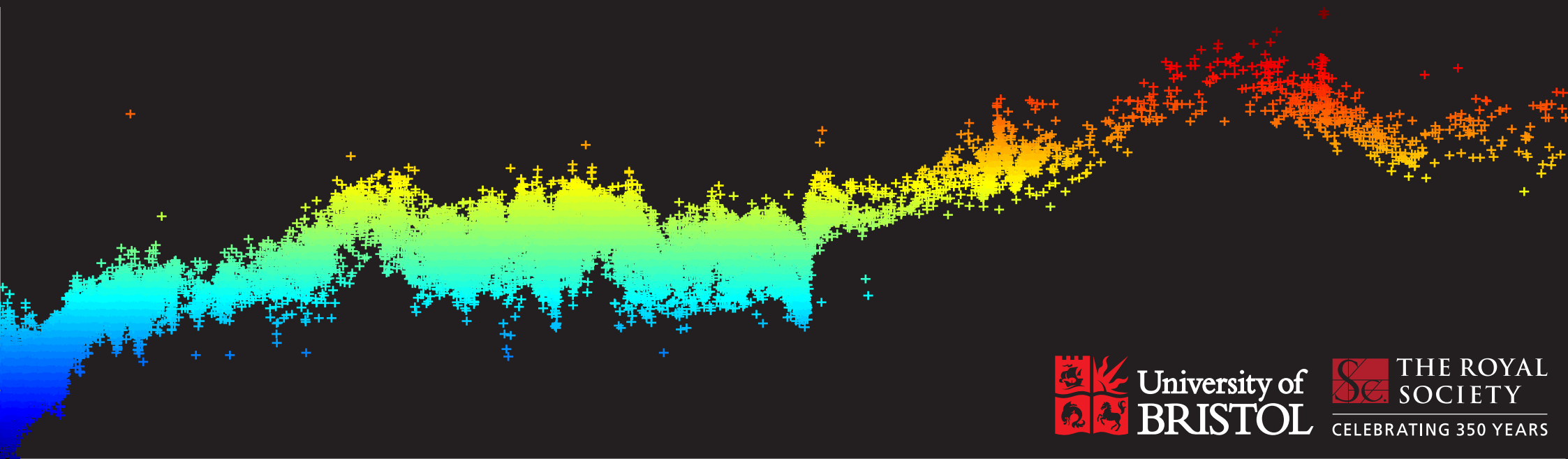


The Geological Record of Ocean Acidification

Andy Ridgwell





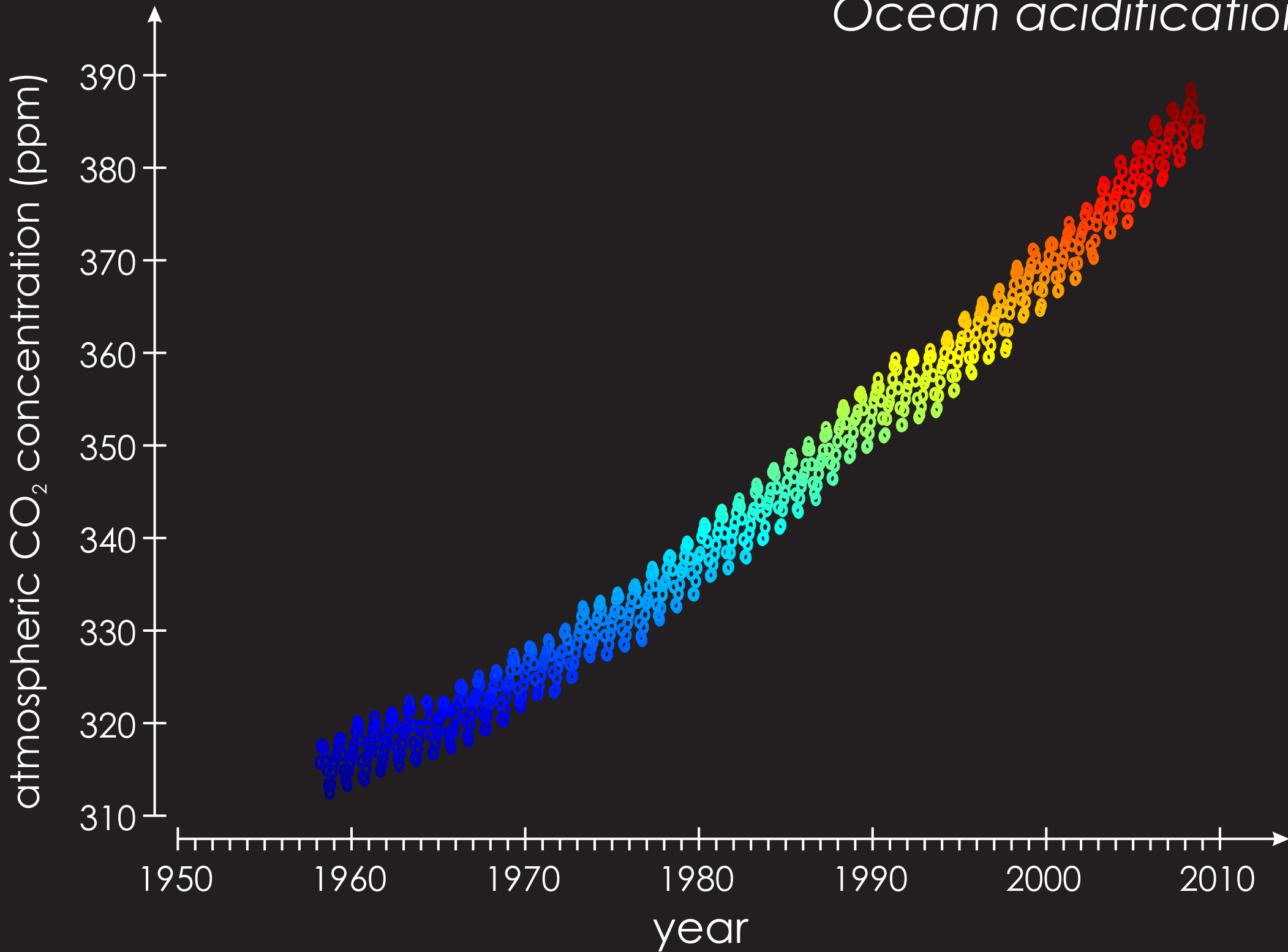




Google



Ocean acidification



Ocean acidification



Rising carbon emissions could wipeout marine species with oceans acidifying at fastest rate

By [Daily Mail Reporter](#)

Last updated at 12:10 PM on 2nd March 2012

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This is all just guesses made from tiny samples of imperfect information by people who are looking for the answer they want to find.

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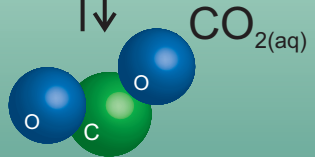
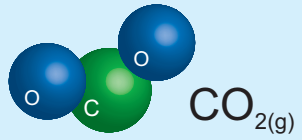
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atmosphere



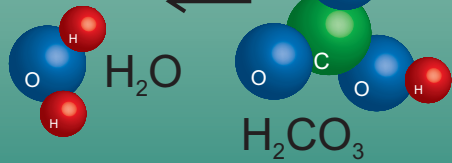
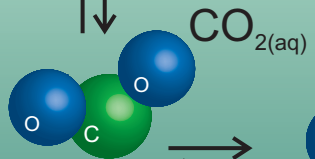
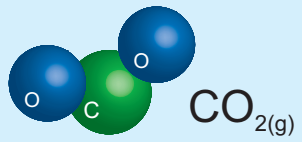
ocean

CO_2 chemistry in seawater

From: *Barker and Ridgwell* [2012]

<http://www.nature.com/scitable/knowledge/library/ocean-acidification-25822734>

atmosphere

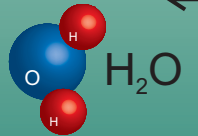
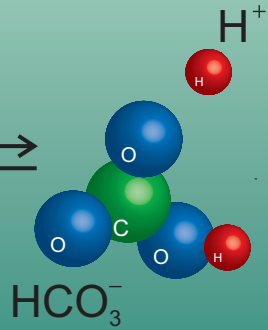
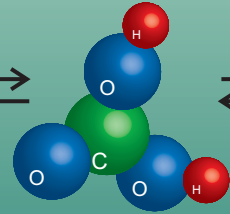
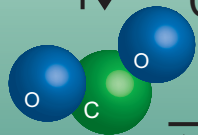
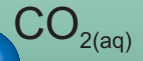
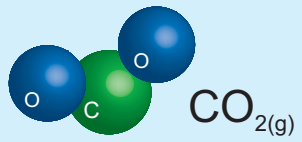


carbonic acid

ocean

CO_2 chemistry
in seawater

atmosphere

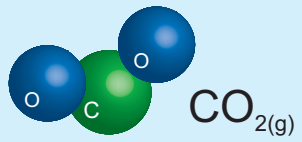


bicarbonate ion

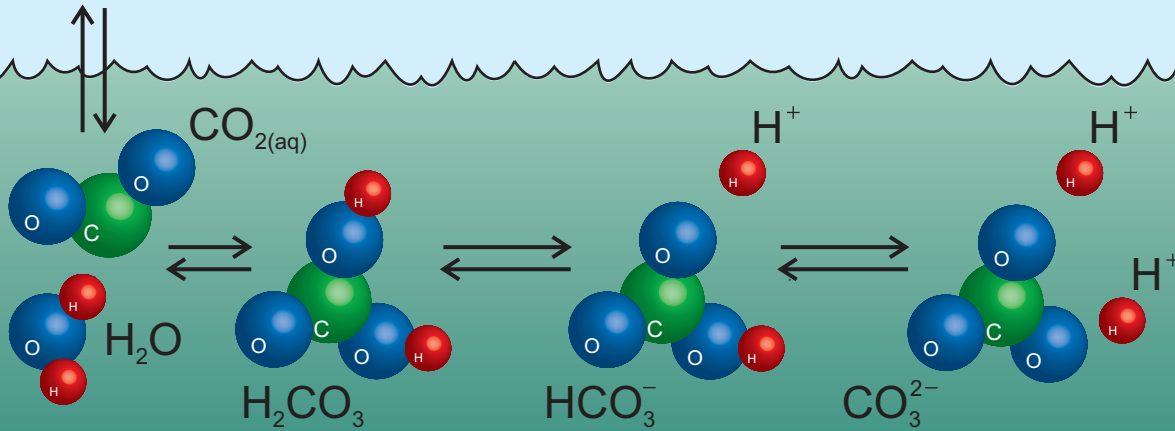
ocean

CO_2 chemistry
in seawater

atmosphere



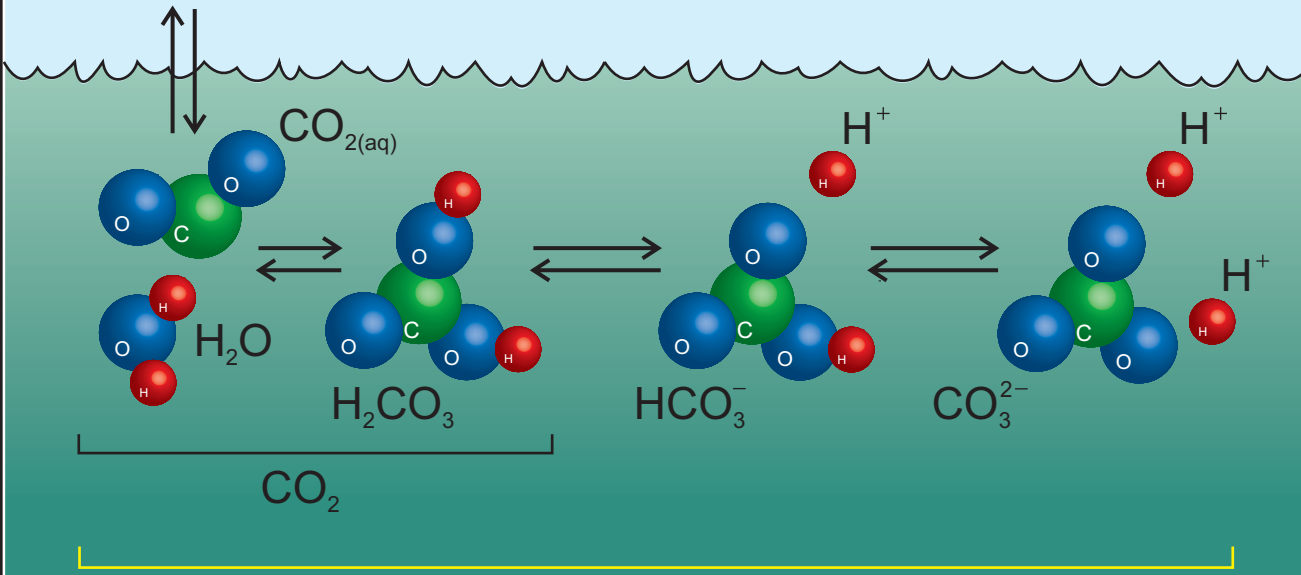
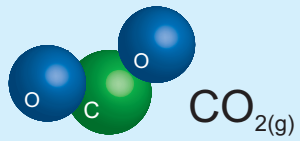
CO_2 chemistry
in seawater



carbonate ion

ocean

atmosphere



'DIC' (dissolved inorganic carbon)

ocean

CO_2 chemistry in seawater

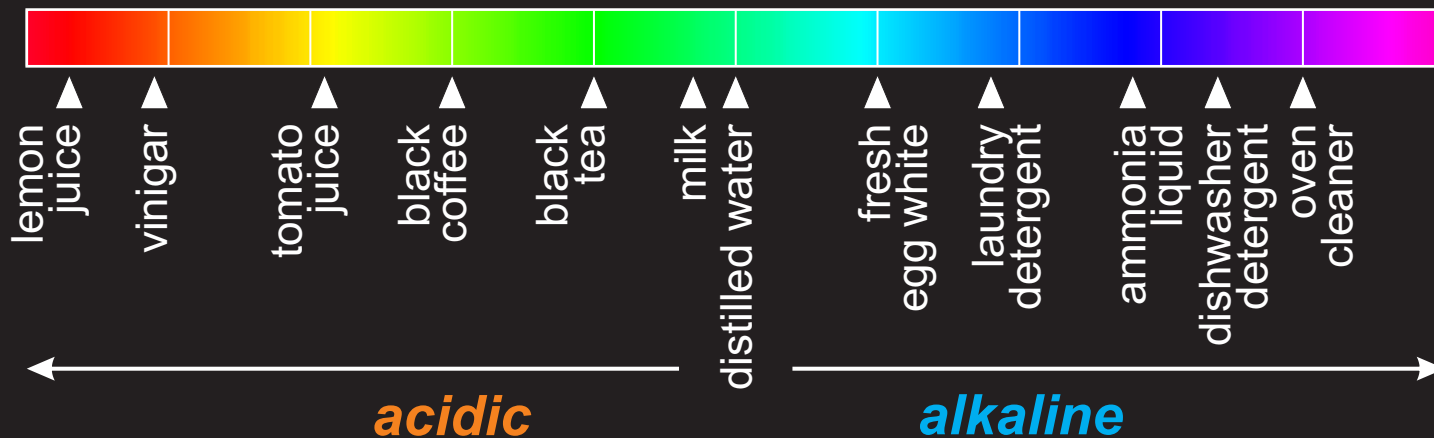
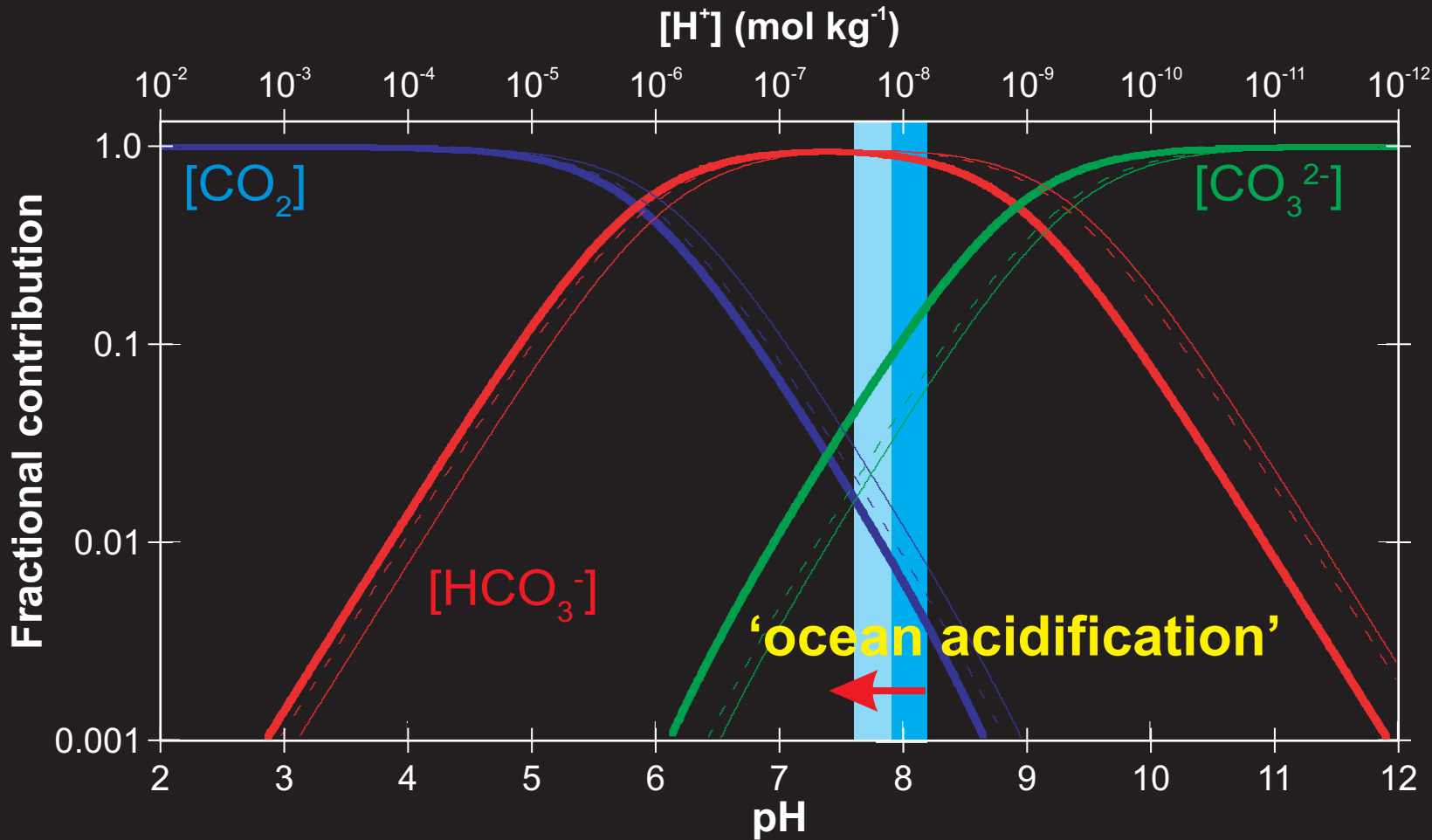
When CO_2 dissolves in seawater, the equilibrium distribution of dissolved carbon between $\text{CO}_{2(aq)}$, HCO_3^- , and CO_3^{2-} , is perturbed.

