CHAPTER 6: GEOCHEMICAL 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 the evolution of life
BIOGEOCHEMICAL CYCLING OF ELEMENTS: examples of major processes

Physical exchange, redox chemistry, biochemistry are involved
HISTORY OF EARTH’S ATMOSPHERE

Outgassing

- \( \text{N}_2 \)
- \( \text{CO}_2 \)
- \( \text{H}_2\text{O} \)

Life forms in oceans

- \( \text{CO}_2 \) dissolves

Onset of photosynthesis

- \( \text{O}_2 \) reaches current levels; life invades continents

4.5 Gy B.P.  4 Gy B.P.  3.5 Gy B.P.  0.4 Gy B.P.  present
EVOLUTION OF O$_2$ AND O$_3$ IN EARTH'S ATMOSPHERE

- Extinction of dinosaurs ~65 MYr.
- Emergence of man ~5 MYr.
- Early civilization ~0.005 MYr.

Geological period:
- Cambrian
- Ordovician
- Silurian
- Devonian
- Carboniferous
- Permian
- Triassic
- Jurassic
- Cretaceous

Ground level oxygen concentration or ozone column abundance as fraction of present atmospheric level

- [O$_2$] < 5 $\times$ 10$^{-9}$ PAL before life

Millions of years before present

4600 4000 3000 2000 1000 800 600 400 300 200 100

4 10$^{-3}$ 10$^{-4}$ 10$^{-5}$ 10$^{-6}$ 10$^{-7}$ 10$^{-8}$ 10$^{-9}$ 1

Oldest sedimentary rocks
Stromatolites
Gunflint blue-green algae
Eucaryotic cells
Ozone
Oxygen
Soft-bodied metazoans
Shelly metazoans
Land plants
Land animals
Mammals
Flowering plants

Precambrian era
### Comparing the Atmospheres of Earth, Venus, 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>CO$_2$ (mol/mol)</td>
<td>0.96</td>
<td>4x10$^{-4}$</td>
<td>0.95</td>
</tr>
<tr>
<td>N$_2$ (mol/mol)</td>
<td>3.4x10$^{-2}$</td>
<td>0.78</td>
<td>2.7x10$^{-2}$</td>
</tr>
<tr>
<td>O$_2$ (mol/mol)</td>
<td>6.9x10$^{-5}$</td>
<td>0.21</td>
<td>1.3x10$^{-3}$</td>
</tr>
<tr>
<td>H$_2$O (mol/mol)</td>
<td>3x10$^{-3}$</td>
<td>1x10$^{-2}$</td>
<td>3x10$^{-4}$</td>
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</tbody>
</table>
RUNAWAY GREENHOUSE EFFECT ON VENUS

Fig. 7-16 Evolution of temperatures in the early atmospheres of Venus and Earth (dashed lines), superimposed on the phase diagram of water.
OXIDATION STATES OF NITROGEN

N has 5 electrons in valence shell ⇒ 9 oxidation states from −3 to +5

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>NH₃ (Ammonia)</th>
<th>NH₄⁺ (Ammonium)</th>
<th>R₁N(R₂)R₃ (Organic N)</th>
<th>N₂</th>
<th>N₂O (Nitrous oxide)</th>
<th>NO (Nitric oxide)</th>
<th>HONO (Nitrous acid)</th>
<th>NO₂⁻ (Nitrite)</th>
<th>NO₂ (Nitrogen dioxide)</th>
<th>HNO₃ (Nitric acid)</th>
<th>NO₃⁻ (Nitrate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>−3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>NH₃</td>
<td>NH₄⁺</td>
<td>R₁N(R₂)R₃</td>
<td>N₂</td>
<td>N₂O</td>
<td>NO</td>
<td>HONO</td>
<td>NO₂⁻</td>
<td>NO₂</td>
<td>HNO₃</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>+1</td>
<td>NH₃</td>
<td>NH₄⁺</td>
<td>R₁N(R₂)R₃</td>
<td>N₂</td>
<td>N₂O</td>
<td>NO</td>
<td>HONO</td>
<td>NO₂⁻</td>
<td>NO₂</td>
<td>HNO₃</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>+2</td>
<td>NH₃</td>
<td>NH₄⁺</td>
<td>R₁N(R₂)R₃</td>
<td>N₂</td>
<td>N₂O</td>
<td>NO</td>
<td>HONO</td>
<td>NO₂⁻</td>
<td>NO₂</td>
<td>HNO₃</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>+3</td>
<td>NH₃</td>
<td>NH₄⁺</td>
<td>R₁N(R₂)R₃</td>
<td>N₂</td>
<td>N₂O</td>
<td>NO</td>
<td>HONO</td>
<td>NO₂⁻</td>
<td>NO₂</td>
<td>HNO₃</td>
<td>NO₃⁻</td>
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<tr>
<td>+4</td>
<td>NH₃</td>
<td>NH₄⁺</td>
<td>R₁N(R₂)R₃</td>
<td>N₂</td>
<td>N₂O</td>
<td>NO</td>
<td>HONO</td>
<td>NO₂⁻</td>
<td>NO₂</td>
<td>HNO₃</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>+5</td>
<td>NH₃</td>
<td>NH₄⁺</td>
<td>R₁N(R₂)R₃</td>
<td>N₂</td>
<td>N₂O</td>
<td>NO</td>
<td>HONO</td>
<td>NO₂⁻</td>
<td>NO₂</td>
<td>HNO₃</td>
<td>NO₃⁻</td>
</tr>
</tbody>
</table>

