Now that we have looked at the physical processes involved with the exchange of CO₂ between the atmosphere and the ocean let’s turn to the chemical processes.

### Chemical 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
Solubility of Gases as a Function of Temperature

- Solubility of all gases decreases with increasing $T$
- Differences result from molecular interactions between gas & water

**CO$_2$ Solubility is a Function of Temperature**

- Demonstrations of the temperature dependence

- Solubility decreases as $T$ increases
- $p$CO$_2$ increases as $T$ increases (implying the liquid can hold less of the gas at higher $T$, resulting in higher gas pressure)
Gas Solubility Decreases as Salinity Increases

Natural Range of Seawater NaCl (Salinity)

CO₂ is more soluble in cold waters than in warm waters (the thermal pump), & more soluble in fresher waters than saltier waters (the salt pump).

- If alkalinity (see following discussion) were uniform throughout the ocean & if both cold & warm surface waters equilibrated their \( p_{CO₂} \) with the atmosphere, then cold surface waters would have a higher dissolved CO₂ content than warm surface waters.

- As these cold surface waters circulate into the deep interior of the ocean, deep waters will have more CO₂ than warm surface waters.
Chemical Processes Influencing Air-Sea Exchange of CO$_2$

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

2. Chemical Processes
   - CO$_2$ solubility = f (temperature, salinity) ["The Solubility Pump"]
   - Carbonate chemical equilibrium

3. Biological Processes ["The Biological Pump"]
   - Photosynthesis & respiration
   - Calcium carbonate production

CO$_2$ Uptake by the Ocean: the Carbonate System

- The ocean can take up CO$_2$ from the atmosphere in amounts that far exceed what would be expected based on solubility alone
- The extra absorbing power is caused by the carbonate buffer system

- CO$_2$ gas dissolves in seawater to become aqueous CO$_2$
  \[ \text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) \]
- Henry’s Law describes the equilibrium between CO$_2(g)$ & CO$_2(aq)$
  \[ K_H = \frac{[\text{CO}_2(aq)]}{p\text{CO}_2} \quad \text{(a function of T & S)} \]
- CO$_2(aq)$ combines with water to produce carbonic acid
  \[ \text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \]
- At the pH of surface seawater (~8.2), carbonic acid rapidly dissociates into a hydrogen ion and a bicarbonate ion
  \[ \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \]
- The hydrogen ion then reacts with a carbonate ion to produce a second bicarbonate ion
  \[ \text{H}^+ + \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^- \]
CO₂ Uptake by the Ocean: DIC

- Since only ~1% of CO₂(aq) exists as H₂CO₃ it is usually left out of the sum of dissolved inorganic carbon (DIC) species

\[
\text{DIC} = \text{CO}_2(\text{aq}) + \text{HCO}_3^- + \text{CO}_3^{2-}
\]

- The molar ratio of these three species in seawater is about 1 : 100 : 10

CO₂ Uptake by the Ocean: Conservative Quantities

- DIC is a **conservative** quantity in seawater, meaning
  - Its concentration can only be changed by mixing & advection
  - It can be mixed linearly
  - Non-conservative properties (e.g., O₂ & PO₄³⁻) are altered by biological & chemical processes

- An example would be mixing in an estuary, where the DIC concentration changes linearly from the low value in rivers to the high value in seawater:
*** Start Here Tues 2/10/09 ***

Clarifications

Eddies

• Small-scale (~$10^0$-$10^2$ km), time-varying components of the circulation
• Spatio-temporal integrations produce the large-scale “steady” flows
• Contain 90-99% of the kinetic energy of the flow (Wunsch, 2004, 2007, in press)
• Ubiquity & importance recognized since ’70s; widely observed since ’90s

Without eddies (1° grid size)

With eddies (1/6° grid size)

http://www.cre.noaa.gov/climate/images/modeling_oceansim.jpg
- Another conservative quantity in seawater that is important for understanding the exchange of CO$_2$ between the atmosphere & the ocean is **Alkalinity**, the best definition of which I have ever read is:

  *The negative charge deficit in seawater that is compensated by ions which can exist in more than one charge state.* (Broecker, 2005)

- Seawater must be **electrically neutral**
- Though comprised primarily of ions with a fixed electrical charge, such as the cations Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, and the anions Cl$^-$ & SO$_4^{2-}$, there is a slight deficit of negative charge, the **alkalinity**

  - That deficit is made up by protonating & deprotonating acids & bases until charge balance is achieved.
CO₂ Uptake by the Ocean: Alkalinity (cont’d.)