To a first approximation, the net outcome can be written:

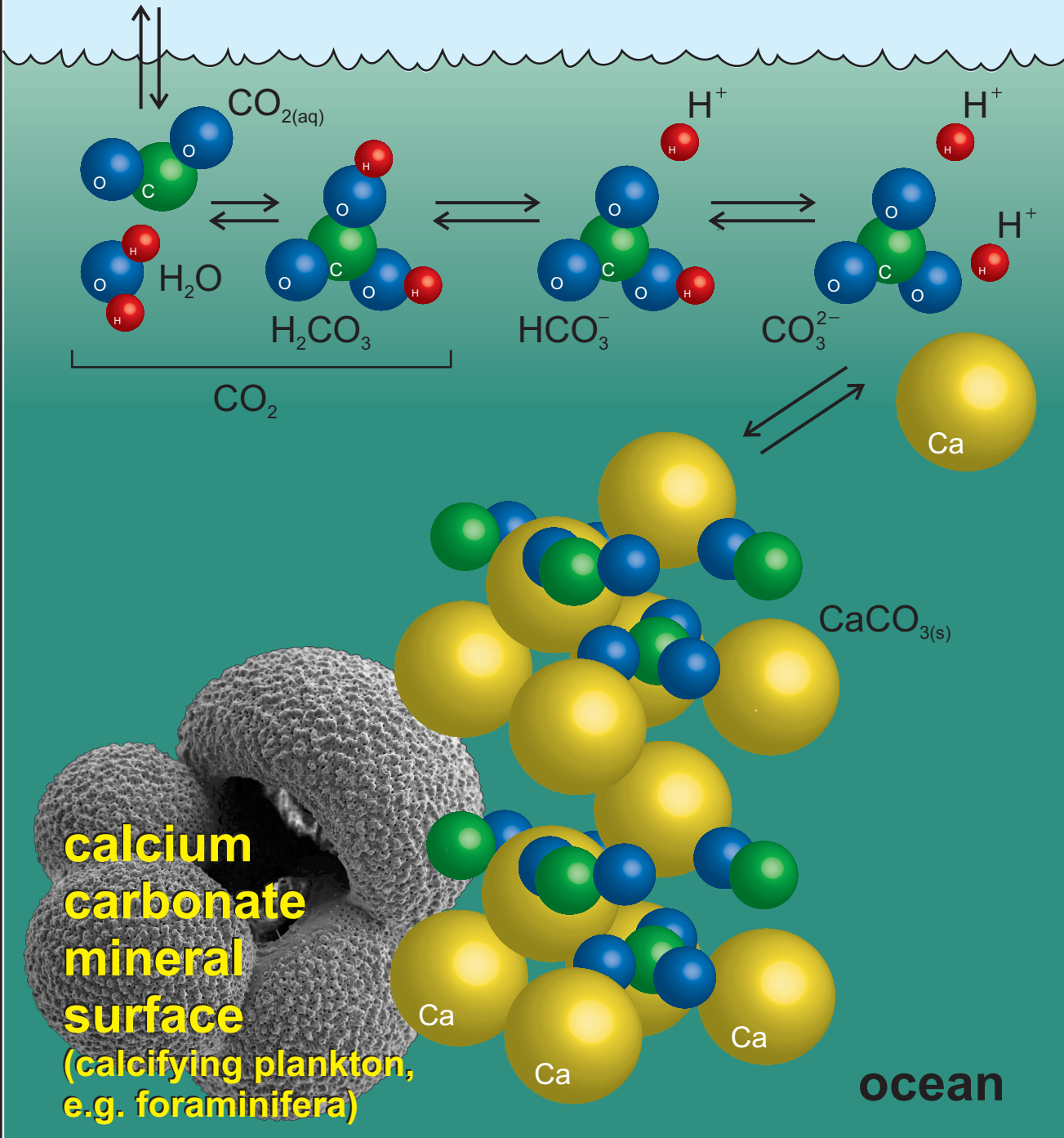
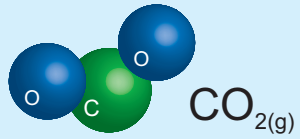


(However, a small part of the resulting HCO_3^- dissociates into CO_3^{2-} and H^+ , which is where the 'acidification' in ocean acidification comes from.)

The nature of pH (and acidity vs. alkalinity)



atmosphere



**calcium
carbonate
mineral
surface**

(calcifying plankton,
e.g. foraminifera)

CO_2 chemistry & mineral phases

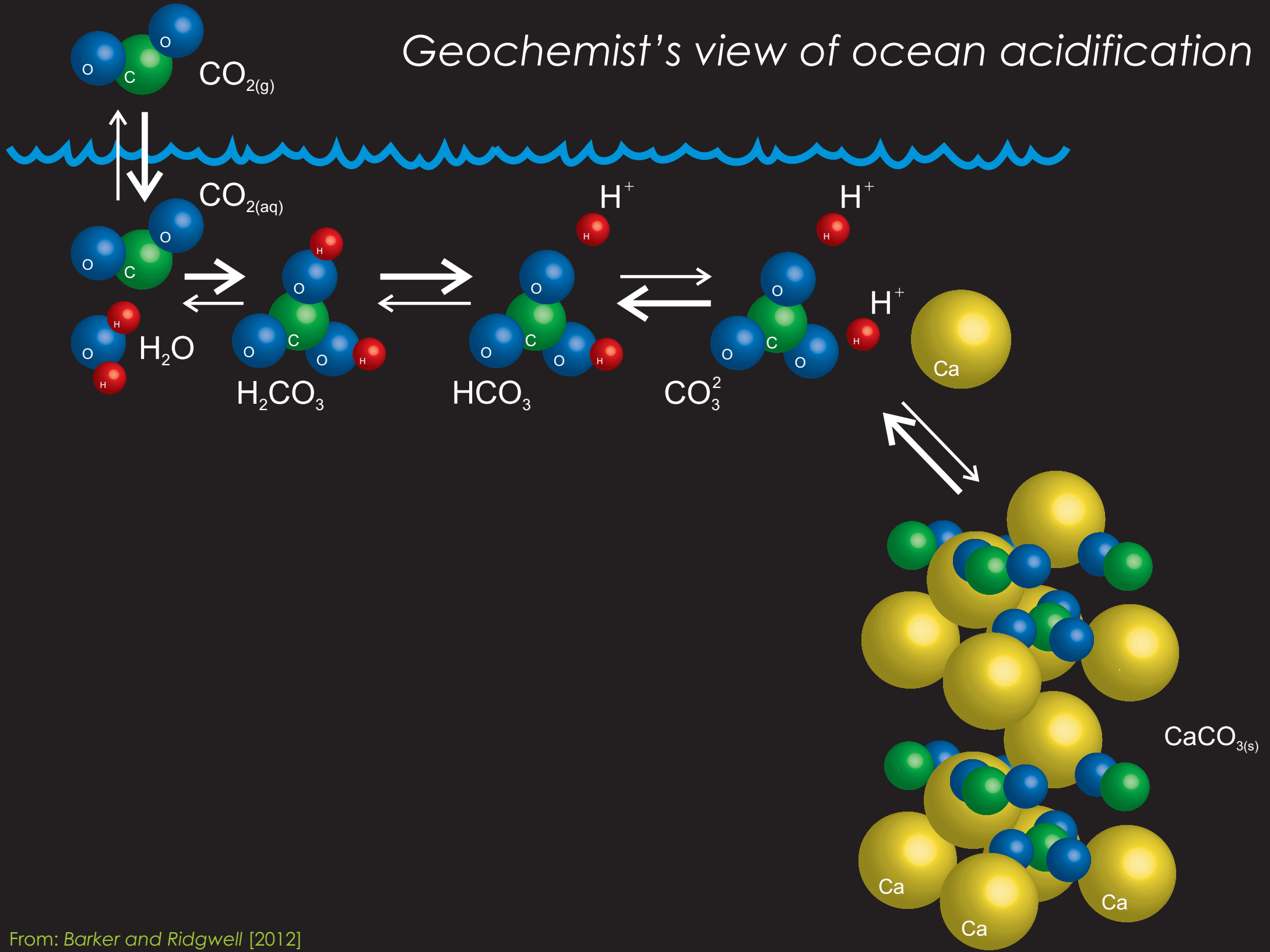
In decreasing the ocean carbonate ion (CO_3^{2-}) concentration, the stability of CaCO_3 , defined by its saturation state:

$$\Omega = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] / k$$

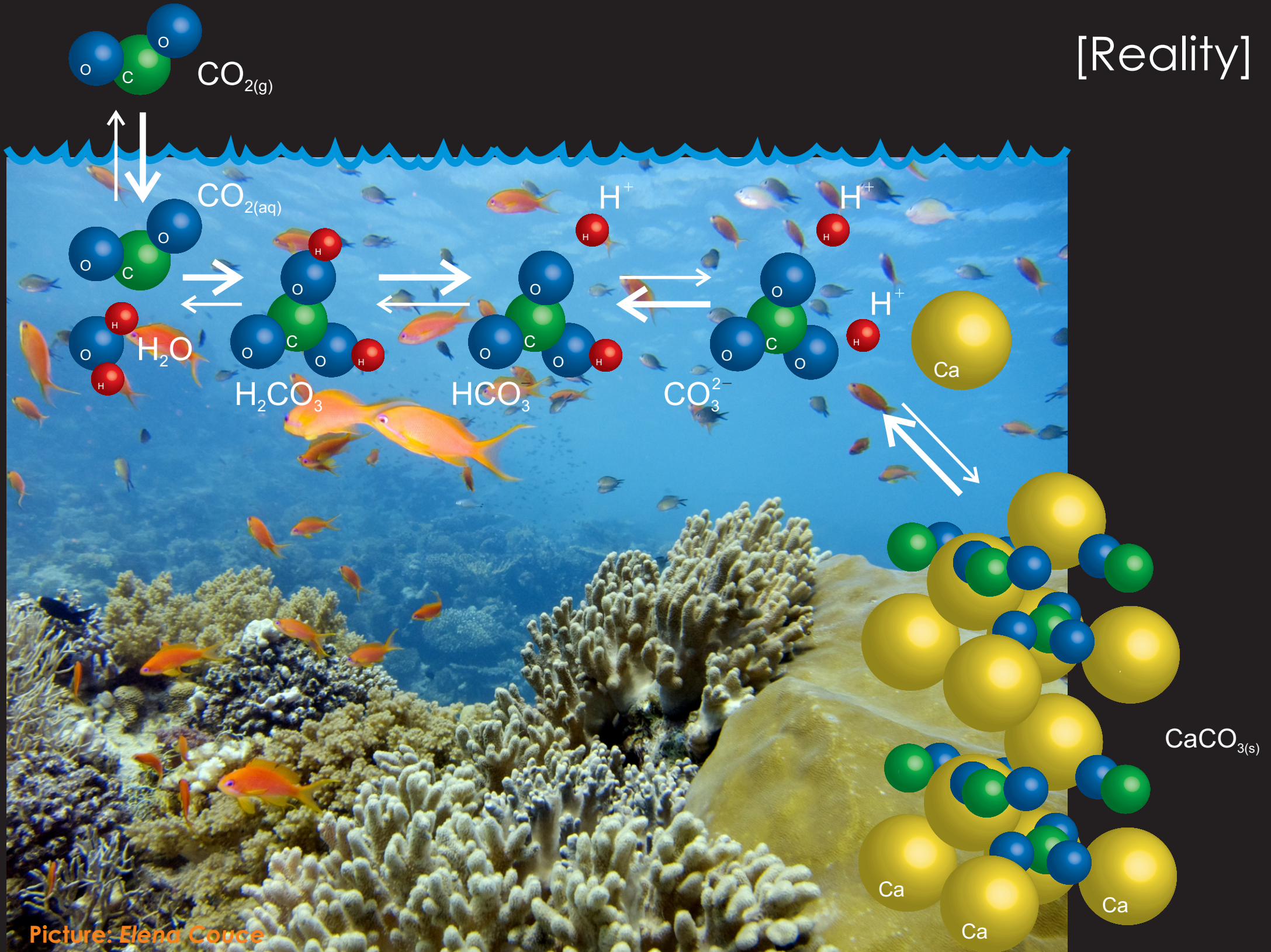
is suppressed.

Ω is simply a (normalized) measure of how thermodynamically favourable it is to precipitate CaCO_3 .

Geochemist's view of ocean acidification

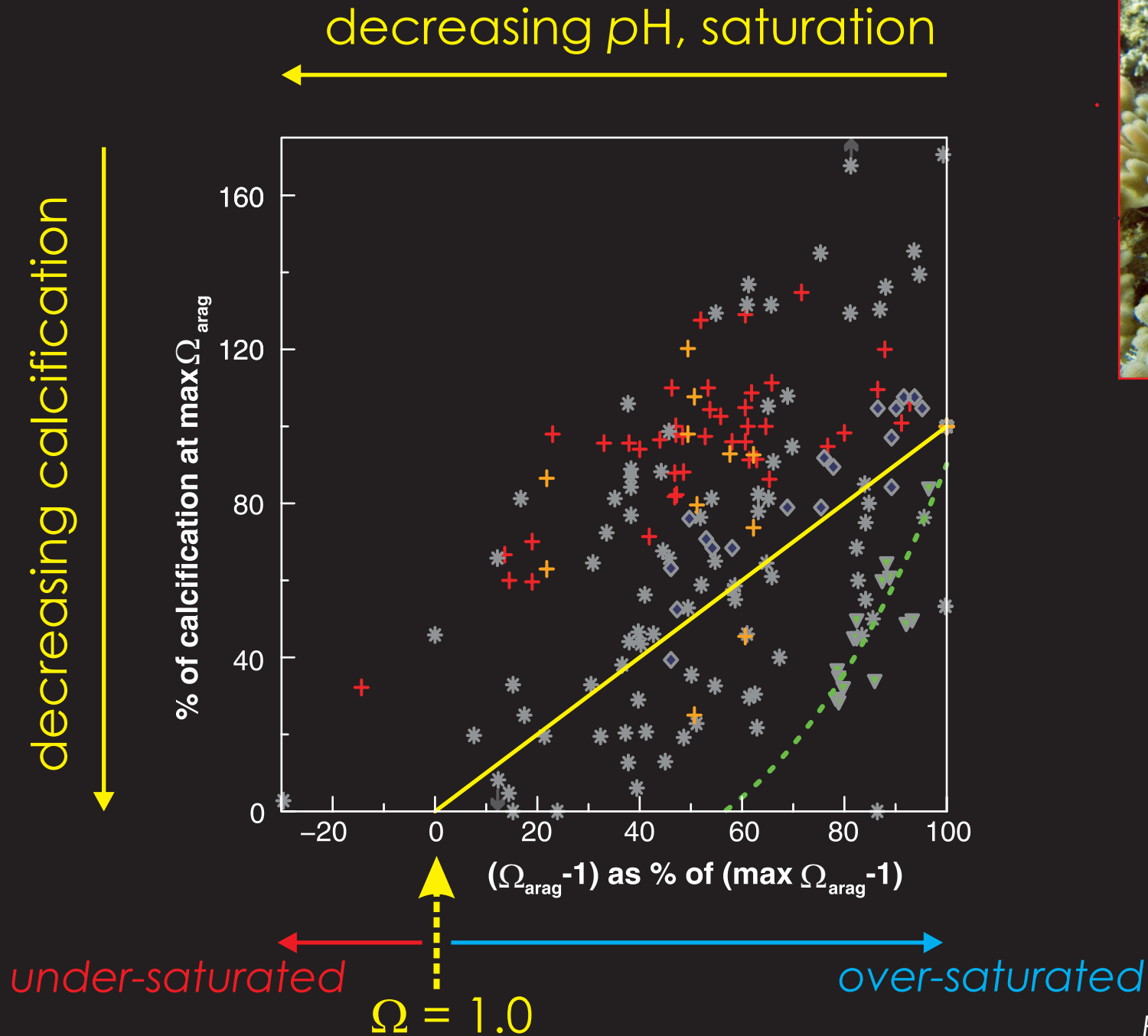


[Reality]

