Carbonate Chemistry
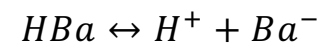
- General acid / base chemistry

- Carbonate speciation

- Carbonate saturation

- Response of ocean to different scenarios
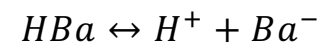
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Acids and Bases in SW

- Dissolving species HBa in water gives H^+ and Ba^-

$$HBa \leftrightarrow H^+ + Ba^-$$

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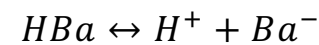
$$HBa \leftrightarrow H^+ + Ba^-$$

$$K' = \frac{[H^+]x[Ba^-]}{[HBa]} \qquad (1)$$

Note: for carbonate chemistry we will use K' – "apparent" equilibrium constants.
- These are determined experimentally using near-seawater concentrations of ions
- Include impact of activity w/o additional calculation

Acids and Bases in SW

- Dissolving species HBa in water gives H^+ and Ba^-

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$$K' = \frac{[H^+]x[Ba^-]}{[HBa]} \qquad (1)$$

- Total amount of Ba in solution is the combination of [HBa] and [Ba$^-$]

$$[Ba]_T = [HBa] + [Ba^-] \qquad (2)$$

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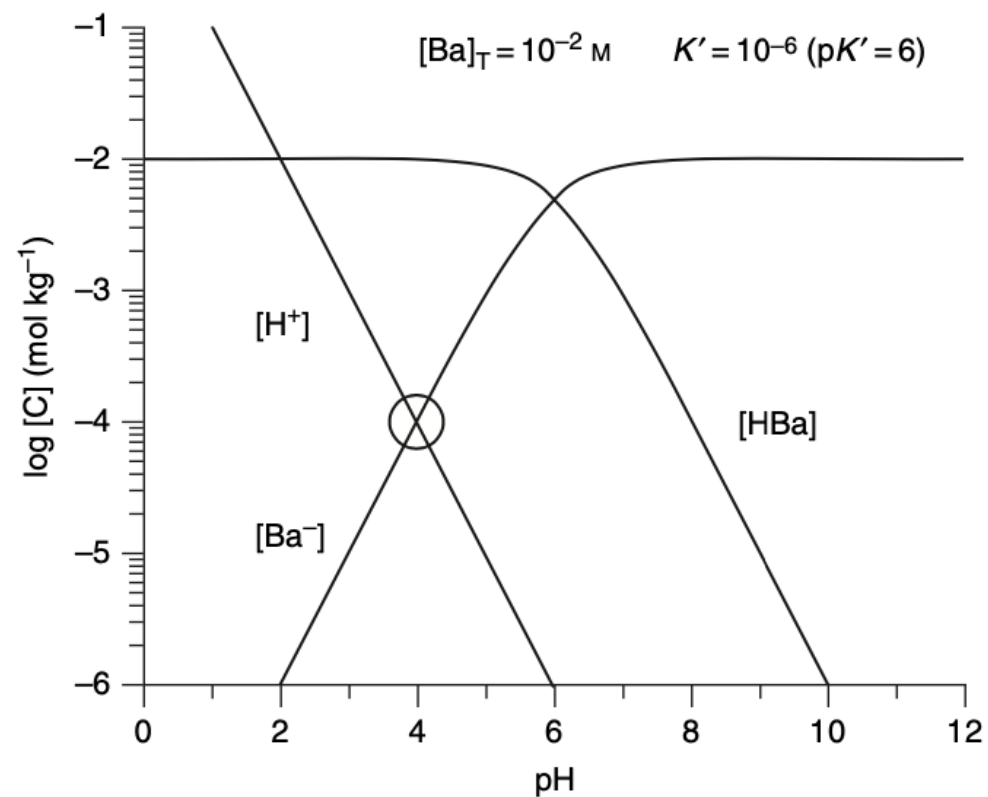- Seawater is neutral, so charge balance must be maintained

$$HBa \leftrightarrow H^+ + Ba^-$$

$$K' = \frac{[H^+] x [Ba^-]}{[HBa]} \qquad (1)$$

$$[Ba]_T = [HBa] + [Ba^-] \qquad (2)$$

$$0 = [H^+] - [Ba^-] \qquad (3)$$

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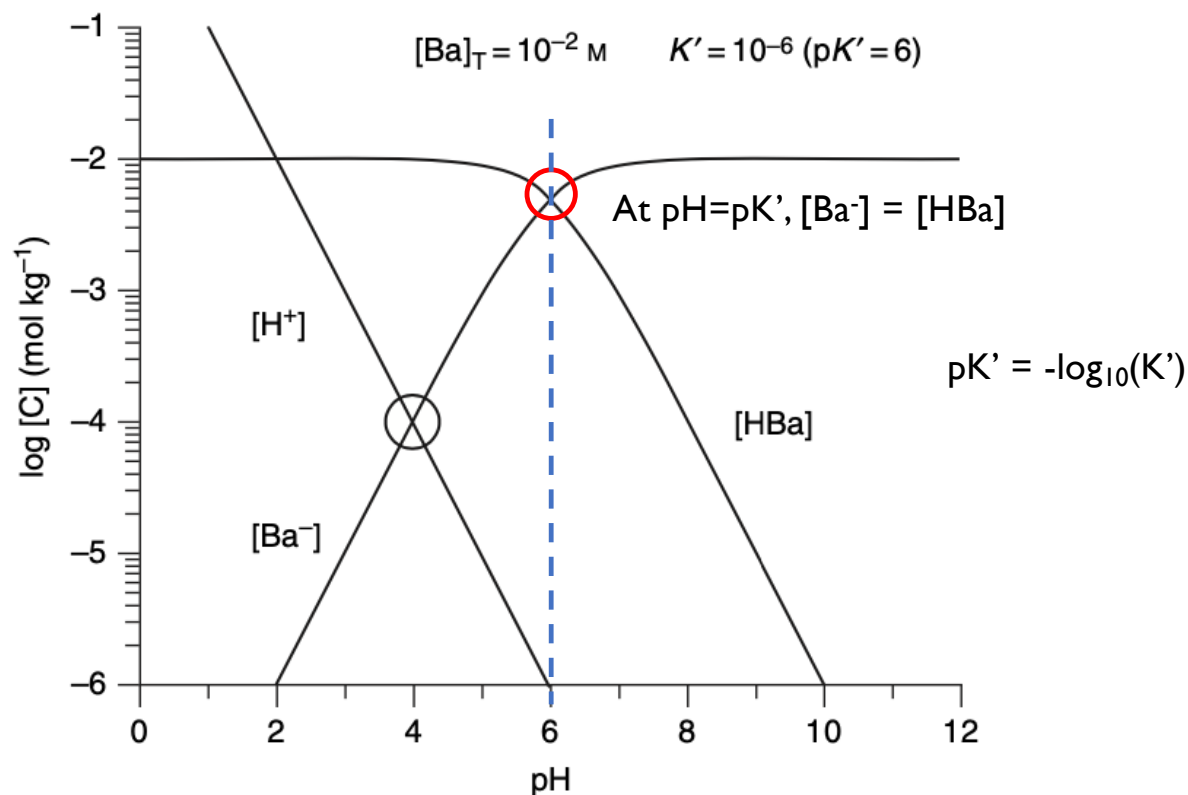
Acid-Bases: Log species distribution vs. pH

$[Ba]_T = 10^{-2}$ M $K' = 10^{-6}$ (p$K' = 6$)

$[H^+]$

$[HBa]$

$[Ba^-]$

log [C] (mol kg^{-1})

pH

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$[Ba]_T = 10^{-2}$ M $K' = 10^{-6}$ (p$K' = 6$)

At pH=pK', $[Ba^-]$ = $[HBa]$

pK' = -$\log_{10}$(K')

$[H^+]$

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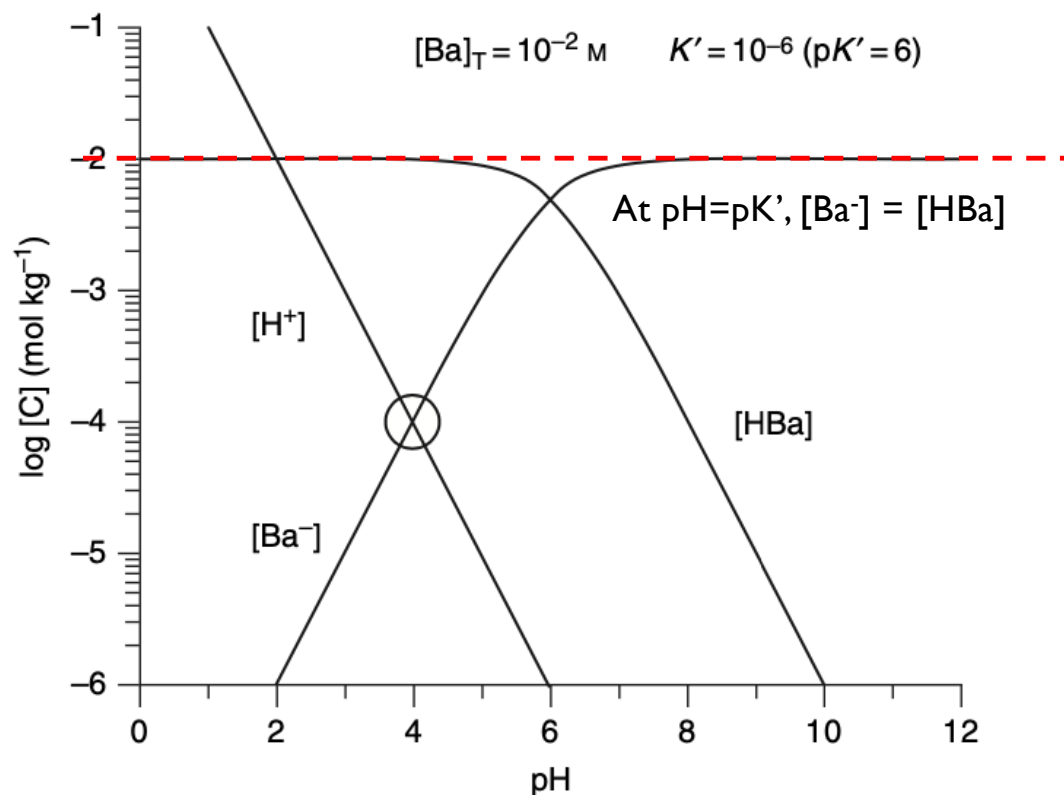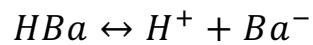$[Ba]_T = 10^{-2}$ M $\qquad K' = 10^{-6}$ (p$K' = 6$)

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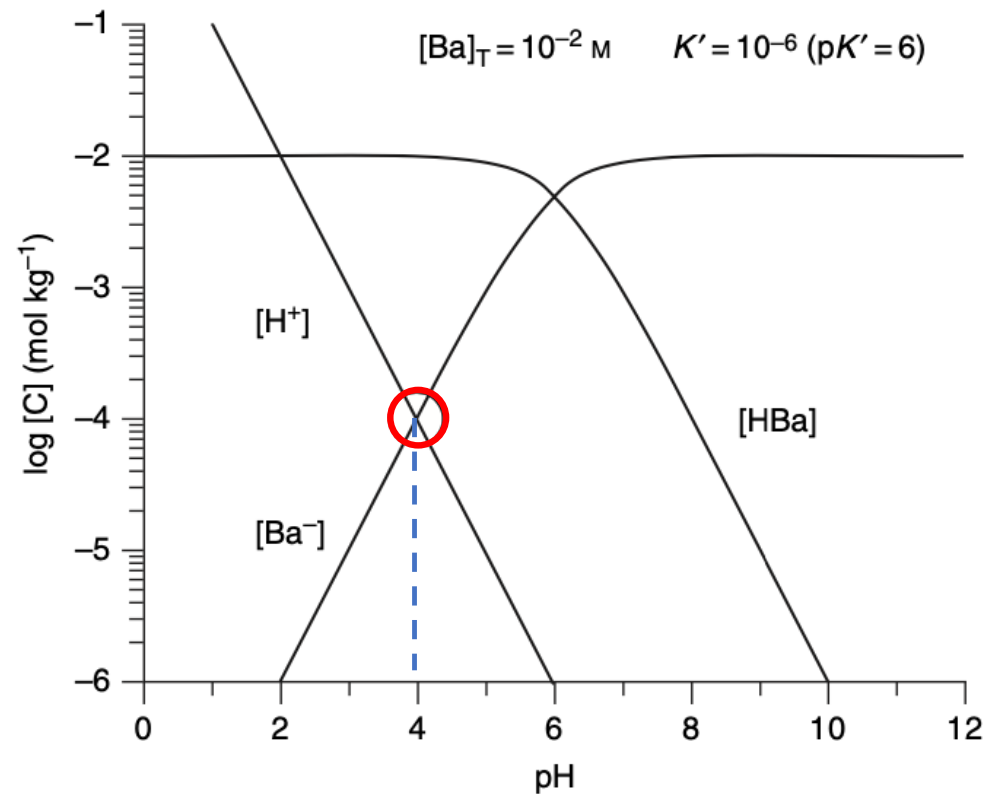$[Ba]_T = 10^{-2}$ M $\qquad K' = 10^{-6}$ (p$K' = 6$)

