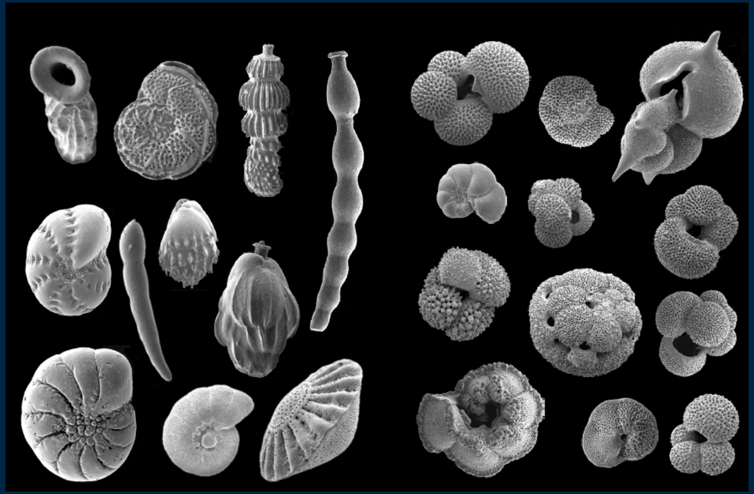

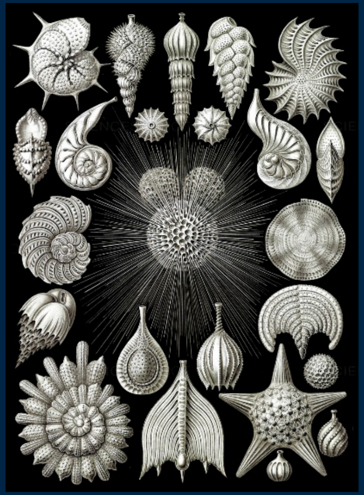

APPLICATIONS OF FORAMINIFERA IN PALEOCLIMATOLOGY – GEOCHEMICAL ANALYSES

AARHUS UNIVERSITY
DEPARTMENT OF GEOSCIENCE

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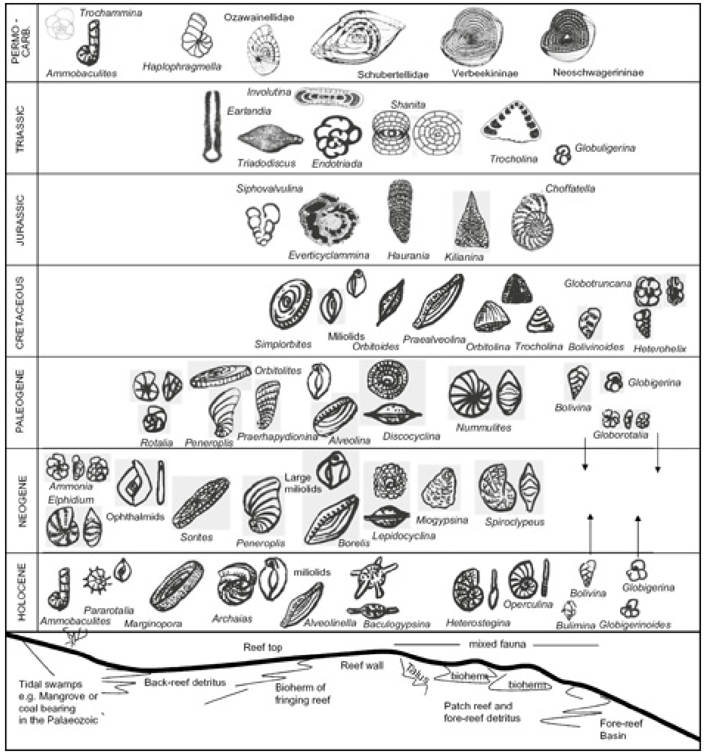
PHD

WHY ARE FORAMINIFERA SUITED FOR PALEOCLIMATOLOGICAL RECONSTRUCTIONS?

- Calcium carbonate test → fossil record
- Abundance, diversity
- Species existing through time
- Test precipitates from surrounding sea-water → it reflects the geochemical signature of the water

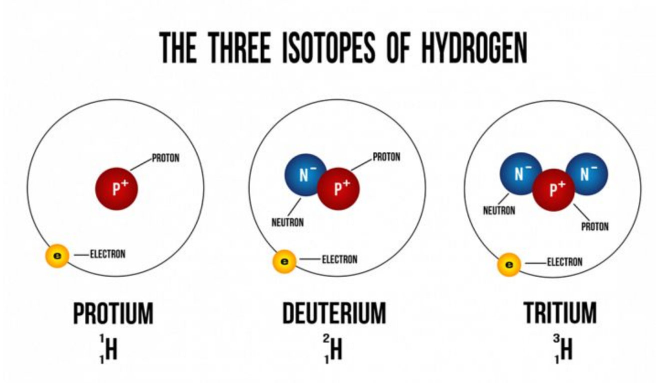


Source: ucldigitalpress.co.uk

1. STABLE ISOTOPE ANALYSIS

What are the isotopes of an element?

Atoms of the same element that have different numbers of neutrons → they have the same number of protons (positive charge) and electrons (negative charge), but differ in molecular weight due to different numbers of neutrons (neutral charge).



Source: www.worldatlas.com

Types of isotopes:

- Radioactive (unstable): prone to decay to another state: ^{14}C
- Stable: have a stable proton-neutron combination: ^{13}C, ^{12}C, ^{1}H, ^{2}H, ^{3}H, ^{18}O, ^{16}O. These isotopes occur naturally in the environment, but their natural abundance differs with different environmental conditions.