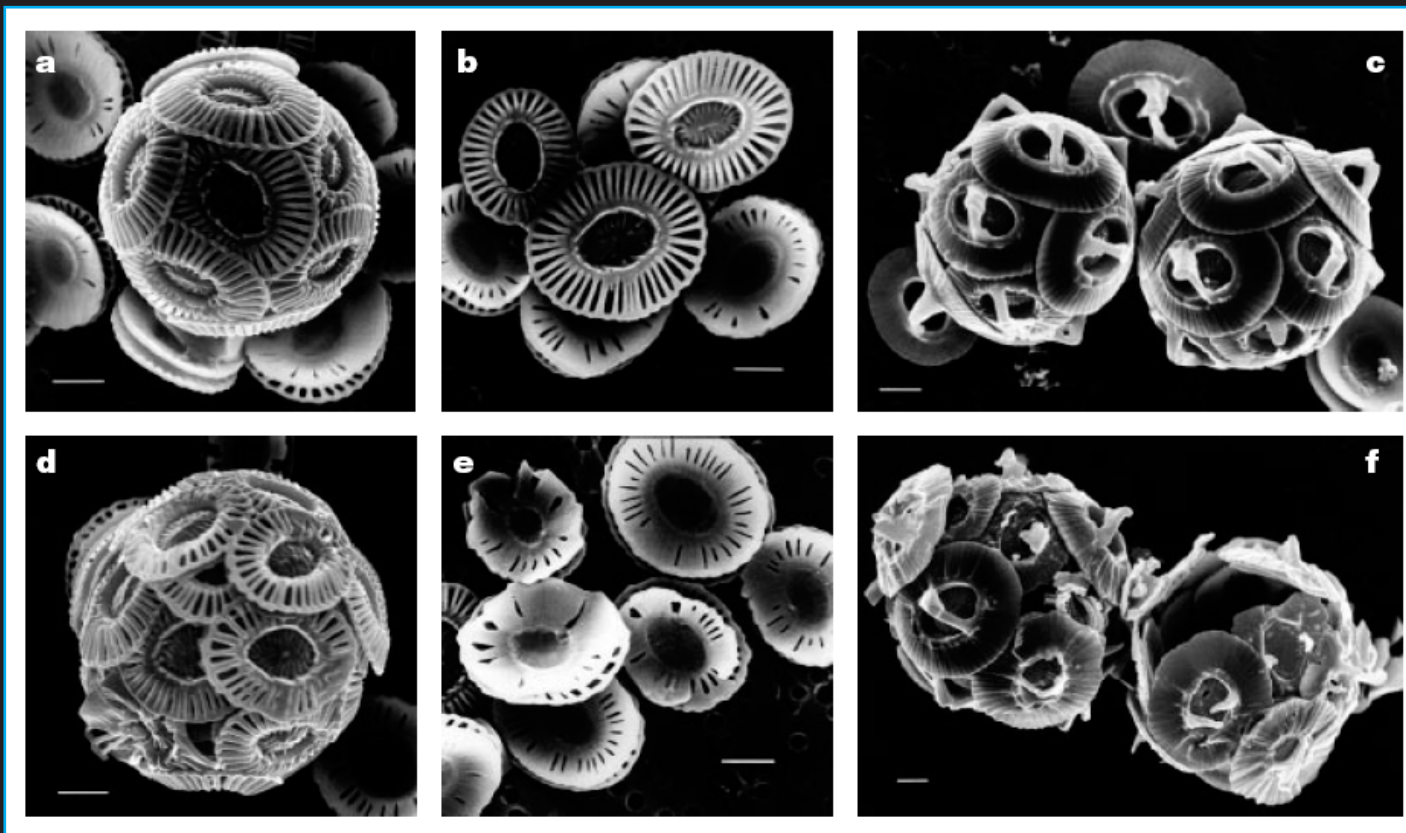


Picture: Elena Couce

Ocean biological consequences(?)



Ocean biological consequences(?)



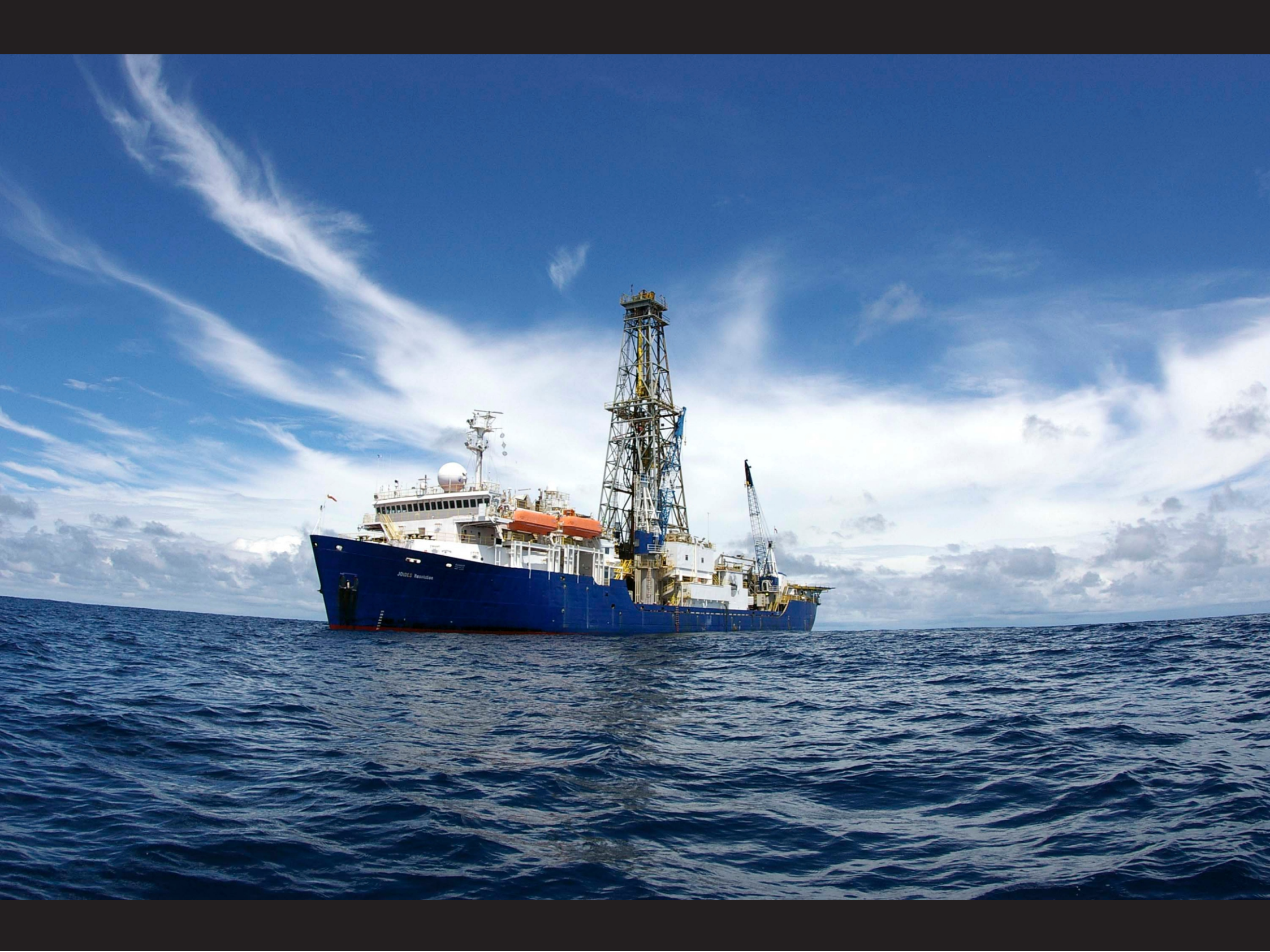
low CO₂ (high pH)

high CO₂ (low pH)

SEM micrographs of coccolithophorids under different CO₂ conditions
Riebesell et al. [2000] (Nature 407)

The geological record of ocean acidification

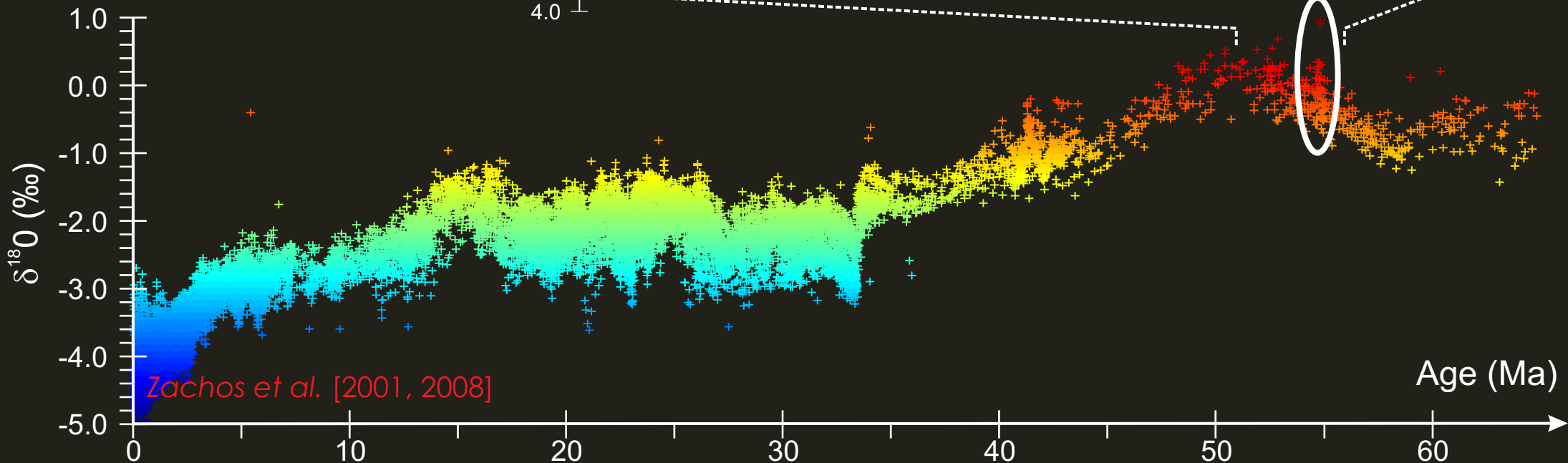
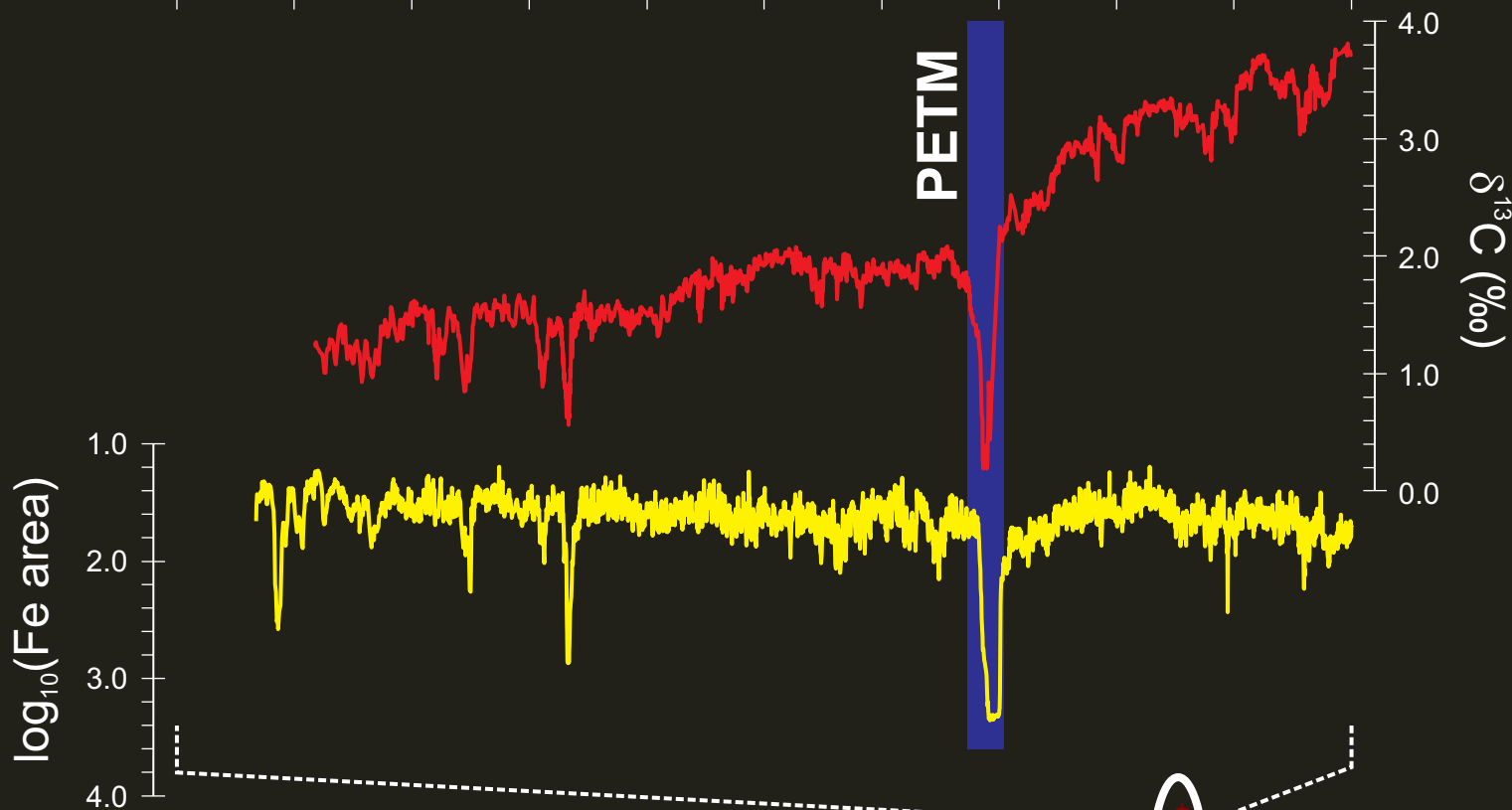




Zachos et al. [2010]
Lunt et al. [2011]

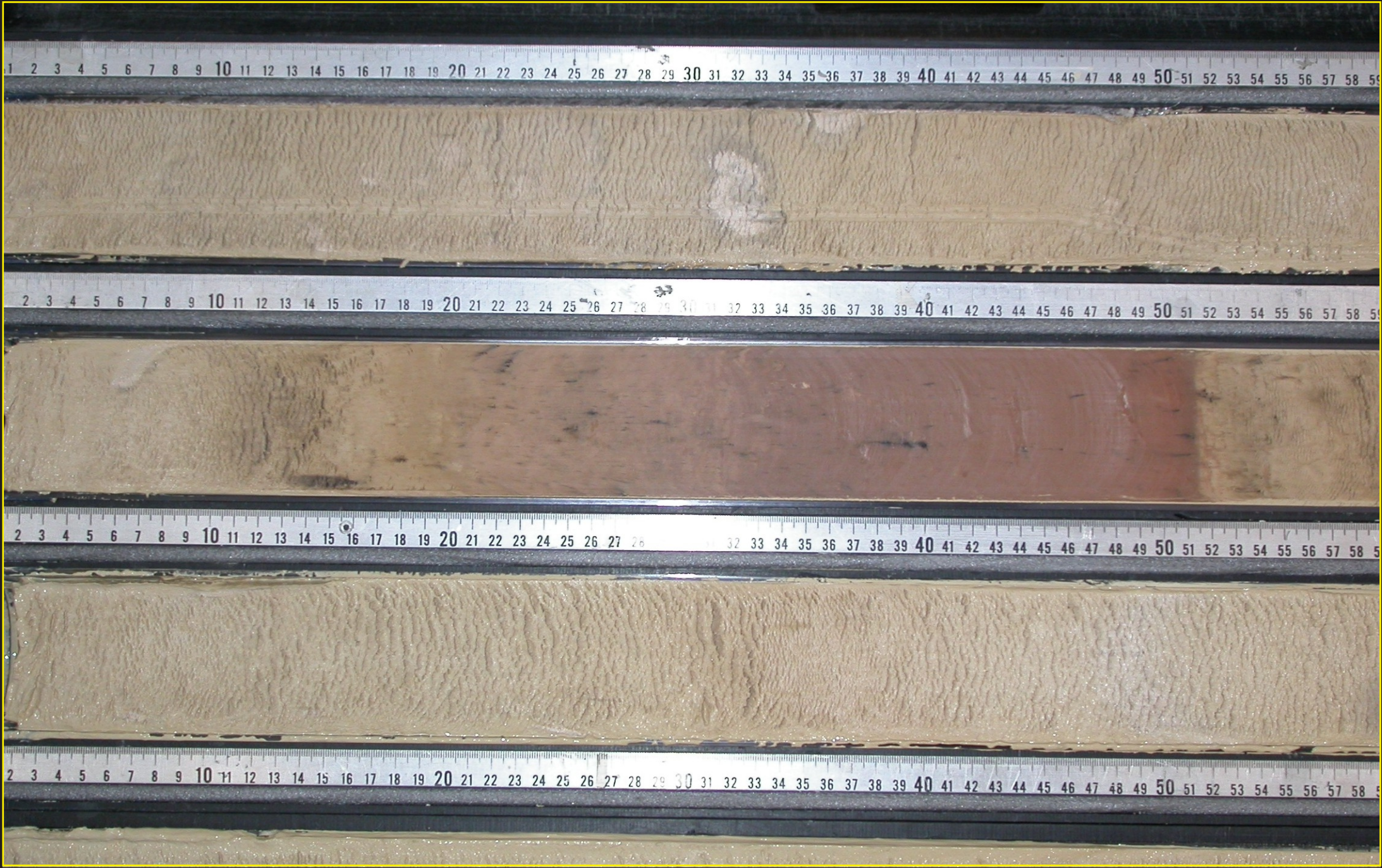
Age relative to the PETM (Ma)

-3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5



Zachos et al. [2001, 2008]

Age (Ma)



Sediments spanning the Palaeocene-Eocene boundary recovered from ODP Leg 208 (Walvis Ridge)
Picture courtesy of Daniela Schmidt (University of Bristol)

