Biogeochemical Cycles

1) Biological cycling
2) Gas exchange
3) Global sources/sinks
4) Chemical reactions

…and circulation, of course.

WF: Chap. 5: Biological Fundamentals
“ ” 6: Carbonate Chemistry Fundamentals
Biological coupling of element cycles: the equation of life in the oceans

The elemental composition of average marine plankton

\[ 106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 + 78\text{H}_2\text{O} \]

photosynthesis/growth \quad \uparrow \quad \text{remineralization/respiration/oxidation}

\[ \text{C}_{106}\text{H}_{175}\text{O}_{42}\text{N}_{16}\text{P} + 150\text{O}_2 \]

Simpler version (with glucose): \[ 6\text{CO}_2 + 6\text{H}_2\text{O} \leftrightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \]

The transformations of primary elements of life are closely connected by the biomass requirements of plankton. The proportions, known as “Redfield ratios”, are relatively constant when averaged over large plankton communities.
Composition of Phytoplankton:

**Carbohydrates @ 26%**: energy storage and building blocks of most cellular components (e.g., glucose).

**Lipids @ 16%**: energy storage and building blocks for membranes.

**Proteins @ 54%**: structural components and enzymes that catalyze biochemical reactions.

**Nucleic acids @ 4%**: agents of reproduction and blueprints for development.
The Biological Pump:

The recycling exchanges between organic matter, mostly created in the euphotic zone from light and inorganic nutrients, and inorganic matter, created by remineralization/respiration/decay, mostly by the action of bacteria on dead organic matter, both in the interior and in the euphotic zone.

The Food Web:

**Autotrophs**: organisms that can create organic matter directly from inorganic matter.

**Heterotrophs**: organisms that gain energy and nutrition only from organic matter.

… and then there are **Mixotrophs**.
Schematic depiction of biogeochemical cycling of nutrients between simple inorganic molecules and complex (and innumerable) organic compounds. Organic matter (OM) is formed primarily through photosynthesis in the surface ocean (<100m). [P]articles of OM are subject to sinking, while [D]issolved OM is transported only by the flow. POM vs. DOM is defined operationally by size. Much of the remineralization occurs within the euphotic zone as local recycling.
Dissolved Nutrients

1) Phosphate section

Depth-Latitude section of phosphate (PO$_4$ [mmol/m$^3$], the sole form of dissolved inorganic phosphorus) along **30W in the Atlantic** and **170W in the Pacific** from World Ocean Atlas [2005]. Upper ocean is depleted in PO$_4$ due to its uptake by plankton for photosynthesis. Deep ocean has high PO$_4$ due to remineralization of organic P, increasing from NADW to NPDW. High polar values are due to vertical exchange.
Concept: Oceanic biogeochemists use a variety of units to express fractional concentration ... a tower of Babel.

It helps to stick with SI units: A basic unit is a molar mass, often abbreviated as [mole] or [mol].

1 mole = atomic mass \times 10^{-3} \text{ kg/mole [kg]}.  

Mass fraction is relative to seawater [mol/kg, which is non-dimensional]. This can alternatively be expressed as a mass density after multiplying by seawater density \( \rho_0 \approx 1025 \text{ kg/m}^3 [\text{kg/m}^3] \).

E.g., \( \text{O}_2 = 300 \text{ mmol/m}^3 = 300 \times 10^{-3} \times 2.16 \times 10^{-3} = 0.96 \times 10^{-2} \text{ kg O/m}^3 \).

\( \text{DIC} = 2075 \text{ } \mu \text{mol/kg} = 2075 \times 10^{-6} \times 12 \times 10^{-3} \times 1025 = 2.55 \times 10^{-2} \text{ kg C/m}^3 \).
**Concept:** A common chemical notation for isotope abundance is the relative anomaly, often expressed in o/oo:

For a quantity $c$, $\delta c$ or $\Delta c = \frac{c_{\text{in situ}} - c_{\text{standard}}}{c_{\text{standard}}}$,

where the standard is either the preindustrial atmosphere as recorded in old wood samples (for $\Delta ^{14}C'$) or Standard Mean Ocean Water (SMOW) (for $O_2$, $H_2$) or air (for $N_2$), etc.

*E.g.*, for $\Delta ^{14}C'$, the value of - 150 o/oo means a relative anomaly of - 0.15.

