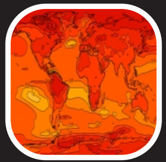
The Geological Record of Ocean Acidification

Andy Ridgwell







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```
! 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
```

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loc_ALK_DIC = dum_ALK &
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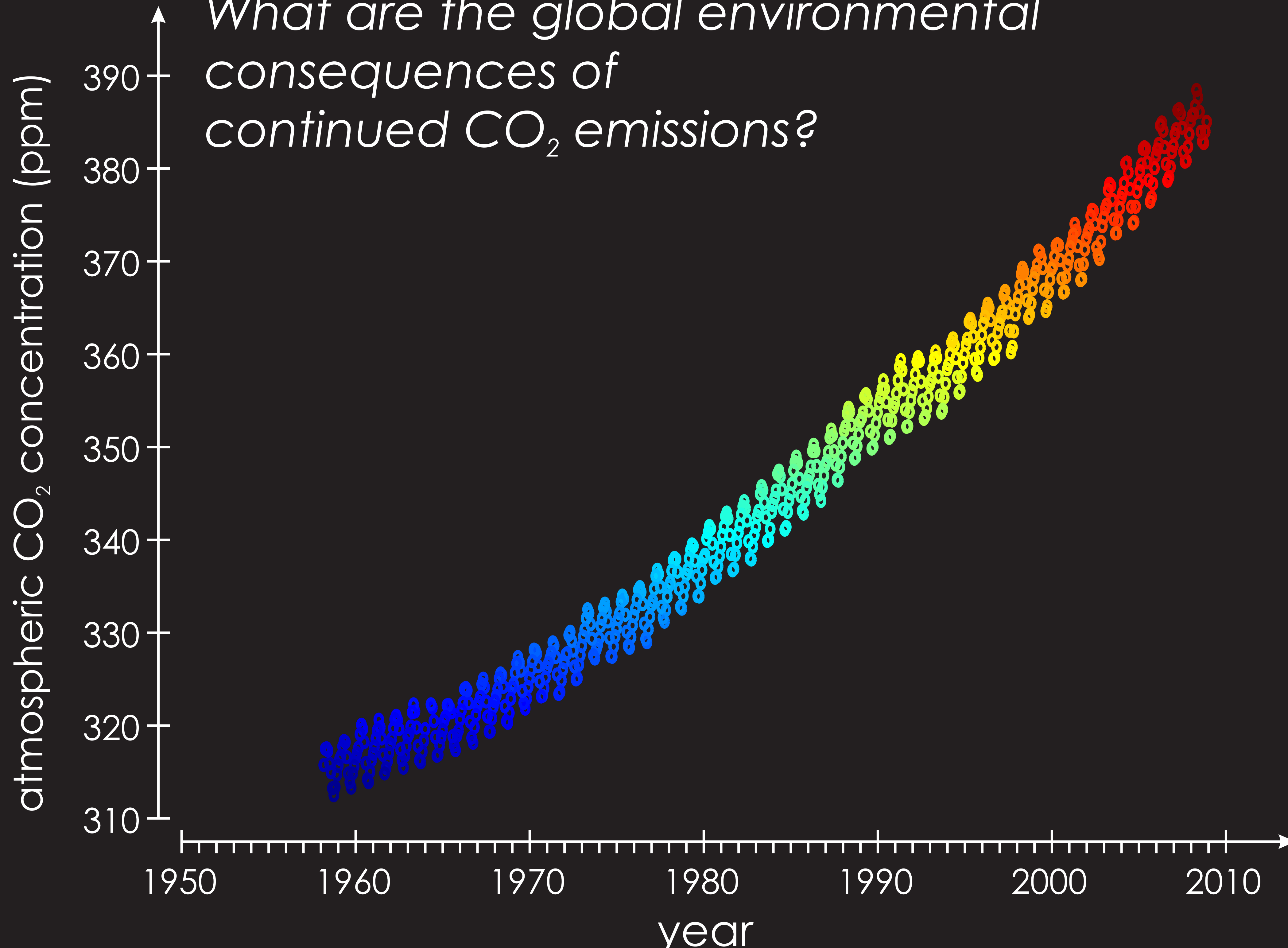
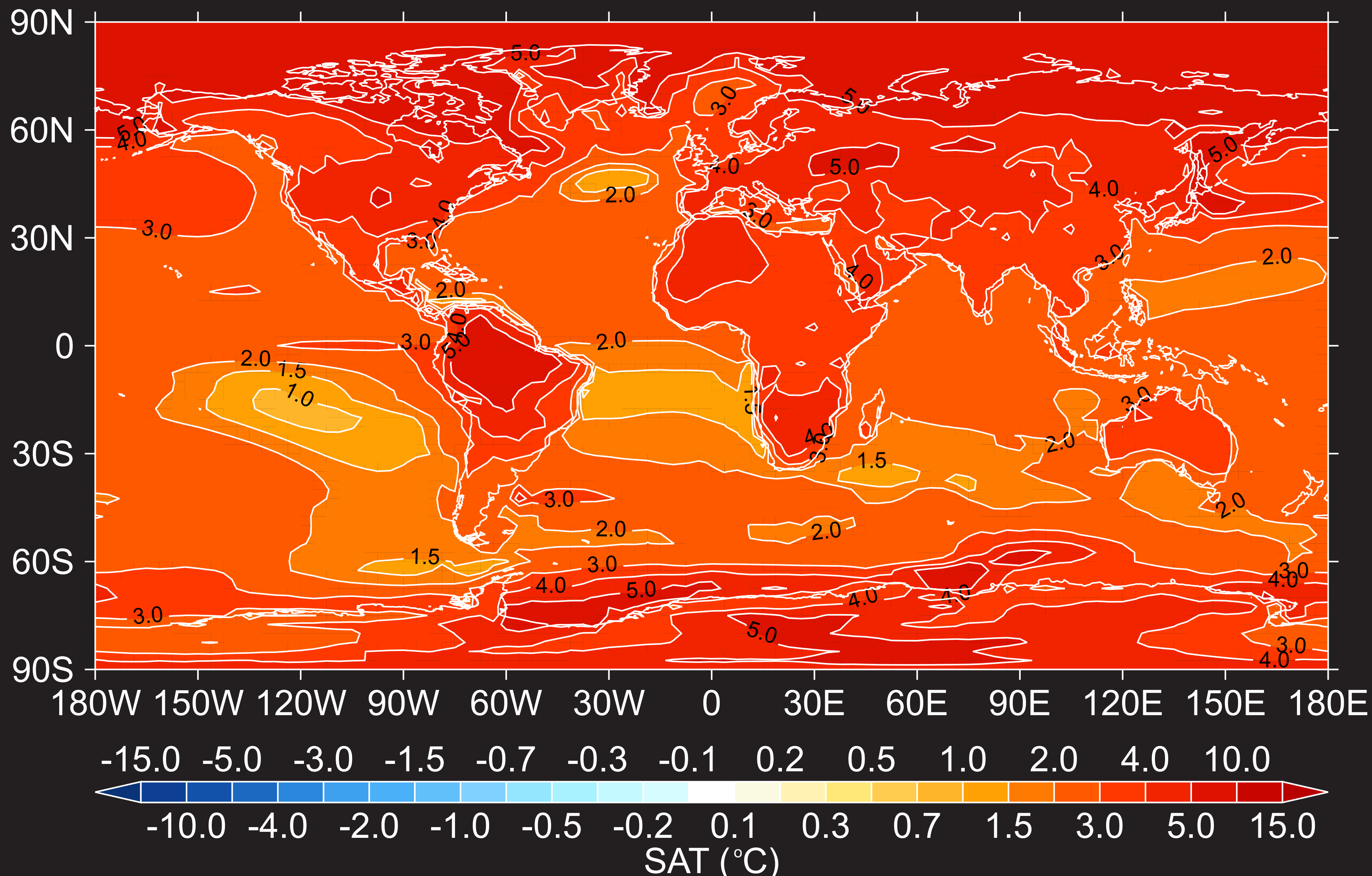
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))
loc_H1 = dum_carbconst(icc_k1)*loc_conc_CO2/loc_conc_HCO3
loc_H2 = dum_carbconst(icc_k2)*loc_conc_HCO3/loc_conc_CO3
```

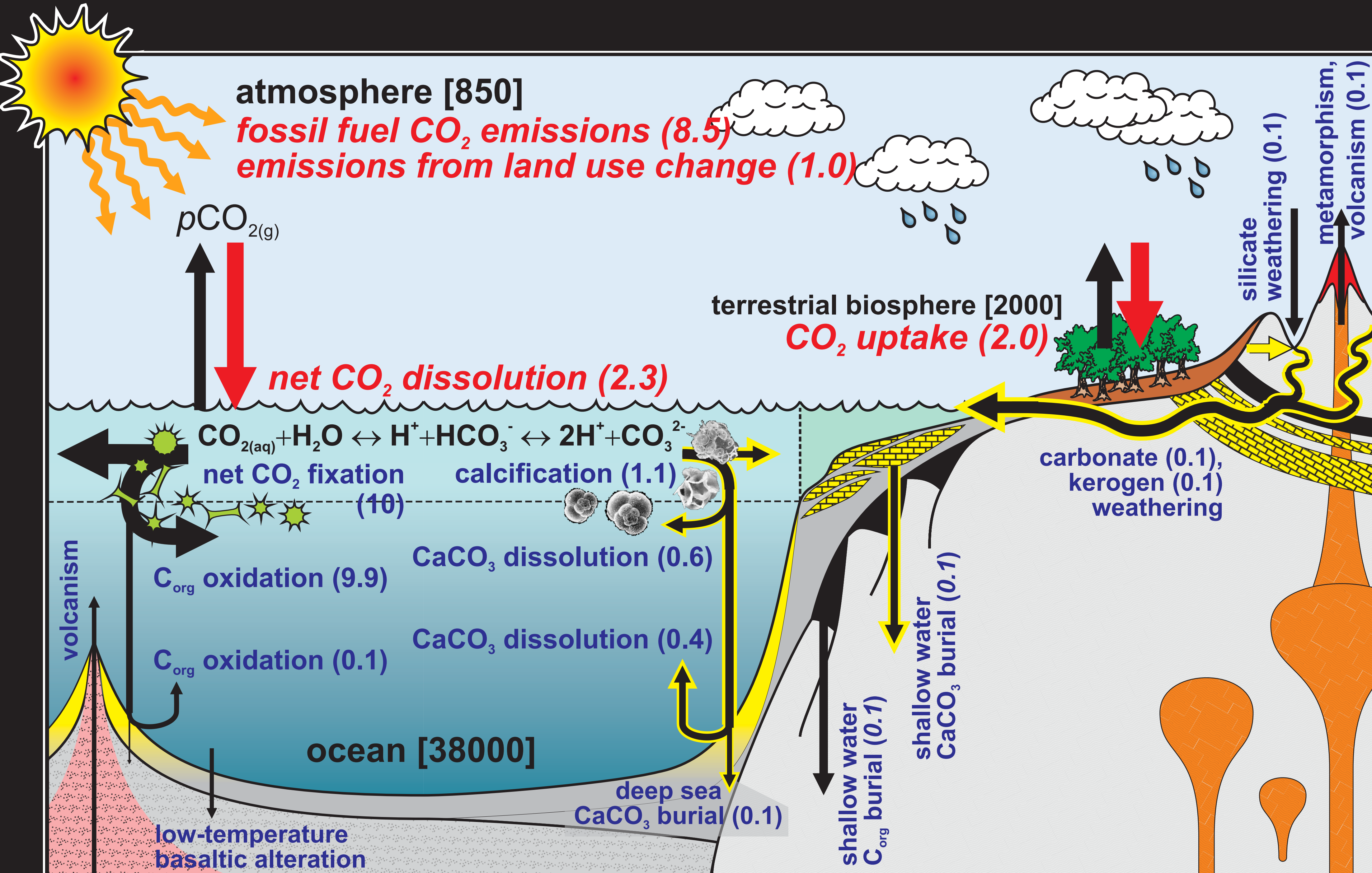
What are the global environmental consequences of continued CO_2 emissions?



~~(projected) climatic consequences~~

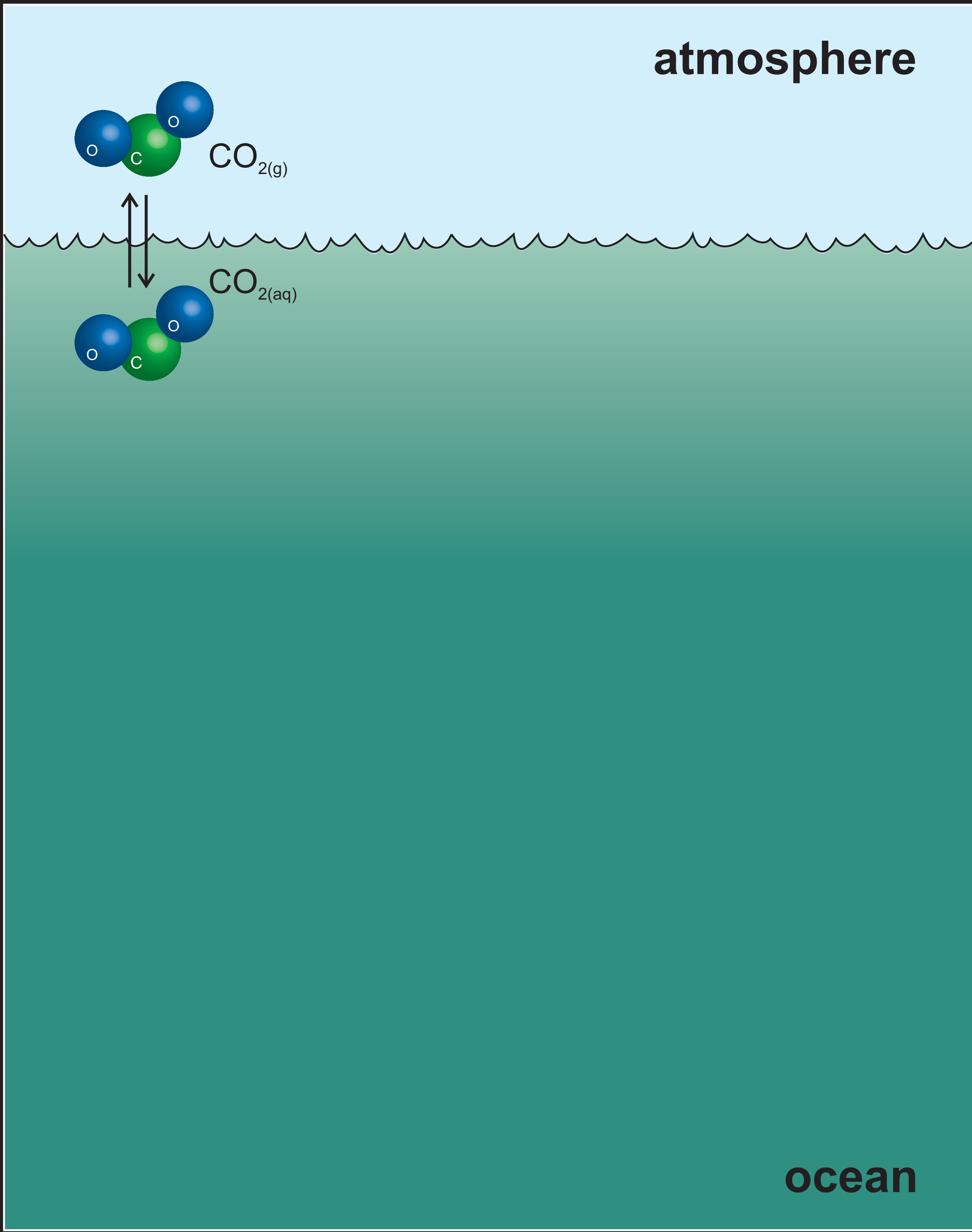


Ocean chemical consequences

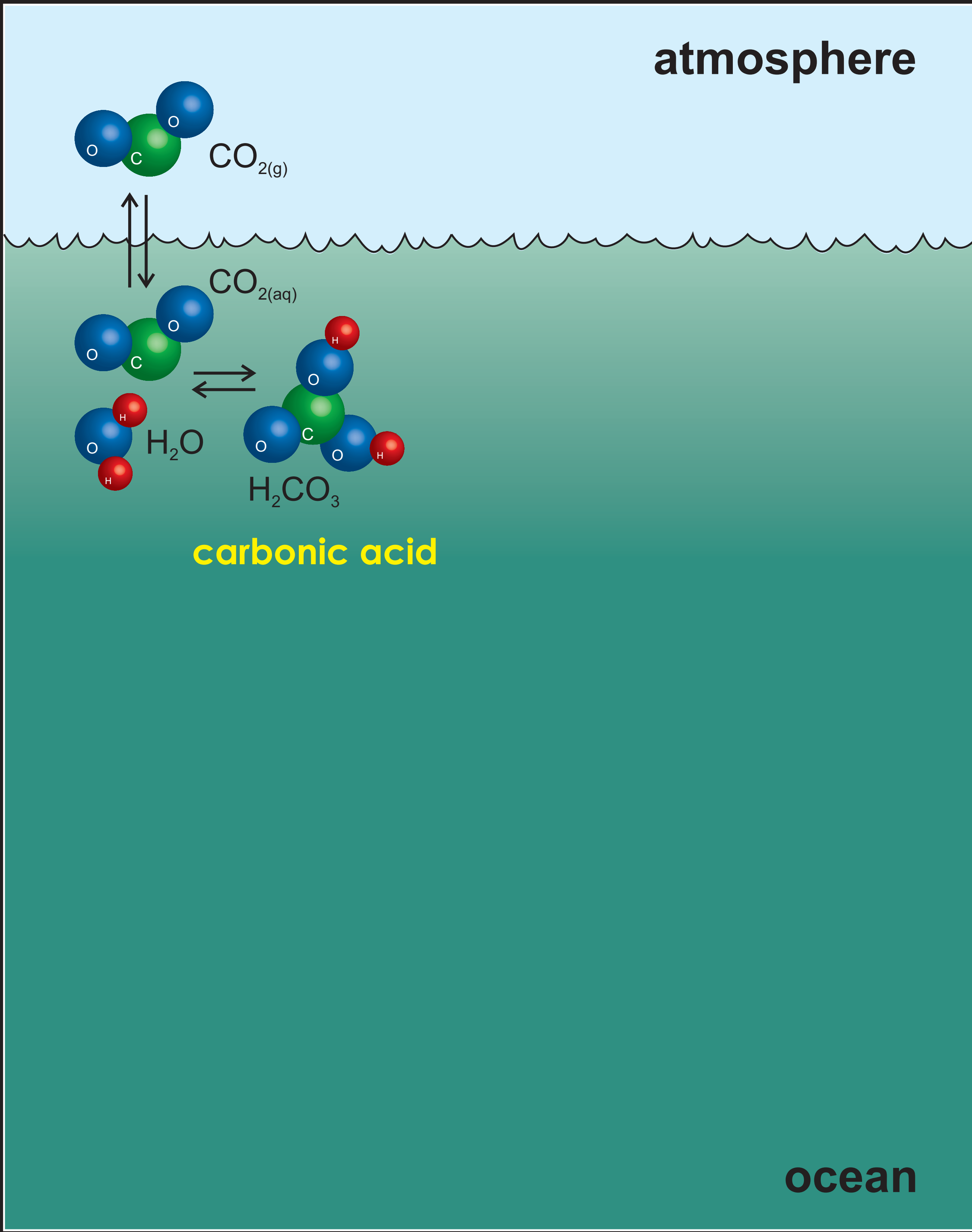



AMMONIUM
HYDROXIDE
NH OH

CO_2 chemistry in seawater



From: *Barker and Ridgwell* [in press]



CO_2 chemistry in seawater

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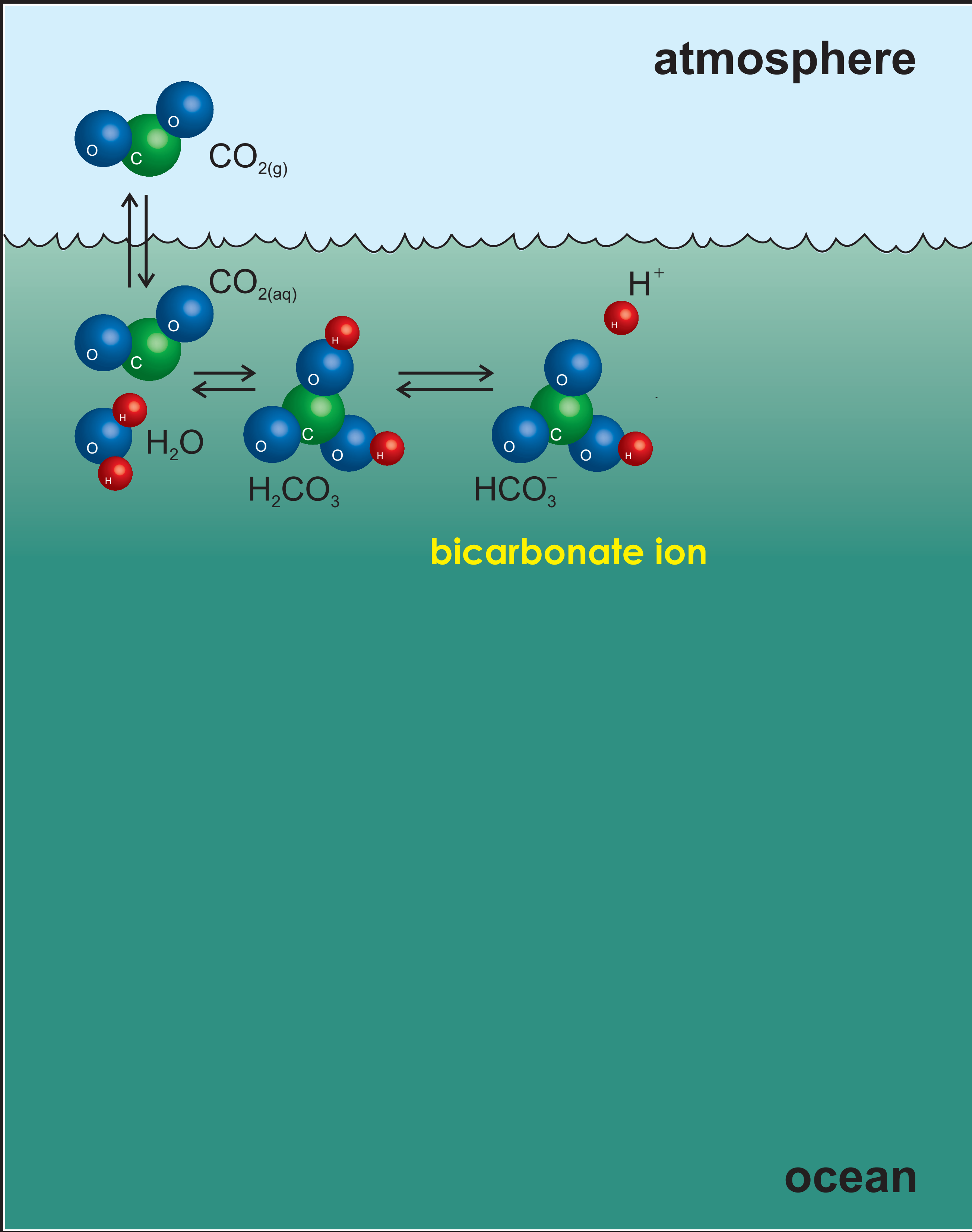
CO_2 chemistry in seawater



