LIMNOLOGY AND OCEANOGRAPHY
ASLO e-Lectures

Ocean Acidification

A Paleo Perspective

Adina Paytan
University of California Santa Cruz

Bärbel Hönisch
LDEO Columbia University

Image credit: NOAA

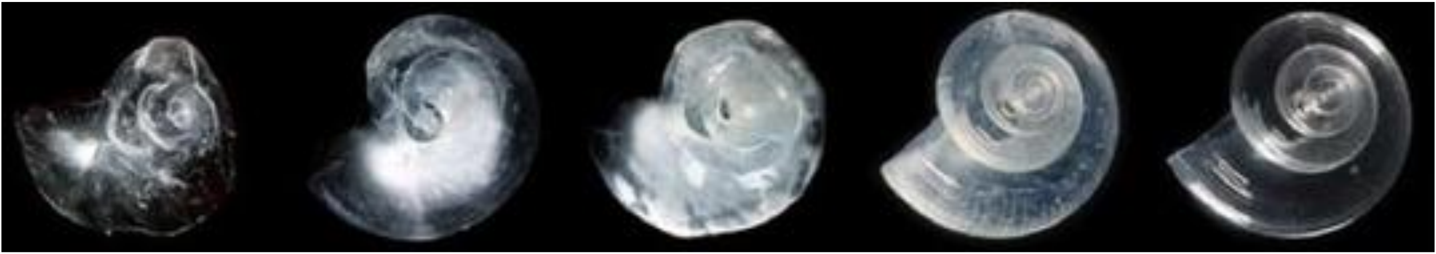
Outline

1. Ocean acidification: a brief overview
2. What can we learn from the geological record?
3. Archives and proxies for pCO_2 and marine carbonate chemistry reconstruction
4. Past records of pCO_2 and acidification events

doi:10.1002/loe2.10003

CO_2 | Carbonic acid | Bicarbonate ion | Hydrogen ion | Carbonate ion

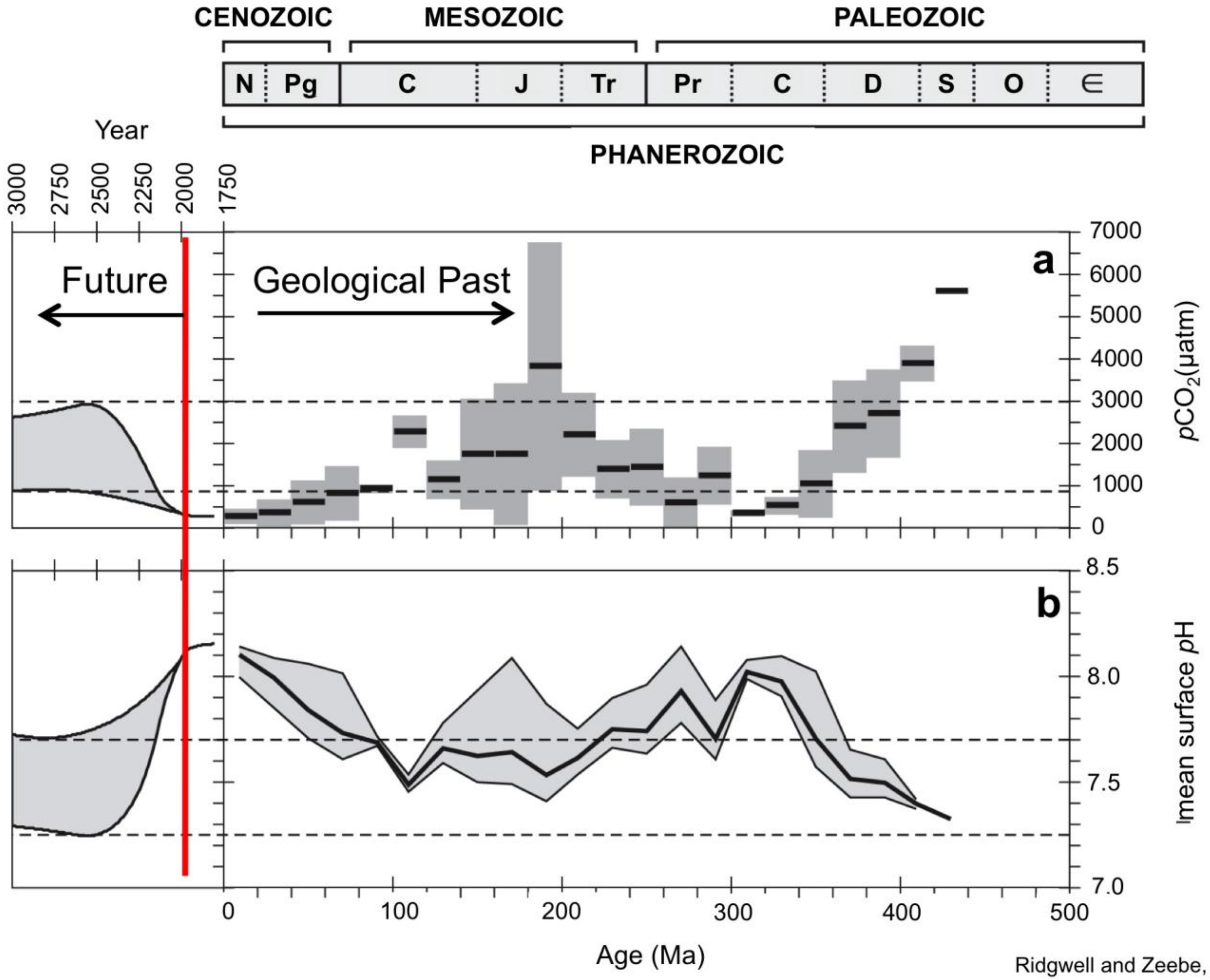
$$CO_2 + H_20 \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+$$



More acidic ↔ More basic

modified from Feely and Doney, 2011

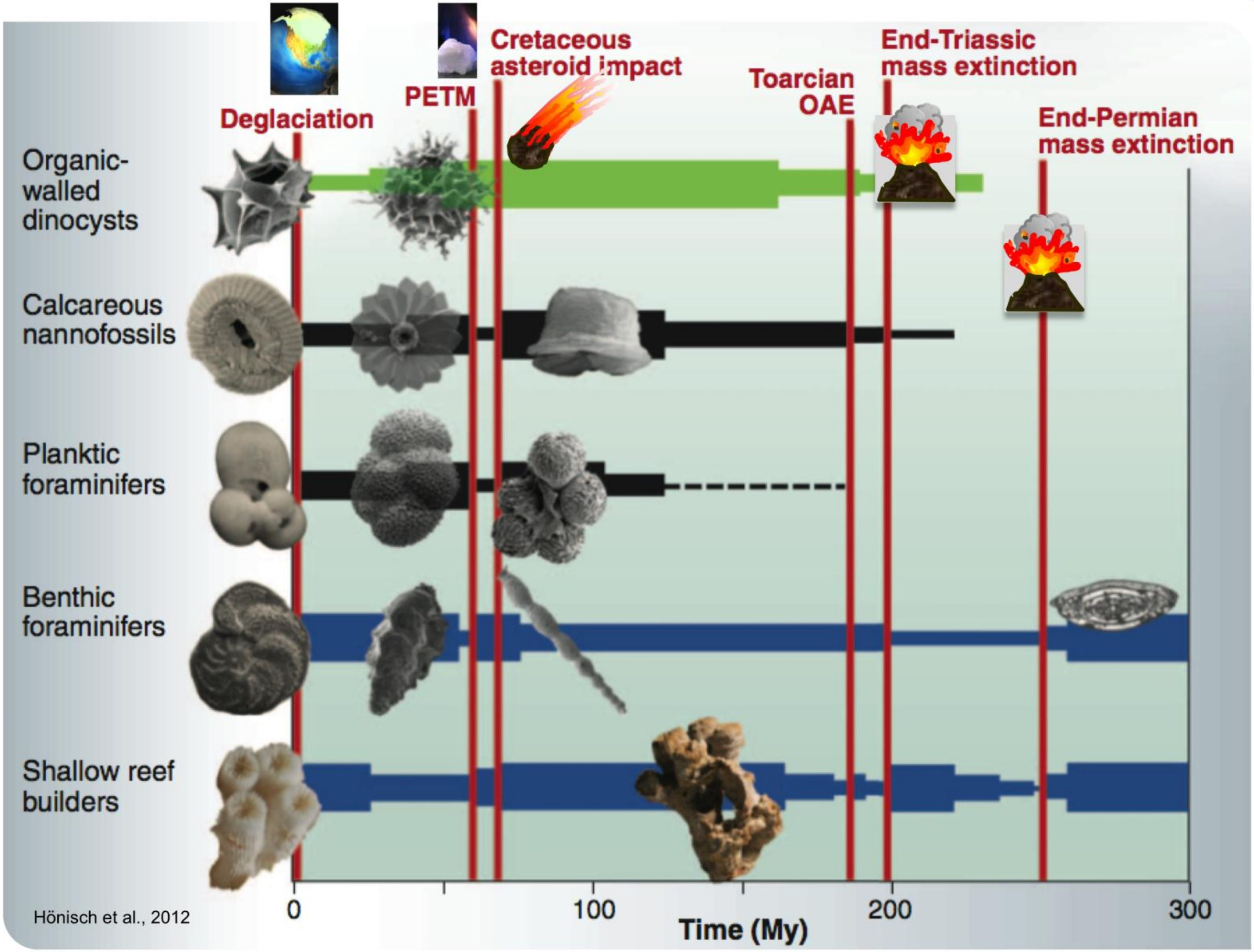
Carbon dioxide in the atmosphere has varied in the past



Ridgwell and Zeebe, 2005

doi:10.1002/loe2.10003

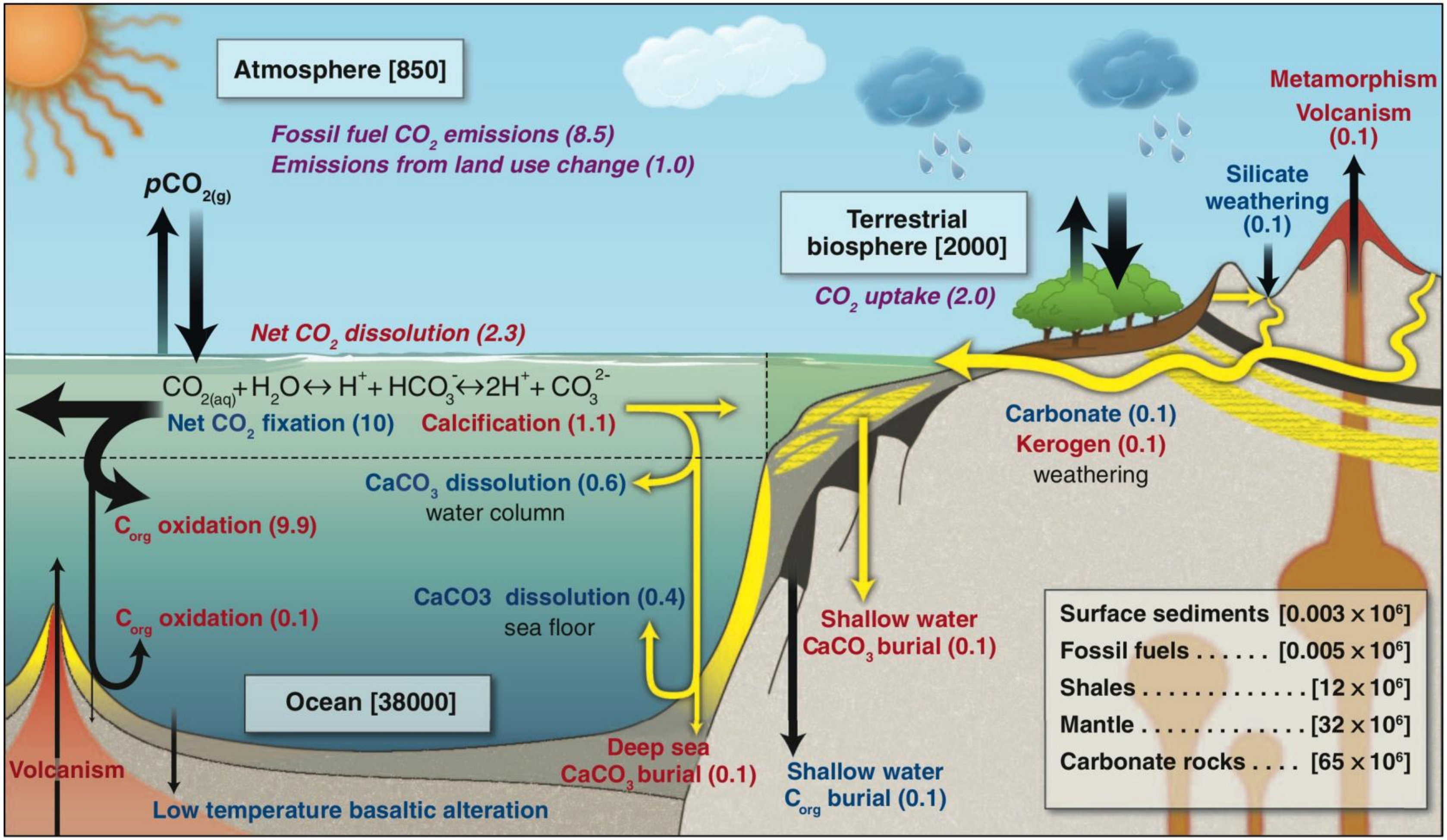
Insights from the Geological Record



Hönisch et al., 2012

doi:10.1002/loe2.10003

The Carbon Cycle



Atmosphere [850]

Fossil fuel CO_2 emissions (8.5)
Emissions from land use change (1.0)

$pCO_{2(g)}$

Net CO_2 dissolution (2.3)

$CO_{2(aq)} + H_2O \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$

Net CO_2 fixation (10)

Calcification (1.1)

$CaCO_3$ dissolution (0.6) water column

C_{org} oxidation (9.9)

CaCO3 dissolution (0.4) sea floor

C_{org} oxidation (0.1)

Ocean [38000]

Volcanism

Low temperature basaltic alteration

Deep sea $CaCO_3$ burial (0.1)

Shallow water C_{org} burial (0.1)

Shallow water $CaCO_3$ burial (0.1)

Terrestrial biosphere [2000]

CO_2 uptake (2.0)

Metamorphism
Volcanism
(0.1)

Silicate weathering (0.1)

Carbonate (0.1)
Kerogen (0.1)
weathering

Surface sediments	$[0.003 \times 10^6]$
Fossil fuels	$[0.005 \times 10^6]$
Shales	$[12 \times 10^6]$
Mantle	$[32 \times 10^6]$
Carbonate rocks	$[65 \times 10^6]$

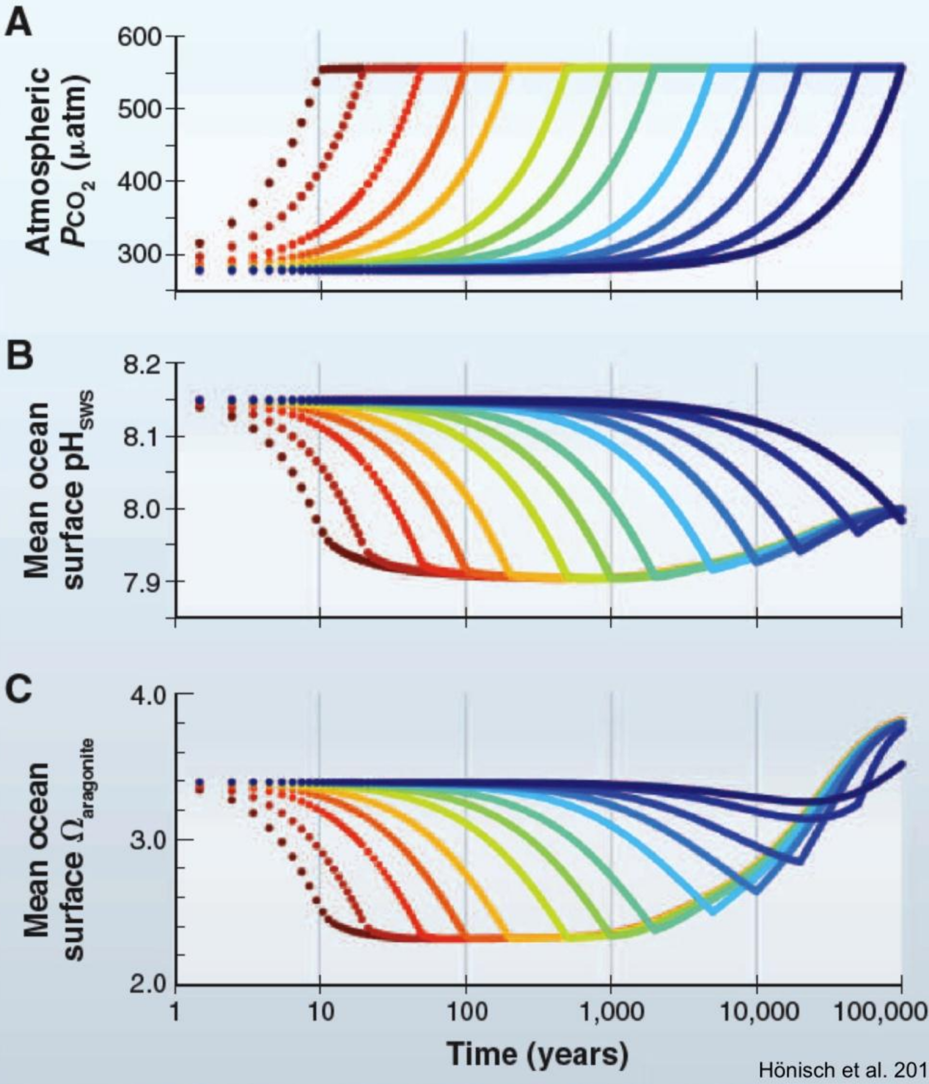
Hönisch et al. 2012

Decoupling of pH and $CaCO_3$ Saturation State

Decoupling of seawater-pH and saturation state on long time scales

An 'ocean acidification *event*' is a time interval in Earth's history that involved geologically 'rapid' changes of ocean carbonate chemistry on timescales <10,000 years.

