

# Ocean Acidification

Global Warming Science, EPS101

**Eli Tziperman**

<https://courses.seas.harvard.edu/climate/eli/Courses/EPS101/>

# Two reminders

## First:

$$\text{pH} \equiv -\log_{10}([H^+])$$

lower pH (<7) ➡ acid

# Two reminders

## First:

$$\text{pH} \equiv -\log_{10}([H^+])$$

lower pH (<7) ➔ acid

## Second:

In a chemical reaction of the form

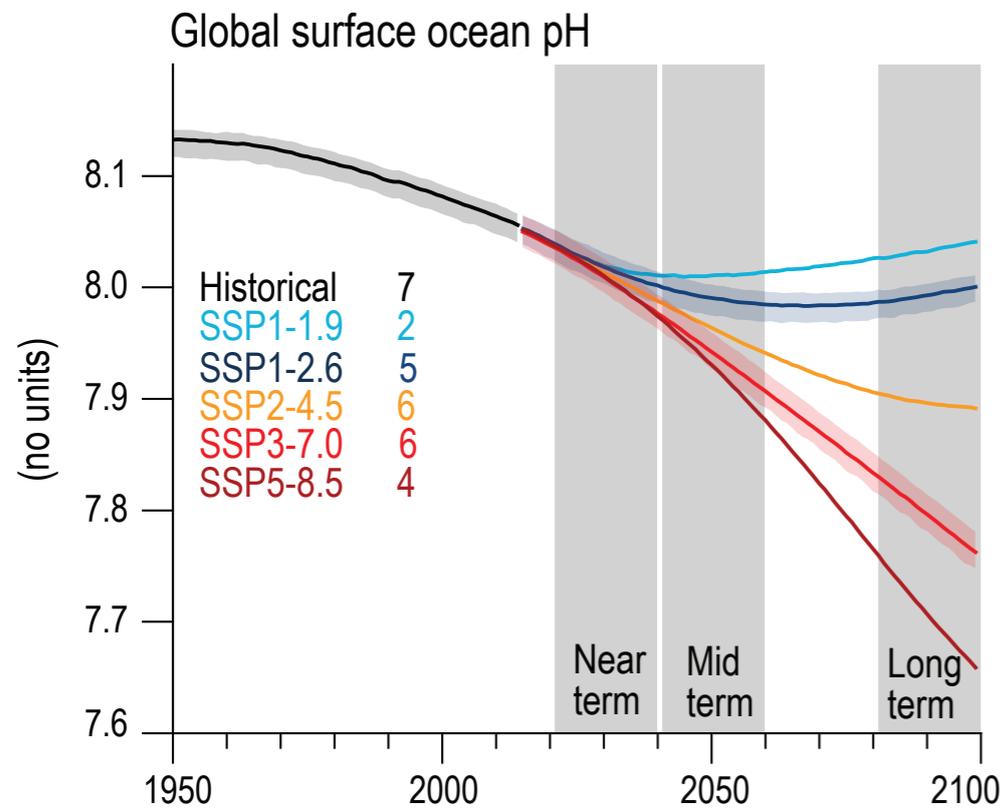


the equilibrium concentrations (moles per liter, denoted  $[A]$ ,  $[B]$ ,  $[C]$ ) satisfy

$$K = \frac{[B][C]}{[A]},$$

where the known equilibrium constant  $K(T, P)$  is a function of temperature and pressure.

# CO<sub>2</sub> is increasing, ocean is becoming more acidic

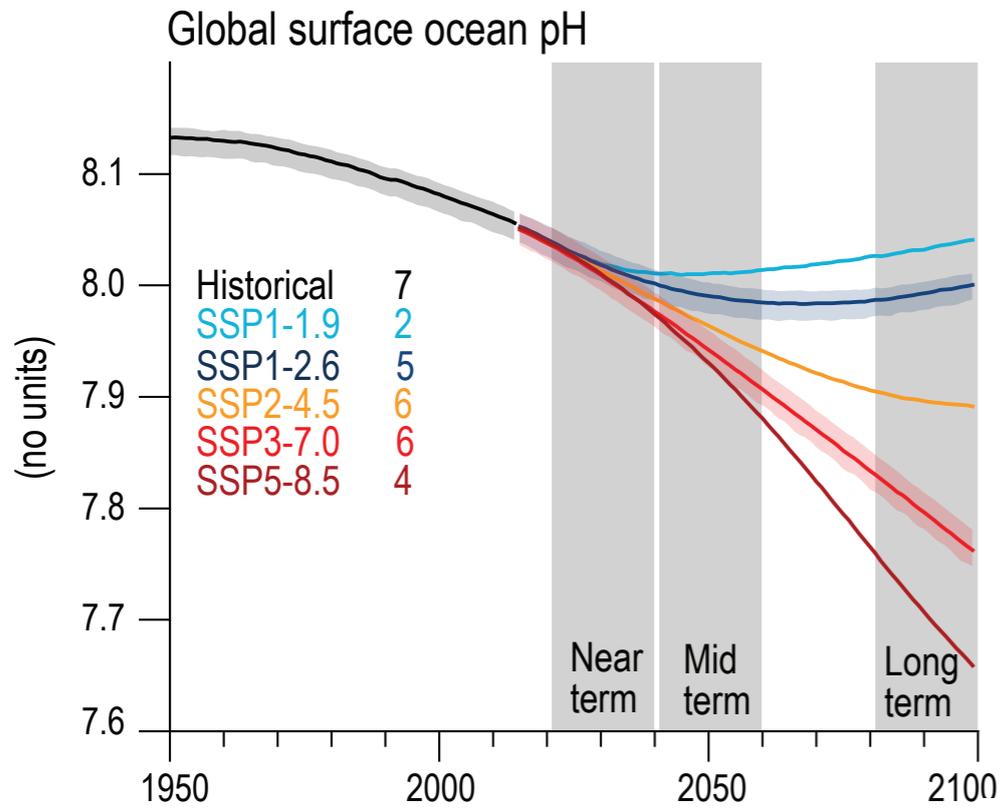


## Figure 4.8 | Global average surface ocean pH.

Shadings around SSP1-2.6 and SSP5-7.0 curves: 5–95% ranges across ensembles. Numbers inside each panel: # of model simulations. Results from CO<sub>2</sub> concentration-driven simulations.

**IPCC AR6, 2022**

# CO<sub>2</sub> is increasing, ocean is becoming more acidic



**Figure 4.8 | Global average surface ocean pH.**

Shadings around SSP1-2.6 and SSP5-7.0 curves: 5–95% ranges across ensembles. Numbers inside each panel: # of model simulations. Results from CO<sub>2</sub> concentration-driven simulations.

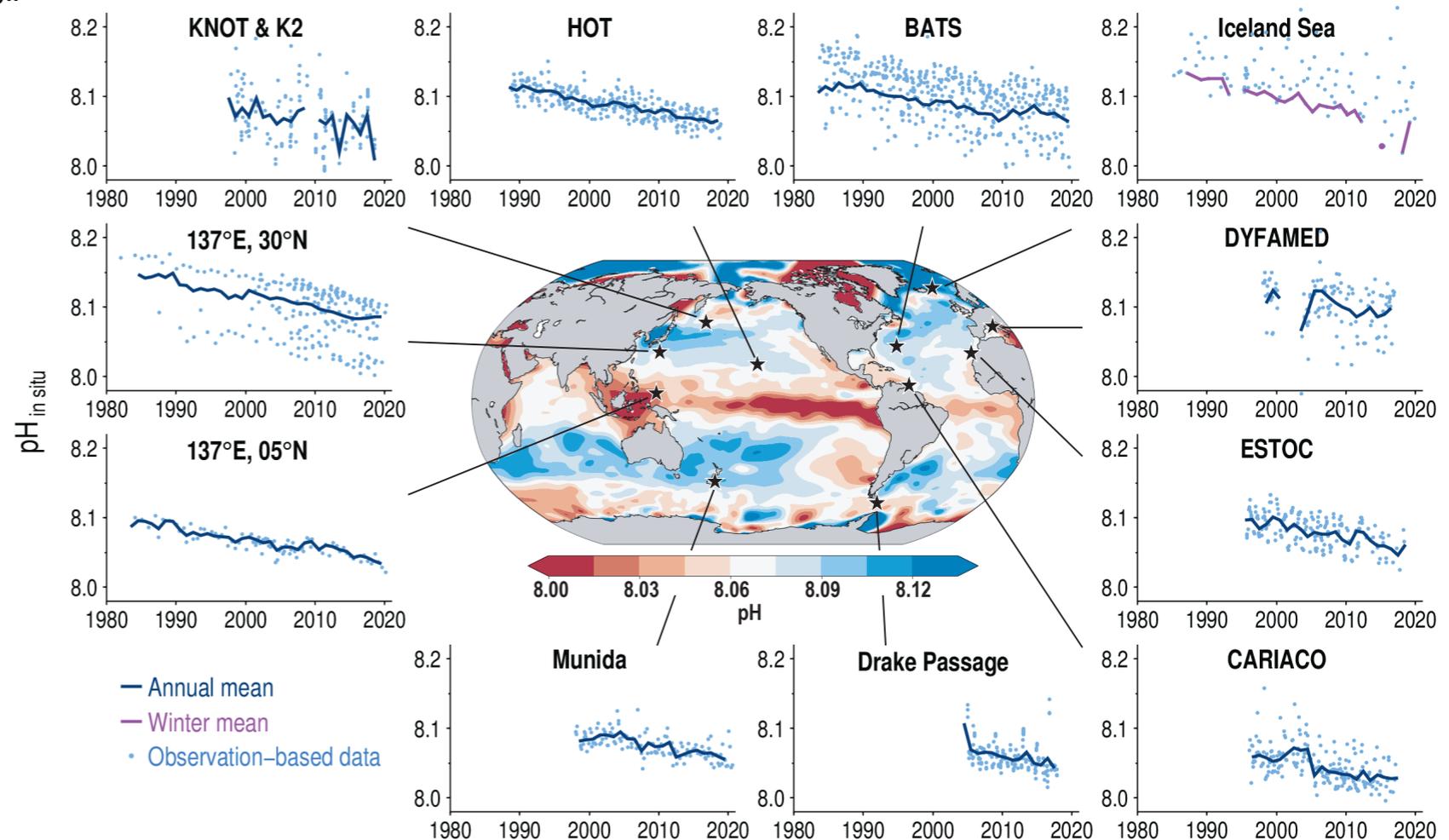
**IPCC AR6, 2022**

**Figure 5.20 | Multi-decadal trends of pH in surface layer at various sites and a global distribution of annual mean pH adjusted to year 2000.**

**Panels:** Time-series data of pH.

**Map:** annual mean pH evaluated from data of surface ocean pCO<sub>2</sub>.

Dore et al. (2009), Olafsson et al. (2009), González-Dávila et al. (2010), Bates et al. (2014), Takahashi et al. (2014), Wakita et al. (2017), Merlivat et al. (2018), Ono et al. (2019), and Bates and Johnson (2020); (Bakker et al., 2016; Jiang et al., 2019).



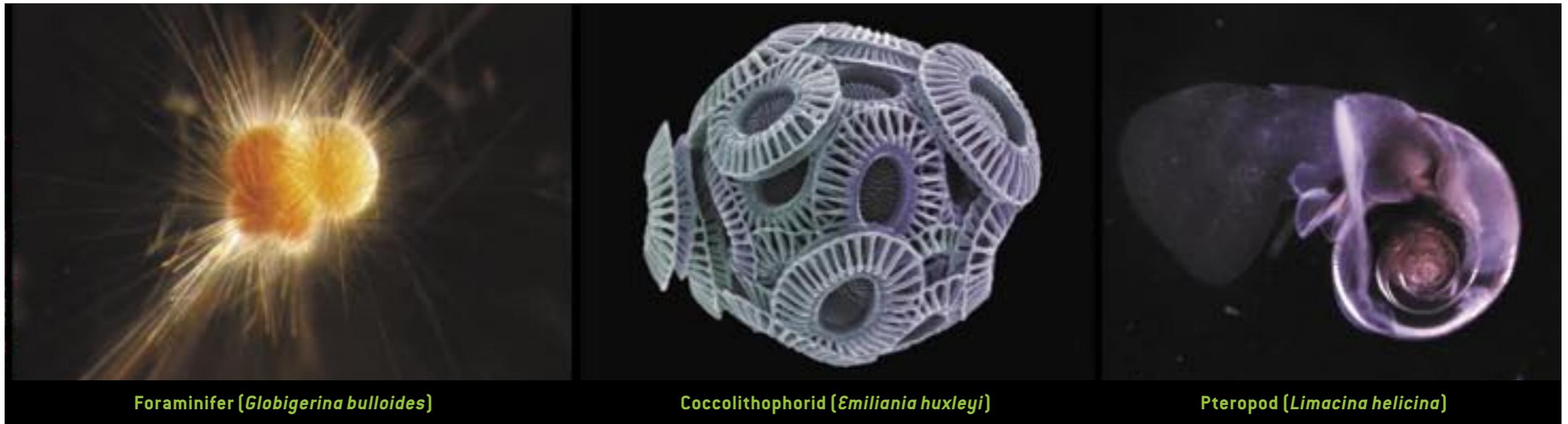
# Farming Oysters Despite Acidic Seas

<https://ocean.si.edu/ocean-life/invertebrates/farming-oysters-despite-acidic-seas>

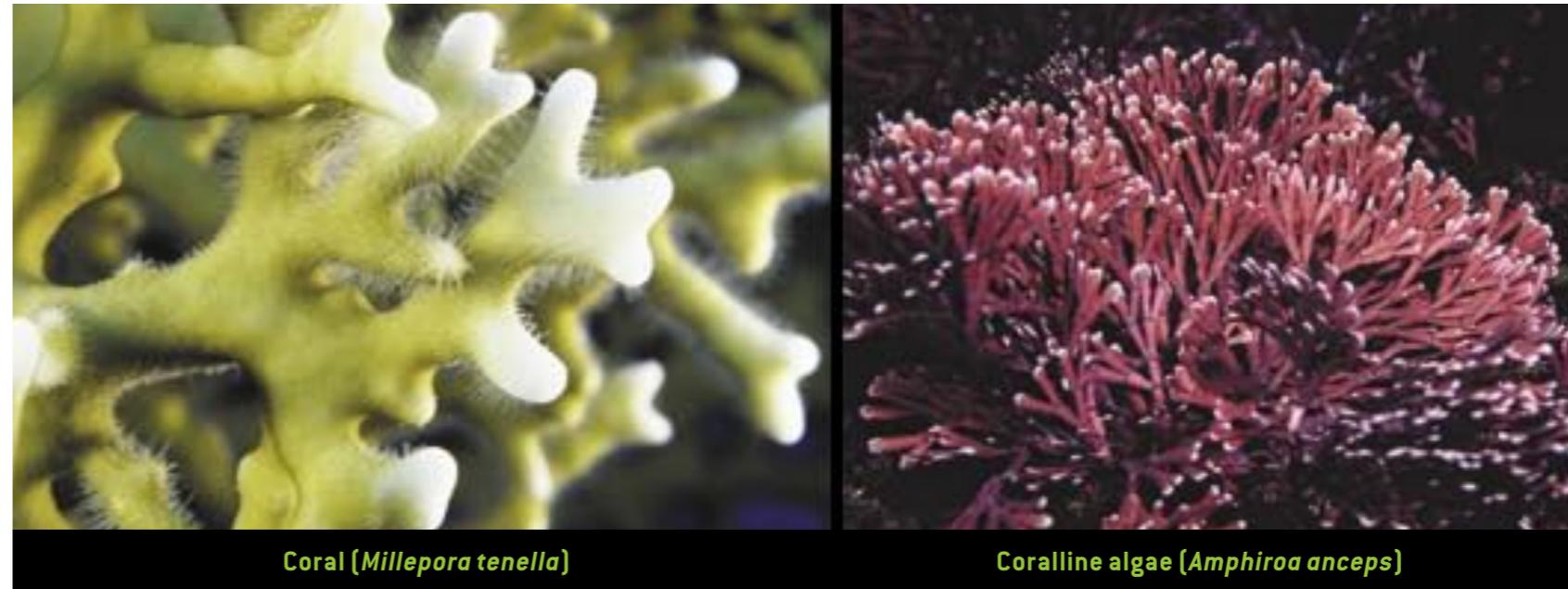
# Farming Oysters Despite Acidic Seas

<https://ocean.si.edu/ocean-life/invertebrates/farming-oysters-despite-acidic-seas>

# why do we care about pH changes: plankton, corals, have $\text{CaCO}_3$ skeletons that may be affected



**Doney et al 2006**



MARINE ORGANISMS at risk from the increasing acidification of the ocean include the corals and coralline algae commonly found in reef communities, as well as foraminifera and coccolithophorids, which are abundant in most surface waters. Also under threat, particularly in cold, polar waters, are a variety of small marine snails called pteropods.

