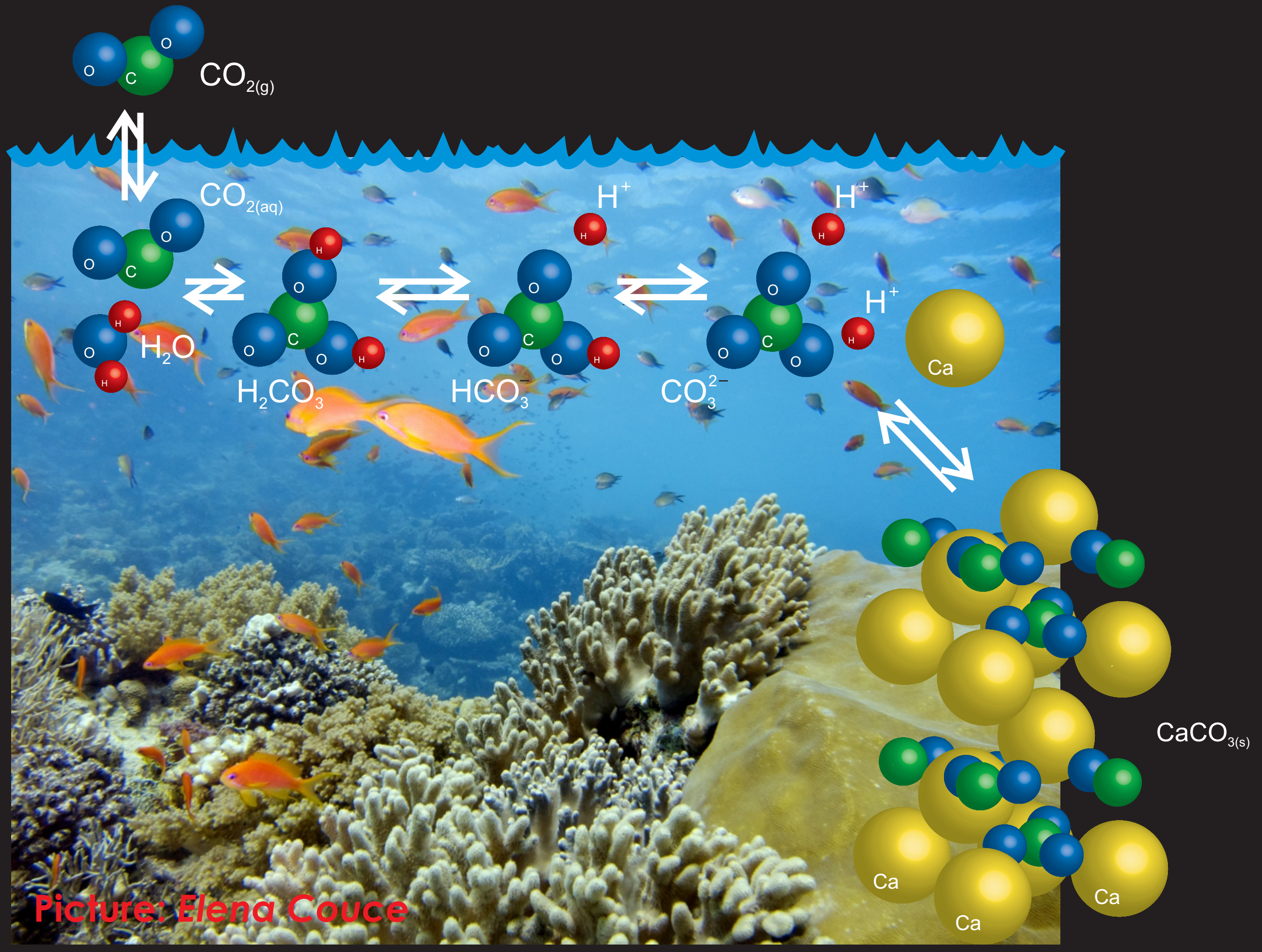
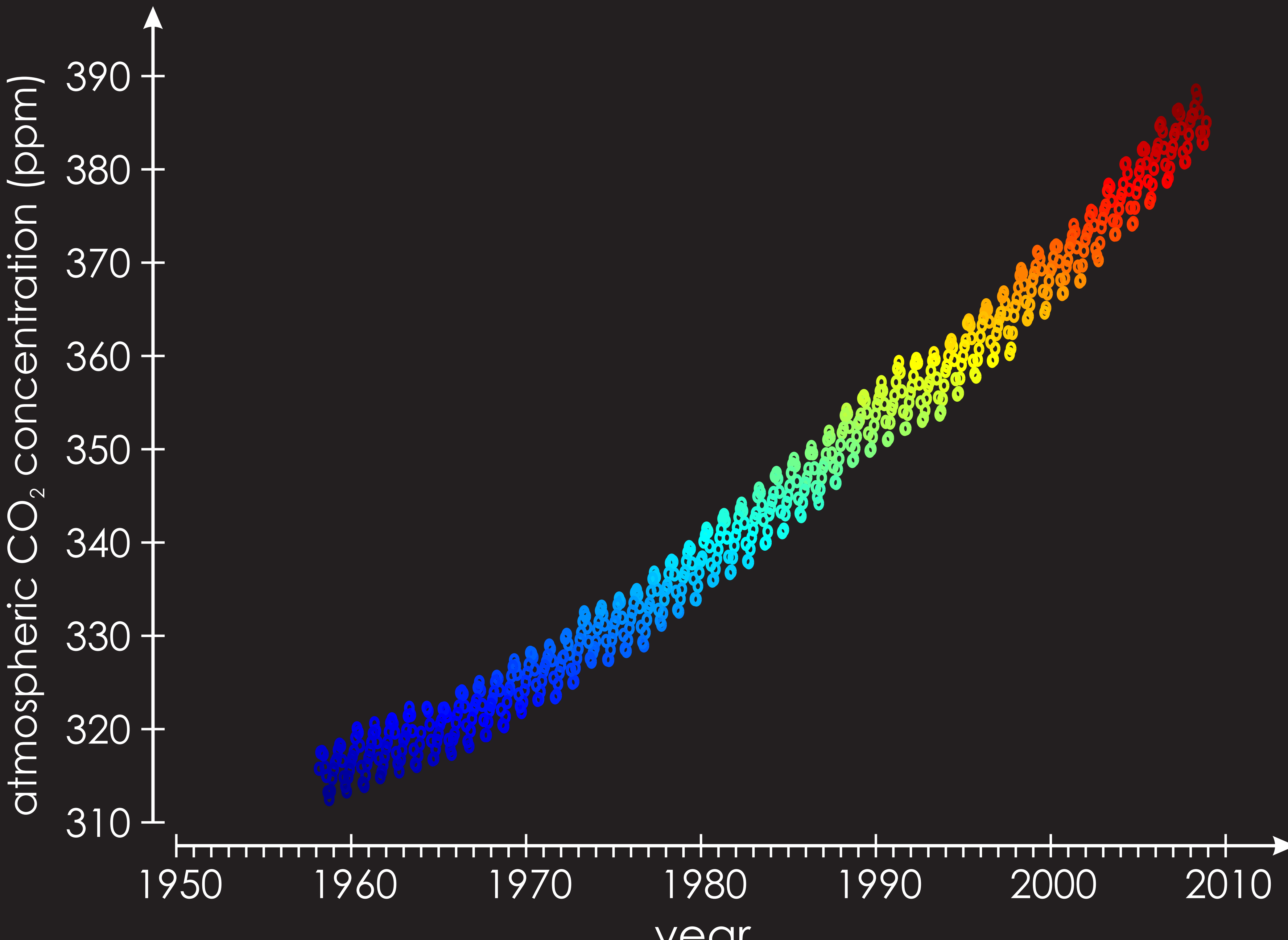
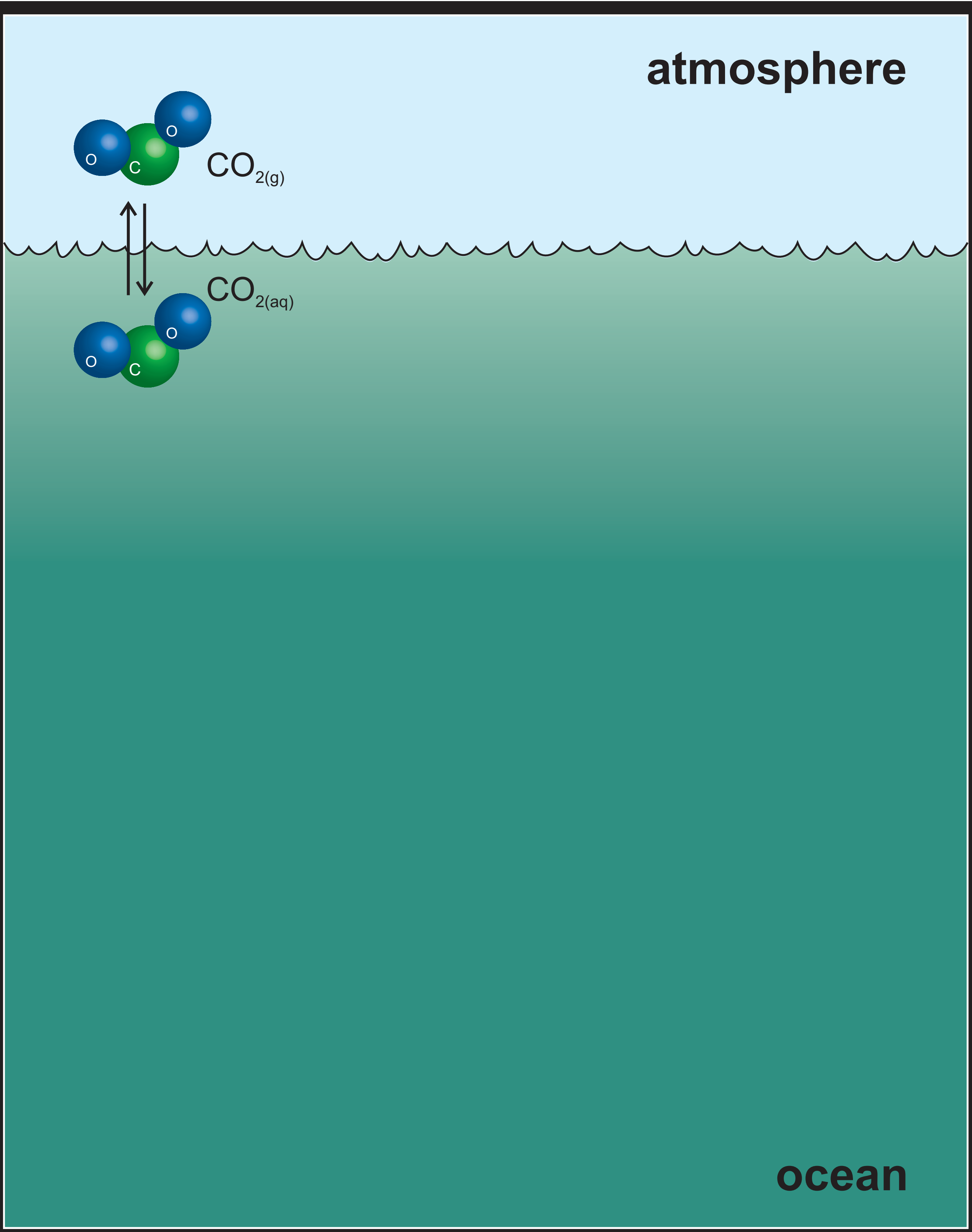
Ocean Acidification



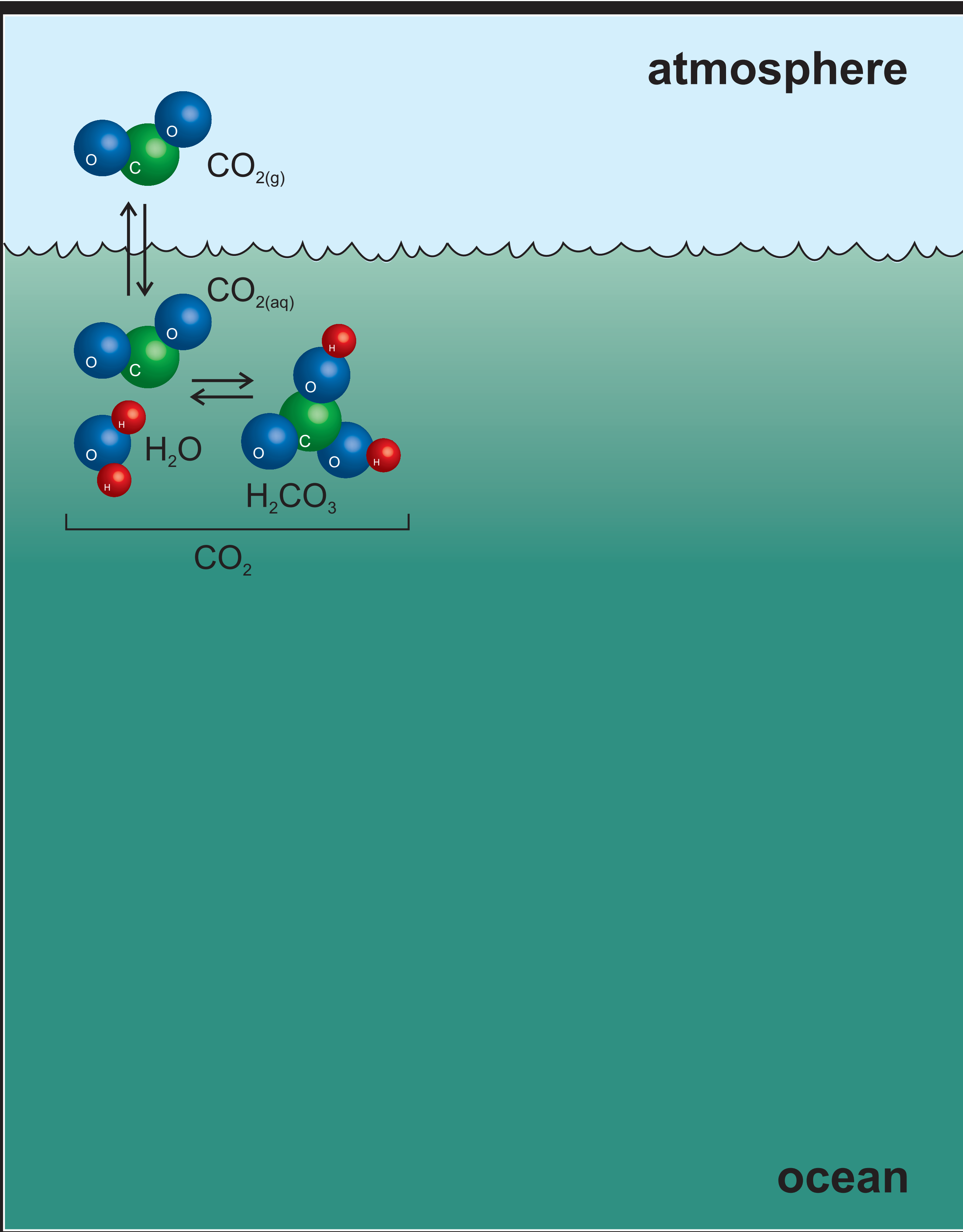


atmospheric CO_2 concentration (ppm)
390
380
370
360
350
340
330
320
310
1950
1960
1970
1980
1990
2000
2010
year