STABLE ISOTOPES

Abundance of stable isotopes:

Element	Isotope	Abundance [%]
Hydrogen	^{1}H	99.985
	^{2}H	0.015
Oxygen	^{16}O	99.76
	^{17}O	0.04
	^{18}O	0.2
Carbon	^{12}C	98.9
	^{13}C	1.1

Criss & Farquhar, 2008

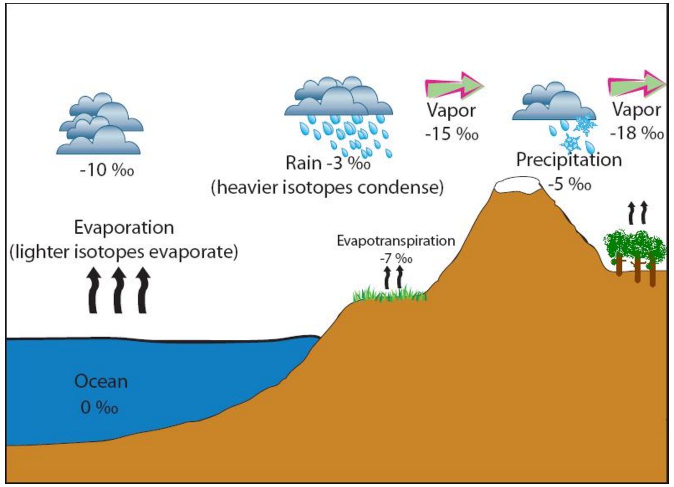
Isotopic ratio:

Measure of the relative abundance of the isotopes: $^{18}O/^{16}O$

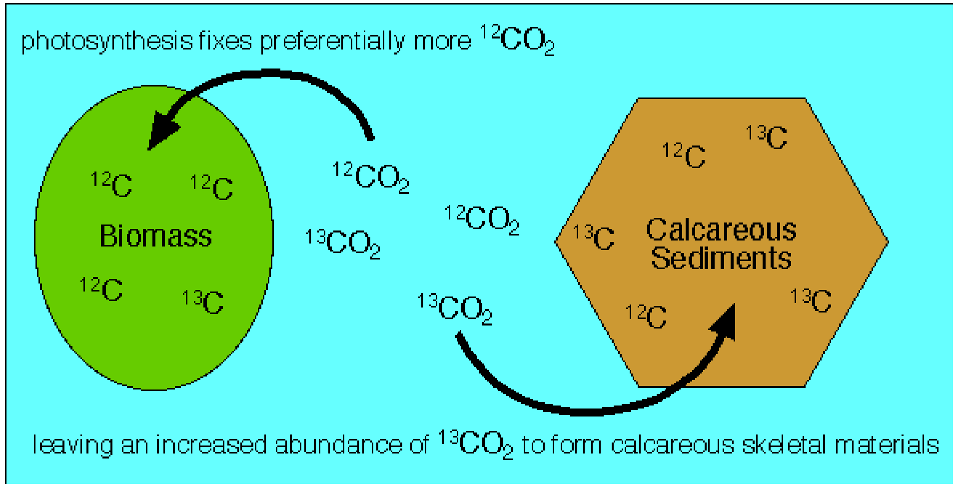
$^{13}C/^{12}C$

ISOTOPE FRACTIONATION

Enrichment of one isotope relative to another in a chemical or physical process (e.g., evaporation, diffusion, metabolism).



Source: serc.carleton.edu



Source: www.columbia.edu

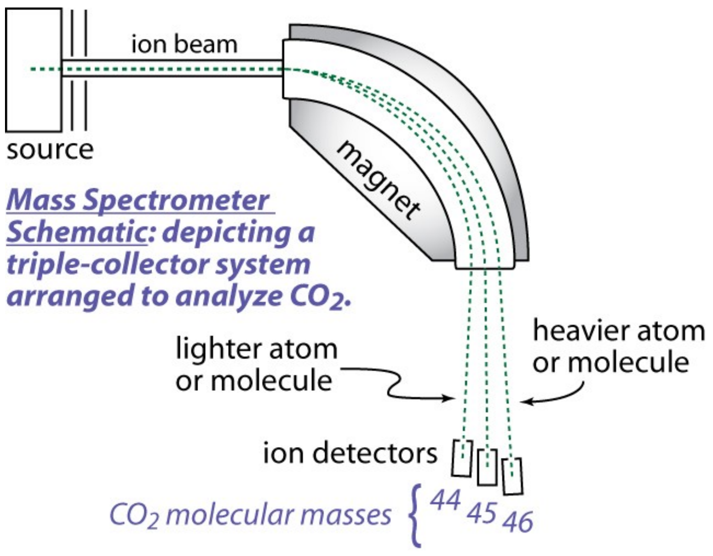
- Water evaporating from the sea: enriched in the light ^{16}O isotope.
- Precipitate: enriched in the heavy ^{18}O isotope, resulting in a further concentration of ^{16}O in atmospheric water vapor.

- During photosynthesis plants are enriched in the lighter ^{12}C isotope. Consequently the atmosphere and oceans become depleted in ^{12}C and enriched in ^{13}C.

MEASUREMENT TECHNIQUE

The isotopic ratio is measured using an isotope ratio mass spectrometer (IRMS): separates elements in function of their weight.

Gas source IRMS: the principal instruments used for measuring isotopic ratios of light elements, including H, C, N and O. The sample is introduced in gaseous form. Fundamental parts:



Source: serc.carleton.edu

(1) a "source" of positively charged ions or molecular ions
(2) a magnetic analyzer
(3) ion collectors

RESULTS OF ISOTOPIC ANALYSES

The isotopic composition of a substance is measured with respect to a standard and it is expressed as delta notation.

Standards used:

O → SMOW (Standard Mean Ocean Water)

C → PDB (Pee Dee Belemnite)

Delta value:

$$\delta^{18}O = \frac{(^{18}O/^{16}O)sample - (^{18}O/^{16}O)SMOW}{(^{18}O/^{16}O)SMOW} \times 1000$$

$$\delta^{13}C = \frac{(^{13}C/^{12}C)sample - (^{13}C/^{12}C)PDB}{(^{13}C/^{12}C)PDB} \times 1000$$

