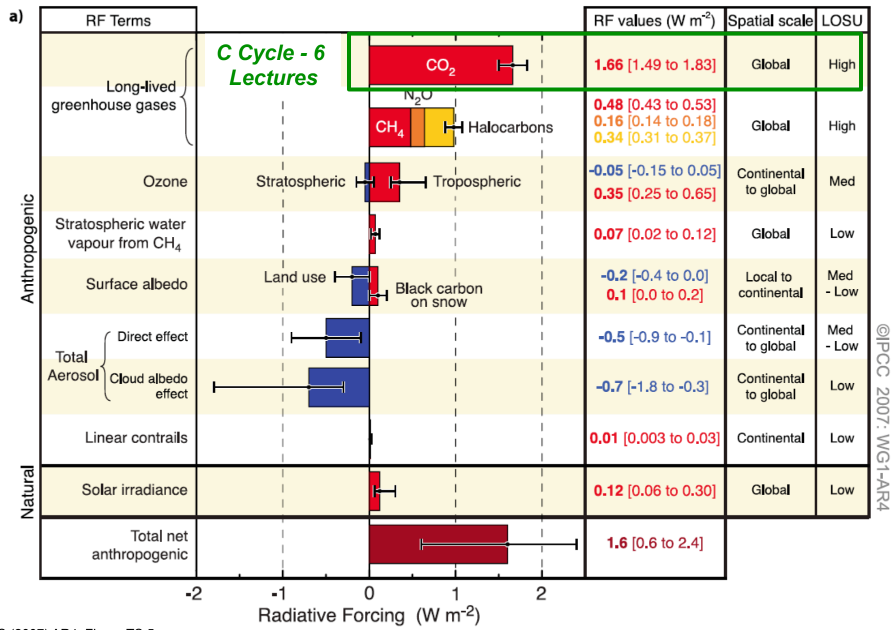
Global Mean Radiative Forcings



IPCC (2007) AR4, Figure TS.5.

PCC 588, Pt. II: The Global Carbon Cycle

Thurs 1/29 Long-term carbon cycle (10^5-10^8 yr)
- *Broecker 2005 pp. 79-130*

Tues 2/3 Short-term C Cycle (10^0-10^2 yr). Atmosphere-ocean CO_2 exchange I
- *Emerson & Hedges 2007 Ch. 11*

Thurs 2/5 Atmosphere-ocean CO_2 exchange II

Tues 2/10 Atmosphere-ocean CO_2 exchange III. Glacial-Interglacial CO_2 (Mid-term C cycle, 10^3-10^5 yr)

Thurs 2/12 Paper Discussion (or lecture if needed)

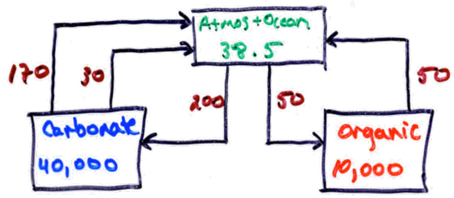
Tues 2/17 Mid-term exam

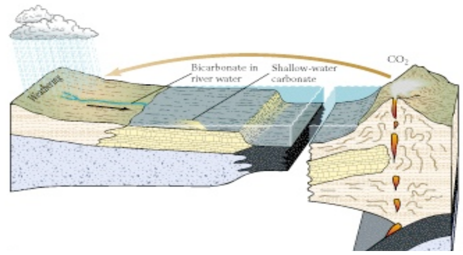
Thurs 2/19 Anthropogenic perturbation of C cycle
- *Broecker 2005 pp. 130-156*

Tues 2/24 Terrestrial C cycle (LJ)
- *Homework #3 out (due 3/3)*

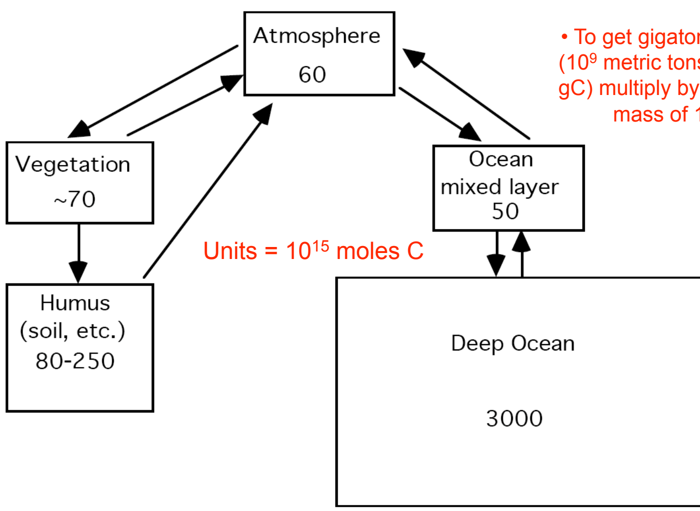
Thurs 2/26 Paper Discussion

Reservoirs, fluxes & the Long-Term Carbon Cycle





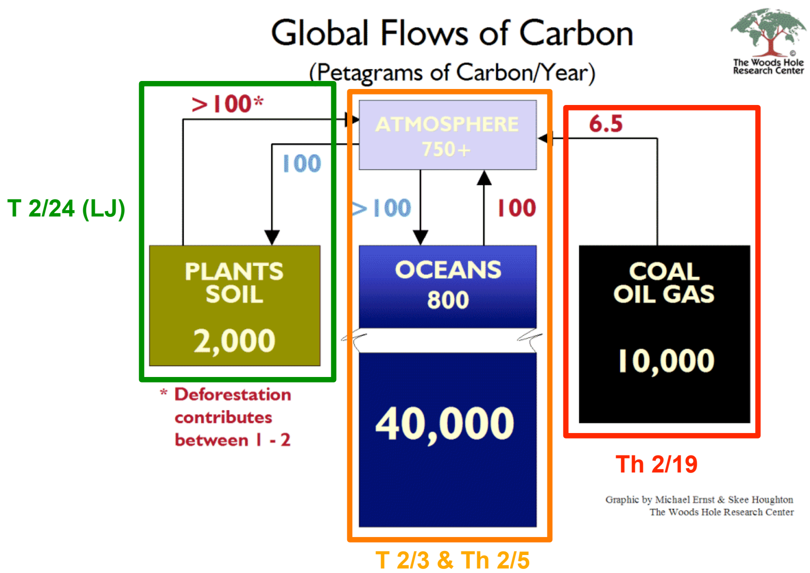
Carbon Reservoirs on Earth's Surface



• To get gigatons of C (10^9 metric tons = 10^{15} gC) multiply by atomic mass of 12

• Large size of ocean w.r.t. atmosphere reservoir + rapid exchange between = focus on ocean-atmosphere CO_2 interactions

Primary Carbon Fluxes Today



Petagram = 10^{15} g = Gt, gigaton

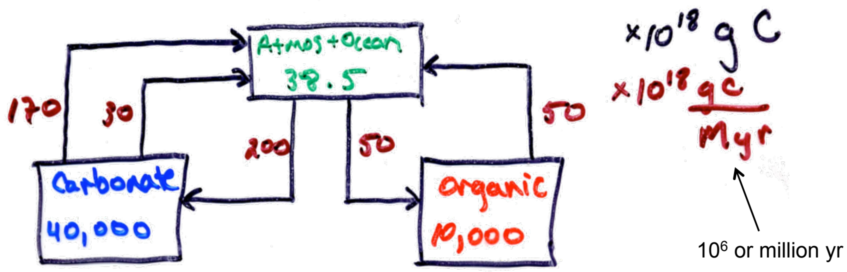
The Long-Term Carbon Cycle: Tectonics & Weathering

On the Million to Billion Year Time Scale:

- Weathering of rocks consumes CO_2 [10^6 yr]
- Seafloor spreading releases mantle CO_2 [10^7 yr]
  - Its rate varies through time for reasons largely unknown
- Continental drift can result in increased or decreased weathering rates [10^8 yr]
  - depending on rainfall & temperature regime
- Mountain building increases weathering rates [10^8 yr]
  - by producing fresh, easily eroded rock, focusing precipitation, providing steep slopes for rapid runoff

Carbon Reservoirs & Fluxes – The Long-Term View

- Most carbon in Earth's crust occurs in carbonate rocks (~10,000x more than in ocean + atmosphere) & as organic material (kerogen) in rocks (~2,500x more than in ocean + atmosphere)
- Ocean + atmosphere C reservoir is small w.r.t. rock reservoir & the transfer rates between those reservoirs
- Transfer of C between rocks & ocean + atmosphere (>10^6 yr) can strongly perturb the CO_2 greenhouse effect



(units are 1000x larger than in previous figures!)

