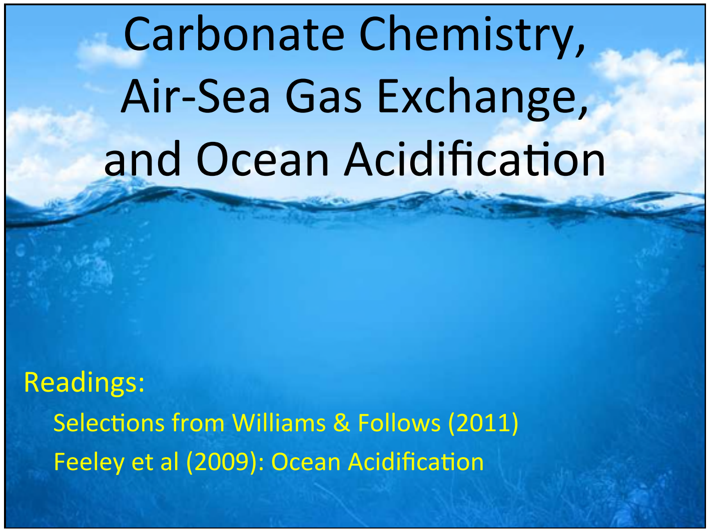


Carbonate Chemistry, Air-Sea Gas Exchange, and Ocean Acidification

Readings:

- Selections from Williams & Follows (2011)
- Feeley et al (2009): Ocean Acidification

Notation and Units

Square brackets [ ] mean the concentration of the stuff inside the bracket, dissolved in seawater. Example: $[CO_3^{2-}]$ or $[HCO_3^-]$

Units of concentration are typically either *moles per kg* or *equivalents per kg*

Equivalents are moles of solute times the charge on each ion of solute.
Example: $[CO_3^{2-}] = 10^{-3}$ mol kg^{-1} = 2x10^{-3} equiv kg^{-1}

Chemical Kinetics

For a chemical reaction in which reagents A and B react to form product C, we write:

$$A + B \xrightarrow{k} C$$

If k is the reaction rate constant, we write

$$\frac{dC}{dt} = k[A][B]$$

Chemical Equilibrium

Most chemical reactions in seawater "go both ways" so it's arbitrary which side of the reaction is "reagents" and which is "products"

$$A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C + D$$

Now we refer to k_f as the rate constant of the forward reaction and k_f as the rate constant of the backward reaction

$$\frac{dC}{dt} = k_f[A][B] \qquad \frac{dA}{dt} = k_b[C][D]$$

Chemical Equilibrium

$$A + B \underset{k_b}{\overset{k_f}{\rightleftarrows}} C + D$$

At equilibrium, the rates of the forward and backward reactions are equal, so that

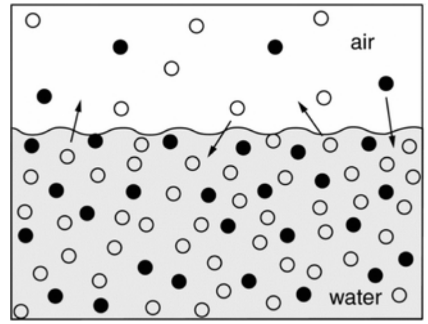
$$k_f[A][B] = k_b[C][D]$$

and we can write

$$\frac{[C][D]}{[A][B]} = \frac{k_f}{k_b} \equiv K_{eq}$$

K_{eq} is the ratio of products to reagents. It's called the equilibrium constant for the reaction

Solubility of CO_2 in Water



Williams_Fig. 6.2

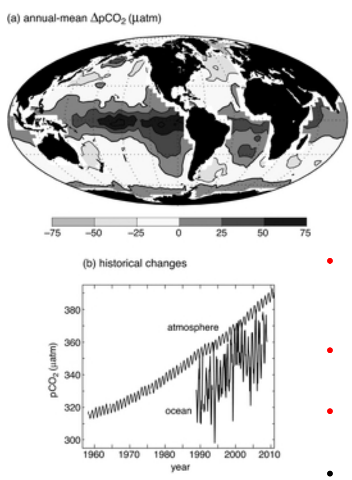
Henry's Law

$$\frac{[CO_2^*]}{pCO_2} = K_0.$$

(really just a definition for K_0)

When the rate at which molecules of gas dissolve into the water equals the rate at which they come out of solution into the air, the gas is in equilibrium with the aqueous (dissolved) form of the compound

We define the partial pressure of CO_2 in seawater as the partial pressure of CO_2 in air that would be in equilibrium with dissolved CO_2 at a given concentration



Williams_Fig. 6.1

Differences of pCO_2 (μatm) between the atmosphere and ocean

- Tropical oceans have high pCO_2, typically 50 μatm greater than atmosphere!
- High latitude oceans have low pCO_2
- Global ocean pCO_2 is less than atmosphere
- Both are increasing fast!

