Carbon Dioxide, Alkalinity and pH

OCN 623 – Chemical Oceanography

15 March 2018

Reading: Libes, Chapter 15, pp. 383 – 389

(Remainder of chapter will be used with the classes "Global Carbon Dioxide" and "Biogenic production, carbonate saturation and sediment distributions")

Student Learning Outcomes (SLOs)

At the completion of today's section, students should be able to:

1. Identify the chemical species involved in the marine CO_2/carbonate system
2. Explain CO_2 dissolution in seawater and subsequent reactions
3. Explain the concepts of pH, alkalinity, and dissolved inorganic carbon, and write the equations defining these quantities
4. Explain the relationship between carbonate dissolution/precipitation and pCO_2.

Why is it important to understand the CO_2 system?

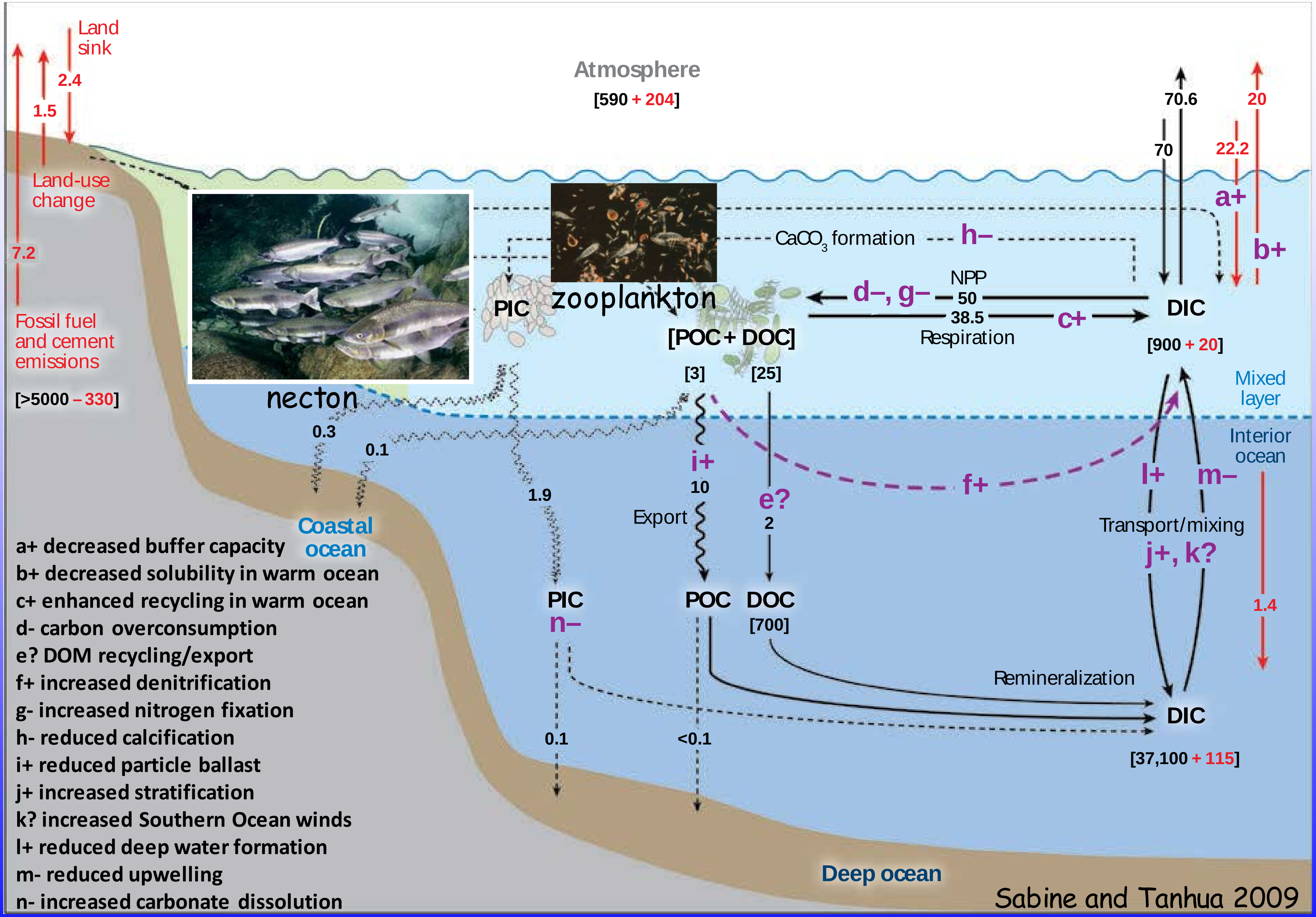
- CO_2 controls the fraction of inbound radiation that remains trapped in the atmosphere (greenhouse effect), which in turn strongly influences planetary climate

- CO_2 is the raw material used to build organic matter

- CO_2 controls the pH of the oceans

- Distribution of CO_2 species affects preservation of $CaCO_3$ deposited on the sea floor