Fragile



Robust



Robust

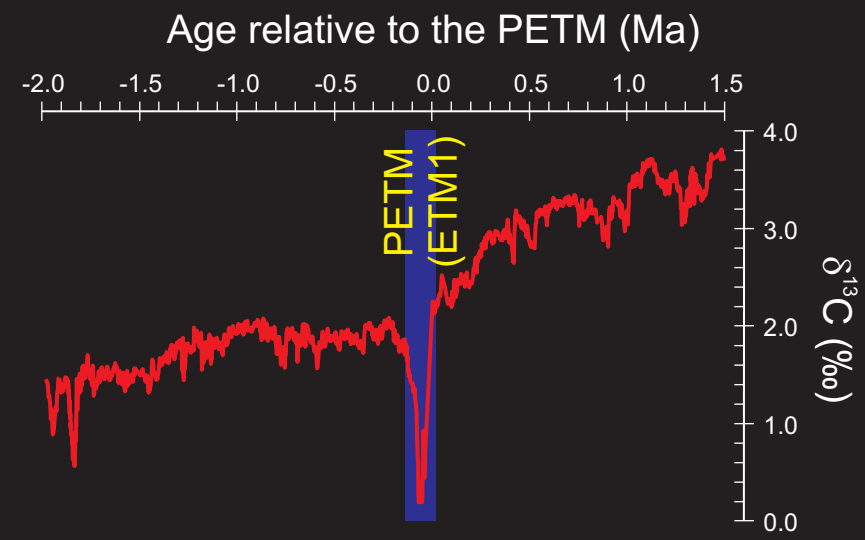
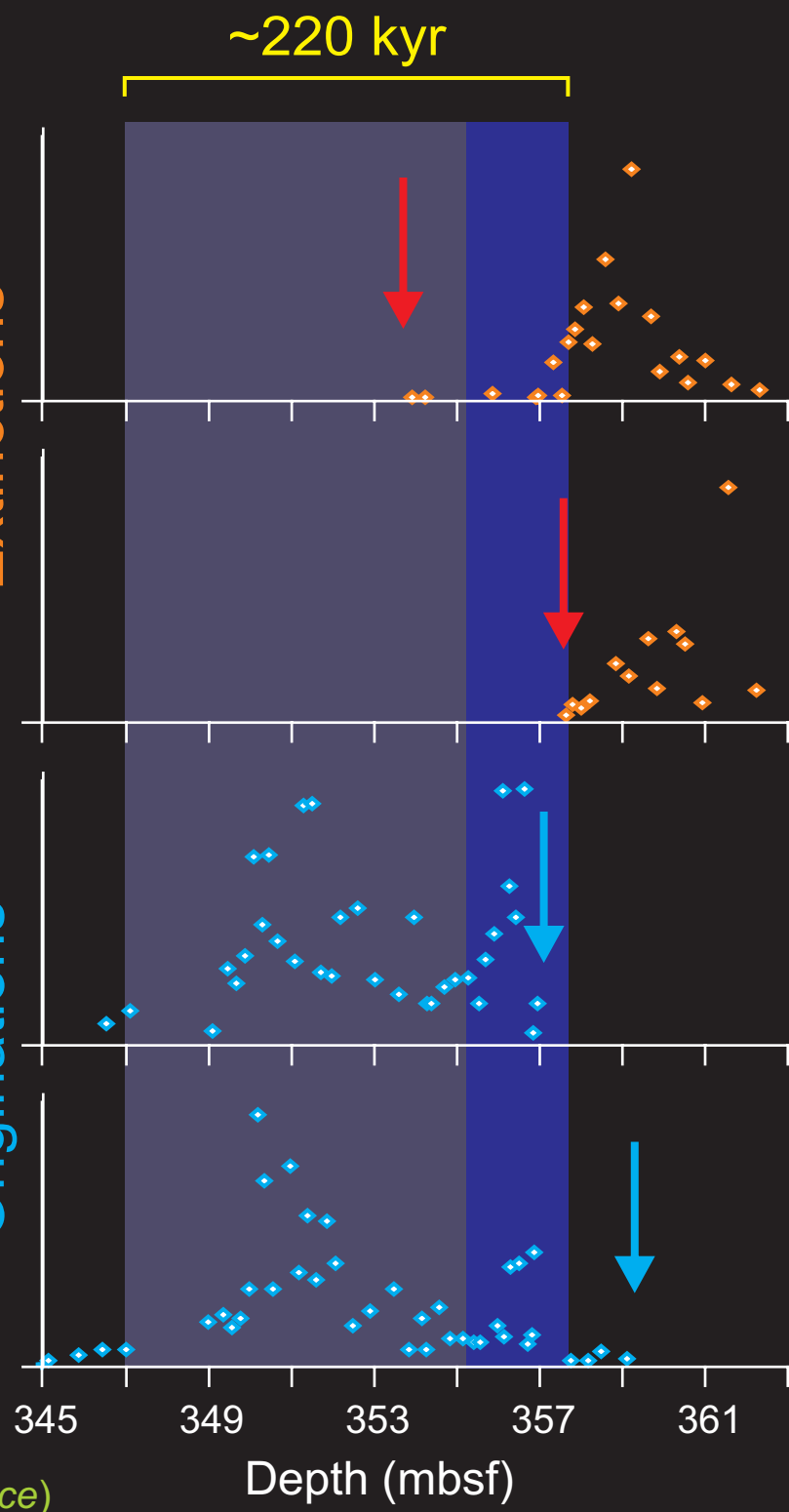


Fragile



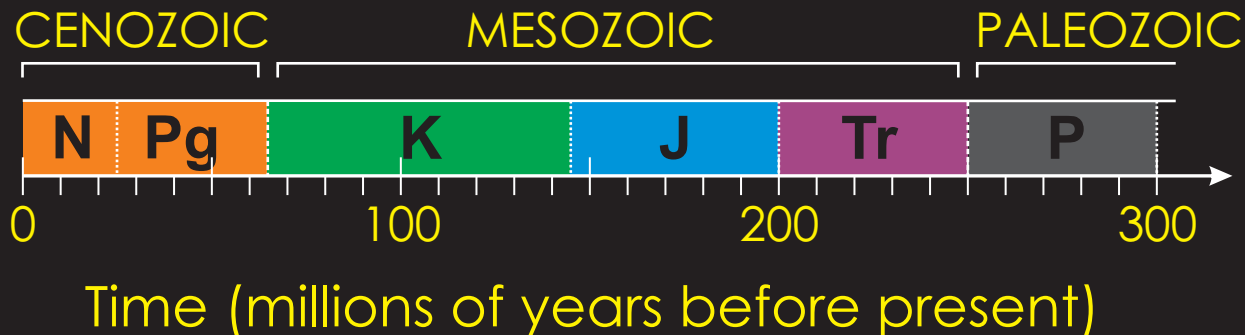
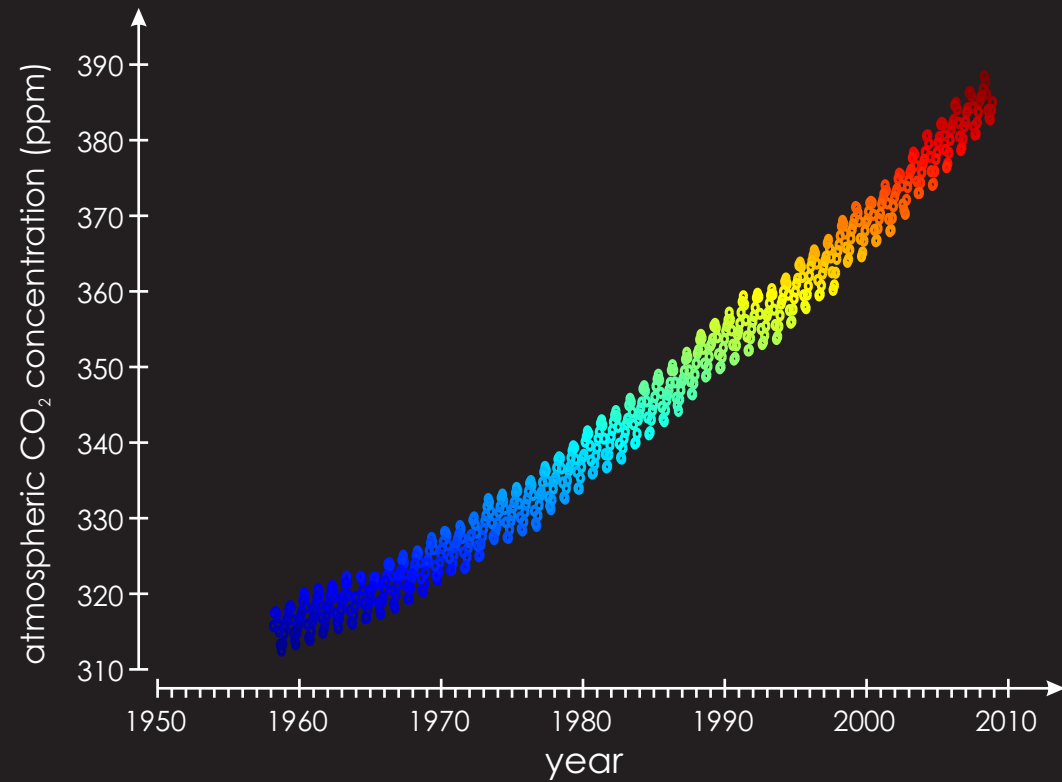
Extinctions

Originations

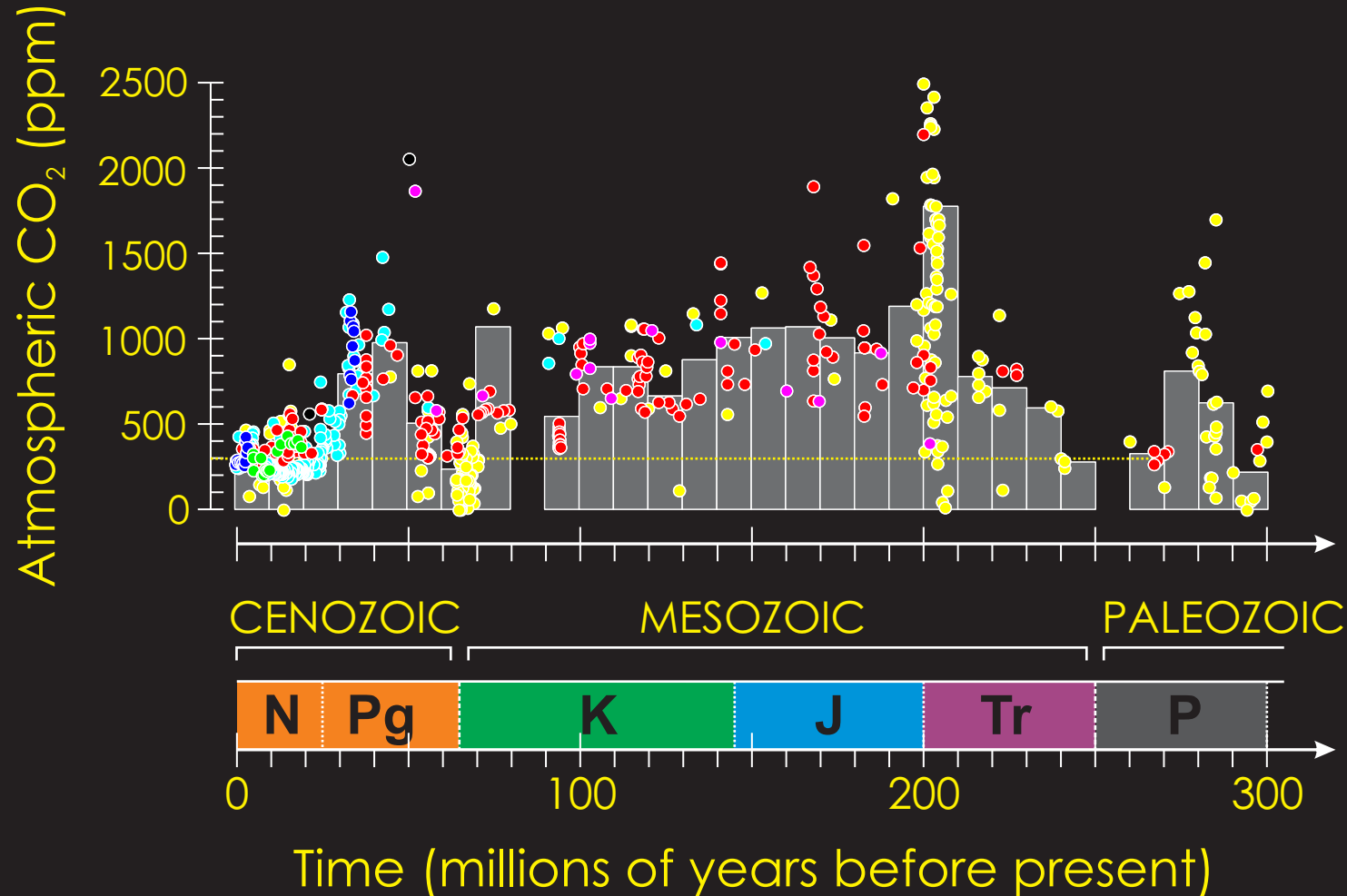


observed nanoplankton
assemblage
response to
environmental change
across the PETM

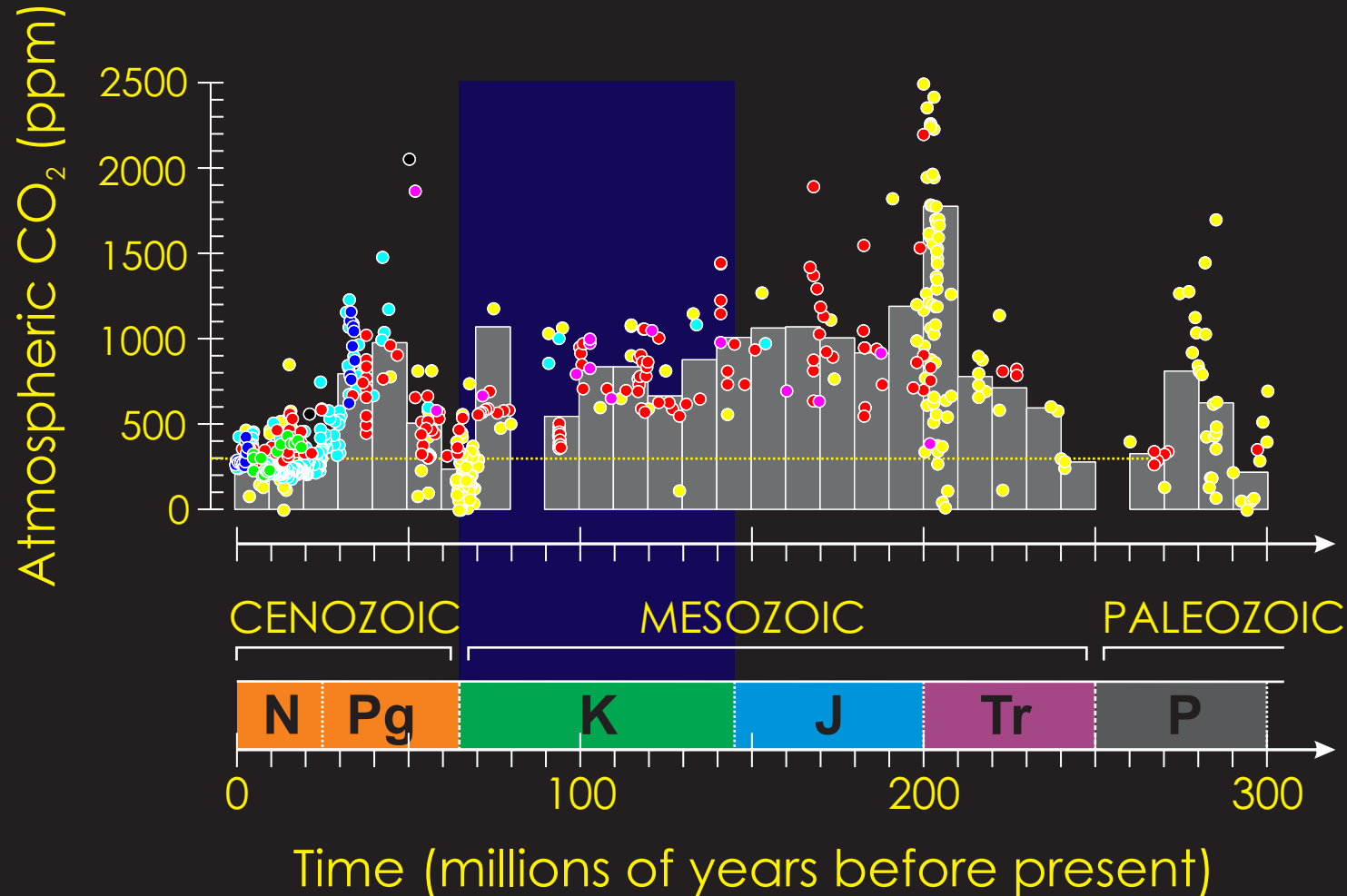
The Geological Record of Ocean Acidification



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ChrisM, Ashford, England, 2/3/2012 12:07



