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

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

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

*largely based on Falkowski and Godfrey 2008

Phil. Trans. R. Soc. B, 363:2705-2716
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?
Electrons, life and the evolution of Earth’s chemical cycles

2 key supplemental readings:
Libes Web Supplement 8.6
Falkowski and Godfrey (2008)

- Early Earth
- Origins of life
- The great oxidation event
- Linkage between global O & N cycles
- Alternate explanations for the great oxidation event
- The rise of O$_2$ and the evolution of life
- The Phanerozoic

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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.
Earth’s geological, geochemical and biological co-evolution since formation
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 H\(_2\)O
- 45 atm CO\(_2\)
- 10 atm HCl, S + N gases

Very reactive solution: giant acid base reaction

Igneous rock + acid gases + H\(_2\)O → sediments + ocean + atmos

Earth cools to critical point, H\(_2\)O in atmosphere condenses

At 200˚C most H\(_2\)O liquid, most CO\(_2\) in atmosphere
composition: (in atms) 30CO\(_2\)/15 H\(_2\)O/1HCl

Earth cools to <100˚C ~3.5 Ga

First evidence of life follows closely
Earth, \(\sim 3.5 \text{ Ga}\)

- 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
  - \(\text{CO}_2\)-rich, no \(\text{O}_2\)
  - UV-drenched landscape
Faint Sun paradox

apparent contradiction between observations of liquid water early in the Earth's history and the astrophysical expectation that the Sun's output would be only 70% as intense (Sagan & Mullen, 1972)

High atmospheric CO$_2$ important in early Earth
balanced weak Sun & maintained temperature

CO$_2$ oceanic uptake & carbonate formation could have cycled toward Snowball Earth
Weathering of silicates on land cycles atmospheric CO₂

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

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

**Deposition in the oceans**

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

Release of CO₂ during carbonate precipitation

**Metamorphic reactions**

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

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

If no recycling all CO₂ removed from atmosphere in ~ 1 million yrs
Estimated atmospheric CO$_2$ levels through Earth’s history
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)
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” $= \text{no O}_2$
  - Early organics from space $\rightarrow$ accumulate
    - Organic “broth” in sea
The Miller-Urey experiment: Abiotic synthesis of organics

- Simulated early Earth
  - Reducing atmosphere
    - H₂O, H₂, CH₄, NH₃
  - 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
Some perspective on coevolution

- The history of life on earth is overwhelmingly microbial
- The earth is ~4.5 billion yrs old,
  - microbes arose 3.8 billion years ago (bya)
  - animals-0.7 bya  -- humans-0.001 bya

Jan. 1-Earth Forms

The Microbial Age-3.1 Billion Years

- Jan 1-Earth Forms
- Late Feb-Microbes
- ~Nov. 5th-Animals (oceans)
- Dec. 11th-Land Plants
- Dec. 27th-Mammals
- Dec. 31st- 10:00 PM Humans
- 11:59:30 PM Written History
3.0 to 1.6 Ga titration of Earth’s oceans and atmosphere with $O_2$
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\textsubscript{2}
- Cyanobacteria, photosynthetic organisms that split water and produce O\textsubscript{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.
Figure 26.5  Banded iron formations are evidence of the vintage of oxygenic photosynthesis.
Oxygen combines with Fe(II) to form Fe₃O₄ (magnetite), which deposit as BIF.

Banded Iron Formations (BIF)

Initial O₂ 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 both ocean and atmospheric chemistry were from today’s, and in what ways they may have dramatically changed. Pictured is one scenario for how the formations may document Earth’s transition to an oxygen-rich atmosphere.

1. Iron from the deep
   Iron from Earth’s interior enters the ocean through hydrothermal vents, which are essentially hot springs on the ocean floor. Modern vents dot spreading ridges, where blocks of ocean crust are moving apart and making room for magma from below to travel upward and create new ocean crust.

2. Iron from the land
   Continental crust on land also contains iron. Water and weather break the crust down, and rivers carry dissolved iron particles into the ocean.

3. Oxygen makers
   Oxygen could have entered the scene as it was produced in large enough quantities by cyanobacteria, microbes that perform photosynthesis.
4 Iron back down
The ocean of early Earth contained much more dissolved iron than today’s ocean. One way iron leaves water is if it reacts with dissolved oxygen. The reaction forms a type of iron that precipitates out of water, falling as iron oxide particles onto the ocean floor.

5 Oxygen up
Being a gas, oxygen can travel between atmosphere and ocean. One question is whether oxygen first built up in the atmosphere, then flooded the water and caused iron to precipitate out; or whether oxygen accumulated in the water and then spent time using up the iron supply until enough oxygen was available to fill the atmosphere.

6 Banding beginnings
Particles of silica also drop out of water onto the ocean floor. The layering of banded iron formations shows that sometimes ocean precipitates were mostly silica and other times they were mostly iron. Why remains unclear.

7 Sediment to rock
Over time, sediments accumulate atop sediments. As the particles are buried deeper and deeper, they undergo changes that form them into rock. Over millions of years, as continents and oceans change, the rocks are uplifted and exposed on the continents. Pictured is Dales Gorge, part of the Brockman Iron Formation in Western Australia.
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 sediment type distribution; where is the C deposition?