# Response of Pteropod shells to increased CO<sub>2</sub>

“The Pteropod or `sea butterfly’, is a tiny sea creature about the size of a small pea, eaten by Juvenile salmon, tiny krill and whales” (<http://oceanacidificationwherewelive.weebly.com>)



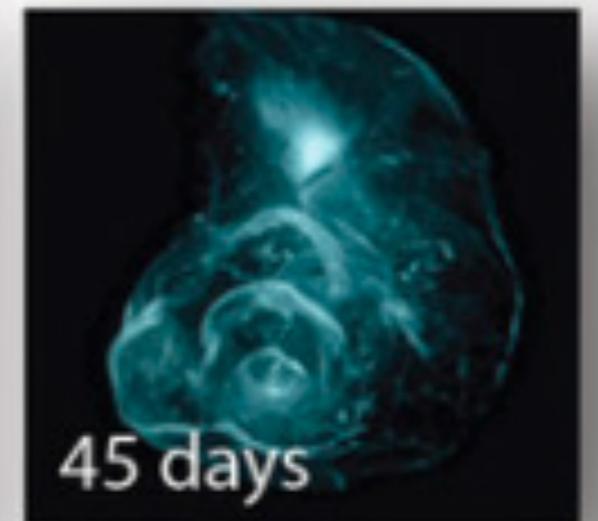
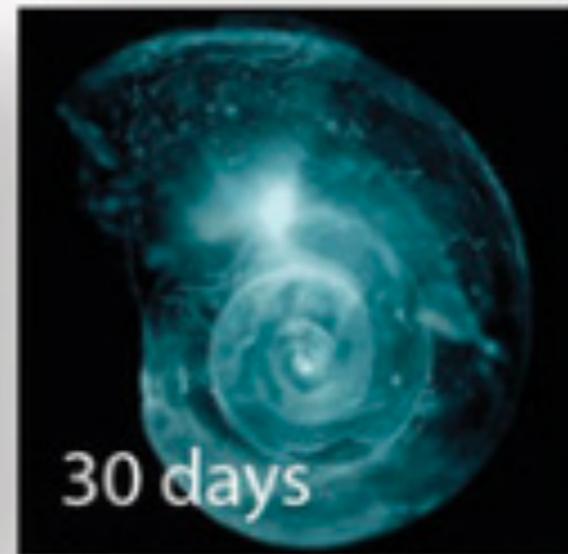
<https://www.nationalgeographic.com/news/2014/5/140502-ocean-snail-shell-dissolving-acidification-climate-change-science/>

# Response of Pteropod shells to increased CO<sub>2</sub>

“The Pteropod or ‘sea butterfly’, is a tiny sea creature about the size of a small pea, eaten by Juvenile salmon, tiny krill and whales” (<http://oceanacidificationwherewelive.weebly.com>)



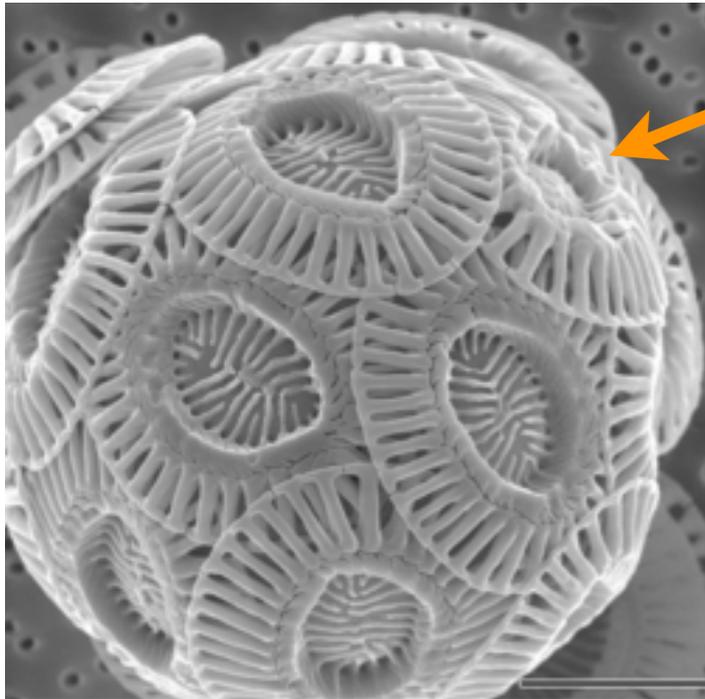
<https://www.nationalgeographic.com/news/2014/5/140502-ocean-snail-shell-dissolving-acidification-climate-change-science/>



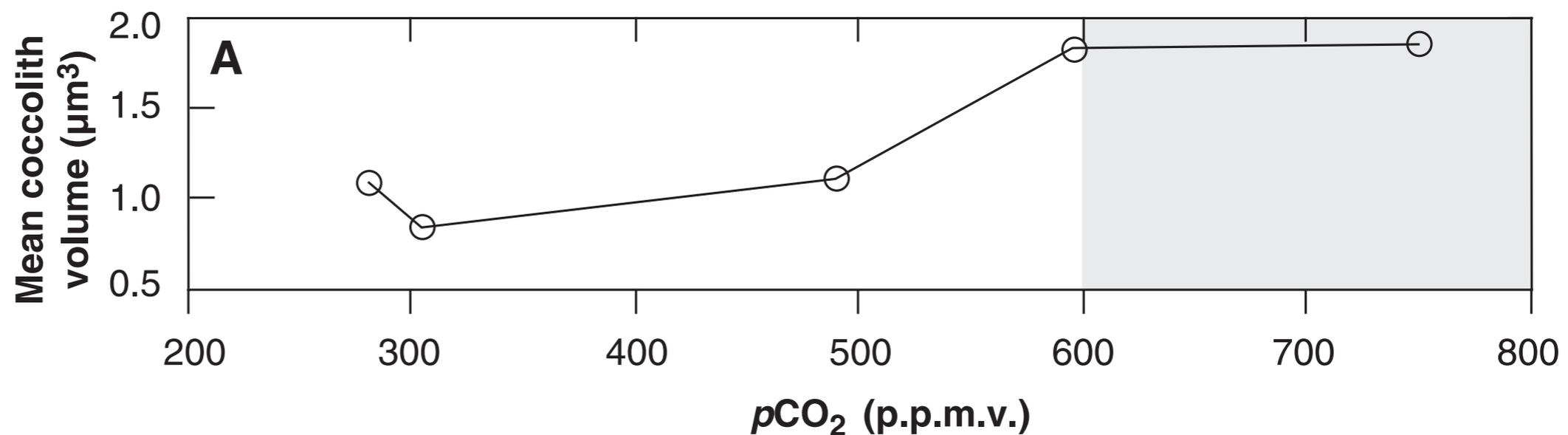
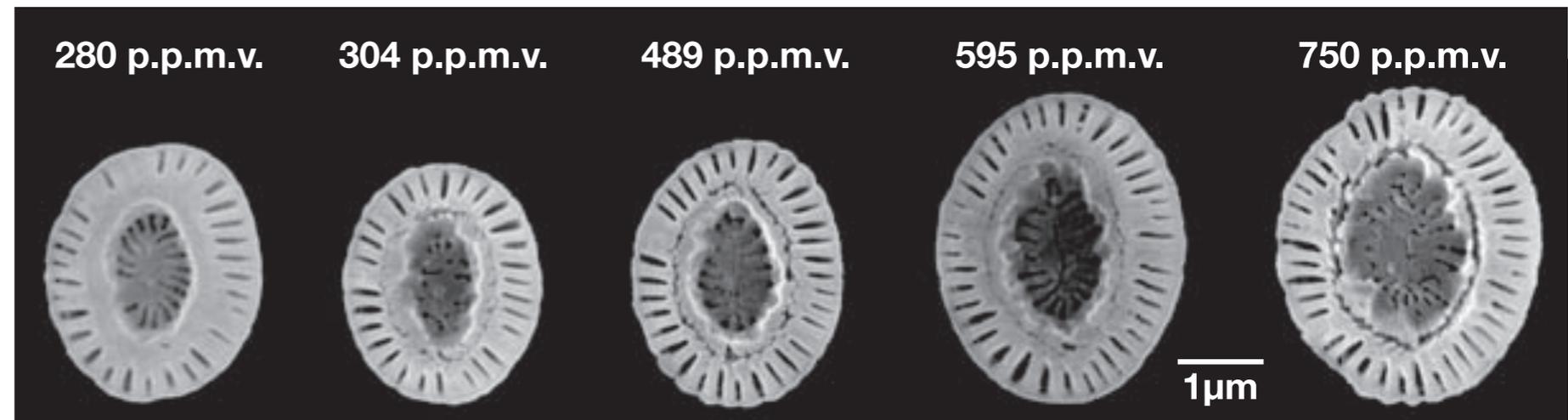
The photo above show what happens to a **Pteropod's shell when placed in sea water with pH and carbonate levels projected for the year 2100**. The shell slowly dissolves after 45 days.

**National Geographic Images**

# Response of Coccolithophore plates to increased CO<sub>2</sub>



Emiliana Huxley, the most common coccolith in the seas today, Wikipedia



## Debora Iglesias-Rodriguez 2008

Fig. 2. Coccolith volume and CaCO<sub>3</sub> per cell. Increasing coccolith volume is closely coupled with increasing CaCO<sub>3</sub> per cell, indicating down-core measurement of coccolith mass to be representative of CaCO<sub>3</sub> production. Scanning electron microscope (SEM) images show typical coccoliths from each culture with P<sub>CO<sub>2</sub></sub> values from 280 to 750 ppmv of CO<sub>2</sub>, of where the measured volume was converted to length using the formula for a heavily calcified coccolith.

# Our goals today

1. Understand calcium carbonate  $\text{CaCO}_3$  dissolution.

## Our goals today

1. Understand calcium carbonate  $\text{CaCO}_3$  dissolution.
2. The ocean carbonate system: how pH is affected by atmospheric  $\text{CO}_2$ .

## Our goals today

1. Understand calcium carbonate  $\text{CaCO}_3$  dissolution.
2. The ocean carbonate system: how pH is affected by atmospheric  $\text{CO}_2$ .
3. The carbonate system buffer effect: why the ocean can absorb so much carbon.

## Our goals today

1. Understand calcium carbonate  $\text{CaCO}_3$  dissolution.
2. The ocean carbonate system: how pH is affected by atmospheric  $\text{CO}_2$ .
3. The carbonate system buffer effect: why the ocean can absorb so much carbon.
4. A positive feedback on warming due to the response of the carbonate system to warming:  
Higher  $\text{CO}_2$  ➡ rising temperature ➡ more  $\text{CO}_2$  emitted by ocean

## Our goals today

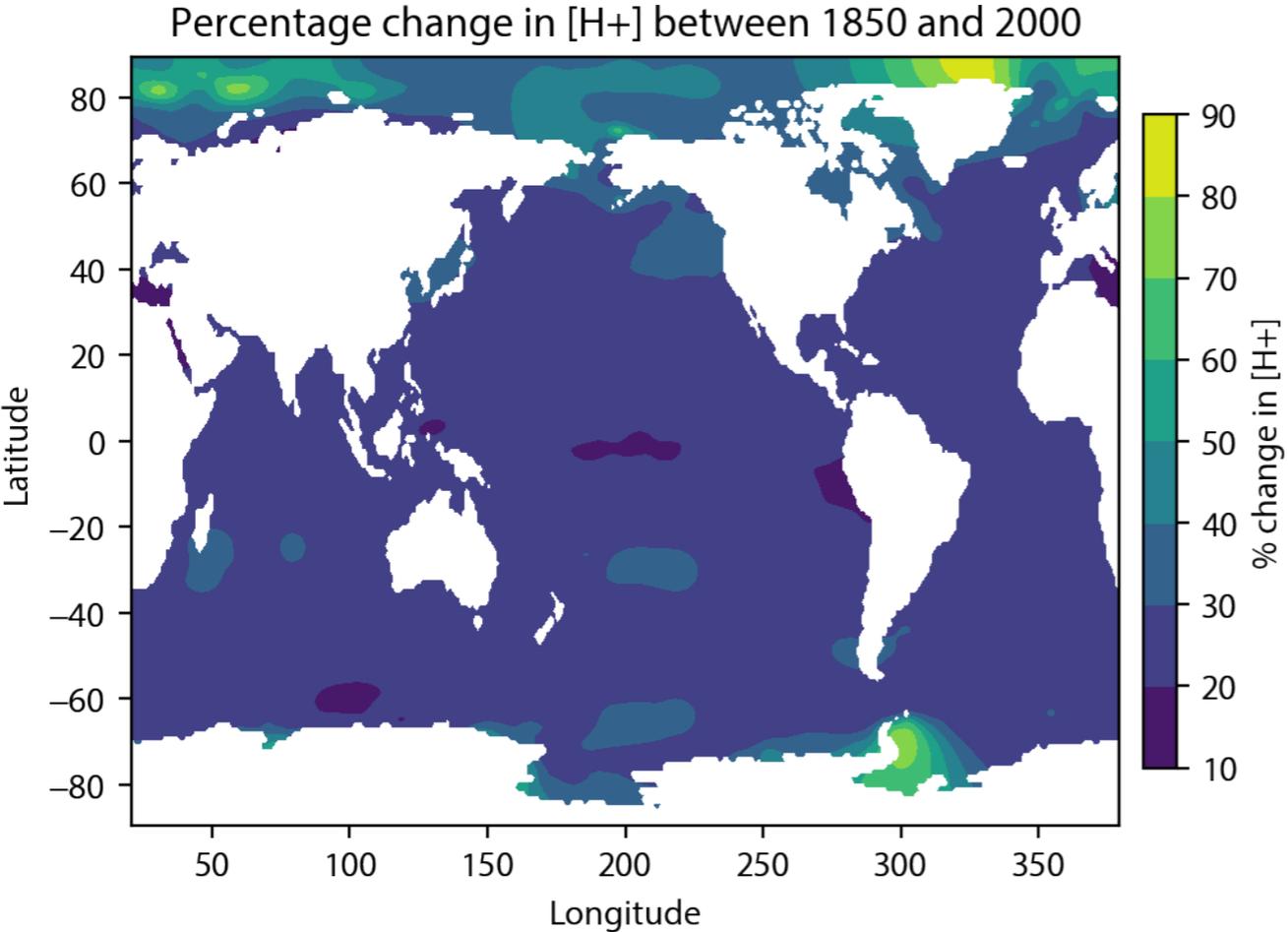
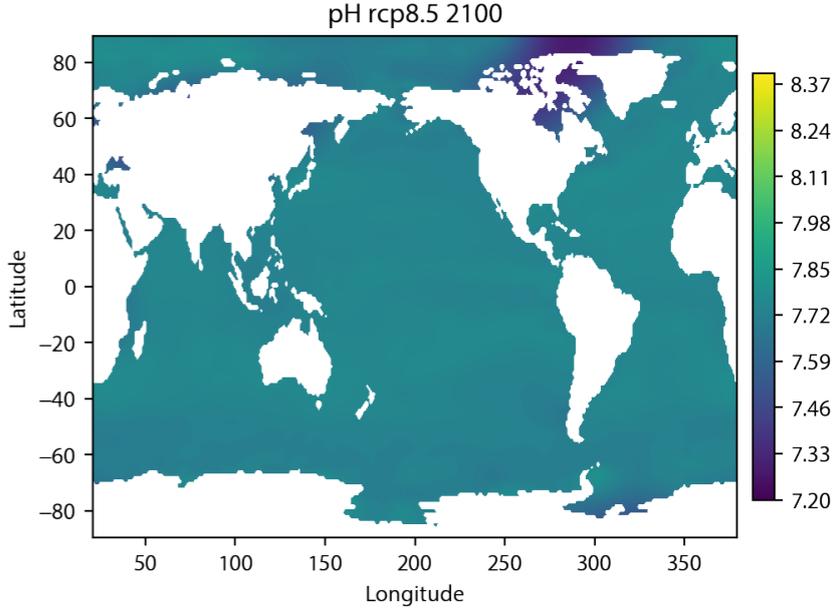
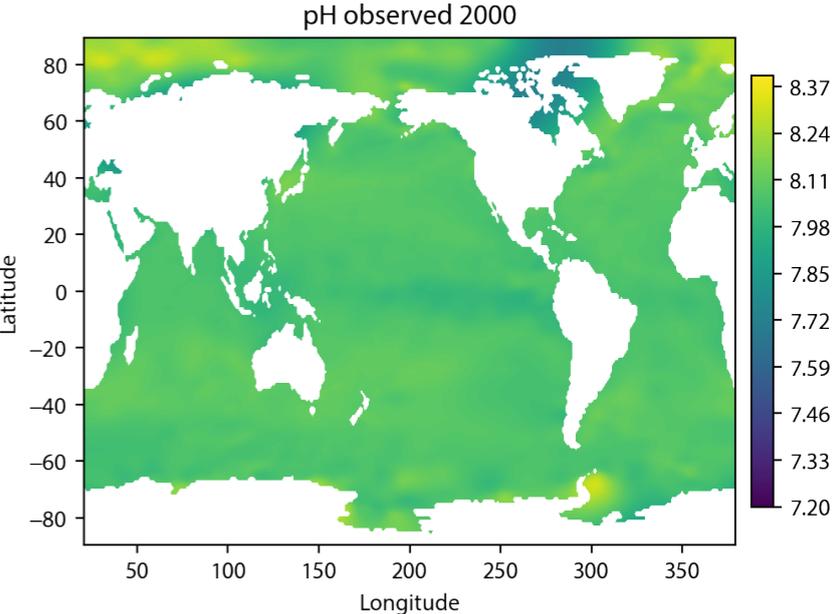
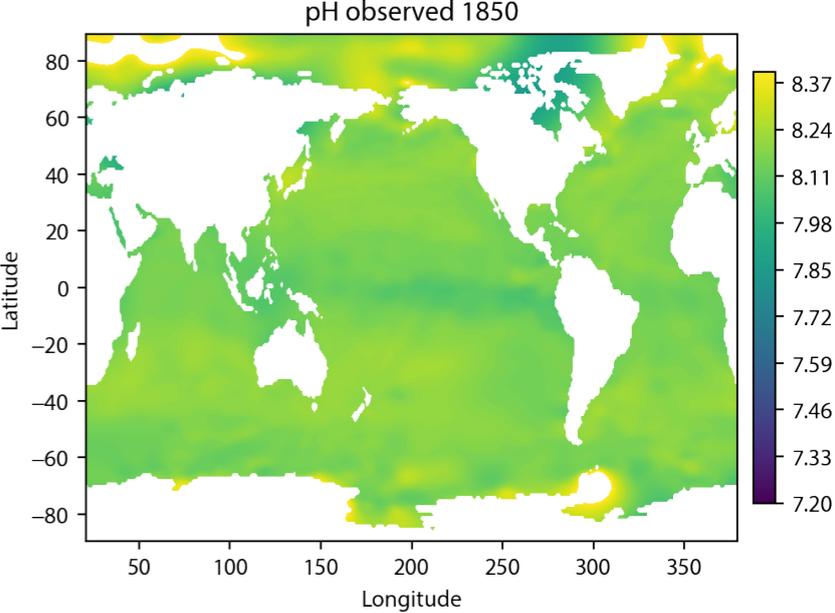
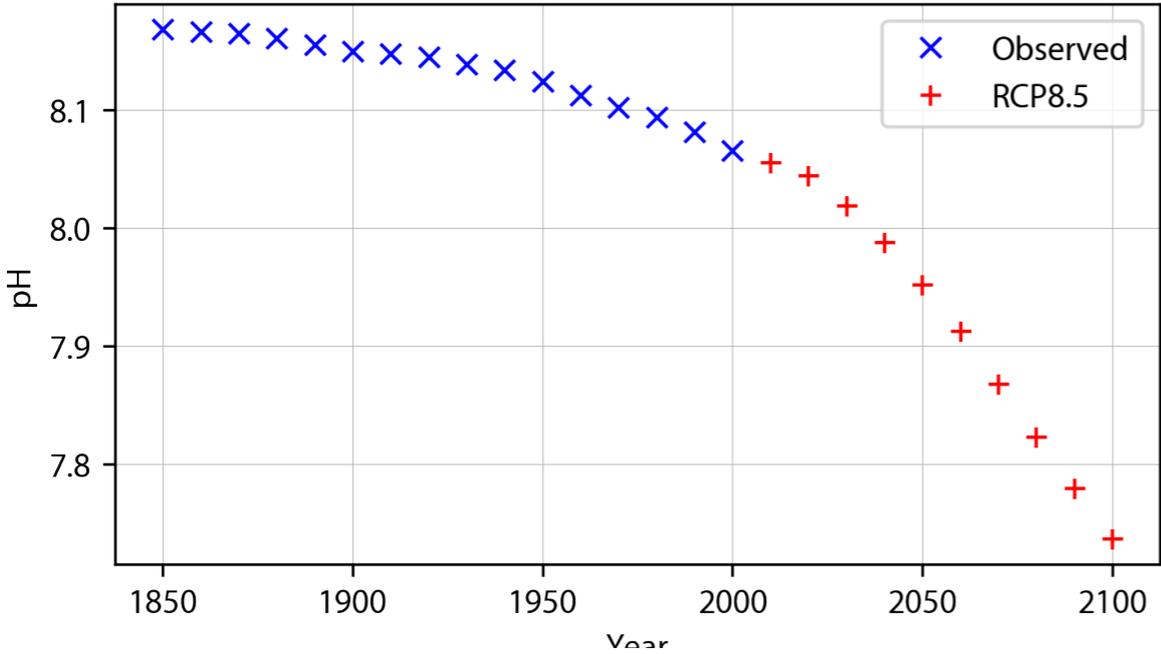
1. Understand calcium carbonate  $\text{CaCO}_3$  dissolution.
2. The ocean carbonate system: how pH is affected by atmospheric  $\text{CO}_2$ .
3. The carbonate system buffer effect: why the ocean can absorb so much carbon.
4. A positive feedback on warming due to the response of the carbonate system to warming:  
Higher  $\text{CO}_2$  ➡ rising temperature ➡ more  $\text{CO}_2$  emitted by ocean
5. The long-term fate of anthropogenic  $\text{CO}_2$ : how/why will it decline.

