Geologic Carbon Cycle
Distribution of Carbon;  
$10^{15}$ grams = 1 Petagram (Pg)
1) Name an important negative feedback between the rock cycle and atmospheric CO$_2$ for inorganic C and organic C? How does it work?

**Figure 3.1** (a) The geological carbon (C) cycle; (b) fluxes affecting the concentration of carbon dioxide (CO$_2$) in the surface reservoir of the carbon cycle. Notes: fluxes that are discussed in detail and quantified in the present work are solid arrows: $B_{POC}$ (burial of POC in marine sediments), $B_{CH4}$ (burial of methane in marine sediments), $B_{BC}$ (burial of biogenic carbonates in marine sediments), $B_{AC}$ (burial of authigenic carbonates in marine sediments), $D_{POC}$ (metamorphic degassing of POC), $D_C$ (metamorphic degassing of carbonate minerals), $D_M$ (degassing of the mantle), $W_{POC}$ (weathering of POC on the continents), $W_C$ (weathering of carbonates on the continents), $A_{OC}$ (alteration of oceanic crust), $W_{CSIL}$ (weathering of silicate minerals on the continents), $W_{OSIL}$ (weathering of silicate minerals in marine sediments). Other carbon fluxes are (dashed arrows): $E_{POC}$ (erosion and transport of POC to the ocean), $A_{POC}$ (accretion of POC during continental collision), $E_C$ (erosion and transport of carbonate minerals to the ocean), $A_C$ (accretion of carbonate minerals during continental collision), $S_{POC}$ (subduction of POC in the mantle), $S_C$ (subduction of carbonate minerals in the mantle).
Chemical weathering (dissolving rocks)

Rocks + H₂O + CO₂ → secondary minerals + dissolved ions + HCO₃⁻ (bicarbonate ion)

Removes CO₂ from the atmosphere and puts it in soluble form (where it can be transported eventually to the ocean)

Releases “base” cations that provide necessary nutrients for life.
Plankton - Primary Producers in the Surface Ocean (a primary producer makes its own food using photosynthesis) Some kinds grow hard shells

Foraminifera – calcium carbonate

Diatoms
Silica
Weathering: Rocks (Ca, Si, O) + H₂O + CO₂ → HCO₃⁻ + Dissolved ions (Ca⁺⁺) + Silica

Carbonic acid bicarbonate

In the ocean – Ca⁺⁺ and HCO₃⁻ can combine to make Calcium carbonate (limestone)
Usually this is mediated by biology – organisms build calcium carbonate shells
The rock cycle regulates atmospheric $CO_2$ over millions of years.

1. Carbon dioxide released from volcanoes.

2. $CO_2$ dissolves in water, making a weak acid that will react with rocks in crust. $CO_2$ also forms organic matter.

3. Calcium carbonate (ocean salts) and organic matter accumulate in sediments on ocean floor.

4. Subducted sediments are heated, which causes them to release carbon dioxide again – $CO_2$ travels up to be released in volcanic gases.
Weathering rates increase with pCO$_2$ (acidity) and temperature (also increases with pCO$_2$).

**Figure 4.4** Dissolution of Ca-feldspar (plagioclase) as a function of soil CO$_2$ concentrations in watersheds of the Sierra Nevada (California), subject to differential hydrothermal activity.
Response time for CO$_2$ with these processes is long –

CO$_2$ in the atmosphere
(70 x $10^{16}$ grams C)

Added by Volcanoes
(~35 x $10^{12}$ grams C/ year)

Removed by dissolution in water, reaction with rocks on sea floor
⇒ Weathering

In contrast rates of fossil fuel burning add $7x10^{15}$ grams C/year to the atmosphere
Average CO$_2$ concentration last 0.5 Myr was 230 ppm (but actually it shifted between low CO$_2$ state of $\sim$180 ppm and high CO$_2$ state of $\sim$280 ppm)
Volcanic gases emitted from the Pacific ‘ring of fire’ indicate predominantly carbonates contribute to the CO₂ emitted.
2) Why do we think it is reasonable that the early atmosphere had relatively high atmospheric CO$_2$ compared to today?
Where did the atmosphere come from?

