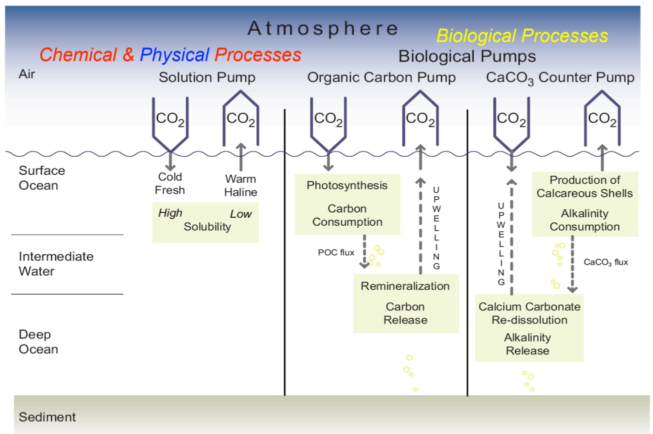
Now that we have looked at the physical processes involved with the exchange of CO_2 between the atmosphere and the ocean let's turn to the chemical processes



IPCC 2007 Fig. 7.10

Chemical Processes Influencing Air-Sea Exchange of CO_2

1. Physical Processes
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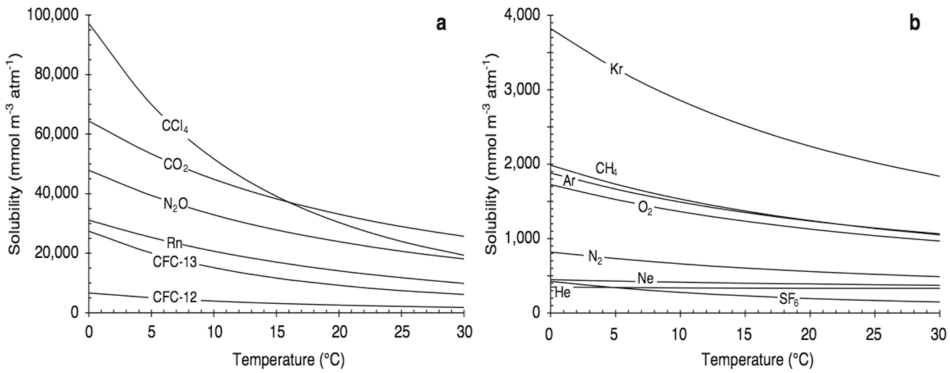
   - Ocean circulation
2. Chemical Processes
   - CO_2 solubility = f (temperature, salinity) ["The Solubility Pump"]
   - Carbonate chemical equilibrium
3. Biological Processes ["The Biological Pump"]
   - Photosynthesis & respiration
   - Calcium carbonate production

Solubility of Gases as a Function of Temperature



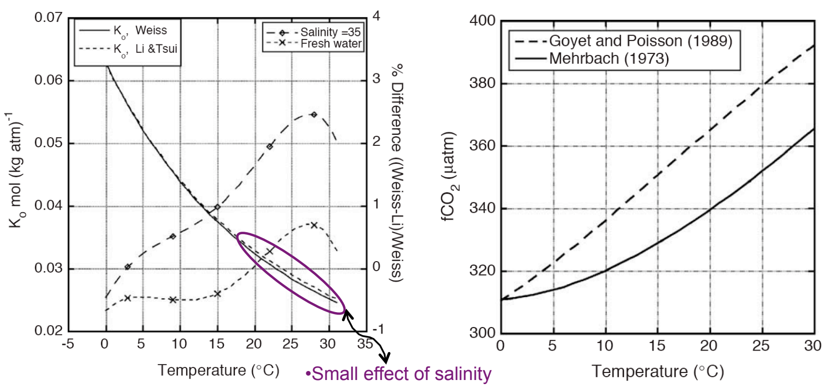
• Solubility of all gases *decreases with increasing T*

• Differences result from molecular interactions between gas & water

Sarmiento and Gruber (2006)

CO_2 Solubility is a Function of Temperature

• Demonstrations of the temperature dependence

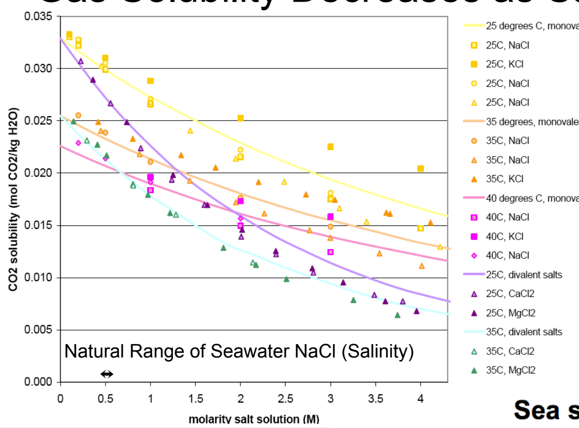


• Solubility decreases as T increases

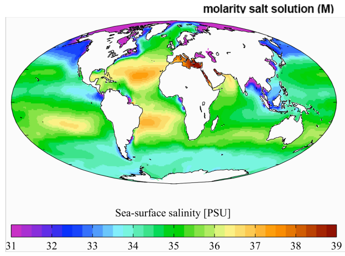
• pCO2 increases as T increases (implying the liquid can hold less of the gas at higher T, resulting in higher gas pressure)

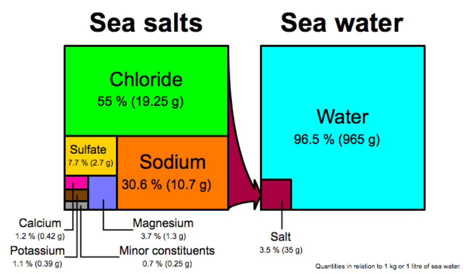
McGillis & Wanninkhof (2006) Aqueous CO_2 gradients for air-sea flux estimates, Mar. Chem. Vol. 98: 100-108