OR

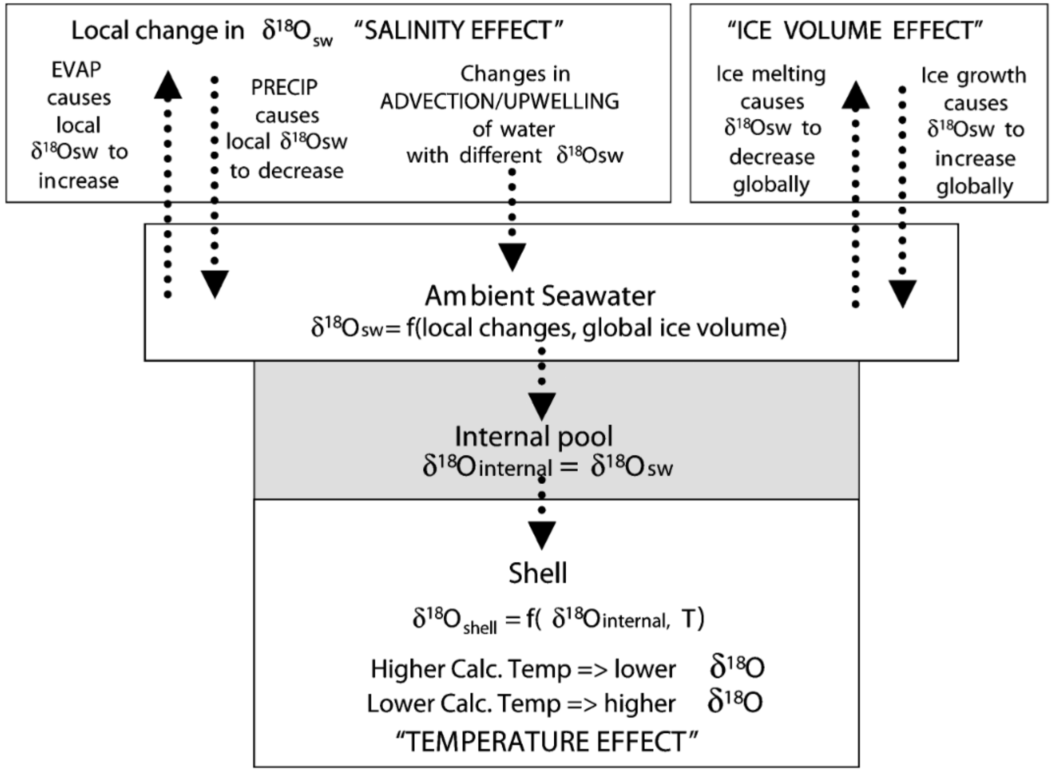
$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000$$

Concentration unit: ‰

δ > 0 → sample enriched in heavy isotopes relative to the standard

δ < 0 → sample depleted in heavy isotopes relative to the standard

FORAMINIFERAL $\delta^{18}O$ AS ENVIRONMENTAL PROXY



Ravelo & Hillaire-Marcel, 2007

Stable oxygen isotope ratios ($\delta^{18}O$) of shell carbonate are controlled by the ratio in the seawater and the calcification temperature.

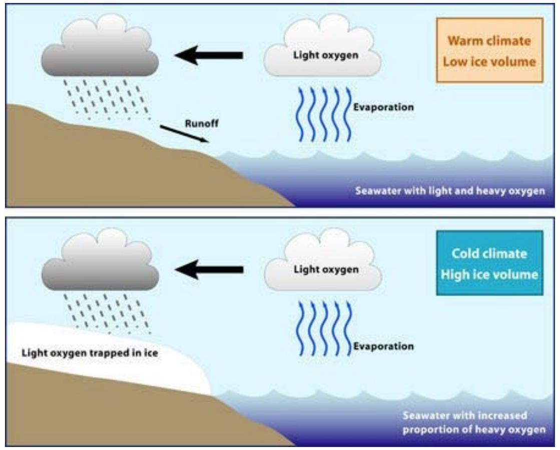
Paleotemperature equation of O´Neil et al. (1969):