- **First atmosphere** – gases inherited from planet formation; this largely was blown away by high energy ‘solar wind’ that began when the sun ignited
- **Second atmosphere** – volcanic gases accumulate also some gases inherited from comets striking Earth
- **This atmosphere** was substantially modified (and still is) by the presence of life
Composition of Volcanic gases

Examples of volcanic gas compositions, in volume percent concentrations (from Symonds et. al., 1994)

<table>
<thead>
<tr>
<th>Volcano Tectonic Style Temperature</th>
<th>Kilauea Summit Hot Spot 1170°C</th>
<th>Ertă' Ale Divergent Plate 1130°C</th>
<th>Momotombo Convergent Plate 820°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (water)</td>
<td>37.1</td>
<td>77.2</td>
<td>97.1</td>
</tr>
<tr>
<td>CO₂ (carbon dioxide)</td>
<td>48.9</td>
<td>11.3</td>
<td>1.44</td>
</tr>
<tr>
<td>SO₂ (sulfur dioxide)</td>
<td>11.8</td>
<td>8.34</td>
<td>0.50</td>
</tr>
<tr>
<td>H₂ (hydrogen gas)</td>
<td>0.49</td>
<td>1.39</td>
<td>0.70</td>
</tr>
<tr>
<td>CO (carbon monoxide)</td>
<td>1.51</td>
<td>0.44</td>
<td>0.01</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.04</td>
<td>0.68</td>
<td>0.23</td>
</tr>
<tr>
<td>HCl</td>
<td>0.08</td>
<td>0.42</td>
<td>2.89</td>
</tr>
<tr>
<td>HF</td>
<td>---</td>
<td>---</td>
<td>0.26</td>
</tr>
</tbody>
</table>

http://www.physics.gla.ac.uk/~martino/gasMonitoring/
<table>
<thead>
<tr>
<th></th>
<th>VENUS</th>
<th>EARTH</th>
<th>MARS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SURFACE</strong></td>
<td><strong>PRESSURE</strong></td>
<td>100,000 mb</td>
<td>1,000 mb</td>
</tr>
<tr>
<td><strong>COMPOSITION</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>&gt;98%</td>
<td>0.03%</td>
<td>96%</td>
</tr>
<tr>
<td>N₂</td>
<td>1%</td>
<td>78%</td>
<td>2.5%</td>
</tr>
<tr>
<td>Ar</td>
<td>1%</td>
<td>1%</td>
<td>1.5%</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0%</td>
<td>21%</td>
<td>2.5%</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.0%</td>
<td>0.1%</td>
<td>0-0.1%</td>
</tr>
</tbody>
</table>
Greenhouse effect on other planets

<table>
<thead>
<tr>
<th></th>
<th>Relative distance from Sun</th>
<th>Albedo (fraction reflected)</th>
<th>radiative equilibrium surface temperature (Celsius)</th>
<th>Surface temperature (Celsius)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun</td>
<td></td>
<td></td>
<td></td>
<td>5800</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.39</td>
<td>0.11</td>
<td>164</td>
<td>260</td>
</tr>
<tr>
<td>Venus</td>
<td>0.72</td>
<td>0.72</td>
<td>-43</td>
<td>480</td>
</tr>
<tr>
<td>Earth</td>
<td>1</td>
<td>0.33</td>
<td>-17</td>
<td>15</td>
</tr>
<tr>
<td>Mars</td>
<td>1.52</td>
<td>0.25</td>
<td>-55</td>
<td>-55</td>
</tr>
</tbody>
</table>
Comparison of terrestrial planetary atmospheres

Venus
- 90 atmospheres
- 96% CO$_2$
- 4% N$_2$

Earth
- 1 atmosphere
- 77% N$_2$
- 21% O$_2$
- 1% Ar
- H$_2$O (var)
- 0.03% CO$_2$

Mars
- 0.007 atmosphere
- 95% CO$_2$
- 2.7% N$_2$
- 1.6% Ar
'runaway greenhouse'

H₂O + light $\rightarrow$ H + H + O

H escapes to space, leaving O

O reacts with rocks (FeO $\rightarrow$ Fe₂O₃)
The Faint Young Sun Paradox

• The paradox comes from two seemingly inconsistent observations: (1) the sun's luminosity is thought to have increased by ~30% over the last 4 billion years
  (2) the earth has had liquid water at its surface for most of that time
    as evidenced by the presence of sedimentary rocks or metamorphic rocks derived from sediments

• We know....The radiative balance of the Earth (which balances the amount of absorbed radiation (incoming minus reflected radiation) with radiation emitted because the Earth has temperature) requires a 'greenhouse' atmosphere (some CO₂ and H₂O vapor in the air) to explain today's surface temperatures.

• Explanations for similar surface temperatures several billion years ago, if there was only 70% as much sunlight reaching earth, have been based on increasing the atmosphere's greenhouse gases (either as CO₂ or CH₄).
Solar (mostly visible light)  Earth (mostly infrared light)

Atmospheric window

Greenhouse gases
3) What happened to the CO$_2$ that was initially in the atmosphere over geologic time?