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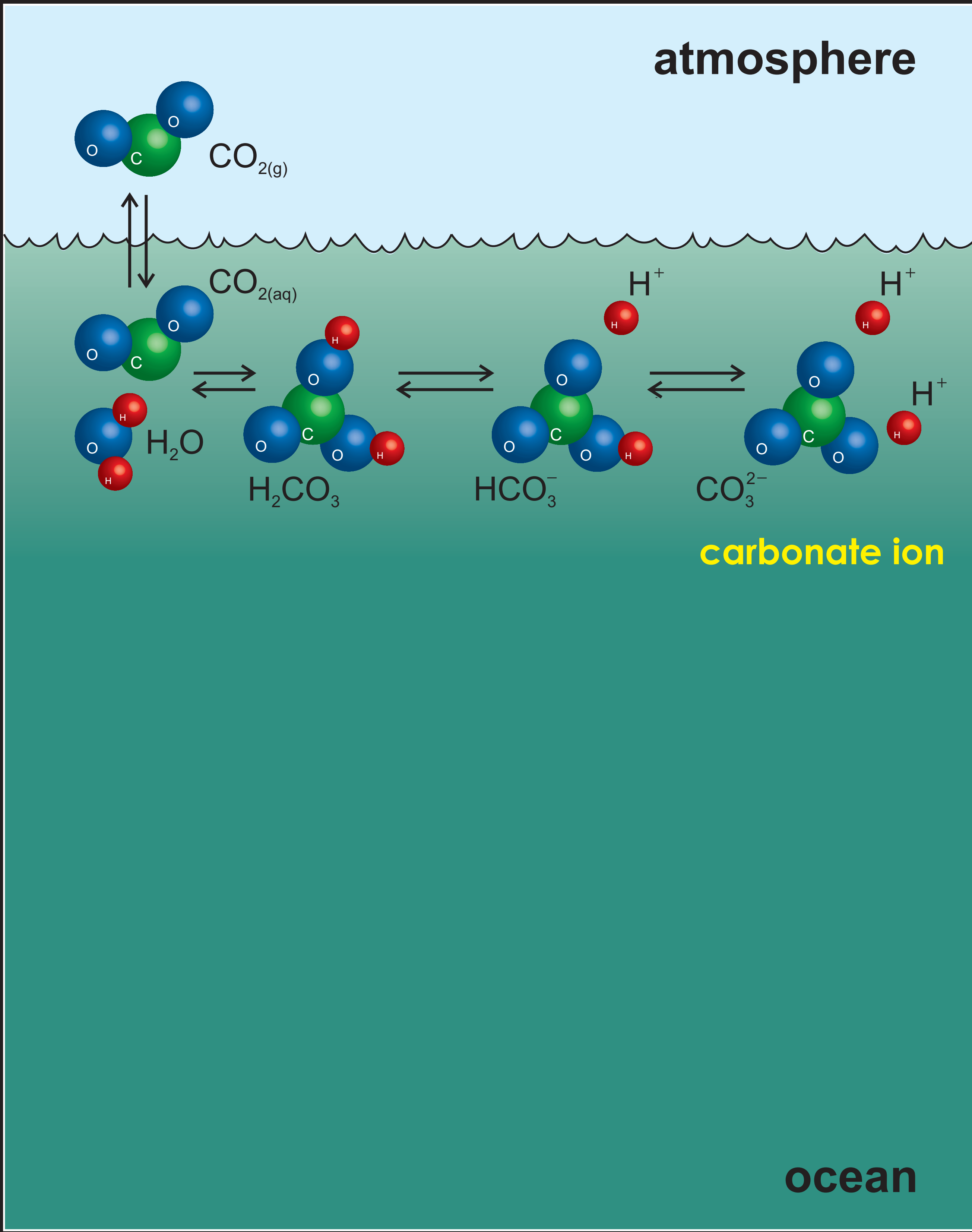
CO_2 chemistry in seawater



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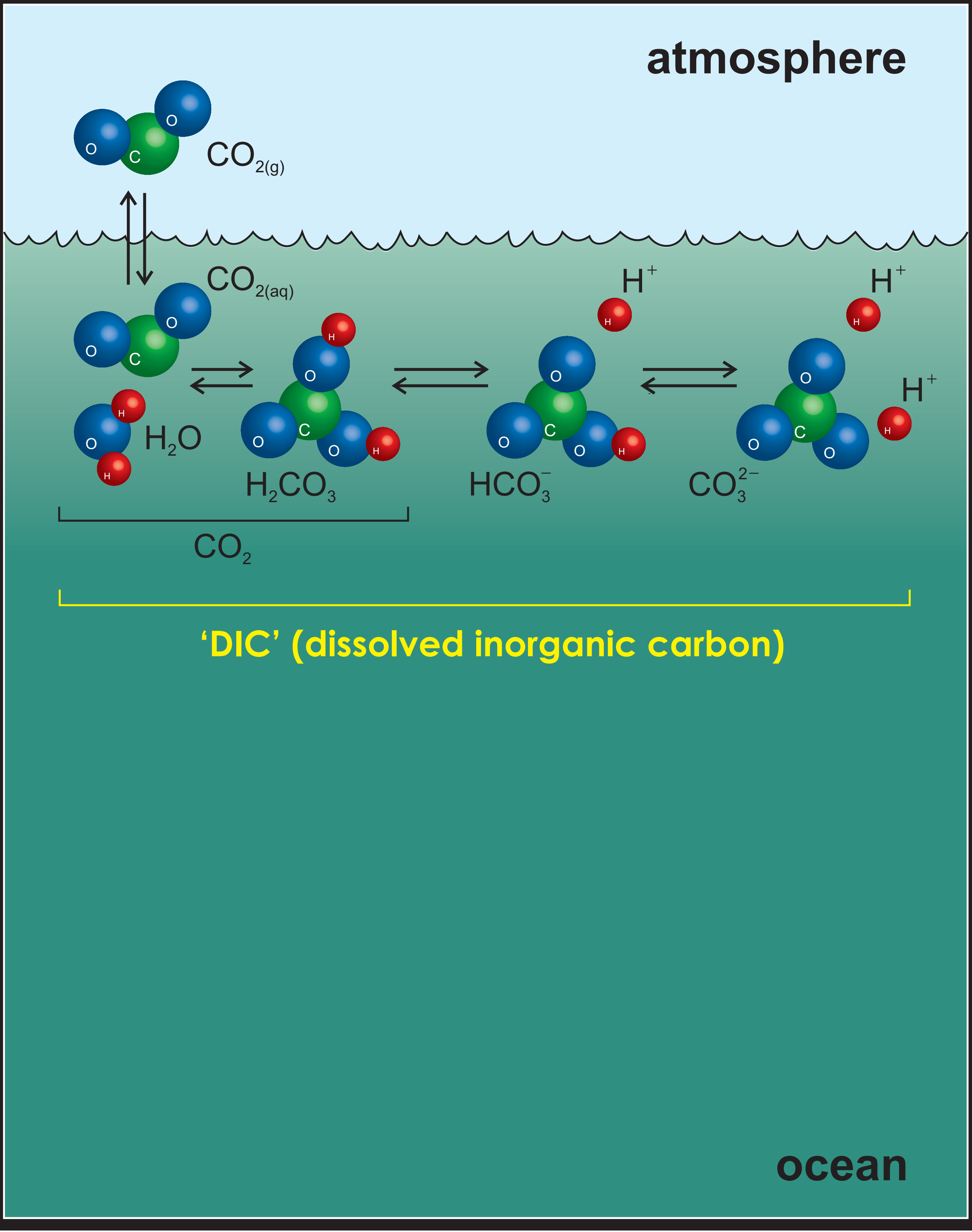


CO_2 chemistry in seawater

So ... when CO_2 dissolves in seawater, the complex equilibrium distribution of dissolved carbon between $CO_{2(aq)}$, HCO_3^-, and CO_3^{2-}, is perturbed.

While there is more total dissolved carbon, carbonate ion (CO_3^{2-}) concentrations do not increase because the hydrogen ion (H^+) equilibrium is also perturbed.

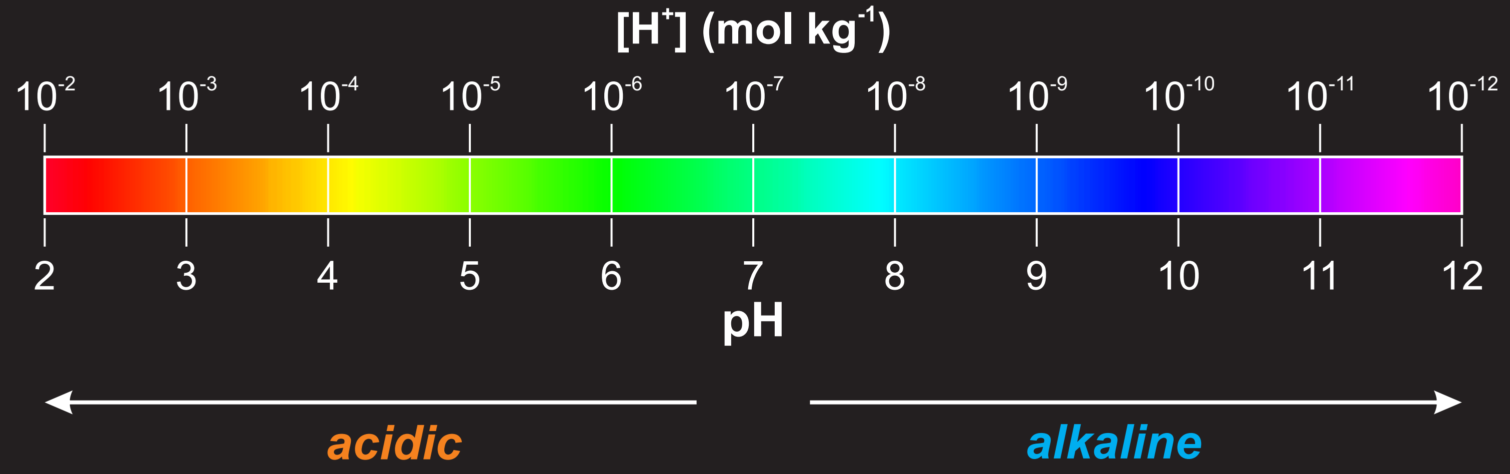
To a first approximation, the net outcome can be written:

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

(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.)

From: *Barker and Ridgwell* [in press]

The nature of pH (and acidity vs. alkalinity)



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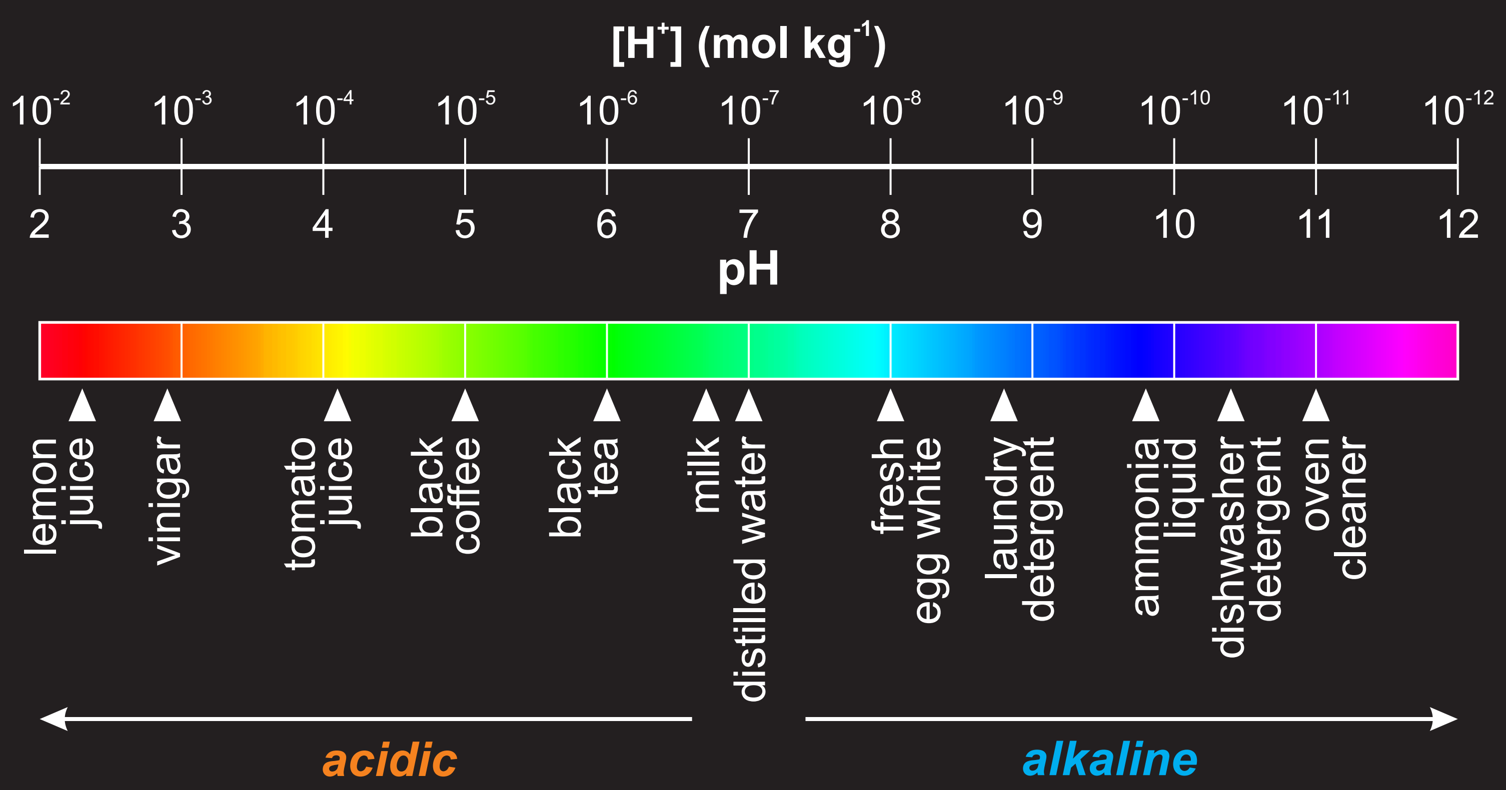

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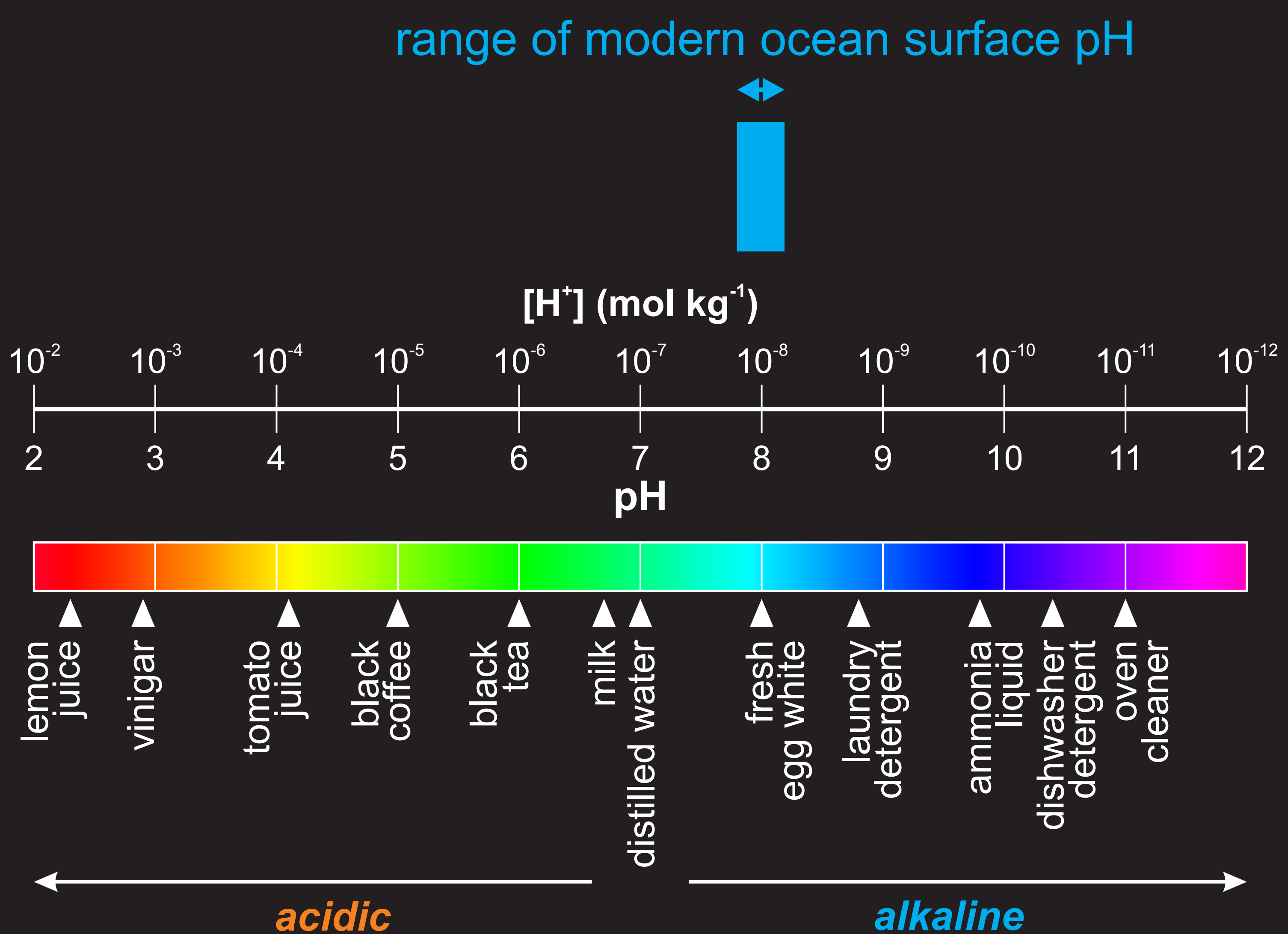

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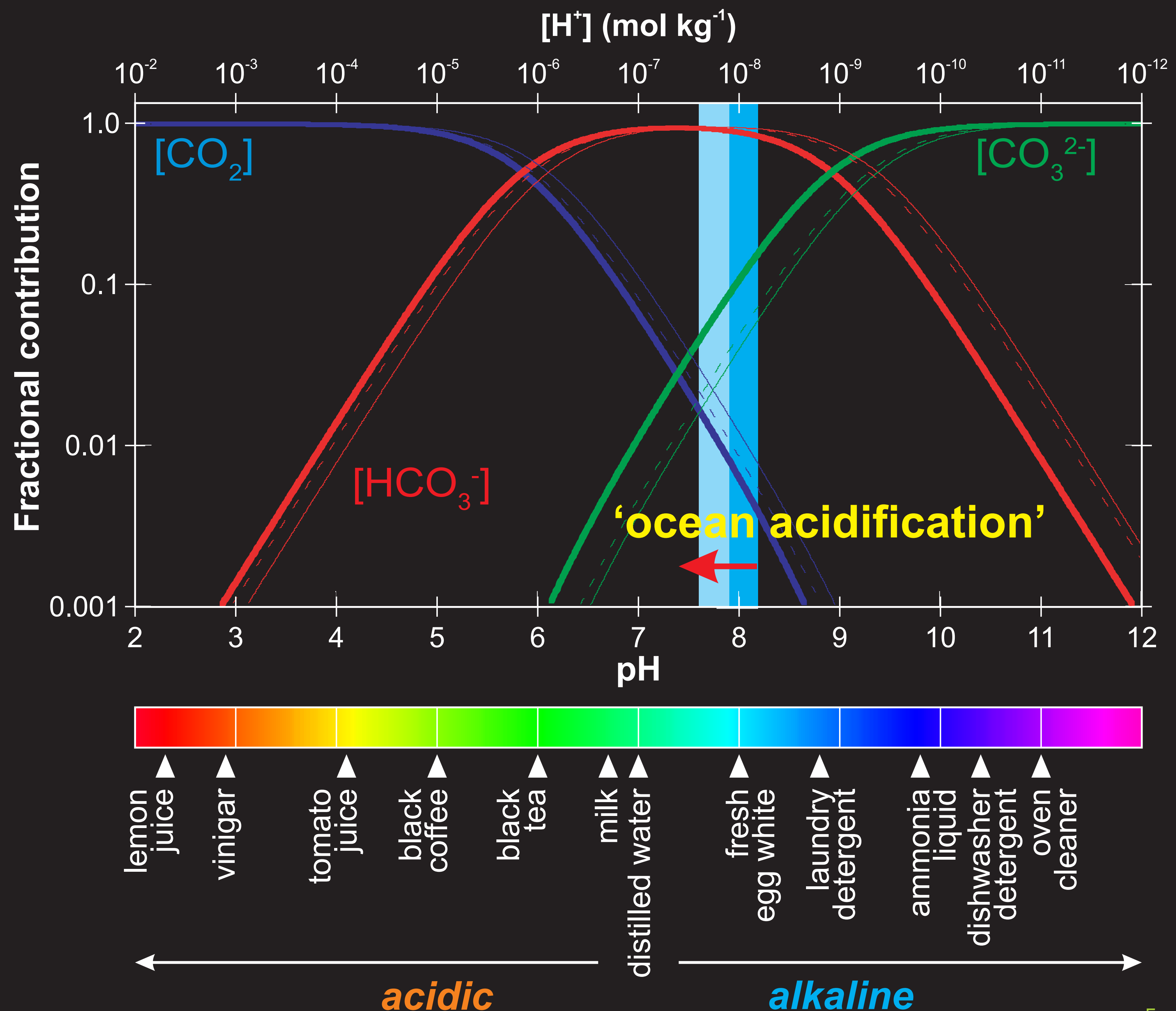
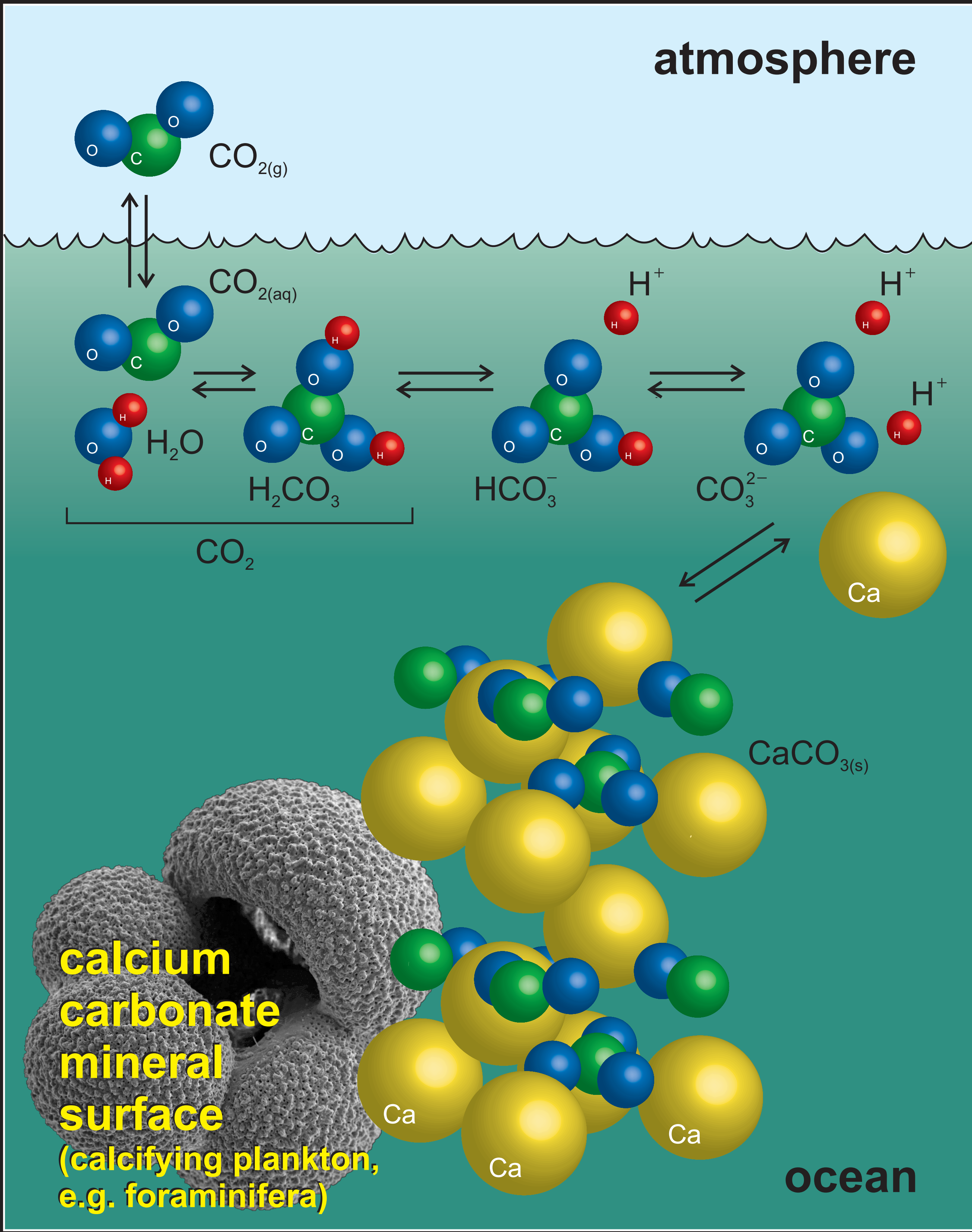
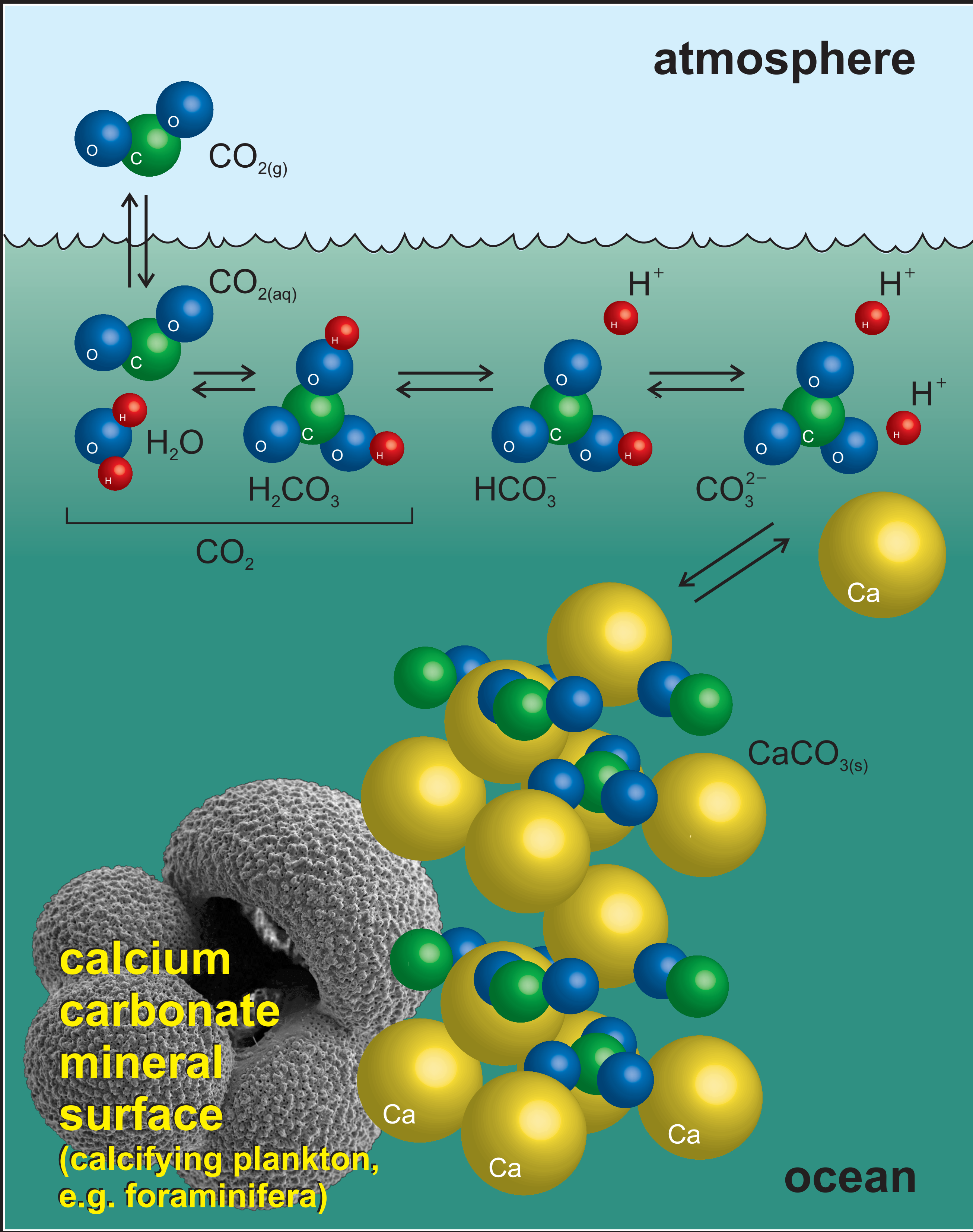