Numerical modelling of The global carbon(ate) cycle

```
! calculate carbonate alkalinity
loc_ALK_DIC = dum_ALK &
& - loc_H4BO4 - loc_OH - loc_HPO4 - 2.0*loc_PO4 - loc_H3SiO4 - loc_NH3 -
loc_HS &
& + loc_H + loc_HSO4 + loc_HF + loc_H3PO4

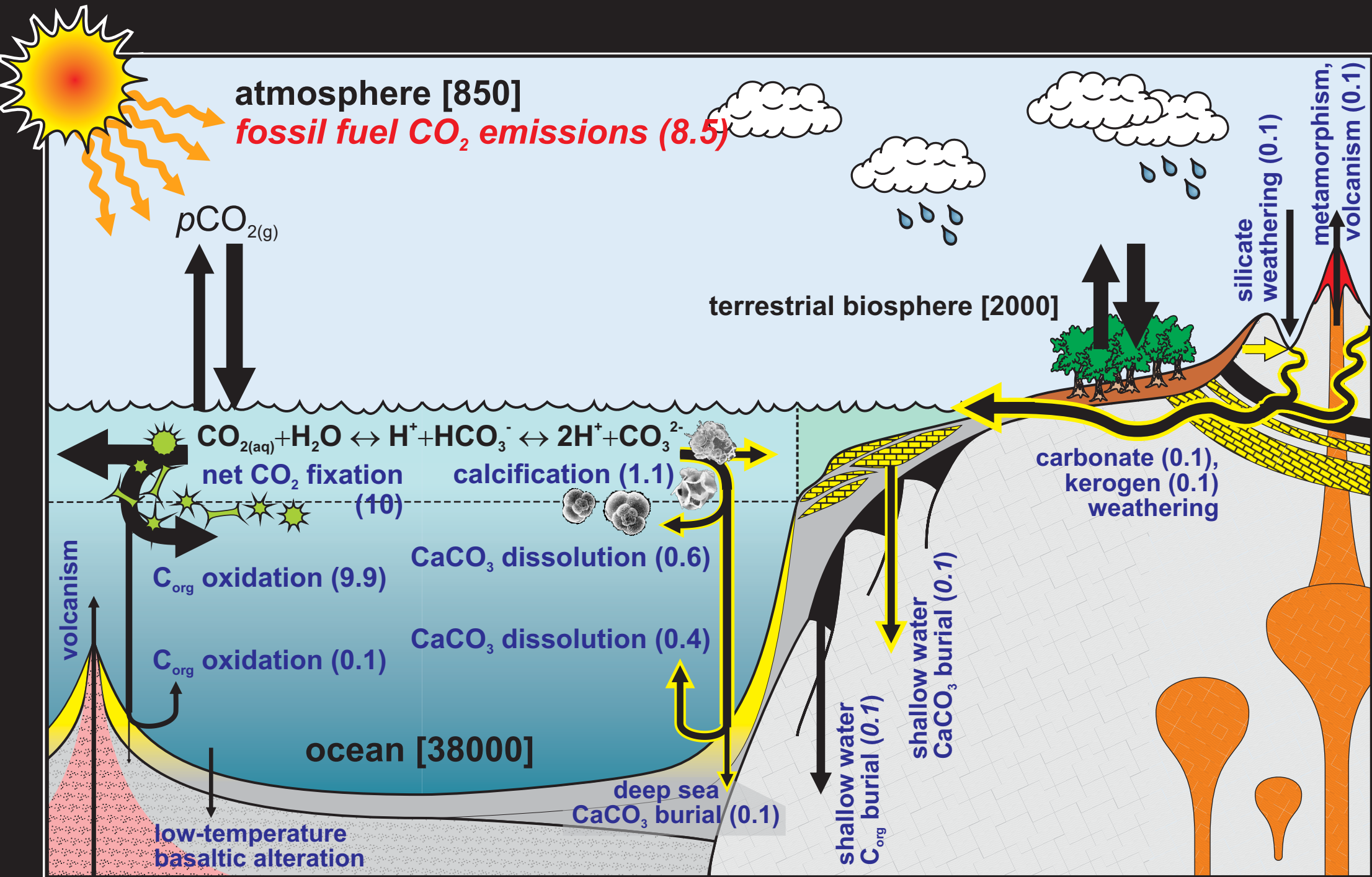
! estimate the partitioning between the aqueous carbonate species
loc_zed = ( &
& (4.0*loc_ALK_DIC + dum_DIC*dum_carbconst(icc_k) -
loc_ALK_DIC*dum_carbconst(icc_k))**2 + &
& 4.0*(dum_carbconst(icc_k) - 4.0)*loc_ALK_DIC**2 &
& )**0.5      loc_conc_HCO3 = (dum_DIC*dum_carbconst(icc_k) -
loc_zed)/(dum_carbconst(icc_k) - 4.0)

loc_conc_CO3 = &
& ( &
& loc_ALK_DIC*dum_carbconst(icc_k) - dum_DIC*dum_carbconst(icc_k) - &
& 4.0*loc_ALK_DIC + loc_zed &
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))

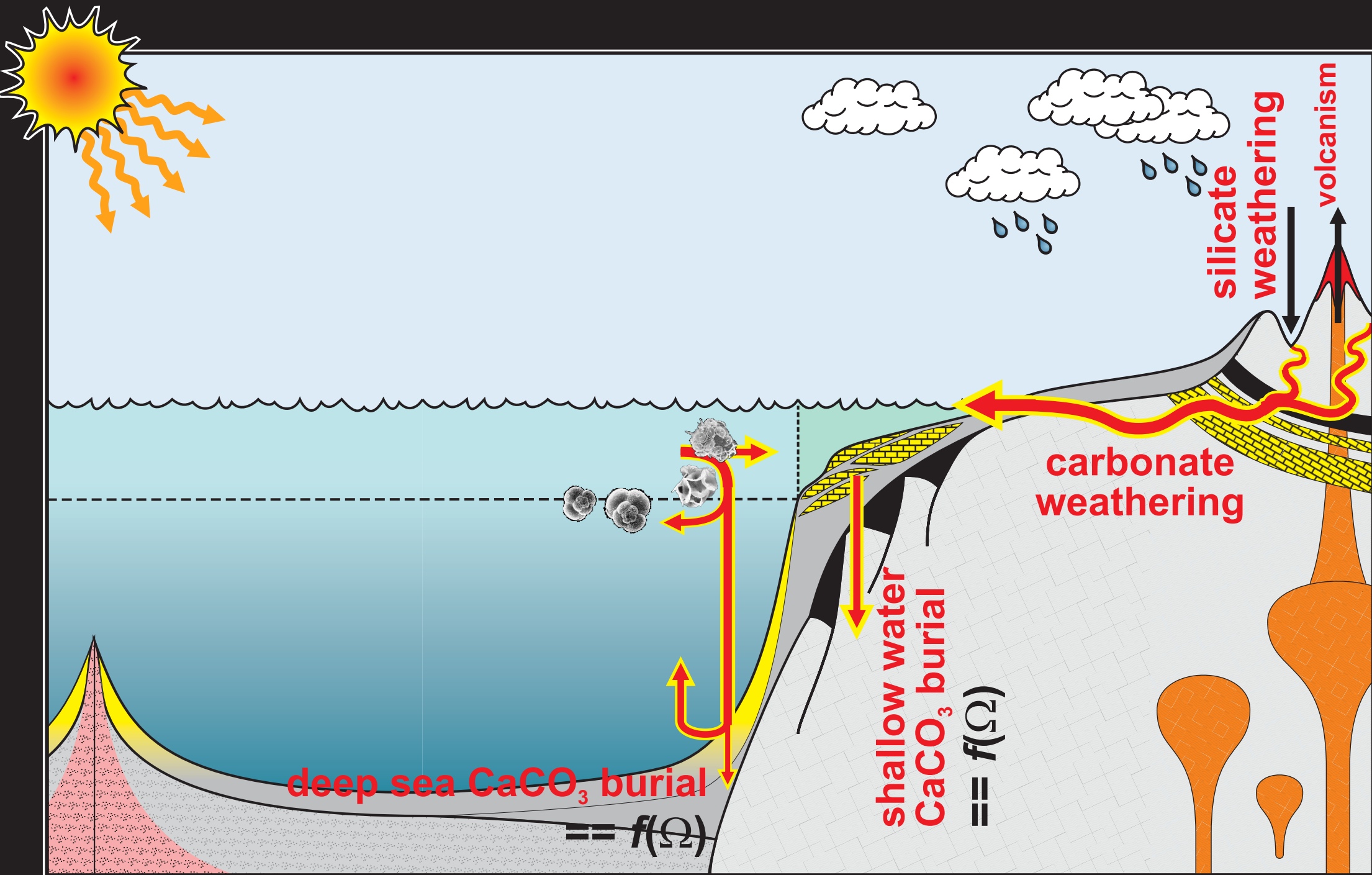
loc_conc_CO2 = dum_DIC - loc_ALK_DIC + &
& ( &
& loc_ALK_DIC*dum_carbconst(icc_k) - dum_DIC*dum_carbconst(icc_k) - &
& 4.0*loc_ALK_DIC + loc_zed &
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))

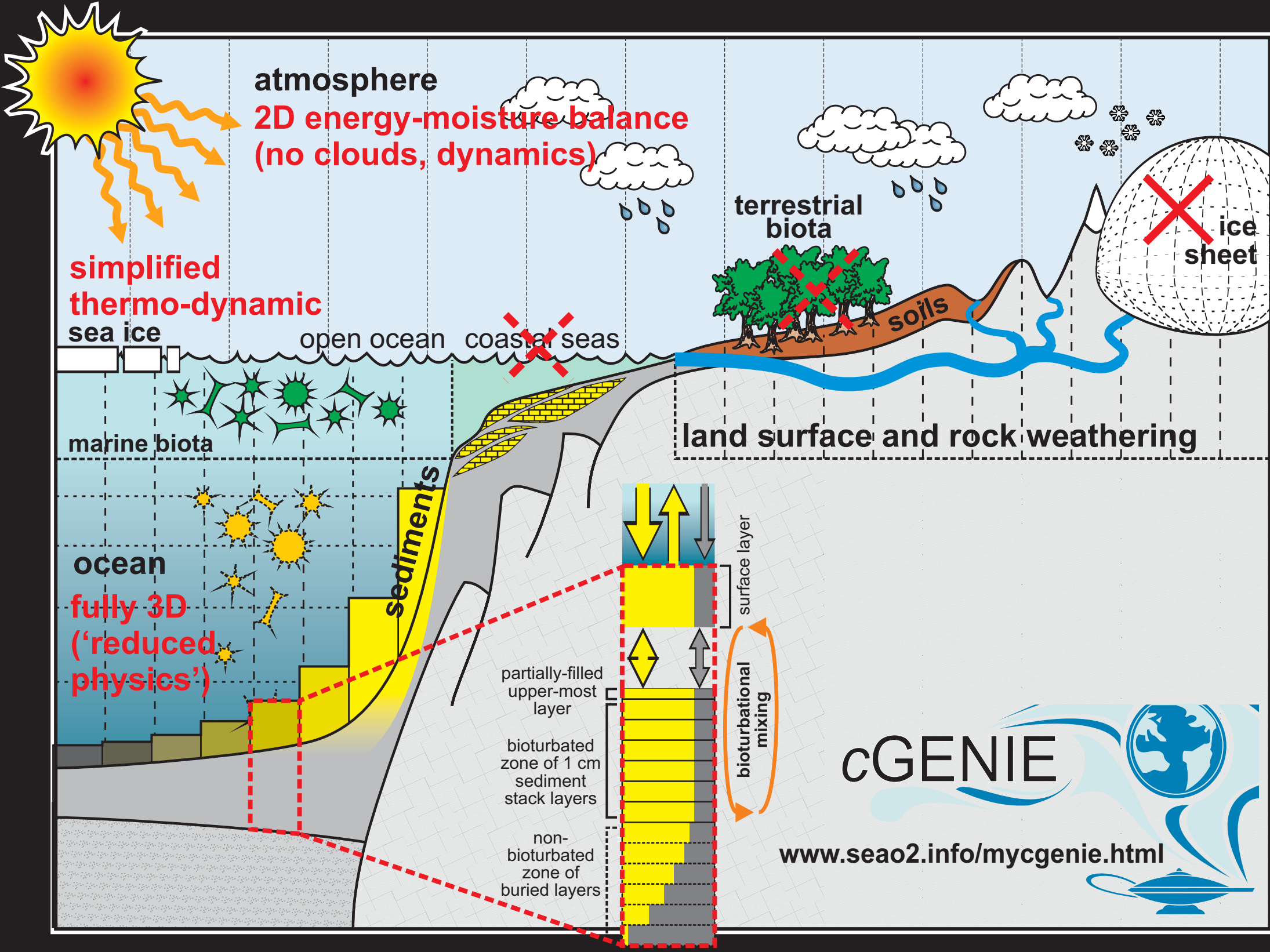
loc_H1 = dum_carbconst(icc_k1)*loc_conc_CO2/loc_conc_HCO3
loc_H2 = dum_carbconst(icc_k2)*loc_conc_HCO3/loc_conc_CO3
```

The global carbon cycle



The global carbon(ate) cycle: Control of saturation (and CO_3^{2-})

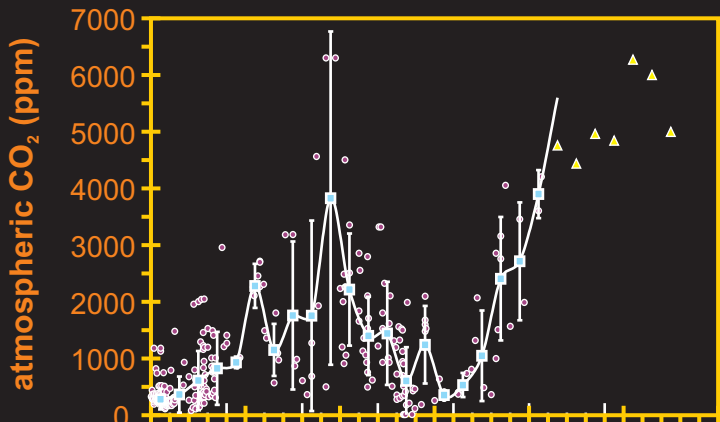




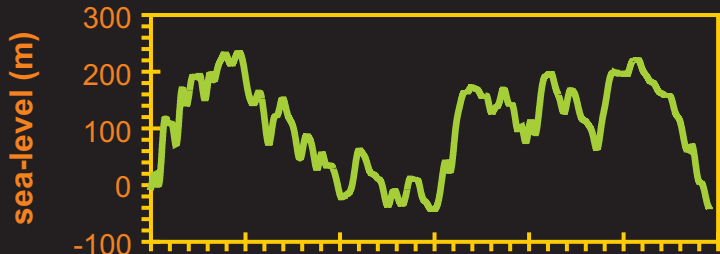
CENOZOIC MESOZOIC PALEOZOIC PRECAMBRIAN

N:Pg C J Tr Pr C D S O E

Royer et al. [2004]

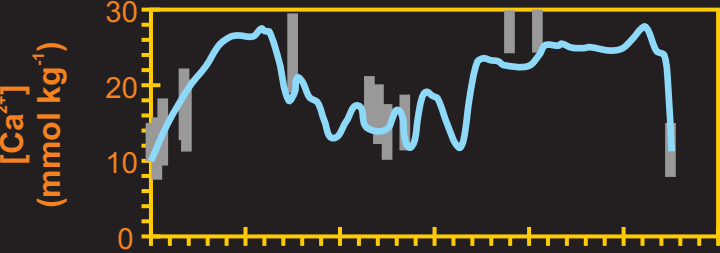


Haq et al. [1988]

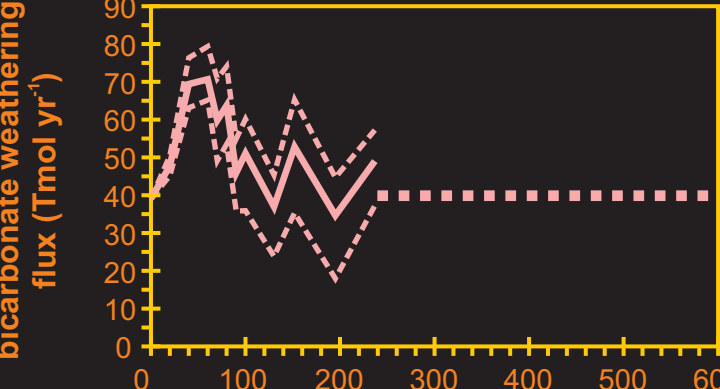


Stanley and Hardie [1998]

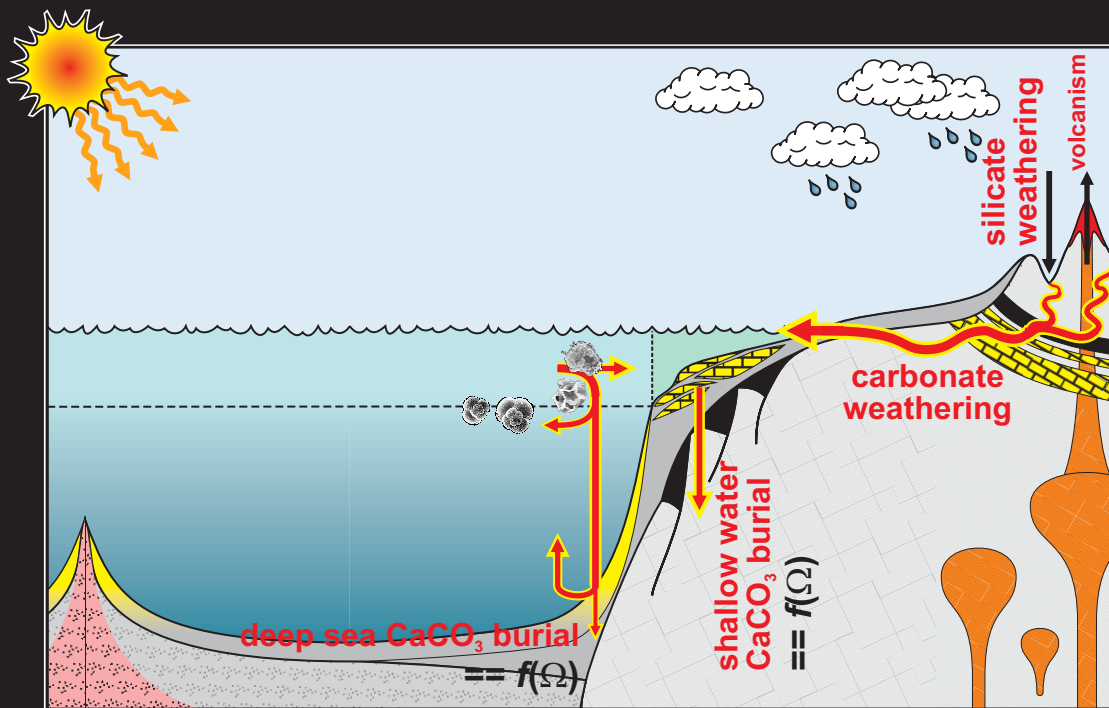
Horita et al. [2002]