Dissolved Organic Matter

DOP ~ 0-0.5 µmol/kg (mostly “labile”)
DON ~ 2-6 µmol/kg (partly “refractory”)
DOC ~ 40-80 µmol/kg (mostly “refractory”)

Distribution of Dissolved Organic Carbon (DOC) along 3 ocean transects. Nitrogen and phosphorus content (DON, DOP) are less frequently measured but follow a similar pattern, indicating conversion from inorganic to organic matter by biota. Lowest values indicate the component of DOM that is resistant to uptake/degradation (“refractory”).
The flux of sinking particles measured in sediment traps, at sites in the Eastern Pacific. The decrease with depth (flux divergence) is a measure of rates of organic matter respiration/remineralization. The vertical structure may depend on temperature, particle size and composition, \( \text{O}_2 \), bacteria, etc. Rates of remineralization get slower with depth. Horizontal variations are usually not directly measured, but can be inferred (e.g., from \( \text{O}_2 \)). Only a tiny fraction makes it to the bottom, the benthic sediments.
Oxygen Distribution

Depth-Latitude section of oxygen ($O_2$ [mmol/m$^3$]) from Atlantic to Pacific [SG06]. Oxygen reaches a minimum at mid-depths due to remineralization of organic matter and a long circulation pathway between ventilation exposures. This pattern is reminiscent of other global water mass measures such as $S$ and $^{14}C$, though with quantitative differences.
Oxygen concentration reflects different biological/physical balances:
In mixed layer (depth $z_{ML}$), photosynthesis balances gas exchange. In F, $k_w$ is the transfer coefficient, called the piston velocity [m s$^{-1}$]. In oceanic interior, respiration is balanced by circulation and mixing transports.
Annual mean oxygen ($O_2$ [mmol/m$^3$]) in the upper 50 m, from World Ocean Atlas [2005]. The close correspondence to SST reflects the (inverse) relationship between temperature and solubility, and the near equilibrium with the atmosphere (Henry’s law): $O_2^{\text{sat}} = S \ pO_2^{\text{atm}}$, where $S \sim 1500 \ $mmol m$^{-3}$ atm$^{-1}$ is the solubility for oxygen; for most gases, $\partial S / \partial T < 0$. 
Annual mean oxygen disequilibrium, \( O_2^{\text{diseq}} = -O_2^{\text{sat}} + O_2 \) [mmol/m\(^3\)] in the upper 50 m, from World Ocean Atlas [2005]. Supersaturations \( (O_2^{\text{diseq}} > 0) \) are due to heating and photosynthesis, and undersaturations \( (O_2^{\text{diseq}} < 0) \) are due to cooling and upward transport that delay coming into equilibrium saturation with the atmosphere over a time \( \sim 1 \) month.
Depth-Latitude section of Apparent Oxygen Utilization (AOU = $O_2^{sat}(T,S) - O_2$, [mmol/m$^3$]) from Atlantic to Pacific [Sarmiento & Gruber, 2006]. AOU approximates the total amount of $O_2$ consumed since isolation from atmosphere, ignoring surface disequilibrium.
Deep Ocean Respiration

Oxygen Utilization Rate:

\[ \text{OUR} = \frac{\text{AOU}}{\text{age}} \]

It takes \(~8\) years for \(^{14}\text{C}\) to decay by 1 permil. So estimated abyssal OUR \(~0.1\) mmol/m\(^3\)/yr.

Rate of oxygen utilization due to respiration \((\text{OUR}=S_{\text{resp}}(\text{O}_2))\) can be estimated by OUR=AOU/age, where age time since isolation from the atmosphere which can be derived from transient tracers (e.g. \(^{14}\text{C}, \text{CFC}, ^{3}\text{H}\)). In the deep ocean, OUR \(~0.1\) mmol/m\(^3\)/yr.
Rate of oxygen utilization (OUR) due to respiration can be estimated by $\text{OUR} = \frac{\text{AOU}}{\text{age}}$, where age is derived from transient tracers (e.g. CFC, $^3\text{H}$). In the thermocline, OUR $\sim 10 \text{ mmol/m}^3/\text{yr}$, $\sim 100\times$ larger than the deep ocean.
Conservative tracers