Jargon & Notation

- Carbonic Acid: H_2CO_3
- $[CO_2^*]$ = "Aqueous CO_2" + Carbonic Acid
  = $[CO_2(aq)] + [H_2CO_3]$
- Bicarbonate: HCO_3^-
  single-charged anion, dominant form of DIC
- Carbonate: CO_3^{2-}
  doubly-charged anion, much less abundant
- DIC = "Dissolved Inorganic Carbon"
  = ΣC = $[CO_2^*] + [HCO_3^-] + [CO_3^{2-}]$

More Jargon & Notation

- Cation: an ion in solution with a positive charge
- Anion: an ion in solution with a negative charge
- TA = Titration alkalinity = concentrations of all "proton acceptors" minus "proton donors" = concentration of weak acid anions minus weak acids minus $[H^+]$
- pH = $-\log_{10}[H^+]$, a measure of the acidity
- $pK_{eq} = -\log_{10}[K_{eq}]$

Carbonate Equilibria

Three equations (equilibria) in five unknowns

$$CO_2(gas) \longleftrightarrow CO_2(dissolved) \qquad [CO_2(aq)] = K_0 pCO_2 \qquad 6.1$$

$$[CO_2(aq)] + H_2O \longleftrightarrow [H^+] + [HCO_3^-] \qquad K_1 = [H^+][HCO_3^-]/[CO_2(aq)] \qquad 6.6$$

$$[HCO_3^-] \longleftrightarrow [H^+] + [CO_3^{2-}] \qquad K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \qquad 6.7$$

Add two more constraints

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [NO_3^-] + [OH^-] - [H^+] \pm \text{minor species}$$

("Titration Alkalinity")

$$B(OH)_3 + H_2O \leftrightarrow H^+ + B(OH)_4^-, \qquad K_b = [H^+][B(OH)_4^-]/[B(OH)_3]$$

(Boric acid dissociation)

$$\Sigma B = 1.179 \times 10^{-5} S \text{ mol/kg}$$

(S = Salinity)

Solving the Ocean Carbonate System

- Combine equations 6.1, 6.6, and 6.7 to write

$$DIC = \left(1 + \frac{K_1}{[H+]} + \frac{K_1 K_2}{[H+]^2}\right)[CO_2^*] \qquad (7)$$

$$CA = \left(\frac{K_1}{[H+]} + \frac{2K_1 K_2}{[H+]^2}\right)[CO_2^*] \qquad (8)$$

- Divide (7) by (8) to get quadratic for $[H^+]$

$$(CA)[H^+]^2 + K_1(CA - DIC)[H^+] + K_1 K_2 (CA - 2\,DIC) = 0 \qquad (9)$$

Ocean Carbonate System (cont'd)

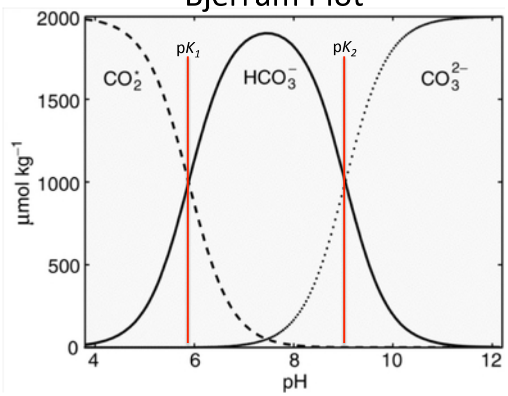
$$(CA)[H^+]^2 + K_1(CA - DIC)[H^+] + K_1 K_2 (CA - 2\,DIC) = 0 \qquad (9)$$

$$CA = TA - \frac{K_B}{K_B + [H+]}[Boron] \qquad (10)$$

- Start with first guess of [H+] (e.g., pH=8)
- Substitute into (10) to get CA then solve quadratic (9)
- Iterate (9) and (10) until pH converges

Speciation vs pH

"Bjerrum Plot"



Williams_Fig. 6.7

Partition of Marine DIC

- Using surface values for DIC, alkalinity, and salinity, we obtain pCO_2 = 278 μatm and pH = 8.18
- These are very close to preindustrial values
- Speciation:

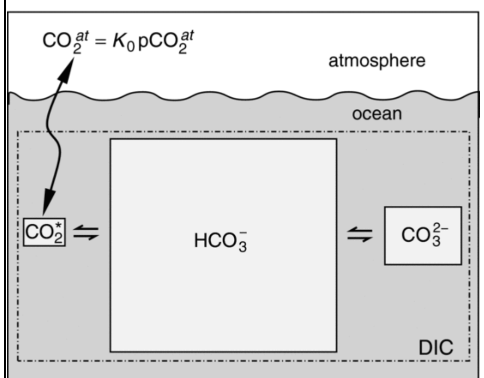
  $[CO_2^*]$ = 10 μMol kg^{-1}

  $[HCO_3]$ = 1769 μMol kg^{-1}

  $[CO_3]$ = 223 mMol kg^{-1}

By far most dissolved CO_2 is bicarbonate!

Buffering of Marine DIC



Williams_Fig. 2.20

Only a small fraction of DIC (CO_2^*) is in chemical equilibrium with atmospheric CO_2

Buffering of Marine DIC

divide eqn 6.6 by eqn 6.7

$$K_1/K_2 = [HCO_3^-]^2/([CO_2(aq)][CO_3^{2-}])$$

$$CO_2(aq) + CO_3^{2-} \longleftrightarrow 2HCO_3^-$$

- As CO_2 is added to the atmosphere, $[CO_2(aq)]$ increases in the ocean
- Most of it reacts with CO_3^{2-} to form additional HCO_3^-
- Absorption of atmospheric CO_2 by the oceans is limited by $[CO_3^{2-}]$, which is quite low
- Ratio of fractional change in pCO_2 per fractional change in DIC is called the *Revelle Factor : R ~ 10*
- This means doubling the amount of atmospheric CO2 would only increase DIC by about 10%

Partition of Anthropogenic CO_2

- Suppose we add CO_2 to the atmosphere by combustion of fossil fuel … what happens to dissolved carbon species in the oceans?
- Add 10% to atmospheric pCO_2 (and $[CO_2(aq)]$), and find new equilibria

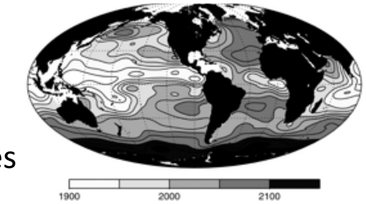
Species	Old	New	Change
pCO2 (ppm)	278	305.8	10.0%
CO2(aq)	10	11	10.0%
HCO3	1769	1800	1.8%
CO3	223	210	-5.8%
DIC	2002	2021	0.9%

10% increase in pCO_2 produces less than 1% increase in DIC!

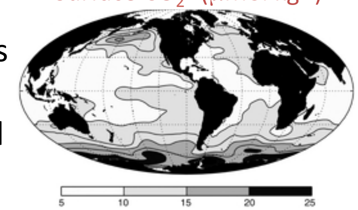
Global Variations

- Surface DIC varies by about 5%
- Atlantic vs Pacific
- Low DIC in tropics
- $CO_2^* << DIC$
- More CO_2^* in cold water

Surface DIC (μMol kg^{-1})



Surface CO_2^* (μMol kg^{-1})

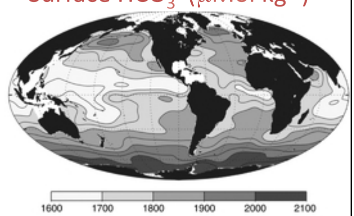


Williams_Fig. 6.4a,b

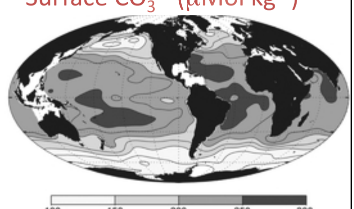
Global Variations

- HCO_3^- ~ DIC
- Variations in CO_3^{2-} by factor of 2
- Speciation much more variable than amount of DIC

Surface HCO_3^- (μMol kg^{-1})



Surface CO_3^{2-} (μMol kg^{-1})