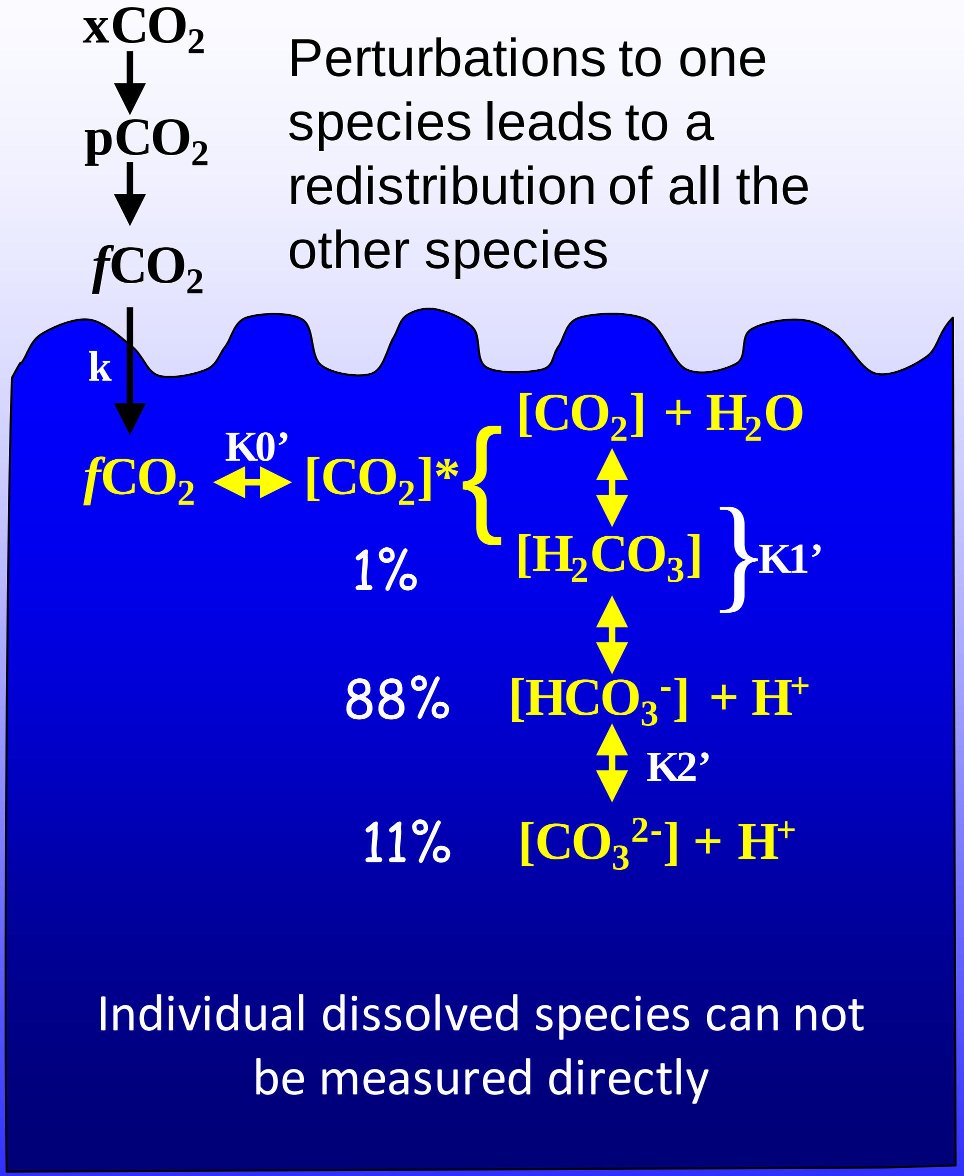
Ocean Carbon Cycle in a Global Context



CO_2 Speciation

Perturbations to one species leads to a redistribution of all the other species

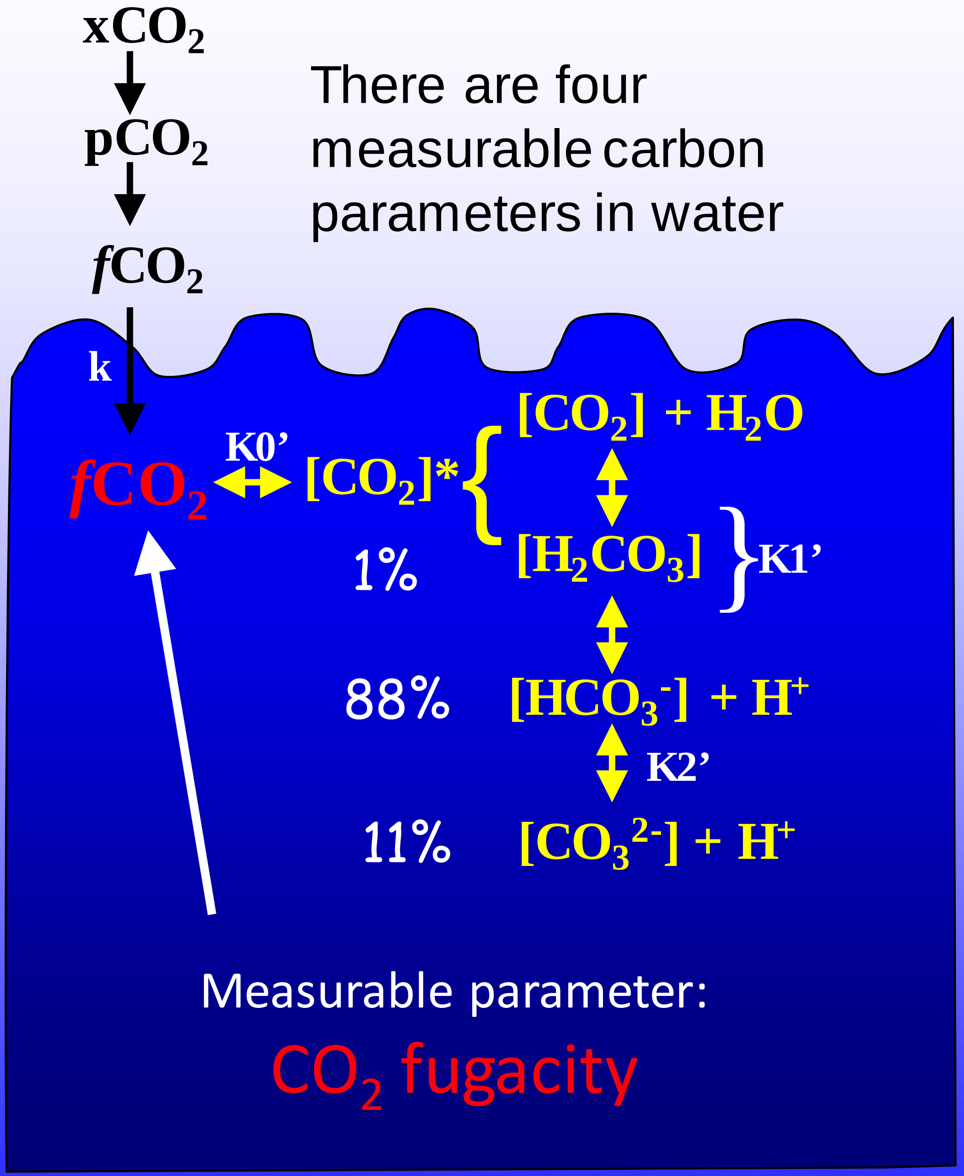
There are many forms of dissolved inorganic carbon in water



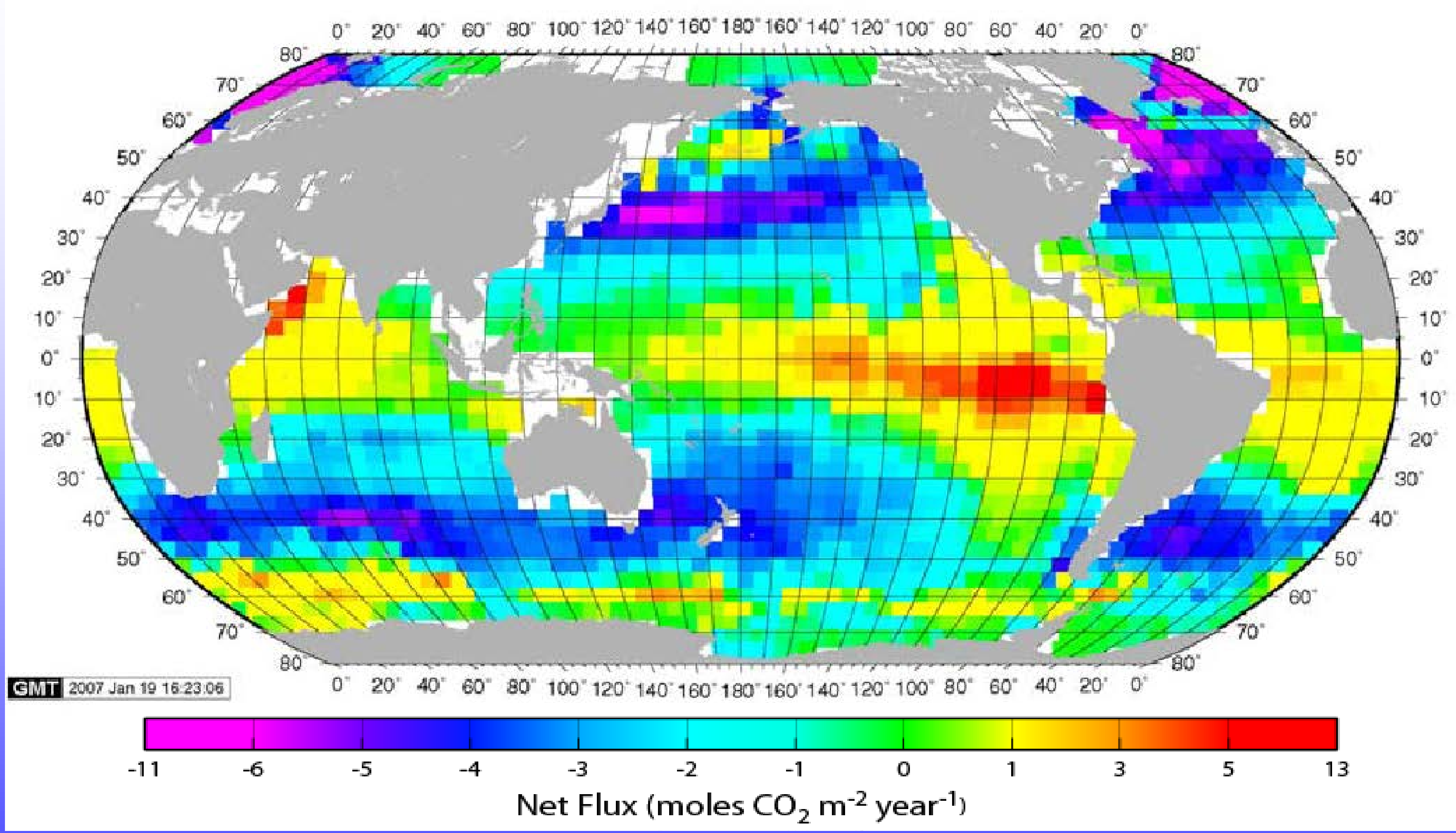
Using the thermodynamic constants (Kx), any two measured parameters can be used to calculate the concentration of all the species

CO_2 Speciation

There are four measurable carbon parameters in water



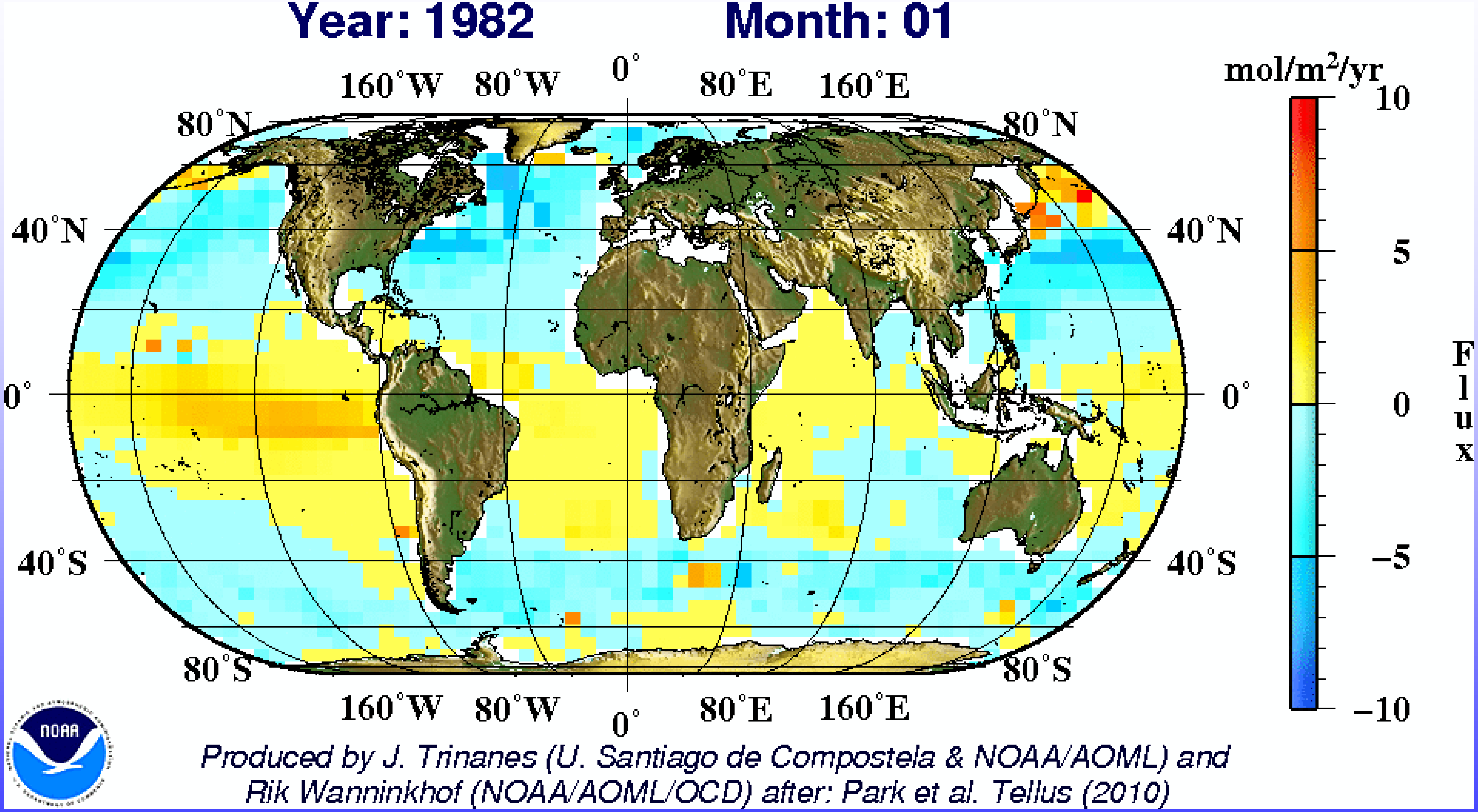
Takahashi climatological annual mean air-sea CO_2 flux for reference year 2000



Based on ~3 million measurements since 1970 and NCEP/DOE/AMIP II reanalysis.
Global flux is 1.4 ±0.7 Pg C/yr

Takahashi et al., Deep Sea Res. II, 2009

The global mean air-sea CO_2 flux for the period from 1982 to 2009 gives an average contemporary net uptake of 1.47±.23 Pg C yr^{-1}



Surface observations have large variability over a wide range of time and space scales making it very difficult to properly isolate the anthropogenic increases. Uptake of 2 Pg C yr^{-1} only requires a $DpCO_2$ of 8ppm.

