Electrons, Life and the Evolution of Earth’s Chemical Cycles

OCN 623 – Chemical Oceanography

Outline

• How does the earth work as a biosphere?

• Earth’s geological, geochemical and biological co-evolution since formation
  - Early Earth
  - Origins of life
  - The great oxidation event
  - Linkage between global O and N cycles
  - Alternate explanations for the great oxidation event
  - The rise of oxygen and the evolution of life
  - The Phanerozoic

Modification of Brian Glazer’s lecture, based on Falkowski and Godfrey 2008 (Phil. Trans. R. Soc. B, 363: 2705-2716)
How Does the Earth Work as a Biosphere?

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

All substrates and products must ultimately be recycled.

All metabolic processes on Earth are prokaryotic and were developed 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 is from outgassing and late accretion)

• Volatile components were liberated from a molten and slowly convecting mixture of silicates, metals, and trapped gases

• The gravitational field of Earth was sufficient to retain most of the gases released from the interior, including CH₄, H₂O, N₂, NH₃, and H₂S, but not H₂

Outgassing (if completed quickly) would lead to:

Surface temperature ≈ 600°C

Atmosphere composition:

- 300 atm H₂O
- 45 atm CO₂
- 10 atm HCl
- S + N gases

Photolysis of H₂O, NH₃, and H₂S produced free O₂, N₂, and S, respectively. O₂ was rapidly consumed by oxidation of CH₄ and H₂S to form CO₂, CO, and SO₂.

Very reactive solution; giant acid-base reaction:

Igneous rock + acidic volcanic gases + H₂O →
sediments + ocean + atmosphere
Earth cools to critical point; H$_2$O in atmosphere condenses

With surface temp $\approx 200^\circ$C, atmosphere composition is:
- 30 atm CO$_2$
- 15 atm H$_2$O
- 1 atm HCl

Earth cools to <100$^\circ$C $\sim$3.5 Ga ago

First evidence of life follows closely

**Earth, $\sim$3.5 Ga Ago**

- Shallow sea environment
  - Land covered by low egg-shaped hills and pillow lavas
  - Silt layers
  - Scattered volcanic islands and evaporite lagoons
- Tides higher
  - Moon closer to Earth, days shorter
- Atmosphere
  - CO$_2$-rich, no O$_2$
  - UV-drenched landscape
High atmospheric CO$_2$ and CH$_4$ important in early Earth; balanced weak Sun

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Weathering Of Silicates On Land Removes Atmospheric CO$_2$

Liquid water on early Earth allowed a hydrologic cycle and silicate mineral weathering to develop.

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

Uptake of atmospheric CO$_2$ 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 CO$_2$ during carbonate precipitation

**Metamorphic reactions**

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

Release of CO$_2$ and return to atmosphere via volcanic/hydrothermal activity

If no recycling, all CO$_2$ removed from atmosphere in ~1 million yrs
Estimated Atmospheric CO₂ Levels Through Earth’s History

How Did CHON Monomers Arise on Early Earth?

- Oparin (1924)
  - Life is simple → complex
  - Photoautotrophs ↔ heterotrophs (complex)
  - No “plants” → no O₂
  - Early organics from space → accumulate
    - Organic “broth” in sea

- Stanley Miller (1951)
  - H₂, N₂, CO₂, H₂O, NH₃, CH₄
  - Reducing atm + UV or lightening → organics
  - Produced amino acids
The Miller-Urey Experiment: Abiotic Synthesis of Organics

- Simulated early Earth
  - Reducing atmosphere
    - $\text{H}_2\text{O}$, $\text{H}_2$, $\text{CH}_4$, $\text{NH}_3$
  - 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

- Life began 3.9-3.5 Ga ago
  - Planetesimal heavy bombardment to 3.9 Ga ago (led to lunar cratering)
- Problems for origin’s 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

Evidence Dating the Origin of Life on Earth

- Fractionated carbon isotopes at 3.8 Ga (Isua Fm., Greenland)
- Filaments of cyanobacteria (blue-green algae) 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 Evolution

- 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 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec

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

Atmospheric O₂ Began Accumulating ~2.7 Ga Ago – The Great Oxidation Event

- Early ocean was anoxic and Fe rich
- Photosynthesis probably evolved very early in prokaryotic history.
  - Early versions of photosynthesis did not split water or liberate O₂ (“anoxygenic photosynthesis”)
- Cyanobacteria - photosynthetic organisms that split water and produce O₂ - evolved ~2.7 Ga Ago
- This early oxygen initially reacted with dissolved iron to form the precipitate iron oxide (titration of Earth’s oceans and atmosphere with O₂, 3.0 -1.6 Ga ago)
  - This can be seen today in banded iron formations -- which contain equivalent of 20x current atmospheric O₂
Banded Iron Formations - Evidence of the Oxygenic Photosynthesis

Oxygen combines with Fe$^{2+}$ to form Fe$_3$O$_4$ (magnetite), which deposits in sediments called Banded Iron Formations (BIF).

