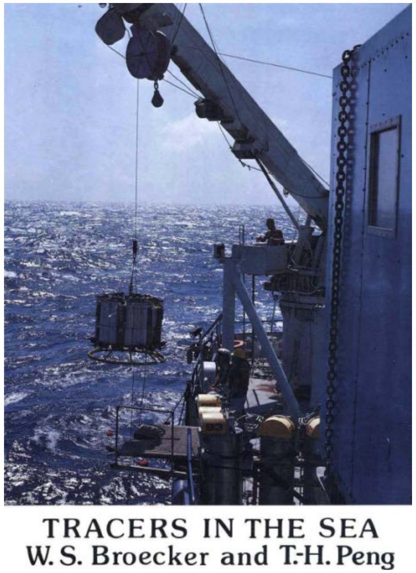
Tracers

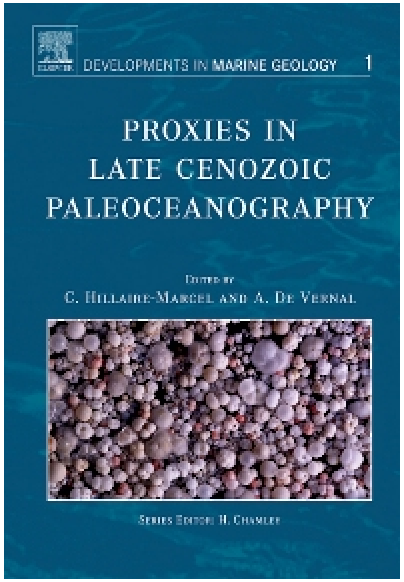
1. Conservative tracers

Temperature, salinity, SiO_2, Nd, ^{18}O…

2. Non-conservative tracers

dissolved oxygen, phosphate, nitrate…





Temperature itself is a tracer but other tracers (like oxygen isotopes) can provide proxies of parameters such as (paleo)-temperature

proxy data are preserved physical characteristics of the environment

Tracers

Chemical tracers…

Radiotracers…

Water transport tracers

- transient tracers
- steady state tracers

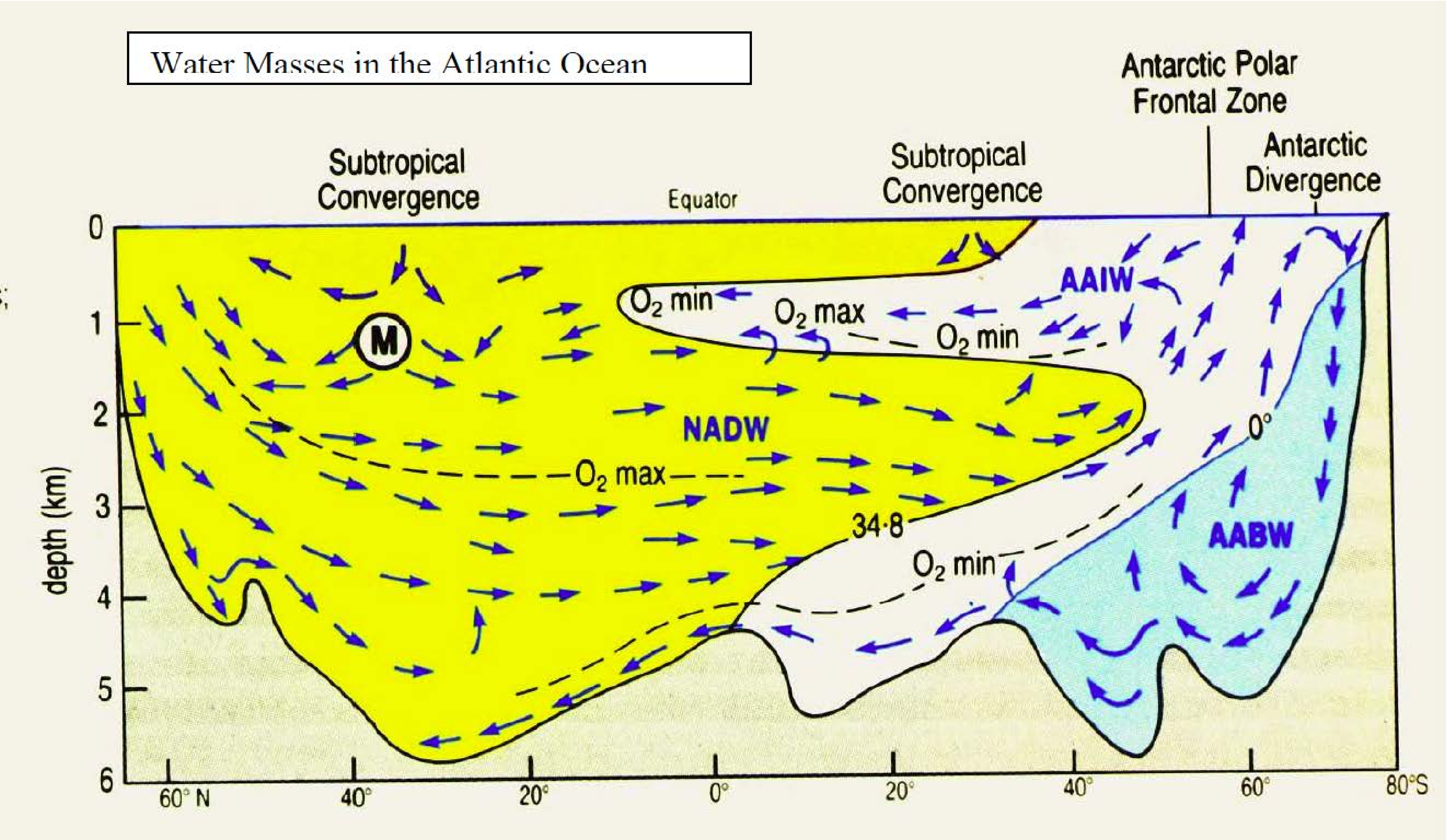
Table 15.1 Ocean Tracers Currently in Use[a]

Isotope	Half-life (years)	Origin			
		Cosmic rays	U+Th series	Weapons testing	Other anthro.
^{14}C	5730	√		√	
^{226}Ra	1600		√		
^{32}Si	250	√			
^{39}Ar	270	√			
^{137}Cs	30.2			√	
^{90}Sr	28.6			√	
^{3}H	12.4	√		√	
^{3}He	—	√	√	√	
^{85}Kr	10.7			√	√
^{228}Ra	5.8		√		
^{7}Be	0.15	√			
^{222}Rn	0.01		√		
Freons	—				√
^{239}Pu	24,400			√	√
^{240}Pu	6540			√	√
^{210}Pb	22.3		√		
^{228}Th	1.9		√		
^{210}Po	0.38		√		
^{234}Th	0.07		√		

a. In the column headed Isotopes, freons and all entries above it are water tracers; all entries below freons are particulate tracers.

W. Broecker (1992)

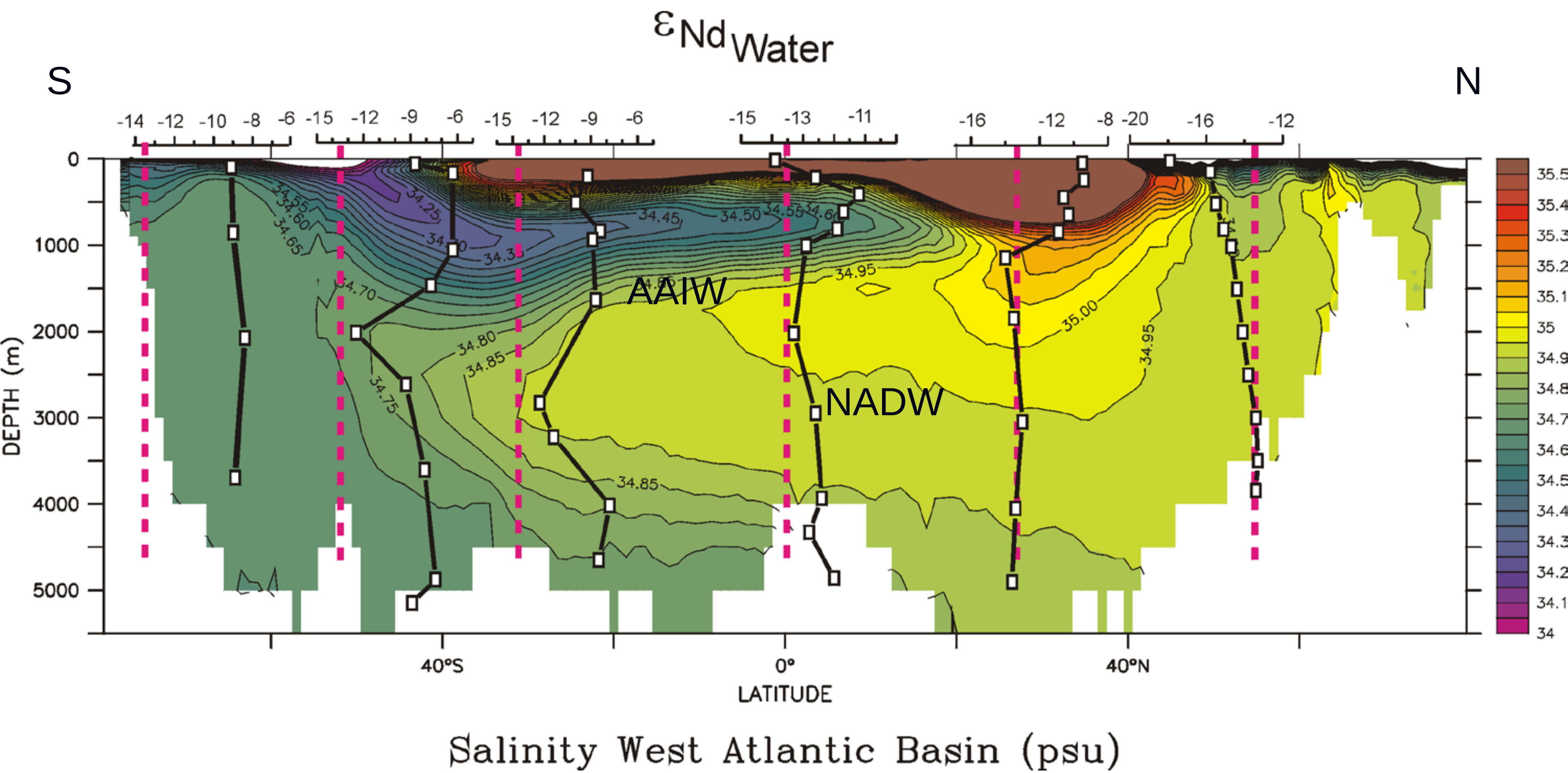
Tracing water masses in the Atlantic ocean



model after Stowe (1979)

Nd tracer

Nd-isotope ratio and salinity profiles in the Atlantic



Goldstein & Hemming: Long-lived isotopic tracers in oceanography, paleoceanography, and ice-sheet dynamics (Treatise on Geochemistry – The Oceans)

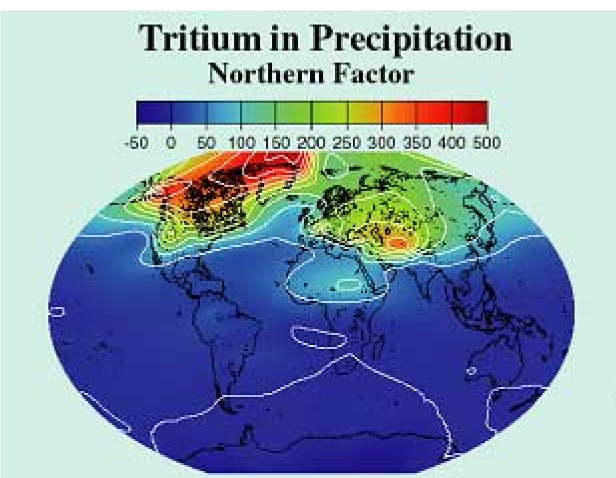
Tritium tracer

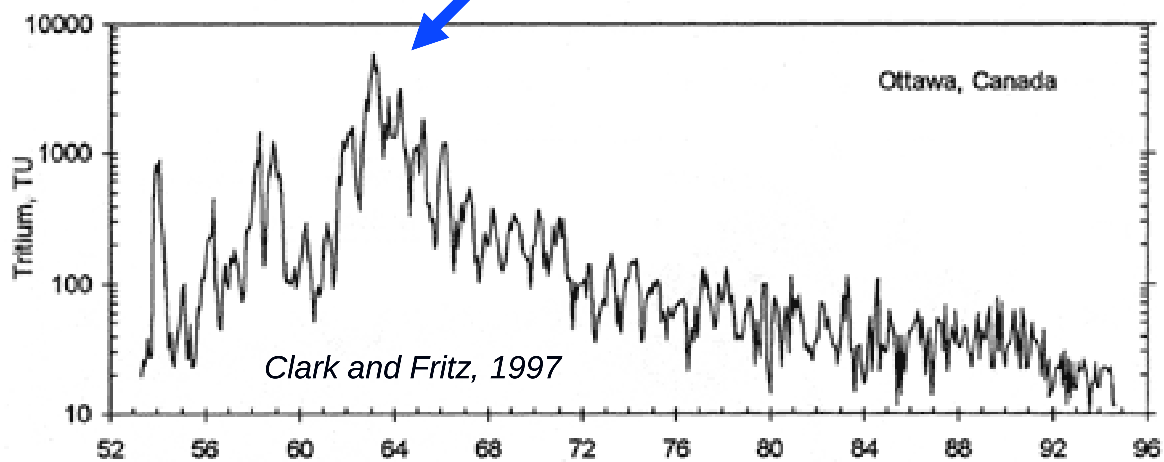
Bomb Tritium

Most of the tritium produced by atmospheric testing of nuclear devices that began in 1952 and reached a maximum in 1963/1964.

The bulk of this tritium was released in the northern hemisphere, and entered the oceans.

bomb spike





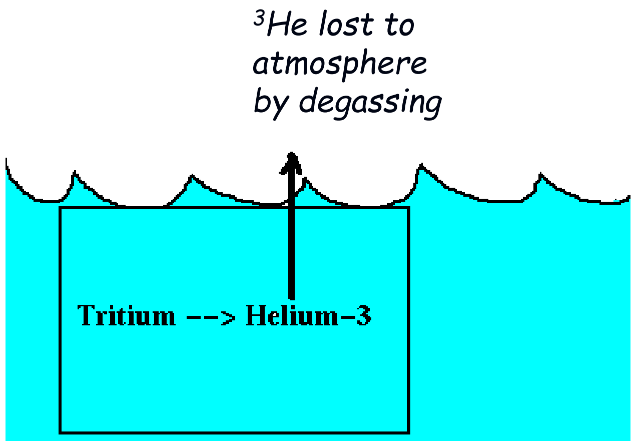
rainfall tritium concentrations

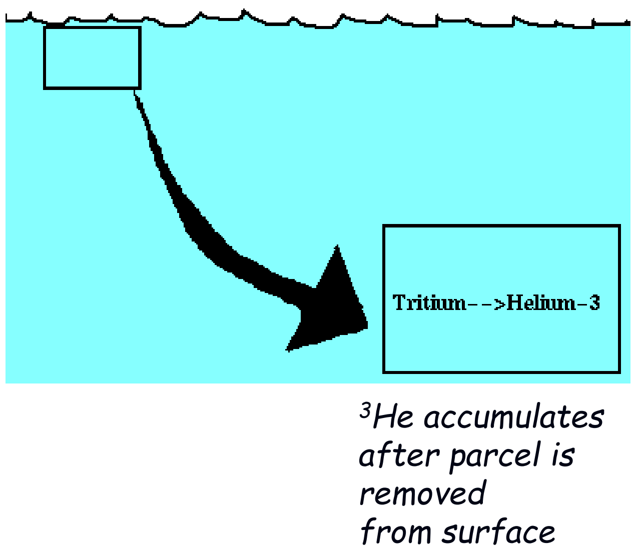
Tritium /^{3}He age

The tritium/^{3}He age is an **apparent age**

Advantage: It is independent of the initial tritium concentration of the water sample.

