

## Carbon Cycle 1: Summary Outline

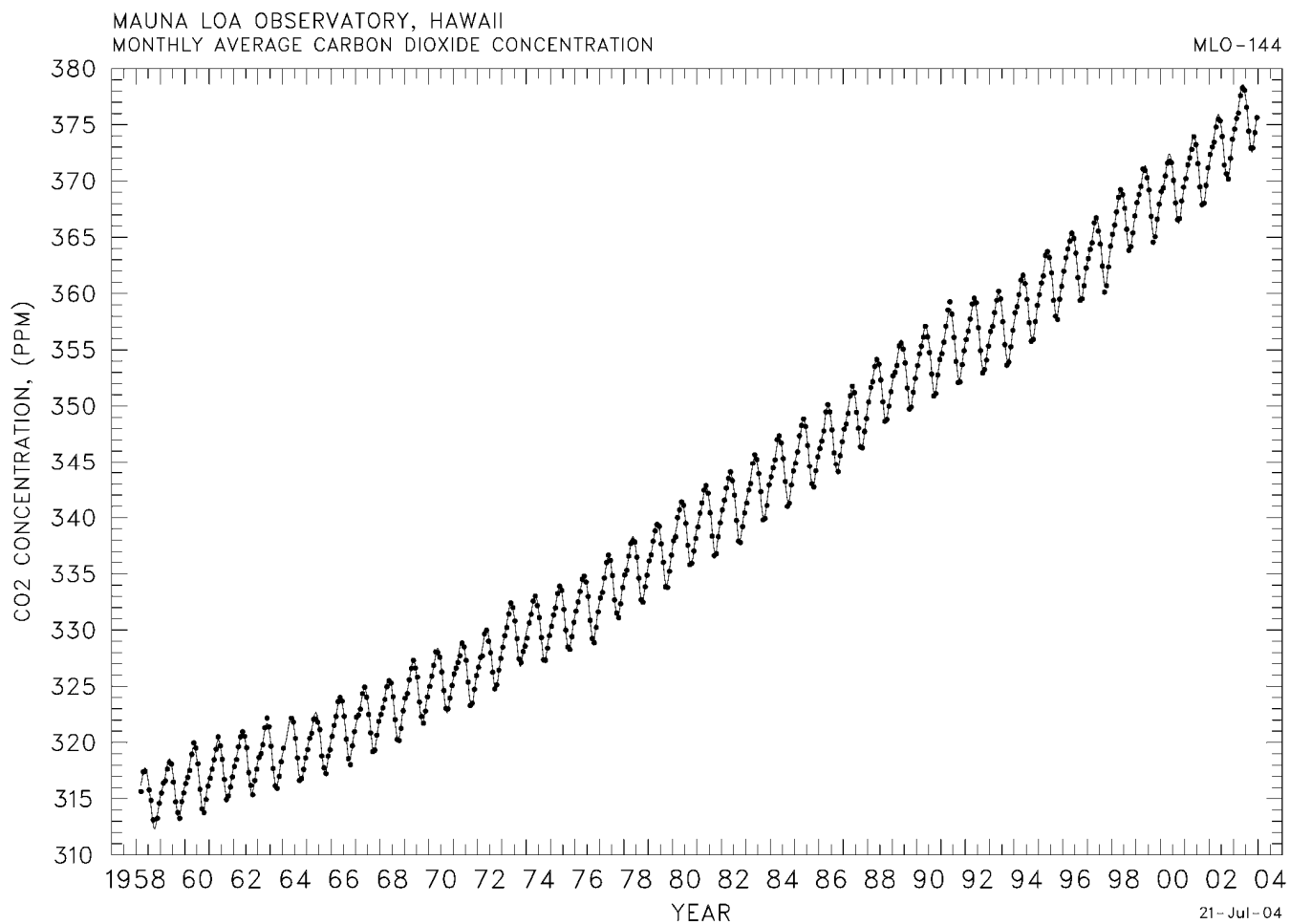
- I. Rising atmospheric CO<sub>2</sub> - observations and questions: how fast? Why not faster? How will it change in the future?
- II. Carbon fluxes through the ocean/atmosphere/biosphere system: overview
- III. Carbon reservoirs; equilibrium controls on transfer between ocean and atmosphere
- IV. CO<sub>2</sub>: physical and biological cycling within the ocean. The ocean carbon pumps
- V. Use of natural radioactivity in estimating the rates of chemical transfer in the ocean
- VI. Gas exchange between the ocean and atmosphere
- VII. Estimating the rate of fossil fuel CO<sub>2</sub> uptake by the ocean. Principles of the estimation techniques. The “missing sink”.
- VIII. Paleo clues for mechanisms controlling atmospheric carbon dioxide.
- IX. Evolution of the anthropogenic carbon transient into the distant future.

### Some useful URLs:

[www.ngdc.noaa.gov](http://www.ngdc.noaa.gov)  
[cdiac.esd.ornl.gov/trends/trends.htm](http://cdiac.esd.ornl.gov/trends/trends.htm)  
<http://www.ldeo.columbia.edu/res/pi/CO2/>  
<http://www.ipcc.ch/pub/online.htm>

### I. How will atmospheric CO<sub>2</sub> concentrations change in the future?

- A. The answer to this question is largely sociopolitical; earth scientists can't predict how people will behave, e.g. fuel consumption behavior, etc. However, it is reasonable to expect that given a scenario for CO<sub>2</sub> emissions, earth scientists should be able to predict what will happen to the CO<sub>2</sub> and how it will change the earth's climate.
- B. What controls CO<sub>2</sub>?: - dominantly the ocean, on time scales of tens to thousands of years - on shorter and longer terms, other factors become important
- C. Pre-anthropogenic CO<sub>2</sub> was about 280 ppmV; now, it's about 365 ppmV (as determined by ice core measurements and modern measurements). During the past 42 years, it has been monitored continuously at Mauna Loa (by D. Keeling in the early years, and NOAA in more recent years):



source: CDIAC

Image courtesy of DOE.

D. CO<sub>2</sub> rise (at present) in atmosphere is about half of the rate of fossil fuel consumption - where does the rest go? Answer to follow: about half goes into the ocean and about half goes into organic matter storage (almost certainly on the continents).

2. CO<sub>2</sub> emissions:

3. CO<sub>2</sub> emissions compared to atmospheric build-up:

E. At what rate will CO<sub>2</sub> go into the ocean in the future? (Can we assume that it will continue to apportion as at present?)

To answer this and other questions, we need to know more about the distribution of carbon on the earth's surface.

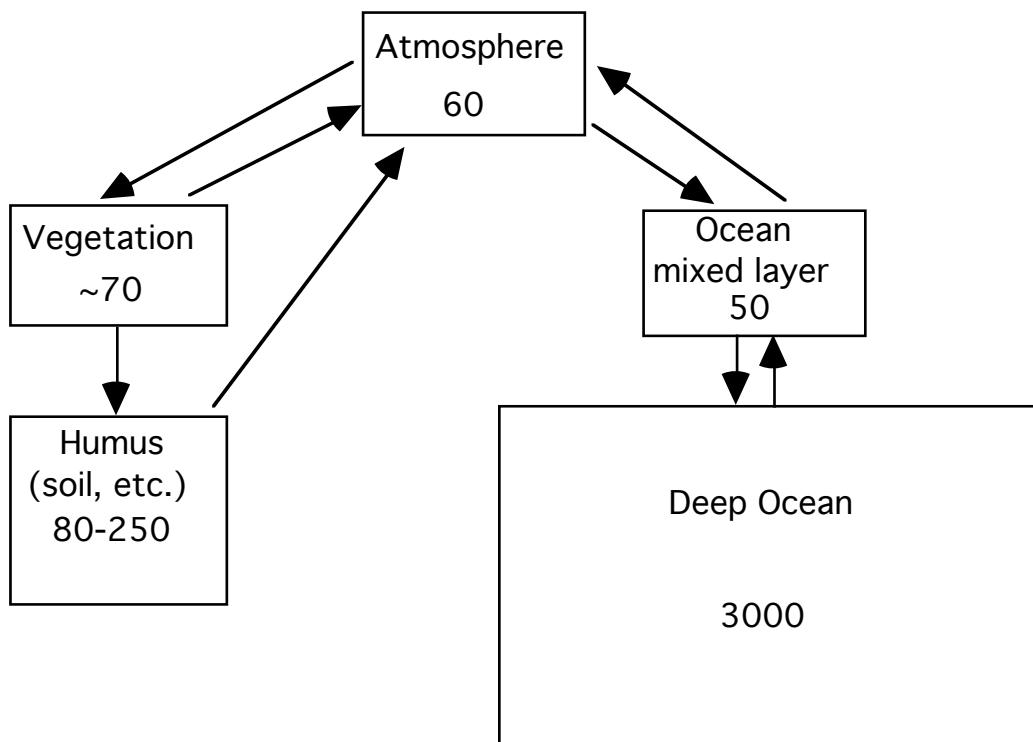
## **II. Carbon fluxes at the earth's surface: overview**

