The oceans carbon cycle

- The main components:
  - DIC, DOC, PC (includes POC and PIC)
- The major biologically mediated processes involved in carbon transformations (photosynthesis, respiration, calcification)
- Reactivity of ocean components
- The importance of ocean biology

Carbon pools and fluxes

- Carbon reservoirs:
  - Inorganic carbon system: DIC (H_2CO_3, HCO_3^-, CO_3^{2-}), total alkalinity, pH, pCO_2
    - Coulometry (DIC), potentiometric titration (total alkalinity), spectrophotometric (pH), pCO_2 equilibrator
  - Dissolved organic carbon (DOC)
    - High temperature combustion
  - Particulate carbon (POC and PIC)
    - High temperature combustion (POD); acidification/IR detection (PIC)
- Carbon fluxes:
  - Biological carbon production (POC and DOC)
    - ¹⁴C-bicarbonate assimilation (primary production), changes in carbon and oxygen inventories
  - Particulate carbon export
    - Sediment trap particle collections
Vertical variations in carbon concentrations in the open sea

Concentrations of inorganic carbon increase with depth.

Concentrations of organic carbon decrease with depth.

CO₂ in oceans ~39,120,000,000,000,000,000 g C
CO₂ in the atmosphere ~750,000,000,000,000,000 g C
Dissolved organic carbon ~700,000,000,000,000,000 g C
Living and dead particles ~3,000,000,000,000,000 g C

What processes control inorganic carbon gradients in the sea?

• Both abiotic and biotic processes control carbon distributions in the sea.
• Atmospheric CO₂ levels are directly linked to feedbacks involving oceanic inorganic and organic carbon reservoirs.
**Dissolved inorganic carbon in seawater**

\[ \text{H}_2\text{O} + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{CO}_3 \]

\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]

\[ \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \]

- \( K_0 = [\text{H}_2\text{CO}_3]/p\text{CO}_2 \)
- \( K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] \)
- \( K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \)

**Concentration of inorganic carbon in seawater is partly controlled by thermodynamics**

Solubility of CO\(_2\) in seawater and speciation of the different inorganic carbon components (H\(_2\)CO\(_3\), HCO\(_3^-\), CO\(_3^{2-}\)) depends on seawater temperature, pressure, salinity, pH, and alkalinity.

**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

**Processes influencing carbon cycling in the upper ocean**

Adapted from Keeling et al. (2004)
Temporal variability in mixed layer inorganic carbon

- Interannual variations in DIC concentrations closely coincide with changes to upper ocean salinity.

Interannual variability in inorganic carbon concentrations

- Annual accumulation (0-150 m) of nDIC ~ 0.1 mol C m⁻² yr⁻¹
- Interannual variations in the E-P balance and mixing important controls on carbon inventories

Winn et al. 1994, Dore et al. 2003, 2009

The oceanic laboratory: World Ocean Circulation Experiment hydrographic transects

Opportunity to evaluate distributions and inorganic carbon throughout the world’s oceans

Annual mean flux [μmol/m²/s] for 2005

$pCO_2 = pCO_2(W) - pCO_2(A)$

Regions of negative $pCO_2$ flux are regions where the ocean is a net sink for atmospheric $CO_2$
Penetration of anthropogenic carbon partly reflects ocean conveyor belt model of thermohaline circulation.

Measurements of DIC concentrations combined with carbon isotope ratios (\(^{13}C/^{12}C\)) and stoichiometry of \(O_2/CO_2\) makes it possible to reconstruct how much anthropogenic carbon has penetrated into the ocean. Note that the Southern Ocean remains poorly characterized. In addition, note that anthropogenic carbon has penetrated significantly below about 2000 meters of the water column only in the North Atlantic, where surface waters sinks to depth on time-scales relevant to anthropogenic CO\(_2\) emission.

1 Gt = 1 billion tonnes = 1 Petagram = 10\(^{15}\) g C

Arrows show the fluxes (in gigatonnes of carbon per year) between the atmosphere and its two primary sinks, the land and the ocean, averaged over the 1990s. Anthropogenic fluxes are in red; natural fluxes in black. The net flux between reservoirs is balanced for natural processes but not for the anthropogenic fluxes. Within the boxes, black numbers give the preindustrial sizes of the reservoirs and red numbers denote the changes resulting from human activities since preindustrial times.

Carbonate chemistry plays a major role in controlling seawater pH.

Vertical profiles of DIC and pH at Station ALOHA.

Long-term record of seawater pCO\(_2\) (surface ocean) and pH at 3 depth strata at Station ALOHA in the subtropical North Pacific. Physical and biological processes combine to alter the rate of acidification along a depth continuum.
Increasing oceanic DIC has two important implications

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

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

### Saturation state:

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

- When $\Omega > 1$, CaCO$_3$ supersaturated, shell formation favored.
- When $\Omega < 1$, CaCO$_3$ undersaturated, dissolution occurs.

- Aragonite: Pteropods and corals
- Calcite: Coccolithophores and foraminifera

Dissolution and formation of shells changes $[\text{Ca}^{2+}] < 1\%$; thus changes in $[\text{CO}_3^{2-}]$ largely control $\Omega$.
Biology also plays an important role in controlling carbon exchange between the ocean and atmosphere.

**Biologically mediated carbon transformations in the sea**

- Photosynthesis and respiration

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

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

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

**Organic Carbon Pump**

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

- Decomposition:
  
  \[ \text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O} \]

**Calcium carbonate pump**

- Photosynthesis:
  
  \[ \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{O}_2 \]

- Decomposition:
  
  \[ \text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O} \]
The biological carbon pump

Carbon is the currency of life

Biology establishes direct linkages between carbon cycling and the cycling of other elements