Gas Solubility Decreases as Salinity Increases

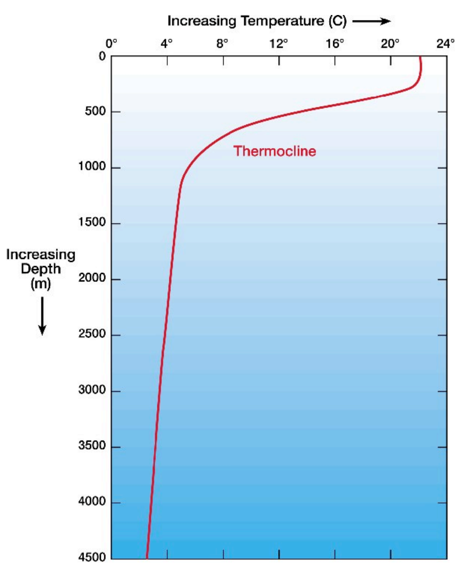


Hangx (2005) CATO Workpackage WP 4.1, Fig. 6c
http://upload.wikimedia.org/wikipedia/commons/2/2c/Sea_salt-e-dp_h
http://upload.wikimedia.org/wikipedia/commons/3/3e/Wiki_plot_04.p





The Carbon "Solubility Pump"



- CO_2 is more soluble in cold waters than in warm waters (the thermal pump), & more soluble in fresher waters than saltier waters (the salt pump).
- If alkalinity (see following discussion) were uniform throughout the ocean & if both cold & warm surface waters equilibrated their p_{CO2} with the atmosphere, then cold surface waters would have a higher dissolved CO_2 content than warm surface waters.
- As these cold surface waters circulate into the deep interior of the ocean, deep waters will have more CO_2 than warm surface waters.

Chemical Processes Influencing Air-Sea Exchange of CO_2

1. Physical Processes
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3. Biological Processes ["The Biological Pump"]
   - Photosynthesis & respiration
   - Calcium carbonate production

CO_2 Uptake by the Ocean: the Carbonate System

- The ocean can take up CO_2 from the atmosphere in amounts that far exceed what would be expected based on solubility alone
- The extra absorbing power is caused by the carbonate buffer system

•CO_2 gas dissolves in seawater to become aqueous CO_2

$$CO_2(g) \leftrightarrow CO_2(aq)$$

• *Henry's Law* describes the equilibrium between $CO_2(g)$ & $CO_2(aq)$

$$K_H = [CO_2(aq)]/pCO_2 \qquad \text{(a function of T \& S)}$$

• $CO_2(aq)$ combines with water to produce carbonic acid

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

• At the pH of surface seawater (~8.2), carbonic acid rapidly dissociates into a hydrogen ion and a bicarbonate ion

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

• The hydrogen ion then reacts with a carbonate ion to produce a second bicarbonate ion

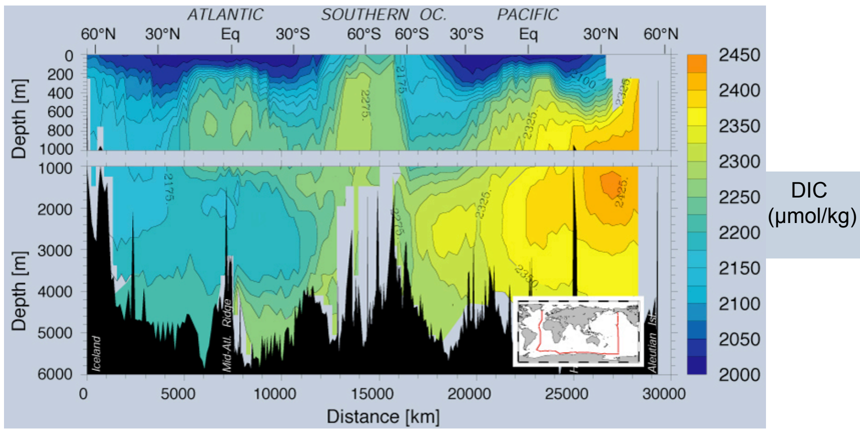
$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$$

CO_2 Uptake by the Ocean: DIC

• Since only ~1% of $CO_2(aq)$ exists as H_2CO_3 it is usually left out of the sum of dissolved inorganic carbon (DIC) species

$$DIC = CO_2(aq) + HCO_3^- + CO_3^{2-}$$

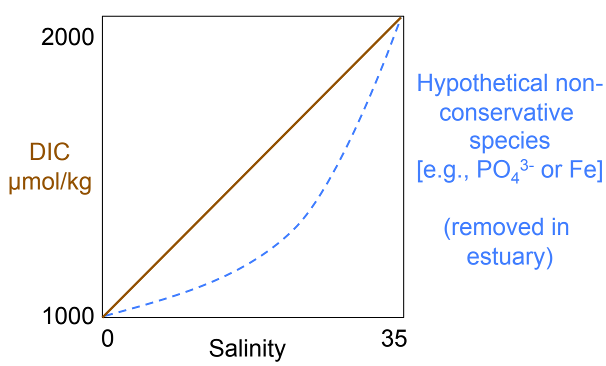
• The molar ratio of these three species in seawater is about **1 : 100 : 10**



CO_2 Uptake by the Ocean: Conservative Quantities

- DIC is a **conservative** quantity in seawater, meaning
  - Its concentration can only be changed by mixing & advection
  - It can be mixed linearly
  - Non-conservative properties (e.g., O_2 & PO_4^{3-}) are altered by biological & chemical processes

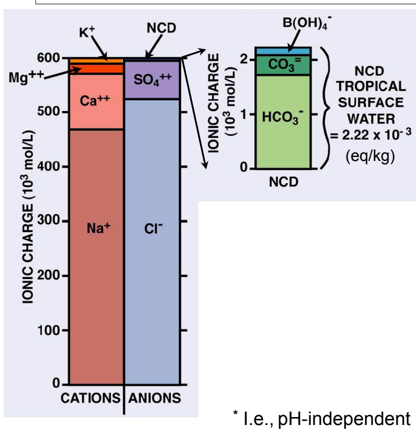
• An example would be mixing in an estuary, where the DIC concentration changes linearly from the low value in rivers to the high value in seawater:



CO_2 Uptake by the Ocean: Alkalinity

▪ Another conservative quantity in seawater that is important for understanding the exchange of CO_2 between the atmosphere & the ocean is **Alkalinity**, the best definition of which I have ever read is:

The negative charge deficit in seawater that is compensated by ions which can exist in more than one charge state. *(Broecker, 2005)*



• Seawater must be electrically neutral

• Though comprised primarily of ions with a fixed electrical charge*, such as the cations Na^+, K^+, Mg^{2+}, Ca^{2+}, and the anions Cl^- & SO_4^{2-}, there is a *slight* deficit of negative charge, the alkalinity

• That deficit is made up by protonating & deprotonating acids & bases until charge balance is achieved

* I.e., pH-independent species; strong acids & bases

Broecker (2005) *The Role of the Ocean in Climate Yesterday, Today and Tomorrow*, Eldigio Press, NY. Emerson & Hedges (2007) Ch.4. *Updated 2/9/09*

CO_2 Uptake by the Ocean: Alkalinity (cont'd.)