• pH is a 3rd important quantity in determining ocean uptake of CO₂

\[ \text{pH} = -\log[H^+] \]

• The NCD is compensated by adding & removing protons (H⁺) to ions that can exist in more than one charge state

• Important for ocean CO₂ uptake are acids & bases that can exist in more than one charge state in the pH range of seawater, ~7-9.

• So a more precise definition of alkalinity would be:

“If the negative charge deficit that is compensated by acids & bases that can exist in more than one charge state in the pH range of seawater.”

• Because of their high concentration in seawater and their tendency to protonate / deprotonate at pH 7-9, HCO₃⁻, CO₃²⁻, B(OH)₃, & B(OH)₄⁻ are by far the most abundant such species

CO₂ Uptake by the Ocean: Alkalinity (cont’d)

• The high concentrations of carbonate & borate ions make HCO₃⁻, CO₃²⁻, B(OH)₃, & B(OH)₄⁻ the most important contributors to alkalinity in seawater since its pH is ~8.2

CO₂ Uptake by the Ocean: Alkalinity (cont’d.)

Thus in seawater:

\[
\text{NCD} = \text{Alkalinity} = \text{HCO}_3^- + 2*\text{CO}_3^{2-} + \text{B(OH)}_4^- 
\]

More precise definitions of alkalinity exist that include more species:

- They include ions that contribute < 1% to alkalinity because they become protonated/deprotonated at:
  - seawater pH, but have low &/or variable concentrations (e.g., H₃SiO₄⁻, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻, OH⁻)
  - pH levels << 8 (e.g., Cl⁻, SO₄²⁻, F⁻)
- In practice, even borate is left out since it comprises < 5% of alkalinity
- The term Carbonate Alkalinity is then used as a simplifying approximation:
  \[
  \text{Carbonate Alkalinity} = \text{HCO}_3^- + 2*\text{CO}_3^{2-} 
  \]

Borate contribution to Alkalinity:

\[
\frac{108.6}{2216} \times 100 = 4.9\%
\]

Adapted from Broecker (2005) and Emerson & Hedges (2007) Chap. 4

How is Alkalinity Determined?

- Alkalinity is measured by titration: strong acid is added to seawater until all proton acceptors have been protonated
- “The precise definition of alkalinity of seawater is based on the method by which it is determined and the species that exchange protons during the titration.” (Emerson & Hedges (2007) p. 4.10)
- Operationally carbonate alkalinity is defined as the # of equivalents of acid required to bring a sample to the CO₂ endpoint, or equivalence point —i.e., when # moles acid added = moles HCO₃⁻ + 2*moles of CO₃²⁻.
  - Acid dropped from a burette into seawater until indicator changes color permanently—the endpoint.
  - At this equivalence point, all the CO₃²⁻ & HCO₃⁻ have been converted to CO₂.
  - The carbonate alkalinity is 3.8 meq/L
Alkalinity Titration of Seawater with Strong Acid

\[ \text{Alkalinity in the Ocean} \]

- Alkalinity is greater in the deep ocean than in the surface b/c Ca\(^{2+}\) ions are incorporated into CaCO\(_3\)\(^*\) (removing alkalinity & NCD) in surface waters & released by dissolution of CaCO\(_3\) in deep waters (adding alkalinity & NCD)

\[ \text{Alkalinity} \ (\text{uMol or } \mu\text{eq/kg}) \]

WOCE Pacific Ocean
Line 18 along 105°W


* A biological process we will discuss shortly
CO₂ Uptake by the Ocean: the Revelle Factor

- The amount of CO₂ the ocean can absorb from the atmosphere beyond the amount of CO₂ gas that can be dissolved in it is referred to as its buffering capacity.
- The buffering capacity of the ocean is quantified by the Revelle Factor.
- The RF (aka buffer factor) relates the fractional change in atmospheric pCO₂ to a fractional change in DIC (after re-equilibration).
- RF is directly proportional to the ratio of DIC : Alkalinity.

