Ocean pH and the carbon cycle

AdOc Spring 2013

Anthropogenic carbon intrusion:
http://vimeo.com/7644529

Ischia experiment:
http://www.physorg.com/news/2011-09-oceans-acidity-biodiversity.html
(http://www.physorg.com/news/2011-09-oceans-acidity-biodiversity.html)

hydrochloric acid (HCl) — 10^0
gastric fluid (1.0–3.0) — 10^{-1}
lemon juice, some acid rain — 10^{-2}
vinegar, wine, beer, oranges — 10^{-3}
tomatoes — 10^{-4}
bananas
black coffee
bread — 10^{-5}
typical rainwater
urine (5.0–7.0) — 10^{-6}
milk (6.6)
pure water — ($H^+ = OH^-$) — 10^{-7}
blood (7.3–7.5)
egg white (8.0) — 10^{-8}
seawater (7.8–8.3)
baking soda — 10^{-9}
phosphate detergents
bleach, Tums
soapy solutions, milk of magnesia — 10^{-10}
household ammonia (10. 5–11.9) — 10^{-11}
— 10^{-12}
hair remover — 10^{-13}
oven cleaner
sodium hydroxide (NaOH) — 10^{-14}

Electroneutrality principle and pH

All water solutions are electrically neutral: the total abundance of cation charges (+) is exactly matched by the total abundance of anion charges (-)

Pure water pH

- a *tiny* fraction of H_2O dissociates into hydrogen (H^+) and hydroxide (OH^-)
- since these are the only ions in pure water, their abundances must be equal, i.e., $[H^+] = [OH^-] = 10^{-7}$ mol/kg
- pH = -log $[H^+]$, = 7 for pure water (neutral)

- *experiment:* add a strong acid (HCl) to pure water:
  - HCl dissociates into H^+ and Cl^-
  - new charge balance is: $[H^+] = [Cl^-] + [OH^-]$
  - $[H^+]$ rises (acidic pH, <7)

Seawater alkalinity

• most elements dissolved in seawater have "conservative charge," meaning that the charge of their ions does not change (e.g., Na^+ and Cl^-)

• seawater contains an excess of conservative cations+ over conservative anions-

• this excess charge is called the alkalinity:

Alk = Σ(conserv. Cation+ charges) - Σ(conserv. anion-charges)

ie: $([Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K+]\ldots) - ([Cl^-] + 2[SO_4^{2-}]\ldots) > 0$
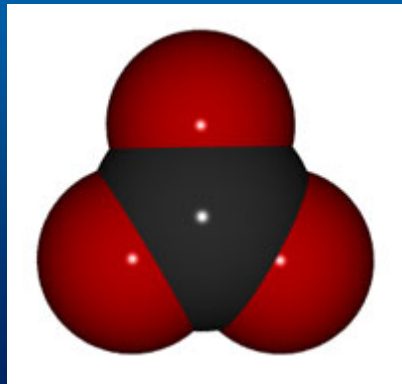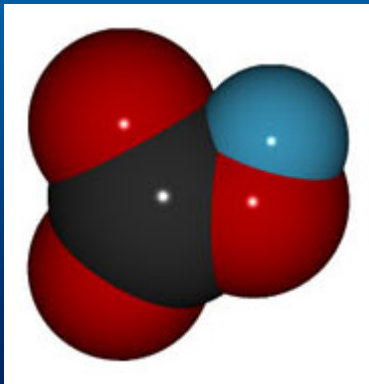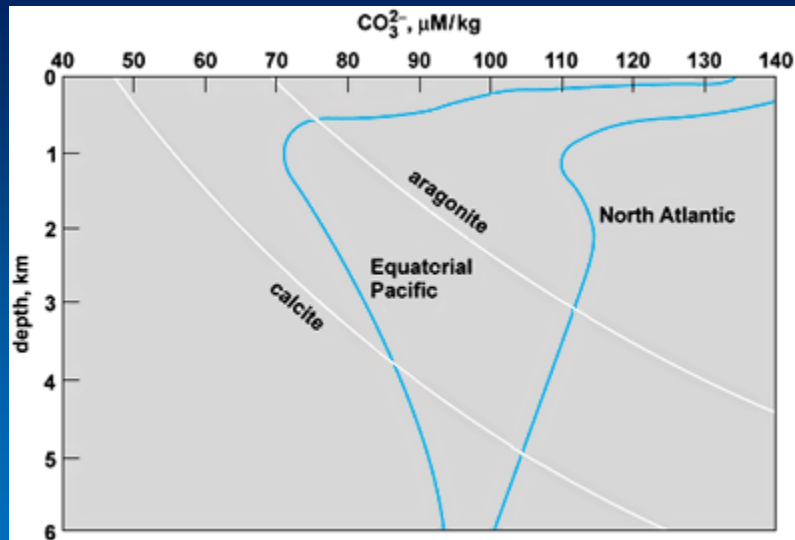
Seawater pH

- H^+ and OH^- could theoretically balance alkalinity by having more OH^- than H^+ ("non-conservative charge")
- *if no other ions could change their charge*, $[OH^-]$ would have to be very high and seawater would be very basic
- in reality, molecules of *two other* important elements can change their charge to provide more anions to balance the alkalinity: carbon and boron ("non-conservative charge")