• The negative charge deficit is compensated by adding & removing protons (H^+) to ions that can exist in more than one charge state (pH-dependent species; weak acids & bases). Note: $pH = -log[H^+]$

• Important for ocean CO_2 uptake are those acids & bases that can exist in more than one charge state in the pH range of seawater, ~7-9.

• So a more precise definition of alkalinity than Broecker's would be:

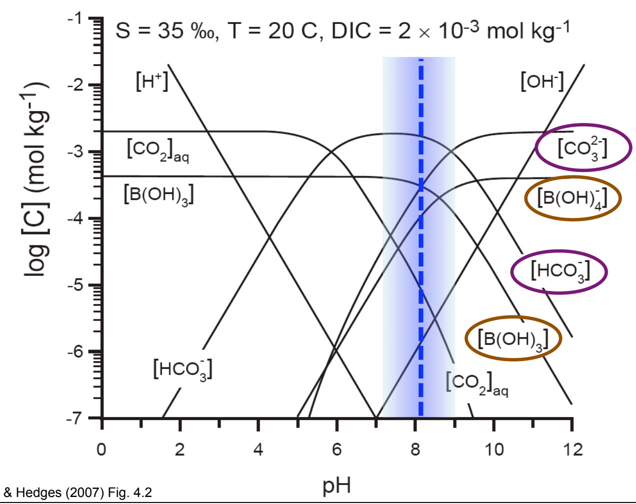
"The negative charge deficit that is compensated by acids & bases that can exist in more than one charge state in the pH range of seawater."

• Because of their high concentration in seawater and their tendency to protonate / deprotonate at pH 7-9, HCO_3^-, CO_3^{2-}, $B(OH)_3$, & $B(OH)_4^-$ are by far the most abundant such species

Adapted from Broecker (2005), Emerson & Hedges (2007) Chap. 4.

CO_2 Uptake by the Ocean: Alkalinity (cont'd)

• The high concentrations of carbonate & borate ions make HCO_3^-, CO_3^{2-}, $B(OH)_3$, & $B(OH)_4^-$ the most important contributors to alkalinity in seawater since its pH is ~8.2



Adapted from Emerson & Hedges (2007) Fig. 4.2

CO_2 Uptake by the Ocean: Alkalinity (cont'd.)

PROPERTIES	TROPICAL SURFACE	DEEP PACIFIC	UNITS
WATER DEPTH	0	4000	meters
TEMPERATURE	25.0	1.5	°C
SALINITY	35.0	34.7	g/kg
p_{CO_2}	280	510*	10^{-6} atm
NCD	2216.0	2450.0	10^{-6} mol/kg
ΣCO_2	1858.0	2340.0	10^{-6} mol/kg
$(CO_2)_{aq}$	7.9	29.9	10^{-6} mol/kg
(HCO_3^-)	1601.5	2215.0	10^{-6} mol/kg
$(CO_3^=)$	248.5	95.0	10^{-6} mol/kg
ΣB	410.6	407.1	10^{-6} mol/kg
$B(OH)_3^0$	302.0	362.6	10^{-6} mol/kg
$B(OH)_4^-$	108.6	44.5	10^{-6} mol/kg
(OH^-)	8.8	0.4	10^{-6} mol/kg
pH	8.15	7.77	

*AT SEA SURFACE PRESSURE

Borate contribution to Alkalinity:

108.6 / 2216 *100 = 4.9%

• Thus in seawater:

NCD = Alkalinity = HCO_3^- + $2*CO_3^{2-}$ + $B(OH)_4^-$

• More precise definitions of alkalinity exist that include more species

• They include ions that contribute < 1% to alkalinity b/c they become protonated / deprotonated at:

  ○ seawater pH, but have low & variable *concentrations* (e.g., $H_3SiO_4^-$, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-})

  ○ pH levels << 8 (e.g., Cl^-, SO_4^{2-}, F^-)

• In practice, even borate is left out since it is < 5% of alkalinity

• The term *Carbonate Alkalinity* is then used as a simplifying approximation:

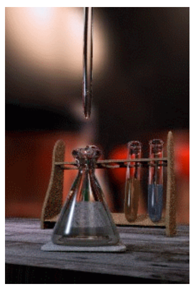
Carbonate Alkalinity = HCO_3^- + $2*CO_3^{2-}$

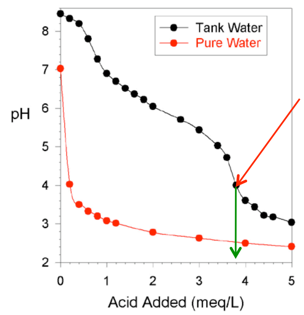
Adapted from Broecker (2005) and Emerson & Hedges (2007) Chap. 4

How is Alkalinity Determined?

- Alkalinity is measured by titration: strong acid is added to seawater until all proton acceptors have been protonated
- “The precise definition of alkalinity of seawater is based on the method by which it is determined and the species that exchange protons during the titration.” *(Emerson & Hedges (2007) p. 4.10)*
- Operationally carbonate alkalinity is defined as the # of equivalents of acid required to bring a sample to the CO_2 endpoint, or equivalence point—I.e., when # moles acid added = moles HCO_3^- + 2*moles of CO_3^{2-}

- Acid dropped from a burette into seawater until indicator changes color permanently--the endpoint.

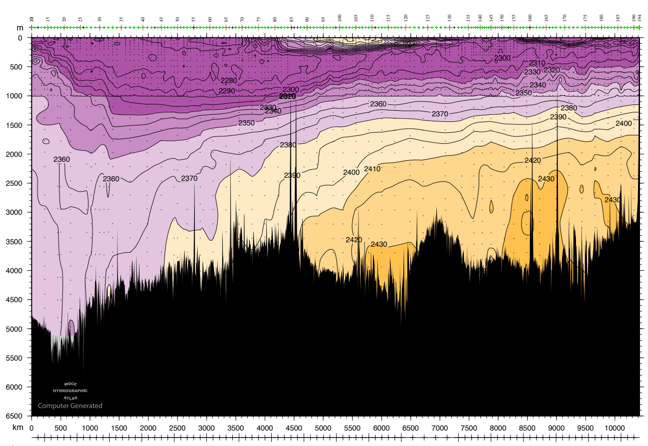




- At this equivalence point all the CO_3^{2-} & HCO_3^- have been converted to CO_2
- The carbonate alkalinity is 3.8 meq/L