Starting from:

\[ \frac{D(AOU)}{Dt} = S_{\text{resp}}(O_2), \quad AOU(z=0) = 0 \]

\[ \frac{DPO_4}{Dt} = S_{\text{resp}}(PO_4), \quad PO_4(z=0) = P_c \]

\[ S_{\text{resp}}(O_2) = r_{O:P} \cdot S_{\text{resp}}(PO_4) \]

Define:

\[ PO_4^{pre} = PO_4 - \frac{1}{r_{O:P}} AOU \]

Then:

\[ \frac{D(PO_4^{pre})}{Dt} = 0, \quad PO_4^{pre}(z=0) = P_o \]

Oxygen and Phosphate can be combined to estimate the component of PO_4 that is transported from the surface to the interior ocean, “pre-formed” PO_4. It is a parcel-conservative water mass tracer, whose value is set at the surface and unchanged by subsurface respiration but for mixing. The Redfield value is \( r_{O:P} = 150 \).
"Pre-formed" Phosphate

Depth-Latitude section of pre-formed PO$_4$ (PO$_4^{pre}$, mmol/m$^3$) from Atlantic to Pacific. Most of the deep ocean PO$_4$ arrives via transport rather than remineralization. Deep gradient understood as a tracer of Southern versus Northern water mass origins (AABW vs. NADW) that are largely preserved following the circulation. This is a repeated slide.
Preformed $[\text{PO}_4^{3-}]$ (carried in the water from the surface)

Regenerated $[\text{PO}_4^{3-}]$ (produced from degradation of sinking organic matter)

Sarmiento and Gruber, 2006
Annual mean PO$_4$ [mmol/m$^3$] in the upper 50 m, from World Ocean Atlas [2005]. In most of the ocean, nutrients are extremely scarce because they have been consumed, limiting further photosynthesis. Exceptions are regions of strong vertical exchange with the remineralized subsurface reservoirs, or insufficient sunlight or micronutrients (e.g., dust).
Southern Ocean: leak in the biological pump

**low latitude**
- **CO₂**
- Low [PO₄³⁻]
- Regenerated
- CO₂ excess

**high latitude**
- **CO₂**
- High [PO₄³⁻]
- Preformed
Diagram of a simple biogeochemical model (here for P) that uses observed nutrient distributions ($P_{obs}$) to infer hard-to-observe rates of biological processes ($S_{photo}$, $S_{resp}$) and particle fluxes, $F_p(z_c)$, with $z_c$ the base of the euphotic zone. Some OGCMS have much more sophisticated models.
Particle (POM)) Export

Flux $F_p$ of POM (mol C/m²/yr) out of the surface ocean (75m), from four OGCMs (Princeton, MIT, NCAR, Hadley Center). Globally integrated values are 5-15 GtC/yr. [1 Gt = 1 Pg] An additional ~ 2 GtC is transported to the deep ocean as dissolved organic carbon. Spatial pattern of export can be used to estimate infer primary productivity (fueled by new nutrients into the euphotic zone) because the two roughly balance. Model differences in $F_p$ are mainly due to circulation differences in nutrient supply.
Distributions of dissolved organic carbon (DOC; µmol/kg) at 30 m. Meridional and zonal lines of data are observed values, while the background field is modeled; notice moderate model-data differences where they overlap. DOC is mainly the waste products of biology, not the same as abundance (biomass; e.g., Chl) or growth (productivity). Low subpolar DOC is partly rapid vertical exchange with interior water with high DIC, but is also lack of iron for growth (in south).
The Nitrogen Cycle

- Several bioavailable forms of N (mostly NO$_3^-$). Vast reservoir of N$_2$ is nearly inert.

- N$_2$ can be converted to bioavailable N (i.e., fixed) by specialized organisms (diazotrophs), unlike other nutrients.

- Biological sources of N are much larger than non-biological sources (atmosphere, rivers), apart from agricultural eutrification locally.

- N$_2$O (greenhouse gas) is produced in reactions, emitted to atmosphere, by denitrification where O$_2$ is low or in sediments.