## Workshop #1

# Characterizing pH changes

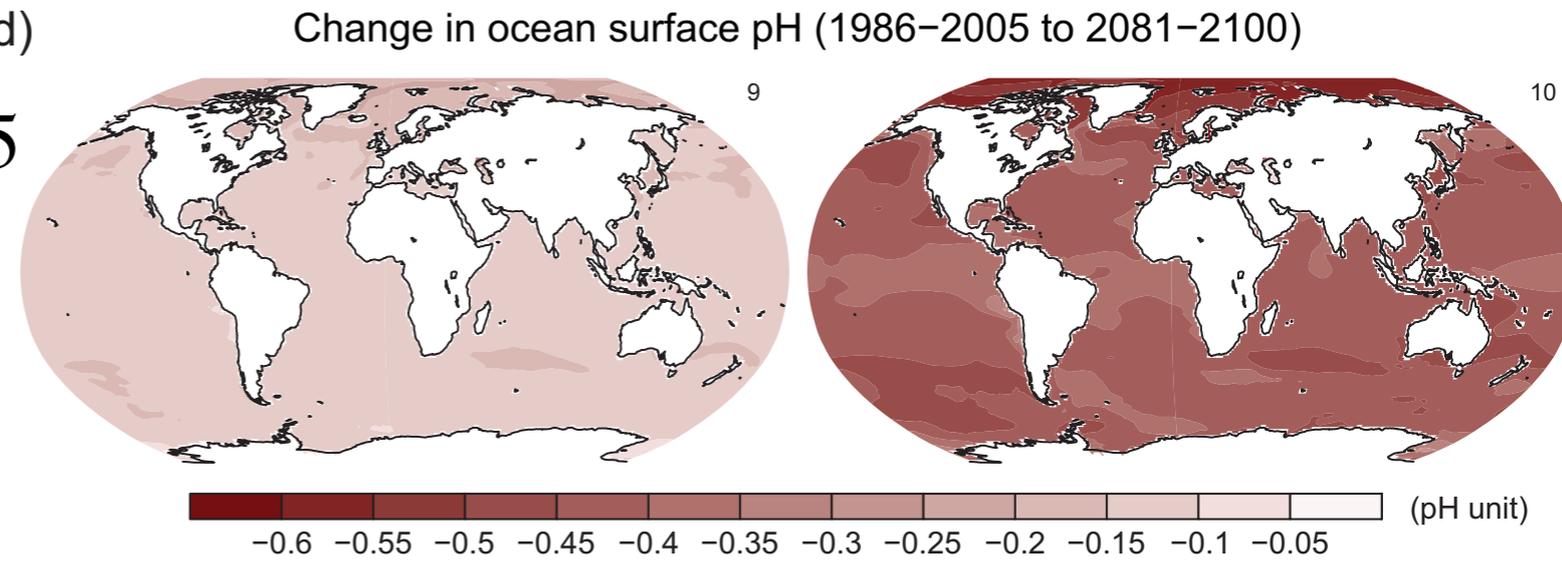
# Workshop #1

## Characterizing pH changes



# Projections: ocean will become much more acidic

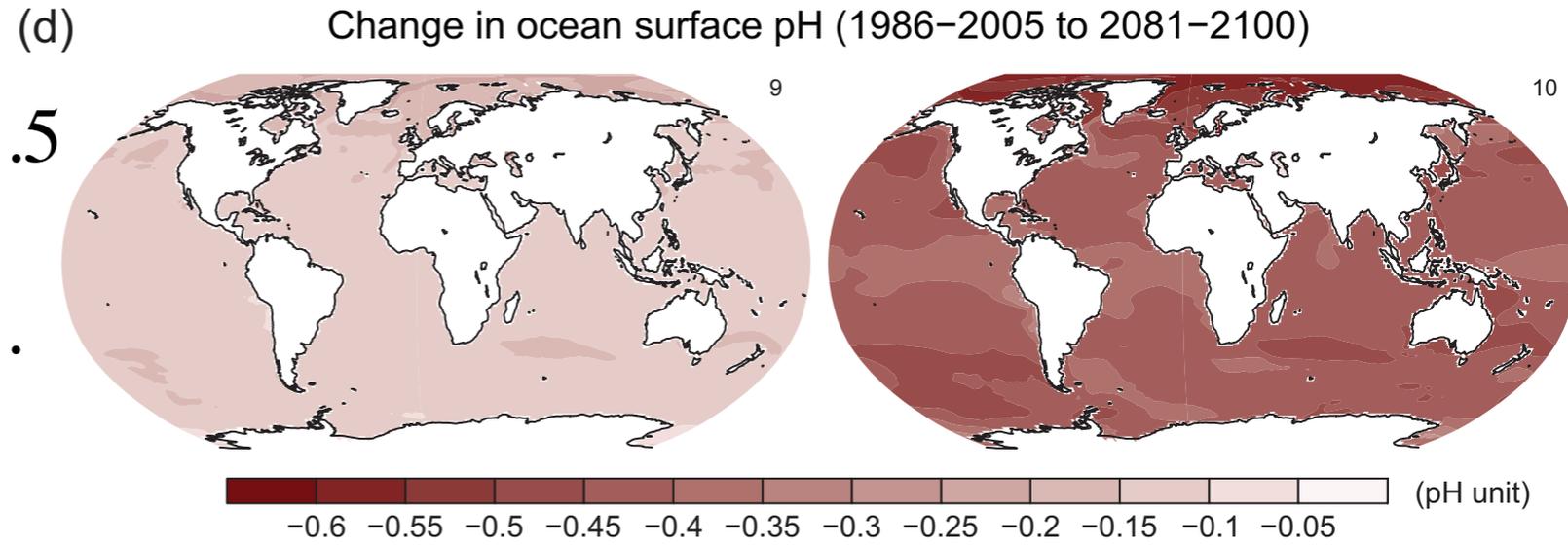
**Figure SPM.8 |** CMIP5 multi-model mean for RCP2.6 & RCP8.5 in 2081–2100 of change in ocean surface pH relative to 1986–2005. Number of models used is in the upper right corner of each panel.



**IPCC AR5, 2013**

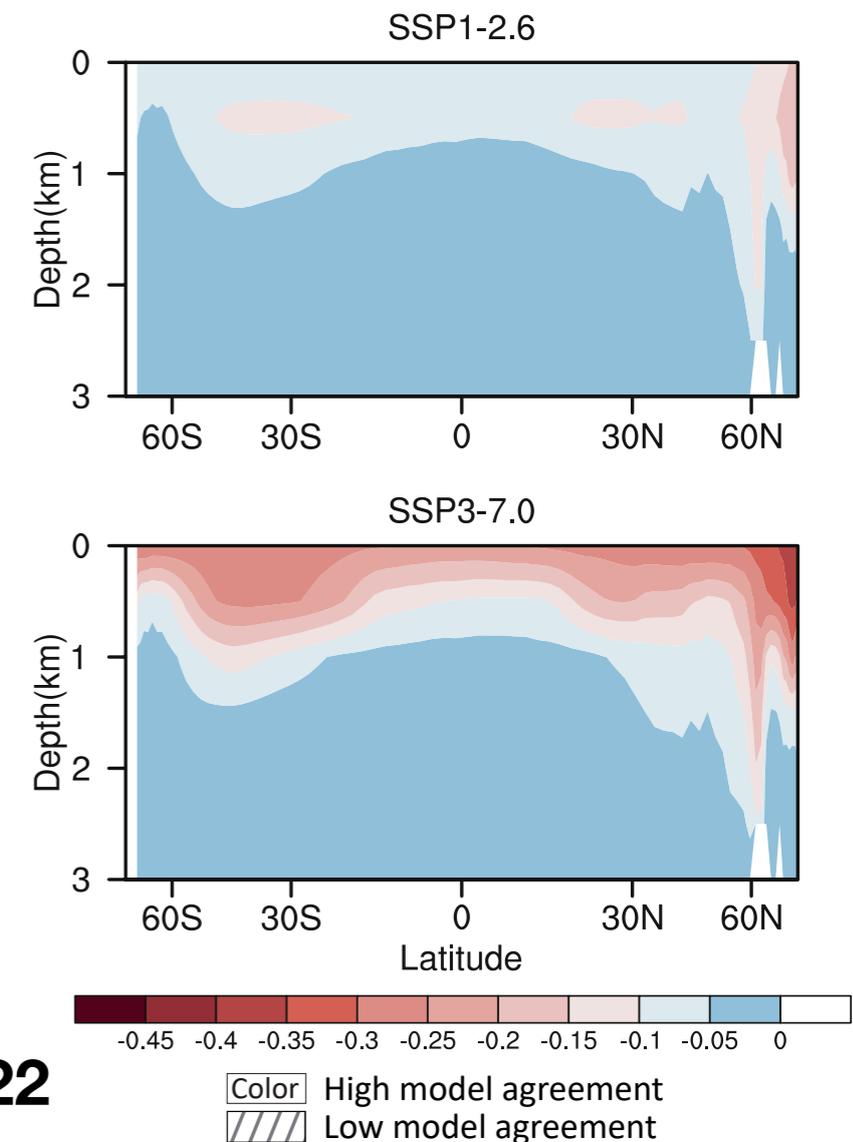
# Projections: ocean will become much more acidic

**Figure SPM.8 |** CMIP5 multi-model mean for RCP2.6 & RCP8.5 in 2081–2100 of change in ocean surface pH relative to 1986–2005. Number of models used is in the upper right corner of each panel.



**IPCC AR5, 2013**

**Figure 4.29 | Long-term change of annual and zonal mean ocean pH.** Multi-model mean change in annual and zonal pH in 2081–2100 relative to 1995–2014 for SSP1-2.6 and SSP3-7.0, respectively. Eleven CMIP6 models are used.



**IPCC AR6, 2022**

notes section 5.1:  
pH and  $\text{CaCO}_3$  dissolution

# pH and $\text{CaCO}_3$ dissolution

The equilibrium reaction between solid calcium carbonate and the ions



# pH and $\text{CaCO}_3$ dissolution

The equilibrium reaction between solid calcium carbonate and the ions



The equilibrium concentrations are related via the solubility product

$$K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$$

# pH and $\text{CaCO}_3$ dissolution

The equilibrium reaction between solid calcium carbonate and the ions



The equilibrium concentrations are related via the solubility product

$$K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$$

The saturation state is given by omega. **When  $\Omega < 1$ ,  $\text{CaCO}_3$  tends to dissolve.**

$$\Omega = \frac{[\text{Ca}^{2+}] [\text{CO}_3^{2-}]}{K_{sp}}$$

# pH and $\text{CaCO}_3$ dissolution

The equilibrium reaction between solid calcium carbonate and the ions



The equilibrium concentrations are related via the solubility product

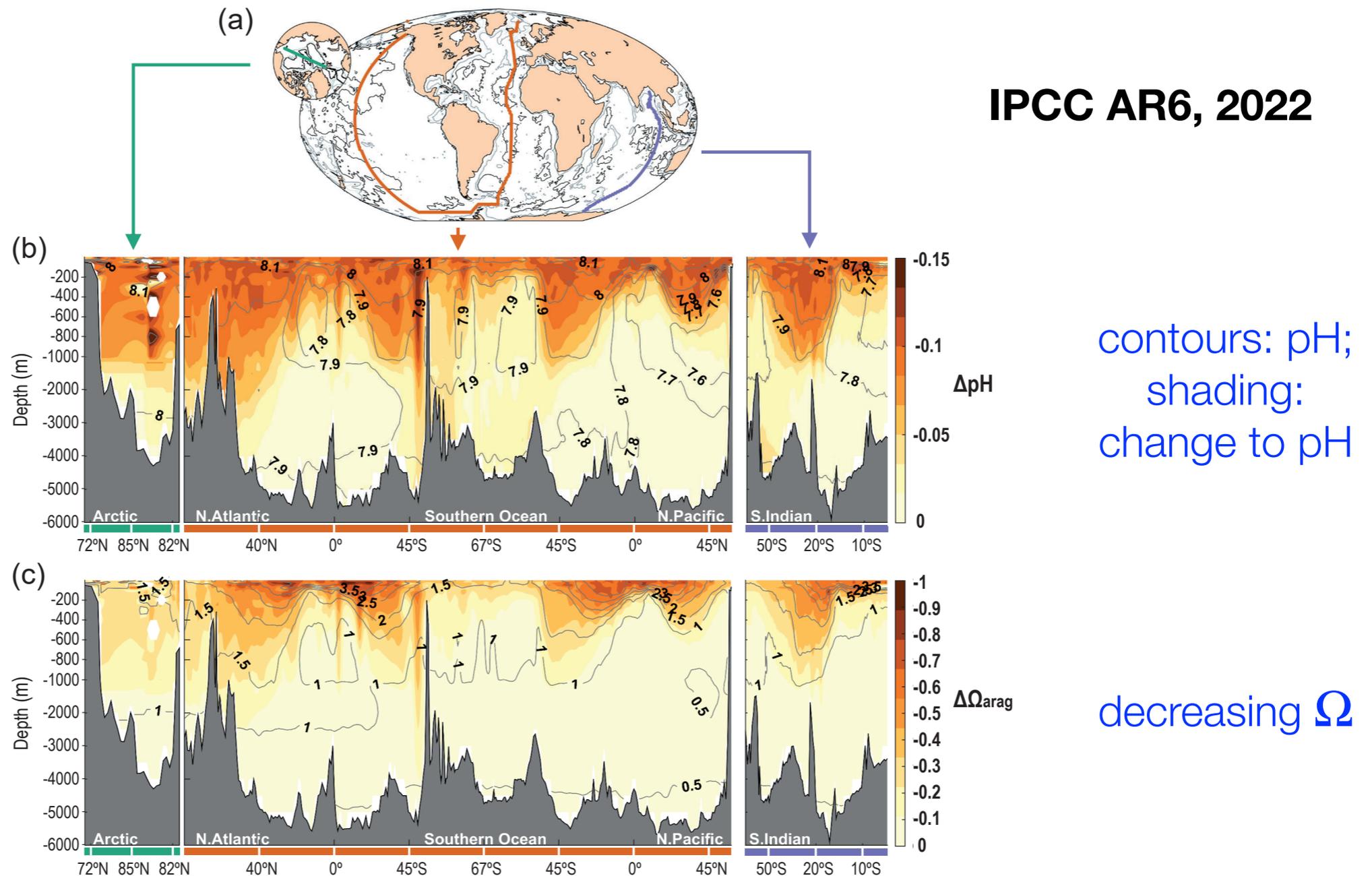
$$K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}]$$

The saturation state is given by omega. **When  $\Omega < 1$ ,  $\text{CaCO}_3$  tends to dissolve.**

$$\Omega = \frac{[\text{Ca}^{2+}] [\text{CO}_3^{2-}]}{K_{sp}}$$

We will see next that as ocean pH decreases due to the increase in atmospheric  $\text{CO}_2$ , the carbonate ion concentration,  $\text{CO}_3^{2-}$  decreases as well, making omega smaller and leading toward more dissolution.