- pH of this system will equal 4

Acid-Bases: Log species distribution vs. pH

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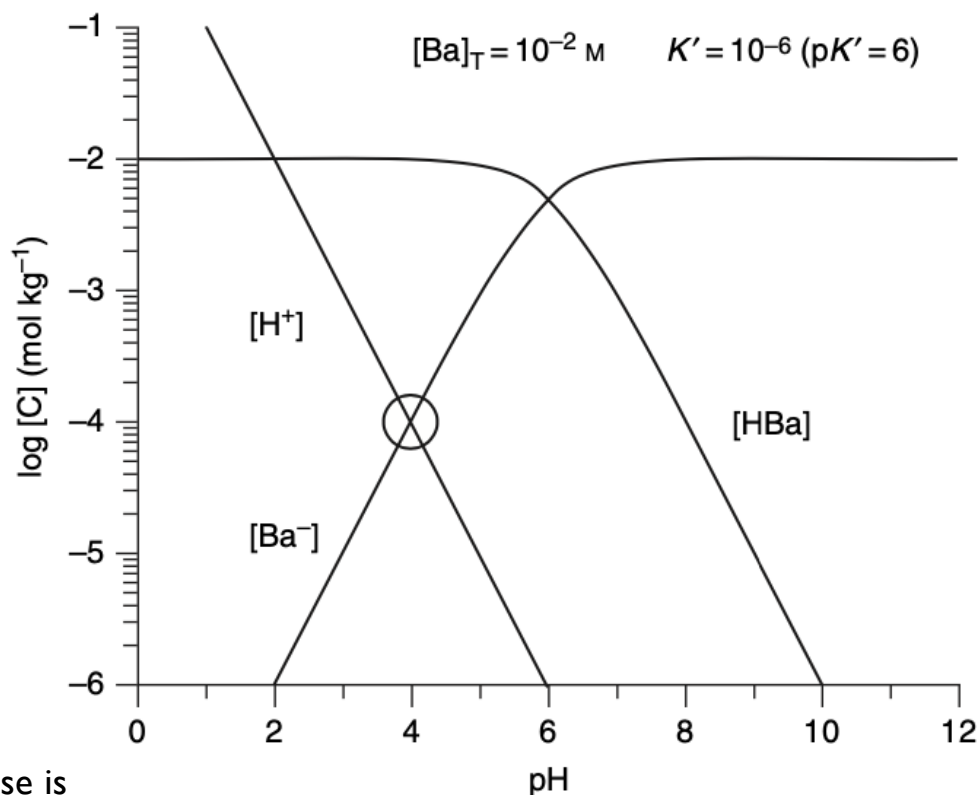
$K' = \dfrac{[H^+] x [Ba^-]}{[HBa]}$ (1)

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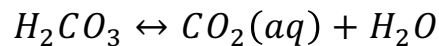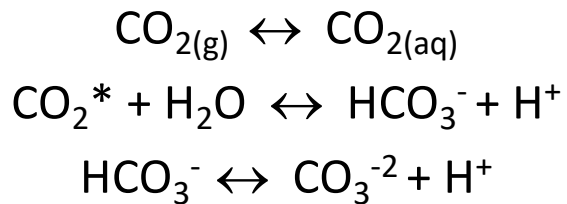
$0 = [H^+] - [Ba^-]$ (3)

- 3 equations, 4 unknowns (H, Ba, HBa, $[Ba]_T$)
- Charge balance sets pH, but don't know concentrations of species unless something else is measured ($[Ba]_T$)
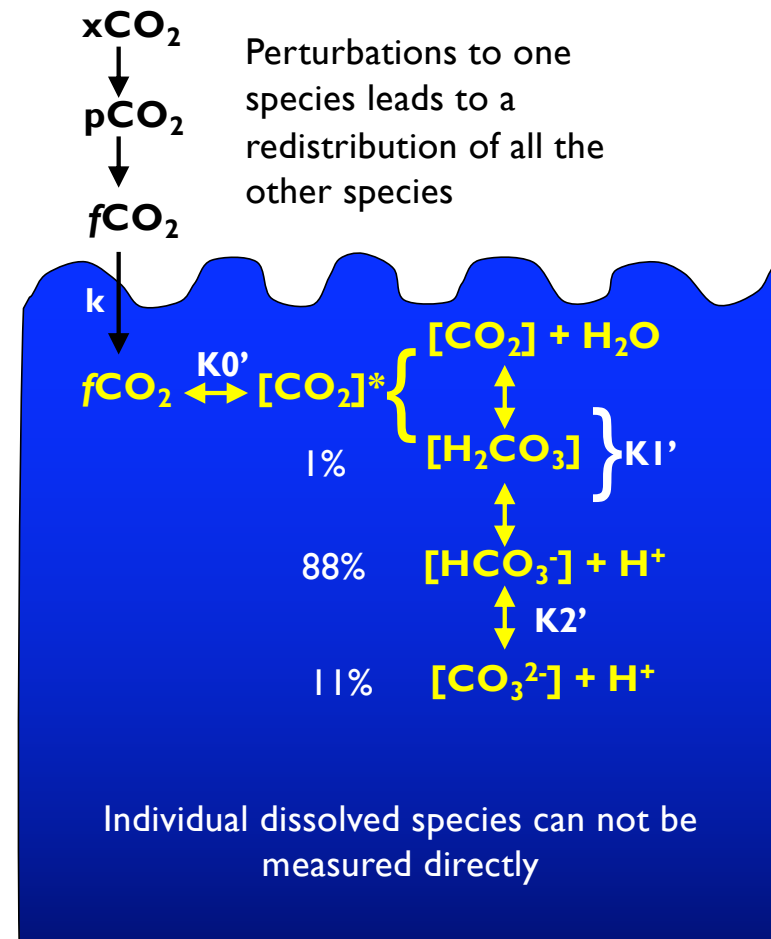

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[HBa]

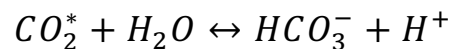pH

Why do we study 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

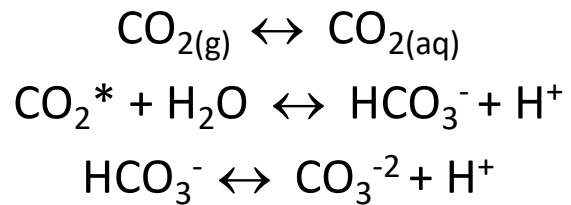- Distribution of CO_2 species affects preservation of $CaCO_3$ deposited on the sea floor

CO$_2$ Speciation

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$
$$CO_2{}^* + H_2O \leftrightarrow HCO_3^- + H^+$$
$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$$

$$H_2CO_3 \leftrightarrow CO_2(aq) + H_2O$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

- Dissolved CO_2 hydrates to form carbonic acid (H_2CO_3) which then dissociates to form HCO_3^-
- In practice, very little dissolved CO_2 exists as carbonic acid and it is not possible to distinguish between carbonic acid and CO_2(aq), so a composite equation is used:
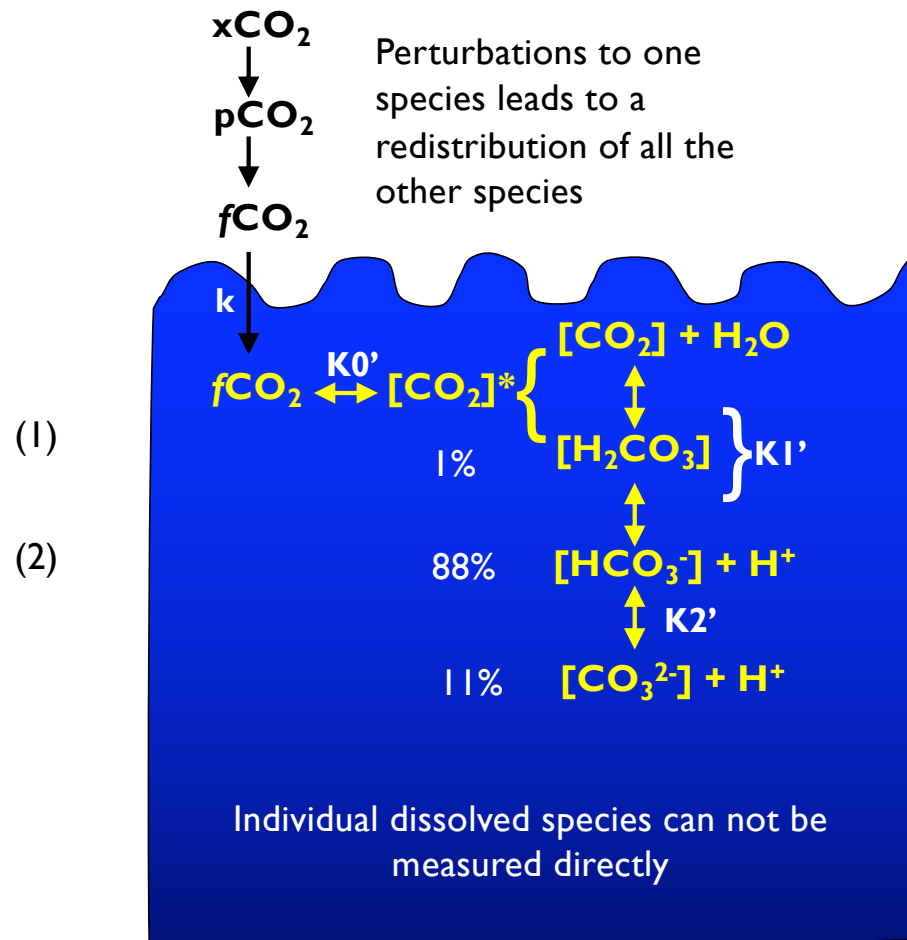
$$CO_2^* + H_2O \leftrightarrow HCO_3^- + H^+$$

xCO$_2$
pCO$_2$
fCO$_2$

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

k

fCO$_2$ $\xleftrightarrow{K0'}$ [CO$_2$]* $\begin{cases}\end{cases}$

[CO$_2$] + H$_2$O

1%   [H$_2$CO$_3$] } K1'

88%   [HCO$_3^-$] + H$^+$

K2'

11%   [CO$_3^{2-}$] + H$^+$

Individual dissolved species can not be measured directly

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CO₂ Speciation

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xCO₂

↓

pCO₂

↓

fCO₂

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- 4 equations, 6 unknowns (H$^+$, HCO$_3^-$, CO$_2$, CO$_3^{2-}$, DIC, TA)

xCO$_2$ → **pCO$_2$** → **fCO$_2$**

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Distribution of CO$_2$ Species at Different pH Values

