April 7, 2009

Introduction

Will look at C and N (maybe) cycles with respect to how they influence CO2 levels in the atmosphere. Ocean chemistry controls CO2 levels in atmosphere.

<u>Carbon Reservoir Sizes</u> (PgC, 10^{15}gC) (Sarmiento and Gruber, 2002)
Atmosphere = 600
Surface Ocean = 1020
Intermediate and Deep Ocean = 38100
Surface Sediments = 150
Marine Biota = 3
DOC = 700
Vegetation/Soil/Detritus = 2314
Fossil Fuels = 3800 (223 have been burned)

Ocean Carbon Chemistry, specifically in the high latitudes, controls atmospheric CO_2 concentrations - over long timescales (years) atmosphere equilibrates with surface ocean.

CO2 in atmosphere is influenced by pCO2 of surface water (partial pressure of water is the CO2 (gas) that would be in equilibrium with water).

Global map of ΔpCO_2 is mostly dictated by surface ocean conditions since atmosphere is relatively well mixed relative to timescale of processes that alter surface ocean pCO_2, and relative to time it takes to equilibrate surface ocean with atmosphere (6-10 months).

- locally, CO2 is not in equilibrium with ocean, transfer of CO_2 between air-sea would tend to eliminate ΔpCO_2, but takes 6-10 months to equilibrate 50m thick surface layer with atmosphere, so biological and physical processes dominate ΔpCO_2 distribution because the timescale of these processes is faster.
- globally, it is in equilibrium with ocean under steady state conditions

Since the atmosphere is fairly well mixed, the difference in pCO2 of the ocean versus atmosphere is dictated by variations in the pCO2 of the ocean **which is controlled by what?**

- CARBON CHEMISTRY (discuss details later)
- surface ocean temperature (warming increases pCO_2, and cooling lowers pCO_2)
- surface ocean salinity (much smaller effect than temperature)

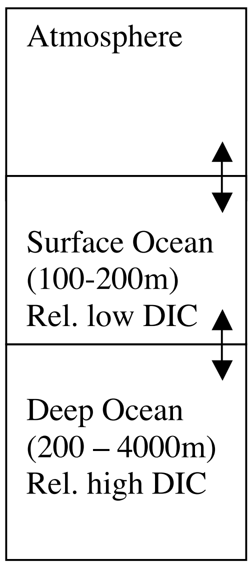
CARBON CHEMISTRY can be broken down to:
- Total amount of carbon (DIC) **which in influenced by what?**
  - **PRODUCTIVITY** (discuss this now), which decreases DIC
  - UPWELLING, which increases DIC
- Alkalinity (balance of strong acids and bases) **which is influenced by what?**
  - River input versus sedimentation influences long term whole ocean alkalinity
  - Formation of minerals in sea water influences distribution of ocean alkalinity

- Dissolution of minerals formed in sea water influences distribution of ocean alkalinity

Deep ocean concentration of [DIC] and [Alk] ultimately control surface concentration of [DIC] and [Alk], and hence pCO_2. Upwelling in low latitudes releases carbon to atmosphere (warming of upwelled waters increases pCO_2 dramatically), but is not thought to control atmospheric pCO_2.

In sum: Variations in pCO2 stem from physical (T and S and upwelling) and biological processes – these will be the focus of this lecture.

PRODUCTIVITY – Biological Pump (transfer of carbon from the surface ocean to the deep ocean). First focus on the effect of productivity on DIC.



It is convenient to think about the ocean as a two-box system, with fluxes between them. Atmosphere is passive – trying to equilibrate with ocean.

If there was no biological productivity today, (surface and deep layers were mixed), then DIC in surface ocean would be higher and atmosphere would be 440 ppm, compared to 280 ppm (pre-anthropogenic today).

If all surface nutrients were utilized and pump was totally efficient, then DIC in surface ocean would be lower and atmosphere would be 145 ppm (LGM was 195 ppm).