The Long-Term Biogeochemical Carbon Cycle

1. Organic Carbon Burial and Weathering

$$CO_2 + H_2O \underset{\text{Weathering}}{\overset{\text{Burial}}{\rightleftharpoons}} CH_2O + O_2$$

2. Tectonics: Seafloor Spreading Rate

   - Mantle CO_2 from Mid-Ocean Ridges

3. Carbonate-Silicate Geochemical Cycle

   - Chemical Weathering <u>Consumes</u> CO_2
   - Carbonate Metamorphism <u>Produces</u> CO_2

Chemical Weathering = chemical attack of rocks by dilute acid

$CO_2 + H_2O \leftrightarrow H_2CO_3$

The Geochemical (or non-biological part of the) LT Carbon Cycle

1. **Carbonate Weathering:**

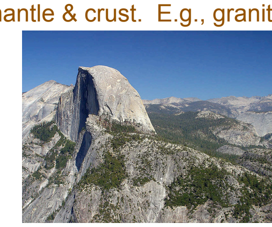
$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2\,HCO_3^-$

Carbonate Rocks (e.g., limestone)

2. **Silicate Weathering:**

$CaSiO_3 + 2\,H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2 + H_2O$

Silicate Rocks (most of the mantle & crust. E.g., granite)



- 2x CO_2 consumption for silicates
- Carbonates weather faster than silicates

http://en.wikipedia.org/wiki/Image:Yosemite_20_bg_090404.jpg http://en.wikipedia.org/wiki/Image:Burren_karst.jpg

Granite (silicate)

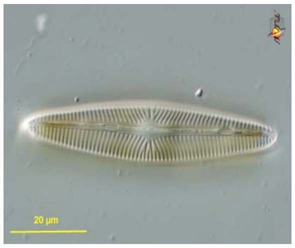
Carbonate rocks weather faster than silicate rocks!

- Rivers transport dissolved ions to ocean

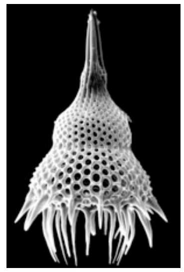
Limestone (carbonate)

Adapted from Kump et al. (1999)

Products of weathering precipitaed as $CaCO_3$ & SiO_2 in ocean

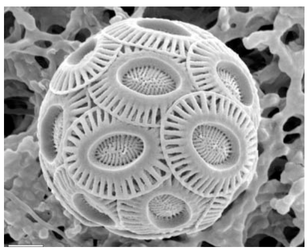


Diatom (SiO_2)

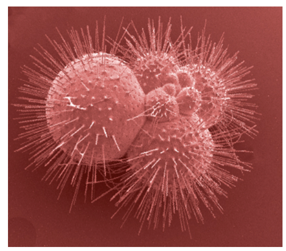


Radiolarian (SiO_2)

R, Protozoans
L, Eukaryotic Phytoplankton



Coccolithophorid ($CaCO_3$)



Foraminifer ($CaCO_3$)

Net reaction of geochemical carbon cycle (Urey Reaction)

Net Reaction of Rock Weathering
+
Carbonate and Silica Precipitation in Ocean

$$CaSiO_3 + \boxed{CO_2} \rightarrow CaCO_3 + SiO_2$$

- CO_2 consumed (~ 0.03 Gt C/yr)
- Would deplete atmospheric CO_2 in 20 kyr
- Plate tectonics returns CO_2 via Volcanism and Metamorphism

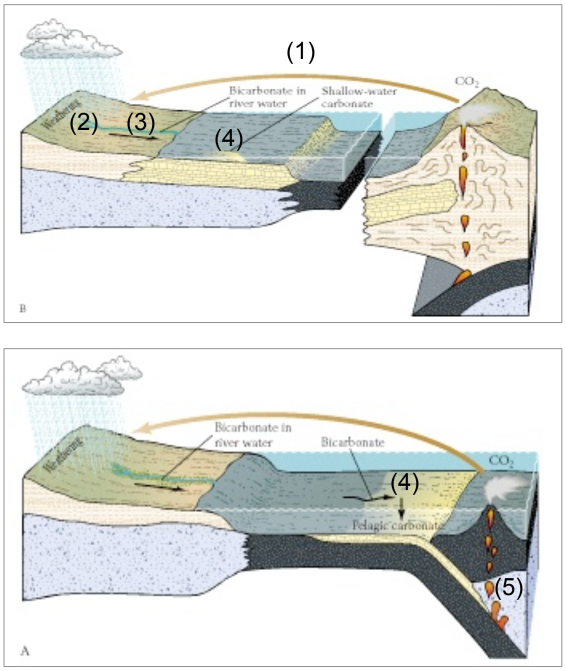
----

Carbonate Metamorphism

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + \boxed{CO_2}$$

- CO_2 produced from subducted marine sediments

- On geologic time scales, rock weathering balanced by carbonate metamorphism
- Any *imbalance* can cause changes in atmospheric CO_2

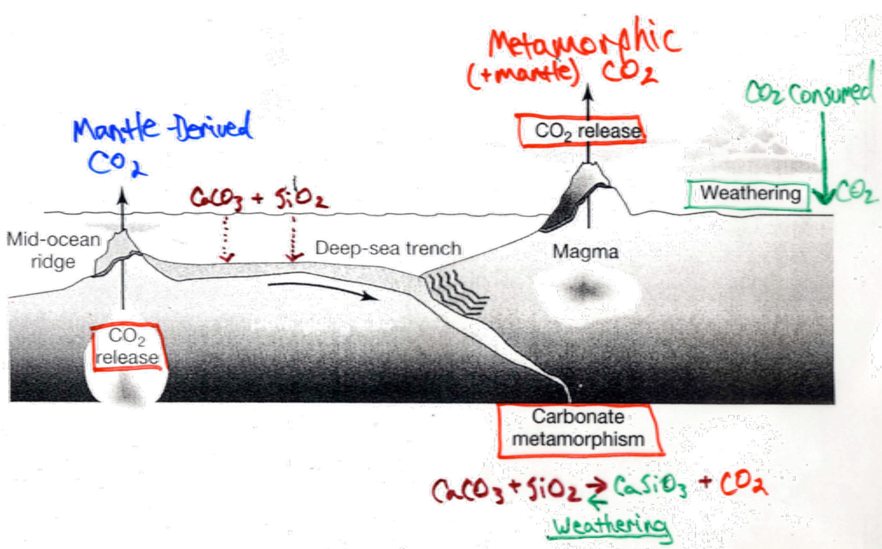


Carbonate-Silicate Geochemical Cycle

1. CO_2 released from volcanism dissolves in H_2O, forming carbonic acid
2. H_2CO_3 dissolves rocks
3. Weathering products transported to ocean by rivers
4. $CaCO_3$ precipitation in shallow & deep water
5. Cycle closed when $CaCO_3$ metamorphosed in subduction zone or during orogeny.

Stanley (1999)

Carbonate-Silicate Geochemical Cycle



Kump et al. (1999)

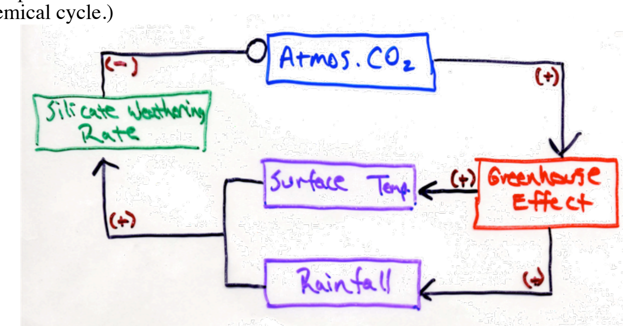
- Geologic record indicates climate has rarely reached or maintained extreme Greenhouse or Icehouse conditions....
- Negative feedbacks between climate and Geochemical Carbon Cycle must exist
- Thus far, only identified for Carbonate-Silicate Geochemical Cycle:

  Temp., rainfall enhance weathering rates

  (Walker et al, 1981)

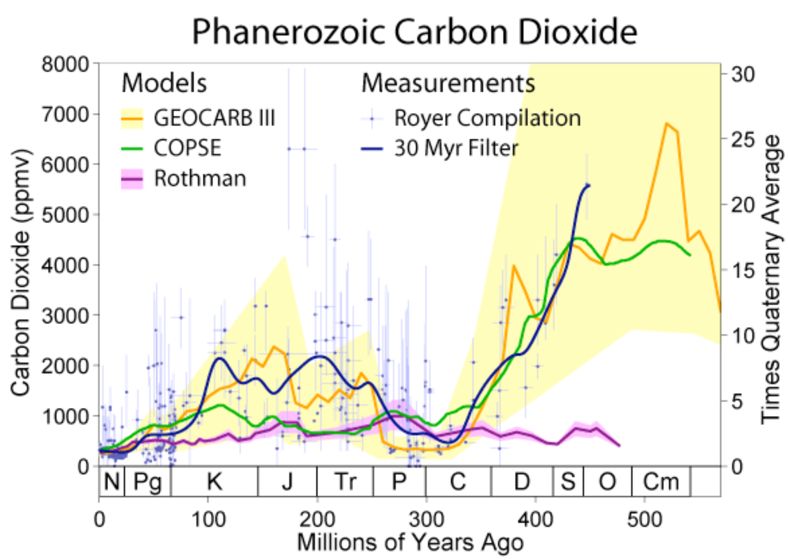
  (I.e., no obvious climate dependence of tectonics or organic carbon geochemical cycle.)