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- Addition of CO_2?
  - DIC? TA? pH?
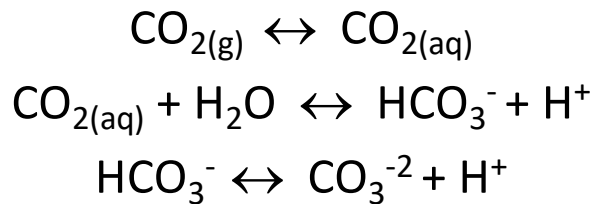
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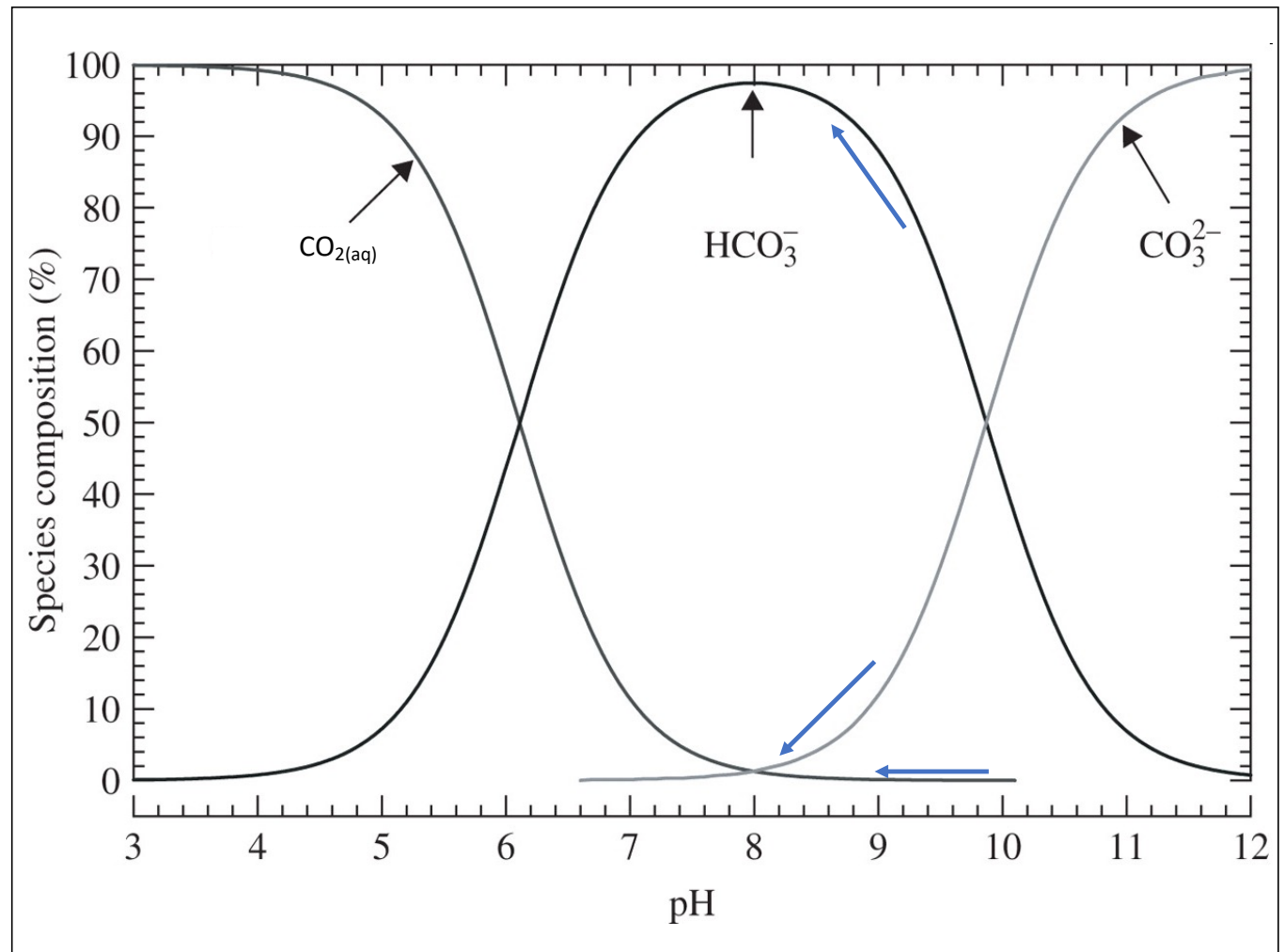
- 4 equations, 6 unknowns (H⁺, HCO₃⁻, CO₂, CO₃²⁻, DIC, TA)

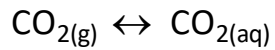- What happens when we start perturbing the system?
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$$CO_{2(g)} \rightarrow CO_{2(aq)}$$

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

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

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

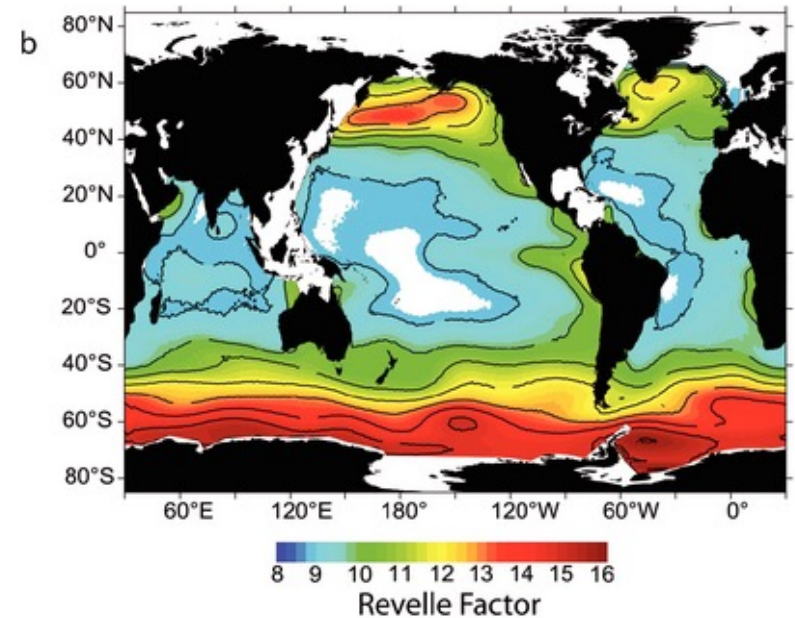- What about impact on alkalinity?

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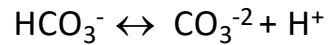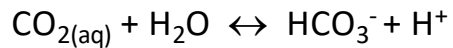
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Revelle factor – buffer capacity of seawater

- How much will a given change in carbon content impact seawater pCO_2?

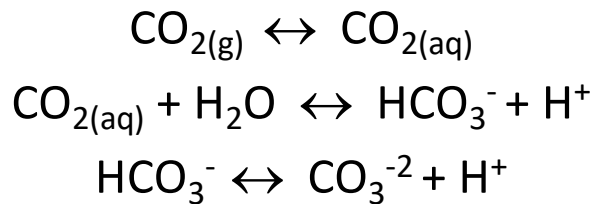$$R_{Rev} = \frac{\Delta fCO_2 / fCO_2}{\Delta DIC / DIC}$$
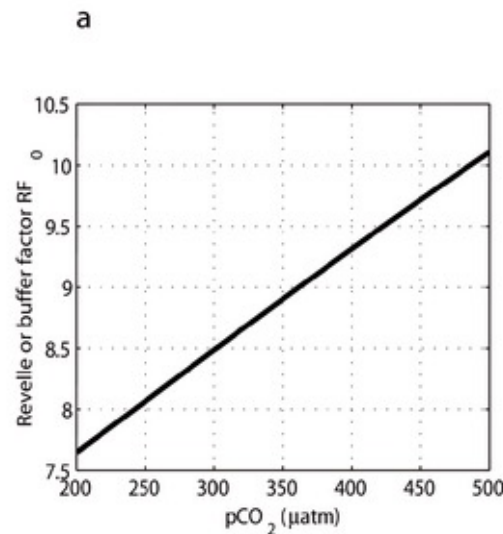
IPCC AR4, Fig. 7-11

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- 4 equations, 6 unknowns (H$^+$, HCO$_3^-$, CO$_2$, CO$_3^{2-}$, DIC, TA)

Precipitation of CaCO$_3$?

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$
(consumption of CO_3^{2-})
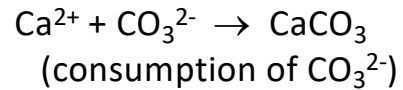
Does this reduce the CO_2 (pCO_2)
level of the seawater?

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

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

But this H^+ release causes:

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

Thus, CaCO$_3$ precipitation causes
a decrease in DIC and TA, but
an <u>increase</u> in pCO_2
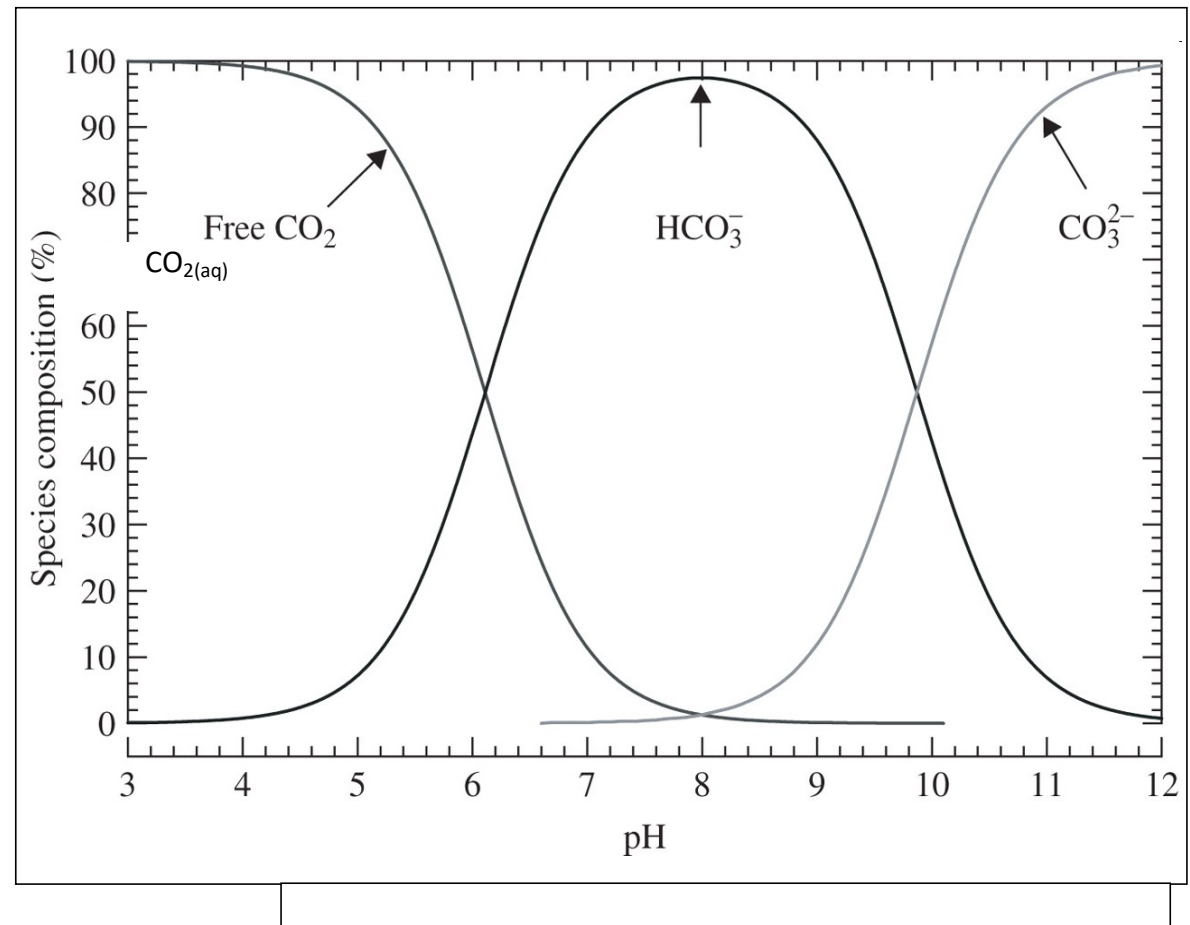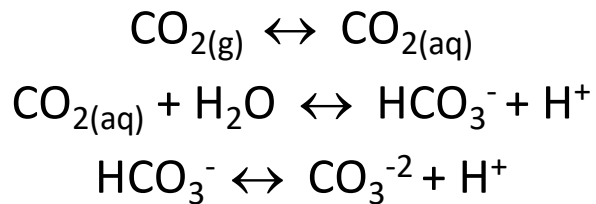
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Species composition (%) vs pH plot showing Free CO_2 ($CO_{2(aq)}$), HCO_3^-, and CO_3^{2-}.