$$T(°C) = 16.9 - 4.38(\delta_c - \delta_w) + 0.1(\delta_c - \delta_w)^2$$

δ_c: $\delta^{18}O$ of (equilibrium) calcite
δ_w: $\delta^{18}O$ of the seawater

LR04 STACK

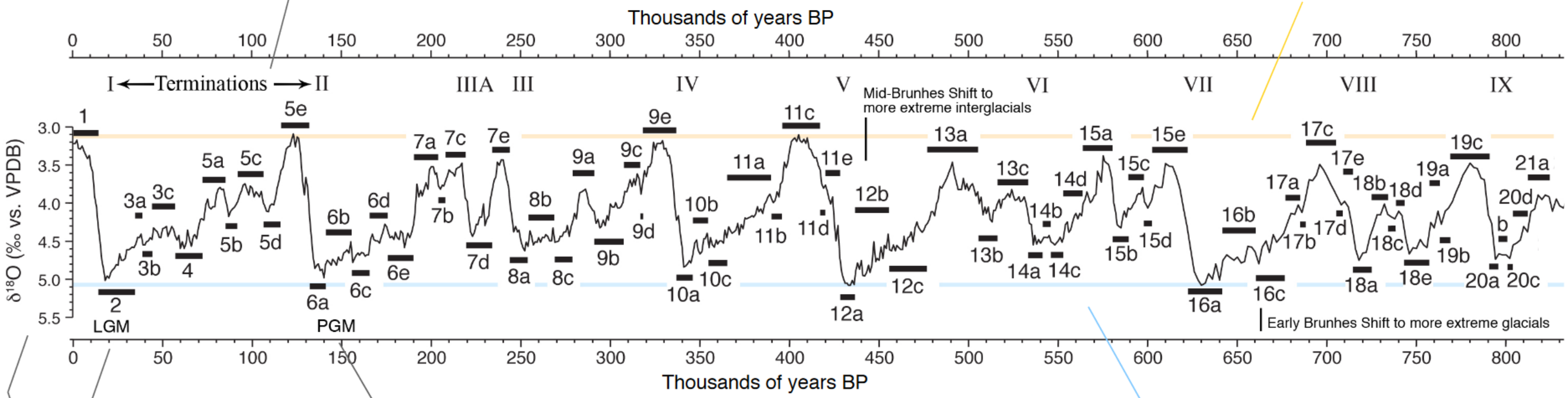
Source: www.filthymonkeymen.com



Marine isotope stages:
LR04 stack of Lisiecki & Rayamo, 2005

Terminations: transitions from glacial to interglaciol stages

Minimum δ^{18}O typical in glacials after Mid-Brunhes Transition, but not before



Last glacial maximum

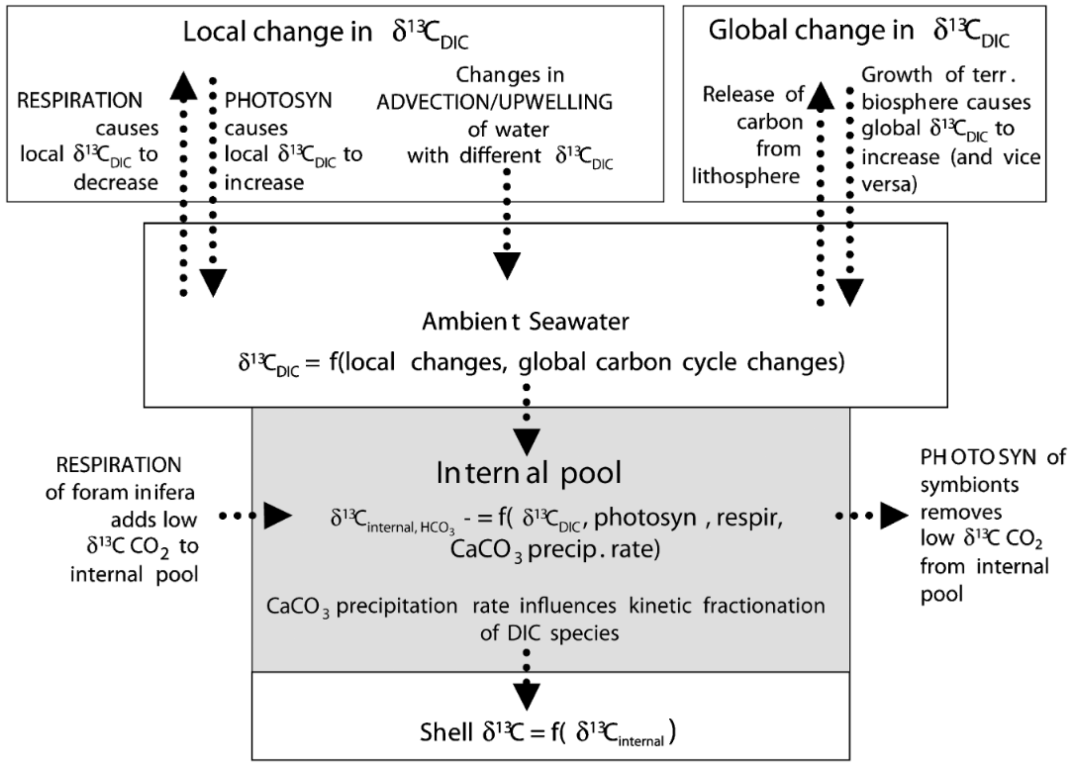
Penultimate glacial maximum

Maximum δ^{18}O typical in glacials after Early Brunhes Transition, but not before

The inverted scale puts higher temperatures and higher sea-level up, and lower temperatures and lower sea-level down.

Source: railsback.org

FORAMINIFERAL $\delta^{13}C$ AS ENVIRONMENTAL PROXY

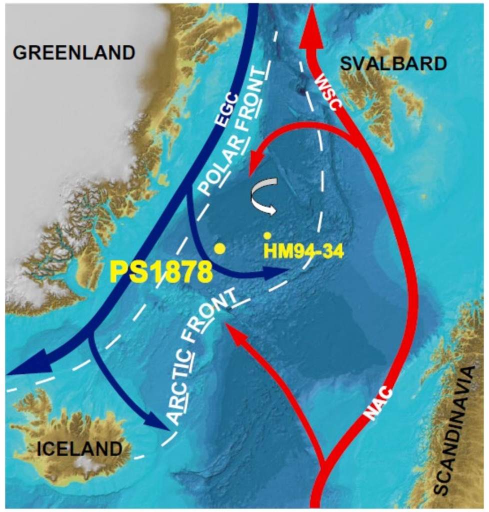


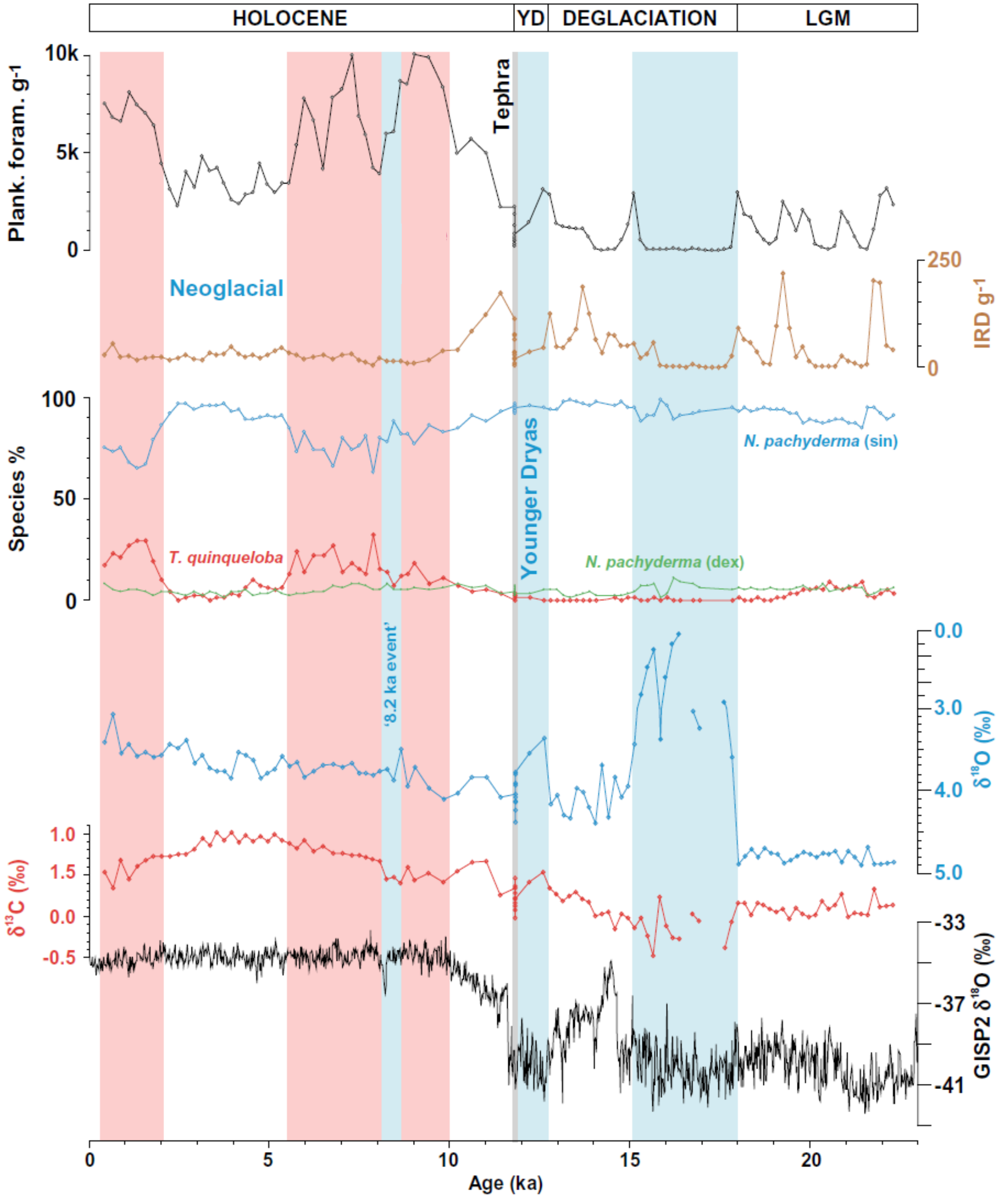
Ravelo & Hillaire-Marcel, 2007

Stable carbon isotope ratios ($\delta^{13}C$) of shell carbonate are a function of the ratio of dissolved inorganic carbon in the surrounding water.

