Updates

- Grad proposal new deadlines
  - Outline by Oct 28
  - Optional deadline for grading early version Nov 16
  - Final due Dec 7
- Next week breakout/presentation Thurs
  - Presentation Readings are posted
  - They are not required if you have already started on another paper – just suggestions

Global carbon cycle, 1990’s (IPCC Ch7)
black = natural fluxes, red = anthropogenic fluxes

Ocean biogeochemistry -
Part 1: Gas exchange and the carbonate system

Global C cycle - key points:
- Petagrams = $10^{15}$ gm; in atmosphere 1 Pg = ~0.5 ppm
  - A petagram (Pg) = a gigaton (Gt); both terms are used.
- Relative sizes of reservoirs (in Gt or Pg)
  - Atmosphere 762
  - Veg/soils 2350 (veg ~750, soils ~1600)
  - Surface ocean 918
  - Deep ocean 37,200
  - Ocean seds 150
  - Carbonate rocks 66-100 x $10^6$
  - Fossil fuels (var.) 3500
- Scale of anthropogenic fossil fuel perturbation relative to natural fluxes: generally small
  - 1980’s: 5.4 Gt/yr
  - 1990’s: 6.4 Gt/yr
  - 2009: 8.7 Gt/yr
- Note processes that move C around depend on climate, so change as climate changes
Ocean C cycle processes

*critical on a broad range of time scales*

- **Years/decades**: equilibration of CO$_2$ at surface; biological productivity
- **Centuries**: sequestration of C in deeper water via sinking of surface water to great depths (thermohaline circulation)
- **Millennia**: changes in amount of carbonate preserved or dissolved on ocean floor
- **Geologic scales**: burial of C-bearing sediments

**Anthropogenic CO$_2$ in the ocean**

Sabine et al. 2004, *Science*

- Fig: total inventory of anthropogenic CO$_2$ (all depths)
- 48% of anthropogenic CO$_2$ emitted (1800-1994) is in ocean
- (this leaves little room for biosphere to be a big net sink over this time frame)

The ocean carbon system - overview

- **Surface water - atmosphere exchange of CO$_2$**
  - Gas diffusion between ocean and atm. - depends on conc. gradient
  - Max concentration determined by solubility: f(T, S, P)
  - Key role of winds in determining rate of exchange
- **What happens next?**
  - **Reacts** to produce other forms of inorganic C: HCO$_3^-$, CO$_3^{2-}$
  - Balance of forms depends on pH
  - **Used** by biological productivity to form organic C tissue and calcium carbonate shells (next week!)
- **Transport to deep sea**
  - Solubility pump - sinking waters hold lots of CO$_2$
  - Biological pump - productivity incorporates C into particles that sink
  - Carbonate pump - related to biological; can increase surface CO$_2$
- **Other important processes (for the future):** ocean acidification, thermohaline circulation, nutrient biogeochemistry, ocean stratification

Exchange between ocean and atmosphere depends on

- **Concentration gradient** (difference in the partial pressure of CO2 in atmosphere vs ocean)
  - Solubility depends on specific conditions: T, sal, P
  - **Circulation:** Upwelling vs. nonupwelling
- **Wind speed** determines exchange rate
  - Nonlinear
- **CO$_2$ exchange is 2-way!**
  - Some ocean regions are a source, some a sink
  - Ever-increasing atmospheric CO2 drives net invasion
  - Areas of upwelling are sources locally
Air-sea CO₂ exchange

- Driven by concentration gradient
  - Yellow-red: CO₂ evasion to atmosphere
  - Blue-purple: CO₂ invasion from atmosphere

**Total dissolved inorganic carbon**

- Upwelling of deep water = source of CO₂ to atmosphere
- Recall ocean C reservoirs
  - Surface ~900 Gt
  - Deep ~37,000 Gt
- Deep water is enriched
  - Decay of sinking organic particles

**Gas solubility in seawater**

**Solubility** determines the maximum amount of CO₂ that seawater can hold under specific conditions.

- **Temperature** (more soluble in cold)
- **Salinity** (more soluble in fresher water; effect is small)
- **Pressure** (more soluble under high P)

From Bigg, 1998, *The Oceans and Climate*
**CO₂ solubility compared to other gases**

- CO₂ is off the charts - why?
- Reacts to form other compounds of dissolved inorganic C
  - HCO₃⁻ and CO₃²⁻: a reservoir of carbon
  - allow more CO₂ to enter at surface
  - (concentration gradient is determined only by CO₂, not the others)

From Bigg, 1998, *The Oceans and Climate*

**Forms of dissolved inorganic carbon (DIC)**

- Depends on pH
- Acidic: carbon in CO₂ form
- Basic: carbon mostly in carbonate (CO₃²⁻) form
- Ocean pH around 8: carbon mostly in bicarbonate (HCO₃⁻) form
  - 90% HCO₃⁻, 10% CO₃²⁻, <1% CO₂

*Figure* from Girard, *Environmental Chemistry*. The α stands for the fraction of total dissolved inorganic carbon present in the given form (CO₂, CO₃, or HCO₃⁻)

**CO₂ buffering in seawater**

- CO₂ enters ocean via gas diffusion, but most converts rapidly to HCO₃⁻
- Reaction:
  - CO₂ + CO₃²⁻ + H₂O → H⁺ + HCO₃⁻ + CO₃²⁻ → 2HCO₃⁻
- Thus addition of CO₂ draws down CO₃²⁻
  - Reduces ocean’s ability to absorb more: As CO₂ in atmosphere rises, strength of ocean C uptake will weaken.
  - Negative consequences for calcifying organisms such as corals (reduced calcification, weaker skeletons)
  - CO₂ is a weak acid, so adding more and keeping it as CO₂ makes ocean more acidic (but rate of change is buffered by change to HCO₃, CO₃ forms)

