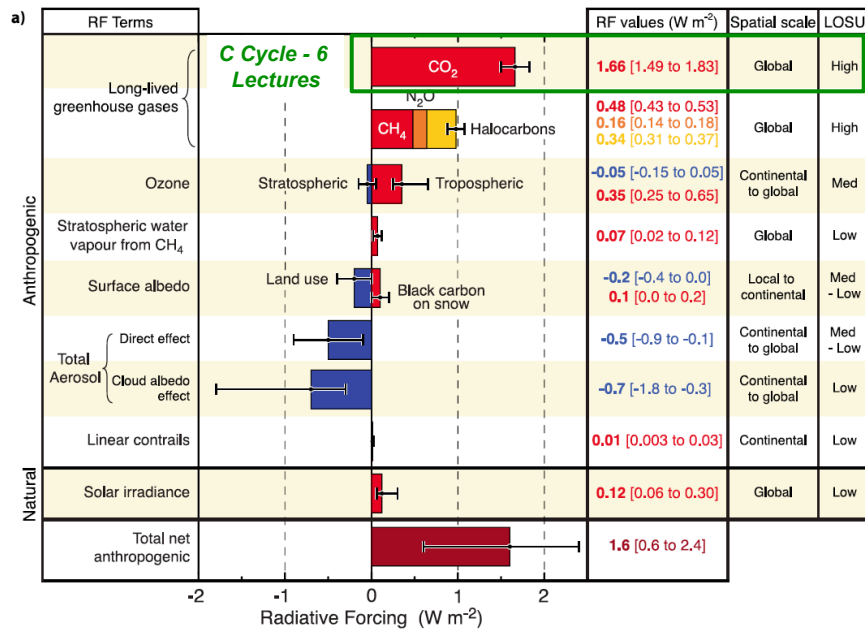


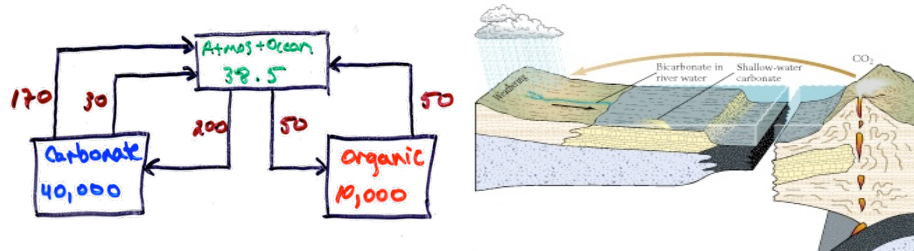
Global Mean Radiative Forcings



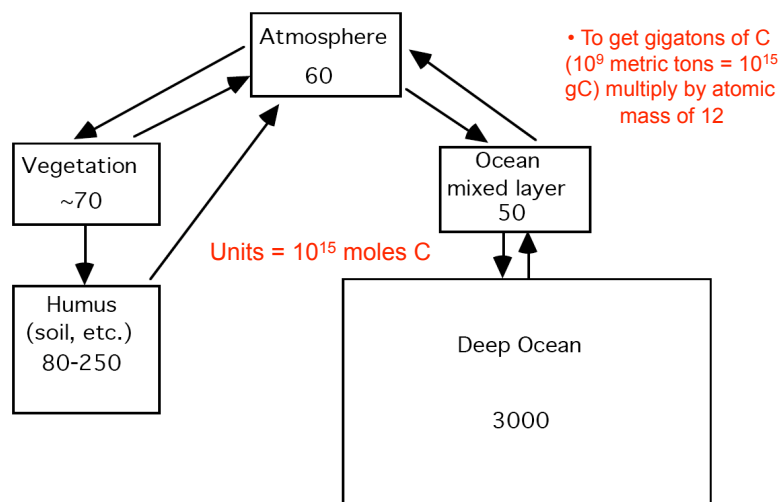
PCC 588, Pt. II: The Global Carbon Cycle

- 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 CO₂ exchange I
- Emerson & Hedges 2007 Ch. 11
- Thurs 2/5 Atmosphere-ocean CO₂ exchange II
- Tues 2/10 Atmosphere-ocean CO₂ exchange III. Glacial-Interglacial CO₂ (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

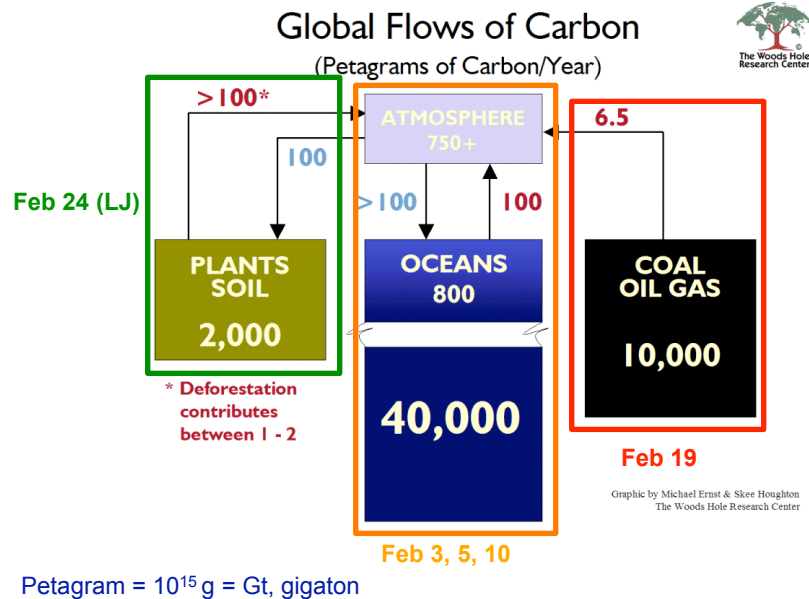


Carbon Reservoirs on Earth's Surface



- Large size of ocean w.r.t. atmosphere reservoir + rapid exchange between = focus on ocean-atmosphere CO₂ interactions

Primary Carbon Fluxes Today



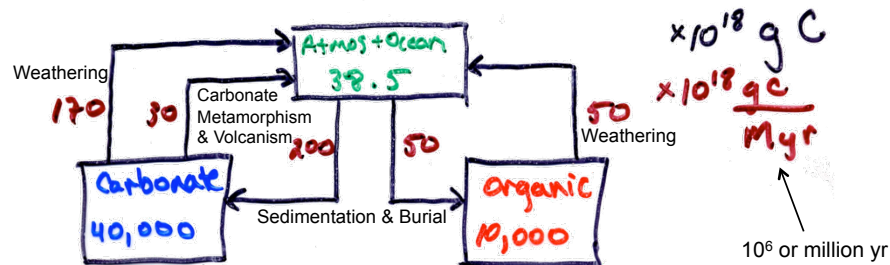
The Long-Term Carbon Cycle: Tectonics & Weathering

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** (~1000x more than in **ocean + atmosphere**) & as **organic material (kerogen)** in rocks (~250x 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 CO₂ greenhouse effect



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

Amended 1/30/09

The Long-Term Biogeochemical Carbon Cycle

1. Organic Carbon Burial and Weathering

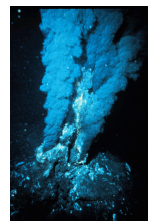


2. Tectonics: Seafloor Spreading Rate

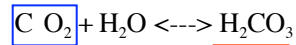
- Mantle CO₂ from Mid-Ocean Ridges

3. Carbonate-Silicate Geochemical Cycle

- Chemical Weathering Consumes CO₂
- Carbonate Metamorphism Produces CO₂



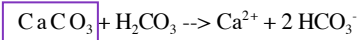
Chemical Weathering = chemical attack of rocks by dilute acid



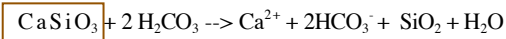
The **Geochemical**
(or non-biological
part of the)
LT **Carbon Cycle**

1. Carbonate Weathering:

Carbonate Rocks (e.g., limestone)



2. Silicate Weathering:



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



- 2x CO₂ 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)

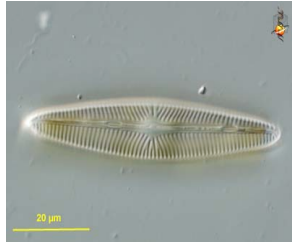
Carbonate rocks
weather faster
than silicate
rocks!