# Spread of ocean acidification from the surface into the interior of ocean since pre-industrial times.



**Figure 5.21 | Spread of ocean acidification from the surface into the interior since pre-industrial times. (a) three transects used to create the cross sections shown in (b) and (c); vertical sections of the changes in (b) pH and (c) saturation state of aragonite ( $\Omega_{\text{arag}}$ ) between 1800–2002 due to anthropogenic  $\text{CO}_2$  invasion (color). Contour lines: contemporary values in 2002.**



Lamont-Doherty Earth Observatory  
COLUMBIA UNIVERSITY | EARTH INSTITUTE

<https://www.youtube.com/watch?v=Qdj6z5my58U>



Lamont-Doherty Earth Observatory  
COLUMBIA UNIVERSITY | EARTH INSTITUTE

<https://www.youtube.com/watch?v=Qdj6z5my58U>

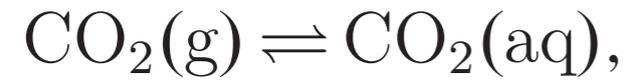
notes:

section 5.2 The carbonate system

section 5.2.1 Carbonate system equations

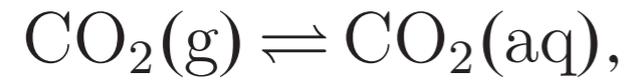
# The ocean carbonate system

Atmospheric  $\text{CO}_2(\text{g})$  is in equilibrium with dissolved  $\text{CO}_2(\text{aq})$ , (Henry's Law)



# The ocean carbonate system

Atmospheric  $\text{CO}_2(\text{g})$  is in equilibrium with dissolved  $\text{CO}_2(\text{aq})$ , (Henry's Law)

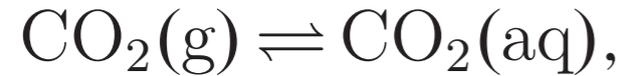


its reaction with water is given by



# The ocean carbonate system

Atmospheric  $\text{CO}_2(\text{g})$  is in equilibrium with dissolved  $\text{CO}_2(\text{aq})$ , (Henry's Law)



its reaction with water is given by

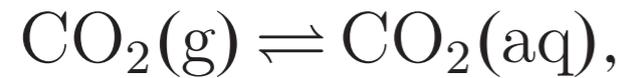


treated together as a single variable



# The ocean carbonate system

Atmospheric  $\text{CO}_2(\text{g})$  is in equilibrium with dissolved  $\text{CO}_2(\text{aq})$ , (Henry's Law)



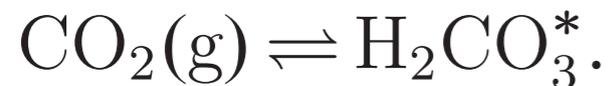
its reaction with water is given by



treated together as a single variable

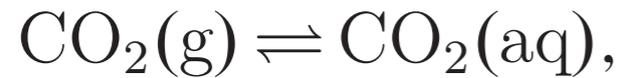


Henry's law is now,



# The ocean carbonate system

Atmospheric  $\text{CO}_2(\text{g})$  is in equilibrium with dissolved  $\text{CO}_2(\text{aq})$ , (Henry's Law)



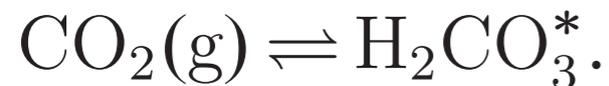
its reaction with water is given by



treated together as a single variable



Henry's law is now,

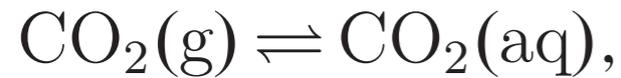


Carbonic acid releases two protons



# The ocean carbonate system

Atmospheric  $\text{CO}_2(\text{g})$  is in equilibrium with dissolved  $\text{CO}_2(\text{aq})$ , (Henry's Law)



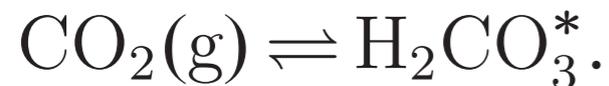
its reaction with water is given by



treated together as a single variable



Henry's law is now,



Carbonic acid releases two protons

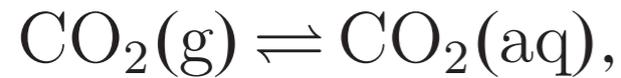


Water dissociation



# The ocean carbonate system

Atmospheric  $\text{CO}_2(\text{g})$  is in equilibrium with dissolved  $\text{CO}_2(\text{aq})$ , (Henry's Law)



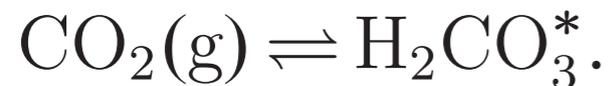
its reaction with water is given by



treated together as a single variable



Henry's law is now,



Carbonic acid releases two protons



Water dissociation



$$K_H \equiv K_0(T, S, p) = \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(\text{g})]}$$

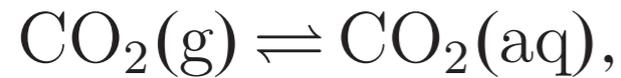
$$K_1(T, S, p) = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]}$$

$$K_2(T, S, p) = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$K_w(T, S, p) = [\text{H}^+][\text{OH}^-]$$

# The ocean carbonate system

Atmospheric  $\text{CO}_2(\text{g})$  is in equilibrium with dissolved  $\text{CO}_2(\text{aq})$ , (Henry's Law)



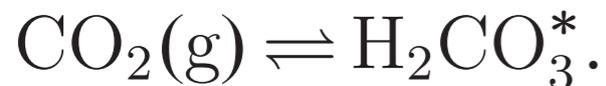
its reaction with water is given by



treated together as a single variable



Henry's law is now,



Carbonic acid releases two protons



Water dissociation



$$K_H \equiv K_0(T, S, p) = \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(\text{g})]}$$

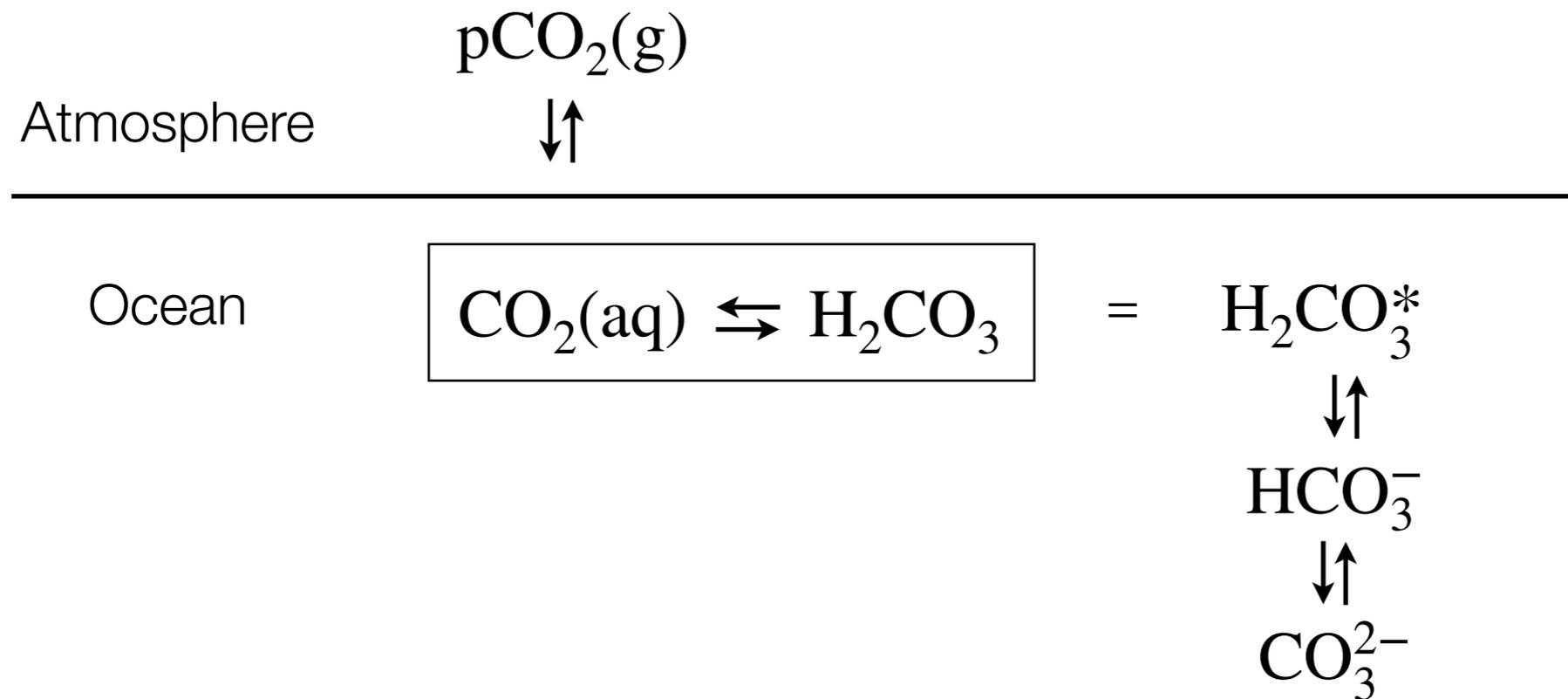
$$K_1(T, S, p) = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]}$$

$$K_2(T, S, p) = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$K_w(T, S, p) = [\text{H}^+][\text{OH}^-]$$

➔ **6 unknown**  $[\text{CO}_2(\text{g})]$ ,  $[\text{H}_2\text{CO}_3^*]$ ,  $[\text{OH}^-]$ ,  $[\text{H}^+]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ , **and only four equations**

# The ocean carbonate system



# Charge conservation and carbon mass conservation

Charge conservation:

$$0 = \left( [\text{H}^+] - [\text{OH}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{HBO}_3^-] \right) \left| \begin{array}{l} \text{Weak acids/bases: concentration} \\ \text{changes as we change the pH} \end{array} \right.$$

$$+ \left( [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] \right) \left| \begin{array}{l} \text{Strong, don't change} \end{array} \right.$$

$$- 2[\text{SO}_4^{2-}] - [\text{NO}_3^-].$$

Use that to define Alkalinity:

$$\begin{aligned} \text{Alk} &\equiv [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{HBO}_3^-] + [\text{OH}^-] - [\text{H}^+] \\ &= [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] \\ &\quad - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-]. \end{aligned}$$

And carbonate Alkalinity, good enough approximation for our purposes:

$$\begin{aligned} \text{Alk}_C &\equiv [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \\ &\approx [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]. \end{aligned}$$

Two more equations!

And total carbon mass: also does not change in carbonate system reactions:

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3^*].$$

# Complete equations for the ocean carbonate system

Charge conservation (alkalinity)

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

← Carbonate alkalinity  $\text{Alk}_C$  →

$T, S, p$ : the ocean temperature, salinity, and pressure where the carbonate system is solved.

# Complete equations for the ocean carbonate system

Charge conservation (alkalinity)

$$\text{Carbonate alkalinity } Alk_C$$
$$Alk = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Mass conservation (total CO<sub>2</sub>)

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3^*].$$

$T, S, p$ : the ocean temperature, salinity, and pressure where the carbonate system is solved.

# Complete equations for the ocean carbonate system

Charge conservation (alkalinity)

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Carbonate alkalinity  $Alk_C$

Mass conservation (total  $\text{CO}_2$ )

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3^*].$$

plus the carbonate equations

$$K_H \equiv K_0(T, S, p) = \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(\text{g})]}$$

$$K_1(T, S, p) = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]}$$

$$K_2(T, S, p) = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$K_w(T, S, p) = [\text{H}^+][\text{OH}^-]$$

$T, S, p$ : the ocean temperature, salinity, and pressure where the carbonate system is solved.

# Complete equations for the ocean carbonate system

Charge conservation (alkalinity)

$$\text{Carbonate alkalinity } Alk_C$$

$$Alk = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Mass conservation (total CO<sub>2</sub>)

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3^*].$$

plus the carbonate equations

$$K_H \equiv K_0(T, S, p) = \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(\text{g})]}$$

$$K_1(T, S, p) = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]}$$

$$K_2(T, S, p) = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$K_w(T, S, p) = [\text{H}^+][\text{OH}^-]$$

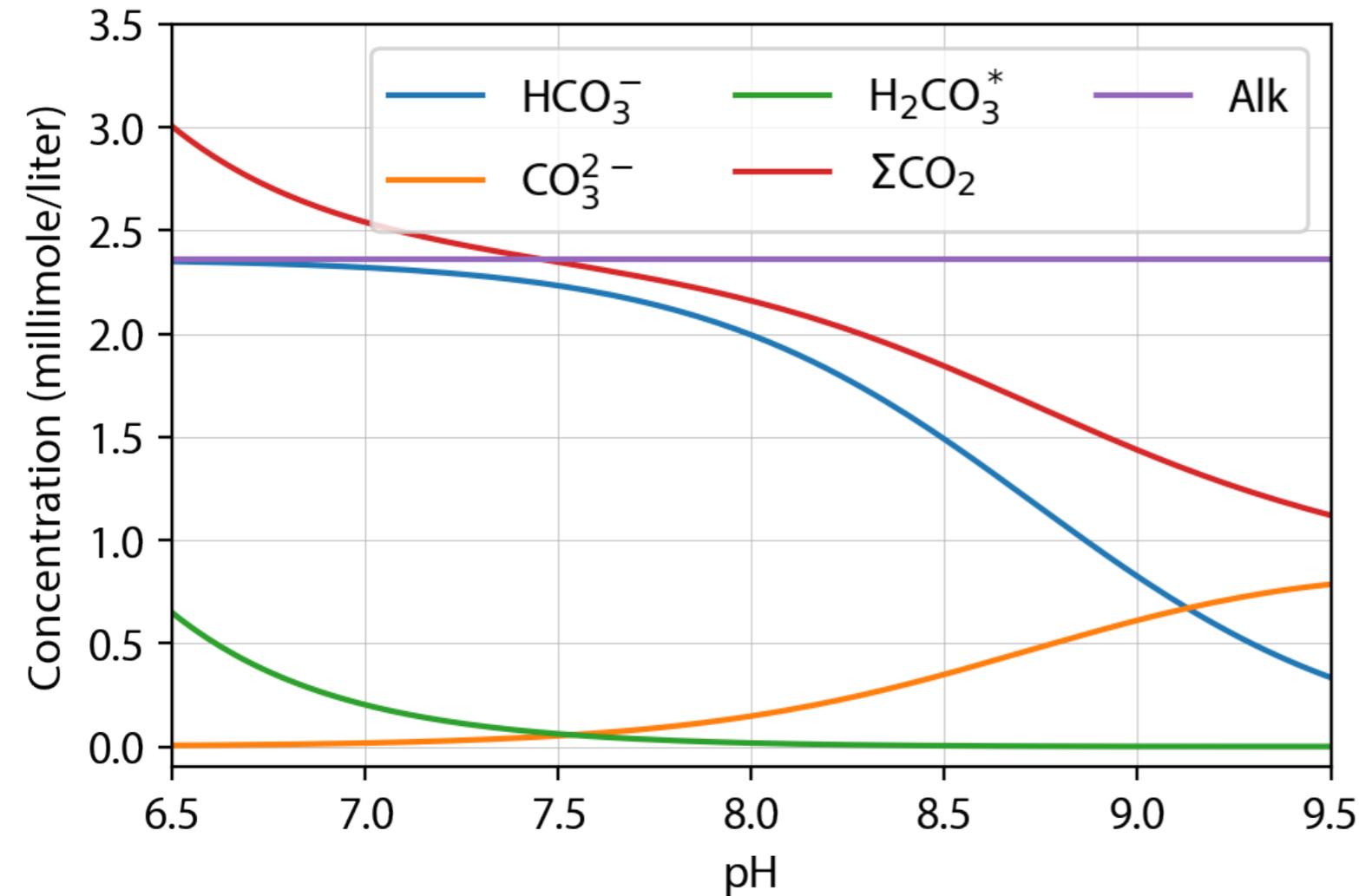
*T, S, p*: the ocean temperature, salinity, and pressure where the carbonate system is solved.