PRODUCTIVITY **is influenced by what?**

- Sunlight (won't really discuss this, but it is obvious that there are multiple climate effects on productivity – clouds, or anything that influences water turbidity.
- **nutrients**, macro and micro (relevance to Nitrogen cycle)
- temperature, salinity (to a lesser extent since there are organisms adapted to different regions)

NUTRIENTS – what influences nutrient distribution in surface water?

- upwelling of deeper dissolved nutrients (wind strength, direction, internal source from recycled nutrients)
- river clay (external source to ocean)
- aeolian dust (external source to ocean)
- atmospheric gases (external source to ocean)

NUTRIENTS – what are the timescales of changes to surface water nutrients due to these processes?

- upwelling (instantaneous)
- river sources (geologic – 1000's to millions)
- aeolian sources (instantaneous to geologic)
- atmospheric sources (instantaneous)

NUTRIENTS – name some nutrients that fall into these categories?

- upwelling (any nutrients enriched in subsurface water)
- river sources (P, metals, N, Si – usually plenty of nutrients near rivers, but quickly become metal-limited when go away from river sources)
- aeolian sources (metals – vast regions of the ocean are metal-limited, especially in upwelling regions where there are excess major nutrients)
- atmospheric sources (N – and this is why the N-cycle and biological transformations of N are so important to the C cycle. Nitrogen is thought to be a limiting nutrient in many locations over vast regions of the ocean).

A note on the importance of NITROGEN: Carbon Cycle – influenced by Productivity among other things, which is influenced by nitrogen fixation and denitrification, among other things.

1. N2 to organic-N; called **"N-fixation"** (plants and humans): enzyme-catalyzed reduction of N2 to NH3 (ammonia), NH4+ (ammonium), or any organic nitrogen compound.
2. Organic-N to NH4+; **"mineralization" or "ammonification"** (by bacteria and fungi): breakdown of organic N to NH4+ or NH3.
3. NH4+ or NH3 to NO3-(nitrate) or NO2-(nitrite); **"nitrification"** (by bacteria): as a means of producing energy.
4. NO3- to N2 or N2O; **"denitrification"** (by bacteria): reduction of NO3- to any gaseous nitrogen species
5. NH4+ or (NO3- to NH4+) to organic-N; **"photosynthesis/assimilation"** (uptake by plants): assimilation or uptake of ammonium by organism to form biomass.

Inorganic Carbon Species

$CO_{2\,(aq)}$ = dissolved CO_2 gas
H_2CO_3 = carbonic acid

$CO_{2\,(aq)}$ and H_2CO_3 are analytically indistinguishable from each other and are lumped together as CO_2^*. CO_2^* comprises 0.5 – 1.5% of the total carbon in ocean

$CO_3^=$ = carbonate ion, comprises 2.5 – 9.5% of total carbon in ocean
HCO_3^- = bicarbonate ion, comprises 90 – 96% of total carbon in ocean

The following reactions describe the relationships between these species – we assume thermodynamic equilibrium between species (reactions are fast)

$$CO_{2\,(gas)} <==> CO_{2\,(aq)} \qquad (1)$$

$$CO_{2\,(aq)} + H_2O <==> H_2CO_3 \qquad (2)$$

$$H_2CO_3 <==> H^+ + HCO_3^- \qquad (3)$$

$$HCO_3^- <==> H^+ + CO_3^= \qquad (4)$$

Using CO_2^* we redefine (1) through (3):

$$CO_{2\,(gas)} <==> CO_2^* \qquad (5)$$

$$CO_2^* + H_2O <==> H^+ + HCO_3^- \qquad (6)$$

Temp. dependant equilibrium equations for reactions (5), (6), and (4):

$$K_o = [CO_2^*] / pCO_2 \qquad (7)$$

$$K_1 = [H^+][HCO_3^-] / [CO_2^*] \qquad (8)$$

$$K_2 = [H^+][CO_3^=] / [HCO_3^-] \qquad (9)$$

DIC – Dissolved Inorganic Carbon

$$[DIC] = [HCO_3^-] + [CO_3^=] + [CO_2^*] \qquad (10)$$

Alkalinity – a measure of the acid-neutralizing capacity of sea water. It is a measure of excess of bases (proton acceptors) over acids (proton donors) measured by titration with H^+ of all weak bases. pH of the ocean is 8.2 – a weak basic solution.

