# The Geological Record of Ocean Acidification

Andy Ridgwell










THE ROYAL SOCIETY
CELEBRATING 350 YEARS

University of BRISTOL

**The Geological Record of Ocean Acidification**
Bärbel Hönisch, et al.
Science **335**, 1058 (2012);
DOI: 10.1126/science.1208277

Mail Online

# 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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How can anyone believe any thing these proven Liers have to say..just look at globle warming not one shread of Real proof that people have any thing to do with it..and now this...
If they want to keep there jobs that badly ,Do some real work...before starting to make up scare stores

*green_hackle, LONDON/ENGLAND, 03/3/2012 12:41*

Alarmist garbage.
This is all just guesses made from tiny samples of imperfect information by people who are looking for the answer they want to find.
None of them have any real evidence for what happened 300 years ago, never mind 300 million. It's 2+2=5 at its finest. They also always fail to mention that the causes of mass extinctions in prehistory are only theoretical, and that those extinctions took place over millions of years.
Any sense of any kind of impending disaster is just Hollywood hyperbole and fundraising. Even if any of what they say is true, there won't be any serious impact for the human race for millions of years, and there will be plenty of engineering and technological solutions before then.

*dave, Dystopia, UK, 1/3/2012 23:54*

More dodgy science, all the records show that CO2 levels in the Atmosphere follow temperature not the other way round, CO2 is only soluble in water at lower temperatures so as the temperature rises more is released to the air. To prove it to yourself take some cold fizzy drink from the fridge and pour it into a mug, heat a spoon in hot water and put it in the mug. You will see bubbles of Carbon dioxide released as the spoon heats the liquid. That is why we all like cold soft drinks and beer they do not go flat as quickly. So the myth of more temperature causing acidification cannot happen because there would be less CO2 in the ocean not more.

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

# *The Geological Record of Ocean Acidification*

# The Geological Record of Ocean Acidification

```
! 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 Geological Record of Ocean Acidification*

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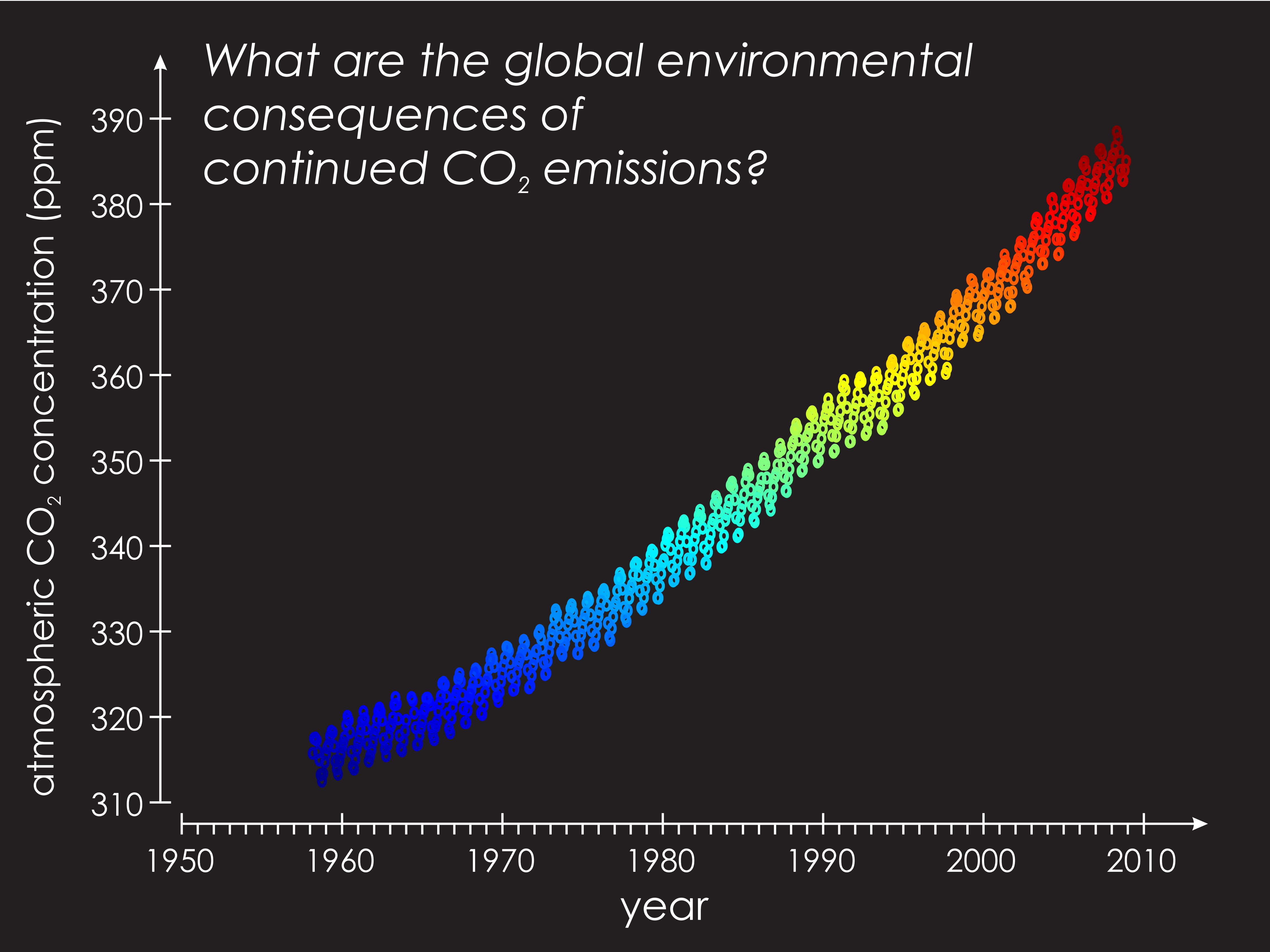
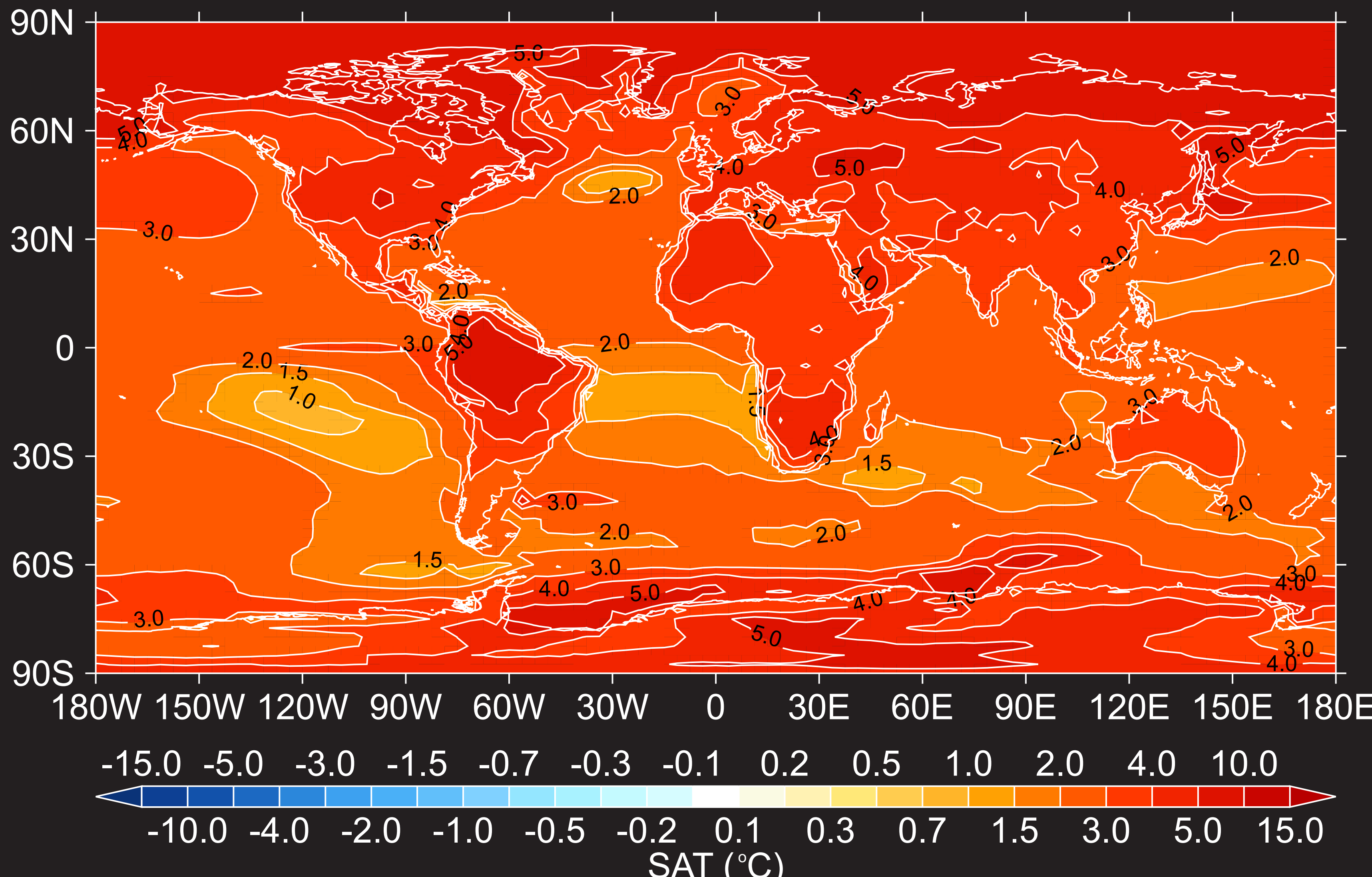
loc_H1 = dum_carbconst(icc_k1)*loc_conc_CO2/loc_conc_HCO3
loc_H2 = dum_carbconst(icc_k2)*loc_conc_HCO3/loc_conc_CO3
```

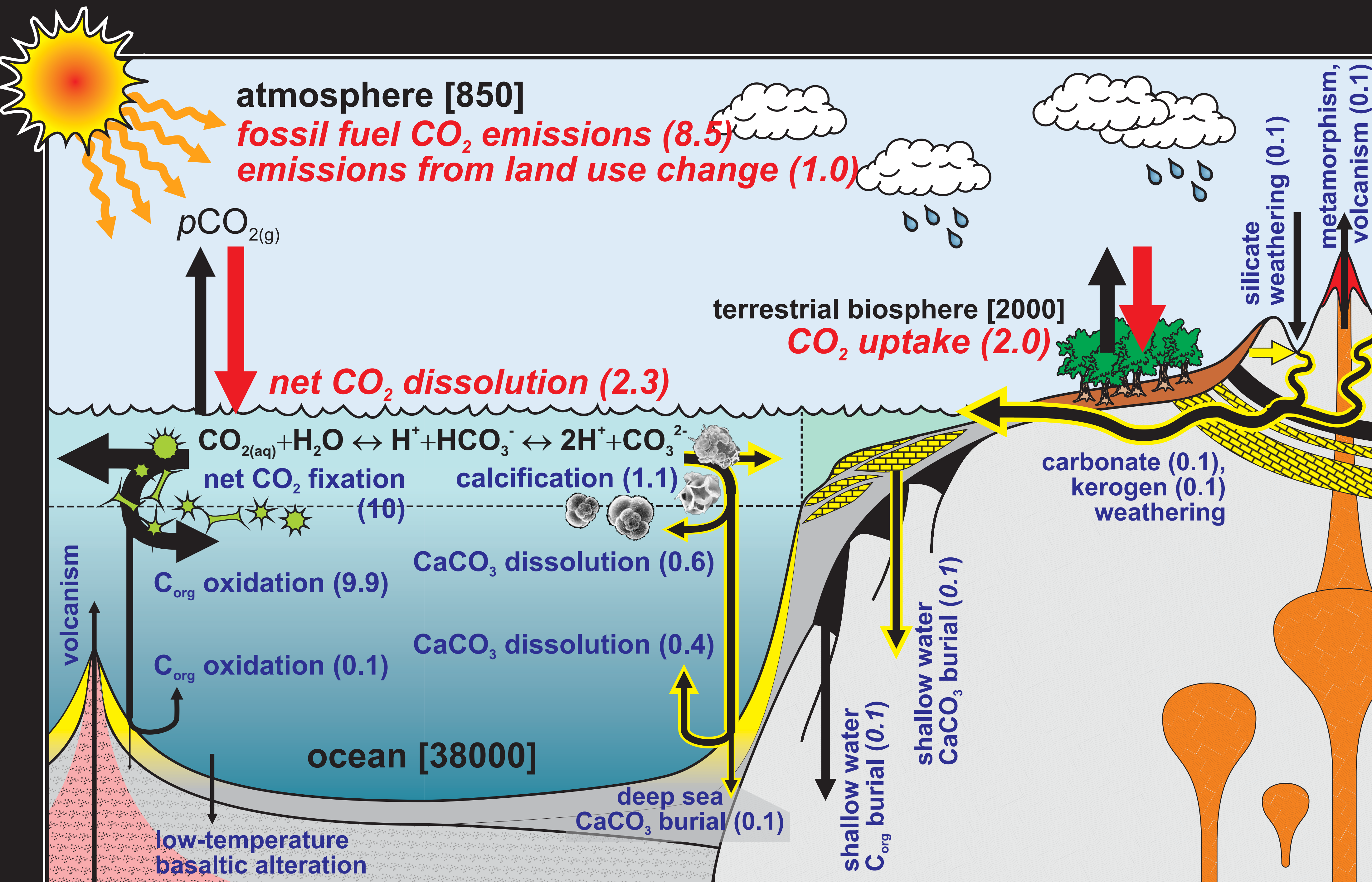



What are the global environmental consequences of continued $CO_2$ emissions?
atmospheric $CO_2$ concentration (ppm)
390
380
370
360
350
340
330
320
310
1950
1960
1970
1980
1990
2000
2010
year

# (projected) climatic consequences

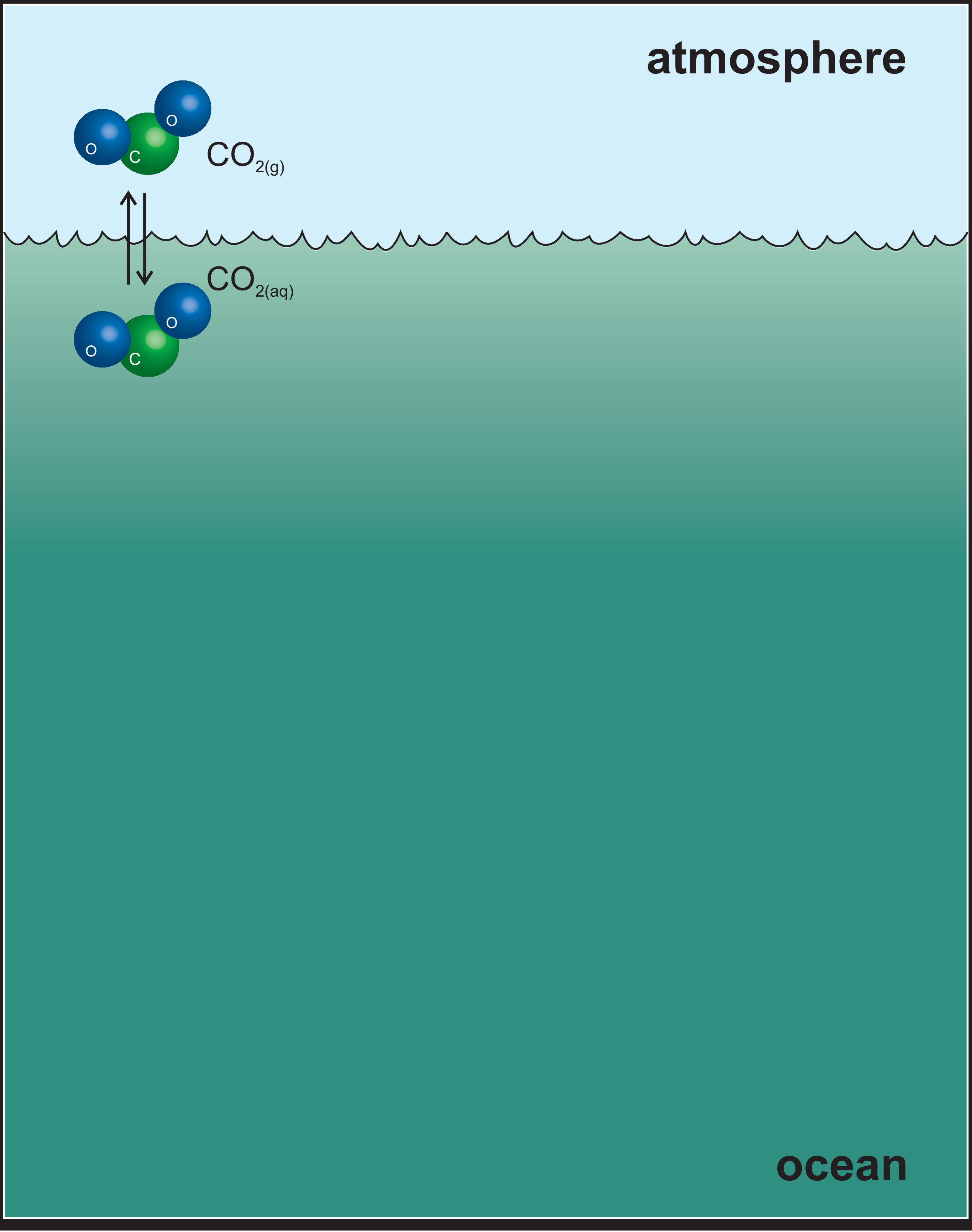


# Ocean chemical consequences



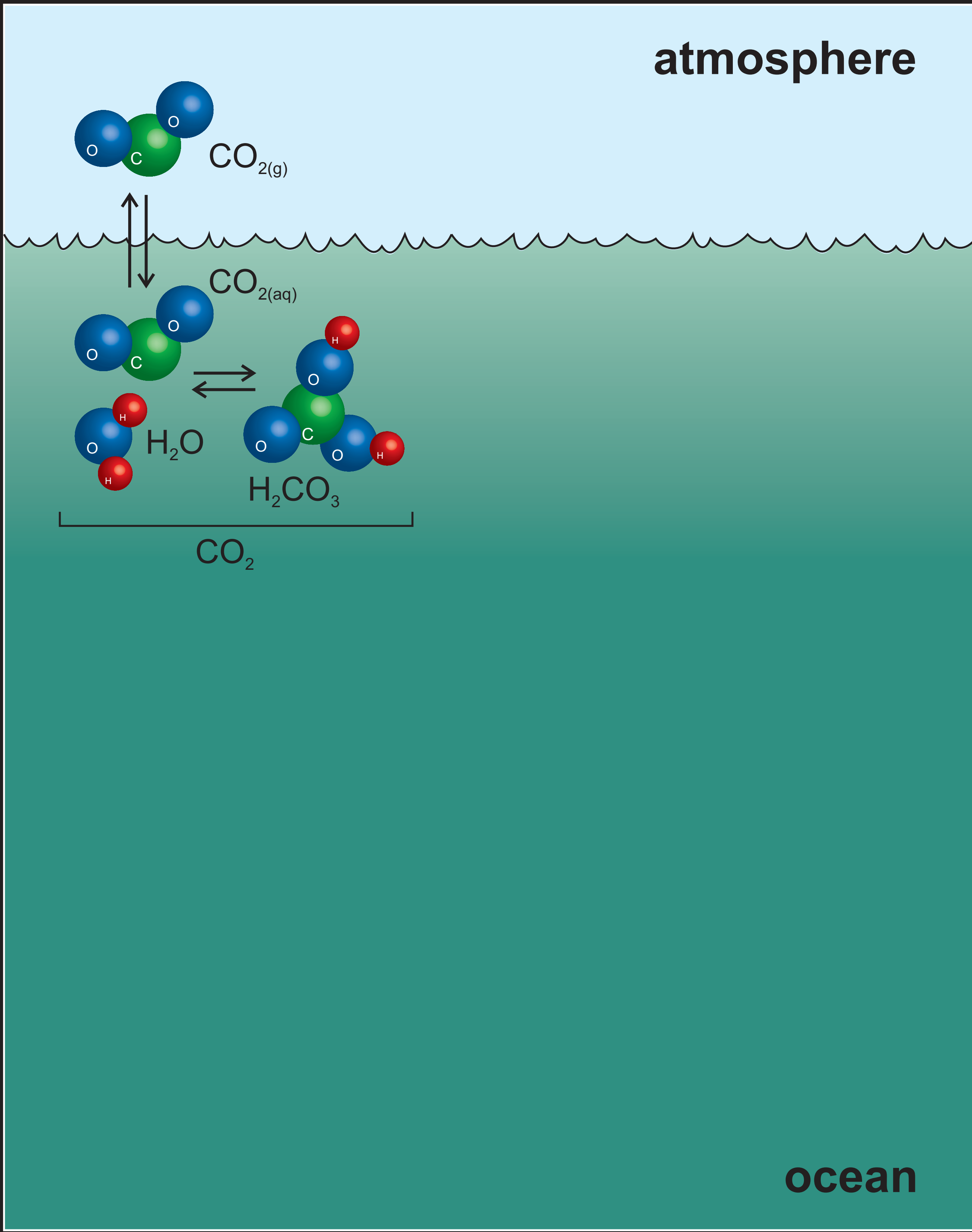
AMMONIUM
HYDROXIDE
NH OH

# $CO_2$ chemistry in seawater




From: *Barker and Ridgwell* [in press]