Have the ratios of these two burial mechanisms varied over time and how can we use isotopes to know? )
Processes modifying atmospheric composition include:

- **Water** – formed the oceans

- **Carbon dioxide, sulfur gases, HCl** are very soluble in water and would likely have mostly **dissolved in the oceans**. When dissolved in water carbon dioxide can form minerals like calcium carbonate (limestone) that accumulate over time (CO$_2$ went into rocks)

- escape of H and He from Earth's gravitational field

LIFE The rise of oxygen in the atmosphere is related to process of photosynthesis by which plants convert CO$_2$ + water into organic carbon (plant tissue) plus O$_2$
Evolution of the Terrestrial Planet Atmospheres

• Venus, Earth, & Mars received their atmospheres through outgassing.
  • most common gases: $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{N}_2$, $\text{H}_2\text{S}$, $\text{SO}_2$

• Chemical reactions caused $\text{CO}_2$ on Earth to dissolve in oceans and go into carbonate rocks (like limestone.)
  • this occurred because $\text{H}_2\text{O}$ could exist in liquid state
  • $\text{N}_2$ was left as the dominant gas; $\text{O}_2$ was exhaled by plant life
  • as the dominant gas on Venus, $\text{CO}_2$ caused strong greenhouse effect

• Mars lost much of its atmosphere through impacts
  • less massive planet, lower escape velocity
If $\text{CO}_2$ concentrations were higher in the early Earth – as they are in the other terrestrial planet atmospheres AND in volcanic emissions – then we can offset the faintness of early sunlight with an enhanced greenhouse effect.

$\text{CO}_2$ concentrations would have had to be $1000 - 10,000$ times present levels in the early earth atmosphere for temperatures to be above freezing.
Where did all that $\text{CO}_2$ go?

Limestone rock
(calcium carbonate)
Stable carbon isotope evidence

Qualitatively, if all CO$_2$ remains in the atmosphere (and CO$_2$ accumulates over time, as in the “ice-house” earth), the $^{13}$C/$^{12}$C will be the same as volcanic source.

If a lot of organic matter is preserved, the remaining C in the oceans will have high $^{13}$C/$^{12}$C ratio compared to volcanic CO$_2$ source.
Stable carbon isotope evidence

Qualitatively, if all CO₂ remains in the atmosphere (and CO₂ accumulates over time, as in the “ice-house” earth), the $^{13}$C/$^{12}$C will be the same as volcanic source.

If a lot of organic matter is preserved, the remaining C in the oceans will have high $^{13}$C/$^{12}$C ratio compared to volcanic CO₂ source.
After Figure 15 in Hoffman and Schrag.

Today's values
Image from Och and Zhou, Earth Science Reviews, 2012
The model described in the paper is very complex – for a simplified form, take a look at the online GEOCARB model - see: http://climatemodels.uchicago.edu/geocarb/geocarb.doc.html

Try the following:– set “Transition spike” to zero, and change the CO₂ degassing rate from 1.5 to 11.5 x 10^{12} mole/year. How does atmospheric pCO₂ vary? Does the ratio of weathering of C to organic C vary? What happens if you turn on plants (and why?))?
The earth has been cold enough for ice sheets to form on land only a few times in its history. We are currently in such an “icehouse” climate now. This is also accompanied by very low (in terms of earth’s history) CO2 concentrations. What is one explanation given for the low CO2 in the last millions of years?
CO₂ and land ice over the past 400 million years

AGU Fall 2009 - Bjerknes Lecture
RB Alley: The Biggest Control Knob: Carbon Dioxide in Earth's Climate History
http://www.agu.org/meetings/fm09/lectures/videos.ph
II. Snowball Earth

- The idea that runaway ice-albedo feedback led to complete freezing of the Earth’s surface ~700 million years ago
- First suggested by geologists who found evidence of glacial rock deposits on continents that would have been at the equator at this time
- Models show that if you have too much ice near the equator, a completely frozen earth will result
What was the world like 700 million years ago?

• Continents were likely clustered in one large ‘megacontinent’ near the equator
• The atmosphere had free oxygen (since 2000 million years ago)
• Life was made up only of single celled organisms, though cells with a nucleus (Eukaryotes) had evolved
Evidence for glaciation: the presence of ‘drop-stones’ or ice-rafted debris. In this photo, Paul Hoffman and Dan Schrag, two of the principal proponents of the renewed Snowball hypothesis, point to a cap carbonate deposit overlying glacial-derived debris. The photo below shows elaborate crystal structure of aragonite preserved in the cap carbonate deposit. Both deposits have paleomagnetic signatures that put them in tropical latitudes in the late Proterozoic. (photos and figures are adapted from http://wwweps.harvard.edu/people/faculty/hoffman/snowball_paper.html)
In a mostly snow- and ice-covered Earth, surface temperatures are estimated to have been very cold (-50 degrees C, well below freezing) – hence, Snowball Earth

**BUT..**
- No production of sediments in nearly lifeless oceans
- No reaction of liquid water with CO₂ dissolved in it to react with rocks and add salts to oceans
- No water vapor, little precipitation

**CO₂ still added by volcanoes**

**NO Processes to remove CO₂ from the atmosphere**
What got us out of the icehouse?

$\text{CO}_2$ builds up because it is added faster than it is removed.