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$$CO_2 + H_2O + \text{Nutrients} \rightarrow CH_2O + O_2$$

$$K_1' = \frac{\{H^+\}[HCO_3^-]}{[CO_2]^*} \tag{1}$$

Usage of P:N:C = 1:16:106

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

- 1 mol of OM formed = decrease of DIC by 1

$$DIC\ (\text{or}\ TCO_2) = [CO_2]^* + [HCO_3^-] + [CO_3^{2-}] \tag{3}$$

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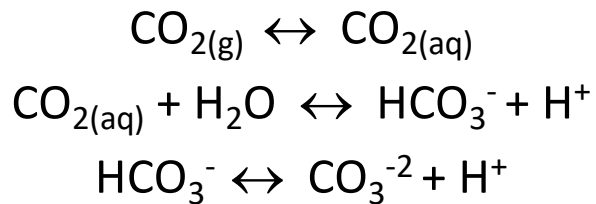- 4 equations, 6 unknowns (H$^+$, HCO$_3^-$, CO$_2$, CO$_3^{2-}$, DIC, TA)

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$$CO_2 + H_2O + \text{Nutrients} \rightarrow CH_2O + O_2$$

Usage of P:N:C = 1:16:106

- 1 mol of OM formed = decrease of DIC by 1
- Nitrate incorporation / degradation changes H+

$$NH_3(OM) + 2O_2 \leftrightarrow NO_3^- + H^+ + H_2O$$
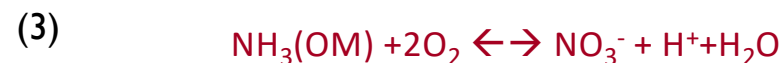
- Changes alkalinity in a -16/106 ratio (0.15, opposite sign to DIC change)

Carbonate changes

- What happens when we start perturbing the system?
- Addition of CO_2?
- Precipitation of $CaCO_3$?
- Formation of organic matter?

- Zeebe (2012)
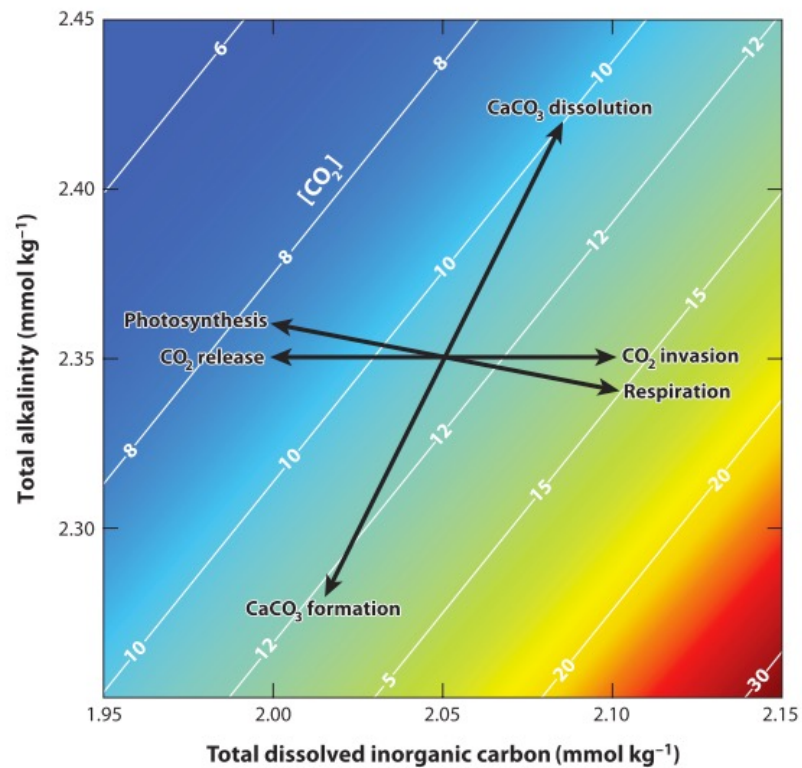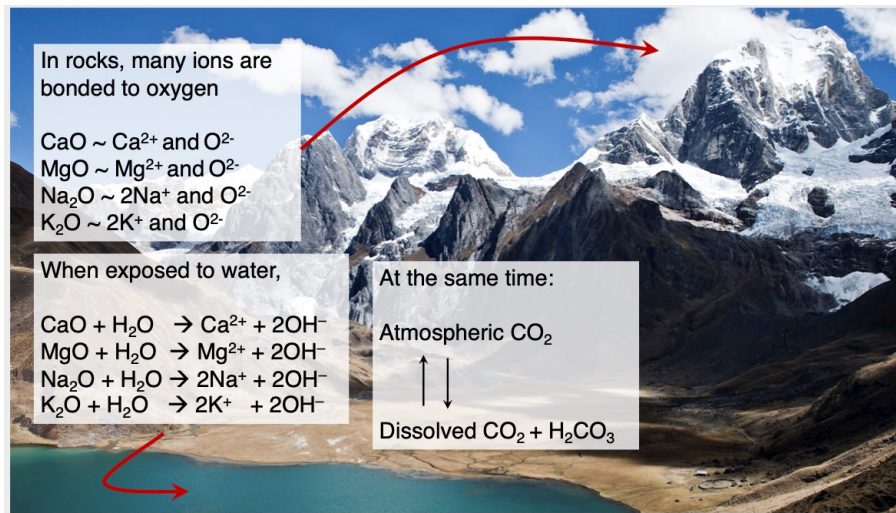
Seawater carbon content vs. freshwater

In rocks, many ions are bonded to oxygen

$CaO \sim Ca^{2+}$ and O^{2-}
$MgO \sim Mg^{2+}$ and O^{2-}
$Na_2O \sim 2Na^+$ and O^{2-}
$K_2O \sim 2K^+$ and O^{2-}

When exposed to water,

$CaO + H_2O \rightarrow Ca^{2+} + 2OH^-$
$MgO + H_2O \rightarrow Mg^{2+} + 2OH^-$
$Na_2O + H_2O \rightarrow 2Na^+ + 2OH^-$
$K_2O + H_2O \rightarrow 2K^+ + 2OH^-$

At the same time:

Atmospheric CO_2

Dissolved $CO_2 + H_2CO_3$

Weathering of rocks forms HCO_3^- and CO_3^{2-}
These additional pools of carbon allow seawater to take up much more carbon than freshwater

|	Pure water	Ocean water
Dissolved CO_2 + carbonic acid	☐ 0.4 mg/L	☐ 0.4 mg/L
Bicarbonate + Carbonate	▫ < 0.04 mg/L	>90 mg/L
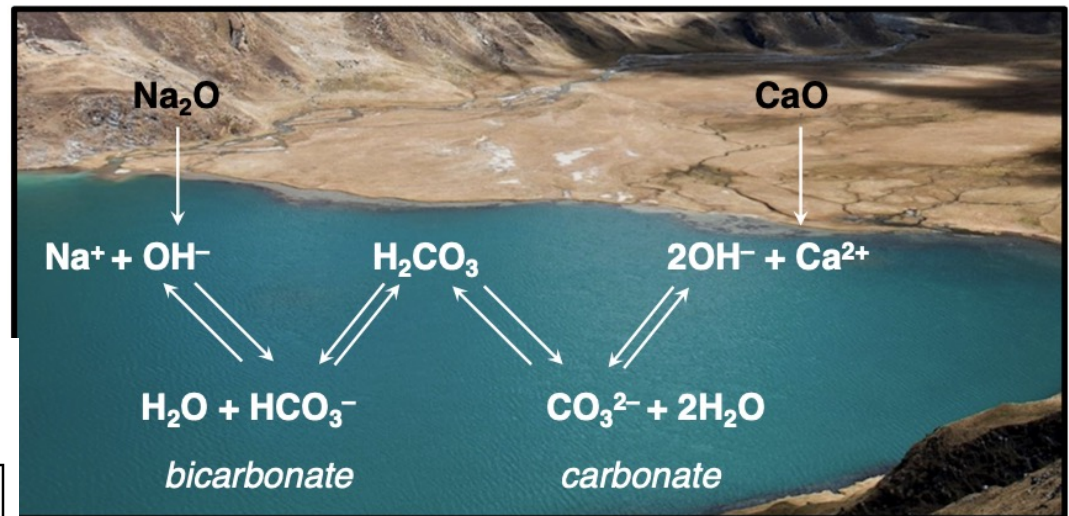
SW can hold ~ 200x more carbon than FW

CO$_2$ Speciation – fCO$_2$

Takahashi climatological annual mean air-sea CO$_2$ flux for reference year 2000

- fCO$_2$ is measured by equilibrating seawater with a headspace, then measuring the CO$_2$ molecules in that headspace using infrared adsorption

GMT 2007 Jan 19 16:23:06

Net Flux (moles CO$_2$ m^{-2} year^{-1})
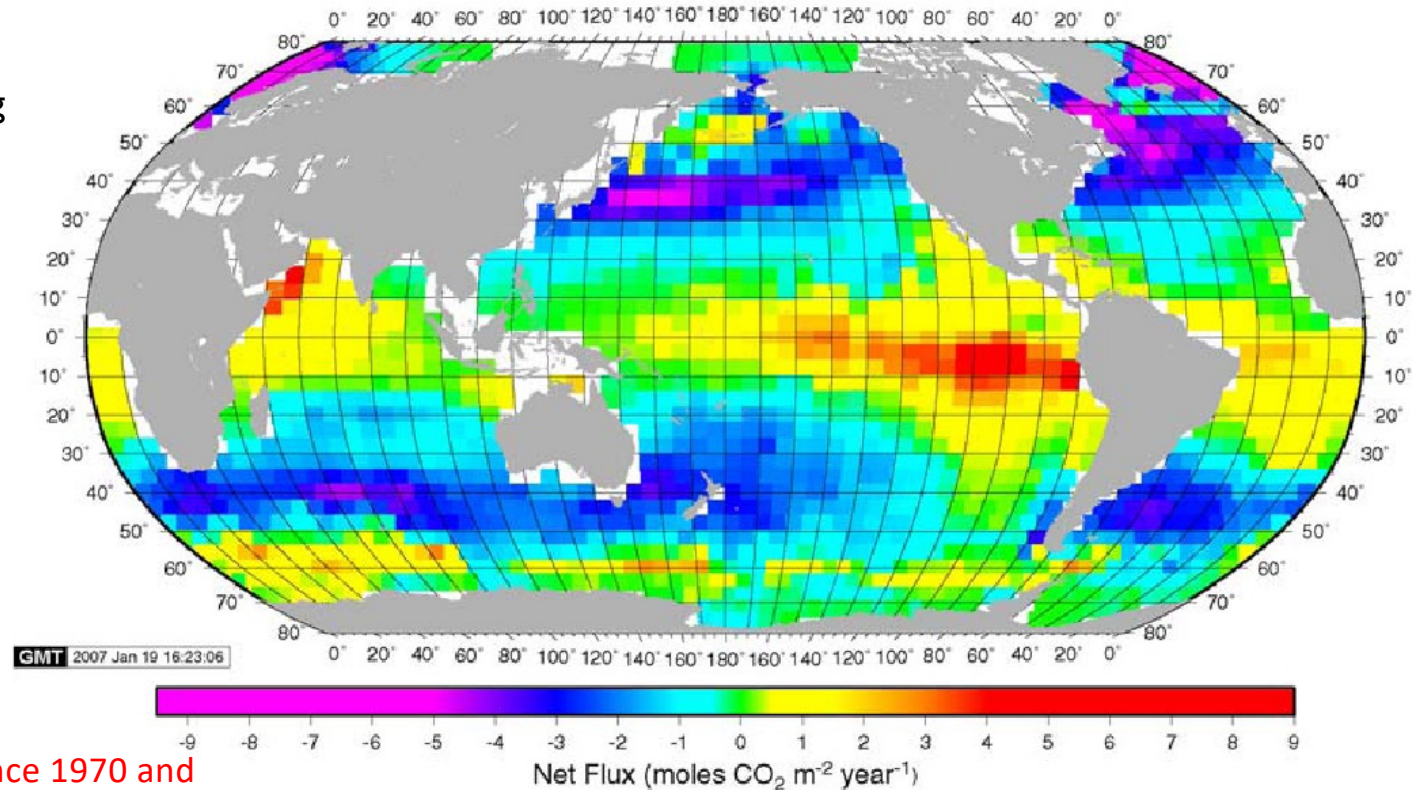
Based on ~3 million measurements since 1970 and NCEP/DOE/AMIP II reanalysis. Global flux is 1.4 ±0.7 Pg C/yr

- (Current SOCAT database has >21 million measurements)

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CO$_2$ Speciation – Total Alkalinity