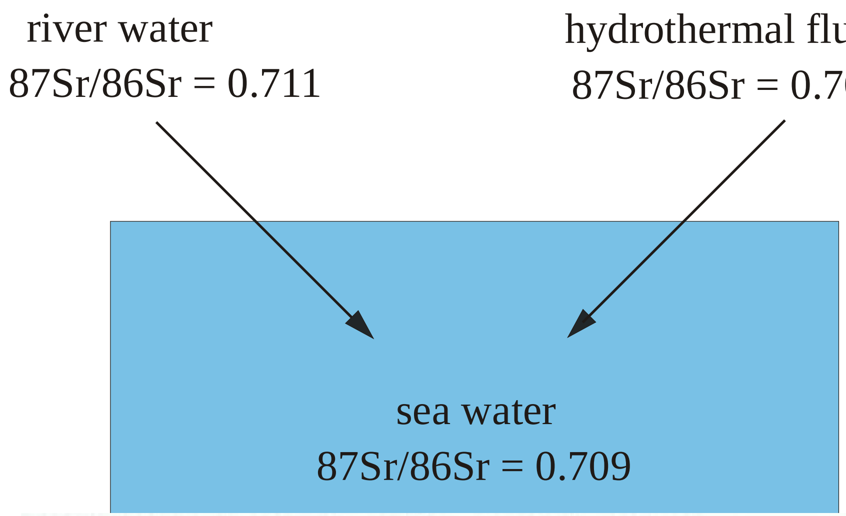
Potential problem: tritium/^{3}He age is affected by mixing and dispersion





The marine $^{87}Sr/^{86}Sr$ ratio

Sr isotope composition of the oceans is determined by the relative contributions of Sr from river waters and hydrothermal sources



At steady state, two equations (WS7.1.1 and WS7.1.2 following) can then be set up and solved to estimate the hydrothermal water flux.

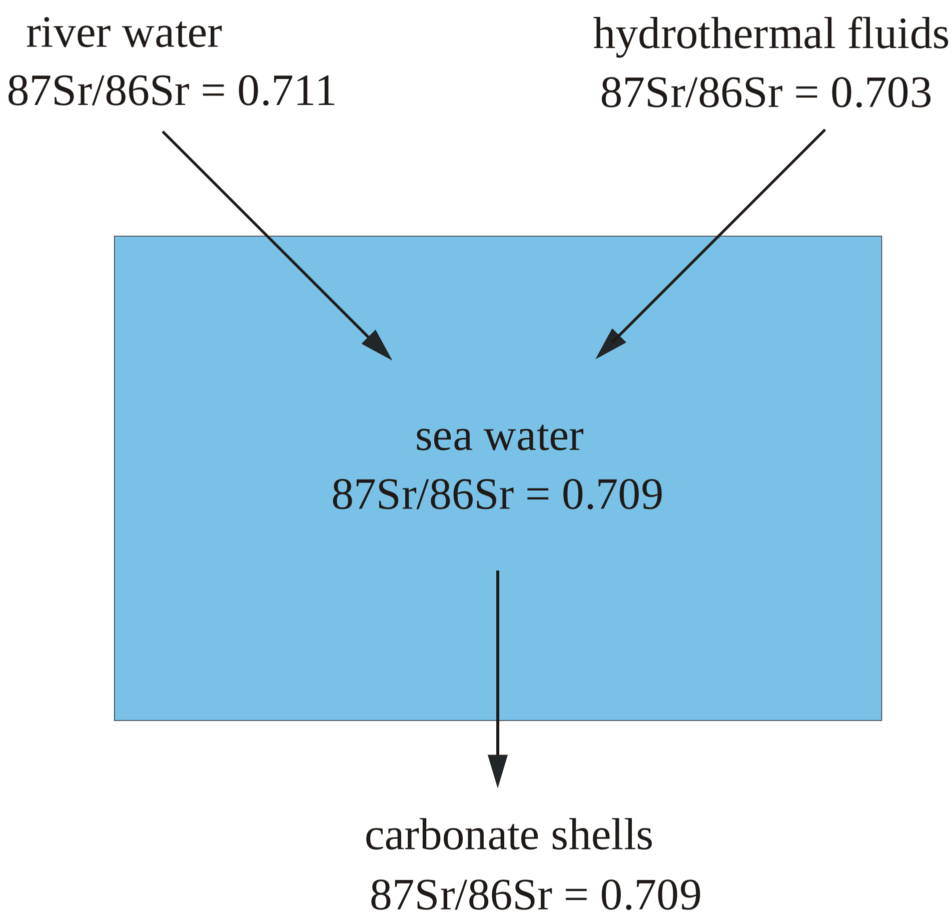
$$\frac{FSr(riv)\times R(riv)+FSr(hydro)\times R(hydro)}{FSr(riv)+FSr(hydro)} = R(seawater) \qquad (WS7.1.1)$$

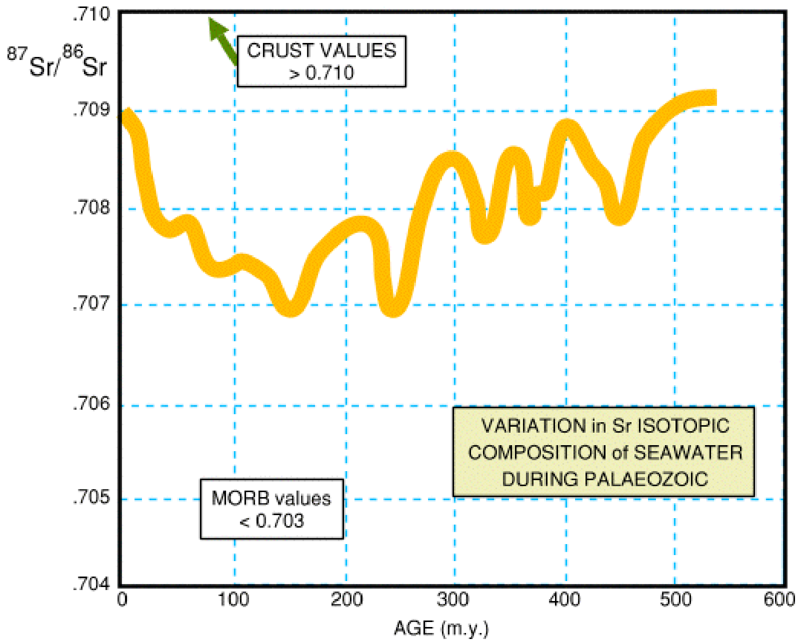
$$FSr(hydro) = [Sr]\times H \qquad (WS7.1.2)$$

where FSr is Sr flux through rivers(riv) or hydrothermal systems (hydro), R is strontium isotopic composition of rivers (riv), hydrothermal systems (hydro), seawater [Sr](hydro) is the concentration of Sr in hydrothermal fluids and H is the total water flow through hydrothermal systems.

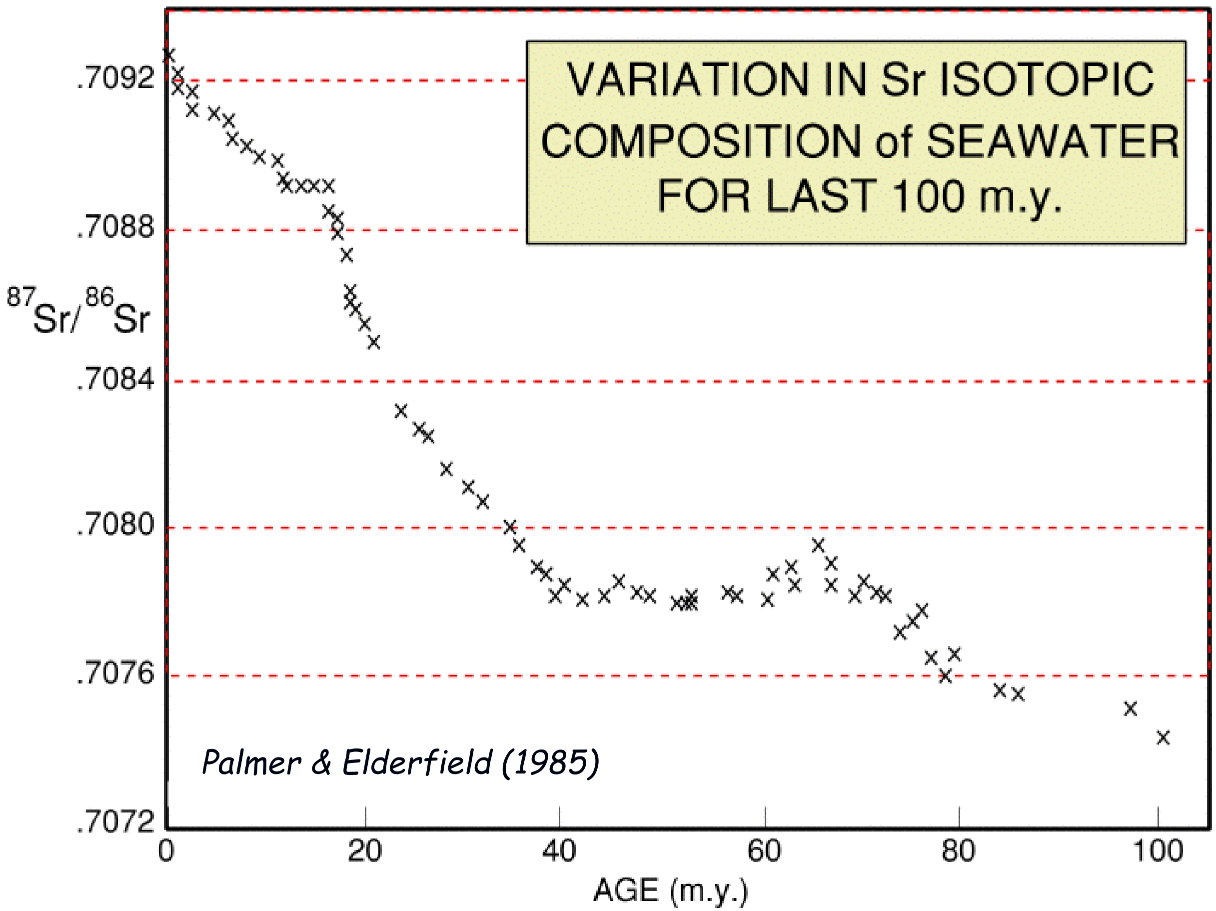
The marine $^{87}Sr/^{86}Sr$ ratio

Sr isotope composition of the oceans is determined by the relative contributions of Sr from river waters and hydrothermal sources





The marine $^{87}Sr/^{86}Sr$ ratio

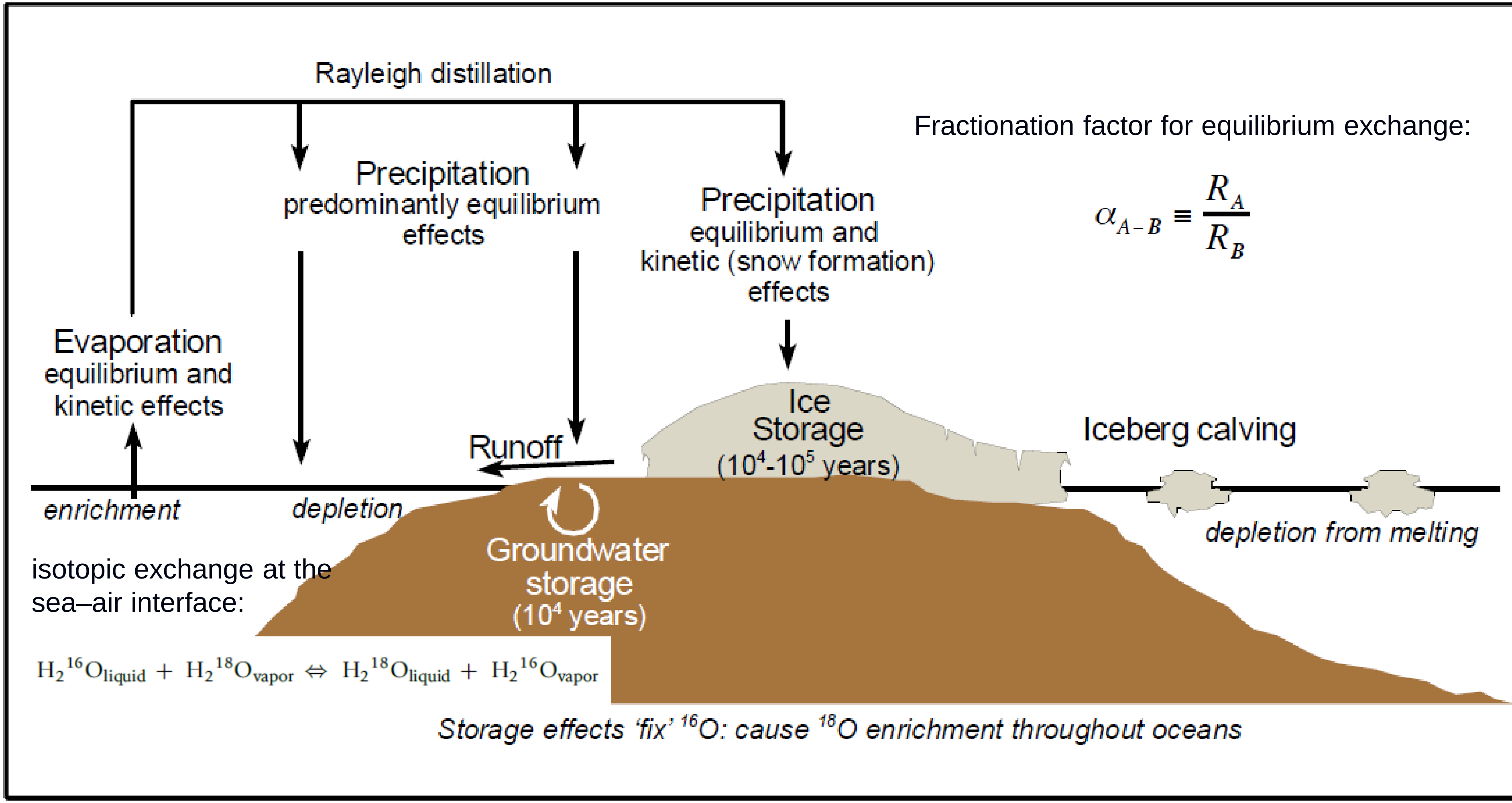


Continental weathering is major sink for atmospheric CO_2

$CaSiO_3 + 2CO_2 + 3H_2O \rightarrow Ca2^{+} + 2HCO_3^{-} + SiO_2 + H_2O$

High Sr ratio in the oceans means higher continental weathering rates

Oxygen isotopes in seawater

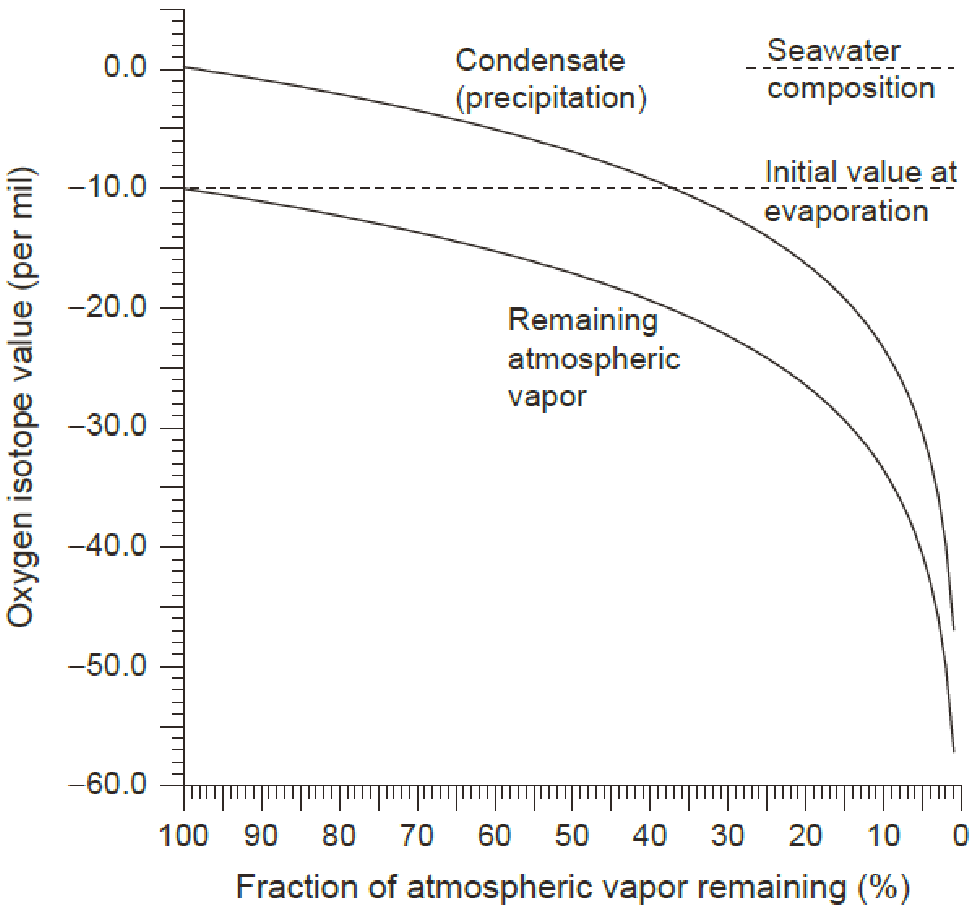


$$R = \frac{^{18}O}{^{16}O} = \frac{0.205}{99.757} = 0.002055$$

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

Rohling (2013) Encyclopedia of Quaternary Science

Oxygen isotopes in seawater



Rohling (2013) Encyclopedia of Quaternary Science

$$R = \frac{^{18}O}{^{16}O} = \frac{0.205}{99.757} = 0.002055$$

$$\delta^{18}O = \left[\frac{R_{sample} - R_{standard}}{R_{standard}}\right] \times 1000$$