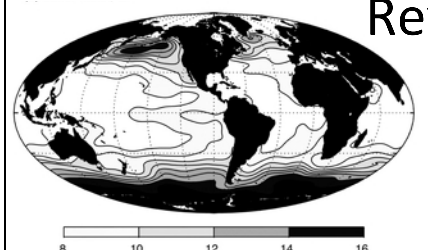


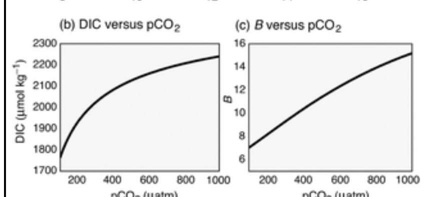
Williams_Fig. 6.4c,d

Revelle Buffer Factor

- fractional change in DIC per fractional change in pCO_2
- Logarithmic response of DIC to DCO_2

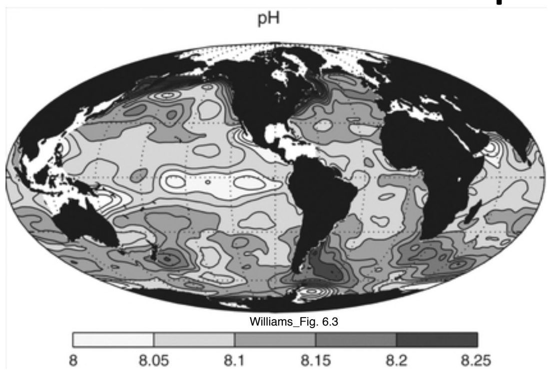
Buffer Factor





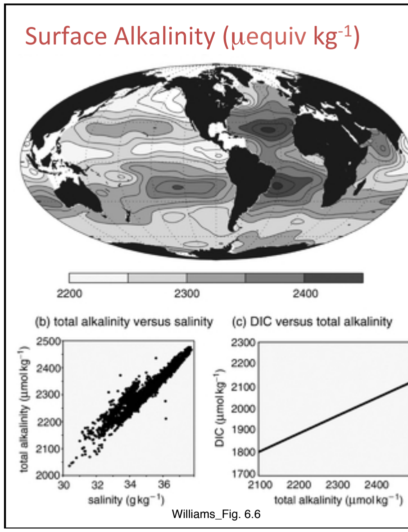
Williams_Fig. 6.12

Global Variations: pH



pH is low where water is warm

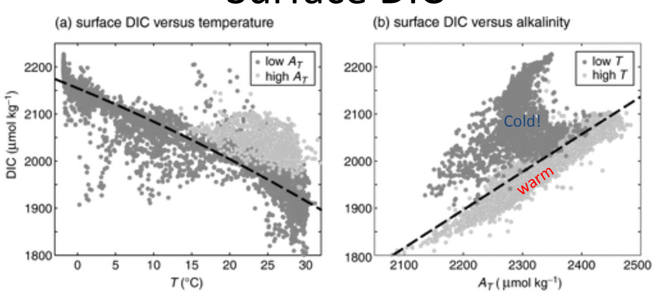
Global Variations



- Alkalinity varies with salinity – dilution!
- Explains most of surface DIC variations too

Global Variations:

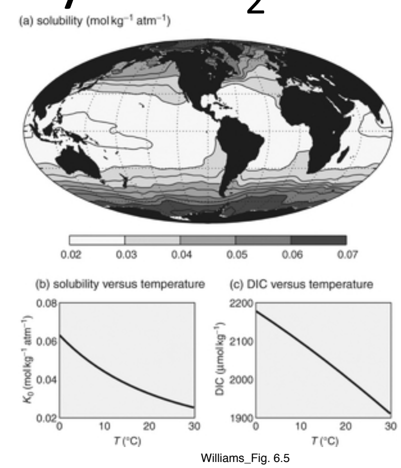
Surface DIC



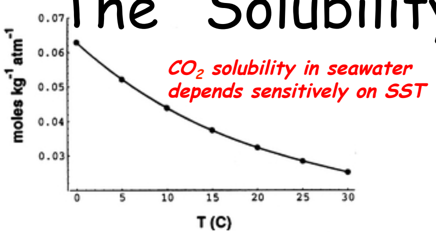
- DIC decreases with temperature
- Warm ocean DIC ~ Alk, not so in cold ocean

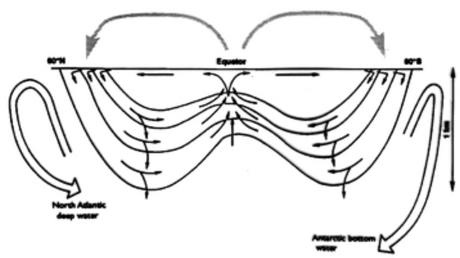
Solubility of CO_2

- Henry's Law coefficient
- Varies by a factor of 2 with temperature!
- Accounts for most of variance of surface DIC