How are CO_2 levels kept in balance on >10^6-yr time scales? ***Feedbacks***



Adapted from Kump et al. (1999)

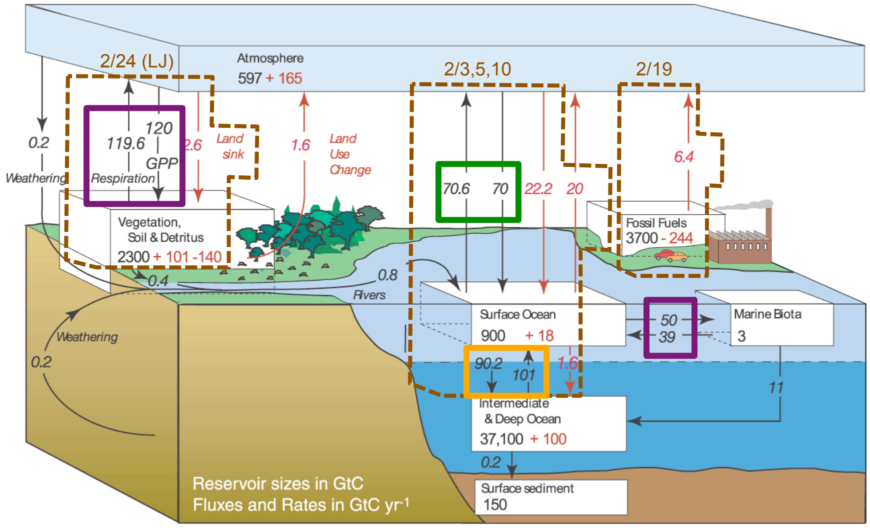
Atmospheric CO_2 During the Last 545 Ma



http://commons.wikimedia.org/wiki/File:Phanerozoic_Carbon_Dioxide.png

Short-Term (10^0-10^2 yr) Carbon Cycle – Our Focus

- Photosynthesis, Respiration, Air-Sea Gas Exchange, Ocean Circulation



Black arrows → natural fluxes

Red arrows → anthropogenic fluxes

IPCC 2007, Fig. 7.3

Global Carbon Fluxes & Reservoirs – Details

Reservoirs (Pg):

Atmosphere: CO2 (288 ppm in 1850)	612
(369 ppm in 2000)	784
Oceans: Biota	1-2
DOC	700
Org C in sediments (1 meter)	1,000
DIC	38,000
Terrestrial: Biota	600
Soil Humus (1 meter)	1,500
Fossil Fuels (identified reserves), gas	44
oil	90
coal, oil sand & shale	3440

Fluxes (Pg yr^{-1}):

Atmosphere-Ocean exchange	90
Gross Primary Production Ocean	100
Land	120
Net Primary Production Ocean	45
Land	60
Net C export from the surface ocean	8-15
Sedimentation of Org. C. in the ocean	0.2

Anthropogenic Changes (Pg or Pg yr^{-1}):

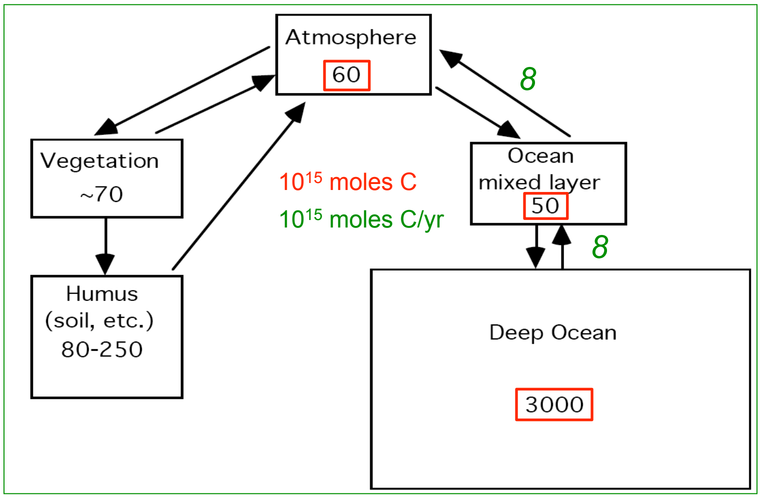
Cumulative Changes (Pg): (1800-1994)	
Fossil Fuels Burnt & Cement Prod.	244
Atmospheric Increase	165
Storage in the Ocean	118
Inferred Terrestrial Change	-39
Partitioning of Anthropogenic Fluxes (1990s) (Pg yr^{-1})	
Fossil Fuel and Cement Production	6.3 ± 0.4
Atmosphere Accumulation	3.2 ± 0.1
Uptake by Terrestrial Biosphere	-1.4±0.7
Ocean Uptake	-1.7±0.5

- Excludes crustal rocks (& mantle!) other than coal, oil & gas

Pg, petagram = 10^{15} g = Gt, gigaton

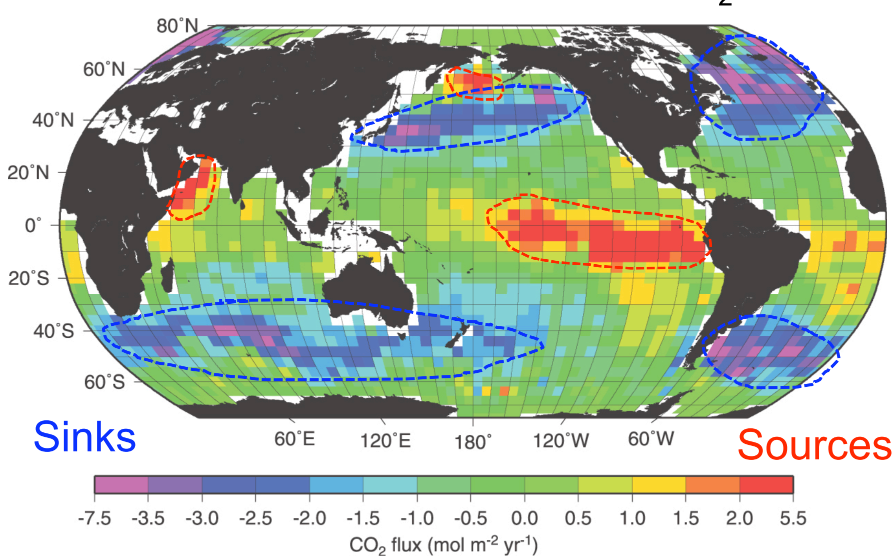
Emerson & Hedges (2007) Table XI-1

Because ocean reservoir is large w.r.t. atmosphere, & rapid exchange occurs between them, the processes affecting these reservoirs & fluxes are central in controlling atmospheric CO_2 (& GG forcing) on 10^1-10^2 time scales



• To get gigatons of C (10^9 metric tons = 10^{15} gC) multiply by atomic mass of 12

