XI. the natural carbon cycle

with materials from
J. Kasting (Penn State)
outline

• properties of carbon
• the terrestrial biological cycle of carbon
• the ocean cycle of carbon
• carbon in the rock cycle
• overview of carbon stocks and exchanges
• timescales of exchange and renewal
• the silicate weathering “thermostat”
the carbon cycle

- flow of matter and energy between reservoirs (stocks and flows naturally in or near balance)

- linked to other biogeochemical and life cycles thru nutrient and energy flows

- linked to climate via greenhouse effect (and direct influence of vegetation on climate)

- to understand, first need to know something about carbon itself
organic and inorganic carbon

C is cycled between reduced and oxidized forms by natural processes

<table>
<thead>
<tr>
<th>organic carbon (reduced)</th>
<th>inorganic carbon (oxidized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘CH₂O’</td>
<td>CO₂ carbon dioxide</td>
</tr>
<tr>
<td>example:</td>
<td>H₂CO₃ carbonic acid</td>
</tr>
<tr>
<td>Glucose -- C₆H₁₂O₆</td>
<td>HCO₃⁻ bicarbonate ion</td>
</tr>
<tr>
<td></td>
<td>CO₃⁻ carbonate ion</td>
</tr>
<tr>
<td></td>
<td>CaCO₃ calcium carbonate</td>
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</table>

example of transfer of oxidized to reduced C that also involves a flow of energy?
photosynthesis

energy + CO$_2$ + H$_2$O $\rightarrow$ CH$_2$O + O$_2$

plants harness sun’s energy to make chemical energy (carbohydrate) from inorganic CO$_2$ (& water)
photosynthesis

energy + CO₂ + H₂O → CH₂O + O₂

degradation and decay

energy + CO₂ + H₂O ← CH₂O + O₂

photosynthesis requires an input of (light) energy, respiration and decay release stored chemical energy (on land, photosynthesis is roughly balanced by respiration and decay....)
As biomass ages, it takes on different forms, becoming organic carbon (reduced).
inorganic carbon (oxidized)

seashells

limestone

CO$_2$, DIC

coral
carbon

• **can bond readily and reversibly with H, O, N and any number of additional carbon atoms**

• **provides molecular “backbone” for life**

• **can store and release energy via change in “oxidation” state**
<table>
<thead>
<tr>
<th>oxidation state</th>
<th>oxidized</th>
<th>intermediate</th>
<th>reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>simplest example</td>
<td>CO₂</td>
<td>CH₂O</td>
<td>CH₄</td>
</tr>
<tr>
<td>carbon oxidation state</td>
<td>+4</td>
<td>0</td>
<td>-4</td>
</tr>
<tr>
<td>general category</td>
<td>inorganic carbon</td>
<td>carbohydrate</td>
<td>hydrocarbon</td>
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Oxygen is hungry for electrons and generally leaves bonded atoms depleted in electrons and therefore positively charged.
# Oxidation State

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- **simplest example**
  - CH₄
  - CH₂O
  - CO₂

- **carbon oxidation state**
  - oxidized: +4
  - intermediate: 0
  - reduced: -4

- **general category**
  - inorganic carbon
  - carbohydrate
  - hydrocarbon

---

**oxidized state most stable, so organic C will tend to move to this state over time**
the terrestrial biological C-cycle

photosynthesis

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

respiration and decay

- on land, production of organic carbon by photosynthesis is largely balanced by respiration and decay
  
  -- respiration: used by both plants and animals to produce energy for metabolism
  
  -- decay: consumption of dead organic matter by (aerobic or anaerobic) microorganisms
natural carbon stocks and flows

on a global scale, we measure quantities of carbon in gigatons (Gt)

1 Gt = 1 billion metric tons

1 metric ton = 1,000 kilograms

(so, 1 Gt = $10^{15}$ grams)

Typically, we only count the weight of the carbon itself, i.e., for CH$_2$O we neglect the weight of the H$_2$O. So, we write these units as Gt(C) or GTC.
Plants respire all the time, offsetting much of new photosynthesis. The values here are for net photosynthesis which is offset by respiration by consumers on various timescales.