Gibbs et al. [1999]



Age (Ma)

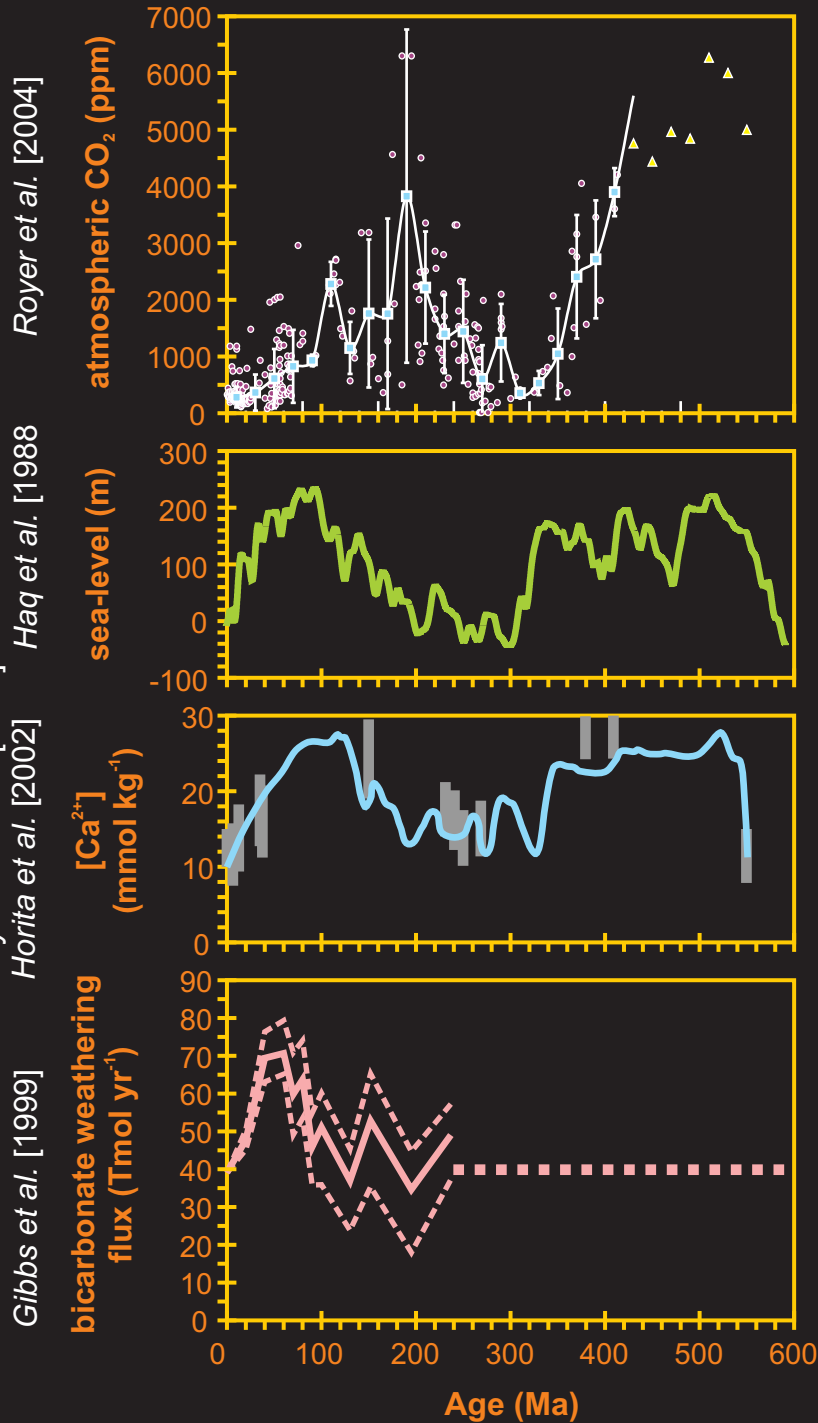


whatever model [Ridgwell, 2005]

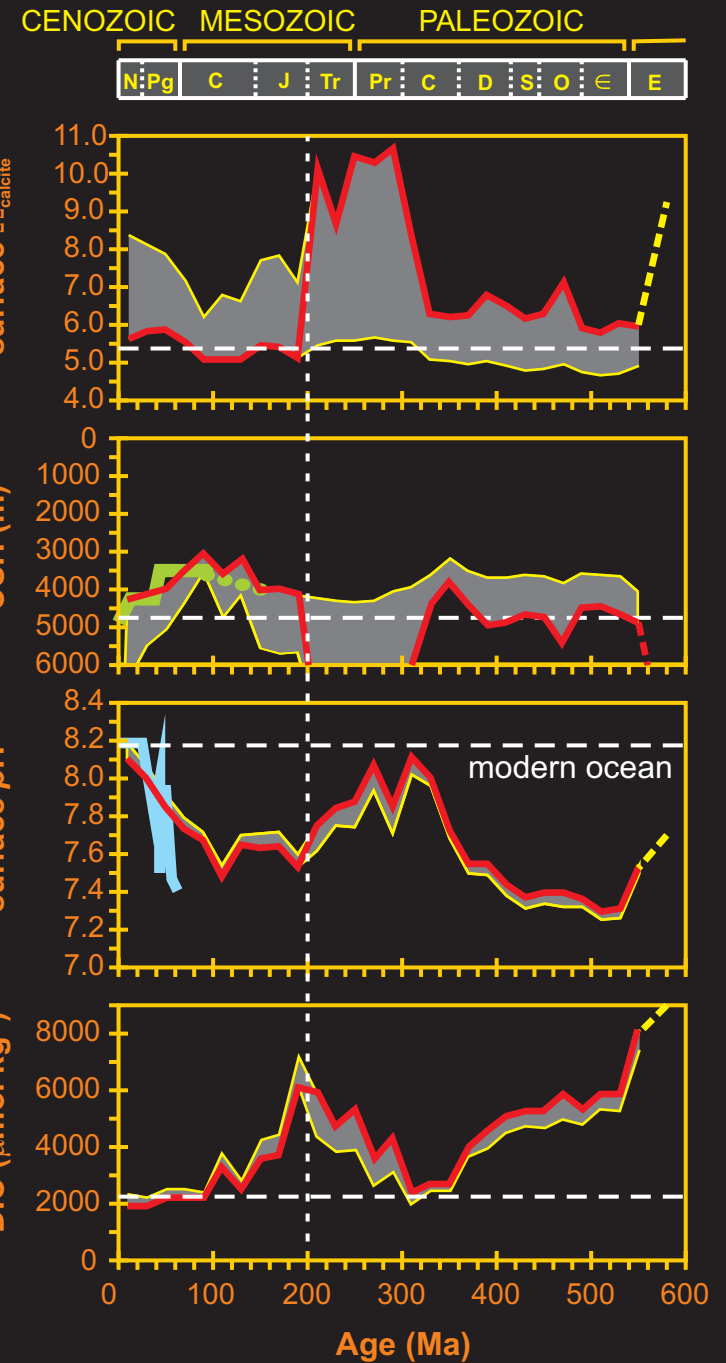
Model projections

CENOZOIC MESOZOIC PALEOZOIC PRECAMBRIAN

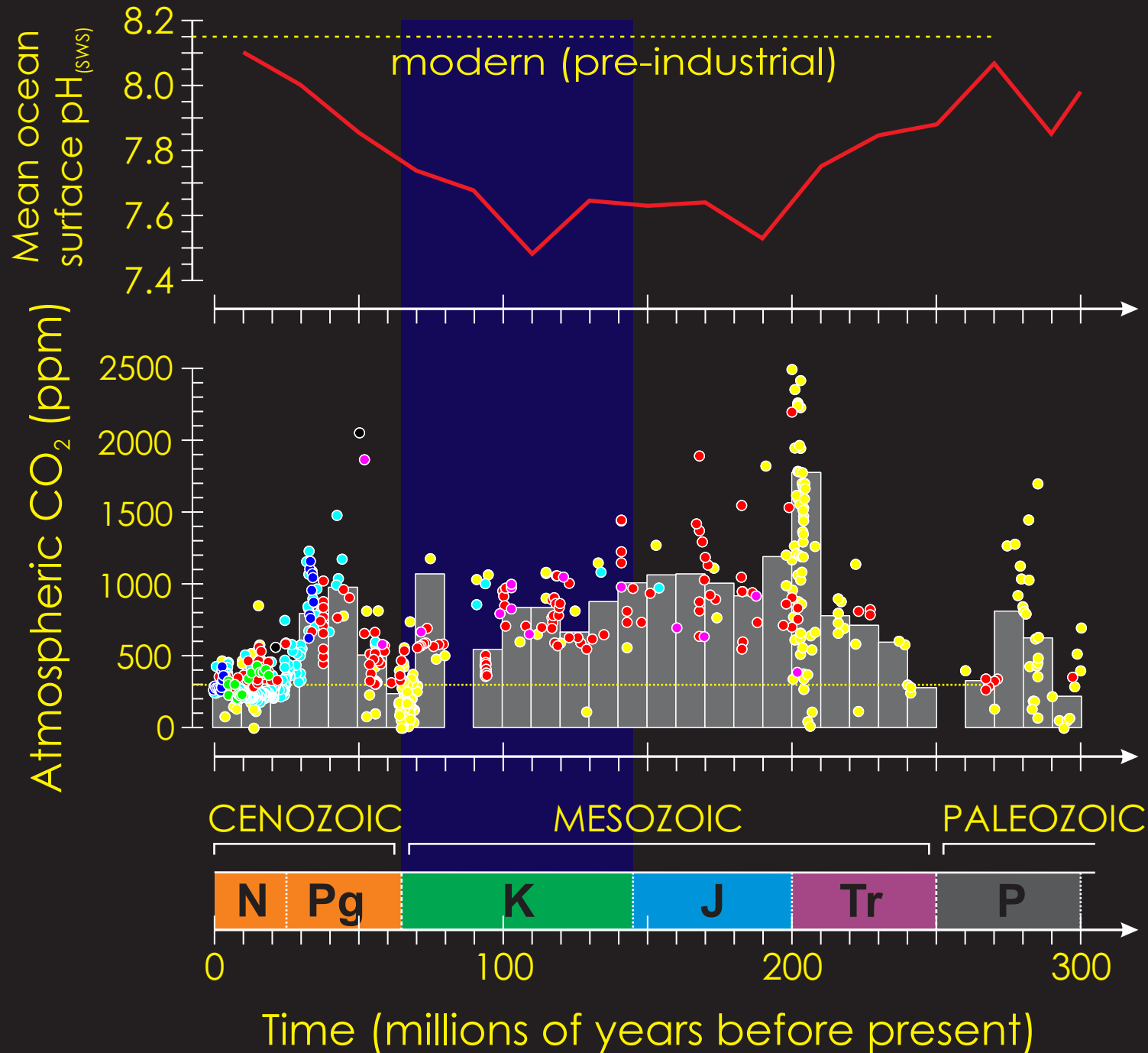
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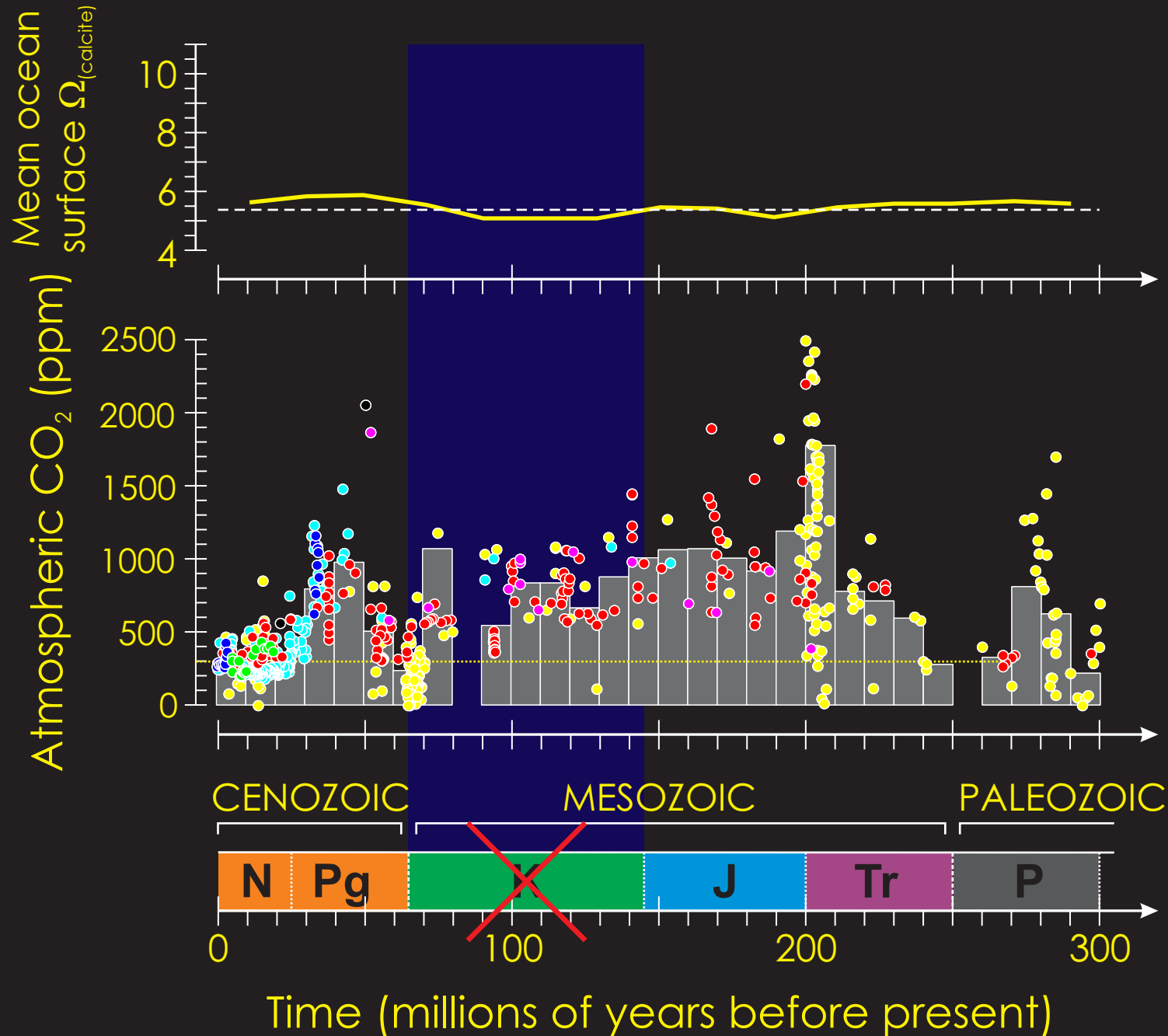
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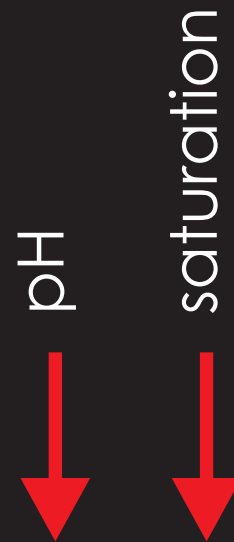


The Geological Record of Ocean Acidification





'slow'
(quasi steady-state)



'fast'
(geologically abrupt)

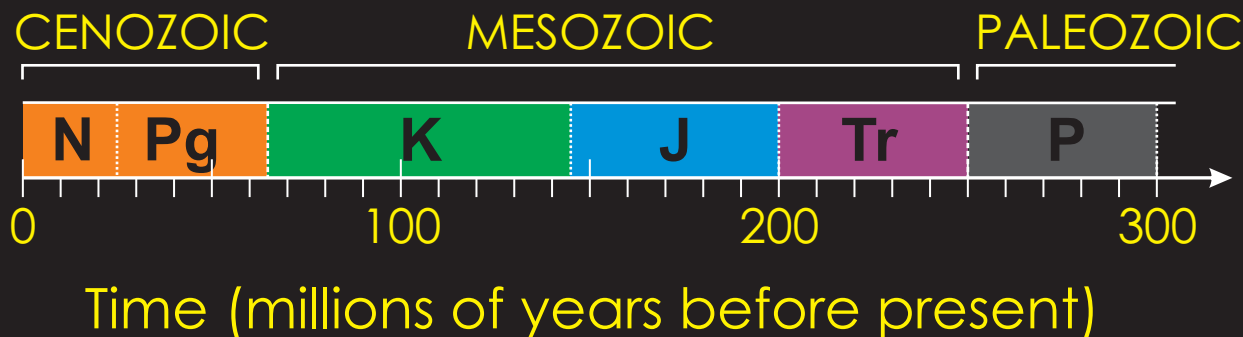
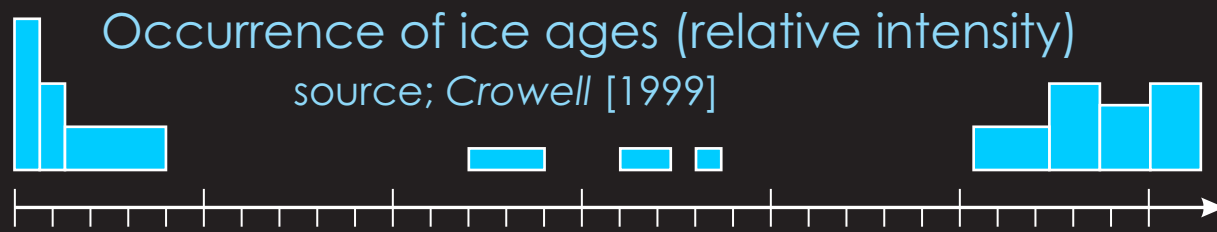
Rate of change (magnitude of CO₂ emissions)

Is there a past 'analogue' for the future consequences of massive CO₂ release and ocean acidification?

