Electrons, life and the evolution of Earth’s chemical cycles*

\[ 2\text{H}_2\text{O} \rightarrow 4\text{e}^- + 4\text{H}^+ + \text{O}_2 \]

\[ \text{CO}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow (\text{CH}_2\text{O}) + \text{H}_2\text{O} \]

OCN 623 – Chemical Oceanography

*largely based on Falkowski and Godfrey 2008
Phil. Trans. R. Soc. B, 363:2705-2716
Libex Web Supplement 8.6

How does the Earth work as a biosphere?
- geological, geochemical, and (micro)biological coevolution of planet & life

Where did we come from?
- origin of life questions

Are we alone?
- how does Earth “work”
- what kind of disequilibria do we look for in distant atmospheres?

How did O$_2$ become the 2nd most abundant gas in the atmosphere?
Oxygen chemistry

mainly found as oxidation state (-II)
water, oxide & hydroxide metals
also as (-I); \( \text{H}_2\text{O}_2 \)
also as superoxide anion
also as hydroxyl radicals

moderately soluble: \( \approx 284\mu\text{M} @ 20\,^\circ\text{C} \)
slow kinetics for abiotic oxidation of organic matter
faster abiotic oxidation of reduced iron and sulfur species
slower abiotic oxidation of reduced manganese, ammonium, methane

Oxygenic photosynthesis

\[
2\text{H}_2\text{O} + \text{light} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2 \\
\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow (\text{CH}_2\text{O})_n + \text{H}_2\text{O}
\]

Coupled on a microscopic scale:

Oxygenic photosynthesis

\[
2\text{H}_2\text{O} + \text{CO}_2 \rightarrow (\text{CH}_2\text{O})_n + \text{O}_2
\]

Aerobic Respiration

\[
(\text{CH}_2\text{O})_n + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2
\]
Sustaining life on a planet

All organisms derive energy for growth and maintenance by moving electrons from a substrate to a product.

All substrates and products must ultimately be cycled.

Biological processes are paired;
  e.g., photosynthesis and respiration,
  this will often mediate spatial and temporal gradients.

All metabolic processes on Earth are prokaryotic and were derived in the Archean and/or Proterozoic Eons.
Early Earth

Formed by accretion 4.6 billion years B.P. (4.6 Ga)
Initially molten from kinetic energy of impacts

Early atmosphere lost to space (present atmosphere from outgassing and late accretion)

Outgassing (if completed quickly)

would lead to:
- Surface temperatures of 600°C
- Atmosphere with 300 atm H₂O
- 45 atm CO₂
- 10 atm HCl, S + N gases

Very reactive solution: giant acid base reaction

Igneous rock + acid gases + H₂O → sediments + ocean + atmos

Earth cools to critical point, H₂O in atmosphere condenses

At 200°C most H₂O liquid, most CO₂ in atmosphere
composition: (in atms) 30CO₂/15 H₂O/1HCl

Earth cools to <100°C ~3.5 Ga

First evidence of life follows closely
Earth’s geological, geochemical and biological co-evolution since formation

Earth, ~3.5 Ga

- Shallow sea environment
  - Land covered by low egg-shaped hills, diameter 20-50 km
  - Pillow lava
  - Silt layers
  - Scattered volcanic islands evaporite lagoons

- Tides higher
  - Moon closer to Earth, days shorter

- Atmosphere
  - CO₂-rich, no O₂
  - UV-drenched landscape
**Weathering of silicates on land cycles atmospheric CO₂**

\[
\begin{align*}
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} & = \text{Ca}^{2+} + 2\text{HCO}_3^- \\
\text{CaSiO}_3 + 2\text{CO}_2 + 3\text{H}_2\text{O} & = \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{H}_2\text{SiO}_4^- \\
\end{align*}
\]

Uptake of atmospheric CO₂ during weathering on land, delivery of dissolved form to oceans

**Deposition in the oceans**

\[
\begin{align*}
\text{Ca}^{2+} + 2\text{HCO}_3^- & = \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \\
\text{H}_4\text{SiO}_4 & = \text{SiO}_2 + 2\text{H}_2\text{O} \\
\end{align*}
\]

Release of CO₂ during carbonate precipitation

**Metamorphic reactions**

\[
\begin{align*}
\text{CaCO}_3 + \text{SiO}_2 & = \text{CaSiO}_3 + \text{CO}_2 \\
\end{align*}
\]

Release of CO₂ and return to atmosphere via volcanic/hydrothermal activity

*If no recycling all CO₂ removed from atmosphere in ~ 1 million yrs*

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**Chemistry of life centers on the disequilibrium redox chemistry of “the big six”**

H, C, N, O, P, and S

Primary role of P is in forming phosphates, binding to C, forming organics, whereas other 5 facilitate electron transfer

…and at least 54 other “trace elements” (Fe)

Life is electric.
How did CHON monomers arise on early Earth?