- Rivers
transport
dissolved ions to
ocean

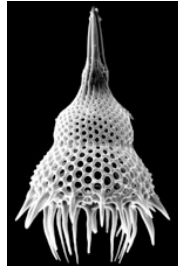


Limestone (carbonate)

Adapted from Kump et al. (1999)



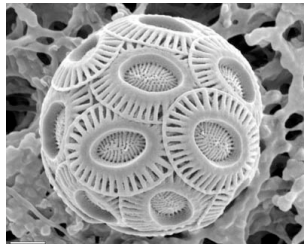
Diatom
(SiO₂)



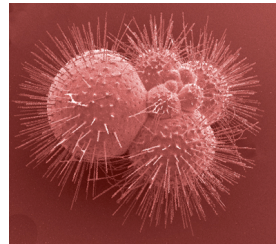
Radiolarian
(SiO₂)

Products of
weathering
precipitated as
CaCO₃ & SiO₂ in
ocean

R, Protozoans
L, Eukaryotic Phytoplankton

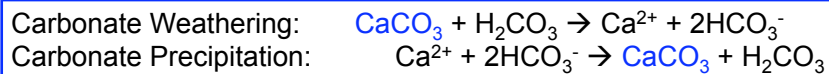


Coccolithophorid
(CaCO₃)



Foraminifer
(CaCO₃)

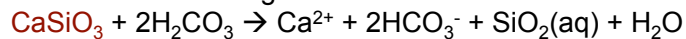
Net reaction of Rock Weathering on Land & (Biogenic) Mineral Precipitation in the Ocean



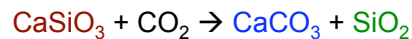
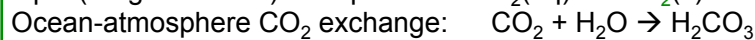
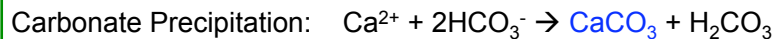
0

Note: Both reactions occur at Earth surface conditions

Calcium-Silicate Weathering:

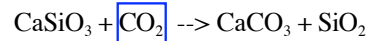


Note: Silicate minerals do not re-form at Earth surface conditions



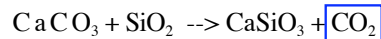
- Ca²⁺ liberated from silicate weathering leaves ocean as CaCO₃
- 2 mol H₂CO₃ req'd to weather CaSiO₃ *but* only 1 mol H₂CO₃ liberated during CaCO₃ precipitation

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



- CO₂ consumed (~ 0.03 Gt C/yr)
- Would deplete atmospheric CO₂ in 20 kyr (τ_R w.r.t. weathering)
- Plate tectonics returns CO₂ via Volcanism and Metamorphism

Carbonate Metamorphism

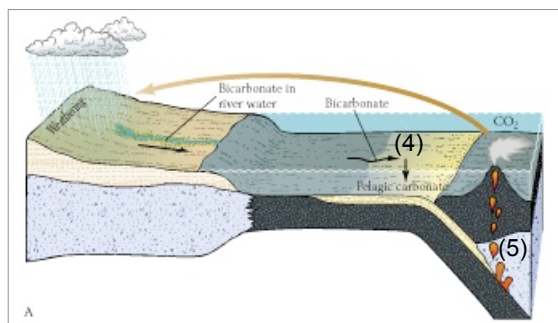
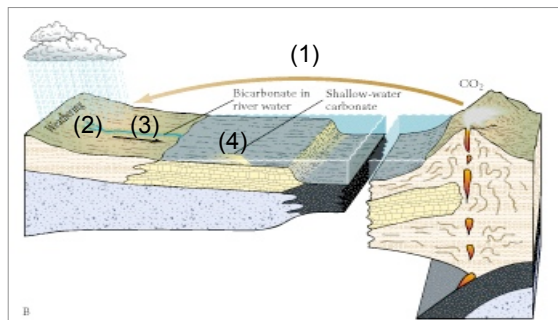


- CO₂ produced from subducted marine sediments

**Net reaction of
geochemical
carbon cycle
(Urey Reaction)**

- On geologic time scales, rock weathering balanced by carbonate metamorphism

- Any *imbalance* can cause changes in atmospheric CO₂

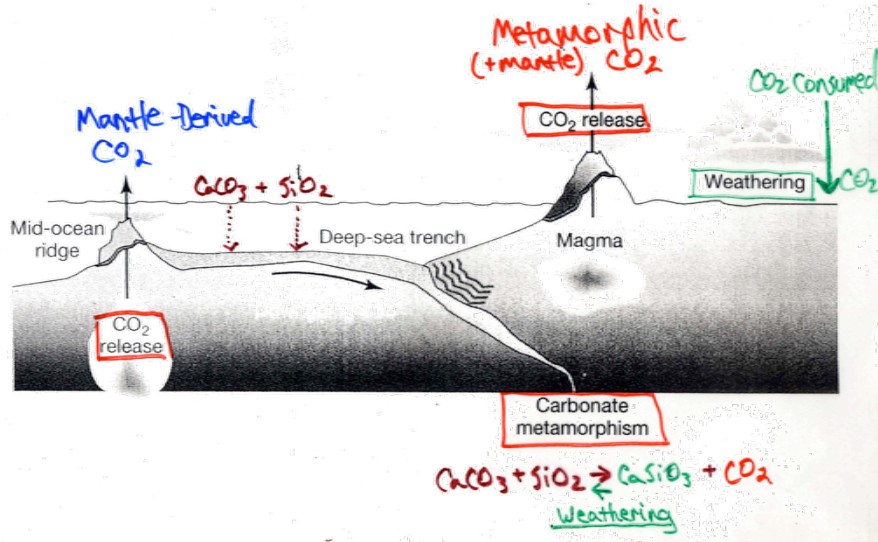


Stanley (1999)

**Carbonate-
Silicate
Geochemical
Cycle**

1. CO₂ released from volcanism dissolves in H₂O, forming carbonic acid
2. H₂CO₃ dissolves rocks
3. Weathering products transported to ocean by rivers
4. CaCO₃ precipitation in shallow & deep water
5. Cycle closed when CaCO₃ metamorphosed in subduction zone or during orogeny.

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:

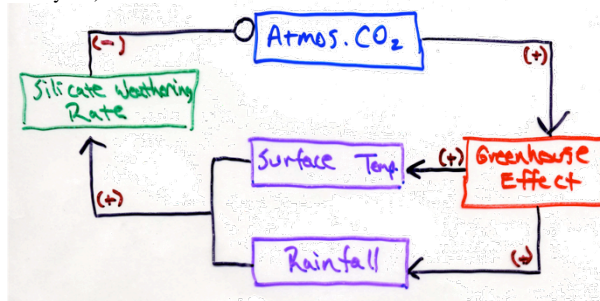
Temp., rainfall enhance weathering rates

(Walker et al, 1981)

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

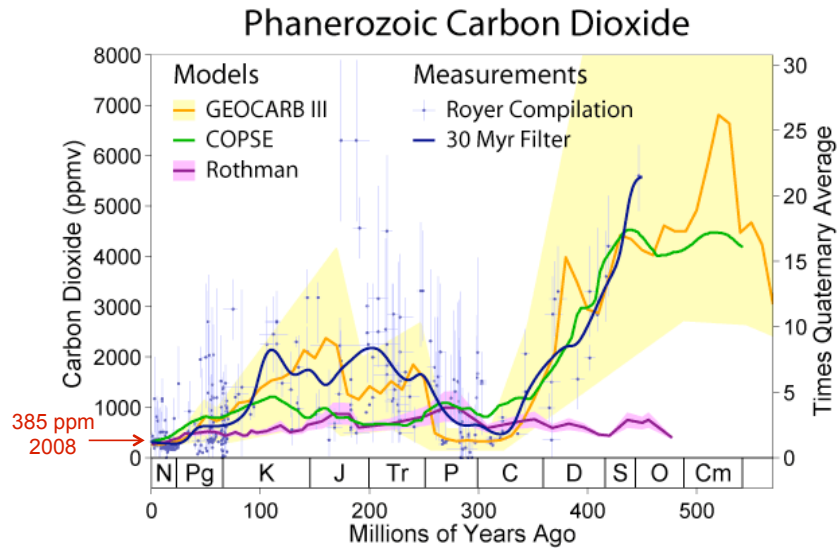
How are CO₂ levels kept in balance on >10⁶-yr time scales?