Initial O$_2$ used up in oxidizing Fe, CH$_4$ etc., but after precipitation of available Fe, O$_2$ builds up in ocean. O$_2$ is toxic to cyanobacteria, which die and form a chert layer.
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 vent fields 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. Weathering breaks the crust up, and even carries 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 oceans. 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 into 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 dissolved iron, 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 in layers. As the particles are tested 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 Hamersley Iron Formation in Western Australia.
The Oxygen Conundrum #1

Assume $O_2$ evolution by $\sim3000$ Ma ago, demonstrated by:
- Cyanobacterial microfossils (Knoll 1996)
- Biomarkers (Summons 1999)

But large increase in atmospheric $O_2$ not until 2400-2200 Ma ago, demonstrated by:
- S stable isotopic ratio loses variability $\sim2450$ Ma ago (Farquhar 2000)

Thus, a delay between the emergence of oxygenic photosynthesis and the rise of free atmospheric $O_2$ by $\sim600$ Ma
To produce an oxidized atmosphere Earth, reduced (organic) carbon must be removed before it is reoxidized. 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?
Oxygen Accumulation

- This "corrosive" O$_2$ had an enormous impact on life, dooming many prokaryote groups (only known life)
  - Some species survived in habitats that remained anaerobic (these are "obligate anaerobes")

- Other species evolved mechanisms to use O$_2$ in cellular respiration, which uses oxygen to help harvest the energy stored in organic molecules

- Thus, prokaryotes altered the planet through O$_2$ evolution, making aerobic respiration possible and paving the way for other forms of life (eukaryotes)

- At 1.6 Ga ago, Eukaryotes appear
  - Can use oxygen for respiration
  - FeS$_2$, Uranites disappear from sediments

So, the great oxidation event story is all well and good, but you can’t get the O$_2$ really accumulating (i.e., photosynthesis can’t be very extensive) without a source of biologically usable nitrogen

.....and what about the BIFs from 3.8 Ga ago?
One possibility:
Abiotic, photocatalyzed reduction of N₂ to NH₃, coupled to oxidation of Fe(II) to Fe(III):

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

This reaction is totally inhibited by even low O₂ concs

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**Master Equations in the N/C/O/P Cycle**

**Photosynthesis/Remineralization**

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

**Nitrogen fixation (inhibited by O₂)**

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

**Nitrification (requires O₂)**

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

**Denitrification (inhibited by O₂)**

\[
C_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 84.8\text{HNO}_3 \rightarrow 106\text{CO}_2 + 55.2\text{N}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4 + 1177.2\text{H}_2\text{O}
\]
Fennel et al. (2005):

...the extraordinary delay in the oxidation of the atmosphere and oceans was caused by a biogeochemical "bottleneck" imposed by metabolic feedbacks between carbon burial, net oxygen production, and the evolution of the nitrogen cycle in the Proterozoic oceans.

Whereas under anoxic conditions oceanic ammonium would have been relatively stable, as oxygen concentrations rose, nitrification and subsequent denitrification would have rapidly removed fixed inorganic nitrogen from the oceans.

Denitrification would have imposed a strong constraint on the further rise of free oxygen by depriving oxygenic photoautotrophs of an essential nutrient (that is, fixed inorganic nitrogen). "

Nitrification: >20uM O₂
Denitrification: <5uM O₂
...in the process of oxidizing the early Proterozoic ocean, the system had to go through a nitrogen-limited phase during which time export production was severely attenuated.

...the presence of shallow seas with increased organic matter burial (!!!) was a critical factor determining the concentration of oxygen in the ocean and atmosphere

...the phosphate concentration played a key role in determining the rate of oxygenation of the deep ocean

...Only after the ocean-atmosphere system moved past the denitrification feedback was a new stable state with abundant nitrate reached.

More On Linkage of O to N and C Cycles

Falkowski & Godfrey (2008)

Free O2 allowed ammonium to be oxidized to nitrate. Nitrate was subsequently denitrified (when O2 was absent) and lost as N2.