The isotopic exchange at the sea–air interface is given by:

$$H_2{}^{16}O_{liquid} + H_2{}^{18}O_{vapor} \Leftrightarrow H_2{}^{18}O_{liquid} + H_2{}^{16}O_{vapor}$$

Fractionation factor for equilibrium exchange:

$$\alpha_{A-B} \equiv \frac{R_A}{R_B}$$

$$\alpha_{l-v} = \exp\{(1.137\ T^{-2}) \times 10^3 - (0.4156\ T^{-1}) - 2.0667 \times 10^{-3}\}$$

→ decrease in fractionation with increasing temperature

$$T(°C) = 16.5 - 4.3(\delta^{18}O_{cc} - \delta^{18}O_{sw}) + 0.14(\delta^{18}O_{cc} - \delta^{18}O_{sw})^2$$

Oxygen isotopes in seawater

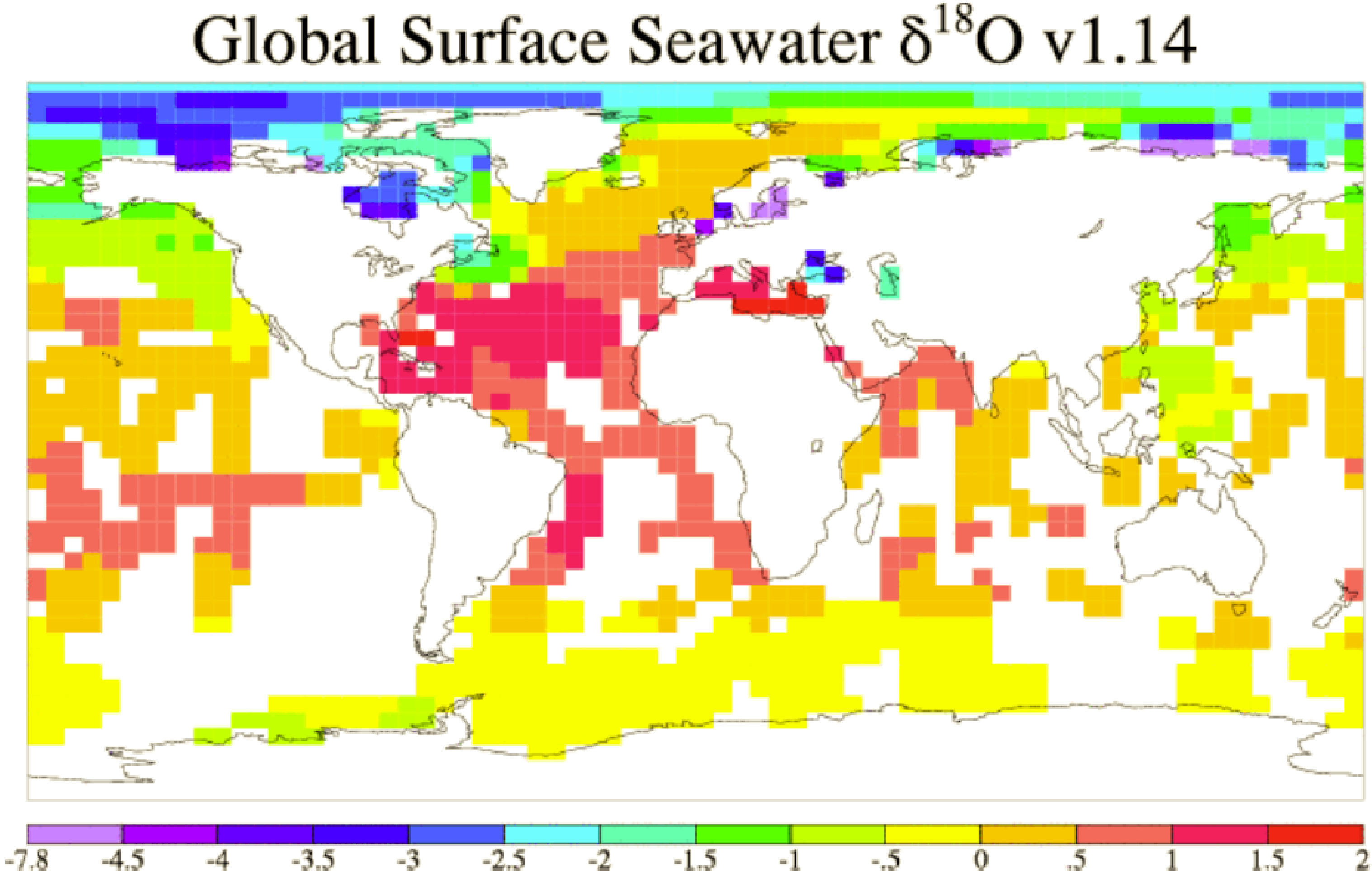


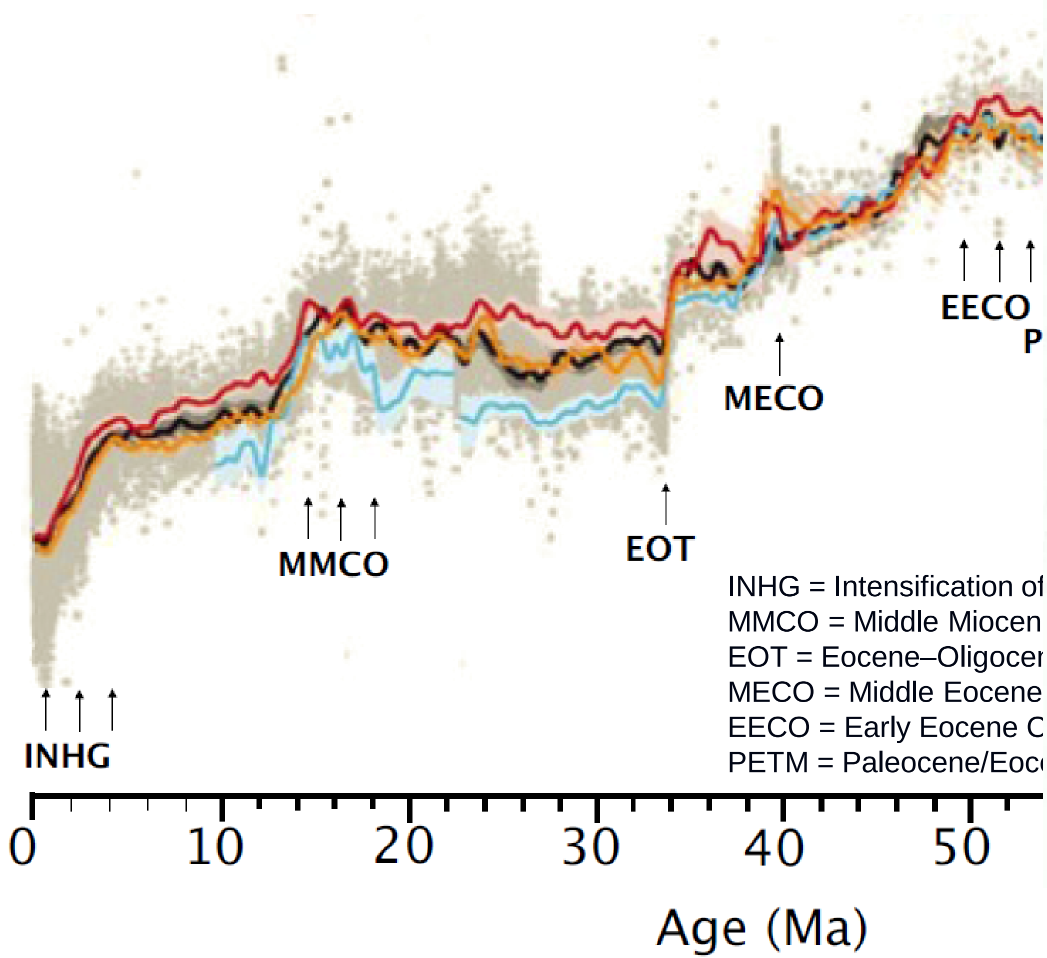
Figure 3. Example of output from the Schmidt et al (1999) global sea-water $\delta^{18}O$ database (extracted 1 February 2006). The image shows surface-water $\delta^{18}O$ integrated over the top 50 m on a 4° x 5° degree grid.

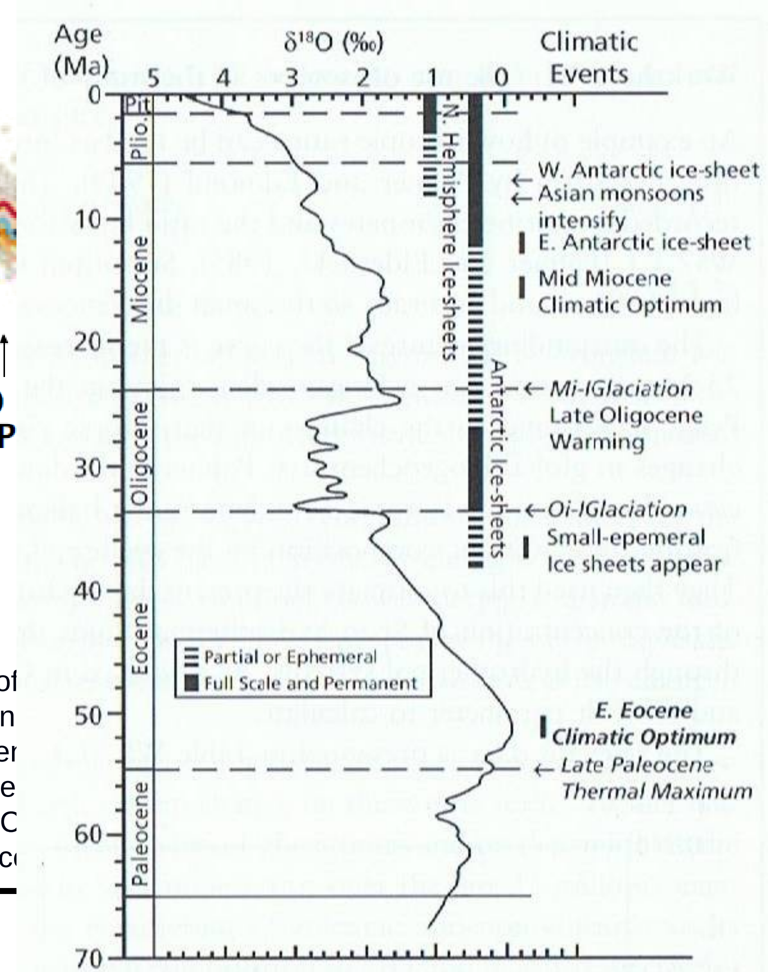
E.J. Rohling (2013)

Calcite tests of selected benthic (left) and planktonic (right) foraminifera from well-preserved Paleogene sediments of Tanzania (33–45 Ma)

Oxygen isotope tracer

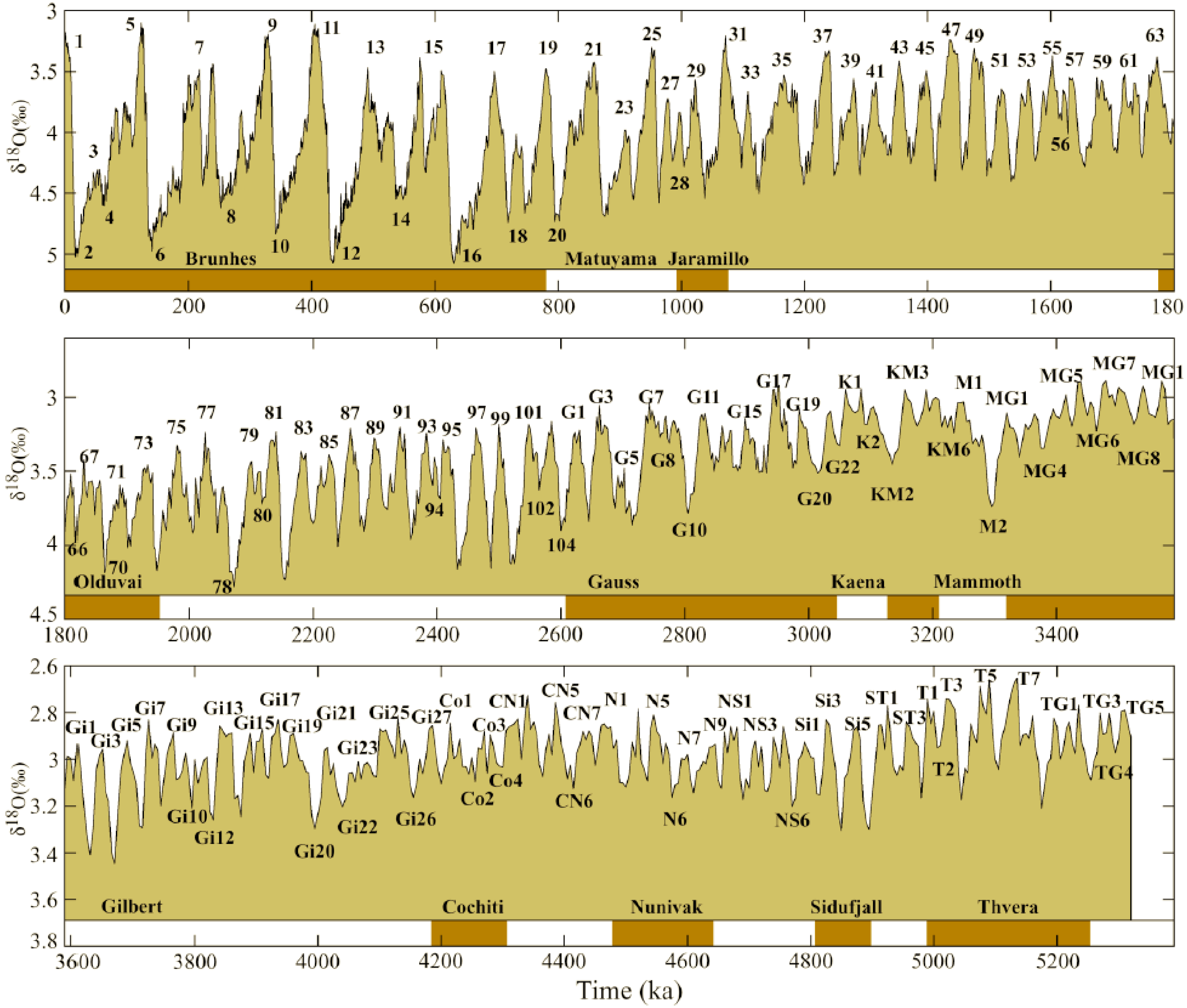
Compilation of deep-sea benthic foraminifera δ[18]O values obtained for the last 80 Ma