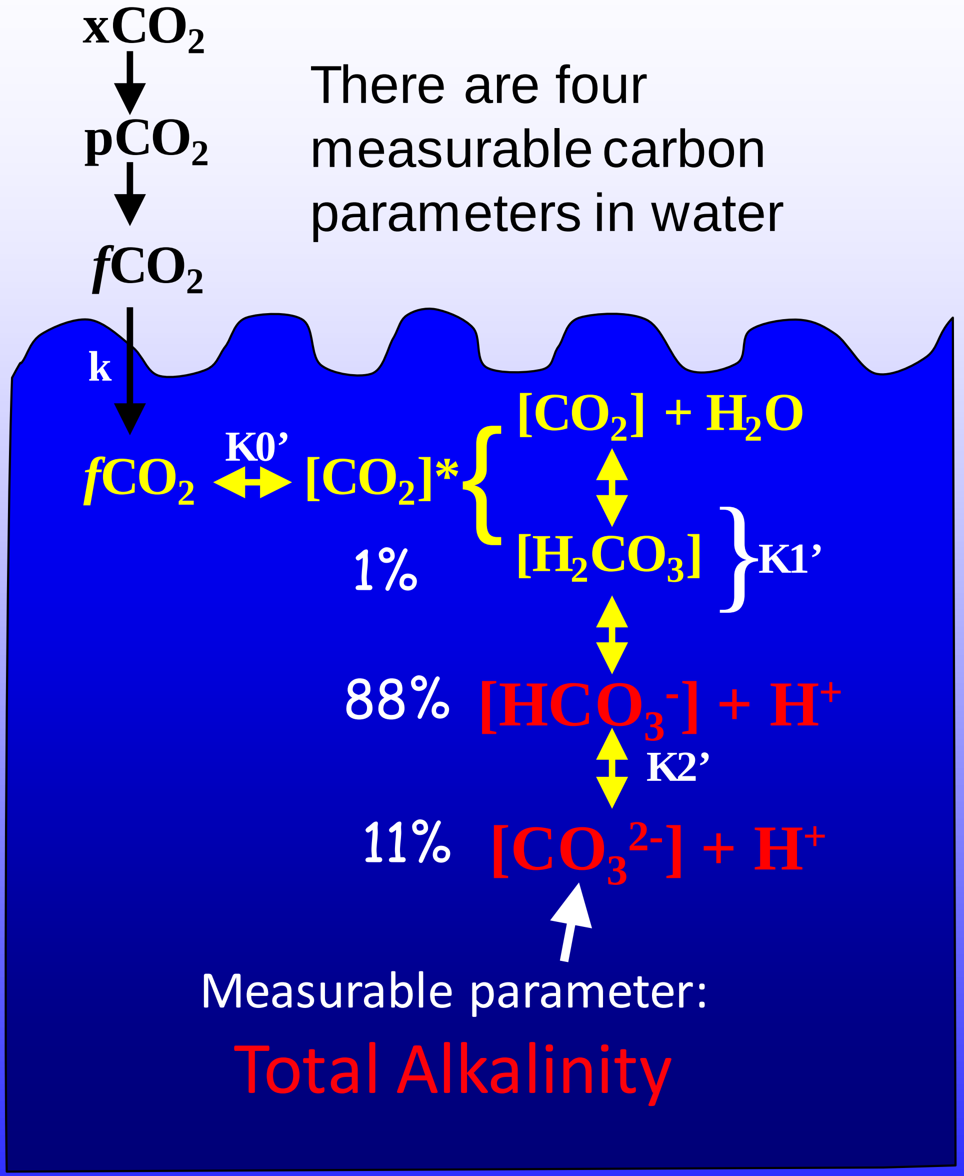
CO_2 Speciation

GENERAL DEFINITION:
The acid-buffering capacity of seawater

Total Alkalinity (TA) represents ability of seawater to resist pH change upon addition of acid

Remember the concept of a "buffer" (from basic chemistry): a substance that resists pH change upon addition of acid or base

There are four measurable carbon parameters in water



Carbonate Alkalinity

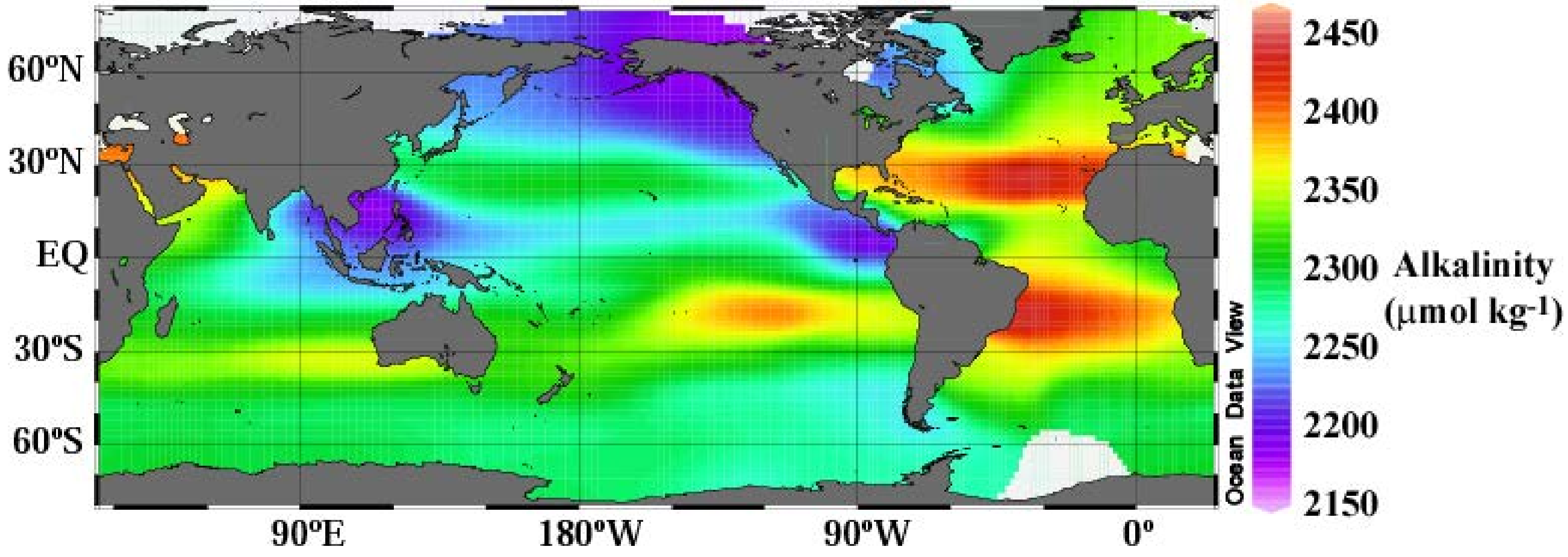
$CA \equiv 2[CO_3^{-2}] + [HCO_3^-]$

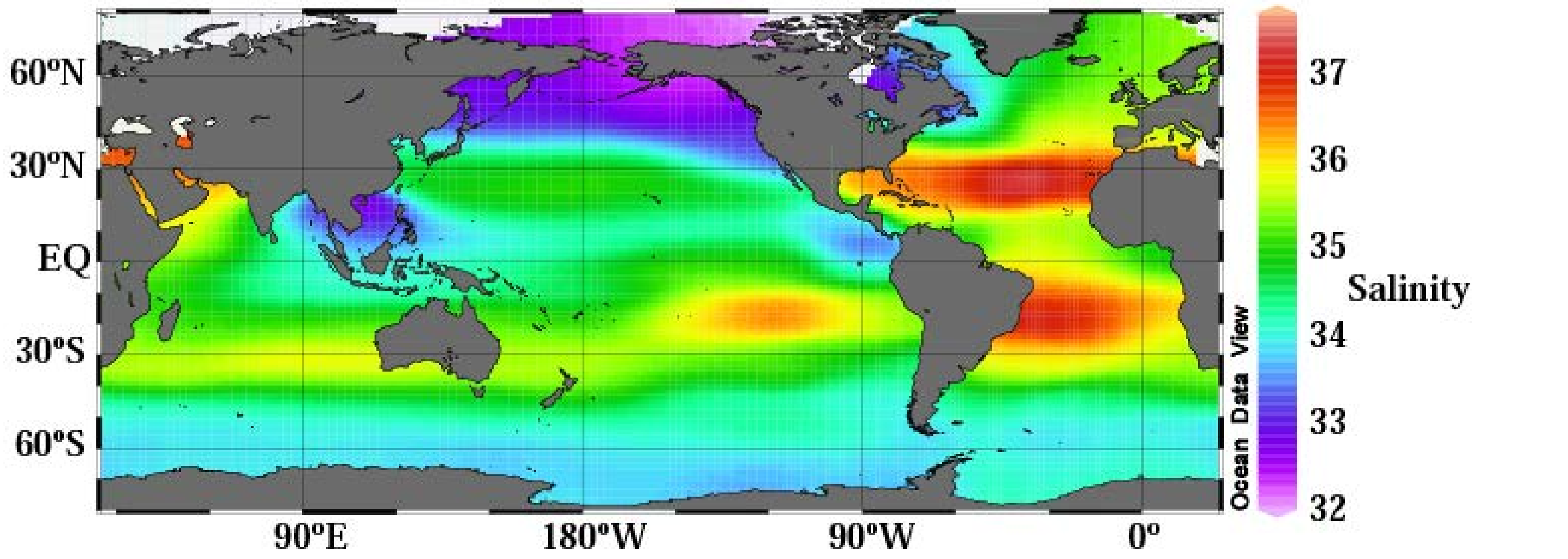
Typically, HCO_3^- and CO_3^{-2} are present at ~1000x conc of other proton acceptors