- Alexander Oparin (1924) “The Origin of Life”
  - Theory, no experiments
  - Life is simple organics $\rightarrow$ complex organics
  - Photoautotrophs $\rightarrow$ heterotrophs (complex)
  - No “plants” no $O_2$
  - Early organics from space $\rightarrow$ accumulate
    - Organic “broth” in sea

The Miller-Urey experiment: Abiotic synthesis of organics

- Simulated early Earth
  - Reducing atmosphere
    - $H_2O, H_2, CH_4, NH_3$
  - Simple inorganic molecules
  - Electric sparks (lightning)
  - Produced amino acids and other organic molecules
  - Couldn’t happen under modern conditions
  - Oxidizing atmosphere attacks organic bonds
  - Or: possibly Earth was contaminated with organics from space
The Age of Earth’s Life

• Problems for the “origins hunt”
  – Biology – 99.9% efficient at recycling organic material; few “soft” materials get fossilized
  – Geology – endogenic / exogenic processes
    • Internal Earth T increases 20-30°C / km
    • Organic fossils destroyed at 150°C

• Began 3.9-3.5 bya
  – Planetesimal heavy bombardment to 3.9 bya (lunar cratering)

Evidence for the timing of the origin of life on Earth

• Fractionated carbon isotopes at 3.8 Ga (Isua Fm., Greenland)
• Filaments of cyanobacteria in 3.4 Ga cherts (in western Australia, South Africa)
• Stromatolites at 3.3-3.5 Ga (Warrawoona Group, Australia)

• Anaerobic: evolved outside the presence of free oxygen (free oxygen would probably poison it!)
• Heterotrophic: a consumer, absorbing molecules from water
• “Prokaryotic”: no nucleus nor other complex organelles
Life processes fractionate isotopes, precipitation does not lighter isotopes react faster

Leaves heavier isotopes behind
  i.e. heavier isotopes more enriched in medium lighter isotopes enriched in organism

Isotopically light C in marine sediments from Greenland 3.83 Ga

S isotopes at 3.4 Ga ~0

As move forward in time see evidence of isotope disproportionation

Sulphate reducing bacteria?

Some evidence for inorganic fractionation of S isotopes in atmosphere from reactions with UV
Atmospheric oxygen began accumulating 2.7 billion years ago

The great oxidation event

- Photosynthesis probably evolved very early in prokaryotic history.
  - Early versions of photosynthesis did not split water or liberate $O_2$
- Cyanobacteria, photosynthetic organisms that split water and produce $O_2$ evolved over 2.7 billion years ago.
- This early oxygen initially reacted with dissolved iron to form the precipitate iron oxide.
  - This can be seen today in banded iron formations.

Oxygen combines with Fe(II) to form $Fe_3O_4$ (magnetite), which deposit as BIF

Banded Iron Formations (BIF)

Initial $O_2$ consumed in oxidizing Fe, CH₄ etc., but after precipitation of available Fe, oxygen accumulates in ocean — is toxic to anaerobes

Microcrystalline quartz layers (chert) between magnetite layers
Building a banded iron formation

Banded iron formations began as sediments accumulating on the ocean floor of early Earth. The formations record how different atmospheric and oceanic chemistries have changed from today's, and in what ways they may still be changing. The diagrams illustrate this.

1. Iron from the deep ocean floor
   - Iron from the deep ocean floor can rise through hydrothermal vents and encountered by iron-carrying fluids from sedimentary layers, where iron-rich oceanic crust is forming.

2. Iron from the land
   - Continental rocks can later be broken down, releasing iron to iron-carrying fluids that flow to the oceans, where new iron-carrying sediments are created.

3. Oxygen creation
   - Oxygen is produced by photosynthesis, which is the process by which plants convert sunlight into energy.

4. Iron back down
   - The iron is then eventually transported to the ocean floor, where it is deposited as sediments.

5. Oxygen up
   - Oxygen is produced by photosynthesis, which is the process by which plants convert sunlight into energy.

6. Banded beginnings
   - The oxygen is then transported to the ocean, where it is carried by iron-carrying fluids to the ocean floor, where it is deposited as sediments.