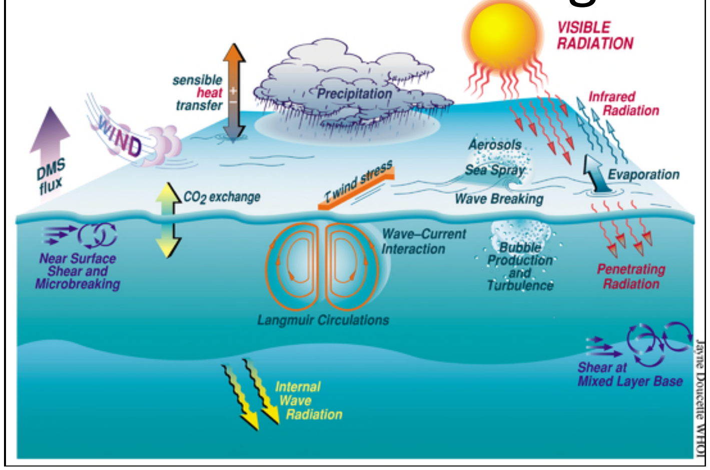
The "Solubility Pump"





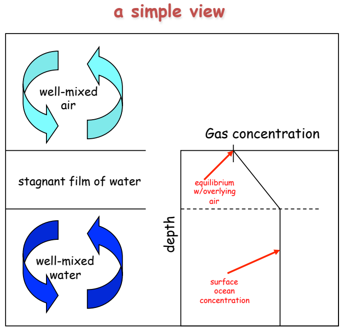
- CO_2 is highly soluble in cold high-lat waters
- Transported to deep ocean by convection and isopycnal mixing
- Dynamically-driven equatorial upwelling brings high-CO_2 water to surface
- Atmospheric transport closes the loop

Air-Sea Gas Exchange



Air-Sea Gas Exchange

a simple view



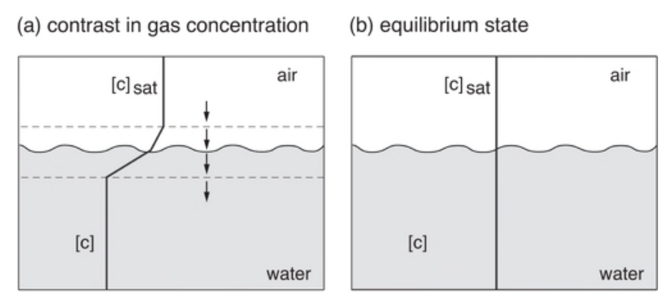
After Broecker and Peng (1982)
Tracers in the Sea

- Two well-mixed reservoirs, separated by a thin film of "stagnant" water at the surface
- Air-sea gas flux depends on:
  - Thickness of film
  - Diffusivity of gas molecules within film
  - Magnitude of disequilibrium

$$F = D\frac{[gas]_{top} - [gas]_{bottom}}{z_{film}}$$

- Equivalently, we can describe this process in terms of "pistons" of gas moving upward and downward, with net gas flux being the difference between the two fluxes

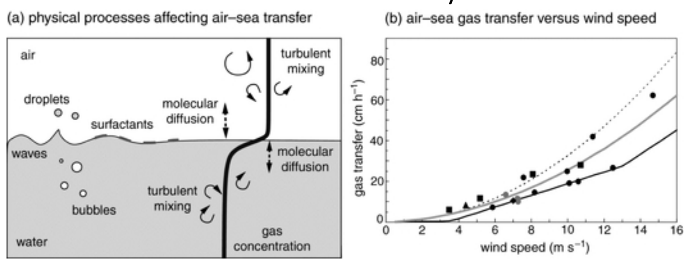
Air-Sea Gas Exchange



Williams_Fig. 6.13

Gas Exchange Coefficient

The "Piston Velocity"



Williams_Fig. 6.14

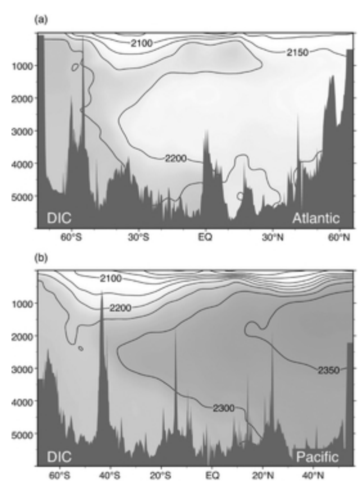
- Very strong dependence (quadratic? cubic?) on windspeed
- Turbulence disrupts stagnant film, must be "regrown" each time
- "Regime-shifts" at higher wind speeds

Atmospheric CO_2 in Equilibrium with the Deep Ocean

- Mix deep seawater with surface and warm it to 16° C (global mean SST)
- pCO_2 would be 938 ppm!
  (observed is only 400 after 200 years of industry!)
- pH would be 7.73
  (observed is about 8.1)
- How is this possible?