# $CO_2$ chemistry in seawater




From: *Barker and Ridgwell* [in press]

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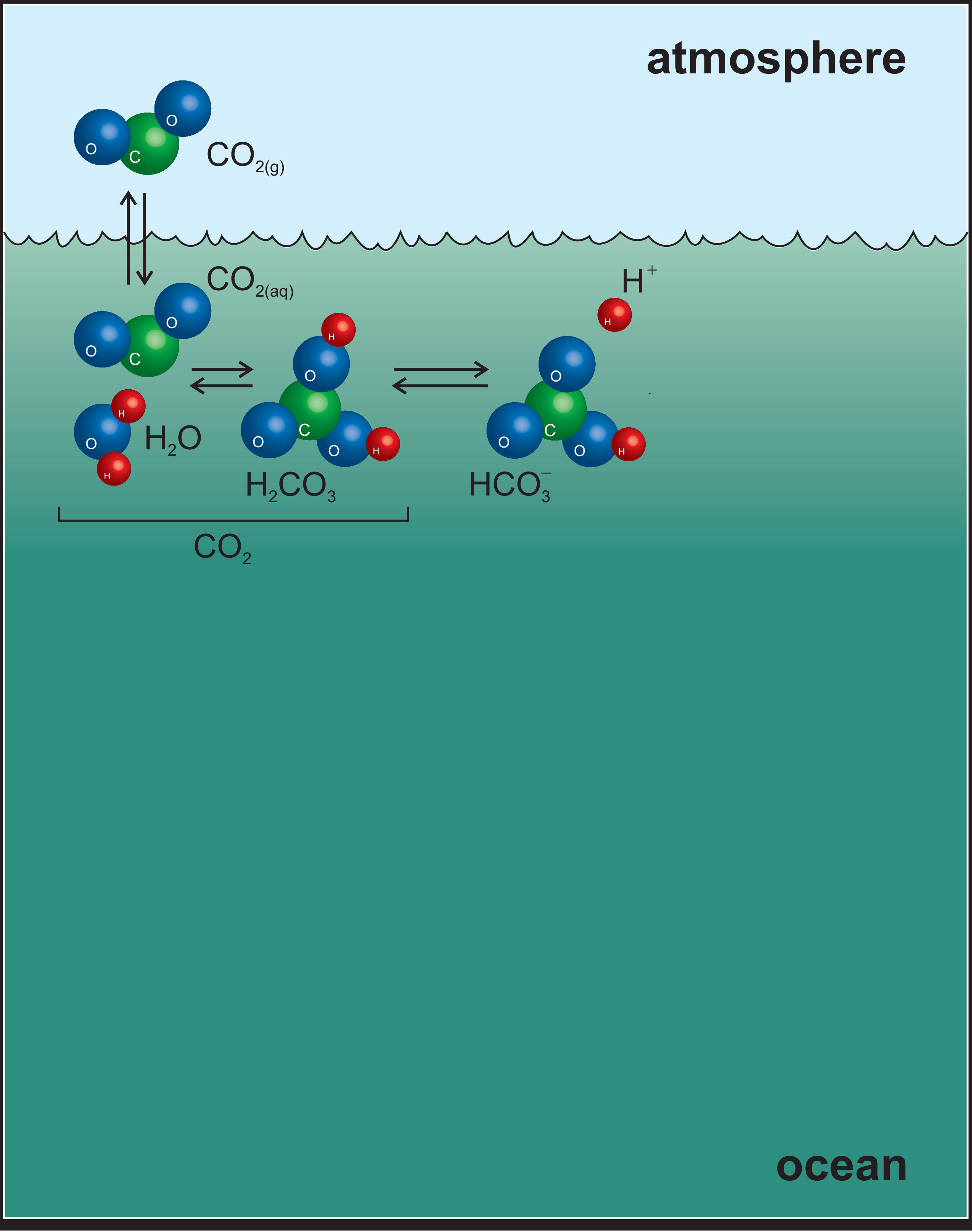


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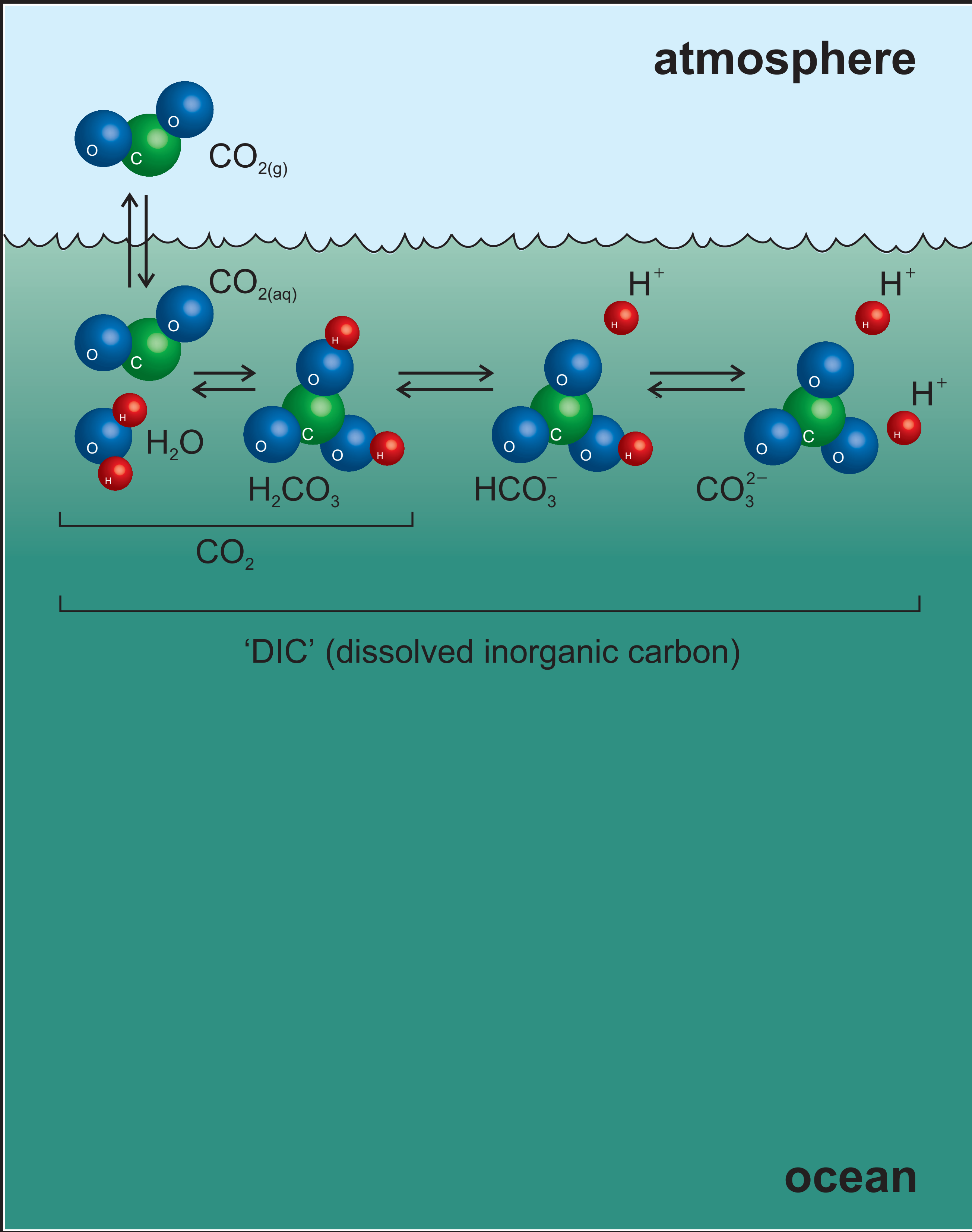


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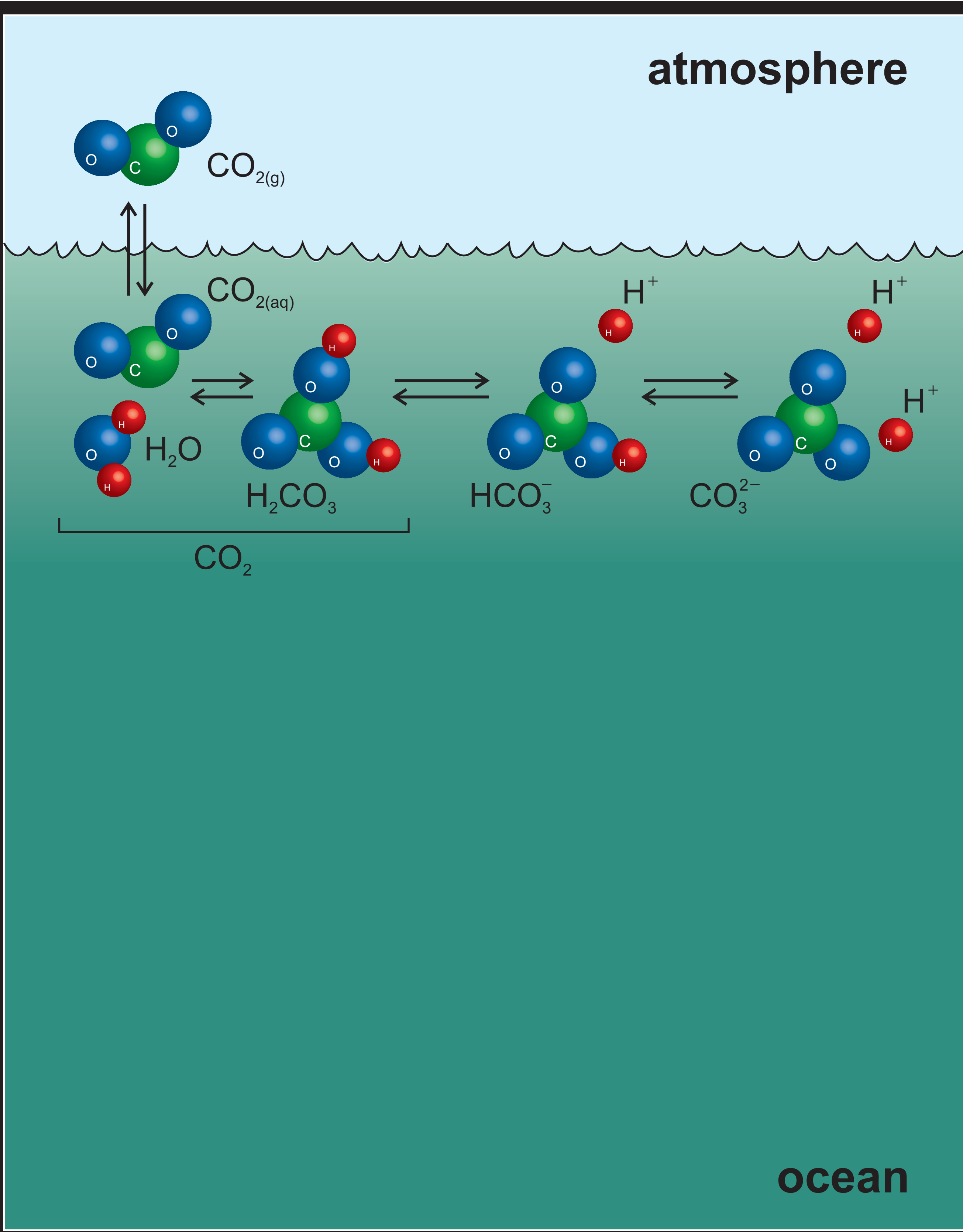



# $CO_2$ chemistry in seawater

When $CO_2$ dissolves in seawater, the $CO_{2(aq)}$ concentration changes only slightly because the system is buffer by carbonate ions: $CO_3^{2-}$

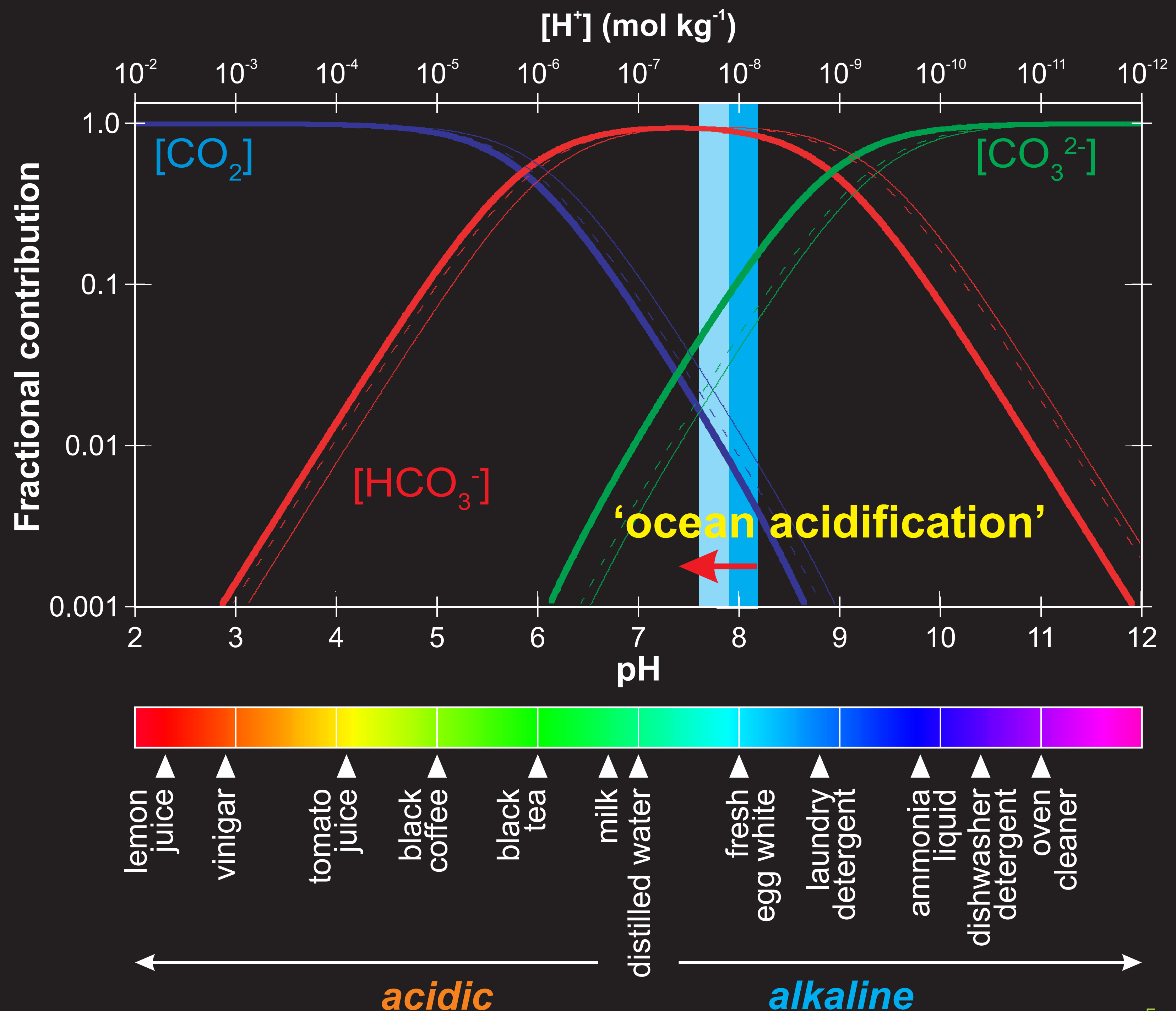
$CO_2$ is scavenged according to the reaction:

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

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.

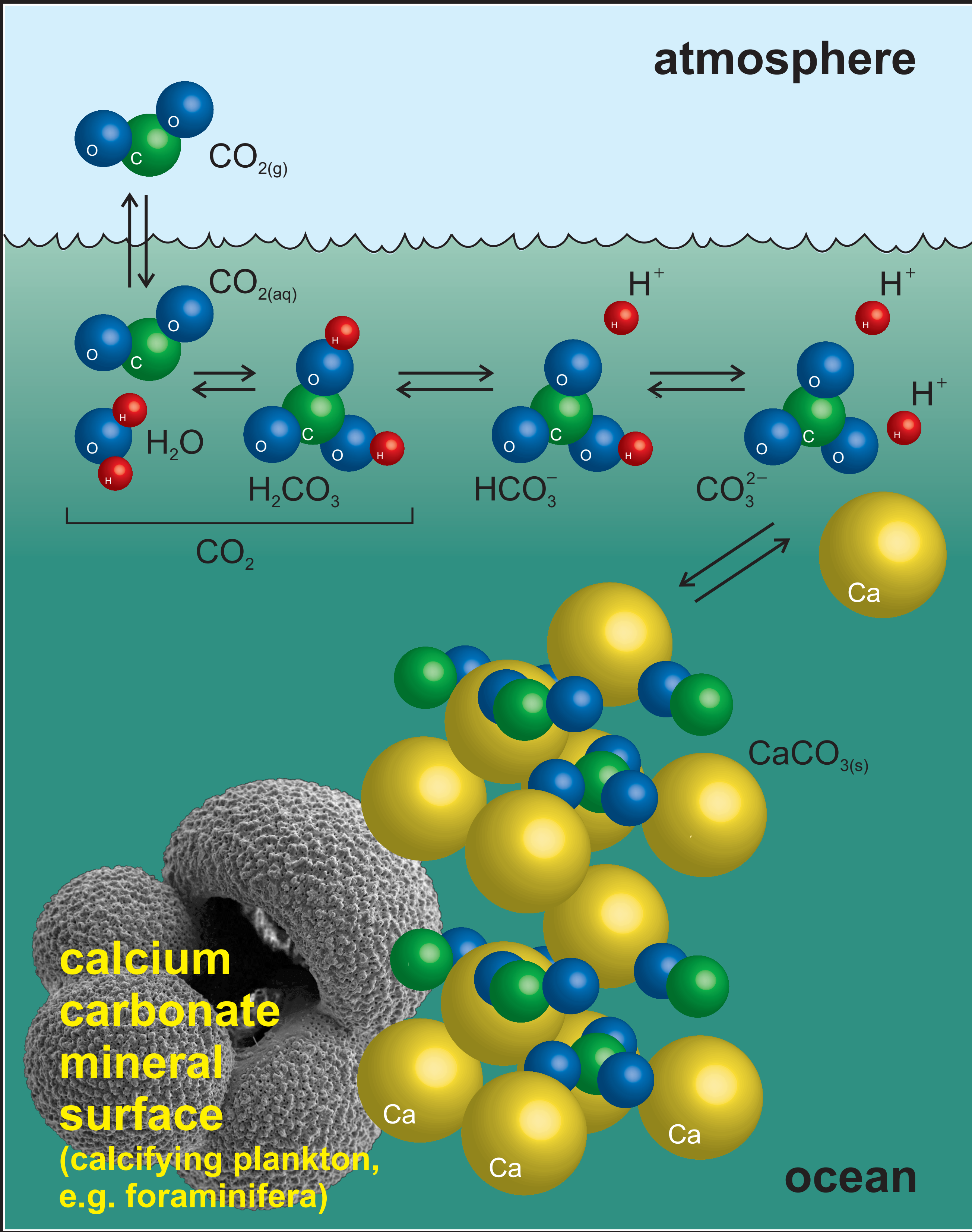
From: *Barker and Ridgwell* [in press]

# The nature of pH (and acidity vs. alkalinity)

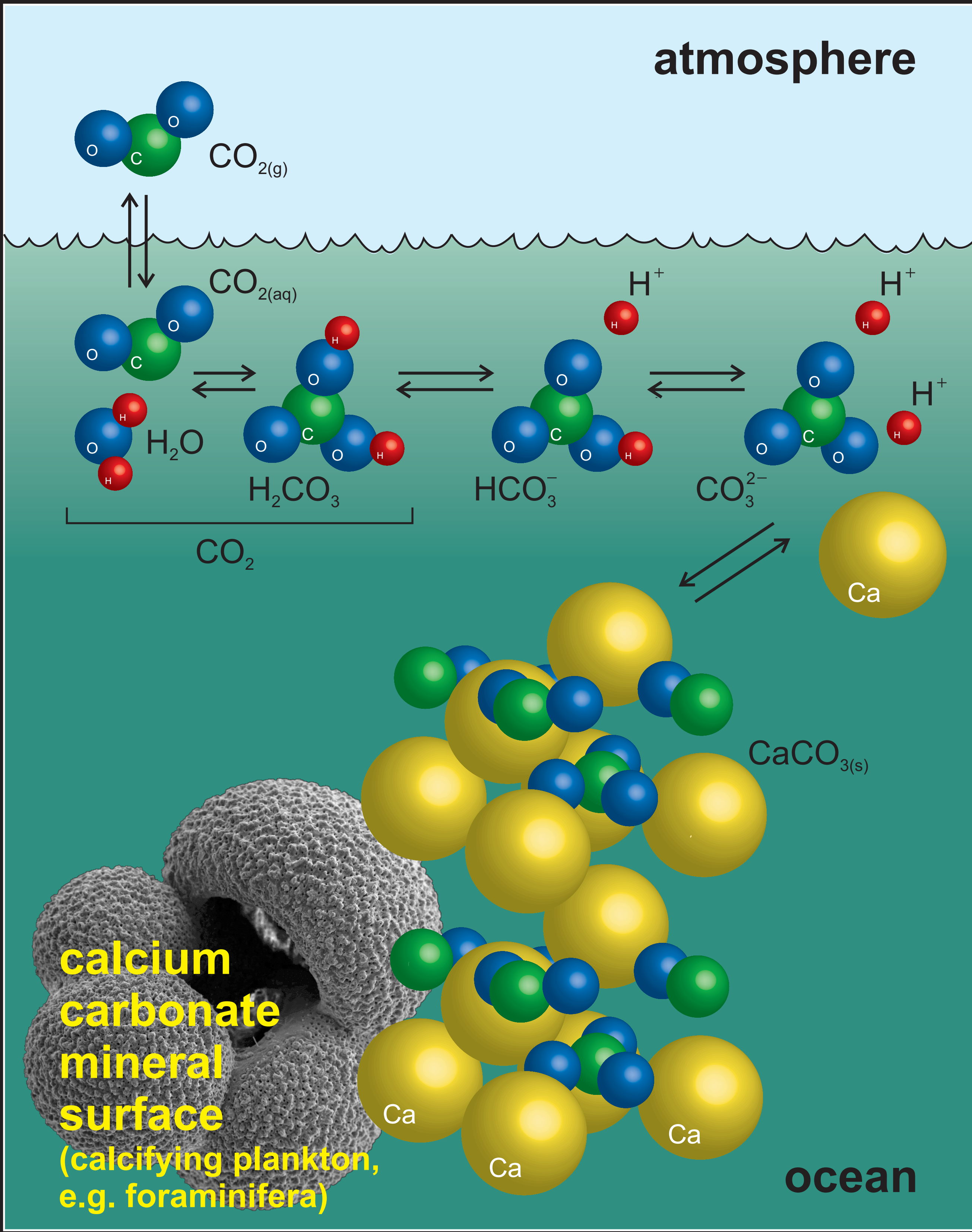



From: *Barker and Ridgwell* [in press]