Alkalinity in the Ocean

- Alkalinity is greater in the deep ocean than in the surface b/c Ca^{2+} ions are incorporated into $CaCO_3$* (removing alkalinity & NCD) in surface waters & released by dissolution of $CaCO_3$ in deep waters (adding alkalinity & NCD)



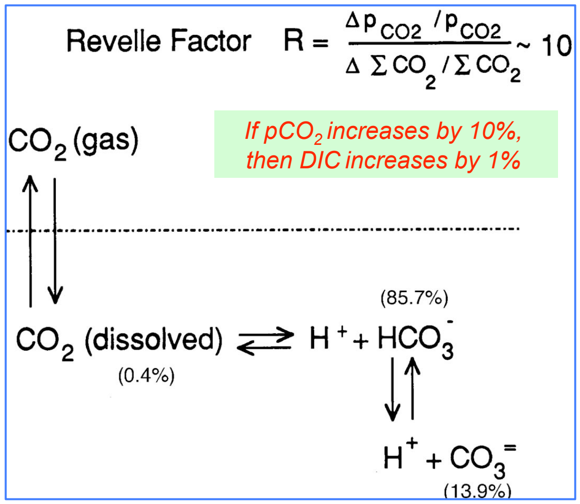
Alkalinity
(uMol or μeq/kg)

WOCE Pacific Ocean Line 18 along 105°W

Adapted from Broecker (2005). WOCE Pacific Ocean Atlas.

*A biological process we will discuss shortly

CO_2 Uptake by the Ocean: the Revelle Factor



- The amount of CO_2 the ocean can absorb from the atmosphere beyond the amount of CO_2 gas that can be dissolved in it is referred to as its buffering capacity
- The buffering capacity of the ocean is quantified by the Revelle Factor
- The RF (*aka* buffer factor) relates the fractional change in atmospheric pCO_2 to a fractional change in DIC (after re-equilibration)
- RF is directly proportional to the ratio of DIC : Alkalinity *(see next page…)*

Figure adapted from Ed Boyle 12.842 Lecture Notes (2008)

Buffering Capacity of the Ocean

- Because Carbonate Alkalinity = HCO_3^- + $2*CO_3^{2-}$ it is clear that the greater the alkalinity of a solution the greater its potential for neutralizing acid (H^+), such as CO_2 :

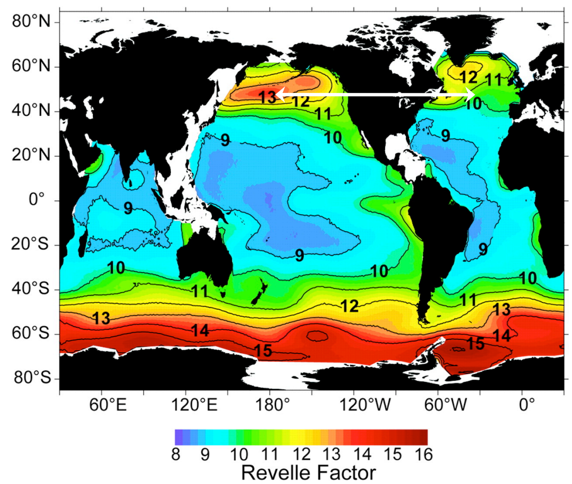
$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$$

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

- The more CO_3^{2-}, or Alkalinity, contained in the water, the more CO_2 (acid) it will be able to absorb
- But the total amount of DIC is also a factor, because with low concentrations of DIC there cannot be large amounts of CO_3^{2-} to neutralize CO_2 at any pH
- That is why the Revelle factor is proportional to (DIC / Alkalinity). Low values of either quantity imply greater capacity to buffer added CO_2.

Buffering Capacity of the Ocean: The Revelle Factor

1994 distribution of the Revelle factor averaged over upper 50m of water.



• Lower RF = Greater buffering capacity

• Low RFs occur in warm tropical-subtropical waters; high RFs in cold high latitude waters

• The capacity for seawater to take up CO_2 from the atmosphere is inversely proportional to the RF

• Hence, the lower the RF, the higher the oceanic equilibrium concentration of CO_2 for a given atmospheric CO_2 increase

• North Pacific surface waters have a higher RF at comparable latitudes & consequently lower anthropogenic CO_2 concentrations

• This difference results from North Pacific alkalinity values about 100 mol/kg lower than in the North Atlantic

• Current RFs are about one unit higher than in the preindustrial ocean.

Sabine et al. (2004) *Science* Vol. 305: 367-371

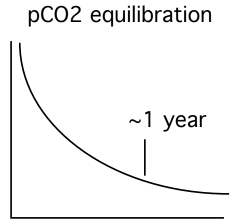
Equilibration Time for Atmospheric Gases in Ocean Mixed Layer

Simple Gas Exchange
(e.g. O2, Ar)

• For mixed layer depth of 100m & piston velocity of 2000 m/yr

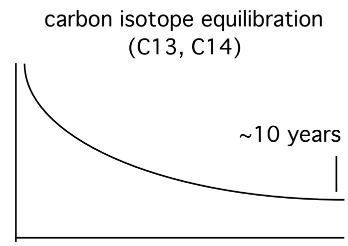
• Equilibration time =100m/2000m yr^{-1} =0.05yr = 18d

Equilibration Time for Atmospheric Gases in the Ocean Mixed Layer



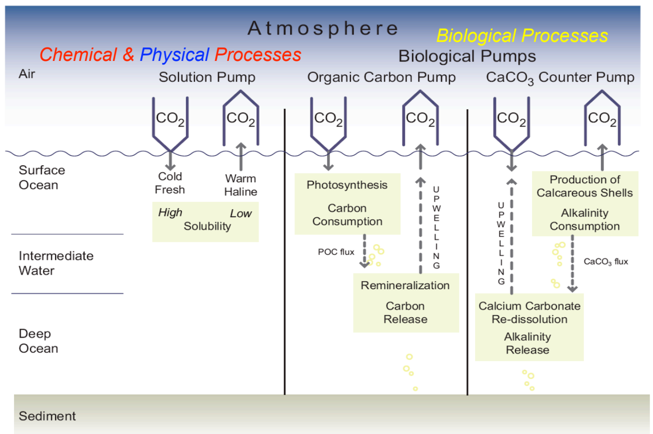
- Change in pCO_2 causes equal change in CO_2(aq)
- Revelle factor: fractional change in pCO_2 is ~10x greater then DIC change
- Since CO_2(aq)=0.5% of DIC it takes 10/0.5, or 20x longer to equilibrate DIC then to equilibrate CO_2(aq)
- Equilibration time $=(100m / 2000m\ yr^{-1})*20=1yr$