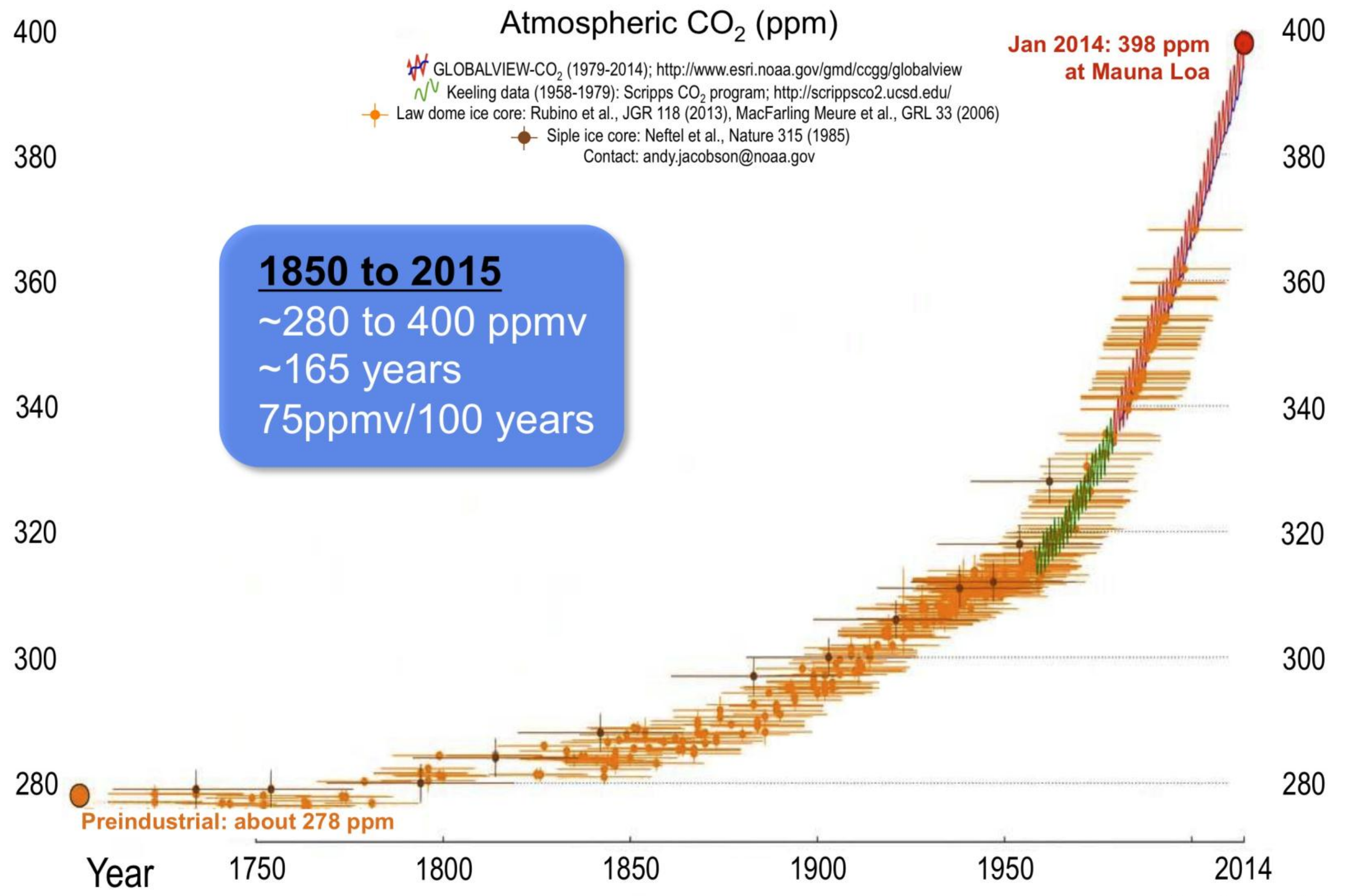
Such time scales are too rapid for weathering – the process that restores carbonate saturation in the ocean - to respond.



Hönisch et al. 2012

doi:10.1002/loe2.10003

Ice-core data before 1958. Mauna Loa data after 1958



1850 to 2015

~280 to 400 ppmv

~165 years

75ppmv/100 years

Andy Jacobson, NOAA

doi:10.1002/loe2.10003

Archives and Proxies for Ocean Acidification Reconstruction

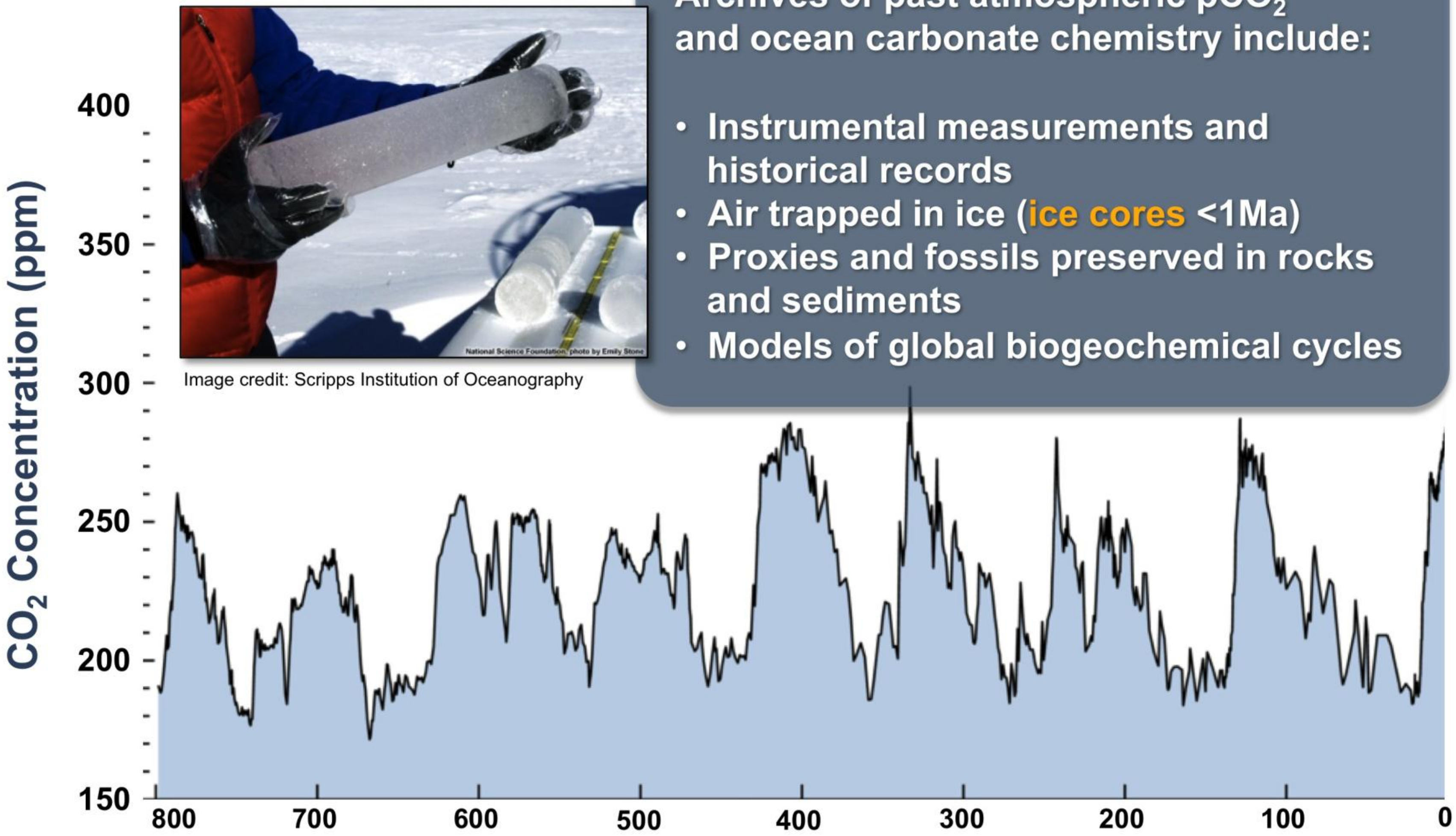


Image credit: Scripps Institution of Oceanography

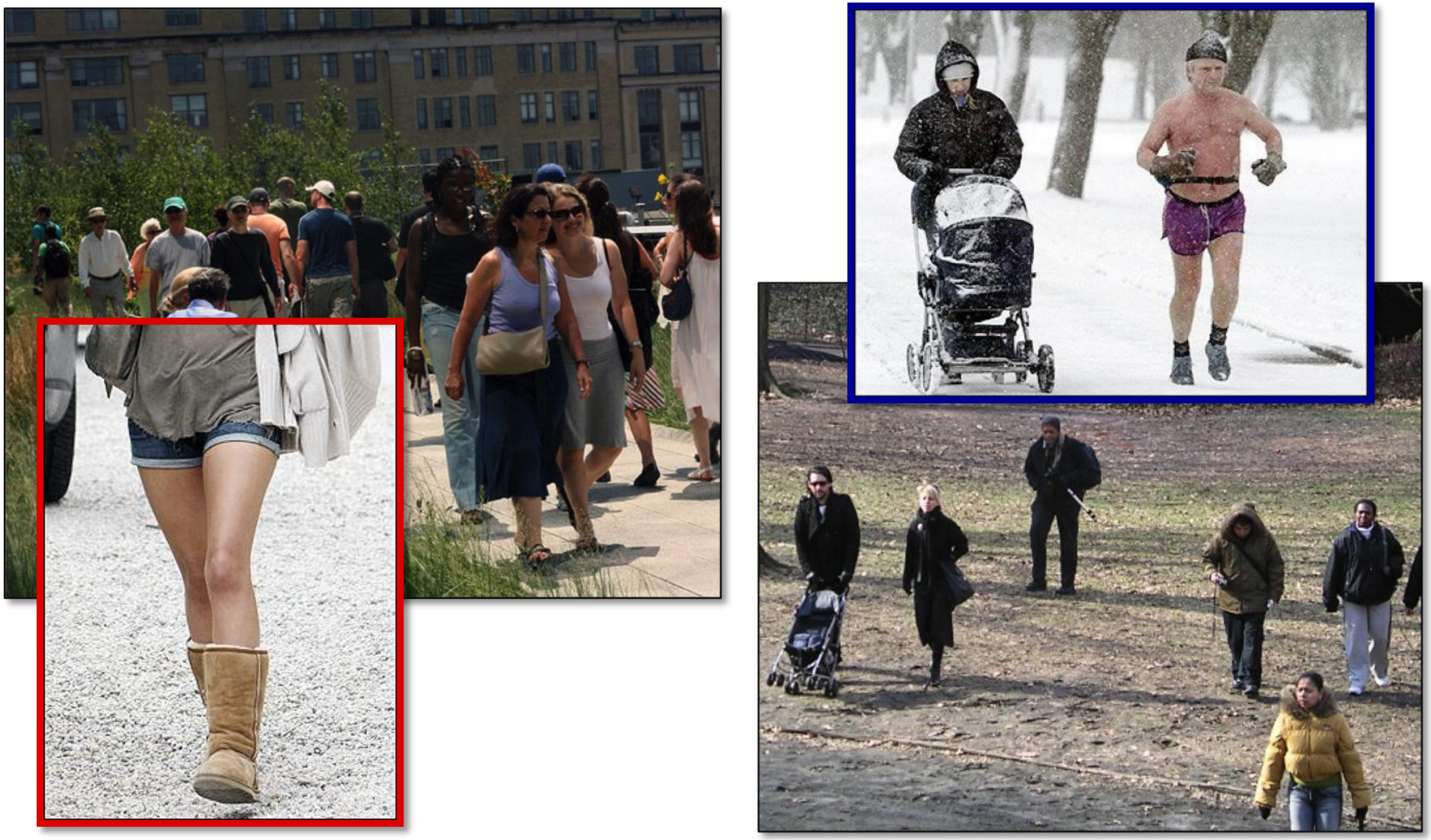
Archives of past atmospheric pCO_2 and ocean carbonate chemistry include:

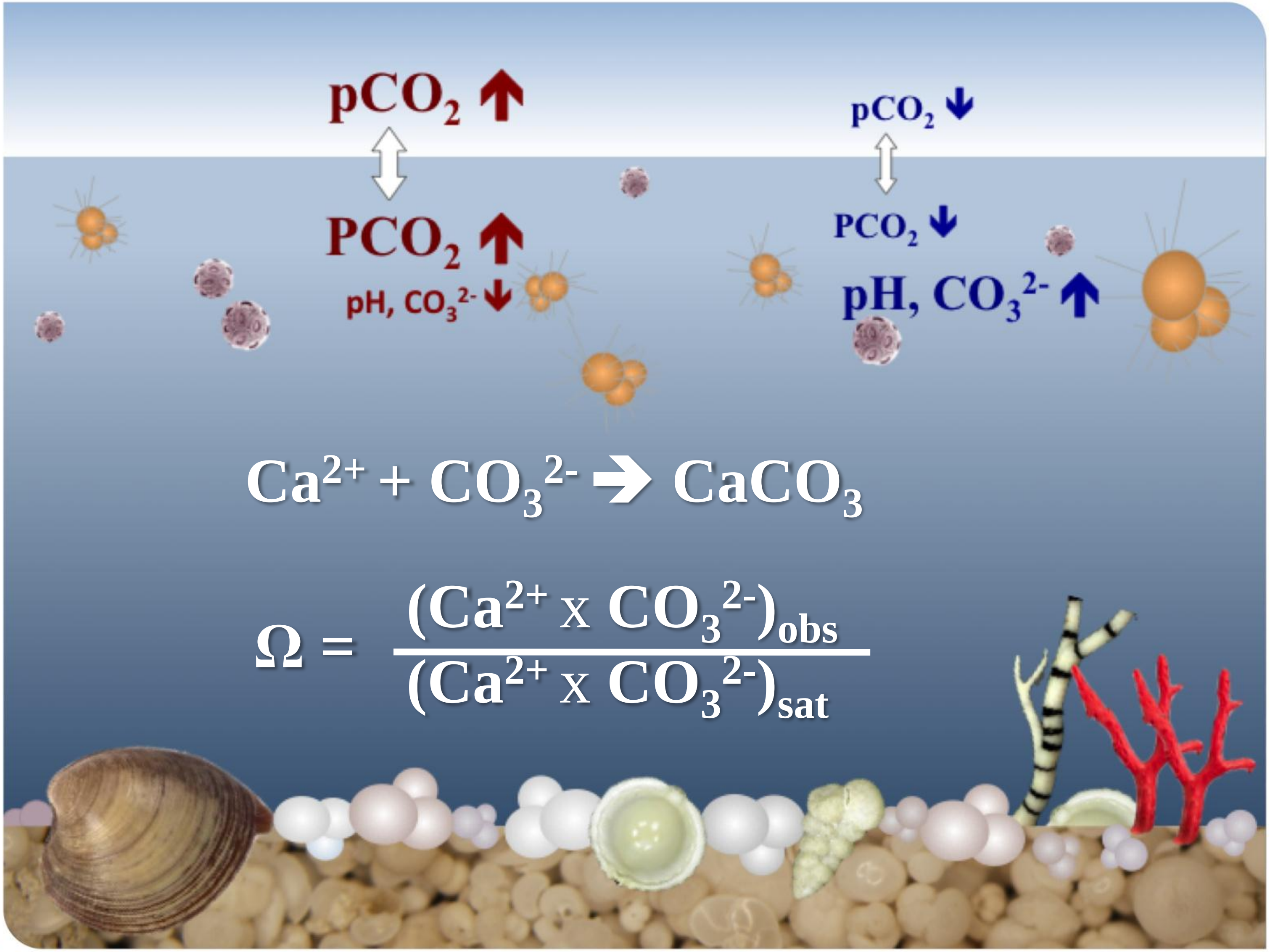
- Instrumental measurements and historical records
- Air trapped in ice (ice cores <1Ma)
- Proxies and fossils preserved in rocks and sediments
- Models of global biogeochemical cycles

Petit et al. 1999, Siegenthaler et al. 2005, Lüthi et al. 2008

doi:10.1002/loe2.10003

Proxies are stand-ins for environmental parameters that can no longer be measured directly.





$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

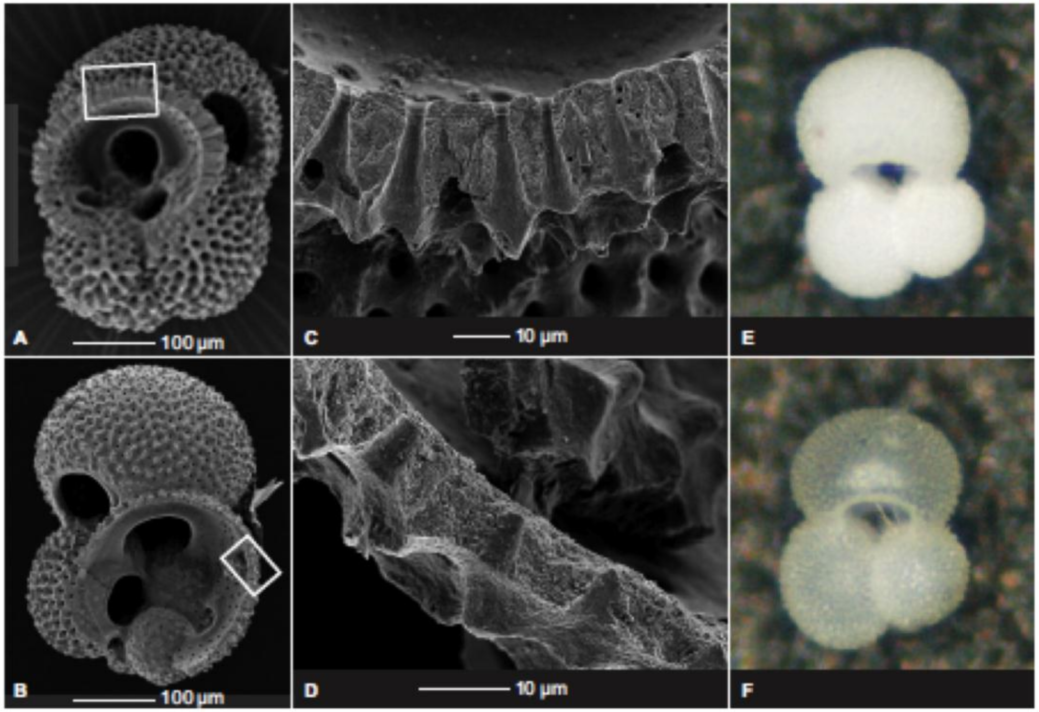
$$\Omega = \frac{(Ca^{2+} \times CO_3^{2-})_{obs}}{(Ca^{2+} \times CO_3^{2-})_{sat}}$$

doi:10.1002/loe2.10003

Calcification and carbonate preservation

If carbonate saturation is low, $CaCO_3$ will dissolve

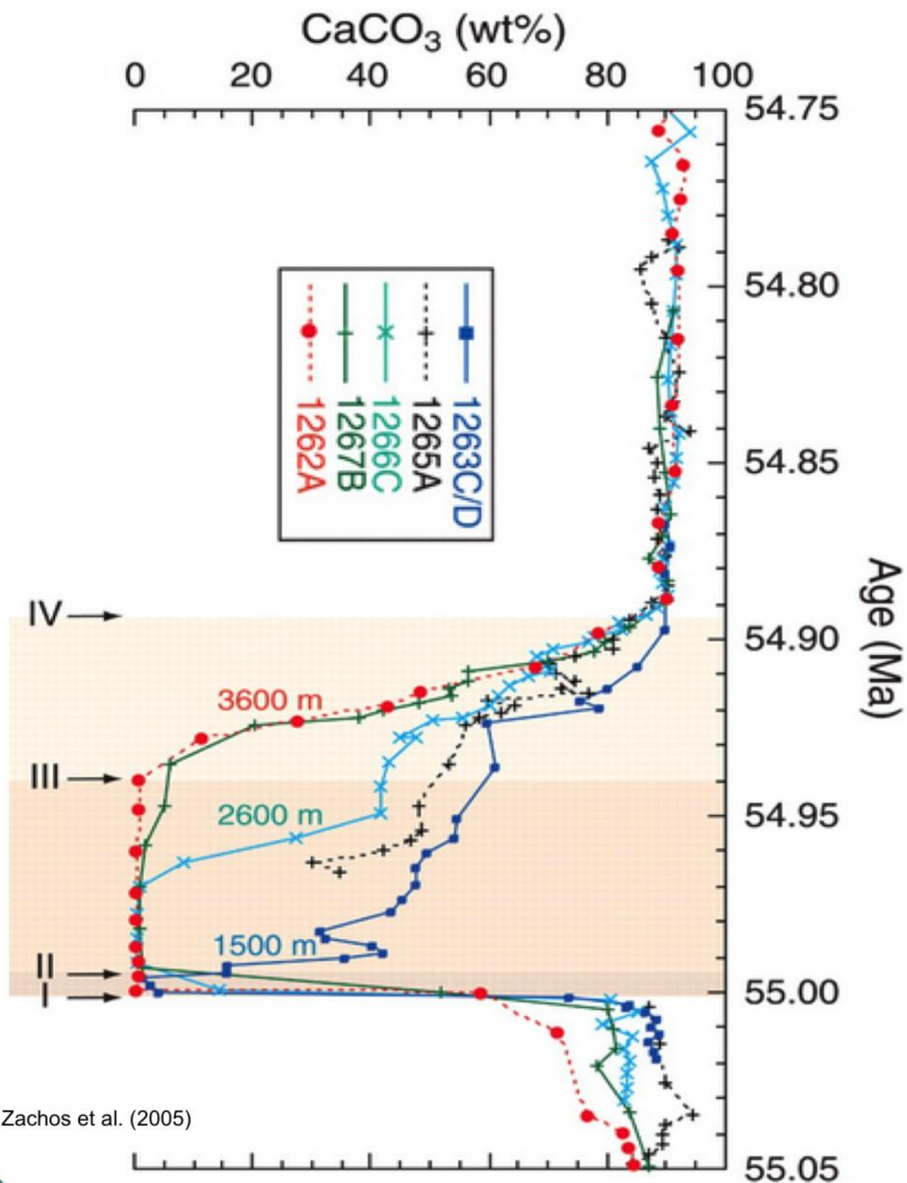
- Fossil shell weight, fragmentation, assemblages
- Changes in the calcite compensation depth (CCD)