EXAMPLES OF PALEORECONSTRUCTION

Telesinski et al., 2014





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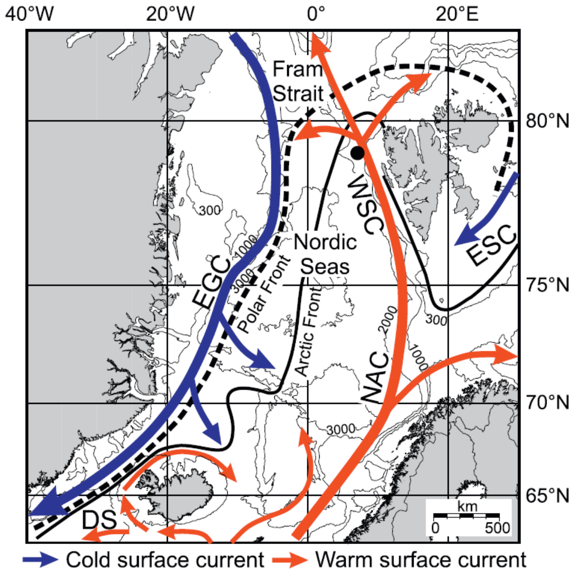
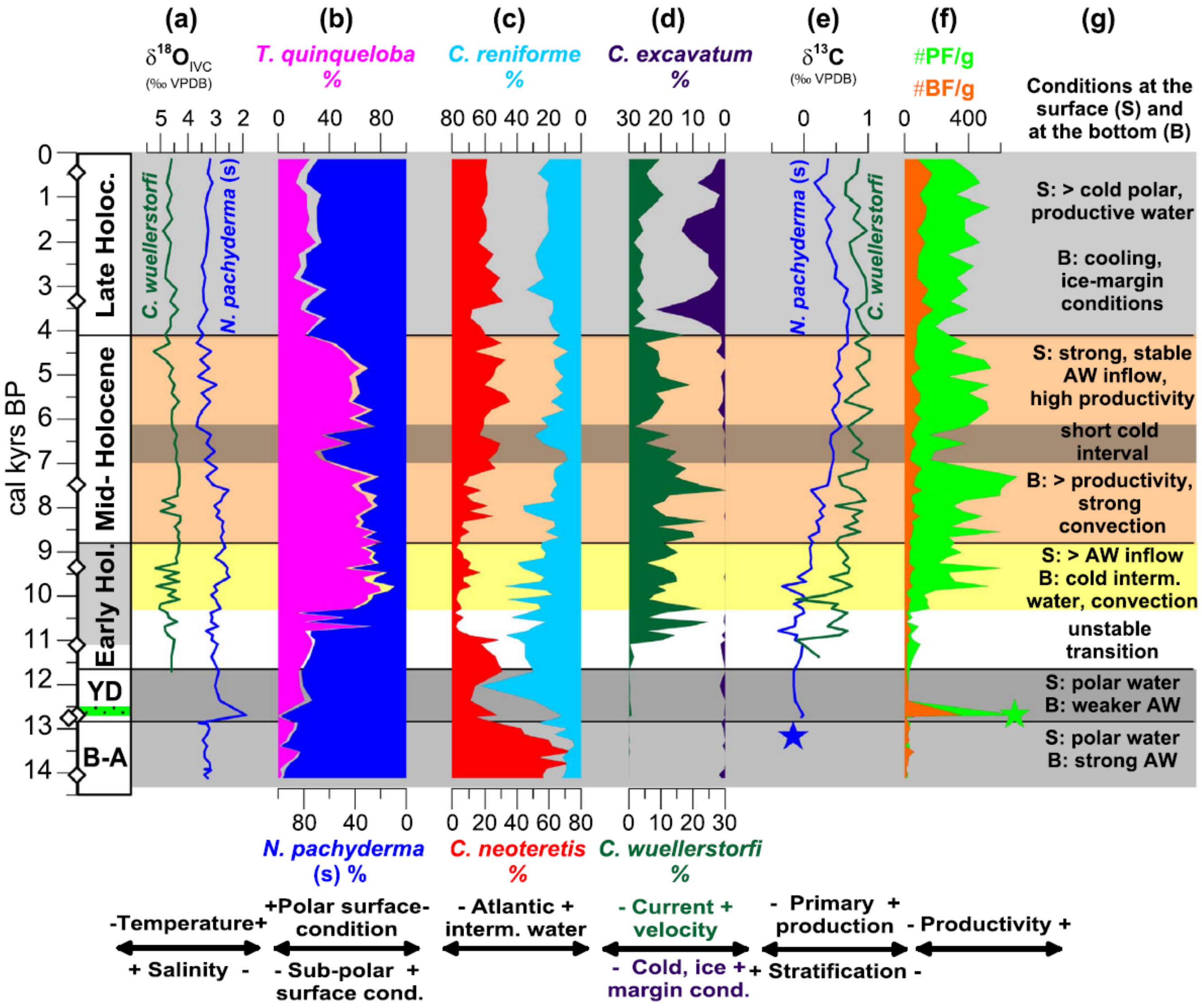
EXAMPLES OF PALEORECONSTRUCTION

Consolaro et al., 2018





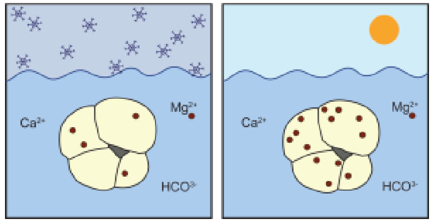
2. Mg/Ca THERMOMETRY

The calcium atom in the calcite skeletons of marine organisms is often replaced by other cations (Mg, Cd, Ba, Sr, Fe, Co, Zn, Ni):

1. substitution is directly dependent upon the concentration of the element in the surrounding seawater in which the organism lives

2. the organism itself controls the incorporation of the element into the calcite skeleton, independently of the chemical signal of the surrounding water masses

Foraminifera: substitution of Mg into the calcite is temperature dependent → more Mg incorporated into their tests when they grow in warmer waters.