Equilibration Time for Atmospheric Gases in the Ocean Mixed Layer



- Total DIC must equilibrate with atm. CO_2
- $1m^2$ of upper 100m of ocean contains: 10^5kg water * $(2000*10^{-6}$mol C/kg water) = 200 moles C
- CO_2 gas exchange rate = 20 mol/m^2/yr (see prev. lec.)
- Equilibration time = (200 mol) / (20 mol/m^2/yr) = 10yr

Now that we have looked at the physical & chemical processes involved with the exchange of CO_2 between the atmosphere & the ocean let's turn to the biological processes



IPCC 2007 Fig. 7.10

Biological Processes Influencing Air-Sea Exchange of CO_2

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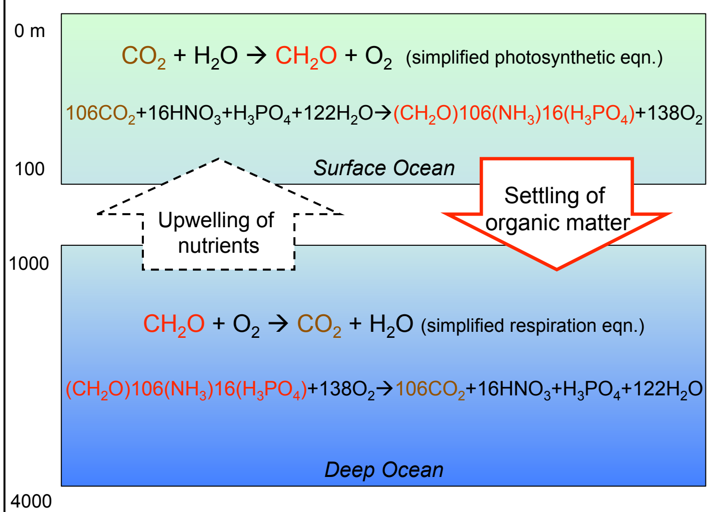
The "Biological Carbon Pump"

• *The biologically mediated transfer of CO_2 & nutrients from the surface to the deep ocean*



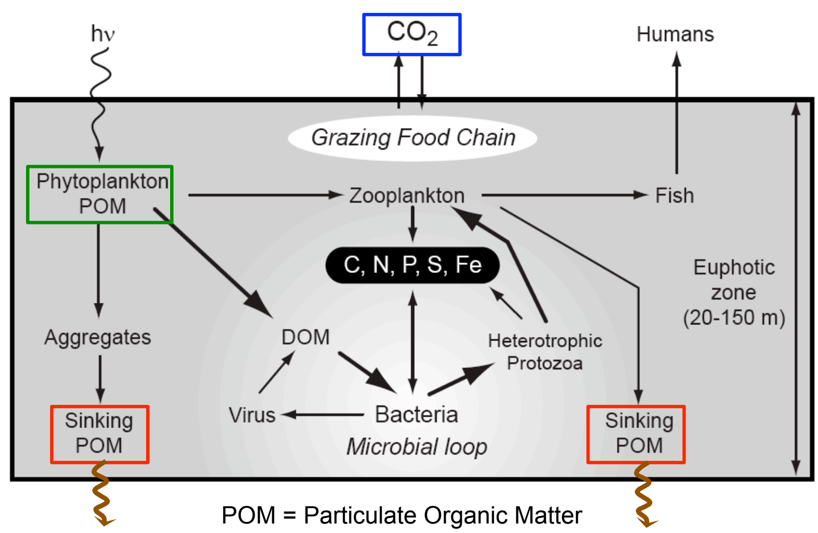
• The elemental composition of phytoplankton in the ocean is amazingly constant, as 1st noted by A.C. Redfield*

• This "Redfield ratio" characterizes both phytoplankton & seawater!

• Grazing of phytoplankton by zooplankton produces fecal pellets that sink & transport algal biomass to the deep sea where it is "remineralized" back to inorganic nutrients

* Redfield, Ketchum & Richards (1963) "The influence of organisms on the composition of sea-water." In: M.N. Hill (Ed.), *The Sea 2:* 26-77, Interscience, NY.

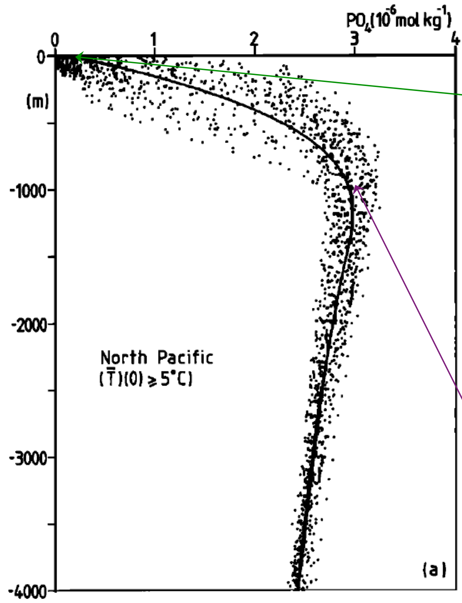
A More Realistic View of Biological Processes in the Surface Ocean "Box"



POM = Particulate Organic Matter
DOM = Dissolved Organic Matter

Emerson & Hedges (2007) *Chem. Oceanogr.*, Fig. 6.5

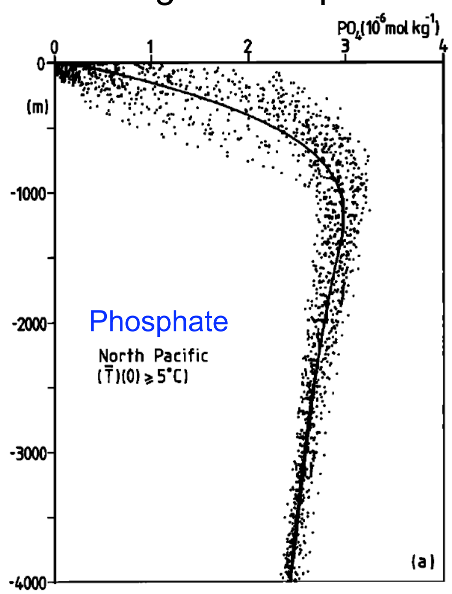
Biological Pump Effect on Nutrient Distributions