Pearson (2012) *Reconstructing Earth's Deep-Time Climate*

Oxygen isotope tracer

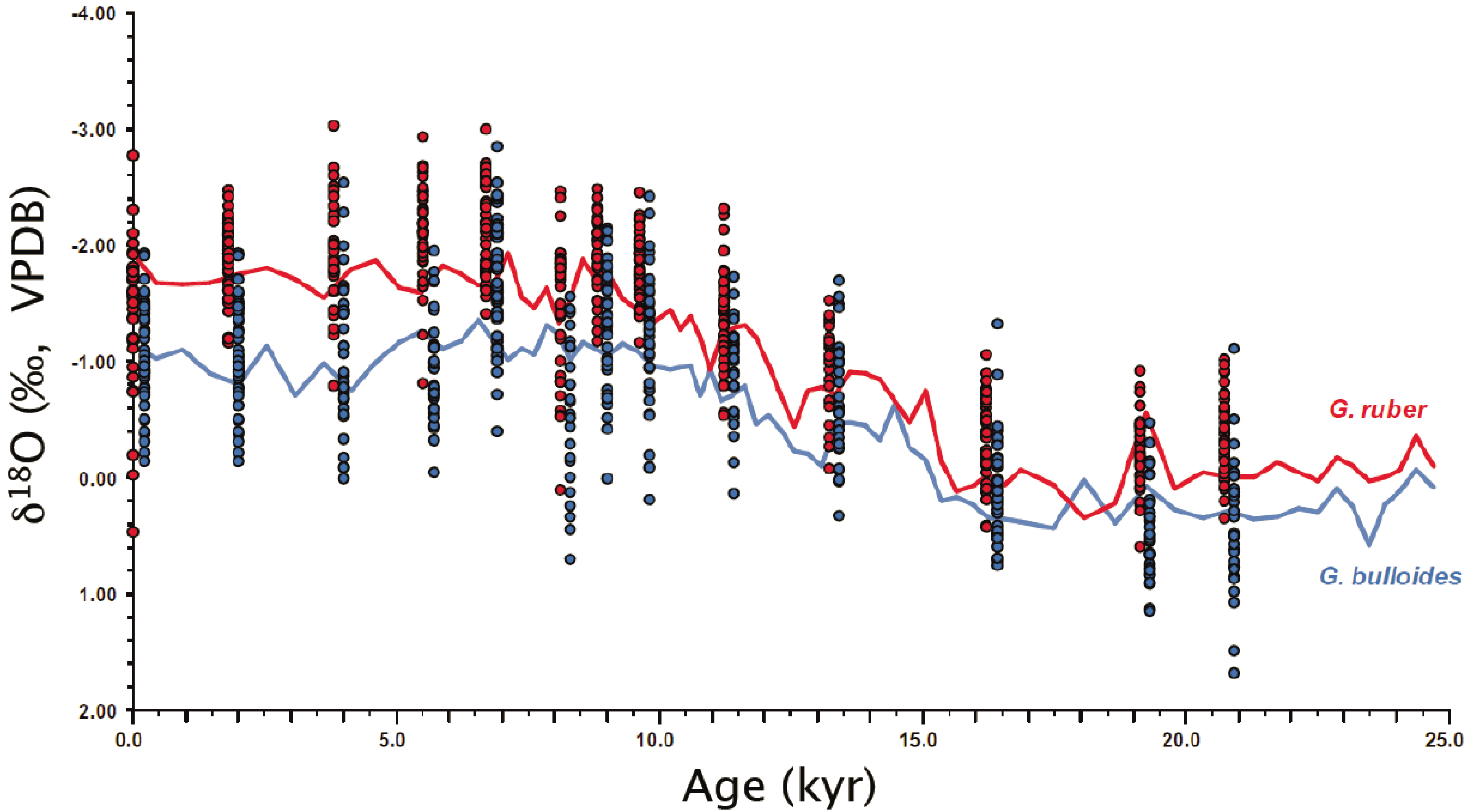


benthic foraminiferal oxygen record

Rohling (2013) Encyclopedia of Quaternary Science

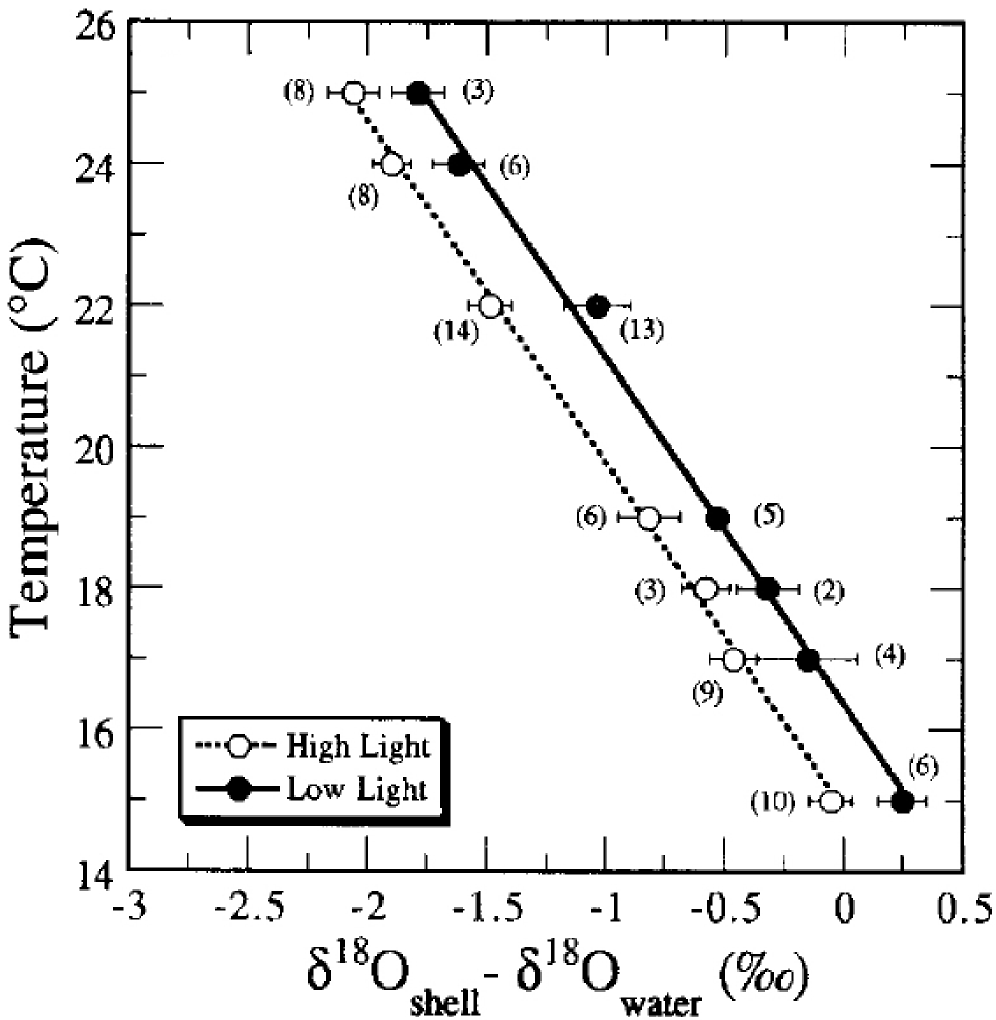
Oxygen isotope tracer

Oxygen isotope ratios of individual tests of the planktonic foraminifera Globigerinoides ruber and Globigerina bulloides in a core that spans the last deglaciation



Pearson (2012) *Reconstructing Earth's Deep-Time Climate*

Oxygen isotopes and paleo-temperature



historic Epstein et al. (1953) paleo-temperature equation:

$T(°C) = 16.5 - 4.3(\delta^{18}O_{cc} - \delta^{18}O_{sw}) + 0.14(\delta^{18}O_{cc} - \delta^{18}O_{sw})^2$

$\delta^{18}O_{cc}$ measured in calcium carbonate

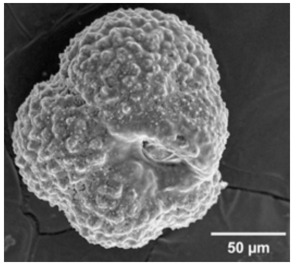
$\delta^{18}O_{sw}$ isotope ratio of the water from which it is precipitated

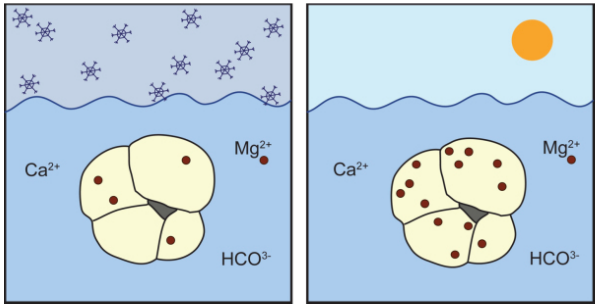
The slope of the equation means that 0.23‰ increase in $\delta^{18}O_{cc}$ corresponds to a difference of about 1°C

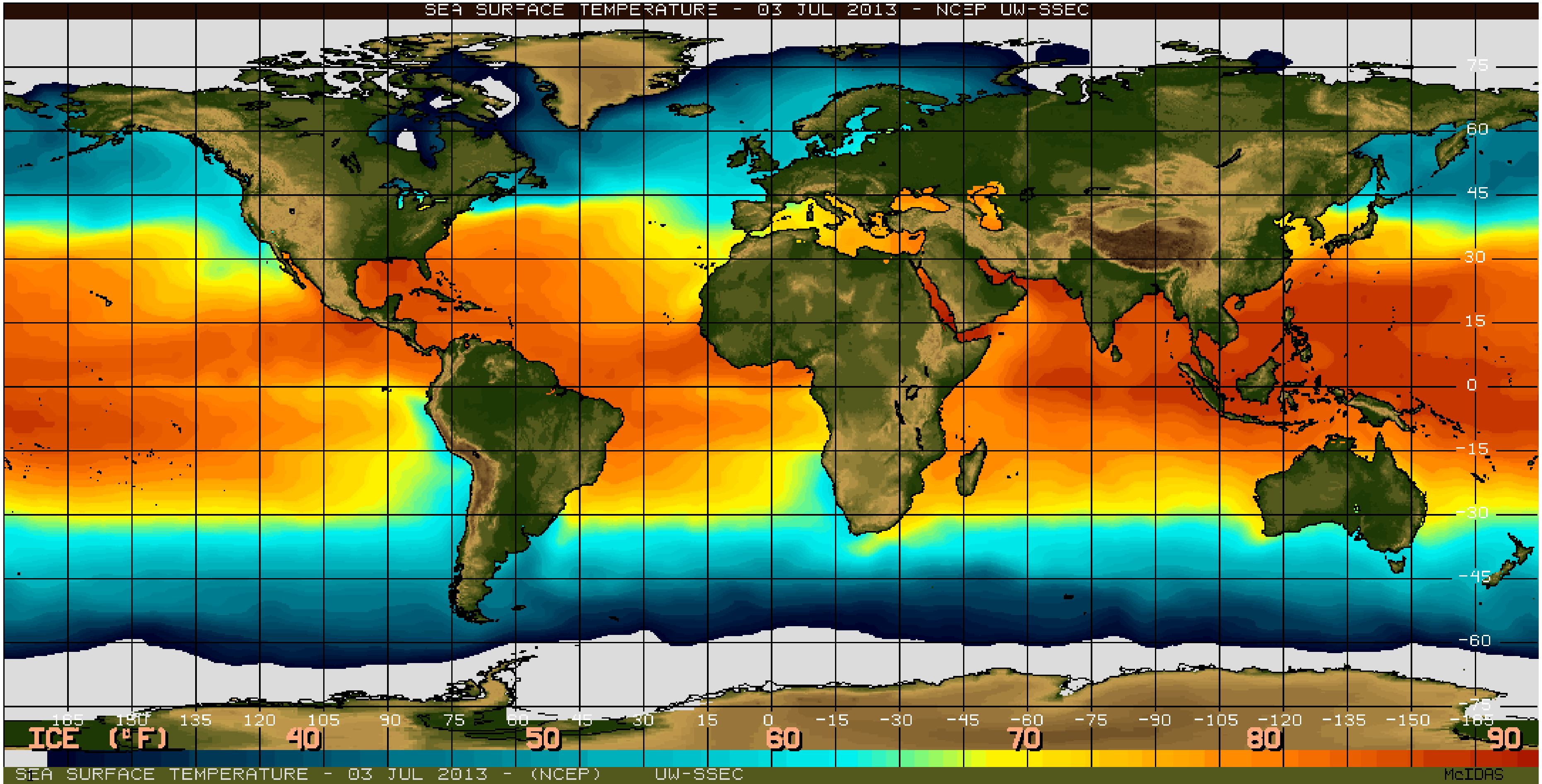
Pearson (2012) *Reconstructing Earth's Deep-Time Climate*

Mg/Ca-ratio as proxy for past oceanic temperature

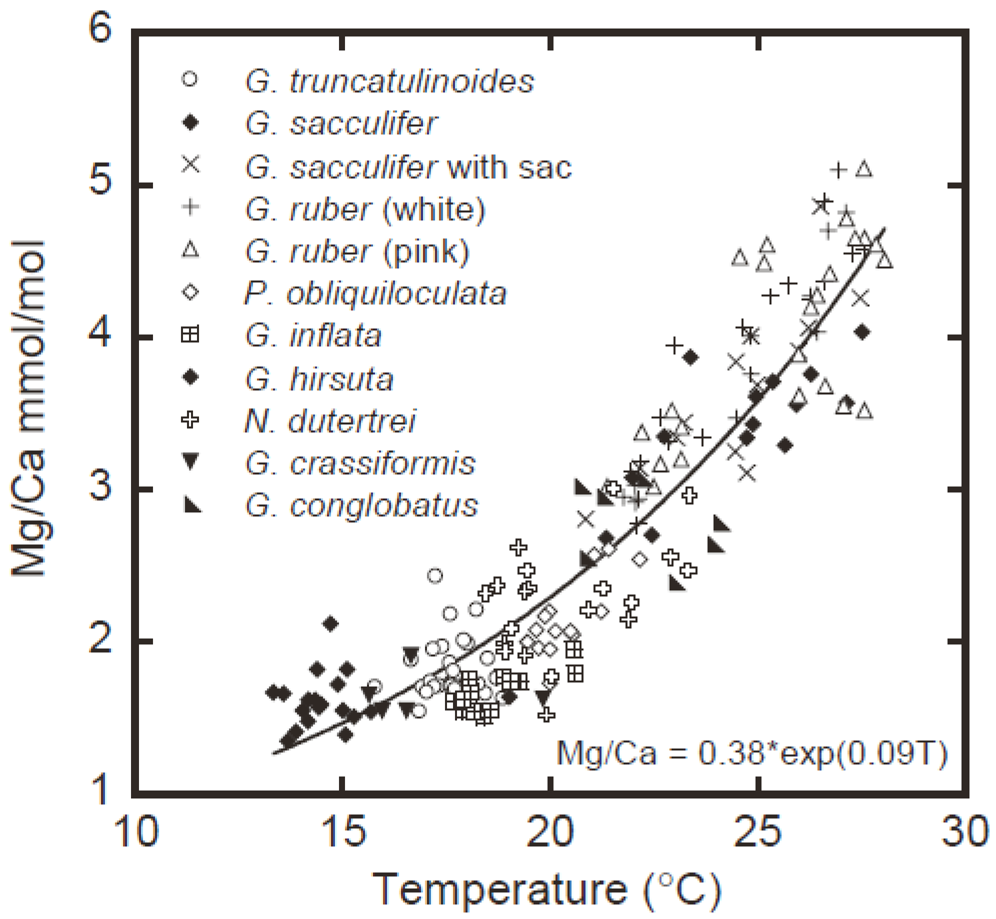
take up of Mg in calcite ($CaCO_3$)
in shell of foraminifera is temperature dependent
→ estimating seawater temperatures in the past







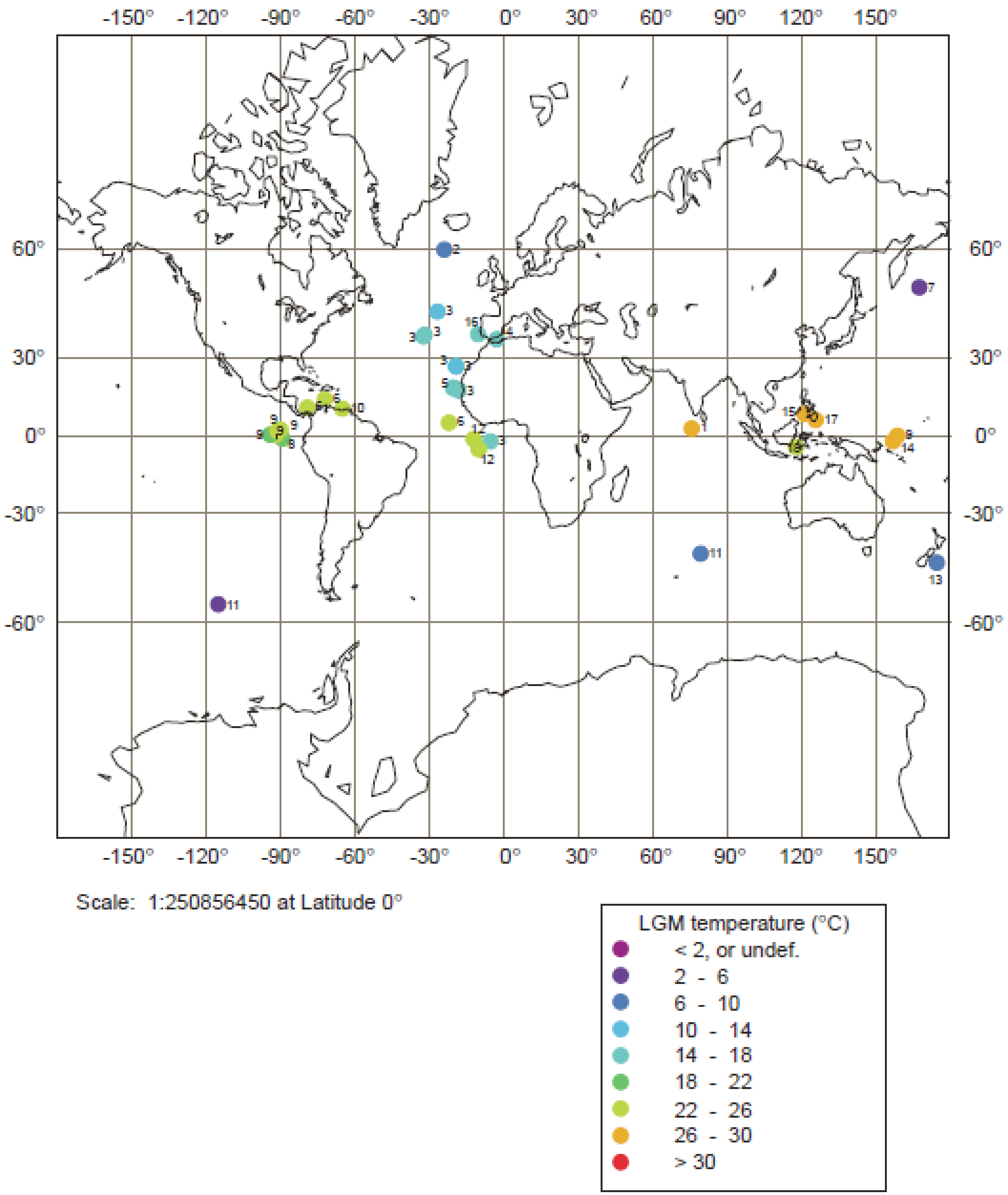
Mg/Ca-ratio as proxy for past oceanic temperature