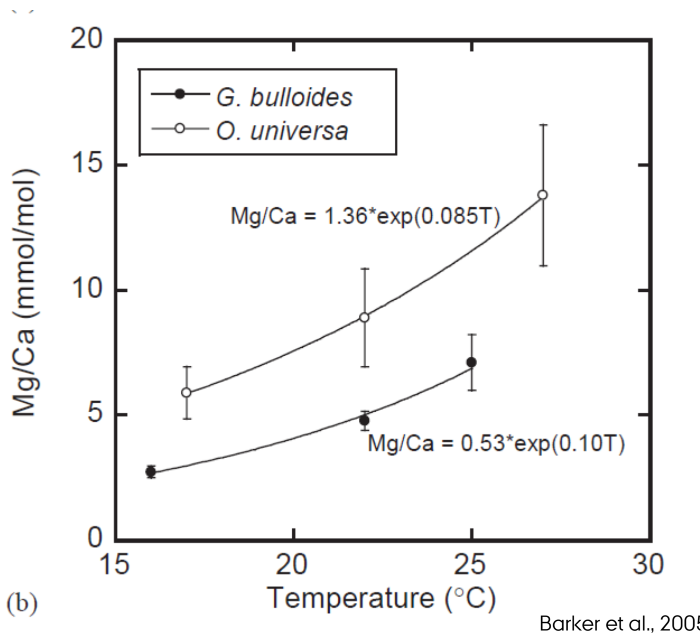


Source: foramsetal.wordpress.com

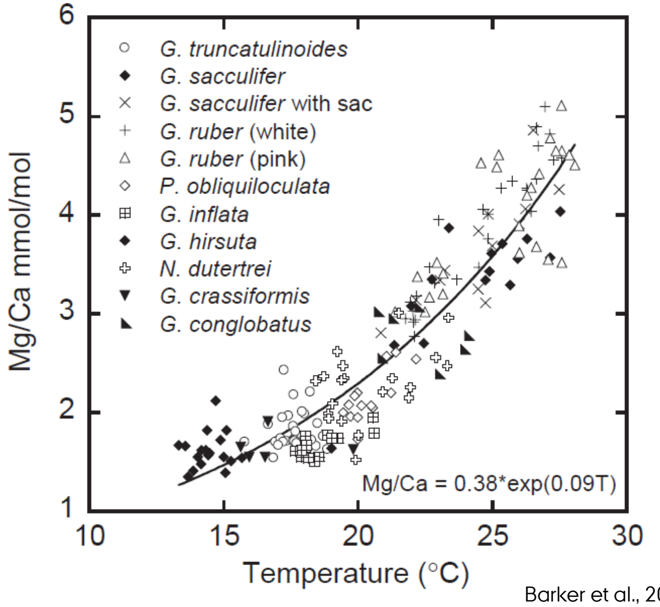
Mg/Ca-TEMPERATURE CALIBRATIONS

Essential for quantitative paleo-temperature reconstructions → species specific Mg/Ca vs. temperature relationship:

$$Mg/Ca = B \exp(A \times T)$$



Barker et al., 2005



Barker et al., 2005

MEASUREMENT TECHNIQUES

- ICP-MS (inductively coupled plasma mass spectrometry): the sample is dissolved, ionized, and then separated into ions grouped by mass-to-charge ratios.
- ICP-OES (OES = optical emission spectrometry): ionizes the sample and then looks at the different wavelengths produced by the excited atoms.
- Laser-ablation ICP-MS: removes very small, precise portions of a sample prior to ionization (beneficial if you want to examine how a sample varies spatially).
- Electron probe microanalysis (EPMA or EMPA): detecting spatial variations in elemental ratios. It involves hitting a sample with an electron beam, followed by analysis of x-rays produced by the different elements within the sample.

ADVANTAGES/DISADVANTAGES

Advantages:

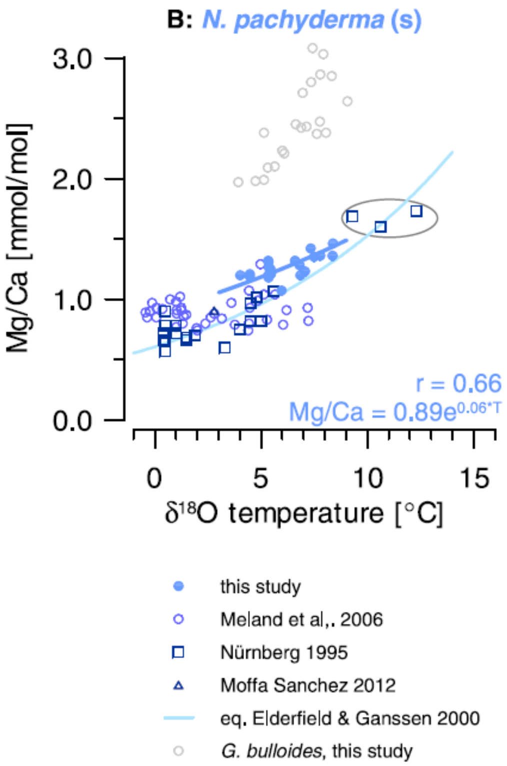
- Mg/Ca ratio of seawater may be considered to be constant over glacial/interglacial timescales
- Combination of Mg/Ca and $\delta^{18}O$ measurements in the same samples theoretically allows to reconstruct both temperature and $\delta^{18}O_w$ changes distinctly
- Temperature dependence of Mg/Ca is species-specific → possible to reconstruct temperatures from different depths in the water column depending on the species' habitat preferences
- Measurement of Mg/Ca ratios is straightforward with elemental analysis → high resolution records may be attained in a relatively short time

Disadvantages:

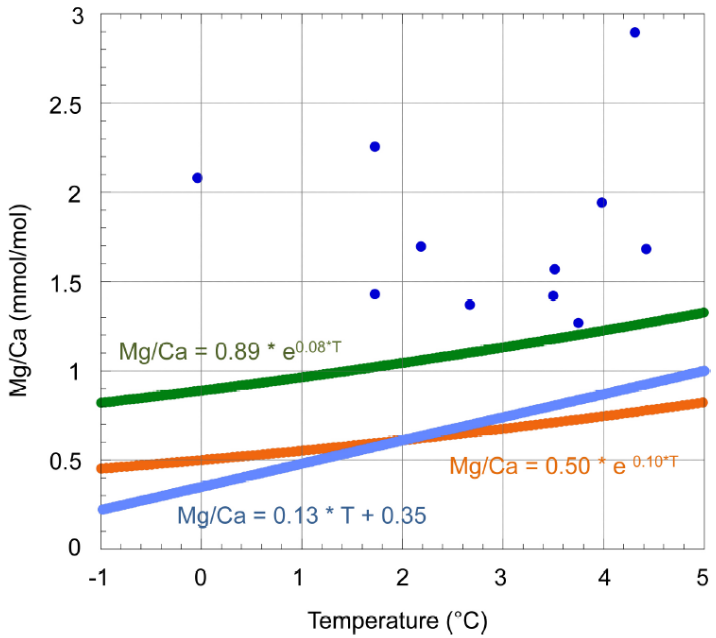
- Partial dissolution may cause removal of Mg-enriched calcitic parts
- High latitudes: the Mg/Ca of some species has no correlation with temperature

HIGH LATITUDES, *N. pachyderma* (sin.)