High $\text{CO}_2$ levels increase the greenhouse effect.
Ice melts (rapidly due to ice-albedo (reflectivity) feedback)
Freeze-Fry Scenario

High CO2 levels, no ice reflecting sunlight – it is HOT!!! Carbonates precipitate in the oceans

Over time, faster weathering takes CO₂ out of the atmosphere again
What might you look for to test this hypothesis?

- Fluctuating carbon dioxide concentrations
  (hard to get a direct measure so long ago)
- Evidence that carbon dioxide accumulating in the atmosphere was from volcanoes (other volcanic gases? Isotopes of C in CO$_2$)
- Reduction of oxygen content of the oceans that are frozen over. Organic matter still decomposes removing O$_2$, but no exchange with the air through ice to replenish it. (Banded iron formations)
- Evidence of very slow weathering rates during the ice period and fast rates in the subsequent warm period (change chemistry of the ocean?)
  (hard to say, cold period is mostly a hiatus in sediment formation, so not many deposits exist)
87Rb-87Sr decay scheme

87Rb = 27.83%
85Rb = 72.17%
- decays to 87Sr by β⁻, half-life = 48.8 billion years

88Sr = 82.53%
87Sr = 7.04%
86Sr = 9.87%
84Sr = 0.56%

All stable

Mass balance of Parent (N) and Daughter (D) isotopes – the problem of initial (unknown) 87Sr

- normalize to stable 86Sr (mainly it is easier to measure isotopic ratios):

\[ D = D_0 + N \left( e^{\lambda t} - 1 \right) \]

\[ \frac{^{87}Sr}{^{86}Sr} = \left( \frac{^{87}Sr}{^{86}Sr} \right)_0 + \frac{^{87}Rb}{^{86}Sr} \left( e^{\lambda t} - 1 \right) \]

\[ y = b + x(m) \quad t = [\ln(m+1)] \lambda. \]
As long as the minerals all crystallized from the same melt, the initial $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ should be about the same (not much mass-dependent fractionation by comparison). However different minerals will have very different Rb/Sr ratios.
At time $t_1$, some arbitrary time after time $t_0$, some of the $^{87}\text{Rb}$ has decayed to $^{87}\text{Sr}$. The more Rb in the rock the more $^{87}\text{Sr}$ is produced.
\[
\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = (\frac{^{87}\text{Sr}}{^{86}\text{Sr}})_i + \frac{^{87}\text{Rb}}{^{86}\text{Sr}}(e^{\lambda t} - 1)
\]

Notice that no matter how much time has passed, a straight line through a series of cogenetic samples will always give us the initial \(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\) ratio, i.e. the same y-intercept.
<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Age (billion years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Juvinas (achondrite)</td>
<td>Mineral isochron</td>
<td>4.60 ± 0.07</td>
</tr>
<tr>
<td>Allende (carbonaceous chondrite)</td>
<td>Mixed isochron</td>
<td>4.5-4.7</td>
</tr>
<tr>
<td>Colomera (silicate inclusion, iron meteorite)</td>
<td>Mineral isochron</td>
<td>4.61 ± 0.04</td>
</tr>
<tr>
<td>Enstatite chondrites</td>
<td>Whole-rock isochron</td>
<td>4.54 ± 0.13</td>
</tr>
<tr>
<td>Enstatite chondrites</td>
<td>Mineral isochron</td>
<td>4.56 ± 0.15</td>
</tr>
<tr>
<td>Carbonaceous chondrites</td>
<td>Whole-rock isochron</td>
<td>4.69 ± 0.14</td>
</tr>
<tr>
<td>Amphoterite chondrites</td>
<td>Whole-rock isochron</td>
<td>4.56 ± 0.15</td>
</tr>
<tr>
<td>Bronzite chondrites</td>
<td>Whole-rock isochron</td>
<td>4.69 ± 0.14</td>
</tr>
<tr>
<td>Hypersthene chondrites</td>
<td>Whole-rock isochron</td>
<td>4.48 ± 0.1</td>
</tr>
<tr>
<td>Krahenberg (amphoterite)</td>
<td>Mineral isochron</td>
<td>4.70 ± 0.01</td>
</tr>
<tr>
<td>Norton County (achondrite)</td>
<td>Mineral isochron</td>
<td>4.7 ± 0.1</td>
</tr>
</tbody>
</table>

Note: All ages are based on a value of $1.39 \times 10^{-11} \text{ y}^{-1}$ for the decay constant of $^{87}\text{Rb}$. The currently accepted value of $1.42 \times 10^{-11} \text{ yr}^{-1}$ has the effect of lowering these ages slightly.