From: *Barker and Ridgwell* [in press]

CO_2 chemistry & mineral phases

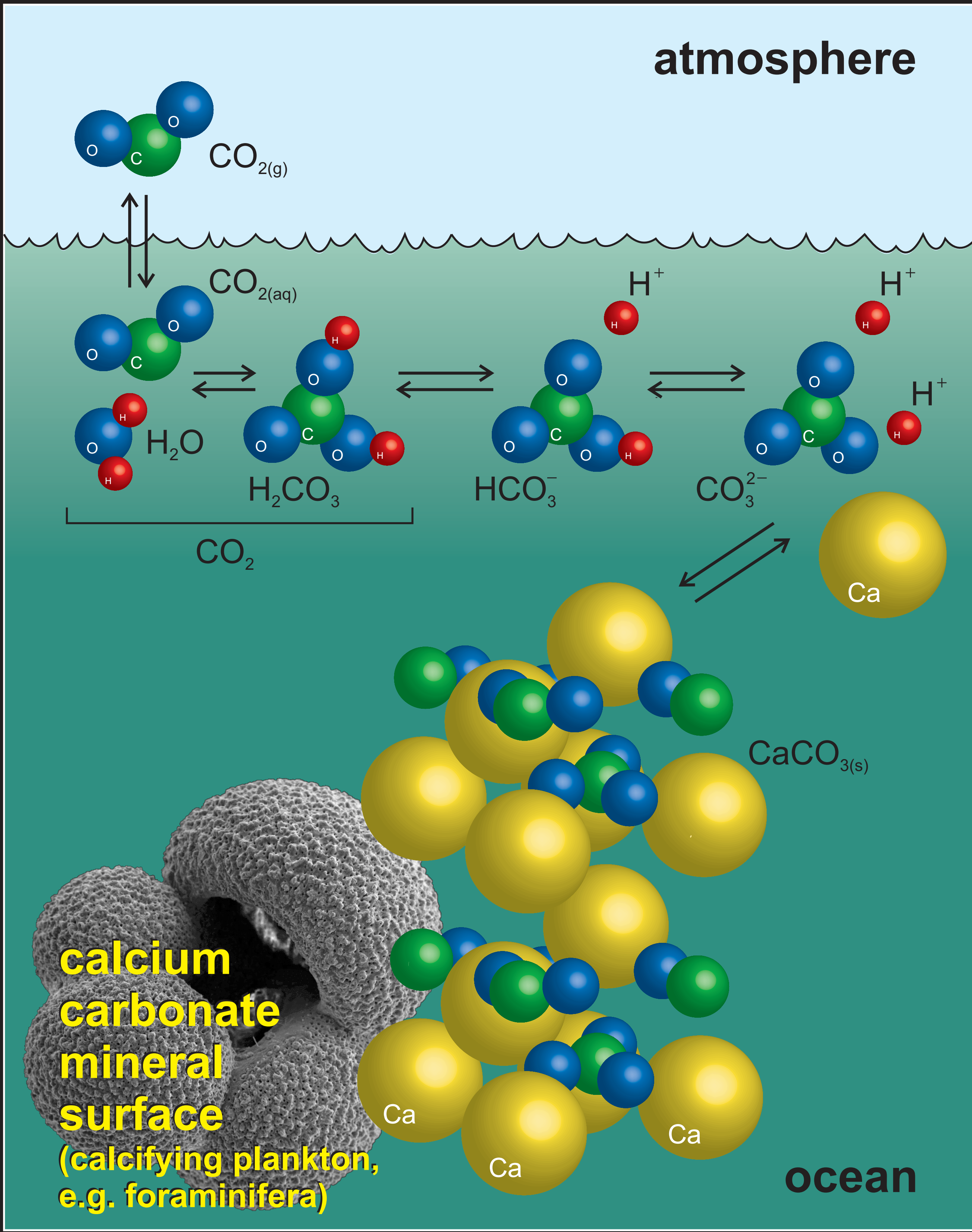


CO_2 chemistry & mineral phases



Aragonite: less stable
orthorhombic polymorph (e.g., many corals, pteropods)

Calcite: more stable
(and more abundant)
trigonal polymorph (e.g., coccolithophorides, foraminifera)

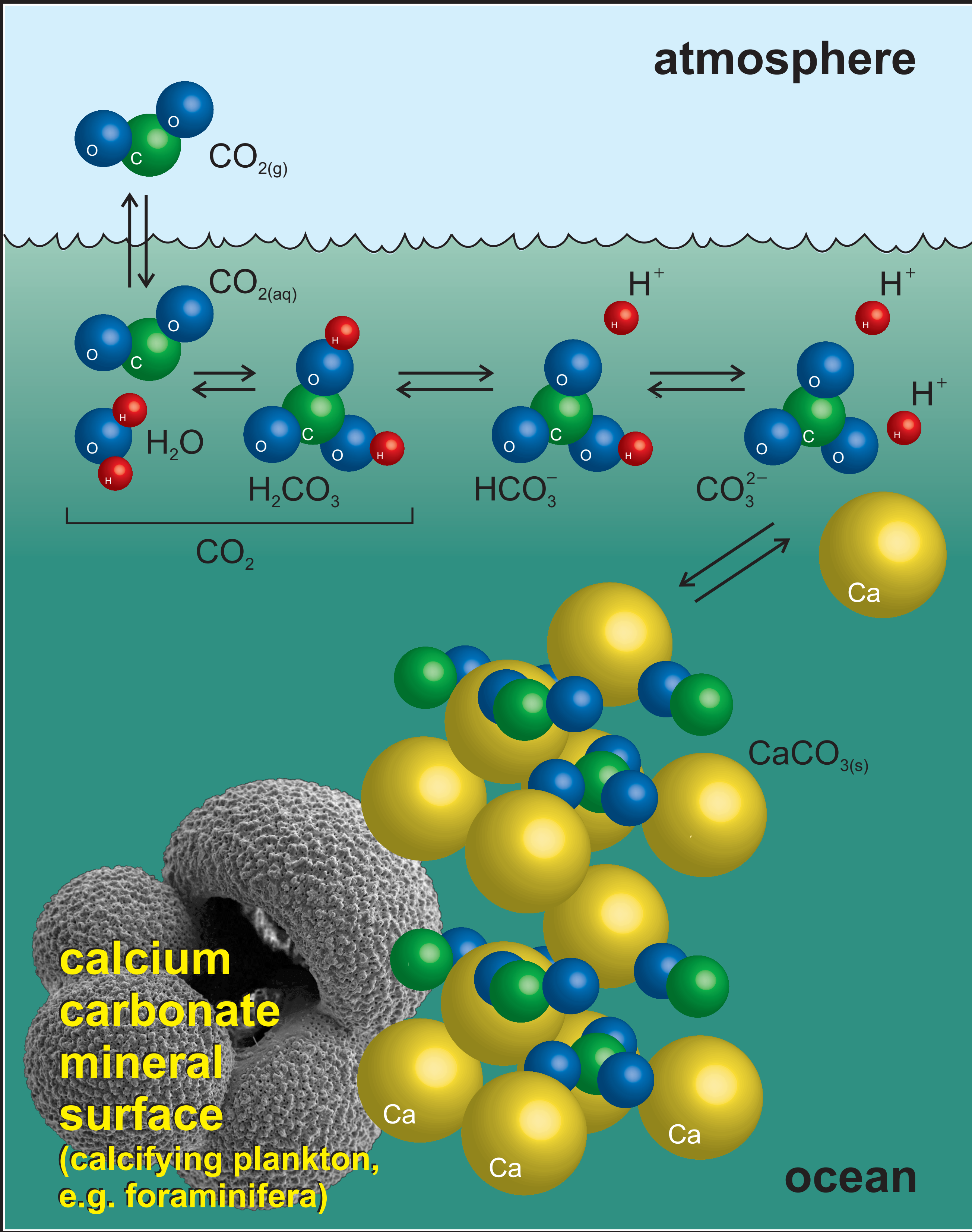


CO_2 chemistry & mineral phases

The addition of (fossil fuel) CO_2 to seawater results in a decrease in carbonate ion (CO_3^{2-}) concentration and 'ocean acidification'. A decrease in CO_3^{2-}, in turn, suppresses the stability of $CaCO_3$, defined by its *saturation state*:

$$\Omega = [Ca^{2+}]\times[CO_3^{2-}]\,/k$$

$\Rightarrow$ The thermodynamic efficiency of precipitating $CaCO_3$ is a function of $[CO_3^{2-}]$ (and carbonate 'saturation').



CO_2 chemistry & mineral phases

The bottom-line:

more (fossil fuel) CO_2

→

less CO_3^{2-} (& lower pH)

→

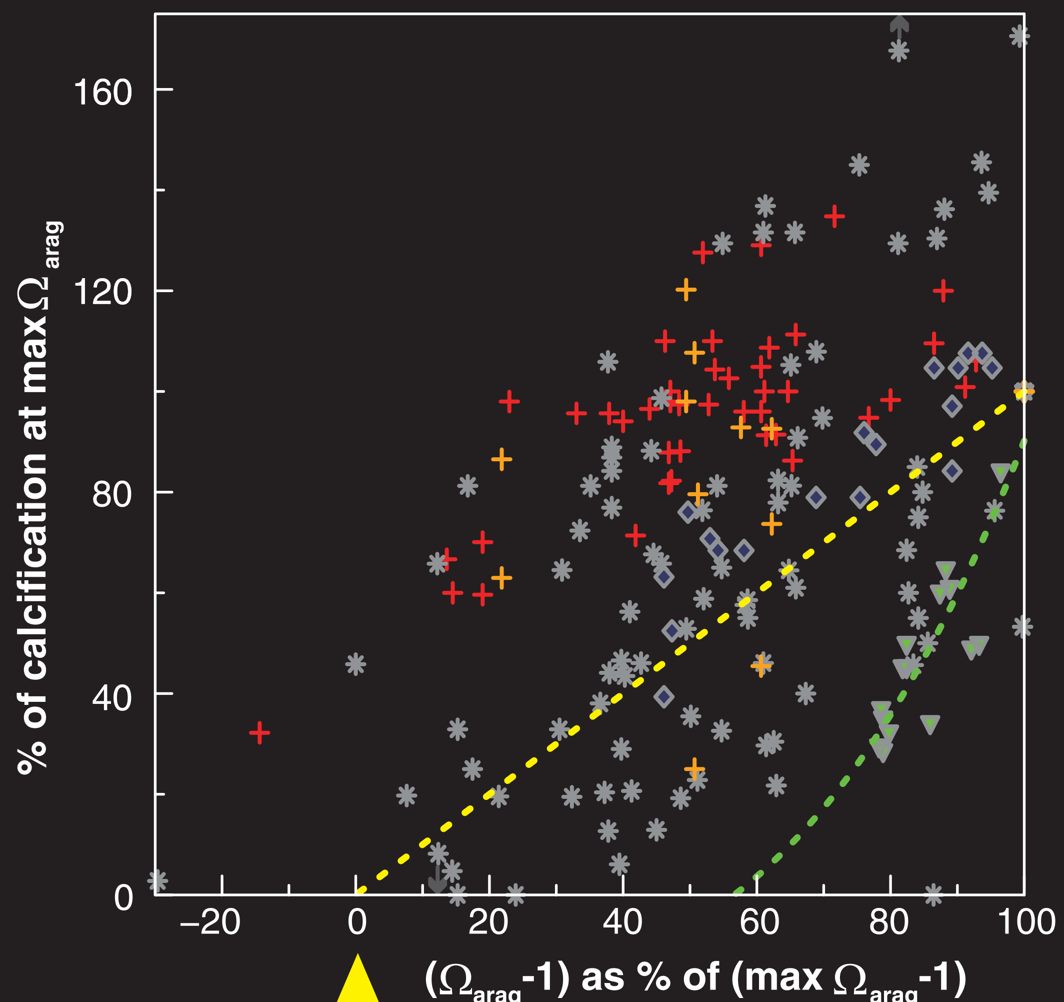
lower saturation (Ω) & less stable $CaCO_3$

(i.e., calcite and aragonite will dissolve more readily or be less easily precipitated by organisms)

Ocean biological consequences(?)

decreasing pH, saturation

decreasing calcification



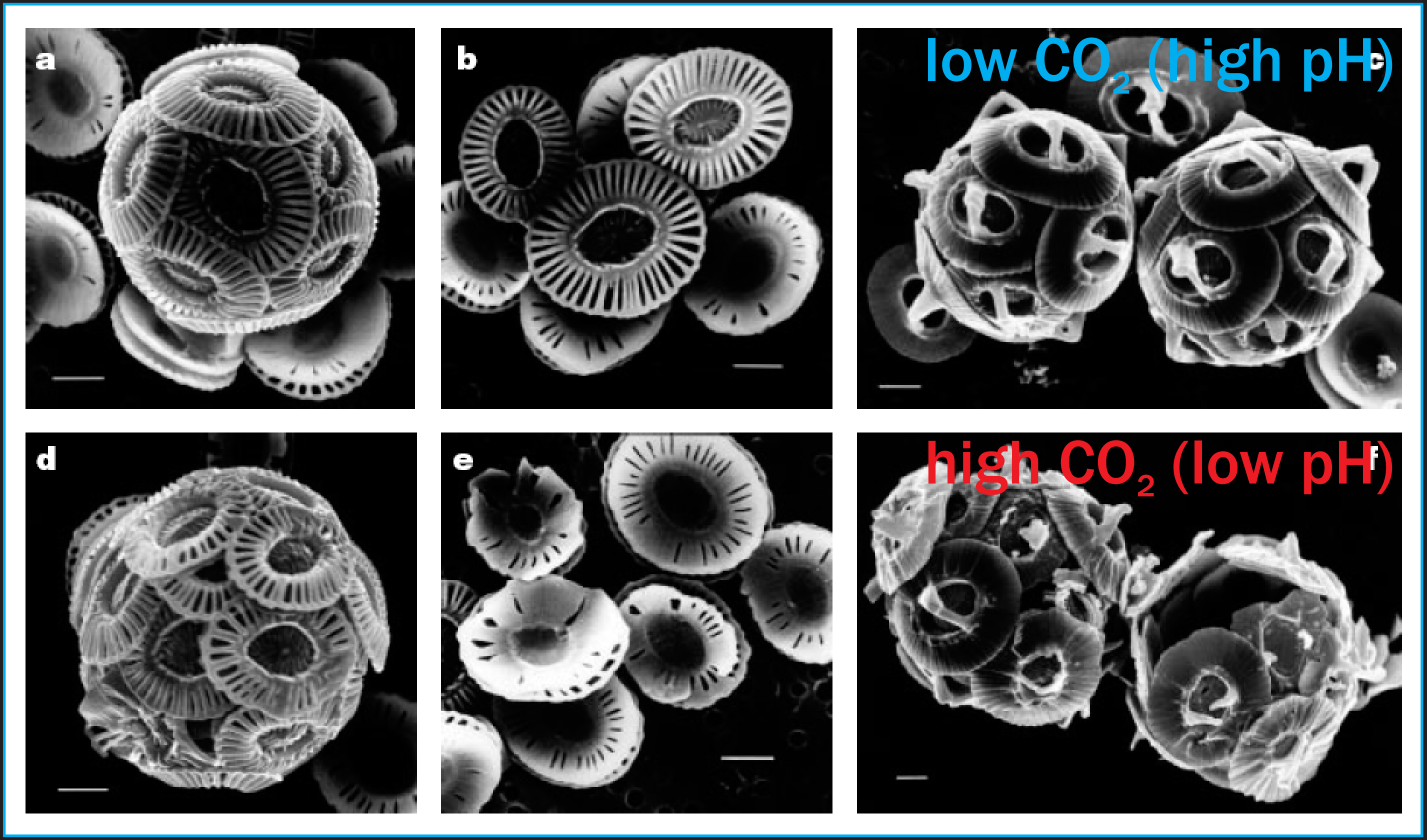
Ω = 1.0

under-saturated

over-saturated

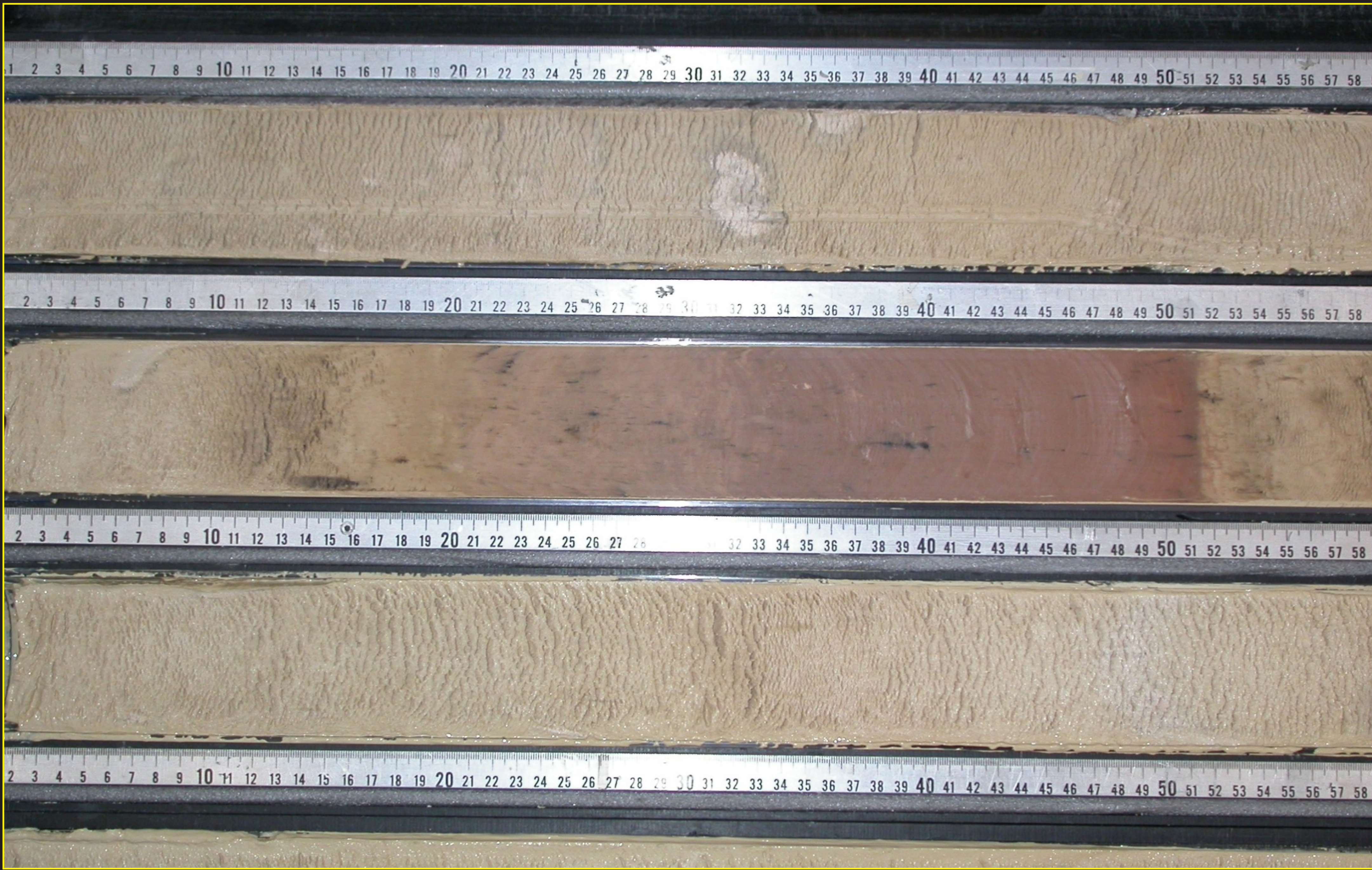
Pandolfi et al. [2011] (*Science*)

Ocean biological consequences(?)