Feedbacks



Adapted from Kump et al. (1999)

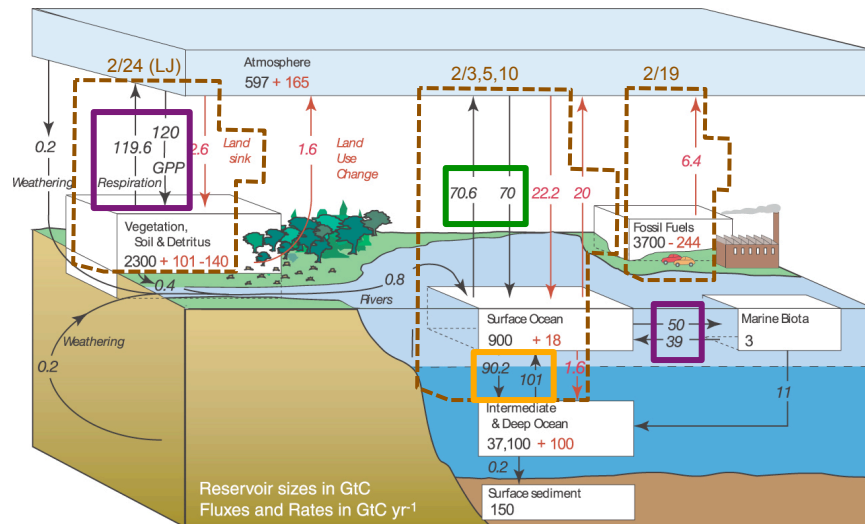
Atmospheric CO₂ During the Last 545 Ma



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: CO ₂ (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):

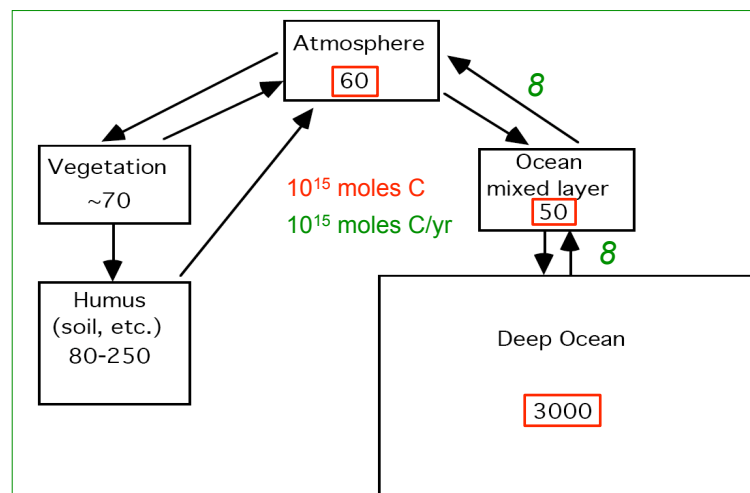
Cumulative Changes (Pg): (1800-1994)	
Fossil Fuels Burnt & Cement Prod.	244
Atmospheric Increase	165
Storage in the Ocean	118
Inferred Terrestrial Change	-39
Partitioning of Anthropogenic Fluxes (1990s) (Pg yr ⁻¹)	
Fossil Fuel and Cement Production	6.3 ± 0.4
Atmosphere Accumulation	3.2 ± 0.1
Uptake by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

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

Pg, petagram = 10¹⁵ g = Gt, gigaton

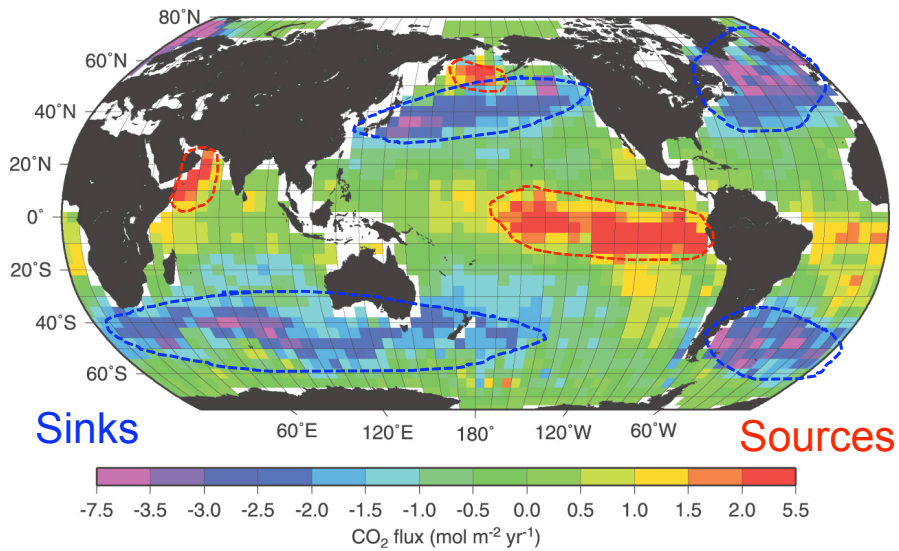
Emerson & Hedges (2007) Table XI-1

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 CO₂ (& GG forcing) on 10¹-10² time scales