Scanning Electron Microscope (SEM) images of a thick **(A)** and thin **(B)** walled shell, with a close-up of the cross-section of the shell wall **(C–D).** Microphotographs of a thick **(E)** and thin **(F)** specimen.

de Moel et al., 2009

doi:10.1002/loe2.10003

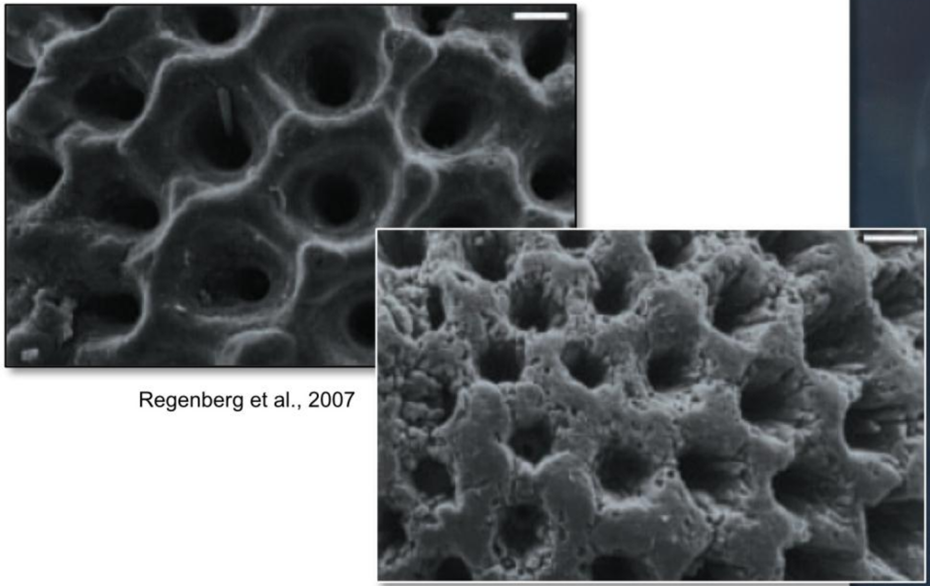


Zachos et al. (2005)

Changes in the carbonate compensation depth (CCD)

Advantages and Disadvantages of Carbonate Preservation Proxies

- The records yield high resolution continuous data sets
- Very easy to weigh shells or measure the carbonate content in the sediment



Regenberg et al., 2007

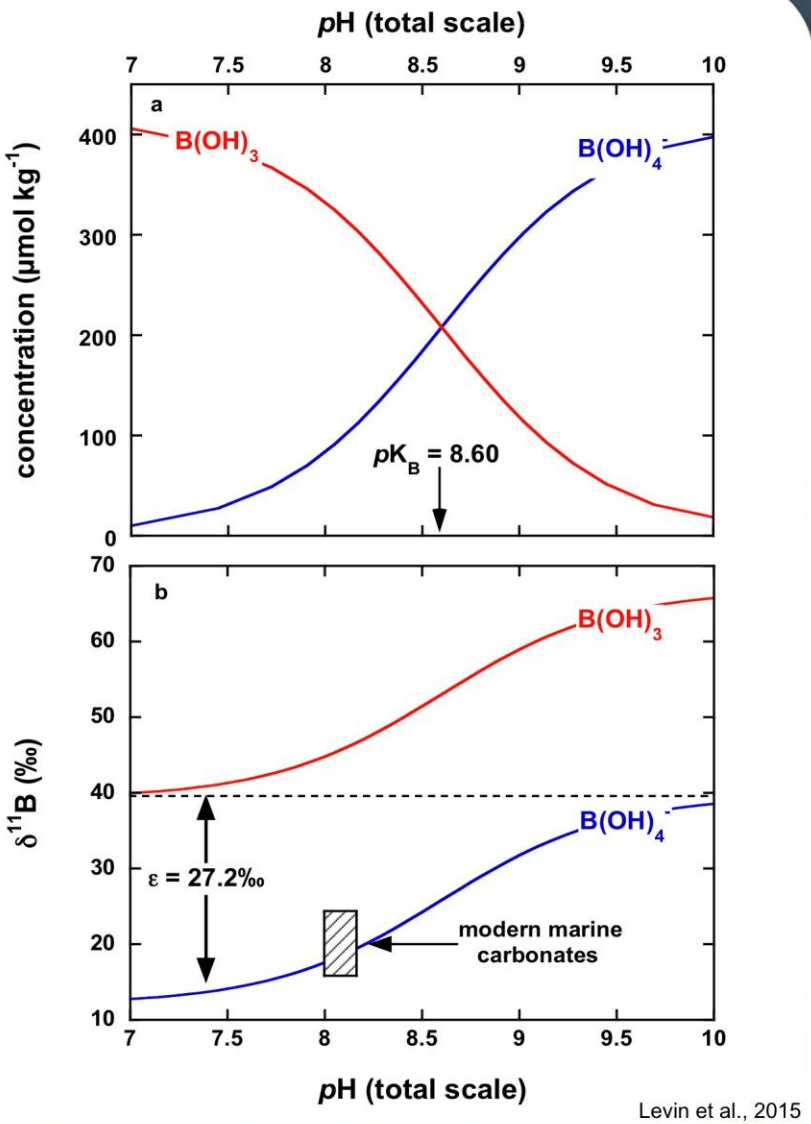
- The proxies typically do not yield quantitative estimates of ocean carbonate system or atmospheric pCO_2.
- Dissolution in the sediment and/or post burial carbonate precipitation from pore fluids may complicate interpretation
- Surface ocean pH and temperature determine original (i.e. undissolved) shell weights

doi:10.1002/loe2.10003

Boron isotopes and B/Ca

The relative abundance and isotopic composition of dissolved B species are a function of seawater pH.

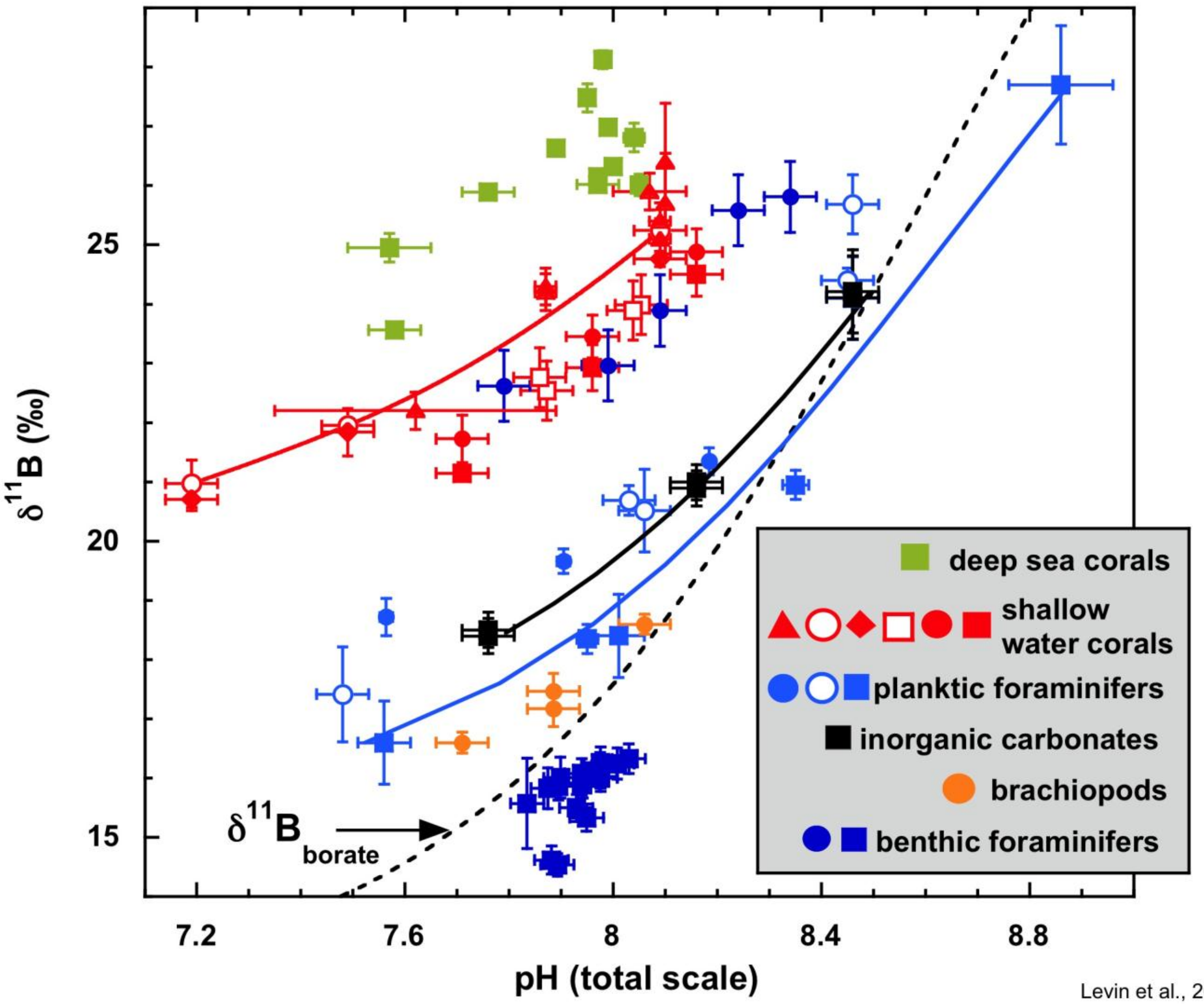
- $B(OH)_4^-$ is incorporated into carbonate shells and $\delta^{11}B$ and B/Ca can be measured in the carbonate.
- It is possible to use living calcifying organisms in controlled lab experiments or field observations to obtain quantitative calibrations



Levin et al., 2015

doi:10.1002/loe2.10003

Boron isotope calibrations



Levin et al., 2015

doi:10.1002/loe2.10003

Laboratory calibrations of B/Ca in planktic foraminifers

photo: A. Patel

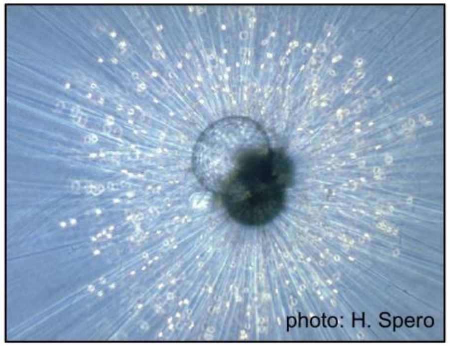


photo: H. Spero

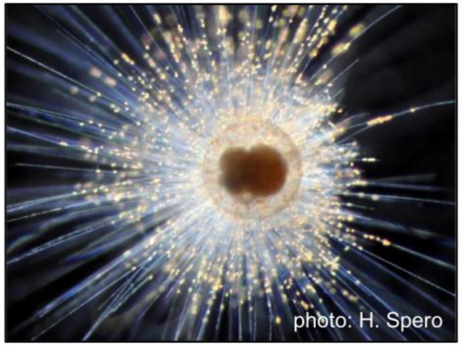
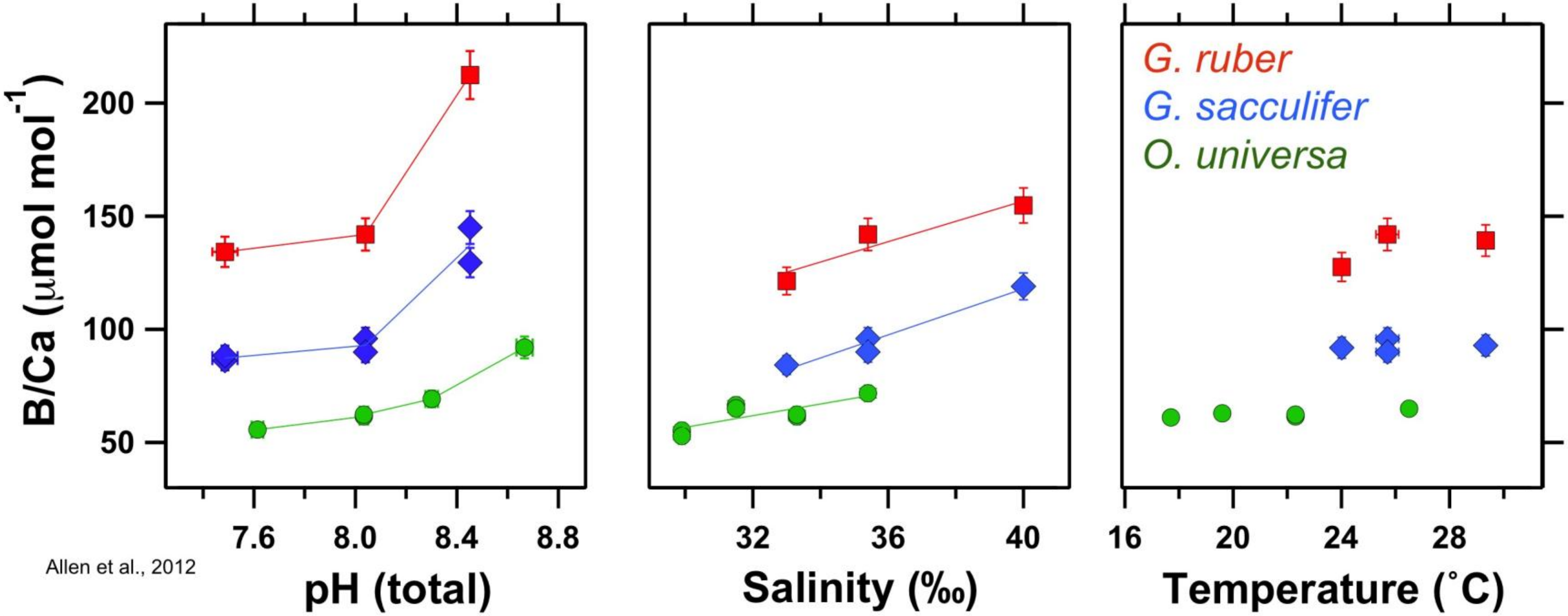
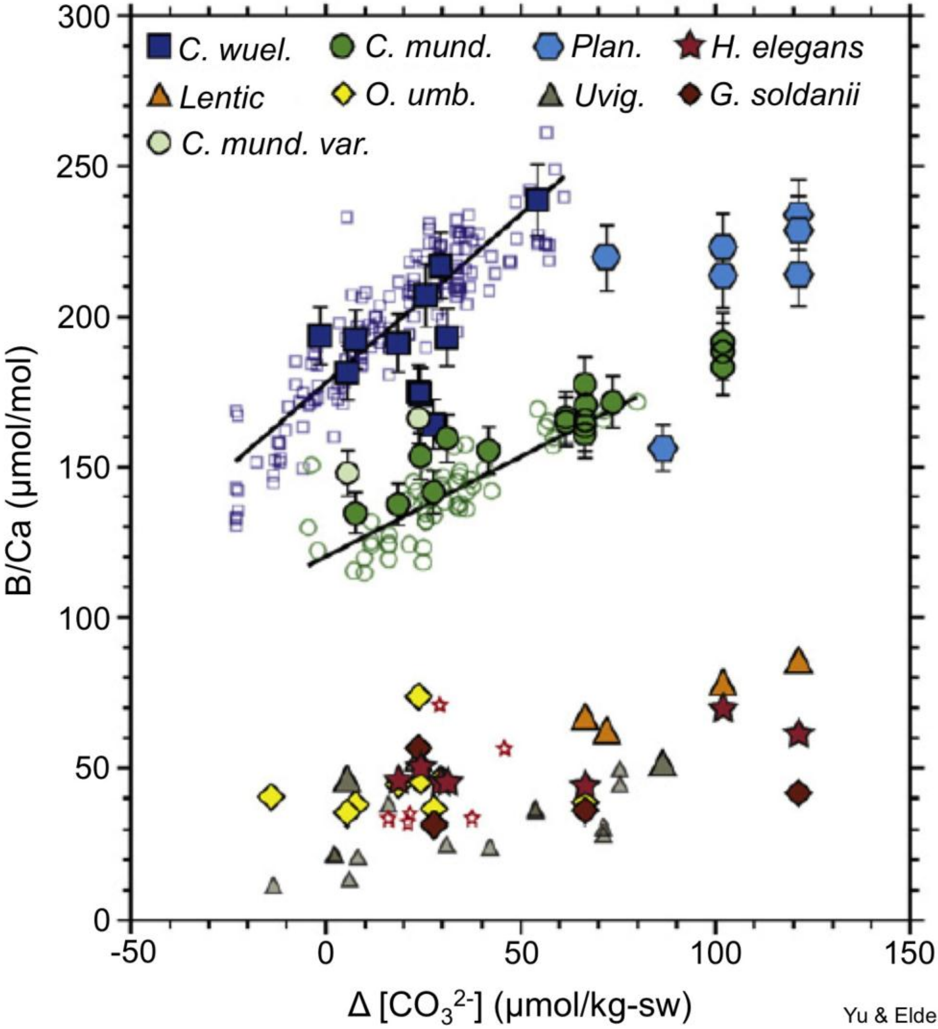