# $CO_2$ chemistry & mineral phases



# $CO_2$ chemistry & mineral phases

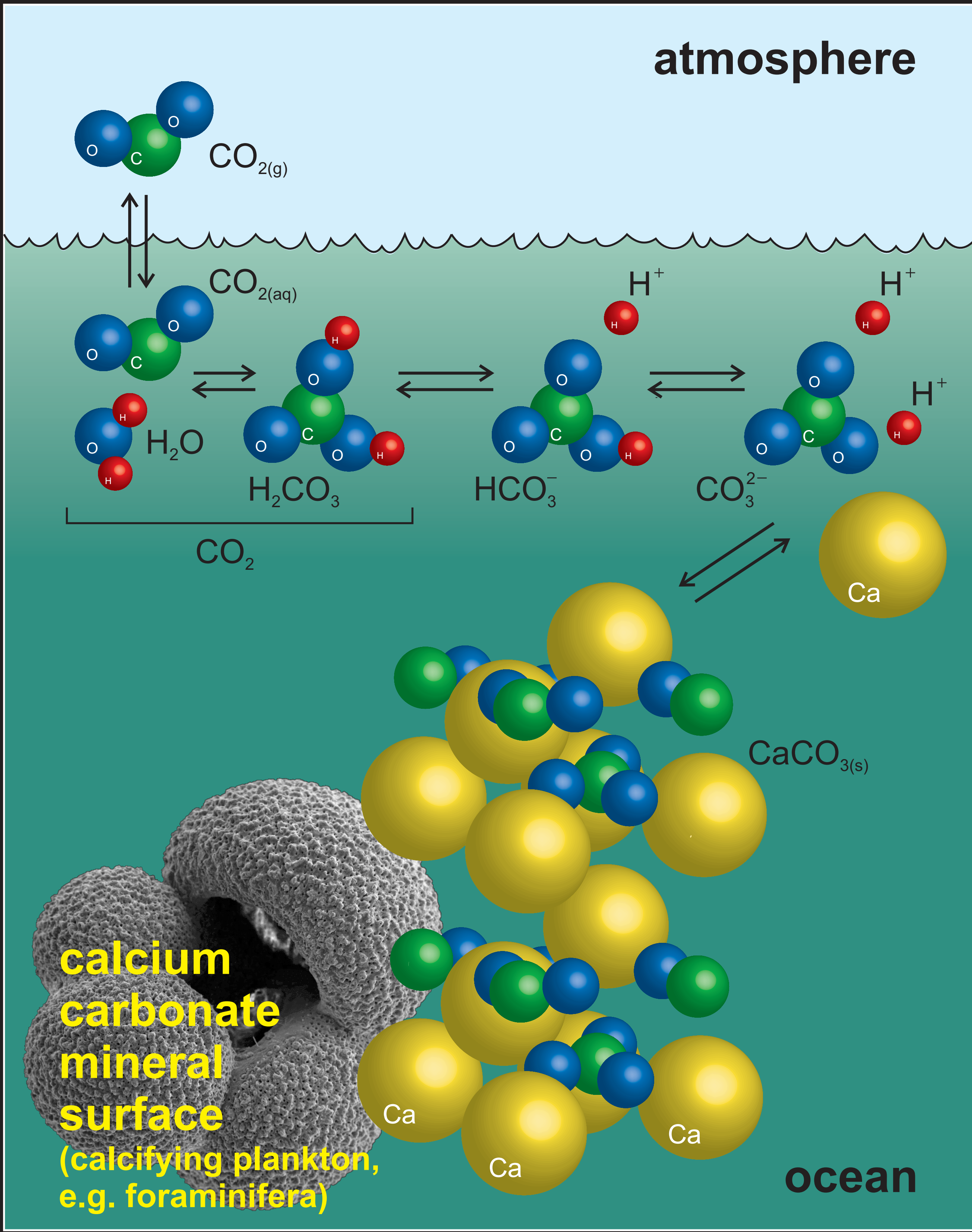



**Aragonite: less stable**

orthorhombic polymorph (e.g., many corals, pteropods)

**Calcite: more stable**

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

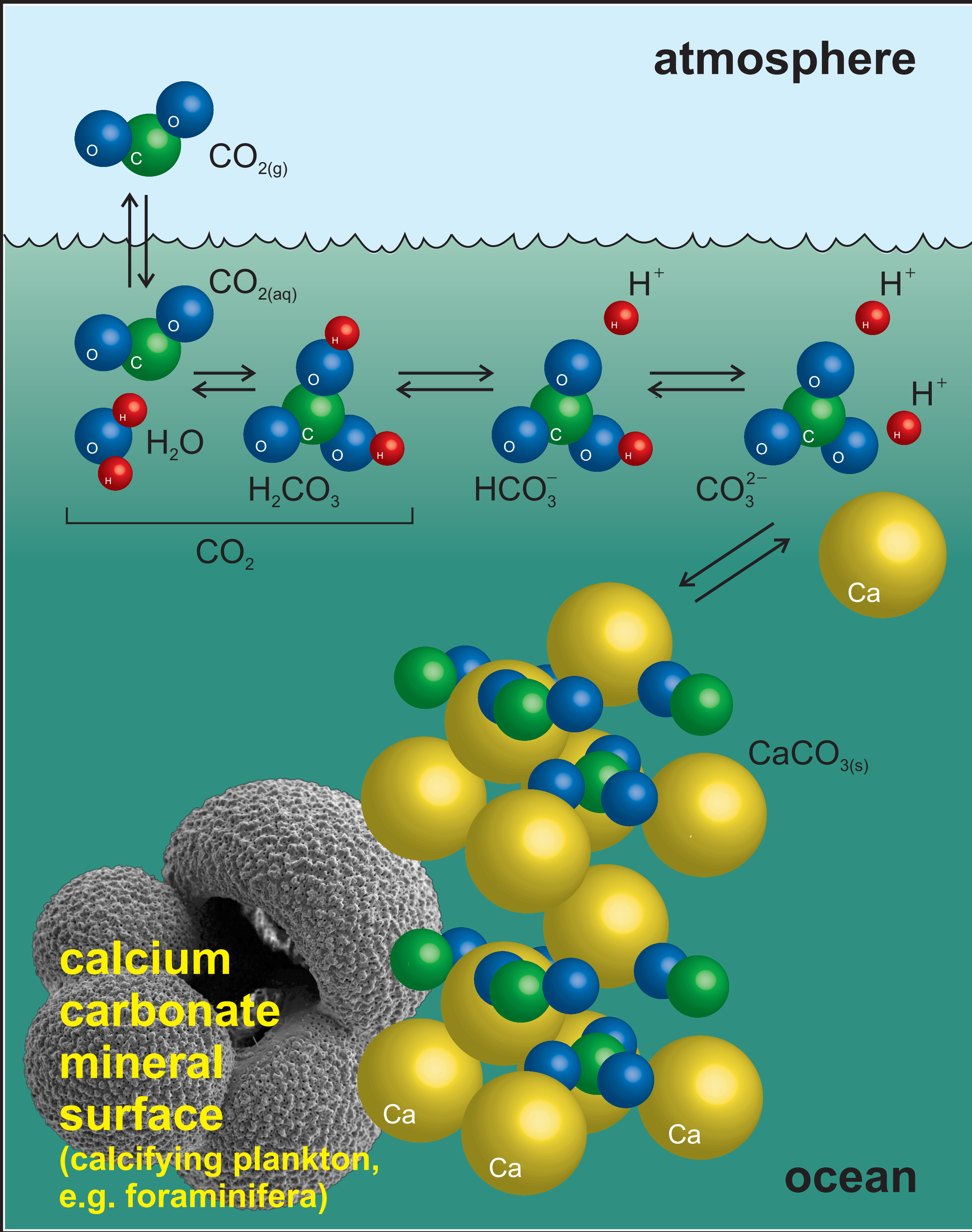



# $CO_2$ chemistry & mineral phases

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*:

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

⇒ 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)

→

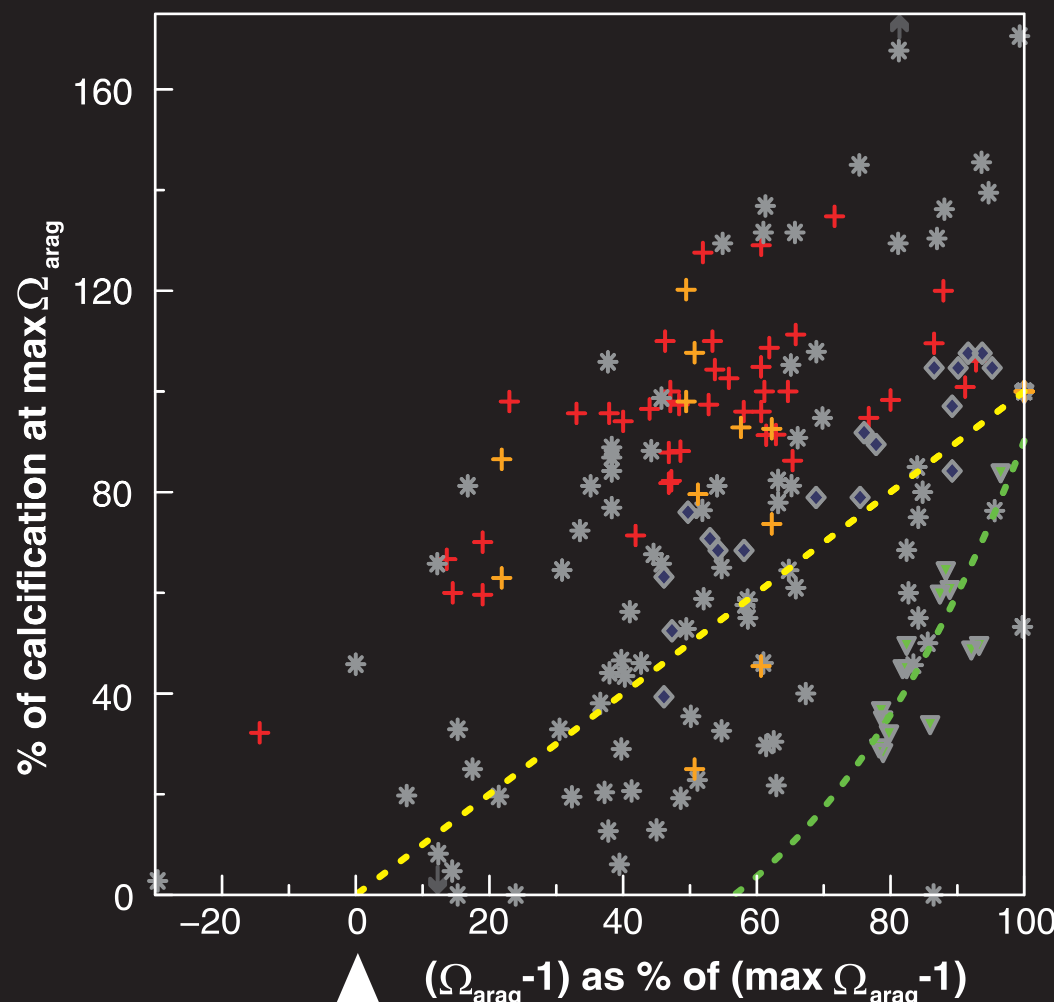
lower saturation (Ω) & less stable $CaCO_3$

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

# *Ocean biological consequences(?)*

decreasing pH, saturation

decreasing calcification rates
(% compared to Preindustrial conditions)



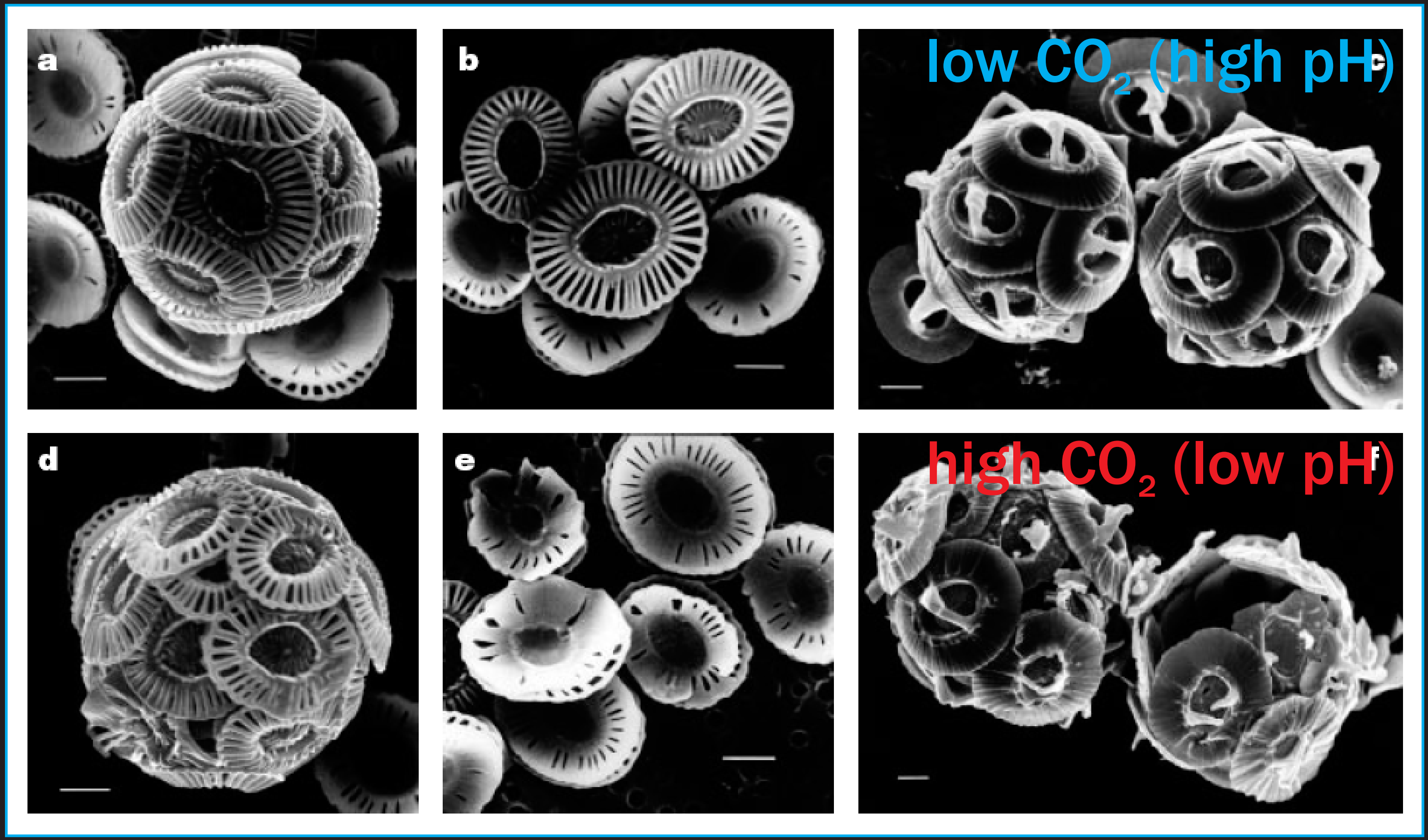

*under-saturated*

$\Omega$ = 1.0

*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)

# Calcification responses ($CaCO_3$ per cell per day) at elevated (~ ×2 to ×3) $CO_2$

| Species | Strain | Year location | Exp. design | Manipulation | | Reference |
|---|---|---|---|---|---|---|
| Emiliania huxleyi | PML B92/11A | 1992 North Sea | laboratory culture | acid/base | ↓ | Riebesell et al. [2000] Zondervan et al. [2001] |
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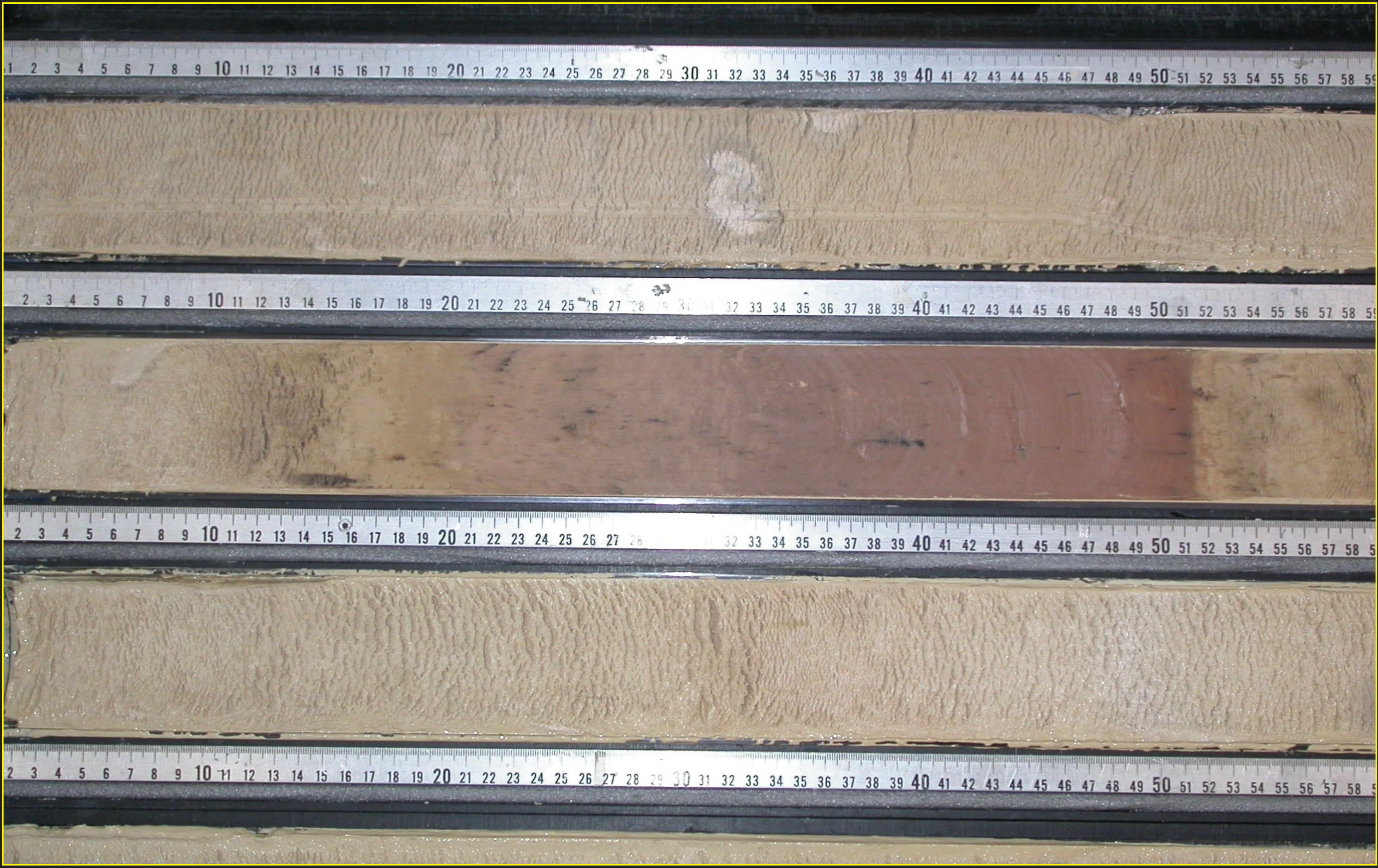
| Emiliania huxleyi | CAWPO6 | 1992 South Pacific | laboratory culture | $CO_2$ bubbling | ↑ | Iglesias-Rodriguez et al. [2008] |
| Emiliania huxleyi | MBA 61/12/4 | 1991 N. Atlantic | laboratory culture | $CO_2$ bubbling | ↑ | Iglesias-Rodriguez et al. [2008] (pers com) |
| Emiliania huxleyi | CCMP 371 | 1987 Sargasso Sea | laboratory culture | $CO_2$ bubbling | ↓ | Feng et al. [2008] |
| Emiliania huxleyi | CCMP 371 | 1987 Sargasso Sea | laboratory culture | $CO_2$ bubbling | ↓ | Feng et al. [2008] |
| Emiliania huxleyi | TW1 | 2001 W. Mediterranean | laboratory culture | $CO_2$ bubbling | ↓ | Sciandra et al. [2003] |
| Emiliania huxleyi | Ch 24-90 | 1991 North Sea | laboratory culture | $CO_2$ bubbling | ↔ | Buitenhuis et al. [1999] |
| Emiliania huxleyi | CAWPO6 | 1992 South Pacific | laboratory culture | $CO_2$ bubbling | ↑ | Shi et al. [2009] |
| Gephyrocapsa oceanica | PC7/1 | 1998 Portuguese shelf | laboratory culture | acid/base | ↓ | Riebesell et al. [2000] Zondervan et al. [2001] |
| Calcidiscus leptoporus | AC365 | 2000 S. Atlantic | laboratory culture | acid/base | ↓↑ | Langer et al. [2006] |
| Coccolithus pelagicus | AC400 | 2000 S. Atlantic | laboratory culture | acid/base | ↔ | Langer et al. [2006] |