SEM micrographs of coccolithophorids under different CO_2 conditions
Riebesell et al. [2000] (*Nature* 407)

The time-machine on the ocean floor



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

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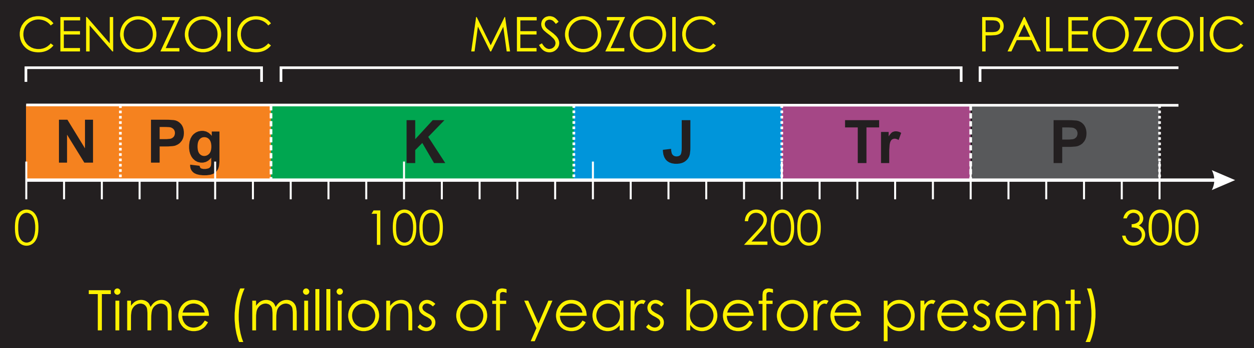
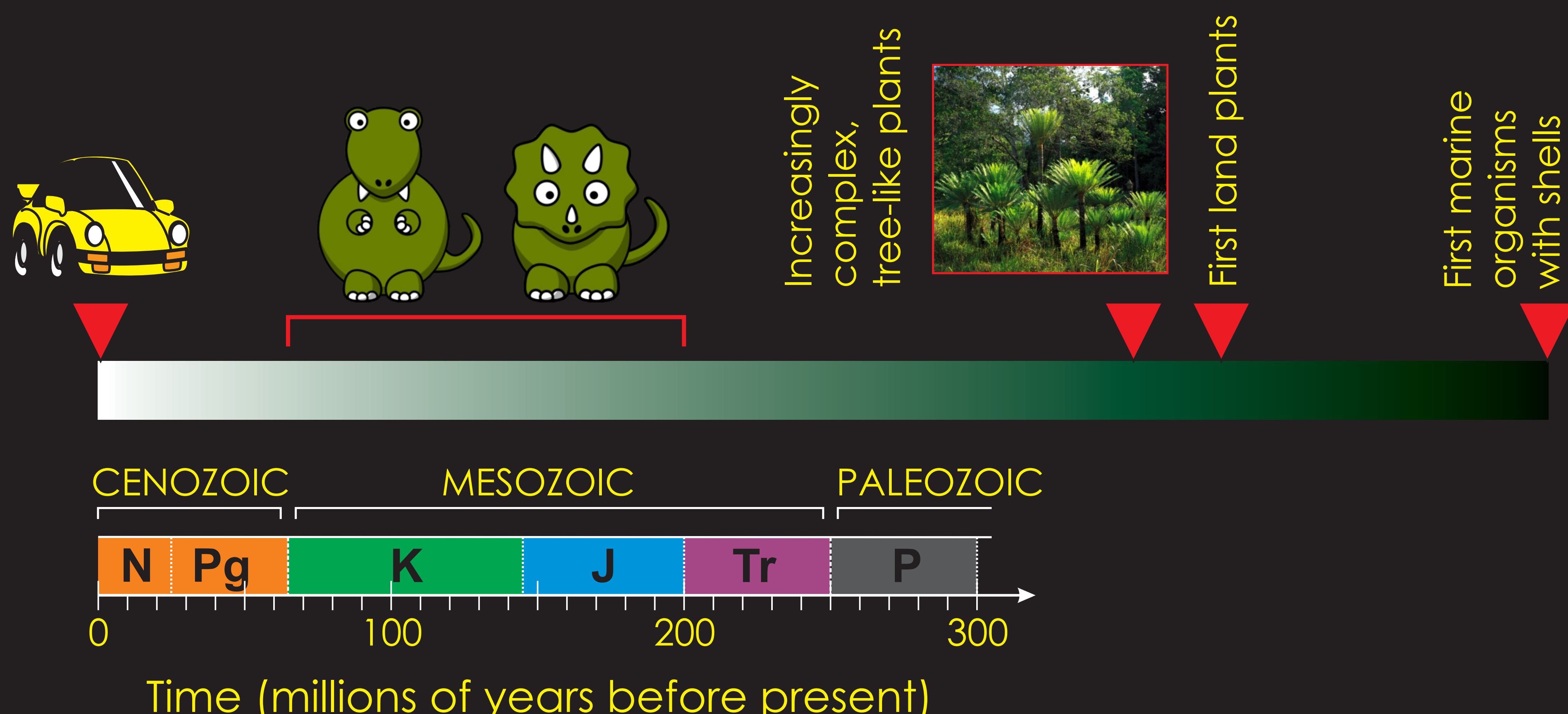


From: *Hönisch et al.* [in press]

The Geological Record of Ocean Acidification



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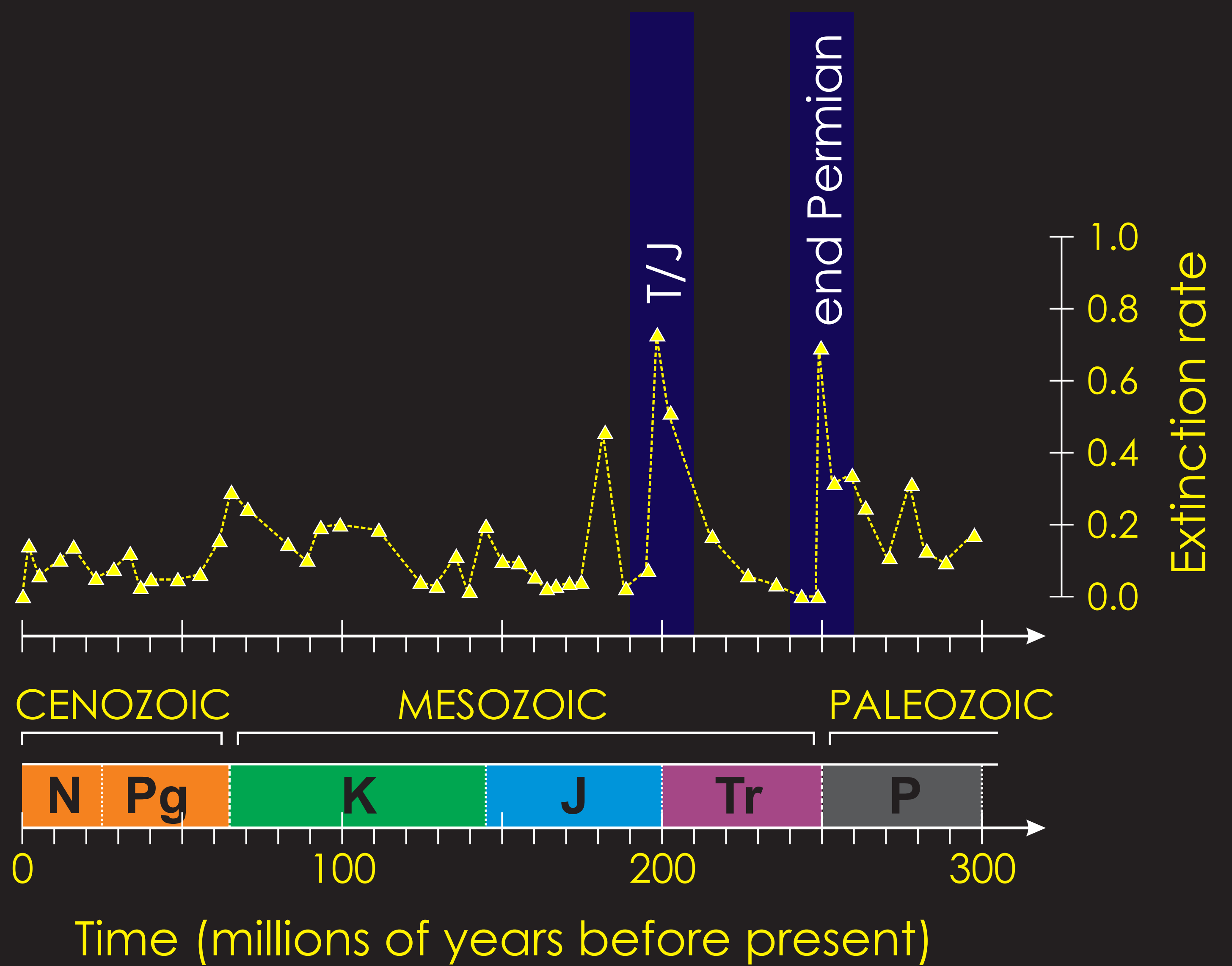

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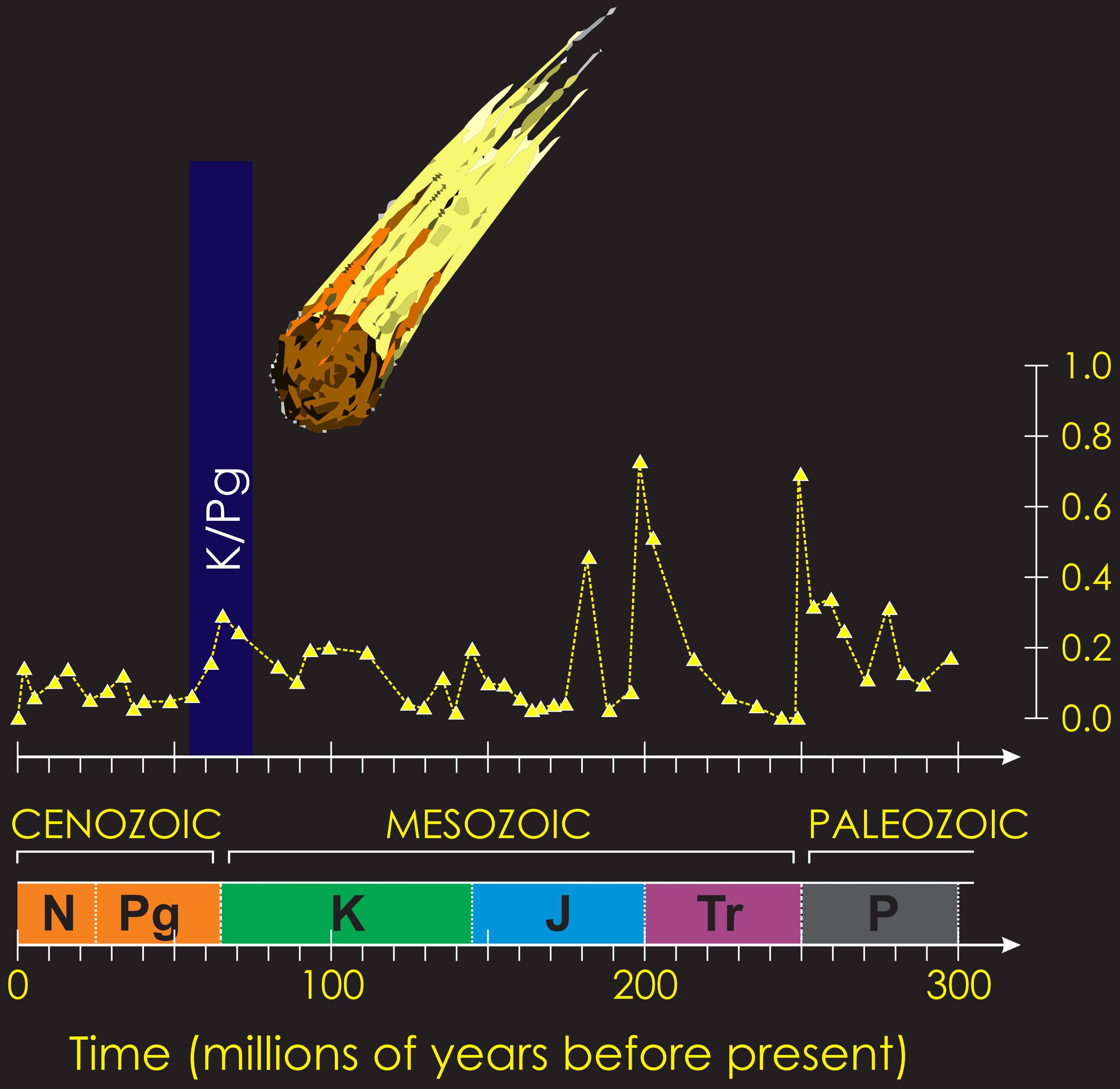
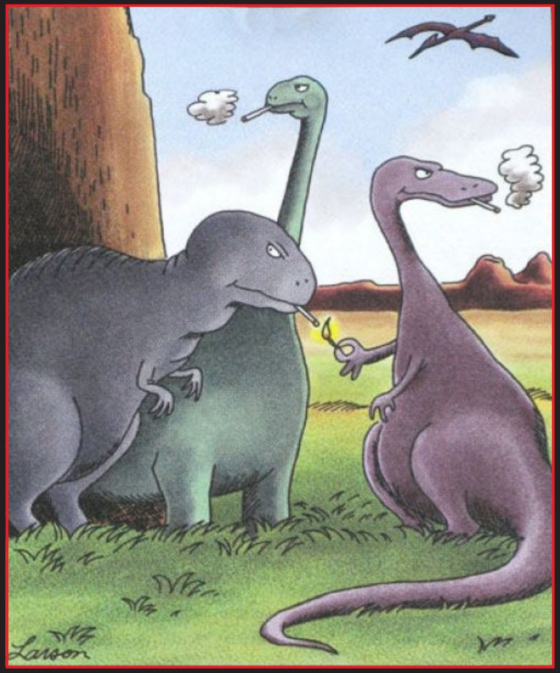
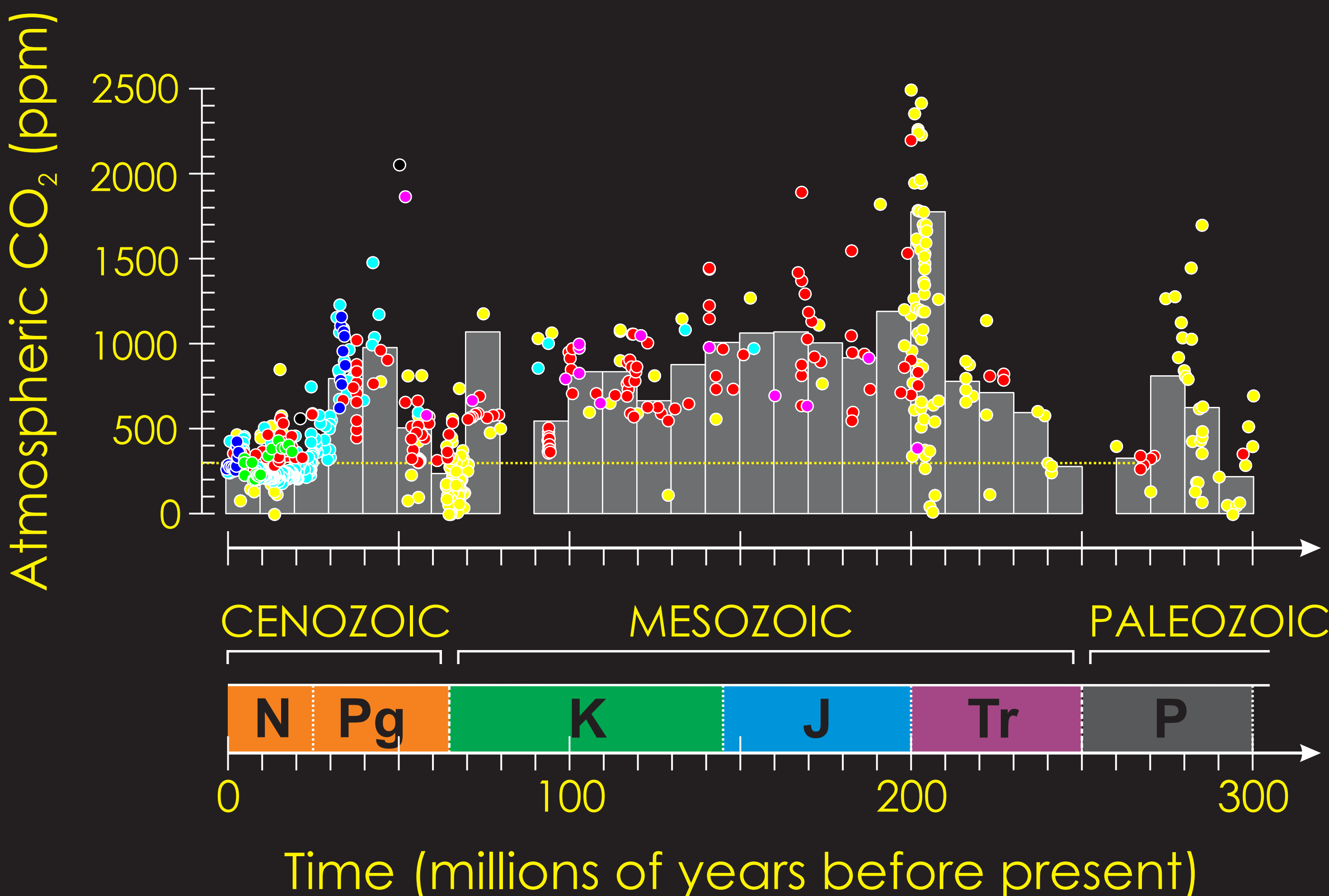
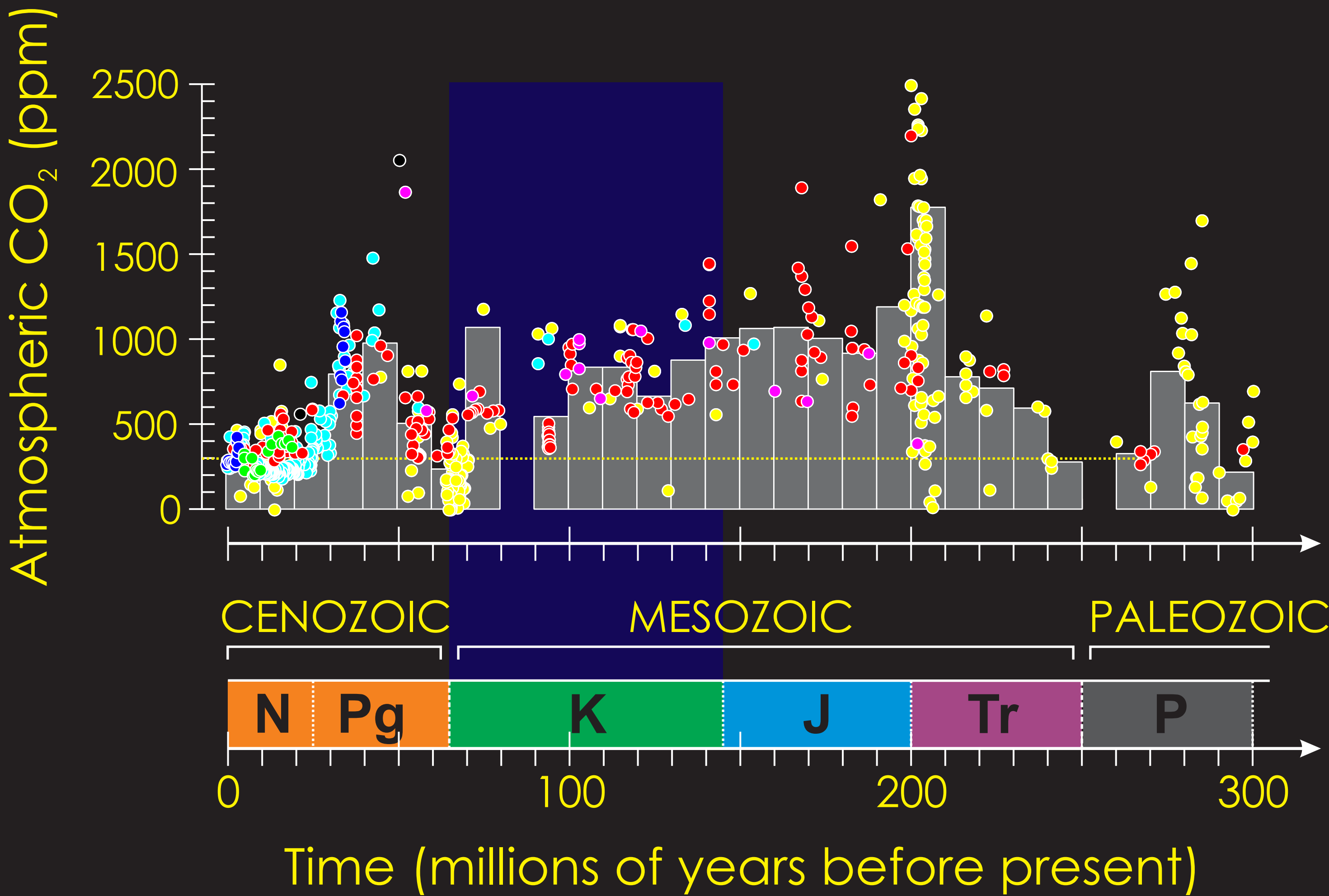