photo: H. Spero



Allen et al., 2012

Coretop calibrations of B/Ca in benthic foraminifers



Yu & Elderfield 2007,
Rae et al. 2011

doi:10.1002/loe2.10003

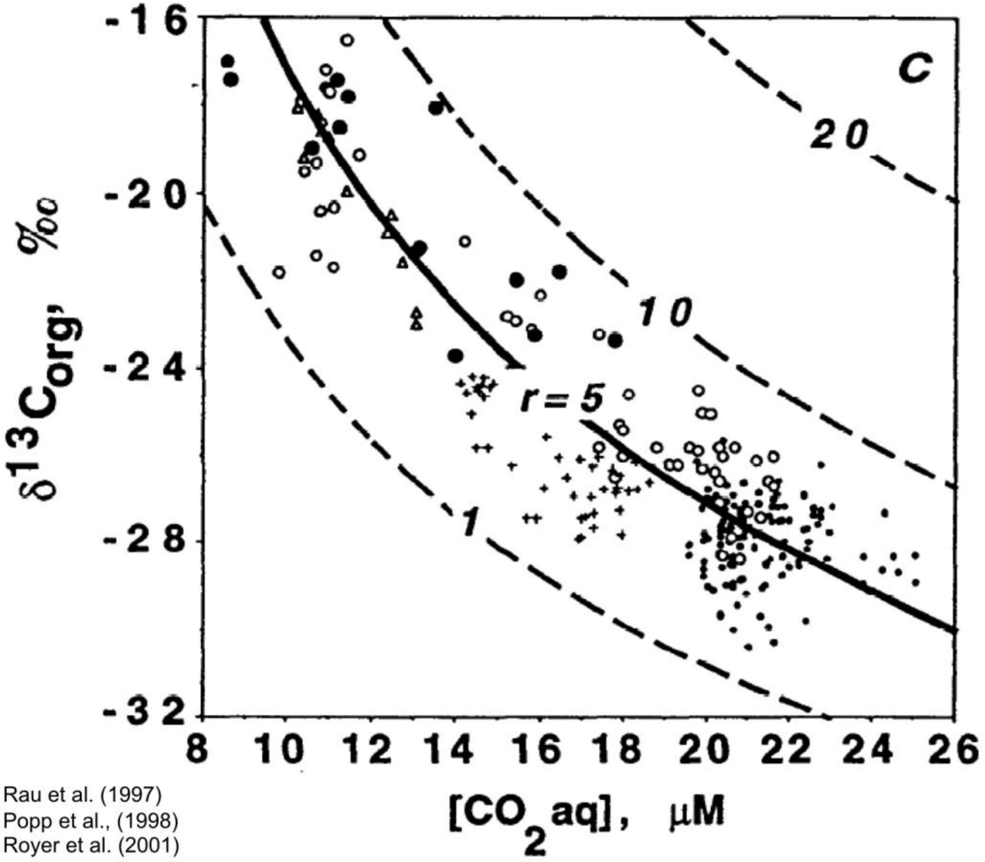
Advantages and Disadvantages of $\delta^{11}B$ and B/Ca Proxies

- Geochemically based; theory very fundamental
- B/Ca ratios relatively easy to measure
- Could be repeated on many existing sediment cores
- Could yield a high resolution continuous record

- $\delta^{11}B$ difficult to measure
- Proxies are species-specific and require species-dependent calibrations. Shell weight and size influence $\delta^{11}B$ and B/Ca
- Subject to uncertainty in seawater B concentration and alkalinity variations over time
- Requires independent estimate of temperature & salinity
- B/Ca proxy relatively new and controls not fully understood

doi:10.1002/loe2.10003

Phytoplankton $\delta^{13}C$



Rau et al. (1997)
Popp et al., (1998)
Royer et al. (2001)
Pagani (2014)

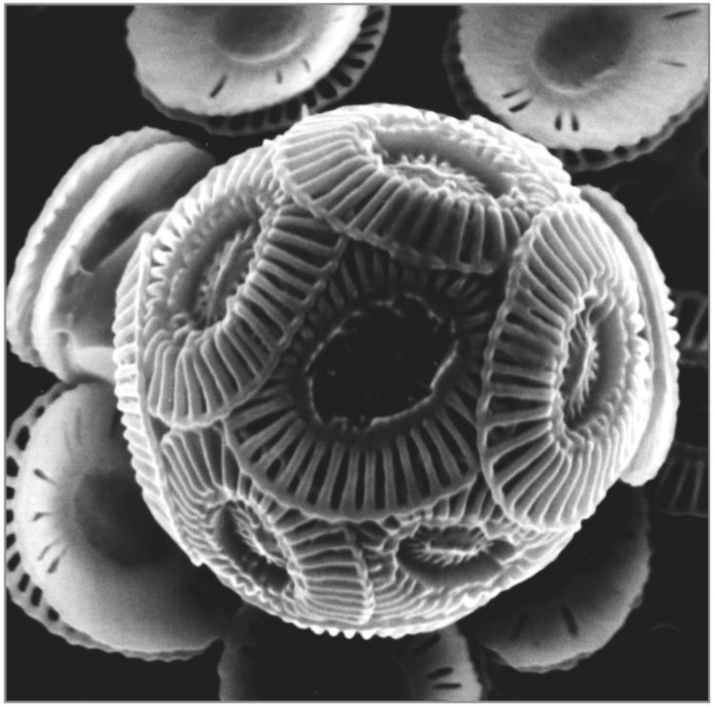
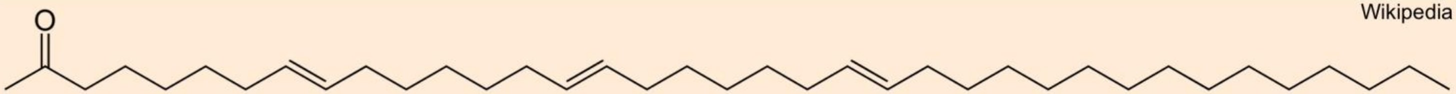


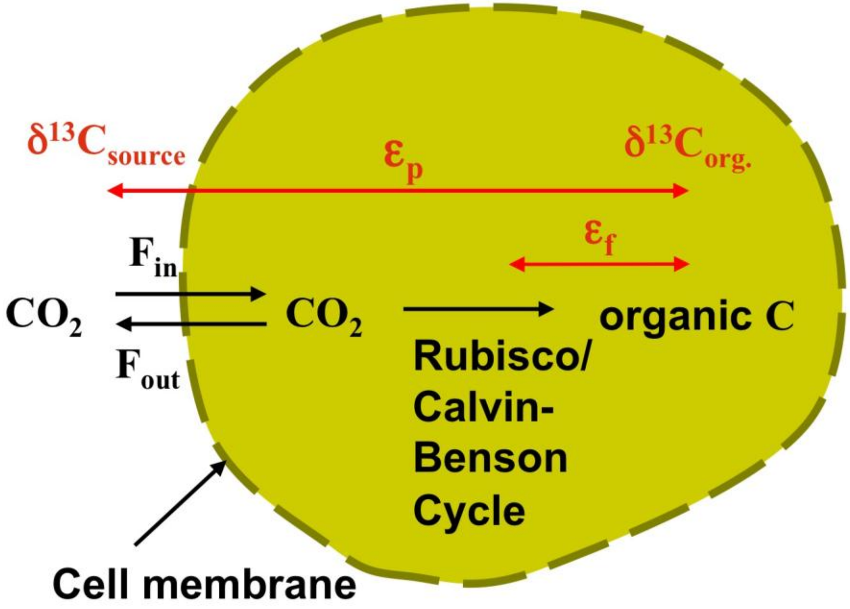
photo: B. Rost

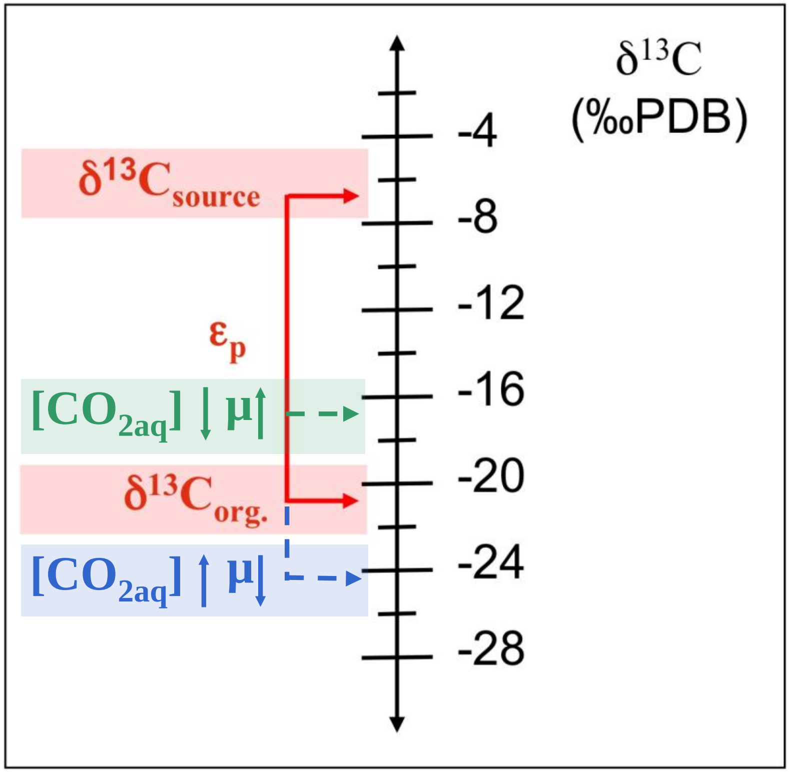


Wikipedia

The structure of a 37:3 alkenone, (8E,15E,22E)-heptatriaconta-8,15,22-trien-2-one, $C_{37}H_{68}O$

Photosynthetic carbon isotope fractionation (ε_p) in alkenones





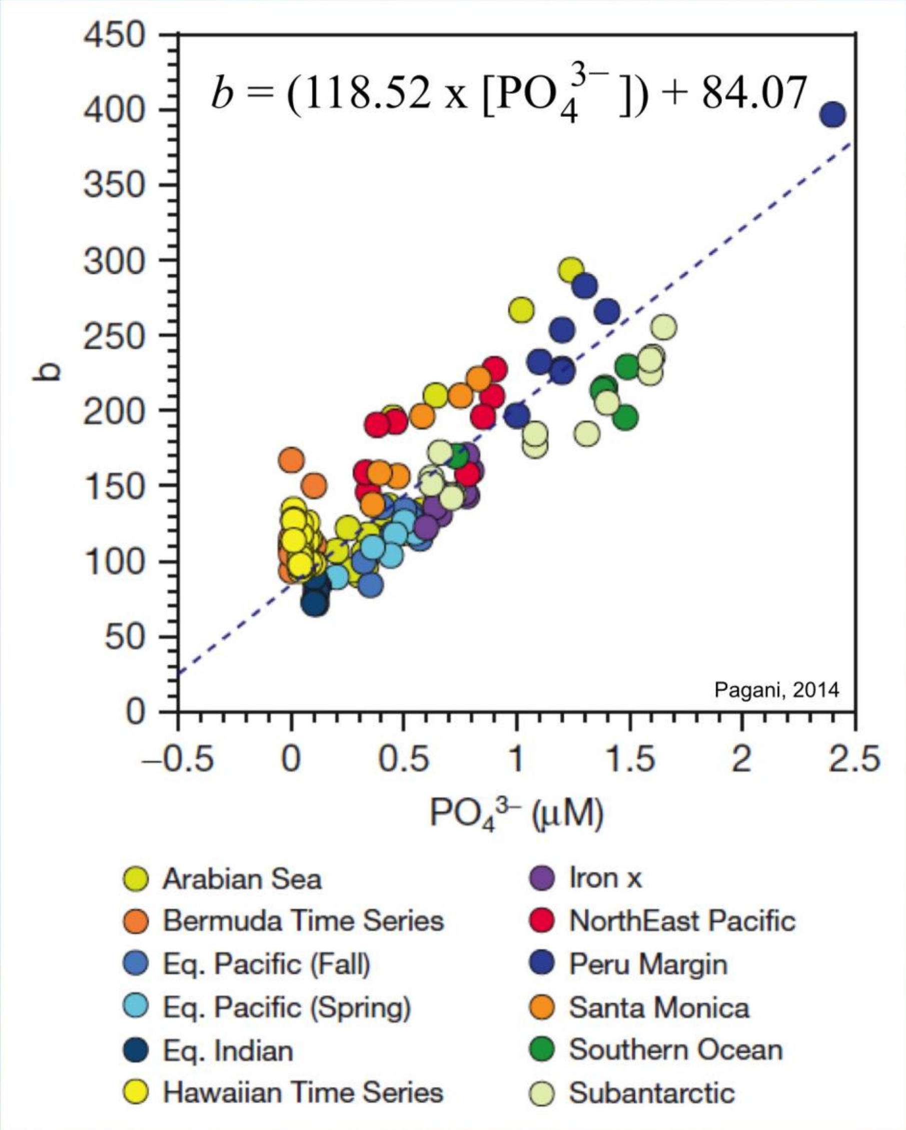
$$\varepsilon_p = \varepsilon_f - b/CO_2 = \varepsilon_f - \mu/CO_2 = \varepsilon_f * F_{out}/F_{in}$$

ε_f = C-fractionation during enzymatic carbon fixation, ~25‰ for Rubisco
b = empirical factor combining the effects of physiological influences
μ = growth rate

Phytoplankton $\delta^{13}C$

$$\varepsilon_\mathrm{p} = \varepsilon_\mathrm{f} - \frac{b}{[\mathrm{CO_2}]'}$$

ε_p also depends on phytoplankton growth rates (μ) which in turn depend on nutrient (PO_4) availability. Factor b in the equation above is related to nutrient concentrations and is estimated from nutrient proxies.



Pagani, 2014

doi:10.1002/loe2.10003

Phytoplankton δ^{13}C

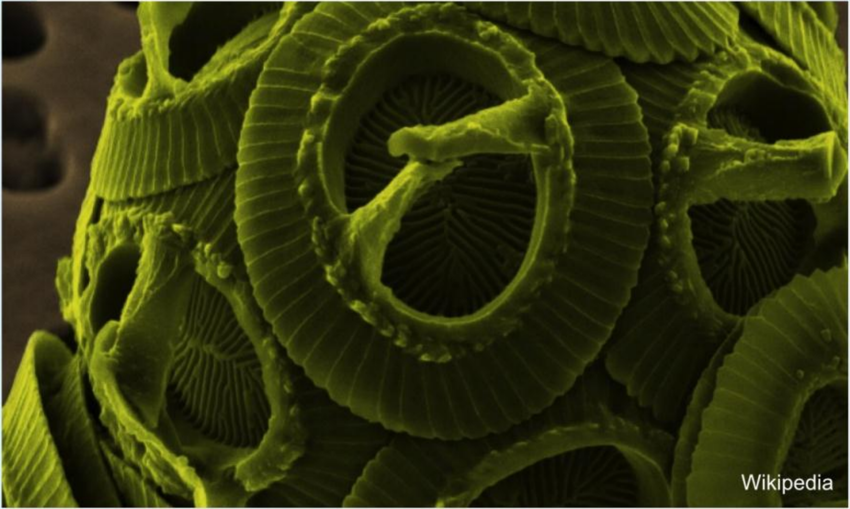
- Phytoplankton preferentially take up ^{12}C relative to ^{13}C.
- This fractionation (ε_p – offset from the isotopic signature of dissolved C in seawater) is greater (δ^{13}C lower) when dissolved CO_2 is more abundant and lower (δ^{13}C higher) when it is less abundant. The fractionation is species specific.
- Metabolic pathways, cell geometry, and growth rates also impact the isotope ratios and the effect of these parameters has to be accounted for.

$$\varepsilon_{\mathrm{p}} = \varepsilon_{\mathrm{f}} - \frac{b}{[\mathrm{CO_2}]'}$$

- By measuring the δ^{13}C value of molecular fossils(alkenones) in conjunction with the δ^{13}C of carbonate shells (DIC) and a measure of growth rates, an estimate of dissolved CO_2 concentrations in surface water can be made.