Lower RF = Greater buffering capacity

Buffering Capacity of the Ocean

- Because Carbonate Alkalinity = HCO₃⁻ + 2*CO₃²⁻ it is clear that the greater the alkalinity of a solution the greater its potential for neutralizing acid (H⁺), such as CO₂:

- The more CO₃²⁻, or Alkalinity, contained in the water, the more CO₂ (acid) it will be able to absorb.
- But the total amount of DIC is also a factor, because with low concentrations of DIC there cannot be large amounts of CO₃²⁻ to neutralize CO₂ at any pH.
- That is why the Revelle factor is proportional to (DIC / Alkalinity). Low values of RF of DIC/Alk imply greater capacity to buffer added CO₂. (Higher Alk = Lower RF = Higher buffering capacity.)
Buffering Capacity of the Ocean: The Revelle Factor

1994 distribution of the Revelle factor averaged over upper 50m of water.

- Low RFs occur in warm tropical-subtropical waters; high RFs in cold high latitude waters
- The capacity for seawater to take up CO$_2$ from the atmosphere is inversely proportional to the RF
- Hence, the lower the RF, the higher the oceanic equilibrium concentration of CO$_2$ for a given atmospheric CO$_2$ increase
- North Pacific surface waters have a higher RF at comparable latitudes & consequently lower anthropogenic CO$_2$ concentrations
- This difference results from North Pacific alkalinity values about 100 mol/kg lower than in the North Atlantic
- Current RFs are about one unit higher than in the preindustrial ocean.

Equilibration Time for Atmospheric Gases in Ocean Mixed Layer

Simple Gas Exchange (e.g. O$_2$, Ar)

- For mixed layer depth of 100m & piston velocity of 2000 m/yr
- Equilibration time = 100m/2000m yr$^{-1}$ = 0.05yr = 18d
**Equilibration Time for Atmospheric Gases in the Ocean Mixed Layer**

- **pCO2 equilibration**
  - ~1 year
  - Change in pCO2 causes equal change in CO2(aq)
  - Revelle factor: fractional change in pCO2 is ~10x greater than DIC change
  - Since CO2(aq)=0.5% of DIC it takes 10/0.5, or 20x longer to equilibrate DIC then to equilibrate CO2(aq)
  - Equilibration time = (100m/2000m yr⁻¹) * 20 = 1yr

- **Total DIC must equilibrate with atm. CO2**
  - Total DIC must equilibrate with atm. CO2
  - 1m² of upper 100m of ocean contains: 10⁵ kg water * (2000 * 10⁻⁶ mol C/kg water) = 200 moles C
  - CO2 gas exchange rate = 20 mol/m²/yr (see prev. lec.)
  - Equilibration time = (200 mol) / (20 mol/m²/yr) = 10yr
Now that we have looked at the physical & chemical processes involved with the exchange of CO$_2$ between the atmosphere & the ocean let’s turn to the biological processes.

![IPCC 2007 Fig. 7.10](image)

### Biological Processes Influencing Air-Sea Exchange of CO$_2$

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   - Photosynthesis & respiration
   - Calcium carbonate production
The “Biological Carbon Pump”

- The biologically mediated transfer of CO$_2$ & nutrients from the surface to the deep ocean

The elemental composition of phytoplankton in the ocean is amazingly constant, as 1st noted by A.C. Redfield*

This “Redfield ratio” characterizes both phytoplankton & seawater!

Grazing of phytoplankton by zooplankton produces fecal pellets that sink & transport algal biomass to the deep sea where it is “remineralized” back to inorganic nutrients.

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 \quad \text{(simplified photosynthetic eqn.)}
\]

\[
106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 + 122\text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 138\text{O}_2
\]

Deep Ocean

Surface Ocean

Upwelling of nutrients

Settling of organic matter

\[
\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{(simplified respiration eqn.)}
\]

\[
(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 138\text{O}_2 \rightarrow 106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 + 122\text{H}_2\text{O}
\]


A More Realistic View of Biological Processes in the Surface Ocean “Box”

Emerson & Hedges (2007) Chem. Oceanogr., Fig. 6.5

POM = Particulate Organic Matter
DOM = Dissolved Organic Matter
Biological Pump Effect on Nutrient Distributions

- Nutrients such as N & P stripped out of surface water by photosynthesis
  - Consuming CO$_2$(aq)
  - Producing O$_2$
- Transported to deep sea by sinking fecal pellets
- Released back into deep water during decomposition by bacteria (remineralization)
  - Consuming O$_2$


Note that O$_2$ has mirror-image profile of PO$_4^{3-}$

Combined Effect of the Biological Pump & Ocean Circulation

\[ \text{PO}_4^{3-} + \text{MOC: John Marshall, MIT.} \]

\[ \text{Biological Pump + Ocean Circulation Effect on Phosphate} \]

- Oldest water in ocean accumulates most remineralized \( \text{PO}_4^{3-} \), the ultimate source of which was photosynthesis in the global surface ocean.
Oldest water in ocean accumulates most respired CO$_2$, the ultimate source of which was photosynthesis in the global surface ocean.