- ‘Residence time’ (inventory/input rate) of N is very short, ~2000 yrs making it susceptible to large changes (cf., $\tau_{\text{PO}_4} \sim 50,000$ yrs). This is slightly shorter than the global mixing time (maximum age).
Annual average surface nitrate (NO$_3$ [mmol/m$^3$]) in the upper 50 m, from World Ocean Atlas [2005]. Note very close correlation to PO$_4$ (slide 18), but generally lower values relative to biomass N:P requirements (i.e. r$_{N:P}$=16), implying a nitrate limitation to growth.
Global correlation between NO$_3$ and PO$_4$. Slope is similar to the Redfield ratio for biomass ($r_{N:P}=16$) indicating dominance of photosynthesis/remineralization. Small deviations from the 16:1 covariation, are caused by denitrification ($S_{\text{denit}}$) and N$_2$ fixation ($S_{\text{Nfix}}$) and can be quantified with the tracer N*$^*$. The geographical differences are real but secondary to the N-P coupling in the equation of sea life.

Starting from:

$$\frac{DPO_4}{Dt} = S_{\text{pho}}(PO_4) + S_{\text{resp}}(PO_4)$$

$$\frac{DNO_3}{Dt} = S_{\text{pho}}(NO_3) + S_{\text{resp}}(NO_3) + ...$$

$$+ S_{\text{Nfix}} - S_{\text{denit}}$$

Define:

$$N^* = NO_3 - r_{N:P}PO_4$$

Then:

$$\frac{DN^*}{Dt} = S_{\text{Nfix}} - S_{\text{deni}}$$
Sequence of reactions for oxidizing organic matter, ranked by energy of reaction. At low O$_2$ levels (<10 mmol/m$^3$), respiration proceeds via denitrification, a process that removes NO$_3$ from the ocean, and accounts for the N limitation of photosynthesis. In current ocean, subsequent reactions (3-6) are confined to sediments. Redfield ratio indicates dominance of aerobic respiration in seawater.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Stoichiometry</th>
<th>Threshold O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Aerobic respiration</td>
<td>$OM + 150 O_2$  $\rightarrow$ 106 CO$_2$ + 16 HNO$_3$ + H$_3$PO$_4$ + 78 H$_2$O</td>
<td></td>
</tr>
<tr>
<td>(2) Denitrification</td>
<td>$OM + 104$ HNO$_3$  $\rightarrow$ 106 CO$_2$ + 60 N$_2$ + H$_3$PO$_4$ + 138 H$_2$O</td>
<td>1-10 mmol/m$^3$</td>
</tr>
<tr>
<td>(3) Manganese reduction</td>
<td>$OM + 260$ MnO$_2$ + 174 H$_2$O  $\rightarrow$ 106 CO$_2$ + 8 N$_2$ + H$_3$PO$_4$ + 260 Mn(OH)$_2$</td>
<td></td>
</tr>
<tr>
<td>(4) Iron reduction</td>
<td>$OM + 236$ Fe$_2$O$_3$ + 410 H$_2$O  $\rightarrow$ 106 CO$_2$ + 16 NH$_3$ + H$_3$PO$_4$ + 472 Fe(OH)$_2$</td>
<td></td>
</tr>
<tr>
<td>(5) Sulfate reduction</td>
<td>$OM + 59$ H$_2$SO$_4$  $\rightarrow$ 106 CO$_2$ + 16 NH$_3$ + H$_3$PO$_4$ + 59 H$_2$S + 62 H$_2$O</td>
<td></td>
</tr>
<tr>
<td>(6) Methane fermentation</td>
<td>$OM + 56$ H$_2$O  $\rightarrow$ 47 CO$_2$ + 59 CH$_4$ + 16 NH$_3$ + H$_3$PO$_4$</td>
<td></td>
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Declining energy yield (J/mol OM)
Oceanic Oxygen in the Interior

Annual mean oxygen, \( \text{O}_2 \) [mmol/m\(^3\)], in the thermocline (400 m), from World Ocean Atlas [2005]. Respiration leads to anoxic conditions in the tropical Pacific and Indian Oceans, where waters are old and underlying high productivity surface waters with local respiration of high POM “marine snow”.
Ocean “Age”

The ideal age tracer:

$$\frac{D\tau}{Dt} = 1 \quad \tau(z = 0) = 0$$

computed from an ocean model (ECCO2). Units: years. In model evaluations, there is also age mixing.

