The Carbon Cycle

**WHY CARBON?**

\[ \text{AN} = 6 \ (6P/6N) \]
\[ \text{AW} = 12.011 \]

Oxidation: -4 to +4
Isotopes: ^1C, ^12C, ^13C, ^14C

**Carbon is the currency of life**

Carbohydrates  
Protein  
Nucleic acids

All living organisms utilize the same molecular building blocks.

**Time Scales of Carbon Exchange in the Biosphere**

4 places carbon is stored:  
1) Lithosphere, 2) Atmosphere,  
3) Ocean, 4) Terrestrial biosphere
The oceans carbon cycle

• The main components:
  – DIC, DOC, PC (includes POC and PIC)
• Primary processes driving the ocean carbon cycle:
  – abiotic: solubility, ventilation, transport;
  – biotic: photosynthesis, respiration, calcification

The ocean holds 50 grams of CO\(_2\) for every 1 gram of CO\(_2\) in the atmosphere.

<table>
<thead>
<tr>
<th>Pool</th>
<th>Mass (g C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2) in the atmosphere</td>
<td>(~750,000,000,000,000,000,000)</td>
</tr>
<tr>
<td>CO(_2) in oceans</td>
<td>(~39,120,000,000,000,000,000)</td>
</tr>
<tr>
<td>Dissolved organic carbon</td>
<td>(~700,000,000,000,000,000,000)</td>
</tr>
<tr>
<td>Living and dead particles</td>
<td>(~3,000,000,000,000,000,000)</td>
</tr>
</tbody>
</table>

*Because of its solubility and chemical reactivity, CO\(_2\) is taken up by the oceans more readily than other atmospheric gases.

* Over the long term (1000s of years) the oceans will consume ~90% of anthropogenic CO\(_2\) emissions.

Pools of Carbon in the Sea

- DIC in the oceans \(~37500 \times 10^{15}\) g C
  - H\(_2\)CO\(_3\)-carbonic acid
  - HCO\(_3\)-bicarbonate
  - CO\(_3^{2-}\)-carbonate
- DOC \(~700 \times 10^{15}\) g C
- POC (living and detrital organic particles) \(~22 \times 10^{15}\) g C
- PIC (CaCO\(_3\)) \(<1 \times 10^{15}\) g C

Vertical profiles of carbon in the North Pacific

- Dissolved Inorganic Carbon (\(\mu\)mol L\(^{-1}\))
- Particulate Carbon (\(\mu\)mol L\(^{-1}\))
- Dissolved Organic Carbon (\(\mu\)mol L\(^{-1}\))

Depth (m)

1900 2000 2100 2200 2300 2400

0 2 4 6 8 10

0 20 40 60 80 100

0 1000 2000 3000 4000 5000

Dissolved Inorganic Carbon (\(\mu\)mol L\(^{-1}\))

Dissolved Organic Carbon (\(\mu\)mol L\(^{-1}\))

Particulate Carbon (\(\mu\)mol L\(^{-1}\))
Dissolved inorganic carbon

- $\text{H}_2\text{O} + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3$
- $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$
- $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$

- Solubility of CO$_2$ in seawater and its equilibrium among these different species depends on temperature, pressure, salinity, pH, and alkalinity.
- The residence time of CO$_2$ in the atmosphere is ~10 years; it exchanges rapidly with the ocean and terrestrial biome.

- Dissolved inorganic carbon (DIC) exchanges rapidly with the ocean and terrestrial biome.

- Surface seawater (pH~8.2): $[\text{H}_2\text{CO}_3]$ : $[\text{HCO}_3^-]$ : $[\text{CO}_3^{2-}]$ = 0.5% : 88.6% : 10.9%

- "Ocean acidification due to increasing atmospheric carbon dioxide" The Royal Society 2005. www.royalsoc.ac.uk

- Vertical profiles of DIC and pH at Station ALOHA

- What processes control DIC gradients in the sea?
  - Abiotic and biotic processes control carbon distributions in the sea.
  - Need to understand controls on the variability of these processes

- Temperature dependent relationship of DIC at atmospheric pCO$_{2,\text{atm}}$ = 280 ppm (preindustrial levels)

- Solubility pump:
  - Cooler water gains CO$_2$-high latitude regions are sinks for CO$_2$
  - Cooler, CO$_2$ rich waters sink
  - Maintains vertical gradient in CO$_2$
  - Air-sea heat fluxes drive air-sea CO$_2$ fluxes
Physics plays a key role in controlling ocean carbon distributions.