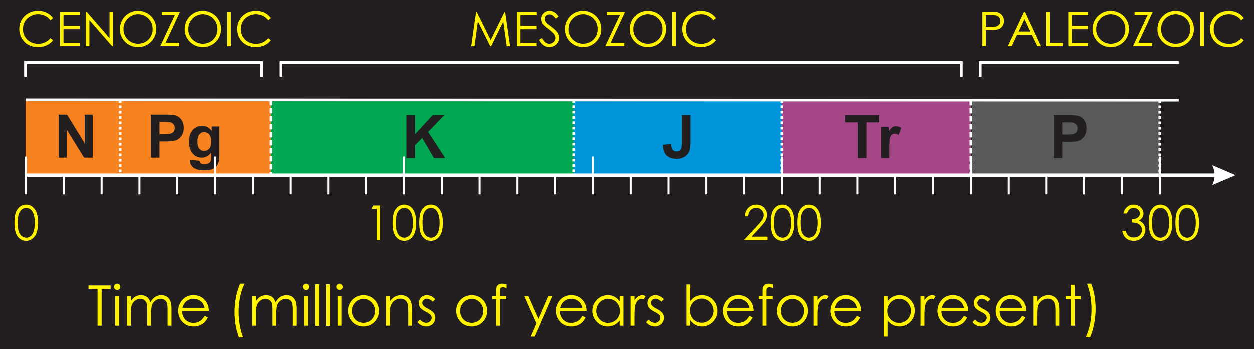
From: *Ridgwell et al.* [2009] (Biogeosciences)

# *The time-machine on the ocean floor*



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

# *The Geological Record of Ocean Acidification*




From: *Hönisch et al.* [in press]

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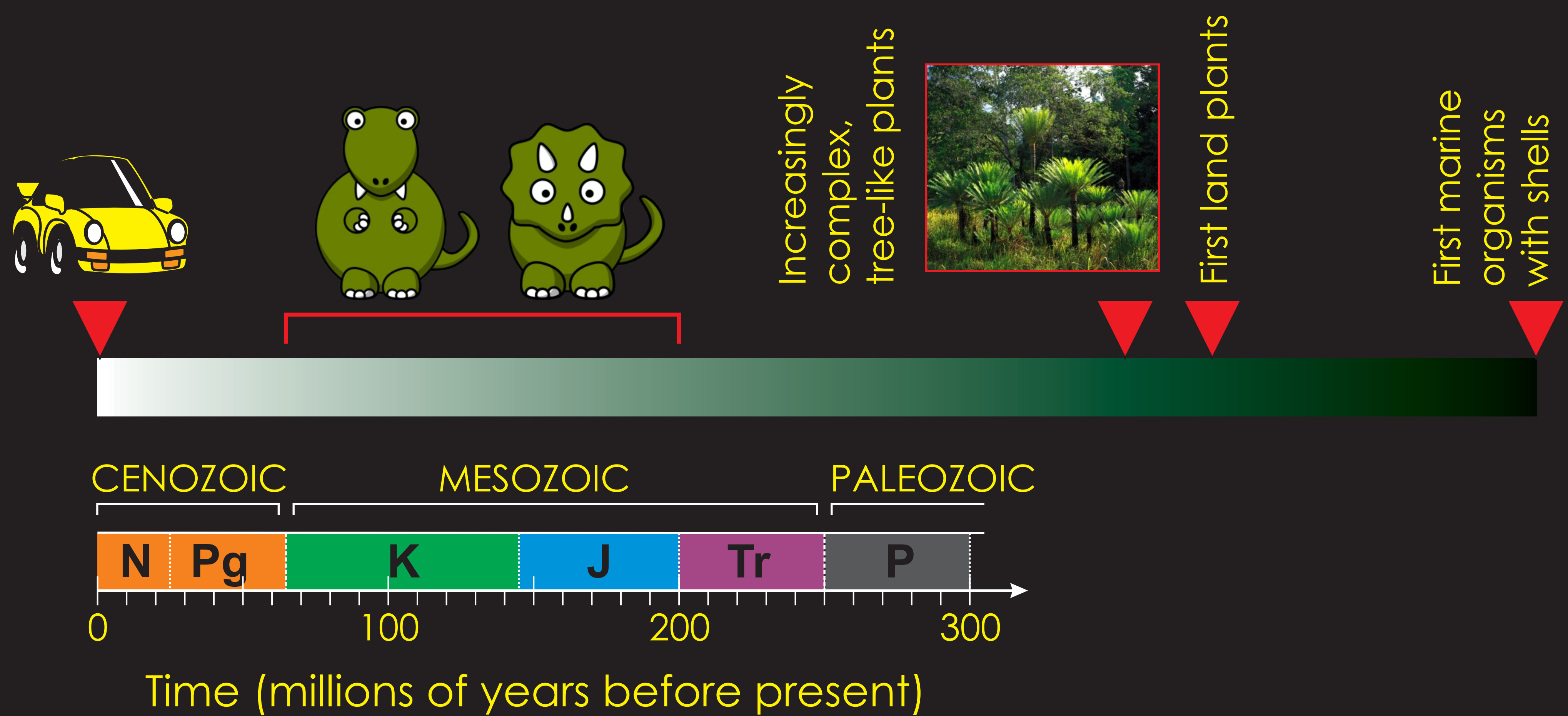

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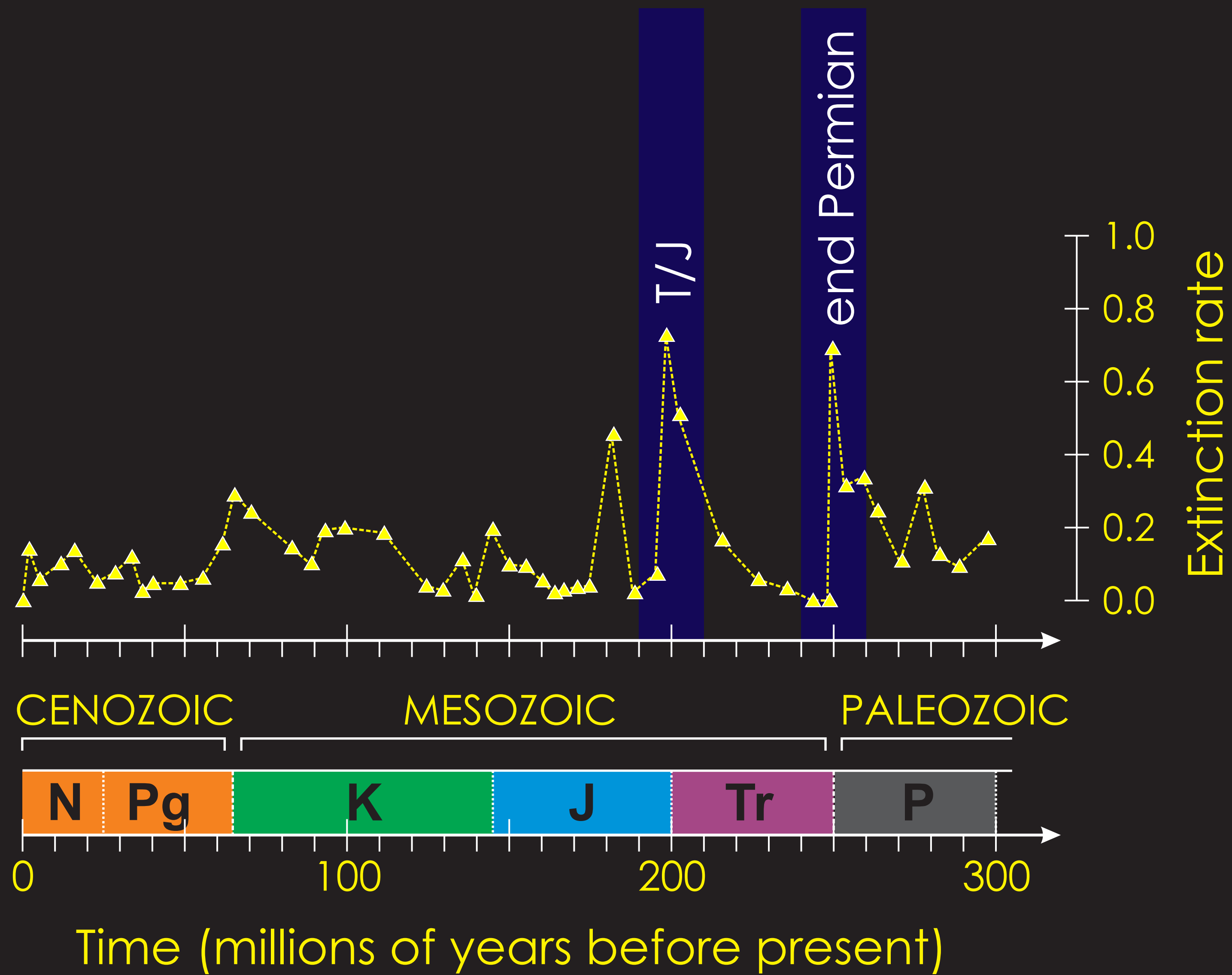


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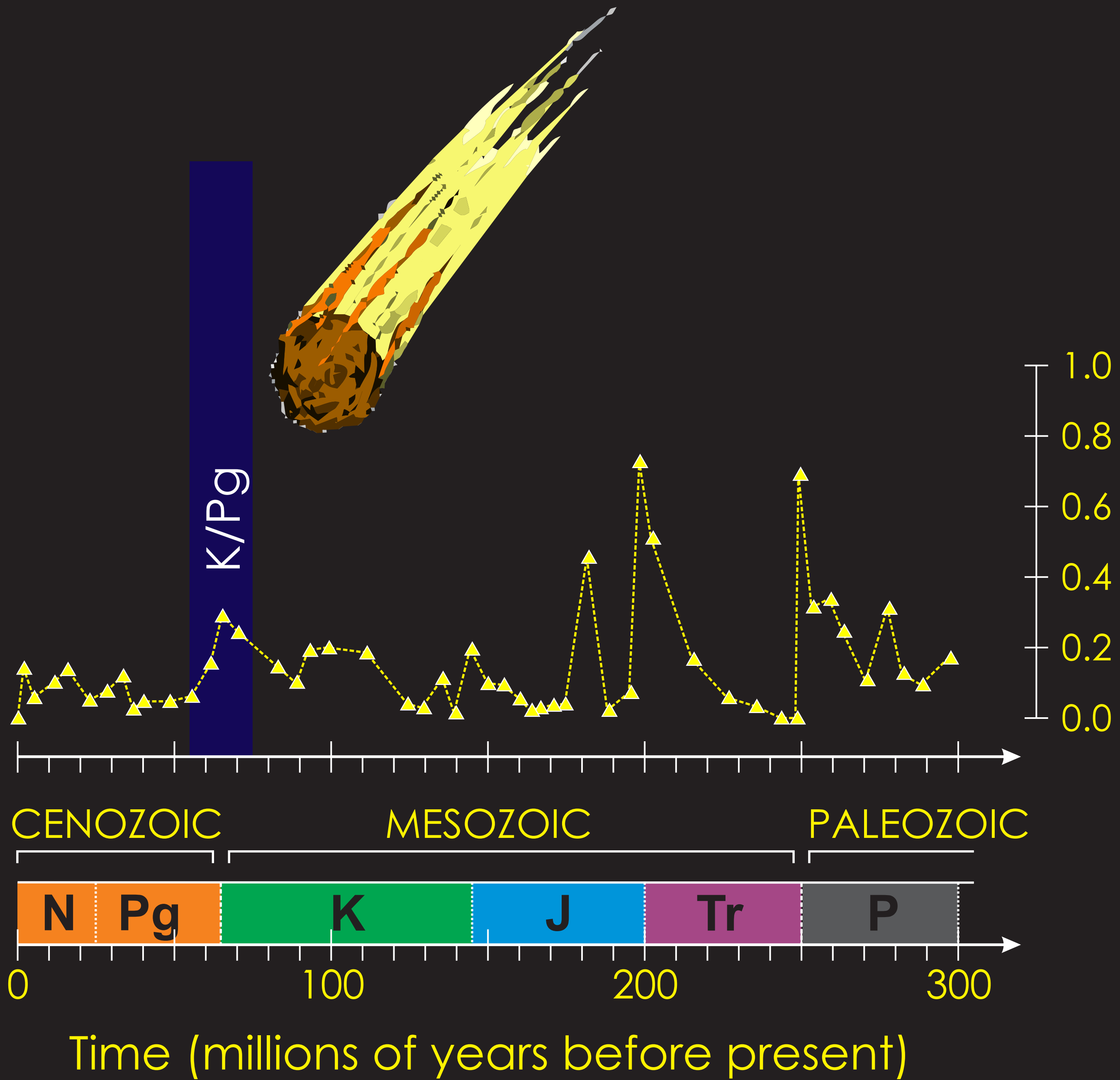


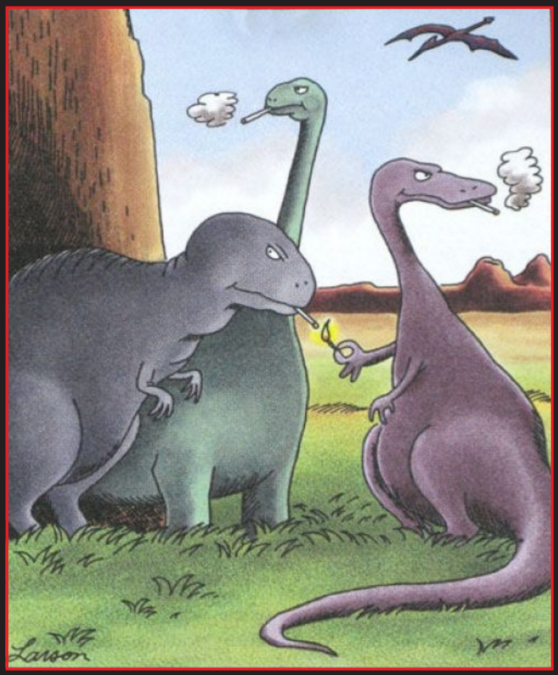

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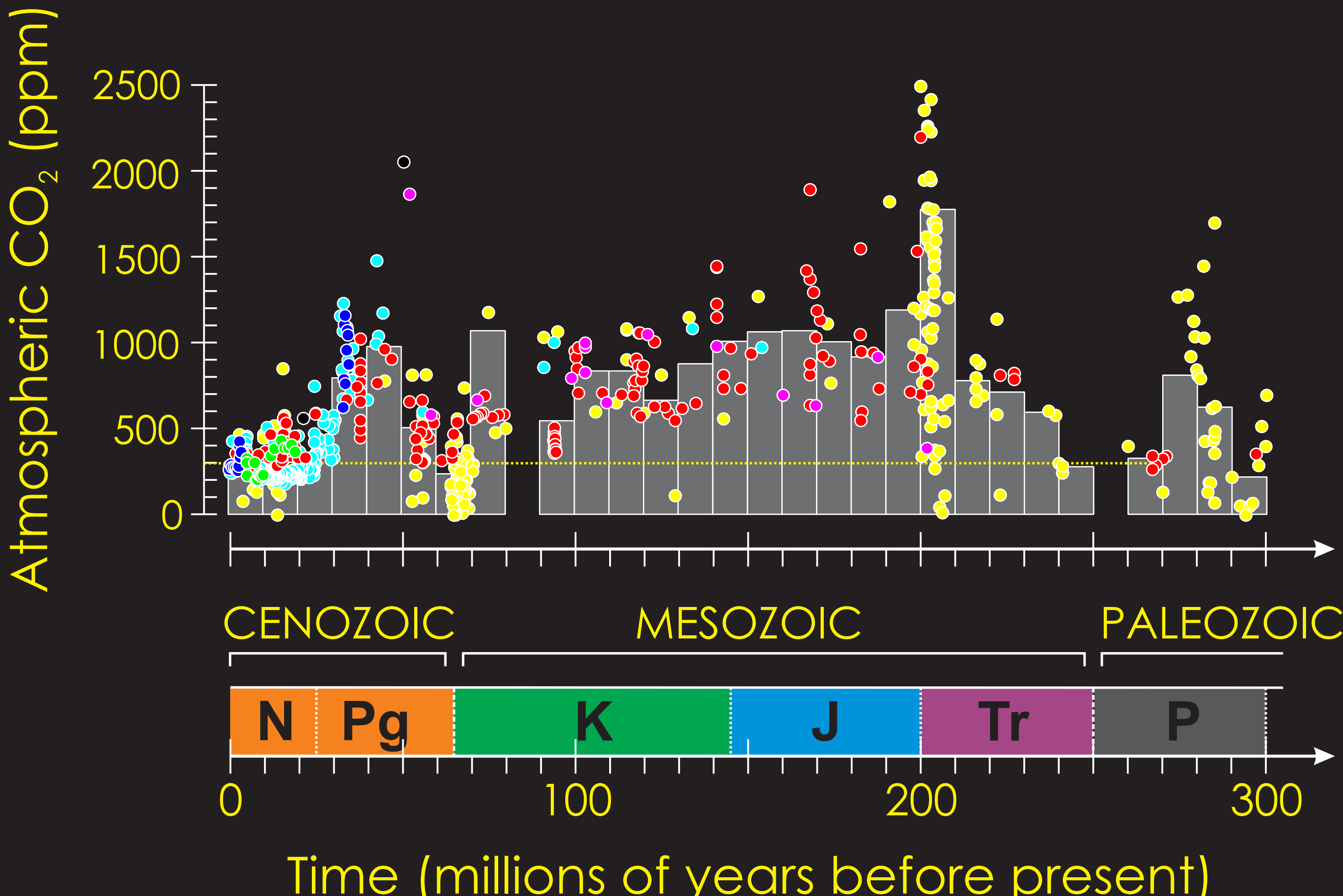


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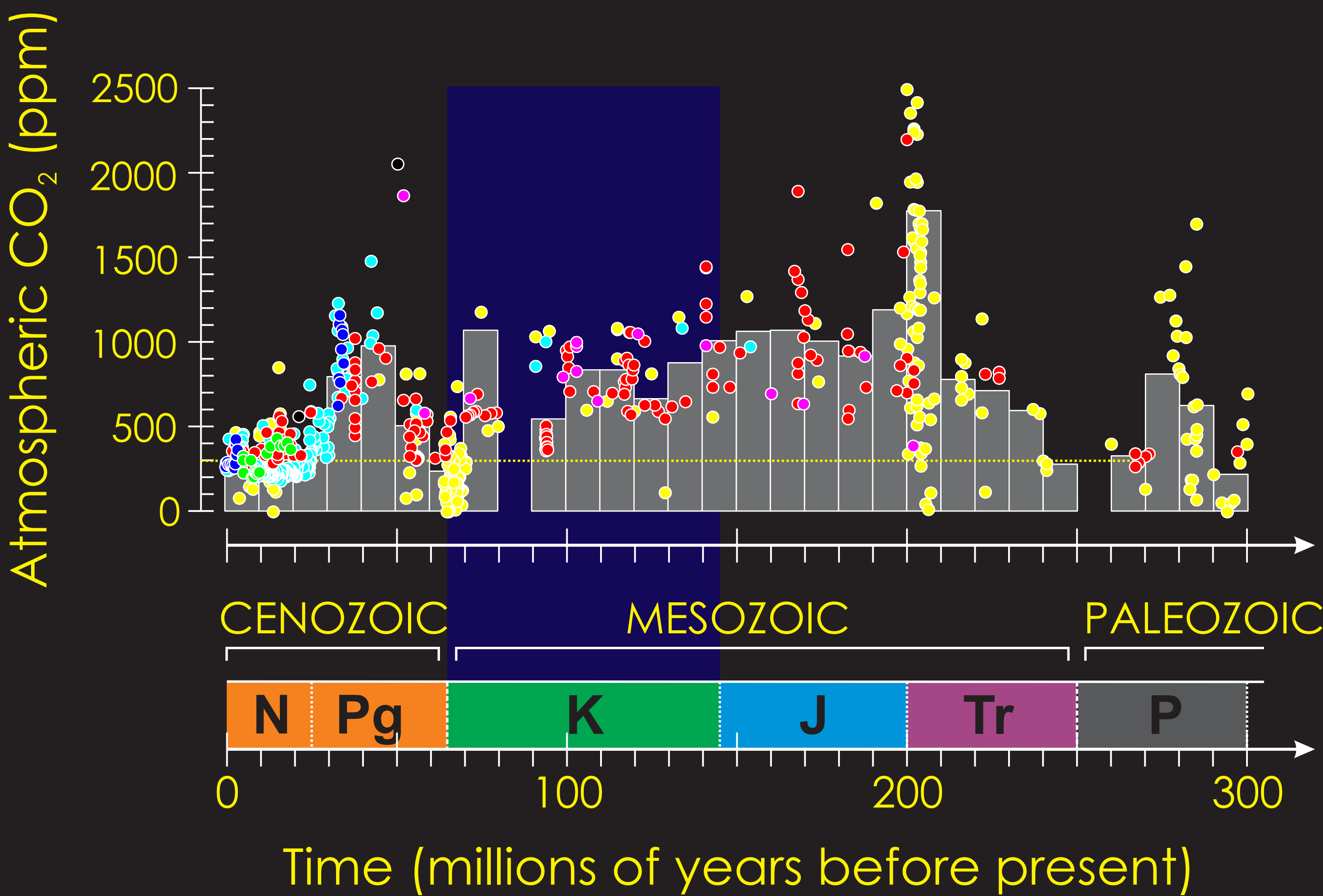