- Oldest water in ocean is most impoverished in O$_2$ because 138 moles of O$_2$ are consumed per mole of PO$_4^{3-}$ liberated during organic matter decomposition.
- From the Redfield ratio of C:N:P:O$_2$ of 106:16:1:-138
Global Nitrate & Water Age at 3000 m

From Key et al. (2005) in Emerson & Hedges (2007), Fig. 6.16.

The best visual depiction of the combined effect of the biological pump & ocean circulation I have seen!

From Key et al. (2005) in Emerson & Hedges (2007), Fig. 6.16.
Hard vs. Soft Parts

- Some organisms precipitate inorganic shells ("hard parts") out of calcium carbonate & silica, the overwhelming majority being coccolithophorids (CaCO$_3$) & diatoms (SiO$_2$)
- On average 22 moles of C as CaCO$_3$ are precipitated for every 106 moles of C converted into phytoplankton biomass ("soft parts")
- Results in a Redfield Ratio of C$_{org}$:N:P:C$_{CaCO3}$:O$_2$ = 106:16:1:22:-138
- Production of CaCO$_3$ is important in air-sea CO$_2$ exchange because it removes carbon and alkalinity from surface water & transfers it to deep sea

Globally the Production of CaCO$_3$ is 0.6 Gt C/yr
(~3% of global marine C fixation)

- SeaWiFS images & Composite
- 50% reduction in coccolith blooms expected in N. Atl (their largest habitat) by 2100 A.D. owing to ocean acidification

Coccolithophorids & Air-Sea CO₂ Exchange (c.)

- Coccolithophorids alter the Corganic:Ccarbonate, or “rain ratio” & increase surface pCO₂ during calcification, producing one molecule of CO₂ for each molecule of CaCO₃ fixed.
- Globally, the rain ratio from the surface ocean is ~ 4:1
- This ratio is largely controlled by the dominant taxon fixing carbon such that a shift in the phytoplankton community structure from calcifiers to silicifiers would affect the capacity of the biological pump
- For example, during a bloom of coccolithophorids, photosynthesis: calcification & the rain ratio can approach 1:1, & the effect of such high calcification rates has been found to change the air-sea gradient of CO₂.
- Considering that coccolithophorid blooms are responsible for up to 80% of surface ocean calcification, the 50% predicted decrease in potential surface coccolithophorid bloom areal extent may potentially lead to a significant increase in the POC:PIC ratio.
- By 2050 an increase in dissolved CO₂ & a decrease in the concentration of CO₃²⁻ will result in an increase in CaCO₃ dissolution.
- A decrease in calcification is a short-term negative feedback in the global carbon cycle.

Ratio of Hard to Soft Parts Produced & Exported from the Surface Ocean Influences pCO₂

- Vector diagrams demonstrate the effect of biological & physical processes on surface ocean pCO₂:
  - Gas exchange
    - Proportionally changes ocean DIC w/ no effect on alkalinity
  - "Soft tissue pump"
    - Photosynthesis reduces DIC & increases alkalinity with a slope of C/N=-106/16=-6.6
  - "Carbonate pump"
    - CaCO₃ production reduces alkalinity by 2 units per unit decrease in DIC b/c CO₃²⁻ contributes 2 moles of alkalinity per mole of DIC

Alkalinity = HCO₃⁻ + 2*CO₃²⁻
DIC = CO₂(aq) + HCO₃⁻ + CO₃²⁻

*Debate continues over the “true” Redfield ratio, with this book taking C:N = 117:16
Sarmiento & Gruber (2007) Fig. 8.3.5
Why is productivity so low in subtropical gyres?
Why is it so high in high latitude oceans? Along equator? On coastal margins?

Ocean color/SeaWiFS: http://oceancolor.gsfc.nasa.gov/SeaWiFS/TEACHERS/sanctuary_7.html