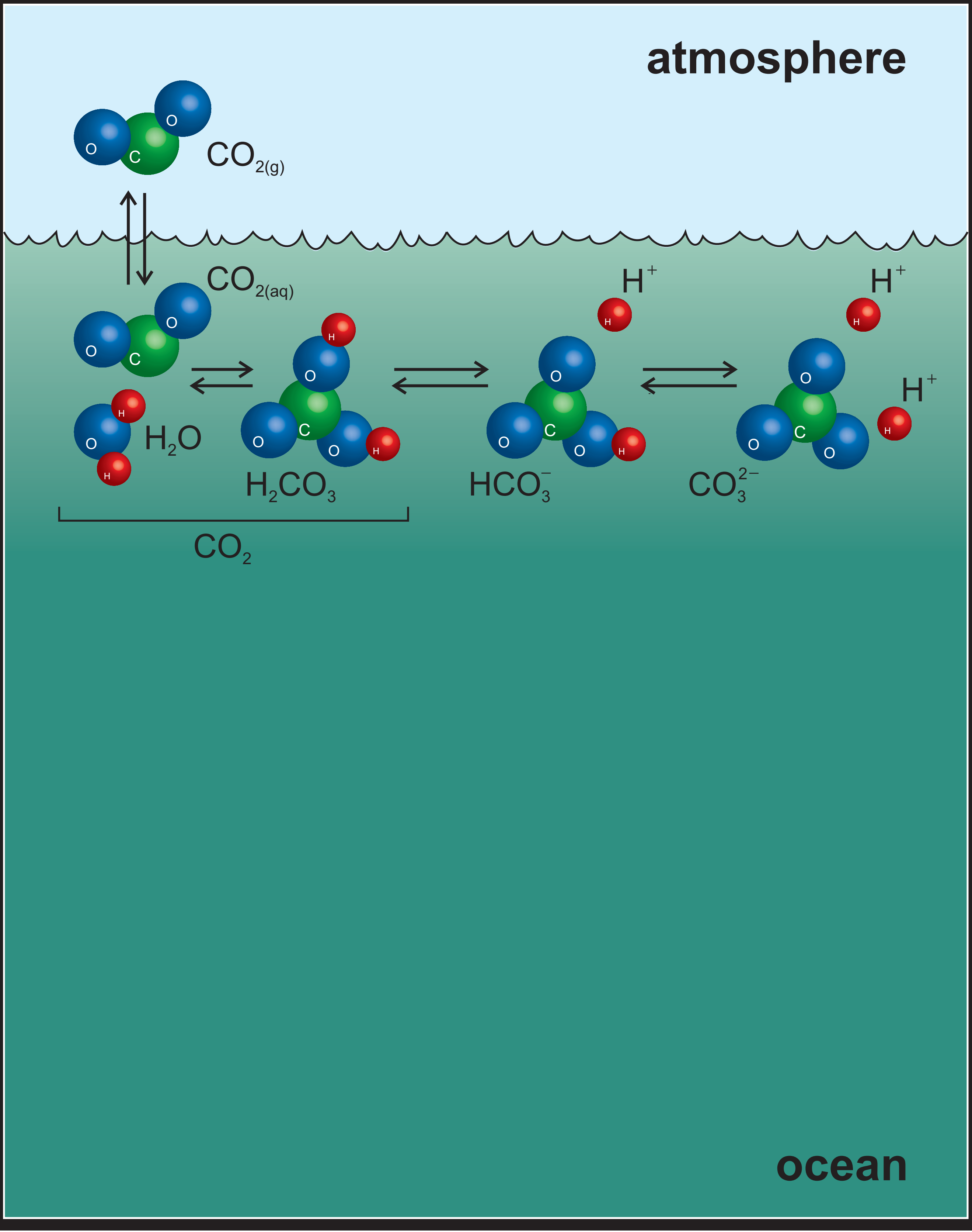


The Geological Record of Ocean Acidification



The Geological Record of Ocean Acidification




atmosphere
$CO_{2(g)}$
$CO_{2(aq)}$
H_2O
H_2CO_3
H^+
HCO_3^-
H^+
H^+
CO_3^{2-}
CO_2
ocean
C
O
H

```
! 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) -
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& ) &
& /(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 &
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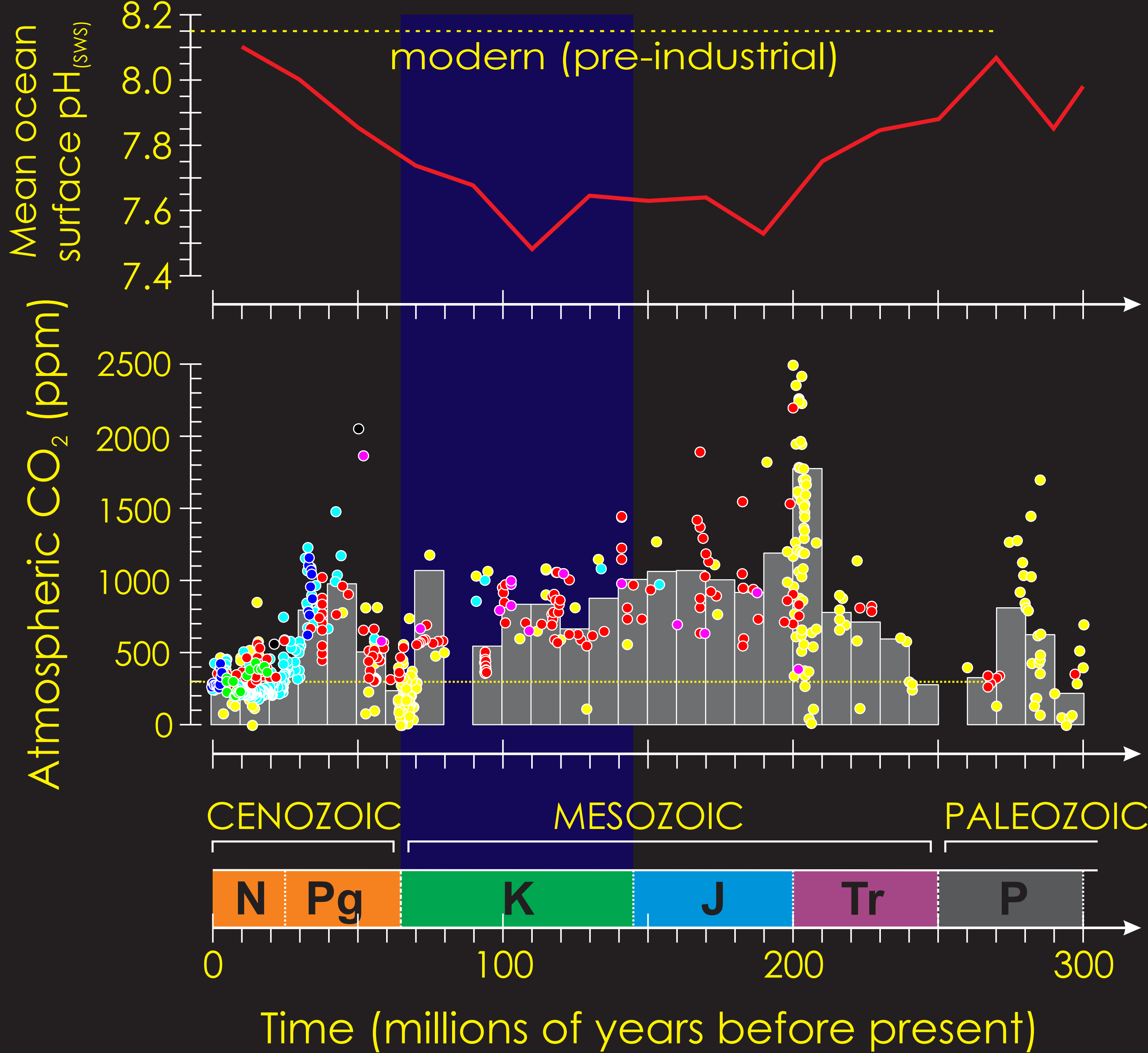
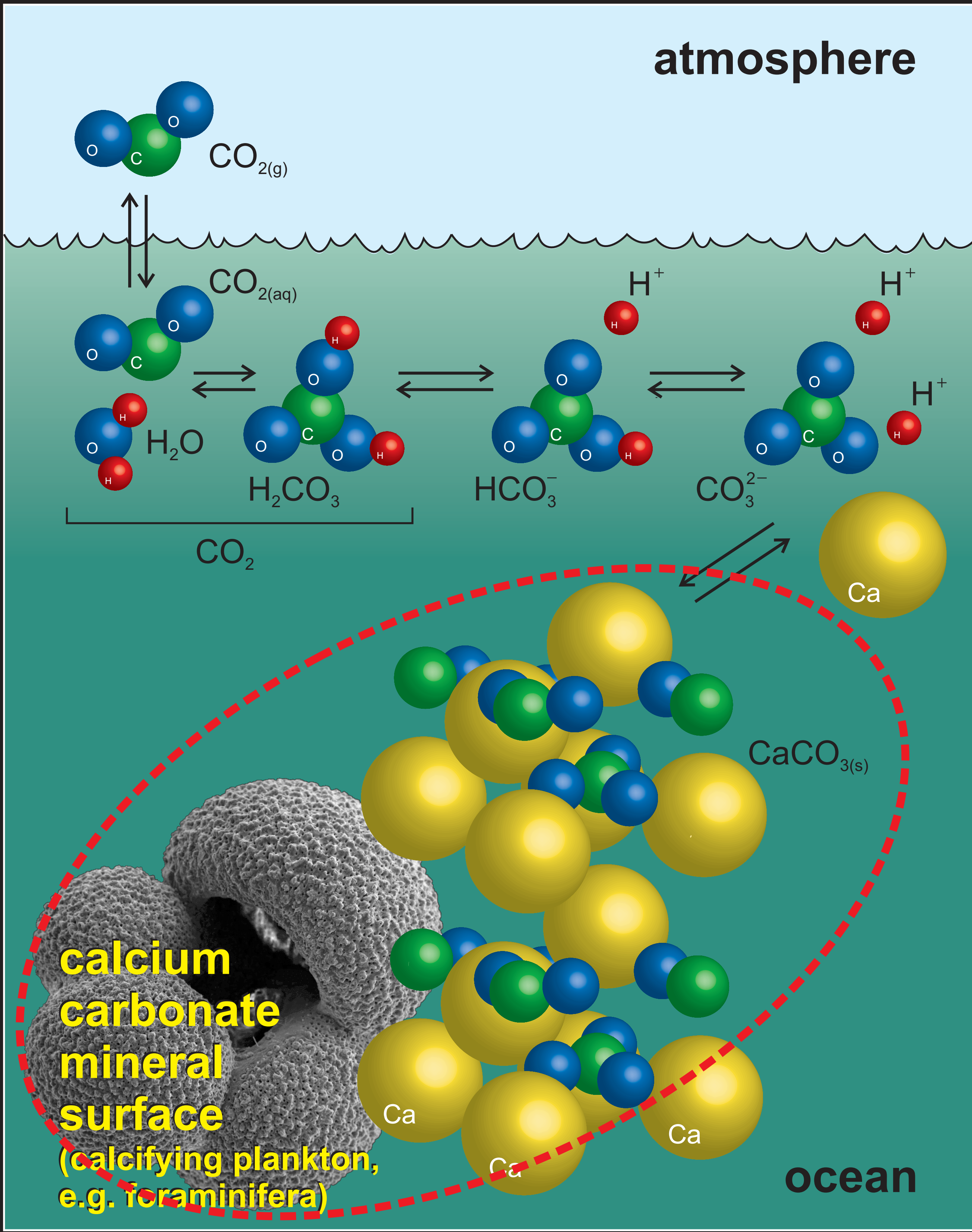
loc_H1 = dum_carbconst(icc_k1)*loc_conc_CO2/loc_conc_HCO3

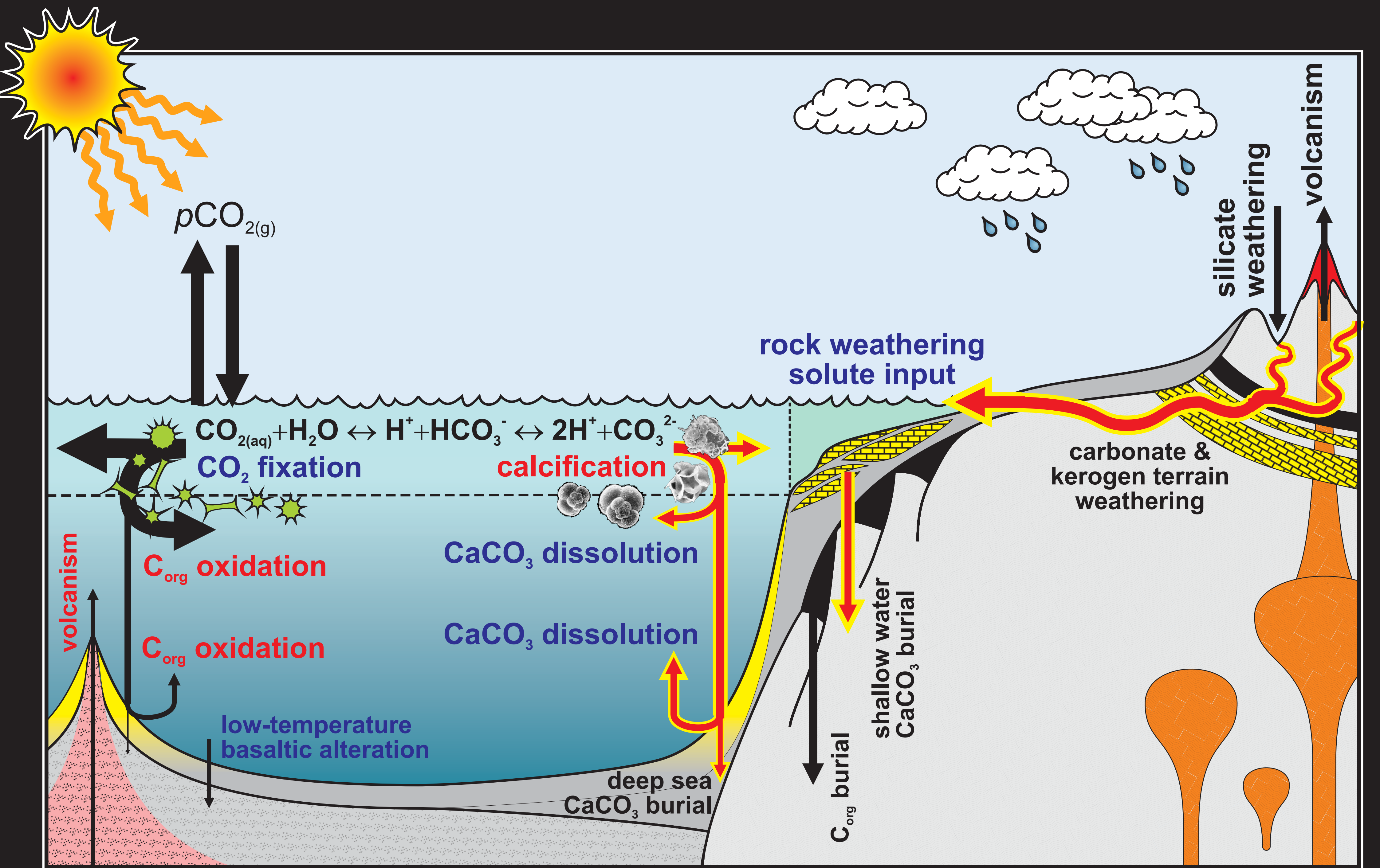
loc_H2 = dum_carbconst(icc_k2)*loc_conc_HCO3/loc_conc_CO3
```

The Geological Record of Ocean Acidification




atmosphere
O
C
O
CO2(g)
CO2(aq)
O
C
O
H
O
H
H2O
H
O
C
O
H
H2CO3
H+
H
O
C
O
H
HCO3−
H+
H
O
C
O
H+
H
CO32−
CO2
Ca
CaCO3(s)
calcium
carbonate
mineral
surface
(calcifying plankton,
e.g. foraminifera)
Ca
Ca
Ca
ocean

The global carbon(ate) cycle: Control of ocean saturation



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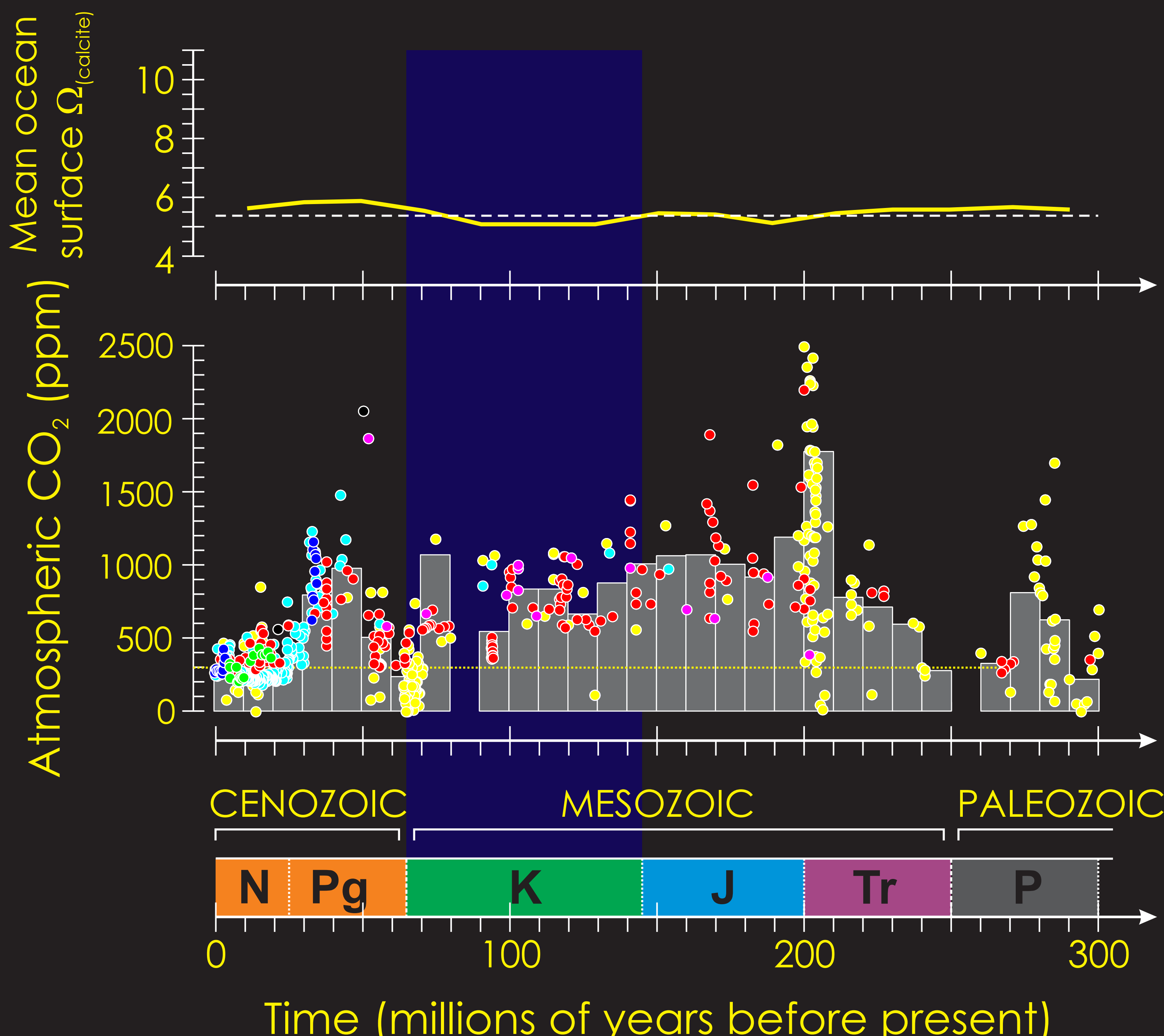