### III. Carbon reservoirs at the earth's surface.

A. Diagram showing the mass distribution and transfer linkages between carbon reservoirs

Units:  $10^{15}$  moles.

[Note that other commonly used units are "gigatons of carbon" ( $10^9$  metric tons of  $^{12}\text{C}$ ) and "petagrams of carbon", i.e.  $10^{15}$  grams of  $^{12}\text{C}$ ), which are equal to one another. To convert from units of  $10^{15}$  moles to these units, multiply by 12 (the atomic weight of carbon).]



1. Discussion: how do we know these numbers?  
how well they are known?

B. Anthropogenic  $\text{CO}_2$  distributes itself between these reservoirs. About half remains in the atmosphere,  $25 \pm 10\%$  goes into the ocean (at present). There is a "missing sink" which must be organic matter and probably is on the continents.

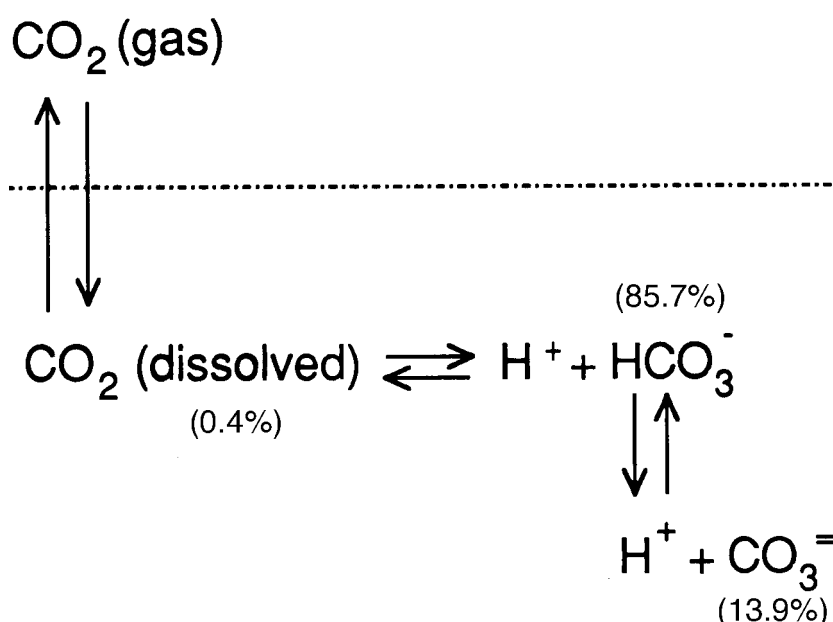
1. How do we estimate the uptake of  $\text{CO}_2$  by the ocean? What physical and chemical processes determine the fraction of oceanic uptake? Will it remain constant?

2. Revelle Factor: the equilibrium thermodynamic fractional change in seawater  $\text{CO}_2$  for a given fractional change in the partial pressure of  $\text{CO}_2$ :

$$R = \frac{\Delta p_{\text{CO}_2} / p_{\text{CO}_2}}{\Delta \Sigma \text{CO}_2 / \Sigma \text{CO}_2} ; \quad \text{this number is a slight function of temperature, salinity, and Alk}/\Sigma \text{CO}_2$$

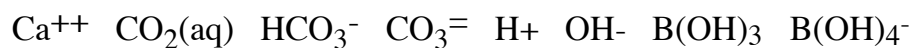
If  $p_{\text{CO}_2}$  increases by 10%, then  $\Sigma \text{CO}_2$  increases by 1%.

$$\text{Revelle Factor } R = \frac{\Delta p_{\text{CO}_2} / p_{\text{CO}_2}}{\Delta \Sigma \text{CO}_2 / \Sigma \text{CO}_2} \sim 10$$

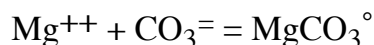


### 3. Carbon system equilibrium thermodynamics

- a. relevant dissolved species:



- i. In seawater a substantial proportion ( $\sim 30\%$  of  $\text{HCO}_3^-$ ,  $\sim 90\%$  of  $\text{CO}_3^{=}$ ) exists as ion pairs e.g.



It is customary to define the "carbonate ion concentration" of seawater as the sum of the complexed and uncomplexed carbonate ion:

$$[\text{CO}_3^{=}] = \sum_i [\text{X}_i(\text{CO}_3^{=})]$$

- ii. Other relevant parameters are the **partial pressure of  $\text{CO}_2$  ( $p_{\text{CO}_2}$ )** and  **$\text{pH} = -\log a_{\text{H}^+}$**

( $a_{H^+}$  is the chemical activity of hydrogen ion - concentration modified by "activity coefficient")

iii. Two useful conservative quantities (relationships linear with mixing) are:

$$\Sigma CO_2 = [CO_2(aq)] + [HCO_3^-] + [CO_3^{2-}]$$

$$\text{Alkalinity} \approx [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$

Conservative properties such as these are important because they can be used in models involving fluid transport and mixing, and because they allow one to control mass balances.

iv. Alkalinity derives from a rearranged form of the charge balance equation:

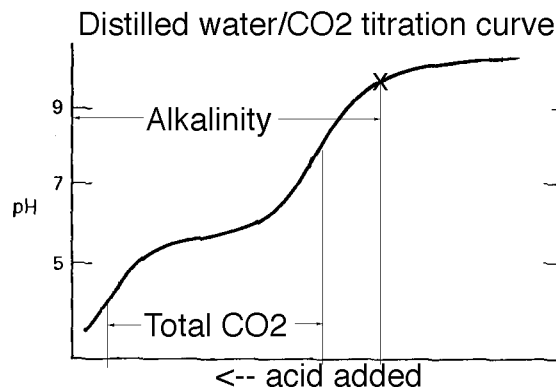
$$\begin{aligned} [Na^+] + 2[Mg^{++}] + 2[Ca^{++}] &= [Cl^-] + 2[SO_4^{2-}] + [HCO_3^-] \\ + [K^+] + [H^+] + (\text{other cations}) &+ 2[CO_3^{2-}] + [B(OH)_4^-] \\ &+ [OH^-] + (\text{other anions}) \end{aligned}$$

If we place all species which are pH-dependent (i.e. weak acids and bases) on the right side of this equation, and all species which are pH-independent (i.e. strong acids and bases) on the left side, we can rearrange it to:

$$\begin{aligned} [Na^+] + 2[Mg^{++}] + 2[Ca^{++}] &= [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] \\ + [K^+] + (\text{other "strong" cations}) &+ [OH^-] \\ - [Cl^-] - 2[SO_4^{2-}] &+ (\text{other "weak" anions}) \\ - (\text{other "strong" anions}) &- [H^+] - (\text{other "weak" cations}) \end{aligned}$$