flows in GTC/year

balanced?
the terrestrial biological C-cycle

not all new plant tissue survives- about as much new dead plant material enters soils as is lost from soils by decay (mostly oxidation)
seasonal var. in CO₂

season to season “breathing” of biosphere (~+/- 60 GTC/yr) leads to clear seasonal var. in amount of atmospheric CO₂
clicker question:

the change in overall CO₂ amount from 1999 to 2000 and 2001 is due primarily to:

a) more respiration
b) less photosynthesis
c) more decay
d) burning of fossil fuels
e) none of the above
monthly mean CO₂
the terrestrial biological C-cycle

output

photosynthesis
60 GTC/yr

atm. CO$_2$

input

respiration & decay
60 GTC/yr

$\text{CO}_2$ reservoir size: 700 GTC

residence time: \[
\frac{700 \text{ GTC}}{60 \text{ GTC/yr}} = \sim 11.7 \text{ yr}
\]

approx. lifetime of $\text{CO}_2$ molecule in atmosphere if there were no exchange with slowly moving deep ocean, sediments and rocks
the ocean C-cycle

carbon uptake and release by the oceans:

1. exchange of CO$_2$ gas across air-sea interface

2. the “biological pump”
the ocean C-cycle

atm. CO₂

air-sea exchange

surface ocean

“DIC”

~100 m

~4 km

deep ocean

“DIC”

biological pump

C in sea water exists largely as “DIC” (dissolved inorganic carbon)

biological activity transfers C from upper O. to deep O., leading to different [DIC] and pCO₂ in upper and deep O.
the ocean’s biological pump

photosynthesis

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

respiration

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

This pumps up the CO\(_2\) of deep water...
the ocean’s biological pump

*transfer of CO$_2$ to the deep ocean:*

photosynthesis creates organic matter; this sinks to the deep ocean, where it decays back to CO$_2$
the ocean’s biological pump

transfer of CO$_2$ to the deep ocean:

deep water becomes enriched in CO$_2$

the carbon is recycled to the surface in ~1,000 years
deep circulation dominated by a continuous circuit associated with formation of deep water in the N. Atlantic (i.e. NADW)
Dissolved Inorganic C (DIC), Pacific

DIC (µmol/kg) in the Pacific

end of conveyor, must come up somewhere

less more

pls. see later note on molar units
The biological pump increases the [DIC] and pCO$_2$ of the deep ocean. When deep water upwells to surface, some excess CO$_2$ escapes to atmosphere, but most is taken back up by the biological pump....
atm. CO$_2$  

**vigorous exchange**  
90 GtC/yr  

**biological pump**  

**DIC: 1,000 GTC**  

**deep ocean**  

**DIC: 37,000 GTC**  

pCO$_2$ = 380 ppmv  

**in equilibrium**  

pCO$_2$ = 380 ppmv  

pCO$_2$ $\approx$ 1000 ppmv  

• deep water has a higher CO$_2$ partial pressure than does surface water

Can say that the partitioning of C between surface and deep ocean by the biological pump helps to set the atmospheric concentration (in unperturbed C-cycle)…
the ocean timescale(s)

the surface ocean-to-atmosphere exchange is large with respect to the size of the atmospheric reservoir, but does not tug on the atmospheric concentration seasonally, because:

• unlike land, there is not a strong hemispheric or seasonal bias in biological production over the ocean (slide)
new production ocean vs. land

June

Dec.