- seawater pH is only slightly basic (~7.8-8.3) because OH^- only needs to provide a small fraction of the anions (C and B provide most of the charge balance)
- seawater pH is also not easily changed, for the same reason (buffered)

Carbon in seawater
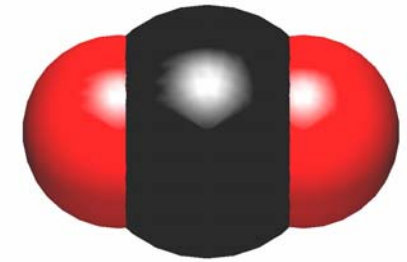
- basic building block of organic molecules
- ~60X more C dissolved in oceans than in atmosphere
- occurs in seawater in several forms:
    - ~98% dissolved inorganic carbon (DIC):
        - ~1% carbon dioxide gas (CO_2)
        - ~90% bicarbonate (HCO_3^-)
        - ~10% carbonate (CO_3^{2-})
        - DIC transforms between 3 to maintain charge balance
    - ~2% dissolved organic carbon (DOC)

Glucose

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Calcium Carbonate Accumulation

Below the CCD, cold water holds more CO_2, which results in more carbonic acid, which dissolves $CaCO_3$ faster.
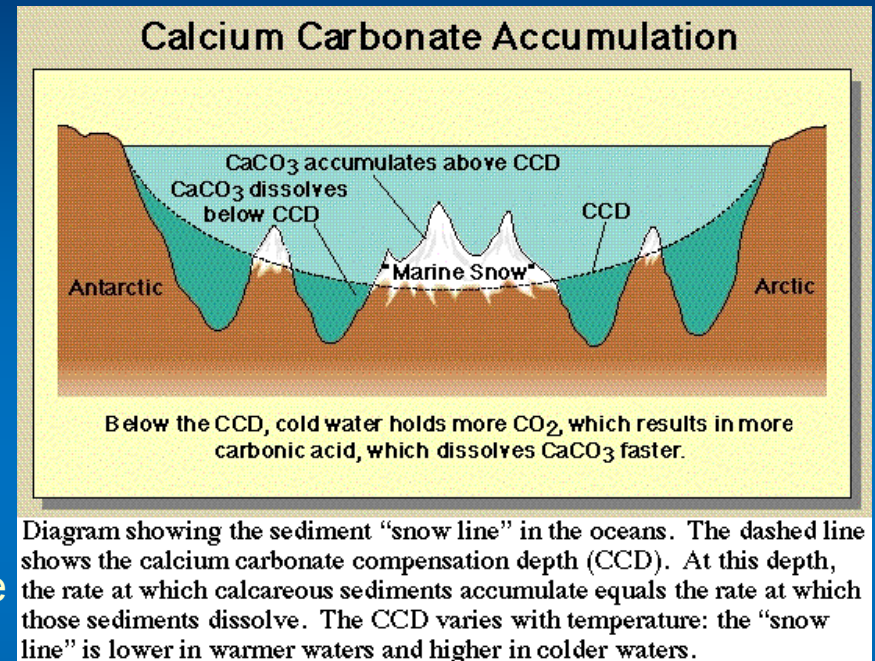
Diagram showing the sediment "snow line" in the oceans. The dashed line shows the calcium carbonate compensation depth (CCD). At this depth, the rate at which calcareous sediments accumulate equals the rate at which those sediments dissolve. The CCD varies with temperature: the "snow line" is lower in warmer waters and higher in colder waters.

Solubility of aragonite and calcite [expressed in terms of carbonate (CO_3^{2-}) ion concentration] in seawater at 2°C as a function of water depths in the North Atlantic and the eastern Equatorial Pacific. The intersections of the solubility curves with the curves for the concentration of the CO_3^{2-} ion indicate the water depths at which the ocean water is saturated with the respective minerals.