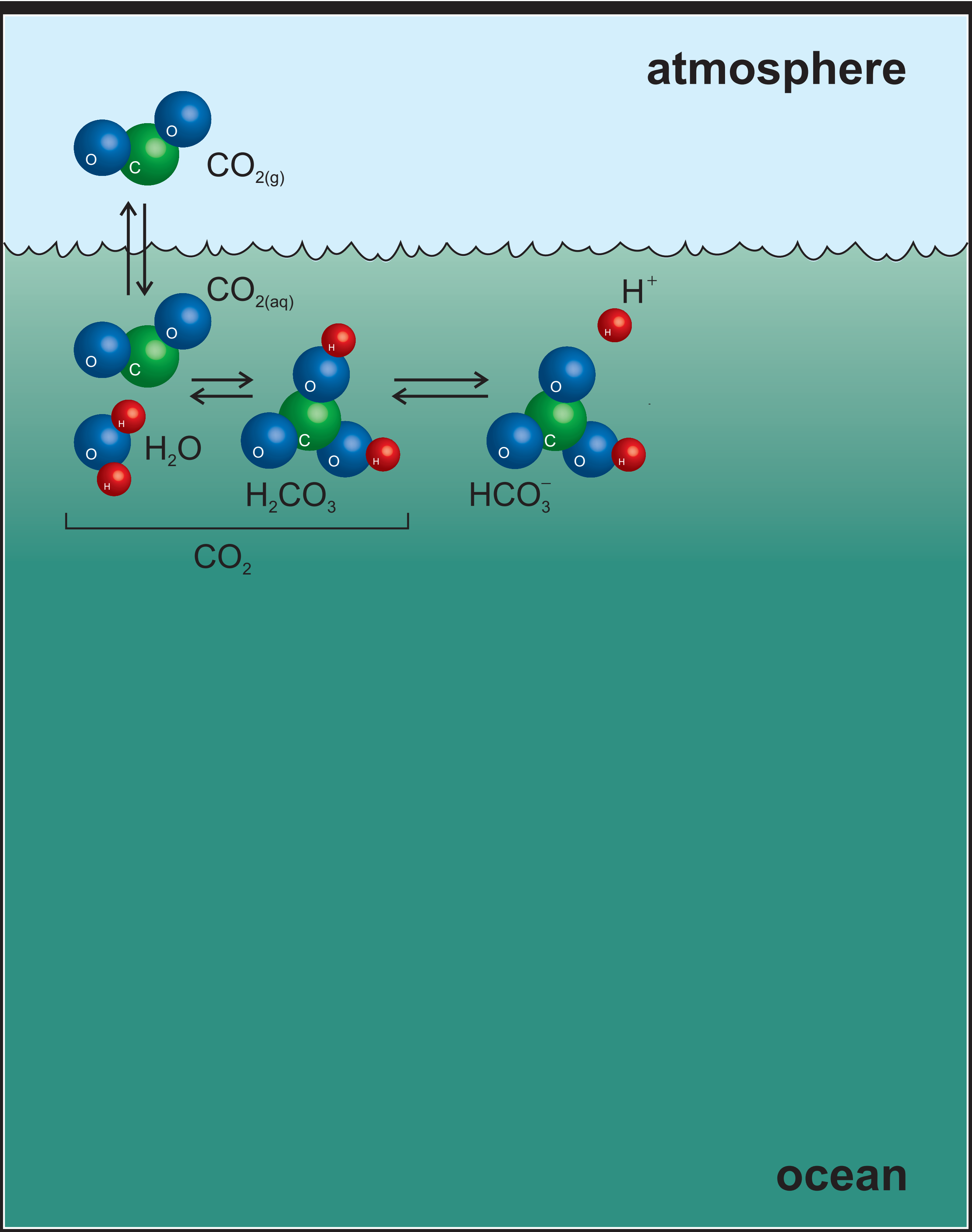
CO_2 chemistry in seawater

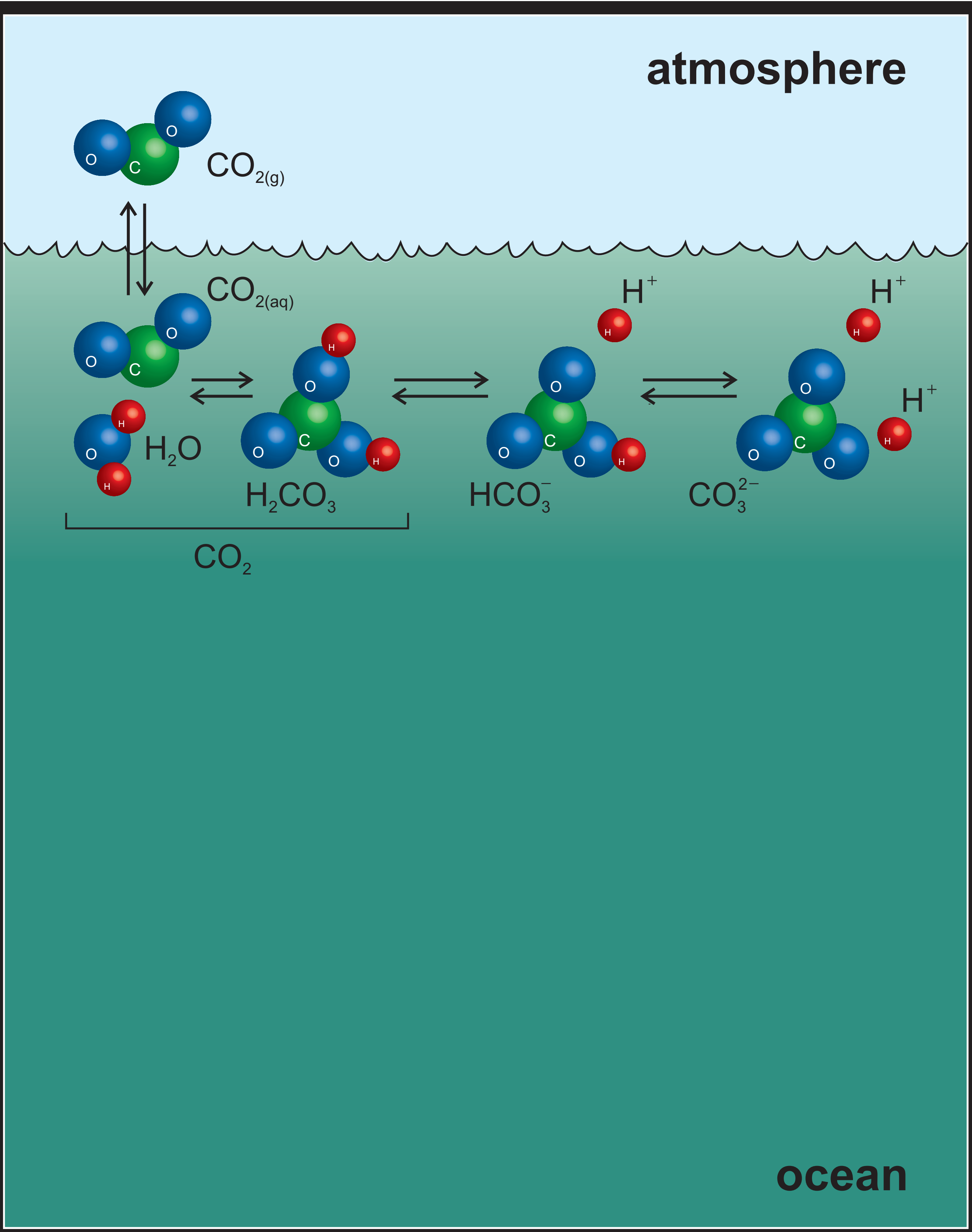


CO_2 chemistry in seawater



CO_2 chemistry in seawater



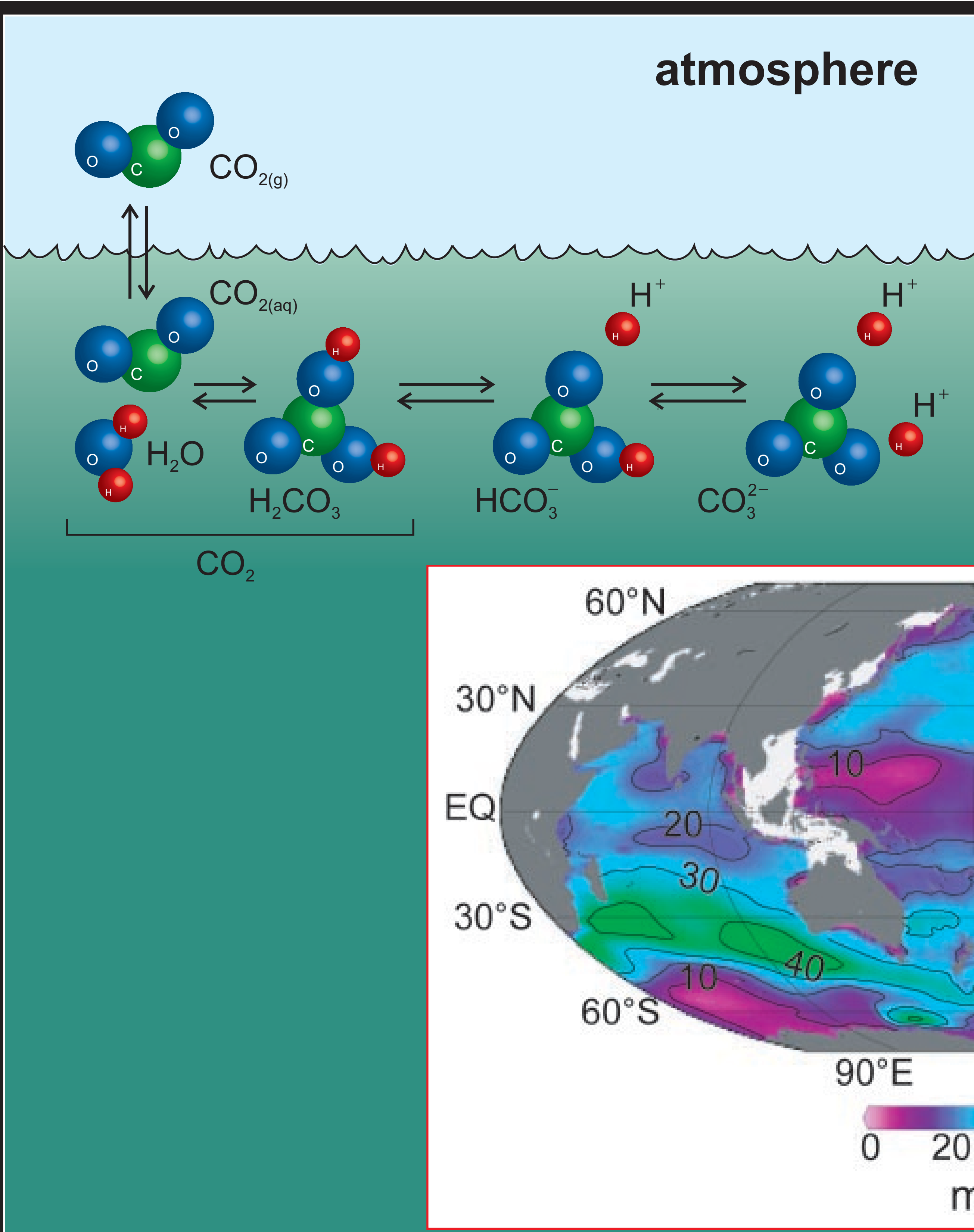


CO_2 *chemistry in seawater*

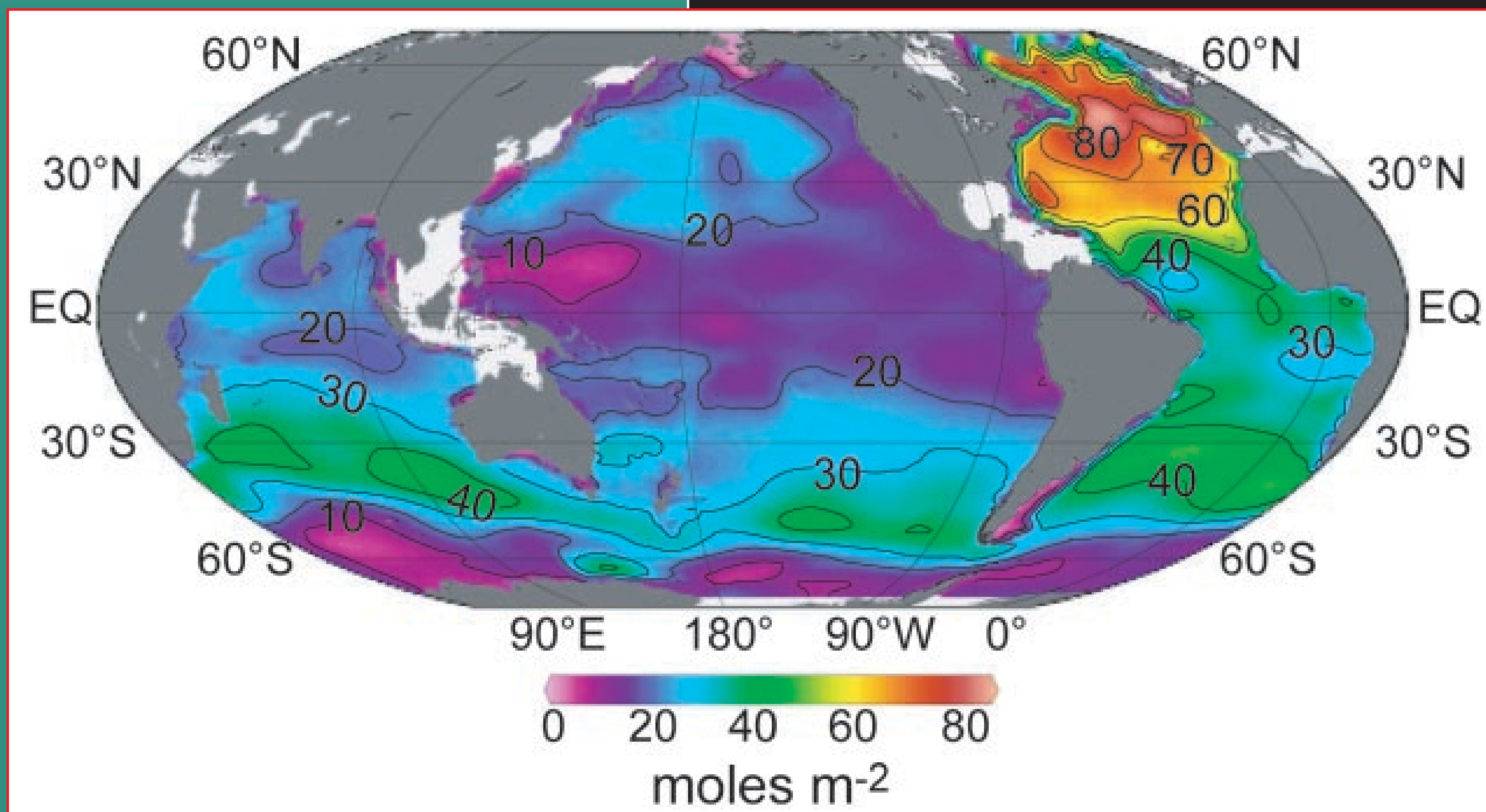
Under typical marine conditions, dissolved carbon dioxide ($CO_{2(aq)}$) will largely hydrate to form a proton (H^+) and a bicarbonate ion (HCO_3^-), which can dissociate to form another hydrogen plus carbonate ion (CO_3^{2-}).

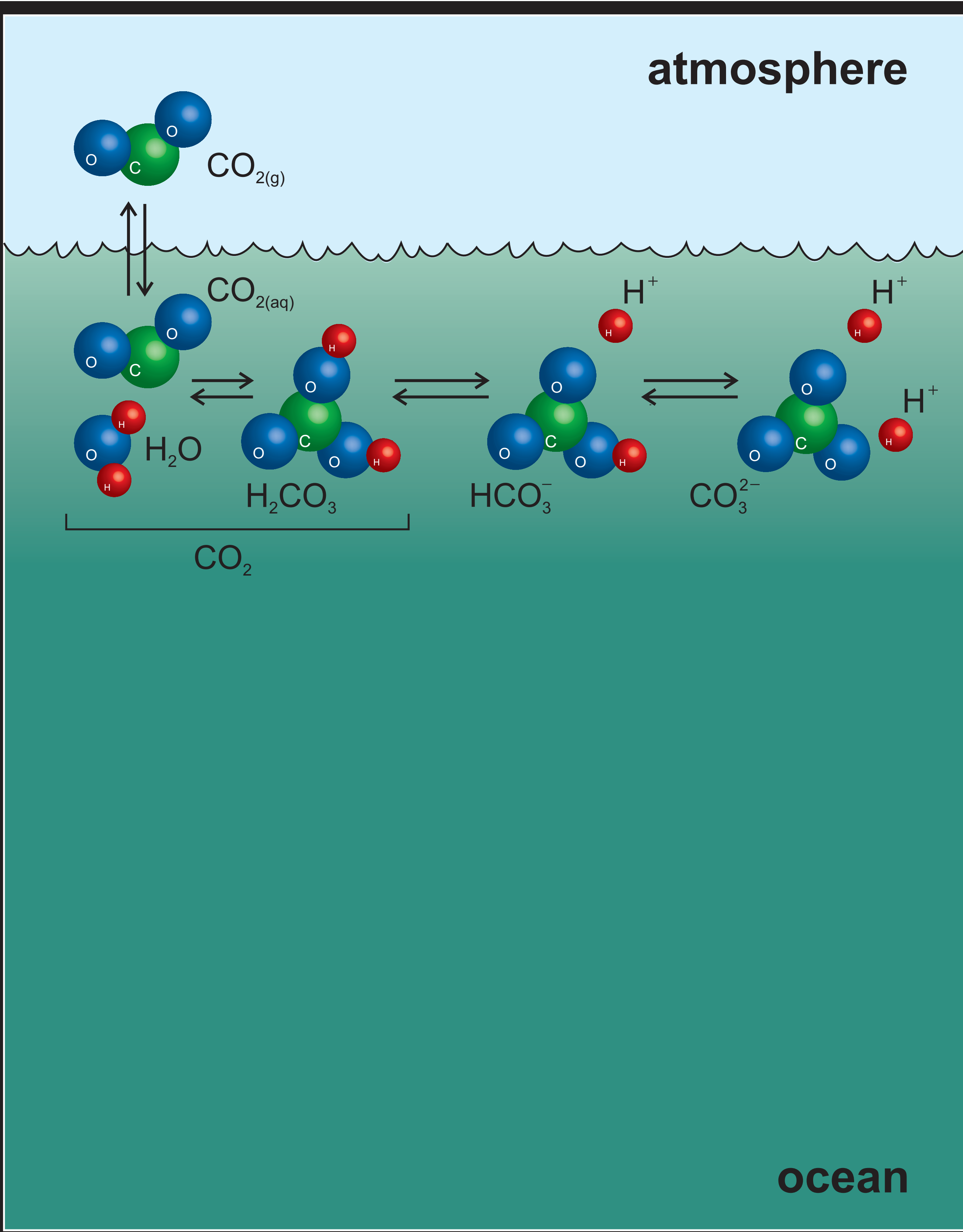
The sum total;
$CO_{2(aq)}$ (+ H_2CO_3) + HCO_3^- + CO_3^{2-}
is collectively termed dissolved inorganic carbon ('DIC').

CO_2 chemistry in seawater



From: *Sabine et al.* [2004] (*Science* 305)





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-}

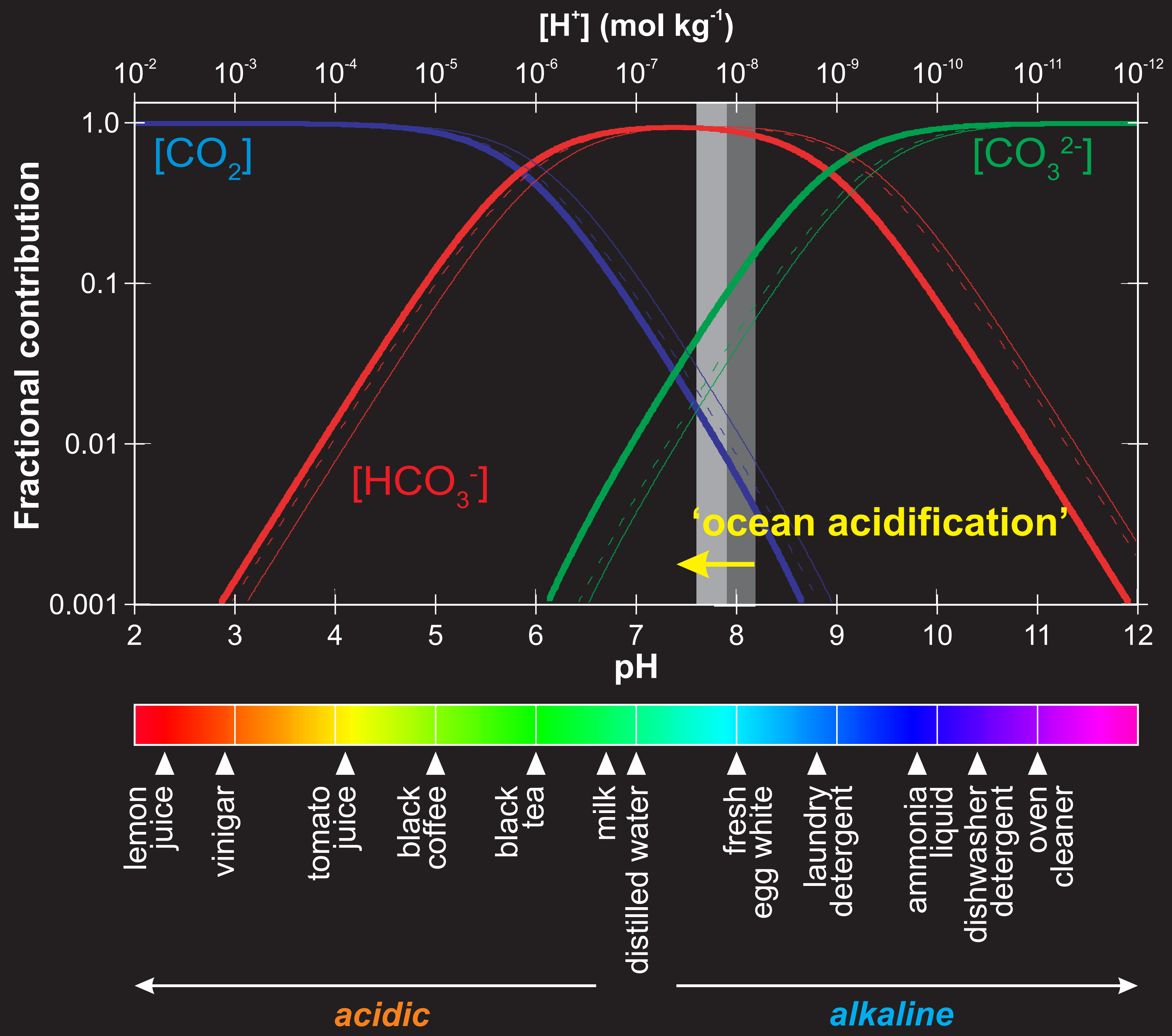
CO_2 is scavenged according to the reaction:

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

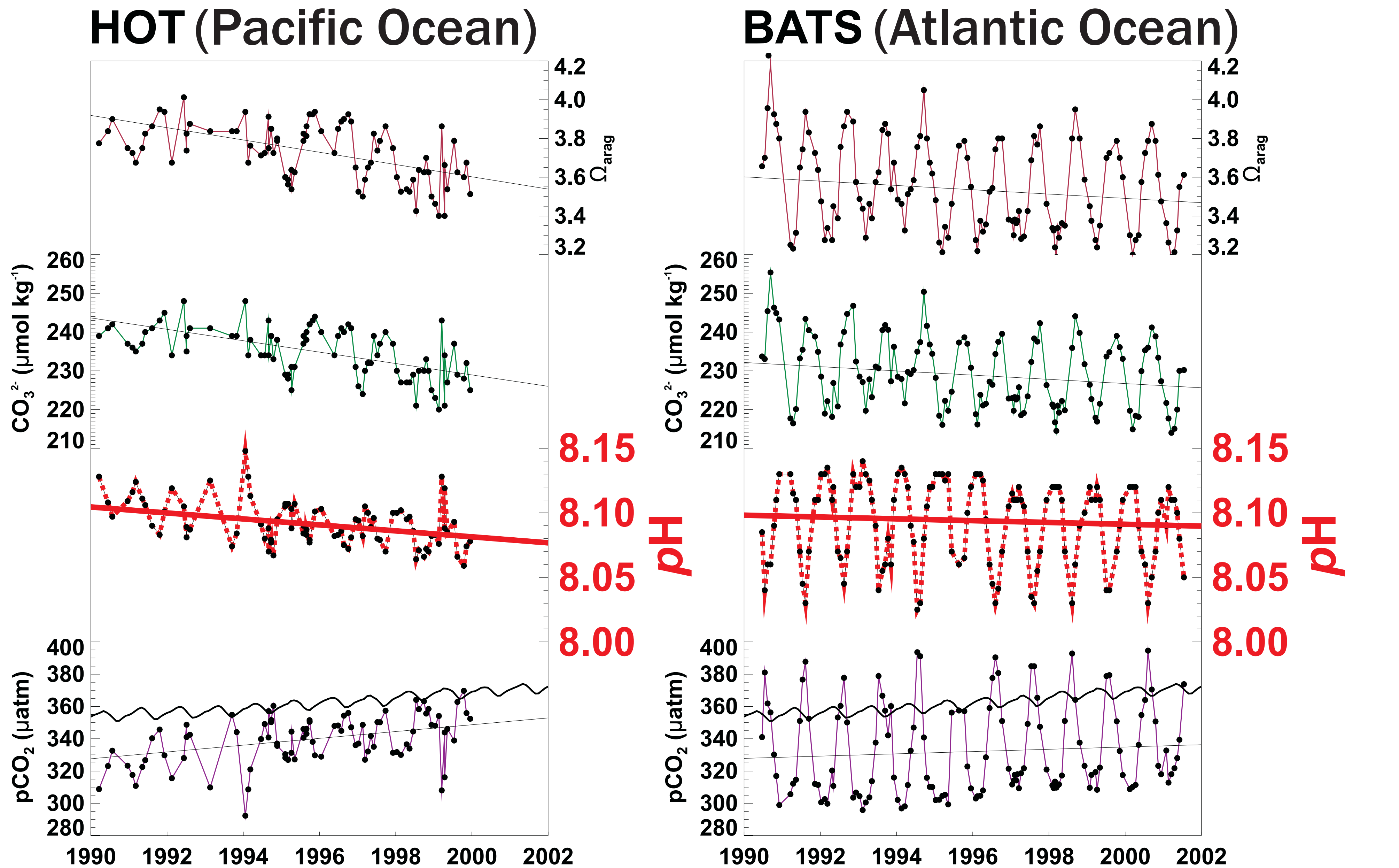
However, a small part of the resulting HCO_3^- dissociates into CO_3^{2-} and H^+, which is where the 'acidification' in ocean acidification comes from.

Don't forget that pH is a log scale, so that a 1.0 unit decrease in pH corresponds to a factor 10 increase in hydrogen ion concentration ($[H^+]$): $pH = -\log_{10}([H^+])$

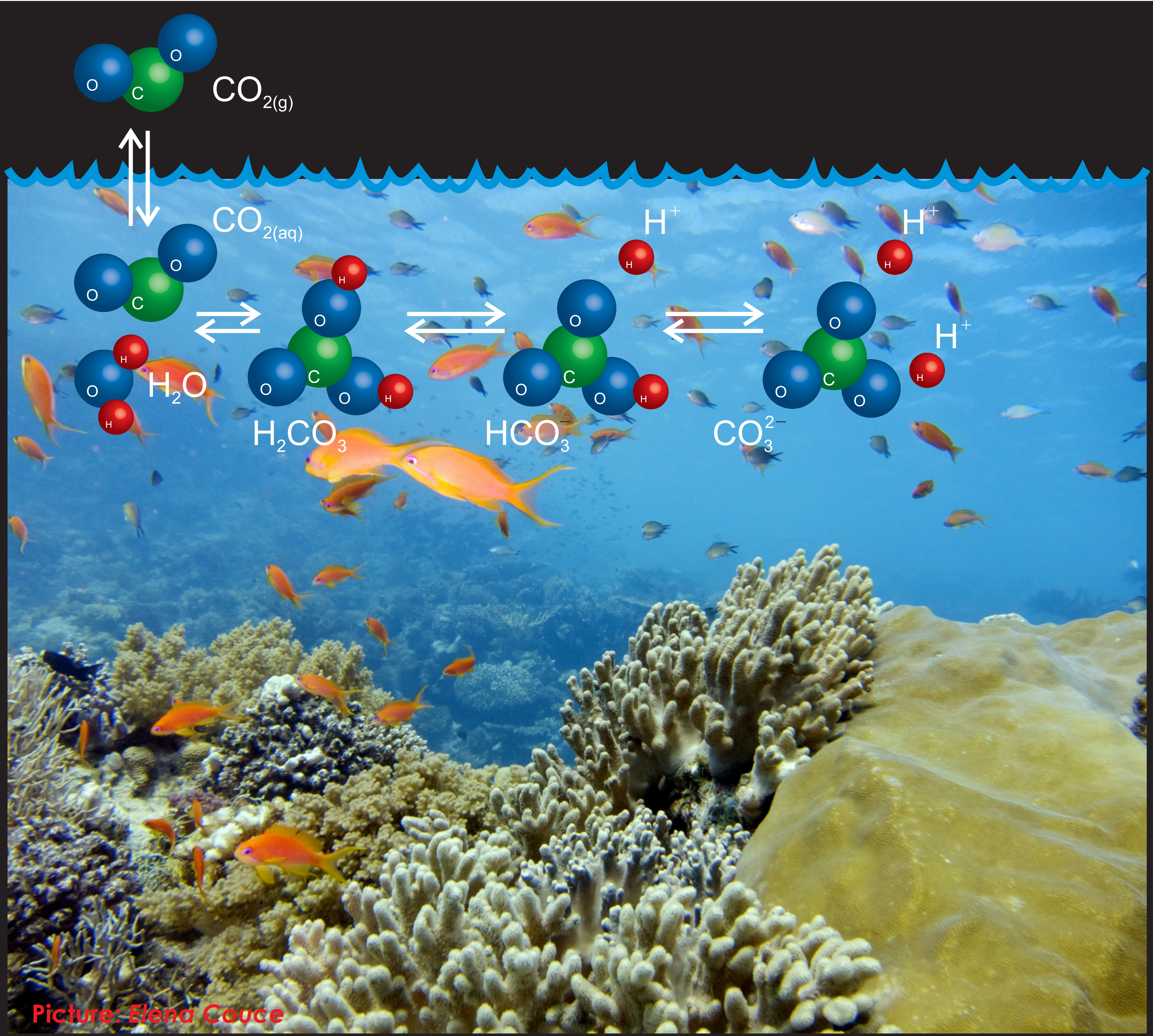
pH (and acidity vs. alkalinity)



Observations of declining ocean surface pH

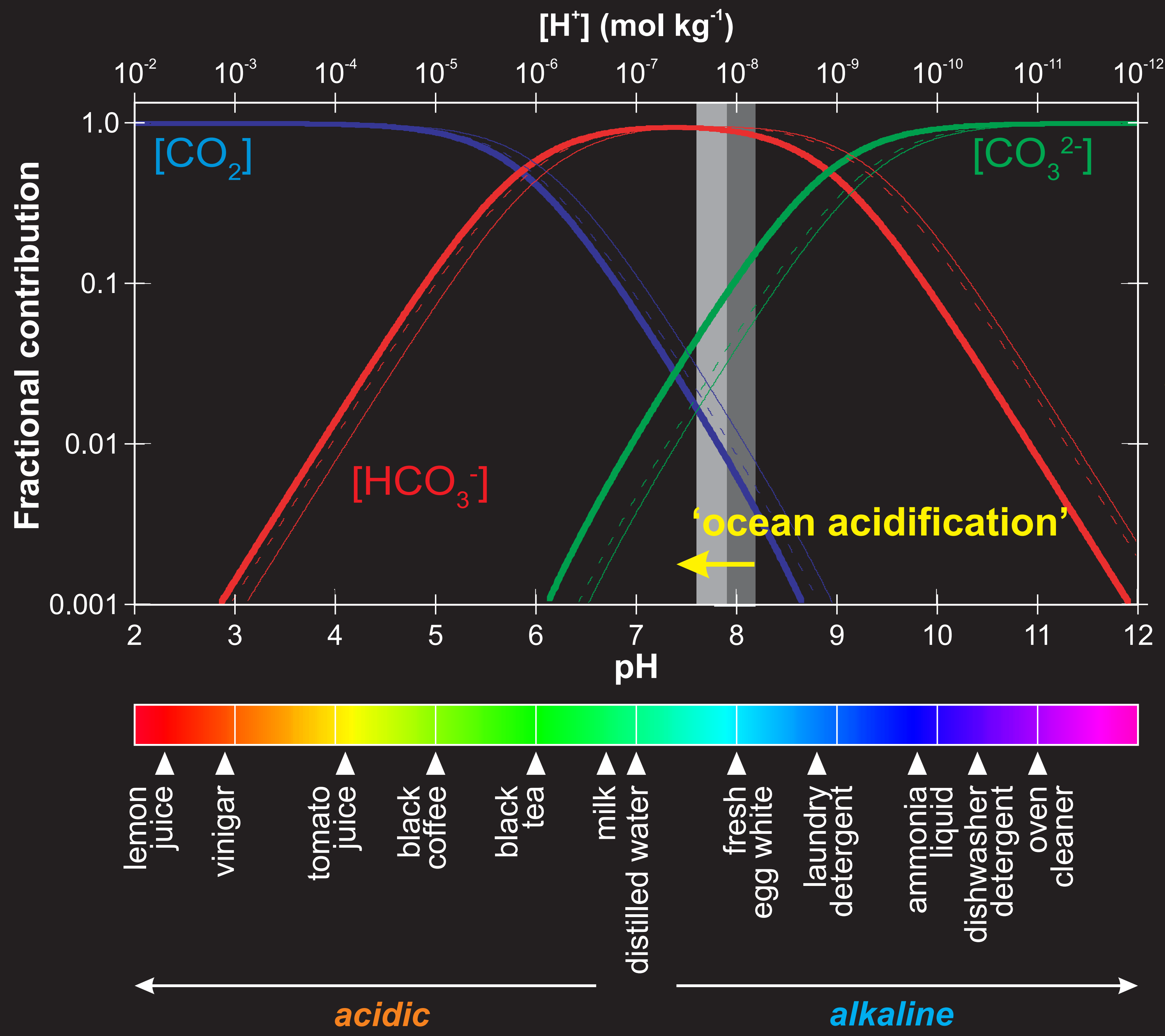


Kleypas et al. [2006]: http://www.ucar.edu/communications/Final_acidification.pdf



$CO_{2(g)}$
$CO_{2(aq)}$
H_2O
H_2CO_3
HCO_3^-
CO_3^{2-}
H^+
H^+
H^+
Picture: Elena Couce

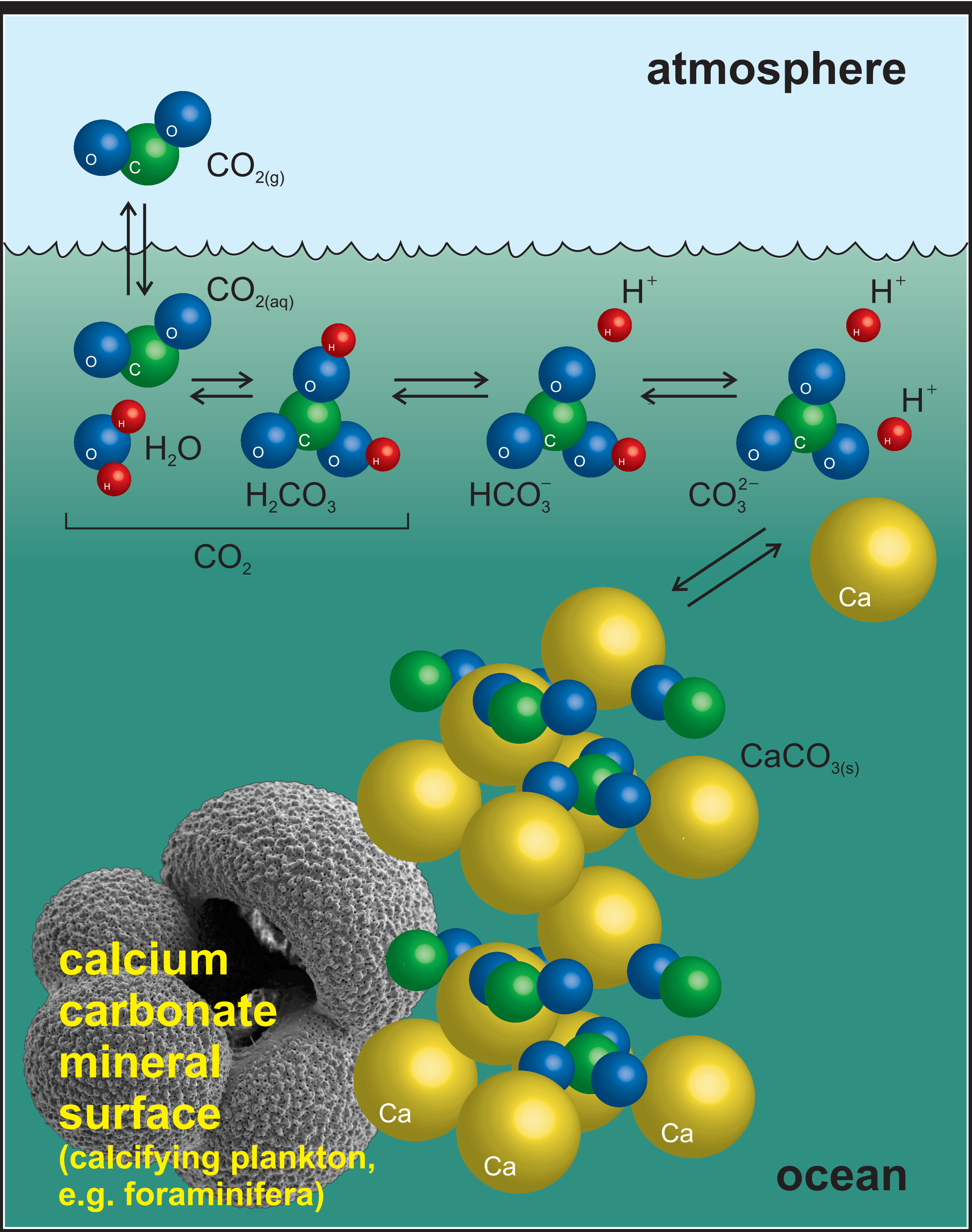
pH (and acidity vs. alkalinity)



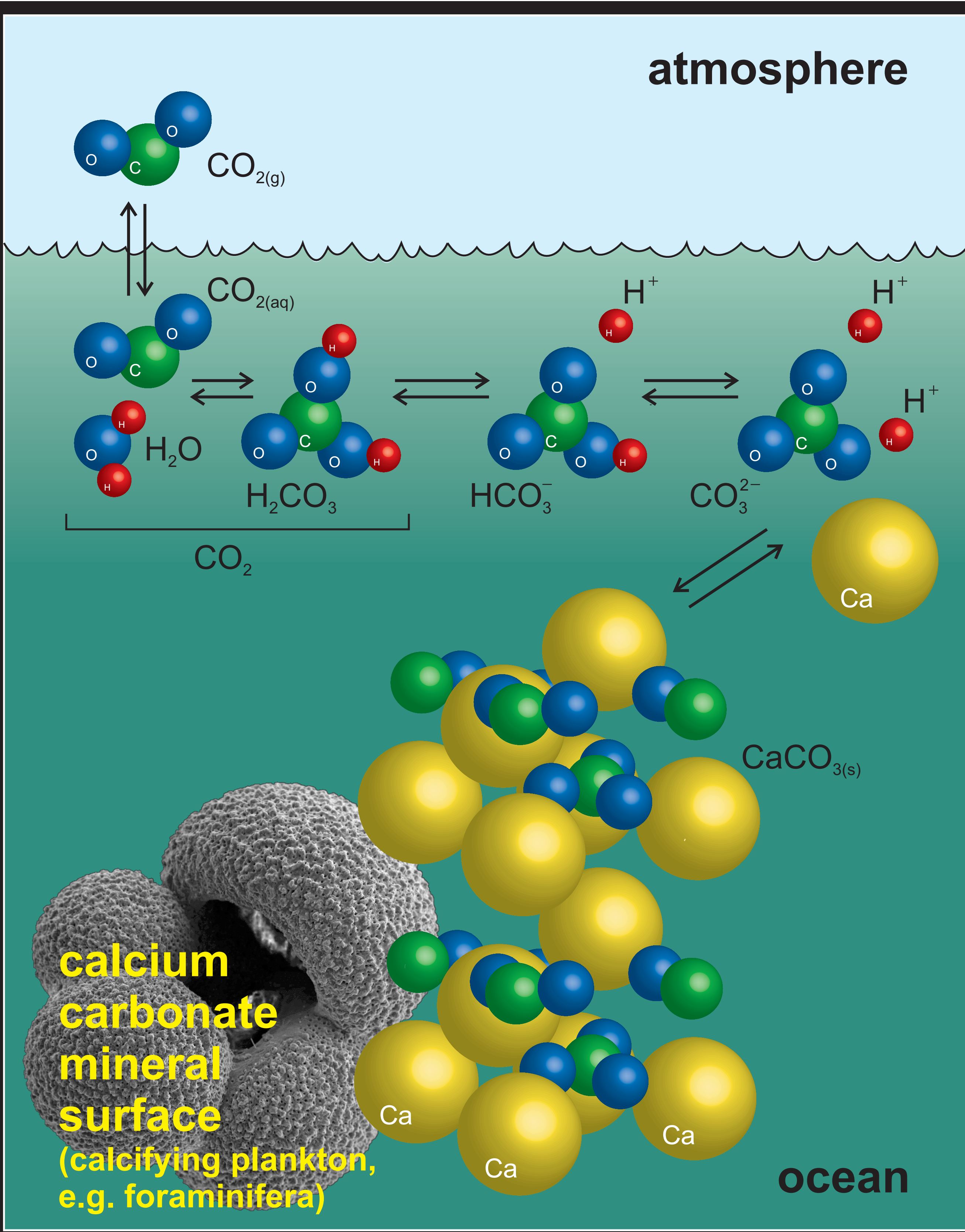
Direct impacts on micro-organisms in the ocean are currently thought likely to be small, although changes in *p*H will affect nutrient concentrations and trace metal speciation.