Jonkers et al., 2013

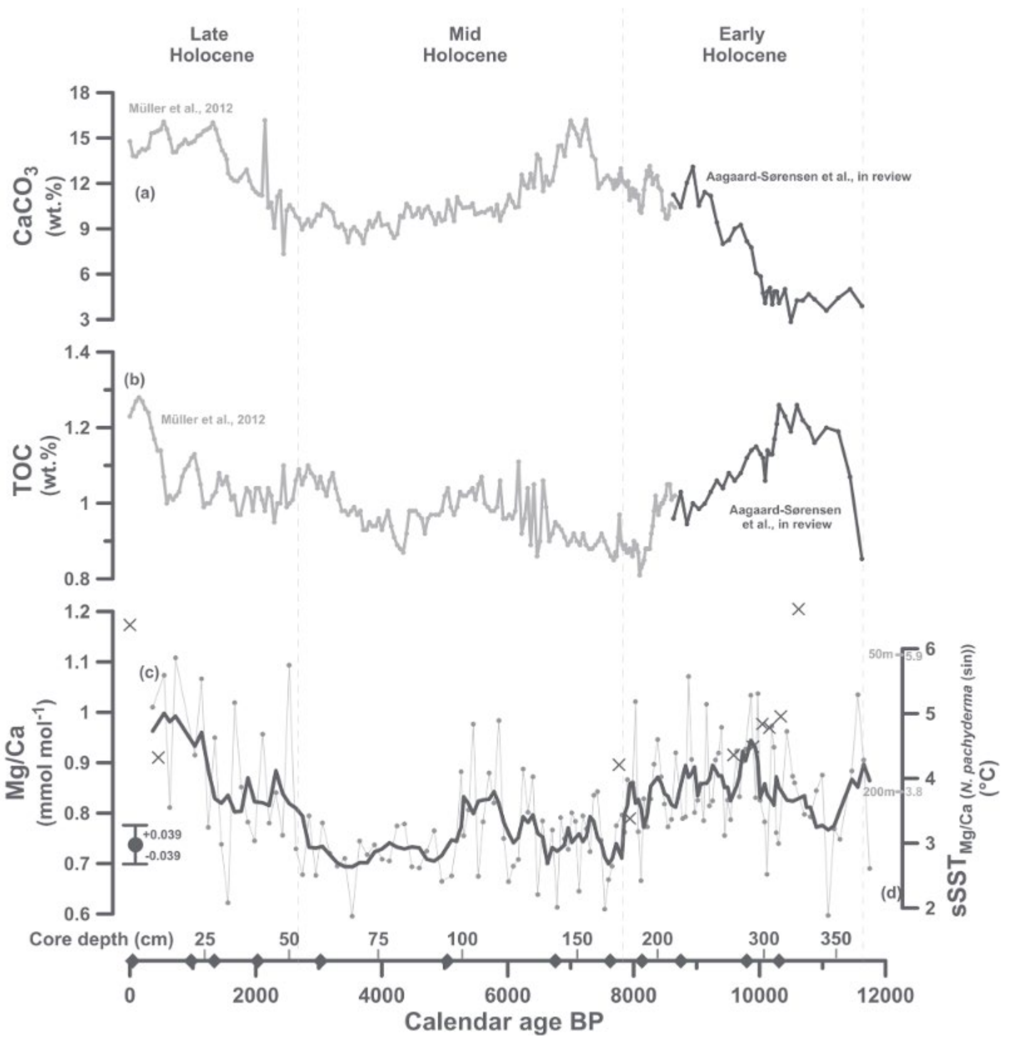


Calibrations:
Elderfield & Ganssen, 2000 (orange)
Kozdon et al., 2009 (blue)
Jonkers et al., 2013 (green)