DIC distribution

• low at the sea surface and high in the deep ocean
• removed by photosynthesis and added by respiration (as CO_2)
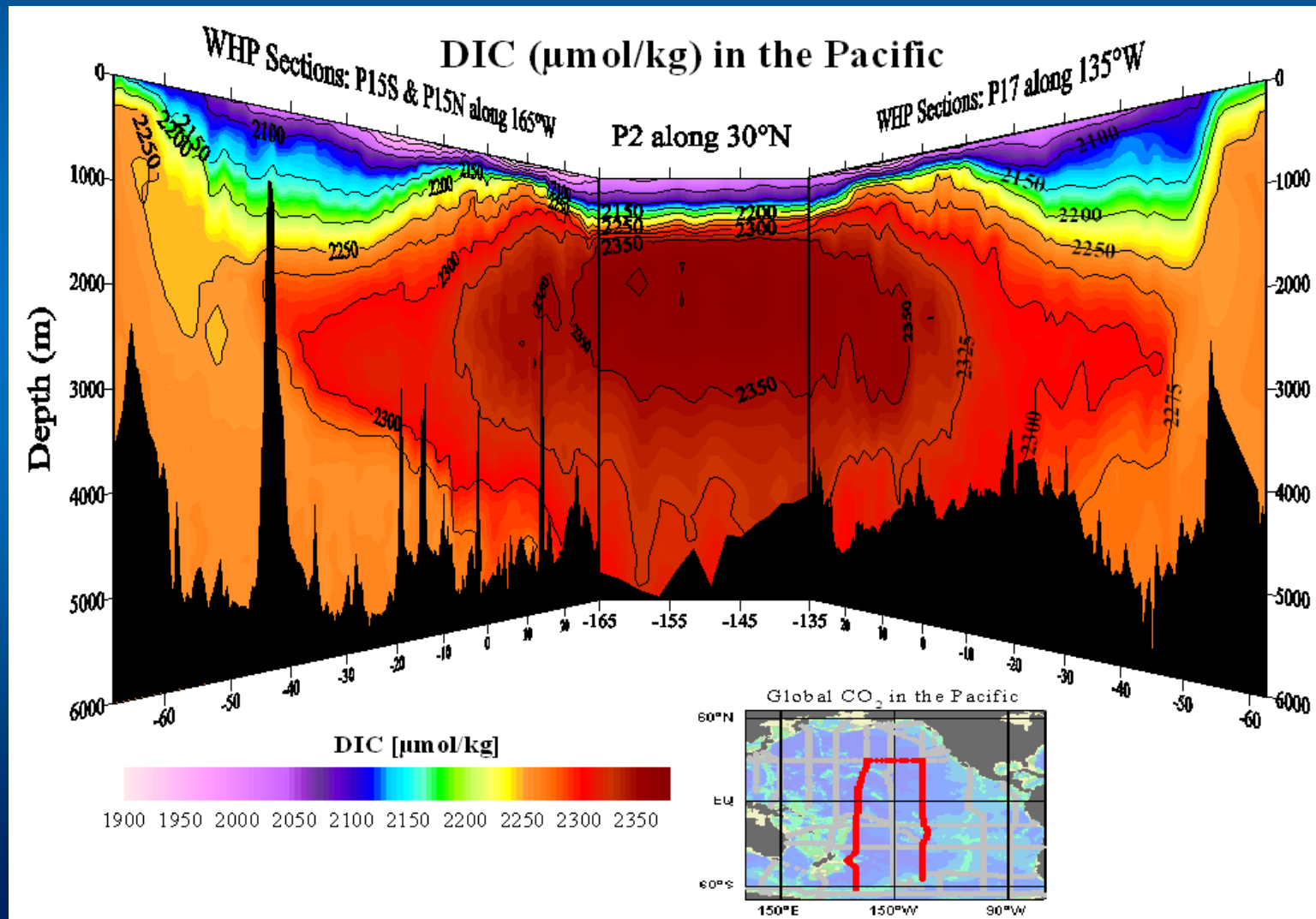
Air-sea exchange of CO_2

Of the three forms of DIC, only CO_2 can enter the atmosphere

At equilibrium, the partitioning of CO_2 between the atmosphere and ocean is determined by Henry's Law:

$$pCO_2 = [CO_2(aq)] / K_0$$

pCO_2 is the concentration ("partial pressure") *in air*

$[CO_2(aq)]$ is the concentration in seawater
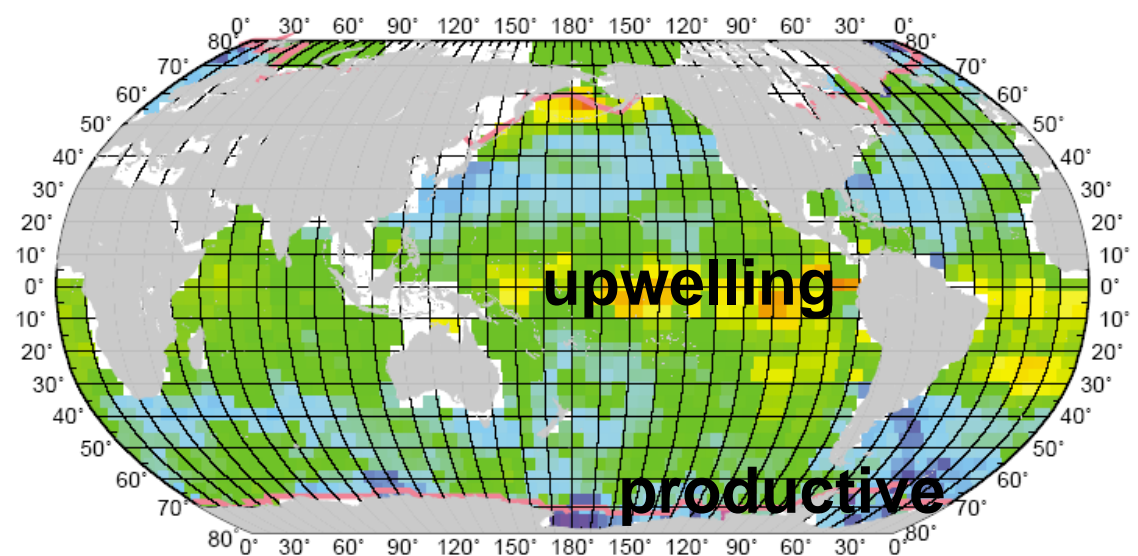- decreases with photosynthesis