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& /(2.0*(dum_carbconst(icc_k) - 4.0))

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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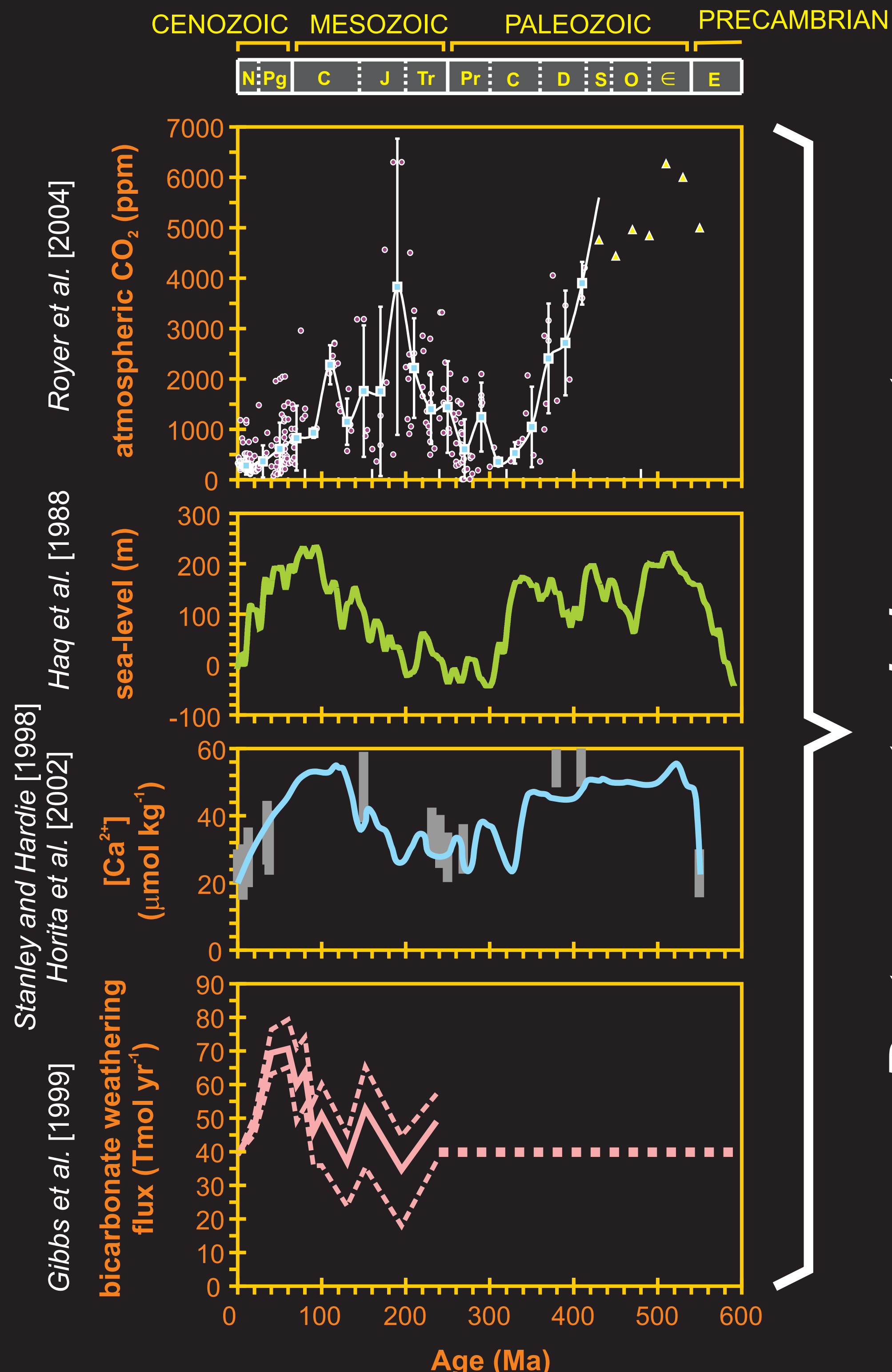
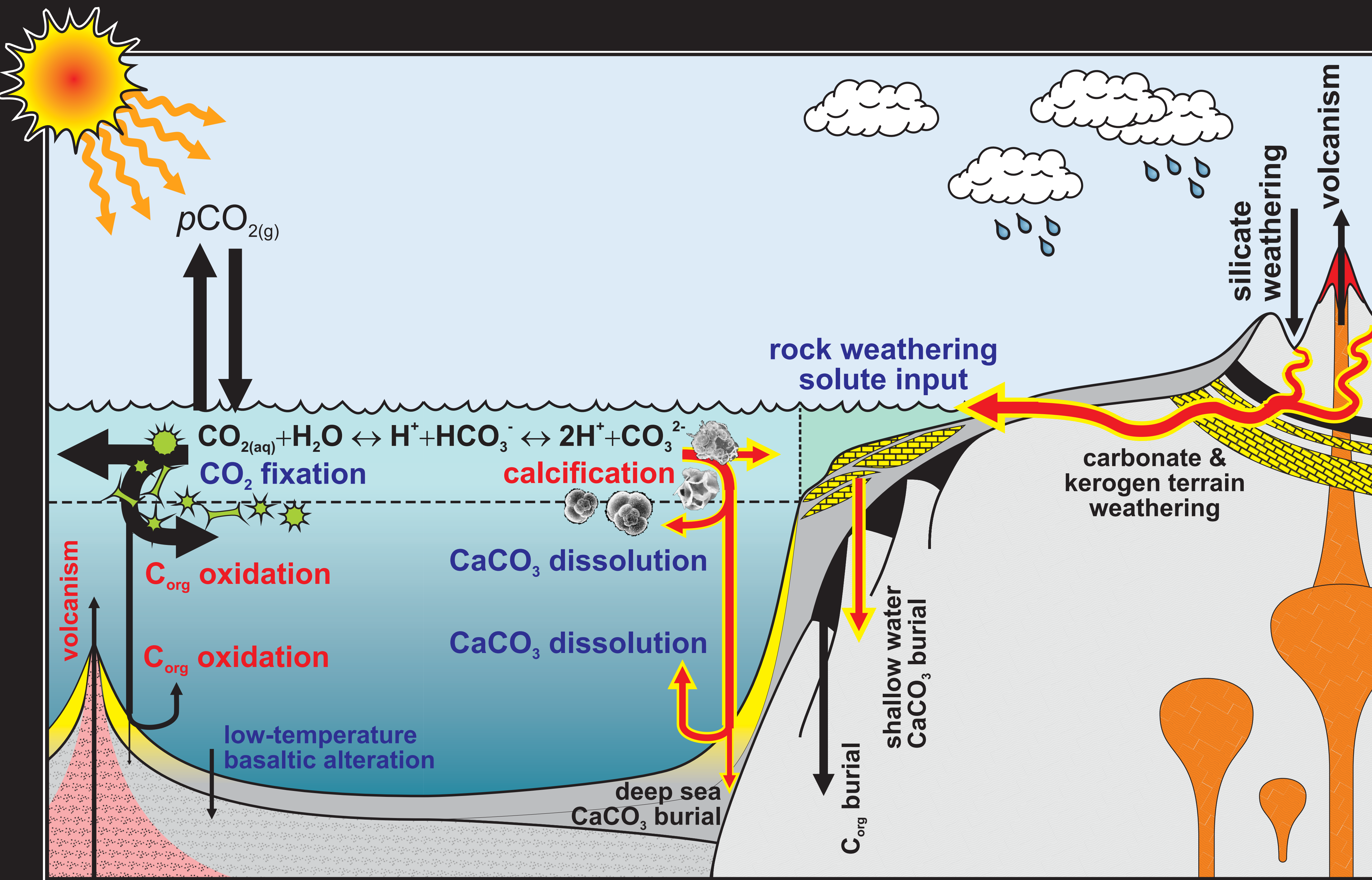
```

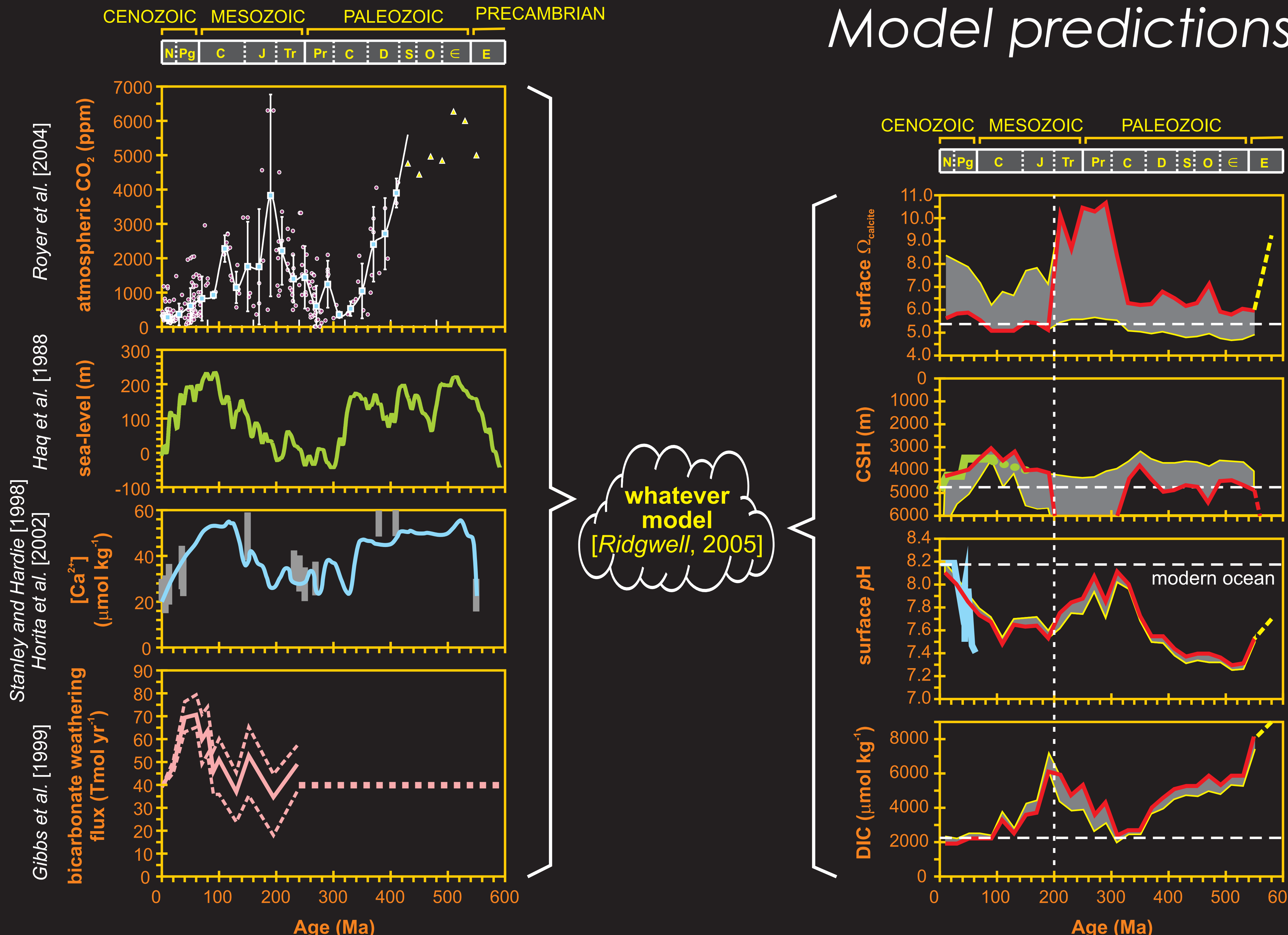



Data constraining past changes in ocean chemistry

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



# Model predictions



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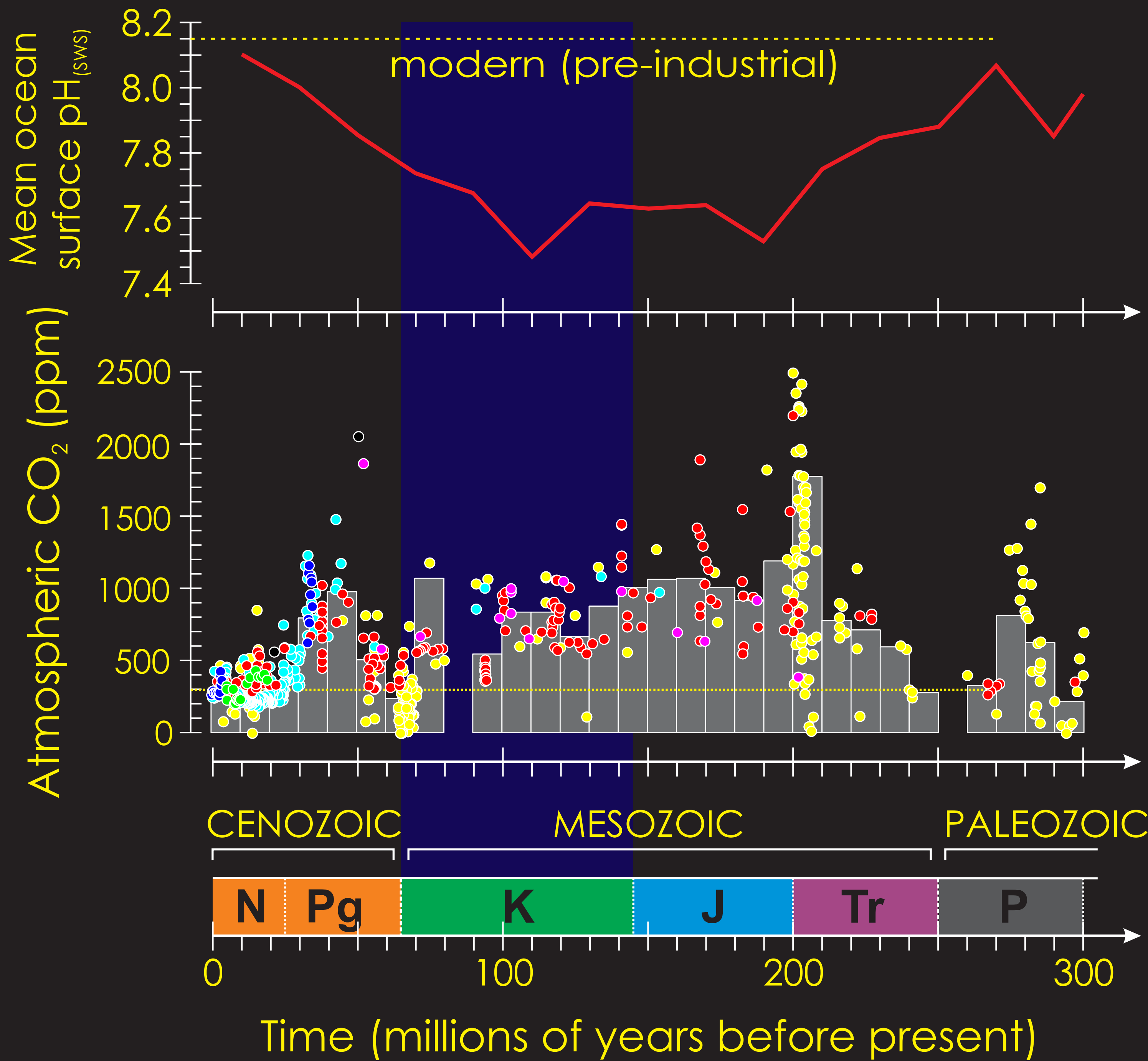
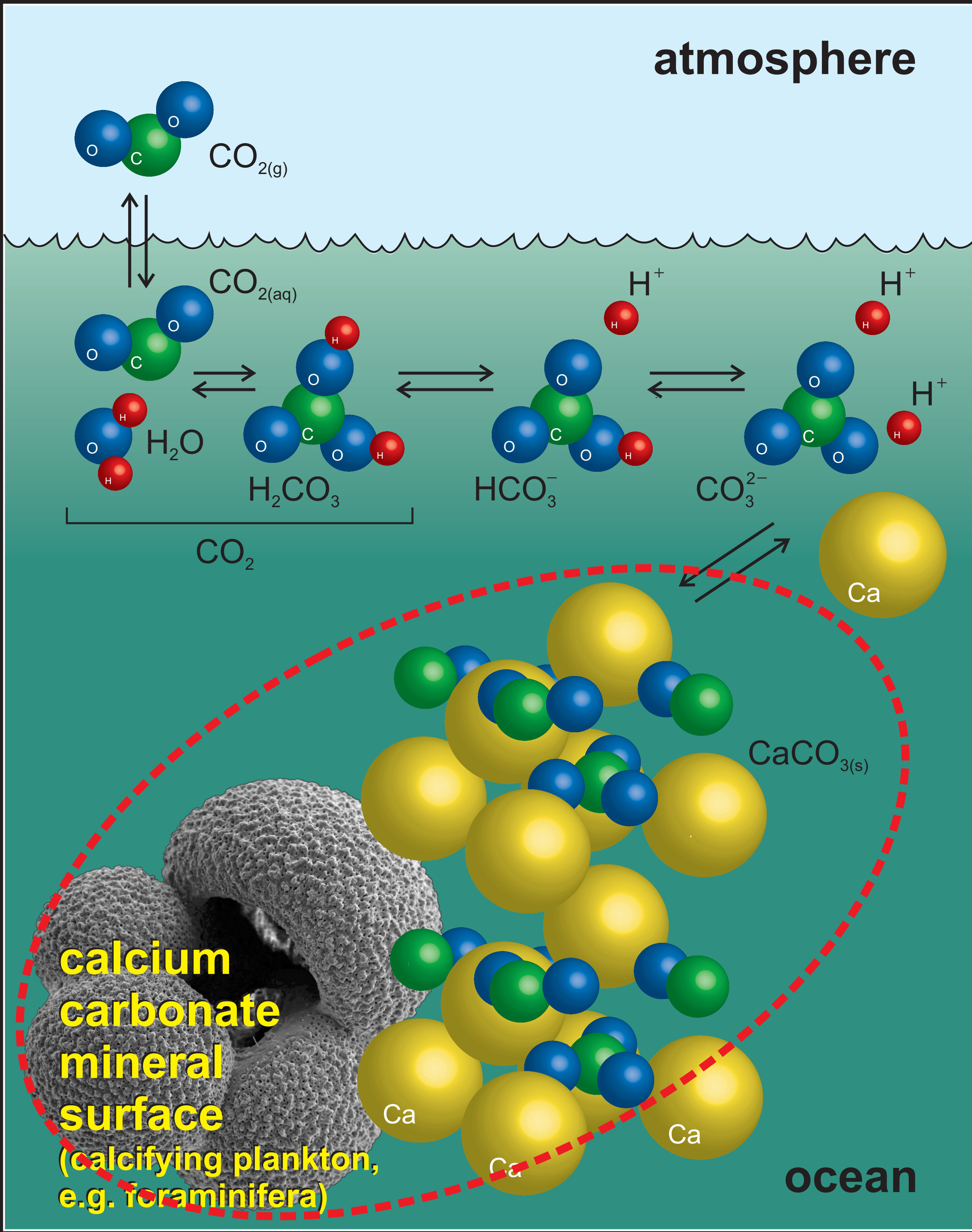
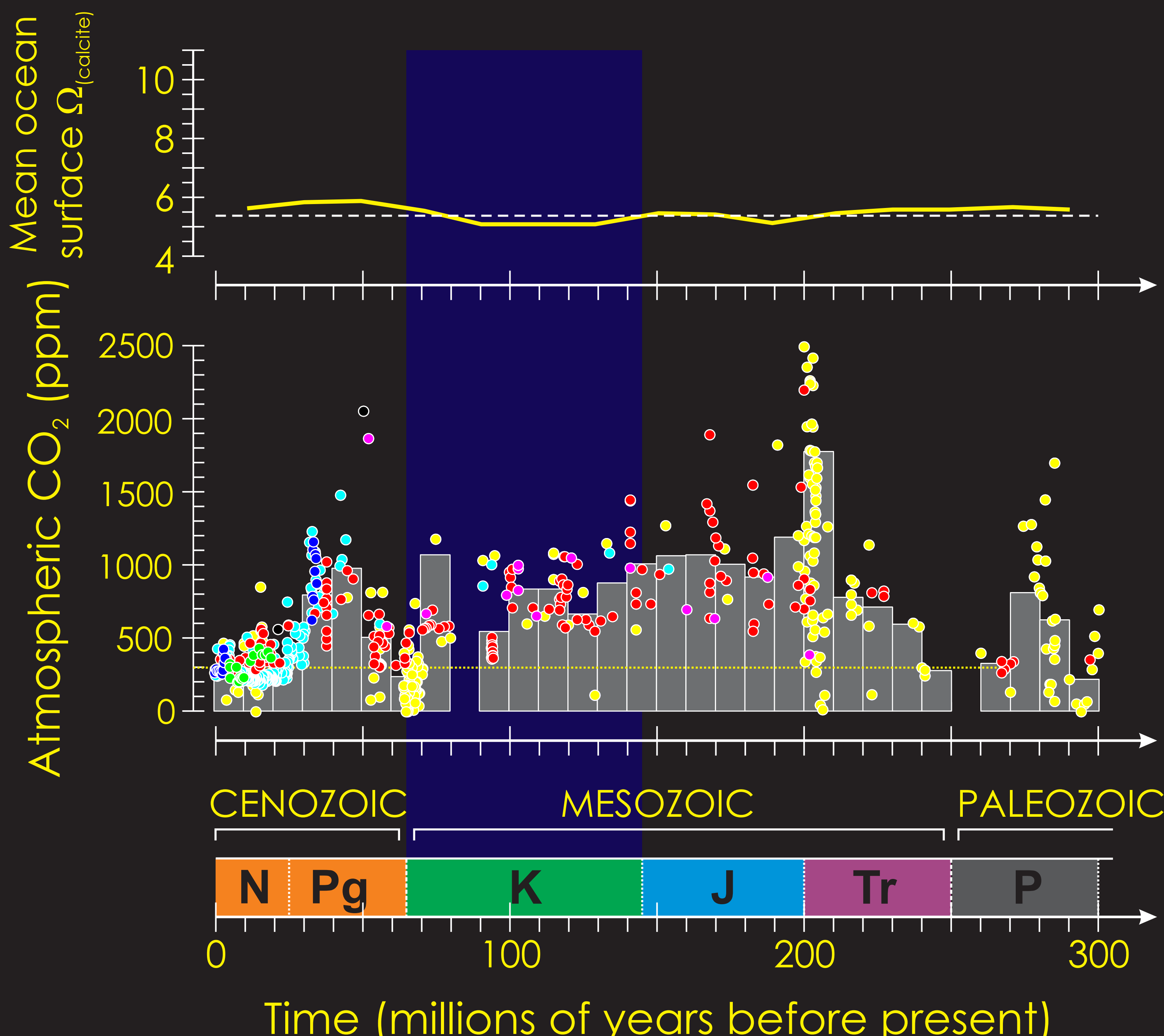


atmosphere
$CO_{2(g)}$
$CO_{2(aq)}$
$H_2O$
$H_2CO_3$
$HCO_3^-$
$CO_3^{2-}$
$H^+$
$H^+$
$H^+$
$CO_2$
Ca
$CaCO_{3(s)}$
calcium carbonate mineral surface
(calcifying plankton, e.g. foraminifera)
ocean

# The Geological Record of Ocean Acidification

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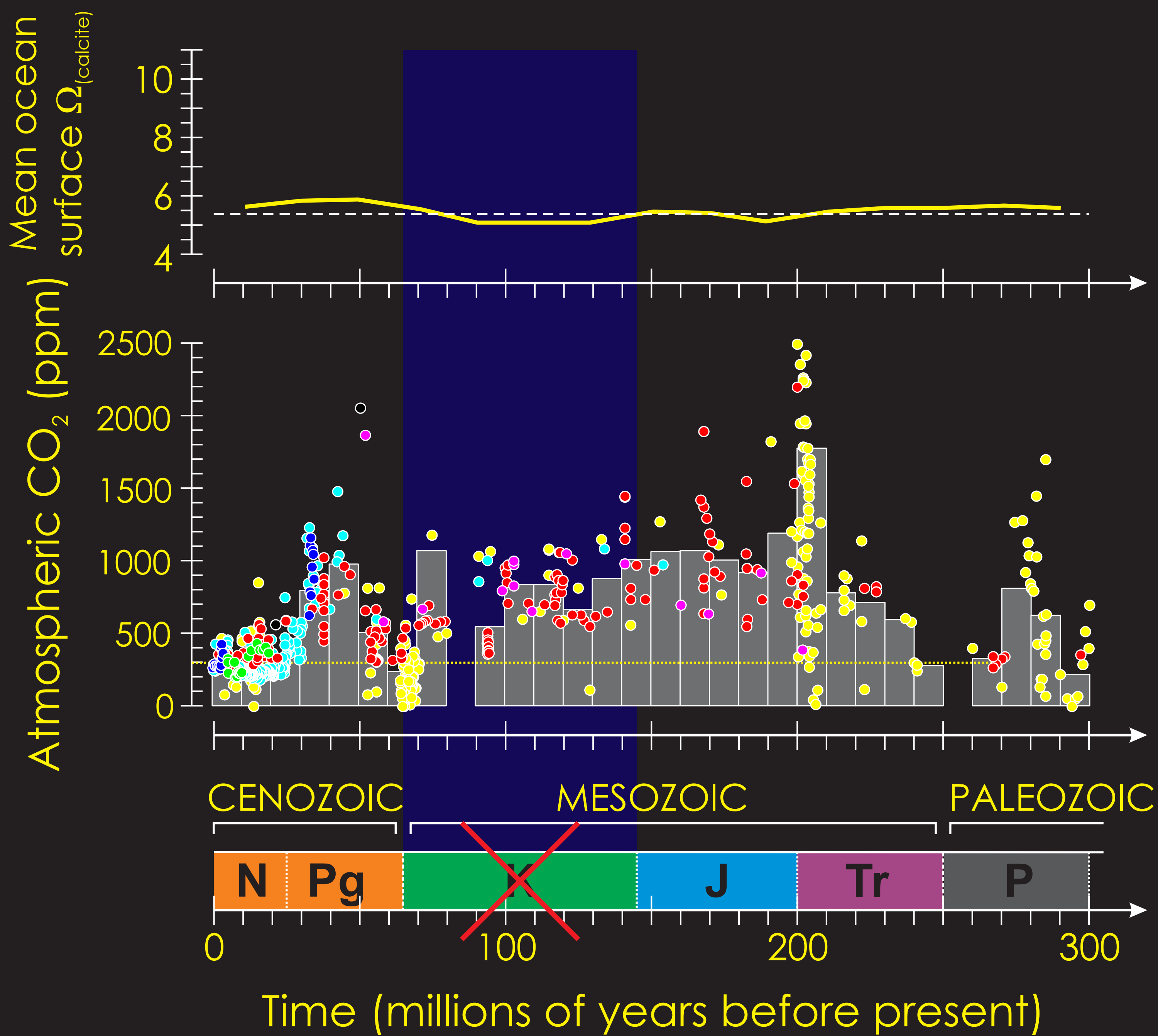
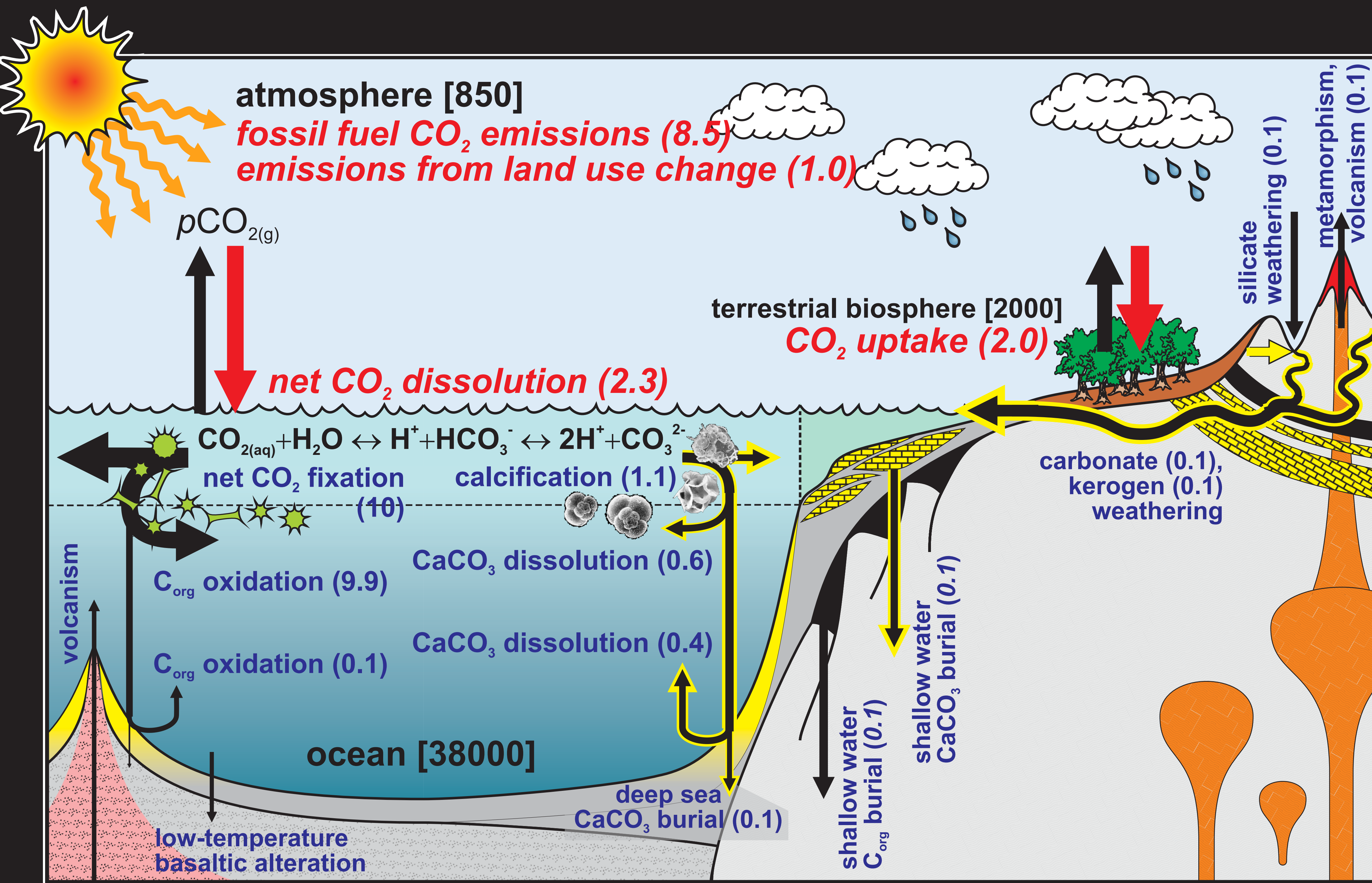
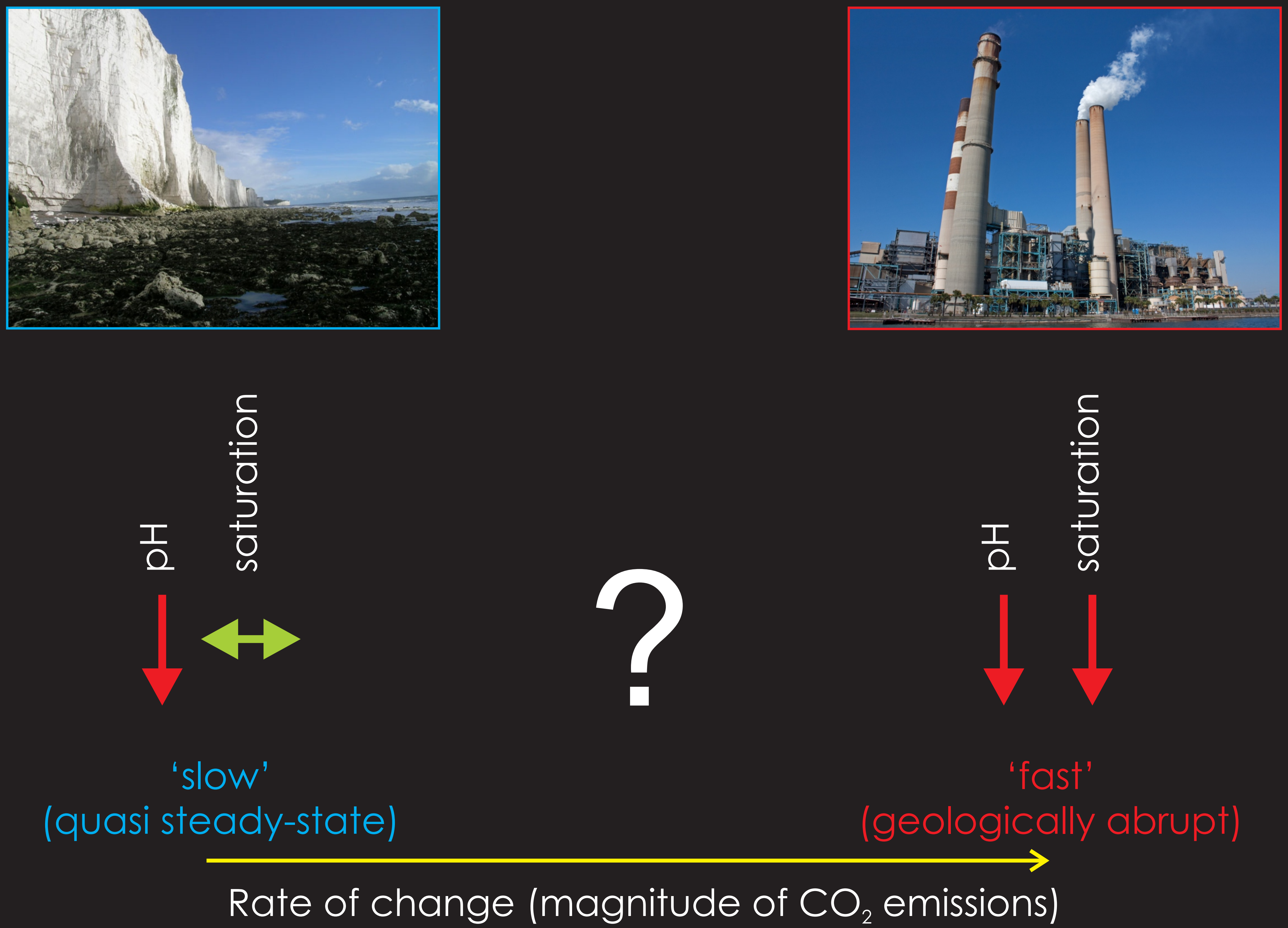



# The modern carbon cycle




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