- TAlk is measured by titrating SW with acid.
- While the the seawater is still being buffered, TA>0 (i.e. there are smaller changes in measured H+ changes than expected)
- Once measured H+ change equals observed H+ change, you know that all weak acids are gone, so TA can be calculated based on the amount of acid added

$$TA = [HCO_3^-] + 2*[CO_3^{2-}] + [B(OH)_4^-] + [HPO_4^{2-}] + 2*[PO_4^{3-}]... + [OH^-] - [H^+]$$
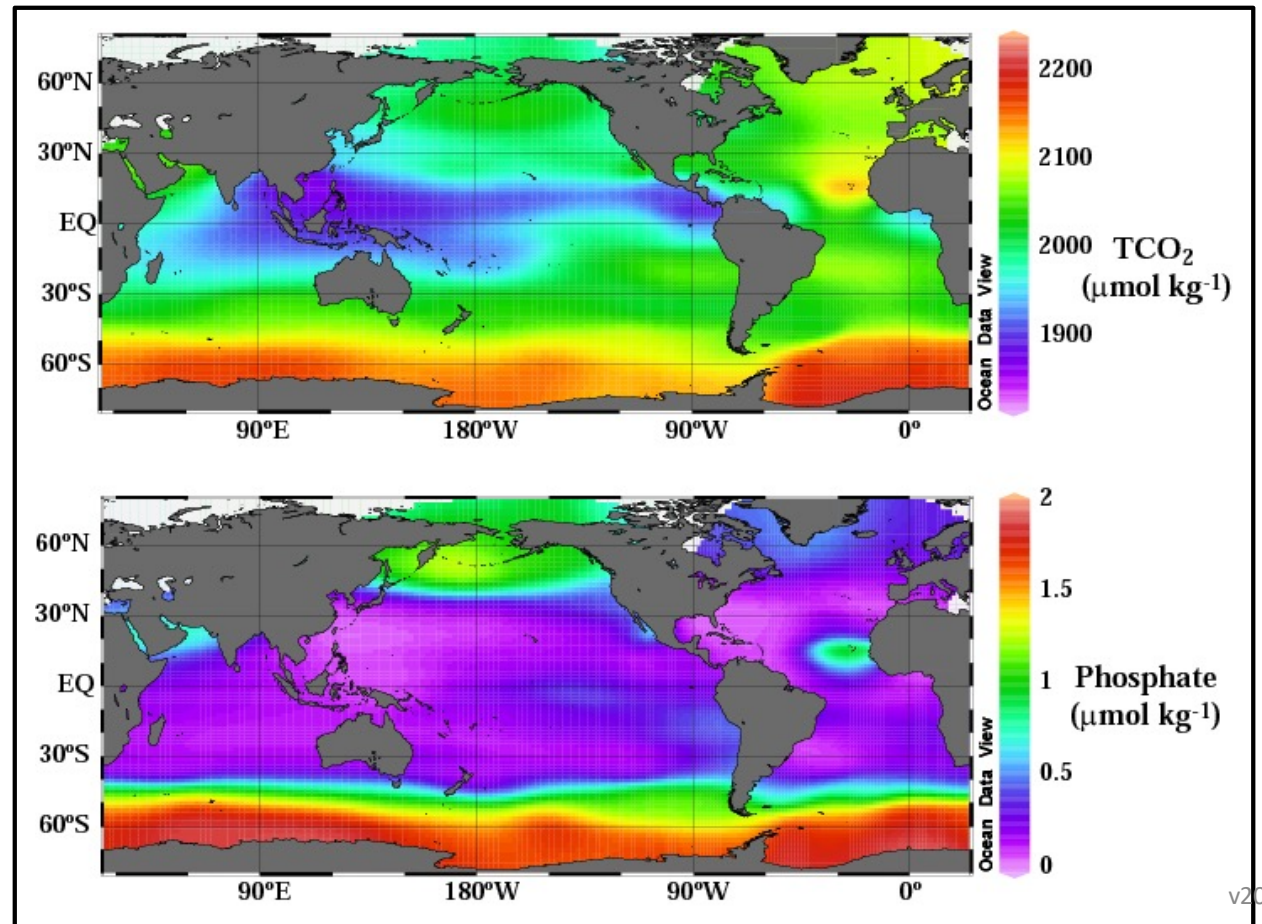
Carbonate alkalinity – simplification for calculation in Psets: $A_C = [HCO_3^-] + 2[CO_3^{2-}]$

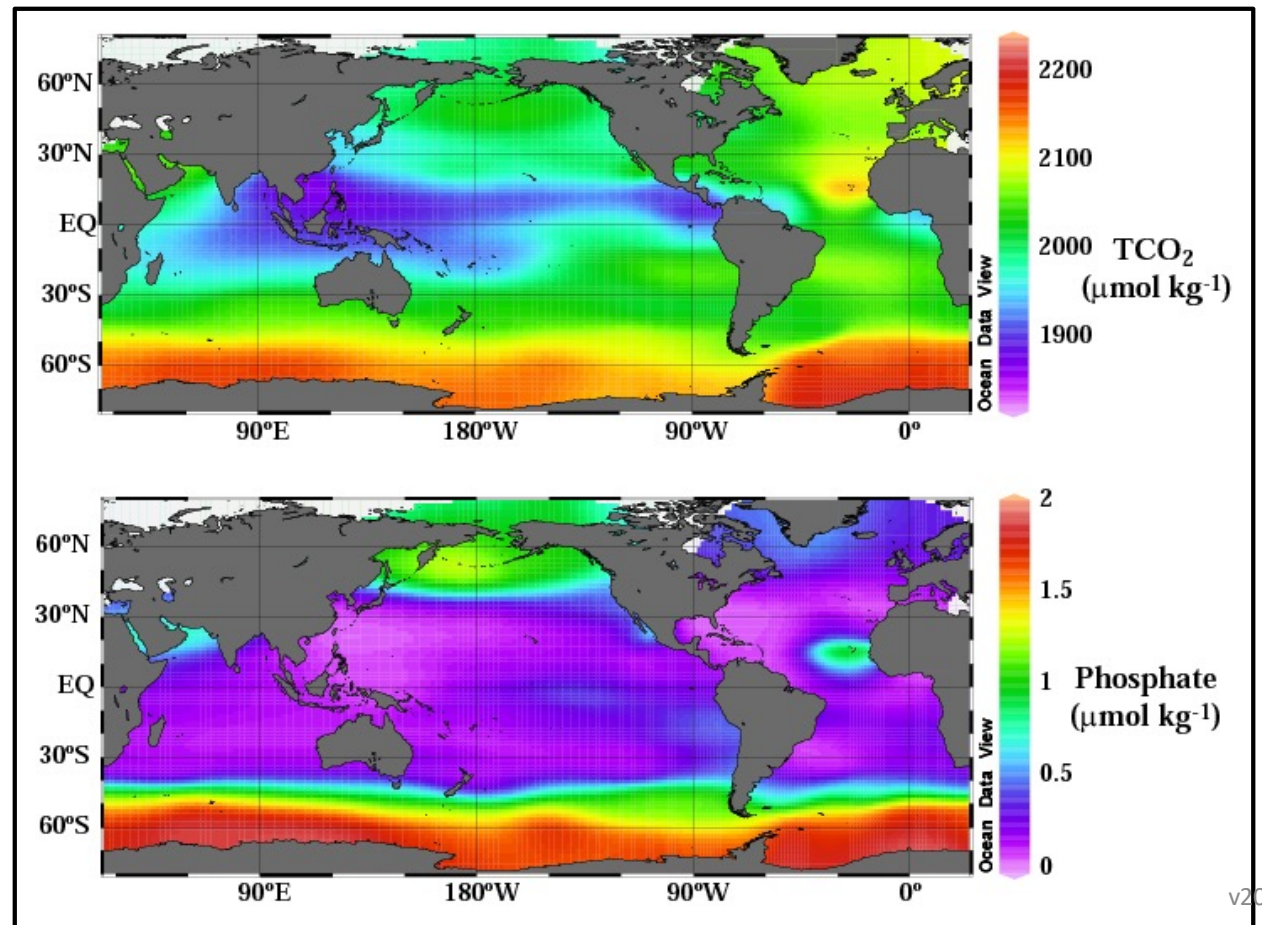## Surface TA/TAlk/Alk/A$_T$ Distribution is Very Similar to Salinity

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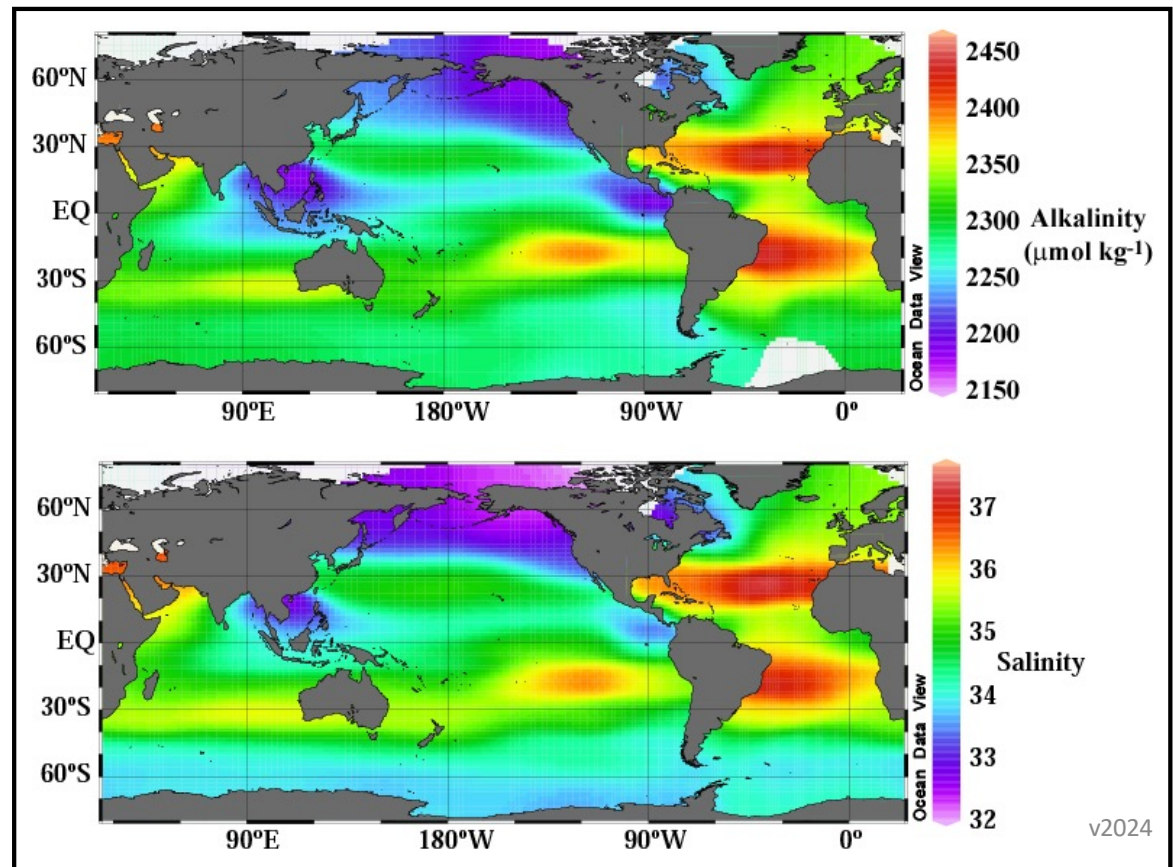
CO$_2$ Speciation – Total CO$_2$

TCO$_2$/DIC/C$_T$: Surface Distribution is Similar to Nutrient Distributions

CO$_2$ Speciation – Total CO$_2$

Shallow Indian Ocean Data
(depth < 100 m)
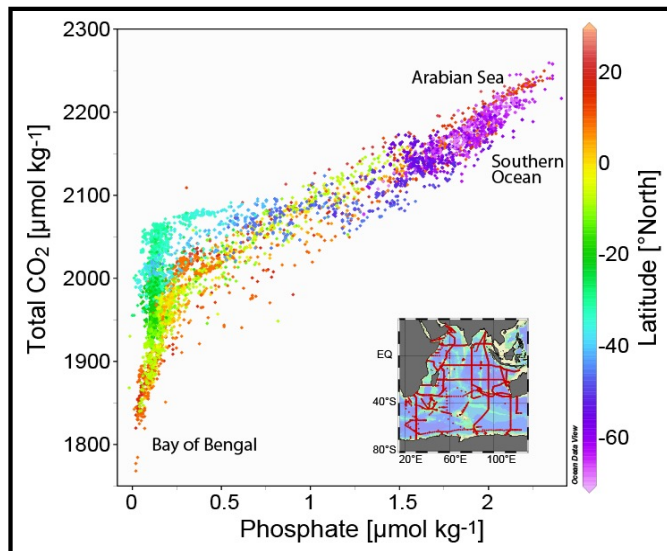
CO$_2$ Speciation – pH