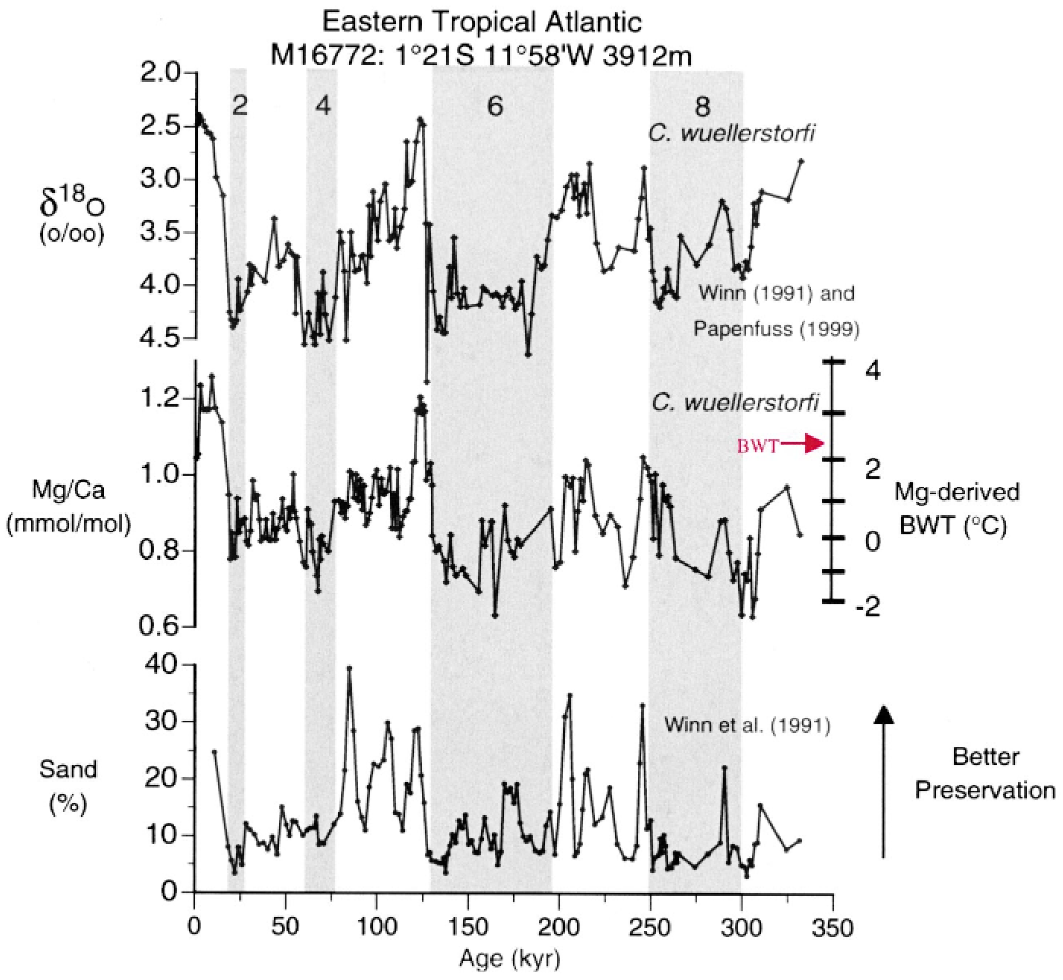
EXAMPLES OF PALEORECONSTRUCTION

Aagard-Sørensen et al., 2014



EXAMPLES OF PALEORECONSTRUCTION

Martin et al., 2002



3. OTHER GEOCHEMICAL PROXIES IN FORAMINIFERA

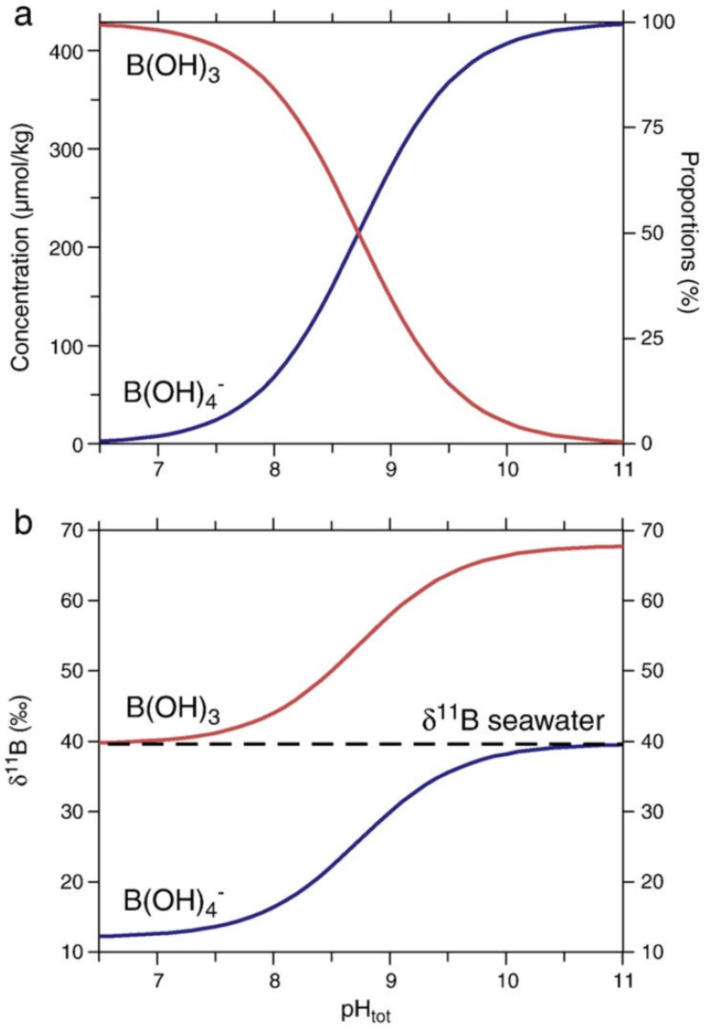
- Clumped isotopes: temperature
- Strontium isotopes: chemostratigraphy
- Neodymium isotopes: past ocean structure, ocean circulation
- Boron isotopes, B/Ca, U/Ca: seawater pH and carbonate ion concentration [CO_3^{-2}]

BORON ISOTOPES - pH

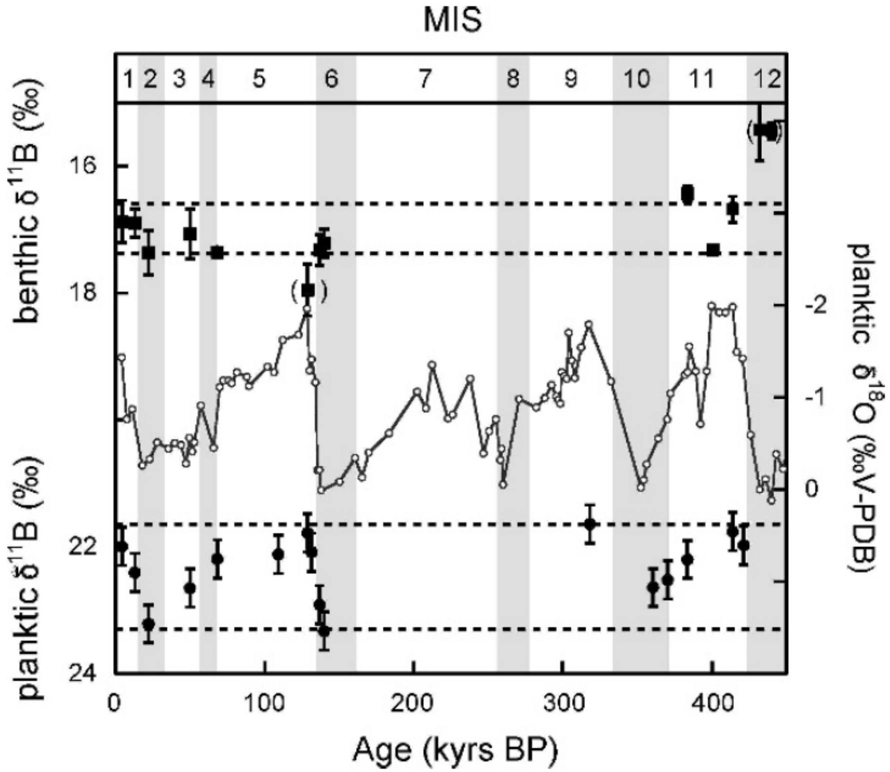
Rae et al., 2011

Boric acid

Borate ion



Hönisch et al., 2008



EXERCISE

Comparison of LR04 stack (Lisiecki & Rayamo, 2005) to the $\delta^{18}O$ data measured in your core (bottom age 52.000 yr BP).

- **Can you relate the GCO3 record to the LR04 stack?**
- **What can be the reason for the deviations?**

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