The Global Carbon Cycle

- Radiative forcing
- Global carbon reservoirs
- Glacial-interglacial cycles
- Anthropogenic CO2
- Ocean-atmosphere partitioning
- Ocean carbon cycle
- Carbon distribution in the ocean
- Solubility pump
  - Carbonate chemistry
- Biological pump
  - Photosynthesis and respiration
- Causes of glacial-interglacial change?
- Fate of anthropogenic CO2?
Radiative forcing due to CO2

(a) Black body normalized emission curves

(b) absorption at 11 Km

(c) absorption at ground level
Global carbon reservoirs

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Mass of Carbon ($10^{15}$ g=Pg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>700</td>
</tr>
<tr>
<td>Ocean dissolved inorganic carbon, DIC</td>
<td>37000</td>
</tr>
<tr>
<td>Ocean dissolved organic carbon, DOC</td>
<td>$685 , ^a$</td>
</tr>
<tr>
<td>Ocean particulate organic carbon, POC</td>
<td>13 to 25 $^b$</td>
</tr>
<tr>
<td>Biota (land+ocean)</td>
<td>600</td>
</tr>
<tr>
<td>Soils</td>
<td>1500</td>
</tr>
<tr>
<td>Fossil Fuels</td>
<td>5000</td>
</tr>
<tr>
<td>Rocks (organic)</td>
<td>140000000</td>
</tr>
<tr>
<td>Rocks (as calcium carbonate)</td>
<td>600000000</td>
</tr>
</tbody>
</table>
Geological timescales
Glacial-interglacial variations

Vostok ice core
(Antarctica)
- What caused CO$_2$ drawdown of \(\sim 100\text{ppmv}\) during glacials?
- Role of oceans?
- Climate drives carbon change or vice versa?

Vostok ice core (Antarctica)
Atmospheric CO2 in the industrial era

LAW DOME, ANTARCTICA ICE CORES

Source: Etheridge et al. (CSIRO)
Atmospheric CO2 in the industrial era

LAW DOME, ANTARCTICA ICE CORES

Source: Etheridge et al. (CSIRO)

Implications for climate?
Measurement of atmospheric CO2
Biological processes: Photosynthesis and respiration

Photosynthesis

\[ 6CO_2 + 6H_2O \xrightarrow{\text{photons}} C_6H_{12}O_6 + 6O_2. \]

Respiration

\[ C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}. \]
- Well mixed throughout atmosphere
- Global increase due to anthropogenic emissions
- Elevated northern hemisphere concentrations due to higher emissions
- High seasonality in northern hemisphere reflects terrestrial ecosystem
  - Summer photosynthesis, winter respiration
- Low seasonality in southern hemisphere due to small land area
Ocean Carbon Cycle

- Why is there so much carbon in the ocean?
- Carbonate chemistry
- “solubility pump”
- “biological pumps”
Carbon dioxide in the ocean

- $\text{CO}_2$ dissolves in seawater
  \[ K_o = \frac{\text{CO}_2^*}{p\text{CO}_2} \]

- Effective partial pressure in surface water
  \[ p\text{CO}_2 = \frac{\text{CO}_2^*}{K_o} \]

- Gas exchange between air and water driven by partial pressure difference
  \[ \text{Flux} \propto p\text{CO}_2^{\text{air}} - p\text{CO}_2 \]
Distribution of carbon in the ocean

- CO$_2$ dissolves in seawater
  \[ p\text{CO}_2 = \frac{\text{CO}_2^*}{K_o} \]

- Carbonate chemistry
  \[ \text{CO}_2^* + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \]
  \[ \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+ \]

- Dissolved Inorganic Carbon, DIC
  \[ \text{DIC} = \text{CO}_2^* + \text{HCO}_3^- + \text{CO}_3^{2-} \]
- $\text{CO}_2^{\text{at}}$ = effective atmospheric concentration
- Gradient in $\text{CO}_2$ drives air-sea exchange
- $\text{CO}_2^*$ is only about 1% of DIC
- Air-sea equilibration (of upper 100m of ocean) takes > 1 year for CO2
- Damps influence of air-sea exchange on seasonal timescales
Equilibrium DIC higher at lower T

\[ A_T = 2.35 \text{ eq m}^{-3} \]
Observing the ocean
Global ocean survey 1980's-2000's
Potential temperature $\theta$ ($^\circ$C)
- Renewal of deep and bottom waters takes on the order of 1000 yrs
Dissolved Inorganic Carbon

DIC (μmol kg⁻¹)
“Solubility Pump” of carbon

- Cooling of high latitude surface waters increases solubility of CO2 and saturation DIC
- Induces uptake of CO2 from atmosphere and increase of DIC
- Cooler waters are denser and form oceans deep waters, sliding under warmer surface layer
- Cool, DIC rich waters underneath warm, DIC-depleted waters
- Sequesters carbon as DIC in deep ocean, away from atmosphere
Biological processes: Photosynthesis and respiration

**Photosynthesis**

\[
6CO_2 + 6H_2O \xrightarrow{\text{photons}} C_6H_{12}O_6 + 6O_2.
\]