**Carbon and Alkalinity**

- **Fundamental control** on how much CO₂ the ocean can take in
- Can define in two ways:

  1. **Excess positive charge among components of seawater salinity** – the sum of cation charges minus sum of anion charges:
     
     \[ [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{HBO}_3^-] \]
     
     (these are the dissolved components of ocean “salt”)

  2. **Sum of HCO₃⁻ and CO₃²⁻**
     
     \[ \text{ALK} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \]
     
     (Easier to measure and balances the excess positive charge above)
**Carbon and Alkalinity**

- Why are these definitions equivalent??
- Excess positive charge must be balanced by negative charges, which come from $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$
- Carbonate systems provides electrical neutrality: forms of inorganic carbon shift to balance the charge precisely:
  \[ \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- \rightleftharpoons \text{CO}_2 \]

- High alkalinity: most C is in $\text{CO}_3^{2-}$ form (double-negative charge); low alkalinity: most C is in $\text{CO}_2$ (or $\text{HCO}_3^-$) form
- Which
- Alkalinity determines the ultimate ability of the ocean to absorb and buffer CO2
  - Alk in turn is determined by rock weathering (= slow!)

**Alkalinity**

- Which can absorb more CO2 from the atmosphere, high alkalinity waters or low alkalinity waters?
  - High alkalinity = high positive charge = high $\text{CO}_3^{2-}$

**Alkalinity**

- What controls alkalinity?
  - Weathering of rocks to produce cations (long time scales, global)
  - Biological productivity that uses Ca++ and others (short time scales, patchy)

- Slow rate of (geological) cation addition means that ability of ocean to take up CO2 will inevitably decrease as anthropogenic CO2 is added (alk cannot keep up)

**Ocean as long-term carbon sink**

- Recall ocean C reservoirs
  - Surface ~900 Gt
  - Deep ~37,000 Gt
- Deep water is enriched
  - Decay of sinking organic particles

- Effectively removing carbon from the atmosphere (for long periods - centuries+) requires that C get into the deep ocean.
How does carbon move from surface to deep ocean?

- **Solubility pump**
  - Where cold waters sink, can transport CO\(_2\) to depth
- **Biological pump**
  - Organic carbon
  - Carbonate counter-pump - enriches surface waters in CO\(_2\) on short term

**Carbon transport to deep sea**

- **Solubility pump**: CO\(_2\) more soluble in cold, saline waters. In the North Atlantic, cold deep waters (denser than surroundings) sink into the depths. This process takes carbon out of surface and into deep.

**Carbon transport to deep sea**

- **Biological pump**: photosynthesis converts inorganic carbon to organic particles, which reduces surface [DIC].
  - Sinking particles (~25%)* remove C from surface to deep waters
  - a very small fraction (1-2% of C)* is buried in seds.
- **Most effective where nutrients are high**

* - Most C is released by decay (respiration) in either surface or deep waters.

**Carbon transport to deep sea**

- **Carbonate counter pump**: Organic productivity is also associated with CaCO\(_3\) production
  - \(\text{Ca}^{++} + \text{CO}_3^{-} \rightarrow \text{CaCO}_3\)
  - CaCO\(_3\) precipitation decreases alkalinity by 2 units (via removal of double-charged Ca\(^{++}\)) but total CO\(_2\) by only one unit (via removal of CO\(_3^{-}\))
  - Due to dominance of alkalinity change, there is a net shift of carbon towards CO\(_2\):
    - \(\text{CO}_3^{-} \leftrightarrow \text{HCO}_3^{-} \leftrightarrow \text{CO}_2\)
  - Formation of CaCO\(_3\) therefore increases surface water CO\(_2\)! (counterintuitive since it also removes C)
The ocean carbon system - overview

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- What happens next?
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- Other important processes (for the future): ocean acidification, thermohaline circulation, nutrient biogeochemistry, ocean stratification
Acidity: Changing ocean chemistry

- As CO$_2$ rises, pH and CO$_3^{2-}$ fall

Notes on carbonate saturation

\[ \text{Ca}^{++} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \]

- Saturation state, $\Omega$: a measure of how saturated the surface ocean is with respect to CaCO$_3$ (how easily can CaCO$_3$ form?)
  - If $\Omega > 1$, supersaturated: precipitation (in fresh water)
  - If $\Omega < 1$, undersaturated: dissolution (in fresh water)

- Increase atmospheric CO$_2$ means that:
  - CO$_2$ is reduced, $\Omega$ decreases
  - CO$_2$ increases, so pH drops.

- Sample values for surface ocean:
  - Today: (365 ppm) $\Omega = 4.0$, pH = 8.05
  - Preindustrial: (280 ppm) $\Omega = 4.6$, pH = 8.16
  - Glacial: (200 ppm) $\Omega = 5.6$, pH = 8.26
  - 2100: (700? ppm) $\Omega = 2.8$, pH = 7.9

More on carbonate saturation state

- Nearly always positive, so why worry?
  - Organisms appear to care about degree of supersaturation; calc decreases even though $\Omega > 1$
  - Expanding regions where $\Omega < 1$ means inorganic dissolution regions are growing.

- Calcification reduced under lower saturation state
  - coccoliths and other plankton (90% of current calc), reef organisms (10% of current calc)