➔ **6 unknown**  $[\text{CO}_2(\text{g})]$ ,  $[\text{H}_2\text{CO}_3^*]$ ,  $[\text{OH}^-]$ ,  $[\text{H}^+]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ , **and six equations**

# Workshop #2

## The carbonate system solution

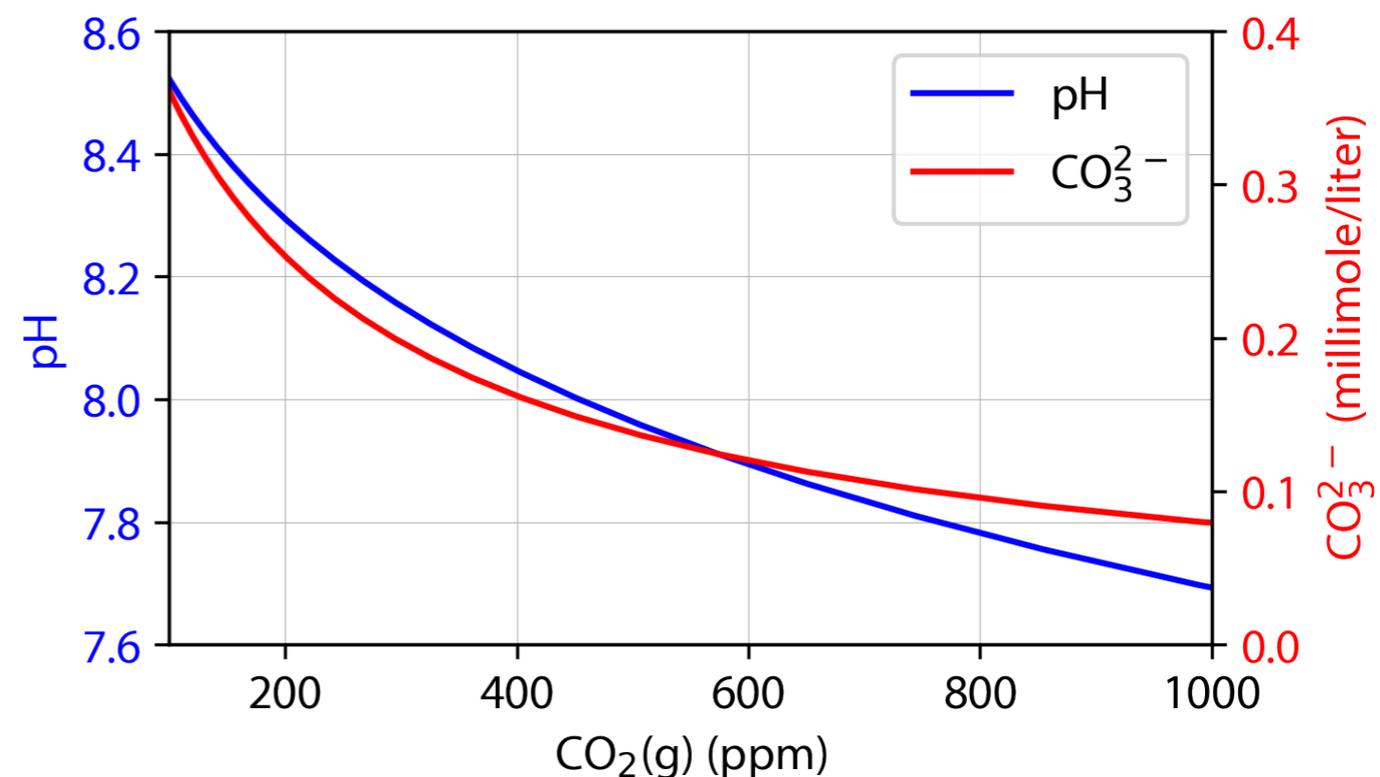
# Carbonate system solution



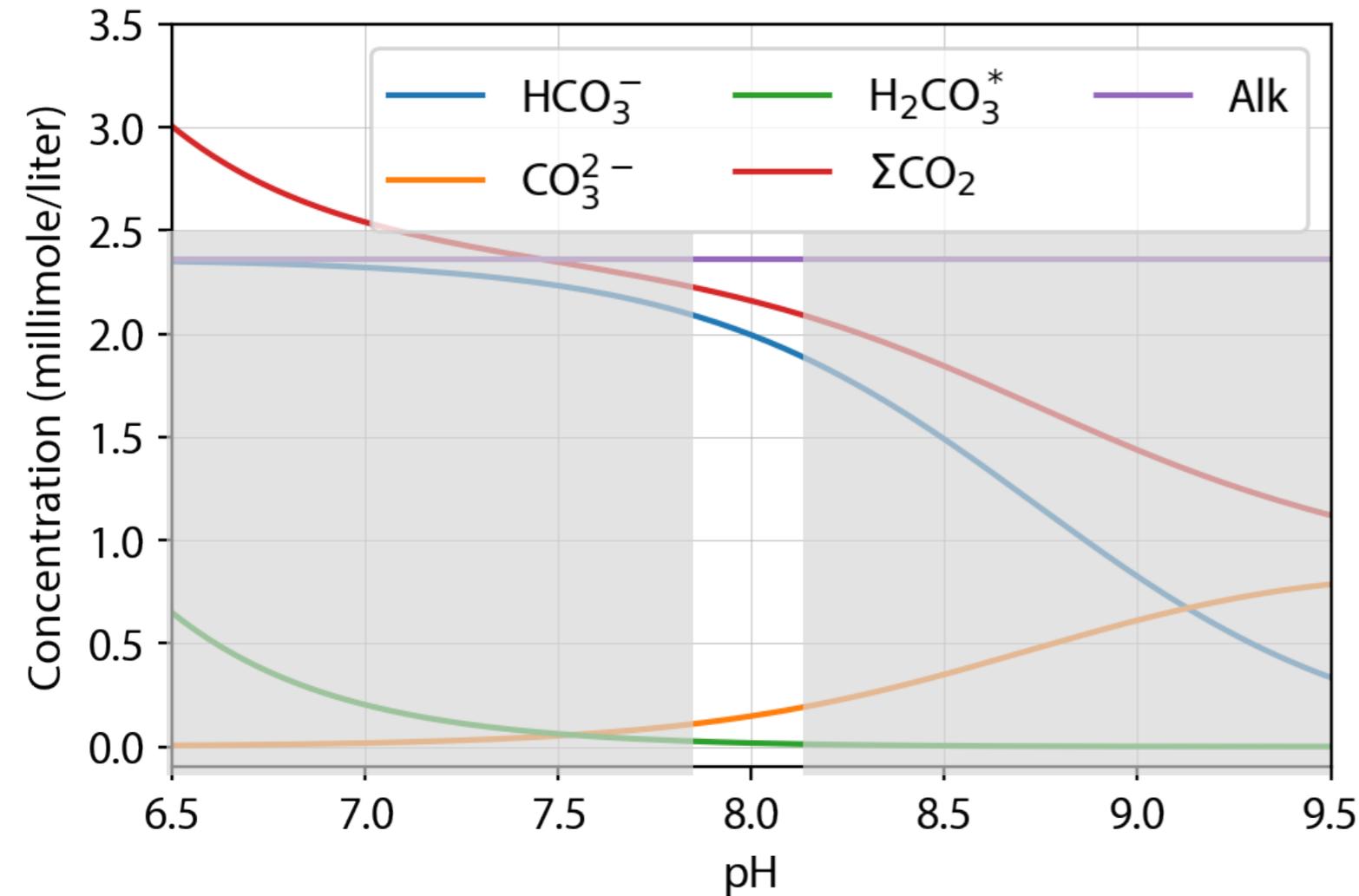
**Figure 5.3: The solution of the carbonate system,** showing the concentration of carbonate species as a function of pH for a fixed alkalinity.

**Figure 5.4: The response of pH and carbonate ion to  $\text{CO}_2$  increase.**

The solution of the carbonate system for a fixed alkalinity as in Figure 5.3, showing the ocean pH (blue) and the carbonate ion  $\text{CO}_3^{2-}$  concentration (red) as a function of atmospheric  $\text{CO}_2$ .



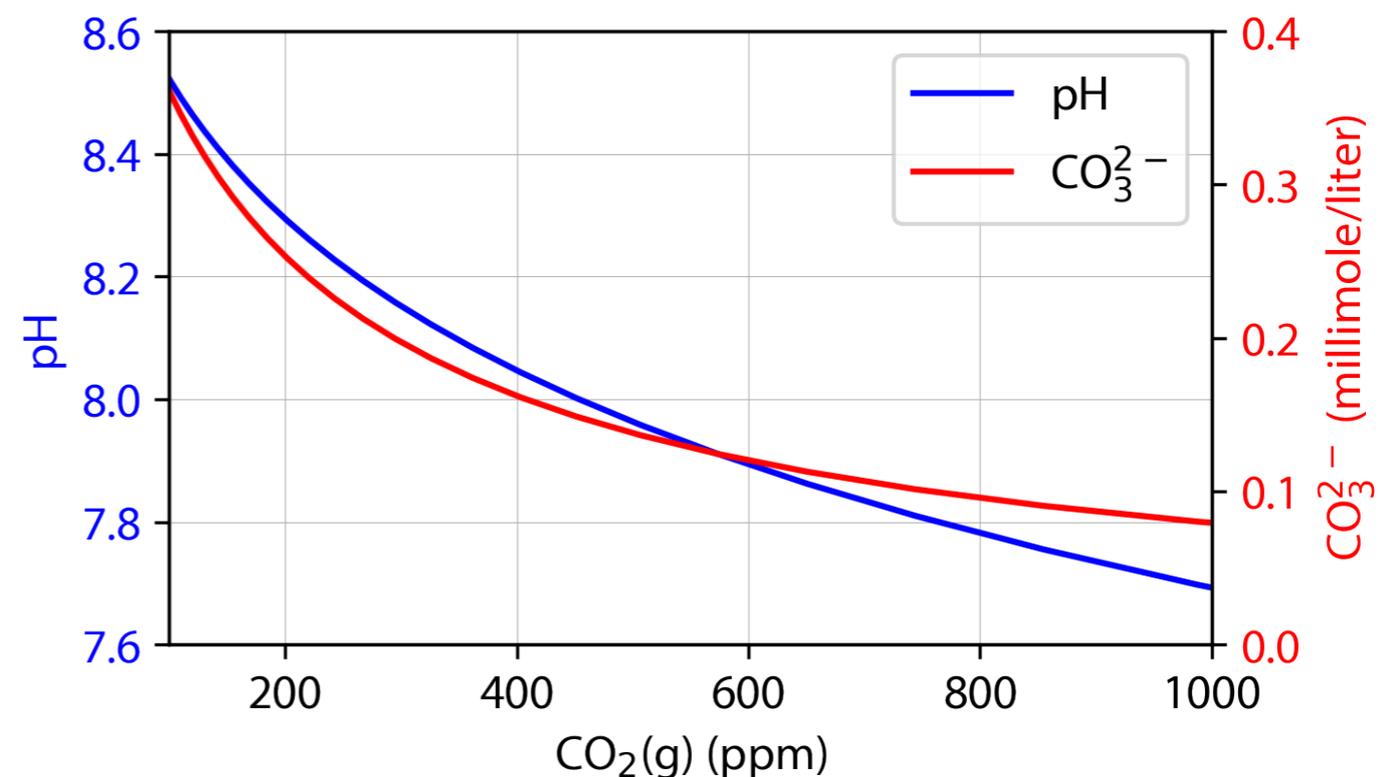
# Carbonate system solution



**Figure 5.3: The solution of the carbonate system,** showing the concentration of carbonate species as a function of pH for a fixed alkalinity.

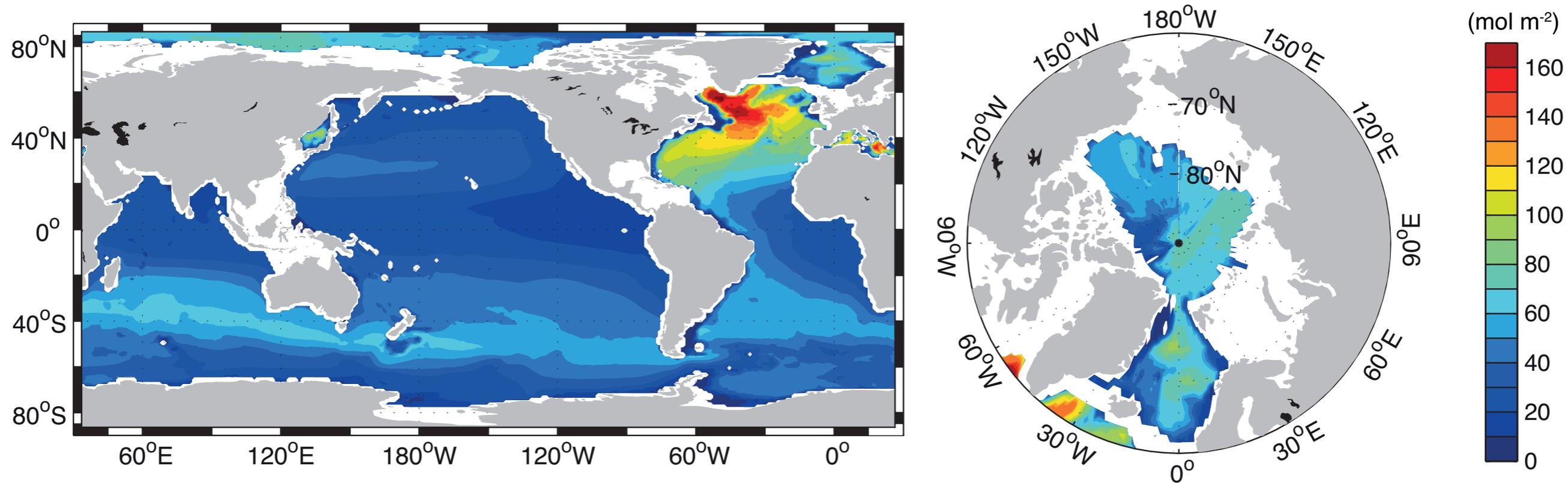
**Figure 5.4: The response of pH and carbonate ion to  $\text{CO}_2$  increase.**

The solution of the carbonate system for a fixed alkalinity as in Figure 5.3, showing the ocean pH (blue) and the carbonate ion  $\text{CO}_3^{2-}$  concentration (red) as a function of atmospheric  $\text{CO}_2$ .



# Oceans are already storing much more carbon

IPCC AR5, 2013



**Figure 3.16** | Compilation of the 2010 column inventories ( $\text{mol m}^{-2}$ ) of anthropogenic CO<sub>2</sub>: the global Ocean excluding the marginal seas (updated from Khatiwala et al., 2009)  $150 \pm 26$  PgC; Arctic Ocean (Tanhua et al., 2009) 2.7 to 3.5 PgC; the Nordic Seas (Olsen et al., 2010) 1.0 to 1.6 PgC; the Mediterranean Sea (Schneider et al., 2010) 1.6 to 2.5 PgC; the Sea of Japan (Park et al., 2006)  $0.40 \pm 0.06$  PgC. From Khatiwala et al. (2013).