7. Sediment to rock
   - The iron is then eventually transported to the ocean floor, where it is deposited as sediments.

The process continues as the ocean floor moves, and the sediments are eventually transformed into rock.
To oxidize Earth, reduced (organic) carbon must be sequestered, not reoxidized.

But only a very small fraction (~0.01%) of the organic matter produced by photosynthesis in the ocean escapes respiration & is buried.

What is the sink for the organic matter on geologic time scales?

**Global distribution of chlorophyll**
• BUT, we’ve covered in this course how difficult it is for reduced organic matter to avoid cycling: re-oxidation.
• This is why ‘give me a tanker of iron & I’ll give you an ice age’ doesn’t work
• A very small portion of organic matter produced by photosynthesis in the oceans is buried in sediments (~0.01%)

So, what is the sink for organic matter on geologic time scales?
Without continents, we wouldn’t have 21% $O_2$.

- to maintain high concentrations of oxygen in Earth’s atmosphere on geological time scales, cratons (and large amounts of silicate-rich rocks) need to be formed allowing the organic matter to be removed from the Wilson cycle and stored on land in rocks (shales).
- Subduction allows for deposition of organic matter from seafloor to land, removing it from biological oxidation on long time scales.

Continental collision ‘resets’ the cycle.

Evolution of oxygenic photosynthesis

- When did it first occur?
  - ~3 Ga or earlier… probably

Cyanobacteria are only bacteria that evolve oxygen.
The Oxygen Conundrum - part II

Assume O$_2$ evolution by ~3000 Ma
- Cyanobacterial microfossils (Knoll 1996)
- Biomarkers (Summons 1999)

But the large increase in atmospheric O$_2$ wasn’t until 2.4-2.2 Ga
- Sulfur isotopes, 2090-2450 Ma (Farquhar 2000)
- Carbon isotopes, 2500-2000 Ma (Des Marais 1992)

Thus a delay between the emergence of oxygenic photosynthesis and the rise of free atmospheric O$_2$ by ~600 Myr

Why?

Prior to ~2.45 Ga, mass-independent sulfur fractionation record implies that sulfate-reducing bacteria did not play a significant role in the global S cycle, so the MIS signal is due to changes in volcanism
Oxygen accumulation

- This “corrosive” O\textsubscript{2} had an enormous impact on life, dooming many prokaryote groups
  - Some species survived in habitats that remained anaerobic (these are “obligate anaerobes”)
- Other species evolved mechanisms to use O\textsubscript{2} in cellular respiration, which uses oxygen to help harvest the energy stored in organic molecules
- Thus, prokaryotes altered the planet through O\textsubscript{2} evolution, making aerobic respiration possible and paving the way for other forms of life (eukaryotes)

Demise of cyanobacteria from oxygen toxicity, reduces oxygen production

But Fe continually added to ocean from weathering

Oxygen levels drop - bacteria make a come back

Excess oxygen production-cycle repeats!

Banded iron formation continues for 800 Ma, BIF contain equivalent of 20 x current atmospheric oxygen level

An elegant battle of biology vs chemistry = coevolution of Earth biosphere!

At 1.6 Ga Eukaryotes appear
  - can use oxygen for respiration
  - FeS\textsubscript{2}, Uranites disappear from sediments

(BUT, some BIFs date back to 3.8 Ga)
The great oxidation event

So, the great oxidation event story is all well and good, but you can’t get primary production really cranking without fixing nitrogen, …and what about those BIFs from 3.8 Ga?
Is there an alternate way to form banded iron formations?

3.8 bya, with no O₂, how to make stable Fe AND supply bioavailable N to the planet?

$$6\text{Fe(II)S}_n + 6\text{H}_2\text{O} + \text{N}_2 \rightarrow 2\text{NH}_3 + 6\text{Fe(III)OH} + 6\text{S}_n$$

Abiotic, UV photocatalyzed oxidation of Fe(II) to Fe(III) by dumping electrons off to N₂

so, reduction of N₂ to NH₃

But this reaction would be totally inhibited by even low O₂
Master Equations in the C-H-O-N Cycle

Photosynthesis/Remineralization

\[ 106\text{CO}_2 + 16\text{NO}_3 + \text{H}_2\text{PO}_4 + 122\text{H}_2\text{O} = \]

\[ C_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 138\text{O}_2 \]

(Geochemical representation of a bacterium)

Nitrogen fixation (inhibited by O\(_2\))

\[ 2\text{N}_2 + 4\text{H}^+ + 3\text{CH}_2\text{O} \rightarrow 4\text{NH}_4^+ + 3\text{CO}_2 \]