Hence: CA nearly equals TA

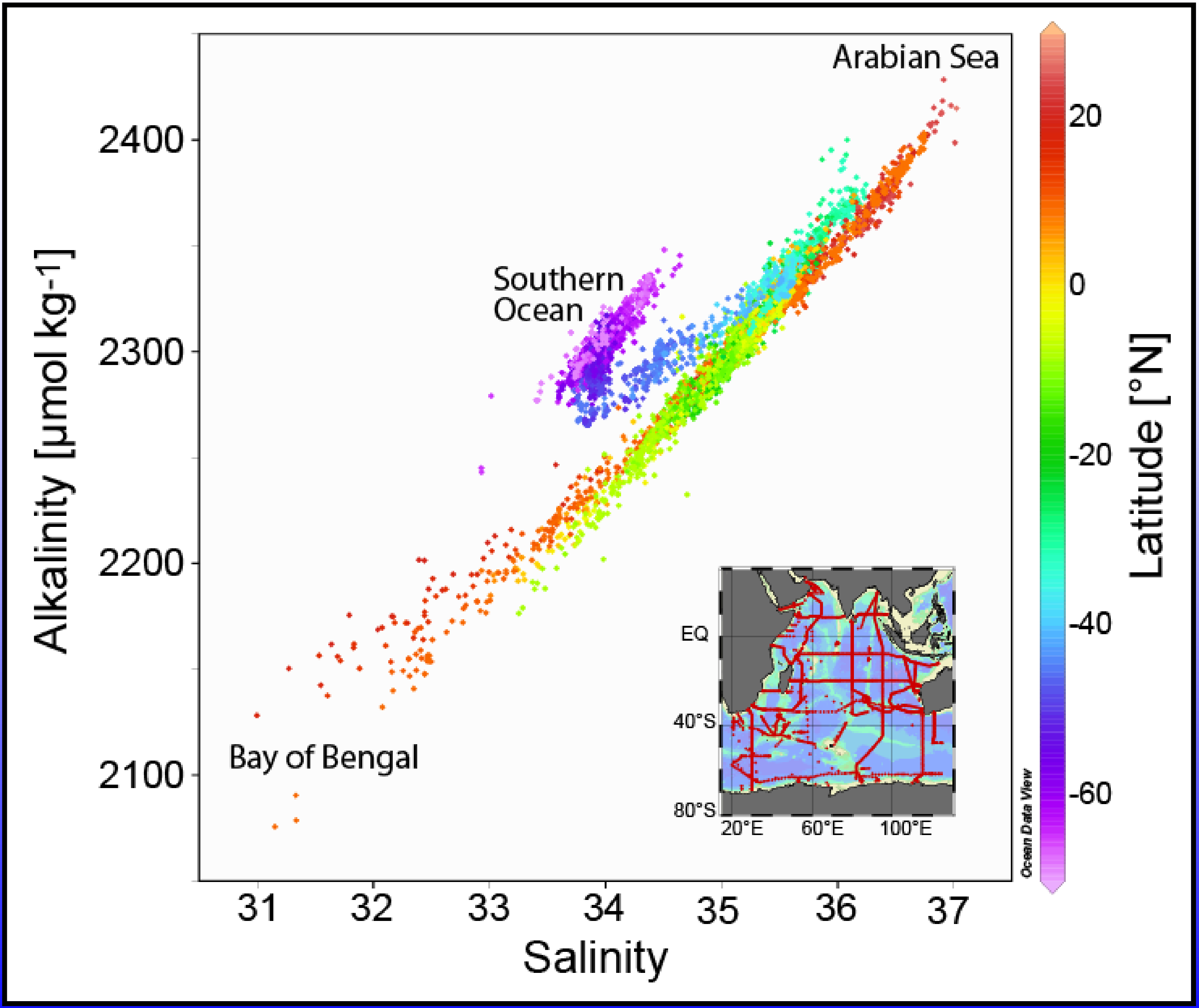
$$TA = [HCO_3^-] + 2*[CO_3^{2-}] + [B(OH)_4^-] + [HPO_4^{2-}] + 2*[PO_4^{3-}]\ldots + [OH^-] - [H^+]$$

Surface TA/Talk/Alk/A_T Distribution is Very Similar to Salinity





Shallow Indian Ocean Data (depth < 100 m)



CO_2 Speciation

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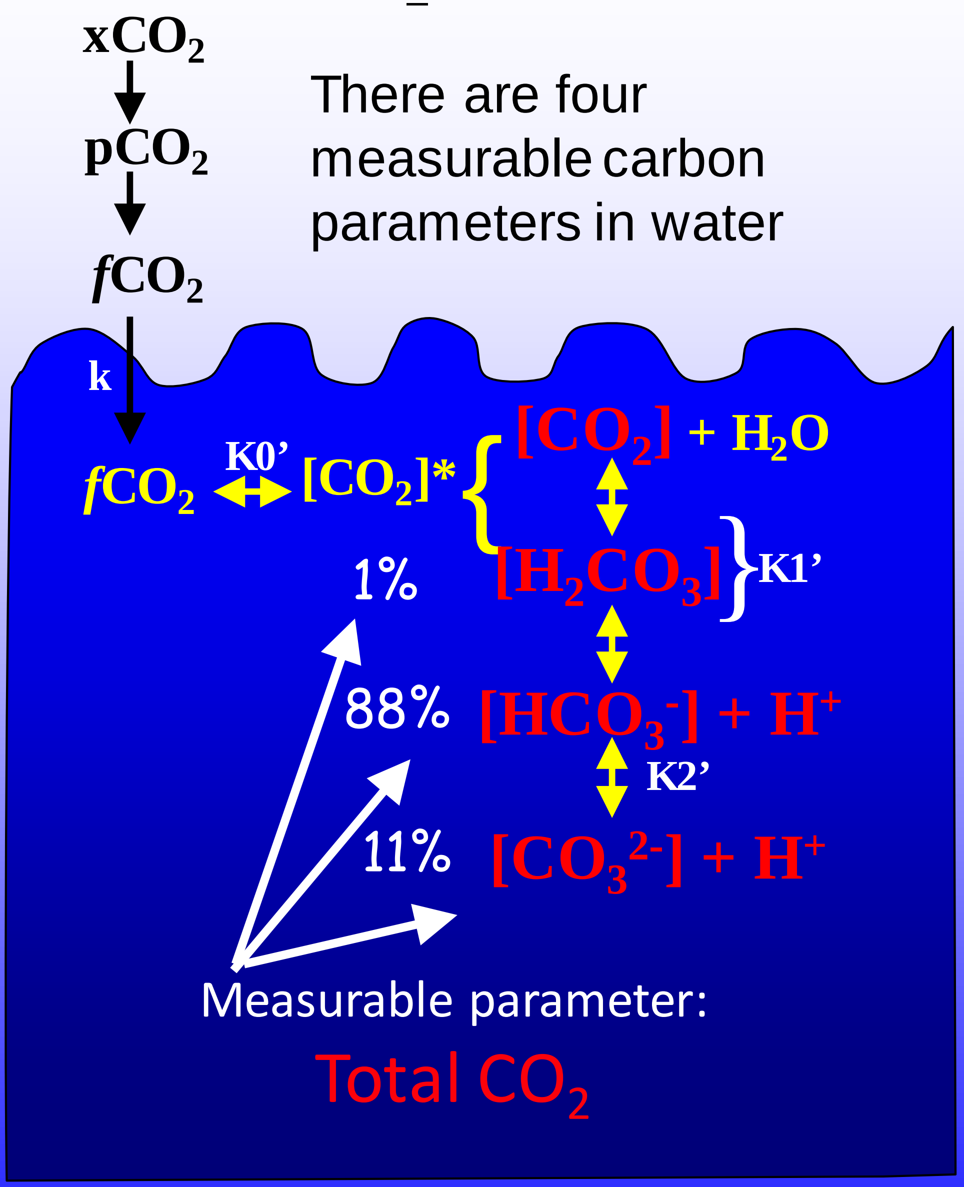
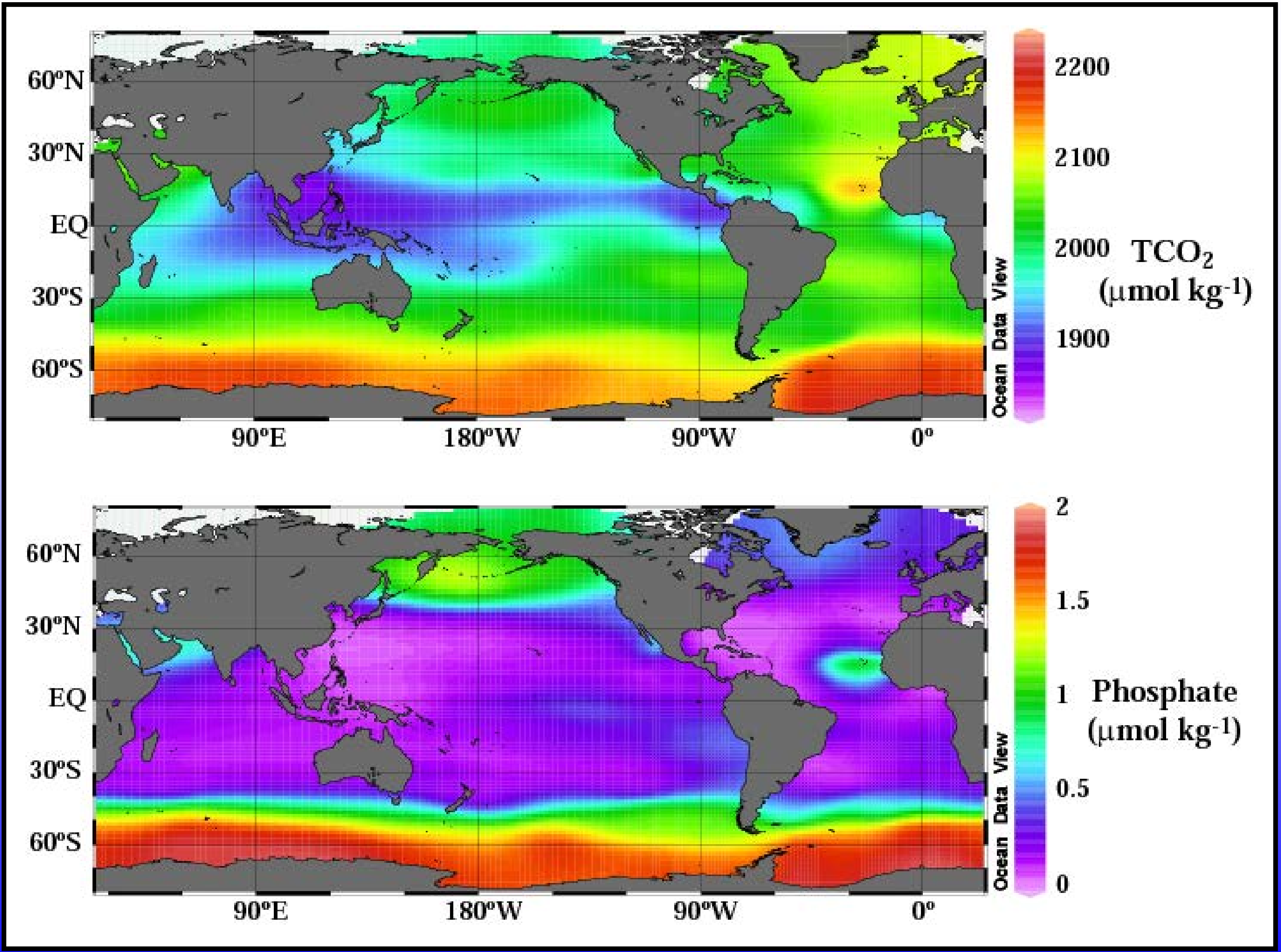