K_0 is the solubility coefficient
- decreases with $\uparrow$ temperature (warm $\rightarrow$ higher pCO_2)
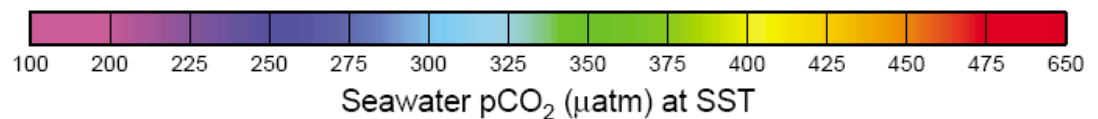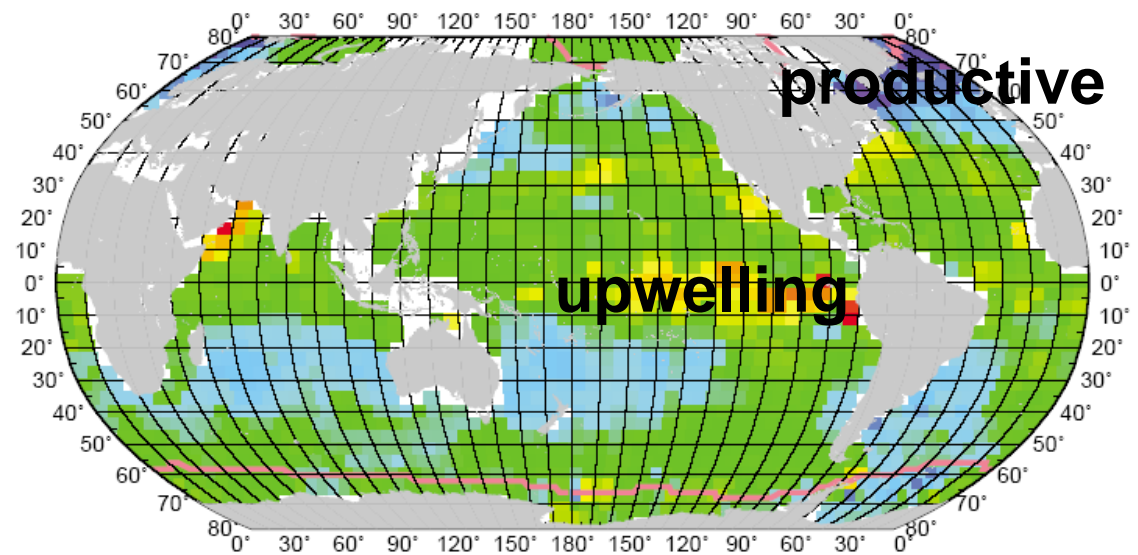- decreases with $\uparrow$ salinity (salty $\rightarrow$ higher pCO_2)

- **globally averaged**, the surface ocean and atmosphere (well-mixed) are close to equilibrium

- **locally** the ocean may be far from equilibrium

- result is net fluxes **into** or **out of** ocean

- high productivity areas (photosynthesis)

- upwelling areas

Takahashi et al. (2002)

Climatological pCO_2 in Surface Water [940K] for February 1995

upwelling

productive

Climatological pCO_2 in Surface Water [940K] for August 1995

productive

upwelling

| 100 | 200 | 225 | 250 | 275 | 300 | 325 | 350 | 375 | 400 | 425 | 450 | 475 | 650 |

Seawater pCO_2 (μatm) at SST

Annual average fluxes: more in than out due to buildup of fossil fuel CO_2 in the atmosphere

Mean Annual Air-Sea Flux for 1995 (NCEP 41-Yr Wind, 940K, W-92)