Surface pH distribution reflects combined patterns of alkalinity and TCO$_2$

- Measured on several different scales (free, Total, seawater)
- Important to be consistent
  - Total scale (pH$_T$) most commonly used in oceanography

pH

8.4
8.3
8.2
8.1
8
7.9
7.8
7.7
7.6
7.5

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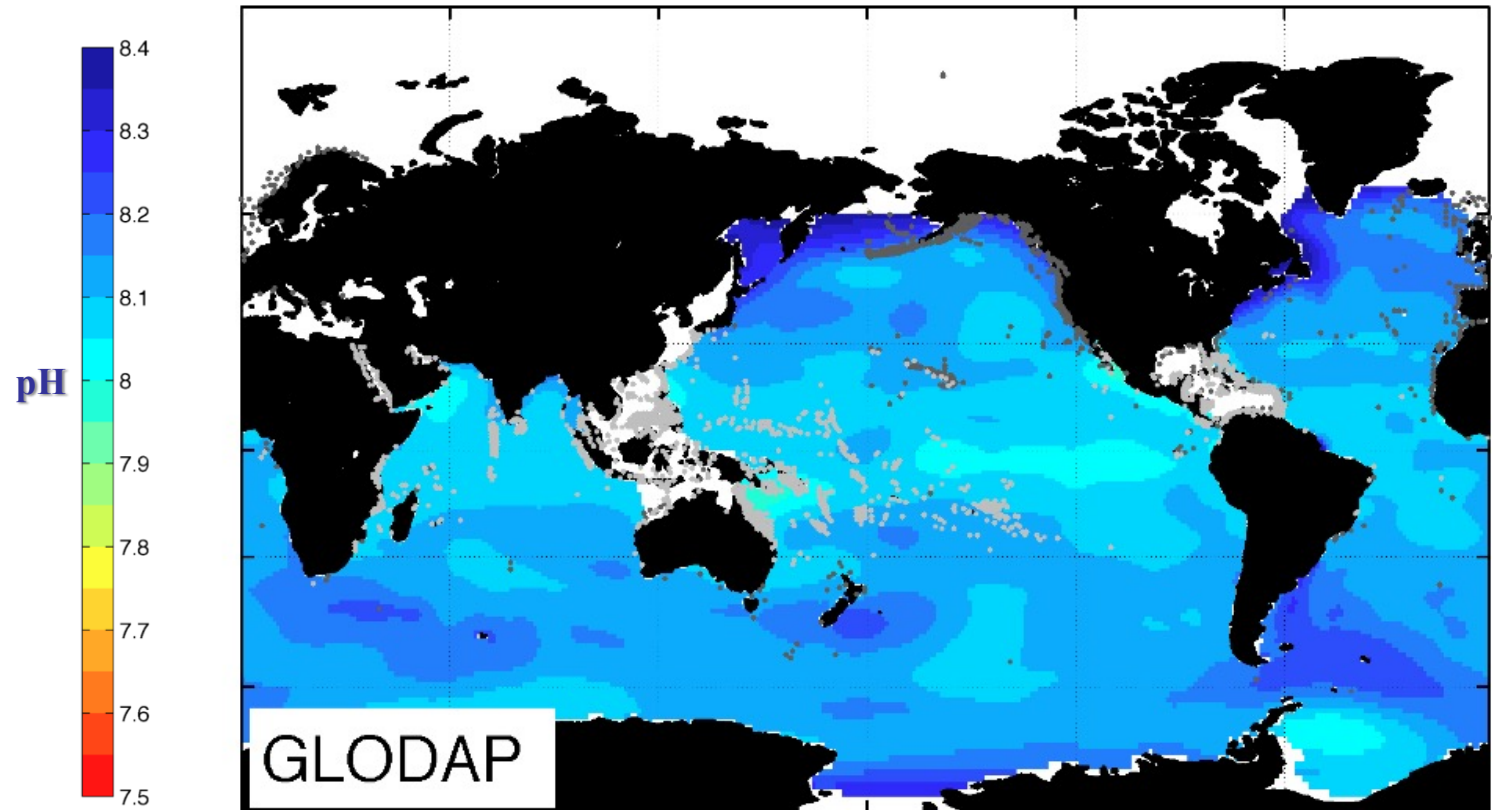
Light gray = warm water corals
Dark gray = cold water corals

Feely, Doney and Cooley, Oceanography (2009)

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CO_2 Speciation

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

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

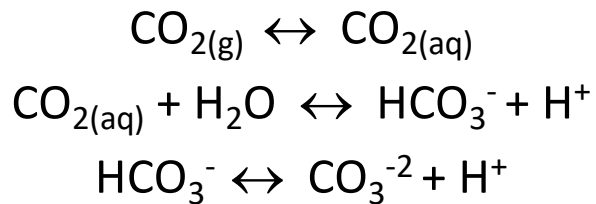$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$$

$$K_1' = \frac{\{H^+\}[HCO_3^-]}{[CO_2]^*} \tag{1}$$

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

$$\text{DIC (or } TCO_2) = [CO_2]^* + [HCO_3^-] + [CO_3^{2-}] \tag{3}$$

$$TA = [HCO_3^-] + 2*[CO_3^{2-}] + [B(OH)_4^-] + [HPO_4^{2-}] + \\ 2*[PO_4^{3-}]\ldots + [OH^-] - [H^+] \tag{4}$$

- 4 equations, 6 unknowns (H^+, HCO_3^-, CO_2, CO_3^{2-}, DIC, TA)
- Measuring 2 allows the system to be constrained

xCO_2

pCO_2

fCO_2

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

k

fCO_2 $\leftrightarrow$ **K0'** $[CO_2]^*$ $\Big\{$ $[CO_2] + H_2O$

1% $[H_2CO_3]$ $\Big\}$**K1'**

88% $[HCO_3^-] + H^+$

           K2'

11% $[CO_3^{2-}] + H^+$

Individual dissolved species can not be measured directly

CO_2 Speciation – For HW

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

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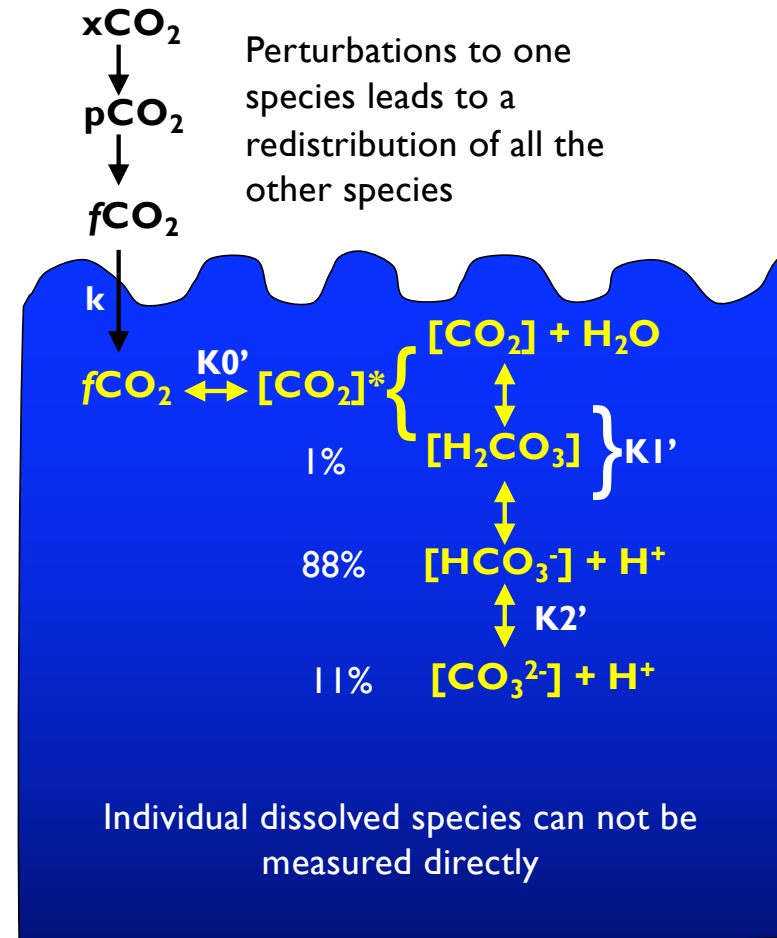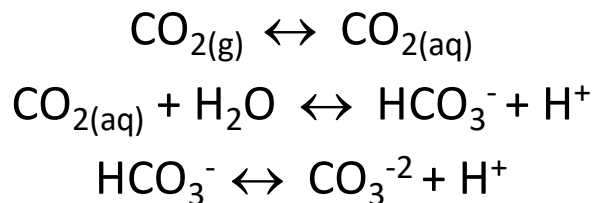
$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$$

$$K_1' = \frac{\{H^+\}[HCO_3^-]}{[CO_2]^*} \quad (1)$$

$$K_2' = \frac{\{H^+\}[CO_3^{2-}]}{[HCO_3^-]} \quad (2)$$

DIC (or TCO_2) = $[HCO_3^-] + [CO_3^{2-}]$ (3)

$$A_C = [HCO_3^-] + 2[CO_3^{2-}] \quad (4)$$

- 4 equations, 6 unknowns (H^+, HCO_3^-, CO_2, CO_3^{2-}, DIC, TA)
- Measuring 2 allows the system to be constrained

xCO$_2$

pCO$_2$

fCO$_2$

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

k

fCO$_2$ $\xleftrightarrow{K0'}$ [CO$_2$]* {

[CO$_2$] + H$_2$O

1%

[H$_2$CO$_3$] } K1'

88%

[HCO$_3^-$] + H$^+$

K2'

11%

[CO$_3^{2-}$] + H$^+$

Individual dissolved species can not be measured directly
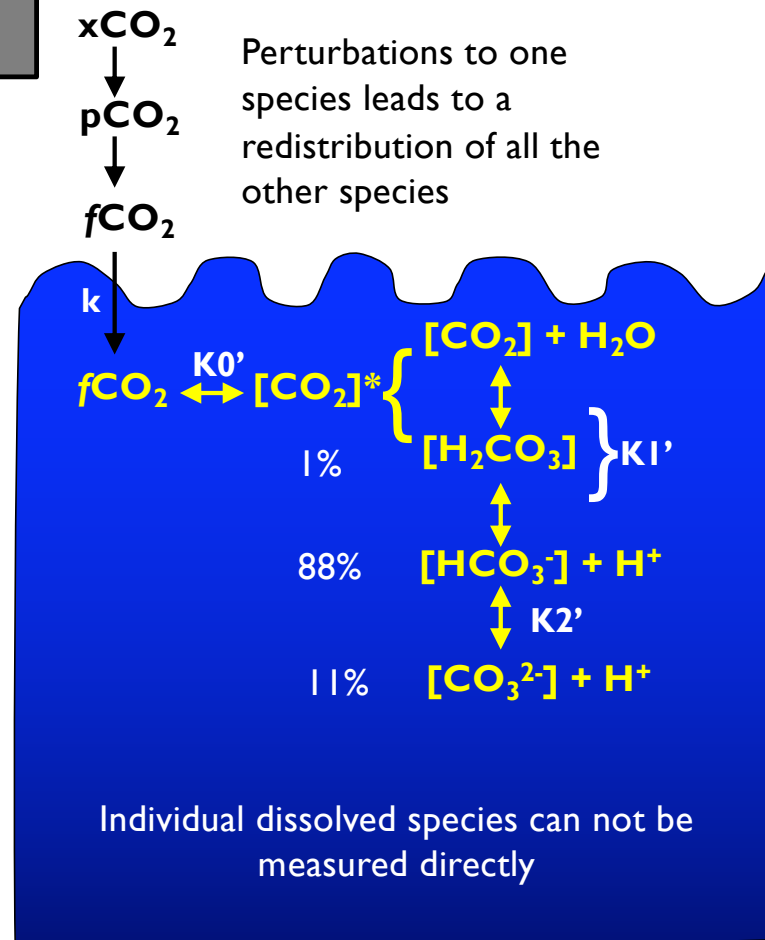
Take home message:
Each of the 4 measurable carbon parameters can tell us something different about the basic processes operating in the Ocean