$$[Alk] = [HCO_3^-] + 2[CO_3^=] + [OH^-] + [B(OH)_4^=] - [H^+] \qquad (11)$$

[$B(OH)_4^=$ (borate) is formed by the dissociation of boric acid.]
[OH^- (hydroxide ion) and H^+ are formed by the dissociation of water.]

Alkalinity can also be viewed as the charge balance of all strong acids and bases unaffected by titration of weak bases, or the excess positive charge that is balanced by the weak bases:

$$[Alk] = [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + \text{minor cations} - [Cl^-] - 2[SO_4^{2-}] - [Br^-] - [NO_3^-] - \text{minor anions} \quad (12)$$

For the purposes of this class we will focus on 'carbonate alkalinity' which are the components of alkalinity related to the carbon species. This approximation is appropriate for understanding the processes that determine primary carbon chemistry and alkalinity distributions.

In reality, borate contributes about 4% of the total alkalinity of the ocean, and the balance between $[OH]^-$ and $[H^+]$ contribute less than 0.5%.

From now on we will make the following assumption:

$$[Alk] \approx [\text{carbonate Alk}] = [HCO_3^-] + 2[CO_3^=] \quad (13)$$

In some cases, we can simplify the expression for [DIC] by assuming that $[CO_3^*]$ is negligible (≈0.5%), and rewrite (10) as:

$$[DIC] \approx [HCO_3^-] + [CO_3^=] \quad (14)$$

Combining (13) and (14) we can come up with expressions that relate $[HCO_3^-]$ and $[CO_3^=]$ to [Alk] and [DIC]:

$$[HCO_3^-] \approx 2[DIC] - [Alk] \quad (15)$$
$$[CO_3^=] \approx [Alk] - [DIC] \quad (16)$$

HOW CARBON SPECIES VARY WITHIN THE OCEAN – mainly has to do with biological processes, although air-sea exchange can also influence DIC.

Biological uptake of carbon in the form of organic matter, and respiration or destruction /oxidation of organic matter have a major influence on DIC and a minor influence on Alk.

Formation of organic tissue (photic zone) will cause [DIC] to decrease due to carbon uptake into organic matter, and [Alk] to increase slightly due to uptake of negatively charged ions [$HPO_4^{=}$] and [NO_3^{-}] (see eqn 12).

Destruction of organic tissue (respiration) will cause [DIC] to increase due to carbon oxidation, and [Alk] to decrease slightly due to oxidation of nutrients P and N.

In the surface water, photosynthesis dominates over respiration, thus organic matter formation would tend to drive [DIC] down, and [Alk] slightly up.

But, the formation and destruction of calcite ($CaCO_3$) is also occurring and has a strong influence on DIC and Alk as well:

Formation of $CaCO_3$ (photic zone) will cause [DIC] to decrease due to carbon uptake into organic matter, and [Alk] to decrease due to uptake of calcium ions [Ca^{2+}]. For every one unit of [DIC] change there is a 2 unit change in [Alk] due to the double charge of calcium ion.

Dissolution of $CaCO_3$ will cause [DIC] to increase and [Alk] to increase, again in a 1:2 ratio.

In the surface water, $CaCO_3$ formation dominates over dissolution, thus driving DIC and Alk down. In the deep water below the lysocline, $CaCO_3$ dissolution is strong, thus driving DIC and Alk up. See handout for position of lysocline – intersection between calcite saturation and carbonate ion content.