(kind of a respiration reaction)

Nitrification (requires O\(_2\))

\[ \text{NH}_4 + 2\text{O}_2 \rightarrow \text{NO}_3 + 2\text{H} + \text{H}_2\text{O} \]

(reverse of N\(_2\) fixation)

Denitrification (inhibited by O\(_2\))

\[ C_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 84.8\text{HNO}_3 \rightarrow \]

\[ 106\text{CO}_2 + 55.2\text{N}_2 + 16\text{NH}_3 + \text{H}_2\text{PO}_4 + 1177.2\text{H}_2\text{O} \]

Oxic-Anoxic Transition of the Black Sea

Konovalov et al. 2005
Adapting a modern OATZ environment as a geologic timeline

(Fennel et al. 2005)

Linking O to N & C cycles

Model of:
continental shelf seas, hi/lo latitude sfc ocean, deep ocean, atmosphere

In the process of oxidizing the early Proterozoic ocean, the system had to go through a N-limited phase during which time export production was severely attenuated. The presence of shallow seas & increased Org-C burial was critical in determining [O₂].

(Fennel et al. 2005)
Normalized nitrification/denitrification rates

Shelf width drastically affects amount of fixed N in model

How can a balance of N & O sources & sinks be achieved despite continued organic matter production?

Nitrification > 20uM
Denitrification <5uM

Linking O to N & C cycles (Falkowski & Godfrey 2008)

Free O\textsubscript{2} allowed ammonium to be oxidized to nitrate

Nitrate was subsequently denitrified when O\textsubscript{2} was absent, “lost” as N\textsubscript{2}

The interaction between the O\textsubscript{2} & N cycles led to a negative feedback, in which increased O\textsubscript{2} production led to decreased fixed inorganic nitrogen in the oceans

This negative feedback, supported by isotopic analyses of fixed N in sedimentary rocks from the late Archaean, continues in the present day

Only after the ocean-atmosphere system moved past the denitrification feedback could a new stable state with abundant nitrate be reached
Linking O to N & C cycles

The rise of O\textsubscript{2} is critically dependent upon the N cycle

The time delay between the evolution of oxygenic photosynthesis and oxidation of the Earth's atmosphere is very sensitive to the areal extent of shallow seas, i.e., carbon burial, net O\textsubscript{2} production, and the evolution of the biological N cycle in the Proterozoic (but not physical mixing??)

The concentration of O\textsubscript{2} in the atmosphere, and to a small extent the timing of oxidation, is also sensitive to the initial PO\textsubscript{4} concentration

The rise of oxygen altered the N-cycle

Oxygen permitted NH\textsubscript{4} to be converted to NO\textsubscript{3} – which can be rapidly reduced to N\textsubscript{2}

There was a critical time in Earth history when the N cycle was a major barrier to oxidizing the planet

Why hasn’t Earth ever gone back to an anoxygenic state? Can it?

As long as mantle convection is slower than the rate of production of oxidants on the surface, the oxidation event was a one-way process
REVIEW
The Microbial Engines That Drive Earth’s Biogeochemical Cycles
Paul G. Falkowski, * Tom Fenchel, ** Edward F. Delong, **

Virtually all nonequilibrium electron transfers on Earth are driven by a set of nanobiological machines composed largely of multimeric proteins complexes associated with a small number of prosthetic groups. These machines evolved exclusively in microbes early in our planet’s history yet, despite their antiquity, are highly conserved. Hence, although there is enormous genetic diversity in nature, there remains a relatively stable set of core genes coding for the major redox reactions essential for life and biogeochemical cycles. These genes created and coevolved with biogeochemical cycles and were passed from microbe to microbe primarily by horizontal gene transfer. A major challenge in the coming decades is to understand how these machines evolved, how they work, and the processes that control their activity on both molecular and planetary scales.
Conclusions

• The establishment of life on Earth had a crucial impact on the evolution of the planet

• The onset of oxygenic photosynthesis was the greatest “pollution” event of all time – relegating the dominant species to niche roles

• N cycle constrained timing of free oxygen on Earth, and provided a major feedback that constrained atmospheric O₂ concentrations

• Global N, C, and O cycles are constantly fluctuating on time scales of up to hundreds of millions of years

• Anthropogenic alterations of these cycles is much faster than observed in the geologic record

Five major biological innovations yield different vertical profiles of ocean chemistry

N cycle responded to changes in biological evolution & ocean chemistry