In marine chemistry, the right hand side of this equation is usually defined as the alkalinity because these are the species involved in acid-base reactions (although obviously the left hand side is also equal to the alkalinity).

v. Operationally in marine chemistry, alkalinity is defined as the number of equivalents of acid needed to bring a sample to the  $CO_2$  endpoint:



b. Relevant equilibria ("apparent" thermodynamic constants). Because seawater is a "high ionic strength" solution (i.e., it is very salty), conventional thermodynamic constants (activity coefficients, etc.) are difficult to define because of strong ionic interactions. But because the

composition of seawater (for major ions) is constant save for variations in total salt content, we can adopt “apparent constants” which incorporate the activity coefficients and ion interactions into the “apparent” constant (denoted by ‘):

$$\text{i. } \text{CO}_2 (\text{gas}) = \text{CO}_2 (\text{aq}) \quad \alpha_s' = \frac{\text{CO}_2 (\text{aq})}{P\text{CO}_2} \approx 10^{-1.5}$$

$$\text{ii. } \text{CO}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^- \quad K_1' = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2(\text{aq})]} \approx 10^{-6.0}$$

$$\text{iii. } \text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{=} \quad K_2' = \frac{[\text{H}^+][\text{CO}_3^{=}]}{[\text{HCO}_3^-]} \approx 10^{-9.1}$$

$$\text{iv. } \text{B}(\text{OH})_3 + \text{H}_2\text{O} = \text{B}(\text{OH})_4^- + \text{H}^+ \quad K_B' = \frac{[\text{H}^+][\text{B}(\text{OH})_4^-]}{[\text{B}(\text{OH})_3]} \approx 10^{-8.7}$$

These apparent constants are functions of temperature, salinity, and pressure.

Once the system of equations relevant to a problem have been set up (and these may include mass balance, alkalinity, or other constraints), they are solved generally by computer, where the underlying method involves substituting terms to create a single polynomial equation with [H+] as the only variable. This equation is then solved with Newton-Rapson or similar method. For the range of values appropriate for seawater, simplifications can be made that reduce this system of equations to a cubic polynomial with an exact solution.

4. So: Using the Revelle Factor, we can explore various equilibrium scenarios for equilibrium between the ocean and atmosphere given hypothetical changes in pCO<sub>2</sub>:

Atmosphere (10 <sup>15</sup> moles)	Mixed Layer	Whole Ocean
60	50	3050
66	50.5	3080

a. **This result indicates that:**

- (1) **The mixed layer on its own can't take up very much fossil fuel CO<sub>2</sub>, and**
- (2) **The whole ocean would take up ~80% at equilibrium.**

In other words, an equilibrium model cannot account for the 50% uptake ratio. It seems that uptake might have been much more or much less than it has, depending on the extent to which the deep ocean equilibrates.

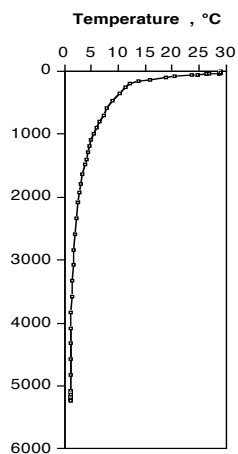
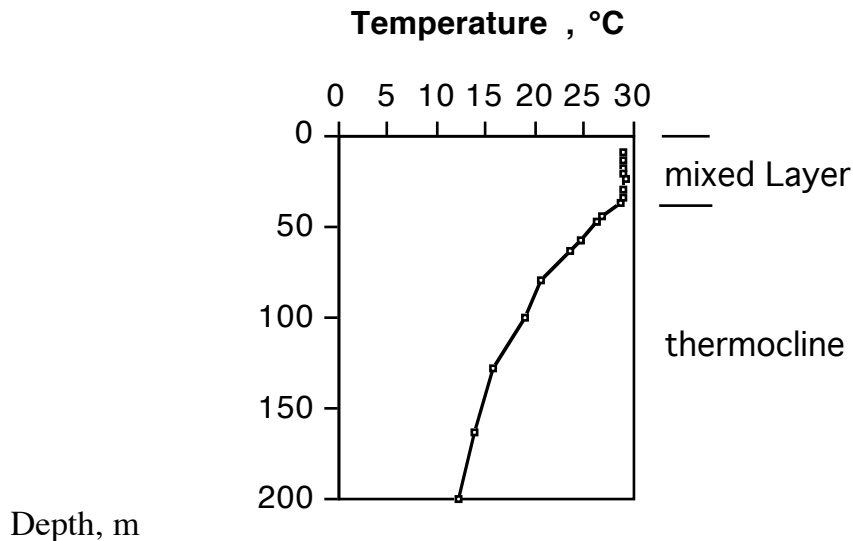


b. So we need to know what controls the uptake of CO<sub>2</sub> by the deep ocean.

#### IV. CO<sub>2</sub>: physical and biological cycling within the ocean. The ocean carbon pumps

##### A. Physical and chemical circulation of the ocean

1. Wind-driven circulation of the ocean; simple ocean dynamics (Coriolis force; Ekman drift, Ekman spiral, coastal upwelling,).
2. Ekman pumping, subduction, ventilated thermocline
3. Meridional Overturning Circulation of the ocean: surface low-latitude warming, wind-driven mixing; high latitude cooling, deep water formation; thermocline as boundary between warm tropical surface water and cold deep water derived from high latitudes. Example: temperature-depth profile from the Northern Indian Ocean (Geosecs Station 400, 9°21'S 95°1'E)

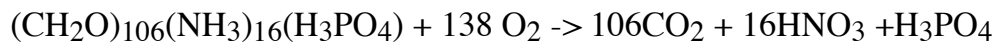


source: GEOSECS

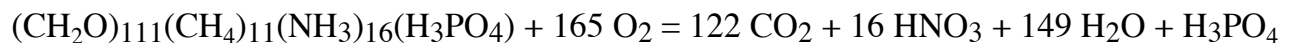
#### 4. The ocean carbon pumps

- a. The solubility pumps:  $\text{CO}_2$  is more soluble in cold waters than in warm waters (the thermal pump), and more soluble in fresher waters than saltier waters (the salt pump). If alkalinity were uniform throughout the ocean and if both cold and warm surface waters equilibrated their  $p\text{CO}_2$  with the atmosphere, then cold surface waters would have a higher dissolved carbon dioxide content than warm surface waters. As these cold surface waters circulate into the deep interior of the ocean, deep waters will have more  $\text{CO}_2$  than warm surface waters.
- b. The biological pump: organisms remove carbon and nutrient elements from the surface ocean (which is equilibrated with atmospheric oxygen; note oxygen solubility is a function of temperature); the debris from these organisms sinks and decomposes, releasing carbon and nutrient elements into the deep water and consuming oxygen.