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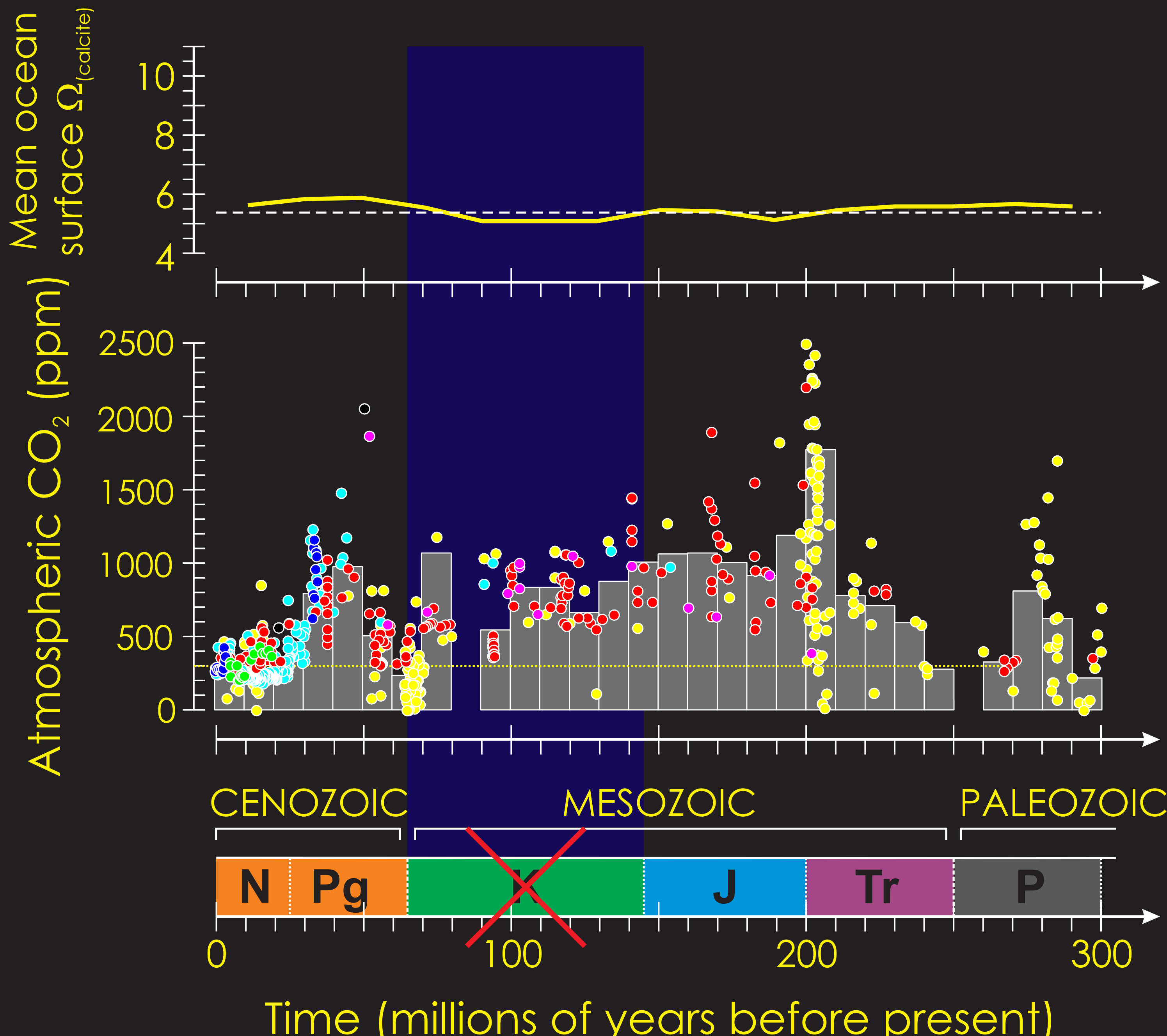
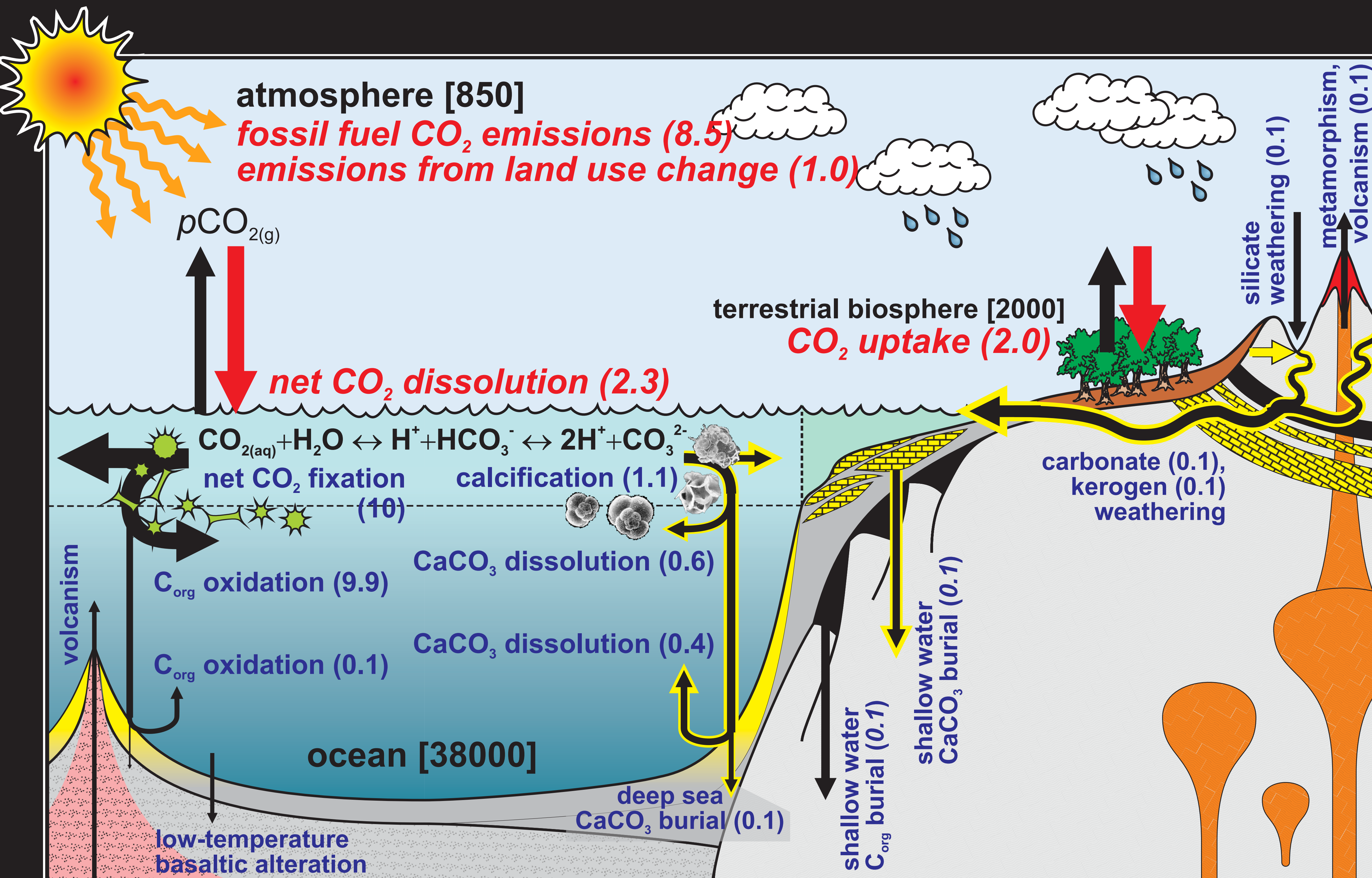
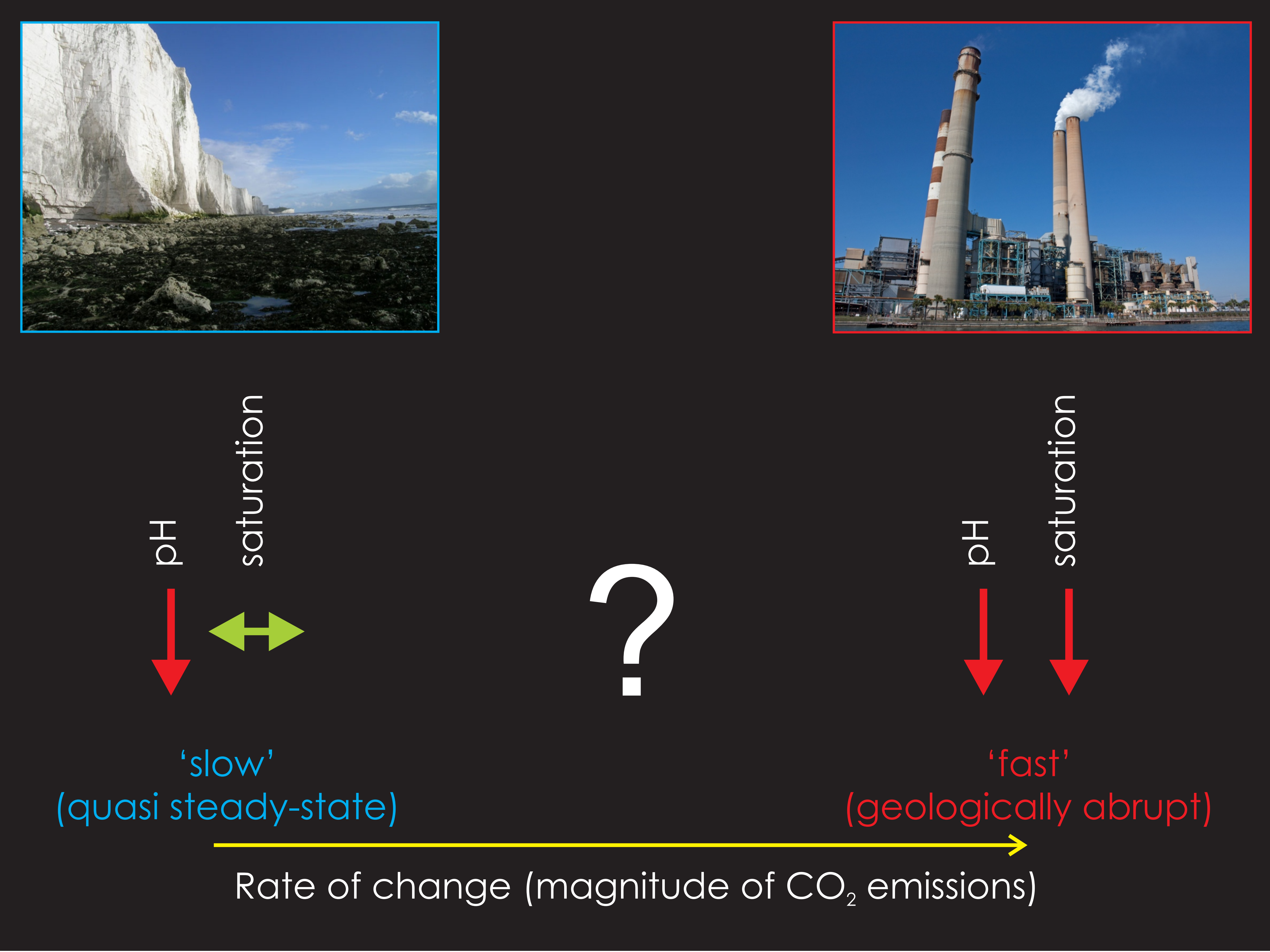


The modern carbon cycle




pH
saturation
?
pH
saturation
'slow'
(quasi steady-state)
'fast'
(geologically abrupt)
Rate of change (magnitude of CO_2 emissions)

```
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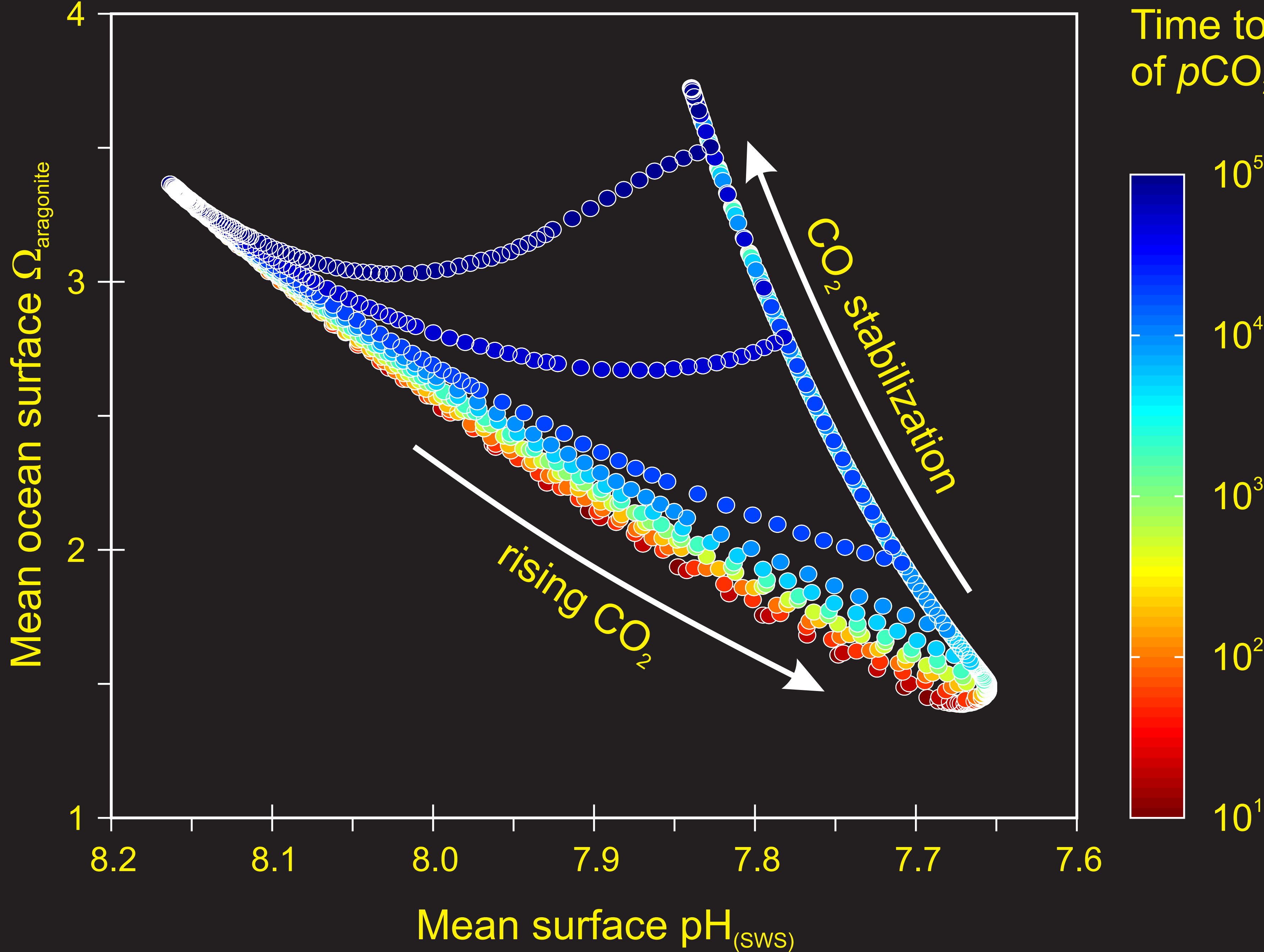
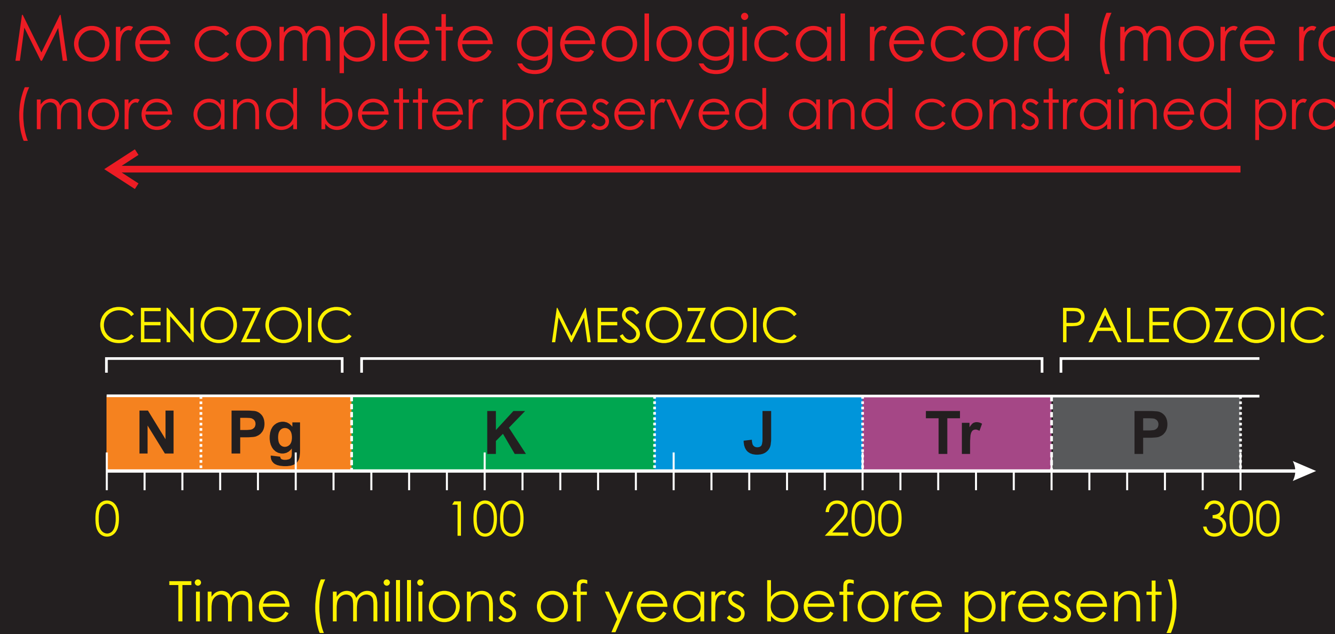
loc_H2 = dum_carbconst(icc_k2)*loc_conc_HCO3/loc_conc_CO3
```

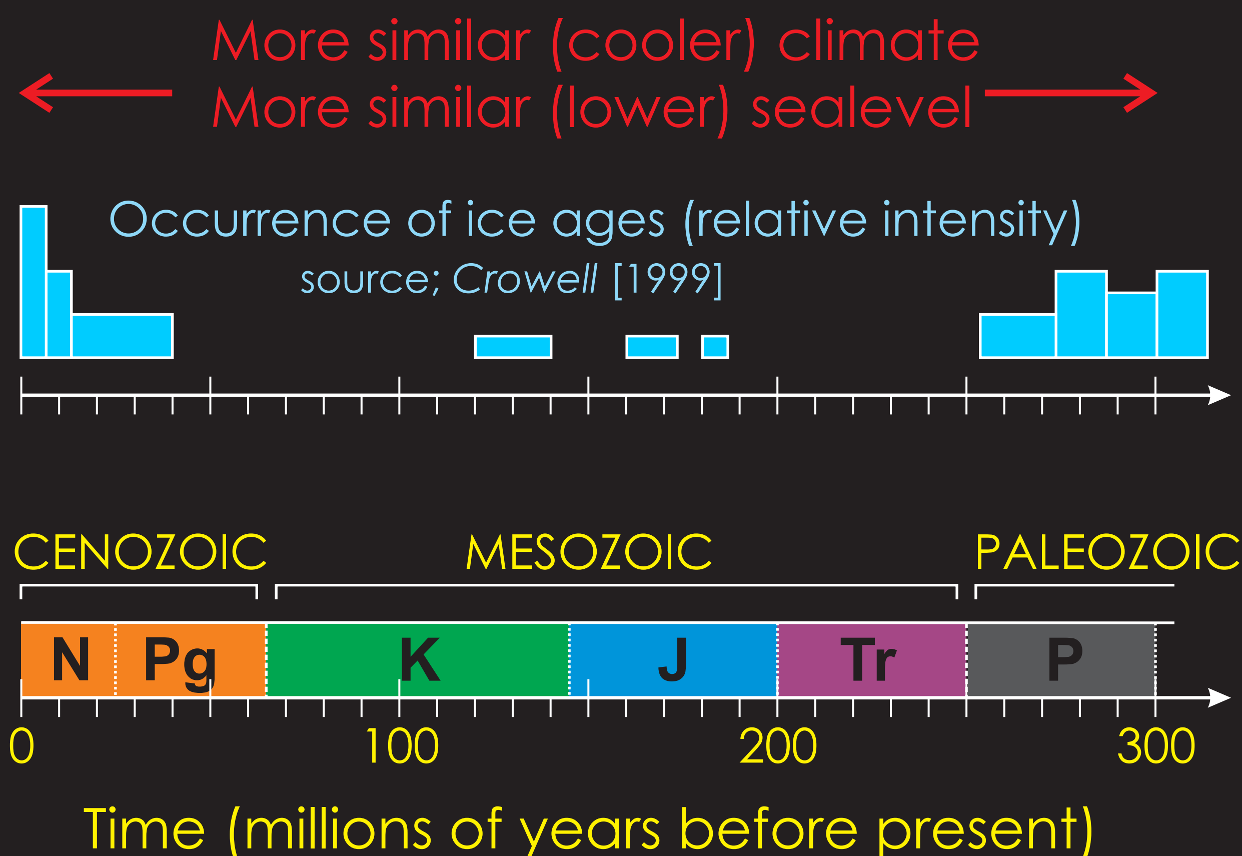
Time-scale dependence of the nature of ocean carbonate chemistry changes



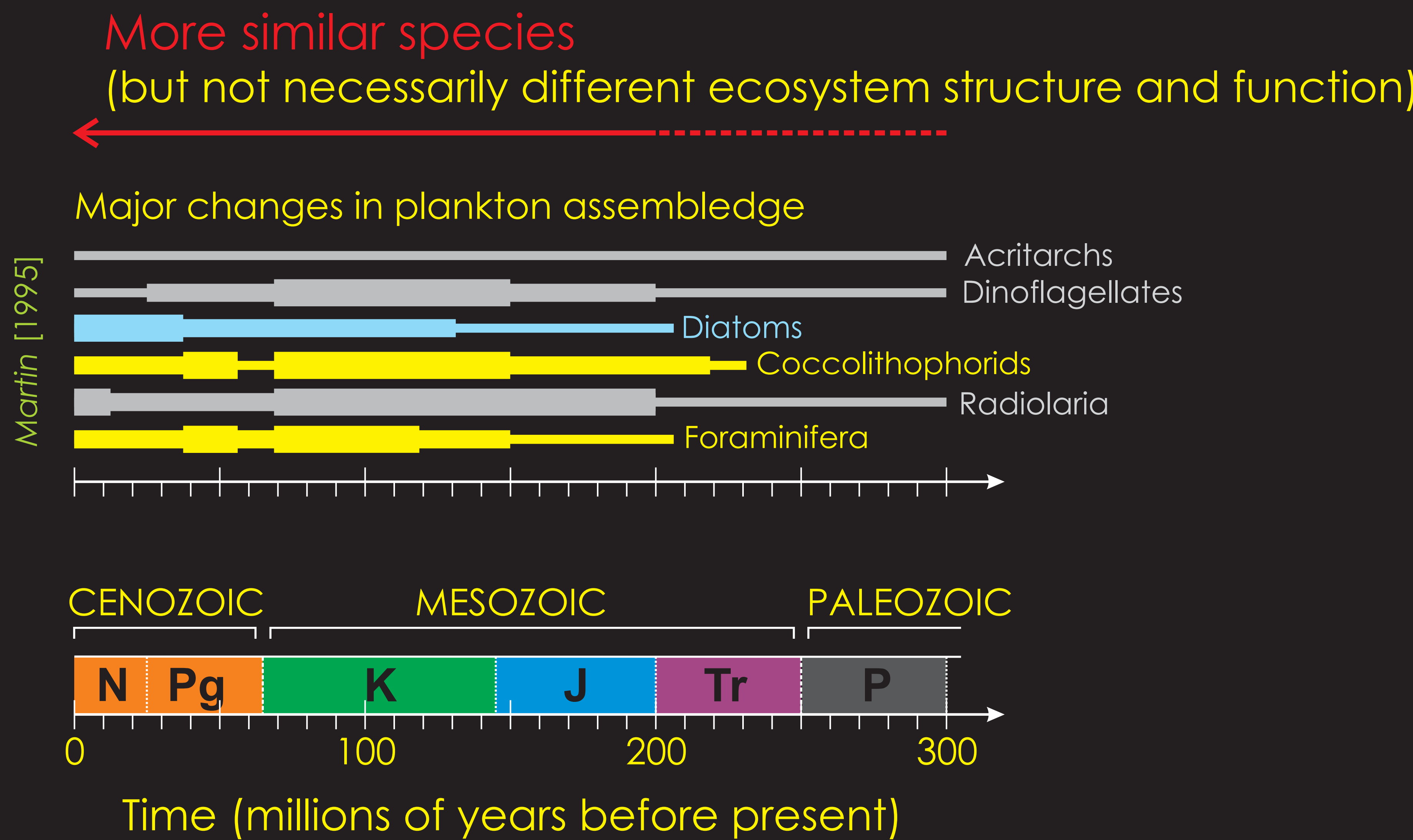
Is there a past 'analogue' for the future consequences of massive CO_2 release and ocean acidification?



Is there a past 'analogue' for the future consequences of massive CO_2 release and ocean acidification?



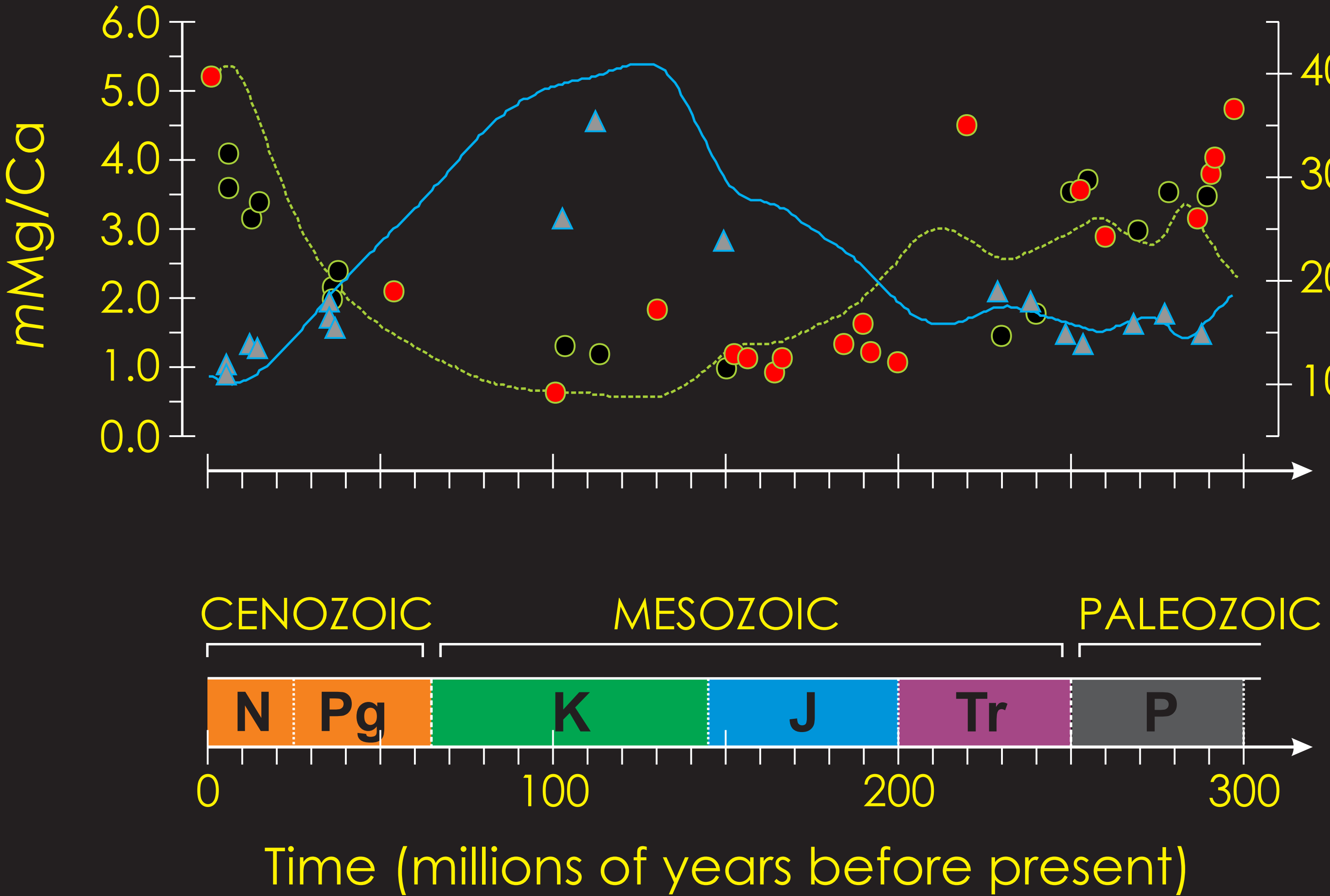
Is there a past 'analogue' for the future consequences of massive CO_2 release and ocean acidification?