Gas Exchange

Ocean Physics

Biology

pCO$_2$

pH

TCO$_2$

TAlk

$CO_2(g)$

Gas Exchange

$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$
Carbonic acid

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
Bicarbonate

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$
Carbonate
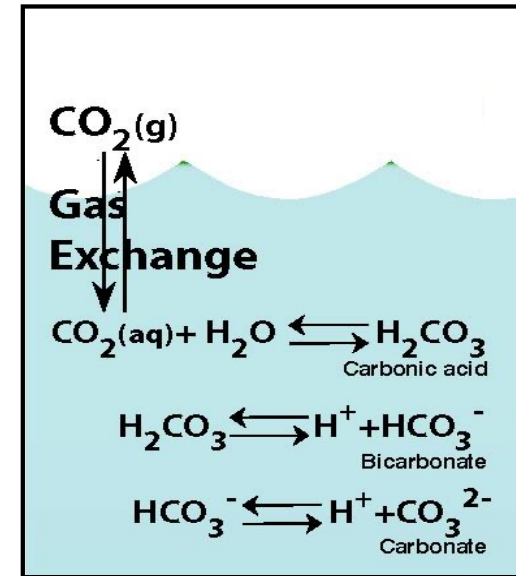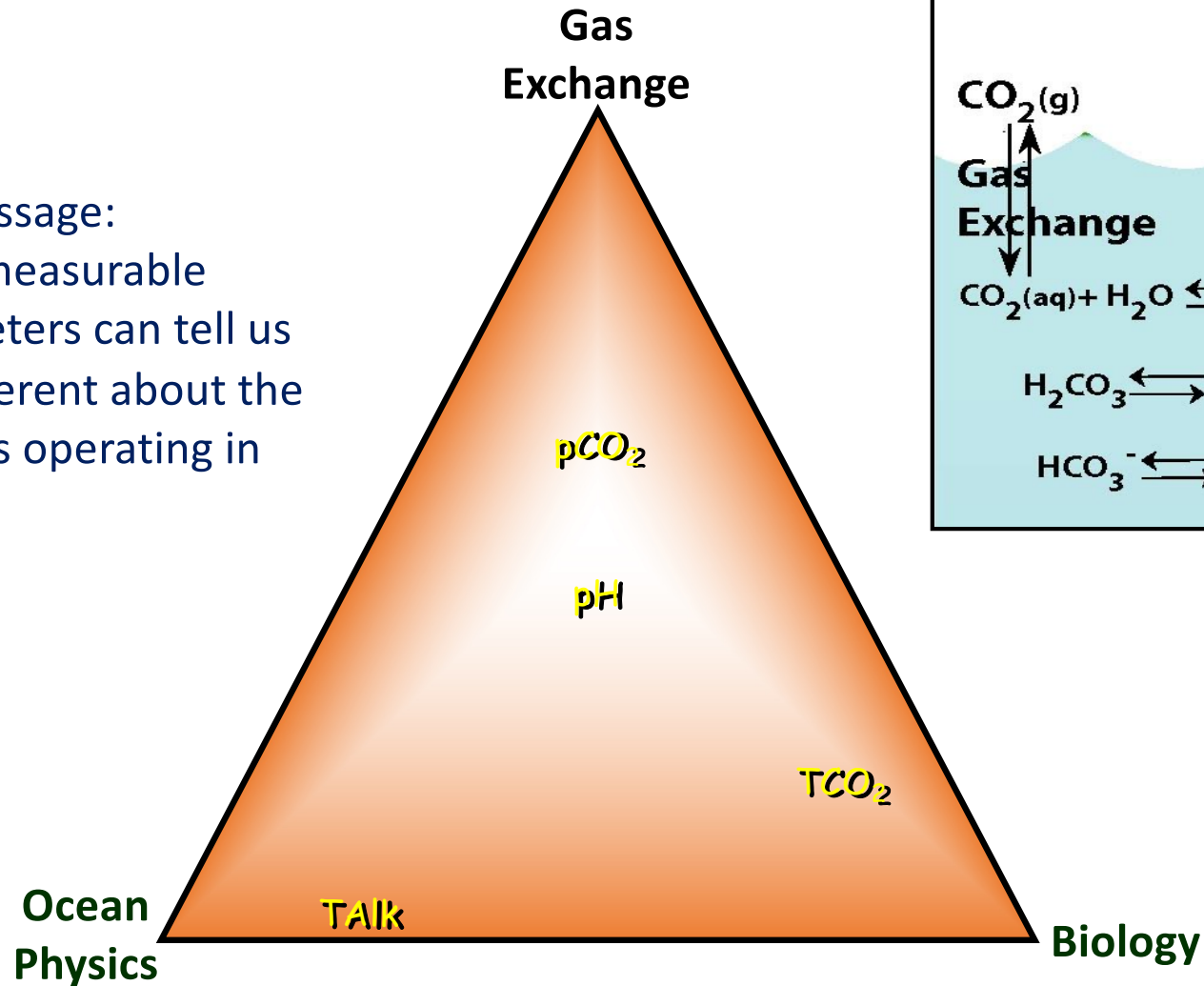
Question:
How will ocean carbon system respond to changes in ocean processes?

Changing Climate

Gas Exchange

Rising CO_2 Levels

Slope = 1.8 ppm per year

pCO_2

pH

TCO_2

TAlk

Ocean Physics

Biology

Changing Biology?

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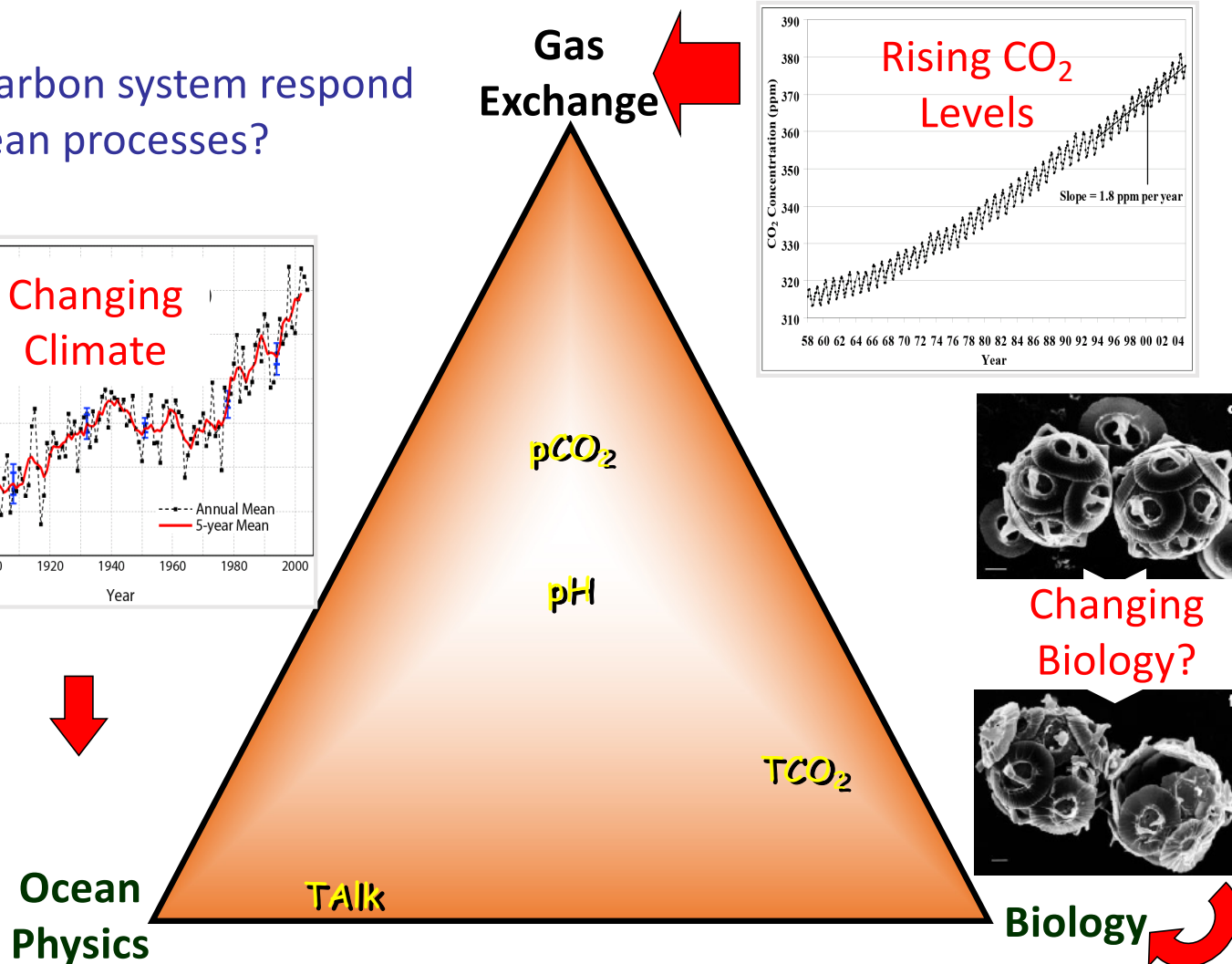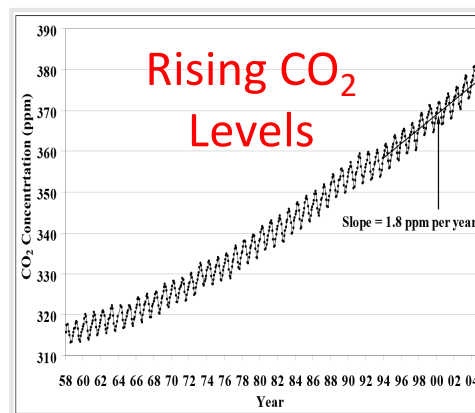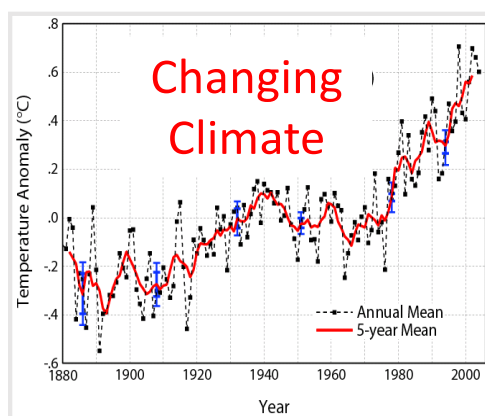
Effects of Pressure on Carbonate Speciation

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

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

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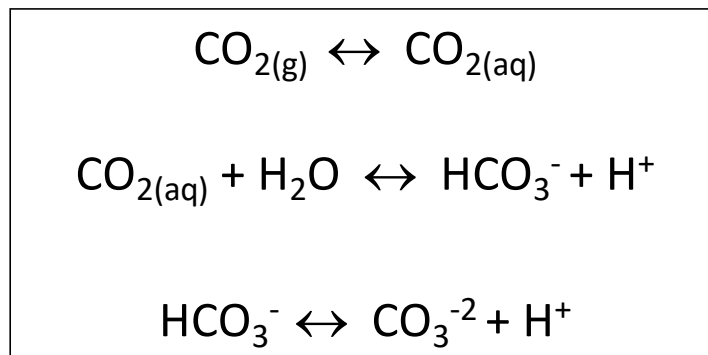
$$HCO_3^- \leftrightarrow CO_3^{-2} + H^+$$

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

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

As you raise a sample from depth:

- Ks' decrease

- Reactions shift to left

- pH increases

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Chemical Reactions of Carbonate Species in Seawater
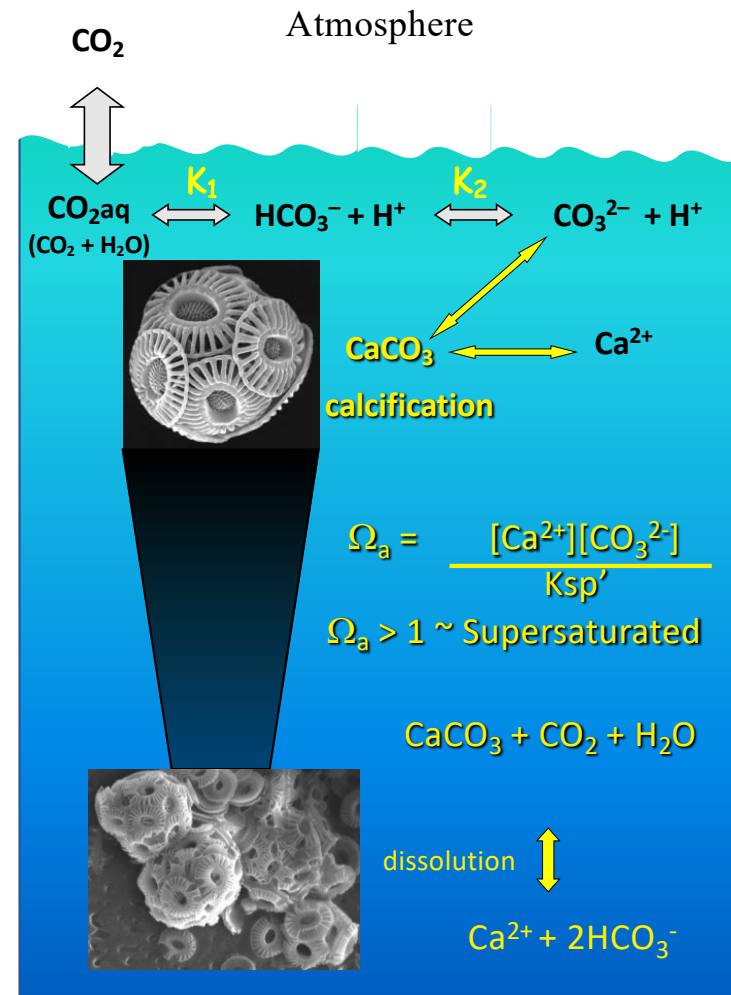
[Ca^{2+}] is one of the 6 major ions in seawater

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

Solubility of CaCO$_3$ increases with decreasing temperature and increasing pressure.