Spatial patterns of carbon storage, affected by ocean circulation

notes:

5.2.2 Approximate solution of the carbonate system

5.3.1 Understanding the response to increased atmospheric  $\text{CO}_2$  concentration

# Approximate solution of the carbonate system

For the values of pH at present/near future:



# Approximate solution of the carbonate system

For the values of pH at present/near future:



So that

$$\text{Alk}_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \cancel{[\text{OH}^-]} - \cancel{[\text{H}^+]}$$

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + \cancel{[\text{H}_2\text{CO}_3^*]}.$$

# Approximate solution of the carbonate system

For the values of pH at present/near future:

$$[\text{HCO}_3^-], [\text{CO}_3^{2-}] \gg [\text{H}^+], [\text{OH}^-], [\text{H}_2\text{CO}_3^*].$$

So that

$$\text{Alk}_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \cancel{[\text{OH}^-]} - \cancel{[\text{H}^+]}$$

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + \cancel{[\text{H}_2\text{CO}_3^*]}.$$

➔ only 5 unknowns ( $\text{OH}^-$  drops out) & the eqns become

$$K_H = \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(\text{g})]},$$

$$K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3^*]},$$

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]},$$

$$\text{Alk}_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

# Approximate solution of the carbonate system

For the values of pH at present/near future:

$$[\text{HCO}_3^-], [\text{CO}_3^{2-}] \gg [\text{H}^+], [\text{OH}^-], [\text{H}_2\text{CO}_3^*].$$

So that

$$\text{Alk}_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \cancel{[\text{OH}^-]} - \cancel{[\text{H}^+]}$$

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + \cancel{[\text{H}_2\text{CO}_3^*]}.$$

➔ only 5 unknowns ( $\text{OH}^-$  drops out) & the eqns become

$$[\text{HCO}_3^-] = 2C_T - \text{Alk}_C,$$

$$[\text{CO}_3^{2-}] = \text{Alk}_C - C_T.$$

$$[\text{H}^+] = K_2 \frac{2C_T - \text{Alk}_C}{\text{Alk}_C - C_T}$$

$$[\text{H}_2\text{CO}_3^*] = \frac{K_2 (2C_T - \text{Alk}_C)^2}{K_1 (\text{Alk}_C - C_T)}$$

$$[\text{CO}_2(\text{g})] = \frac{K_2 (2C_T - \text{Alk}_C)^2}{K_1 K_H (\text{Alk}_C - C_T)}.$$

$$K_H = \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(\text{g})]},$$

$$K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3^*]},$$

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]},$$

$$\text{Alk}_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

and can be solved as

# Approximate solution of the carbonate system

For the values of pH at present/near future:

$$[\text{HCO}_3^-], [\text{CO}_3^{2-}] \gg [\text{H}^+], [\text{OH}^-], [\text{H}_2\text{CO}_3^*].$$

So that

$$\text{Alk}_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \cancel{[\text{OH}^-]} - \cancel{[\text{H}^+]}$$

$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + \cancel{[\text{H}_2\text{CO}_3^*]}.$$

➔ only 5 unknowns ( $\text{OH}^-$  drops out) & the eqns become

$$[\text{HCO}_3^-] = 2C_T - \text{Alk}_C,$$

$$[\text{CO}_3^{2-}] = \text{Alk}_C - C_T.$$

$$[\text{H}^+] = K_2 \frac{2C_T - \text{Alk}_C}{\text{Alk}_C - C_T}$$

$$[\text{H}_2\text{CO}_3^*] = \frac{K_2 (2C_T - \text{Alk}_C)^2}{K_1 (\text{Alk}_C - C_T)}$$

$$[\text{CO}_2(\text{g})] = \frac{K_2 (2C_T - \text{Alk}_C)^2}{K_1 K_H (\text{Alk}_C - C_T)}.$$

$$K_H = \frac{[\text{H}_2\text{CO}_3^*]}{[\text{CO}_2(\text{g})]},$$

$$K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3^*]},$$

$$K_2 = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]},$$

$$\text{Alk}_C = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

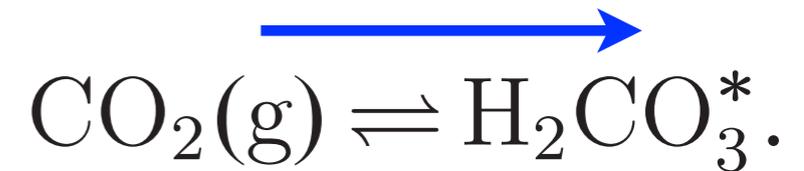
$$C_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

and can be solved as

what could be simpler 🤔

# Understanding the decrease of $\text{CO}_3^{2-}$ in response to $\text{CO}_2$ increase

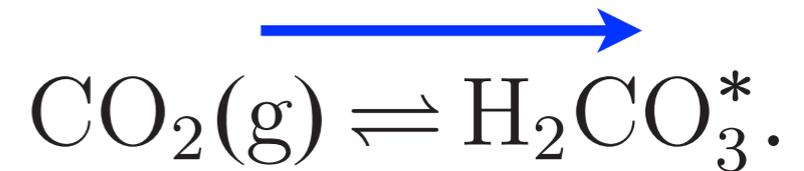
Atmospheric  $\text{CO}_2$  increase implies that Henry's law reaction goes to the right:



(This approach is heuristic, for building intuition only, one needs to consider all reactions simultaneously, not one by one.)

# Understanding the decrease of $\text{CO}_3^{2-}$ in response to $\text{CO}_2$ increase

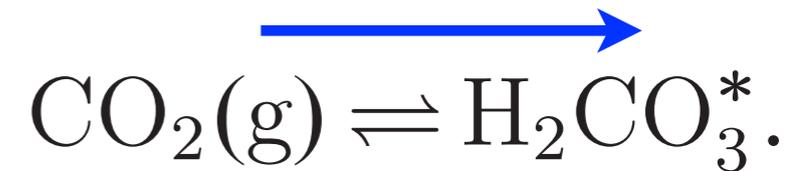
Atmospheric  $\text{CO}_2$  increase implies that Henry's law reaction goes to the right:



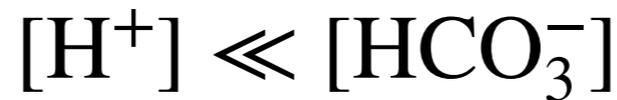
(This approach is heuristic, for building intuition only, one needs to consider all reactions simultaneously, not one by one.)

# Understanding the decrease of $\text{CO}_3^{2-}$ in response to $\text{CO}_2$ increase

Atmospheric  $\text{CO}_2$  increase implies that Henry's law reaction goes to the right:



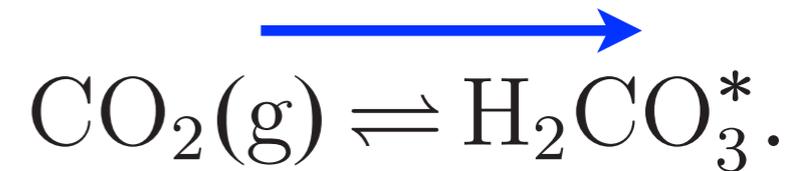
Both increased by same number of ions, but because



the fractional growth of the bicarbonate ion  $[\text{HCO}_3^-]$  is smaller than that of  $[\text{H}^+]$

# Understanding the decrease of $\text{CO}_3^{2-}$ in response to $\text{CO}_2$ increase

Atmospheric  $\text{CO}_2$  increase implies that Henry's law reaction goes to the right:



Both increased by same number of ions, but because

$$[\text{H}^+] \ll [\text{HCO}_3^-]$$

the fractional growth of the bicarbonate ion  $[\text{HCO}_3^-]$  is smaller than that of  $[\text{H}^+]$

therefore  $[\text{H}^+]/[\text{HCO}_3^-]$  increases.

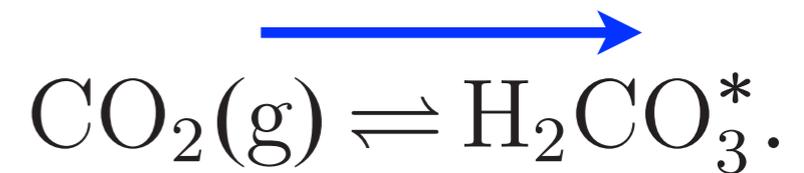
➔ to keep the ratio constant

$$K_2(T, S, p) = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

the carbonate ion  $[\text{CO}_3^{2-}]$  must decrease

# Understanding the decrease of $\text{CO}_3^{2-}$ in response to $\text{CO}_2$ increase

Atmospheric  $\text{CO}_2$  increase implies that Henry's law reaction goes to the right:



Both increased by same number of ions, but because

$$[\text{H}^+] \ll [\text{HCO}_3^-]$$

the fractional growth of the bicarbonate ion  $[\text{HCO}_3^-]$  is smaller than that of  $[\text{H}^+]$

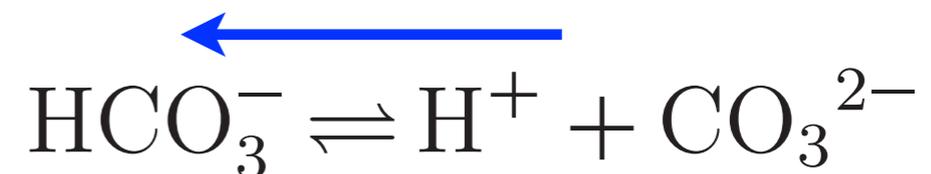
therefore  $[\text{H}^+]/[\text{HCO}_3^-]$  increases.

➔ to keep the ratio constant

$$K_2(T, S, p) = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

the carbonate ion  $[\text{CO}_3^{2-}]$  must decrease

so that this reaction must go to the left:



notes

The carbonate system buffer effect (within section 5.3.1)

The big picture:

# The carbonate system buffer effect

## The big picture: The carbonate system buffer effect

- Most dissolved  $\text{CO}_2$  is converted into bicarbonate  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$  ions

## The carbonate system buffer effect

The big picture:

- Most dissolved  $\text{CO}_2$  is converted into bicarbonate  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$  ions
- ➔ For a given atmospheric  $\text{CO}_2$  increase, the ocean absorbs much more  $\text{CO}_2$  than it would have if the dissolved  $\text{CO}_2$  all stayed as  $\text{H}_2\text{CO}_3^*$

## The carbonate system buffer effect

The big picture:

- Most dissolved  $\text{CO}_2$  is converted into bicarbonate  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$  ions
- ➔ For a given atmospheric  $\text{CO}_2$  increase, the ocean absorbs much more  $\text{CO}_2$  than it would have if the dissolved  $\text{CO}_2$  all stayed as  $\text{H}_2\text{CO}_3^*$
- This is the “buffer effect” of the ocean carbonate system.

## The carbonate system buffer effect

The big picture:

- Most dissolved  $\text{CO}_2$  is converted into bicarbonate  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$  ions
- ➔ For a given atmospheric  $\text{CO}_2$  increase, the ocean absorbs much more  $\text{CO}_2$  than it would have if the dissolved  $\text{CO}_2$  all stayed as  $\text{H}_2\text{CO}_3^*$
- This is the “buffer effect” of the ocean carbonate system.

Understanding it

- Henry's law ( $\text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3^*$ ) controls the concentration of  $\text{H}_2\text{CO}_3^*$ ,
- Without the carbonate reactions, an increase in atm  $\text{CO}_2$  would increase  $\text{H}_2\text{CO}_3^*$  alone.

## The carbonate system buffer effect

The big picture:

- Most dissolved  $\text{CO}_2$  is converted into bicarbonate  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$  ions
- ➔ For a given atmospheric  $\text{CO}_2$  increase, the ocean absorbs much more  $\text{CO}_2$  than it would have if the dissolved  $\text{CO}_2$  all stayed as  $\text{H}_2\text{CO}_3^*$
- This is the “buffer effect” of the ocean carbonate system.

Understanding it

- Henry's law ( $\text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3^*$ ) controls the concentration of  $\text{H}_2\text{CO}_3^*$ ,
- Without the carbonate reactions, an increase in atm  $\text{CO}_2$  would increase  $\text{H}_2\text{CO}_3^*$  alone.
- But, distribution of carbon among [ $\text{H}_2\text{CO}_3^*$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ] is [1%, 10%, 90%]

## The carbonate system buffer effect

The big picture:

- Most dissolved  $\text{CO}_2$  is converted into bicarbonate  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$  ions
- ➔ For a given atmospheric  $\text{CO}_2$  increase, the ocean absorbs much more  $\text{CO}_2$  than it would have if the dissolved  $\text{CO}_2$  all stayed as  $\text{H}_2\text{CO}_3^*$
- This is the “buffer effect” of the ocean carbonate system.

Understanding it

- Henry's law ( $\text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3^*$ ) controls the concentration of  $\text{H}_2\text{CO}_3^*$ ,
- Without the carbonate reactions, an increase in atm  $\text{CO}_2$  would increase  $\text{H}_2\text{CO}_3^*$  alone.
- But, distribution of carbon among [ $\text{H}_2\text{CO}_3^*$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ] is [1%, 10%, 90%]
- ➔ A small increase in  $\text{H}_2\text{CO}_3^*$  due to the  $\text{CO}_2(\text{g})$  increase implies a much larger increase in the bicarbonate ion  $\text{HCO}_3^-$  ➔ a very large increase in total dissolved  $\text{CO}_2$ .

## The carbonate system buffer effect

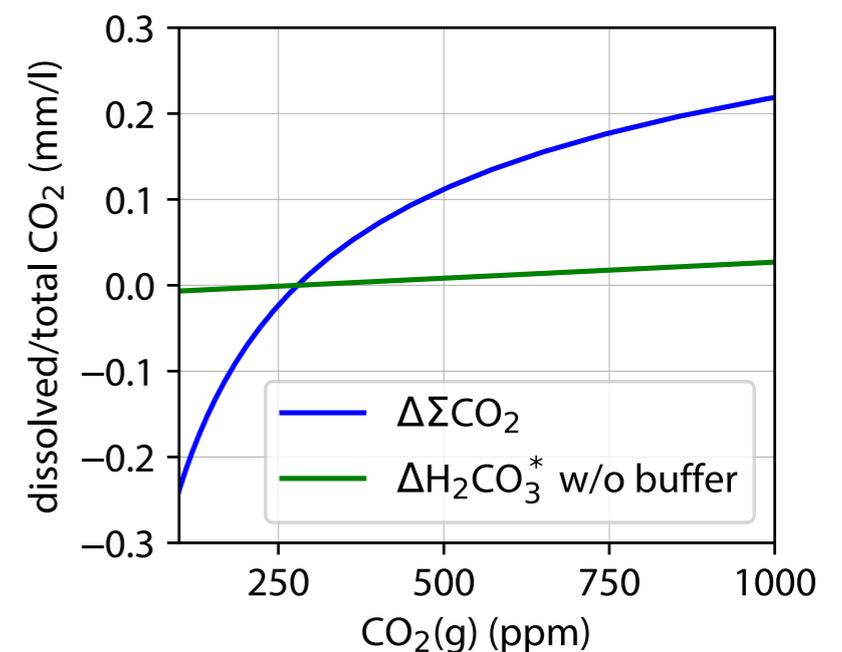
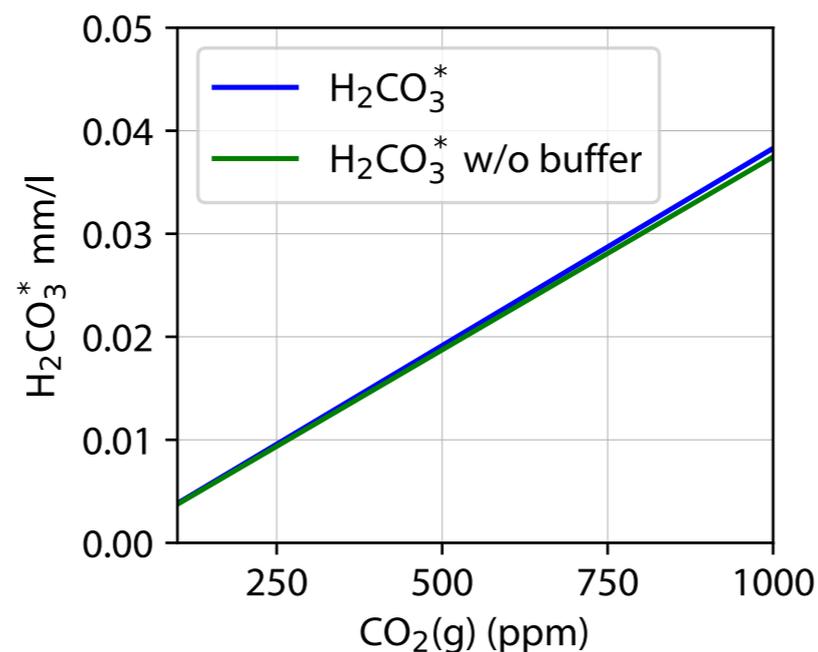
The big picture:

- Most dissolved  $\text{CO}_2$  is converted into bicarbonate  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$  ions
- ➔ For a given atmospheric  $\text{CO}_2$  increase, the ocean absorbs much more  $\text{CO}_2$  than it would have if the dissolved  $\text{CO}_2$  all stayed as  $\text{H}_2\text{CO}_3^*$
- This is the “buffer effect” of the ocean carbonate system.

Understanding it

- Henry’s law ( $\text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3^*$ ) controls the concentration of  $\text{H}_2\text{CO}_3^*$ ,
- Without the carbonate reactions, an increase in atm  $\text{CO}_2$  would increase  $\text{H}_2\text{CO}_3^*$  alone.
- But, distribution of carbon among [ $\text{H}_2\text{CO}_3^*$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ] is [1%, 10%, 90%]
- ➔ A small increase in  $\text{H}_2\text{CO}_3^*$  due to the  $\text{CO}_2(\text{g})$  increase implies a much larger increase in the bicarbonate ion  $\text{HCO}_3^-$  ➔ a very large increase in total dissolved  $\text{CO}_2$ .