Advantages and Disadvantages of Alkenone $\delta^{13}C$ CO_2 Proxy

- Continuous pCO_2 records possible
- Unambiguous marine phytoplankton source
- Quantitative estimates possible



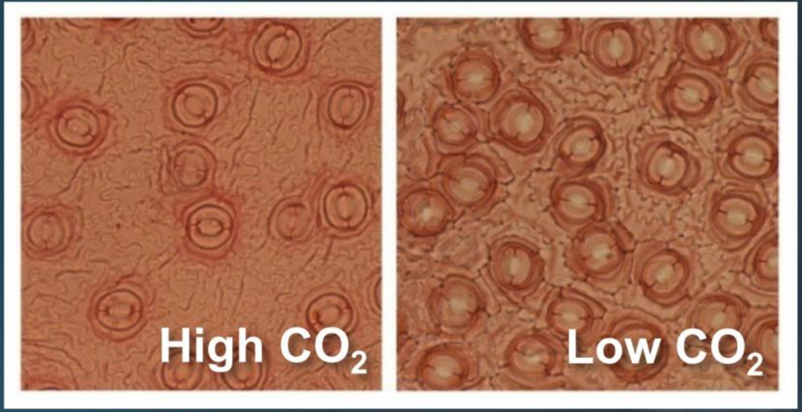
Wikipedia

- Growth rate (nutrients, light, etc.) and cell geometry can influence C isotope fractionation in algae
- Changes in carbon transport mechanisms (active transport of HCO_3^-) may be triggered by low $[CO_2(aq)]$
- Requires knowledge of SST to convert $[CO_2(aq)]$ to pCO_2
- Recent studies consider how carbon isotope fractionation in extinct species may have differed from modern species

doi:10.1002/loe2.10003

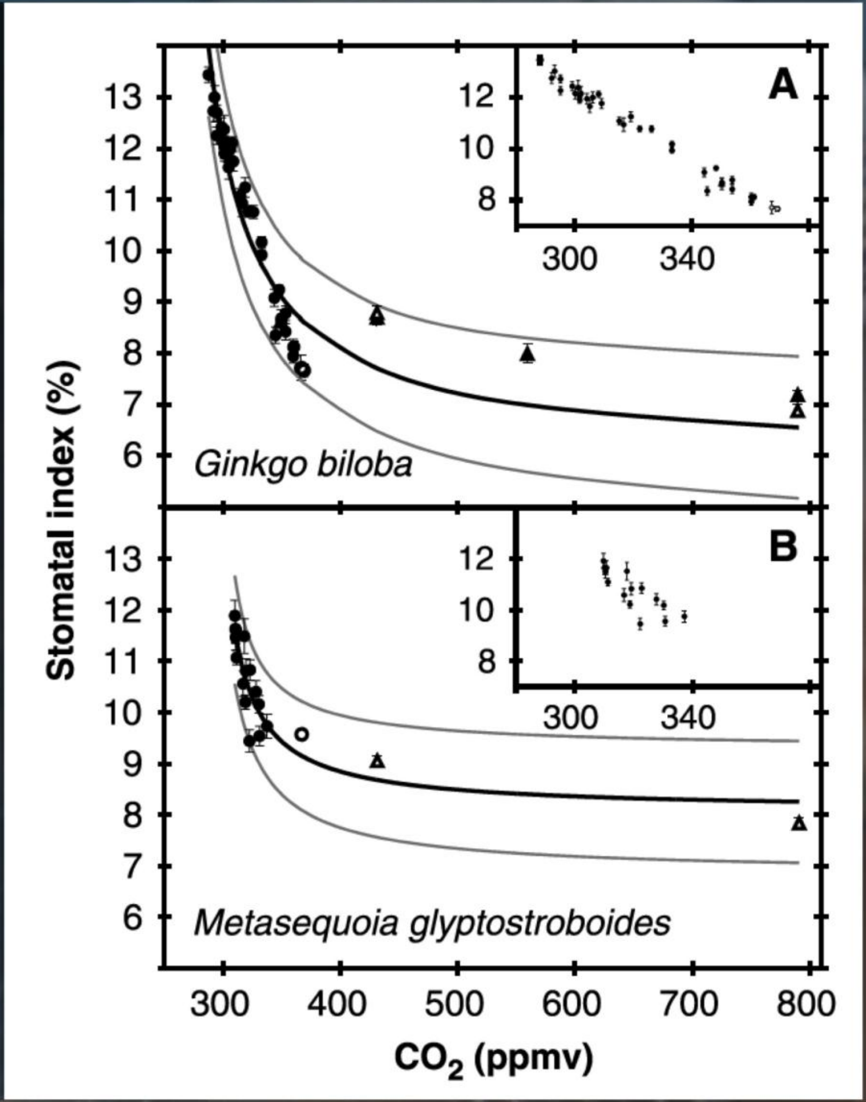
Leaf Stomata Density

The **stomatal density** in some C3 plants will vary inversely with the concentration of atmospheric CO_2.



Emmy Lammertsma

Stomatal Index: the number of stomata on a leaf area divided by the sum of the numbers of stomatal and epidermal cells



Royer et al. (2001) *Science* 292: 2310-2313

doi:10.1002/loe2.10003

Advantages and Disadvantages of the Leaf Stomatal CO_2 Proxy

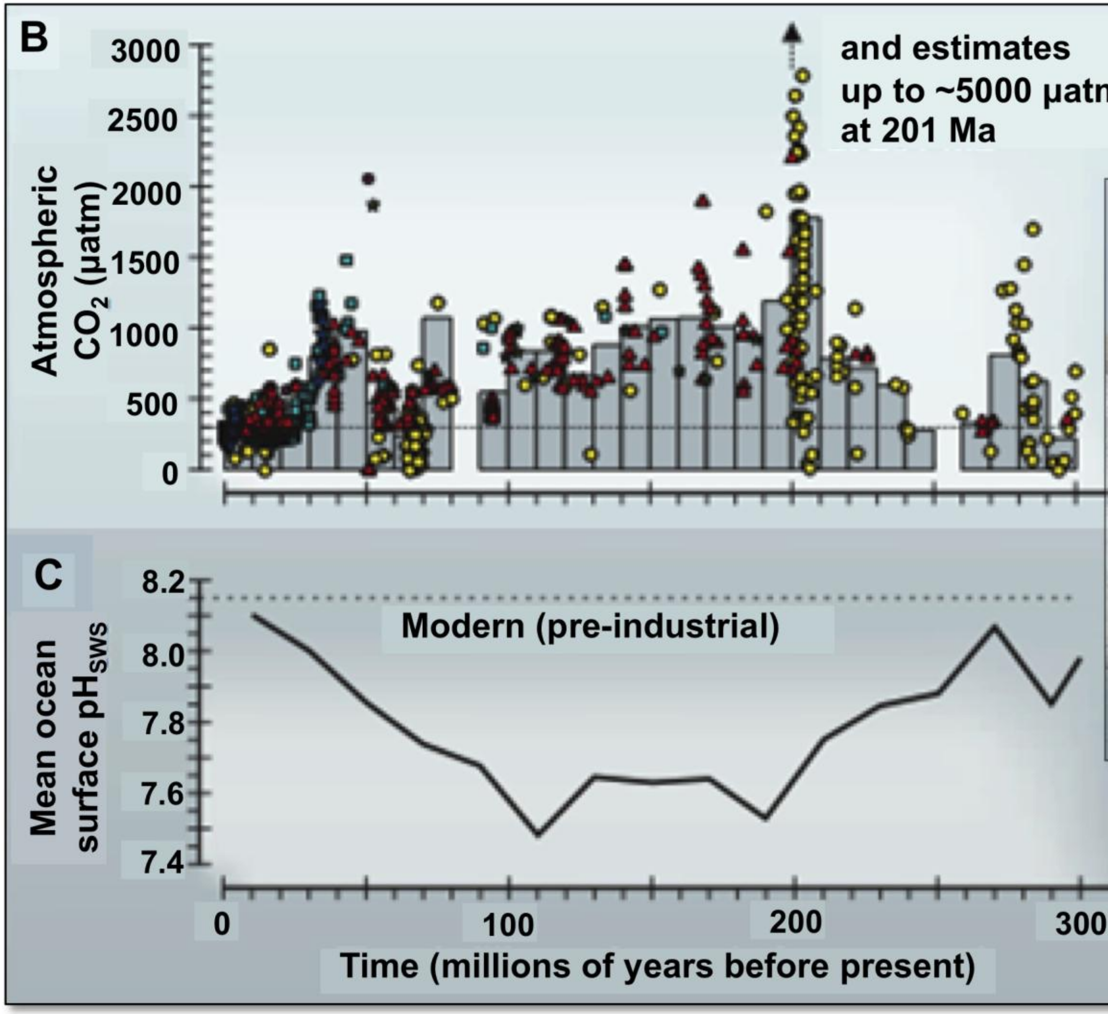
- Biophysical mechanism distinct from geochemical proxies of CO_2
- Applicable whenever suitable leaf fossils exist
- Easy (though tedious) measurement

- Different calibration required for each species
- Altitude also affects stomatal density
- Many tree & plant species from geologic past now extinct, so cannot be calibrated
- Moisture regime may also cause change in stomatal density (not well established)

National Parks Service

doi:10.1002/loe2.10003

Atmospheric CO_2 and ocean acidity



Klaus Wagensonner, Flickr

Hönisch et al. 2012

doi:10.1002/loe2.10003

Ocean Acidification Reconstruction

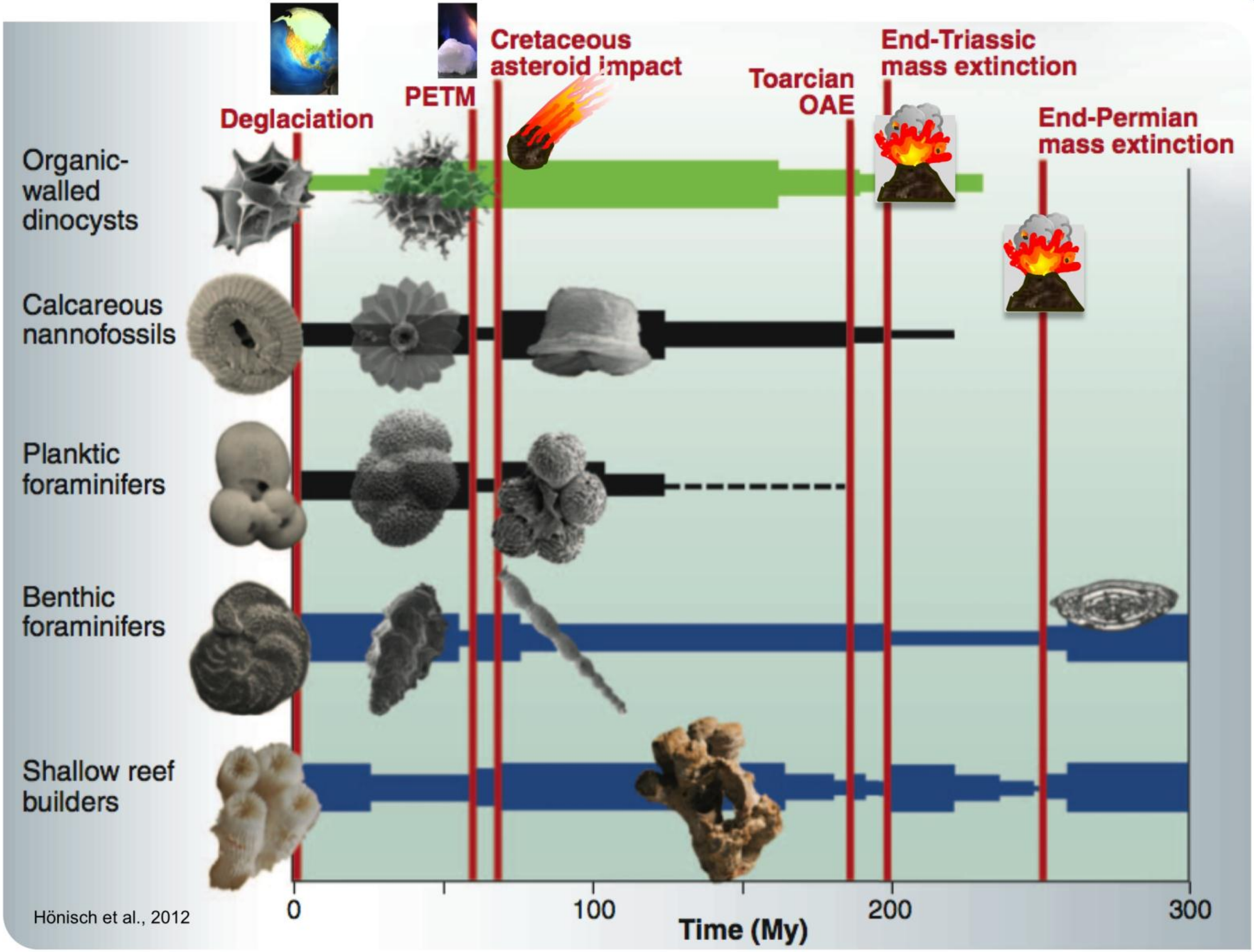
Analogues for current ocean acidification are events of rapid addition of large quantities of carbon into the ocean-atmosphere system.

1) Investigate changes of ocean carbonate chemistry and warming using various geochemical proxies, with particular attention to the rates of change.

2) Investigate evidence for impacts on biology.

Inevitable limitations are the temporal and spatial variability in ocean chemistry, the availability and fidelity of the archives, and the small fraction of organisms preserved in the fossil record.

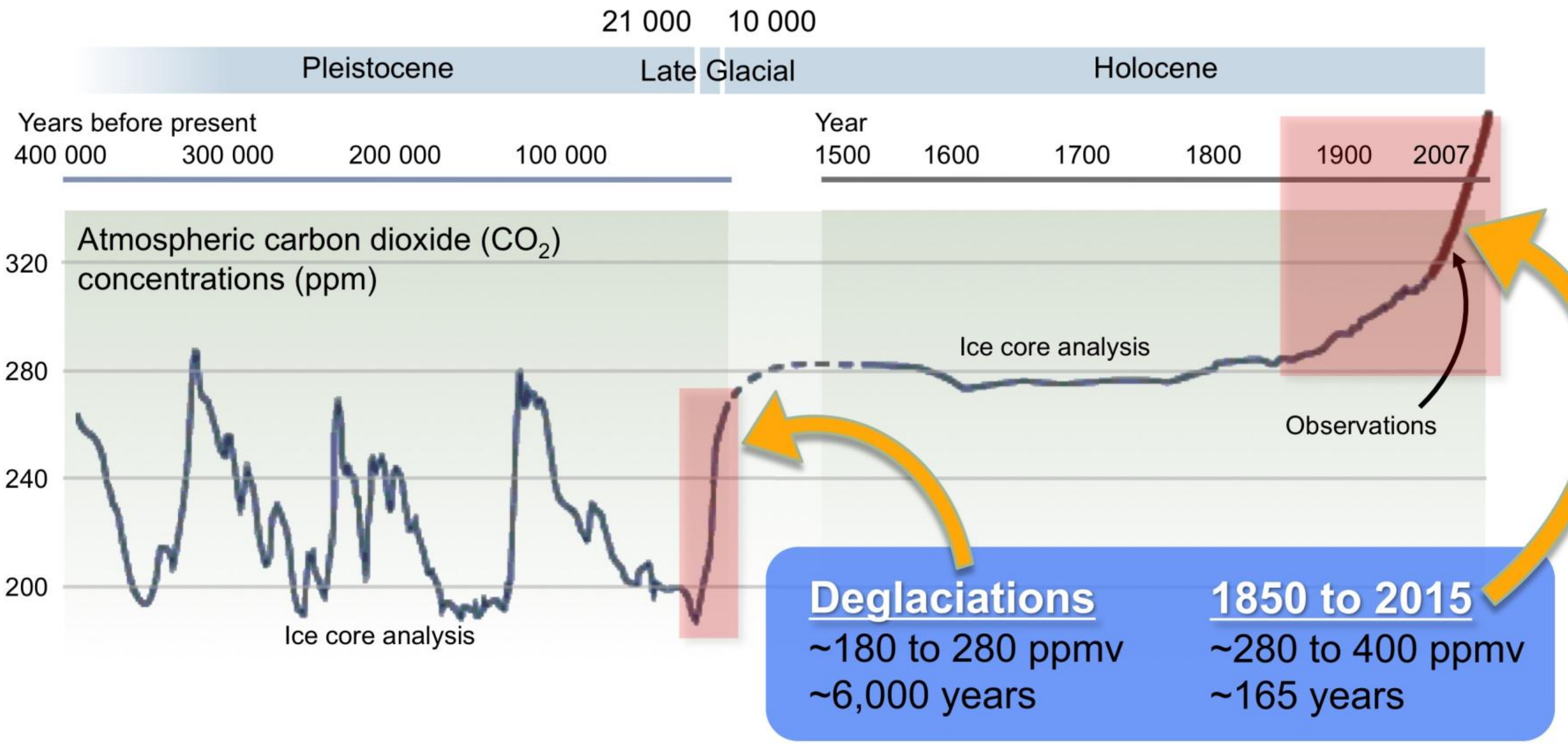
Insights from the Geological Record



Hönisch et al., 2012

doi:10.1002/loe2.10003

Compare modern ocean acidification to Pleistocene deglaciations



Deglaciations
~180 to 280 ppmv
~6,000 years

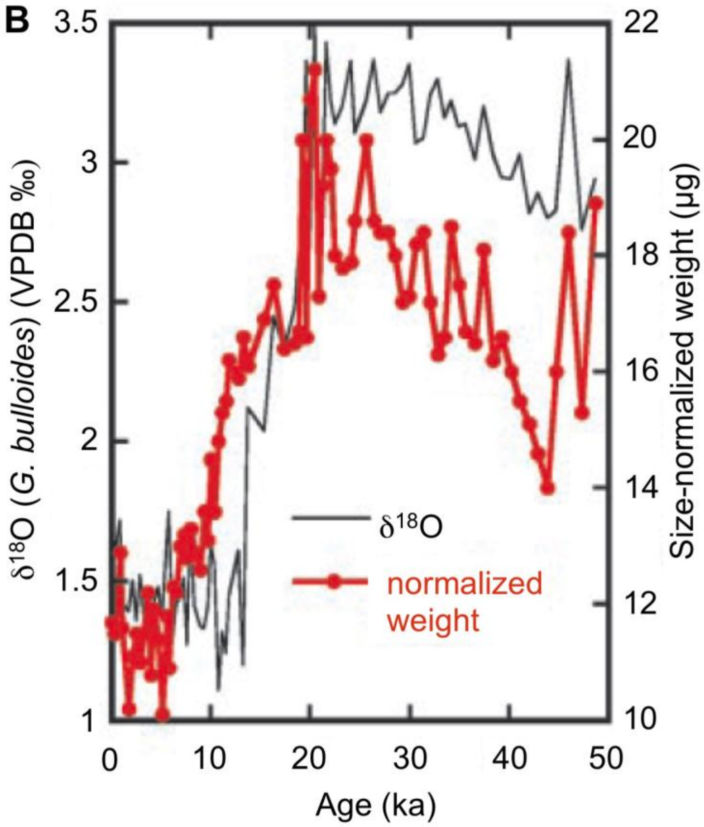
1850 to 2015
~280 to 400 ppmv
~165 years

http://www.unep.org/geo/geo_ice/graphics.asp

doi:10.1002/loe2.10003

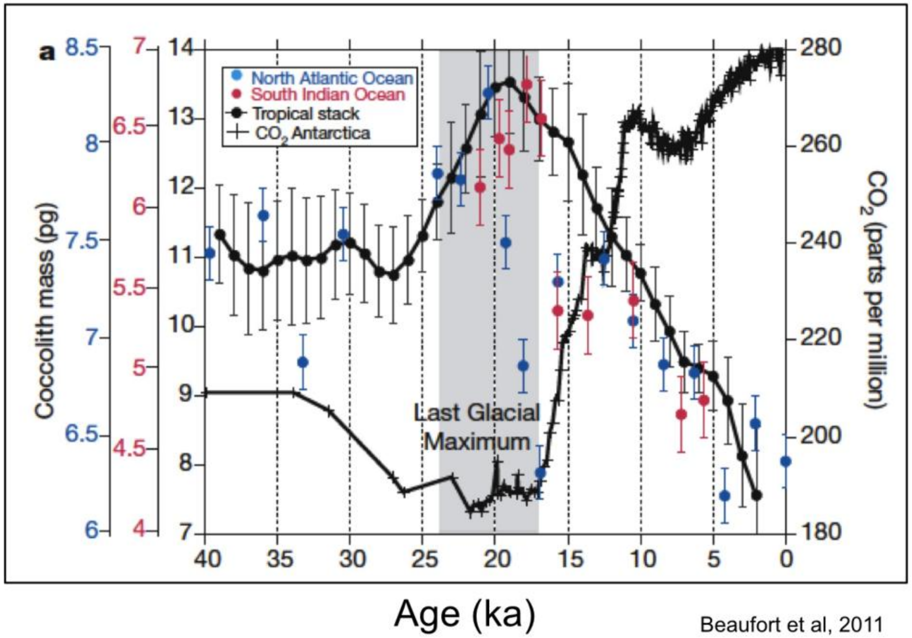
Insights from the Geological Record

The planktic foraminifer *G. bulloides* grows ~35% thinner shells today compared to the last glacial.