Larger (multicellular) animals may be affected as increased CO_2 will acidify the body tissues and fluids and affect the ability of blood to carry oxygen ('hypercapnia').

CO_2 chemistry & mineral phases



CO_2 chemistry & mineral phases



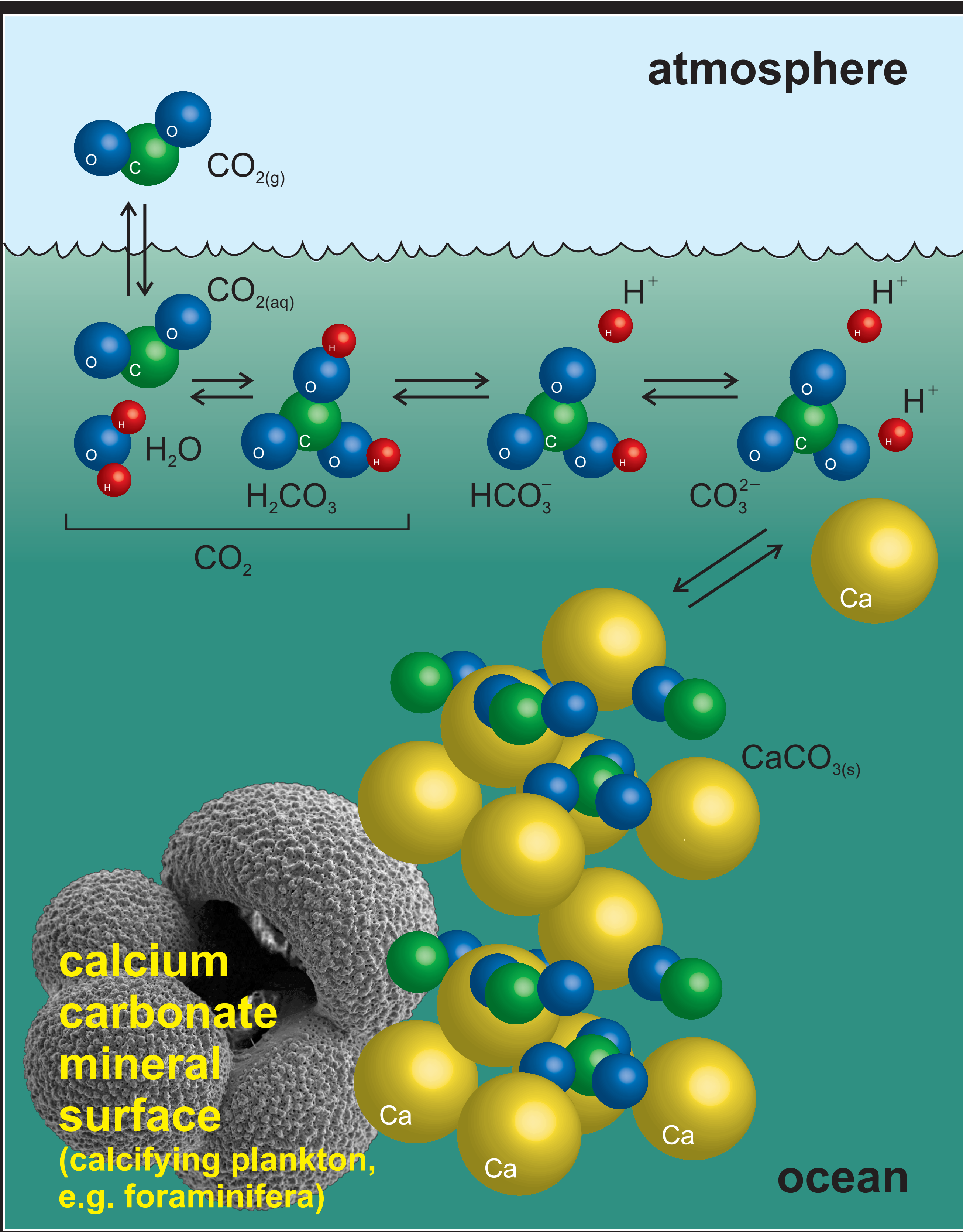
Aragonite: less stable

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

Calcite: more stable

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

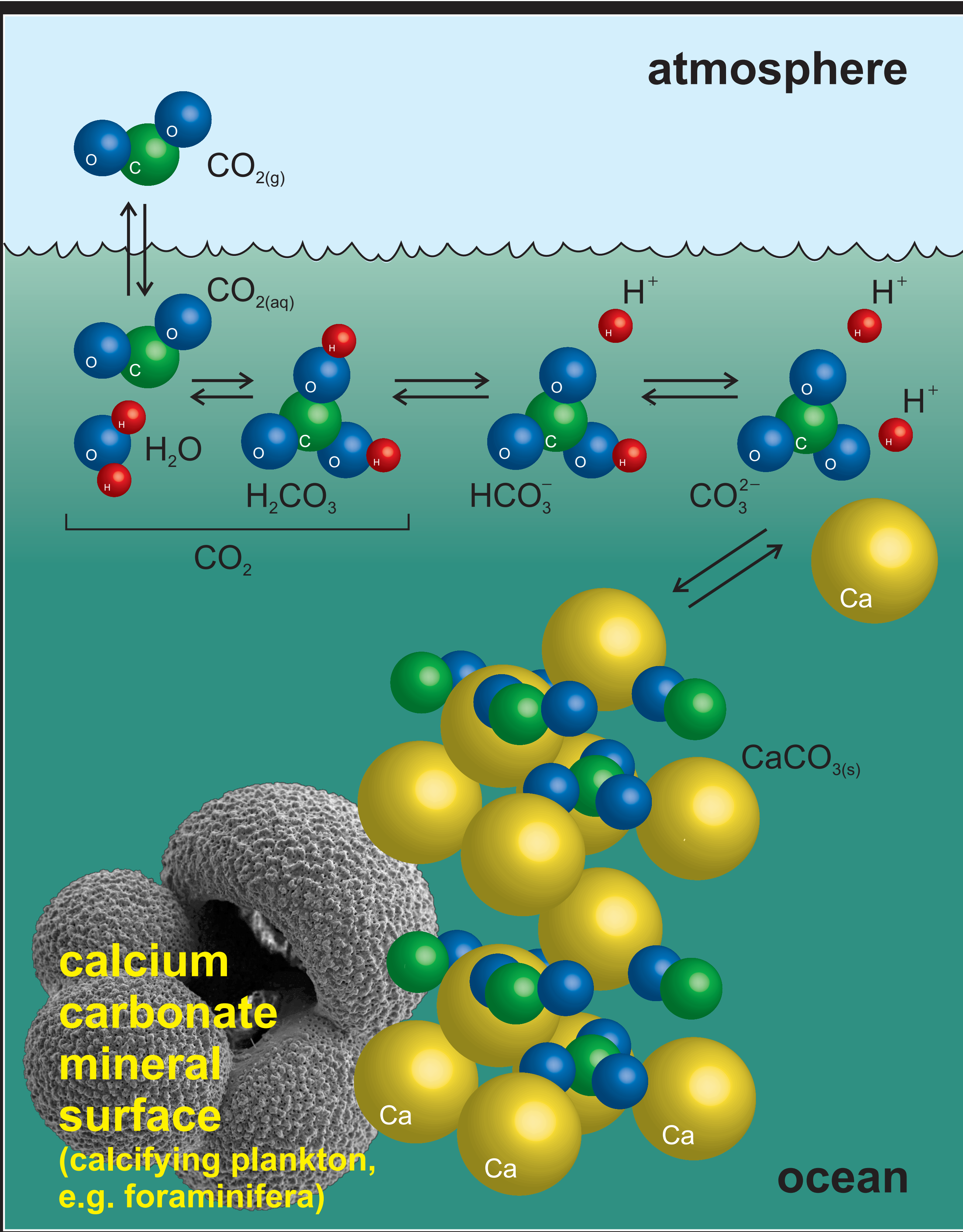
CO_2 chemistry & mineral phases



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

→

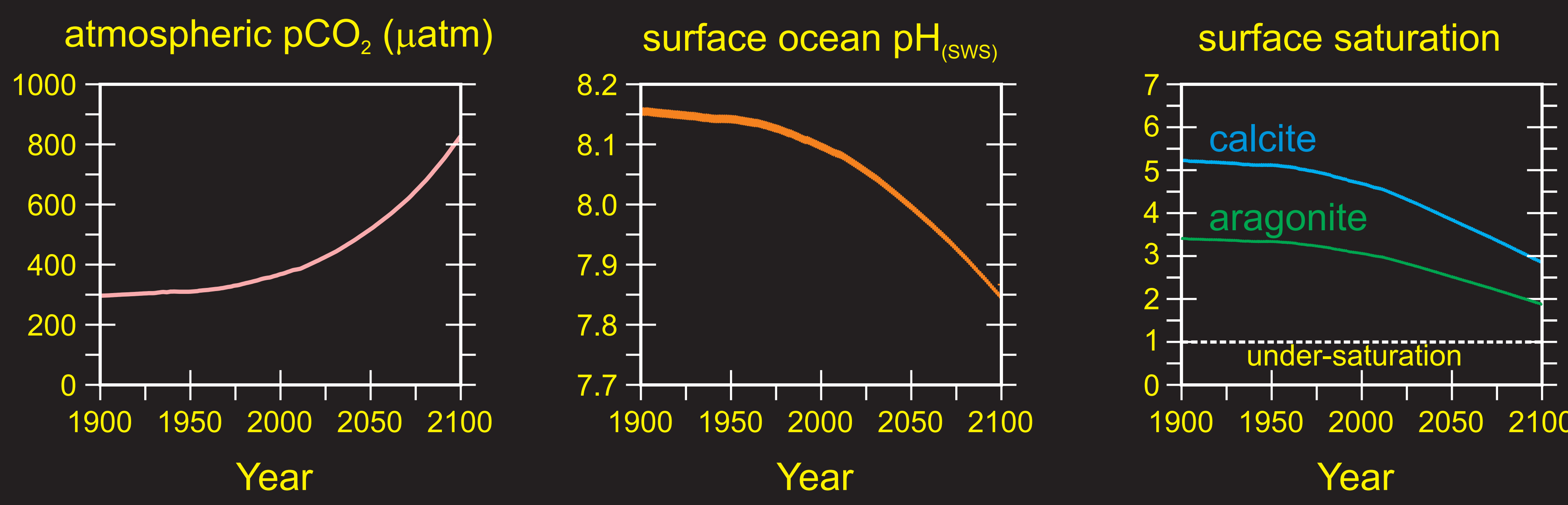
less CO_3^{2-} (& lower pH)

→

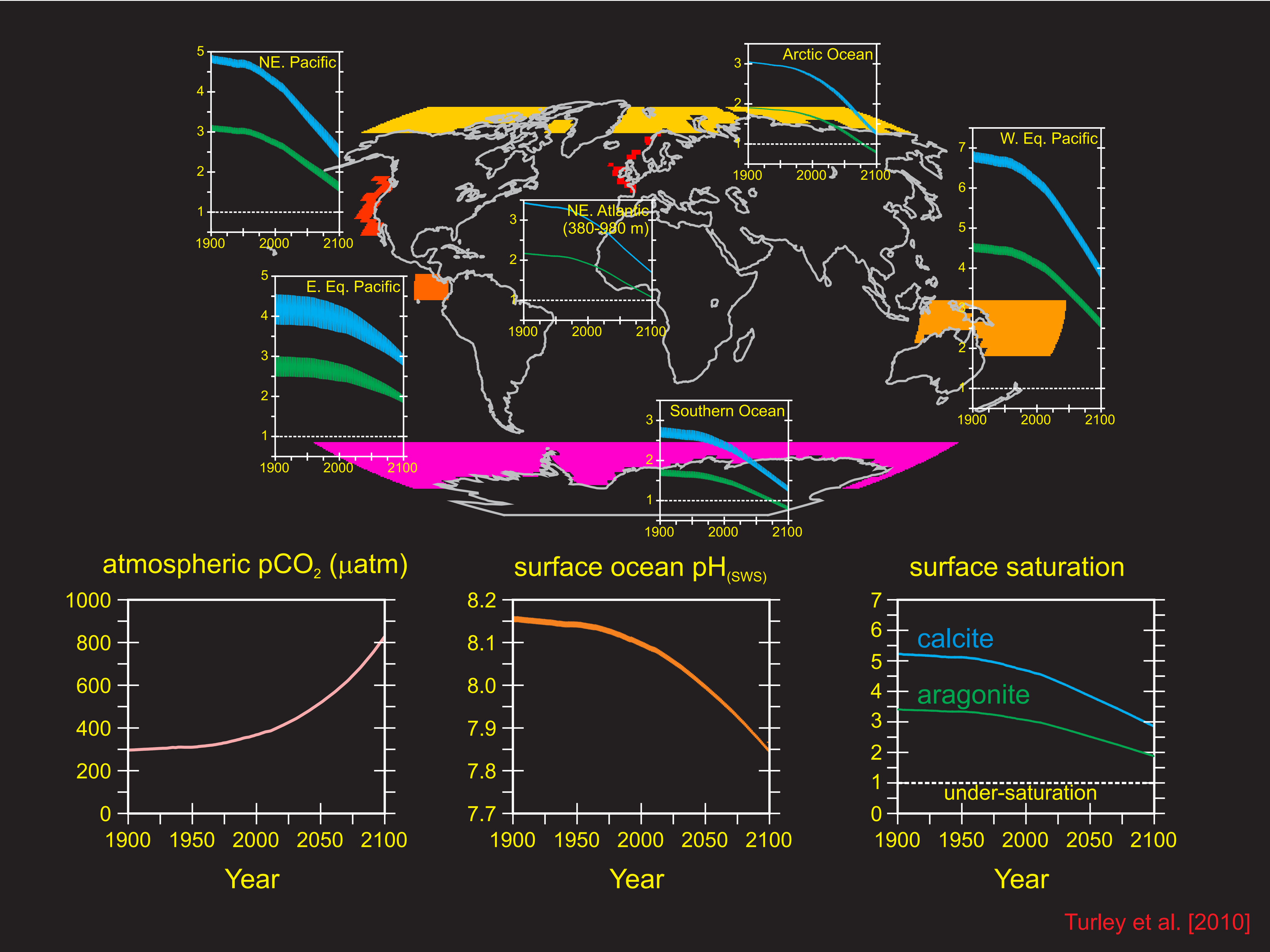
lower saturation (Ω) & less stable $CaCO_3$

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

Changing Ocean Chemsitry

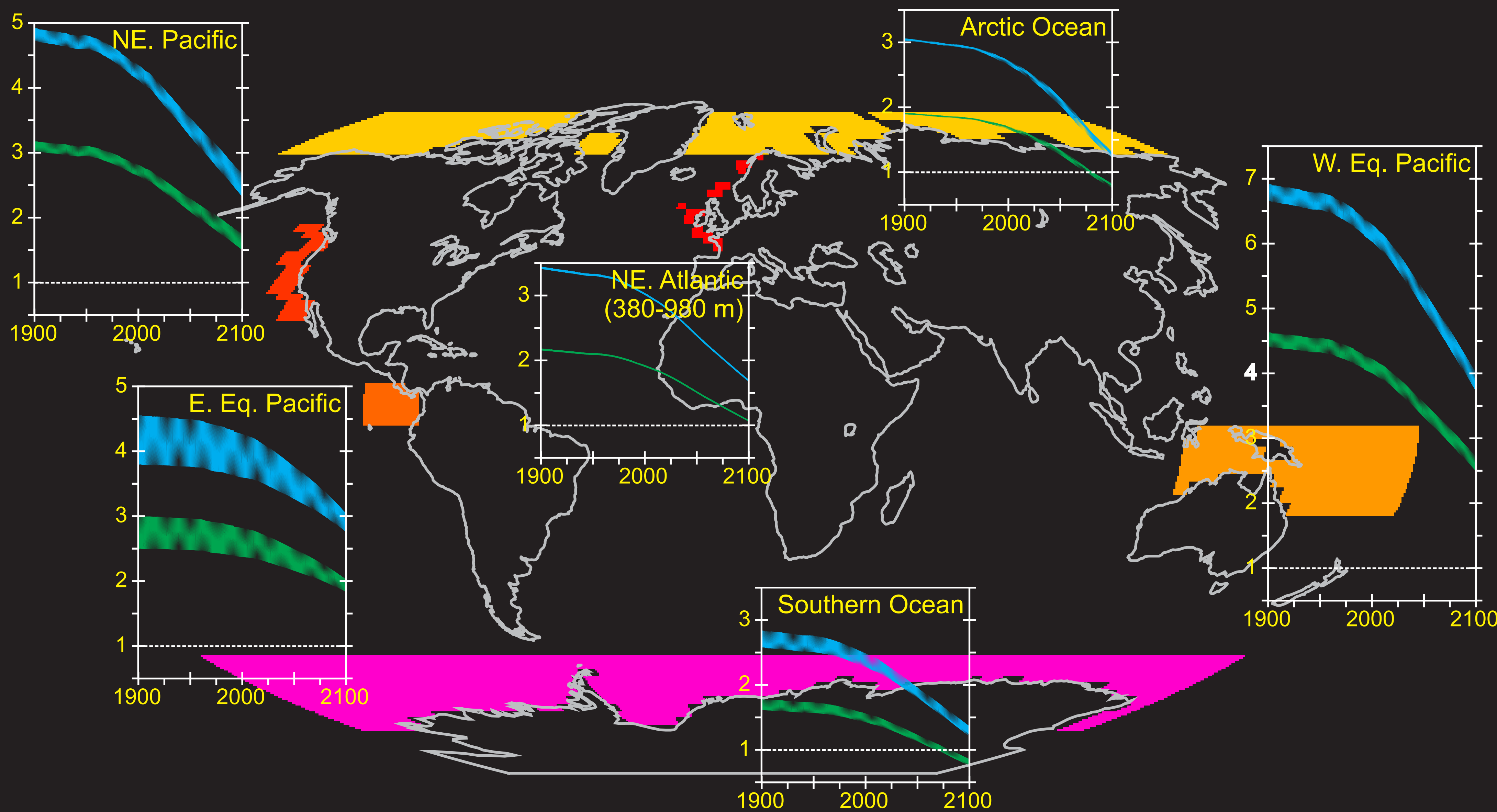


Turley et al. [2010]