Note correspondence between ideal age, $O_2$, and empirical CFC-11 age in the thermocline (Circulation lecture).
Annual mean nitrate deficit (N* [mmol/m³]) in the thermocline (400 m), from World Ocean Atlas [2005]. Largest negative values are found in low-O₂ waters with denitrification where N replaces O in respiration. Highest values found in Atlantic thermocline with higher O₂ and more N₂ fixation. This is non-Redfield.
Iron input via dust

Rate of dust deposition (g/m²/yr) estimated by atmospheric transport and land surface models (note log scale). Continental dust is a major source of iron and other micronutrients to the ocean surface and may limit many biochemical processes, including N₂ fixation and overall productivity. Notice low deposition in tropical Pacific vs. Atlantic, and in polar regions, especially near Antarctica. This causes HNLC (high nutrients, low chlorophyll) regimes.
Biological productivity is limited by available $\text{NO}_3$ throughout most of low-middle latitudes. What explains the incomplete consumption in other areas? …light, micro-nutrients, vertical exchange, gyre circulation, eddy stirring, … Ultimately the quantitative synthesis of these multiple influences can only be done with OGCMs.
What determines the partition of carbon between the atmosphere (~1%), ocean (>90%), and terrestrial biosphere (<10%)? The global carbon cycle for the 1990s, showing the main annual fluxes in GtC yr\(^{-1}\) : pre-industrial ‘natural’ fluxes in black and ‘anthropogenic’ fluxes in red (modified from Sarmiento and Gruber, 2006). Atmospheric carbon content and all cumulative fluxes since 1750 to 1994.
Solubility of CO2 and other gases versus temperature (upper panel) and its subsequent reactions with water (lower), which produce three non-gaseous DIC species --- carbonic acid (H$_2$CO$_3^*$), bicarbonate (HCO$_3^-$), and carbonate (CO$_3^{2-}$) --- in equilibrium reactions. The partition of C depends on pH (next slide). $K_0$ reflects Henry’s Law for air-sea gas exchange. CO$_2^* = CO_2 + H_2CO_3^*$ is total dissolved CO2 in ocean.
**Charge Balance in the Ocean:**

The ocean is electrically neutral to a high degree => it has zero net charge; i.e.,

\[
\text{sum of cations (}+\text{ charge}) - \text{sum of anions (} - \text{ charge}) = 0.
\]

\[
\text{pH} = -\log_{10}([\text{H}^+]) \text{ is a measure of acidity (less is more). The average pH in sea water is about 8.1 --- slightly basic or alkaline.}
\]

**Alkalinity:**

\[
\text{Alk} = \text{sum of charges (anions – cations) from strong electrolytes (highly ionized molecules)} = -\text{sum of charges from weak electrolytes (partially ionized molecules).}
\]
Carbon speciation (log concentration) versus pH, for a fixed total DIC content. At more acidic (lower pH) conditions, CO\(_2\) (i.e. H\(_2\)CO\(_3^\ast\)) is dominant, whereas in basic water, carbonate CO\(_3\) is dominant. Ocean is nearly neutral but slightly basic. As CO\(_2\) is added, H\(^+\) increases (pH lowers) & greater fraction of C atoms present as CO\(_2\), ocean becomes more acidic. CO\(_2^\ast\) is only about 1% of total DIC => large C storage in ocean.
Measured Quantities

To completely specify the chemical speciation of C in seawater, two measurements are needed. Total inorganic carbon concentration (DIC) and pH would be a natural choice, but for practical experimental reasons, Alkalinity is used instead of pH.

**Dissolved Inorganic Carbon (DIC) = all the inorganic C molecules**

\[
DIC = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]
\]

- \( [\text{H}_2\text{CO}_3^*] = 0.5\% \)
- \( [\text{HCO}_3^-] = 88.6\% \)
- \( [\text{CO}_3^{2-}] = 10.9\% \)

**Alkalinity (Alk) = net charge of all species effected by C reactions**

\[
Alk = [\text{HCO}_3^-] + 2 \ast [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + [\text{B(OH)}_4^-]
\]

- \( [\text{HCO}_3^-] = 76.8\% \)
- \( [\text{CO}_3^{2-}] = 18.8\% \)
- \( [\text{OH}^-] = 0.2\% \)
- \( [\text{H}^+] = 4.2\% \)

\[
p\text{CO}_2 \approx \frac{K_2}{K_0 K_1} \frac{(2 \cdot DIC - Alk)^2}{Alk - DIC}
\]

(borate)
**Concept:** CO$_2$ in the ocean is highly buffered; *i.e.*, for any air-sea gas flux of CO$_2$, relatively little change occurs in $[CO_2^*]$. 