Taking the two biological processes together: For every 4 carbon atoms that are sequestered in the surface ocean in organic matter, 1 carbon atom is sequestered in $CaCO_3$. This 4:1 ratio essentially applies for destruction of biogenic particles at depth as well. The net effect is that the change in [Alk] is less than the change in [DIC]:

Net effect of organic matter and $CaCO_3$ production in surface and destruction at depth:

$$\Delta[Alk] \approx 28\% \, \Delta[DIC] \qquad (17)$$

Keeping in mind equation (16): At depth, the increase in [DIC] will be greater than the increase in [Alk] and the [$CO_3^{=}$] will thus be lower than surface water. And, as the water ages and accumulates that respiration products of organic matter and the dissolution products of $CaCO_3$, the [DIC] will increase, the [Alk] will increase, and the [$CO_3^{=}$] will decrease.

<u>CaCO3</u> (calcite)
With reference to the solubility product for calcite:

$K_{sp} = [Ca^{2+}][CO_3^{2-}]$

K_{sp} varies with pressure (and temperature) in the two-box ocean.
Saturation curve – shows you how carbonate concentration at saturation changes as K_{sp} changes with depth. As K_{sp} increases with depth, carbonate concentration at saturation increases.

Below is the $[CO_3^{2-}]$ at saturation with respect to CaCO3.

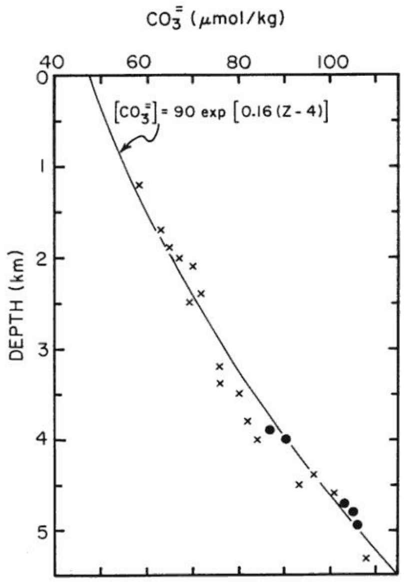


Figure 2-22 Plot of saturation $CO_3^{=}$ ion concentrations obtained using the Weyl-Ben Yaakov <u>in situ</u> saturometer (crosses) and by assuming that the lysocline represents the saturation horizon (solid circles). The curve drawn through these points has the exponential shape demanded by thermodynamic theory. Z in the equation indicates water depth in kilometers. This summary was made by Broecker and Takahashi (463). Broecker; Peng (1982) [OC, Fig. 3.2]

<u>The Lysocline:</u>
$[CO_3^{=}]$ in most of the upper ocean is high enough that $CaCO_3$ is supersaturated with respect to sea water. But, $CaCO_3$ becomes more soluble at lower temperature and higher pressure, and $[CO_3^{=}]$ is low enough in the deep ocean that $CaCO_3$ becomes undersaturated at depth. The depth at which $CaCO_3$ becomes undersaturated is the lysocline. The depth of the lysocline varies from location to location depending on the $[CO_3^{=}]$. In the deep Atlantic, $[CO_3^{=}]$ is higher than in the Pacific, so the lysocline is deeper. Since the deep water residence time is higher in the Indian and Pacific Oceans, it has relatively low $[CO_3^{=}]$ and deep lysocline.

$CaCO_3$ sedimentation is a sink of carbon and alkalinity from the ocean system, and the lysocline depth determines to a large extent how much sedimentation of $CaCO_3$ occurs. Over geological timescales, the lysocline depth adjusts as changes in the ocean chemistry occur, in a way to compensate and diminish misbalances in the carbon cycle.

For example, take the case of increases in volcanic sources of CO_2 to the atmosphere:

CO_2 in atmosphere increases

Temperature increases

Continental weathering increases

Flux of alkalinity and carbon to rivers increases, ocean [Alk] increases

[$CO_3^{=}$] increases (see eqn. 16), lowering pCO_2 of ocean (see eqn. 19). Ocean becomes stronger sink of CO_2 from atmosphere acting as a negative feedback to the elevated levels due to increased volcanism.