**Increasing oxidation number (oxidation reactions)**

**Decreasing oxidation number (reduction reactions)**
THE NITROGEN CYCLE: MAJOR PROCESSES

- **Atmosphere**
  - $N_2$ to NO
  - $NO$ to $HNO_3$ and oxidation

- ** Biosphere**
  - OrgN to NH$_3$/NH$_4^+$
  - NH$_3$/NH$_4^+$ to NO$_3^-$
  - Assimilation, decay, biofixation, nitrification, denitrification

- **Lithosphere**
  - Burial, weathering
BOX MODEL OF THE NITROGEN CYCLE

Inventories in Tg N
Flows in Tg N yr⁻¹
N$_2$O: LOW-YIELD PRODUCT OF BACTERIAL NITRIFICATION AND DENITRIFICATION

Important as
- source of NO$_x$ radicals in stratosphere
- greenhouse gas

IPCC [2001]
**PRESENT-DAY GLOBAL BUDGET OF ATMOSPHERIC N\textsubscript{2}O**

<table>
<thead>
<tr>
<th>SOURCES (Tg N yr\textsuperscript{-1})</th>
<th>18 (7 – 37)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>10 (5 – 16)</td>
</tr>
<tr>
<td>Ocean</td>
<td>3 (1 – 5)</td>
</tr>
<tr>
<td>Tropical soils</td>
<td>4 (3 – 6)</td>
</tr>
<tr>
<td>Temperate soils</td>
<td>2 (1 – 4)</td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>8 (2 – 21)</td>
</tr>
<tr>
<td>Agricultural soils</td>
<td>4 (1 – 15)</td>
</tr>
<tr>
<td>Livestock</td>
<td>2 (1 – 3)</td>
</tr>
<tr>
<td>Industrial</td>
<td>1 (1 – 2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SINK (Tg N yr\textsuperscript{-1})</th>
<th>12 (9 – 16)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis and oxidation in stratosphere</td>
<td></td>
</tr>
</tbody>
</table>

| ACCUMULATION (Tg N yr\textsuperscript{-1}) | 4 (3 – 5) |

Although a closed budget can be constructed, uncertainties in sources are large!

IPCC [2001]
FAST OXYGEN CYCLE: ATMOSPHERE-BIOSPHERE

• Source of $O_2$: photosynthesis
  \[ nCO_2 + nH_2O \rightarrow (CH_2O)_n + nO_2 \]

• Sink: respiration/decay
  \[ (CH_2O)_n + nO_2 \rightarrow nCO_2 + nH_2O \]

$O_2$ lifetime: 5000 years
...however, abundance of organic carbon in biosphere/soil/ocean reservoirs is too small to control atmospheric $O_2$ levels.
Global Distribution of Atmospheric Carbon Dioxide
NOAA CMDL Carbon Cycle Greenhouse Gases

Three dimensional representation of the latitudinal distribution of atmospheric carbon dioxide in the marine boundary layer. Data from the NOAA CMDL cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Principal investigators: Pieter Tans and Thomas Conway, NOAA CMDL Carbon Cycle Greenhouse Gases, Boulder, Colorado, (303) 497-6678 (pieter.tans@noaa.gov, http://www.cmdl.noaa.gov/ccgg).

Illustrates long time scale for interhemispheric exchange
SLOW OXYGEN CYCLE: ATMOSPHERE-LITHOSPHERE

O$_2$: 1.2x10$^6$ Pg O

O$_2$ lifetime: 3 million years

O$_2$: 1x10$^7$ Pg C
FeS$_2$: 5x10$^6$ Pg S

Photosynthesis
decay

Fe$_2$O$_3$
H$_2$SO$_4$

FeS$_2$ runoff
weathering

CO$_2$

orgC

O$_2$

CO$_2$

orgC

sediments

SEDMENTS

microbes

Compression
subduction

CONTINENT

OCEAN
ATMOSPHERIC CO$_2$ INCREASE OVER PAST 1000 YEARS
RECENT GROWTH IN ATMOSPHERIC CO$_2$

Notice:

- atmospheric increase is $\sim$50% of fossil fuel emissions
- large interannual variability

Arrows indicate El Nino events
## GLOBAL CO₂ BUDGET (Pg C yr⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>1980s</th>
<th>1990s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric increase</td>
<td>3.3 ± 0.1</td>
<td>3.2 ± 0.1</td>
</tr>
<tr>
<td>Emissions (fossil fuel, cement)</td>
<td>5.4 ± 0.3</td>
<td>6.3 ± 0.4</td>
</tr>
<tr>
<td>Ocean-atmosphere flux</td>
<td>−1.9 ± 0.6</td>
<td>−1.7 ± 0.5</td>
</tr>
<tr>
<td>Land-atmosphere flux*</td>
<td>−0.2 ± 0.7</td>
<td>−1.4 ± 0.7</td>
</tr>
</tbody>
</table>