$[CO_2^*]$ is only about 0.6% of DIC in the ocean at essentially every location.

This is a negative chemical feedback.

This implies that once a disequilibrium arises in pCO$_2$ between the atmosphere and surface ocean, it will persist for a long time and be removed only slowly ($\Delta t \sim 1$ yr) after a large exchange of CO$_2$ has occurred.
Influences on $pCO_2$: Downward C pumps: solubility, soft-tissue (organic), & carbonate

$\rightarrow$ Alk increases with depth (and DIC usually does too).

$pCO_2 \approx \frac{K_2}{K_0 K_1} \frac{(2 \cdot DIC - Alk)^2}{Alk - DIC}$

$K_0$: Solubility of CO$_2$
$K_1, K_2$: Dissociation constants

$K$ are functions of T and S, but $K_2/K_1$ only weakly so.

Depends on biology (DOC, POC) and gas exchange

Depends on biology (Calcium carbonate in shells):

Increasing acidity in global change reduces Alk and depletes shells.
Simplified Model of Equilibrium Inorganic Carbon Chemistry

Compact notation: $C_1 = [CO_2^*]$, $C_2 = [HCO_3^-]$, $C_3 = [CO_3^{2-}]$, $H = [H^+]$, $D = DIC$, $A = Alk_C \approx Alk_T$, $P = pH = \log_{10}[H^+]$, $pC = pCO_2$.

\[
D = C_1 + C_2 + C_3, \quad A = C_2 + 2C_3 - H
\]

\[
C_1 = K_0 pC, \quad K_1 C_1 = C_2 H, \quad K_2 C_2 = C_3 H.
\]

$\Rightarrow$ 5 equations, 3 rate constants, and 7 unknown concentrations. **Note:** this is not quite the same as WF, Box 6.3.

*E.g.*, For given $(K_0, K_1, K_2)$, $D$, and $A$, what is $P$?

*E.g.*, For given $(K_0, K_1, K_2)$ and $A$, how do $D$ and $P$ change with a change in $pC$?

**Concepts:** The rate constants are functions of $T$ and $S$, biogeochemistry provides sources and sinks for $C_1$ and $C_3$, and $pC$ is highly variable with implications for air-sea $CO_2$ flux.
Carbon storage in deep ocean is enhanced by:

1) Cold temperatures (solubility pump, DIC)
2) Sinking organic material (organic pump, DIC)
3) Sinking CaCO₃ (carbonate pump, Alk)

The organic pump is largest. The carbonate pump is smallest, but has a counterintuitive effect; by reducing Alkalinity, it raises the pCO₂ of the surface ocean, which then escapes to the atmosphere.
Dependence of $pCO_2$ [$\mu$ atm] on temperature and salinity (DIC and Alk held constant):

$$\frac{\partial \ln(pCO_2)}{\partial T} \approx 4.2\% C^{-1}$$

$$\frac{\partial \ln(pCO_2)}{\partial \ln(S)} \approx 1$$

$pCO_2$ vs Temperature, Salinity

Pre-industrial

High $pCO_2$

Low $pCO_2$
Dependence of pCO$_2$ [µ atm] on DIC and Alk (T and S held constant):

$$\frac{\partial \ln(pCO_2)}{\partial \ln(DIC)} \approx 10$$

This quantity (known as the buffer or “Revelle” factor) gives the fractional change in pCO$_2$ required to raise DIC, which depends on pH.

**Arrows:** Formation of OM reduces DIC (can increase Alk slightly): DOC $\sim$ .1 DIC.
Formation of CaCO$_3$ reduces DIC and Alk in a 1:2 ratio. The latter process is $\sim$10x the former.
The distribution of DIC across depth and two ocean basins, caused primarily by the addition of DIC from respiration of OM, but also by solubility and CaCO$_3$ dissolution. E.g., low DIC in Atlantic because younger water with less respiration as yet. Notice the broad similarity with remineralized nutrients (e.g., slide 6).
Analogous to the DIC pumps, the vertical pumps for Alkalinity are (a) P-E decreases $Alk$ (n.b., subtropical surface Atlantic), (b) NO$_3$ remineralization increases $Alk$, and (c) CaCO$_3$ dissolution increases ionization.
A strong sensitivity of atmospheric CO$_2$ to “pre-formed” nutrients (i.e., conditions in the mixed layer) that do not get used by plankton before being transported into ocean interior, and therefore do not transport and DIC to depth. In ice ages, more dust (Fe) and slower MOC lead to greater subpolar consumption, less surface PO$_4$, less pCO$_2$. The ocean has a large, variable C reservoir by DIC partitioning and the 3 carbon pumps.
Preindustrial air->sea CO$_2$ fluxes from model simulations [Murnane et al. 1999]. The flux of CO$_2$ from ocean to atmosphere due to differences in partial pressure ($\Delta$pCO$_2$) due to solubility pump (heating/cooling) and biological pump (mostly photosynthesis/respiration), are generally of opposite sign at high latitudes, relationship is more complex in low latitudes. Carbonate pump is a secondary effect.