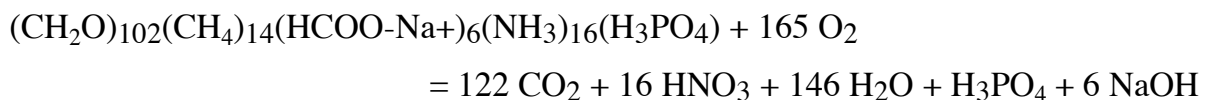
##### **classical Redfield Ratio:**



This stoichiometry proposed by Redfield is based on elemental ratios he observed in ocean water samples and plankton. It considers marine organic matter as if it were a mixture of carbohydrates ( $\text{CH}_2\text{O}$ ), proteins (containing  $\text{NH}_3$ ), and phospholipids and nucleic acids ( $\text{H}_3\text{PO}_4$  bearing). In reality, a broad mixture of compounds occur, and the observed stoichiometry  $\Delta\text{O}_2:\Delta\text{C}$  in deep ocean waters implies a higher value ( $\sim 165$ ), because of the presence more hydrocarbon-like functional groups:



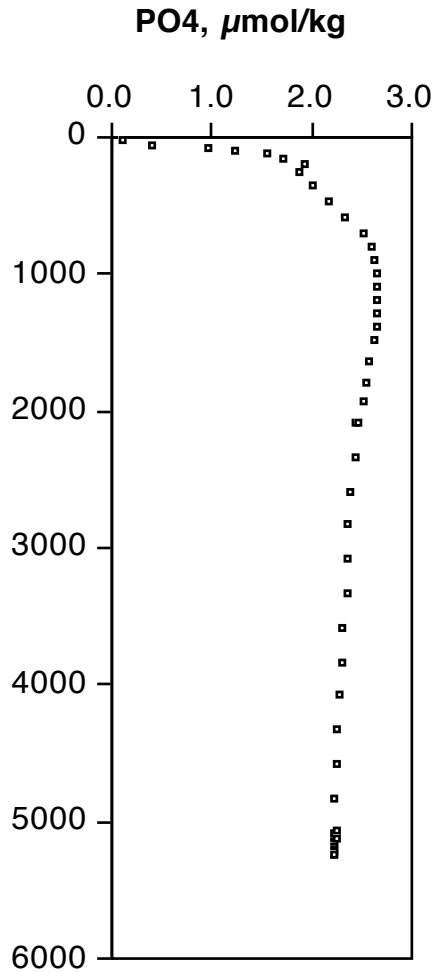
Note the production of nitric and phosphoric acid in this process; this acid changes alkalinity. Once you acknowledge this process, you also need to take into account another effect that reduces the acid effect on alkalinity by about  $1/3$ : the presence of ion-exchanged carboxyl groups:



There is debate on whether the C:P and N:P stoichiometries are fundamental to marine ecosystems, or whether there is some plasticity (e.g., could N:P = 25?). (There is less debate on variable C:N ratios than for C:P).

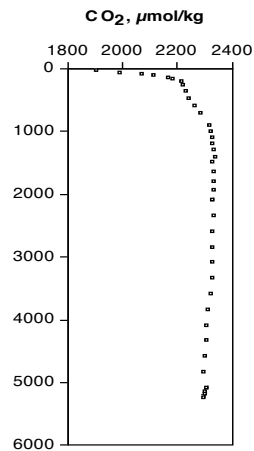
We should also note that some organisms precipitate inorganic shells out of calcium carbonate ( $\text{CaCO}_3$ ) and silica ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ). For example for every 106 organic carbon atoms converted to organic matter, about 22  $\text{CaCO}_3$  molecules are precipitated (ocean-wide average).

Example: phosphorus-depth profile from the Northern Indian Ocean



source: GEOSECS

d. Total dissolved carbon dioxide distribution (combination of solubility pump and biological pump).



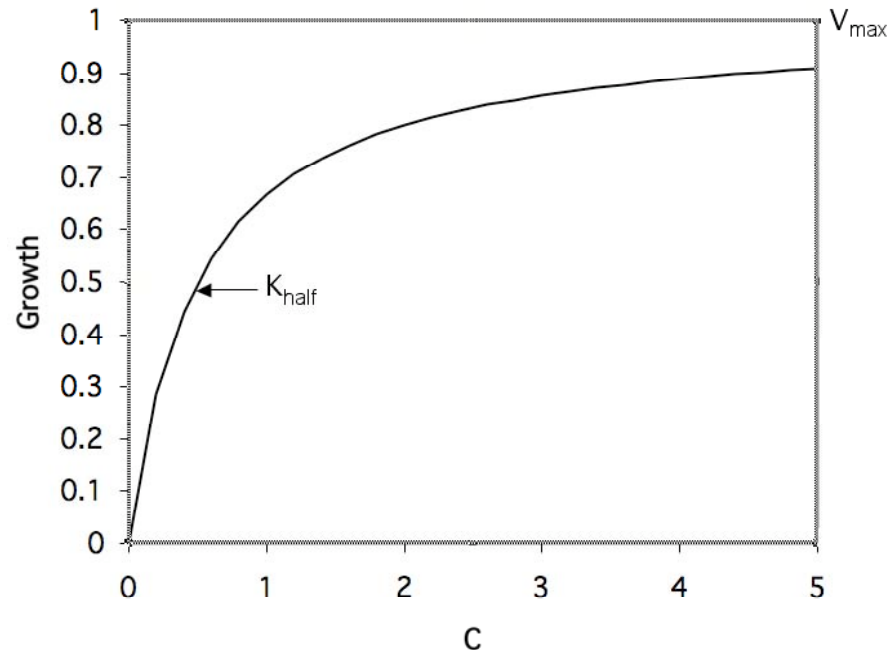
source: GEOSECS

5. If the biological pump were turned off, the pCO<sub>2</sub> of the atmosphere would rise to about 450 ppmV.
6. Concept of the “limiting nutrient”: When light and sufficient nutrients are present, organisms will grow until they deplete the “limiting” nutrient to concentrations that are so low that biological uptake is

severely limited. The effect of nutrient concentrations on biological growth is often likened to the “Michaelis-Menten” function (used for representing enzymatic activities)

$$Growth = V_{\max} \frac{C}{C + K_{half-saturation}}$$

where C is the concentration of the nutrient and  $K_{half-saturation}$  is the concentration at which the growth rate is half of its maximum value  $V_{\max}$



Classically, marine biologists have considered nitrate as the limiting nutrient in most environments (with phosphorus close behind). However, within the past two decades it has been shown that in some environments (so-called “high nutrient low chlorophyll” HNLC), iron is more limiting than iron. Some other trace micronutrients may also be important in some situations (e.g., Zn, Co).

#### B. Factors controlling the rate of uptake of $CO_2$ from the atmosphere

1. On the time scale of tens of thousands of years, anthropogenic  $CO_2$  emissions will be entirely removed by the ocean and oceanic sediments. At present, half of the  $CO_2$  emissions remains in the atmosphere, and about  $25 \pm 10\%$  goes into the ocean. The rate at which carbon is 'ventilated' into the deep sea is the principle control on the ocean uptake of  $CO_2$ , so there is no guarantee that this fraction will remain fixed in the future.
2. What are the fundamental factors controlling the rate of  $CO_2$  uptake by the deep sea?

- a. There are two main ways for carbon to get into the deep sea: On the backs of sinking biogenic particles, and by the physical circulation of the ocean.
- i. Physical mechanisms: First,  $\text{CO}_2$  must enter the sea from the air. There are three major factors controlling this transfer: equilibria, kinetics, and mass balance.
  - ii. Equilibria: Controlled by  $\text{Alk}/\Sigma\text{CO}_2$ , carbonic acid equilibria; simplified as the Revelle Factor.
  - iii. Kinetics: The rate at which gases can transfer across the air-sea interface. The “established” rate for  $\text{CO}_2$  is  $20 \text{ moles/m}^2/\text{yr}$ . Two ways we estimate this number:
    - (1) natural carbon-14 uptake
    - (2) radon-222 deficit
  - iv. Mass Balance: When the ocean and atmosphere is at equilibrium, the total amount stored in the atmosphere and ocean must balance the anthropogenic emissions.