Lysocline depth increases.

More $CaCO_3$ preserved in sediments, sink of Alk and DIC increases to balance increase in source of Alk and DIC.

New steady state achieved, with new lysocline depth and sedimentary sinks of Alk and DIC adjusted to match initial change.

Over shorter timescales, the lysocline adjustment can change the buffering capacity of the ocean. For example, let's look at increases in anthropogenic CO_2.

CO_2 in atmosphere increases and dissolves in ocean

New equilibrium between ocean and atmosphere will be reached within a few hundred to 1000 years. However, equilibrium with respect to river input and sediment output will not be reached so quickly.

Higher DIC in ocean, will cause [$CO_3^{=}$] to decrease (see eqn. 16)

Over long timescales, lysocline depth decreases (shoals)

More $CaCO_3$ will dissolve, rather than being buried, and [Alk] will increase (remember that Alk increase will be larger than DIC increase), thus increasing the buffering capacity of the ocean.

With a shallow lysocline and less $CaCO_3$ burial, the system is out of balance since river input will now exceed sediment output. [ALK] will begin to increase, buffering the original increase in CO2. Eventually, over long geological timescales, the misbalance will make [Alk] increase until it drives the lysocline deep enough so that output = input again.

SHORT-TERM; There is enough carbonate ion in surface ocean to take up about 150 X 10^{14} moles C from atmosphere, or 180 PgC.

HOW DOES OCEAN CONTROL ATMOSPHERIC pCO_2?

Using eqn (7), (8) and (9), we can see how pCO_2 is related to ocean carbon chemistry:

$$pCO_2 = [CO_2^*] / K_0 \tag{18}$$

If we now express CO_2^* as a function of $[HCO_3^-]$ and $[CO_3^=]$, and combine with (18):

$$pCO_2 = K_2 / K_0 K_1 \left([HCO_3^-]^2 / [CO_2^=]\right) \tag{19}$$

(19) provides insight into the connection between lysocline depth and pCO_2.

If we now use the approximations (15) and (16), and combine with (19), we can get a sense of how pCO_2 is related to the balance between [Alk] and [DIC].

$$pCO_2 = K_2 / K_0 K_1 \left((2[DIC] - [Alk])^2 / ([Alk] - [DIC])\right) \tag{20}$$

Here we can distill the major factors that influence pCO_2 of a water mass, and therefore ocean sources and sink of atmospheric CO_2, and the concentration of CO_2 in the atmosphere. The major factors are: (a) temperature (and to a lesser extent salinity) through the $K_2 / K_0 K_1$ term which contains the temperature and salinity dependant equilibrium constants of all three reactions between carbon species (eqn 7, 8 & 9); (b) [DIC], influenced by biological (already discussed) and physical (air-sea exchange) processes; and (c) [Alk], influenced by biological processes (already discussed). Let's look at these factors separately:

(a) Temperature and salinity influence the solubility of CO_2. Solubility increases (pCO_2 decreases) as temperature and salinity decrease. The temperature effect is much stronger than the salinity effect. For temperature, the effect on K_0 is responsible for about 60% of the changes in solubility, and the remaining 40% is accounted for by the temperature effect on K_2 / K_1 (see eqns. 19 and 20). For example, if you take a parcel of water with a pCO_2 of 300 ppm, a one degree increase in temperature will cause pCO_2 to increase by 13 ppm. A one salinity unit increase will cause pCO_2 to increase by 9 ppm. Since the ocean range in T is 30°, but the ocean range in S is only about 5 ppt, temperature is going to have a much stronger influence on the distribution of pCO_2 of surface water.