Net Primary Productivity (kgC/m²/year)
**the ocean timescale(s)**

the surface ocean-to-atmosphere exchange is large with respect to the size of the atmospheric reservoir, but does not tug on the atmospheric concentration seasonally, because:

• unlike land, there is not a strong hemispheric or seasonal bias in biological production over the ocean

• it takes hundreds of years for all ocean water to contact the atmosphere due to slow overturning timescale of the conveyor (~1000 yrs)

• most importantly, reactions between the CO$_2$ and DIC make it hard to change seawater pCO$_2$ (see next lecture on the perturbed C-cycle..)

ocean breathes on timescale of 5,000 year set by slow overturning and chemical reaction with sea sediments (see a later lecture on Ice Age mysteries...)

natural carbon stocks and flows

land:
  600 GTC living
  1500 GTC dead (soils and sediments)

ocean:
  1 GTC living
  600 GTC dead (organic)
  38,000 GTC inorganic

atmosphere:
  700 GTC inorganic (pre-industrial)

rocks:
  50,000,000 GTC inorganic + organic
  5,000 GTC conc. organic (fossil fuel!)

values are approximate
natural carbon stocks and flows

ocean
DIC: 38,000
DOC: 600
living C: 1

land
living C: 500
dead C: 1500

atmosphere
700

90

60 GTC/y

stocks in GTC (gigatons C = 10^{15} g C)
transfer fluxes in GTC/year
natural carbon stocks and flows

**ocean**
- DIC: 38,000
- DOC: 600
- living C: 1

**land**
- living C: 500
- dead C: 1500

**atmosphere**
- 700

**sedimentary rocks**
- CaCO$_3$ + OC: 50,000,000
- fossil fuels: 5000

**transfer fluxes in GTC/year**
- 90 to atmosphere
- 60 GTC/y to land

**stocks in GTC (gigatons C = 10^{15} g C)**

**CaCO$_3$ + SiO$_2$ → CaSiO$_3$ + CO$_2$**

<0.1 GTC/yr

**weathering**

CaSiO$_3$ + CO$_2$ → CaCO$_3$ + SiO$_2$

<0.1 GTC/yr
natural carbon stocks and flows

ocean
DIC: 38,000
DOC: 600
living C: 1

atmosphere
700

land
living C: 500
dead C: 1500

sedimentary rocks
CaCO₃ + OC: 50,000,000
fossil fuels: 5000

CaCO₃ + SiO₂ → CaSiO₃ + CO₂
<0.1 GTC/yr

metamorphism
CaCO₃ + SiO₂ → CaSiO₃ + CO₂
<0.1 GTC/yr

weathering
CaSiO₃ + CO₂ → CaCO₃ + SiO₂
<0.1 GTC/yr

stocks in GTC (gigatons C = \(10^{15}\) g C)
transfer fluxes in GTC/year

90

60 GTC/yr

vigorous exchange

slow exchange
the long term “rock” C-cycle

• dominated by the weathering of Ca-containing silicate minerals and the subsequent use of Ca by organisms to build calcium carbonate shells

• the net result of the two reactions is the uptake of CO₂
silicate rock weathering:

\[ \text{CaSiO}_3 + 2 \text{H}_2\text{O} + 2 \text{CO}_2 \rightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^- + \text{SiO}_2 + \text{H}_2\text{O} \]

carbonate formation:

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

\[ \text{CaSiO}_3 + 2\text{H}_2\text{O} + 2\text{CO}_2 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SiO}_2 + \text{H}_2\text{O} \]

carbonate formation:

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

net reaction:

\[ \text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2 \]
the long term “rock” C-cycle

atmosphere

\[ \text{weathering} \]
\[ \text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2 \]
the long term “rock” C-cycle

weathering

\[ \text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2 \]

atmosphere

CO\(_2\)

 WX

dissolved CaCO\(_3\) & SiO\(_2\)

ocean

sediments
the long term “rock” C-cycle

atmosphere

atmosphere

CO₂

weathering

CaSiO₃ + CO₂ → CaCO₃ + SiO₂

dissolved CaCO₃ & SiO₂

solid CaCO₃ & SiO₂ shells

ocean

sediments
the long term “rock” C-cycle

weathering

\[ \text{CaSiO}_3 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2 \]