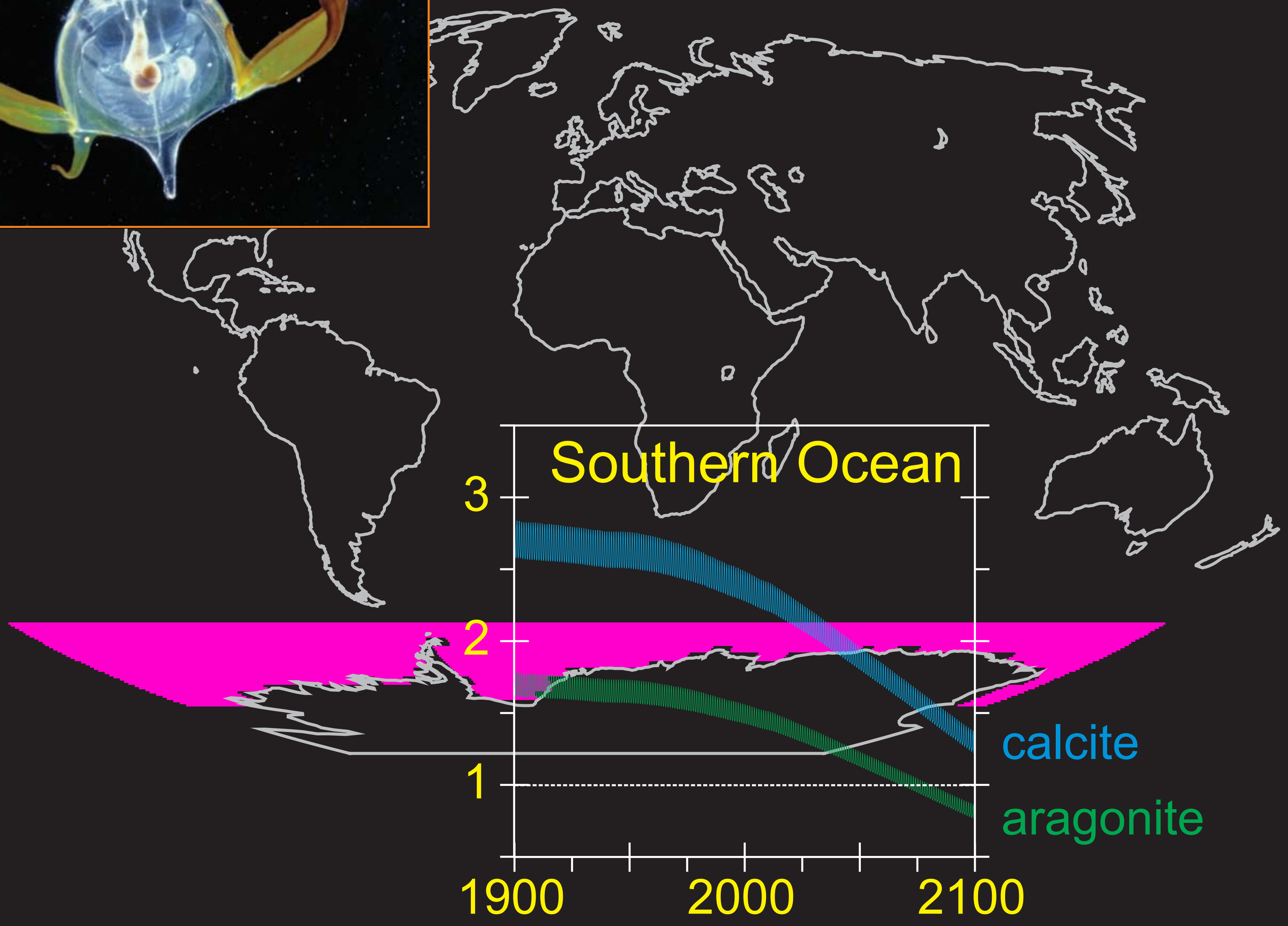
NE. Pacific
Arctic Ocean
W. Eq. Pacific
NE. Atlantic (380-980 m)
E. Eq. Pacific
Southern Ocean
atmospheric pCO$_2$ (μatm)
surface ocean pH$_{(SWS)}$
surface saturation
calcite
aragonite
under-saturation
Year
Year
Year
Turley et al. [2010]

Seasonal/Regional impacts of ocean acidification

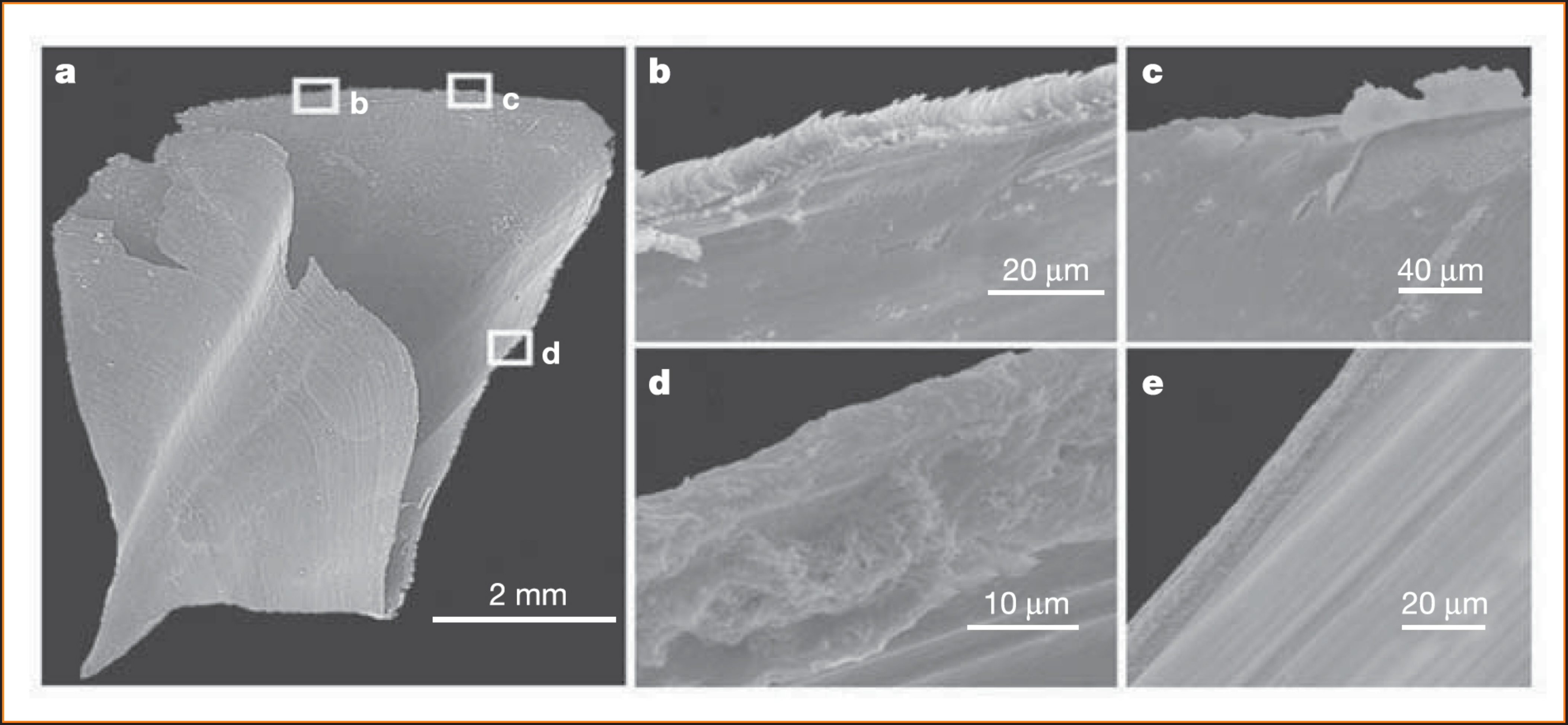


Turley et al. [2010]

Ocean biological consequences(?)

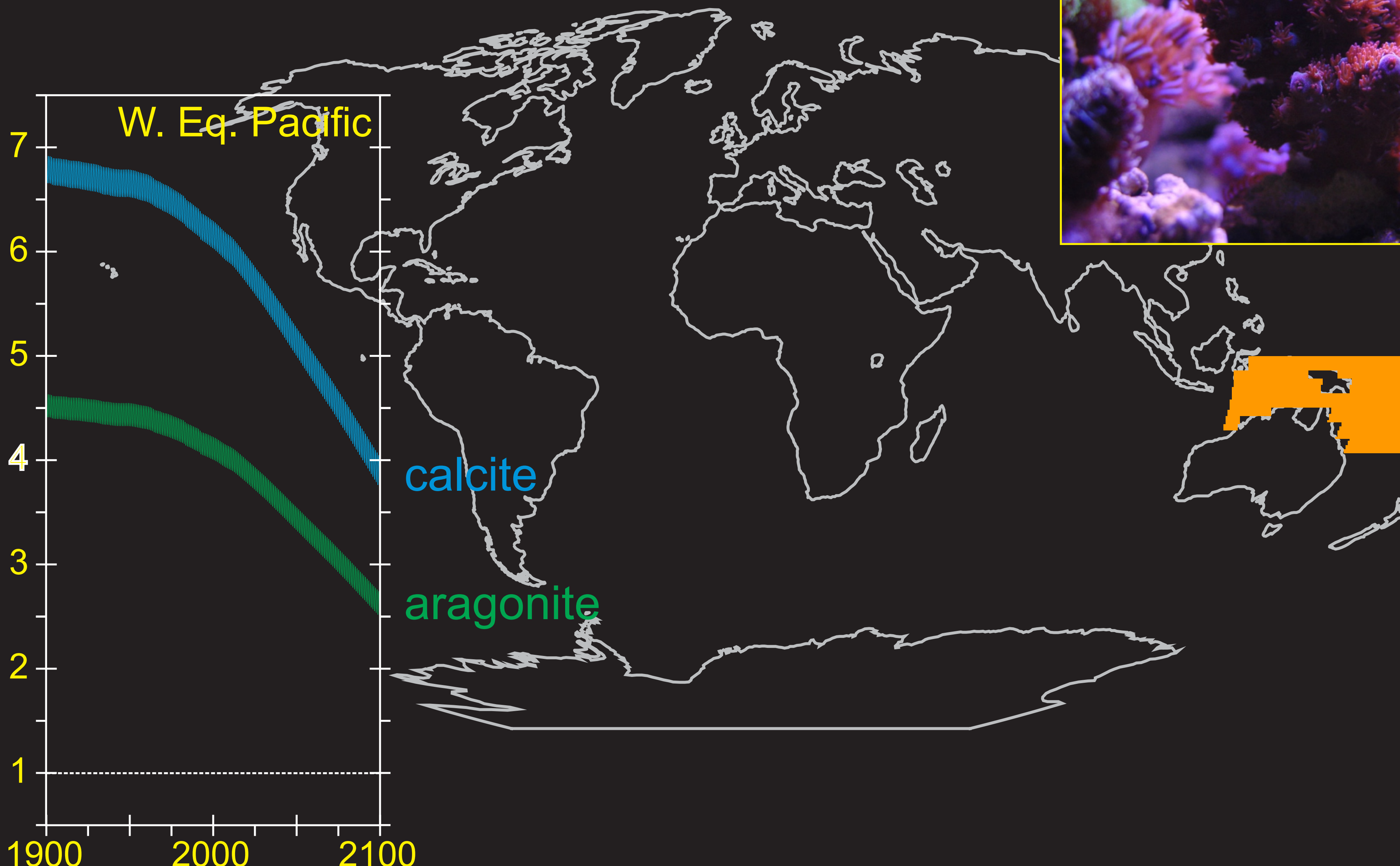


Ocean biological consequences(?)



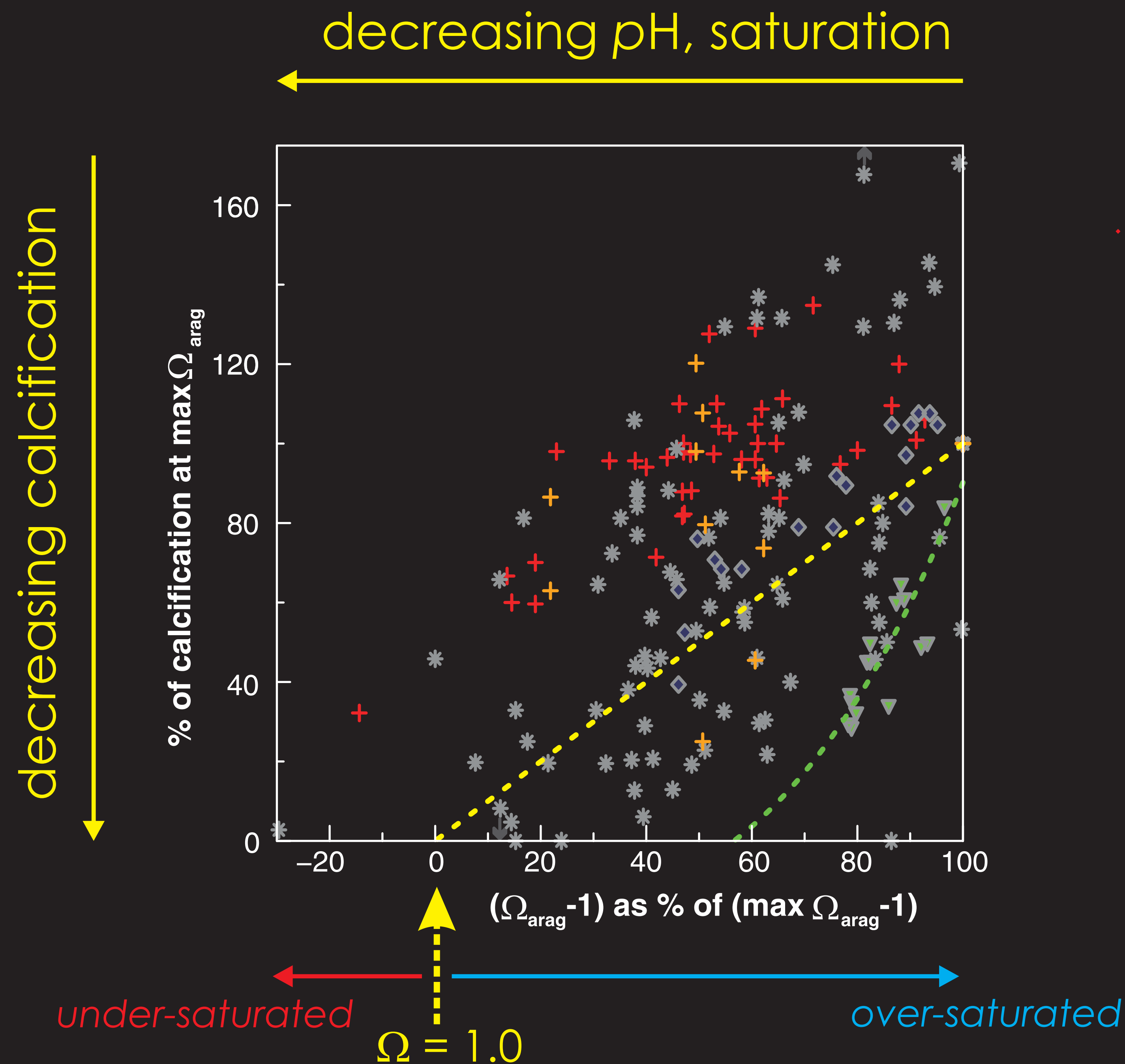
Orr et al. [2005] (Nature 437)

Ocean biological consequences(?)



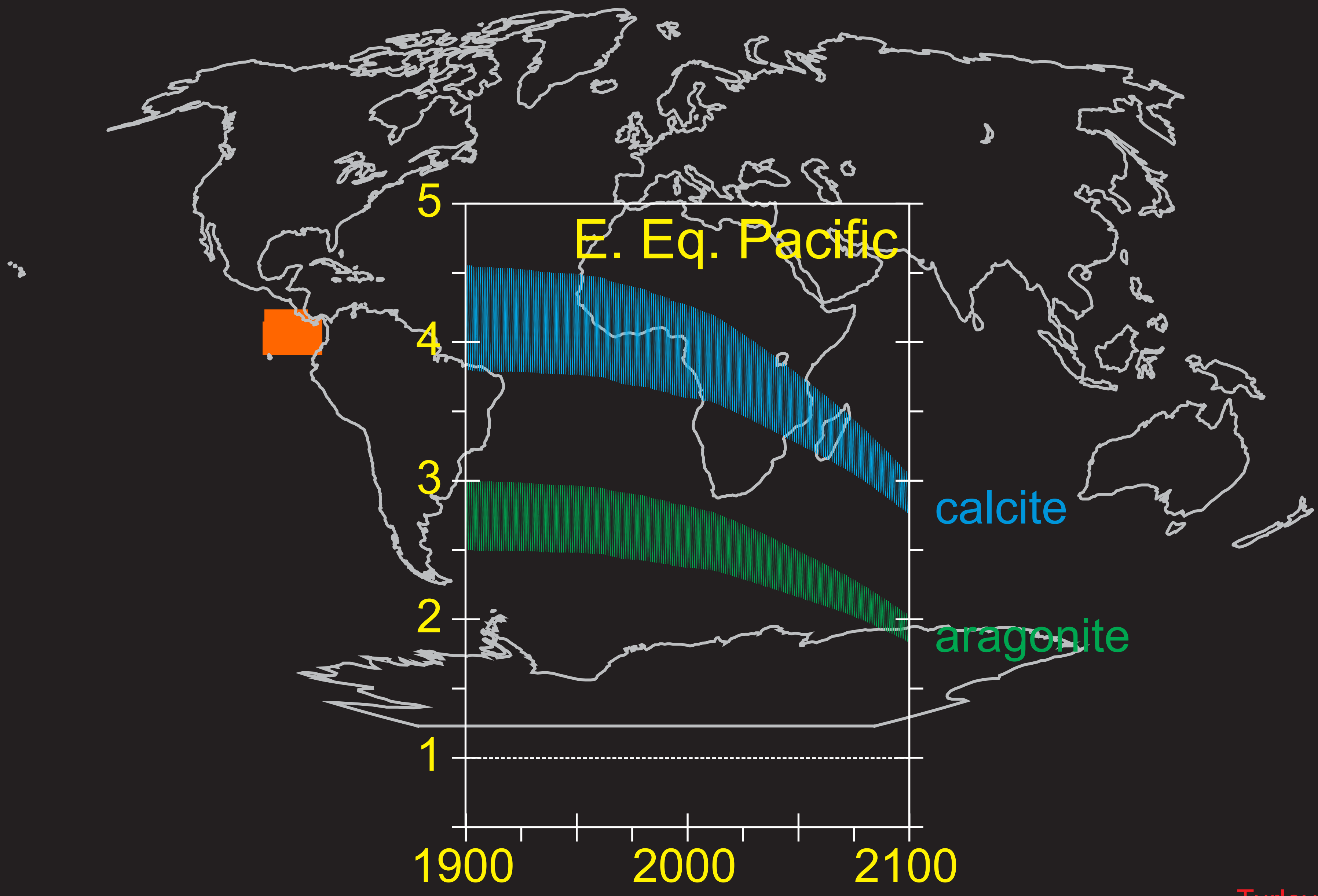
Turley et al. [2010]

Ocean biological consequences(?)