Is there a past 'analogue' for the future consequences of massive CO_2 release and ocean acidification?

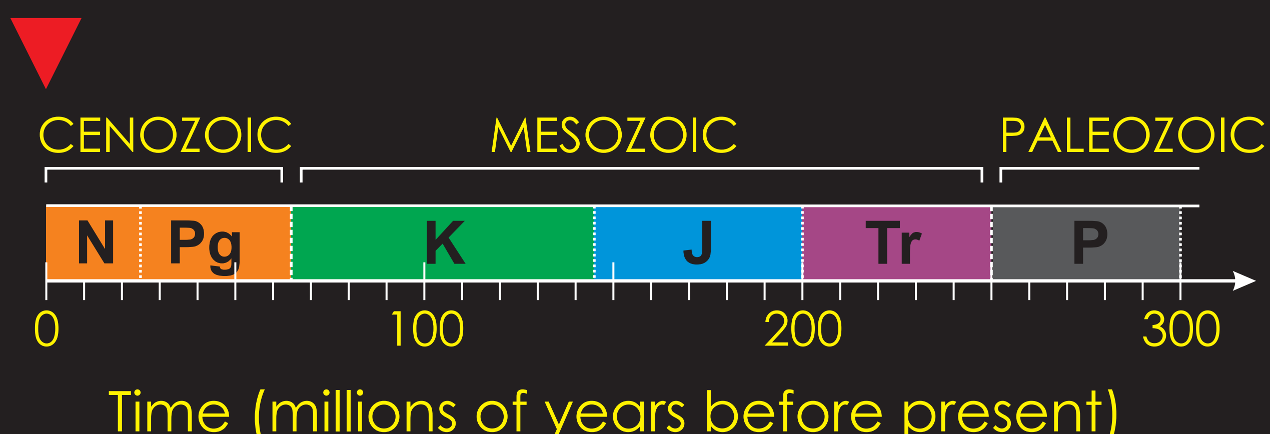
('aragonite' vs. 'calcite' as the dominant reef mineralogy)

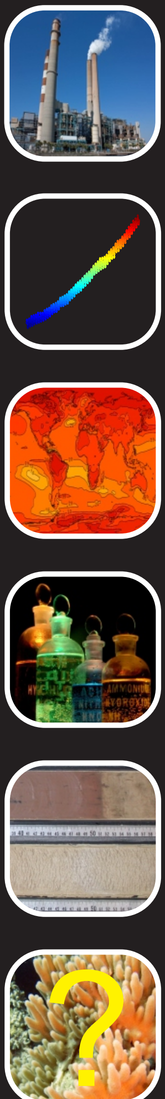
More similar cation chemistry

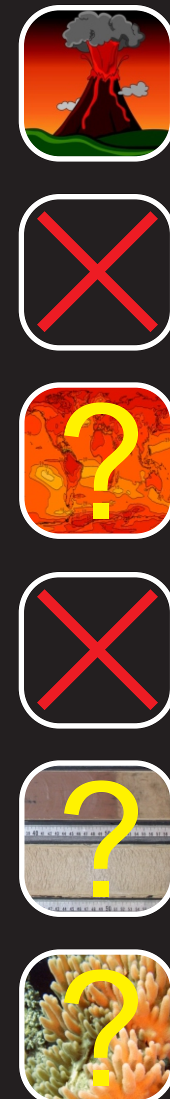


The paleo ocean acidification app store

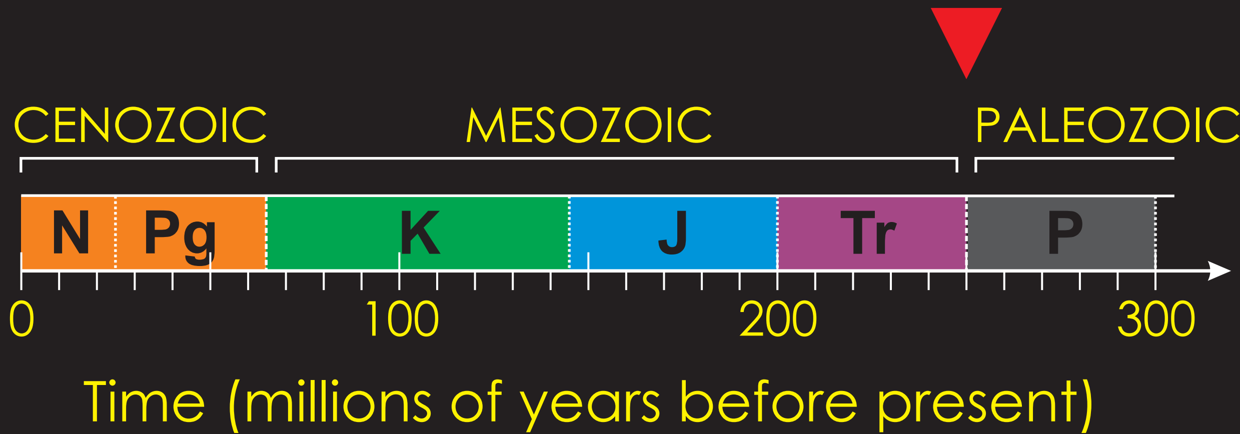
?

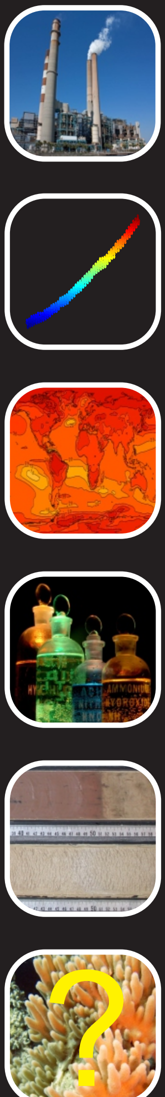


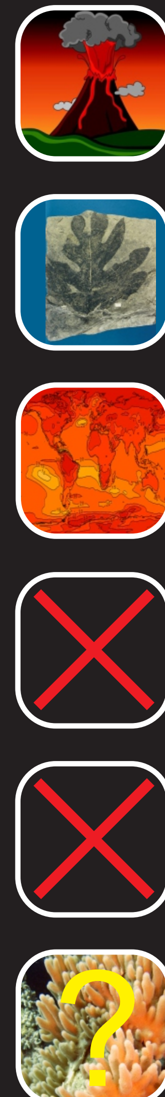


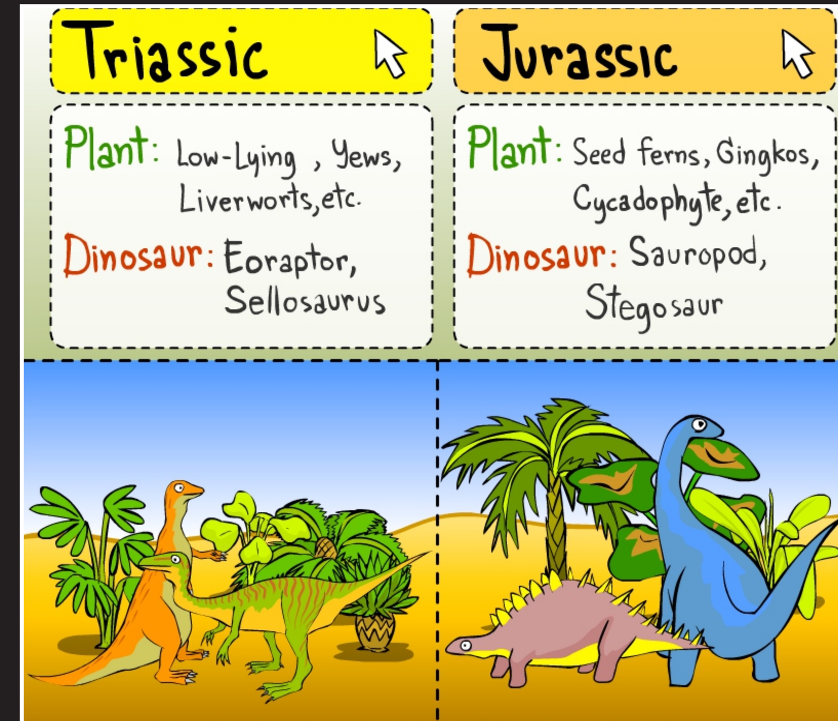


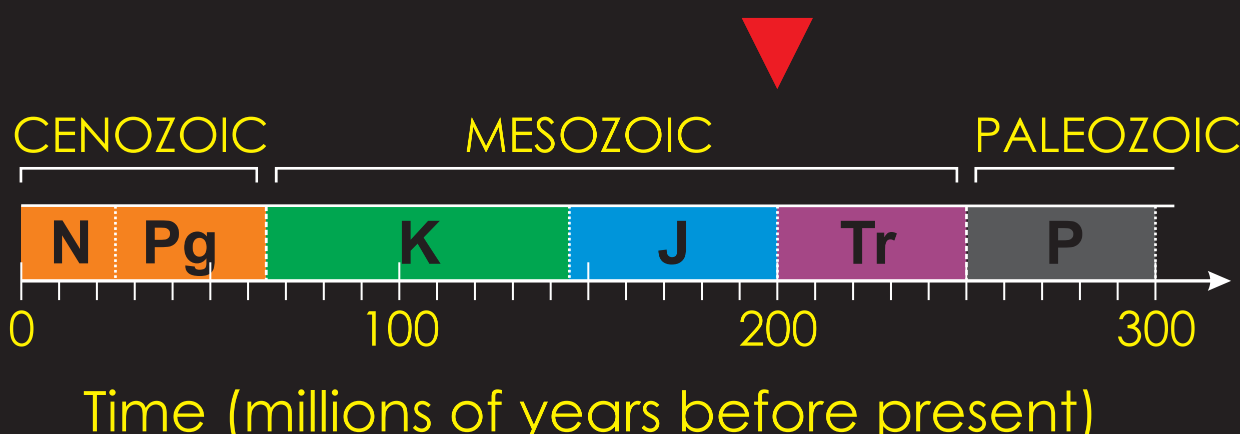

SCIENCEPHOTOLIBRARY


CENOZOIC
MESOZOIC
PALEOZOIC
N
Pg
K
J
Tr
P
0
100
200
300
Time (millions of years before present)

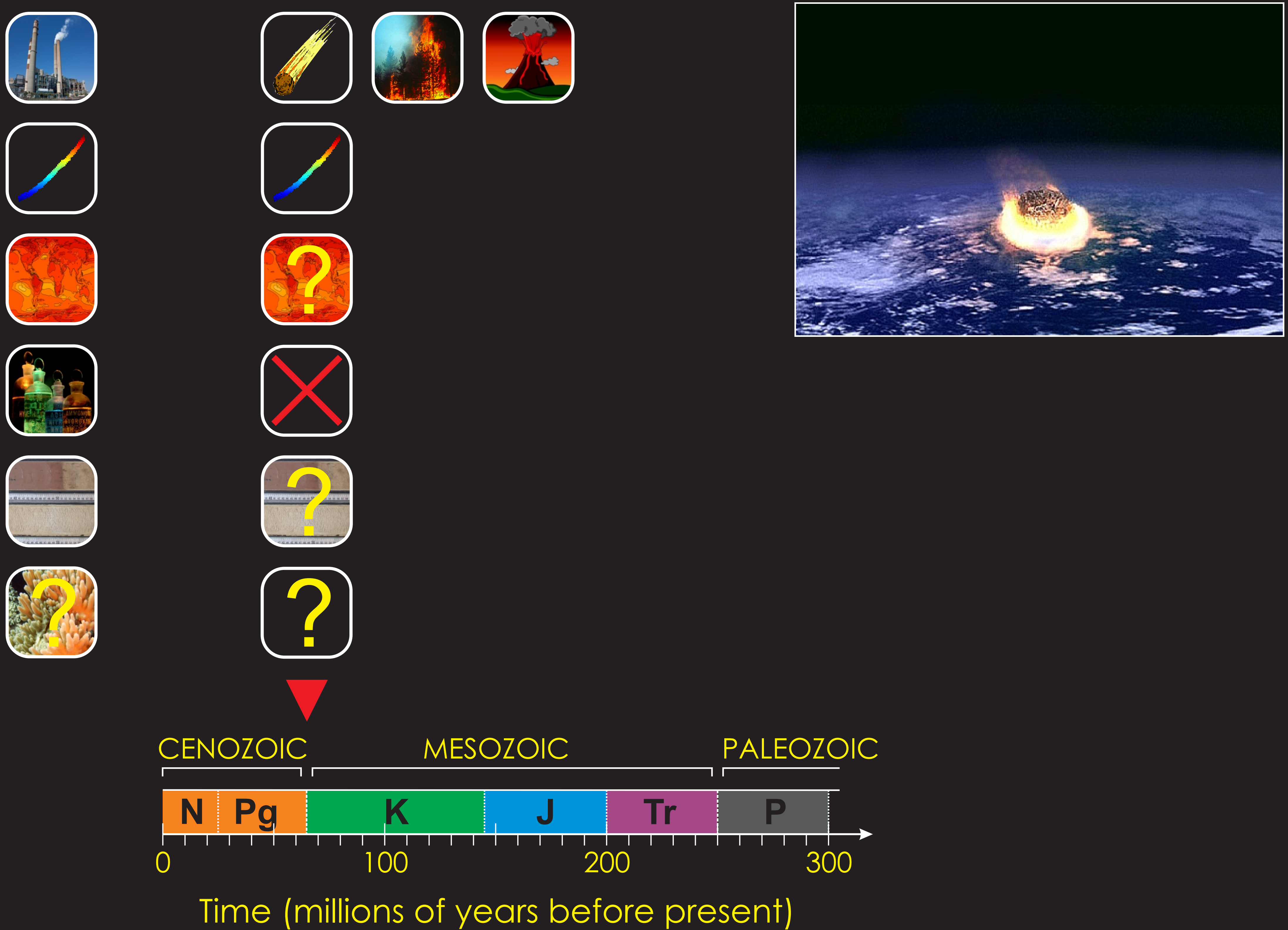


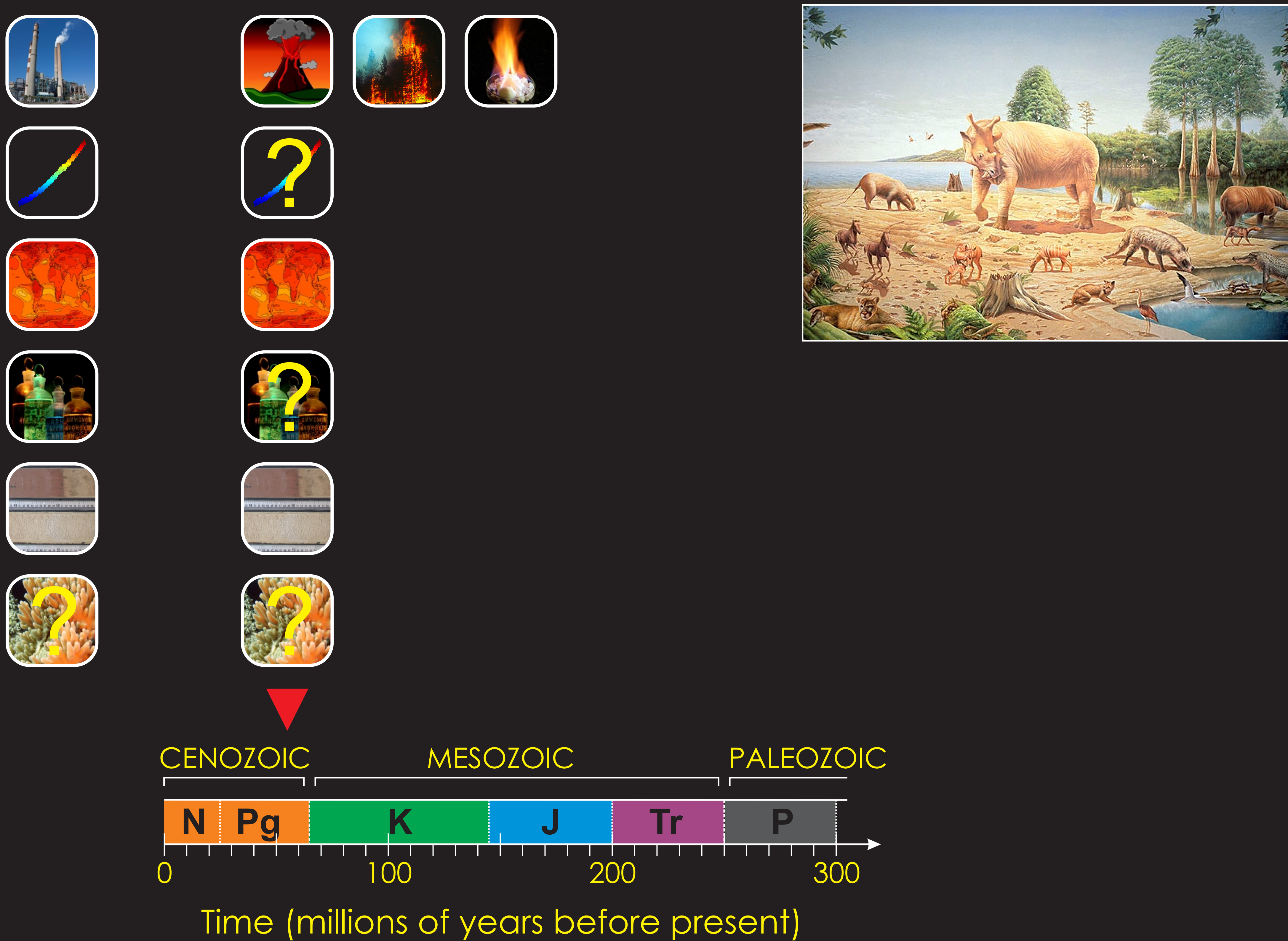



Triassic
Plant: Low-Lying , Yews, Liverworts, etc.
Dinosaur: Eoraptor, Sellosaurus
Jurassic
Plant: Seed ferns, Gingkos, Cycadophyte, etc.
Dinosaur: Sauropod, Stegosaur

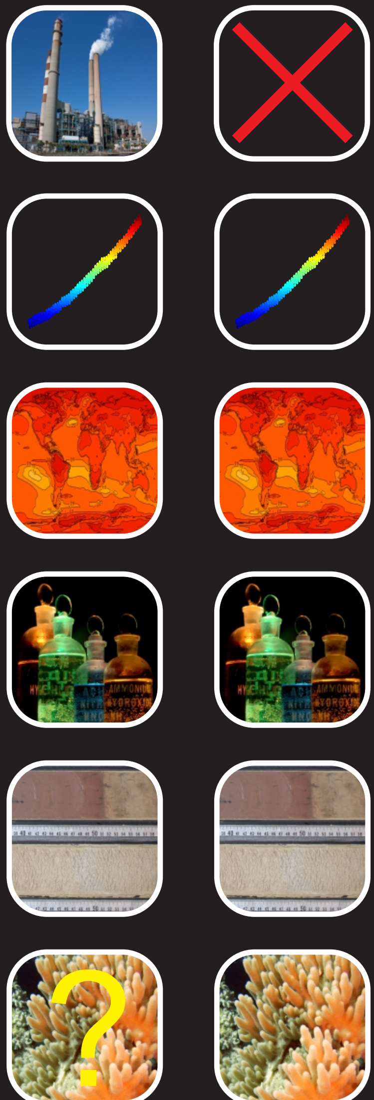

CENOZOIC
MESOZOIC
PALEOZOIC
N
Pg
K
J
Tr
P
0
100
200
300
Time (millions of years before present)

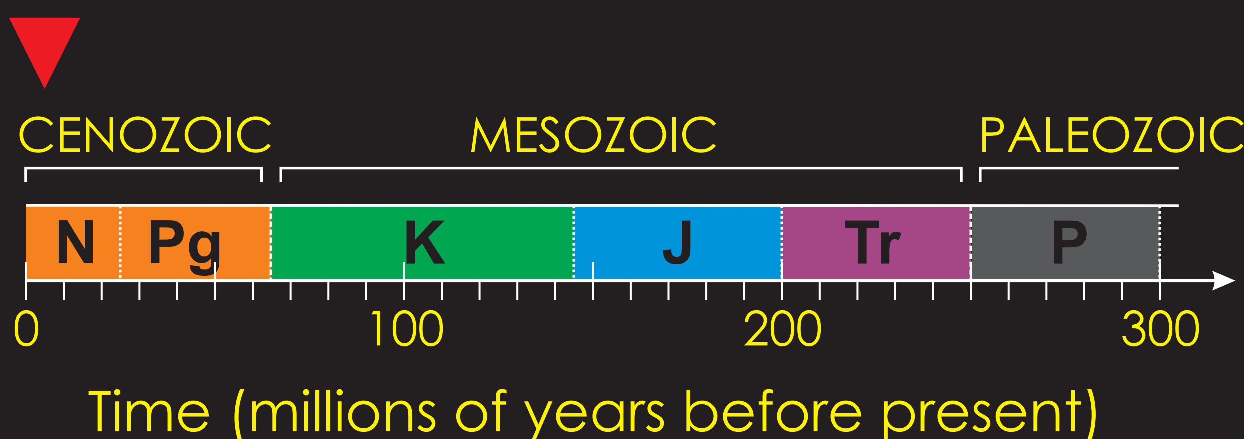

CENOZOIC
MESOZOIC
PALEOZOIC
N
Pg
K
J
Tr
P
0
100
200
300
Time (millions of years before present)


CENOZOIC
MESOZOIC
PALEOZOIC
N
Pg
K
J
Tr
P
0
100
200
300
Time (millions of years before present)



CENOZOIC
MESOZOIC
PALEOZOIC
N
Pg
K
J
Tr
P
0
100
200
300
Time (millions of years before present)