Anand et al. (2003)

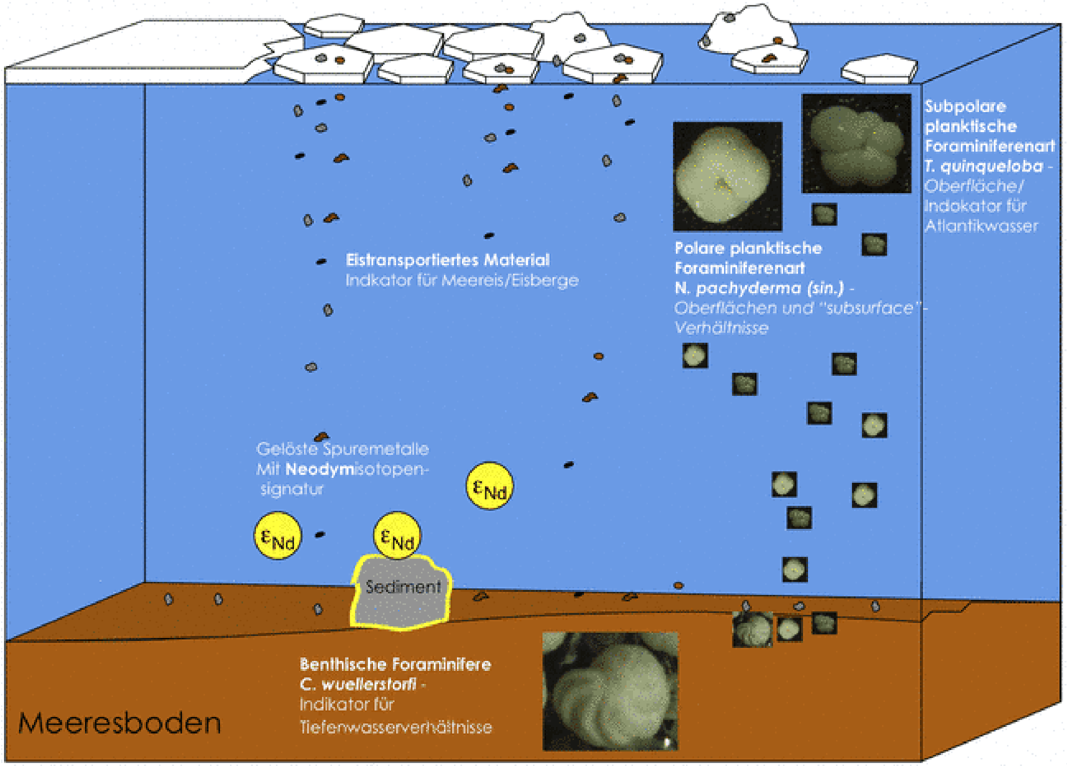
Mg/Ca-ratio as proxy for past oceanic temperature

Mg/Ca temperatures from planktonic foraminifers for the Last Glacial Maximum (LGM)



Barker et al. (2005) QSR

Multiproxy approach: εNd, $\delta^{18}O$, Ca/Mg ratio…

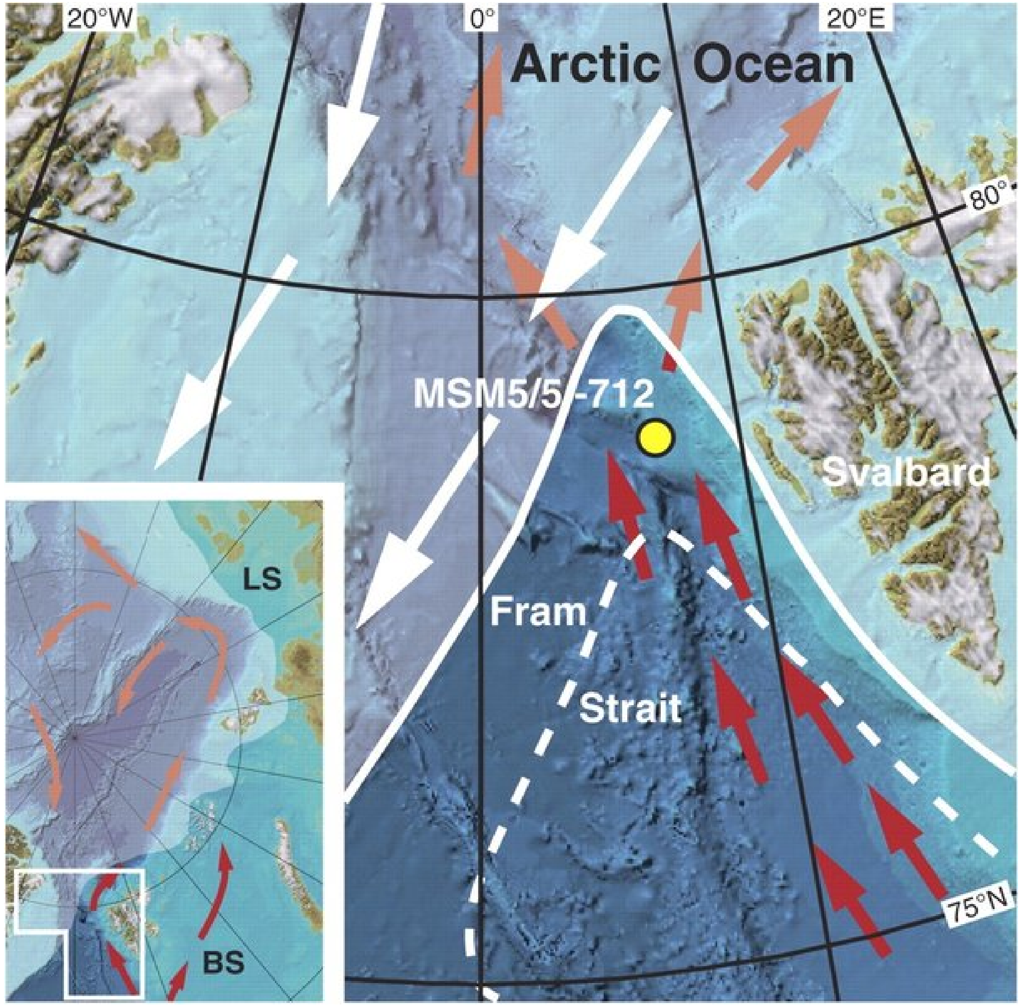


Spielhagen et al. (2011) Science, 331

Multiproxy approach: εNd, $\delta^{18}O$, Ca/Mg ratio…

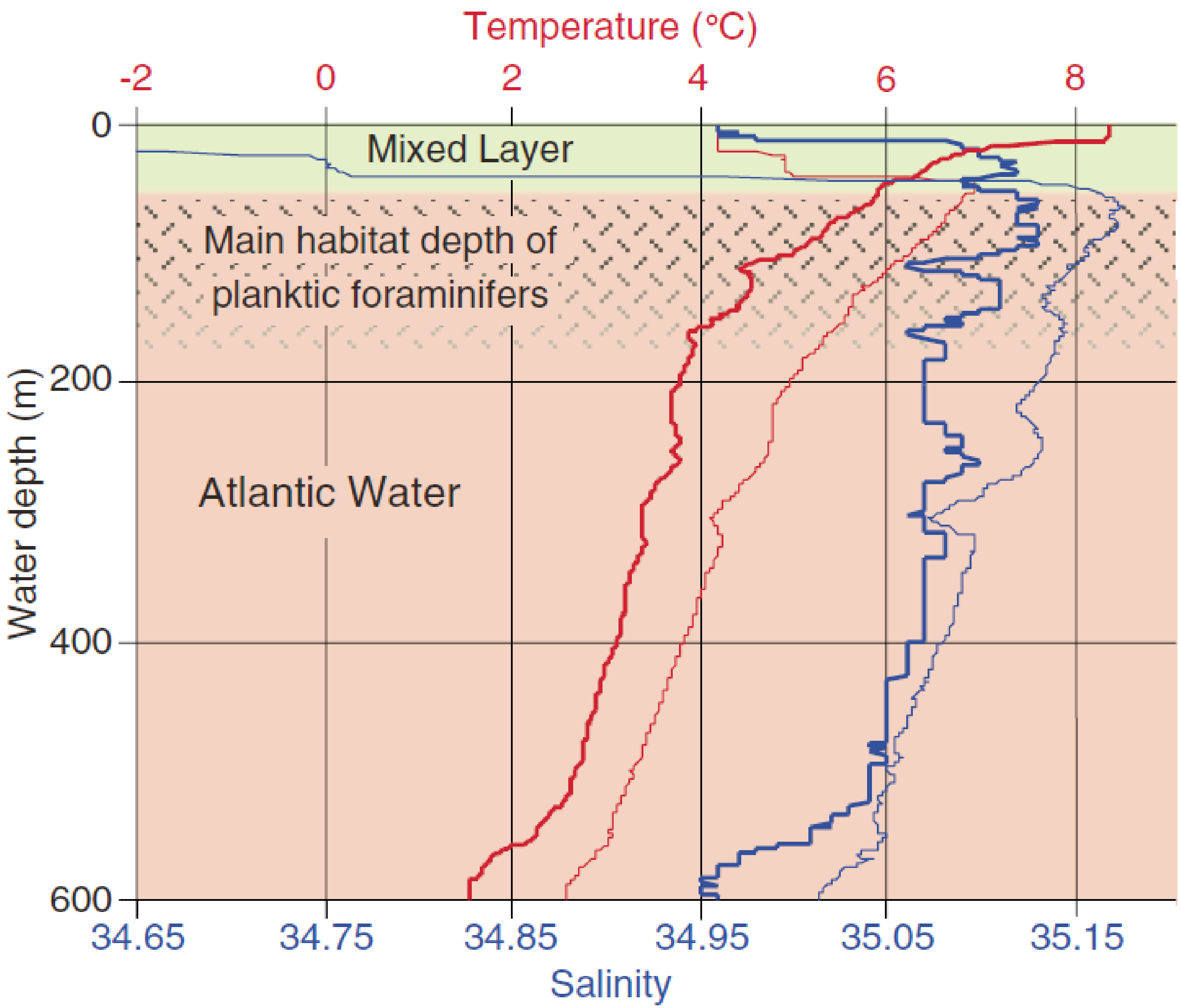
North Atlantic current is a main carrier of heat to the Arctic Ocean through the Fram Strait (red arrows)

Average sea ice cover indicated by white shading; white arrows: ice flow direction



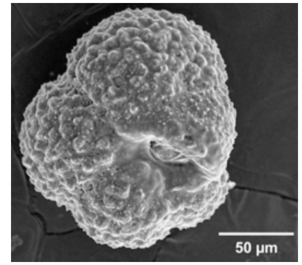
Spielhagen et al. (2011) Science, 331

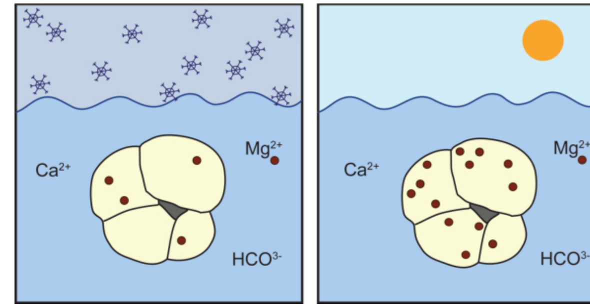
Multiproxy approach: εNd, $\delta^{18}O$, Ca/Mg ratio…