Barker & Elderfield, 2002

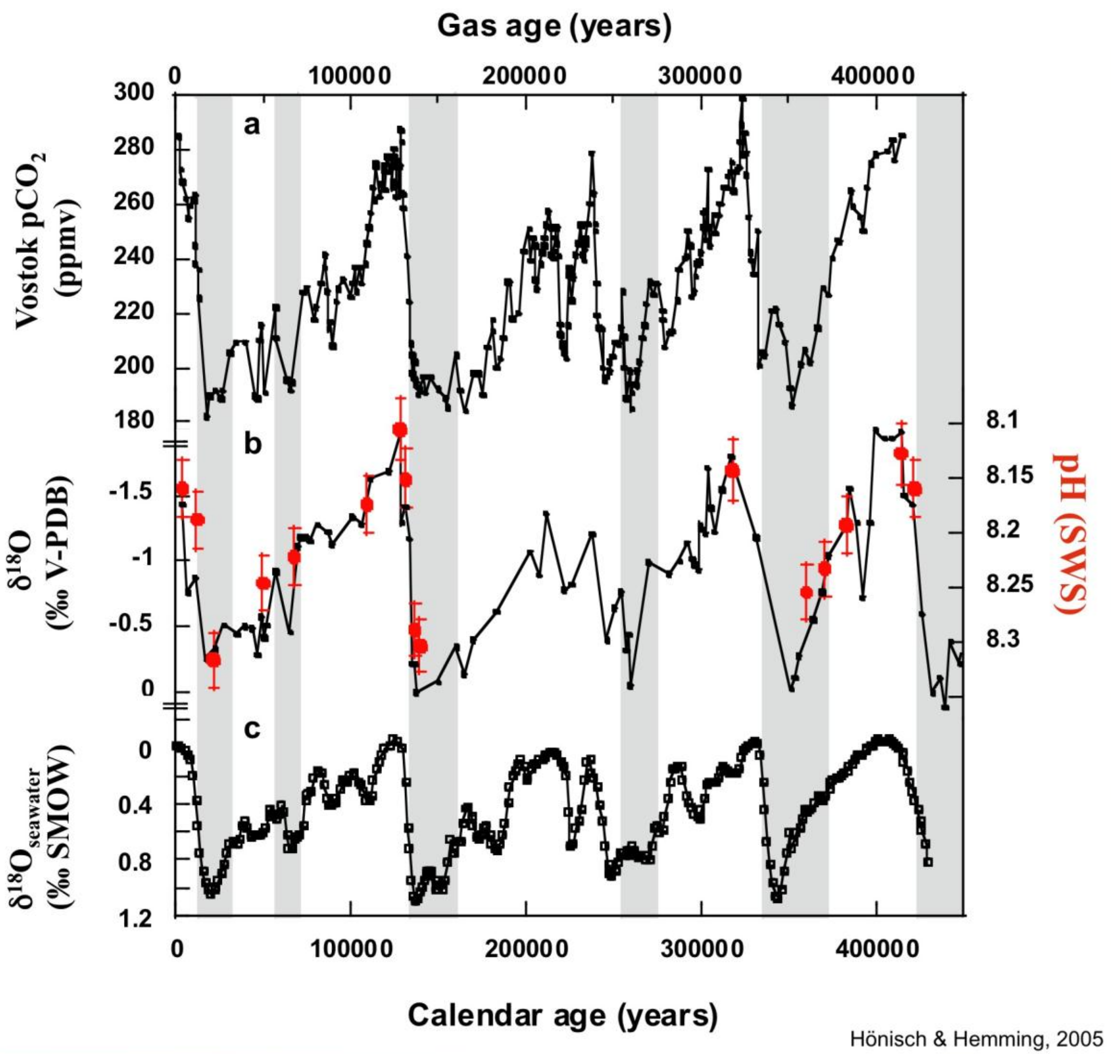
Modern coccoliths are ~20% lighter compared to liths secreted during the last glacial



Beaufort et al, 2011

These changes are consistent with lower preindustrial pH, but by how much?

Boron isotopes and B/Ca

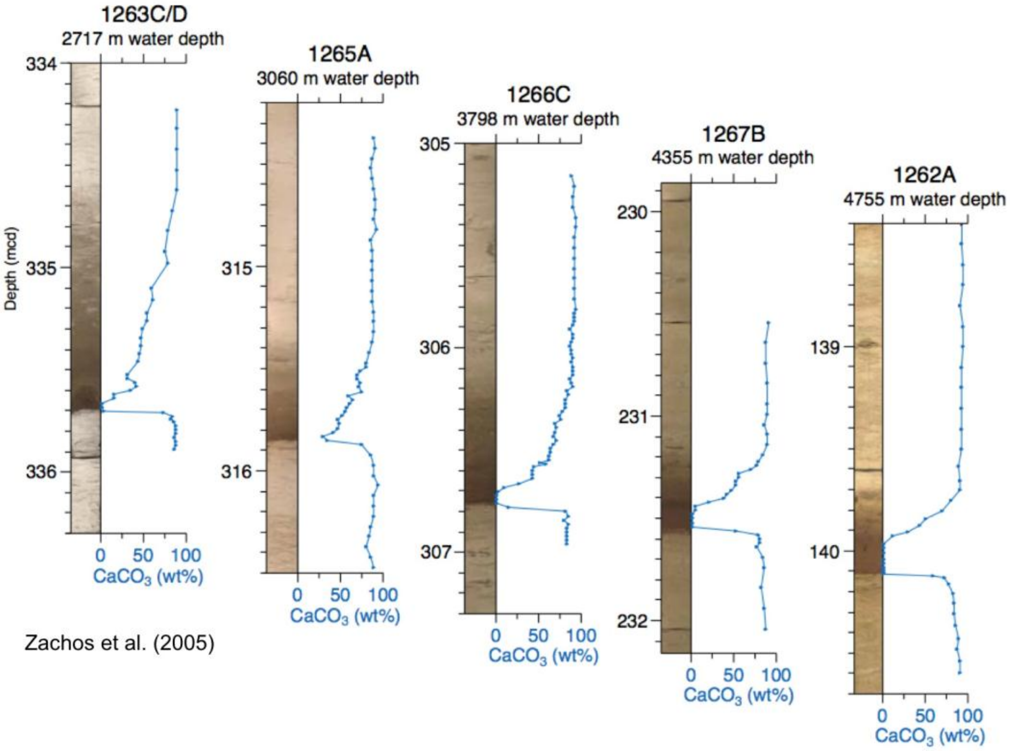


Hönisch & Hemming, 2005

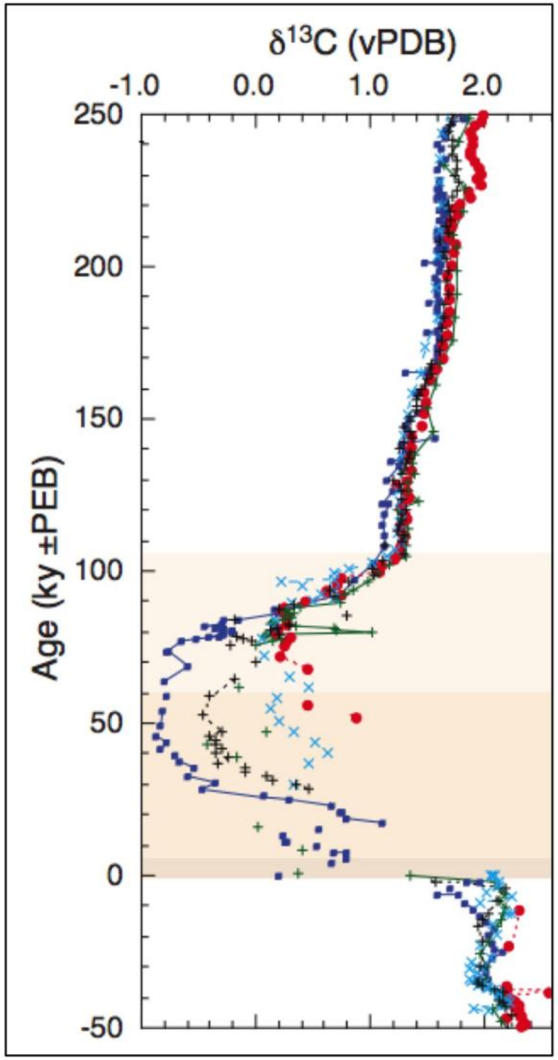
Warming: +2-3°C
pH: -0.15 units
Ω: -2
Calcification changes: ✓
Duration: 6.2 ky
pH change = 0.002 units/century

doi:10.1002/loe2.10003

Paleocene – Eocene Thermal Maximum (PETM)



Zachos et al. (2005)

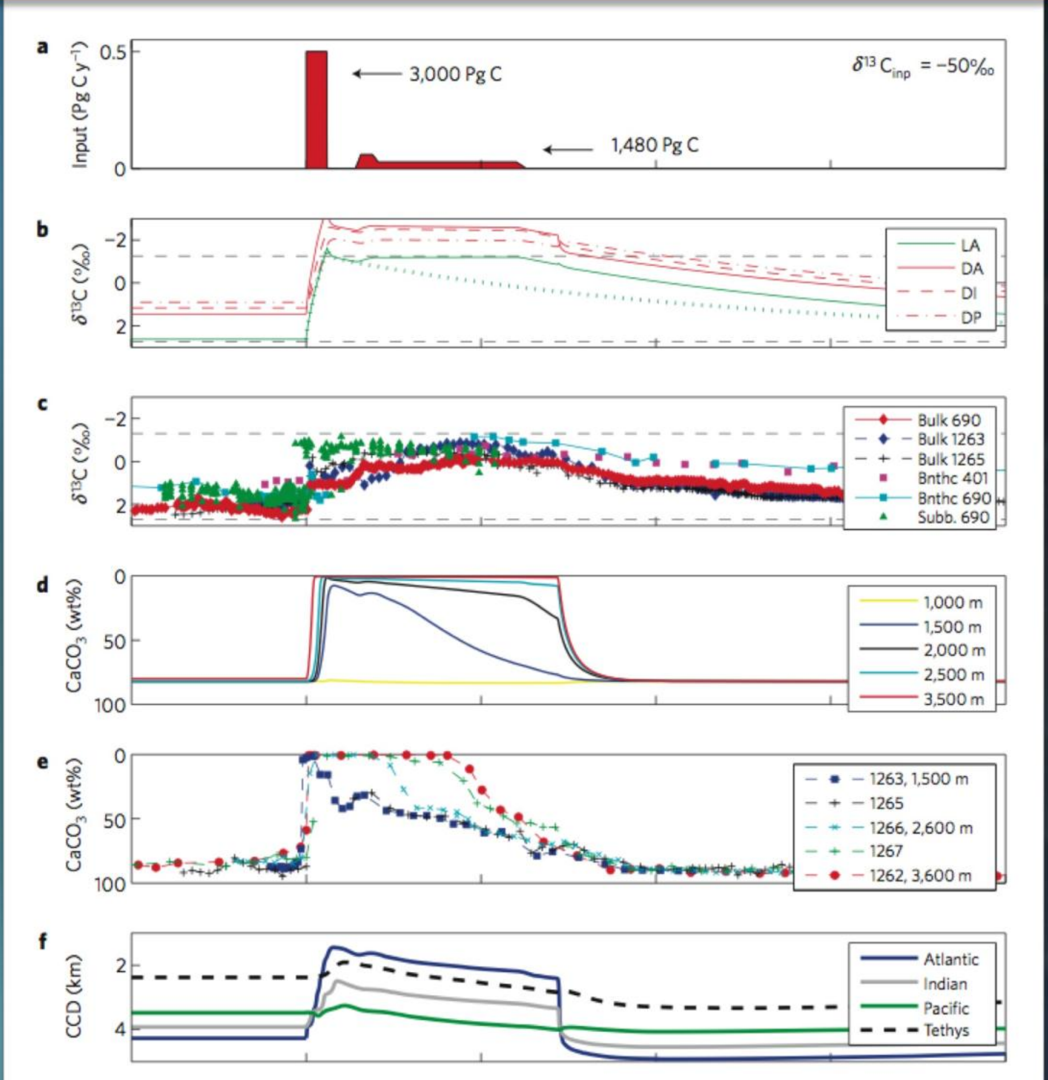


Zachos et al. (2005)

Paleocene-Eocene hyperthermals are characterized by negative carbon isotope excursions and $CaCO_3$ dissolution. Evidence is global, but the PETM (~56 Ma) experienced the most extreme conditions.

doi:10.1002/loe2.10003

Paleocene – Eocene Thermal Maximum (PETM)



Zeebe et al. (2009)

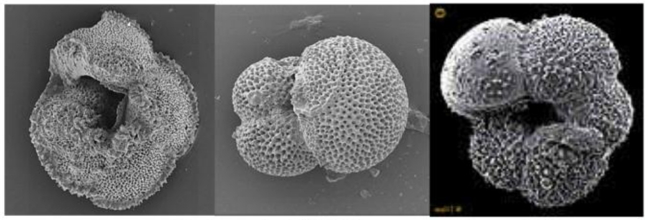
Zeebe et al. (2009) needed a carbon source with an isotopic composition of -50‰ to model the extent of dissolution and δ13C excursion observed in the geological record.

These estimates are consistent with a hydrocarbon source and a total carbon release of ~5,000 PgC.

doi:10.1002/loe2.10003

PETM

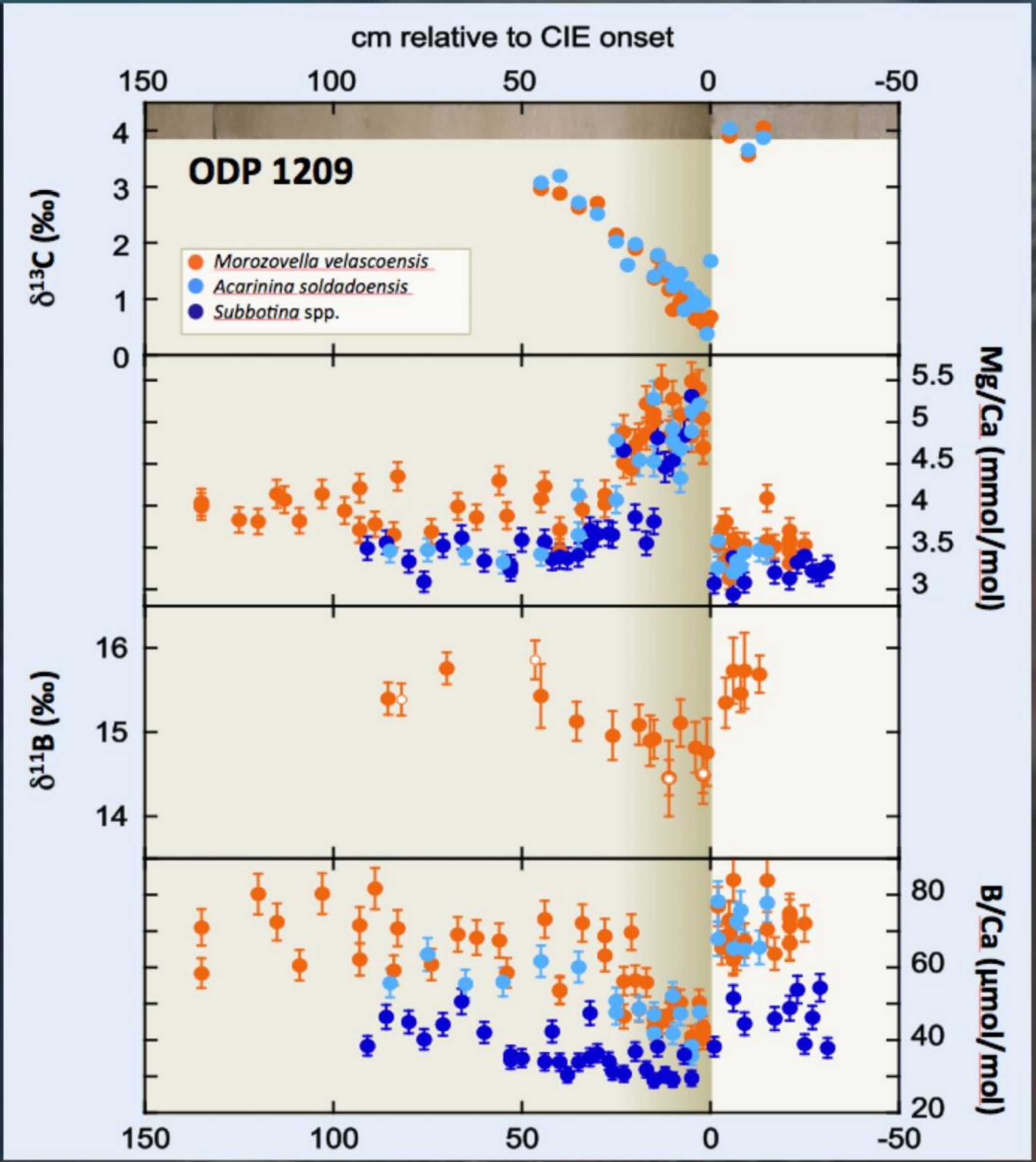
Planktic foraminifers show a ~0.8‰ decrease in $\delta^{11}B$ at the onset of the PETM event, along with a 30–40% reduction in shell B/Ca.



Zachos et al. (2006) Foraminifera.eu

This is consistent with significant, global acidification of the surface ocean (~0.3 pH units) lasting at least 70 kyr and requiring sustained carbon release.