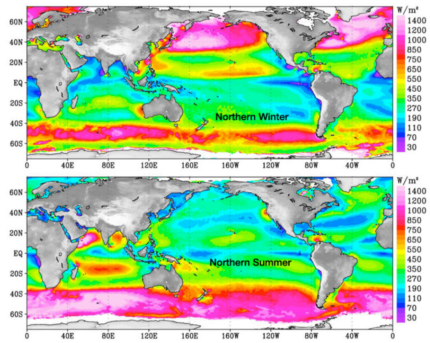
Modern Air-Sea Fluxes of CO_2



▪ *What Determines these Fluxes?*

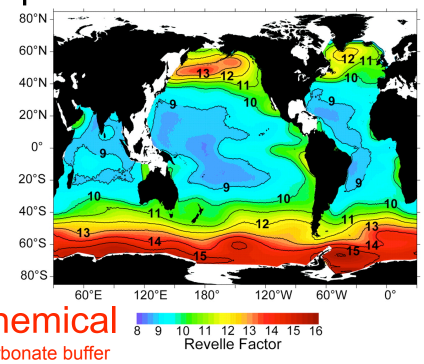
IPCC 2007 Fig. 7.8

Processes Controlling the Exchange Of CO_2 Between the Atmosphere & Ocean



Physical

Quikscat surface wind power density

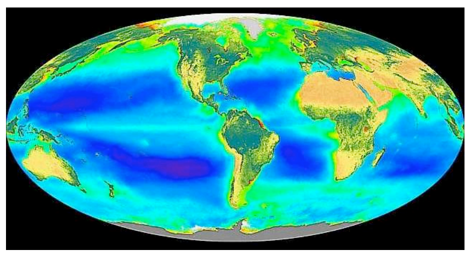


Chemical

Carbonate buffer

Biological

SeaWifs ocean color

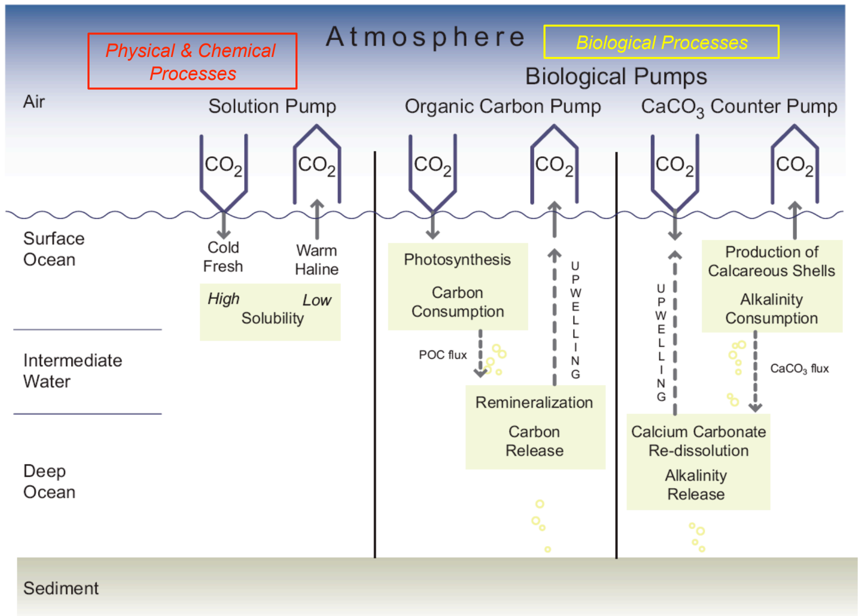


Sabine et al. (2004) *Science* Vol. 305: 367-3
http://www.nasa.gov/images/content/257995main_quikscat-wind-browse.jpg
http://oceancolor.gsfc.nasa.gov/SeaWiFS/TEACHERS/sanctuary_7.html

Material in the following lectures was drawn from several sources

- Broecker (2005) *The Role of the Ocean in Climate Yesterday, Today and Tomorrow*, Eldigio Press, NY.
- Broecker & Peng (1982) *Tracers in the Sea* Eldigio Press, NY.
- Emerson & Hedges (2007) *Chemical Oceanography and the Carbon Cycle*. Cambridge University Press.
- Zeebe & Wolf-Gladrow (2001) *CO_2 in Seawater: Equilibrium, Kinetics, Isotopes*. Elsevier Press.
- Sarmiento & Gruber (2006) *Ocean Biogeochemical Dynamics*. Princeton University Press.
- Ed Boyle (2008) *Lecture Notes for 12.842: Climate Physics & Chemistry*, MIT.

Summary of Processes Influencing Air-Sea Exchange of CO_2



IPCC 2007 Fig. 7.10

Outline of Processes Influencing Air-Sea Exchange of CO_2

1. Physical Processes (kinetics)
   - Air-sea gas exchange = f (wind speed, bubble injection, surfactants)
   - 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

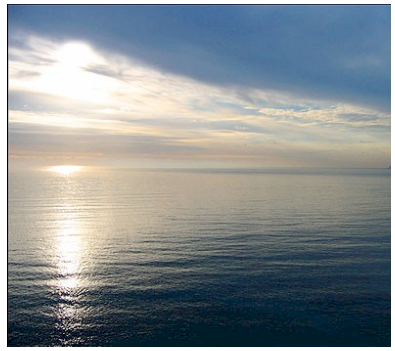
Physical & Chemical Processes Controlling CO_2 Uptake by the Ocean

- Chemical equilibrium determines total possible transfer
  - Carbonate equilibrium, summarized by Revelle Factor; not attained in most of the surface ocean
- Gas exchange dynamics across the air-sea interface determine the rate of approach to chemical equilibrium.
  - Gas exchange = f (wind speed, bubble injection, surfactants)
    - Estimated from ^{222}Rn deficit, ^{14}C uptake, tracer release experiments (SF_6, ^3He, *Bacillus globigii*)
- CO_2 that dissolves into surface mixed layer carried into ocean interior by ocean circulation

Outline of Processes Influencing Air-Sea Exchange of CO_2

1. Physical Processes
   - Air-sea gas exchange = f (wind speed, bubble injection, surfactants)
   - 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

Air-Sea Gas Exchange



• Under which conditions do you expect higher rates of air-sea gas exchange?

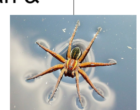
http://z.about.com/d/cruises/1/0/u/k/3/Emerald_Princess_Asea.JPG

http://ninjaradio.files.wordpress.com/2008/08/calm_sea_memory_470x353.jpg

Atmosphere-Ocean Gas Exchange Basics

• Gas exchange is driven by a disequilibrium in the partial pressure of gases between the ocean & atmosphere (e.g., from biological processes, temperature, ocean mixing)

• Although the direction & magnitude of net gas exchange is thermodynamically driven, it is limited by physical transport (diffusion & microadvection) through boundary layers at the surface of the ocean & bottom of the atmosphere.



• Physical motions in the boundary layers are restricted by surface tension (water) & friction (atmosphere)

• Some gas exchange also caused by **bubbles** from breaking waves, esp. in high winds. Can help facilitate equilibrium (e.g., trapped gas can equilibrate with water & return equilibrated gas to surface), but can also create disequilibrium when a submerged bubble completely dissolves the atmospheric gases quantitatively into the water in non-thermodynamic ratios.

• Gas exchange is occurring in both directions at all times (even when gas partial pressures are equal between water & air)

Adapted from Ed Boyle 12.842 Lecture 2008

Atmosphere-Ocean Gas Exchange

- For gas exchange without bubbles, net flux is proportional to the disequilibrium between the dissolved gas at equilibrium with the atmosphere & the dissolved gas concentration in the ocean mixed layer
- The proportionality constant depends on the gas, wind speed (& other factors such as surface slicks)

$$\text{Flux} = k * (C_m - C_o)$$

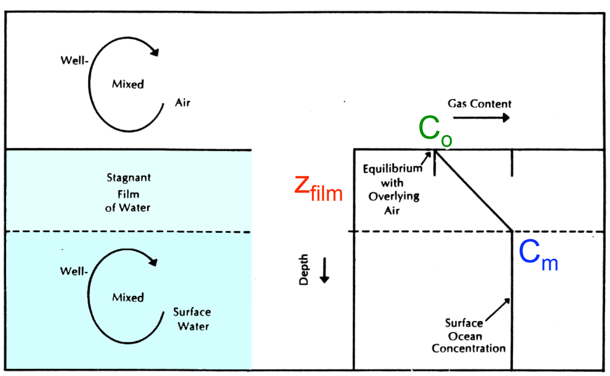
where:

C_m = dissolved gas conc. in ocean mixed layer (mol/m^3)
C_o = dissolved gas conc. at equilibrium w/ atmosphere
= gas conc. in air / H
H = Henry's law const. (ratio of conc. in air to equil. conc. in H_2O,T)
k = proportionality const. relating 1-way gas flux to its conc. in H_2O

- Flux units = $moles/m^2/yr$; k units = $[moles/m^2/yr] / [mol/m^3]$ = m/yr
- Microphysics of gas exchange not well understood. Conceptual models commonly used to estimate gas exchange rates.