```
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loc_ALK_DIC = dum_ALK &
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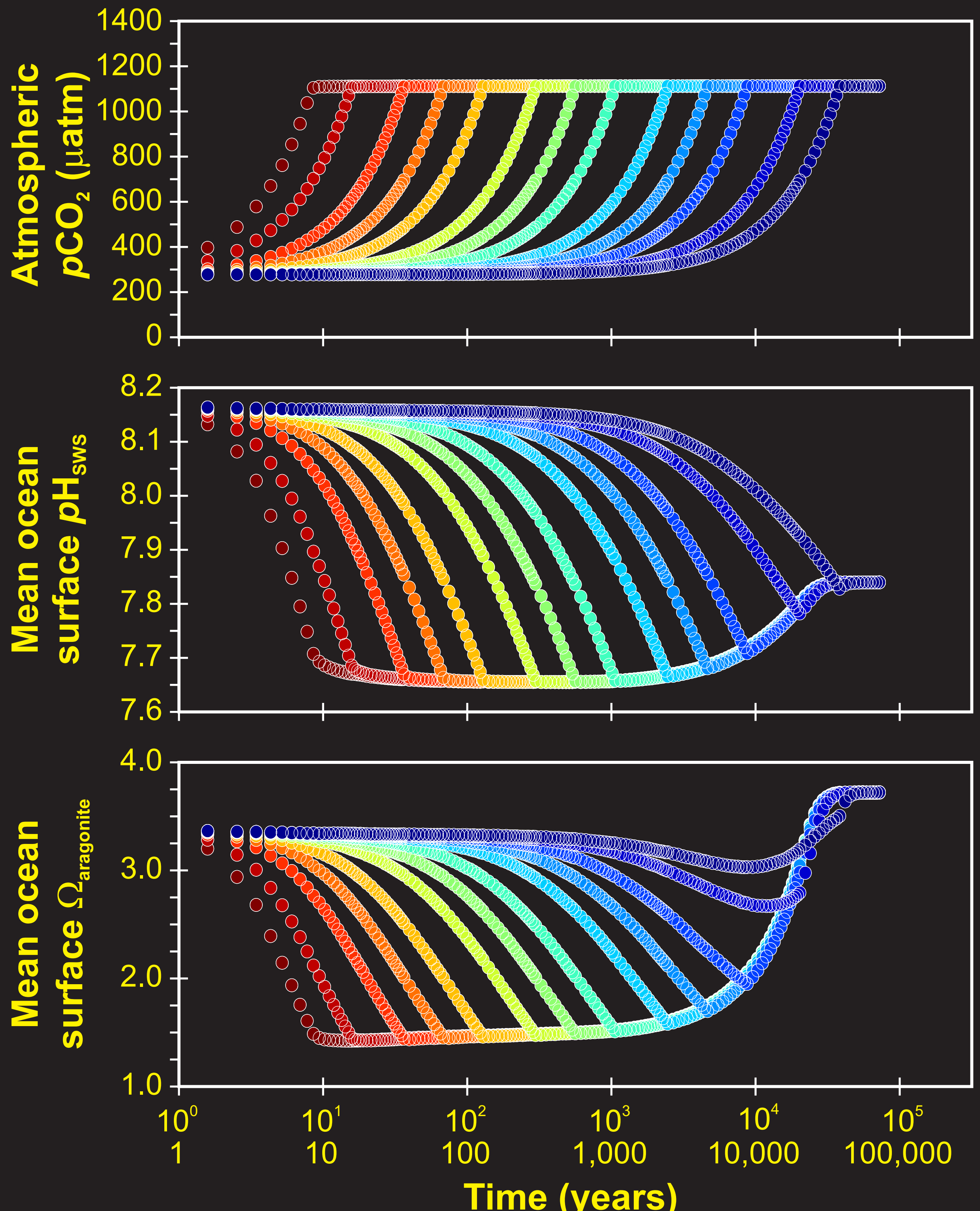
```




```
! 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)

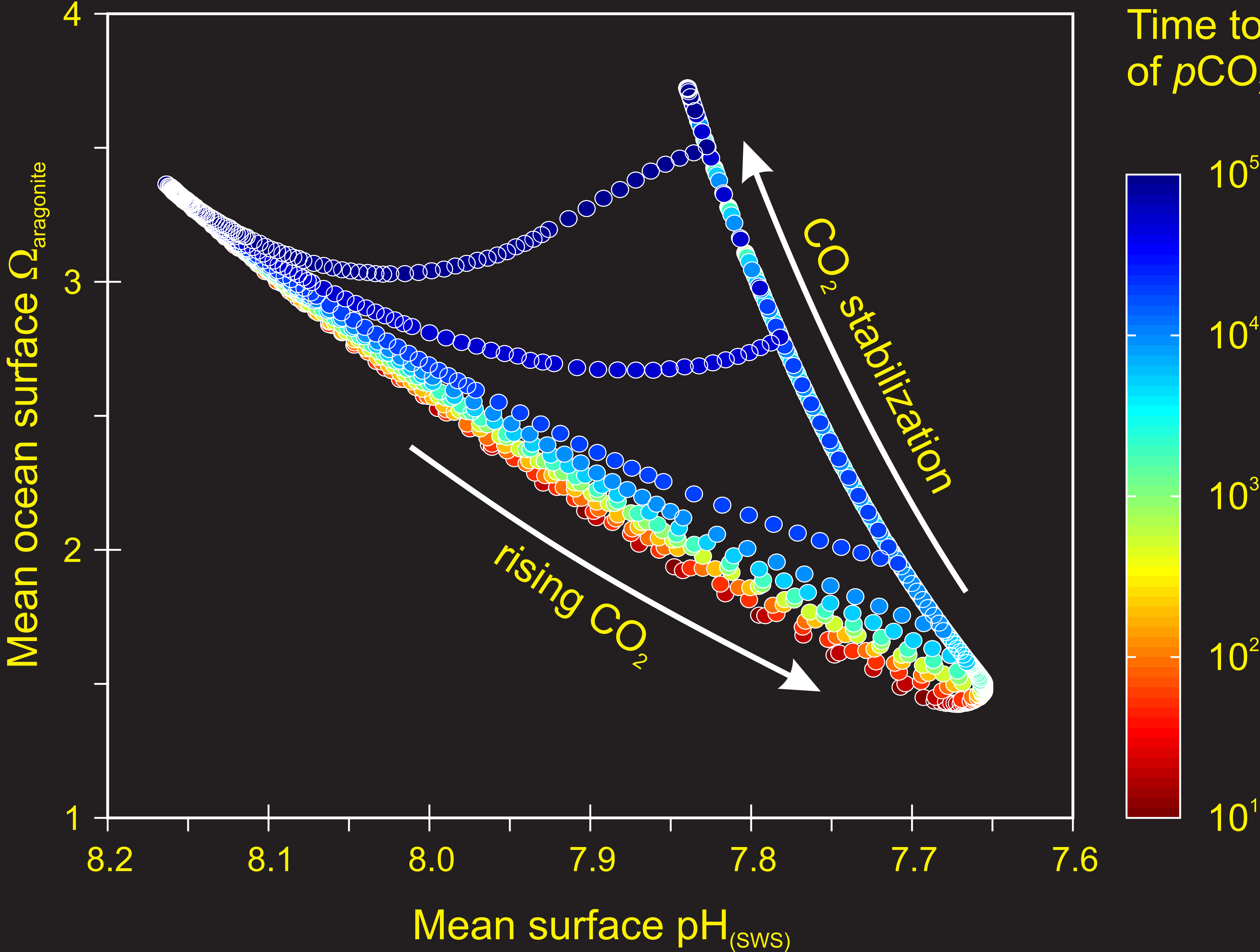
loc_conc_CO3 = &
& ( &
&   loc_ALK_DIC*dum_carbconst(icc_k) - dum_DIC*dum_carbconst(icc_k) - &
&   4.0*loc_ALK_DIC + loc_zed &
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))

