Biogeochemical Cycles and the Carbon Cycle

Required Reading: Jacob Chapter 6

Atmospheric Chemistry
CHEM-5151 / ATOC-5151
Spring 2011
Prof. Jose-Luis Jimenez

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Biogeochemical Cycles

THE EARTH: ASSEMBLAGE OF ATOMS OF THE 92 NATURAL ELEMENTS

• Most abundant elements: oxygen (in solid earth!), iron (core), silicon (mantle), hydrogen (oceans), nitrogen, carbon, sulfur…

• The elemental composition of the Earth has remained essentially unchanged over its 4.5 Gyr history
  – Extraterrestrial inputs (e.g., from meteorites, cometary material) have been relatively unimportant
  – Escape to space has been restricted by gravity

• Biogeochemical cycling of these elements between the different reservoirs of the Earth system determines the composition of the Earth’s atmosphere and oceans, and the evolution of life
Biogeochemical Cycles II

Physical exchange, redox chemistry, biochemistry are involved

Q: where do atmospheric gases come from?
A. Captured by gravity from outside Earth
B. Formed by chemistry on the surface
C. Formed by chemistry on the ocean
D. Spewed by volcanoes
E. I don’t know

Venus, Earth, and Mars

<table>
<thead>
<tr>
<th></th>
<th>Venus</th>
<th>Earth</th>
<th>Mars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (km)</td>
<td>6100</td>
<td>6400</td>
<td>3400</td>
</tr>
<tr>
<td>Surface pressure (atm)</td>
<td>91</td>
<td>1</td>
<td>0.007</td>
</tr>
<tr>
<td>CO₂ (mol/mol)</td>
<td>0.96</td>
<td>3x10⁻⁴</td>
<td>0.95</td>
</tr>
<tr>
<td>N₂ (mol/mol)</td>
<td>3.4x10⁻²</td>
<td>0.78</td>
<td>2.7x10⁻²</td>
</tr>
<tr>
<td>O₂ (mol/mol)</td>
<td>6.9x10⁻⁵</td>
<td>0.21</td>
<td>1.3x10⁻³</td>
</tr>
<tr>
<td>H₂O (mol/mol)</td>
<td>3x10⁻³</td>
<td>1x10⁻²</td>
<td>3x10⁻⁴</td>
</tr>
</tbody>
</table>

Adapted from Jacob, Fig. from http://www.globalchange.umich.edu/globalchange1/current/lectures/Perry_Samson_lectures/evolution_atm/
Runaway Greenhouse Effect on Venus

due to accumulation of water vapor from volcanic outgassing early in its history
…and did not happen on Earth because farther from Sun; as water accumulated it reached saturation and precipitated, forming the oceans

<table>
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<tr>
<th>N₂</th>
<th>CO₂</th>
<th>H₂O</th>
<th>O₂</th>
</tr>
</thead>
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<tr>
<td>oceans form</td>
<td>CO₂ dissolves</td>
<td>O₂ reaches current levels; life invades continents</td>
<td></td>
</tr>
</tbody>
</table>

Outgassing | Life forms in oceans | Onset of photosynthesis

4.5 Gy B.P. | 4 Gy B.P. | 3.5 Gy B.P. | 0.4 Gy B.P. | present

Q: what caused life to move into continents around 0.4 Gy BP?

Adapted from Jacob
Q: How come $O_3$ increased faster than $O_2$?

- Chapman Cycle in the stratosphere:

  \[
  O_2 + h\nu \rightarrow 2 \cdot O \\
  O\cdot + O_2 \rightarrow O_3 \\
  O_3 + h\nu \rightarrow O_2 + O \\
  O_3 + O\cdot \rightarrow 2 \cdot O_2
  \]
Material Supply for Life

A small acorn over time can grow into a huge oak tree. The tree can weigh many tons. Where does most of the mass come from as the tree grows?
A) Minerals in the soil
B) Organic matter in the soil
C) Gases in the air
D) Sunlight
E) I don't know

Fast O Cycle: biosphere-atmosphere

- Source of O₂: photosynthesis
  \[ n\text{CO}_2 + n\text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})_n + n\text{O}_2 \]
- Sink: respiration/decay
  \[ (\text{CH}_2\text{O})_n + n\text{O}_2 \rightarrow n\text{CO}_2 + n\text{H}_2\text{O} \]

O₂ lifetime: 5000 years
...however, abundance of organic carbon in biosphere/soil/ocean reservoirs is too small to control atmospheric O$_2$ levels

**Slow O Cycle: Atmosphere-Lithosphere**

- **O$_2$:** $1.2 \times 10^6$ Pg O
- **O$_2$ lifetime:** 3 million years

From Jacob
Uptake of CO₂ by Oceans

\[ CO_2(g) \rightarrow CO_2\cdot H_2O \]

\[ K_1 = 3 \times 10^{-2} \text{ M atm}^{-1} \]

\[ CO_2\cdot H_2O \rightleftharpoons HCO_3^- + H^+ \]

\[ K_2 = 7 \times 10^{-10} \text{ M} \]

\[ HCO_3^- \rightleftharpoons CO_3^{2-} + H^+ \]

\[ pK_1 = \text{Ocean pH} = 8.2 \]

\[ HCO_3^- \]

\[ CO_3^{2-} \]

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CFC-11 in the Atlantic

1 JUNE 2006

From Jacob
Observed uptake of fossil fuel CO$_2$ by the oceans

Source: Robert Key, Princeton Univ, Sciam March 2006

Compare to ~300 μmoles CO$_2$.

Global Preindustrial C Cycle

Inventories in Pg C
Flows in Pg C a$^{-1}$
Human Influence on C Cycle

Natural fluxes in black; anthropogenic contribution (1990s) in red

From IPCC 2007 via Jacob

EVIDENCE FOR LAND UPTAKE OF CO₂ FROM TRENDS IN O₂,
1990-2000

From Jacob