➔ The ocean absorbs much more total  $\text{CO}_2$  due to the buffer effect than it would have without it, because much of the dissolved  $\text{CO}_2$  is stored as  $\text{HCO}_3^-$  rather than as  $\text{H}_2\text{CO}_3^*$

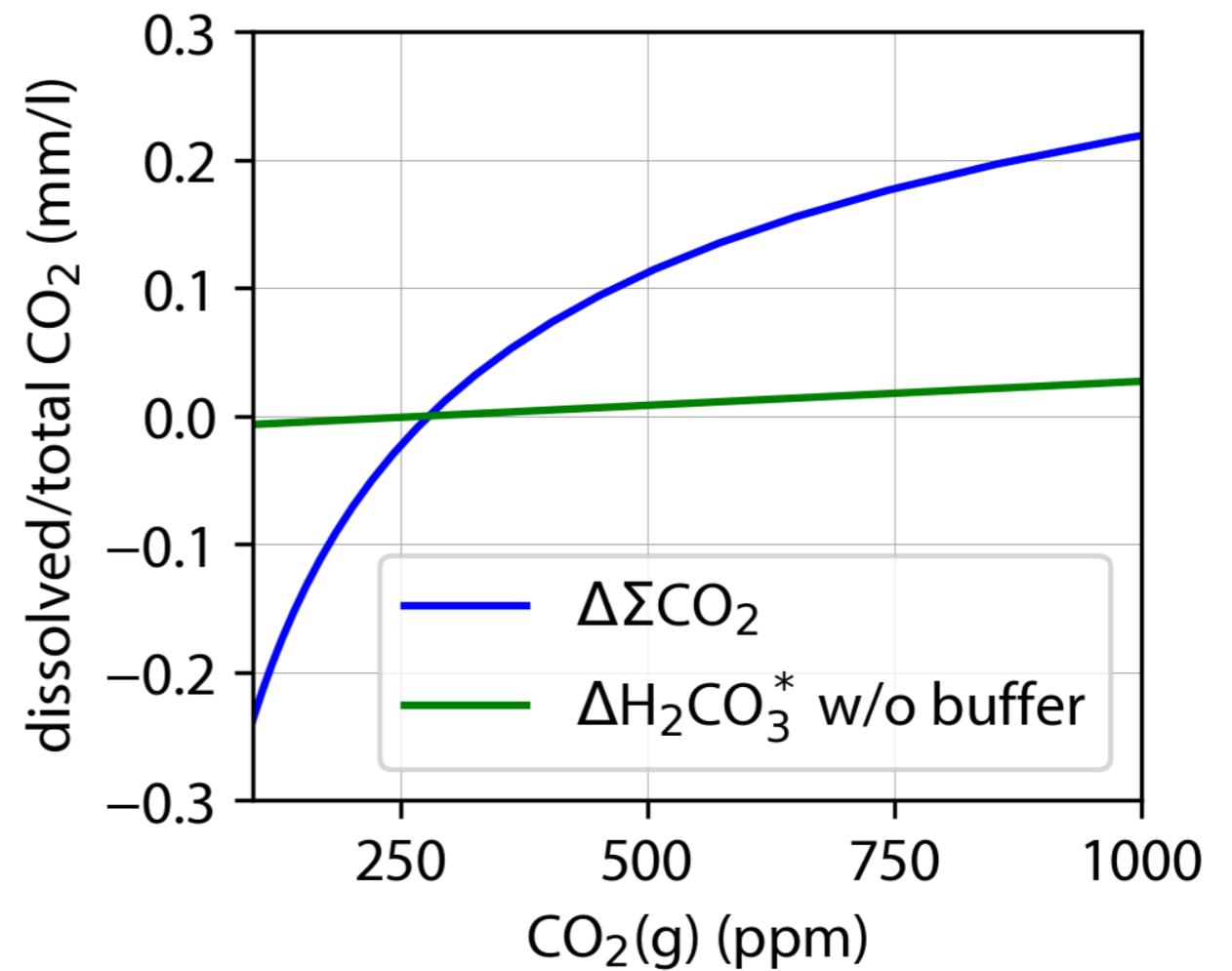
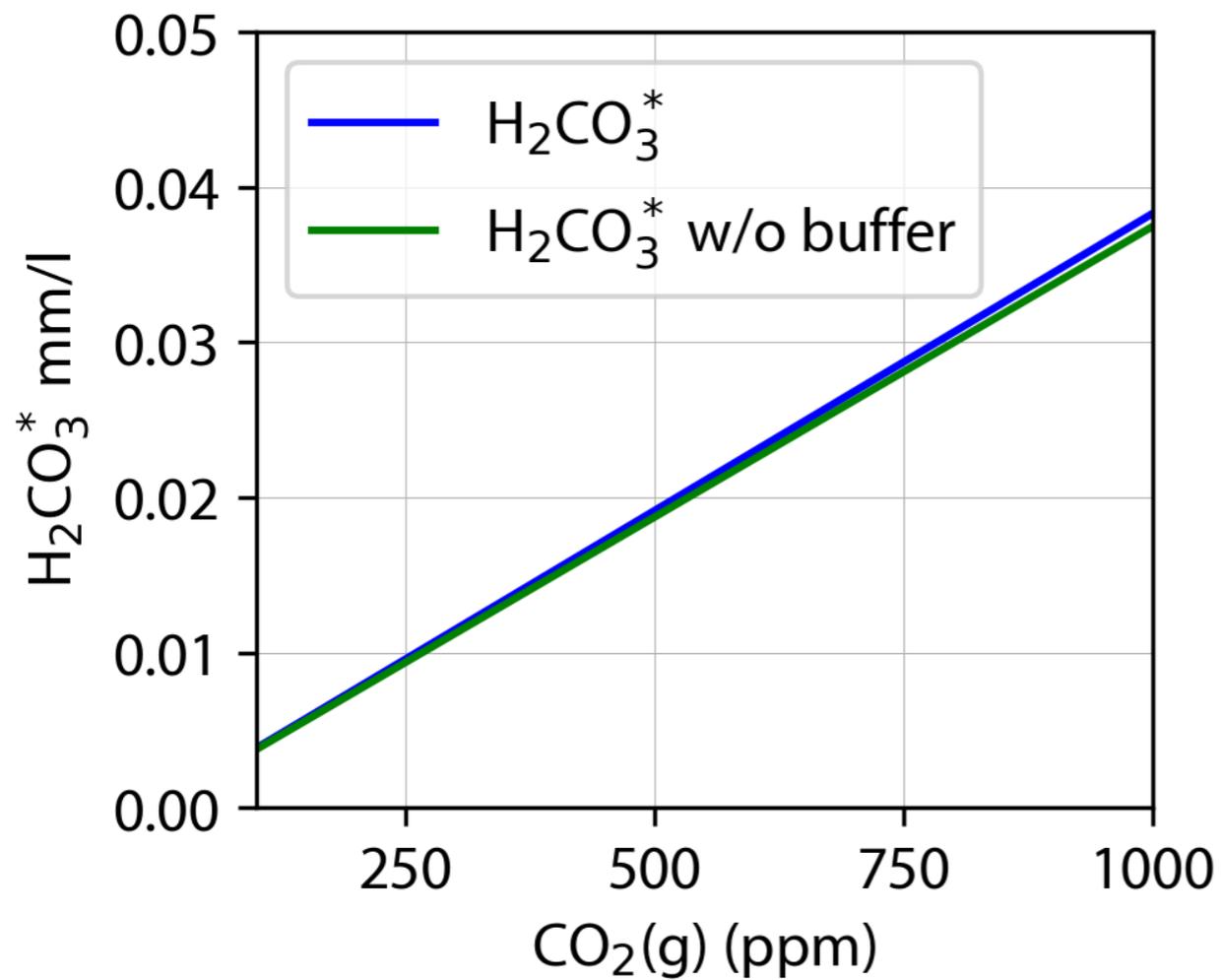


## Workshop #3

### The carbonate system buffer effect

## Workshop #3

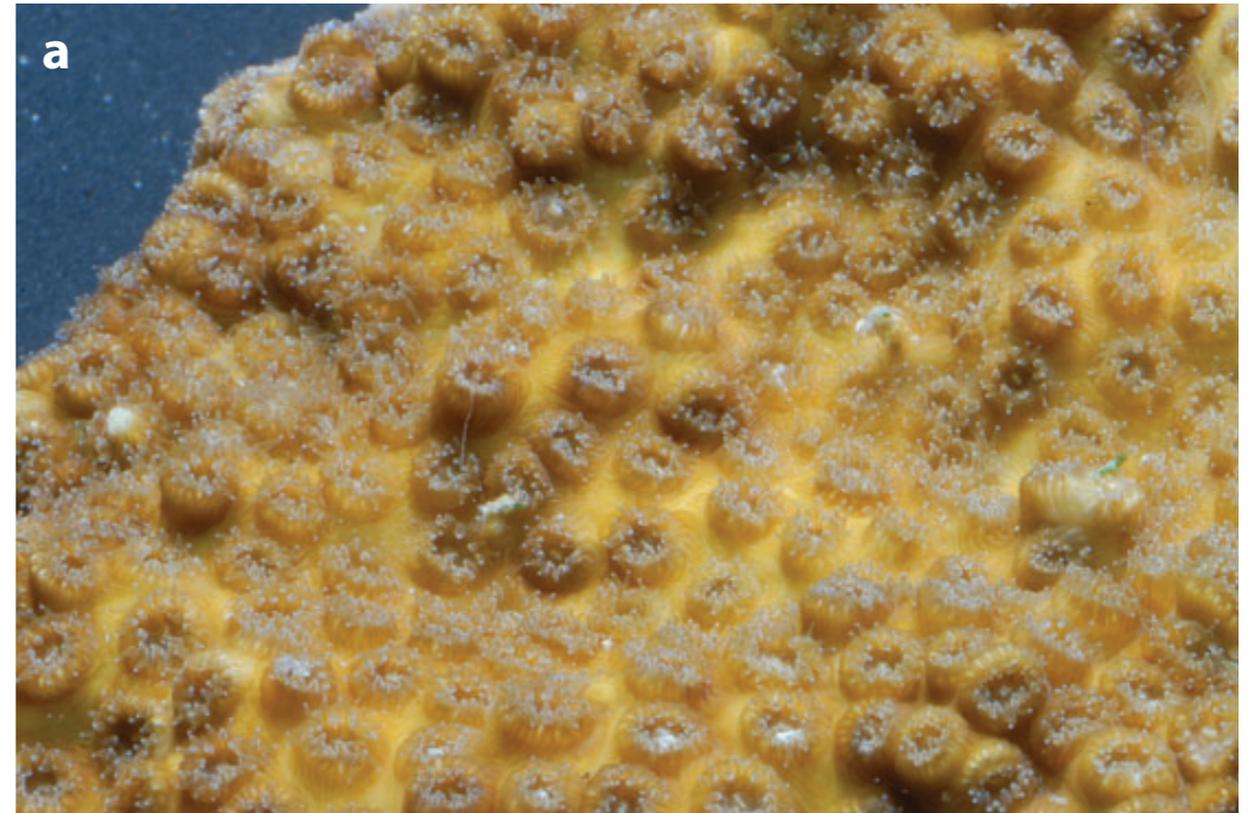
### The carbonate system buffer effect



# Possible consequences for coral reefs

Scleractinian (“stony corals”) **coral** *Oculina patagonica* after being maintained for **12 months in (a) normal seawater (pH = 8.2) and (b) acidified seawater (pH = 7.4).**

From Fine & Tchernov (2007)/ Doney et al 2009.

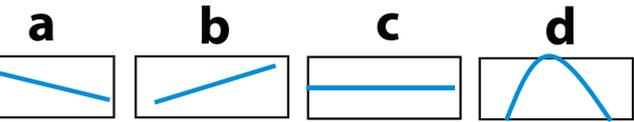


2 mm



2 mm

# Response of different marine organisms to acidification

Response to increasing CO<sub>2</sub>

Physiological response

Major group

Species studied

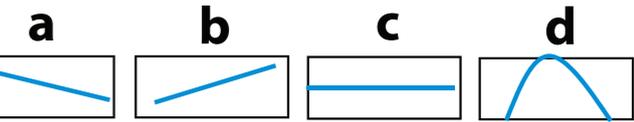
Physiological response	Major group	Species studied	a	b	c	d
<b>Calcification</b> 	Coccolithophores <sup>1</sup>	4	2	1	1	1
	Planktonic Foraminifera	2	2	–	–	–
	Molluscs	4	4	–	–	–
	Echinoderms <sup>1</sup>	3	2	1	–	–
	Tropical corals	11	11	–	–	–
	Coralline red algae	1	1	–	–	–
<b>Photosynthesis<sup>2</sup></b> 	Coccolithophores <sup>3</sup>	2	–	2	2	–
	Prokaryotes	2	–	–	1	–
	Seagrasses	5	–	–	–	–
<b>Nitrogen Fixation</b> 	Cyanobacteria	1	–	1	–	–
<b>Reproduction</b> 	Molluscs	4	4	–	–	–
	Echinoderms	1	1	–	–	–

**1)** Increased calcification had substantial physiological cost; **2)** strong interactive effects with nutrient and trace metal availability, light and temperature; **3)** under nutrient replete conditions

Representative examples of impacts of ocean acidification on major groups of marine biota derived from experimental manipulation studies. The response curves on the right indicate four cases: (a) linear negative, (b) linear positive, (c) level, and (d) nonlinear parabolic responses to increasing levels of seawater pCO<sub>2</sub> for each of the groups. In some cases strains of the same species exhibited different behavior in different experiments.

(Doney et al 2009)

# Response of different marine organisms to acidification

Response to increasing CO<sub>2</sub>

Physiological response	Major group	Species studied	a	b	c	d
<b>Calcification</b> 	Coccolithophores <sup>1</sup>	4	2	1	1	1
	Planktonic Foraminifera	2	2	–	–	–
	Molluscs	4	4	–	–	–
	Echinoderms <sup>1</sup>	3	2	1	–	–
	Tropical corals	11	11	–	–	–
	Coralline red algae	1	1	–	–	–
<b>Photosynthesis<sup>2</sup></b> 	Coccolithophores <sup>3</sup>	2	–	2	2	–
	Prokaryotes	2	–	–	1	–
	Seagrasses	5	–	–	–	–
<b>Nitrogen Fixation</b> 	Cyanobacteria	1	–	1	–	–
<b>Reproduction</b> 	Molluscs	4	4	–	–	–
	Echinoderms	1	1	–	–	–

**1)** Increased calcification had substantial physiological cost; **2)** strong interactive effects with nutrient and trace metal availability, light and temperature; **3)** under nutrient replete conditions

**bottom line:  
it's complicated...**

Representative examples of impacts of ocean acidification on major groups of marine biota derived from experimental manipulation studies. The response curves on the right indicate four cases: (a) linear negative, (b) linear positive, (c) level, and (d) nonlinear parabolic responses to increasing levels of seawater pCO<sub>2</sub> for each of the groups. In some cases strains of the same species exhibited different behavior in different experiments.