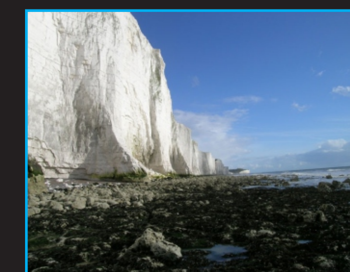
loc_conc_CO2 = dum_DIC - loc_ALK_DIC + &
& ( &
&   loc_ALK_DIC*dum_carbconst(icc_k) - dum_DIC*dum_carbconst(icc_k) - &
&   4.0*loc_ALK_DIC + loc_zed &
& ) &
& /(2.0*(dum_carbconst(icc_k) - 4.0))

loc_H1 = dum_carbconst(icc_k1)*loc_conc_CO2/loc_conc_HCO3

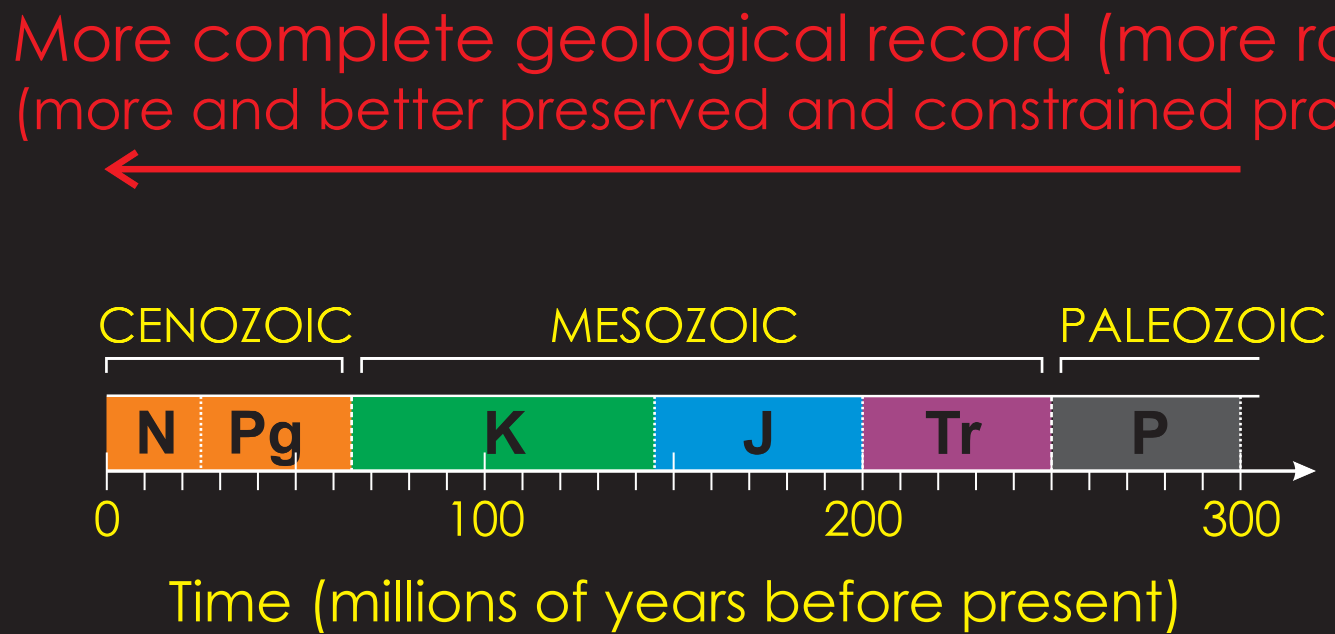
loc_H2 = dum_carbconst(icc_k2)*loc_conc_HCO3/loc_conc_CO3
```

# *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?*



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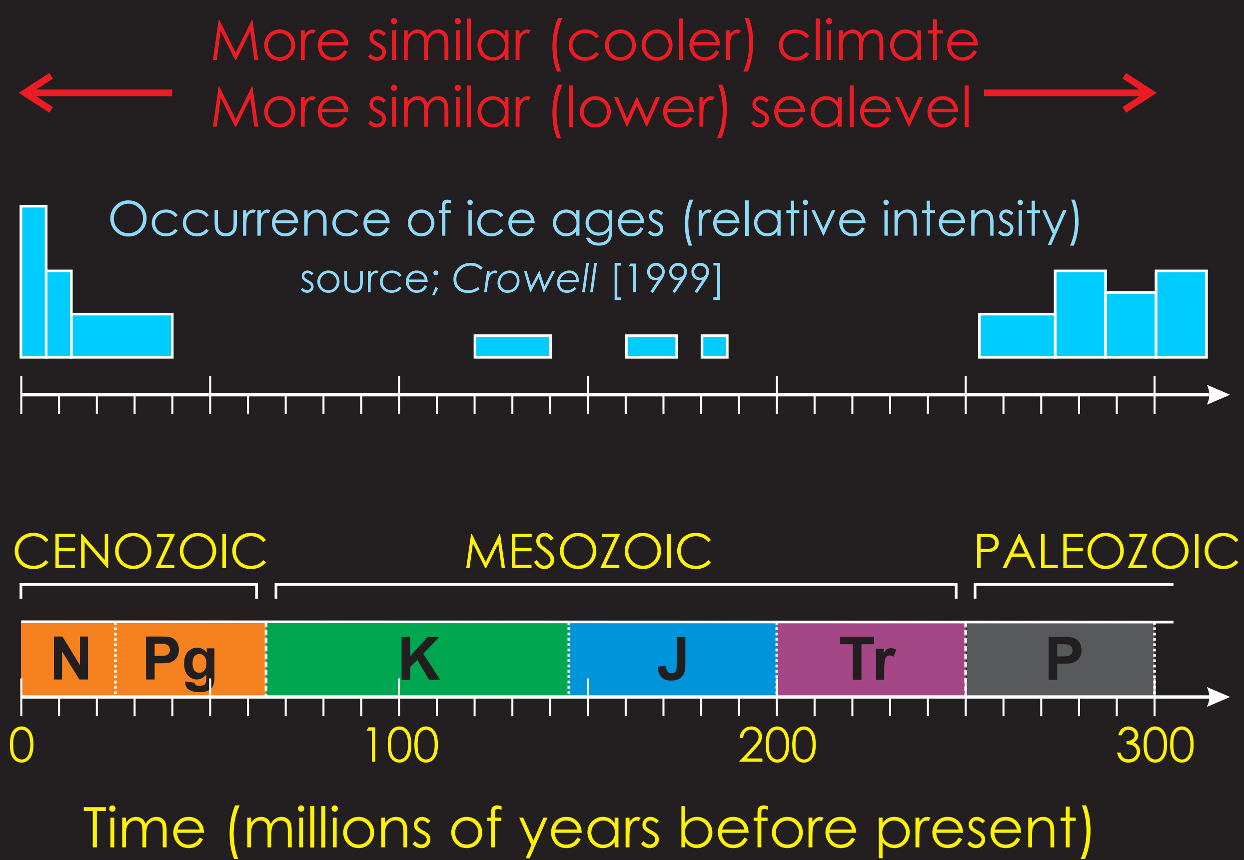


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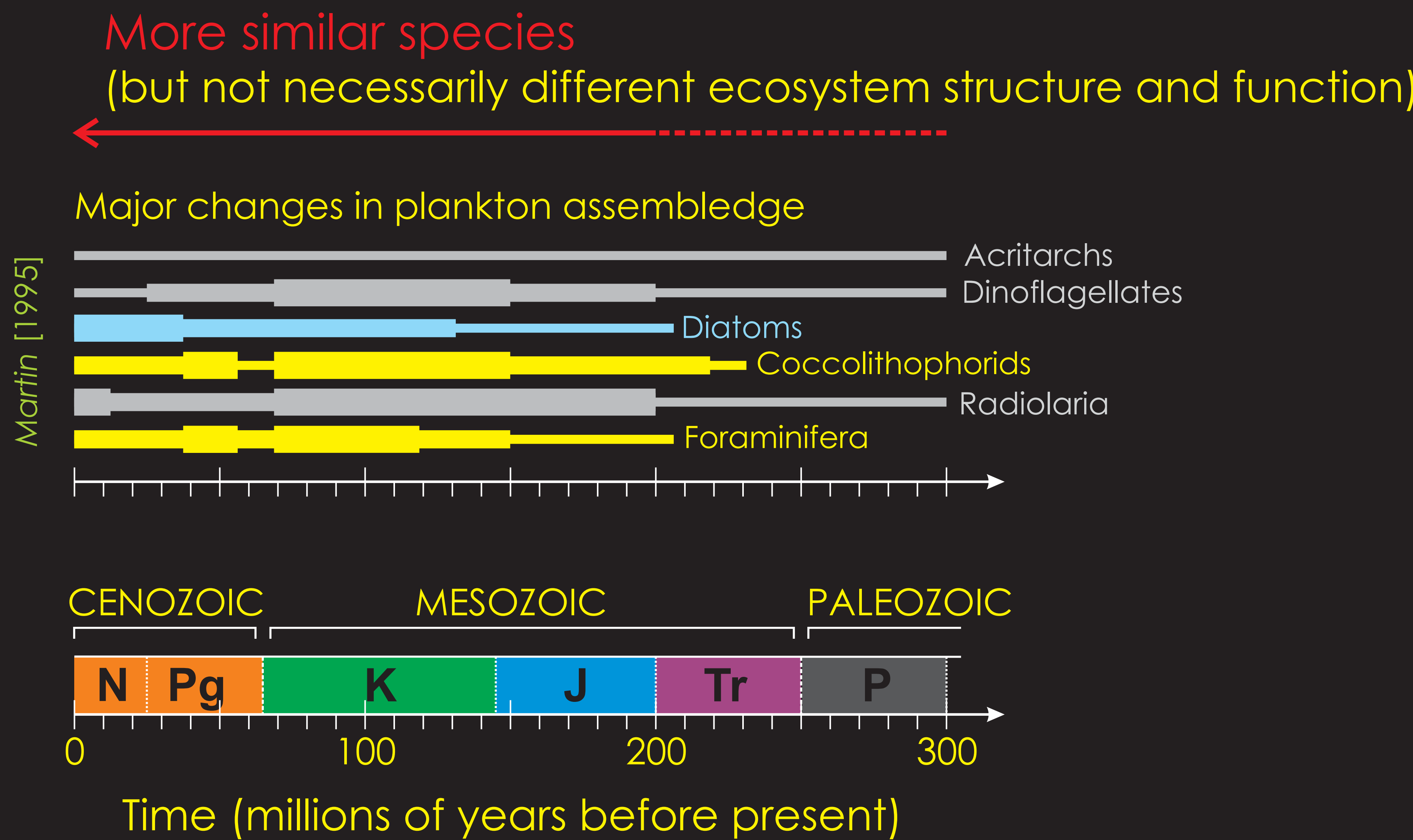
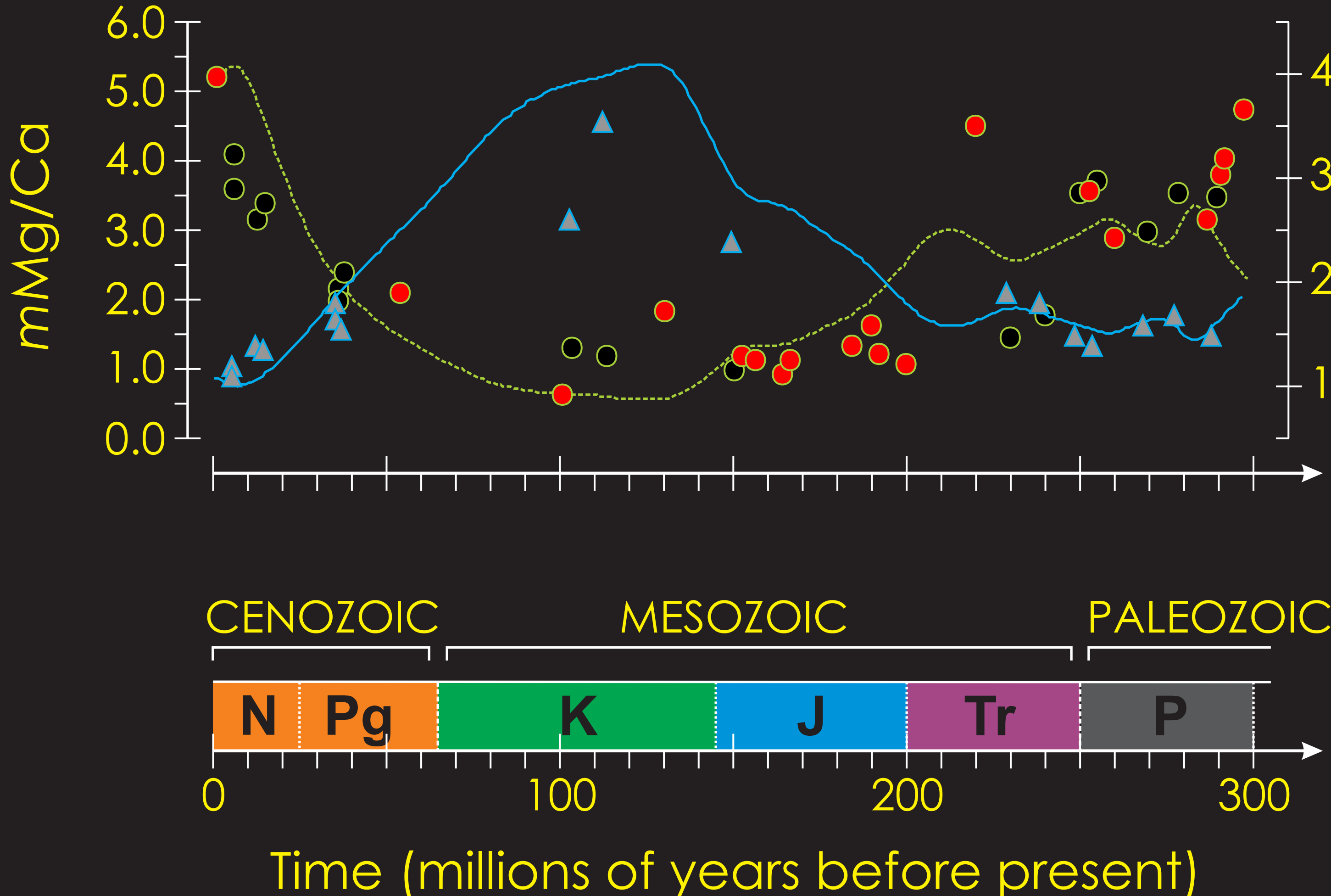


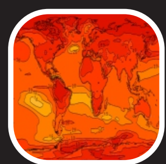
# *Is there a past 'analogue' for the future consequences of massive $CO_2$ release and ocean acidification?*

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

More similar cation chemistry




*The paleo ocean acidification app store*



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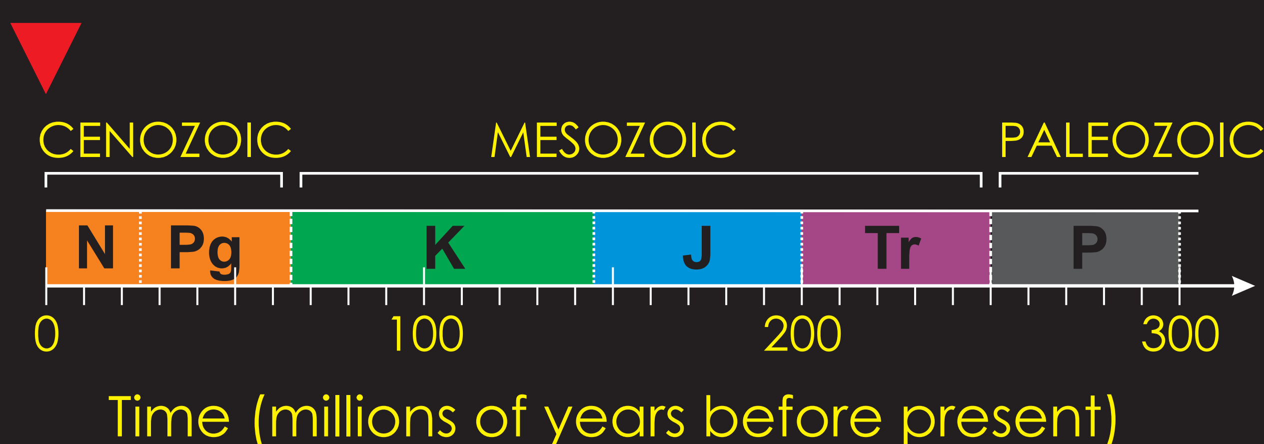


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CENOZOIC
MESOZOIC
PALEOZOIC
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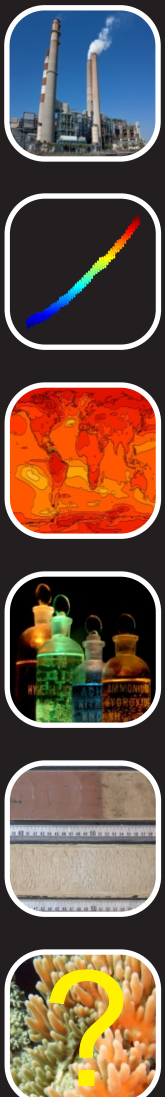