CENOZOIC
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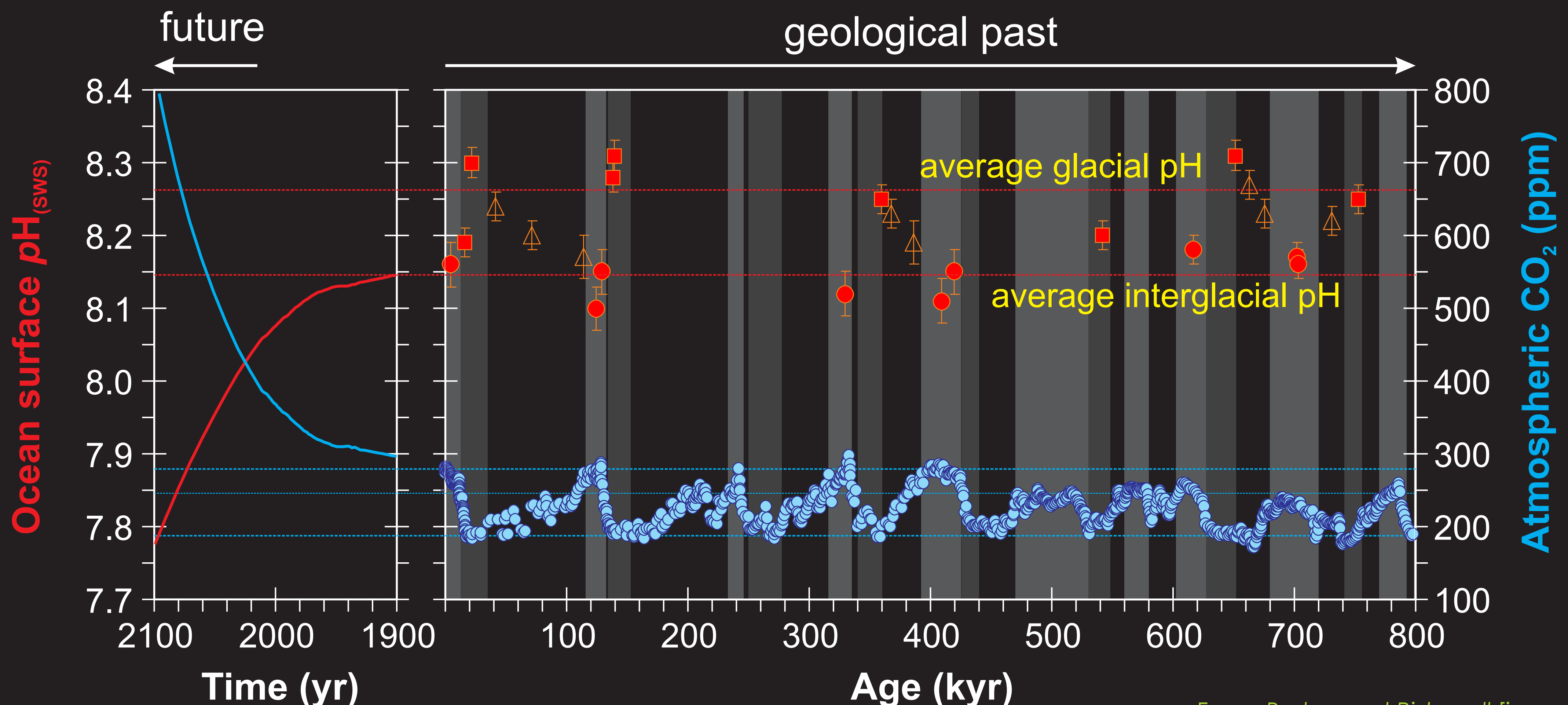
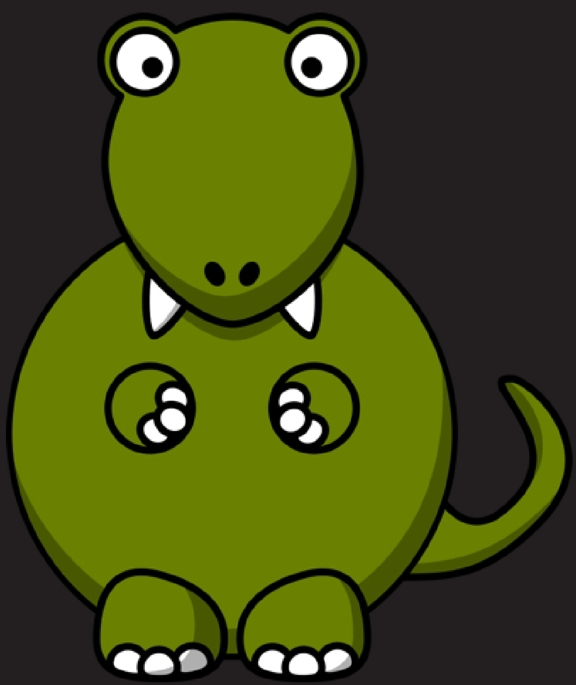
Time (millions of years before present)



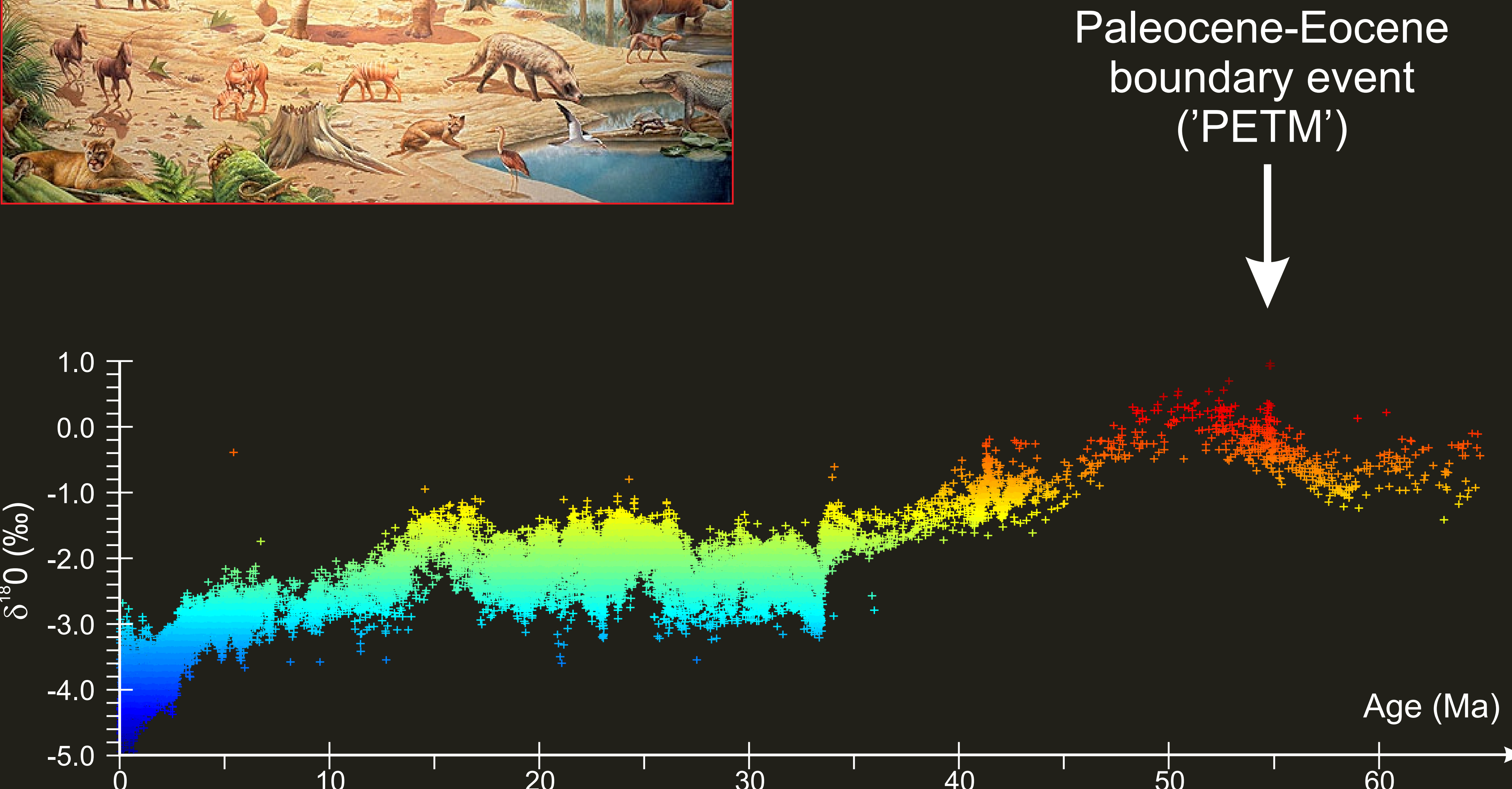
From: *Barker and Ridgwell* [in press]

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



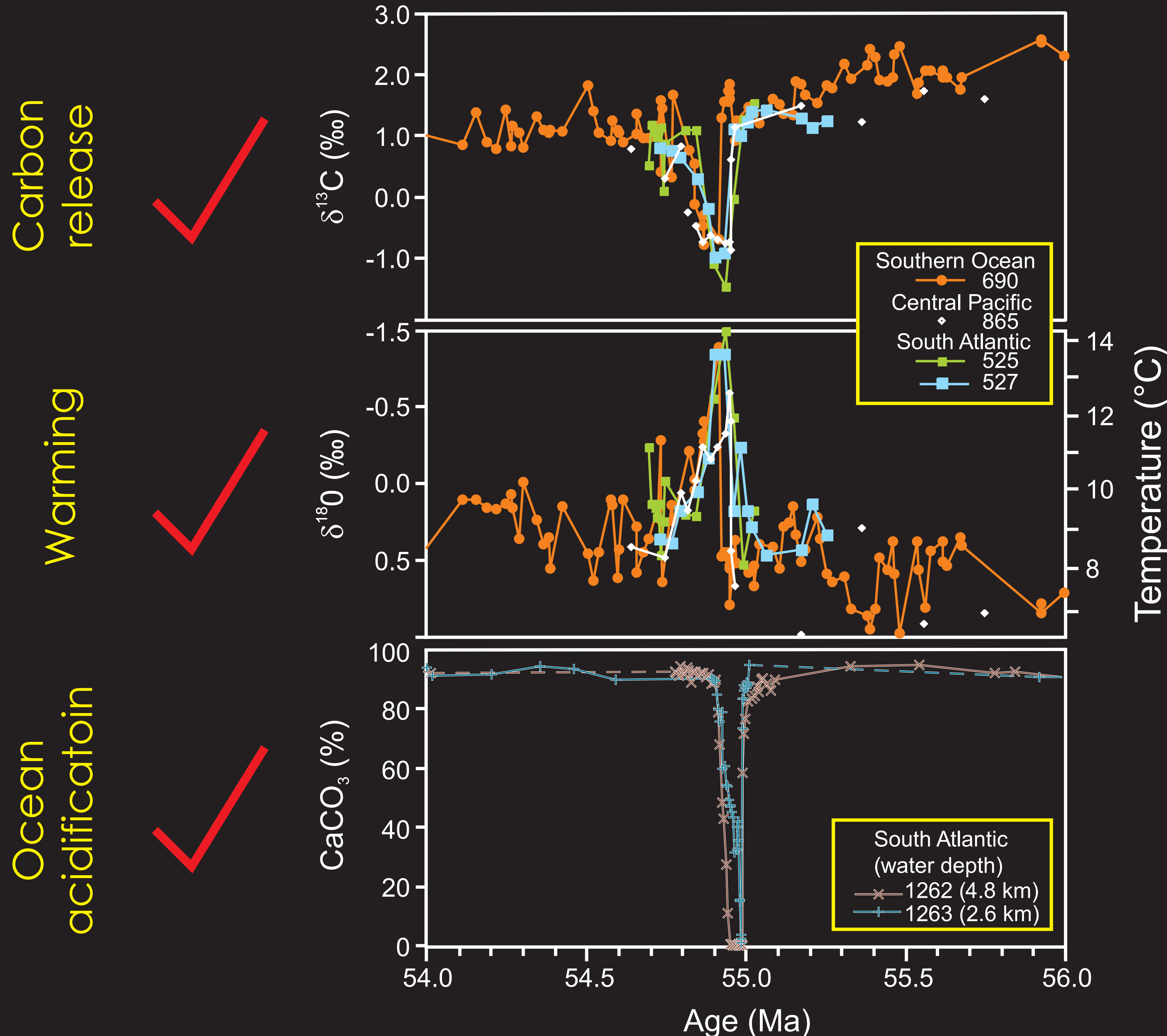
THE ROYAL SOCIETY
CELEBRATING 350 YEARS

University of BRISTOL



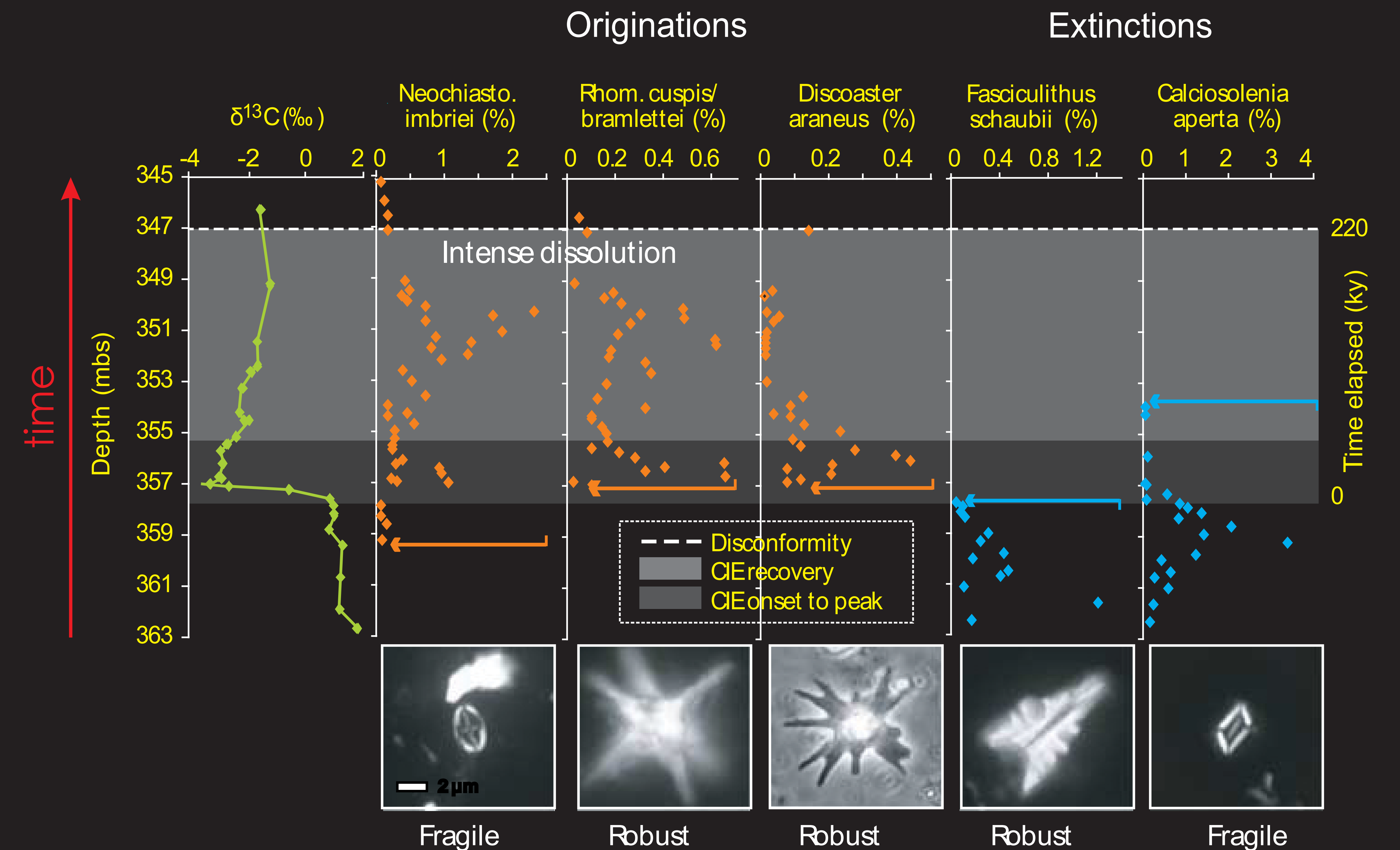
Paleocene-Eocene
boundary event
('PETM')
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
δ18O (‰)
Age (Ma)
0
10
20
30
40
50
60

PETM

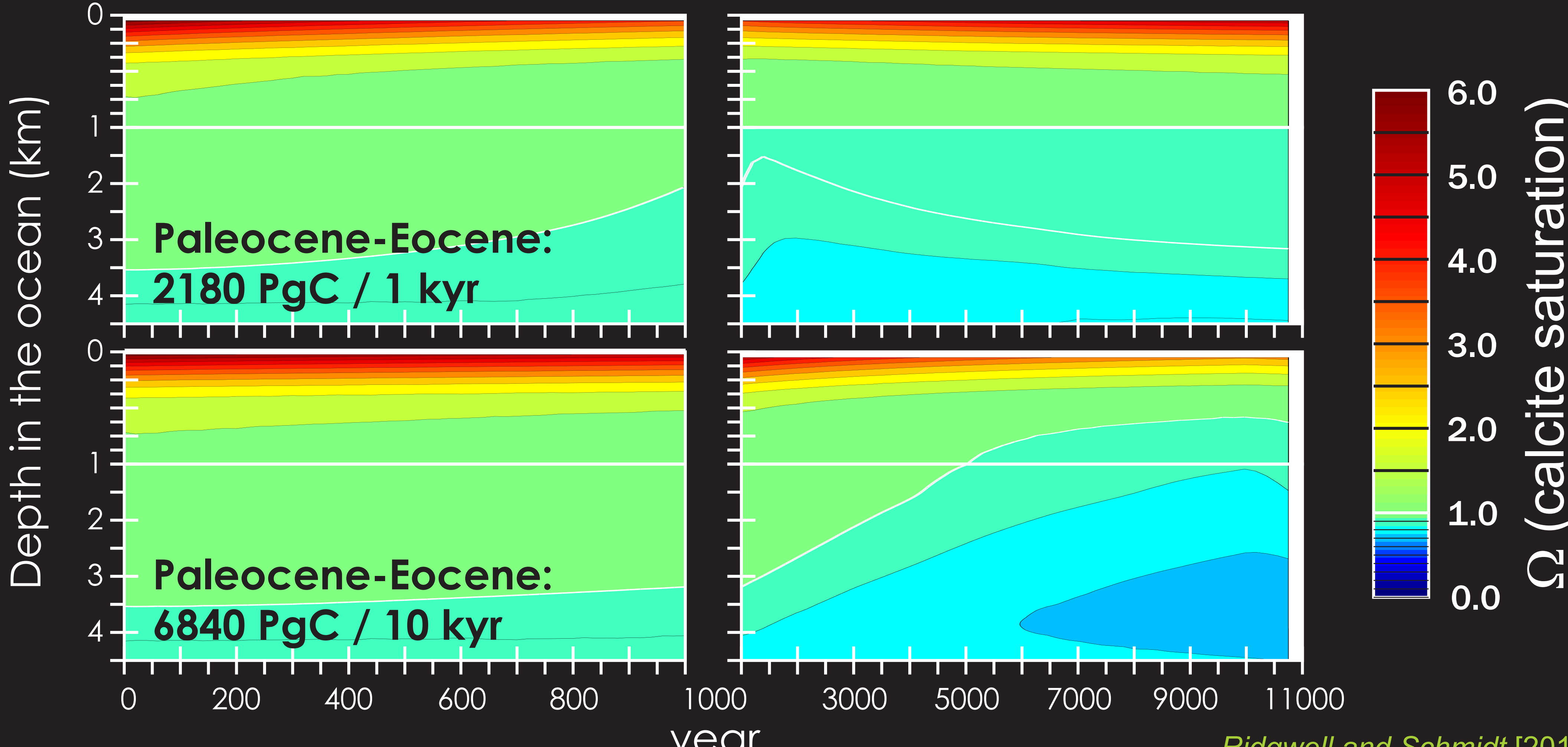


Zachos et al. [2008] (Nature 451)

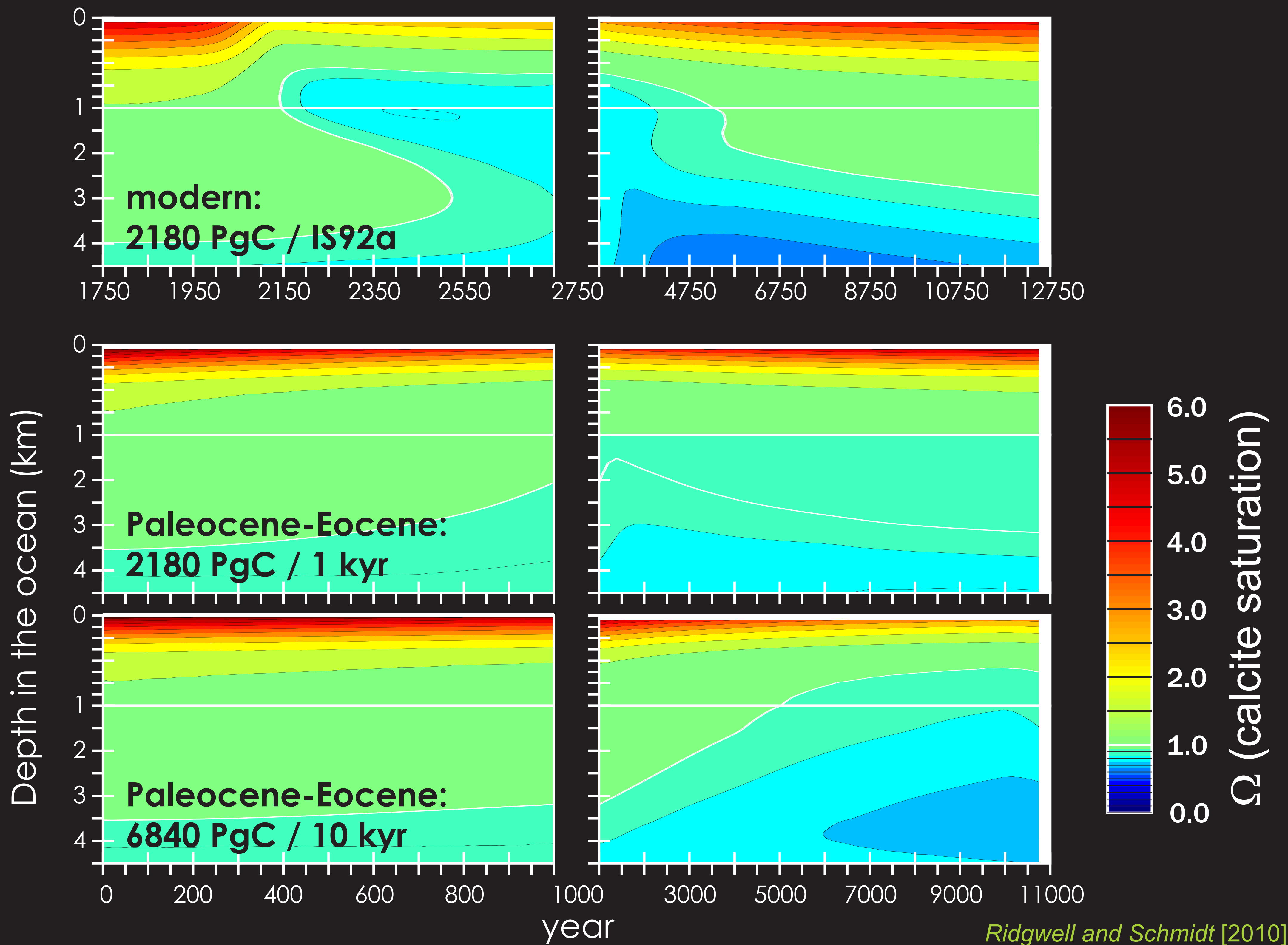
PETM



Gibbs et al. [2006] (Science)

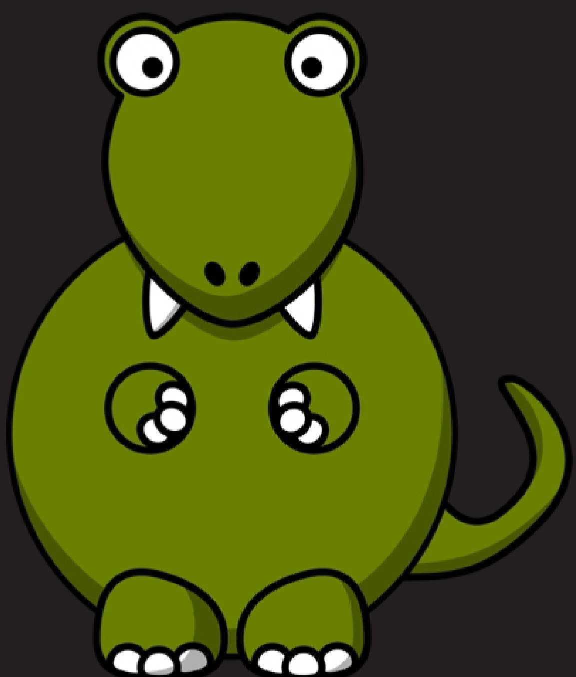


Ridgwell and Schmidt [2010]



modern:
2180 PgC / IS92a
Paleocene-Eocene:
2180 PgC / 1 kyr
Paleocene-Eocene:
6840 PgC / 10 kyr
Depth in the ocean (km)
0
1
2
3
4
1750
1950
2150
2350
2550
2750
4750
6750
8750
10750
12750
0
200
400
600
800
1000
3000
5000
7000
9000
11000
year
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Ω (calcite saturation)
Ridgwell and Schmidt [2010]

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



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