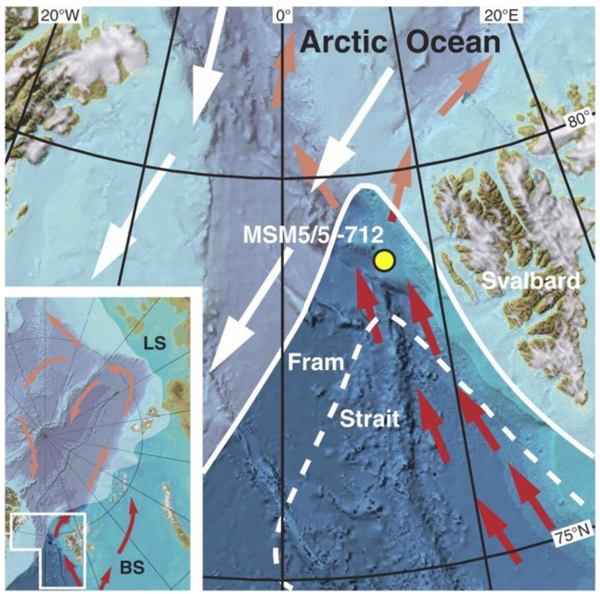


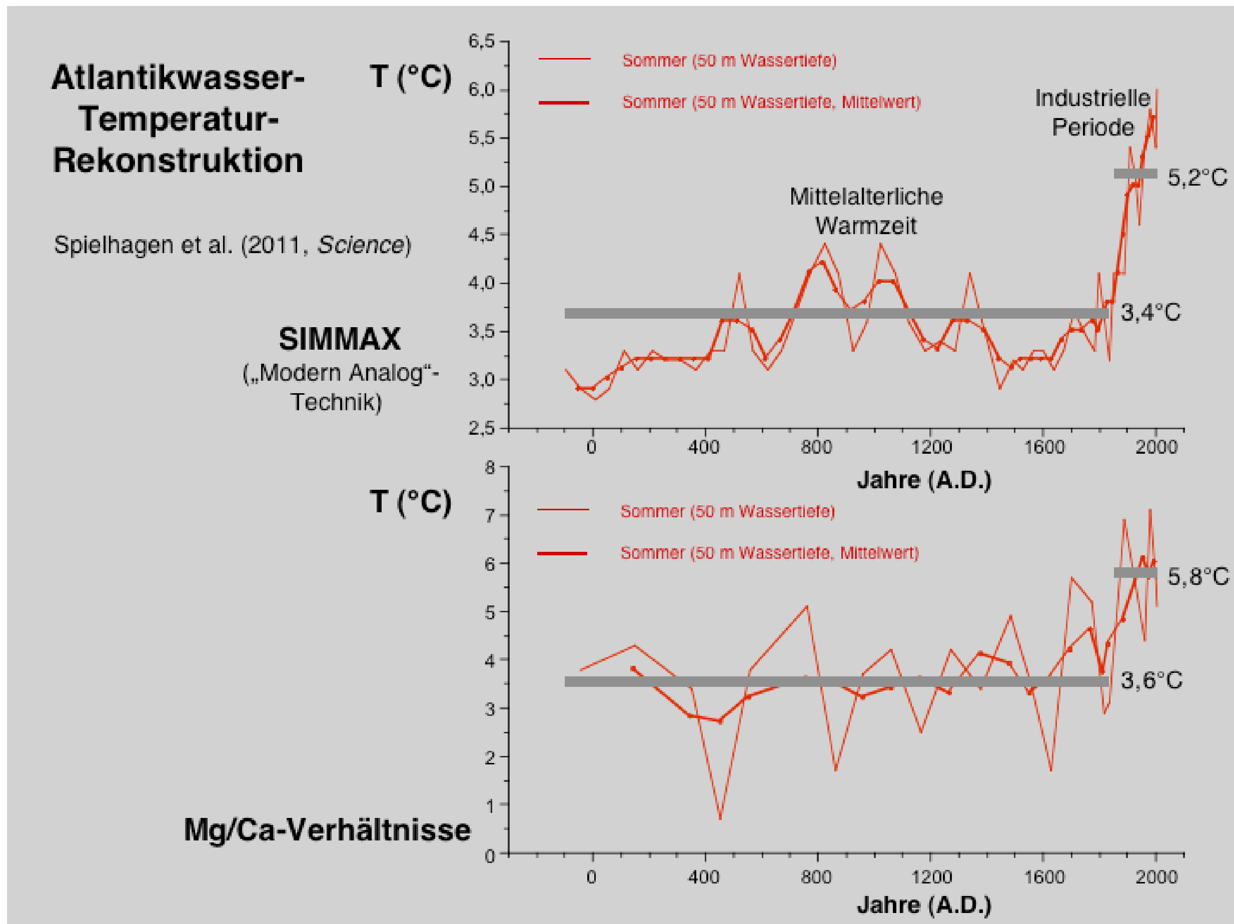
Spielhagen et al. (2011) Science, 331

Multiproxy approach: εNd, $\delta^{18}O$, Ca/Mg ratio…



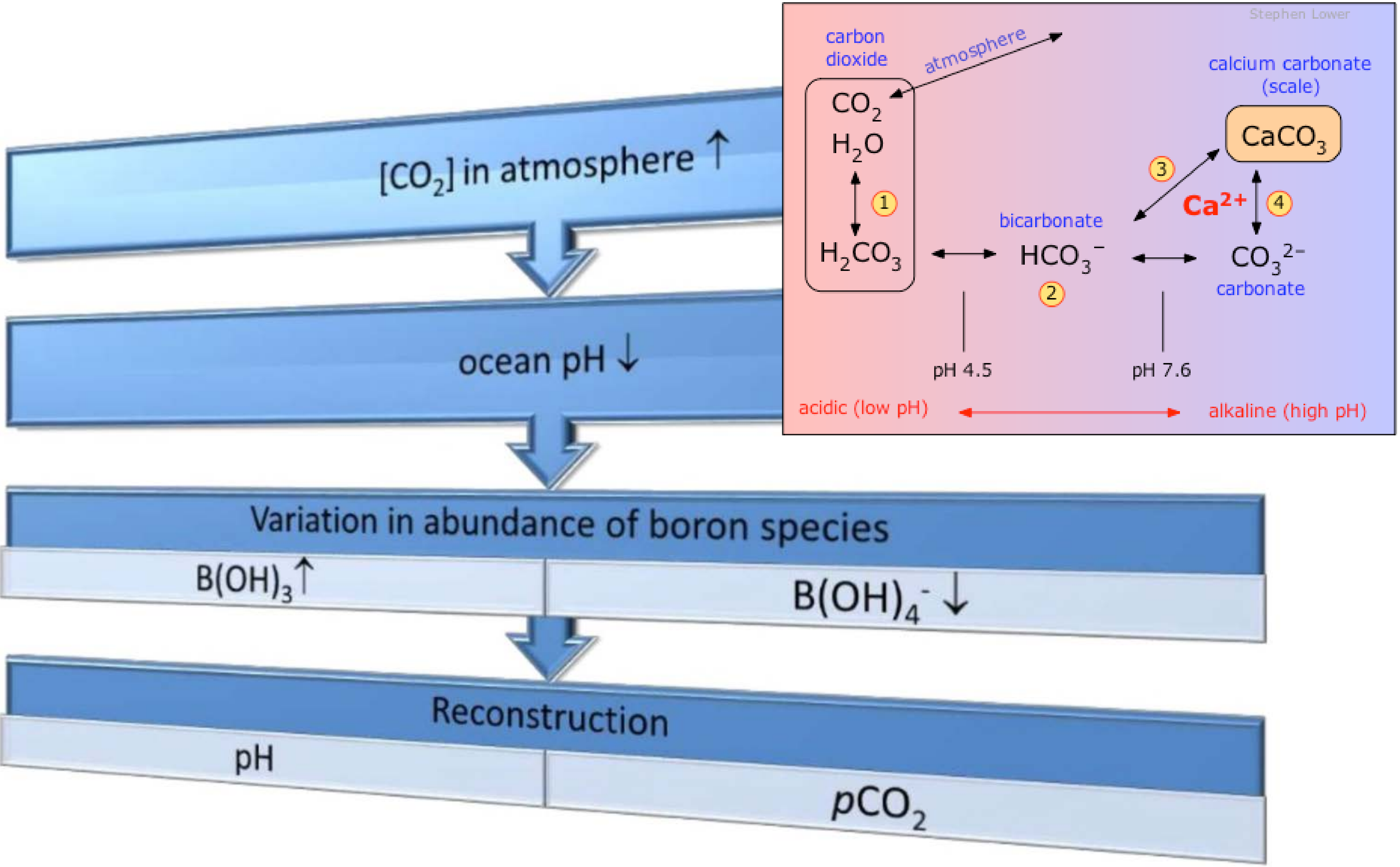






Spielhagen et al. (2011) Science, 331

Paleo-pH proxy

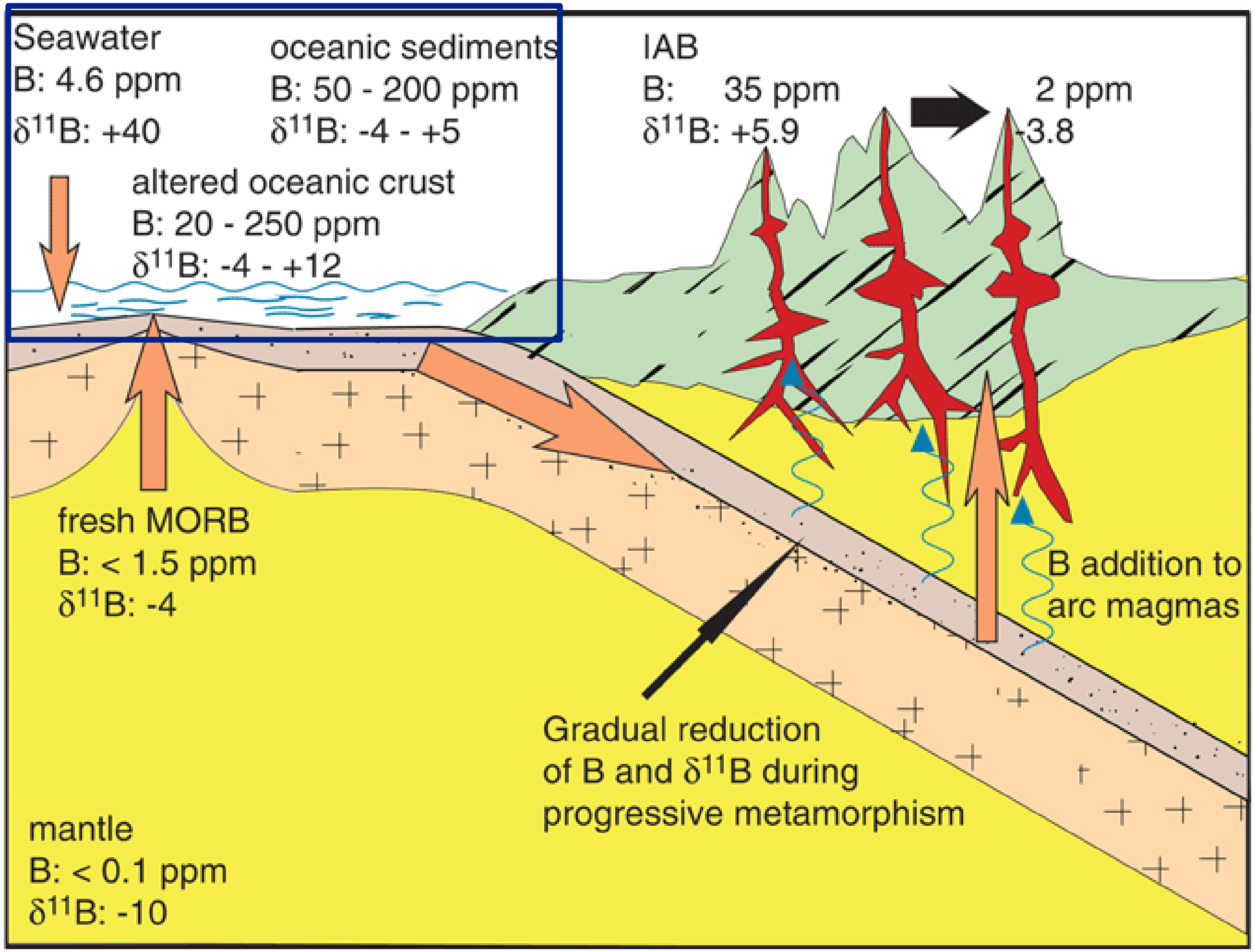


Paleo-pH proxy

boron is adsorbed onto clay particles as they enter the ocean

boron that is removed is isotopically light, leaving seawater isotopically heavy and sediments isotopically light

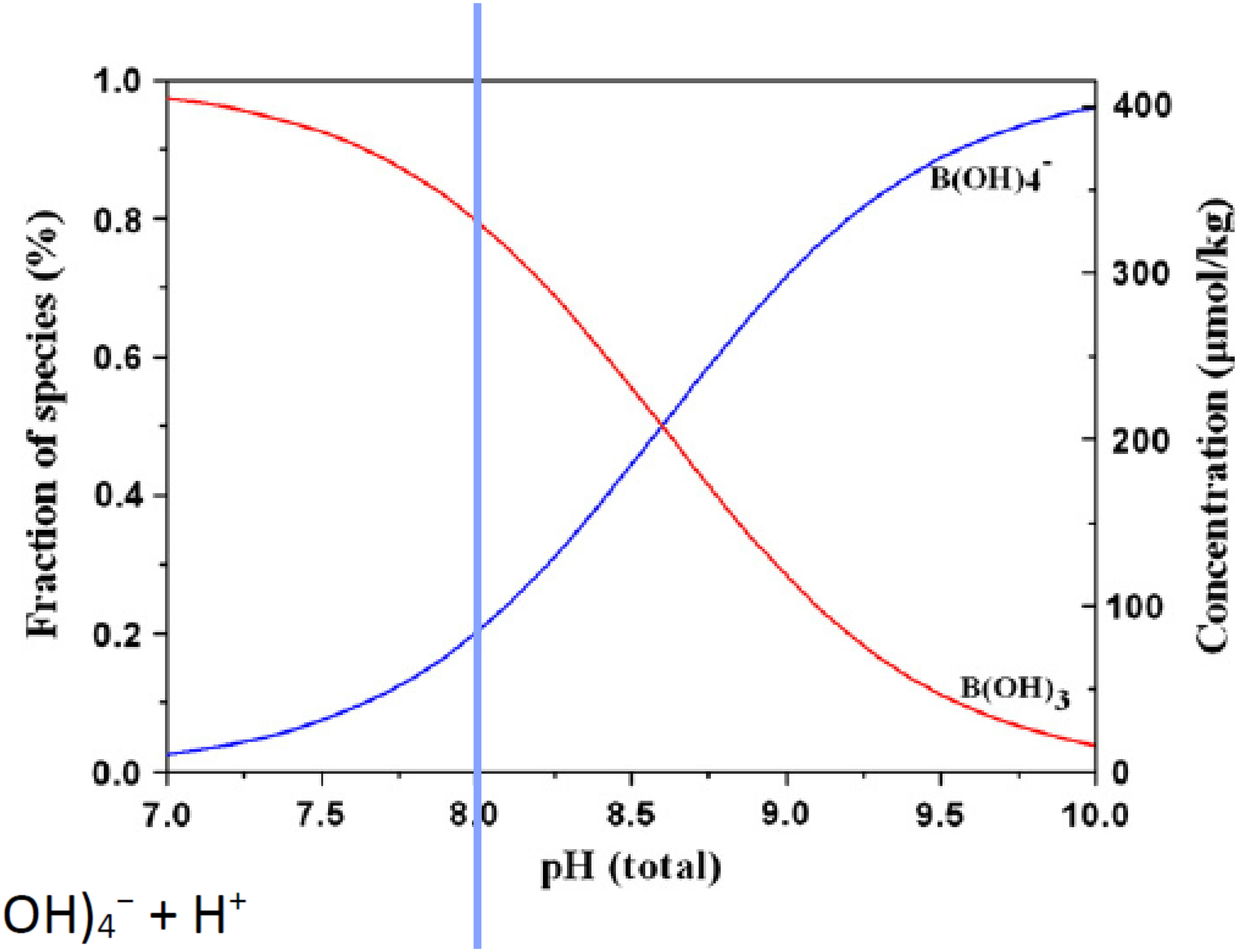
boron does not occur as a metal in seawater



Bor isotopes as paleo-pH proxy

At normal seawater pH boron is present ~80% as trigonal $B(OH)_3$ and ~20% as tetrahedral $B(OH)_4$ species