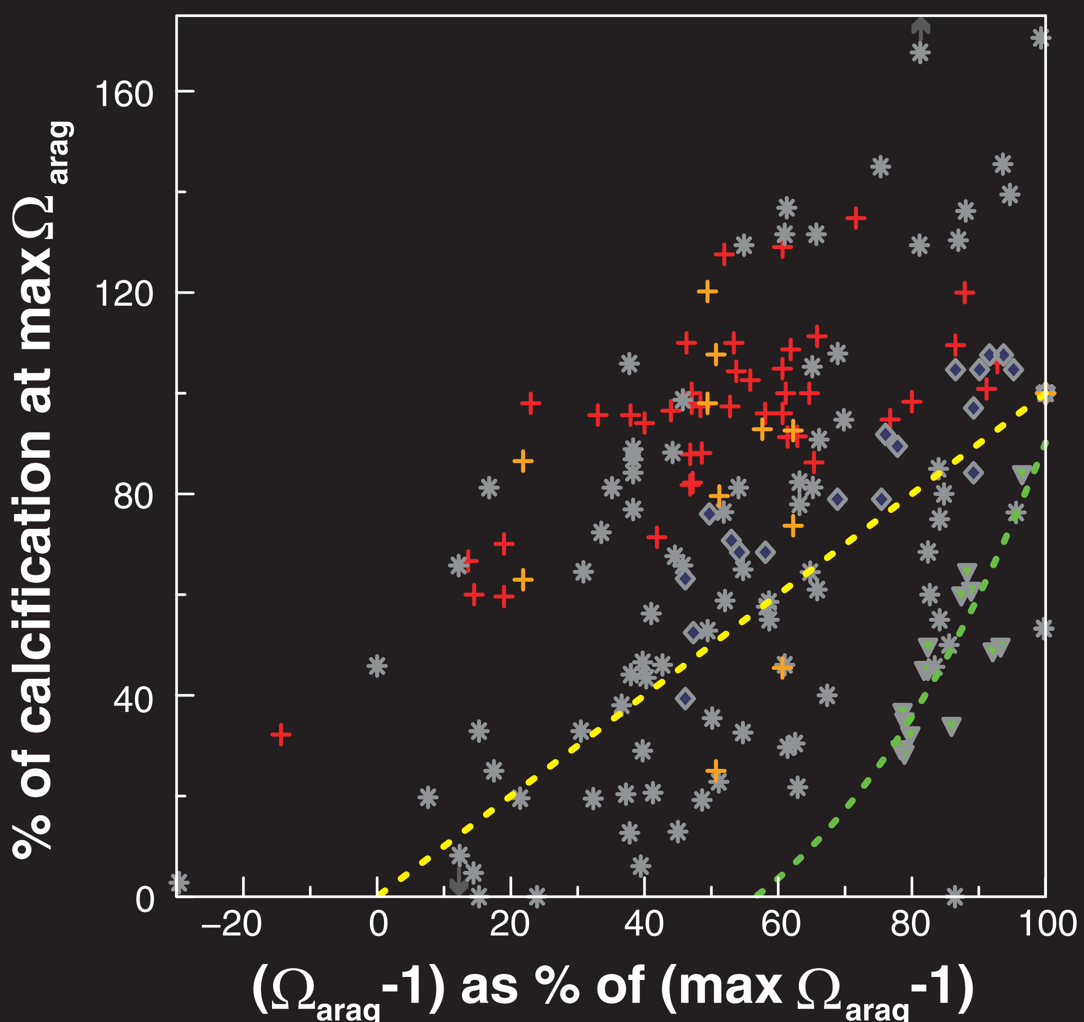
Pandolfi et al. [2011] (*Science*)

Ocean biological consequences(?)



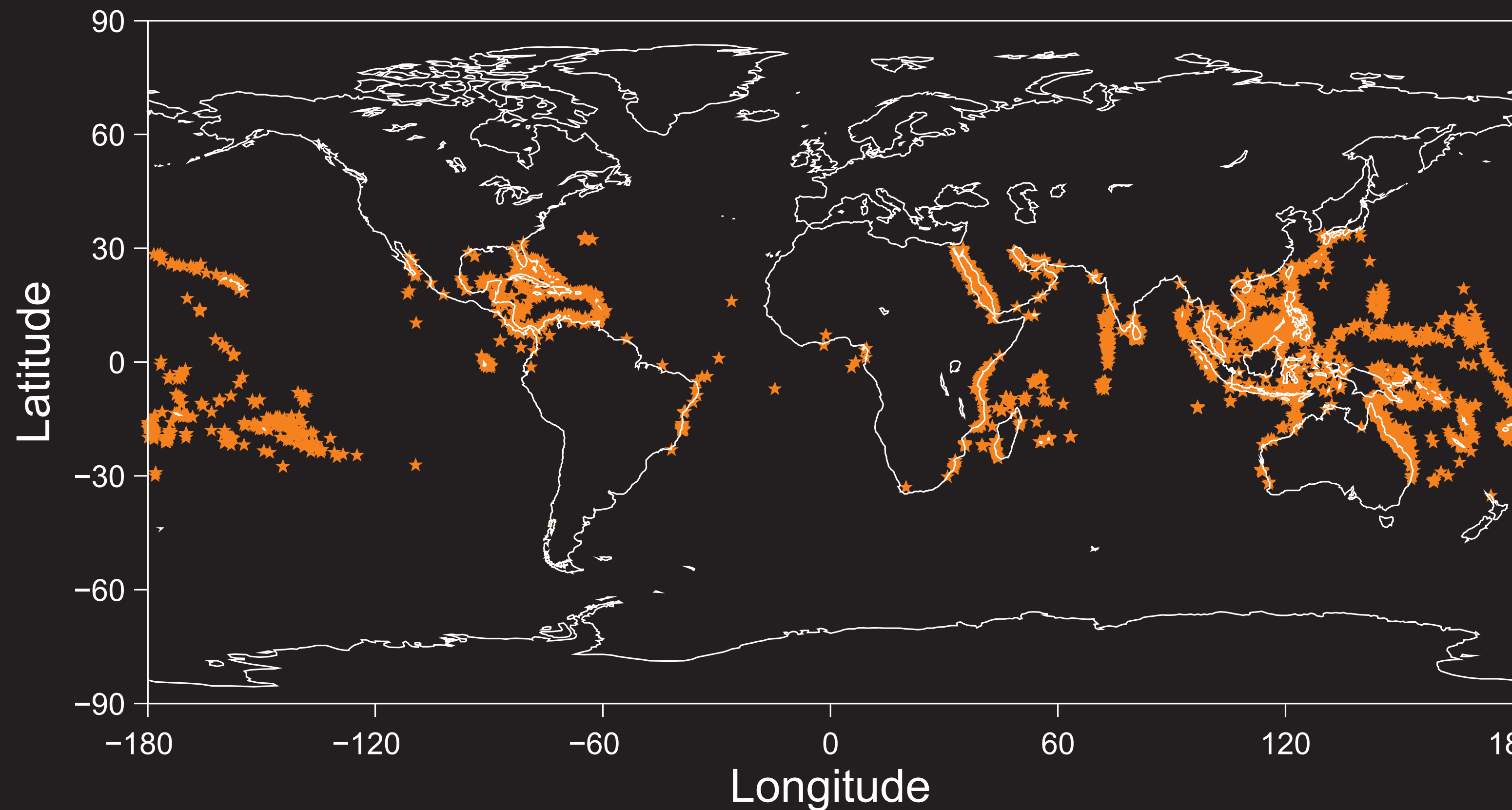
Turley et al. [2010]

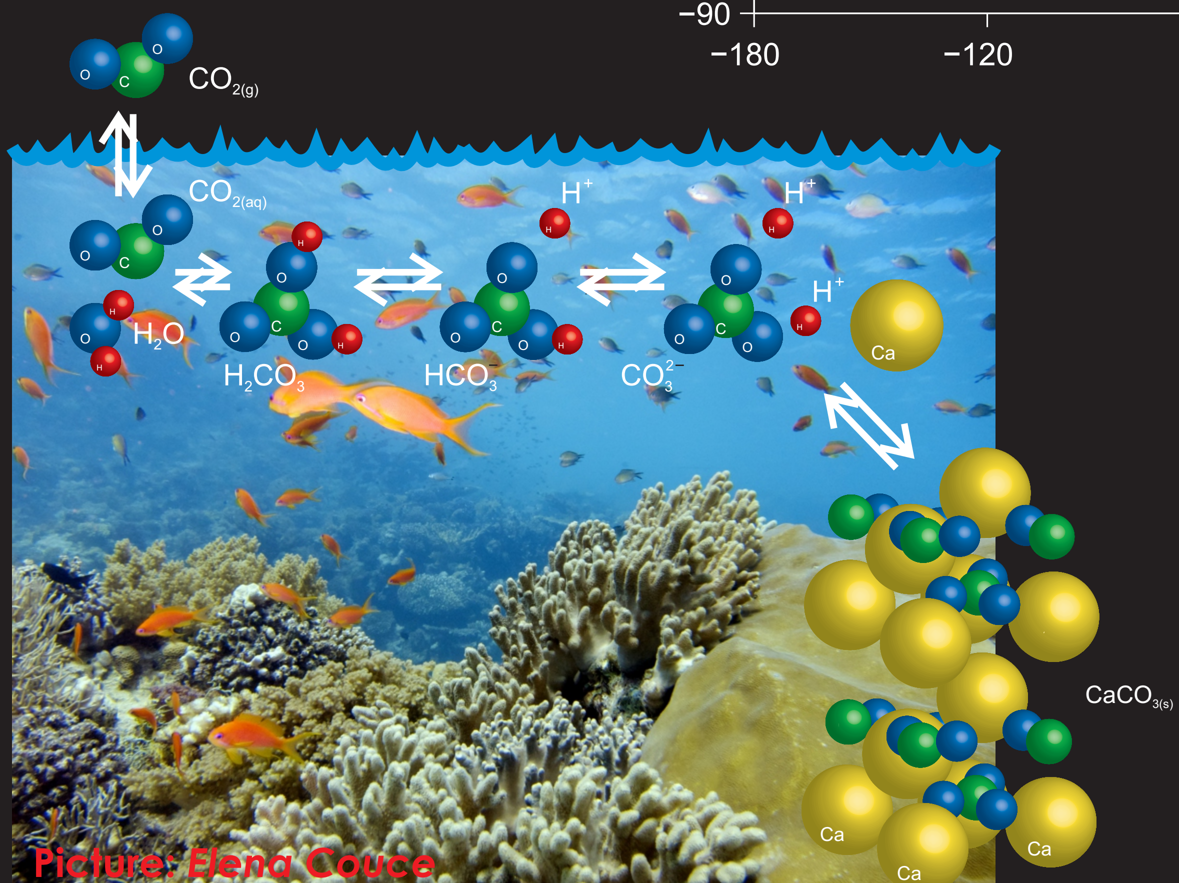
Ocean biological consequences(?)



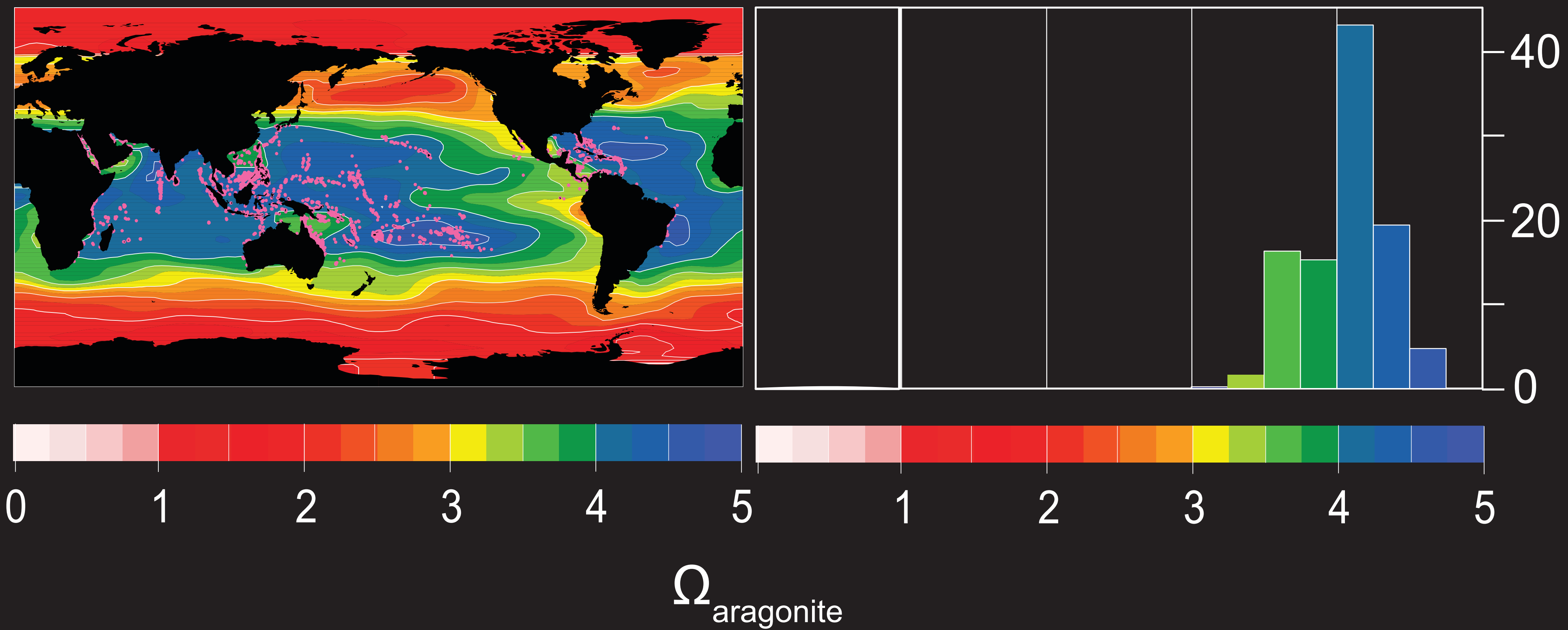
"A 10-20% decrease in $CaCO_3$ production will pose a significant deficit for many coral reefs ... These might include high latitude reefs (for example, Bermuda), reefs in up-welling regions (for example, Galapagos), and many reefs experiencing anthropogenic stresses."

Kleypas et al. [1999] (Science 284)

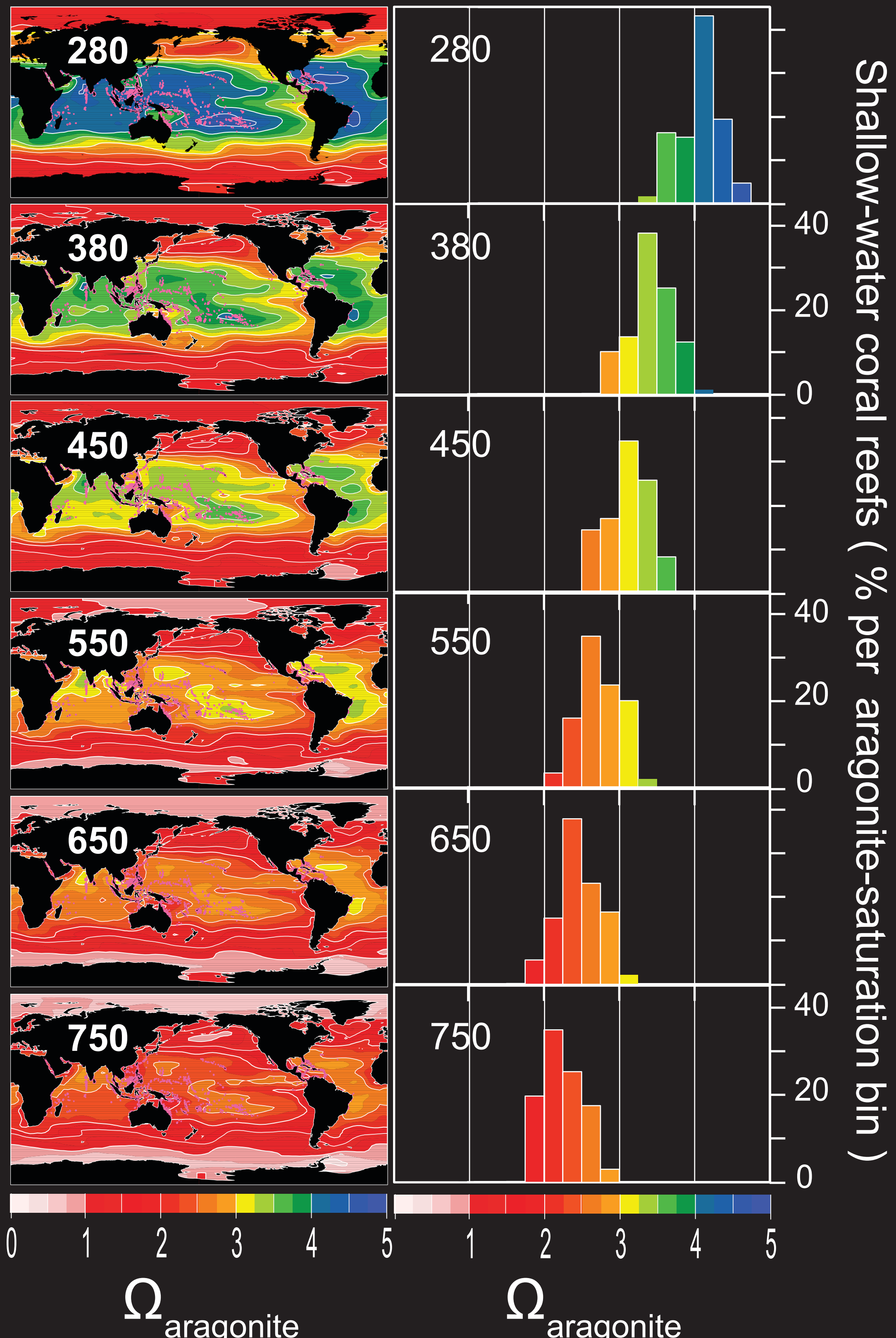

90
60
30
0
−30
−60
−90
Latitude
−180
−120
−60
0
60
120
180
Longitude


$CO_{2(g)}$
$CO_{2(aq)}$
H_2O
H_2CO_3
HCO_3^-
CO_3^{2-}
H^+
H^+
H^+
Ca
$CaCO_{3(s)}$
Ca
Ca
Ca
Picture: Elena Couce

Ocean biological consequences(?)