• To get gigatons of C (10⁹ metric tons = 10¹⁵ gC) multiply by atomic mass of 12

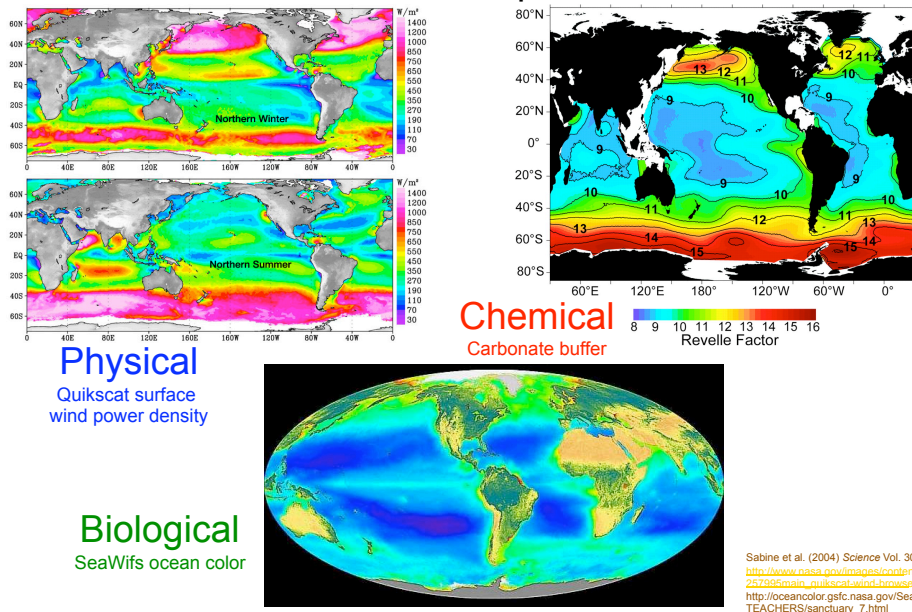
Modern Air-Sea Fluxes of CO₂



■ *What Determines these Fluxes?*

IPCC 2007 Fig. 7.8

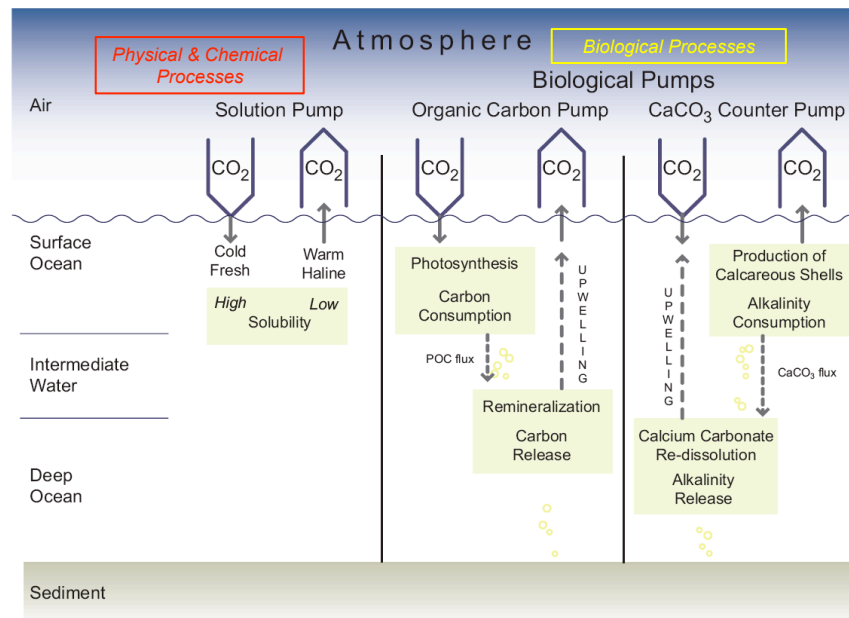
Processes Controlling the Exchange Of CO₂ Between the Atmosphere & Ocean



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) *CO₂ 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 CO₂



IPCC 2007 Fig. 7.10

Outline of Processes Influencing Air-Sea Exchange of CO₂

1. Physical Processes (kinetics)

- Air-sea gas exchange = f (wind speed, bubble injection, surfactants)
- Ocean circulation

2. Chemical Processes

- CO₂ 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 CO₂ 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 ²²²Rn deficit, ¹⁴C uptake, tracer release experiments (SF₆, ³He, *Bacillus globigii*)
- CO₂ that dissolves into surface mixed layer carried into ocean interior by **ocean circulation**

Outline of Processes Influencing Air-Sea Exchange of CO₂

1. Physical Processes

- Air-sea gas exchange = f (wind speed, bubble injection, surfactants)
- Ocean circulation

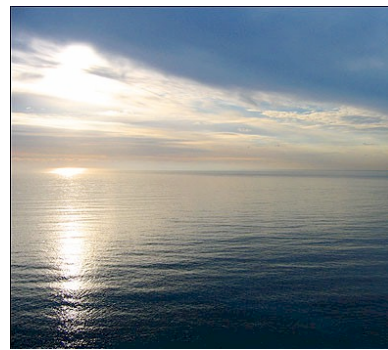
2. Chemical Processes

- CO₂ 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)** that can be enhanced by natural surfactants.
- Some gas exchange also caused by **bubbles** from breaking waves, esp. in high winds. Can help facilitate **equilibrium** (e.g., trapped gas 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

*** Stopped Here - 1/29/09 ***

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/m³)

C_o = dissolved gas conc. at equilibrium w/ atmosphere
= gas conc. in air / H

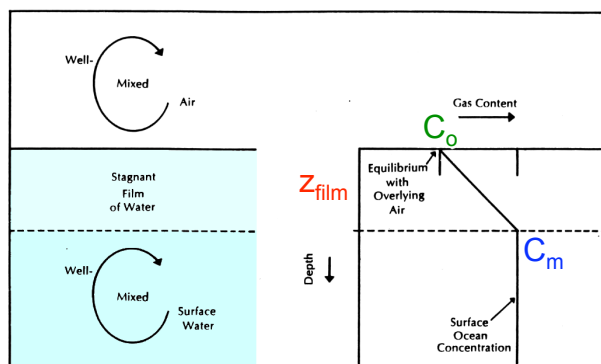
H = Henry's law const. (ratio of conc. in air to equil. conc. in H₂O, T)

k = proportionality const. relating 1-way gas flux to its conc. in H₂O

- Flux units = moles/m²/yr; **k units** = [moles/m²/yr] / [mol/m³] = **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



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

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

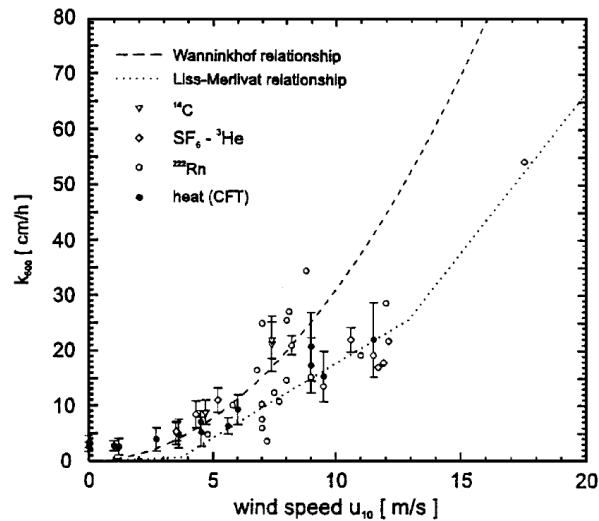
(~ 30 μm, varies with wind)
 D = diffusion coeff. of gas (~ 10⁻⁵ cm²/sec, varies with gas)

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)

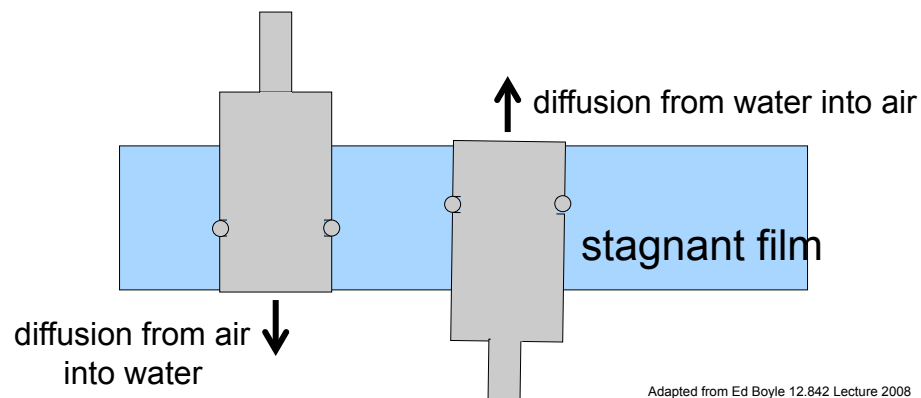
Gas Exchange ($k = D / z_{\text{film}}$) Coefficient Increases With Wind Speed



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

Piston velocity

- k ($= D / z_{\text{film}}$) 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