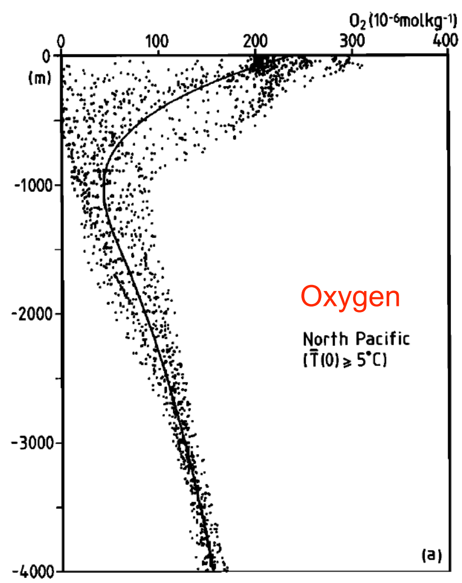


- Nutrients such as N & P stripped out of surface water by photosynthesis
  - Consuming CO_2(aq)
  - Producing O_2
- Transported to deep sea by sinking fecal pellets
- Released back into deep water during decomposition by bacteria (remineralization)
  - Consuming O_2

Shaffer (1996) *J. Geophys. Res.* Vol. 101(C2): 3723-3745.

Biological Pump Effect on Nutrient Distributions

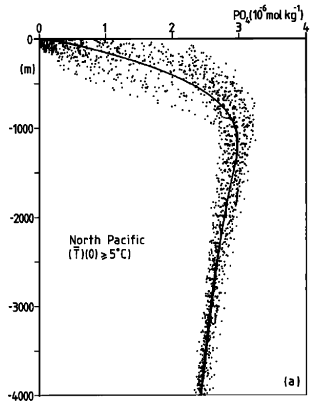




- Note that O_2 has mirror-image profile of PO_4^{3-}

Shaffer (1996) *J. Geophys. Res.* Vol. 101(C2): 3723-3745. GEOSECS data.

Combined Effect of the Biological Pump & Ocean Circulation



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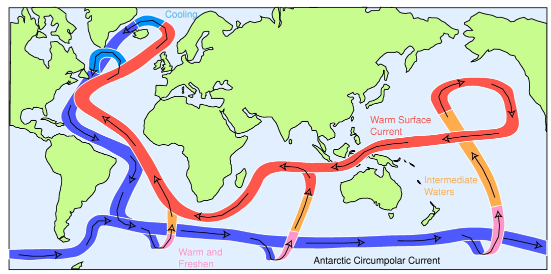

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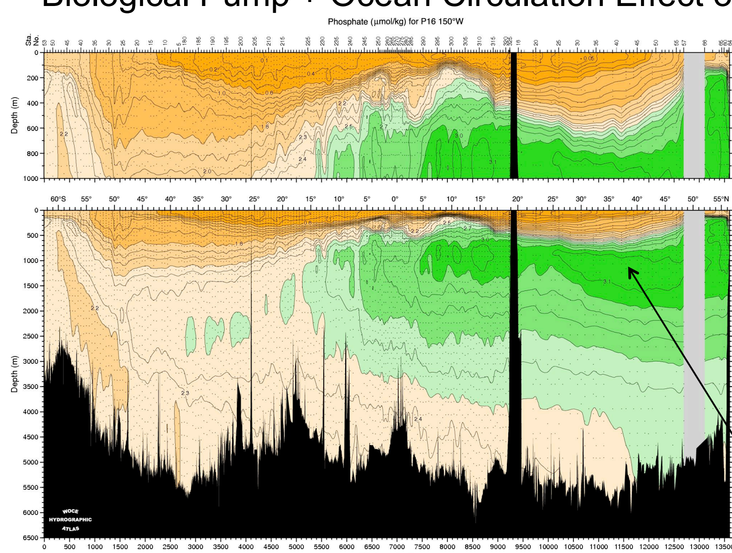
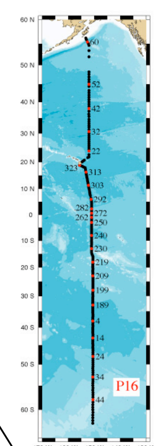
PO4: Shaffer (1996) *J. Geophys. Res.* Vol. 101(C2): 3723-3745. MOC: John Marshall, MIT.

Biological Pump + Ocean Circulation Effect on Phosphate

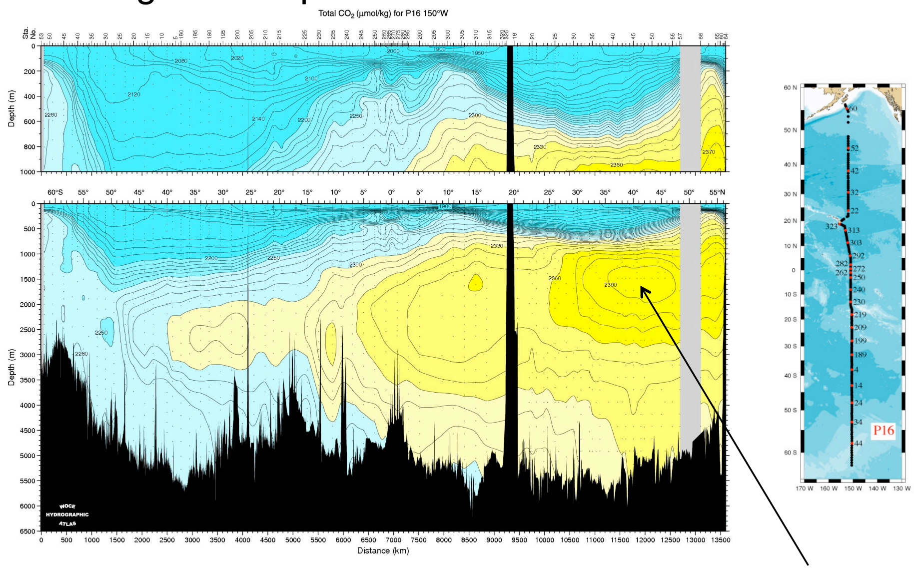




• Oldest water in ocean accumulates most remineralized PO_4^{3-}, the ultimate source of which was photosynthesis in the global surface ocean.