Adapted from Ed Boyle 12.842 Lecture 2008

Stagnant Film Model



$$\text{Flux} = D*(C_m - C_o) / z_{film}$$

Where:

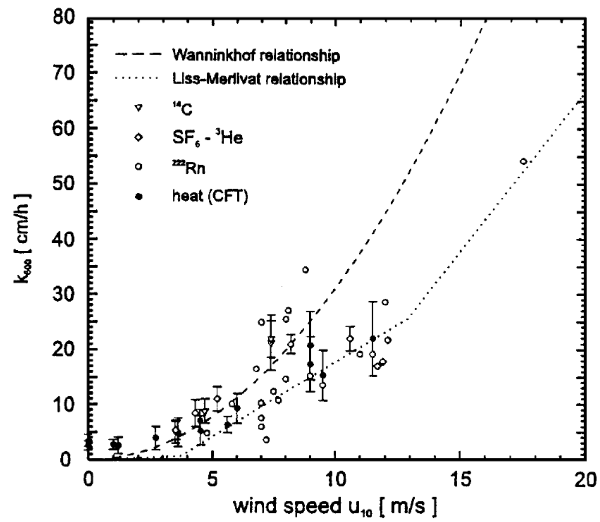
C_m = dissolved gas conc. in ocean mixed layer
C_o = dissolved gas conc. at surface (equil. w/ atmos.)
z_{film} = thickness of stagnant film (~ 30 μm, varies with wind)
D = diffusion coeff. of gas (~ 10^{-5} cm^2/sec, varies with gas)

Note: $k = D / z_{film}$

- Thin film of "stagnant" water separates well-mixed air from well-mixed water
- Gases transferred between air & water by molecular diffusion through film
- Assumes gas conc. at equilibrium w/ air at top of film & = surf. ocean @ bottom
- Film thickness decreases as agitation (i.e., wind speed) increases (~30 μm)

Adapted from Ed Boyle 12.842 Lecture 2008, Broecker & Peng (1984)

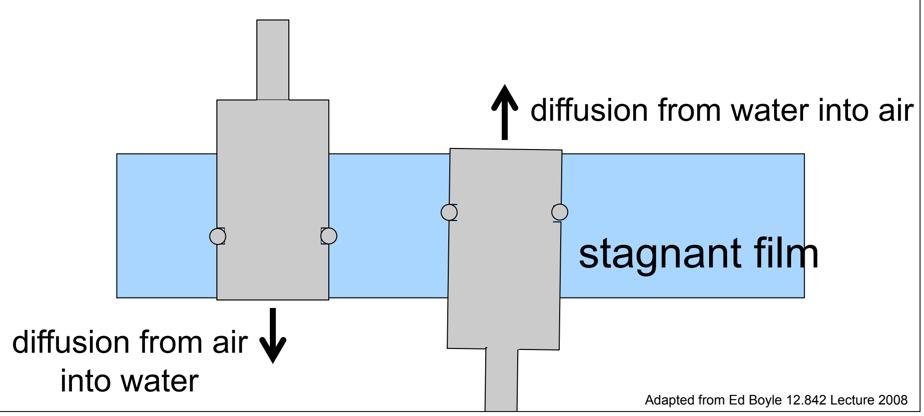
Gas Exchange (k = D / z_{film}) Coefficient Increases With Wind Speed



Jahne & Haußecker (1998) Air-water gas exchange, *Ann. Rev. Fluid. Mech.* Vol. 30: 443-468.

Piston velocity

- k (= D / z_{film}) is called the "**piston velocity**" because it has units of length per time & behaves like two pistons driving dissolved gases into & out of ocean mixed layer
  - May be more logical & intuitive to interpret k as an "exchange coefficient" instead of literally as a ratio of diffusion to film thickness
- The piston velocity for CO_2 in the ocean is about 2000 m/yr!



Adapted from Ed Boyle 12.842 Lecture 2008

Ballpark Estimate of Exchange of CO_2 Exchange Rate Between Ocean & Atmosphere

$$2000 \text{ m yr}^{-1} * 10^{-5} \text{ moles kg}^{-1} * 1000 \text{ kg m}^{-3} = 20 \text{ moles m}^{-2} \text{ yr}^{-1}$$

Piston velocity	conc. of gaseous dissolved CO_2	conversion Factor for H_2O	Exchange rate of CO_2 across air/sea interface

How are Gas Exchange Rates (Coefficients) Determined?

- Radon-222 deficit
- Atmosphere-ocean ^{14}C difference
- Tracer release experiments (SF_6, ^3He)
- Eddy covariance

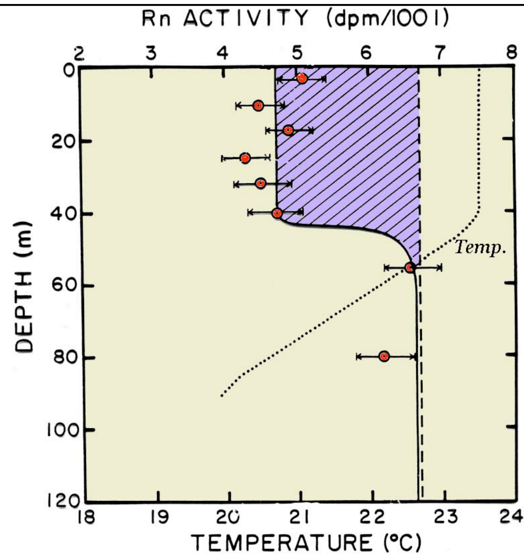


Figure 3-3. Concentration of radon gas as a function of depth at Atlantic GEOSECS station 57 (24°S 35°W). The concentration expected if no radon were escaping to the atmosphere is shown by the dashed line. The difference between this equilibrium value and the observed value is a measure of the amount of radon lost to the atmosphere. The shaded area is a measure of the total amount of radon lost to the air. From the amount of missing radon it is possible to determine the piston velocity for gas exchange. The dotted line is the temperature profile at this station defining the depth of the wind stirred layer. These results were obtained as part of the GEOSECS program (175). *Broecker and Peng (1984)*

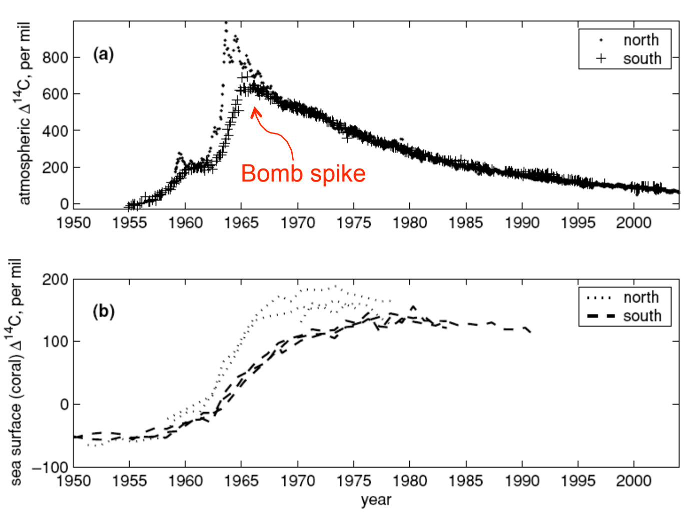
^{222}Rn Deficit Method For Determining Gas Exchange Rates

$z_{film} = D / k$

$= [D_{Rn\text{-}222}/\lambda_{Rn\text{-}222} * h] * [1/(A_{Ra\text{-}226}/A_{Rn\text{-}222})-1]$

Adapted from Ed Boyle 12.842 Lecture 2008

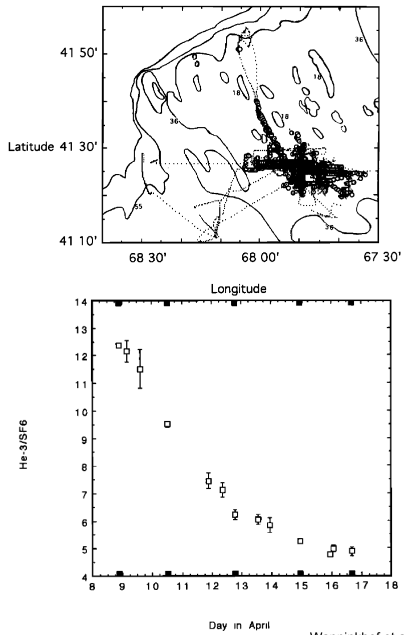
Air-Sea CO_2 Exchange from "Bomb ^{14}C"



- Above-ground nuclear bomb tests in 1950s-1960s doubled the inventory of ^{14}C in the atmosphere
- Attenuated bomb ^{14}C signal in ocean places strong constraint on CO_2 gas exchange rate