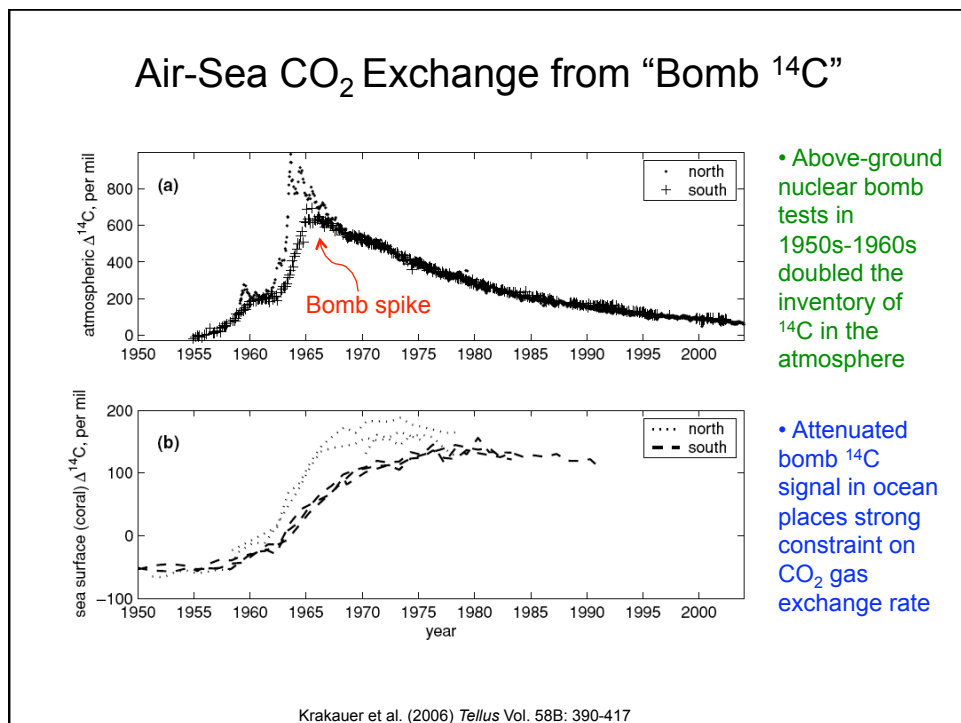
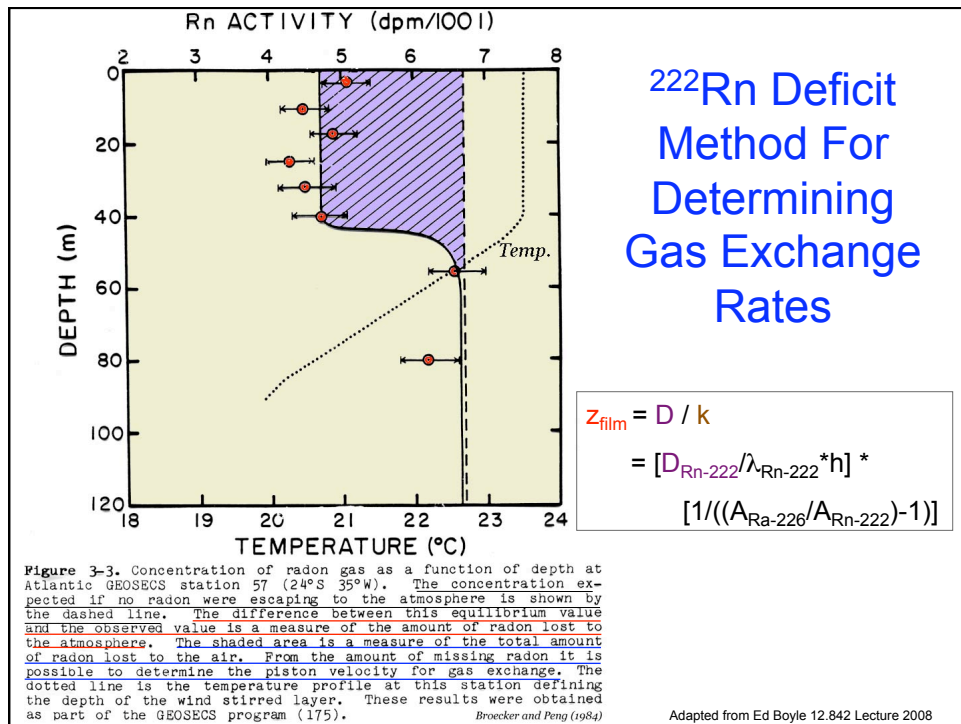
Ballpark Estimate of Exchange Rate of CO₂ Between Ocean & Atmosphere

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

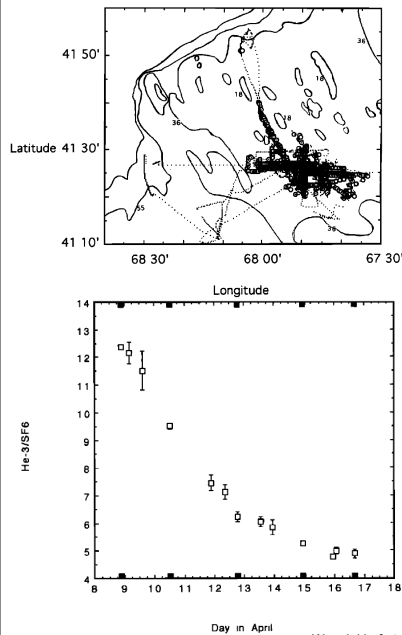
Piston velocity	conc. of gaseous dissolved CO ₂	conversion Factor for H ₂ O	Exchange rate of CO ₂ across air/sea interface
--------------------	--	--	---

How are Gas Exchange Rates (Coefficients) Determined?

- Radon-222 deficit
- Atmosphere-ocean ¹⁴C difference
- Tracer release experiments (SF₆, ³He)
- Eddy covariance



Dual Gaseous Tracer Release Technique



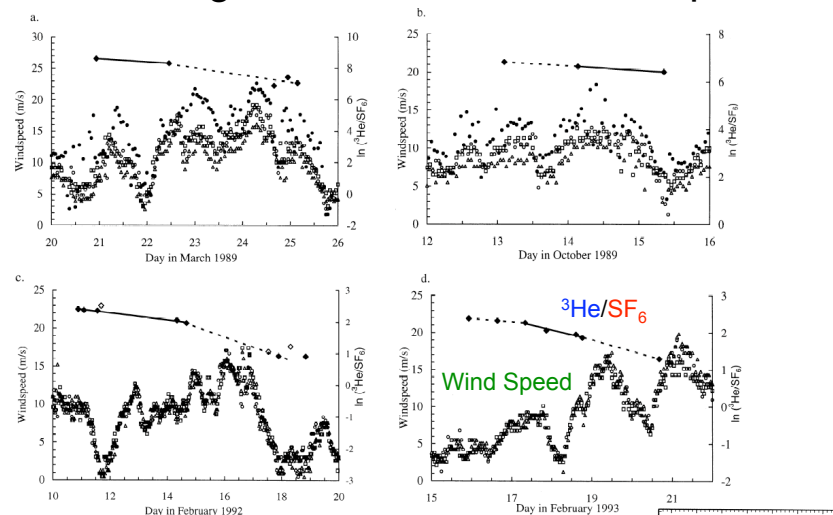
- Used to separate advective & gas transfer components of mass loss in a deliberate tracer experiment
- Two gaseous tracers with widely different (known) rates of escape
- Nonvolatile tracer used to monitor dispersion of patch while change in nonvolatile to volatile tracer ratio over time near center 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 .

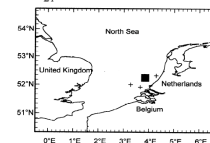
Wanninkhof et al. (1993) *J. Geophys. Res.*, 98(C11), 20237-20248.