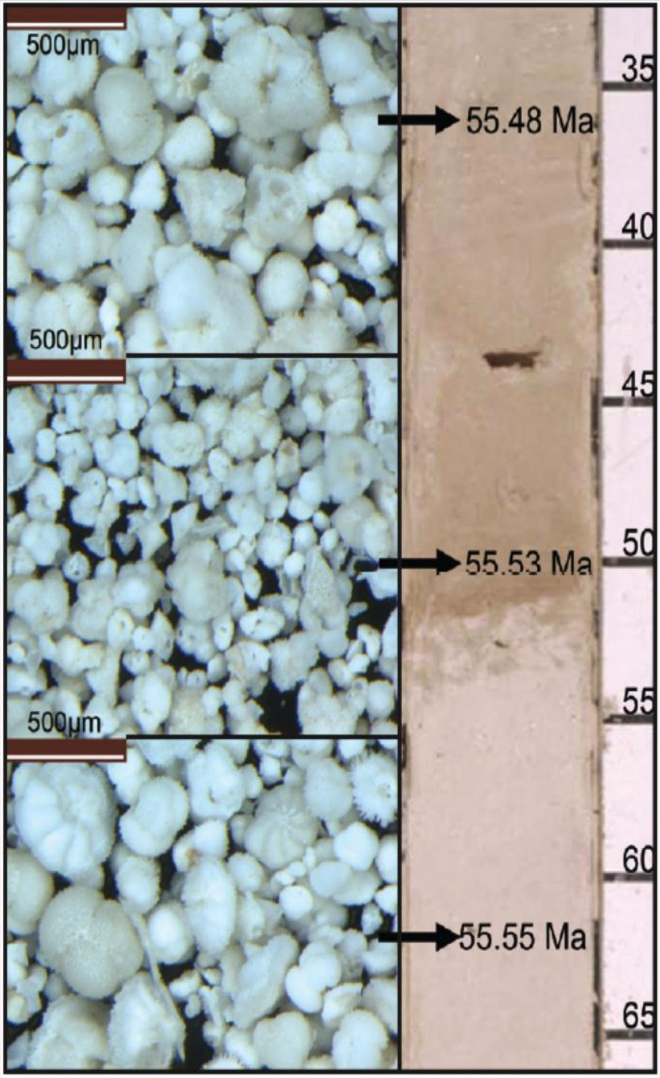
Penman et al., 2014



doi:10.1002/loe2.10003

PETM – Biological evidence for acidification

- 50% of benthic foraminifera species became extinct
- Surface-dwelling organisms were less affected but showed differences in size, reduced abundance, deformities, excursion taxa, some extinction followed by evolution of new species
- Collapse of coral-algal reefs



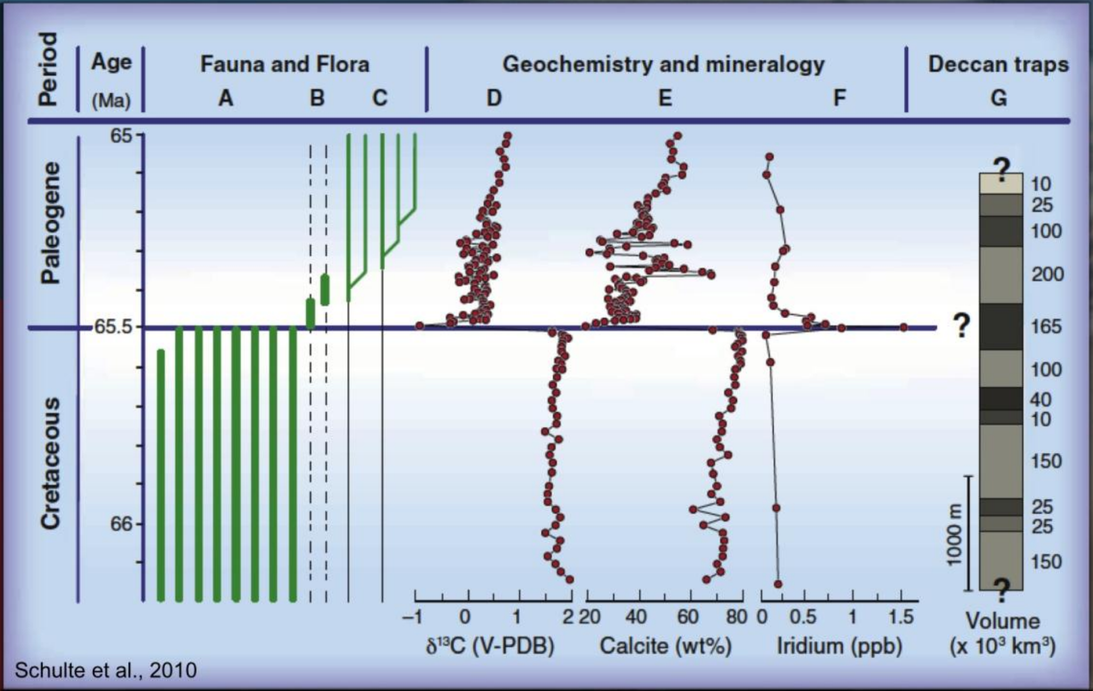
Hönisch et al., 2011

Warming: +5-9°C
pH: -0.3 units
Ω: -?
Deep-sea dissolution: ✓
Changes in calcifier composition: ✓
Duration: 5-19 ky
pH change ~ 0.006 units/century

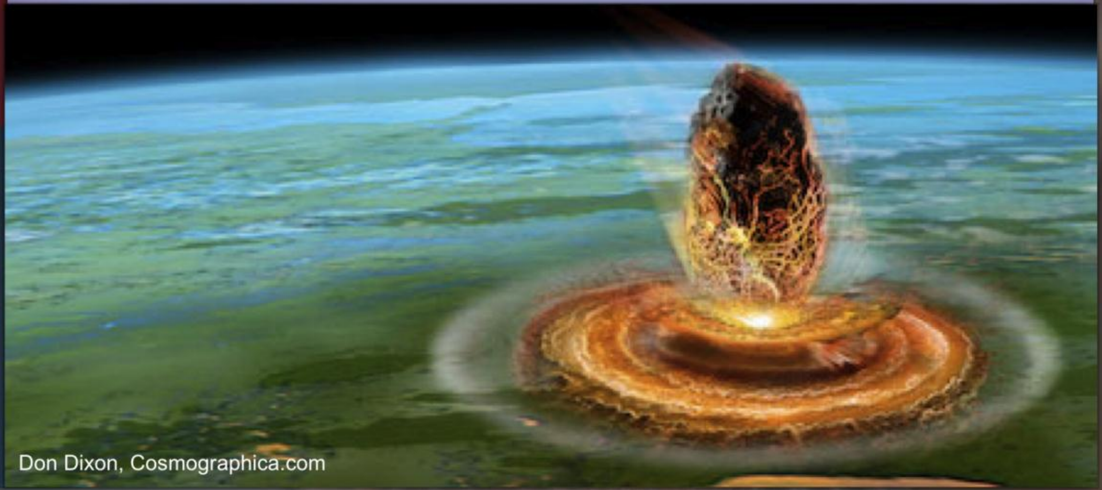
doi:10.1002/loe2.10003

End of Cretaceous

warming: ✔
pH and Ω: ?
deep-sea dissolution: ✔
planktic calcifier extinction: ✔
reef crisis: ✗
benthic foraminifer extinction: ✗

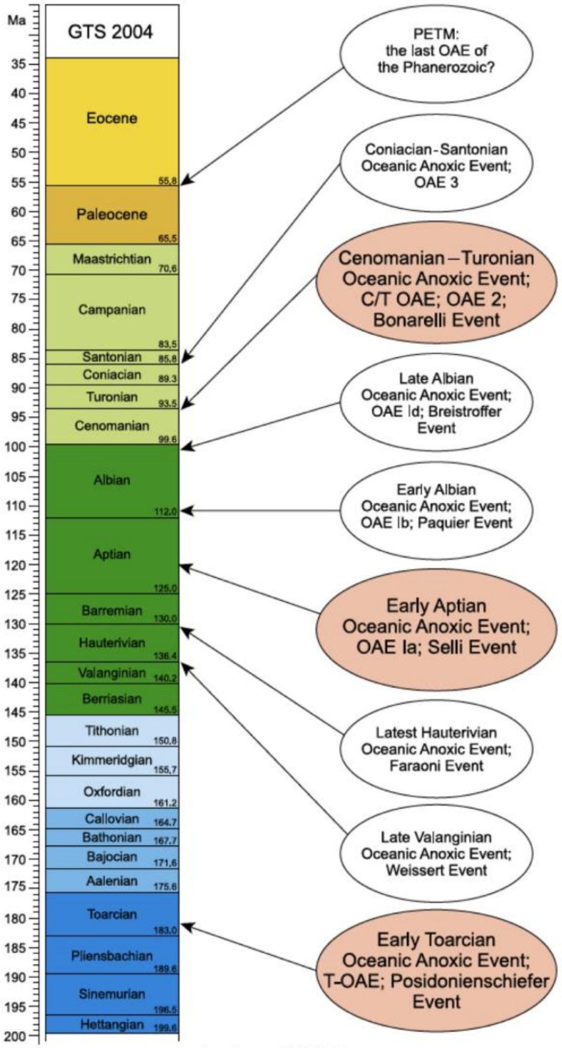


Schulte et al., 2010

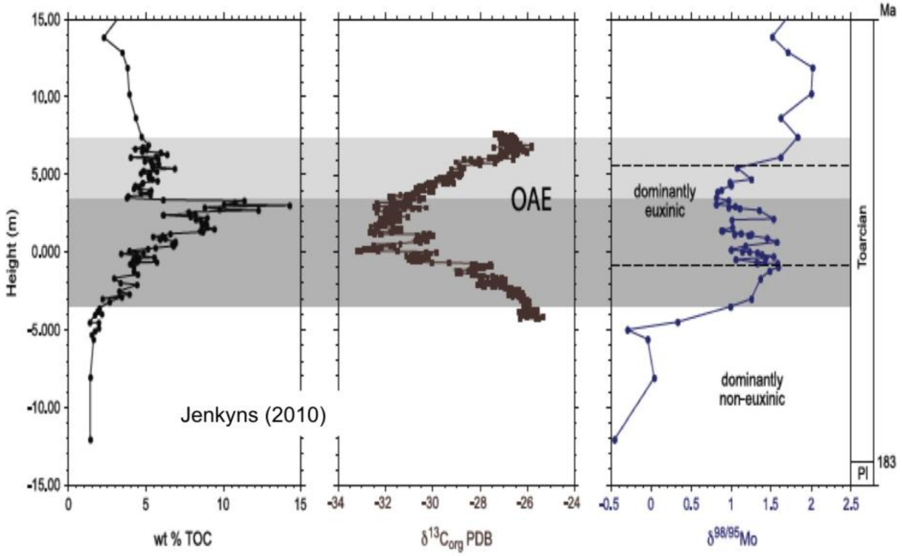


Don Dixon, Cosmographica.com

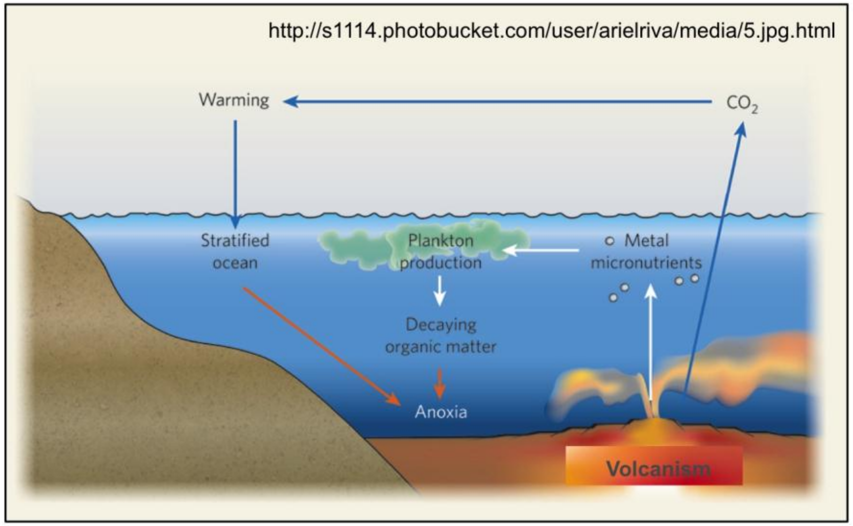
Oceanic Anoxic Events



Jenkyns (2010)



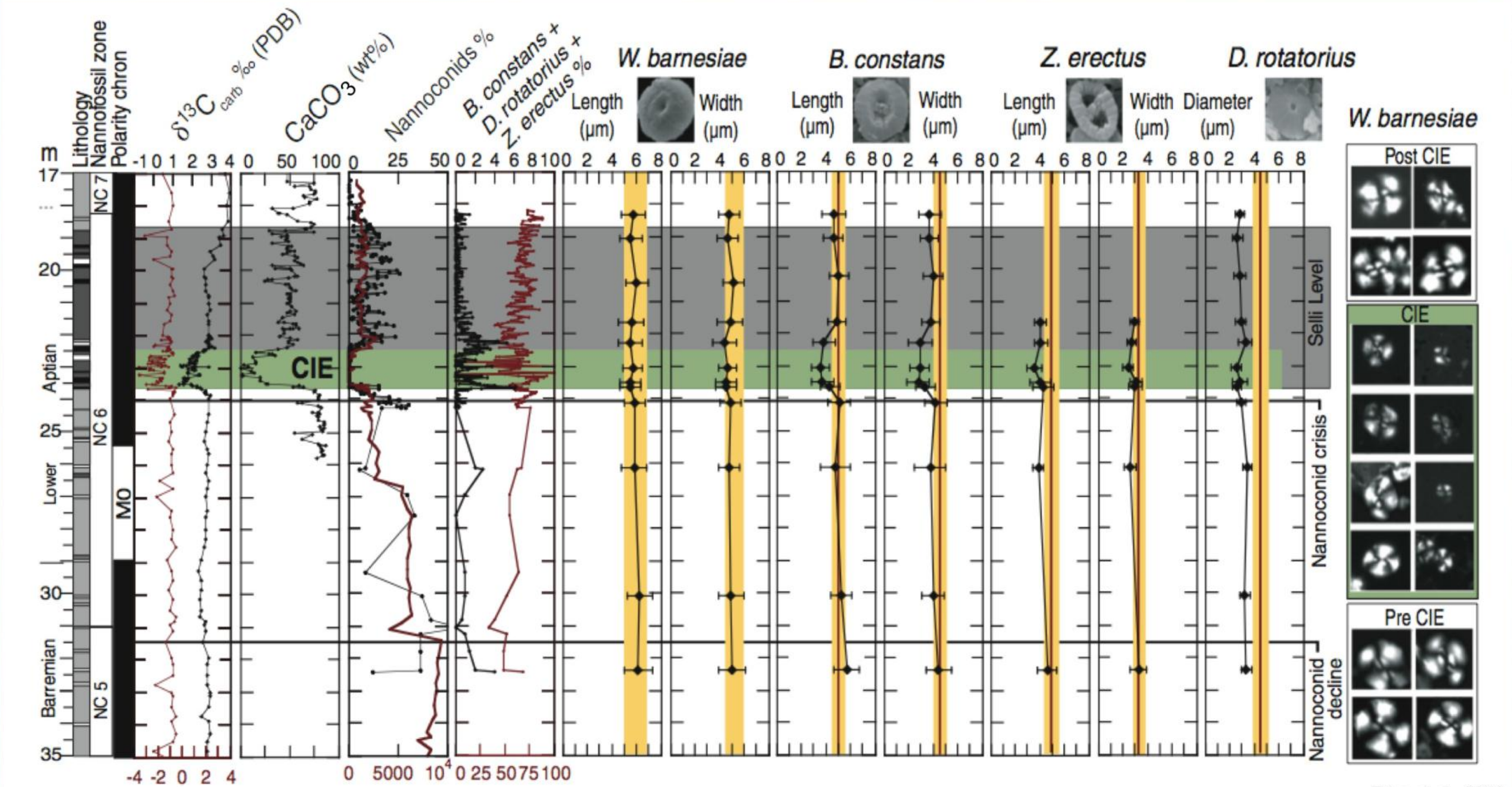
Jenkyns (2010)


http://s1114.photobucket.com/user/arielriva/media/5.jpg.html

doi:10.1002/loe2.10003

Oceanic Anoxic Events

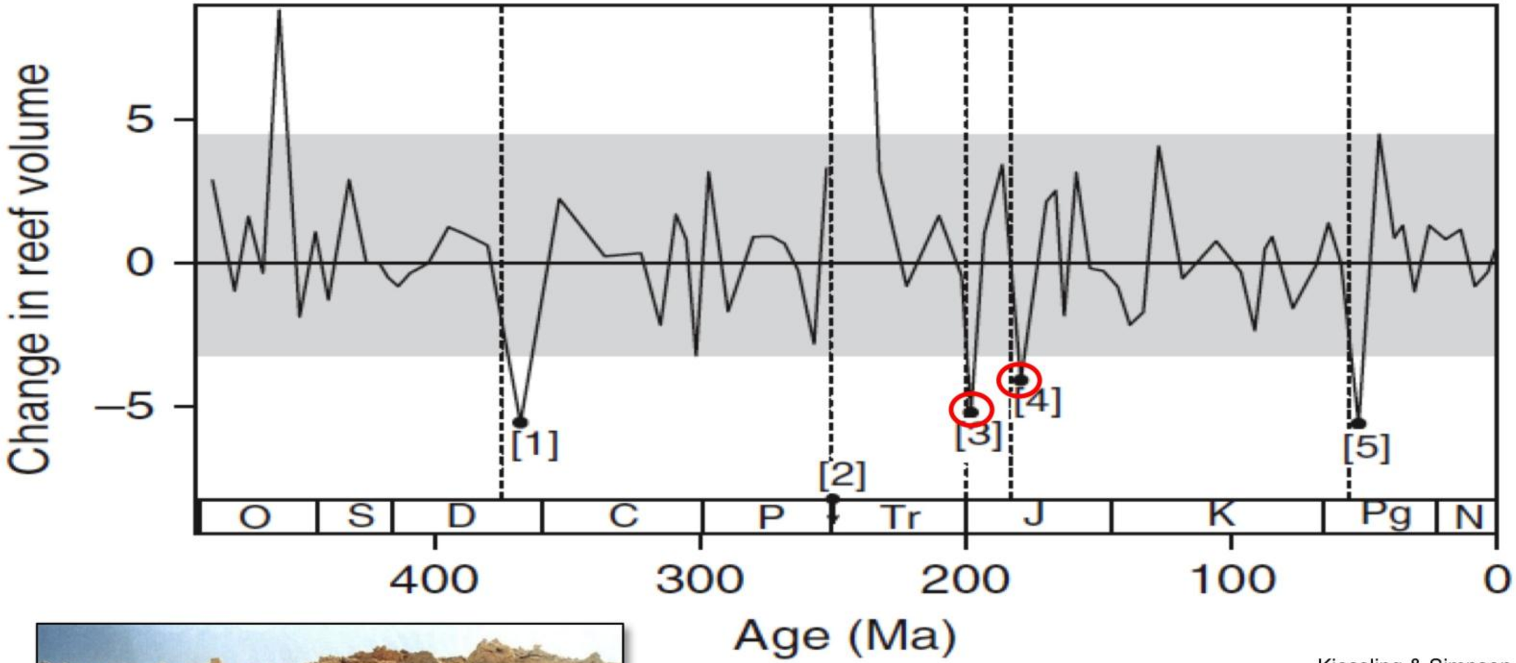
Malformation and size reduction in nanoplankton coincided with decreased $CaCO_3$ accumulation during OAE 1a.