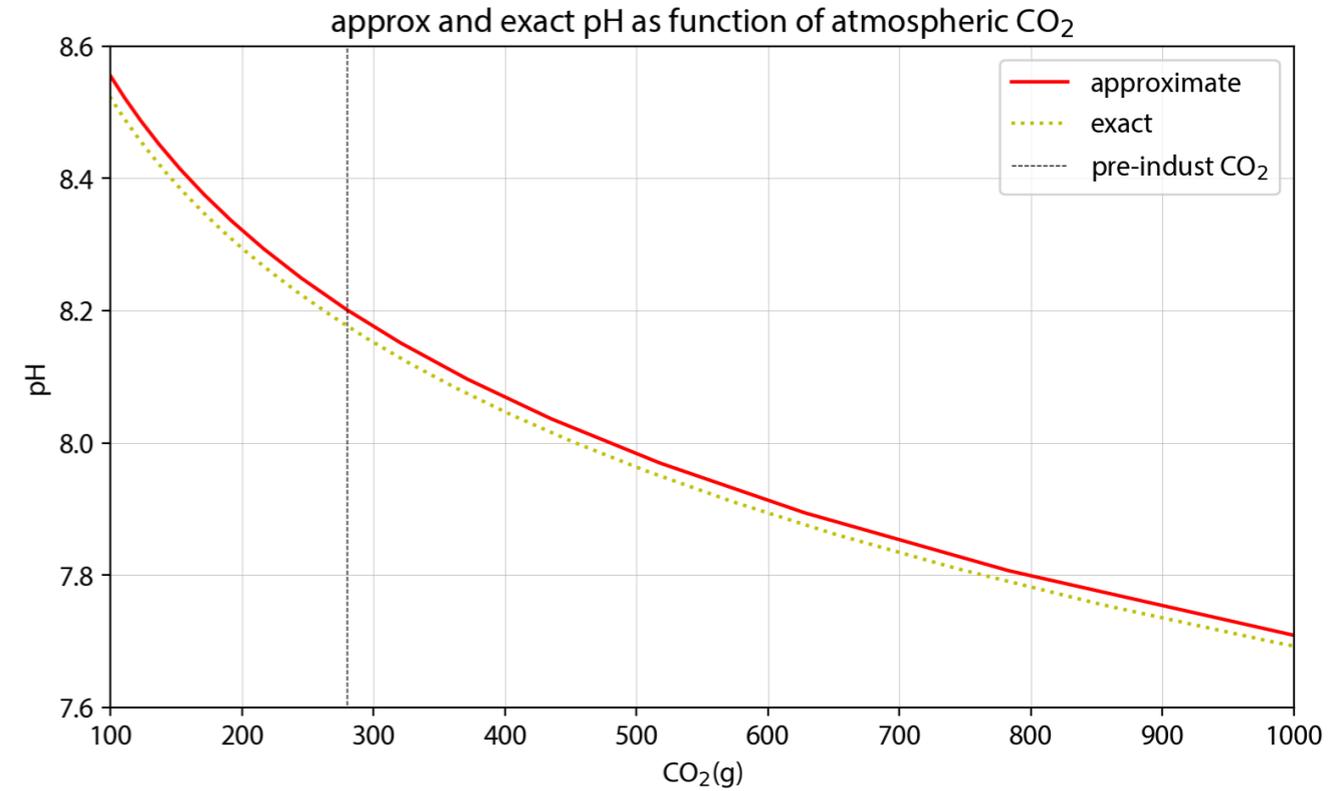
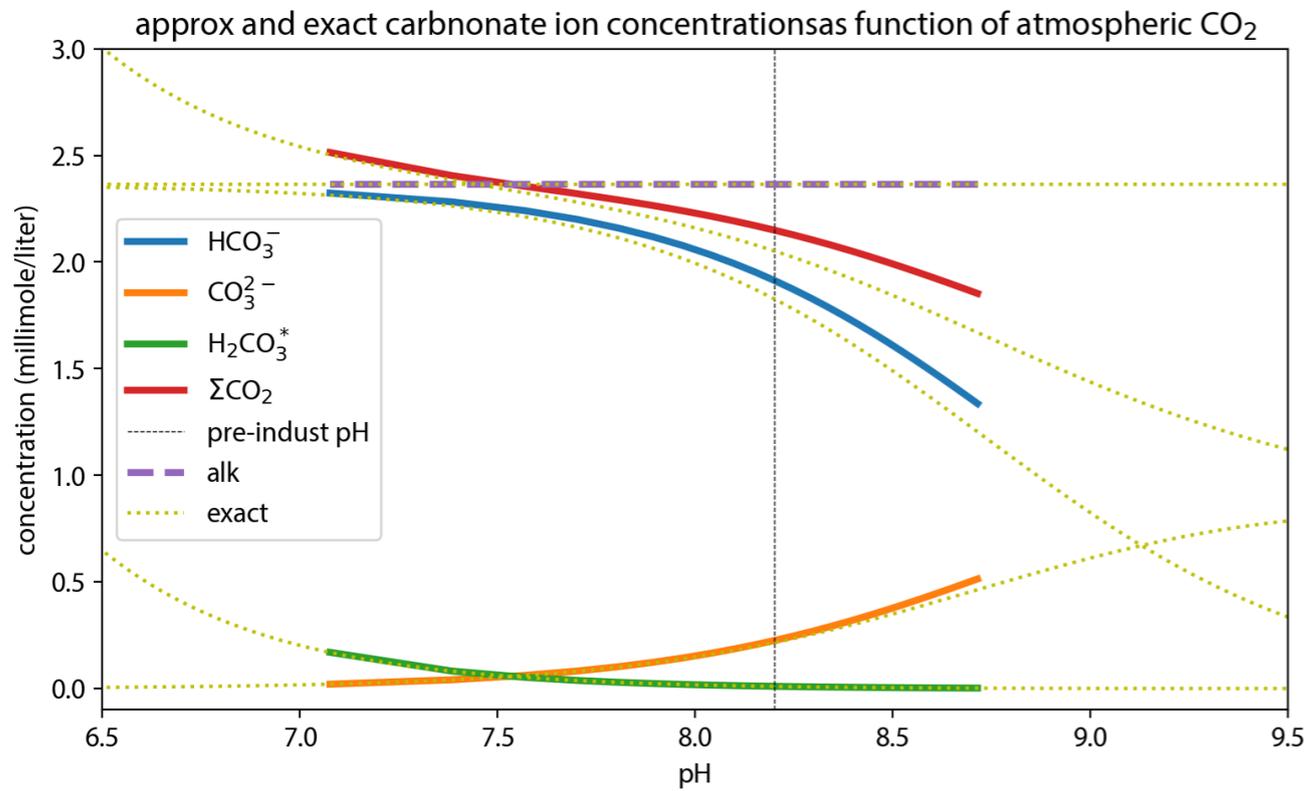
(Doney et al 2009)

## Workshop #4

Understanding the response to atmospheric CO<sub>2</sub>

# Workshop #4

## Understanding the response to atmospheric CO<sub>2</sub>



notes

5.3.2 response to warming,  
5.3.3 long-term decline of CO<sub>2</sub>

(use next two slides)

# Response to warming

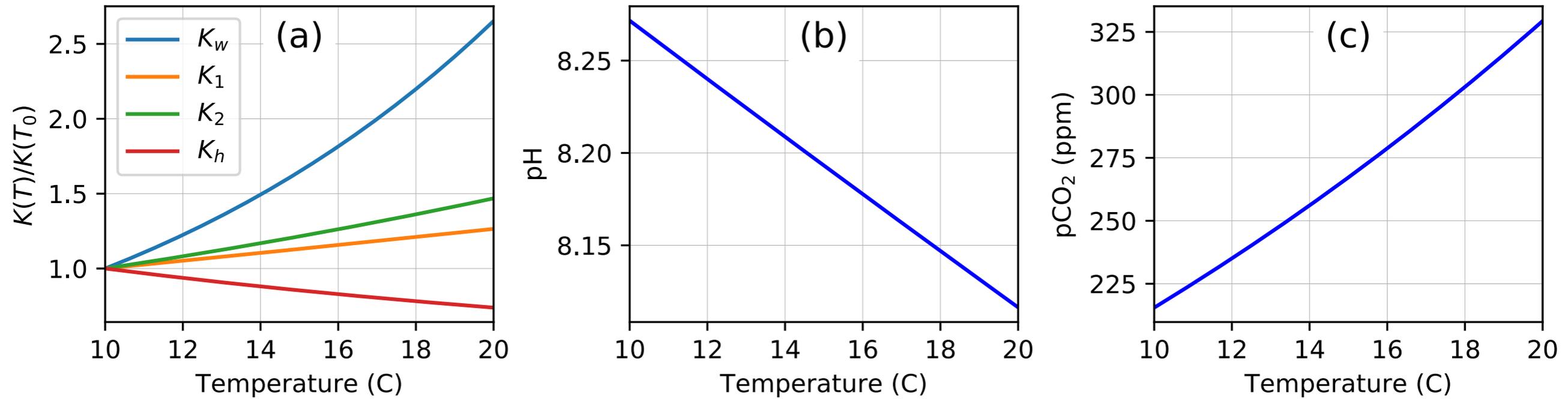


Figure 5.5: Response of the carbonate system to warming, as a function of the ocean temperature. The DIC and alkalinity are assumed fixed. (a) Reaction constants normalized by their values at 10 °C. (b) pH. (c) Atmospheric  $p\text{CO}_2$ .

# Response to warming

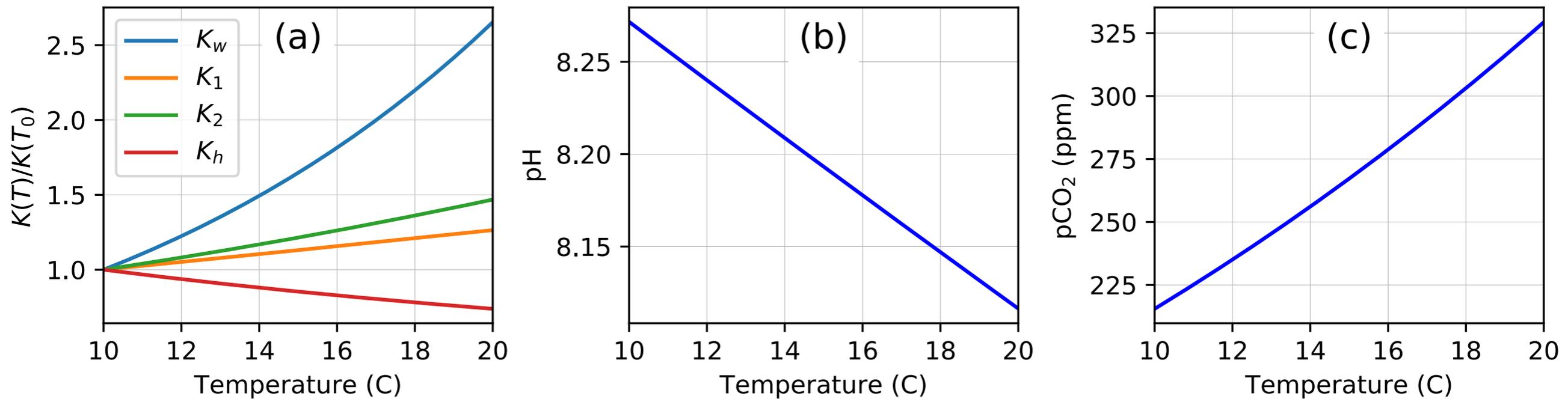


Figure 5.5: Response of the carbonate system to warming, as a function of the ocean temperature. The DIC and alkalinity are assumed fixed. (a) Reaction constants normalized by their values at 10 °C. (b) pH. (c) Atmospheric  $p\text{CO}_2$ .

$$[\text{H}^+] = K_2 \frac{2C_T - \text{Alk}_C}{\text{Alk}_C - C_T}, \quad [\text{CO}_2(\text{g})] = \frac{K_2}{K_1 K_H} \frac{(2C_T - \text{Alk}_C)^2}{\text{Alk}_C - C_T}.$$

$K_1$ ,  $K_2$  and  $K_H$  all play a role, not only Henry's constant responsible for the dissolution of  $\text{CO}_2$ . In solution for the atmospheric  $\text{CO}_2$  concentration,  $K_2/(K_1 K_H)$ , Henry's constant  $K_H$  decreases with temperature, while the other two increase. The ratio overall increases, leading to the increase in atmospheric  $\text{CO}_2$  with warming.

## Long term decline of CO<sub>2</sub>

The dissolution (by the acidic ocean due to CO<sub>2</sub> increase) of one unit of CaCO<sub>3</sub> (say from ocean sediments) into Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> implies the addition of one unit of total CO<sub>2</sub> ( $\Delta C_T$ , in the form of the carbonate ion) and two units of carbonate alkalinity ( $\Delta Alk_C$ ), due to the double negative charge of the carbonate ion.

$$\Delta C_T = \mathbf{1} \uparrow, \quad \Delta Alk_C = \mathbf{2} \uparrow$$

$$[H^+] = K_2 \frac{2C_T - Alk_C + \mathbf{0}}{Alk_C - C_T + \mathbf{1}} \downarrow \Rightarrow pH \uparrow$$

$$[CO_2(g)] = \frac{K_2}{K_1 K_H} \frac{(2C_T - Alk_C + \mathbf{0})^2}{Alk_C - C_T + \mathbf{1}} \downarrow$$

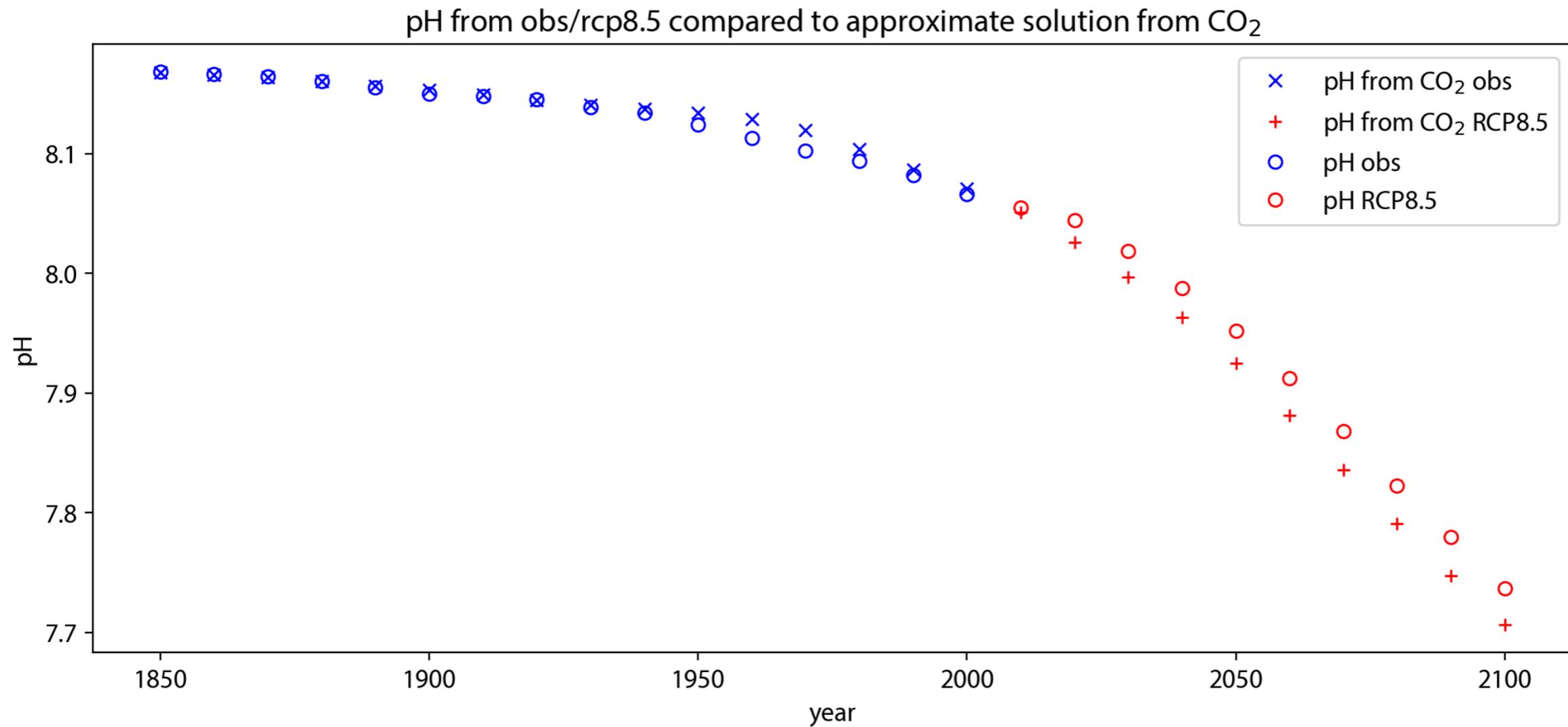
➔ Dissolution of ocean sediments will eventually lead to reduction of atmospheric CO<sub>2</sub>; time scale is thousands of years...

## Workshop #5

Estimating observed and future pH from CO<sub>2</sub>

# Workshop #5

## Estimating observed and future pH from CO<sub>2</sub>



# Ocean Acidification

## Summary

- Acidification: “the other CO<sub>2</sub> problem” already robustly observed.

# Ocean Acidification

## Summary

- Acidification: “the other CO<sub>2</sub> problem” already robustly observed.
- Significant potential effects on ocean life.

# Ocean Acidification

## Summary

- Acidification: “the other CO<sub>2</sub> problem” already robustly observed.
- Significant potential effects on ocean life.
- Unavoidable at high atmospheric CO<sub>2</sub> concentrations.

# Ocean Acidification

## Summary

- Acidification: “the other CO<sub>2</sub> problem” already robustly observed.
- Significant potential effects on ocean life.
- Unavoidable at high atmospheric CO<sub>2</sub> concentrations.
- Very little uncertainty in estimating pH given atmospheric CO<sub>2</sub>, but more uncertain when it comes to effects on ocean life.

# Ocean Acidification

## Summary

- Acidification: “the other CO<sub>2</sub> problem” already robustly observed.
- Significant potential effects on ocean life.
- Unavoidable at high atmospheric CO<sub>2</sub> concentrations.
- Very little uncertainty in estimating pH given atmospheric CO<sub>2</sub>, but more uncertain when it comes to effects on ocean life.
- Buffer effect: allows the ocean to store large amounts of carbon.

# Ocean Acidification

## Summary

- Acidification: “the other CO<sub>2</sub> problem” already robustly observed.
- Significant potential effects on ocean life.
- Unavoidable at high atmospheric CO<sub>2</sub> concentrations.
- Very little uncertainty in estimating pH given atmospheric CO<sub>2</sub>, but more uncertain when it comes to effects on ocean life.
- Buffer effect: allows the ocean to store large amounts of carbon.
- The ocean carbonate system provides a positive feedback due to the release of dissolved CO<sub>2</sub> with warming.

# Ocean Acidification

## Summary

- Acidification: “the other CO<sub>2</sub> problem” already robustly observed.
- Significant potential effects on ocean life.
- Unavoidable at high atmospheric CO<sub>2</sub> concentrations.
- Very little uncertainty in estimating pH given atmospheric CO<sub>2</sub>, but more uncertain when it comes to effects on ocean life.
- Buffer effect: allows the ocean to store large amounts of carbon.
- The ocean carbonate system provides a positive feedback due to the release of dissolved CO<sub>2</sub> with warming.
- CO<sub>2</sub> concentration will eventually drop via the dissolution of ocean sediments, but the residence time of CO<sub>2</sub> is very long...

The End