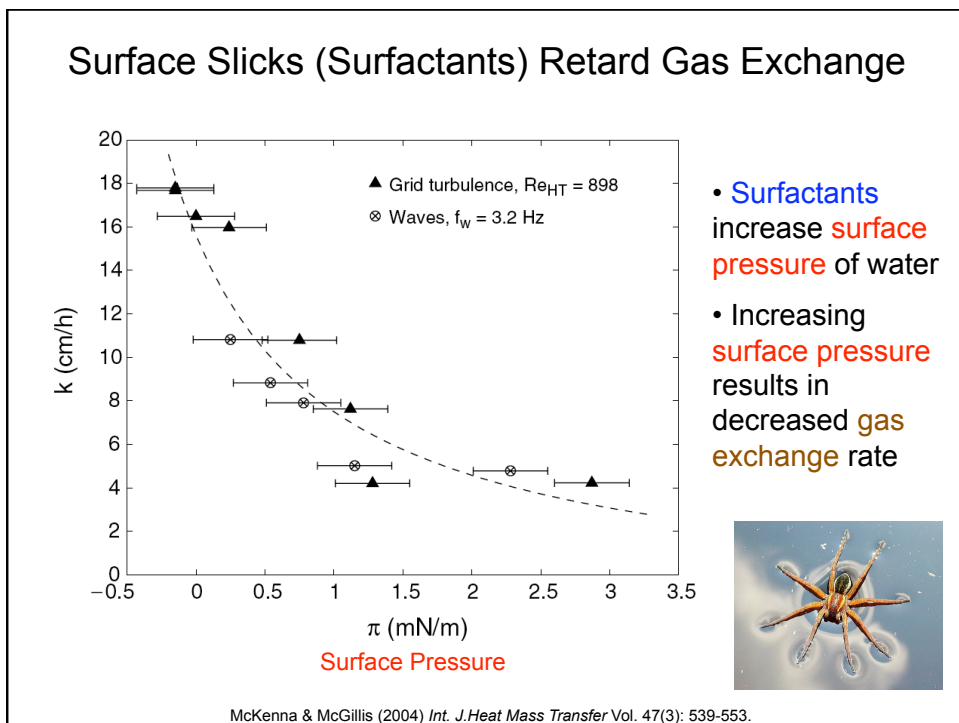
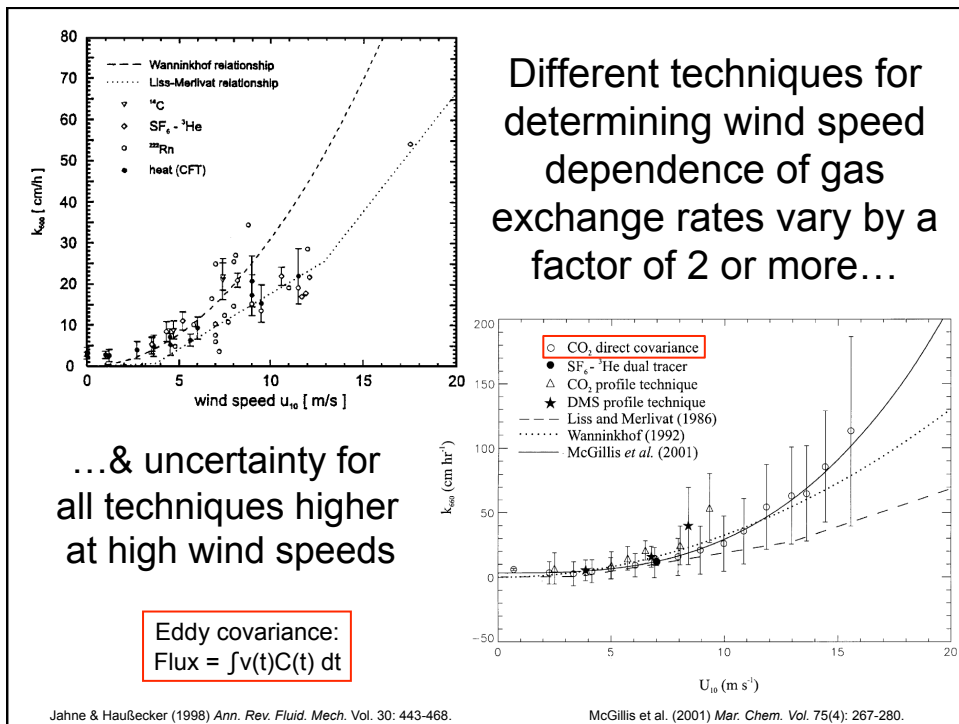
Gas Exchange Increases with Wind Speed



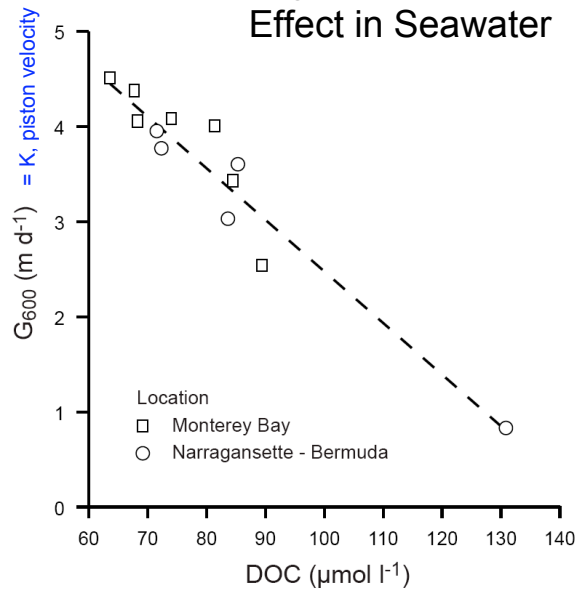
- Higher wind speeds lower $^3\text{He}/\text{SF}_6$ ratio b/c they cause increased loss of less volatile gas (^3He)

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





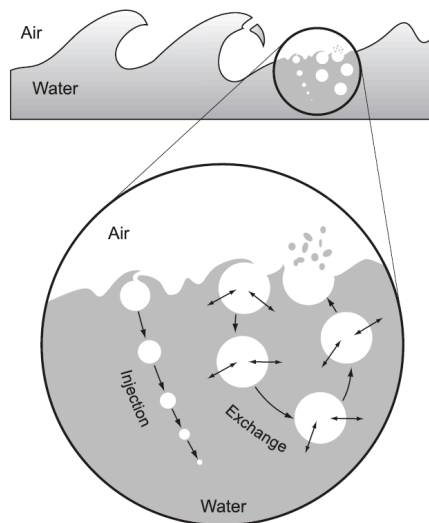
Measuring the Surfactant Effect in Seawater



- Most surfactants are organic
- Gas exchange rates of oxygen were inversely proportional to DOC concentration
- Implies that the organic content affects the interface properties that control gas transfer

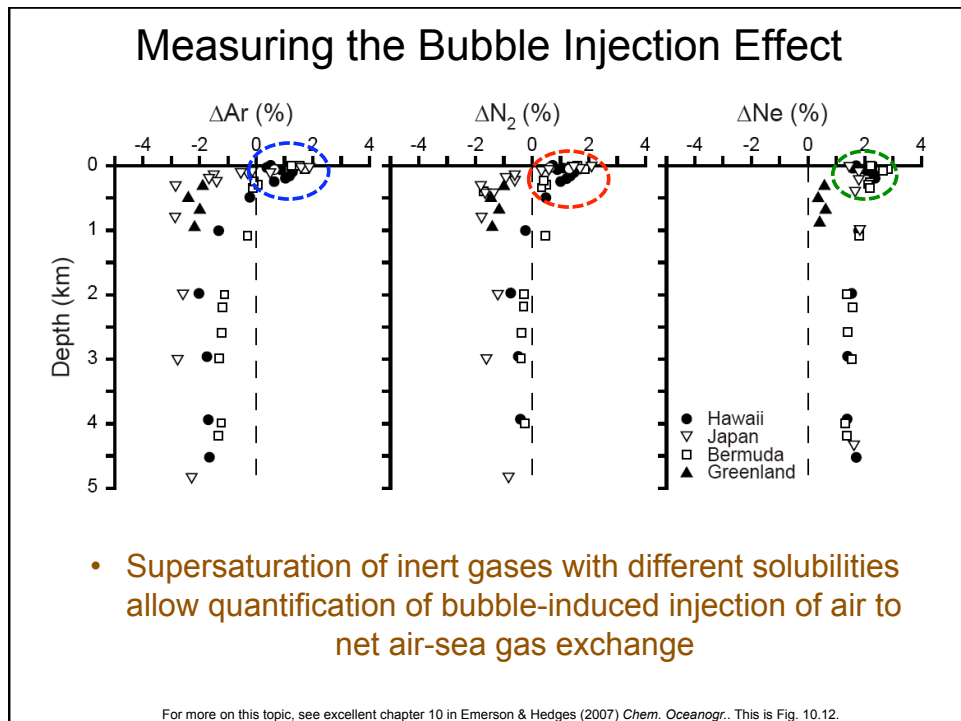
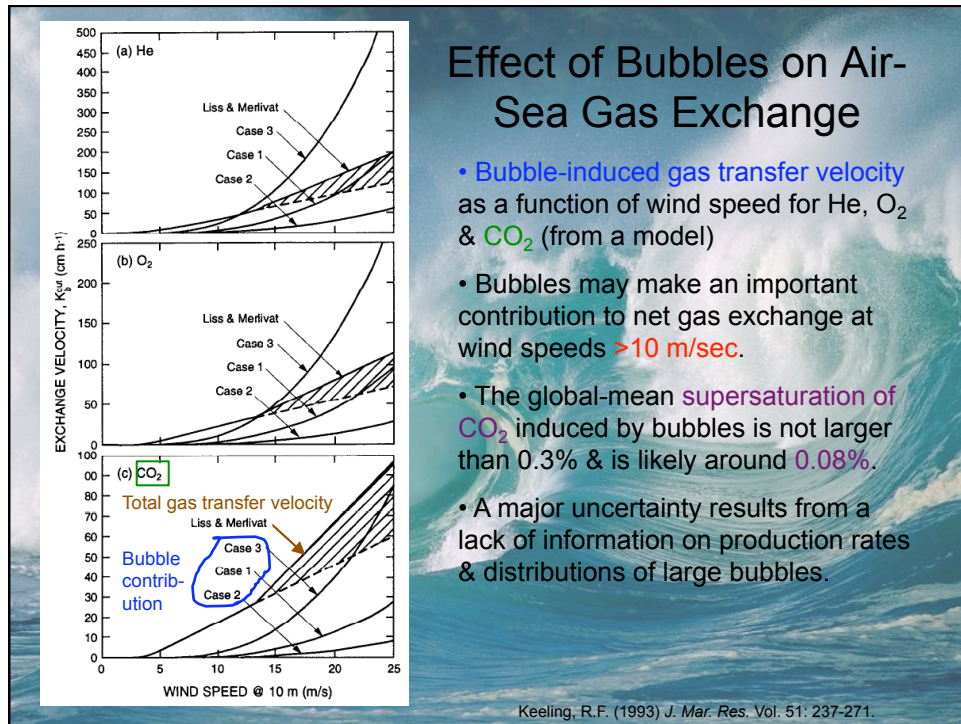
Emerson & Hedges Fig. 10.13, Redrawn from Frew (1997). <http://www.venocoinc.com/images/seepsheen.jpg>