(b) & (c) Using (20) one can calculate how pCO_2 differs as a function of changes in [DIC] and [Alk]. Essentially, the slope of the correlation between a change in pCO_2 relative to a change in [DIC] or [Alk] provides a measure of the sensitivity of a given water mass. The 'sensitivity' of pCO_2 to [DIC] is called the Revelle Factor, or buffer factor. Typically it has values of about 10, and is most accurately calculated when borate is taken into account. Values range from about 8 in low latitudes, to 15 in high latitudes. The 'sensitivity' of pCO_2 to [Alk] is called the Alkalinity Factor. Typically it has values of about –9.5 and varies from about

–7.5 in low latitudes to –13.3 in high latitudes. Note that changes in [DIC] and pCO_2 are positively correlated, while changes in [Alk] and pCO_2 are negatively correlated. The Revelle and Alkalinity factors are dependant not on temperature, but on the [DIC] and [Alk] of the water which differs in the low versus high latitudes. To use these factors, you must know the initial sea water chemistry, and can then estimate how a change in these concentrations will change the pCO_2.

$$\text{Revelle Factor (unitless)} = (\Delta pCO_2/pCO_2) / (\Delta[DIC]/[DIC]) \qquad (21)$$

$$\text{Alkalinty Factor (unitless)} = (\Delta pCO_2/pCO_2) / (\Delta[Alk]/[Alk]) \qquad (22)$$

SUMMARY OF ΔpCO_2 DISTRIBUTION –

The transfer of CO_2 between the ocean and atmosphere determine the atmospheric concentration of CO_2.

Regions with high positive values of ΔpCO_2 are sources to the atmosphere. For example:

tropical upwelling zones are sources: water upwells and warms, pCO_2 is elevated as the water warms. Biological productivity impacts the [DIC] and [Alk], thereby decreasing pCO_2, but on balance warming outweighs biological production and these regions have positive ΔpCO_2 values.

Mid-latitude regions into which warm water is advected and cooled have negative ΔpCO_2 values and are sinks of CO_2 into the ocean.

Mid and high lat North Atlantic is a strong sink: These regions have BOTH biological production and surface water cooling, and therefore ΔpCO_2 values that are strongly negative and are strong sinks of CO_2 out of the atmosphere.

Southern Ocean does not have high enough biological production to bring [DIC] low enough to create a strong sink of CO_2. Although these regions have cold temperatures, they have high [DIC], so they have ΔpCO_2 values that are close to zero.

What is clear is that the strength of the source or sink of CO_2 is determined by multiple processes, both physcial and biological; **Atmospheric CO_2 can be readily influenced by regional changes in any of these processes**.

OCEAN UPTAKE OF ANTHROPOGENIC CO_2

If CO_2 only dissolved in seawater (like other gases), about 70% of the CO_2 emitted by anthropogenic activities would remain in the atmosphere. However, the uptake capacity of the oceans is greatly enhanced by the reaction of CO_2 with carbonate ion to form bicarbonate ion. So, carbonate ion to a large extent, determines the uptake capacity (but carbonate ion is influenced by a number of different things – it is not conservative).

Short timescale (don't consider role of sediment). Upper 75 m of surface ocean were to equilibrate with atmosphere, only about 8% of the emissions would go into the ocean – this occurs in less than one year. Long timescale (don't consider role of sediment). Use entire volume of ocean, and 81% of emissions would go into the ocean. This occurs slowly because of the timescale of vertical mixing of the ocean. Decreasing buffering effect with time as pCO_2 increases.

Now, consider role of sediment:
$CO_2^* + CaCO_3 + H_2O \leftrightarrow Ca^{2+} + 2\ HCO_3^-$

Increases ALK and DIC by same (2 units) for every mole of CO_2^* absorbed.

If you consider the role of sediment in the upper few cm (with a little bit of neutralization by rocks weathered on land), only about 8% of emissions will remain in atmosphere.

Summary: Archer et al., 1997, exact numbers depend on size of pulse.
Carbonate in sea water sequesters 70-80% of atmospheric pulse on timescale of hundreds of years.
$CaCO_3$ in surface seds accounts for an additional 9-15% in about 6000 years
Weathering on land accounts for an additional 3-8% in about 8000 years
Final equilibrium leaves about 8% of the initial pulse in the atmosphere.