The Global Carbon Cycle

- Radiative forcing
- Global carbon reservoirs
- Glacial-interglacial cycles
- Anthropogenic CO2
- Ocean carbon cycle
- Carbonate chemistry and air-sea equilibrium
  - “Solubility pump”
  - “Biological pump”
- 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>600</td>
</tr>
<tr>
<td>Ocean</td>
<td>38 000</td>
</tr>
<tr>
<td>Vegetation/Soils</td>
<td>2 000</td>
</tr>
<tr>
<td>Fossil Fuels</td>
<td>3 700</td>
</tr>
<tr>
<td>Rocks (organic)</td>
<td>14 000 000</td>
</tr>
<tr>
<td>Rocks (as calcium carbonate)</td>
<td>60 000 000</td>
</tr>
</tbody>
</table>

Table 1.3. Carbon budget for the Earth in the pre-industrial era (Sarmiento and Gruber, 2002; Tyrell and Wright, 2001).
Geologic timescales
Figure 1.4: Estimated reservoir sizes (Pg C, boxed numbers) and annual fluxes (Pg C yr$^{-1}$, associated with arrows) for the global carbon cycle in the immediate pre-industrial era. The emissions from fossil fuels is driving fluxes of anthropogenic carbon dioxide (white arrows). Estimates are for the 1990s taken from Sarmiento and Gruber (2002), where a more detailed evaluation can be found.
Present day carbon cycle

Sarmiento and Gruber (Physics Today, 2002)
Atmospheric CO$_2$ in the industrial era

LAW DOME, ANTARCTICA ICE CORES

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

Implications for climate?
Long term fate of anthropogenic carbon?

Source: Etheridge et al. (CSIRO)
Glacial-interglacial variations

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

Vostok ice core (Antarctica)
Measurement of atmospheric CO2
Carbon dioxide in the atmosphere

Global Distribution of Atmospheric Carbon Dioxide
NOAA ESRL Carbon Cycle

Three-dimensional representation of the latitudinal distribution of atmospheric carbon dioxide in the marine boundary layer. Data from the Carbon Cycle cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Contact: Dr. Pieter Tans and Thomas Conway, NOAA ESRL Carbon Cycle, Boulder, Colorado, (303) 497-6678, pieter.tans@noaa.gov, http://www.esrl.noaa.gov/gmd/ccgg/.
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

- At equilibrium, solubility defined
  \[ K_o = [\text{CO}_2^*] / p\text{CO}_2 \]

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

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

- $\text{CO}_2$ 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

$$\text{DIC} = \text{CO}_2^* + \text{HCO}_3^- + \text{CO}_3^{2-}$$
- $\text{CO}_2^{\text{at}} = \text{effective atmospheric concentration}$
- 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
Changes in atmospheric and surface ocean pCO$_2$ at Hawaii
Observing the ocean
Global ocean survey 1980's-2000's
Potential temperature $\theta$ (°C)
Salinity S (psu)

- Renewal of deep and bottom waters takes on the order of 1000 yrs.
Dissolved Inorganic Carbon

DIC (μmol kg⁻¹)
Why does DIC increase with depth?

What causes the gradients in deep Pacific?
Equilibrium DIC higher at lower T

\[ A_T = 2.35 \text{ eq m}^{-3} \]
“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
Air-Sea Flux of CO2

annual–mean $\text{CO}_2$ flux (mol m$^{-2}$y$^{-1}$)

Takahashi et al (2002)
Why does DIC increase with depth?

What causes the gradients in deep Pacific?
Potential temperature $\theta \ (^{\circ}$C)
Biological processes: Photosynthesis and respiration

Photosynthesis

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

Respiration

\[ C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}. \]
Marine food web and carbon cycle
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 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
Nitrate

NO$_3^-$ (µmol kg$^{-1}$)
Dissolved Inorganic Carbon
DIC (μmol kg$^{-1}$)
Vertical profile of DIC in global ocean

- "solubility pump"
- "biological pump"

DIC (μmol kg⁻¹)

Depth (m)
Vertical profile of DIC in global ocean

Killing biological pump would lead to increase in atmos CO2 of ~200ppmv
"Biological Pump" of carbon (carbonate pump)

- Some phytoplankton create mineral calcium carbonate structures
  \[ \text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3 \]
- Sinks and dissolves in deep waters where undersaturated
- Sediments are source/sink of carbon and calcium on multi-millenial timescales
- \( \text{Ca}^{2+} \) ion concentration regulates capacity of water to dissolve \( \text{CO}_2 \)
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 $\sim 3^0C$ 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?
  - Change in phytoplankton community composition?
Biological Pump: 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

Vostok, Antarctica
Fate of anthropogenic CO2?

Gruber and Sarmiento (2002)
CFC-11

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

1990s

Atmospheric mixing ratio

CFC-11

Atlantic

CFC-11

Pacific

Concentration (pptv)

Year

1940 1960 1980 2000
Ocean absorbs anthropogenic CO$_2$

- Solubility pump
- 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
Long term fate – next 1000 years

- About 4000 Pg C of accessible fossil fuels
- Over 1000 years, whole ocean comes to equilibrium with atmosphere
- Most anthropogenic CO$_2$ absorbed by oceans
- Peak atmospheric value depends on rate of emissions
Long term fate – next 10,000 years

- Acidification of deep ocean changes interaction with calcium carbonate sediments
- Increase in $\text{Ca}^{2+}$ concentration increases ocean's capacity to dissolve $\text{CO}_2$

Model of Ridgewell and Hargreaves (2007)
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
  - Over many millenia, most dissolved in oceans
Oxygen

$O_2$ ($\mu$mol kg$^{-1}$)
Carbon partitioning as a function of pH: Bjerrum plot.
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