Effect of Bubbles on Air-Sea Gas Exchange



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

Emerson & Hedges (2007) *Chem. Oceanogr.*, Fig. 10.10



Outline of Processes Influencing Air-Sea Exchange of CO₂

1. Physical Processes

- Air-sea gas exchange = f (wind speed, bubble injection, surfactants)
- Ocean circulation

2. Chemical Processes

- CO₂ 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 CO₂

- CO₂ 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 CO₂.
- But when atmospheric CO₂ rises (e.g., from fossil fuels) the ocean's uptake of that CO₂ is limited by the rate of penetration of surface waters into the ocean interior.
 - That is why the mean age of fossil-fuel CO₂ is ~28 years.
- Ocean circulation & the rate at which surface waters enter the deep sea are therefore central in determining air-sea CO₂ exchange (on 10¹-10² yr time scales).

Ocean Circulation & Air-Sea CO₂ Exchange

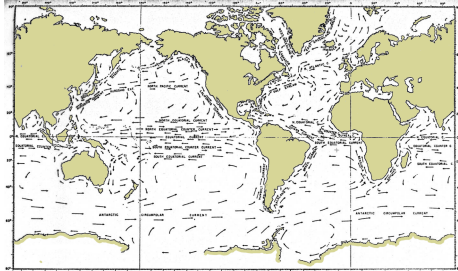
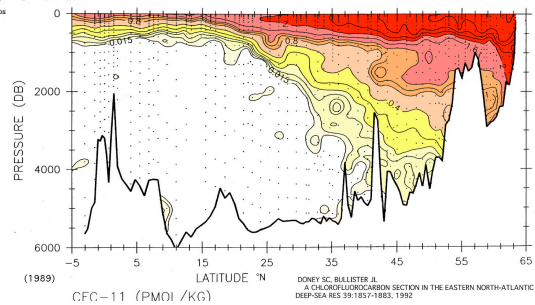


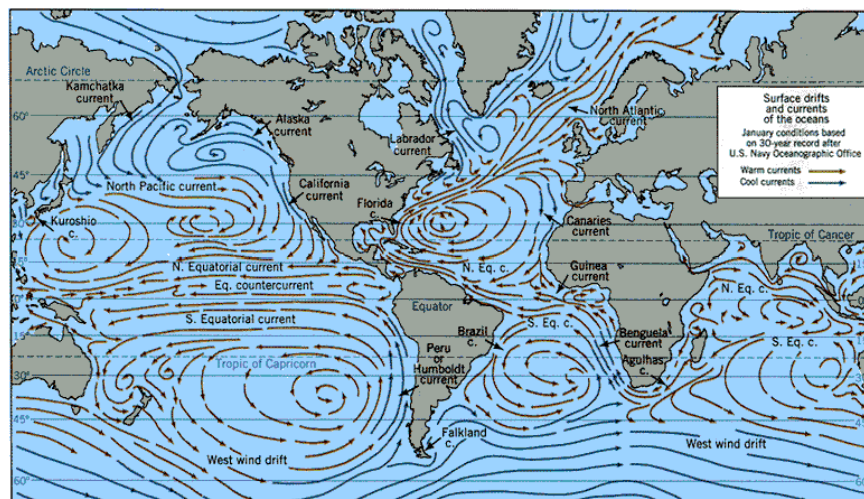
Figure 3-13 Major features of the surface circulation of the oceans. From McLellan, 1965, p. 45. Reprinted by permission of Pergamon Press and H. McLellan.

- Ocean circulation overview

- Transient tracers



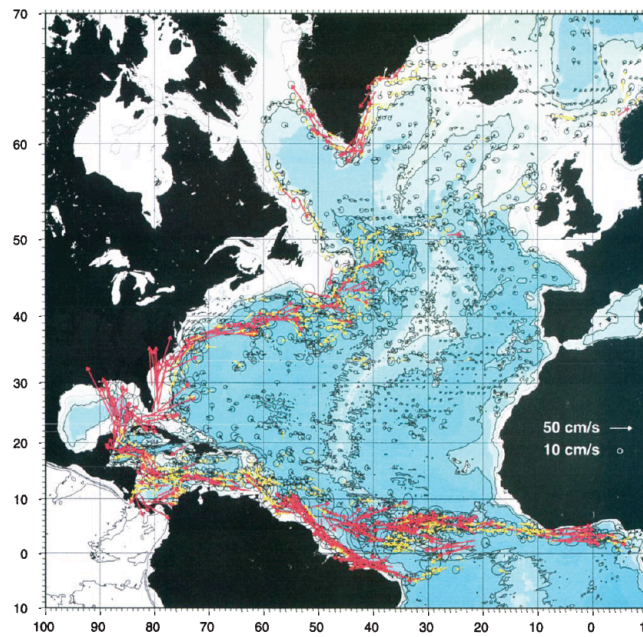
Ocean Surface Currents



- Often called the wind-driven circulation

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

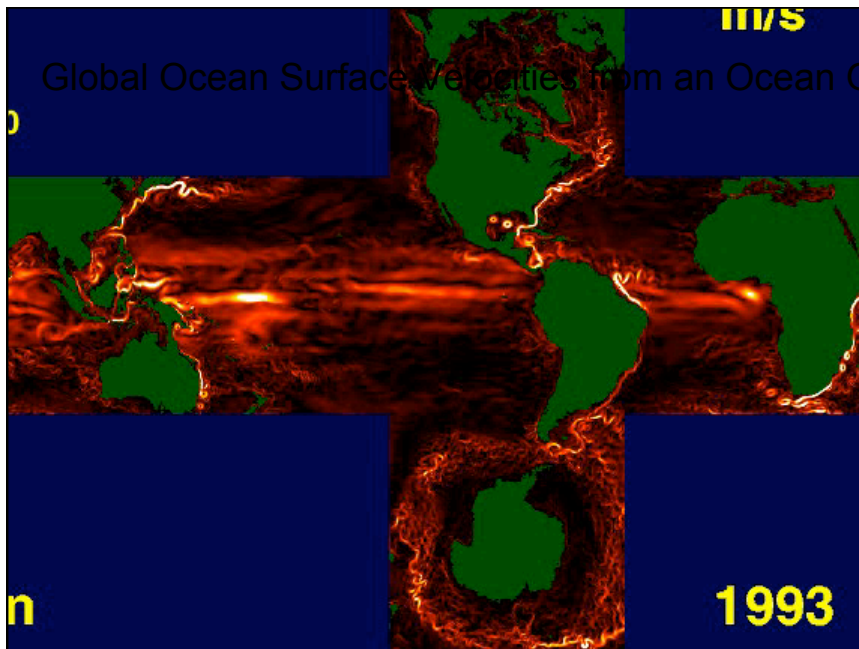
Surface Circulation of the North Atlantic from Drifters



