Now that we have looked at the physical processes involved with the exchange of CO$_2$ between the atmosphere and the ocean let’s turn to the chemical processes.

### 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
Solubility of Gases as a Function of Temperature

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

Sarmiento and Gruber (2006)

CO₂ Solubility is a Function of Temperature

- Demonstrations of the temperature dependence

- Solubility decreases as T increases
- pCO₂ 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

The Carbon “Solubility Pump”

- 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 CO₂

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2. **Chemical Processes**
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   - Photosynthesis & respiration
   - Calcium carbonate production

### CO₂ Uptake by the Ocean: the Carbonate System

- The ocean can take up CO₂ 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

- CO₂ gas dissolves in seawater to become aqueous CO₂
  \[ \text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) \]
- *Henry’s Law* describes the equilibrium between CO₂(g) & CO₂(aq)
  \[ K_H = [\text{CO}_2(aq)]/p\text{CO}_2 \] (a function of T & S)
- CO₂(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:
CO₂ Uptake by the Ocean: Alkalinity

- Another conservative quantity in seawater that is important for understanding the exchange of CO₂ 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⁺, Mg²⁺, Ca²⁺, and the anions Cl⁻ & SO₄²⁻, 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

  I.e., pH-independent species; strong acids & bases

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

- The negative charge deficit is compensated by adding & removing protons (H⁺) to ions that can exist in more than one charge state (pH-dependent species; weak acids & bases). Note: pH = -log[H⁺]
- Important for ocean CO₂ uptake are those 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 than Broecker’s would be:

  “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

![Graph showing pH vs. log [C] (mol kg⁻¹)](image)

Adapted from Emerson & Hedges (2007) Fig. 4.2

Thus in seawater:

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

• More precise definitions of alkalinity exist that include more species
• They include ions that contribute < 1% to alkalinity b/c they become protonated / deprotonated at:
  - seawater pH, but have low & variable concentrations (e.g., H₃SiO₄⁻, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻)
  - pH levels << 8 (e.g., Cl⁻, SO₄²⁻, F⁻)
• In practice, even borate is left out since it is < 5% of alkalinity
• The term Carbonate Alkalinity is then used as a simplifying approximation:

\[ \text{Carbonate Alkalinity} = \text{HCO}_3^- + 2\times\text{CO}_3^{2-} \]

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 CO$_2$ endpoint, or equivalence point—i.e., when # moles acid added = moles HCO$_3^-$ + 2*moles of CO$_3^{2-}$.

- Acid dropped from a burette into seawater until indicator changes color permanently— the endpoint.

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).

Alkalinity

(uMol or μeq/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 (see next page...)

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**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 :

  \[
  \begin{align*}
  \text{CO}_2(\text{aq}) + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3 \\
  \text{H}_2\text{CO}_3 & \leftrightarrow \text{H}^+ + \text{HCO}_3^- \\
  \text{H}^+ + \text{CO}_3^{2-} & \leftrightarrow \text{HCO}_3^- \\
  \hline
  \text{CO}_2(\text{aq}) + \text{H}_2\text{O} + \text{CO}_3^{2-} & \leftrightarrow 2\text{HCO}_3^- \\
  \end{align*}
  \]

- 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 either quantity imply greater capacity to buffer added CO₂.
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)

~2 weeks

- 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

- Simple Gas Exchange (e.g. O2, Ar) ~2 weeks (depth of mixed layer divided by piston velocity - i.e. total gas content divided by gas flux)

- pCO2 equilibration ~1 year

- Carbon isotope equilibration (C13, C14) ~10 years (change in TCO2 required to change pCO2 in seawater is divided by gas flux: e.g. for a 3% increase in pCO2, CO2(aq) rises by 3% and TCO2 rises by 0.3%; but because TCO2 is ~200x CO2(aq), it then takes 200*.3/3=20x longer)

Equilibration Time for Atmospheric Gases in the Ocean Mixed Layer

- For mixed layer depth of 100m & piston velocity of 2000 m/yr

  - Equilibration time = 100m / 2000m yr^-1 = 0.05yr = 18d

- 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 than to equilibrate CO2(aq)

- Equilibration time = (100m / 2000m yr^-1) * 20 = 1yr

- Total DIC must equilibrate with atm. CO2

- 1m^2 of upper 100m of ocean contains: 10^5 kg water * (2000*10^-6 mol C/kg water) = 200 moles C

- CO2 gas exchange rate = 20 mol/m^2/yr (see prev. lec.)

- Equilibration time = (200 mol) / (20 mol/m^2/yr) = 10yr
Now that we have looked at the **physical** & **chemical** processes involved with the exchange of CO₂ between the atmosphere & the ocean let’s turn to the **biological** processes

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

- The biologically mediated transfer of CO₂ & 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

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

- CO₂
- Humans
- Grazing Food Chain
- Phytoplankton
- POM
- Aggregates
- Sinking POM
- Zooplankton
- Fish
- Euphotic zone (20-150 m)
- C, N, P, S, Fe
- DOM
- Heterotrophic Protozoa
- Bacteria
- Viruses
- Microbial loop
- 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\(_2\)


Biological Pump Effect on Nutrient Distributions

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

Combined Effect of the Biological Pump & Ocean Circulation


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!

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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 $22 \text{ moles}$ of C as CaCO$_3$ are precipitated for every $106 \text{ moles}$ of C converted into phytoplankton biomass ("soft parts")
- Results in a Redfield Ratio of $\text{C}_{\text{org}}:\text{N}:\text{P}:\text{CaCO}_3:O_2 = 106:16:1:22:-138$
- 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

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Diatom (SiO$_2$)

Coccolithophorid (CaCO$_3$)
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 CO$_2$ Exchange (c.)

- Coccolithophorids alter the C$_{organic}$:C$_{carbonate}$ or "rain ratio" & increase surface pCO$_2$ during calcification, producing one molecule of CO$_2$ for each molecule of CaCO$_3$ 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 CO$_2$.
- 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 CO$_2$ & a decrease in the concentration of CO$_3^{2-}$ will result in an increase in CaCO$_3$ 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*
Global Ocean 1° Productivity

- 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