Erba et al., 2010

doi:10.1002/loe2.10003

Oceanic Anoxic Events



Kiessling & Simpson, 2011

https://ferrebeekeeper.wordpress.com/tag/rudist/

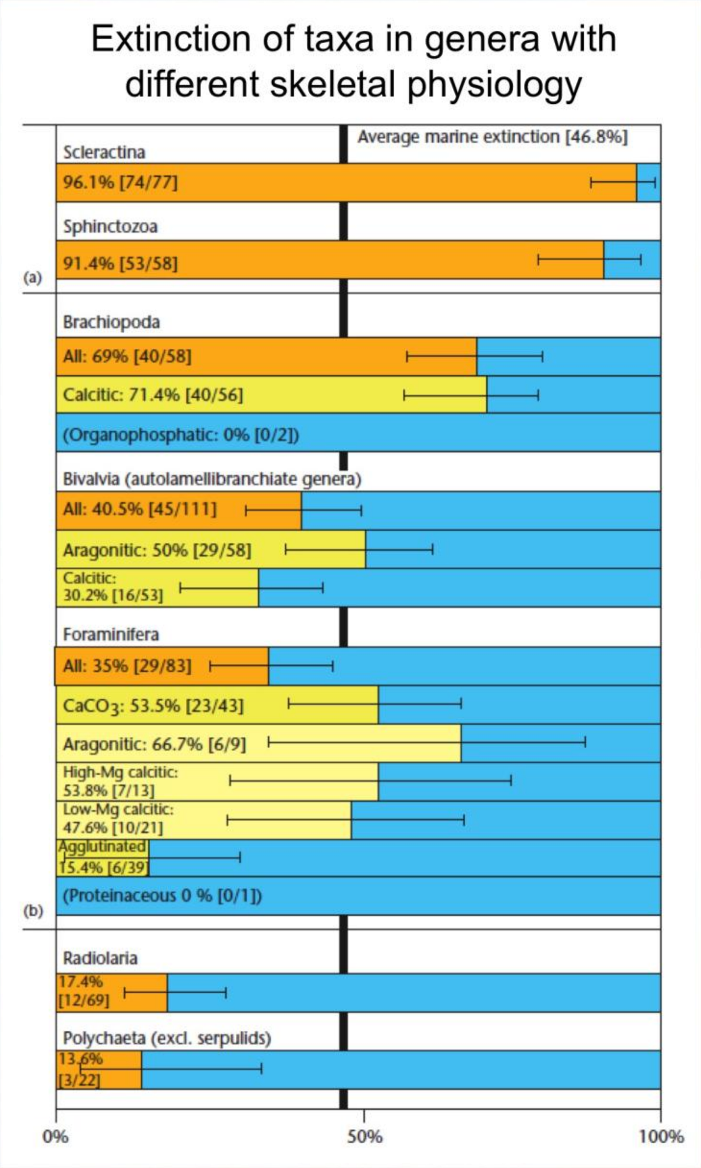
Temperature: ✓
pH and Ω: ?
Shallow water dissolution: ✓
Reef crisis: ✓
deep ocean evidence: ?
Onset: 650 y -20 ky

Triassic – Jurassic (~201 Ma)

- Sudden termination of $CaCO_3$ deposition in pelagic sediments
- Temporal association with CAMP magmatism suggests OA may have been the culprit
- But: tropical species more affected than extra-tropical species, suggesting warming was an important player

Reef crisis: ✓ (but mostly tropical)
$CaCO_3$ accumulation changes: ✓
Duration: 20-600 ky

Črne et al., 2011


Extinction of taxa in genera with different skeletal physiology

Hautmann et al. (2008)

doi:10.1002/loe2.10003

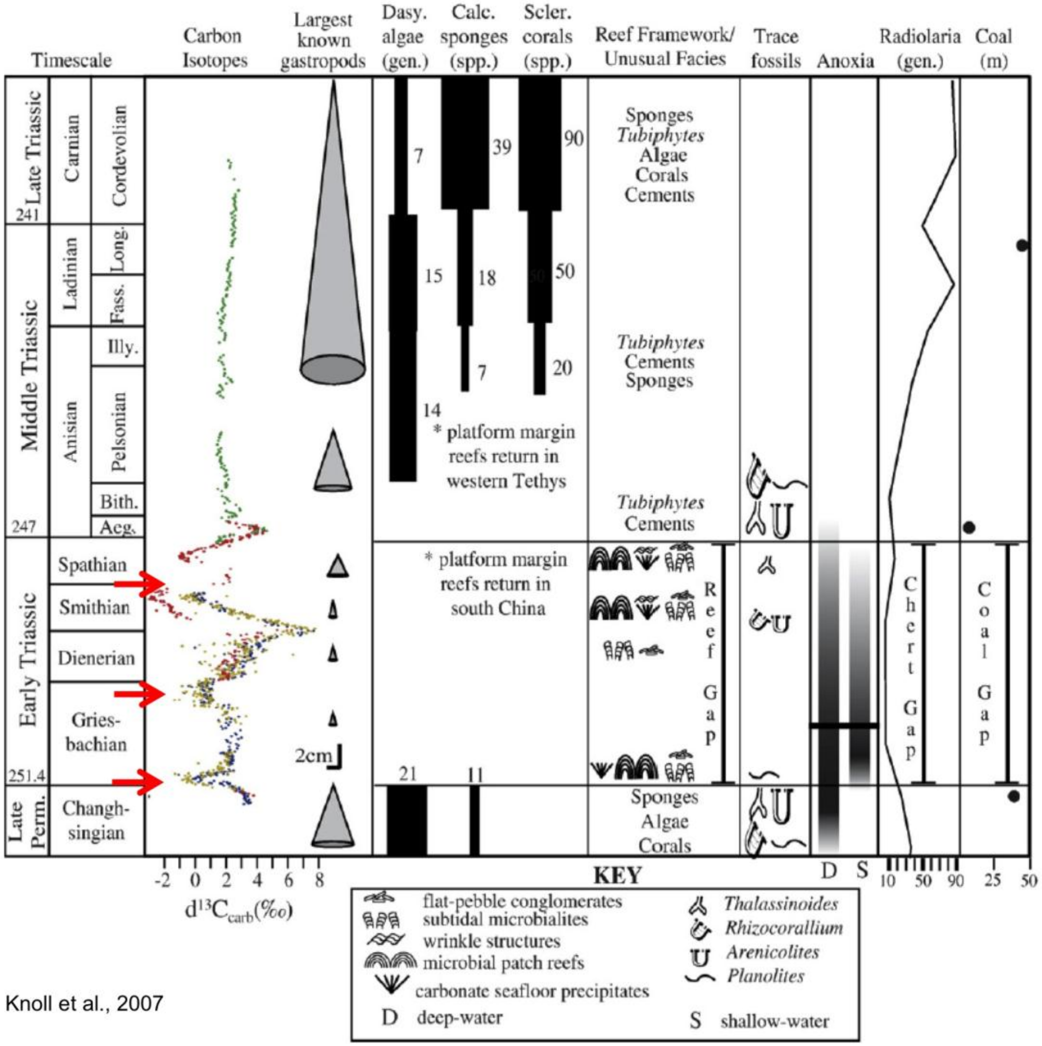
End of Permian (~251 Ma)

Artist's rendering of the landscape during end-Permian extinction.

Credit: José-Luis Olivares/MIT

Selective survival of marine invertebrates best explained by physiological responses to elevated pCO_2 (i.e. hypercapnia)

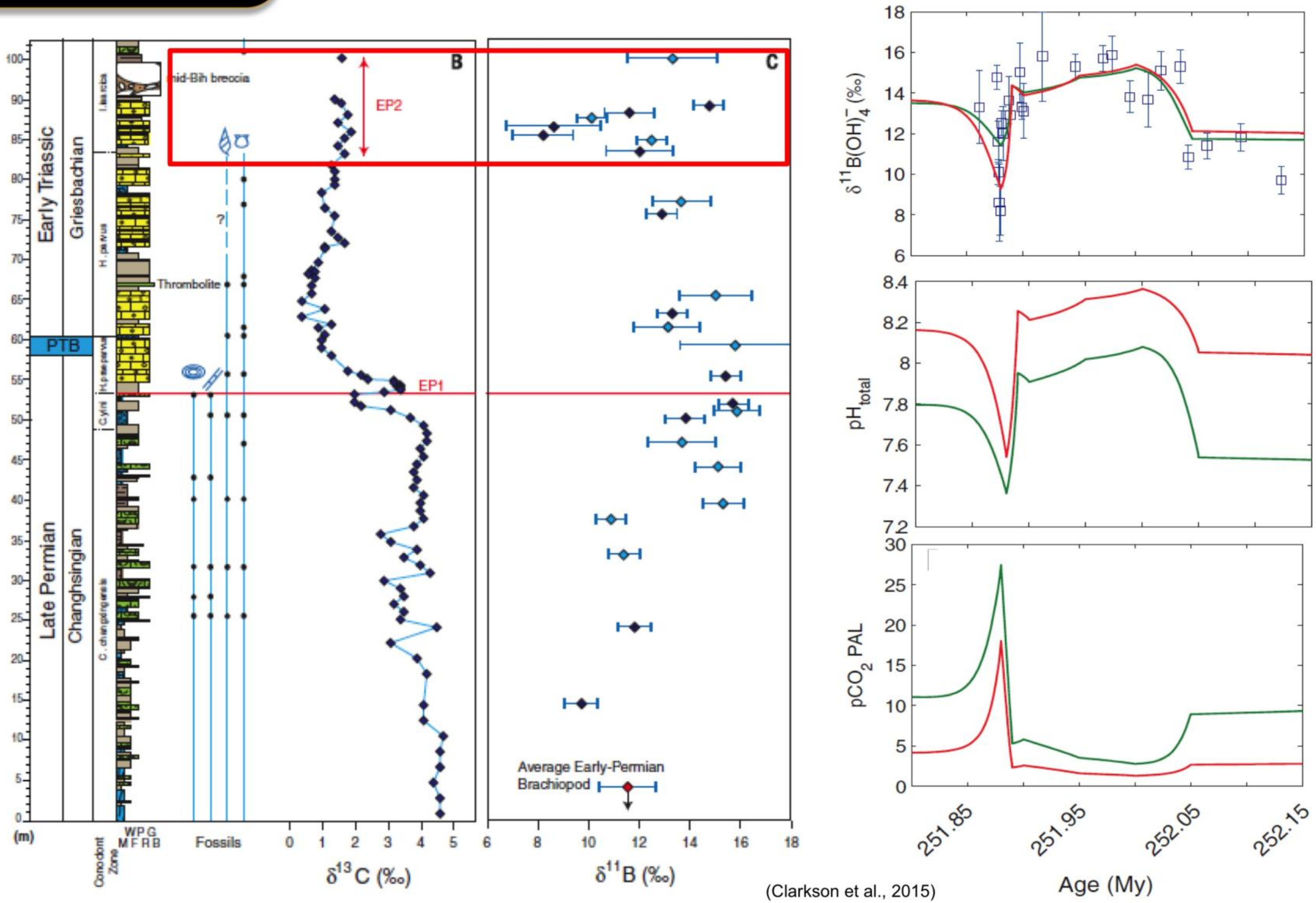
http://www.utas.edu.au/library/exhibitions



Knoll et al., 2007

doi:10.1002/loe2.10003

End of Permian



(Clarkson et al., 2015)

doi:10.1002/loe2.10003

End of Permian

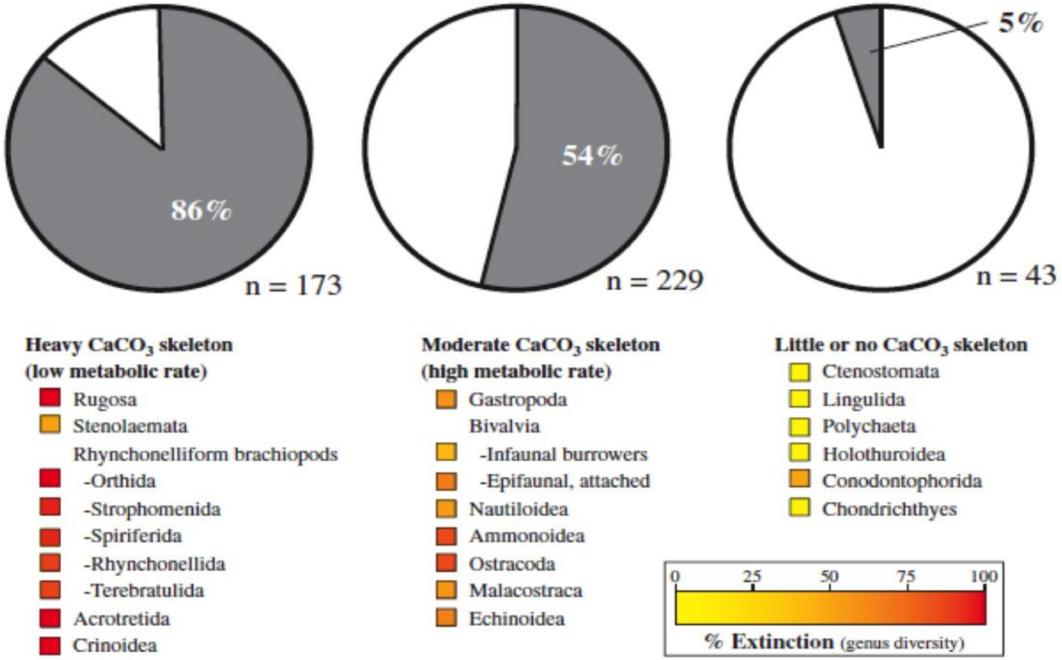


Figure 4.3 Selective extinction during the end-Permian crisis (data from Knoll *et al*. 2007). Hypercalcifers and other animals that have a limited capacity to buffer internal fluids lost 86% of known genera; groups with carbonate skeletons but well-developed physiological mechanisms for buffering internal fluids lost 54% of genera; and groups that use carbonate minerals sparingly or not at all in skeleton formation lost 5% of genera. Colour coding for individual taxa shows how they align along a gradient of increasing extinction severity. The distribution of taxa along this gradient can be predicted from expected variations in vulnerability of these different groups to hypercapnia and ocean acidification as deduced from physiological experiments. See text for discussion and references.

Knoll and Fisher, 2011

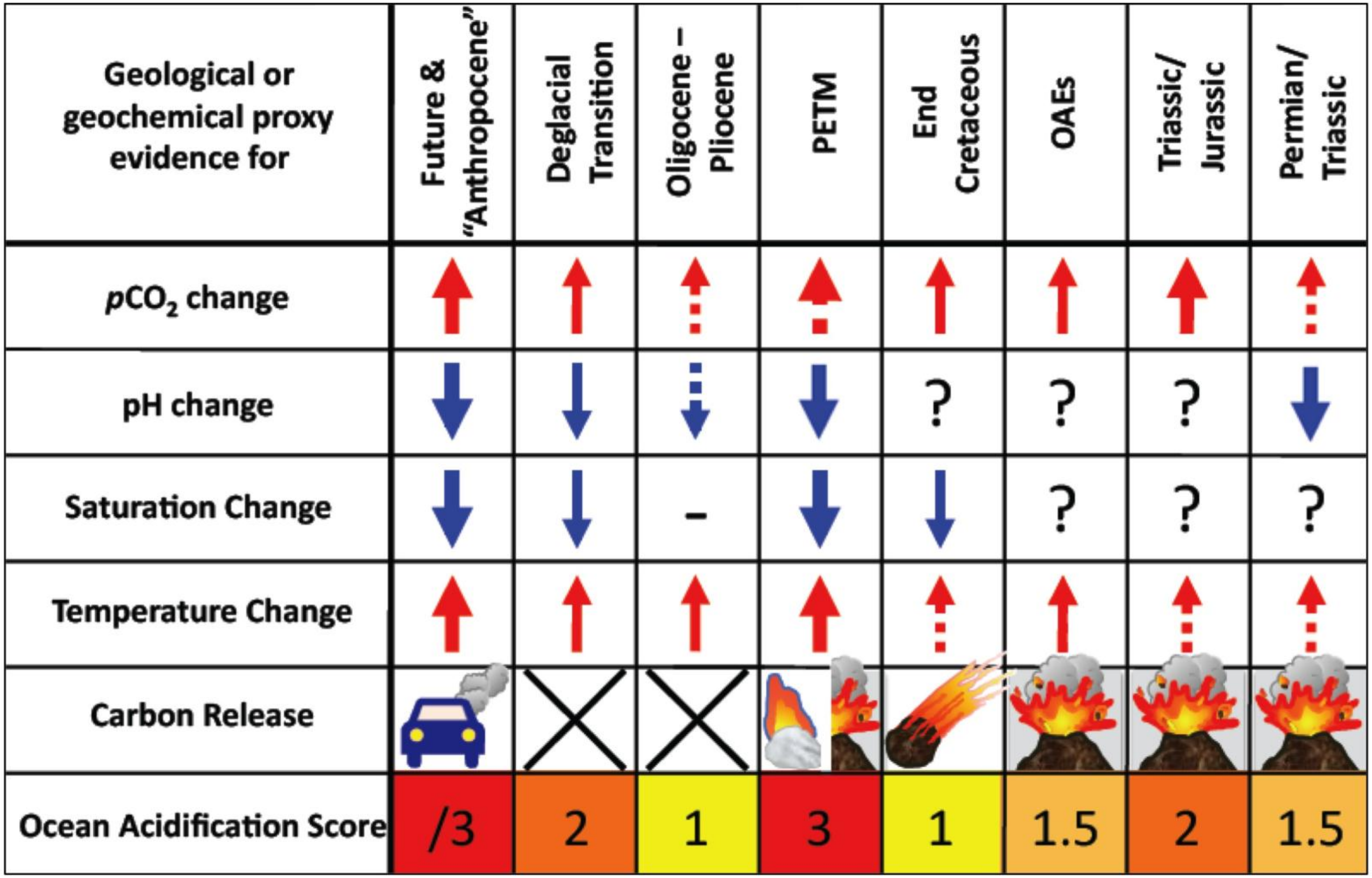

safossils.com


wikipedia.org


britannica.com

Strong warming: ✓
pH: -0.7 units
Reef crisis: ✓
$CaCO_3$ accumulation changes: ✓
Duration: pulses shorter than 60 ky

Does the geological record provide analogues for future OA?



Geological or geochemical proxy evidence for	Future & "Anthropocene"	Deglacial Transition	Oligocene – Pliocene	PETM	End Cretaceous	OAEs	Triassic/ Jurassic	Permian/ Triassic
$p\mathrm{CO_2}$ change	↑	↑	⇡	⇡	↑	↑	↑	⇡
pH change	↓	↓	⇣	↓	?	?	?	↓
Saturation Change	↓	↓	–	↓	↓	?	?	?
Temperature Change	↑	↑	↑	↑	⇡	↑	⇡	⇡
Carbon Release	🚗	✕	✕	🔥 🌋	☄	🌋	🌋	🌋
Ocean Acidification Score	/3	2	1	3	1	1.5	2	1.5

updated after Hönisch et al. 2012

Conclusions

Carbon cycle feedbacks operating on time scales of 100 kyrs and longer may experience high pCO_2 and low ocean pH, but no decrease in carbonate saturation (e.g., the Cretaceous); these intervals are poor analogues for future acidification.

Several extinction events were caused by rapid perturbations in the ocean carbon-cycle, and share some characteristics with anthropogenic ocean acidification.

Estimated rates of CO_2 release during these events are substantially slower than the current anthropogenic CO_2 release, hence it is possible that global biogeochemical cycles will undergo considerable changes, and will include consequences for marine ecosystems.

doi:10.1002/loe2.10003

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http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)2164-0254