WOCE (2007) Atlas Volume 2: Pacific Ocean

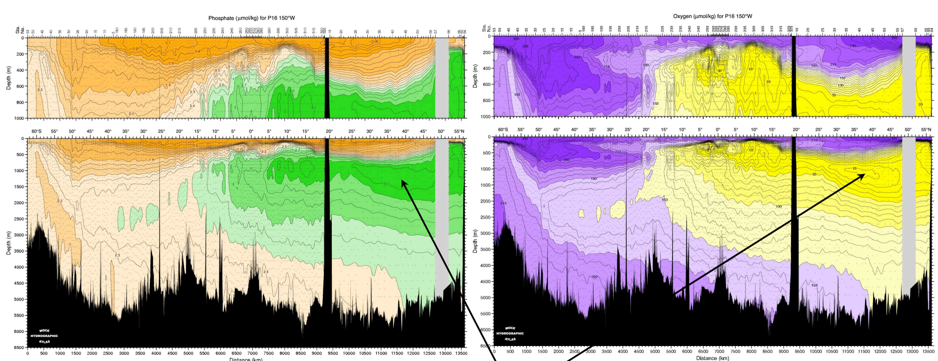
Biological Pump + Ocean Circulation Effect on DIC



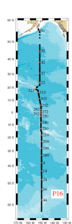
- Oldest water in ocean accumulates most respired CO_2, the ultimate source of which was photosynthesis in the global surface ocean.

WOCE (2007) Atlas Volume 2: Pacific Ocean

Biological Pump + Ocean Circulation Effect on Oxygen

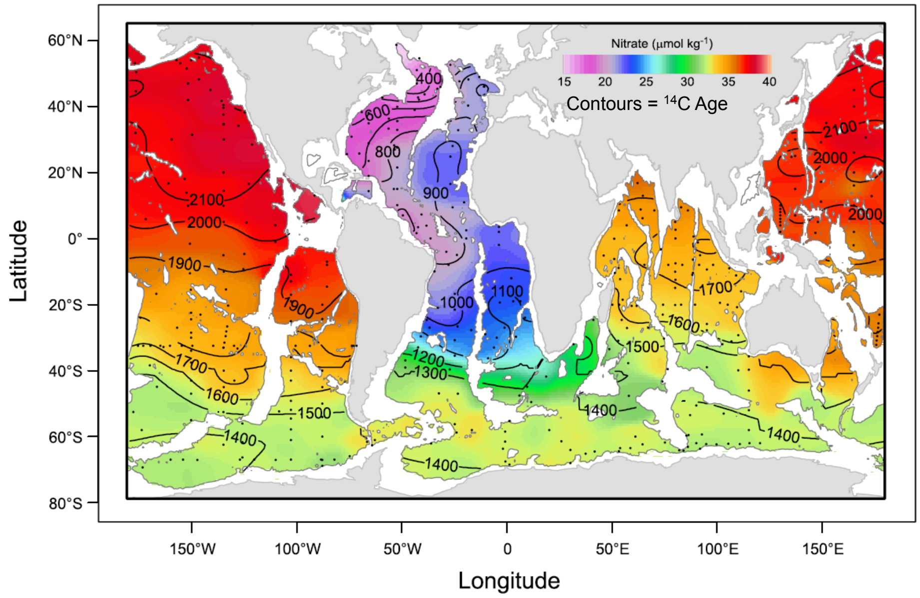


- Oldest water in ocean is most impoverished in O_2 because 138 moles of O_2 are *consumed* per mole of PO_4^{3-} liberated during organic matter decomposition
- From the Redfield ratio of C:N:P:O_2 of 106:16:1:-138



WOCE (2007) Atlas Volume 2: Pacific Ocean

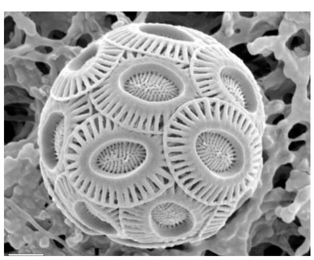
Global Nitrate & Water Age at 3000 m



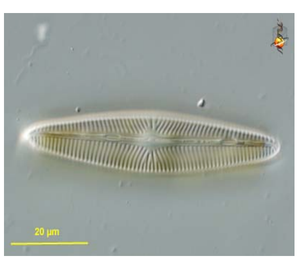
✧ *The best visual depiction of the combined effect of the biological pump & ocean circulation I have seen!*

From Key et al. (2005) in Emerson & Hedges (2007), Fig. 6.16.

Hard vs. Soft Parts



Coccolithophorid ($CaCO_3$)

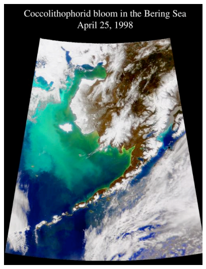


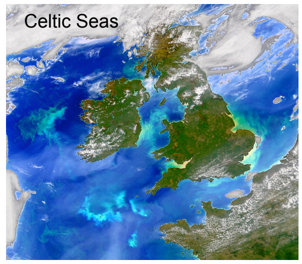
Diatom (SiO_2)

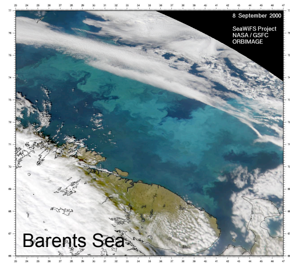
- Some organisms precipitate inorganic shells ("hard parts") out of calcium carbonate & silica, the overwhelming majority being coccolithophorids ($CaCO_3$) & diatoms (SiO_2)
- On average 22 moles of C as $CaCO_3$ are precipitated for every 106 moles of C converted into phytoplankton biomass ("soft parts")
- Results in a Redfield Ratio of C_{org}:N:P:C_{CaCO3}:O_2 = 106:16:1:22:-138
- Production of $CaCO_3$ is important in air-sea CO_2 exchange because it removes carbon *and* **alkalinity** from surface water & transfers it to deep sea

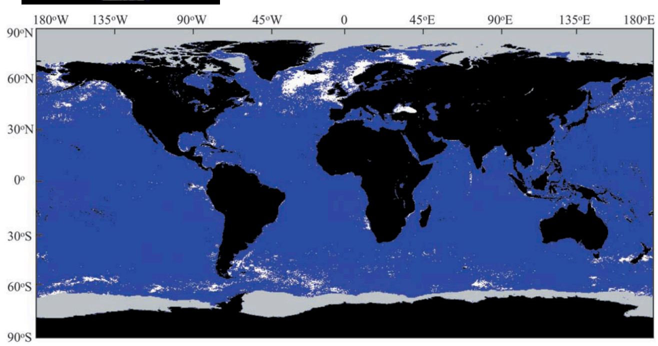
Globally the Production of $CaCO_3$ is 0.6 Gt C/yr