**Respiration**

\[
C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}.
\]
Biological processes: Photosynthesis and respiration

Photosynthesis (schematically)

$$106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O \xrightarrow{\text{photons}} C_{106}H_{263}O_{110}N_{16}P + 138O_2$$

- Key biochemical molecules require other elements
  - e.g. nitrogen rich proteins, phosphorus rich nucleic acids
- Average elemental ratio of plankton
  - C:N:P = 106:16:1
- Carbon typically plentiful
  - Availability of light or other elements limits growth
Photosynthesis requires light and essential nutrients

- Light penetrates about 100m or so in surface ocean
- Carbon plentiful – not generally limiting
- Nutrients (nitrate, phosphate) upwelled from deep waters
- Surface chlorophyll and production of organic matter reflect nitrate distribution
Marine food web and carbon cycle

Sallie Chisholm
Organic particles sink from surface to be respired at depth

- Less than 1% reaches sea floor in deep ocean
- Carbon, nitrogen, phosphorus, iron, etc. returned to inorganic form in the deep waters

Martin et al (1987)
“Biological Pump” of carbon (soft tissue pump)

- Production of organic matter consumes nitrate, DIC in surface waters
- Reduces surface ocean CO$_2$, induces uptake from atmosphere
- Organic particles sink, respired at depth
- Increase deep ocean DIC and reduce atmospheric pCO$_2$
“Biological Pump” of carbon (carbonate pump)

- Some phytoplankton create calcium carbonate
  \[ \text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3 \]
- Sinks but only dissolves in deep waters where undersaturated
- Sediments are source/sink of carbon and calcium on multi-millennial timescales
Vertical profile of DIC in global ocean

Depth (m)

DIC (µmol kg⁻¹)

“solubility pump”

“biological pump”

DIC
DIC saturated 1750
DIC saturated 1990
Killing biological pump would lead to increase in atmos CO2 of ~200ppmv
Did ocean processes cause glacial atmospheric CO$_2$ reduction?

- Rapid changes too swift for sedimentary interaction
- Terrestrial?
- Ocean properties refreshed ~1000yrs
- Solubility and/or biological response to climate change
Glacial pCO$_2$ reduction?

• Solubility pump
  • Deep ocean $\sim$3°C cooler at Last Glacial Maximum (Adkins et al, 2002)
  • Increase in equilibrium DIC equivalent to a reduction of about 30ppmv in atmos pCO$_2$

• Biological pump
  • Iron fertilization?
Iron fertilization?

- Why isn't all nitrate consumed by phytoplankton?
- Iron limitation
  - Iron essential for light harvesting
  - Very low concentrations in deep waters due to scavenging onto sinking particles
  - High nitrate regions photosynthesis limited by iron?
  - Wind-blown dust an important source of iron
Iron fertilization?

- Ice cores show enhanced dust concentrations in Antarctic ice during glacial periods.
- Enhanced biological pump? (Martin and Fitzwater, 1998)
- … models suggest only reduced atmospheric pCO2 by <20ppmv.
- Note implications for deliberate ocean iron fertilization as mitigation.
Fate of anthropogenic CO2?

Gruber and Sarmiento (2002)
CFC-11

CFC-11 (pmol kg$^{-1}$)

1990s
Ocean absorbs anthropogenic CO$_2$

- Not reached deep, old waters yet
- About 2 Pg C per year globally
  - (c.f. 6 Pg C per year emissions)
- Low interannual variability relative to terrestrial exchange
Present day carbon cycle

Gruber & Sarmiento (2002)
Summary

- Ocean has important control over atmospheric pCO2 on timescales from years to millenia
  - Solubility pump
  - Biological pumps
- Ocean processes likely significant in drawing down atmospheric CO2 during glacial periods
  - No “silver bullet” explanation of 100ppmv reduction
  - Combination of processes?
- Climate drives carbon changes with positive feedback (~25% enhancement?)
- Ocean taking up about 1/3 of annual anthropogenic emissions of CO2
  - Confined to shallow waters, reduces pH
Nitrate

$\text{NO}_3^-$ (μmol kg$^{-1}$)
Oxygen

$O_2$ (μmol kg$^{-1}$)
Carbon partitioning as a function of pH: Bjerrum plot.
Air-Sea Flux of CO2

annual–mean CO₂ flux (mol m⁻²y⁻¹)

out of ocean into ocean

Takahashi et al (2002)
Anthropogenic CO$_2$

Mauna Loa time-series: C.D. Keeling  (data from www.esrl.noaa.gov/gmd/cgg/trends)
Consequences of carbonate chemistry

- Buffering

\[
\frac{\delta pCO_2}{pCO_2} = \frac{\delta [CO_2^*]}{[CO_2^*]} = B \frac{\delta DIC}{DIC}
\]

\[B \sim 10\]

- Slow air-sea equilibration timescale
  - About 1 year to equilibrate 50m thick surface ocean mixed layer
  - c.f. 1 month for oxygen