## V. Use of natural radioactivity in studying environmental processes

Radiodecay equations.

$$1. \quad \frac{dN}{dt} = -\lambda N$$

$$2. \quad N = N_0 e^{-\lambda t}$$

3. The radioactive decay constant is often expressed as a half-life ( $t_{1/2}$ ); i.e., the time it would take for half of the original amount to decay. Setting  $N = 1/2 N_0$  in equation 2, then

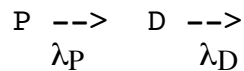
$$t_{1/2} = \ln 2 / \lambda = 0.693 / \lambda$$

B. The concentration of radioactive isotopes is often expressed in terms of its activity, i.e., the rate at which the substance undergoes radioactive decay. This has some obvious advantages (you are expressing the concentration in units similar to the measurement device, e.g. a geiger counter, etc., and it immediately tells you how radioactive the substance is) and one less obvious advantage related to the concept of radioactive equilibrium:

1. Define the activity (A) of a radioisotope as:

$$A = dN/dt = \lambda N$$

2. Consider a radioactive series consisting of an initial amount of a parent isotope ( $P_0$ ) and radioactive daughter isotope ( $D_0$ ):



- a. For the parent isotope:

$$dP/dt = -\lambda_P P \quad ; \quad P = P_0 e^{-\lambda_P t}$$

- b. Assuming that at time = 0,  $D_1 = 0$ , then:

$$\dots dD_1/dt = +\lambda_P P - \lambda_D D \quad ;$$

$$D = \frac{\lambda_P}{\lambda_D - \lambda_P} P_0 (e^{-\lambda_P t} - e^{-\lambda_D t}) + D_0 e^{-\lambda_D t}$$

- c. If  $\lambda_P \ll \lambda_D$  (i.e., the parent is much longer-lived than the daughter), then as  $t \gg t_{1/2}$  for the daughter isotope (and noting that  $P = P_0 e^{-\lambda_P t}$ ),

$$D \cong \lambda_P P / \lambda_D$$

- d. That is,

$$\lambda_D D = \lambda_P P$$

$$A_D = A_P$$

- e. In other words, given a closed system with a long-lived radioactive parent with a succession of shorter-lived radioactive daughter isotopes (and given enough time), the activities of all the isotopes will be equal. Hence we can use activities to estimate

whether or not the system has remained closed for the time appropriate to the half-lives of the given isotopes.

C. Natural radioactive series:  $^{238}\text{U}$ ,  $^{235}\text{U}$ ,  $^{232}\text{Th}$ . These isotopes were created by supernovae nucleosynthesis and incorporated into the earth at the time of its formation. These isotopes then decay into numerous daughter isotopes according to the following chains:

G. Two references on aspects of radioactivity and radiochemistry:

Friedlander, J.W. Kennedy, E.S. Macias, and J.M. Miller, Nuclear and Radiochemistry, Wiley, N.Y., 684 p.

Faure, G., Principles of Isotope Geology, Wiley, N.Y. , 589 p.

## VI. Gas exchange between the ocean and atmosphere

A. Net gas exchange is dictated by a disequilibrium in the partial pressure of gases between the ocean and atmosphere. This disequilibrium can result from changes in temperature; biological production and uptake (e.g.  $\text{O}_2$  and  $\text{CO}_2$ ), and mixing with subsurface waters. Although the direction and magnitude of net gas exchange is thermodynamically driven, it is limited by physical transport (diffusion and microadvection) through boundary layers at the surface of the ocean and the bottom of the atmosphere. In these boundary layers, physical motions are restricted by surface tension (water) and friction (atmosphere). Some gas exchange is also caused by bubbles created by breaking waves, especially at high wind speeds. These bubbles can help facilitate equilibrium (e.g., as a bubble moves through the water, it can equilibrate with the water and bring that equilibrated gas back to the surface), but they can also create disequilibrium when a bubble is brought down so deep that it completely dissolves, injecting the atmospheric gases quantitatively into the water in non-thermodynamic ratios. Gas exchange is occurring in both directions at all times (even when the partial pressures are equal between the water and air).

B. For gas exchange that does not involve dissolving bubbles, the flux is always considered proportional to the disequilibrium between dissolved gas at equilibrium with the atmosphere (at the very surface) and the dissolved gas content of the mixed layer of the ocean. The proportionality constant is considered to depend on the gas, wind speed and perhaps other factors such as surface slicks.

Flux =  $k$  (atm. equilibrium dissolved gas concentration – mixed layer dissolved gas concentration)

where:

atm. equilibrium dissolved gas concentration = air gas concentration /  $H$

$H$  is the Henry's Law Constant, expressed as the ratio of the concentration of gas in air to its (un-ionized) equilibrium concentration in seawater

$k$  is the "transfer velocity" that relates the one-way gas flux to its concentration in water

The flux has units of moles per square meter of surface per year; the dissolved gas concentration has units of moles per cubic meter; hence the proportionality constant  $k$  has units of meters per year. This is referred to as the "piston velocity" because it has units of length per time and it behaves as if there were two imaginary pistons sweeping through

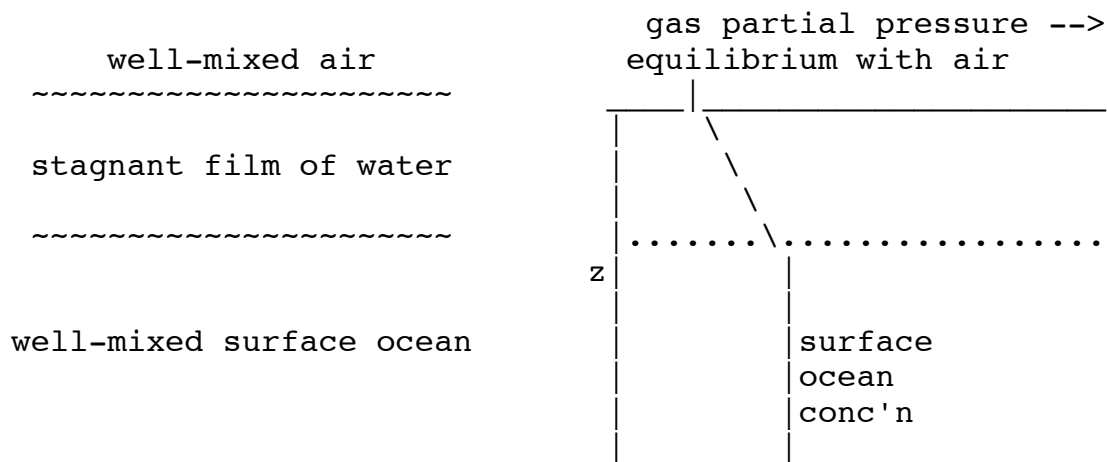
the water driving the dissolved gases simultaneously out into the atmosphere and into the mixed layer. This "piston" has a velocity magnitude of about 2000 m/yr!

C. The physics of gas exchange: not well understood on a microphysical basis. Surfactants and bubbles may play a significant role. The “exchange coefficient” that turns the difference in pressures into a quantitative value is not well understood. It is higher at higher wind speeds, but the functionality is not agreed upon and at high wind speeds, the uncertainty may range over a factor of two.

D. Stagnant film model:

The stagnant film model for gas exchange is a conceptual simplification of the gas exchange process which allows us to estimate the gas exchange rates of some gases from measurements of the gas exchange rates of other gases. It is not “*the law*” – other models are possible, and some of these are more physically realistic. All of these, however, have the same basic feature: there is an impedance between the movement of gases between the physical surface of the seawater into the “interior” several tens to hundreds of microns below the surface.

D (molecular diffusion in water,  $\sim 10^{-5} \text{cm}^2/\text{sec}$ ; depends on gas)  
 $z_{\text{film}}$  ( $\sim 30 \mu\text{m}$ ; depends on wind conditions).



$$\text{Flux} = D \frac{C_m - C_o}{z_{\text{film}}}$$

where  $c_m$  = concentration of dissolved gas in (interior) mixed layer of ocean  
 $c_o$  = concentration of dissolved gas at surface of ocean (equilibrium with atm)  
 $z_{\text{film}}$  = thickness of stagnant film  
 $D$  = diffusion coefficient of dissolved gas

1. For gases like oxygen and nitrogen, which equilibrate entirely between the gas phase and the dissolved aqueous form, gas exchange is very effective and surface waters are almost at equilibrium. For carbon dioxide, where the dissolved aqueous gas equilibrates with the bicarbonate and carbonate ions which occur at much higher concentrations, gas exchange equilibration is slower and surface waters are usually out of equilibrium with the atmosphere - sometimes by up to a factor of two.