Inorganic Carbon is stored in the ocean as Total CO_2 (a.k.a. DIC)

DIC and TA are state variables, meaning they are not a function of temperature or pressure

$$TCO_2 = [CO_2]^* + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

TCO_2/DIC/C_T: Surface Distribution is Similar to Nutrient Distributions



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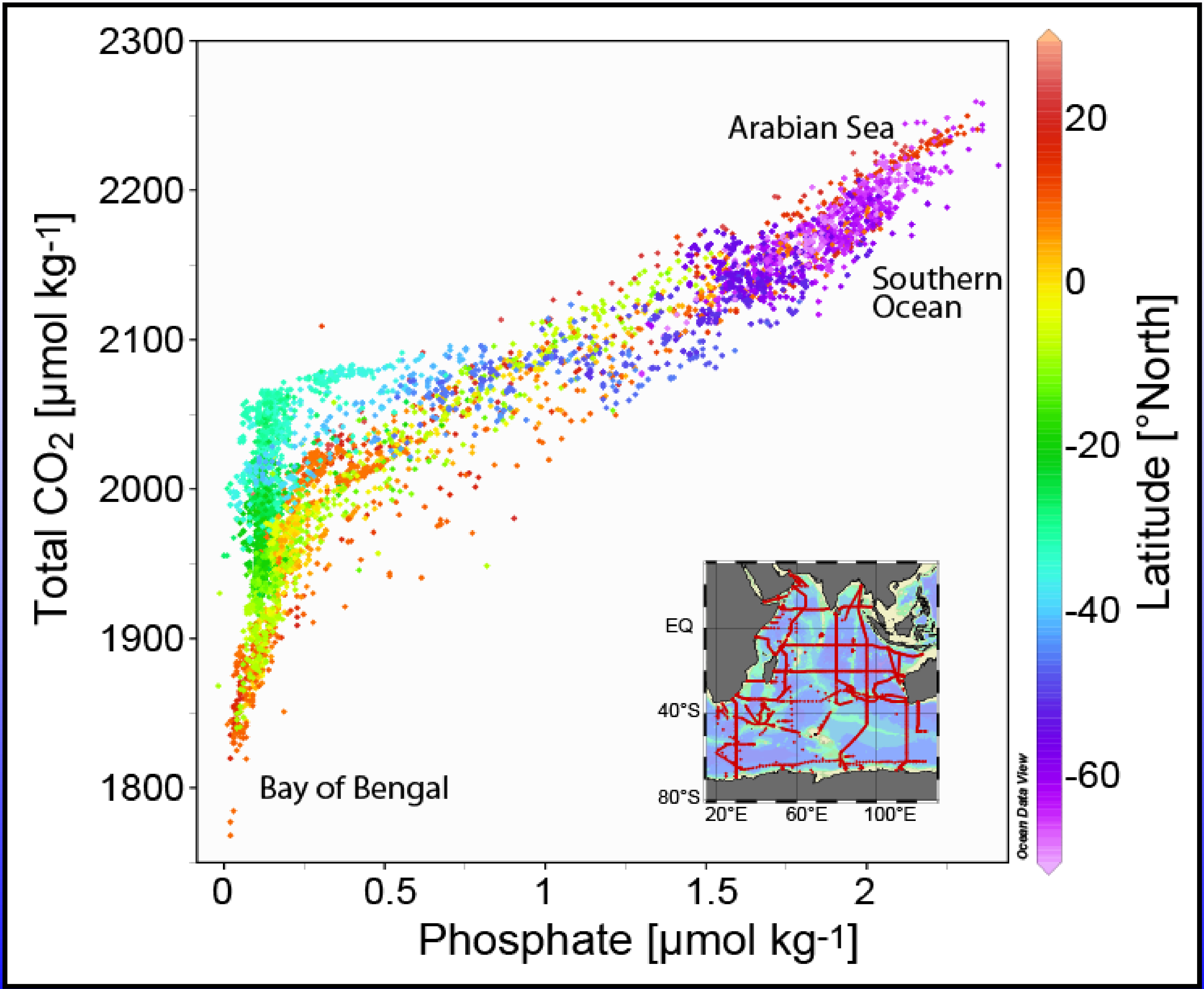

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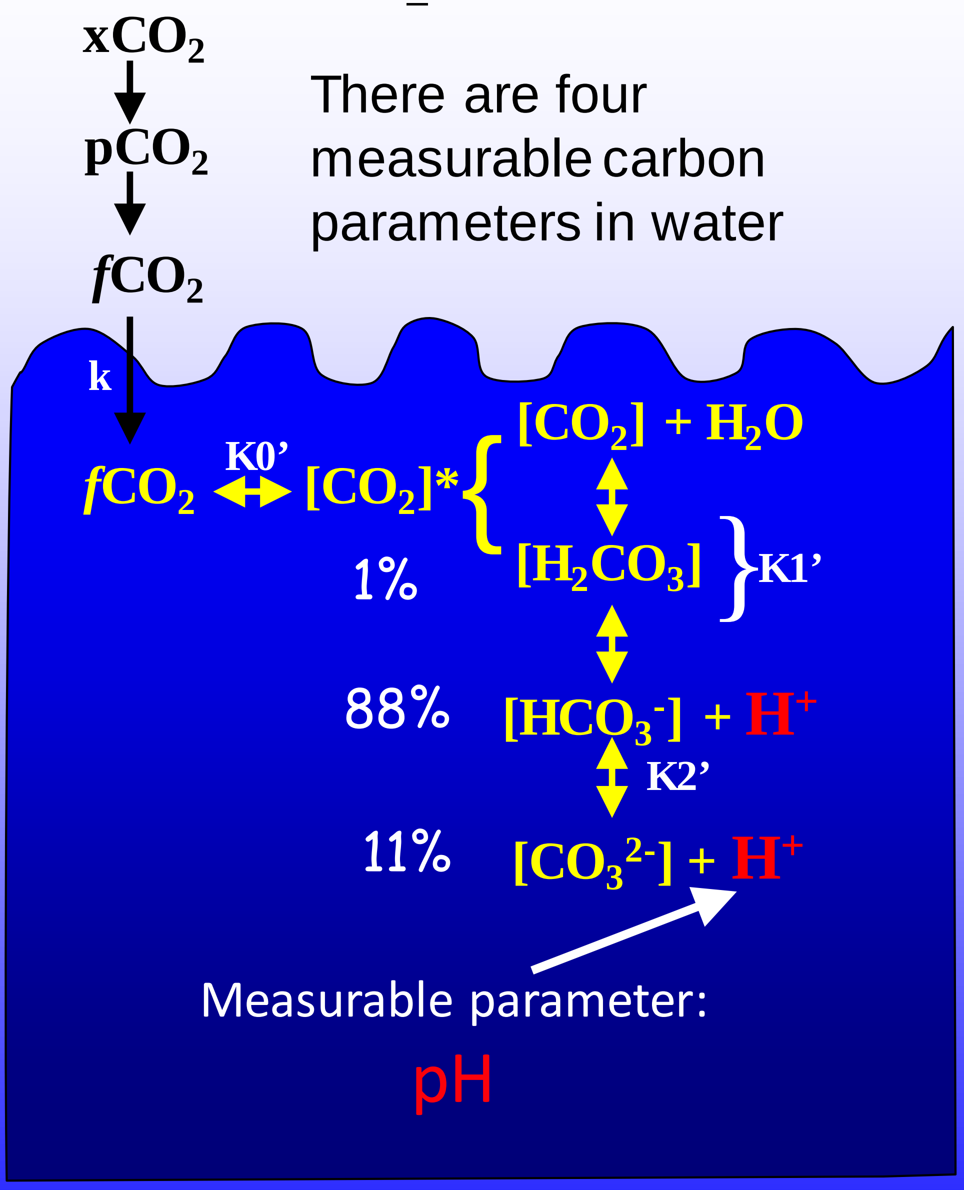