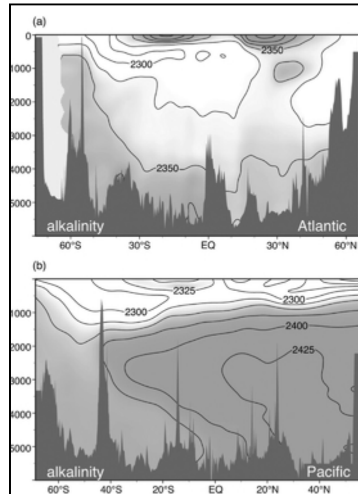
Deep Ocean

- DIC strongly depleted at surface, enhanced at depth
- Enhancement much stronger in Pacific than Atlantic



Williams_Fig. 6.9

Deep Alkalinity

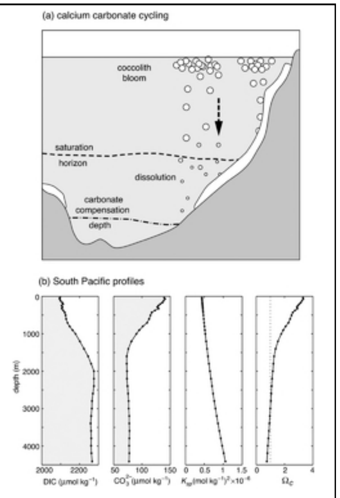


Williams_Fig. 6.10

- Biologically-mediated transfer of alkalinity from surface to deep in subtropical Atlantic
- Progressive increase at depth from Atlantic to Pacific

Calcium Carbonate ($CaCO_3$) Pump

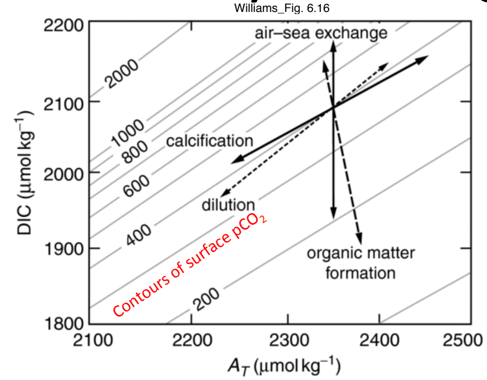
- Coccoliths fix HCO_3^-, make solid $CaCO_3$ shells, sink fast
- Solubility of CaCO3 increases with pressure



Williams_Fig. 6.11

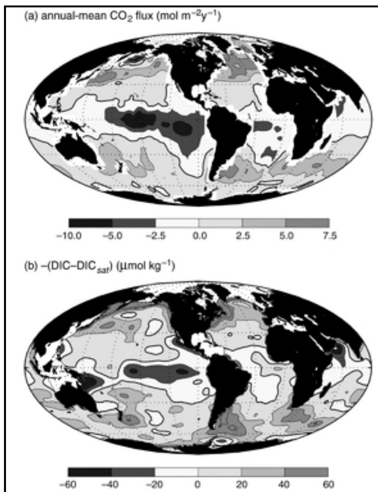
Chemistry & Biology

Williams_Fig. 6.16



- Air-sea gas exchange affects DIC but not alk
- Organic matter and calcification almost orthogonal

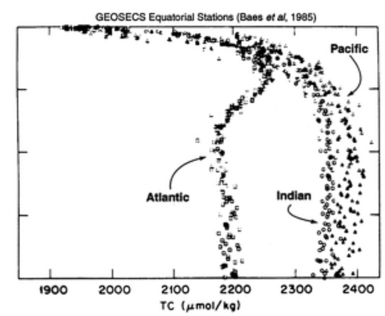
Air-Sea CO_2 Flux



Williams_Fig. 6.15

- Uptake by cold water over large regions
- Emission from tropics, especially from cold upwelling region in Equatorial Pacific

The Biological Pump



- Photosynthesis depletes DIC (and nutrients) in the photic zone
- Decomposition/mineralization deposits DIC and nutrients in deep ocean