- In this model, the ratio of the fluxes of two gases varies linearly with the aqueous diffusion coefficient, and the effect of wind speed in increasing exchange rates is attributed to its role in thinning the stagnant film.

F. Radon technique for determining gas exchange rates:

- rate of radon generation - *in-situ* radio-decay = rate of loss to the atm.

$$D (\lambda_{\text{Ra-226}} C_{\text{Ra-226}} - \lambda_{\text{Rn-222}} C_{\text{Rn-222}}) = \text{Flux to atmosphere}$$

where C = concentration of radioisotope, atoms/cm<sup>3</sup>;

D = depth of mixed layer, cm;

= Flux across surface, atoms/cm<sup>2</sup>/sec

$\lambda$  = decay constant of radioisotope

$$z_{\text{film}} = \frac{D_{\text{Rn-222}}}{\lambda_{\text{Rn-222}}} \left[ \frac{1}{(A_{\text{Ra-226}}/A_{\text{Rn-222}}) - 1} \right]$$

- Natural Carbon-14 method for determining CO<sub>2</sub> exchange rates. Method is based on the 400 year "age" difference between surface ocean waters and the atmosphere: this is because "old" deep water mixes with surface waters which are exchanging with "modern" atmospheric carbon; the "400 yr age" represents a balance between gas exchange with the atmosphere and mixing with deep water.

see supplement!

- Rate of exchange of CO<sub>2</sub> between ocean and atmosphere. Speaking in round terms, we can calculate the average rate at which CO<sub>2</sub> moves across the sea surface:

$$\frac{2000 \text{ m/yr}}{\text{piston velocity}} * \frac{10^{-5} \text{ moles/kg}}{\text{aqueous CO}_2 \text{ conc.}} * \frac{1000 \text{ kg/m}^3}{\text{Conversion factor}} = 20 \text{ moles/m}^2/\text{yr}$$

Given that the upper 75 m of the water column (mixed layer) underneath a square meter contains 150 moles of carbon, full equilibration for carbon isotopes (e.g. <sup>13</sup>C, <sup>14</sup>C) takes years. pCO<sub>2</sub> equilibration takes less time however, because the pH shift induced by gas exchange shifts the water towards equilibrium (e.g., if water is supersaturated with respect to atmosphere, CO<sub>2</sub> is lost and pH of seawater rises, and some aqueous CO<sub>2</sub> is lost to the bicarbonate pool. Hence pCO<sub>2</sub> is moved towards equilibrium both by loss of aqueous CO<sub>2</sub> to atmosphere and by loss of aqueous CO<sub>2</sub> to bicarbonate pool (this is related to the Revelle Factor).

E. Other gas exchange models:

- Film replacement models. In this type of model, the stagnant film is retained but it is periodically replaced by fluid from the mixed layer. More mathematically complex, and in these models, the ratio of the fluxes of two gases varies with the square root of the aqueous diffusion coefficient.
- Boundary-layer models. By analogy to the theoretical and experimental information on the transfer of momentum, heat, and mass at surfaces. k is considered a function of the ratio of the kinematic velocity v (transfer coefficient for momentum) divided by molecular

diffusivity (D); this ratio is referred to as the Schmidt number ( $Sc = \nu/D$ ). In this case, the ratio of the fluxes of two gases varies by the  $2/3$  power of the diffusivities.

3. On the merits of these various models: the thin-film model is conceptually and mathematically simple. The film replacement models are somewhat more physically realistic, but is more mathematically complex and it is difficult to specify the film replacement time. The boundary-layer models are more physically based, but underestimate the transfer coefficients when the water surface is not smooth. None of these models include the effect of bubbles from breaking waves, which are important at high wind speeds.
4. Attempts to estimate the effect of wind velocity on transfer velocities differ by a factor of two. The difference is the largest at high wind speeds where gas exchange is high. One proponent (Wanninkhof) proposes the use of a cubic dependence of transfer velocity on wind speed; other proponents [Liss and Merlivat] propose a “regime change” model where coefficients are linear functions of wind speed within a regime (smooth surface, rough surface, and breaking wave (bubble) regimes] with slope/intercept changes at the regime boundaries.
5. For a more advanced discussion of the gas exchange process:

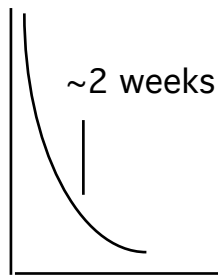
P.S. Liss and L. Merlivat (1986) Air-sea gas exchange rates: introduction and synthesis, in: *The Role of Air-Sea Exchange in Geochemical Cycling* (ed. P. Buat-Menard et al.), D. Reidel Publishing Co.

Asher, W., and R. Wanninkhof, Transient tracers and air-sea gas transfer, *J. Geophys. Res.*, 103, 15939-15958, 1998.

G. Dual tracer technique ( $SF_6/{}^3He$ ) for determining gas exchange rates.

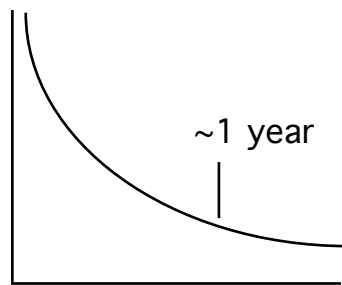
H. Gas exchange equilibration rates of the mixed layer with the atmosphere: one square meter of the the upper 100m of the ocean ( $10^5 kg$ ) contains 200 moles of carbon. 0.5% of this carbon exists as dissolved  $CO_2$ , and the Revelle Factor is  $\sim 10$ , so  $\sim 200 * 0.005 * 10 = 10$  moles of  $CO_2$  needs to be transferred to equilibrate the mixed layer with the atmosphere. The  $CO_2$  gas exchange rate is 20 moles/ $m^2/yr$ , so the mixed layer of the ocean can equilibrate with the atmosphere on a time scale of about a year (note however that  ${}^{13}C$  and  ${}^{14}C$  will take longer to equilibrate because the total carbon dioxide must exchange to fully equilibrate the isotopes, i.e.,  $200/20 = 10$  years).

### Simple Gas Exchange (e.g. O<sub>2</sub>, Ar)



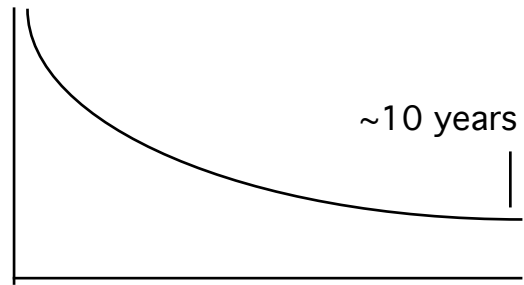
(depth of mixed layer divided by piston velocity - i.e. total gas content divided by gas flux)

### pCO<sub>2</sub> equilibration



(change in TCO<sub>2</sub> required to change pCO<sub>2</sub> in seawater is divided by gas flux: e.g. for a 3% increase in pCO<sub>2</sub>, CO<sub>2</sub>(aq) rises by 3% and TCO<sub>2</sub> rises by 0.3%; but because TCO<sub>2</sub> is ~200x CO<sub>2</sub>(aq), it then takes  $200 \cdot .3 / 3 = 20x$  longer)

### carbon isotope equilibration (C<sup>13</sup>, C<sup>14</sup>)



(total carbon dioxide content divided by total gas flux, ~20 moles/m<sup>2</sup>/yr)

## VII. Factors Controlling the rate of CO<sub>2</sub> uptake by the ocean. Introduction to the missing sink.

### 1. Transient Tracers

Ostlund H. G. and Rooth C. G. H. (1990) The North Atlantic tritium and radiocarbon transients 1972-1983. J. Geophys. Res. 95, 20147-20165.

Doney S. C. and Bullister J. L. (1992) A chlorofluorocarbon section in the eastern North Atlantic. Deep-Sea Res. 39, 1857-1883.