More complete geological record (more rock!)
(more and better preserved and constrained proxies)



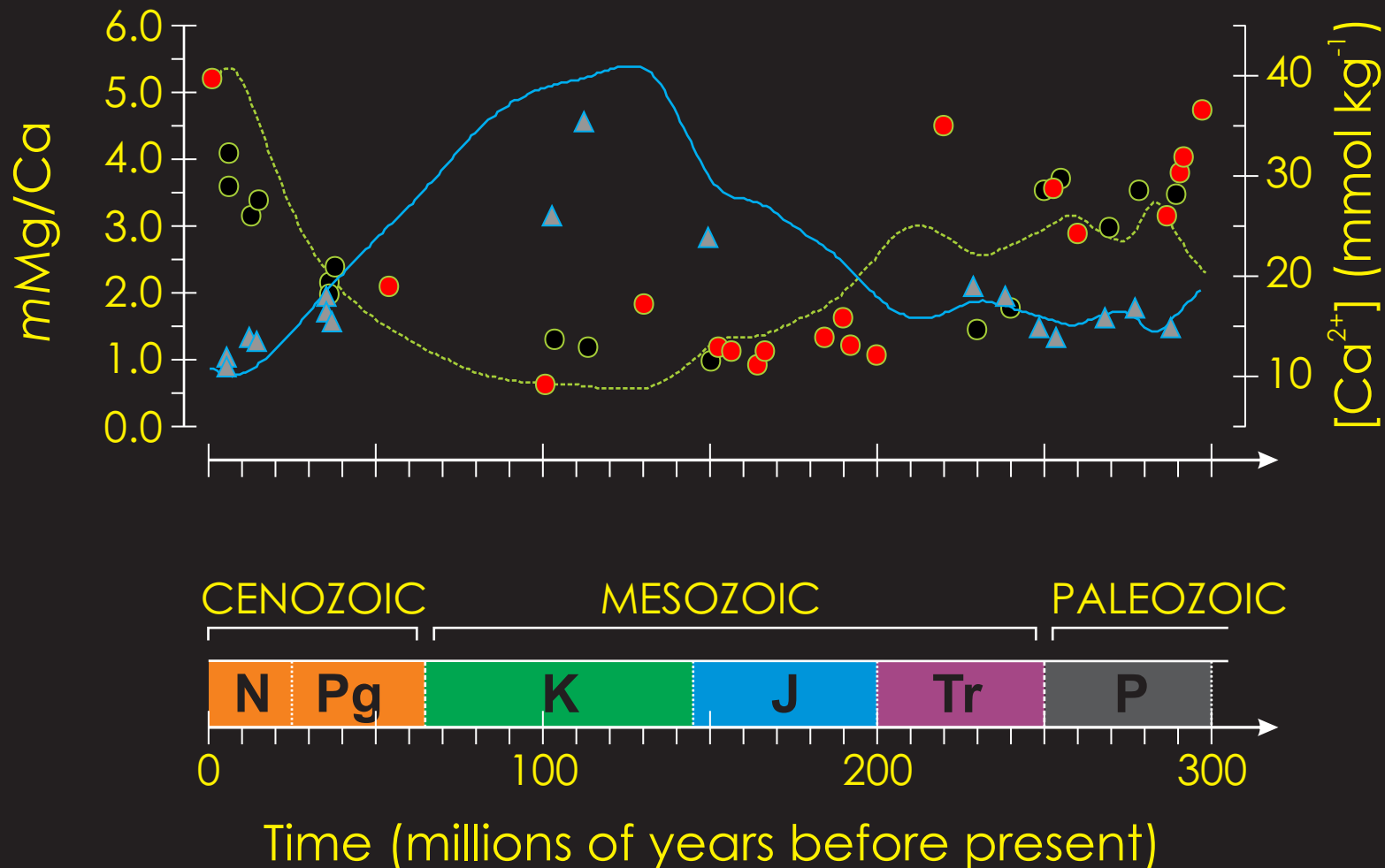
More similar (cooler) climate
More similar (lower) sealevel

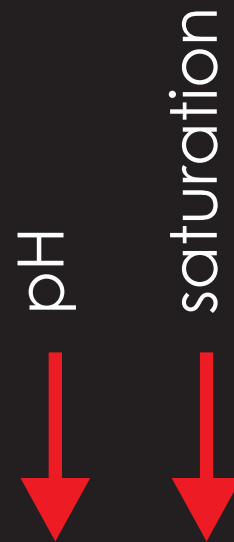


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('aragonite' vs. 'calcite' as the dominant reef mineralogy)

← More similar cation chemistry →





'slow'
(quasi steady-state)

'fast'
(geologically abrupt)



Rate of change (magnitude of CO₂ emissions)

The geological record app store

✓  Massive CO₂ release

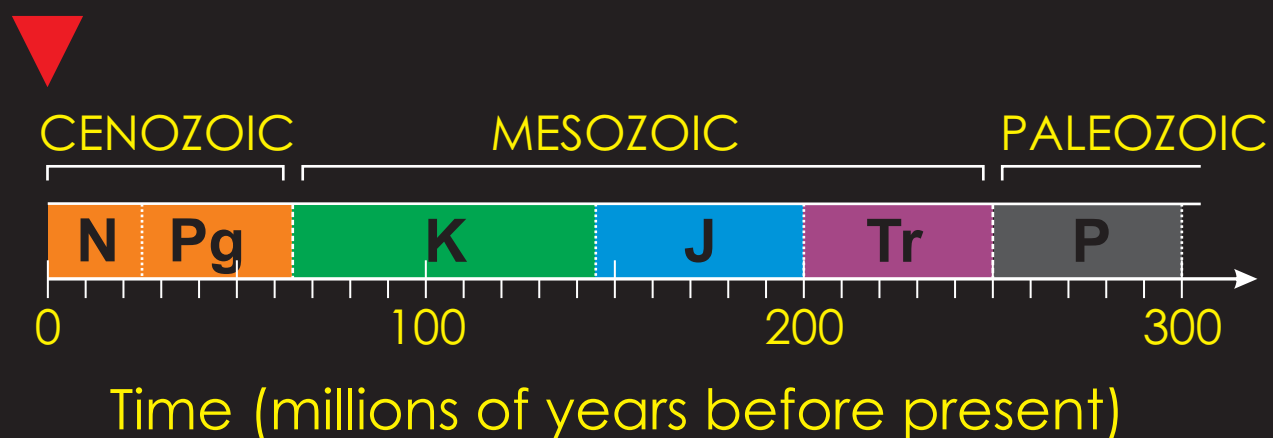
✓  Increasing atmospheric pCO₂

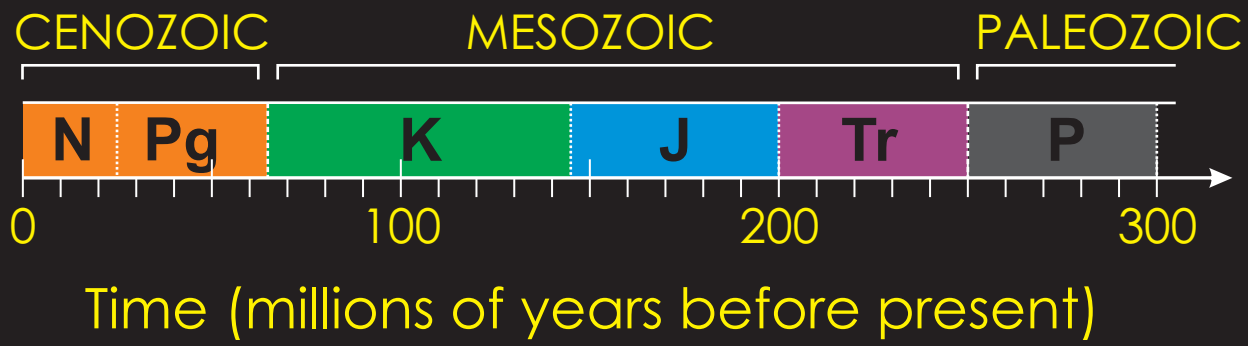
✓  Warming

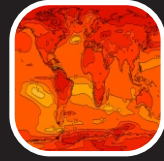
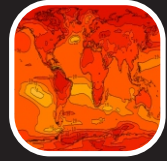
✓  pH decline

✓  Carbonate saturation decline

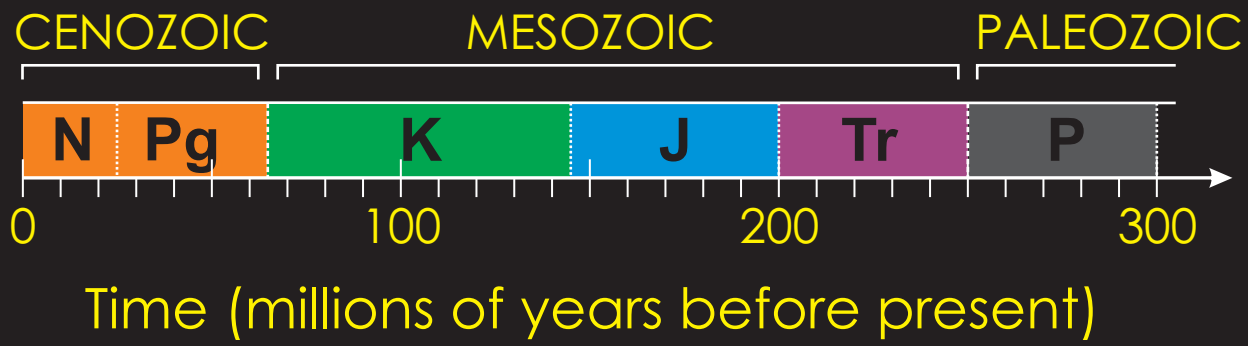
?  Biotic/ecosystem response?

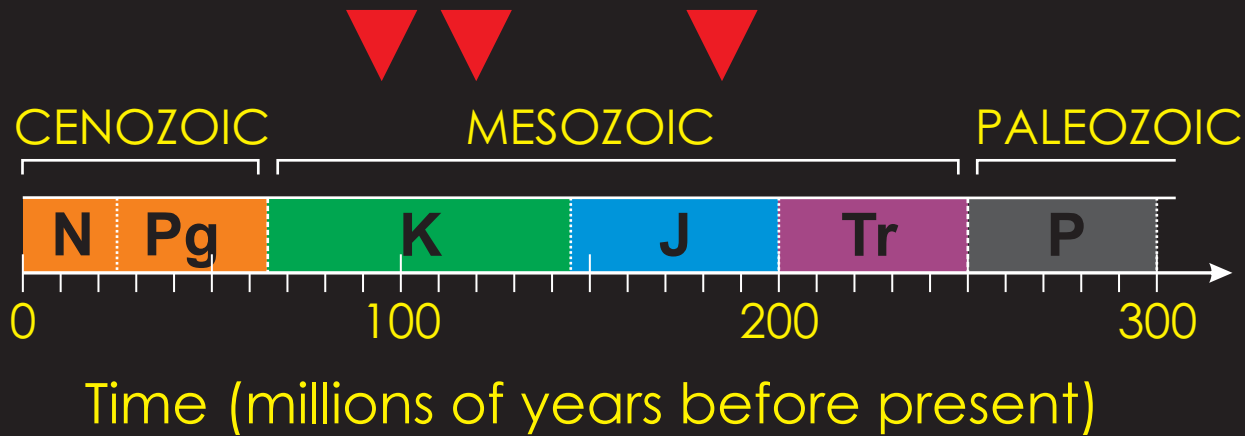
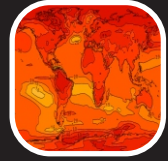
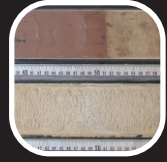
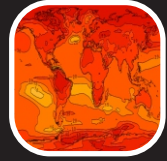


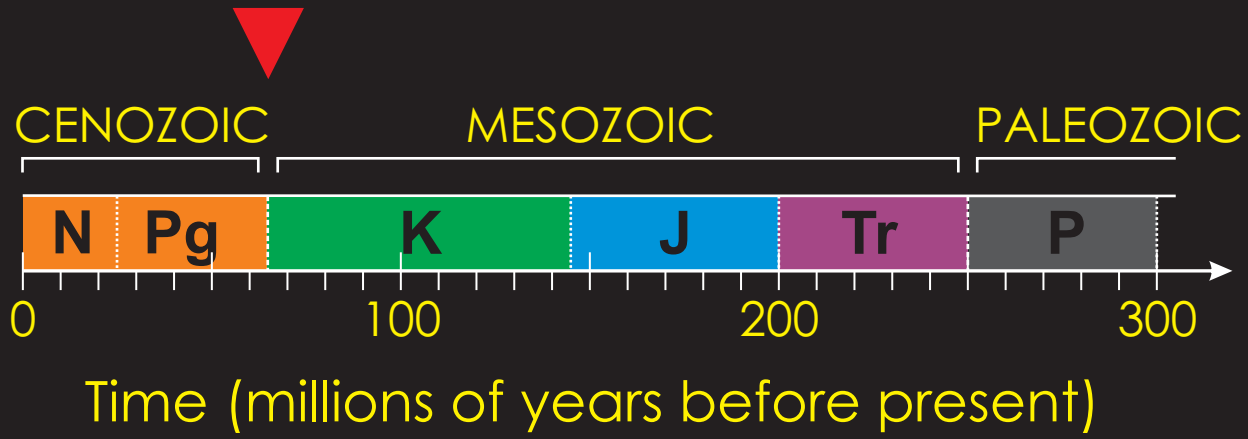


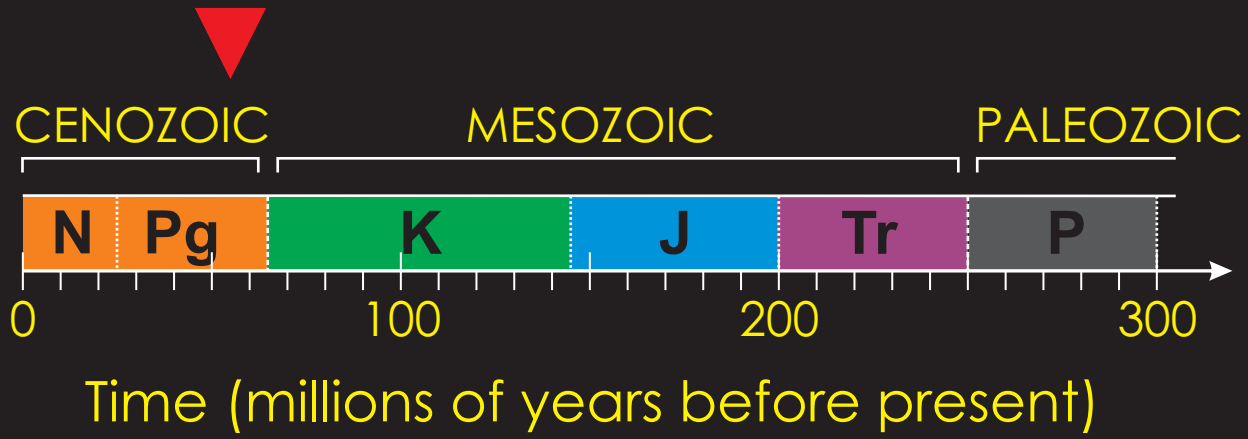


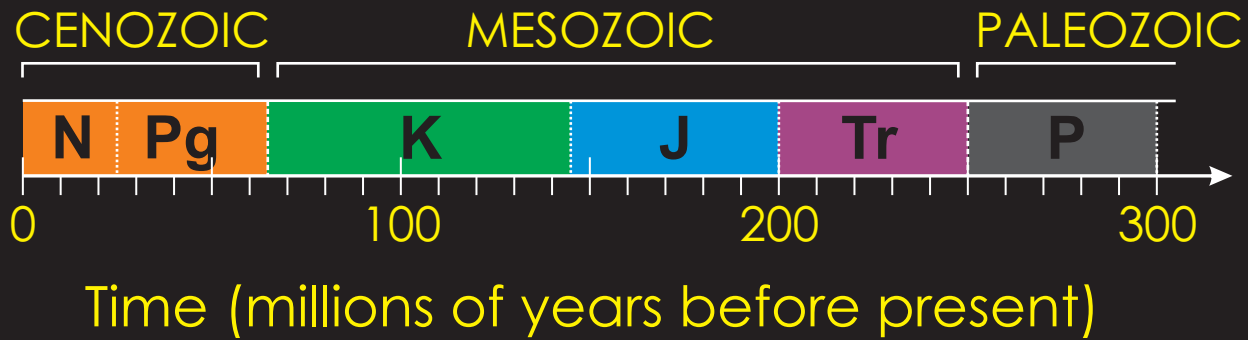
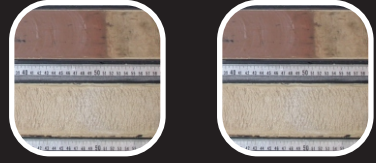
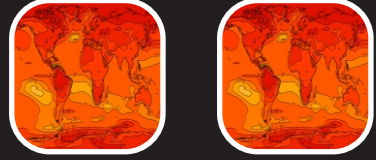
Triassic	Jurassic
Plant: Low-Lying , Yews, Liverworts, etc. Dinosaur: Eoraptor, Sellosaurus	Plant: Seed ferns, Ginkgos, Cycadophyte, etc. Dinosaur: Sauropod, Stegosaur