The biological pump includes both CO$_2$ consumption and burial by organic processes and surfacing of DIC-rich interior water. The net air-sea flux is a generally small residual of the component fluxes (next slide).
Annual mean pCO2 difference ($pCO_2^{\text{ocean}} - pCO_2^{\text{atmosphere}}$, $\mu$atm). The pCO2 differences induces an air-sea flux $F_{CO_2}$ (Henry’s law). Variations are due almost entirely to ocean processes: heating (+), cooling (-), photosynthesis (-), and upwelling of respired DIC (+). Because of buffering, the equilibration time for CO2 is ~20x slower than for other gases, ~1 year. High values in eastern tropical Pacific reflect heating (reduced solubility) and upwelled DIC, countering photosynthesis and leading to CO2 flux into the atmosphere. Low polar values due to cooling and productivity.
As of the mid-1990’s, fossil fuel burning had released about 245 GtC into the atmosphere (currently ~6.5 GtC/yr and accelerating). The amount remaining in the atmosphere is only ~165 GtC. Where’s the other ~80 GtC? Answer: about 120 GtC into the ocean and about -30 GtC from the land surface (deforestation).
In the 1990’s CO$_2$ was measured throughout the ocean. How much was due to “anthropogenic” sources?

\[
C_{\text{obs}} = C_{\text{eq}}^{280} + C_{\text{diseq}} + C_{\text{bio}} + C_{\text{anthr}}
\]

By measuring T and S, we can estimate the equilibrium CO$_2$ concentration under a preindustrial atmosphere (280 ppm).

A preformed disequilibrium is estimated by tracing water mass origins to the surface (assuming constant $C_{\text{diseq}}$).

By measuring AOU and Alk, we can estimate how much CO$_2$ present is due to biology (OM + CaCO$_3$).

The difference is anthropogenic CO$_2$ absorbed by the ocean due to rising atmospheric CO$_2$: the warm water sphere has more because of Ekman MOC (80 Sv) > THC MOC (20 Sv) and because DIC is larger at high latitude. Saturation is approaching as Alk decreases, carbonate decreases, and CO$_2$ increases.

Total $\sim$120 GtC
Ocean acidification

Measured surface pCO$_2$ (left) and pH (right) at time-series sites at Eastern North Atlantic (Canary I.), Central North Pacific (Hawaii), Western North Atlantic (Bermuda).

The most obvious direct consequence of increasing CO$_2$ is the reduction of pH and Alk. This leads toward undersaturation of CO$_3$, hence dissolution of shells and increase of CO$_2$ partition fraction.

Source: IPCC AR4
CaCO$_3$ Undersaturation

Predicted undersaturation of CO$_3$ with respect to the pressure-dependent solubility of CaCO$_3$ shells. (Solubility of CaCO$_3$ increases with pressure.) Marginal saturation lines are drawn on upper plot for past years and indicated global warming scenarios (S650, IS92a); contours are for IS92a. The reduction of [CO$_3^{2-}$] due to ocean acidification will first lead to undersaturation in places where waters are already high in DIC (i.e. upwelling zones). Calcification stops when waters become undersaturated, and may slow down well before that.

Orr et al. [2005]
Projected oceanic uptake of anthropogenic CO$_2$ from a simple ocean model forced by emissions scenarios that stabilize atmospheric CO$_2$ at 450 ppm (S450) and 750 ppm (S750). The acidification of seawater (in “non-linear” models) reduces the buffering capacity to further absorb CO$_2$ from the atmosphere with reduced pH, relative to a non-reactive dye tracer (“linear” models). This is a positive feedback on atmospheric greenhouse concentrations with continuing emissions.