(~3% of global marine C fixation)









- SeaWiFS images & Composite
- 50% reduction in coccolith blooms expected in N. Atl (their largest habitat) by 2100 A.D. owing to ocean acidification

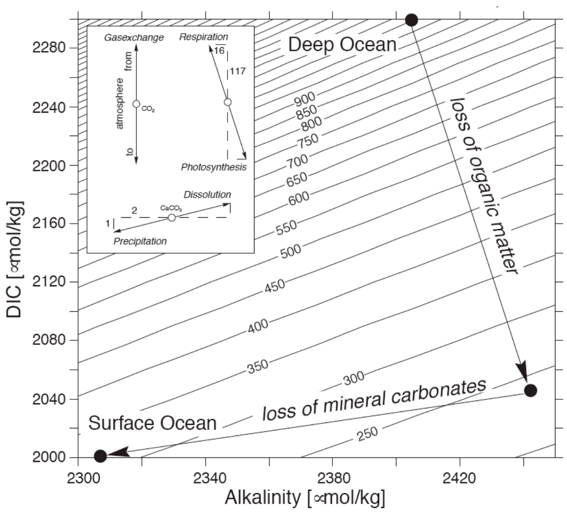
Iglesias-Rodriguez et al. (2002) *Glob. Biogeochem. Cycl.* Vol. 16(4): 1100, doi: 10.1029/GB001454

Coccolithophorids & Air-Sea CO_2 Exchange (c.)

- Coccolithophorids alter the $C_{organic}$:$C_{carbonate}$ or "rain ratio" & increase surface pCO_2 during calcification, *producing one molecule of CO_2 for each molecule of $CaCO_3$ fixed*.
- Globally, the rain ratio from the surface ocean is ~ 4:1
- This ratio is largely controlled by the dominant taxon fixing carbon such that a shift in the phytoplankton community structure from calcifiers to silicifiers would affect the capacity of the biological pump
- For example,during a bloom of coccolithophorids, photosynthesis: calcification & the rain ratio can approach 1:1, & the effect of such high calcification rates has been found to change the air-sea gradient of CO_2.
- Considering that coccolithophorid blooms are responsible for up to 80% of surface ocean calcification, the 50% predicted decrease in potential surface coccolithophorid bloom areal extent may potentially lead to a significant increase in the POC:PIC ratio.
- By 2050 an increase in dissolved CO_2 & a decrease in the concentration of CO_3^{2-} will result in an increase in $CaCO_3$ dissolution.
- A decrease in calcification is a short-term negative feedback in the global carbon cycle.

IGLESIAS-RODRI´GUEZ ET AL. (2002): COCCOLITHOPHORIDS IN OCEAN CARBON CYCLE MODELS

Ratio of Hard to Soft Parts Produced & Exported from the Surface Ocean Influences pCO_2



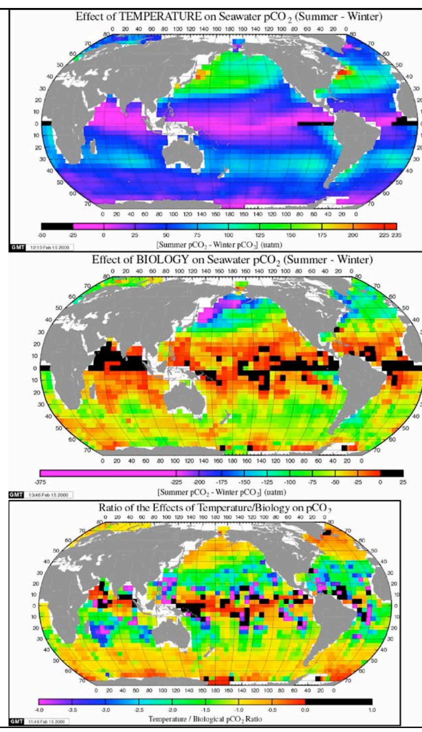
- Vector diagrams demonstrate the effect of biological & physical processes on surface ocean pCO_2:
  - Gas exchange
    - Proportionally changes ocean DIC w/ no effect on alkalinity
  - "Soft tissue pump"
    - Photosynthesis reduces DIC & *increases* alkalinity with a slope of C/N=-106/16=-6.6*
  - "Carbonate pump"
    - $CaCO_3$ production *reduces* alkalinity by 2 units per unit decrease in DIC b/c CO_3^{2-} contributes 2 moles of alkalinity per mole of DIC

Alkalinity = $HCO_3^- + 2*CO_3^{2-}$

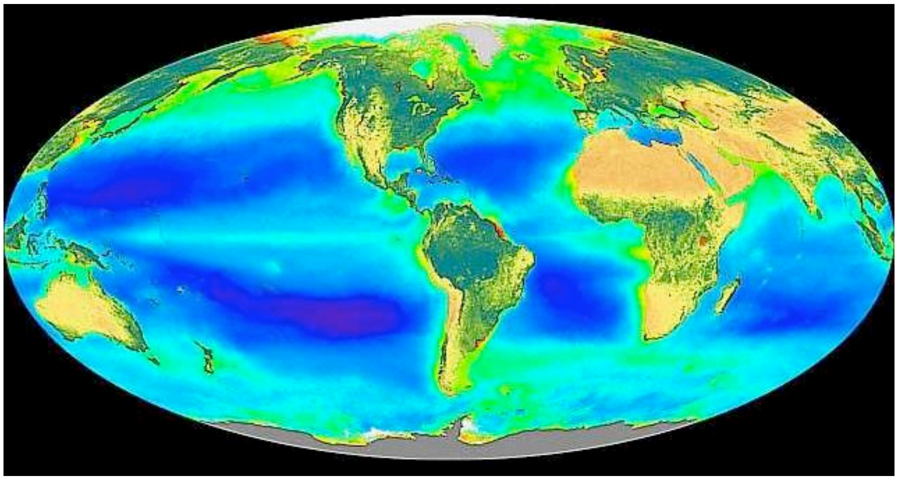
DIC = $CO_2(aq) + HCO_3^- + CO_3^{2-}$

*Debate continues over the "true" Redfield ratio, with this book taking C:N = 117:16

Sarmiento & Gruber (2007) Fig. 8.3.5



Global Ocean 1° Productivity



• Why is productivity so low in subtropical gyres?
• Why is it so high in high latitude oceans? Along equator? On coastal margins?

Ocean color/ SeaWifs: http://oceancolor.gsfc.nasa.gov/SeaWiFS/TEACHERS/sanctuary_7.html