Net Flux (moles CO_2 m^{-2} year^{-1})
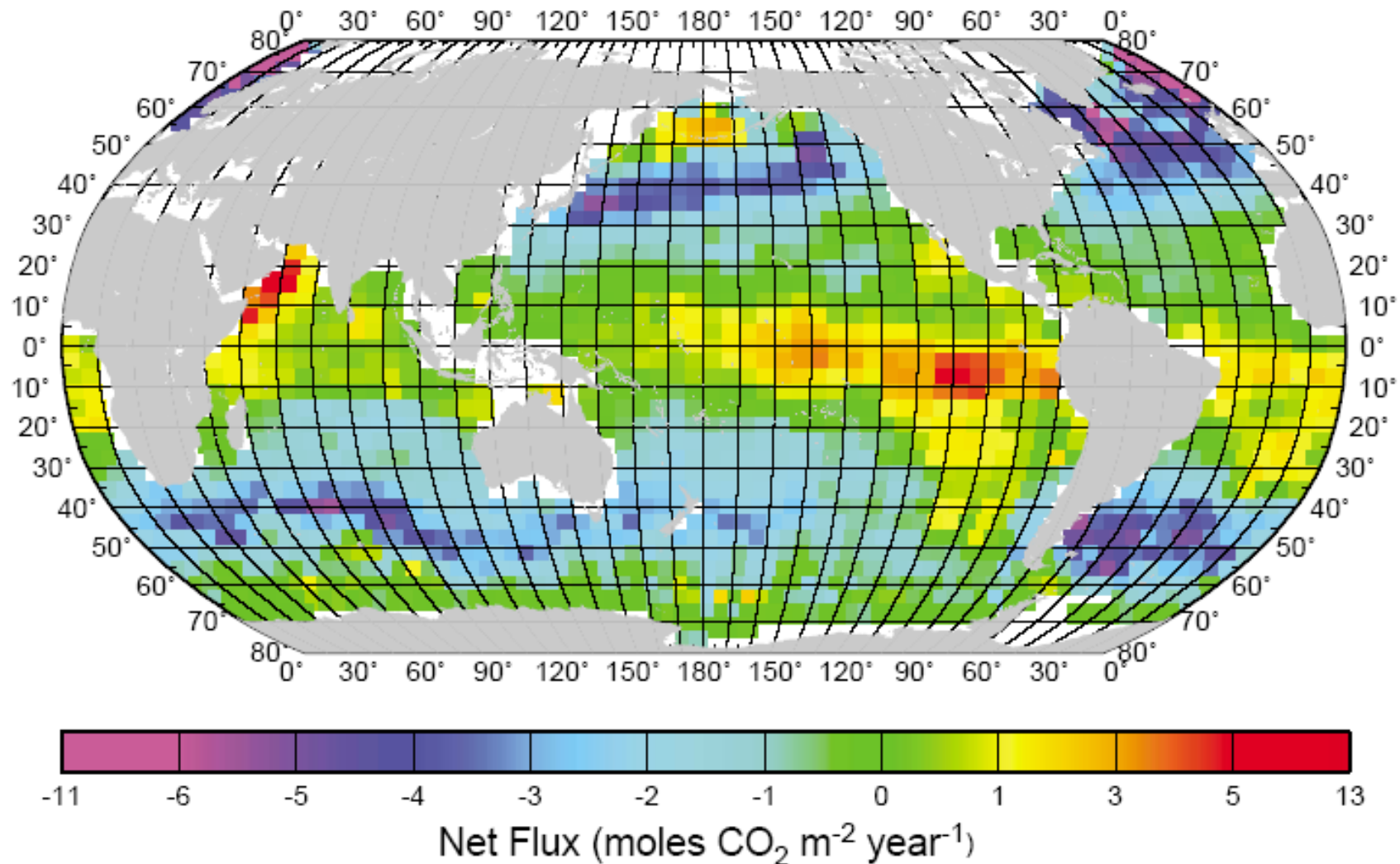
Global biogeochemical cycling of carbon

• natural cycling between seawater, marine biota, marine sediments, atmosphere, and land biota + soils