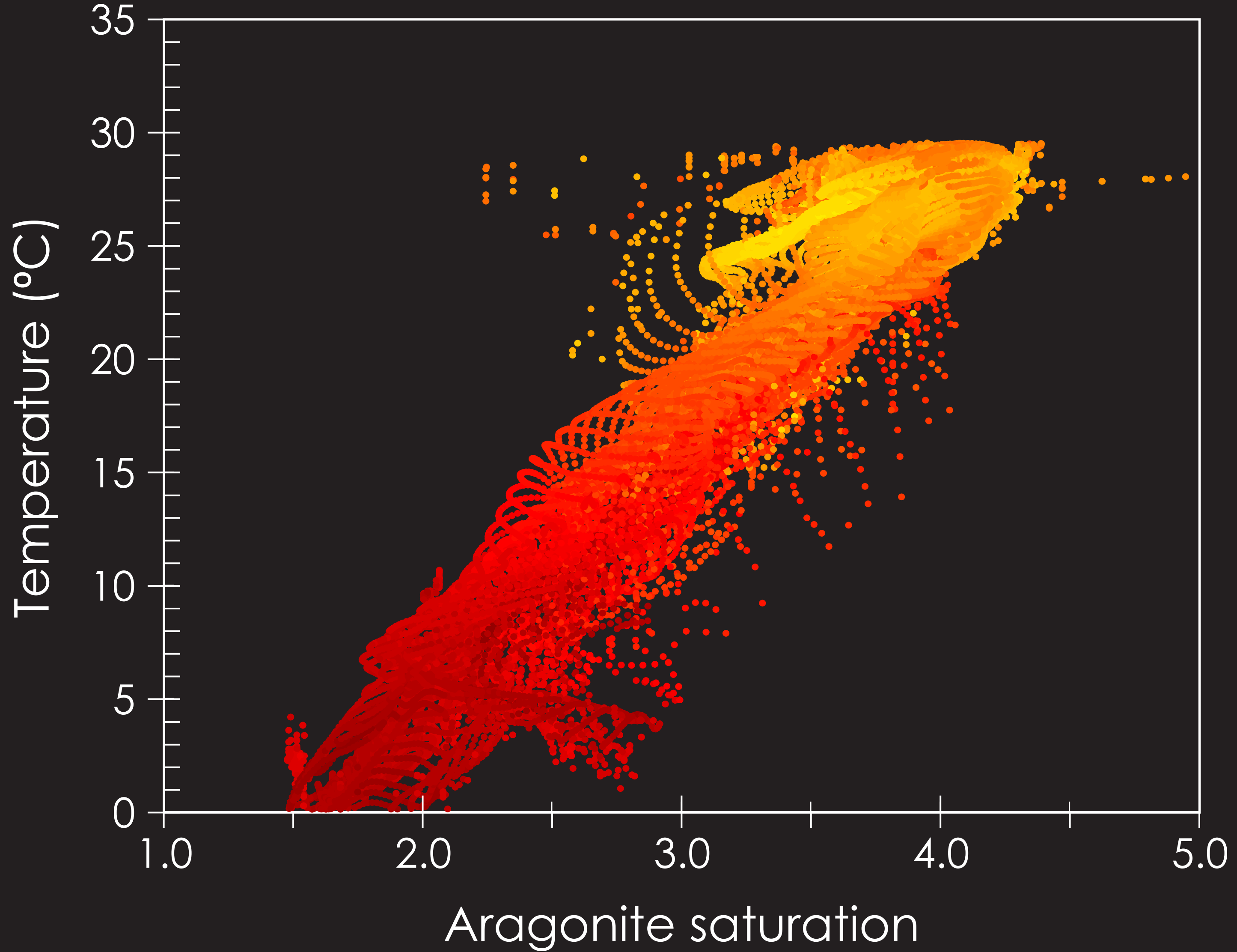


Cao and Caldeira [2008]



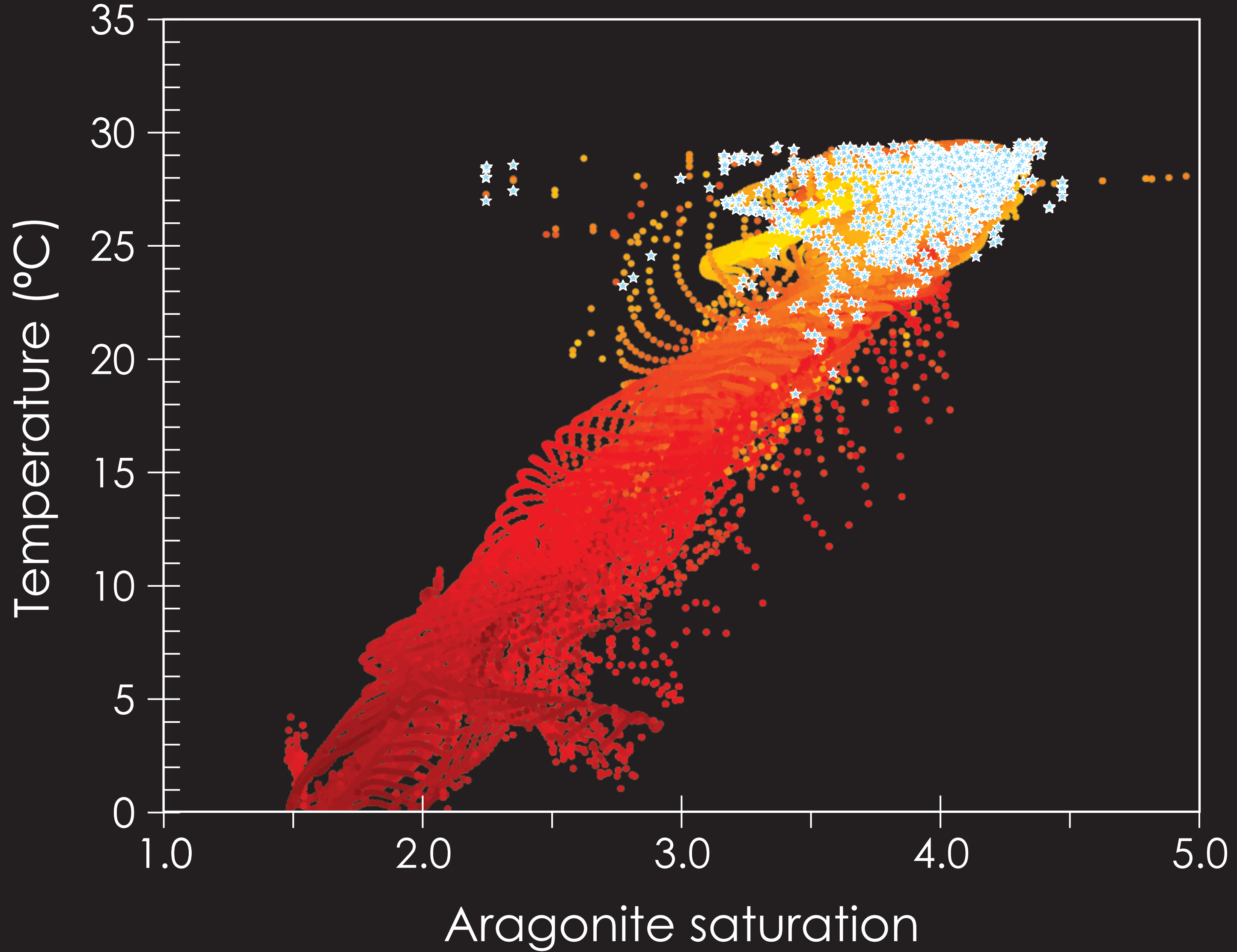
Cao and Caldeira [2008]

Modern ocean surface environmental relationships



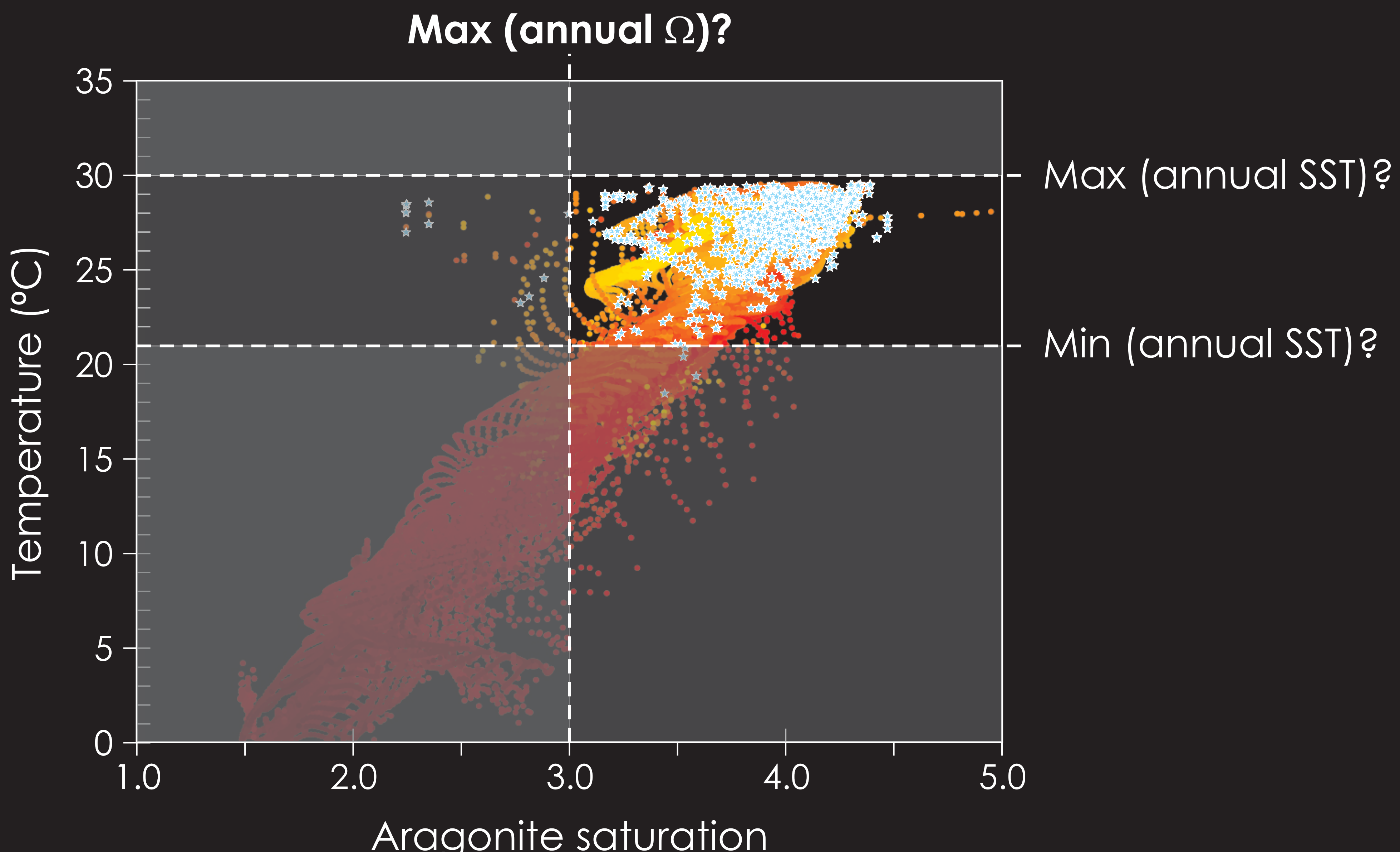
Modern ocean surface environmental relationships

Tropical coral reef locations (ReefBase)



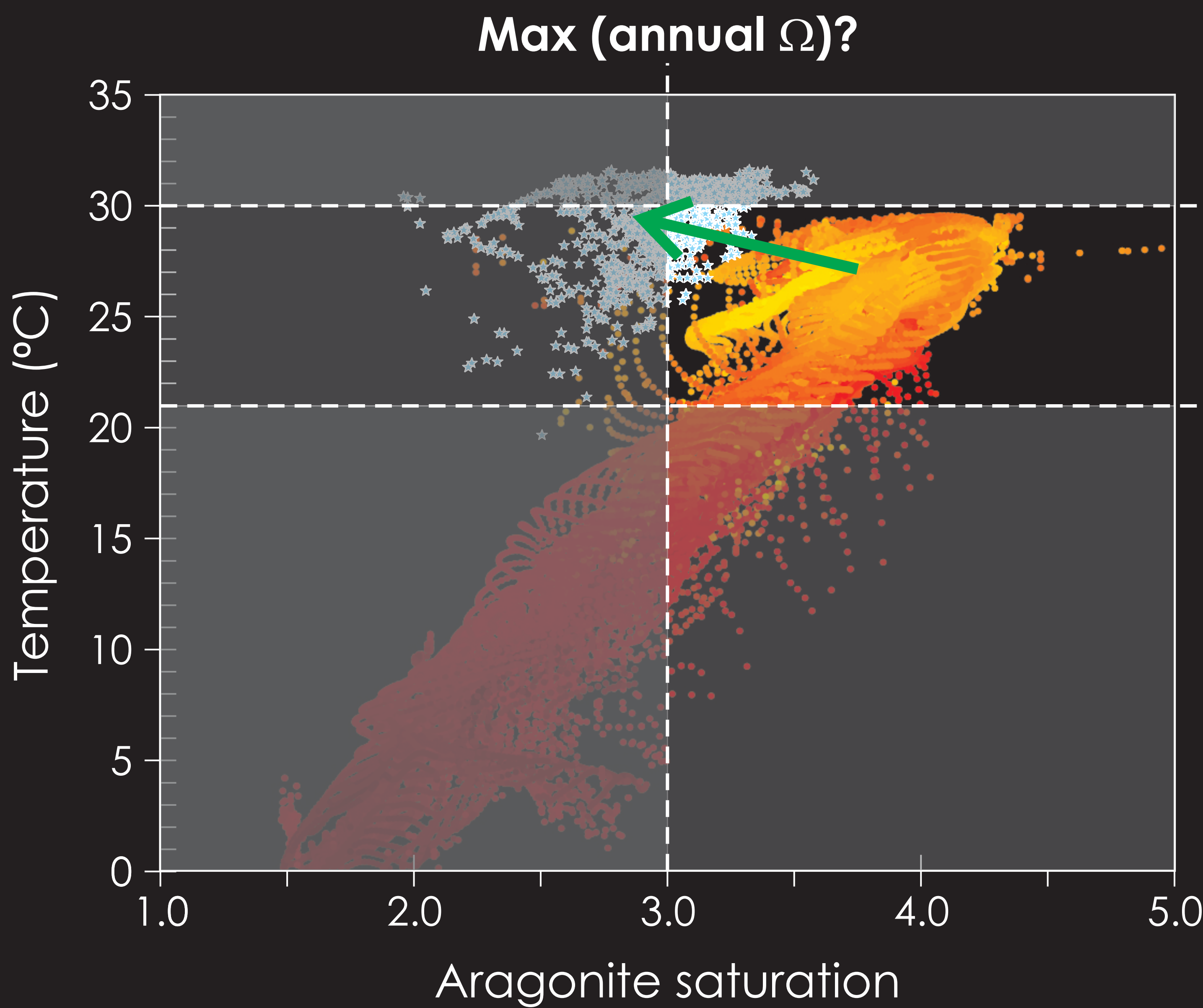
Modern ocean surface environmental relationships

Tropical coral reef locations (ReefBase)

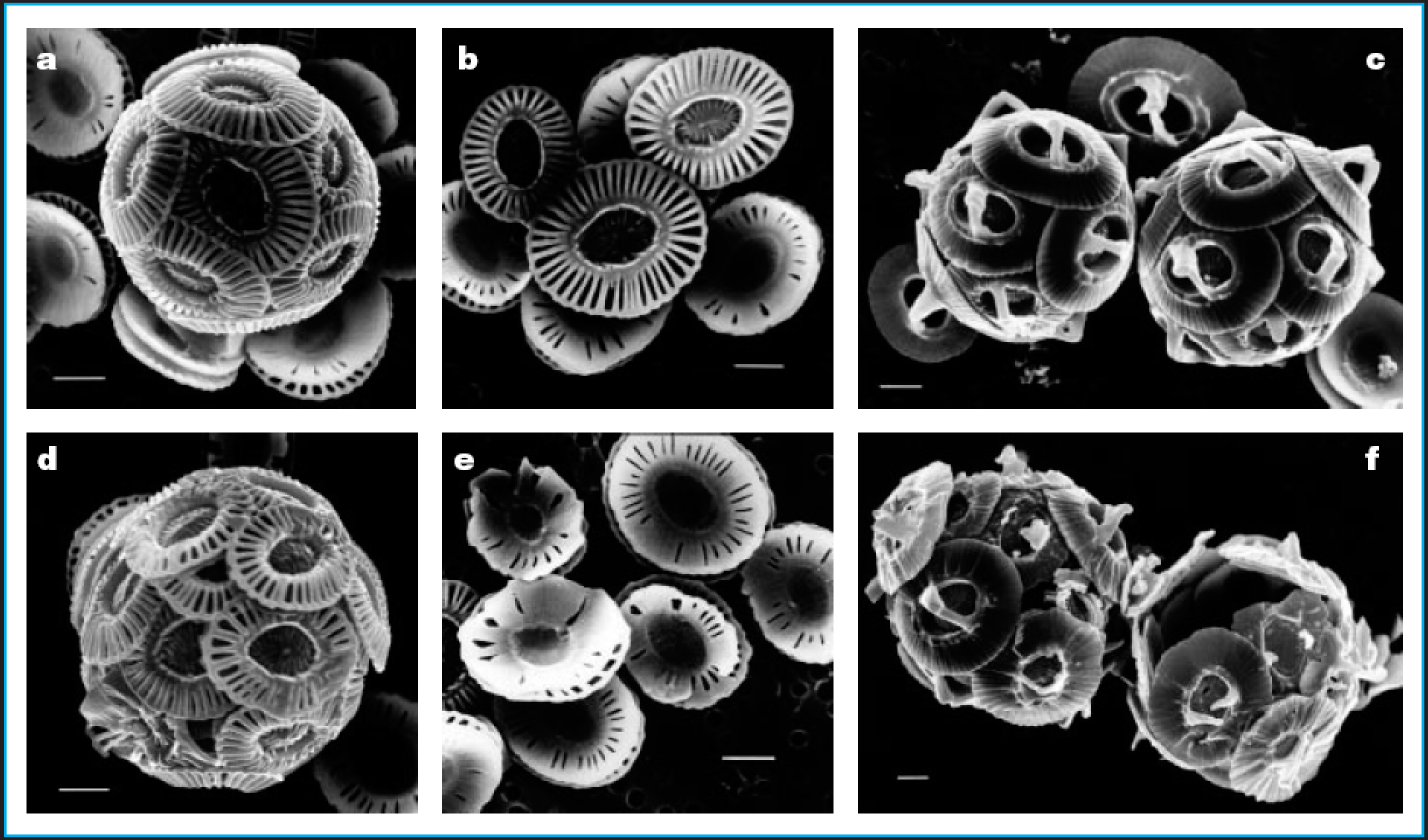


Modern ocean surface environmental relationships

Reef environmental conditions @2070 under RCP 8.5



Ocean biological consequences(?)



low CO_2 (high pH)

high CO_2 (low pH)