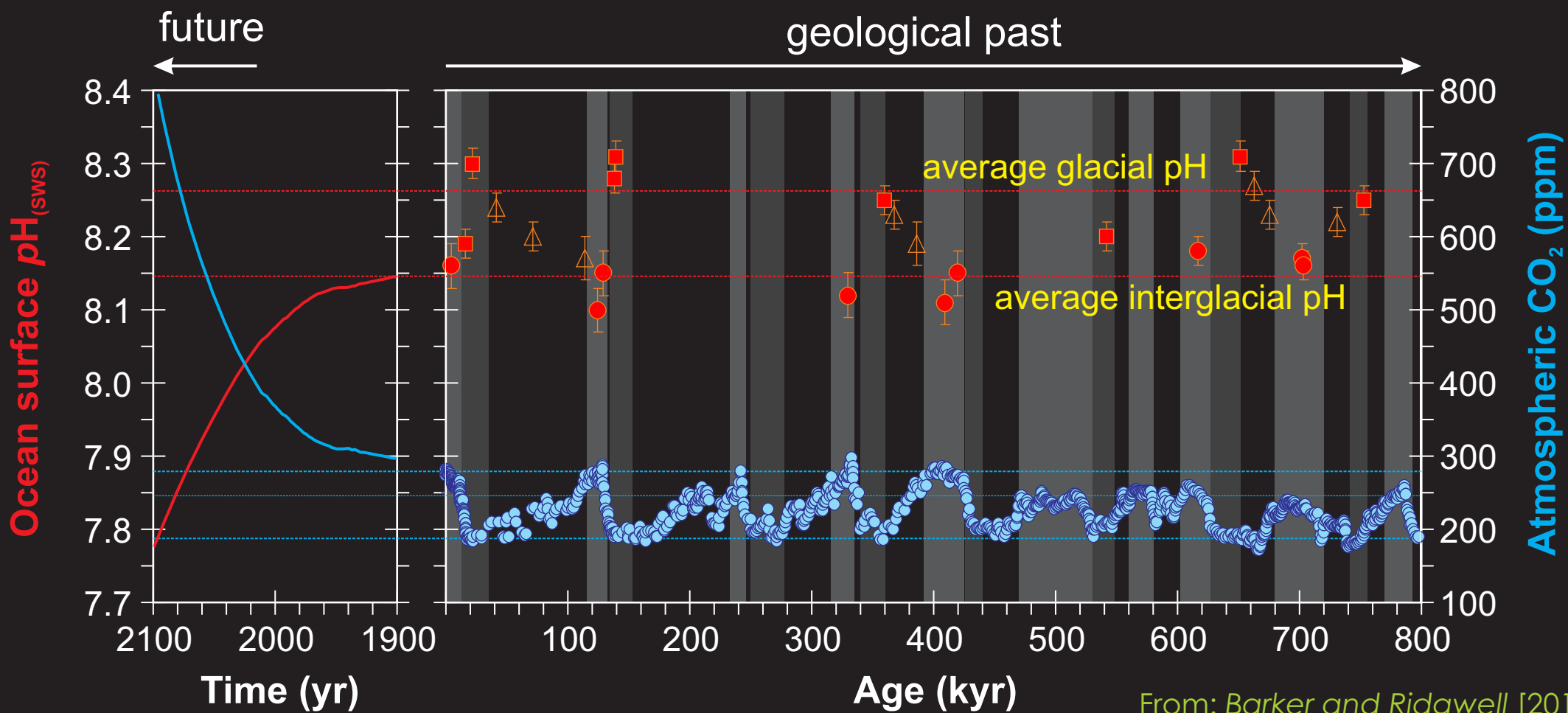










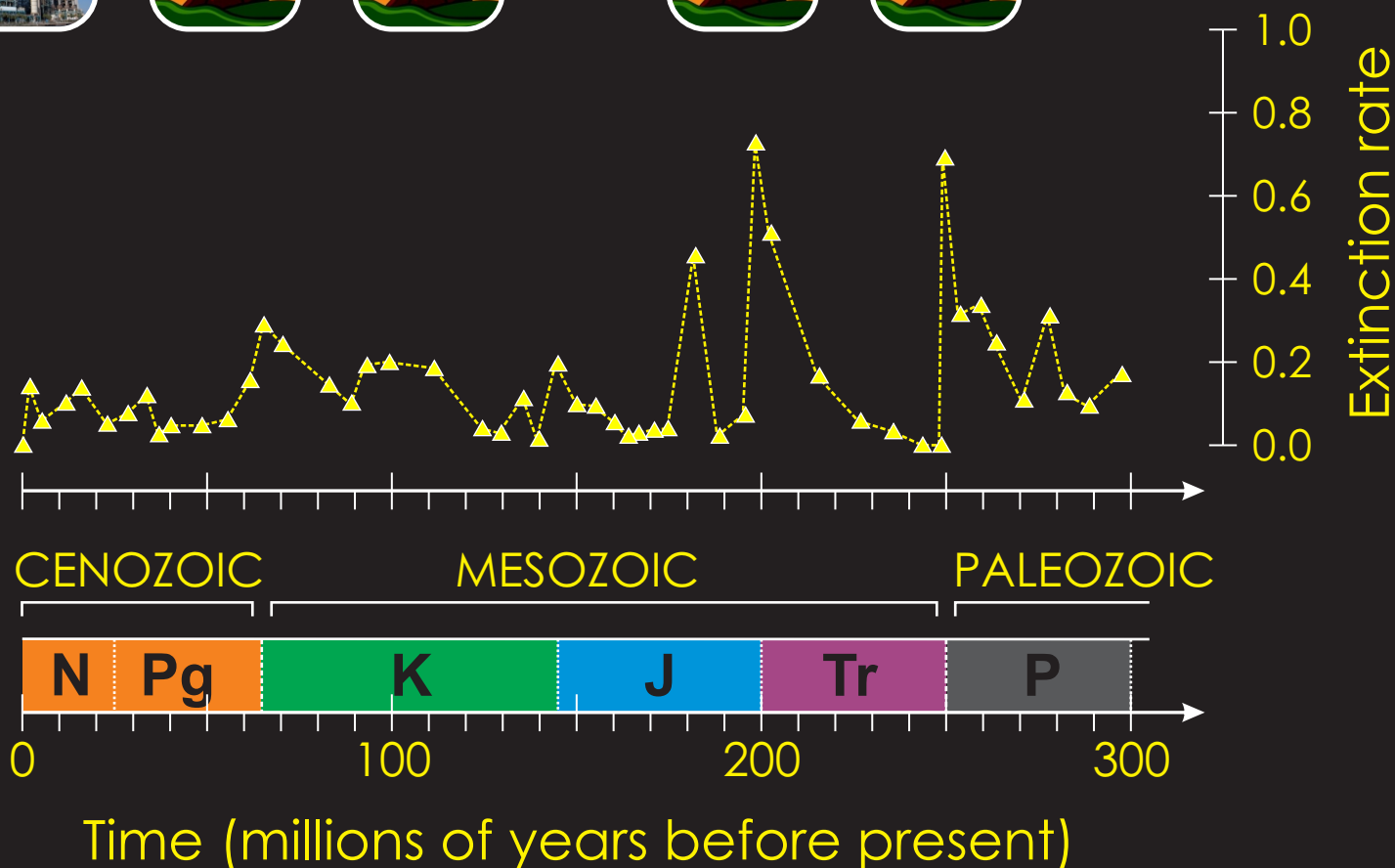


From: *Barker and Ridgwell [2012]*

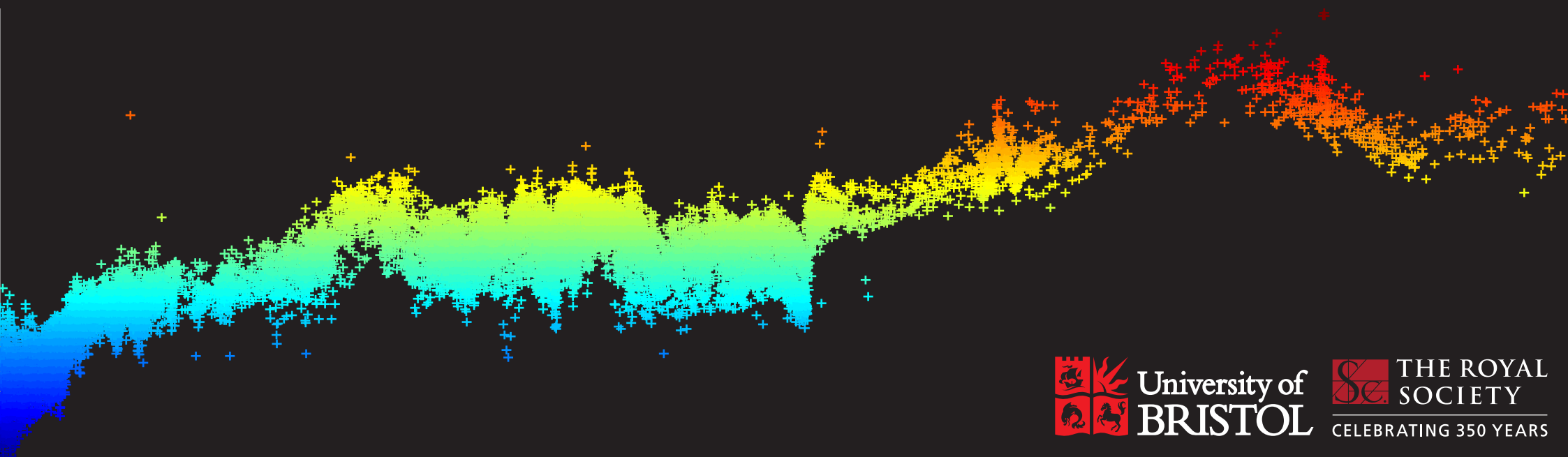
Past potential ocean acidification analogues are characterized by **reduced pH and saturation state**

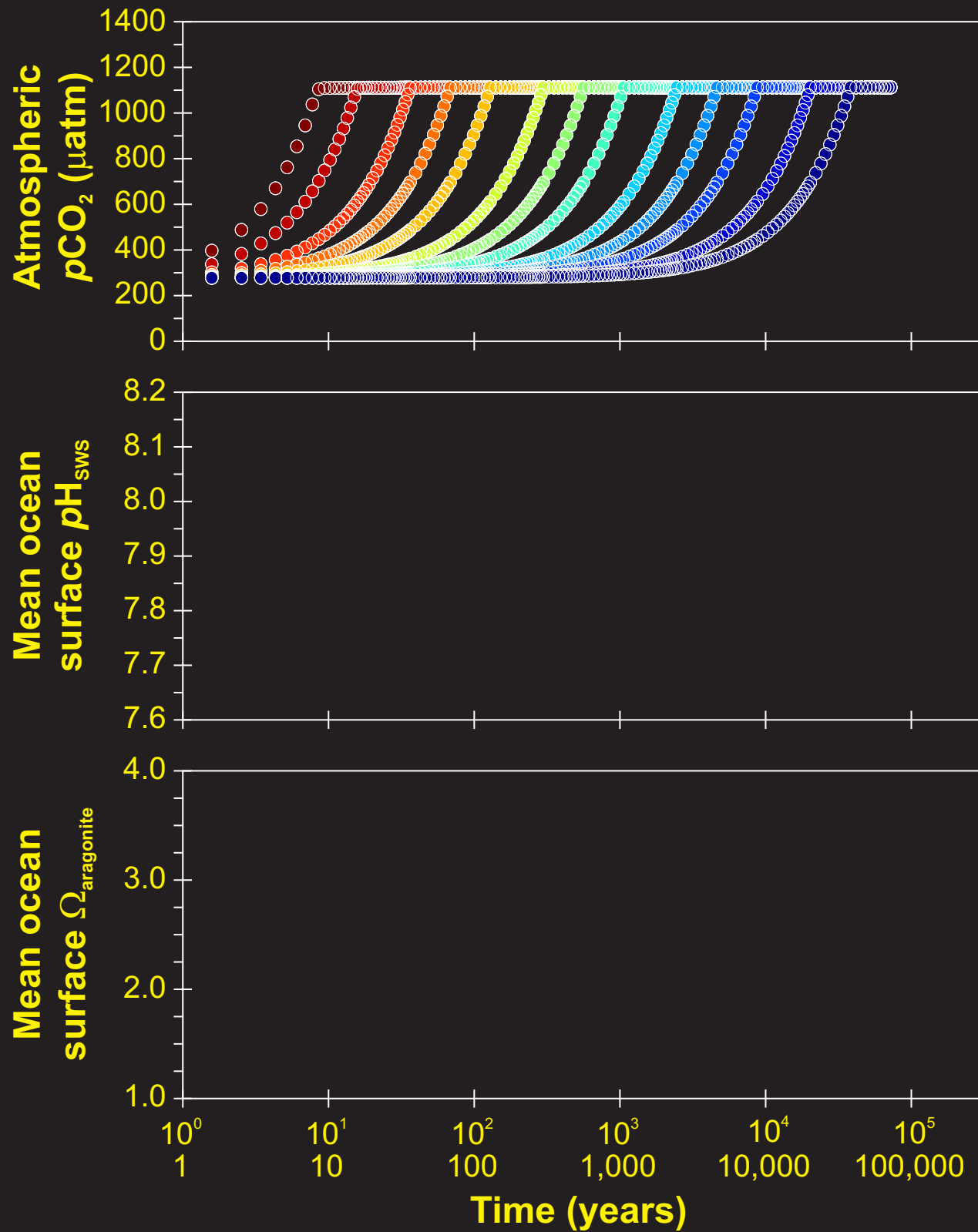
(likely requiring massive and rapid CO₂ release)

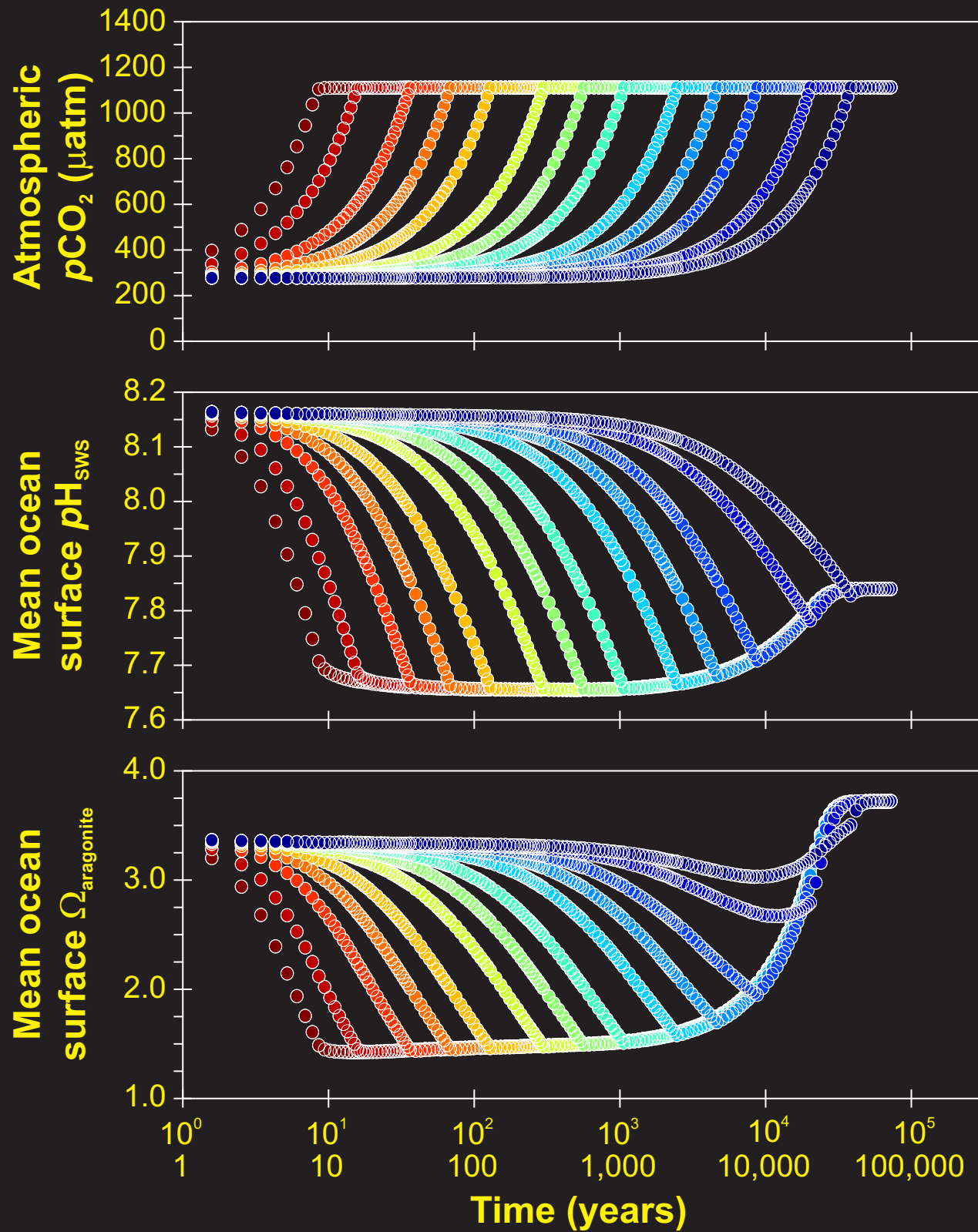
Numerical models can help 'fill in the gaps' by combining 2nd order proxy information to derive 1st order constraints



Bärbel Hönisch, Daniela N. Schmidt, Ellen Thomas, Samantha J. Gibbs, Appy Sluijs, Lee Kump, Richard Zeebe, Rowan Martindale, Sarah E. Greene, Wolfgang Kiessling, Justin Ries, Jim Zachos, Dana L. Royer, Stephen Barker, Thomas M. Marchitto Jr., Ryan Moyer, Carles Pelejero, Branwen Williams, Patrizia Ziveri, Gavin L. Foster, Branwen Williams







Time-scale dependence of the nature of ocean carbonate chemistry changes