• greatly perturbed by human burning of fossil fuels exhausting into the atmosphere

• reservoirs quantified in gigatonnes (Gt = 10^{15} g) of C atoms
• fluxes quantified in Gt C per yr
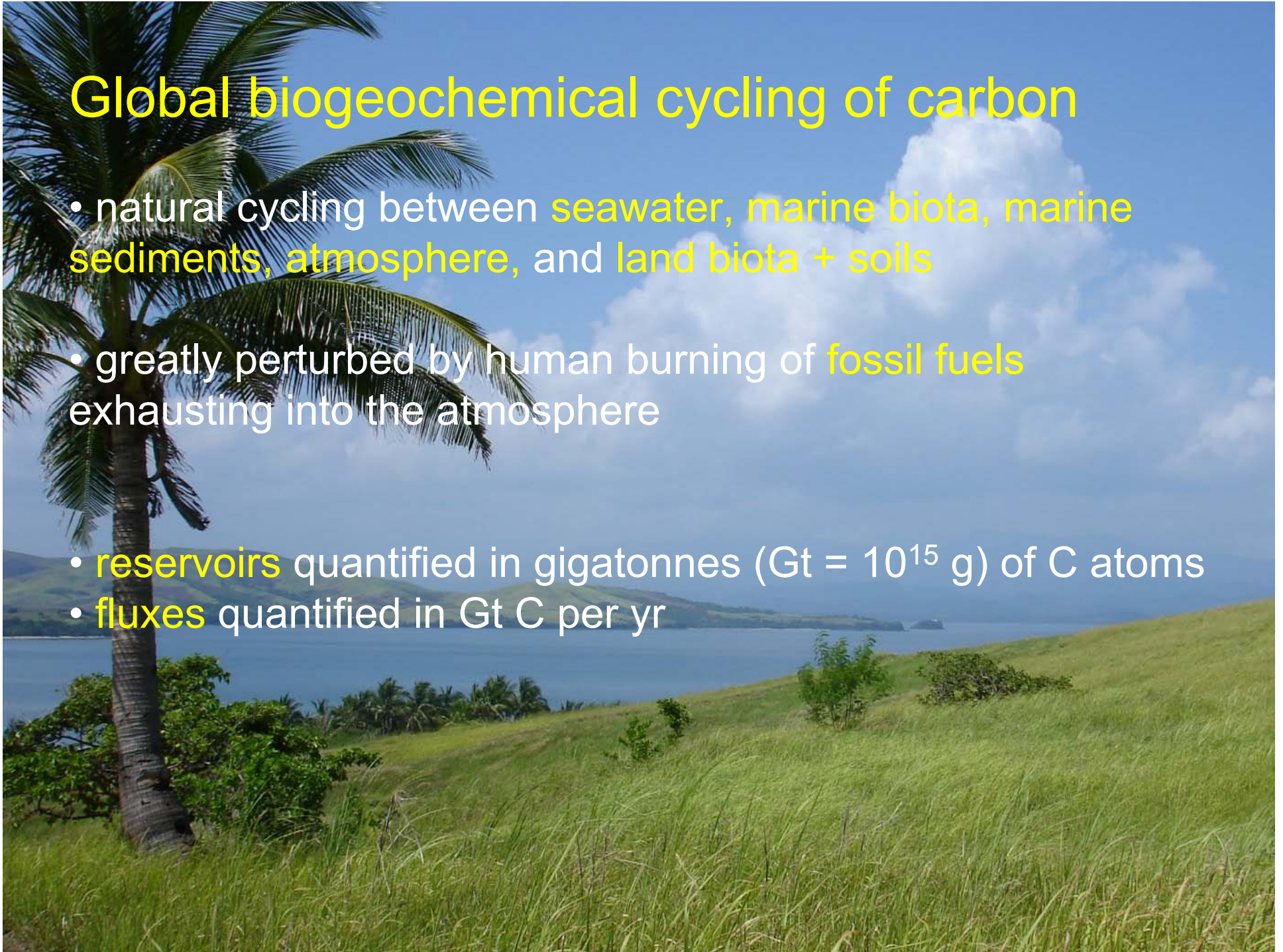
"Perturbed" carbon cycle (1990s, IPCC4)