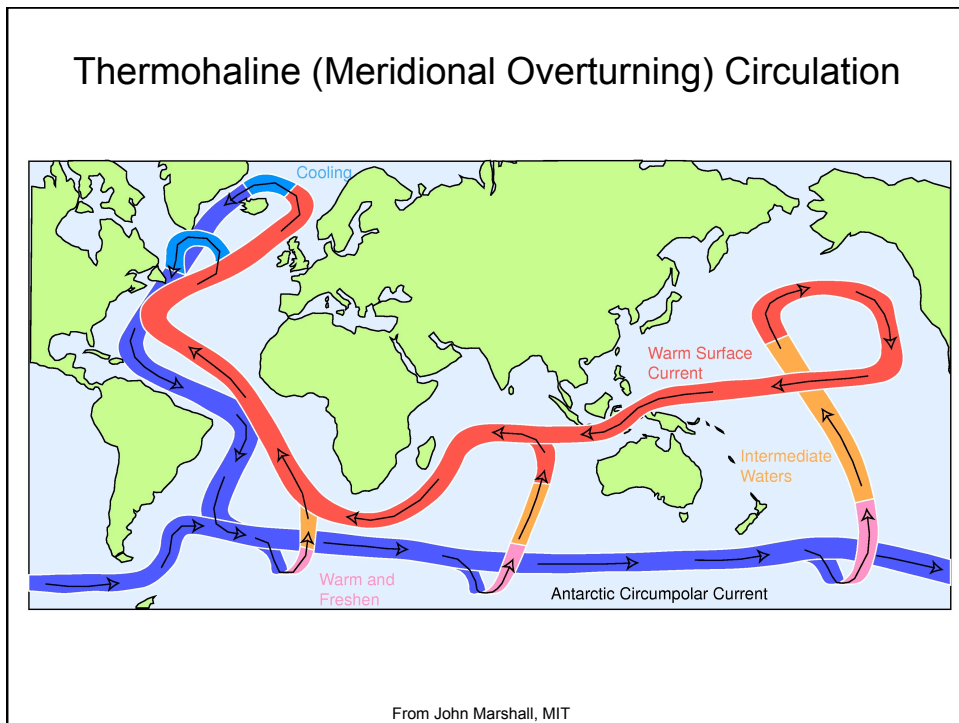
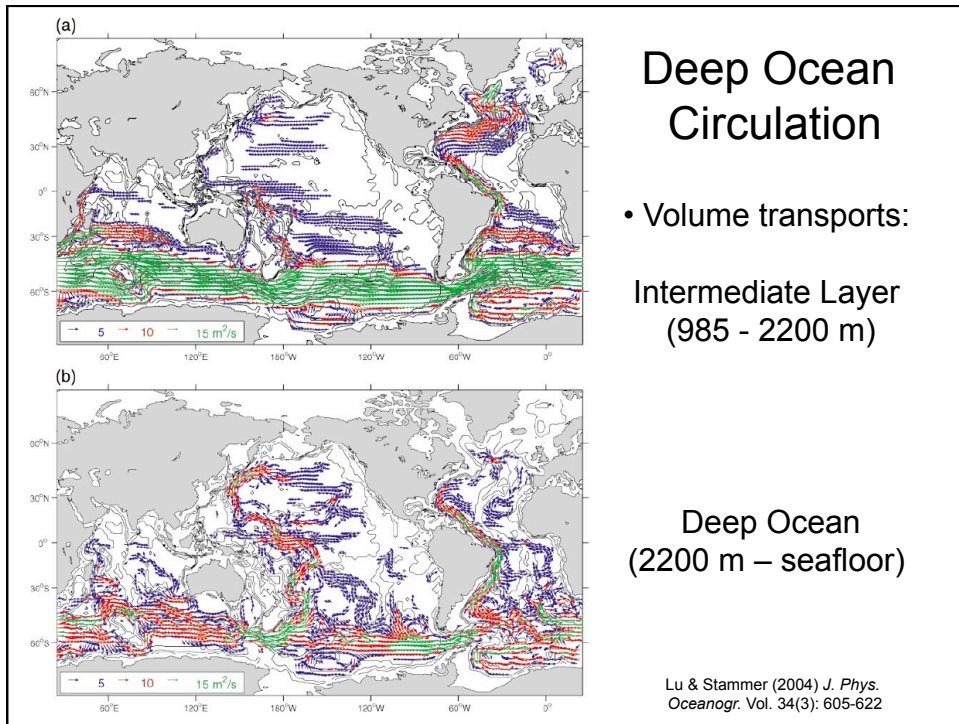
- Decadal average surface velocities in 1° grid boxes

Fratantoni (2001) *J. Geophys. Res.*
Vol. 106(C10): 22067-22093.

Global Ocean Surface Velocities from an Ocean GCM

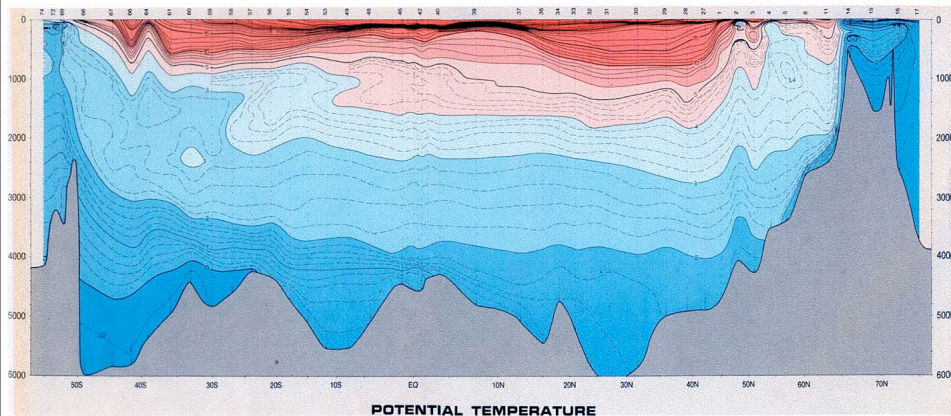


MITgcm - MIT Climate Modeling Initiative - NASA



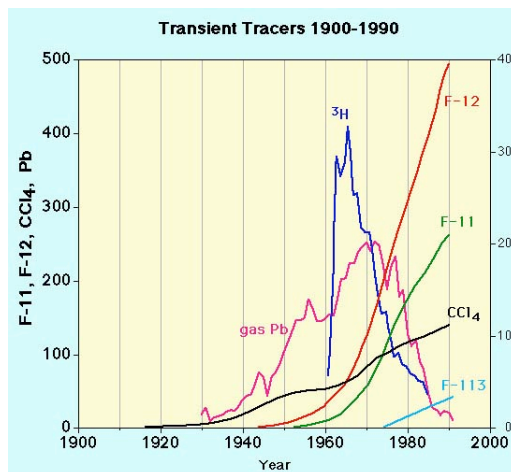
Western Atlantic Potential Temperature* Section

- 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