Krakauer et al. (2006) *Tellus* Vol. 58B: 390-417

Dual Gaseous Tracer Release Technique



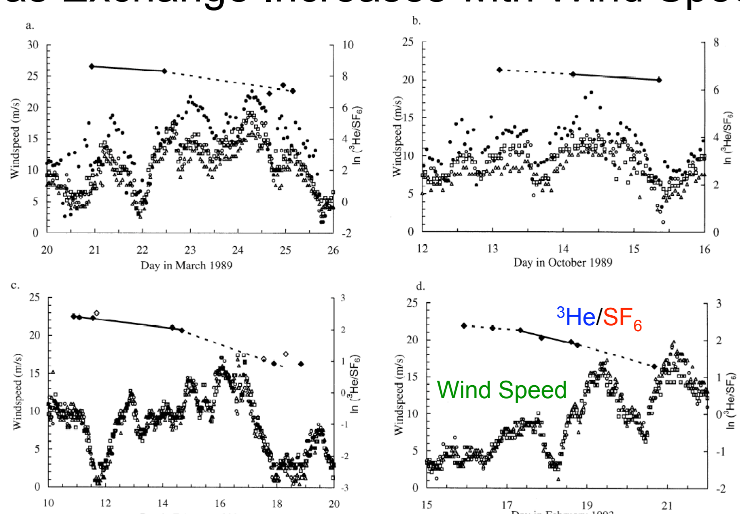
- Used to separate advective & gas transfer components of mass loss in a deliberate tracer experiment
- Two gaseous tracers with widely different (known) rates of escape
- Nonvolatile tracer used to monitor dispersion of patch while change in nonvolatile to volatile tracer ratio over time near center of patch indicates loss due to gas transfer
- Combination of ^3He & SF_6 works well in ocean b/c escape rates differ by 3x, nontoxic, stable, & non-reactive
- Gas transfer velocity expressed as

$$k = h/(t_2 - t_1)\ \ln (R_{wt1}/R_{wt2})$$

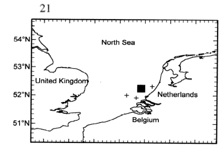
where R_{wt} is the ratio of volatile (SF_6) to nonvolatile (^3He) tracer at time t.

Wanninkhof et al. (1993) *J. Geophys. Res.*, 98(C11), 20237-20248.

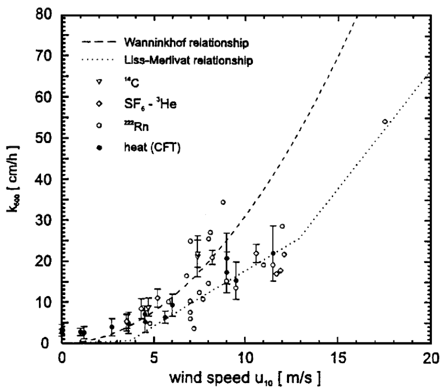
Gas Exchange Increases with Wind Speed



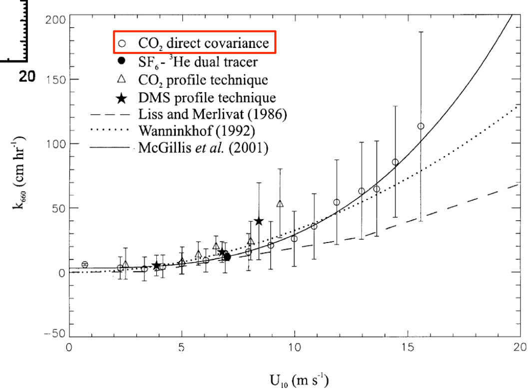
- Higher wind speeds lower $^3He/SF_6$ ratio b/c they cause increased loss of less volatile gas (^3He)



Nightingale et al. (2000) *Glob. Biogeochem. Cycl.* Vol. 14(1): 373-387.



Different techniques for determining wind speed dependence of gas exchange rates vary by a factor of 2 or more…



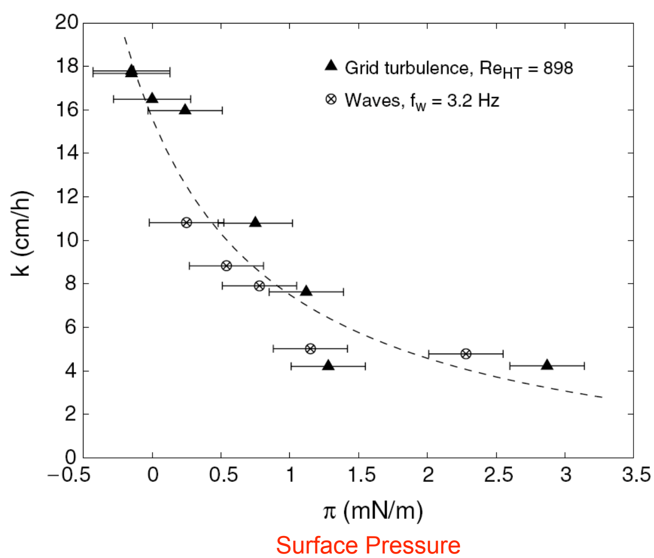
…& uncertainty for all techniques higher at high wind speeds

Eddy covariance:
Flux = ∫v(t)C(t) dt

Jahne & Haußecker (1998) *Ann. Rev. Fluid. Mech.* Vol. 30: 443-468.

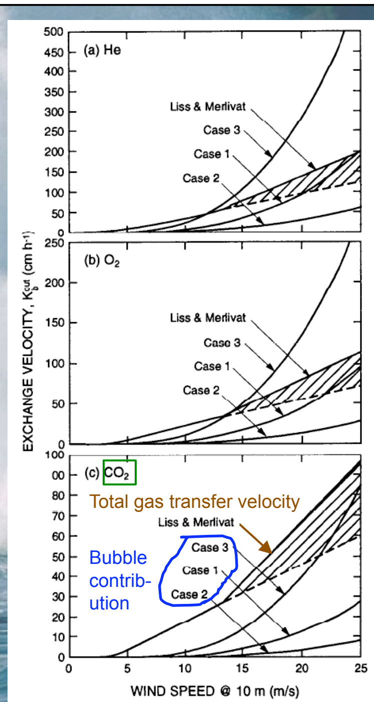
McGillis et al. (2001) *Mar. Chem. Vol.* 75(4): 267-280.

Surface Slicks (Surfactants) Retard Gas Exchange



- Surfactants increase surface pressure of water
- Increasing surface pressure results in decreased gas exchange rate

McKenna & McGillis (2004) *Int. J.Heat Mass Transfer* Vol. 47(3): 539-553.



Effect of Bubbles on Air-Sea Gas Exchange

- Bubble-induced gas transfer velocity as a function of wind speed for He, O_2 & CO_2 (from a model)
- Bubbles may make an important contribution to net gas exchange at wind speeds >10 m/sec.
- The global-mean supersaturation of CO_2 induced by bubbles is not larger than 0.3% & is likely around 0.08%.
- A major uncertainty results from a lack of information on production rates & distributions of large bubbles.

Keeling, R.F. (1993) *J. Mar. Res.* Vol. 51: 237-271.

Outline of Processes Influencing Air-Sea Exchange of CO_2

1. Physical Processes
   - Air-sea gas exchange = f (wind speed, bubble injection, surfactants)
   - 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

The Role of Ocean Circulation in Air-Sea Exchange of CO_2

- CO_2 in the atmosphere equilibrates with the ocean mixed layer on a timescale of ~1 yr.
  - We will do this calculation after discussing the chemistry of ocean uptake of CO_2.
- But when atmospheric CO_2 rises (e.g., from fossil fuels) the ocean's uptake of that CO_2 is limited by the rate of penetration of surface waters into the ocean interior.
  - That is why the mean age of fossil-fuel CO_2 is ~28 years.
- Ocean circulation & the rate at which surface waters enter the deep sea are therefore central in determining air-sea CO_2 exchange (on 10^1-10^2 yr time scales).

Ocean Circulation & Air-Sea CO_2 Exchange

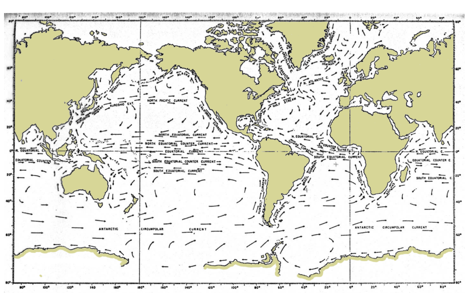
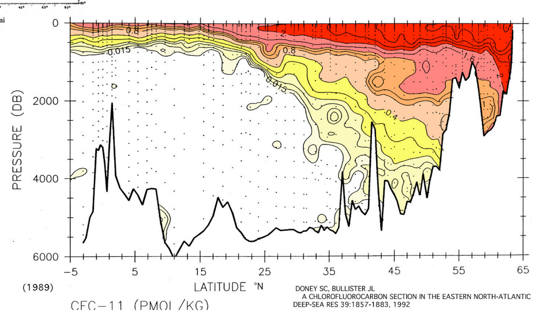