Is photosynthesis-respiration balanced on geologic time scales?
Without continents, we wouldn’t have 21% $O_2$.

Continental collision ‘resets’ the cycle

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)
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 $\sim$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 (Farquhar 2000)
- Carbon isotopes (Des Marais 1992)

Thus a delay between the emergence of oxygenic photosynthesis and the rise of free atmospheric $O_2$ by $\sim$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$_2$, Uranites disappear from sediments
The great oxidation event

Figure 2.7 Cumulative history of \( \text{O}_2 \) released by photosynthesis through geologic time. Of more than \( 5.1 \times 10^{22} \) g of \( \text{O}_2 \) released, about 98% is contained in seawater and sedimentary rocks, beginning with the occurrence of Banded Iron Formations at least 3.5 billion years ago (bya). Although \( \text{O}_2 \) was released to the atmosphere beginning about 2.0 bya, it was consumed in terrestrial weathering processes to form Red Beds, so that the accumulation of \( \text{O}_2 \) to present levels in the atmosphere was delayed to 400 mya. Modified from Schidlowski (1980).
The great oxidation event – an alternative explanation

PSU – Jim Kasting, hydrogen theory

O2 could build up if concurrent with a reduction in gases, e.g., H₂

Possible that more of the O₂ produced ended up buried in the mantle, avoiding reaction with H₂, and allowing H₂ to escape to space

How could O₂ be buried beneath Earth’s crust?
The great oxidation event – an alternative explanation

(1) $O_2$ reacted with Fe in seawater, precipitates buried

(2) oxygen-rich water in seafloor sediments buried within the Earth, leaving $O_2$ in the mantle when the water’s $H_2$ was emitted from volcanoes

(3) oxygen-rich sulfates in hydrothermal systems reacted with Fe in seafloor sediments, which were buried to put $O_2$ into the mantle
So, the great oxidation event story is all well and good, but you can’t get the $O_2$ really accumulating without fixing nitrogen, and what about the BIFs from 3.8 Ga?
Alternate way to form banded iron formations?

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

Abiotic, photocatalyzed reduction of N₂ to NH₃ coupled to oxidation of Fe(II) to Fe(III)

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

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

Photosynthesis/Remineralization

\[106\text{CO}_2 + 16\text{NO}_3 + \text{H}_2\text{PO}_4 + 122\text{H}_2\text{O} = \]
\[\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 138\text{O}_2\]

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

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

Nitrification (requires O\(_2\))

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

Denitrification (inhibited by O\(_2\))

\[\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 84.8\text{HNO}_3 \rightarrow \]
\[106\text{CO}_2 + 55.2\text{N}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4 + 1177.2\text{H}_2\text{O}\]
Oxic-Anoxic Transition of the Black Sea

Ammonium ($\text{NH}_4^+$), $\mu$M

Nitrogen Excess ($\text{N}_2$), $\mu$M

Oxic

Suboxic

Anoxic

Oxygen ($\text{O}_2$) & Sulfide ($\text{H}_2\text{S}$), $\mu$M

Nitrate ($\text{NO}_3^-$), $\mu$M

Mn(II) & NO$_3^-$, $\mu$M

$\sigma_t$

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 [O$_2$]

(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?

(Fennel et al. 2005)
Free $O_2$ allowed ammonium to be oxidized to nitrate.

Nitrate was subsequently denitrified when $O_2$ was absent, “lost” as $N_2$.

The interaction between the $O_2$ & $N$ cycles led to a negative feedback, in which increased $O_2$ 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 $\text{O}_2$ 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 $\text{O}_2$ production, and the evolution of the biological N cycle in the Proterozoic (but not physical mixing??)

The concentration of $\text{O}_2$ in the atmosphere, and to a small extent the timing of oxidation, is also sensitive to the initial $\text{PO}_4$ concentration
Anoxygenic photosynthesis modulating the Proterozoic OMZ

(Johnston et al. 2009)
The rise of oxygen altered the N-cycle

Oxygen permitted $NH_4$ to be converted to $NO_3$ – which can be rapidly reduced to $N_2$

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
Five major biological innovations yield different vertical profiles of ocean chemistry

N cycle responded to changes in biological evolution & ocean chemistry
The rise of oxygen and evolution of life

The cytochrome cyt b/c complex in purple sulfur bacteria was appropriated by anaerobic, heterotrophic host cells and served as a photosynthetic organelle

Oxygen allowed previously anaerobic eukaryotes, which contained a “mitochondria” that operated as a photosynthetic organelle, to use an alternative electron acceptor, O\textsubscript{2} and to function as an oxidative heterotrophic organelle

18x more ATP (!) but metabolically “boring”
The Microbial Engines That Drive Earth’s Biogeochemical Cycles

Paul G. Falkowski,1* Tom Fenchel,2* Edward F. DeLong3*

Virtually all nonequilibrium electron transfers on Earth are driven by a set of nanobiological machines composed largely of multimeric protein 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 $O_2$ 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