dissolved CaCO$_3$ & SiO$_2$

solid CaCO$_3$ & SiO$_2$ shells

CaCO$_3$ & SiO$_2$ sediments

atmosphere

CO$_2$

subduction

ocean
the long term “rock” C-cycle

atmosphere

CO₂

weathering

CaSiO₃ + CO₂ → CaCO₃ + SiO₂

dissolved CaCO₃ & SiO₂

solid CaCO₃ & SiO₂ shells

CaCO₃ + SiO₂ → CaSiO₂ + CO₂

metamorphism

ocean

CaCO₃ & SiO₂ sediments

subduction
long term “rock” inorganic C-cycle

Weathering

CaSiO$_3$ + CO$_2$ → CaCO$_3$ + SiO$_2$
long term “rock” inorganic C-cycle

Weathering

\[ \text{CaSiO}_3 + \text{CO}_2 \]

\(~0.1\) GTC/yr

Volcanism

\[ \text{CaCO}_3 + \text{SiO}_2 \]

\(~0.1\) GTC/yr
What controls silicate weathering rates?

• time
• temperature
• rainfall
• exposure of fresh rock surfaces
• vegetation (roots provide acid)
weathering feedback loop

Atm. CO₂

Silicate weathering rates

Surface Temperature

weathering rates increase with increased temperature
weathering reactions remove CO$_2$, and as CO$_2$ declines, planet temperatures go down.

weathering feedback loop
this is a negative feedback loop and a key factor in helping to stabilize climate and CO$_2$ over long time scales (i.e., millions of years)
key points

• carbon cycle includes atmosphere, ocean, biosphere and lithosphere, but each has different time scale
• time scales depend on size of flux, and size of reservoirs
• the terrestrial biosphere is responsible for seasonal variations in CO$_2$
• other reservoirs must be responsible for longer time scale changes in CO$_2$
• as we will see, human activity and burning of fossil fuels connects the very long time scale of the rock cycle with the much shorter time scales of the atmosphere, ocean and biosphere
the long term “rock” C-cycle

- A small flux of **organic** carbon (0.05 Gt/yr) is also buried in sedimentary rocks, mostly on continental shelves.

- Over time, this small flux has accumulated to create a large reservoir: $\sim 10,000,000$ (or $1 \times 10^7$) Gton C.

- Concentrations of this buried organic carbon include coal, oil and gas--but most carbon is **not** concentrated.

- Organic carbon in sedimentary rocks is ultimately returned as CO$_2$ resulting from **oxidation** by exposure to O$_2$.

- This oxidation is also a **weathering** process.
the natural fate of fossil fuels

- weathering of rocks will ultimately allow the release of fossil fuels as CO$_2$
- this would normally occur over 100s of millions of years
- humans simply speed up this process by burning fossil fuels (10s of years)
- as such, rapid burning of fossil fuels puts the carbon cycle out of balance
concept of the mole

• the last slide gave the sea water concentration of Dissolved Inorganic Carbon (DIC) in moles (i.e. as micro-moles of DIC per kilogram of sea water)

• the number of moles is directly related to the number of molecules of a substance

• 1 mole is $6 \times 10^{23}$ molecules

• the molar mass of C is 12 (‘formula weight’), so 1 mole of C weighs 12 g

• the molar mass of CO$_2$ is 44 (‘formula weight’), so 1 mole of CO$_2$ weighs 44 g

• the molar mass of CO$_3^{2-}$ is 60 (‘formula weight’), so 1 mole of CO$_2$ weighs 60 g

• the amount of C is the same in each…..
learning goals

• be familiar w/ the special chemical attributes of C and how the stability of molecular C relates to its “oxidation” state
• be able to describe the photosynthesis/respiration reaction
• be able to describe the ambient Earth reservoirs of C, their relative sizes (or rank) and the sizes (or rank) of flows between them
• be able to determine a *residence time* from reservoir size and rate of in/output
• use this knowledge to determine which reservoirs exert the greatest influence on atmospheric CO$_2$ on brief (year to year) vs. very long (million year plus) timescales
• be able to describe the roles of *silicate weathering* and *metamorphism* and *volcanism* in the natural cycling of C
• be able to describe where sedimentary C and fossil fuel C come from