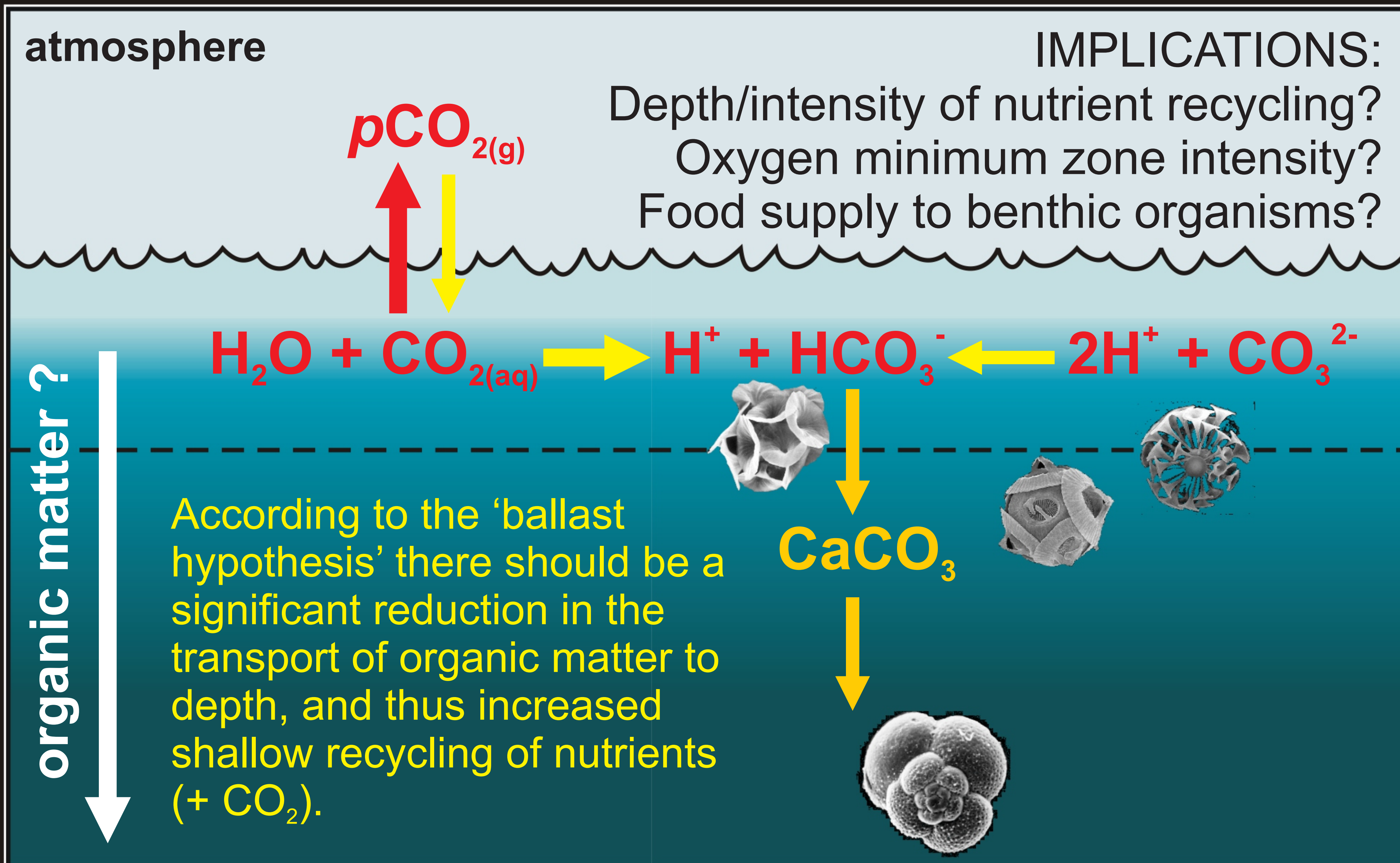
SEM micrographs of coccolithophorids under different CO_2 conditions
Riebesell et al. [2000] (*Nature* 407)

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

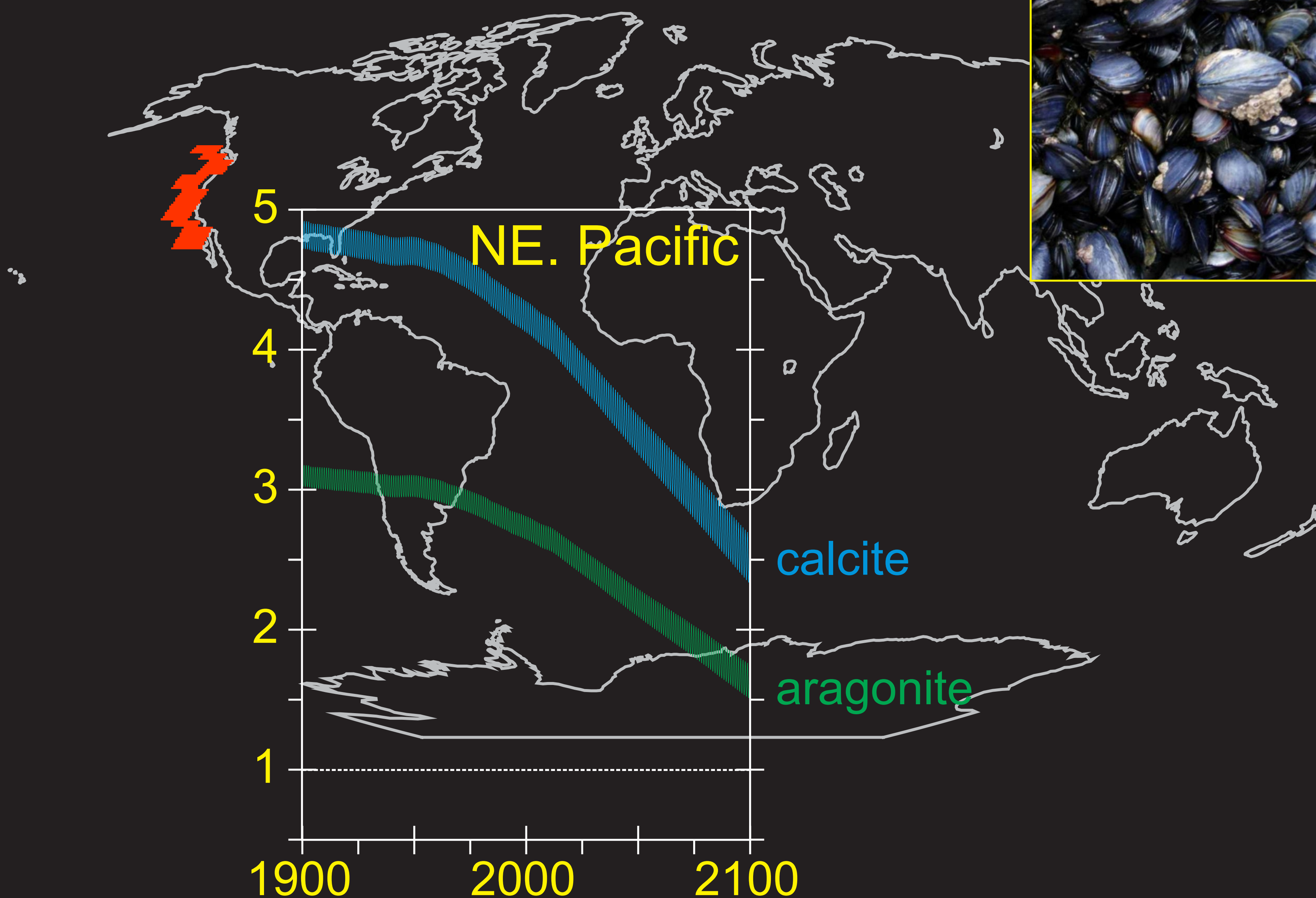
Species	Strain	Year location	Exp. design	Manipulation		Reference
Emiliania huxleyi	PML B92/11A	1992 North Sea	laboratory culture	acid/base	↓	Riebesell et al. [2000] Zondervan et al. [2001]
Emiliania huxleyi	PML B92/11A	1992 North Sea	laboratory culture	acid/base	↓	Riebesell et al. [2000] Zondervan et al. [2001]
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)

Global biogeochemical impacts in a High CO_2 World

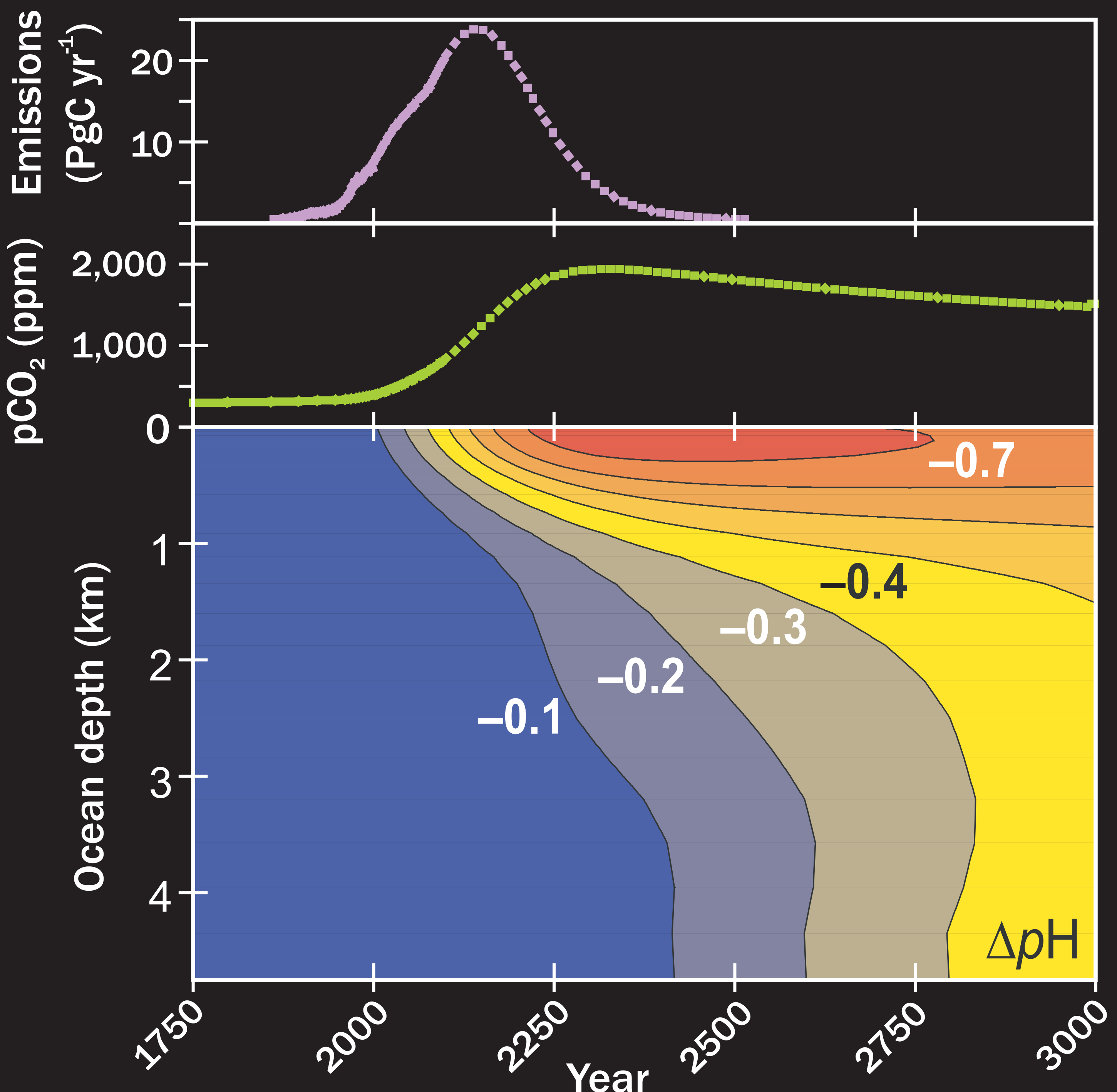


Ocean biological consequences(?)



Turley et al. [2010]

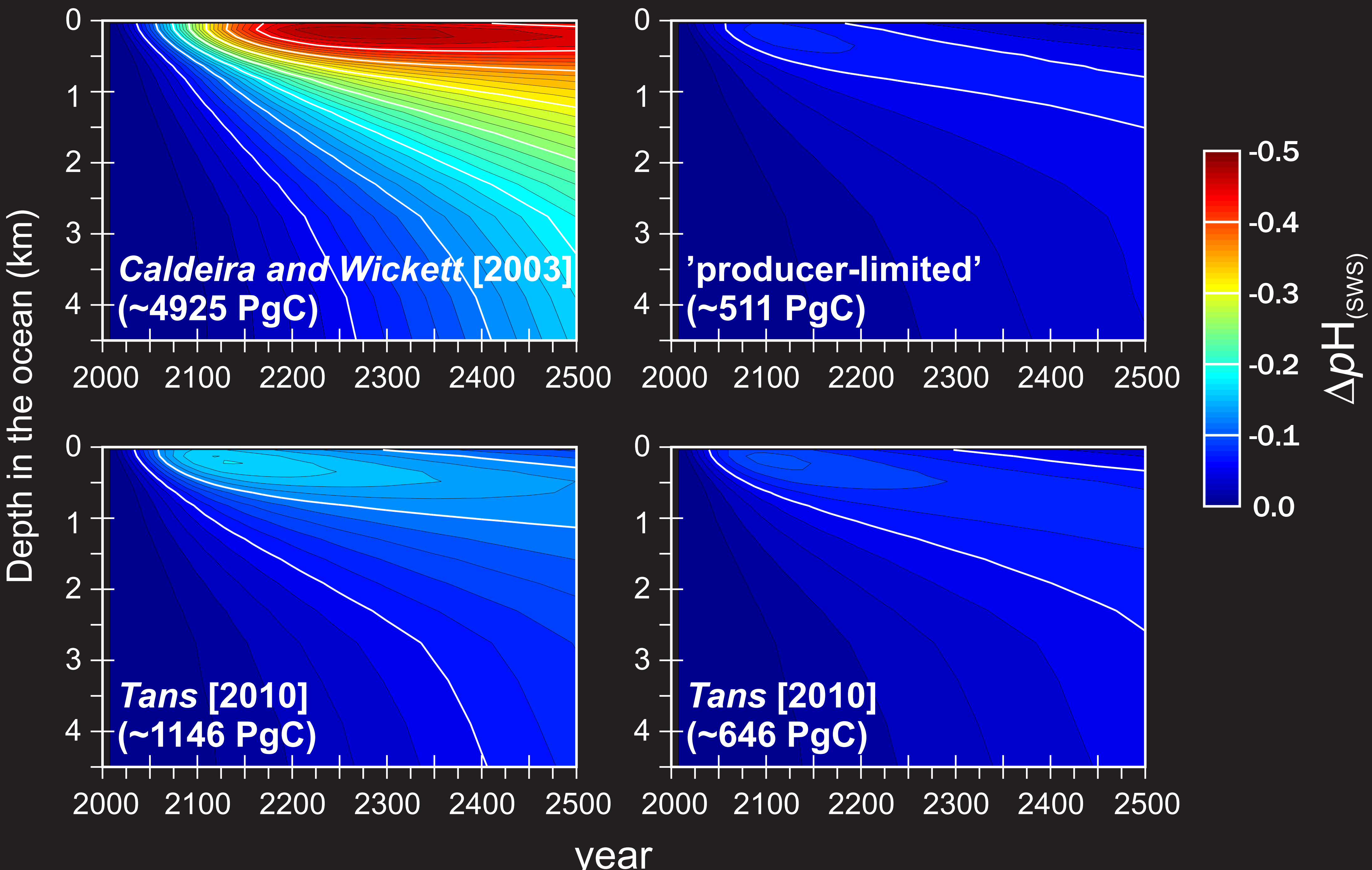
Future trajectories of ocean pH

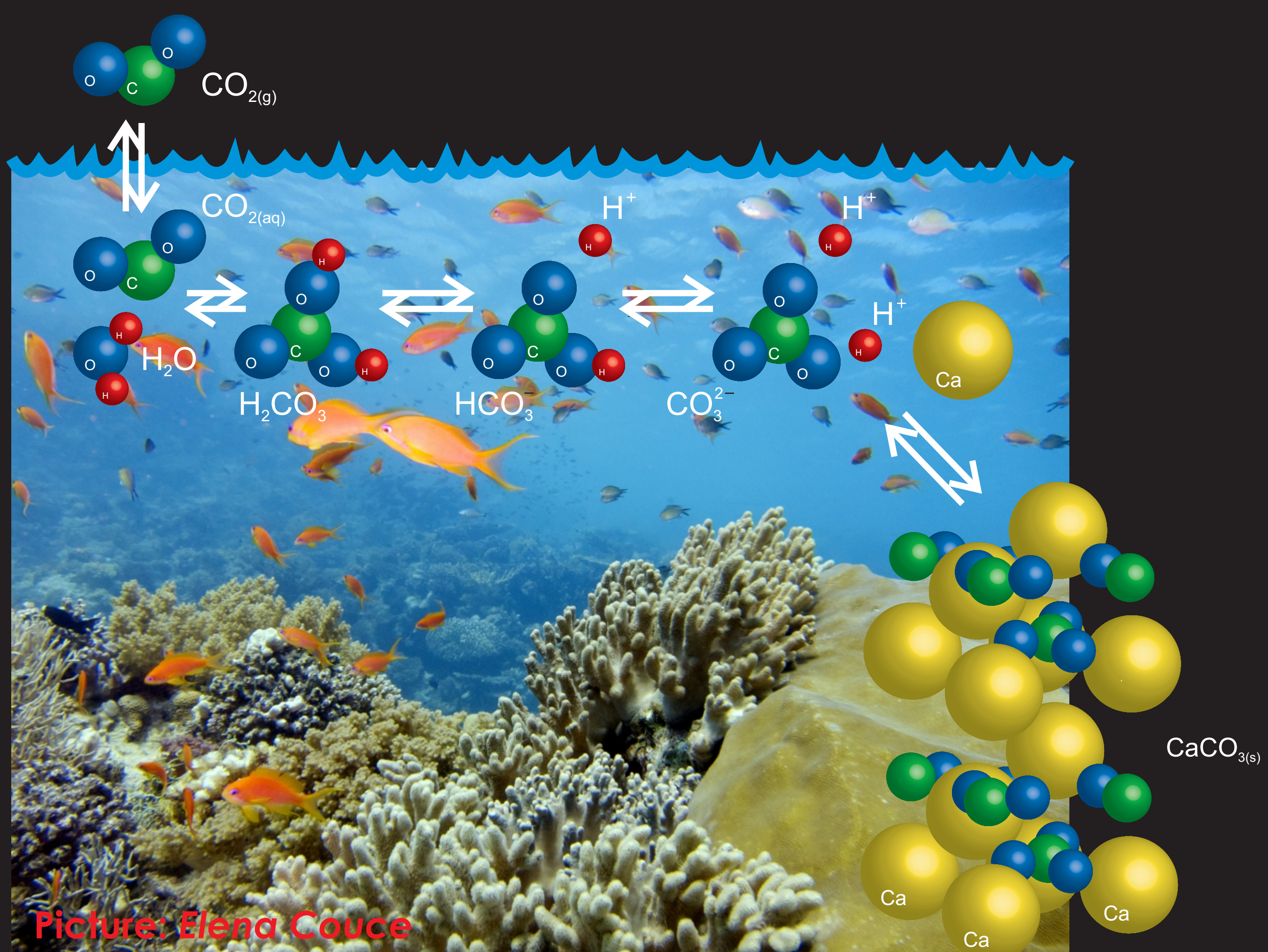


Caldeira and Wickett [2003]

GENIE
Grid ENabled Integrated Earth system model
www.genie.ac.uk

Future ocean pH projections




$CO_{2(g)}$
$CO_{2(aq)}$
H_2O
H_2CO_3
HCO_3^-
CO_3^{2-}
H^+
H^+
H^+
Ca
$CaCO_{3(s)}$
Ca
Ca
Ca
Picture: Elena Couce