*partitioned as follows:

- **Land-use change**
  - 1.7 (0.6 to 2.5)
  - NA

- **Residual terrestrial sink**
  - −1.9 (−3.8 to 0.3)
  - NA

**IPCC [2001]**
The uptake of CO$_2$ by the oceans involves the following reactions:

$$\text{CO}_2(g) + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2\text{H}_2\text{O}$$

$$K_H = 3 \times 10^{-2} \text{ M atm}^{-1}$$

$$K_1 = 9 \times 10^{-7} \text{ M}$$

$$\text{CO}_2\text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$$

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

$$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$$

Net uptake:

$$\text{CO}_2(g) + \text{CO}_3^{2-} \rightleftharpoons 2\text{HCO}_3^-$$
LIMIT ON OCEAN UPTAKE OF CO$_2$:
CONSERVATION OF ALKALINITY

The alkalinity is the excess positive charge in the ocean to be balanced by carbon:

$$\text{Alk} = [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] - [\text{Cl}^-] - 2[\text{SO}_4^{2-}] - [\text{Br}^-]$$

$$= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

It is conserved upon addition of CO$_2$

$\Rightarrow$ uptake of CO$_2$ is limited by the existing supply of CO$_3^{2-}$

Increasing Alk requires dissolution of sediments:

$$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$$

...which takes place over a time scale of thousands of years
EQUILIBRIUM PARTITIONING OF CO$_2$
BETWEEN ATMOSPHERE AND GLOBAL OCEAN

Equilibrium for present-day ocean:

\[
F = \frac{N_{CO_2}(g)}{N_{CO_2}(g) + N_{CO_2}(aq)} = \frac{1}{1 + \frac{V_{oc}PK_H}{N_a}(1 + \frac{K_1}{[H^+] + \frac{K_1K_2}{[H^+]^2}})} = 0.03
\]

varies roughly as \([H^+]\)

\(\Rightarrow\) only 3% of total inorganic carbon is in the atmosphere

But CO$_2$(g) \(\Rightarrow\) \([H^+]\) \(\Rightarrow\) \(F\) \(\Rightarrow\) … positive feedback to increasing CO$_2$

Pose problem differently: how does a CO$_2$ addition \(dN\) partition between the atmosphere and ocean at equilibrium?

\[
f = \frac{dN_{CO_2}(g)}{dN_{CO_2}(g) + dN_{CO_2}(aq)} = \frac{1}{1 + \frac{V_{oc}PK_HK_1K_2}{N_a[H^+][H^+] + 4K_2}} = 0.28
\]

varies roughly as \([H^+]^2\)

\(\Rightarrow\) 28% of added CO$_2$ remains in atmosphere!
FURTHER LIMITATION OF CO$_2$ UPTAKE: SLOW OCEAN TURNOVER (~ 200 years)

Inventories in 10$^{15}$ m$^3$ water
Flows in 10$^{15}$ m$^3$ yr$^{-1}$

Uptake by oceanic mixed layer only ($V_{OC}=3.6\times10^{16}$ m$^3$) would give $f=0.94$ (94% of added CO$_2$ remains in atmosphere)
EVIDENCE FOR LAND UPTAKE OF CO$_2$ FROM TRENDS IN O$_2$, 1990-2000
NET UPTAKE OF CO$_2$ BY TERRESTRIAL BIOSPHERE
(1.4 Pg C yr$^{-1}$ in the 1990s; IPCC [2001]) is a small residual of large atm-bio exchange

- Gross primary production (GPP):
  \[ \text{GPP} = \text{CO}_2 \text{ uptake by photosynthesis} = 120 \text{ PgC yr}^{-1} \]

- Net primary production (NPP):
  \[ \text{NPP} = \text{GPP} - \text{“autotrophic” respiration by green plants} = 60 \text{ PgC yr}^{-1} \]

- Net ecosystem production (NEP):
  \[ \text{NEP} = \text{NPP} - \text{“heterotrophic” respiration by decomposers} = 10 \text{ PgC yr}^{-1} \]

- Net biome production (NBP)
  \[ \text{NBP} = \text{NEP} - \text{fires/erosion/harvesting} = 1.4 \text{ PgC yr}^{-1} \]

Atmospheric CO$_2$ observations show that the net uptake is at northern midlatitudes but cannot resolve American vs. Eurasian contributions.
Inventories in PgC
Flows in PgC yr⁻¹

Time scales are short ⇒ net uptake from reforestation is transitory
GLOBAL PREINDUSTRIAL CARBON CYCLE

Inventories in PgC
Flows in PgC yr\(^{-1}\)
PROJECTED FUTURE TRENDS IN CO$_2$ UPTAKE BY OCEANS AND TERRESTRIAL BIOSPHERE

b) Terrestrial models: CO$_2$ and Climate

d) Ocean models: CO$_2$ and Climate

IPCC [2001]
PROJECTIONS OF FUTURE CO$_2$ CONCENTRATIONS
[IPCC, 2001]