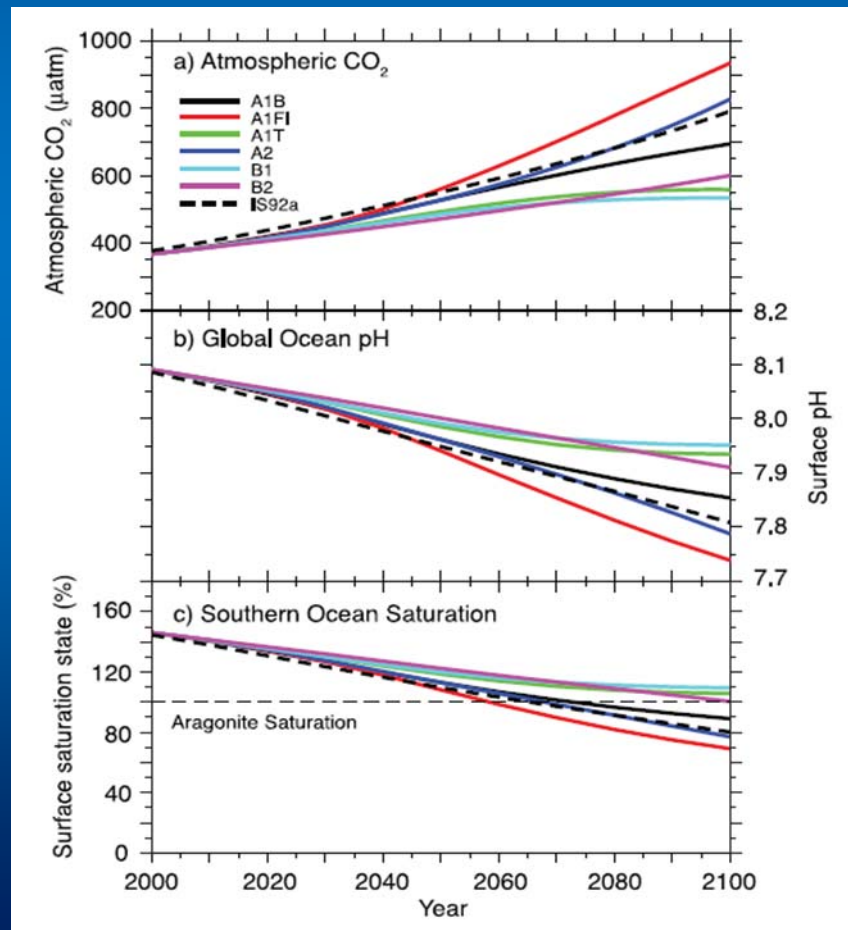Atmosphere: 597 GtC

Pre-industrial

Anthropogenic
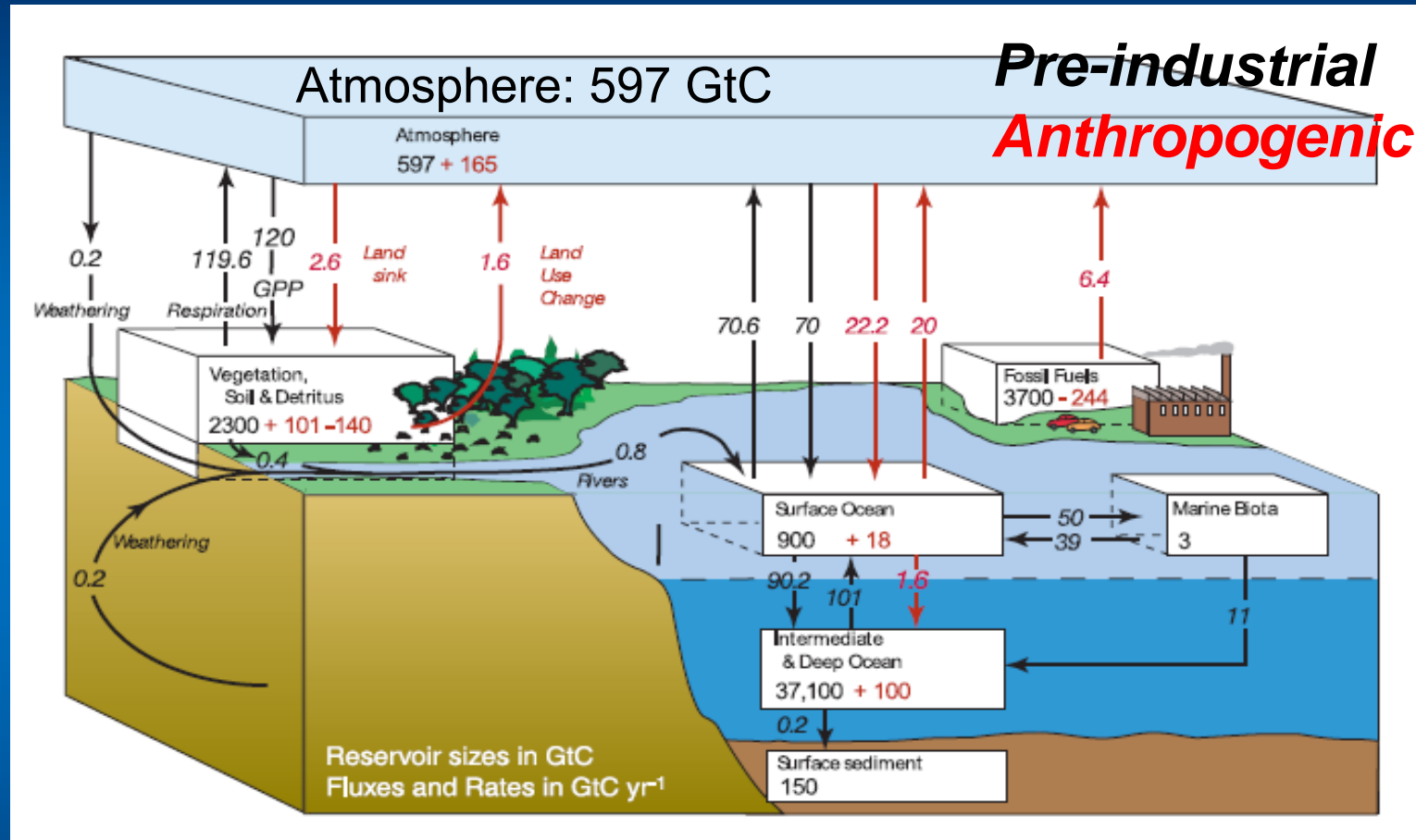
Sources:
Fossil fuels: 244 GtC
Deforestation: 140 GtC

Sinks:
Ocean: 118 ±19 GtC (~30%)
Reforestation & Greening: 101 GtC (~25%)
Atmosphere: 165 GtC (~45%)

Ocean acidification

- CO_2 generates an acid in seawater (pH drop):
    - $CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow HCO_3^- + H^+$
    - surface ocean pH has already dropped by ~0.1

- pH expected to drop by additional 0.2-0.3 by 2100

Cartoon on calcification process:
http://www.whoi.edu/home/oceanus_images/ries/calcification.html

CO2 progression:
http://www.esrl.noaa.gov/gmd/ccgg/trends/history.html

CaCO$_3$ dissolution

- dissolves under high pressure, low temperature, acidic water
- *some* of the H$^+$ combines with CO$_3^{2-}$ (buffering):
    - CO$_3^{2-}$ + H$^+$ $\rightarrow$ HCO$_3^-$
    - saturation state of CaCO$_3$ depends on [Ca^{2+}]*[CO$_3^{2-}$]
    - seawater is then less saturated as pH drops

- aragonite is more soluble than calcite
- organisms with aragonite shells (pteropods, corals) may have difficulty calcifying by 2100 (average surface pH 7.75-7.95)