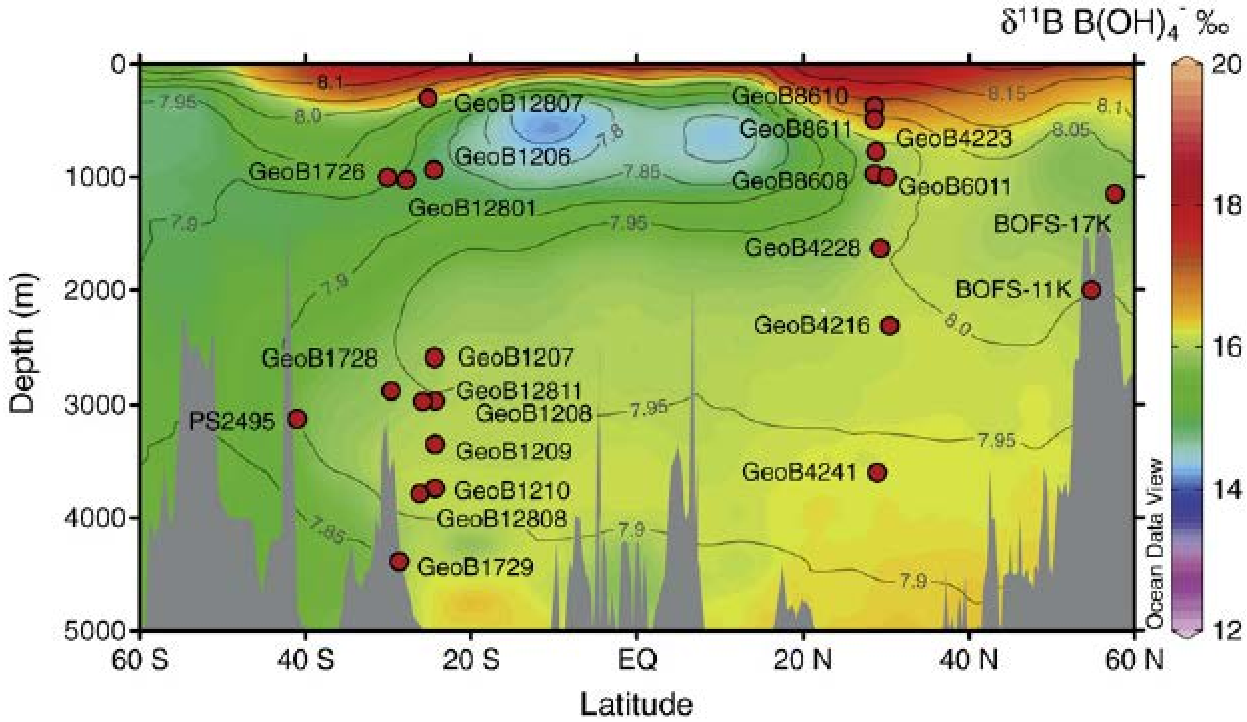
This distribution is pH controlled

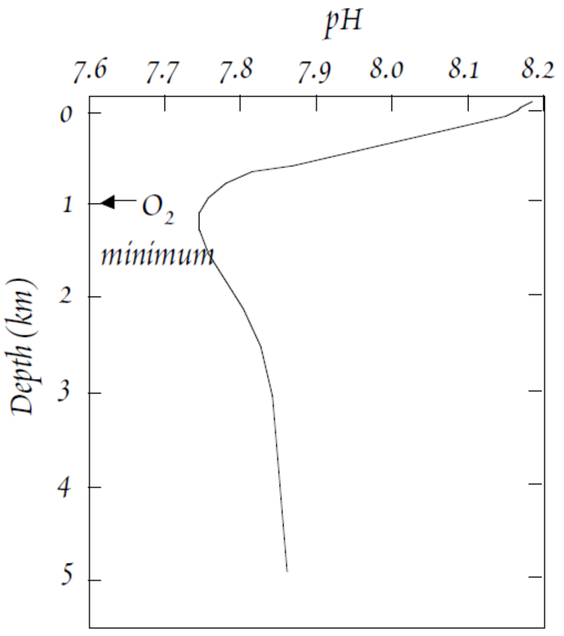


$$B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+$$

$$K_B = \frac{[B(OH)_4^-][H^+]}{[B(OH)_3]}$$

Paleo-pH proxy

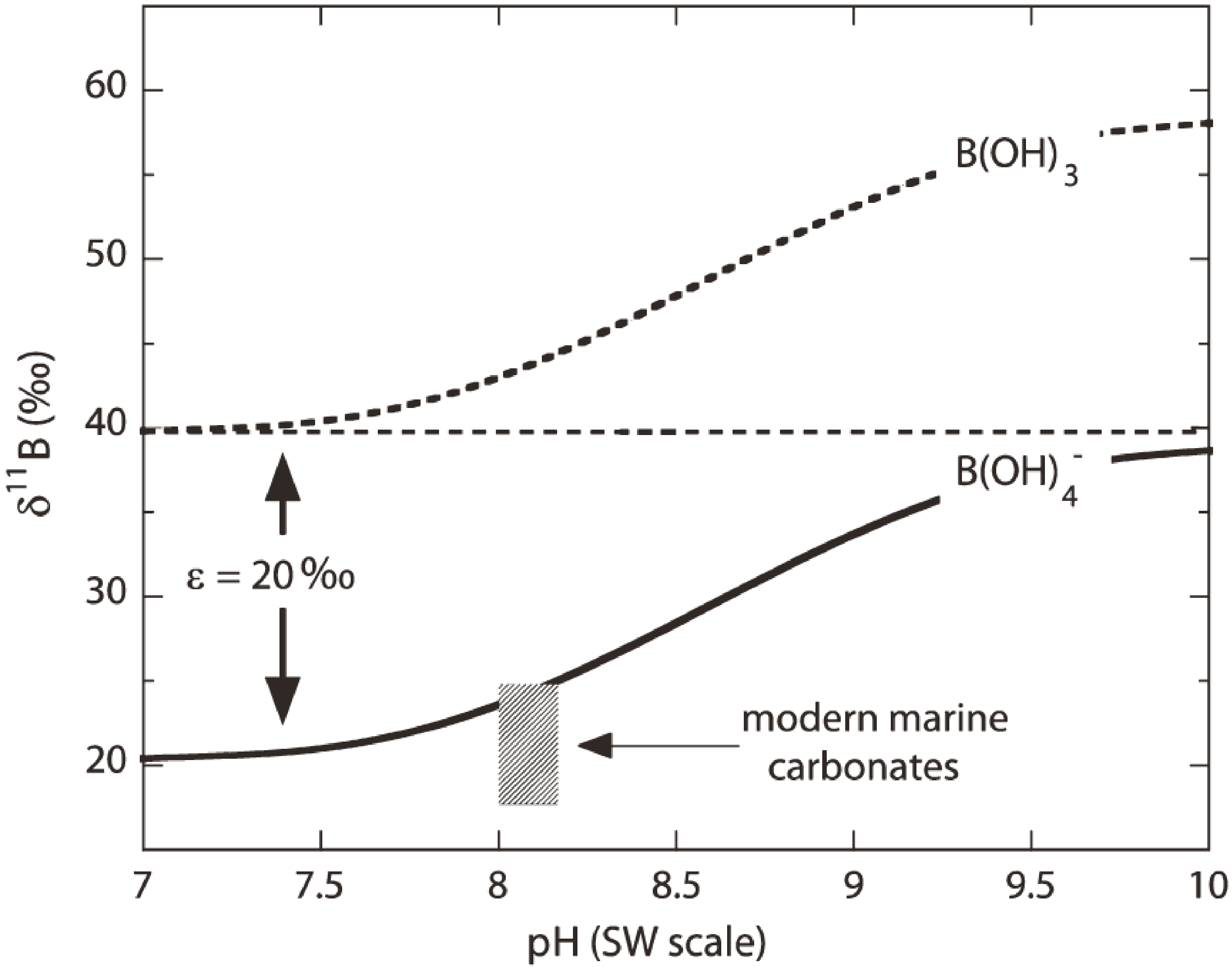




Ni et al. (2005) Core-top calibrations for boron isotope paleo-pH proxy

Bor isotopes as paleo-pH proxy

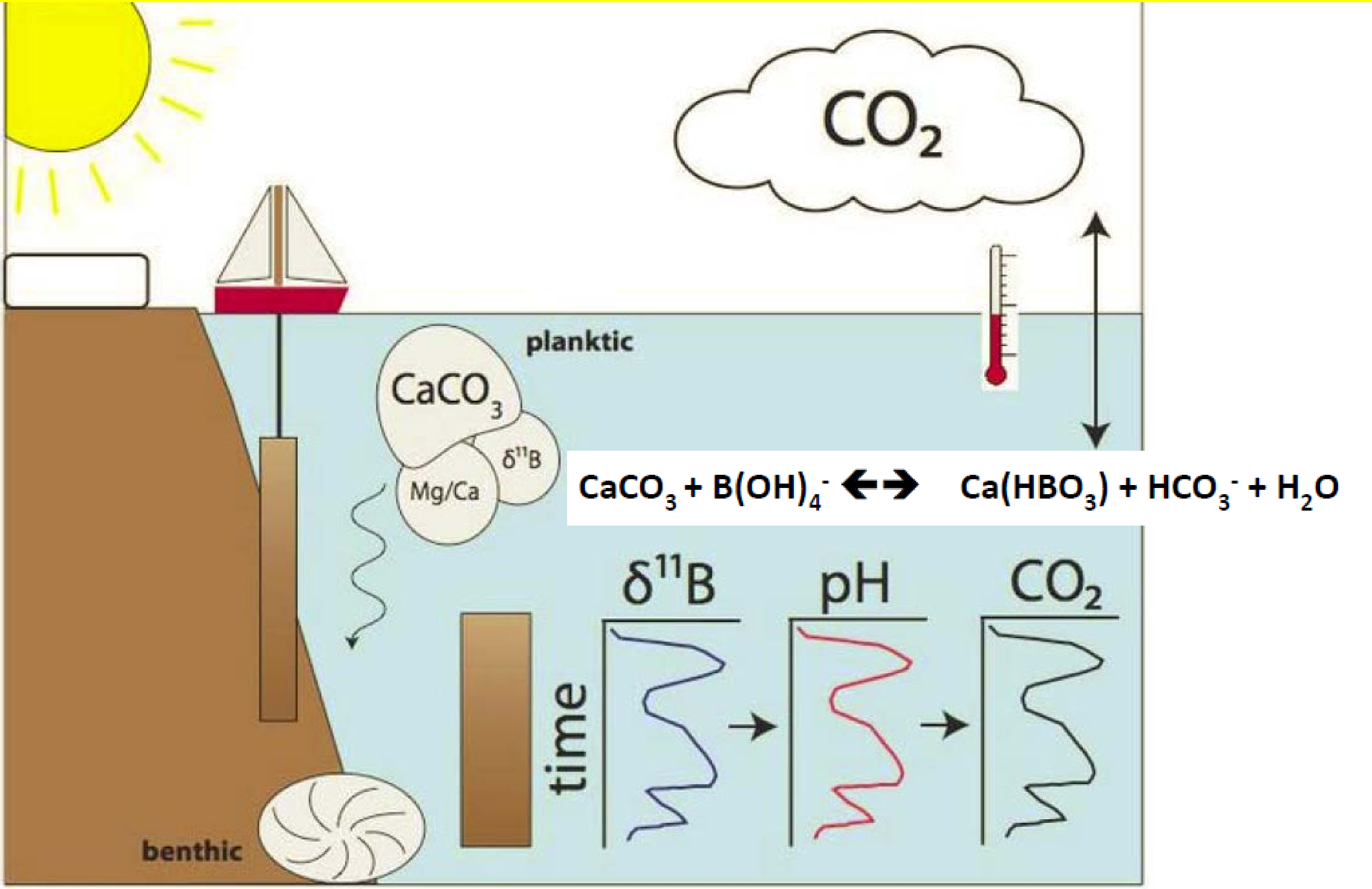
isotopic composition of the dissolved boron species (borate and boric acid) as a function of pH. Boron isotopes are fractionated between the two species



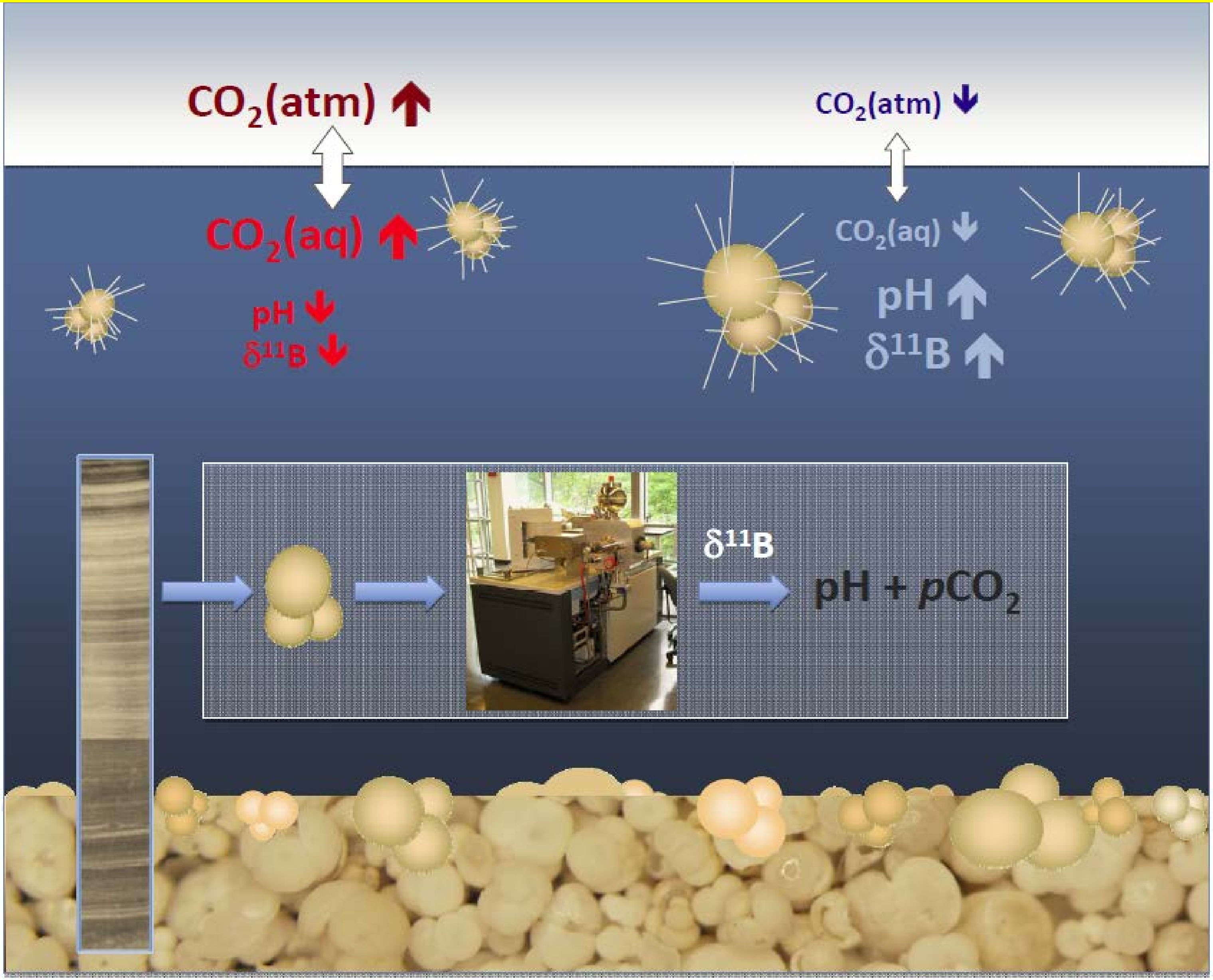
$B(OH)_4$ thought to be the species incorporated into marine carbonates:

$$CaCO_3 + B(OH)_4^- \leftrightarrow Ca(HBO_3) + HCO_3^- + H_2O$$

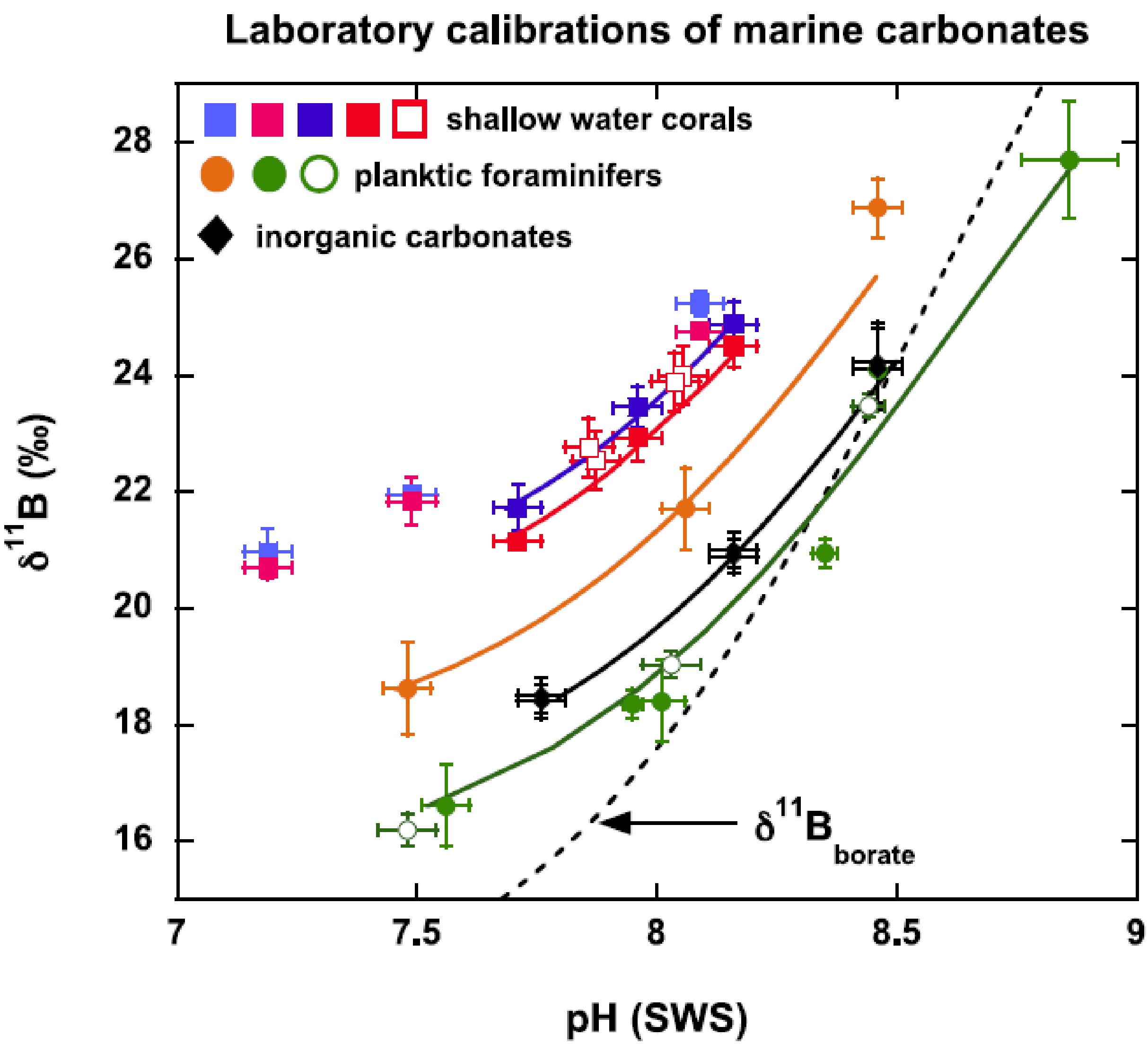
Bor isotopes as paleo-pH proxy



Bor isotopes as paleo-pH proxy



Bor isotopes as paleo-pH proxy



MC-ICP-MS
S. pistillata (Krief et al. 2010)
Porites sp. (Krief et al. 2010)
O. universa (Hönisch & Rae, unpubl.)