Table 7: Summary of Some Rb-Sr Isochron Ages of Meteorites From the Compilation of Faure (49)
Igneous Processes and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios of igneous rocks:

- MORB: 0.7025
- Continents: 0.7119
- Ocean Islands: >0.704
- Meteorites: 0.699

* Remember that $^{87}\text{Rb}$ will partition in melt.
Fig. 1. Three-stage model for the evolution of $^{87}$Sr/$^{86}$Sr in Earth materials through geological time. $^{87}$Sr accumulates in all pools due to $^{87}$Rb decay, with the rate depending on the Rb/Sr of each lithology. Granite1 and Granite2 are examples of rock formation occurring at different times during earth history. Modified from Encyclopedia of Geochemistry (2000) and Capo et al. (1998).
Seawater $^{87}\text{Sr}/^{86}\text{Sr}$ through time
Proxy for relative rate of continental weathering
Speciation of inorganic carbon in aqueous phase as a function of pH

\[
\text{Relative abundance of species}
\]

\[
\begin{align*}
\text{CO}_2 & \quad 1.0 \\
\text{HCO}_3^- & \quad 0.8 \\
\text{CO}_3^{2-} & \quad 0.6
\end{align*}
\]

3 \ 5 \ 7 \ 9

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

Atmosphere

$H^+ + CO_3^{2-} \leftrightarrow H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2 (aq) + H_2O$

Ocean

$HCO_3^- \rightarrow H^+ + CO_3^{2-}$

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ (precipitation)

$Ca^{2+} + CO_3^{2-} \rightarrow HCO_3^- + H^+$ (dissolution)

Sediment

Seawater too basic: $H_2CO_3 \rightarrow HCO_3^- + H^+$ pH drops

Seawater too acidic: $HCO_3^- + H^+ \rightarrow H_2CO_3$ pH rises

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Sediments - They are what lives above them

- **Diatoms**
- **Forams**
- **Washed from land, not much life above**
- **Gyres** - Lifeless - clays
- **Upwelling regions** - More life

Legend:
- **Calcereous ooz**
- **Siliceous ooze**
- **Diatoms**
- **Forams**
- **Pelagic clay**
- **Terrigenous sediment**
- **Glacial-marine sediments**
- **Continental-margin sediments**
Depth Profiles of T, S, O$_2$, NO$_3^-$

32° N, 172° W
North Central Pacific
(mid-gyre region)

Features:
• Main Thermocline (1000m)
  (mixed layer thermocline ~100m)
• Salinity minimum --------
• Oxygen Minimum (400-1500m)
• Nutrient-like profile (at most non-polar locations)
Questions:

Does the concentration at the surface reflect patterns of productivity or temperature? (what would you expect in each case to be the equator-to-pole pattern in concentration?)

How does deep water concentration change at depth from Atlantic to Pacific?

What process would be responsible for the observed change in C content?

How would the picture change with no life?

http://www.pmel.noaa.gov/pubs/outstand/feel2331/images/fig07.jpg
Models predict that on millennial time-scales 65-70% of the emissions would end up in the ocean (no CaCO$_3$ compensation).

From: K. Caldeira

Equilibrium CO$_2$ Concentration, ppm

If we consider the dissolution of CaCO$_3$ sediments this number may be as high as 90%
Fate and impact of emitted CO$_2$ over 1000 yrs

climate model: Bern 2.5CC EMIC
• model sensitivity = 3.2°C for 2xCO$_2$
• warming greater over land
  and at high latitude

not including effect of loss of land ice

*Solomon et al, PNAS, 2009*
‘irreversible climate change’

$\text{CO}_2$ ppmv
~20% in air

mean global surface warming

ocean thermal expansion
Fate of fossil fuel CO$_2$ over 40,000 yrs

**Fig. 1** Schematic breakdown of the atmospheric lifetime of fossil fuel CO$_2$ into various long-term natural sinks. Model results from Archer (2005)

*Archer and Brovkin (2008)*
Also papers by Mysak.