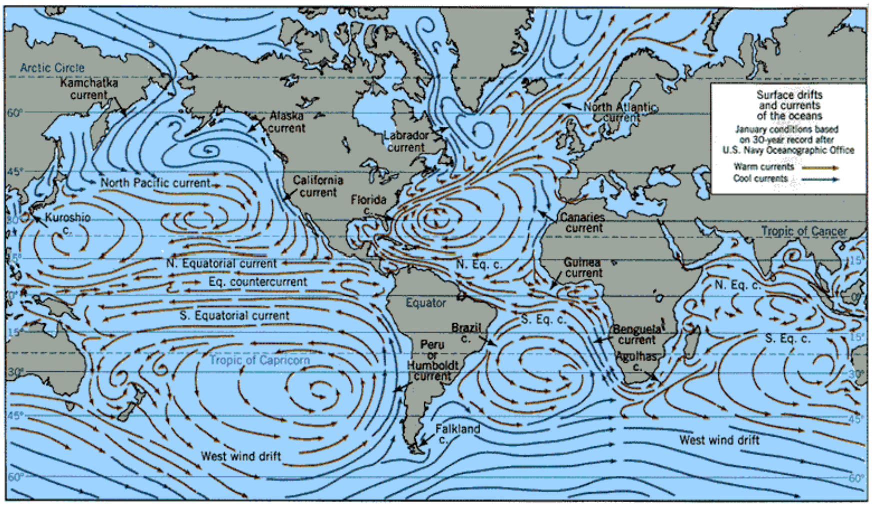
Figure 3-13 Major features of the surface circulation of the oceans. From McLellan, 1965:opposi p. 42. Reprinted by permission of Pergamon Press and H. McLellan.

- Ocean circulation overview

- Transient tracers



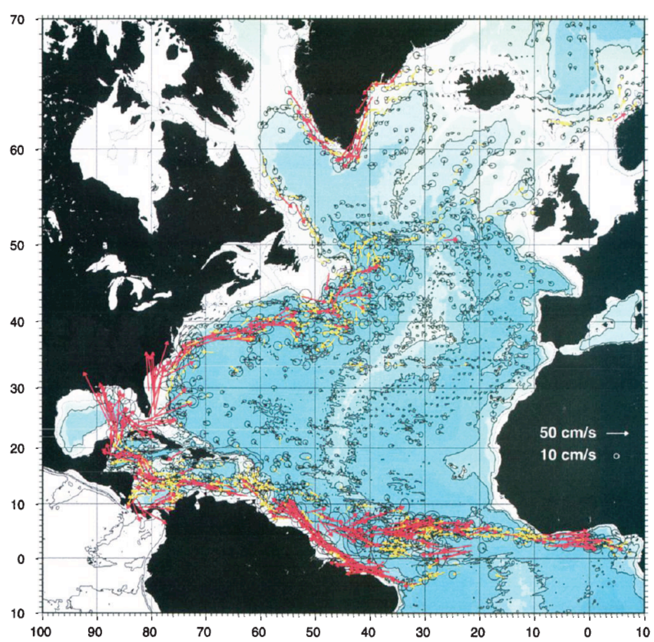
Ocean Surface Currents



• Often called the wind-driven circulation

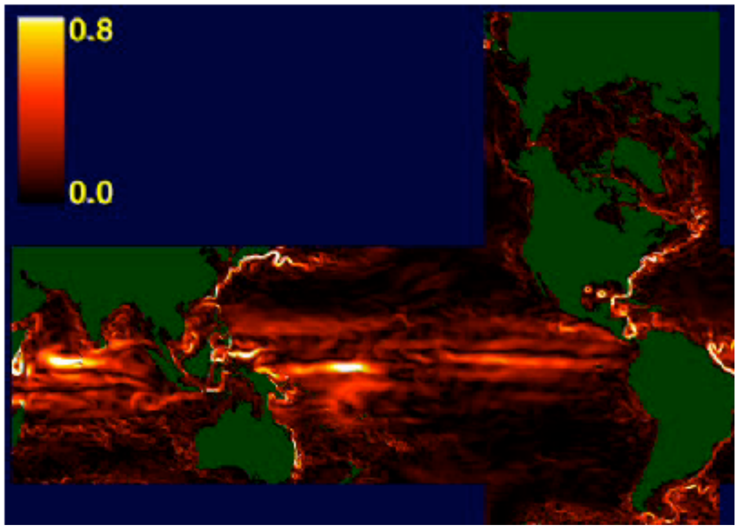
http://mynasadata.larc.nasa.gov/images/L9_OceanCurrentsUSNOO.gif

Surface Circulation of the North Atlantic from Drifters

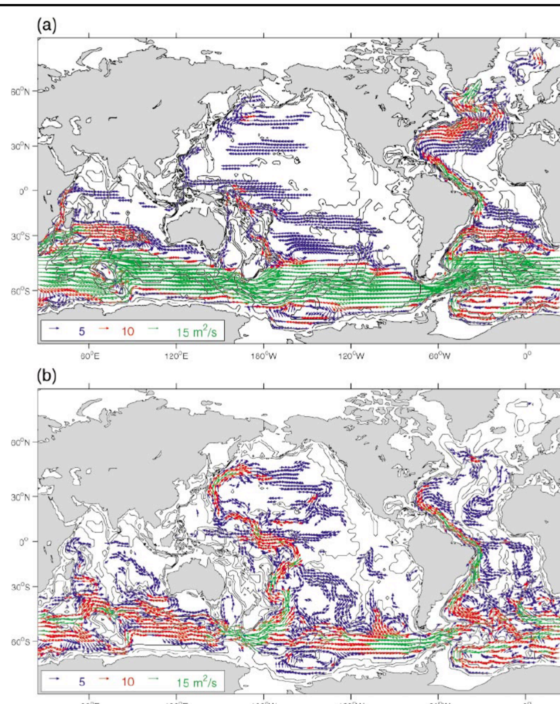


• Decadal average surface velocities in 1° grid boxes

Global Ocean Surface Velocities from an Ocean GCM



MITgcm - MIT Climate Modeling Initiative - NASA



Deep Ocean Circulation

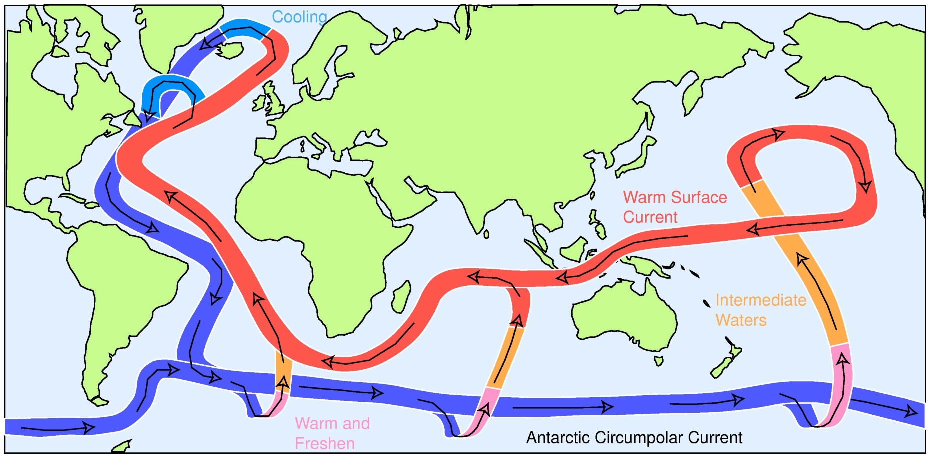
- Volume transports:

Intermediate Layer (985 - 2200 m)

Deep Ocean (2200 m – seafloor)

Lu & Stammer (2004) *J. Phys. Oceanogr.* Vol. 34(3): 605-622

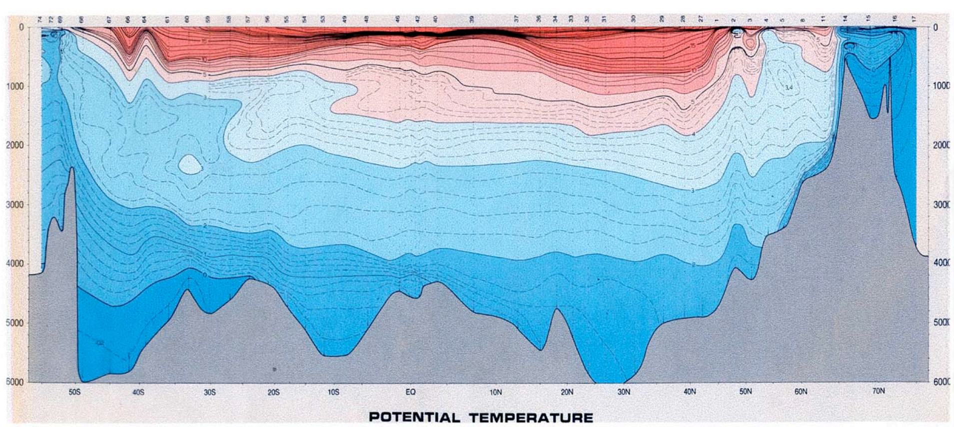
Thermohaline (Meridional Overturning) Circulation



From John Marshall, MIT

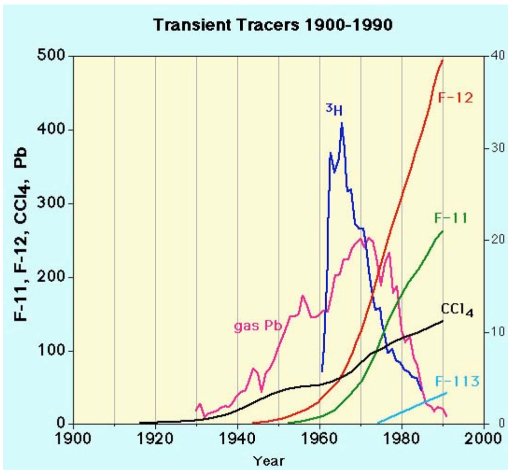
Western Atlantic Potential Temperature* Section

- Combined circulations produce the observed temperature field
- Rather different than might be expected for a stagnant fluid heated at the surface!