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

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Atmosphere

CO$_2$

$$CO_2aq \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + H^+$$
(CO$_2$ + H$_2$O)   K$_1$ K$_2$

CaCO$_3$ $\rightleftharpoons$ Ca^{2+}

calcification

$$\Omega_a = \frac{[Ca^{2+}][CO_3^{2-}]}{Ksp'}$$

$\Omega_a > 1$ ~ Supersaturated

CaCO$_3$ + CO$_2$ + H$_2$O

dissolution

Ca^{2+} + 2HCO$_3^-$

Calcite dissolution

- Remineralization of organic matter in the water column produces CO_2 that reacts with CO_3^{-2}

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

$$CO_2 + CO_3^{-2} + H_2O \rightarrow 2HCO_3^{-}$$

- Higher ΣCO_2 at depth
- Lower CO_3^{-2} at depth

- In the deep ocean, the decrease in $[CO_3^{-2}]$ from this reaction has a marked effect on $CaCO_3$ solubility

Depth, kilometers

ATLANTIC

PACIFIC

Total Dissolved Carbon (ΣCO_2), moles/m³
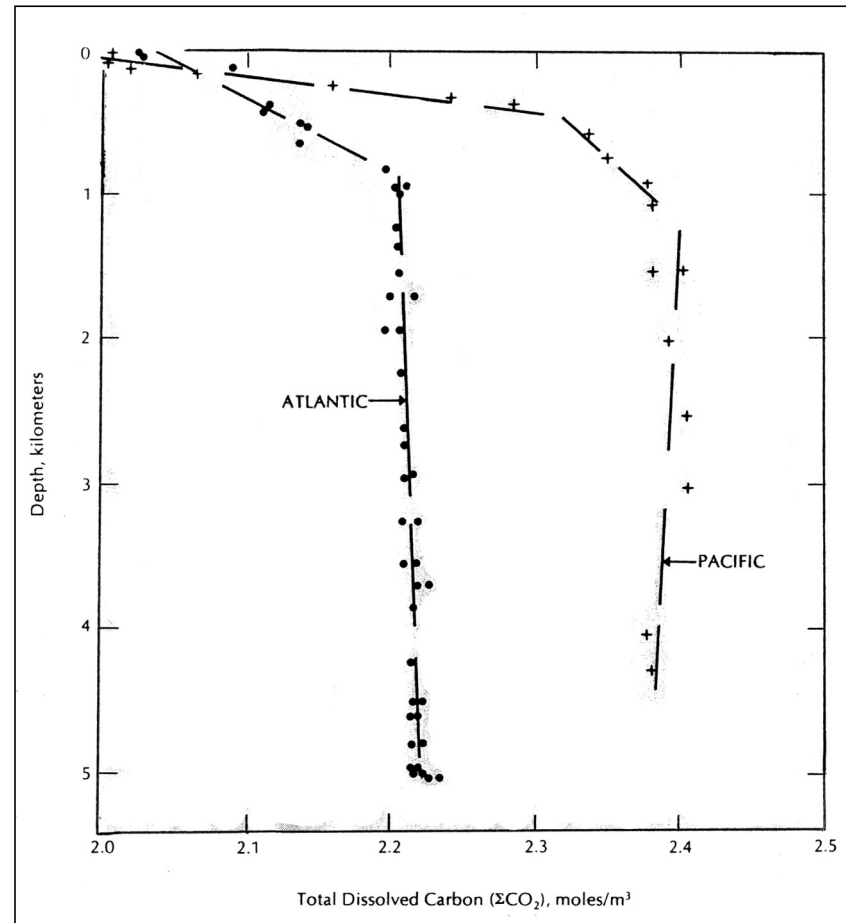
Saturation state of SW

- The saturation state of SW with respect to calcite (and aragonite, Mg-rich calcite, etc.) determines whether these phases will dissolve or not

- Define the *saturation state of SW with respect to calcite* ($CaCO_3$) as:

$$\Omega = \frac{\left(\{Ca^{2+}\}\{CO_3^{2-}\}\right)_{Seawater}}{\left(\{Ca^{2+}\}\{CO_3^{2-}\}\right)_{Calcite-saturated\ seawater}}$$

Assumes $\{CaCO_3\}$ = 1

The denominator is also K_{sp}, the "solubility product"

- Seawater: Changes in $[Ca^{2+}]$ are small $\rightarrow$ changes in Ω largely controlled by $\Delta[CO_3^{2-}]$

Saturation state of SW

$$\Omega = \frac{IAP}{K_{sp}}$$

- **IAP= Ion activity product**

- Depth at which $\Omega = 1$ is called the *saturation horizon*
- **Where** $\Omega > 1$ water is supersaturated with respect to the ion concentrations therefore $CaCO_3$ will precipitate
- **Where** $\Omega < 1$ water is undersaturated with respect to the ion concentrations therefore $CaCO_3$ will dissolve

- K_{sp} dependant on T, P and mineralogy

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Solubility of mixed carbonates

A variety of mixed carbonates, $Ca_{(1-x)}Mg_{(x)}CO_3$:

x = 0	Calcite or aragonite
x < 0.04	Low Mg-calcite
0.04 < x < 0.20	High Mg-calcite
x = 0.5	Dolomite
x = 1	Magnesite

Solubility of Mg-calcite increases with increased Mg content

$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$

$K = \{Ca^{2+}\} \{CO_3^{2-}\} / 1$

Higher K means $CaCO_3$ dissolves with higher activities of Ca^{2+} and CO_3^{2-}

∴ $CaCO_3$ is more soluble
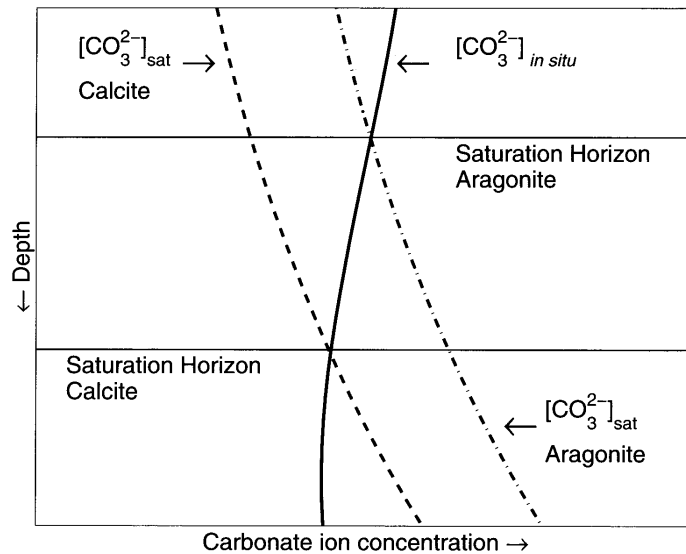

Increasing solubility

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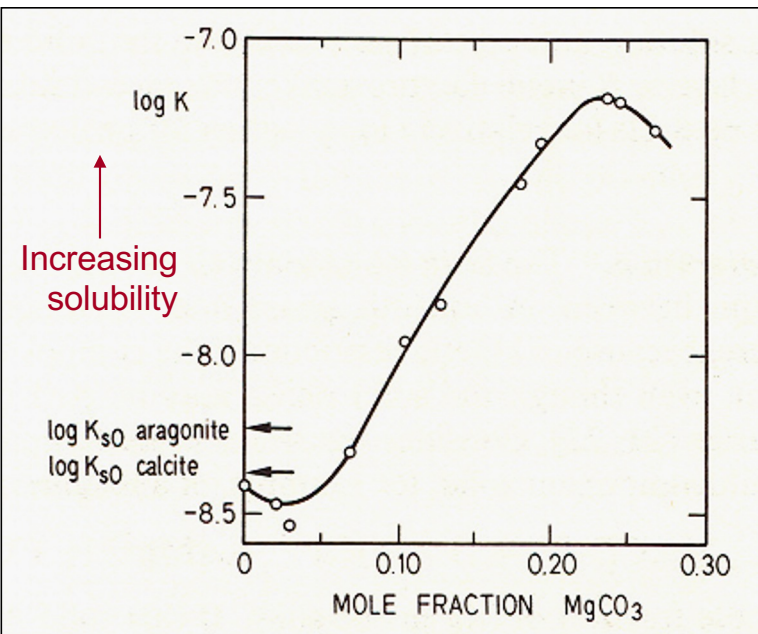
Figure 1.1.6: Illustration of the calcite and aragonite saturation horizon (SH) in the ocean (after Broecker and Peng, 1987). As pressure increases with depth, the solubility of calcite and aragonite increases as well ($[CO_3^{2-}]_{sat}$). The crossover between the *in situ* carbonate ion concentration (solid curve) and the saturation concentration for calcite (dashed curve) and aragonite (dot-dashed curve) determines the saturation horizon of the different mineral phases.
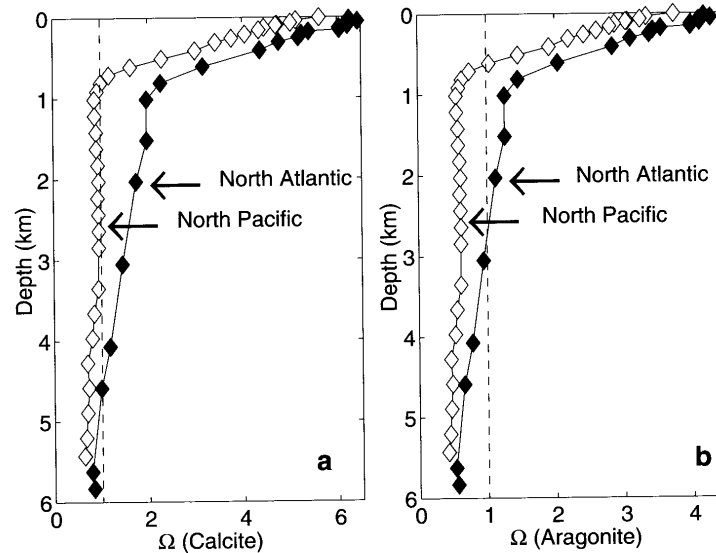
Figure 1.1.7: Saturation state of seawater, Ω, with respect to calcite (a) and aragonite (b) as a function of depth. Ω was calculated using Eq. (1.1.25) and DIC-TA profiles from the North Pacific and North Atlantic Ocean. The dashed vertical line separates areas of supersaturation ($\Omega > 1$) from undersaturation ($\Omega < 1$). Data are from WOCE Section P14N, Stn. 70 (F. Millero and Ch. Winn) and WOCE Section A05, Stn. 84, (F. Millero and S. Fiol), http://cdiac.esd.ornl.gov/oceans/CDIACmap.html.

Zeebe and Wolf-Gladrow (2001)

- The upper ocean is supersaturated wrt both calcite and aragonite

- Aragonite is more soluble than calcite in SW

- Saturation horizon is deeper in Atlantic than in Pacific

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Carbonate Compensation Depth / Lysocline

- ***Saturation Horizon*** is where "Ω" = 1

- ***Lysocline*** is where dissolution effects first appear in carbonate grains
  - Since degree of saturation decreases with depth, dissolution rates should increase with depth

- ***Carbonate Compensation Depth (CCD)*** is where the depositional rate of carbonate is equal to the dissolution rate (*i.e.*, no net accumulation of carbonates on the seafloor)

- The lysocline occurs above the CCD, but is at or below the saturation horizon because of
  - Kinetic effects
  - Protection by organic matter on particulates
  - Inhibitory effect of dissolved species like phosphate which have mid-depth maxima

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