### A. Fluxes and net fluxes of CO<sub>2</sub>

#### 1. As we have seen, there are large and active natural fluxes of CO<sub>2</sub>:

- a. Gas exchange between the surface ocean and the atmosphere, with net fluxes regionally but with near balance globally over the past 2000 years .
- b. "Biological pump" prevents deep ocean CO<sub>2</sub> from exchanging with the atmosphere; reduces the pCO<sub>2</sub> about a factor of 3 below that which would exist if all ocean life were to die off.

2. But these fluxes are at steady-state (prior to anthropogenic perturbations) - i.e., the influxes equal the effluxes and so there have been changes in atmospheric CO<sub>2</sub> over the 11,000 years prior to the recent anthropogenic perturbations have been small. CO<sub>2</sub> rose from about 260 ppmV 6000 years ago to 280 ppmV about 2000 years ago, and has changed little until industrialization began about 200 years ago.

note: "noise" in most recent portion of above record is probably due to proximity to the interconnected "firm" zone (bubbles not completely sealed)

note: this record is probably more reliable for A.D. 1500-1800 because it has a higher accumulation rate and these years are well within the firm zone.

Source: Wahlen, M., D. Allen, B. Deck and A. Herchenroder (1991) Initial measurements of CO<sub>2</sub> concentrations (1530 to 1940 AD) in air occluded in the GISP2 ice core from central Greenland, Geophys. Res. Lett. **18**: 1457-1460.

- a. In particular, note that the "biological pump" is operating independently of anthropogenic changes: the downward pump is driven by the Redfield Ratio to balance the upward flux from upwelling deepwater, and does not "sense" the ongoing rise in atmospheric CO<sub>2</sub> concentrations.
  - b. Also note that the rate of gas exchange between the ocean and atmosphere is sufficiently rapid to prevent large deviations of pCO<sub>2</sub> between the atmosphere and the mixed layer of the ocean.
  - c. Hence, in the absence of some climate-induced change in ocean biology, the "biological pump" and natural gas exchange are not relevant to the disposition of fossil fuel CO<sub>2</sub> by the ocean.
- B. The rate at which the ocean takes up excess CO<sub>2</sub> is partially determined by the equilibrium uptake of fossil fuel CO<sub>2</sub> by the surface ocean, and the rate at which this water can mix into the deep ocean. The rate of CO<sub>2</sub> uptake by the ocean is greater than uptake by the mixed layer alone can account for, but is less than the rate at which the whole ocean could take up CO<sub>2</sub> if it were rapidly stirred. Since the equilibrium uptake of CO<sub>2</sub> by seawater is fixed by thermodynamics, the principle variable controlling the rate of uptake of CO<sub>2</sub> of the ocean is the ventilation rate of the deep ocean.
1. How can we estimate the rate of CO<sub>2</sub> uptake by the ocean? What is limiting?
    - a. We know from observations (1958-1986) that atmospheric CO<sub>2</sub> has only increased by a little more than half (58%) of the total amount of fossil fuel CO<sub>2</sub> emissions.
    - b. In this time, CO<sub>2</sub> has risen from about 315ppmV to >350ppmV (11%). From the Revelle Factor, we know that the total dissolved CO<sub>2</sub> of surface ocean water in equilibrium with this increased CO<sub>2</sub> should then have increased by 1.1%. Can we observe this signal?
      - i. This small change challenges the long-term accuracy of the measurements. Modern measurements can be precise to better than 0.2%, but it is difficult to maintain

long-term accuracy and determine whether the older measurements were well-calibrated. There is a large seasonal cycle and considerable variability throughout the surface waters, particularly at high latitudes. Nonetheless, looking at mid- and tropical- latitude North Atlantic surface waters (mainly in summer), there does appear to be some increase over the past 30 years. But the uncertainties are large enough that we can only say that the uptake estimated by this method is comparable to our preferred method of estimating uptake (below).

- ii. Concept of the mean age of anthropogenic CO<sub>2</sub>: suppose molecules of CO<sub>2</sub> were given just-started stopwatches at the time they are emitted. Later, we gather up these molecules and read their stopwatches and take an average. Currently, this average is about 28 years. It depends on the emission history, and should not be presumed constant as emissions change in the future.

$$\text{Mean Age} = \frac{\int_{-t}^0 -tF(t)dt}{\int_{-t}^0 F(t)dt}$$

t = 0 is the present  
F(t) = CO<sub>2</sub> emissions

- iii. Given the mixed layer equilibration time of about one year (see above) and the fossil fuel mean age of 28 years, gas exchange between the ocean and atmosphere is not limiting.

C. A simple model for the rate of fossil fuel CO<sub>2</sub> uptake by the ocean in 1962-

1990. The goal of this model is to simplify the scenario so that the calculations are trivial, yet the answer is realistic.

1. Assume that the biological pump and "natural" gas exchange are tuned to produce no net change in oceanic CO<sub>2</sub>, so we can ignore them entirely.
2. Assume that the total CO<sub>2</sub> of the ocean mixed layer is at equilibrium with the pCO<sub>2</sub> of the atmosphere, with a Revelle Factor of 10.
3. Consider how much CO<sub>2</sub> in the ocean increases during the 28 year mean life of anthropogenic CO<sub>2</sub> (when about a 10% increase in atmospheric CO<sub>2</sub> occurred):
  - a. The atmosphere, containing  $60 \times 10^{15}$  moles of CO<sub>2</sub>, increased by 10%.
  - b. The mixed layer, containing  $50 \times 10^{15}$  moles of CO<sub>2</sub>, increased by 1%.
  - c. Most of the tritium input to the ocean came from thermonuclear bombs set off in ~1962 (28 years before 1990). This bomb tritium indicates that the mixed layer was in communication with a layer of water of 300 m thickness during that 28 years.
  - d. During this time, high latitude surface water sank to the bottom of the ocean, in an amount equivalent to a layer 4 m/yr if spread uniformly over the seafloor.

e. So our budget for the 28-year period is:

		<i>10<sup>15</sup> moles of carbon</i>		
	<u>thickness</u>	<u>1962</u>	<u>1990</u>	<u>1990-1962</u>
<b>Atmosphere</b>		<b>60</b>	<b>66</b>	<b>6.0</b>
<b>Mixed layer</b>	<b>75m</b>	<b>50</b>	<b>50.5</b>	<b>0.5</b>
<b>Upper Ocean</b>	<b>300m</b>	<b>200</b>	<b>202</b>	<b>2.0</b>
<b>Bottom Water</b>	<b>112m</b>	<b>75</b>	<b>75.8</b>	<b>0.8</b>
-----				
<b>Total</b>				<b>9.3</b>
<b>% taken up by ocean:</b>		<b>3.3/9.3 =</b>	<b>35%</b>	

Note that the above estimate only includes the fraction taken up by the ocean and stored in the atmosphere; it does not include the "missing sink". If the "missing sink" is comparable to the ocean uptake in magnitude, then the ocean has taken up:  $3.3/12.6 = 26\%$  of the total CO<sub>2</sub> emissions.

#### D. Ways to improve on the simple model:

1. Incorporate biology into model (so chemical estimates can be compared to real data, not just to the incremental CO<sub>2</sub> taken up). Allow for pCO<sub>2</sub>/atm. disequilibrium.
2. More tracers and more constraints applied: e.g., use freon and other ocean circulation information as well as tritium.
3. Fully 3D ocean circulation/ chemistry model, constrained to match the pattern of all of the known constraints: T, S, ocean dynamics, chemistry: nutrients, tritium, CFCs, and <sup>14</sup>C.