* The temperature a fluid would have if adiabatically (no heat loss or gain) brought to a standard reference pressure, usually 1000 millibars (used b/c fluid is heated when pressurized)

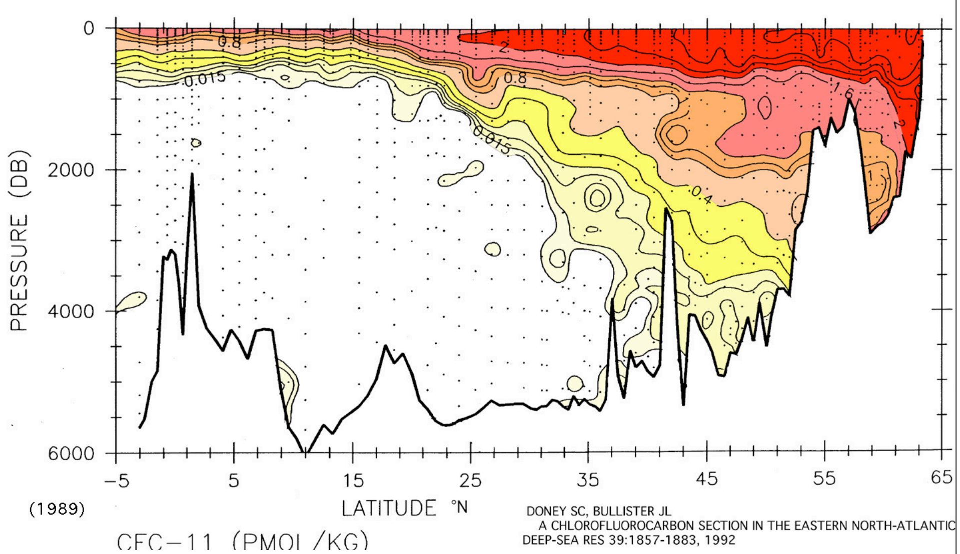
Transient Tracers



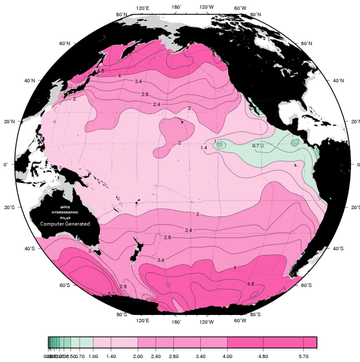
- Tritium (^3H) & ^{14}C were added to the atmosphere from nuclear bomb tests in the 1950's-60's, & chlorofluorocarbons (CFCs) began to be added in ~1950.
- Unlike CO_2 these tracers began entering the ocean only within last ~50 yr.
- They can therefore be used to estimate how much of the ocean has been in contact with the surface during that time.

Adapted from Ed Boyle 12.842 lecture notes, MIT, 2008

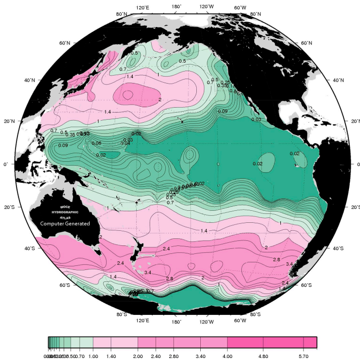
CFC 11 in the North Atlantic Ocean



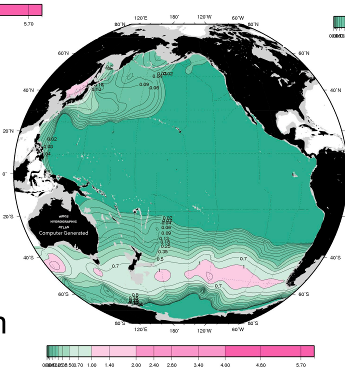
CFC-11 in the Pacific Ocean



100 m



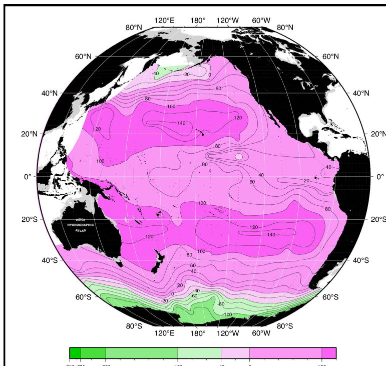
500 m



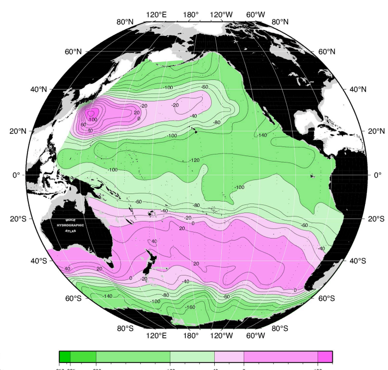
1000 m

WOCE Atlas Vol. 2, Pacific Ocean, 2007

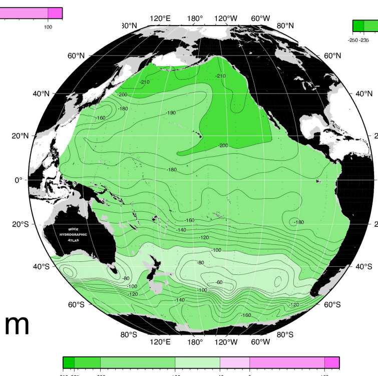
^{14}C in the Pacific Ocean



100 m



500 m

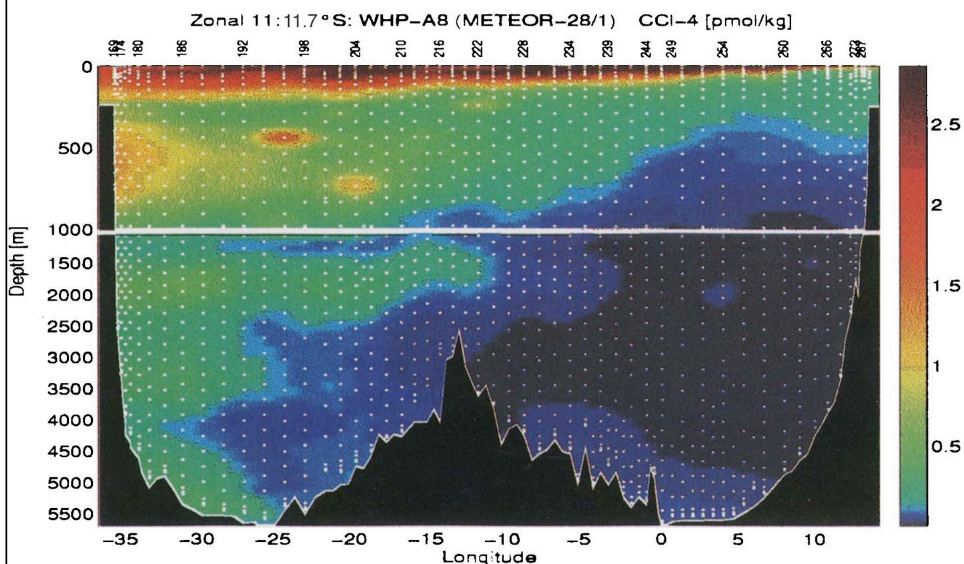


1000 m

Units are $\Delta^{14}C$, or ‰ relative to 1950 wood

WOCE Atlas Vol. 2, Pacific Ocean, 2007

CCl_4 zonal section in the South Atlantic (11.7°S)



Distribution of CCl_4 (pmol/kg) on A8, see Fig. 6.

Roether & Putzka (1996)