$$pH = -\log_{10}\{H^+\}$$

$\{H^+\}$ = Hydrogen ion activity

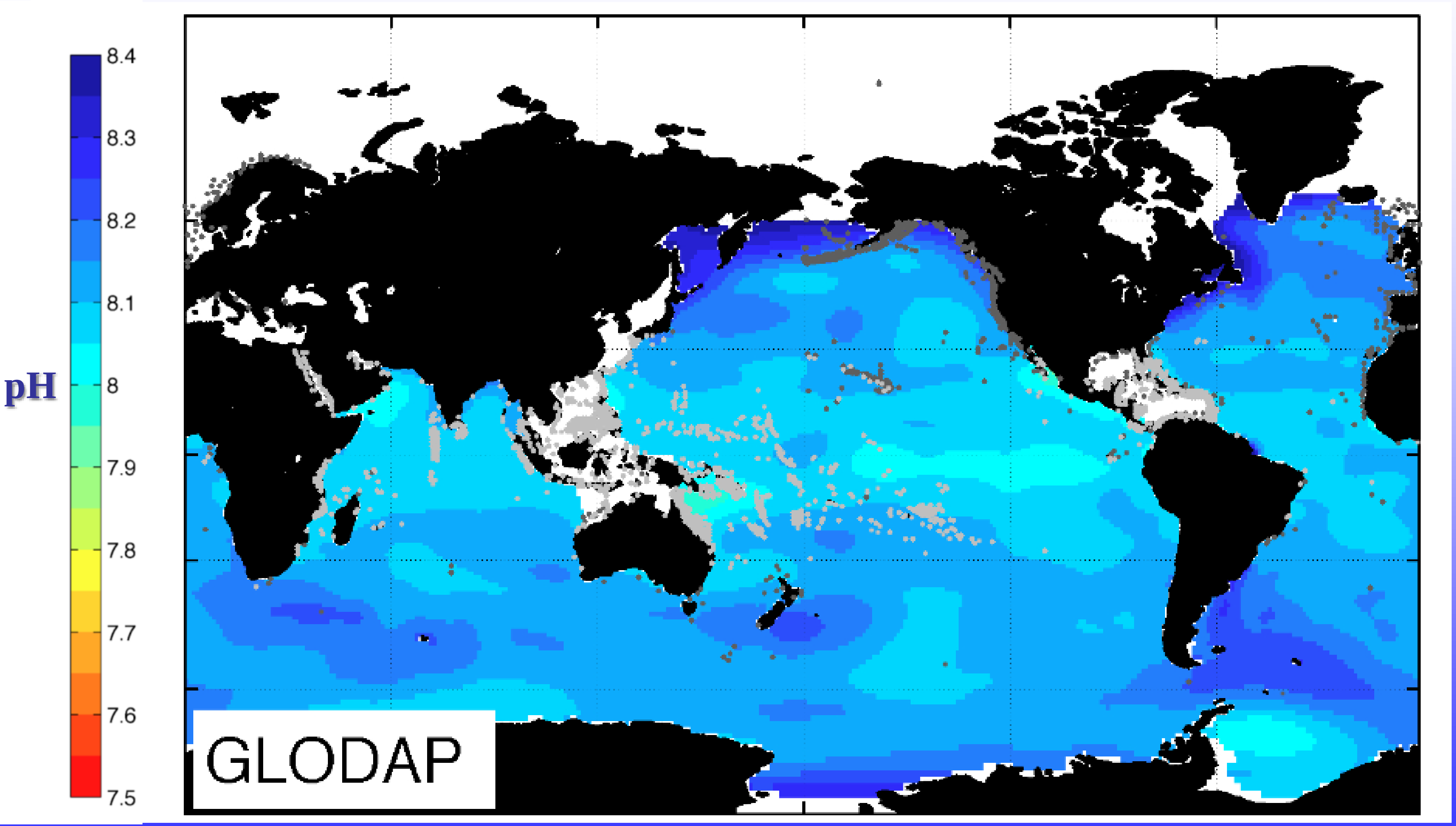
There are 5 different pH scales. The most common are pH_{sws} and pH_T

pH of seawater is slightly basic; acidification is a process, not a state

$\{H^+\}_{sws} = \{H^+\}_f + [HSO_4^-] + [HF]$

$\{H^+\}_T = \{H^+\}_f + [HSO_4^-]$

Surface pH distribution reflects combined patterns of alkalinity and TCO_2



Light gray = warm water corals
Dark gray = cold water corals

Feely, Doney and Cooley, Oceanography (2009)

Group Task

How does seawater pH change when atmospheric CO_2 is added to the ocean?

What are the reactions??

Group Task

How does seawater pH change when atmospheric CO_2 is added to the ocean?

What are the reactions??

Answer: The pH decreases because of the release of hydrogen ions:

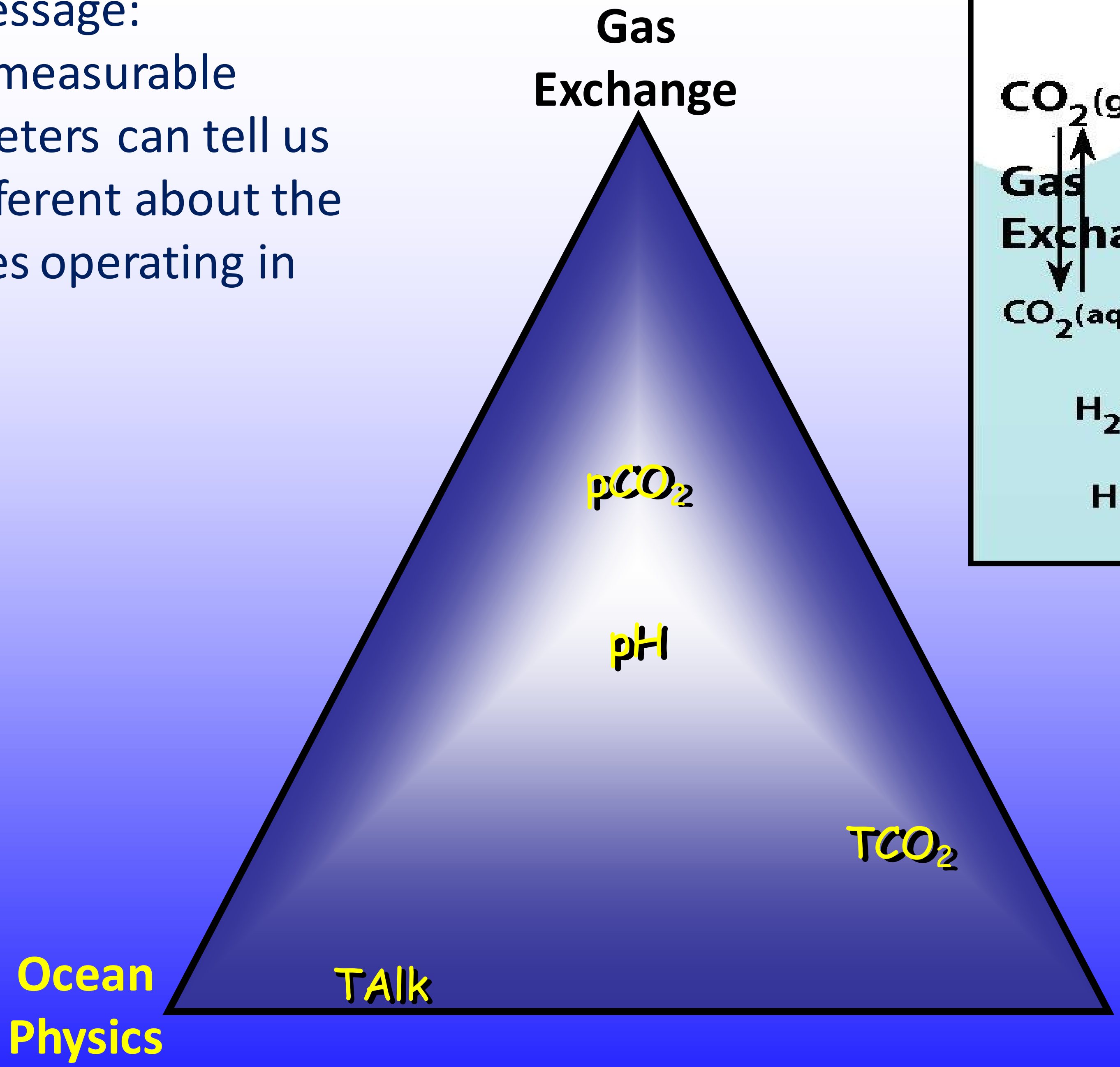
$$CO_{2(g)} \rightarrow CO_{2(aq)}$$

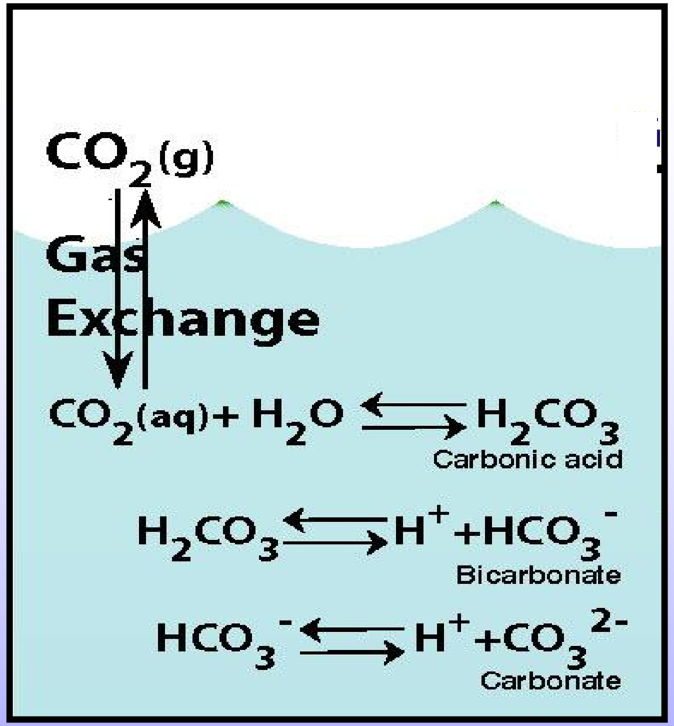
$$CO_{2(aq)} + H_2O \rightarrow HCO_3^- + H^+$$

$$HCO_3^- \leftarrow CO_3^{-2} + H^+$$

The limited amount of CO_3^{2-} available means that not all of the H^+ produced by the middle reaction can be consumed

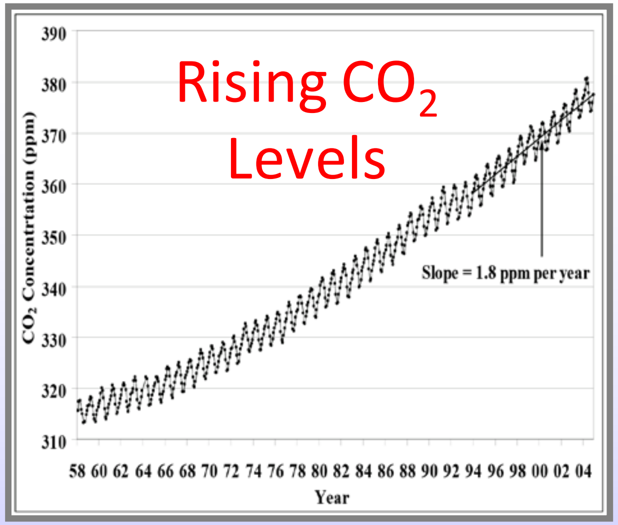
Take home message:
Each of the 4 measurable carbon parameters can tell us something different about the basic processes operating in the Ocean

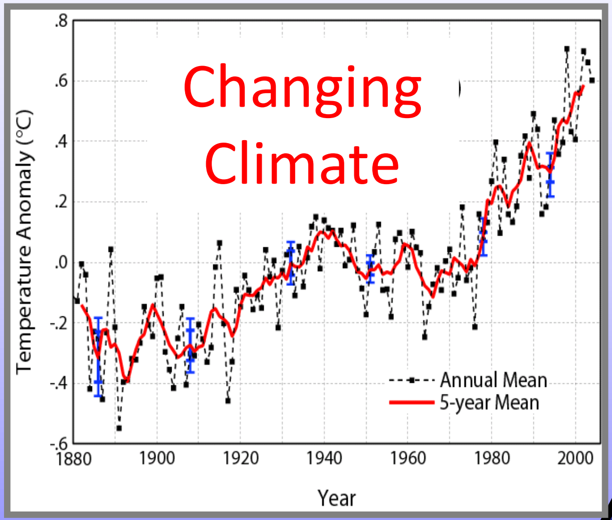


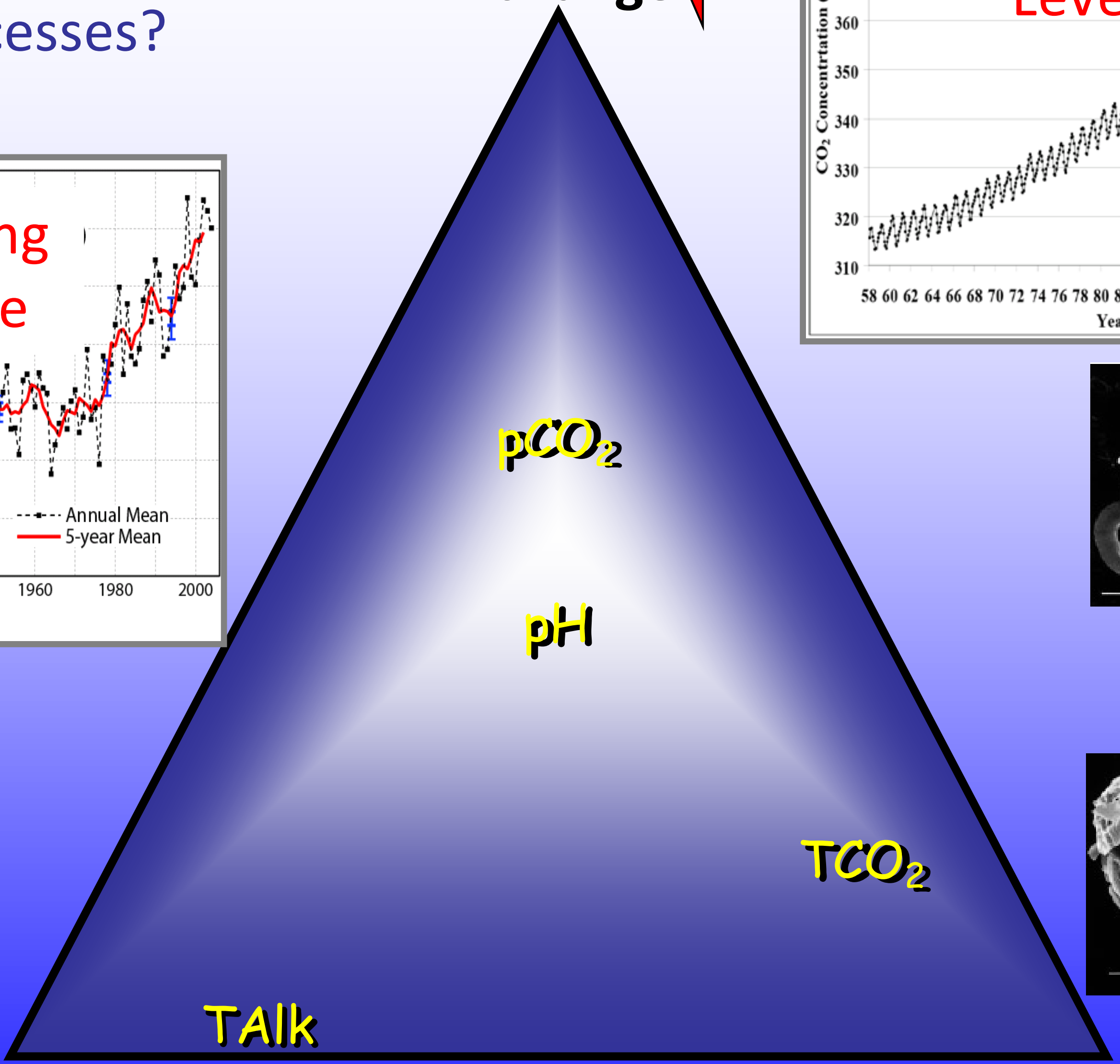


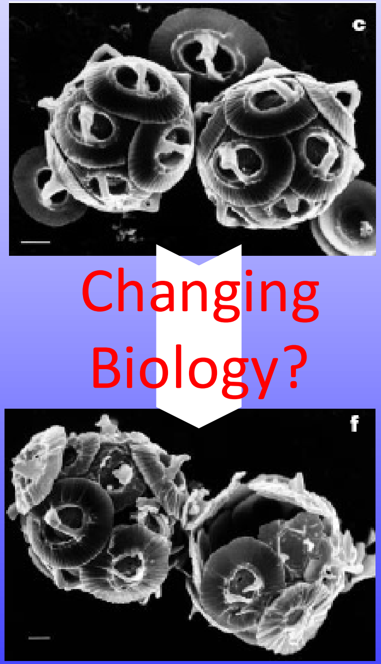
Question:
How will ocean carbon system respond to changes in ocean processes?