#### E. Alternate ways of estimating the uptake of CO<sub>2</sub> by the ocean

1. Integration of fluxes: measure the difference in pCO<sub>2w</sub> between the ocean and atmosphere throughout the ocean as a function of area and season, and estimate the flux from this difference and gas exchange coefficient. You must integrate over the whole area of the ocean (for some length of time - seasonal etc. differences may be expected) to get the net uptake of CO<sub>2</sub> by the ocean. The problem with this technique is the high variability of pCO<sub>2</sub>, and the fact that we are dealing with a small difference between big numbers with large seasonal variability and sparse data coverage. I cannot convince myself that the data coverage is adequate (despite the inclusion of millions of pCO<sub>2</sub> measurements); but at least these estimates do not contradict the "simple robust model" method above.
2. Because most fossil fuel emissions are occurring in the Northern Hemisphere, and because it takes a year or so for the atmosphere to mix, there will be a net gradient in CO<sub>2</sub> between the Northern and Southern Hemisphere.
  - a. The carbon flux due to this gradient can be modeled using atmospheric circulation models, so we can compute the net flux of CO<sub>2</sub> into the southern Hemisphere, and hence the net uptake of CO<sub>2</sub> by the southern Ocean.

- b. While circulation models are not sufficiently realistic to be trusted with this calculation on their own, they can be calibrated by making use of the freon gradient between the hemispheres (most freon is released into the Northern Hemisphere) and from measurements of the interhemispheric gradient (and knowing the production).
  - c. Some problems:
    - i. uptake by the northern hemisphere is determined by difference from emission scenarios;
    - ii. there may have been natural (and perhaps unknown) gradients in  $p\text{CO}_2$  before fossil fuel release began. This situation could arise if the flux of carbon from the northern hemisphere to the southern hemisphere through the atmosphere were balanced by an equal and opposite flux through the ocean. How could we know if this were the case? (Ice cores, possibly, but the precision and accuracy of ice core  $\text{CO}_2$  data may not be adequate to resolve very small gradients).
3. Bomb radiocarbon: atomic bomb tests of the 1960's (and to a lesser extent, 1950's) doubled the radiocarbon content of the atmosphere. As this radiocarbon exchanges with the ocean, we can follow the radiocarbon into the ocean.
- a. Complications:
    - i. This transfer will continue to occur regardless of whether fossil fuel  $\text{CO}_2$  is being emitted; i.e. in order to scale the anthropogenic  $\text{CO}_2$  uptake to  $^{14}\text{C}$  uptake, we must include a model for the gas exchange of  $^{14}\text{CO}_2$  and  $^{12}\text{CO}_2$ .
    - ii. As  $^{14}\text{C}$  is transferred from the atmosphere to the ocean, the scaling factor expands (i.e., a given addition of  $^{14}\text{C}$  to the surface ocean scales to an increasingly larger amount of  $\text{CO}_2$ ). Unless we set off some more bombs, the utility and accuracy of  $^{14}\text{C}$  will diminish into the future.
    - iii. We need to know the distribution of  $^{14}\text{C}$  on a global scale; because measurements of  $^{14}\text{C}$  are expensive (circa \$500 each), it is difficult and costly to undertake a global measurement scheme. One global survey (GEOSECS) was undertaken in the 1970's). From then, until the 1990's only regional studies were undertaken (e.g. North Atlantic, Tropical Atlantic, and South Atlantic studies have been completed in sequence). Finally, in the 1990's, the WOCE program will complete a global picture for the upper 2000 m of the ocean.

#### 4. Carbon-13

a. Definition of  $\delta^{13}\text{C}$ :



units: ‰, permil

- b. Because the  $\delta^{13}\text{C}$  of fossil fuel  $\text{CO}_2$  is  $\sim -27\text{‰}$  compared to  $-6\text{‰}$  for the pre-anthropogenic atmosphere, the  $\text{CO}_2$  that goes into the ocean is depleted in  $^{13}\text{C}/^{12}\text{C}$  compared to the normal oceanic  $\delta^{13}\text{C}$  (which was on average close to equilibrium with the atmosphere. Hence as fossil fuel is released, the  $\delta^{13}\text{C}$  of the atmosphere decreases with time. As some of this  $\text{CO}_2$  goes into the ocean, the  $\delta^{13}\text{C}$  of ocean waters in contact with the atmosphere will move to more negative values. This decrease has been observed, but the use of this technique to estimate  $\text{CO}_2$  uptake has similar caveats as applied to bomb  $^{14}\text{C}$ . Also note: biospheric uptake of  $\text{CO}_2$  will result in larger  $\delta^{13}\text{C}$  fractionation than will solubility-driven ocean uptake, so this data can be used to help resolve ocean vs. continental  $\text{CO}_2$  uptake.

source: Keeling et al. (1996) Glob. Biogeochem. Cycles 10:335



5. “Anthropogenic” CO<sub>2</sub> discrimination by “natural correction”: this method assumes that we know the natural ocean CO<sub>2</sub> system parameters – Redfield ratios, natural alkalinity distribution, etc. – well enough to subtract the large natural CO<sub>2</sub> levels from the present-day observations to give us the “anthropogenic” CO<sub>2</sub>. Problems: uncertainties in the ratios are problematical, particularly in the Southern Ocean. Example: Kortzinger et al. (1998) JGR 103:18861. Nonetheless, the values calculated are in accord with the values calculated the other ways. See Gruber, N., J. L. Sarmiento, et al. (1996). "An improved method for detecting anthropogenic CO<sub>2</sub> in the oceans." Glob. Biogeochem. Cyc. 10: 809-837.
6. Oxygen changes in the atmosphere
- When fossil fuel is burned, O<sub>2</sub> is consumed.
  - O<sub>2</sub> in atmosphere is 200,000 ppmV where CO<sub>2</sub> is 350 ppmV. So a 10% rise in atmospheric CO<sub>2</sub> is roughly matched by an 0.03% fall in oxygen! Hence oxygen must be measured with extreme precision (parts per million).
  - O<sub>2</sub>/CO<sub>2</sub> ratio depends on fuel composition:, e.g.
 
$$\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} \quad , \text{ but}$$

$$\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$$
  - CO<sub>2</sub> uptake by the ocean doesn't change atmospheric O<sub>2</sub>, but CO<sub>2</sub> uptake by the biosphere releases O<sub>2</sub> - so here is a way to separate ocean CO<sub>2</sub> uptake from biospheric CO<sub>2</sub> uptake.
  - Ralph Keeling (Keeling Jr.) uses interferometry to measure changes in the refractive index of air (which depends on O<sub>2</sub> concentration) to measure changes in atmospheric O<sub>2</sub> to the required precision. The O<sub>2</sub>/N<sub>2</sub> ratio can be measured almost as well by mass spectrometry as well (Michael Bender).
  - The first hint of the resolution is given in a paper by R. Keeling et al. where the contributions of ocean uptake and vegetation are resolved by a vector diagram (the next 6 years of data supports this assessment):

## VII. Future evolution of the anthropogenic CO<sub>2</sub> transient.

- A. Unless emission controls are instituted, and assuming some sort of "business as usual" scenario, CO<sub>2</sub> concentrations in the atmosphere will continue to rise to a peak of 3-6 times the preanthropogenic level in the next 200-400 years. At that point, estimated fossil fuel reserves supposedly will be nearly exhausted and CO<sub>2</sub> will fall. Uptake by the ocean will absorb about 70-80% of the total emitted over several

hundreds of years, leaving us 50-100% above preanthropogenic levels. At that point,  $\text{CaCO}_3$  dissolution on the seafloor (and to a lesser extent, by continental carbonates) will become the major sink and take up about  $3/4$  of the residual on time scales of several thousands of years.

source: Caldiera et al. (1993) Nature 366:251-253

source: Archer et al. ,1997. Similar scenarios have been presented previously by Eric Sundquist.

B. Ocean acidification: the pH of the surface ocean has dropped by 0.1 unit during the past 200 years. In projections for the next 100 years, it will drop an additional 0.2 units. This will reduce  $[\text{CO}_3^{2-}]$  and calcifying organisms such as corals will find it more difficult to thrive.