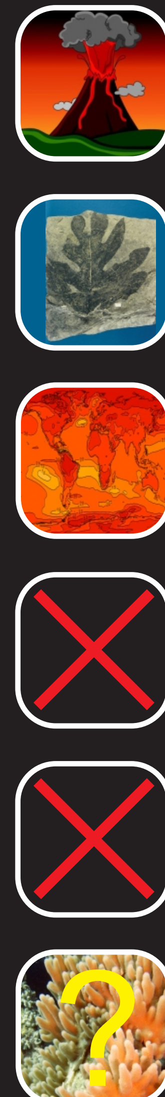
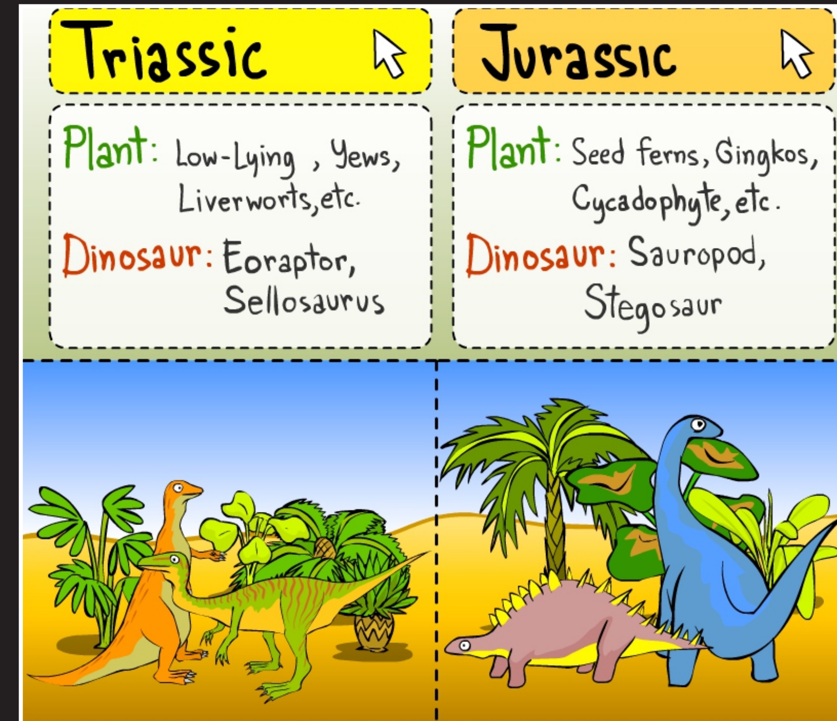
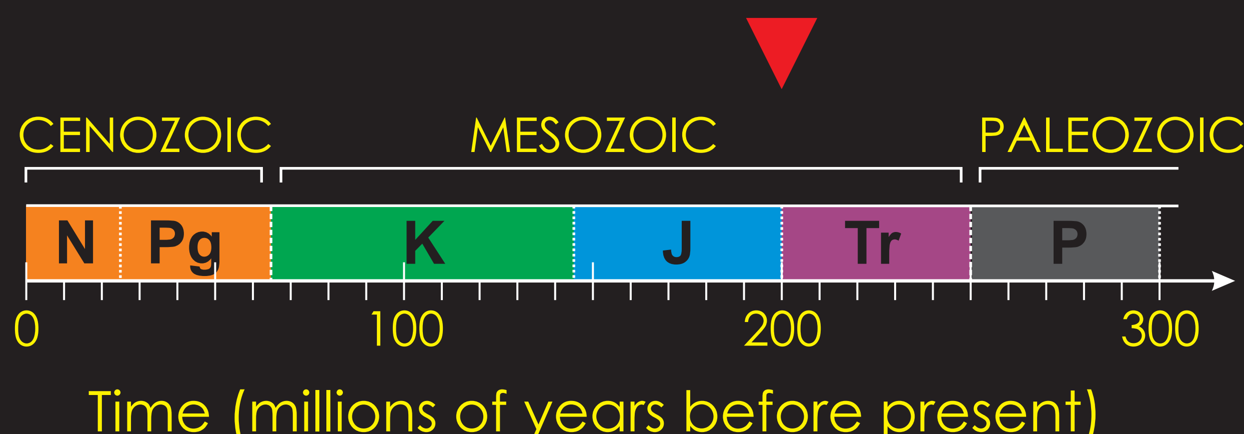
Time (millions of years before present)







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

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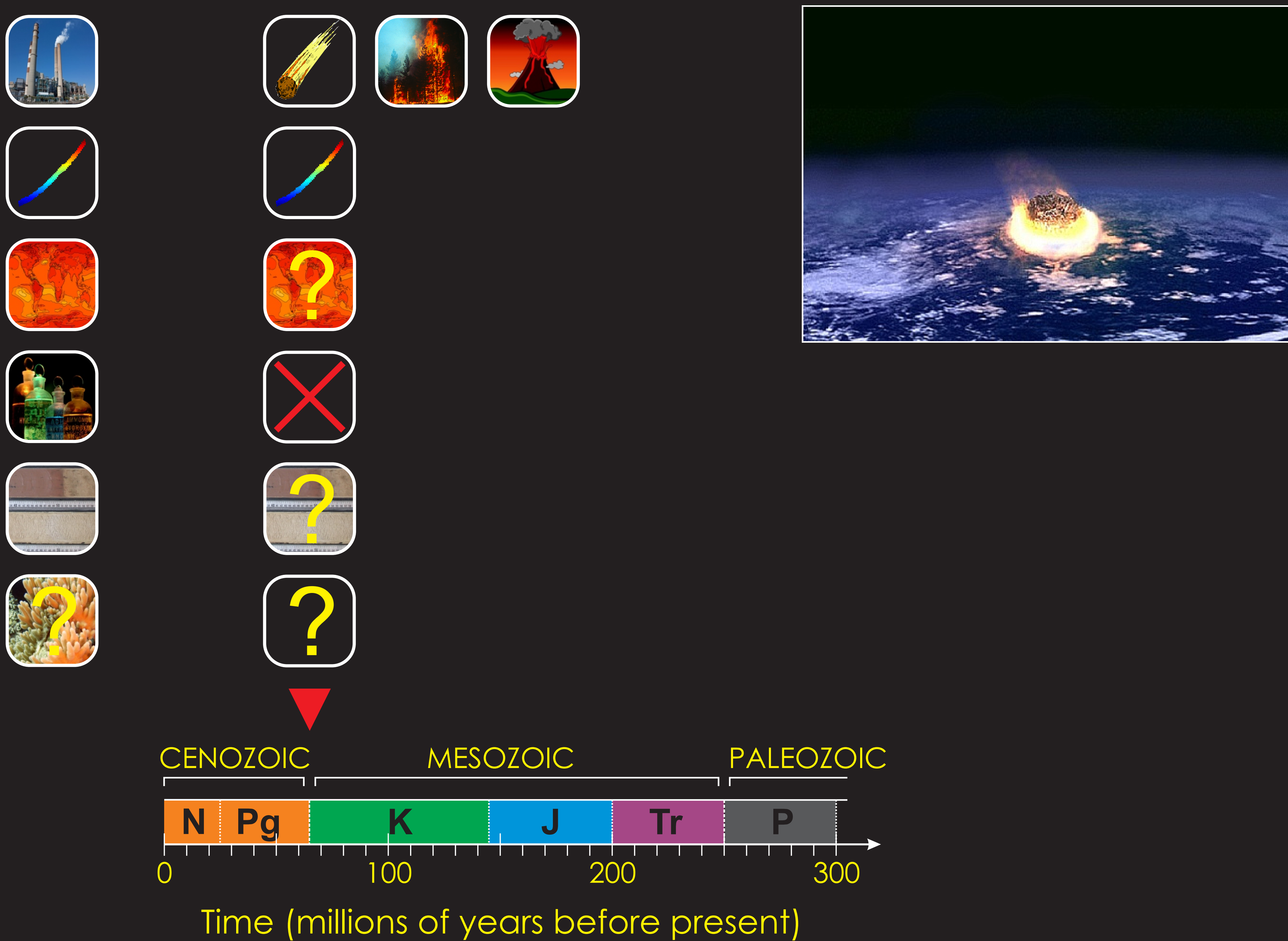

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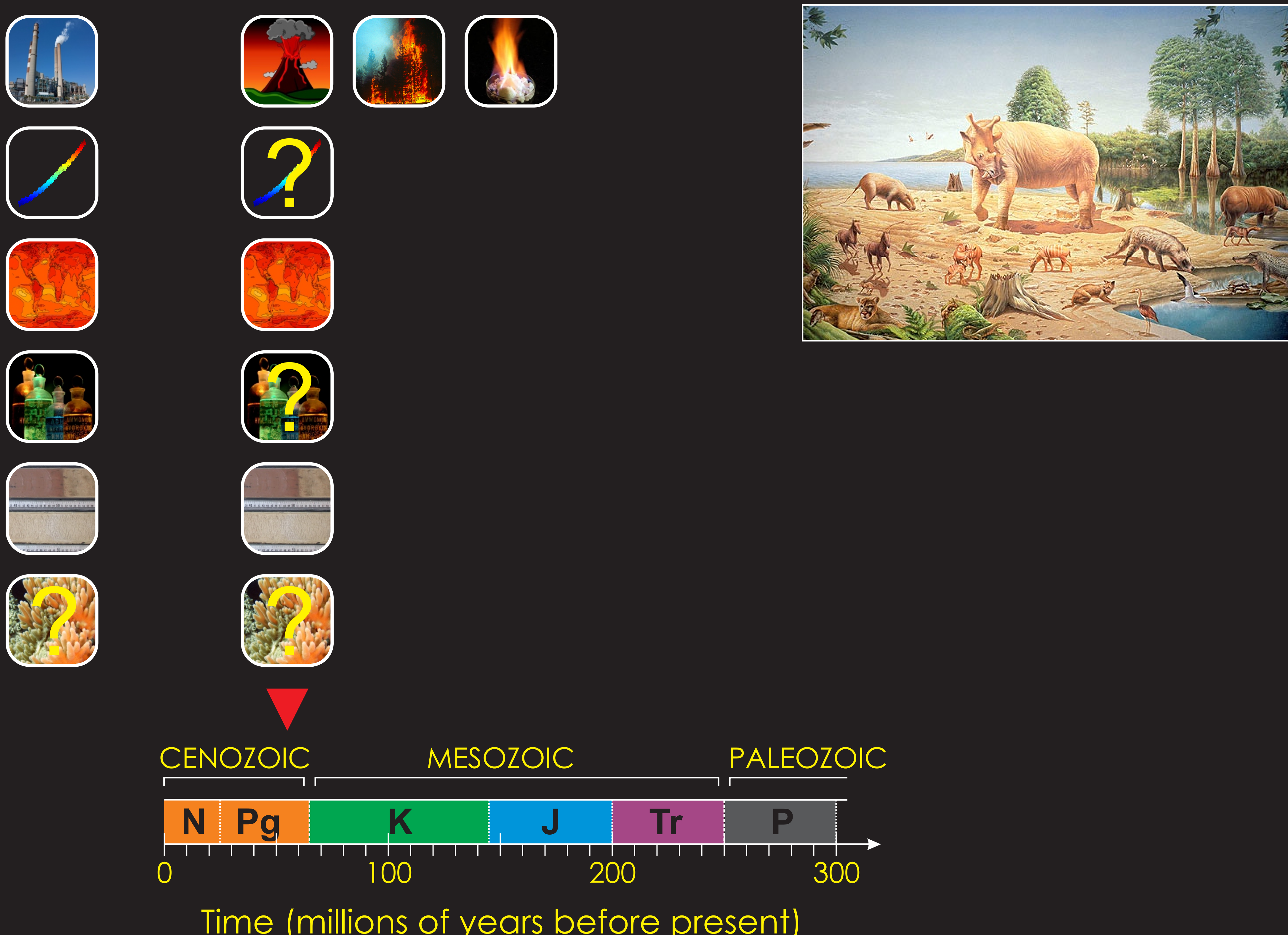
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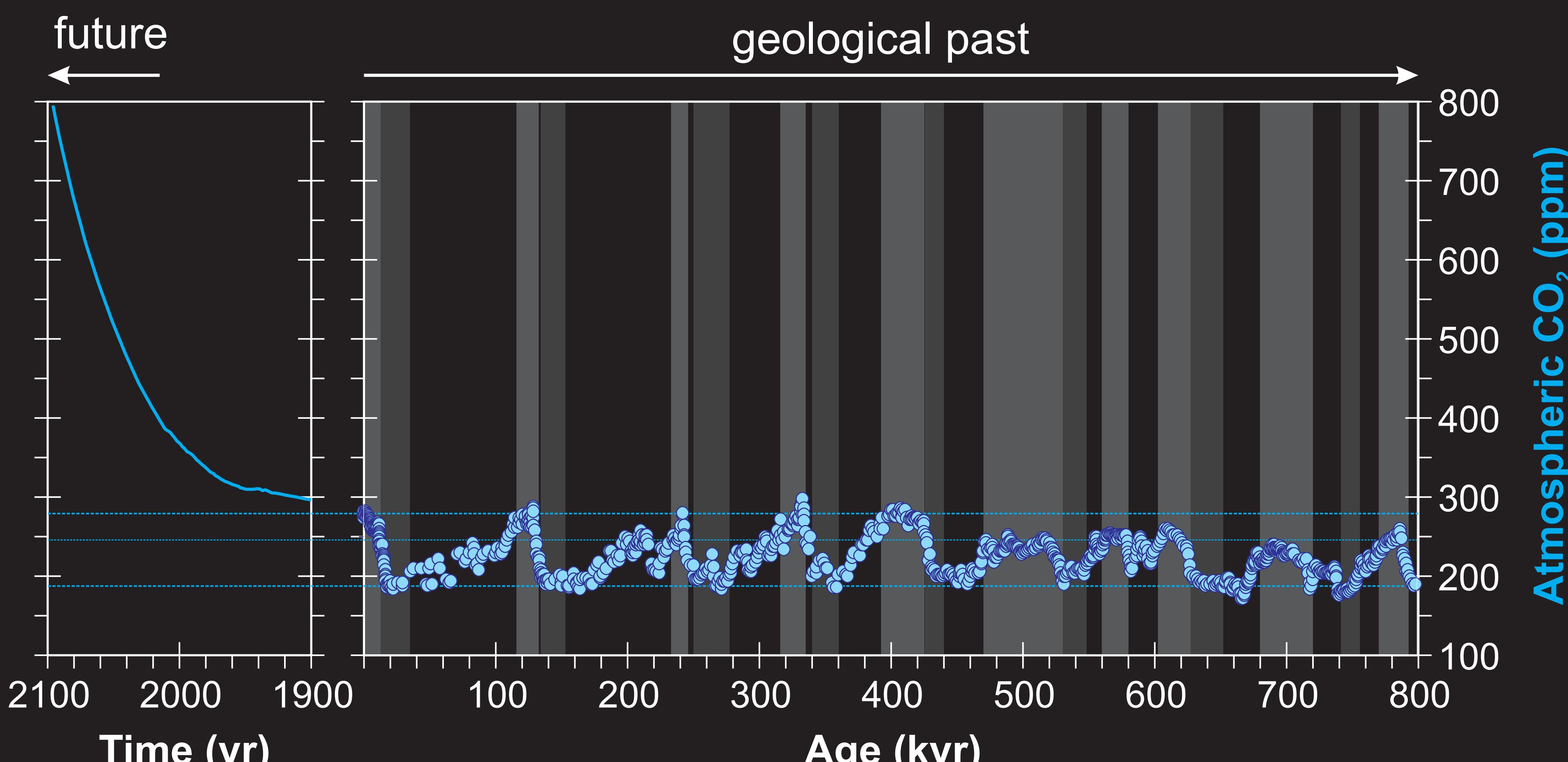
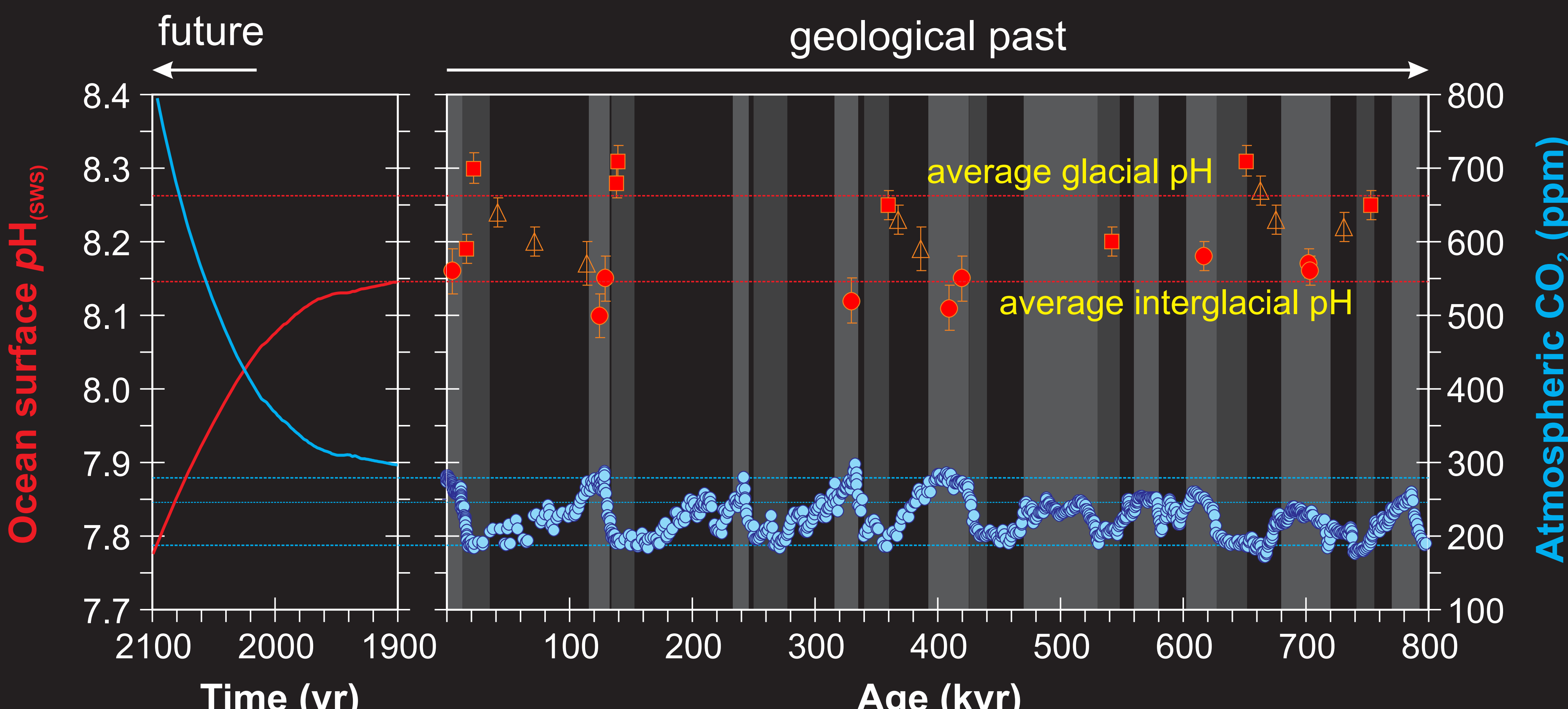



From: *Barker and Ridgwell* [in press]

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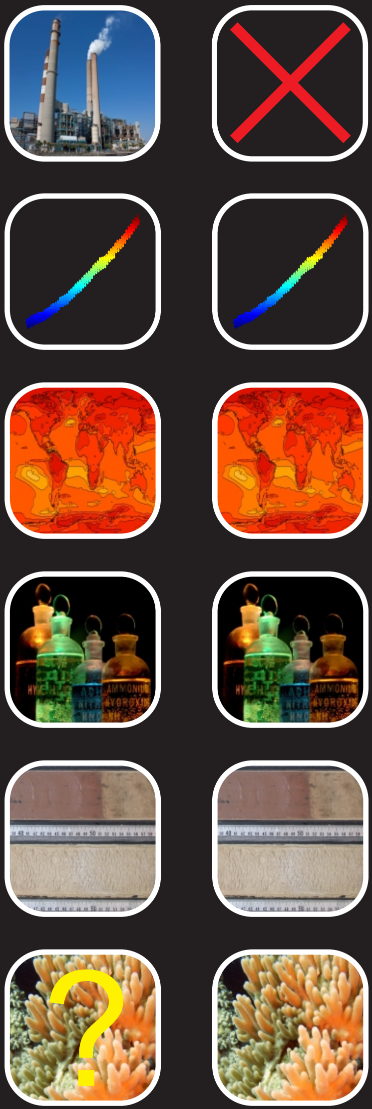

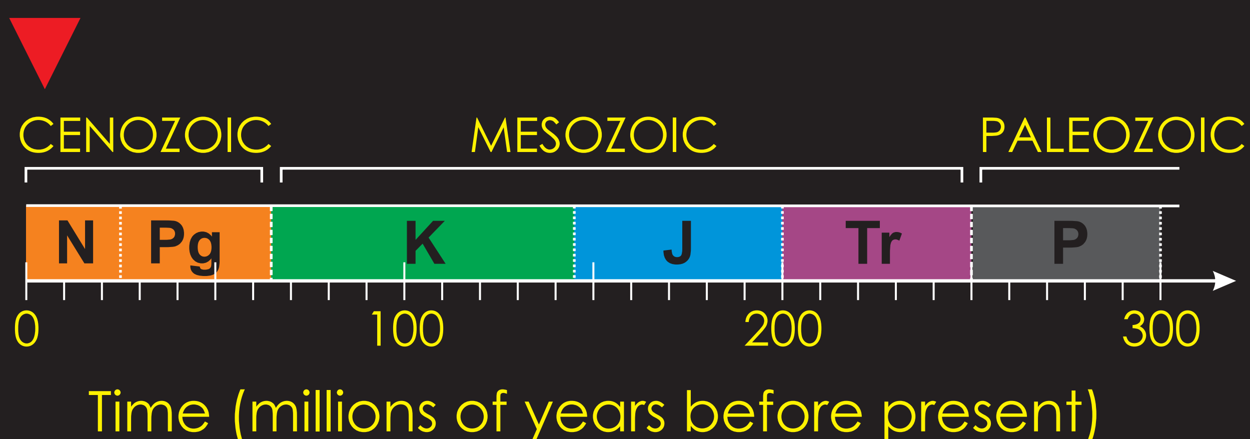
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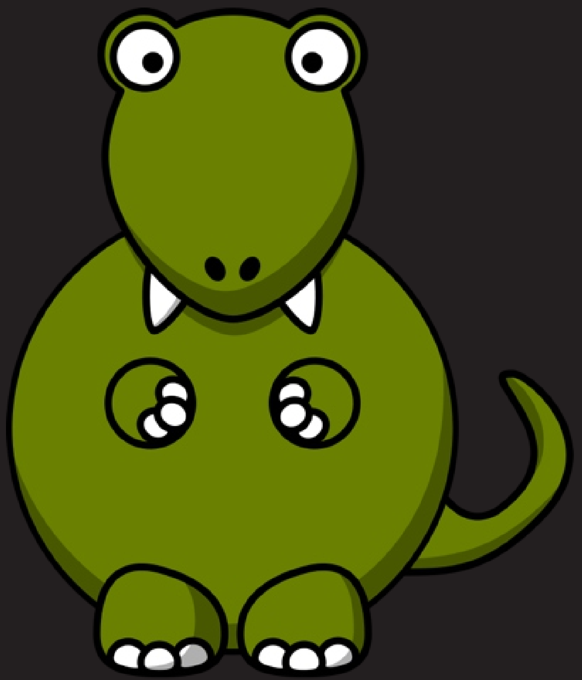
*Bärbel Hönisch, Daniela N. Schmidt, Ellen Thomas, Samantha J. Gibbs, Appy Sluijs, Lee Kump, Richard Zeebe, Rowan Martindale, Sarah E. Greene, Wolfgang Kiessling, Justin Ries, Jim Zachos, Dana L. Royer, Stephen Barker, Thomas M. Marchitto Jr., Ryan Moyer, Carles Pelejero, Branwen Williams, Patrizia Ziveri*



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