The abundances of the DIC ion forms change with pH; at ocean pH's bicarbonate (HCO_3^-) is dominant.
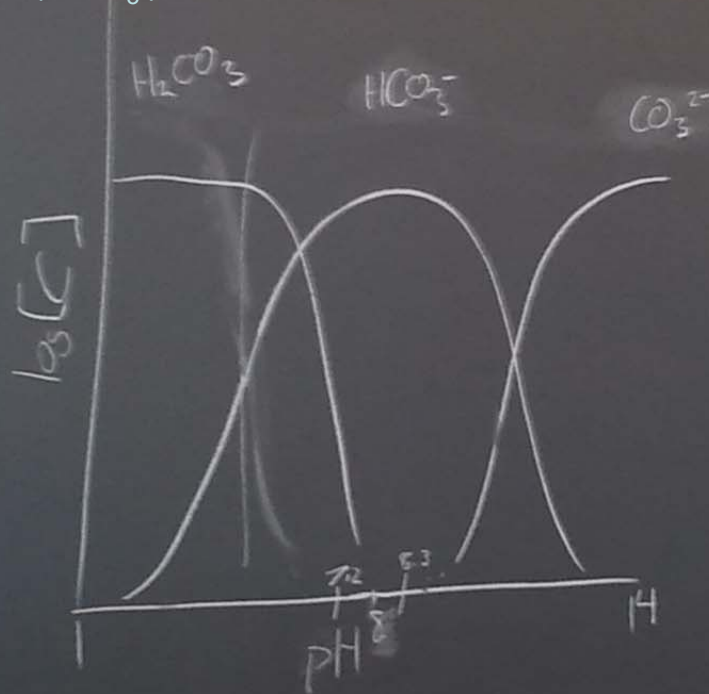
DIC ions by pH

pH at which process is strongest
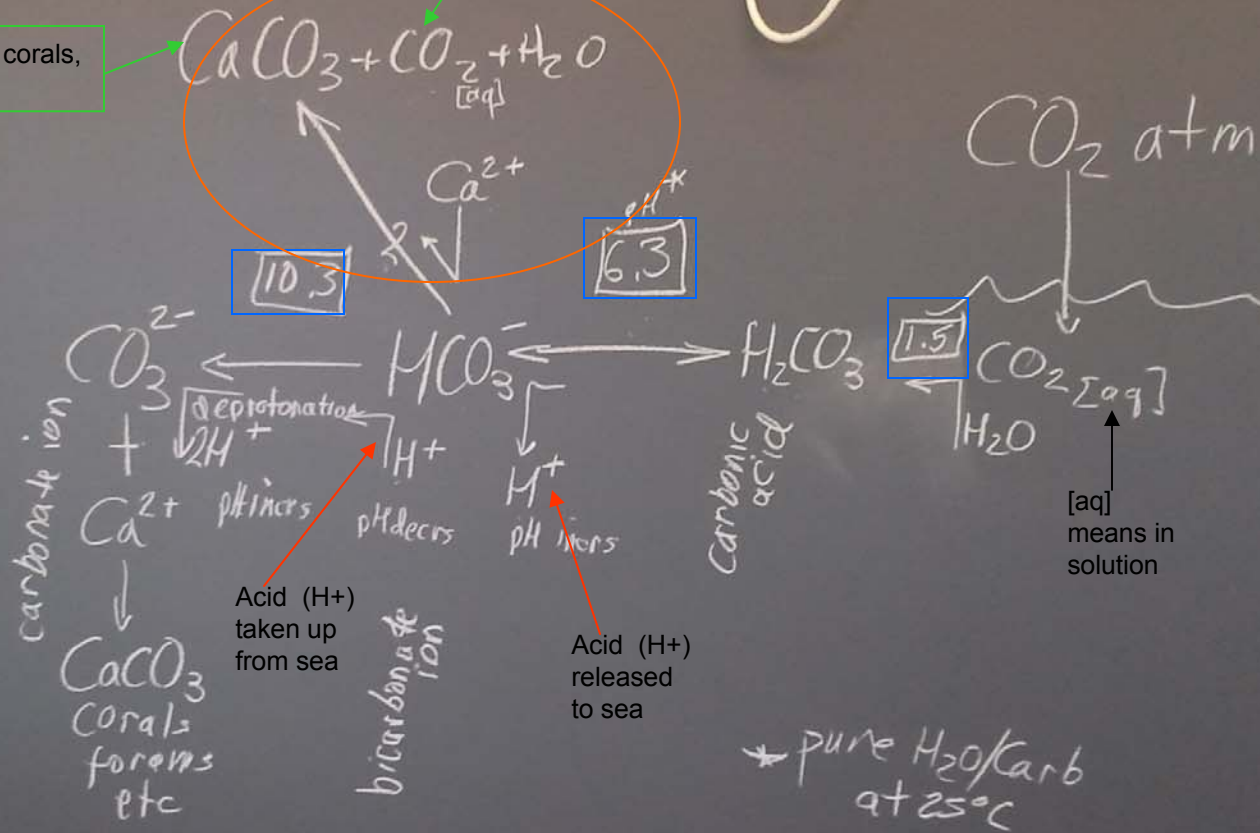
The primary calcification method

CO$_2$ to seawater then atmosph

Shells, corals, etc

$CaCO_3 + CO_2 + H_2O$
[aq]

Ca^{2+}

10.3

6.3

1.5

CO_2 atm

CO_3^{2-} ← HCO_3^- → H_2CO_3 → $CO_{2[aq]}$

carbonate ion

deprotonation

$+ 2H^+$

Ca^{2+} pH incrs

H^+

pH decrs

H^+

pH incrs

carbonic acid

H_2O

[aq] means in solution

$CaCO_3$ corals forams etc

Acid (H+) taken up from sea

bicarbonate ion

Acid (H+) released to sea

★ pure H$_2$O/carb at 25°C

The chemistry:
http://www.co2.ulg.ac.be/pub/frankignoulle_et_al_1995.pdf