Upwelling

Mixing

Upwelling

The oceanic laboratory:
World Ocean Circulation Experiment hydrography transects

Long-term changes in the ocean carbon system in waters off Hawaii. Oceanic uptake of CO₂ also influences seawater pH.

Surface ocean pCO₂
Regions of negative pCO₂ flux are regions where the ocean is a net sink for atmospheric CO₂

Annual mean flux [µmol/m²/s] for 2005

pCO₂ = pCO₂(AIR) - pCO₂(SURFACE)

pH (total scale, in situ)

- 8.06
- 8.08
- 8.10
- 8.12
- 8.14
- 8.08
- 8.06

Sea
Air
"Ocean acidification due to increasing atmospheric carbon dioxide"

The Royal Society 2005. www.royalsoc.ac.uk

The biological carbon pump

Organic Carbon Pump

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 \]

Calcium carbonate pump

\[ \text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]

Increasing oceanic DIC has two important implications

- \( \text{H}_2\text{O} + \text{CO}_2(\text{aq}) \Leftrightarrow \text{H}_2\text{CO}_3 \)
- \( \text{H}_2\text{CO}_3 \Leftrightarrow \text{H}^+ + \text{HCO}_3^- \)
- \( \text{HCO}_3^- \Leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \)

- Increased \( \text{H}_2\text{CO}_3 \) (lowers pH)
- Decreased \( \text{CO}_3^{2-} \) (increases solubility of \( \text{CaCO}_3 \))
Saturation state:

\[
\Omega = \frac{[\text{Ca}^{2+}]_{\text{sea water}} \times [\text{CO}_3^{2-}]_{\text{sea water}}}{[\text{Ca}^{2+}]_{\text{saturated}} \times [\text{CO}_3^{2-}]_{\text{saturated}}}
\]

When \( \Omega > 1 \), CaCO₃ supersaturated, shell formation favored. When \( \Omega < 1 \), CaCO₃ undersaturated, dissolution occurs.

Aragonite: Pteropods and corals
Calcite: Coccolithophores and foraminifera

Dissolution and formation of shells changes [Ca²⁺] < 1%; thus changes in [CO₃²⁻] largely control \( \Omega \).

Distribution of the depths of the undersaturated water (aragonite saturation < 1.0; pH < 7.75) on the continental shelf of western North America. On transect line 5, the corrosive water reaches all the way to the surface in the inshore waters near the coast. The black dots represent station locations.

Primary biologically mediated carbon transformations in the sea

- Photosynthesis and respiration

Photosynthesis:

\[
6\text{CO}_2 + 12\text{H}_2\text{O} \overset{\text{Sunlight}}{\rightarrow} \text{C}_6\text{H}_{12}\text{O}_6 + \text{O}_2 + 6\text{H}_2\text{O} + \text{heat}
\]

Respiration:

\[
\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} + \text{heat}
\]

Note that these reactions are VERY generalized: does not include other bioelements (N, P, S, Fe, etc.) that also are involved in these biological transformations.
The biological carbon pump

![Graph showing the biological carbon pump](image)

**Export and vertical attenuation of particle flux**

- Mixed layer
  - Carbon uptake
  - Carbon flux 100m
- Mixed layer
  - <5 to 10%
- ~1-5%
- U.S. JORPS
  - Carbon flux 1000m
  - ~0.1%

**SEDIMENT TRAPS**

Deep ocean sediment traps. Anchored to the seafloor. Collection interval is determined by the investigator. Provide estimates of sinking particle flux to the deep sea.

**VERTEX program - late 70's - mid 80's**

- Extensive upper ocean trap studies
- Knauer et al., 1979

"Martin curve"

\[ F = F_{100}(z/100)^b \]

- \[ F_{100} = 1.53 \text{ (mol m}^{-2} \text{ y}^{-1}) \]
- \[ b = 0.86 \]
Sinking particles do not sink vertically
- sinking velocity = 10's >500 m/day
- horizontal velocity = 1 - 10's cm/sec

Avg. “sinking” particle:
4 m vertical drop & 520 m horizontal trajectory during 50 min talk

Food web structure is a key determinant on carbon fluxes:
1) Cell size and geometry influence sinking rate
2) Zooplankton repackage material and vertically migrate
3) Small cells support longer food webs = more carbon recycled to CO₂

Zooplankton repackage plankton into rapidly sinking fecal material

Sedimentation of diatom-rich salp fecal pellets > 1 mm long, 350 µm wide, 10 µg C per pellet---these things sink FAST...

Direct aggregation and pulsed export is also important

Flux of labile phytodetritus to the deep North Atlantic