Gas Exchange









Ocean Physics

Biology

Equations for CO_2 Speciation

The equilibrium of gaseous and aqueous CO_2:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$

Subsequent hydration and dissociation reactions:

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

$$K_1^* = \frac{\{H^+\}[HCO_3^-]}{[CO_2]}$$

$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$$

$$K_2^* = \frac{\{H^+\}[CO_3^{2-}]}{[HCO_3^-]}$$

Hint: When you add a CO_2 species to the system, follow the H^+. Thus, the following is a reasonable approximation when pH is between 7.5 and 8.5:

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

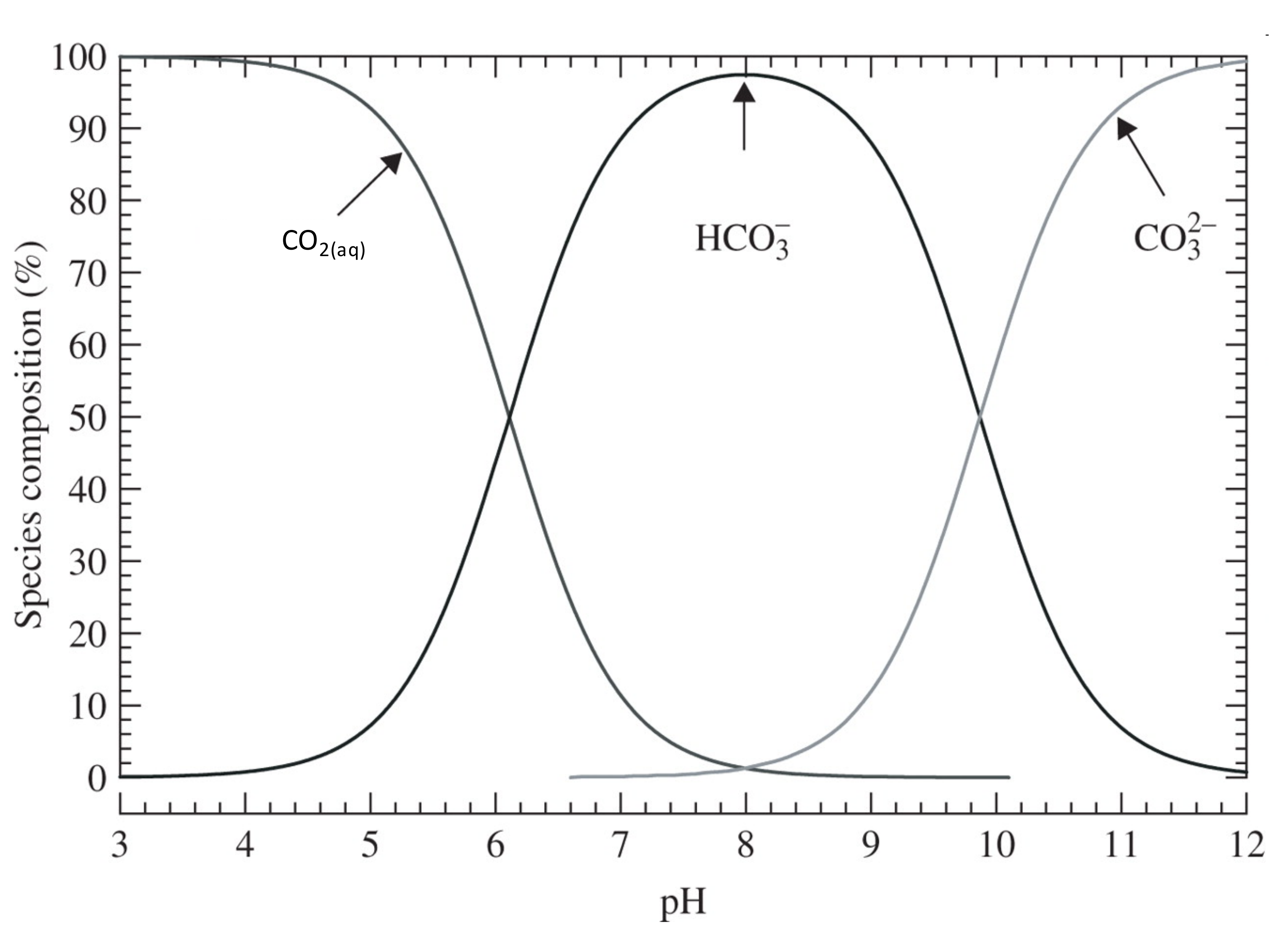
Asterisk (*) indicates a "stoichiometric" constant

Distribution of CO_2 Species at Different pH Values

$CO_{2(g)} \leftrightarrow CO_{2(aq)}$

$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$

$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$



Seawater values shown --- freshwater curves are shifted left

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Effects of Pressure on Carbonate Speciation

	1 atm	1000 atm
K_1*	$10^{-5.89}$	$10^{-5.55}$
K_2*	$10^{-9.13}$	$10^{-8.93}$

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$$

$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$$

$$K_1* = \frac{\{H^+\}[HCO_3^-]}{[CO_2]}$$

$$K_2* = \frac{\{H^+\}[CO_3^{2-}]}{[HCO_3^-]}$$

As you raise a sample from depth:

- Ks' decrease
- Reactions shift to left
- pH increases

Group Task

Why is raising a sample of seawater from depth to the surface like opening a can of soda???

What exactly is happening?

How does the pH change?

Hint: What happens to the dissolved CO_2?

Group Task

Why is raising a sample of seawater from depth to the surface like opening a can of soda???

Answer: In both cases there is:

1) **An aqueous solution containing a large amount of dissolved CO_2**

2) **Pressure is released, causing the CO_2/carbonate reactions to shift to the left (due to decreased Ks)**

3) **CO_2 gas is released and pH increases**

$$HCO_3^- \leftarrow CO_3^{-2} + H^+$$

$$CO_{2(aq)} + H_2O \leftarrow HCO_3^- + H^+$$

$$CO_{2(g)} \leftarrow CO_{2(aq)}$$

$CaCO_3$ Precipitation/Dissolution

A tricky subject when discussing "CO_2"
(or, more properly, pCO_2)

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ (consumption of CO_3^{2-})

Does this reduce the CO_2 (pCO_2) level of the seawater?

$CO_{2(g)} \leftrightarrow CO_{2(aq)}$

$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$

$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$

No! Lost CO_3^{2-} will be replaced:

$HCO_3^- \rightarrow CO_3^{2-} + H^+$

But this H^+ release causes:

$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$

Hint: when pH is between 7.5 and 8.5:

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

Thus, $CaCO_3$ precipitation causes a decrease in DIC and TA,
but an <u>increase</u> in pCO_2

Chemical Reactions of Carbonate Species in Seawater

$[Ca^{2+}]$ is one of the 6 major ions in seawater

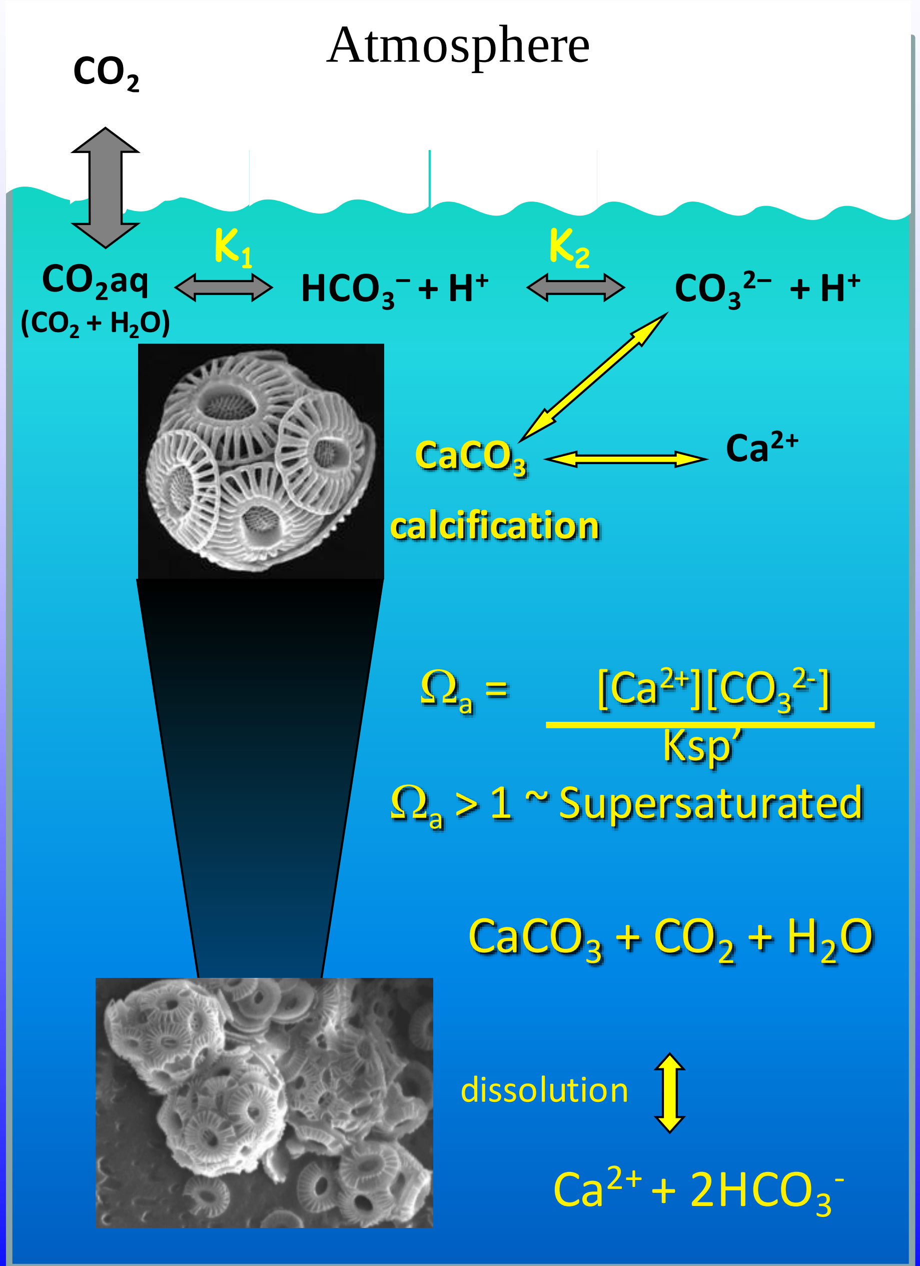
To a first order it is considered conservative with salinity (~10.3 mmol/kg at salinity of 35)

Therefore, $[CO_3^{2-}]$ primarily controls the saturation state of the waters with respect to aragonite, calcite, magnesian calcite

K_{sp} = solubility product of a solid
K_{sp}' = apparent solubility product

Solubility of $CaCO_3$ increases with decreasing temperature and increasing pressure.

Increasing Solubility from left to right:
dolomite < calcite < aragonite < high-magnesian calcite



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