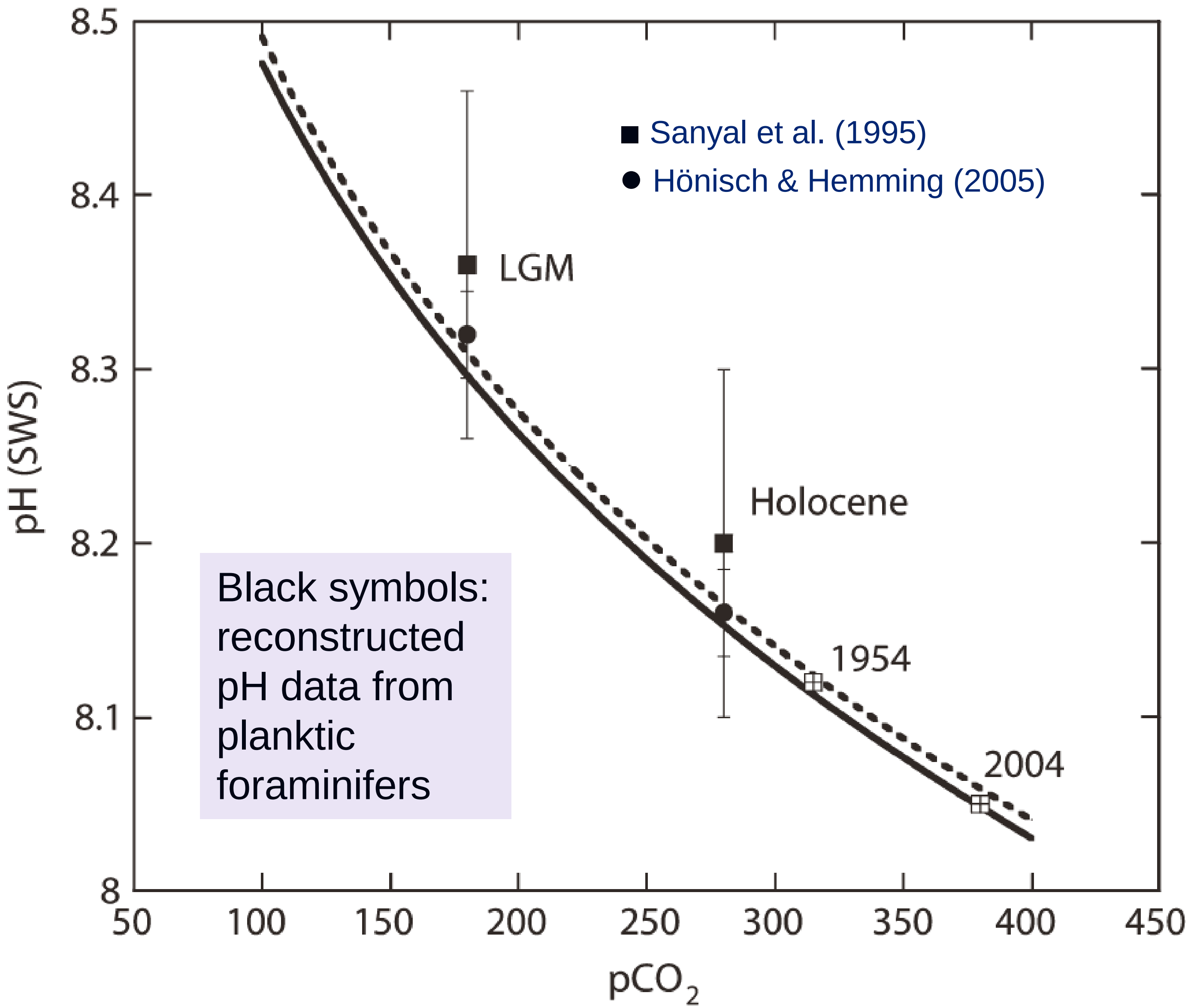
N-TIMS
P. cylindrica (Hönisch et al. 2004)
Acropora sp. (Reynaud et al., 2004)
A. nobilis (Hönisch et al. 2004)
G. sacculifer (Sanyal et al. 2001)
inorganic calcite (Sanyal et al. 2000)
O. universa (Sanyal et al. 1996)

Obstacles: species-specific offsets, effects of seawater secular variation, diagenetic effects ….

Source: http://www.pmc.ucsc.edu/

Bor isotopes as paleo-pH proxy

curves:
surface ocean pH for a given atmospheric pCO_2

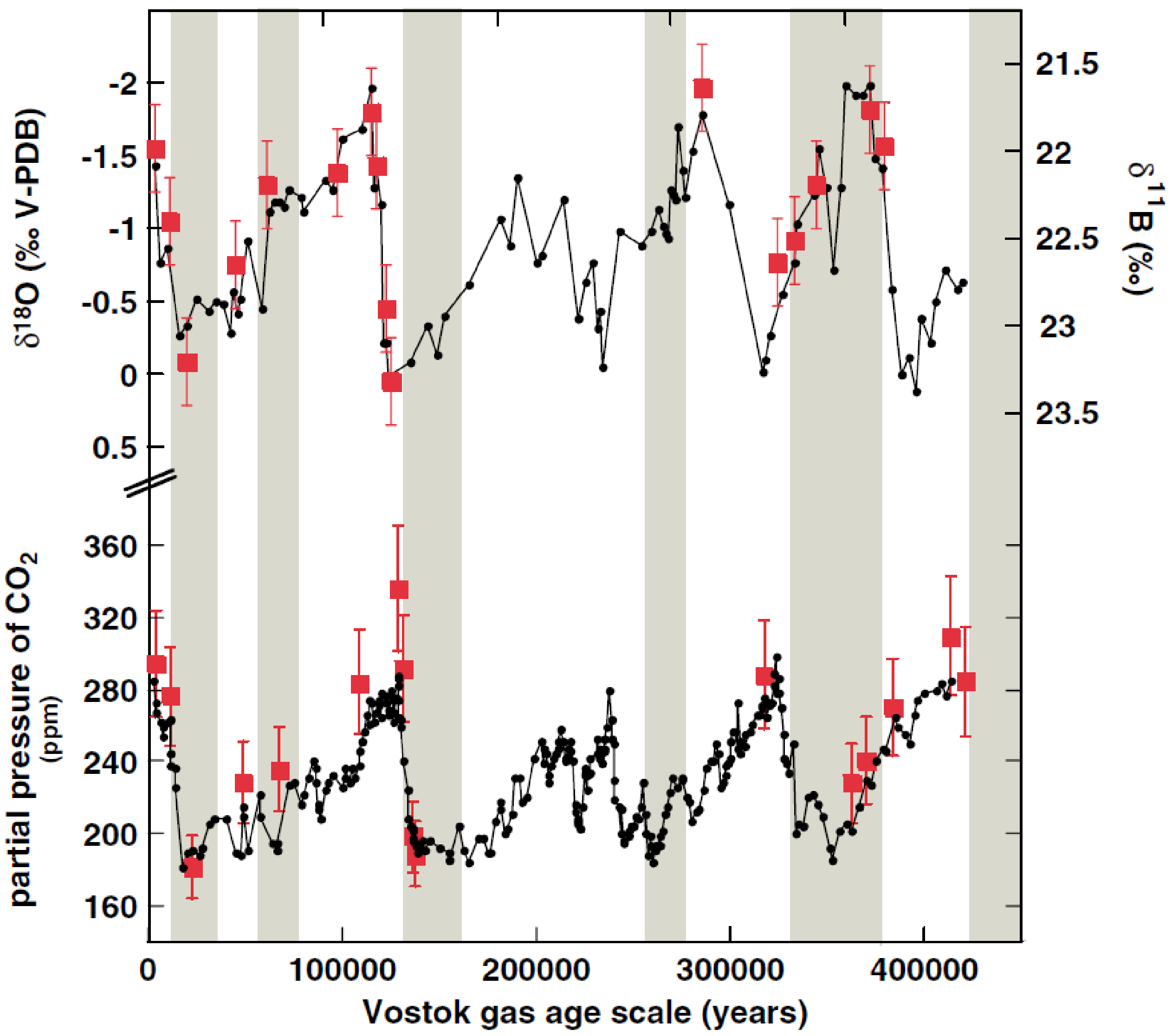


Black symbols: reconstructed pH data from planktic foraminifers

(Hemming & Hönisch 2007)

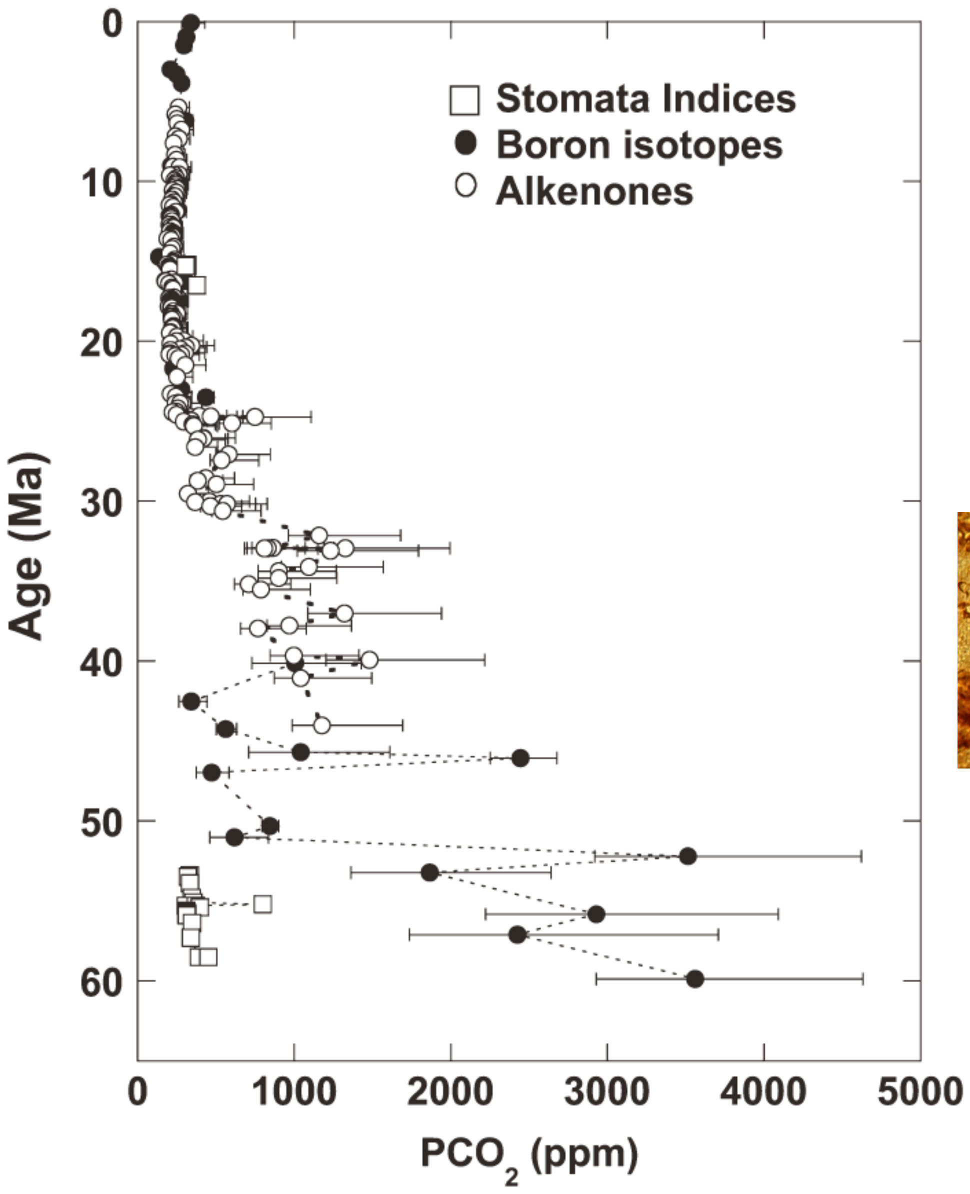
Bor isotopes as paleo-pH proxy

Boron and oxygen isotope data (above) and atmospheric pCO_2 of air trapped in ice core (below) from eastern equatorial Atlantic
(ODP site 668B Vostok ice core)



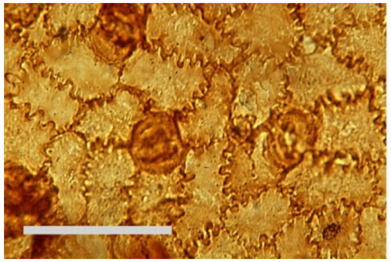
(Hemming & Hönisch 2007)

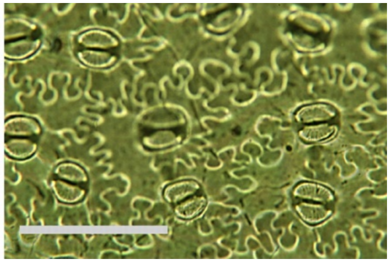
Bor isotopes as paleo-pH proxy



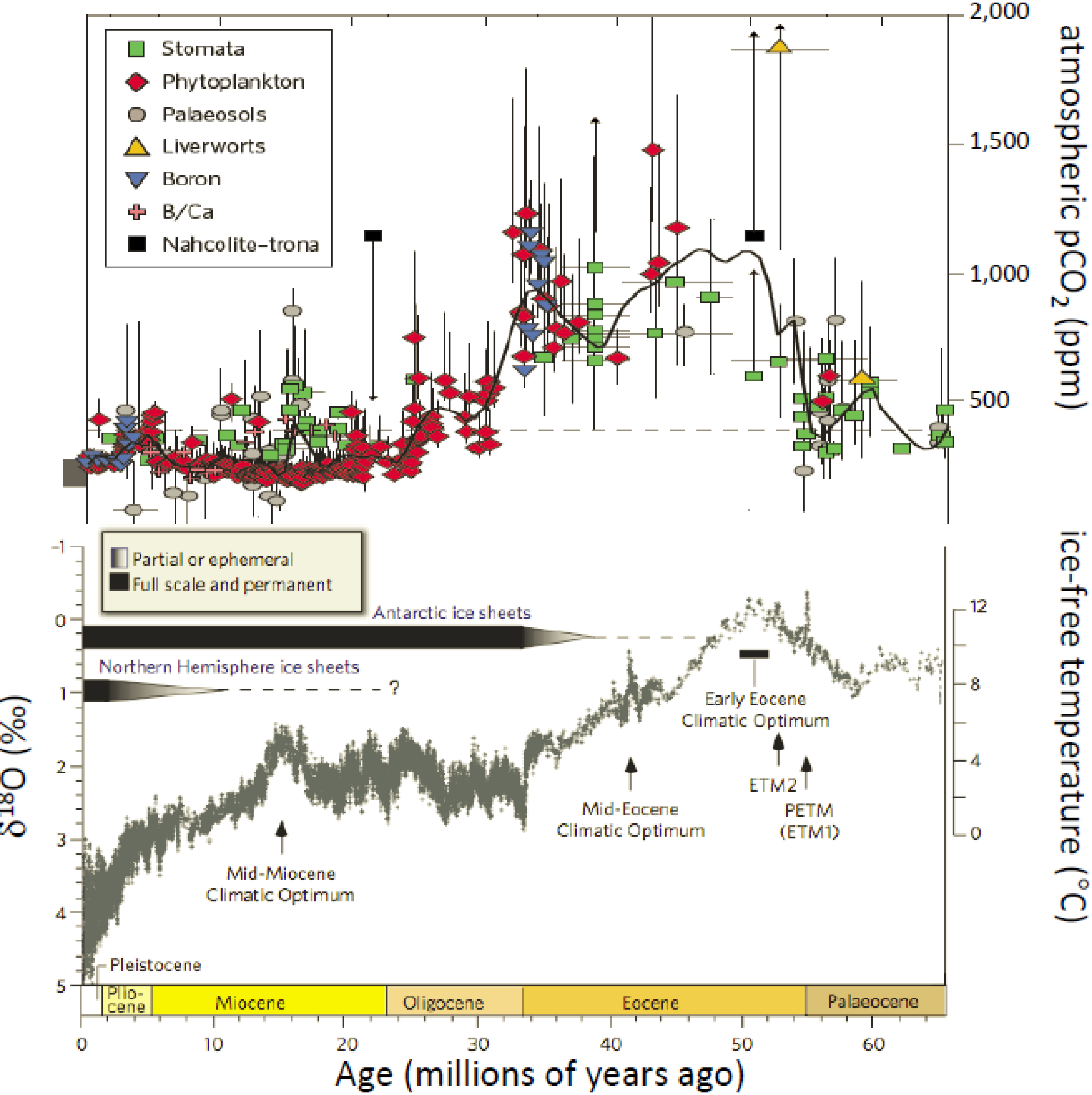
pCO$_2$ through the Cenozoic
(Hemming & Hönisch 2007 and refs. therein)

stomatal CO$_2$ proxy





other paleo-CO_2 proxies



Beerling & Royer, Nature Geoscience, 2011

Zachos et al., Nature, 2008