The interaction between the oxygen and nitrogen cycles in particular led to a negative feedback, in which increased production of oxygen led to decreased fixed inorganic nitrogen in the oceans.

This feedback, which is supported by isotopic analyses of fixed nitrogen in sedimentary rocks from the Late Archaean, continues to the present.
Conclusions on O/N/C Cycles

The rise of $O_2$ is critically dependent upon the N cycle

O & N cycles led to a negative feedback on $O_2$ production, decreasing $O_2$ and decreasing fixed DIN in the oceans

Modeling results:
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

The concentration of $O_2$ in the atmosphere, and to a small extent the timing of oxidation, is sensitive to the initial phosphate concentration
Bjerrum and Canfield, 2002:
Low phosphate availability during the Archean and early Proterozoic eras contributed to low atmospheric oxygen levels by depressing the photosynthetic production of organic matter and hence organic matter burial and net oxygen production.
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?

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**The Great Oxidation Event**

Alternative Explanation #1

Kasting, Science 259, 920-925, 1993

- Very high CH₄ levels in atmosphere (10² – 10³ ppm)
- Photolysis of CH₄ in the atmosphere produces H
- H is lost to space, thereby oxidizing the atmosphere

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**The Great Oxidation Event**

Alternative Explanation #2

Catling et al., Science 293, 839-842, 2001
The Great Oxidation Event

Alternative Explanation #3

Oceanic nickel famine (due to reduced supply) and a methanogen crash before the Great Oxidation Event, which increased the oxidation state of the Earth’s surface.

![Graph showing the concentration of Ni in seawater over time.](image)

Why Did it Take So Long for the Deep Ocean to Become Oxic?

**Johnston et al. (2009):**
Generation of organic matter using sulfide as an electron donor enabled a positive biogeochemical feedback that sustained euxinia (sulfidic, reducing conditions) in the deep ocean.


![Graph showing Mn(II) and NO3 concentration over depth in the Black Sea.](image)
Why hasn’t Earth ever gone back to an anoxygenic state?

Can it?

One theory:
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

The Rise of Free Oxygen and the Evolution of Life

The cytochrome complex in purple sulfur bacteria was incorporated into anaerobic, heterotrophic host cells and served as a photosynthetic organelle (chloroplast) ~1.6 Ga ago

Oxygen allowed previously anaerobic eukaryotes, which contained a “proto-mitochondria” that operated as a photosynthetic organelle, to use an alternative electron acceptor, O₂ and to function as an oxidative heterotrophic organelle

18x (!) more ATP, but metabolically (geochemically) boring

Modern geochemical cycles become established ~1.6 Ga ago
Inorganic Carbon Cycle

Sea floor accumulation of inorganic C (CaCO₃) is established at this time

If no remobilization process, atmosphere would therefore run out of CO₂!

Plate tectonics recycles sedimentary C, and volcanic activity returns CO₂ to atmosphere

Variations in tectonic activity drive long term CO₂ variations

Cycles Through the Phanerozoic Eon
(current geologic eon)

Gondwanaland formed ~ 500-550 Ma ago

Breakup started ~180 Ma ago

Initially low plate tectonic activity, low CO₂, low sea level
Rise in tectonics, rise in CO₂ and sea level, planet warms
• 400 Ma ago, plant life occupies land
• High production on land
• Extensive wetlands, burial of organic C
• High levels of atmospheric oxygen

Breakup of supercontinents may lead to:
• More space on continental shelves for sediments
• Accelerated continental weathering and delivery of nutrients to seawater
  • Fertilizing primary production
  • Increasing organic matter burial
  • Increasing atm O₂

Figure 5.6 Model calculations of atmospheric oxygen during Phanerzoic time. Abbreviations indicate geologic times shown in Figure 1.3. (After Berner and Canfield, 1989.)

Figure 12 Estimated organic carbon burial (×10⁶ g) and atmospheric oxygen concentrations (ppm) through Phanerzoic time, derived from estimates of rock abundance and their relative organic carbon and sulphate content (source Berner and Canfield, 1999).
Conclusions

• 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 hundreds of millions of years to thousands of years

• Anthropogenic alterations of these cycles is much faster than we observe throughout most of the geological record
Phytoplankton’s Influence on the Global Carbon Cycle

The Earth’s carbon cycle can dramatically influence global climate, depending on the relative amounts of heat-trapping carbon dioxide (CO₂) that move into (yellow arrows) and out of (green arrows) the atmosphere and upper ocean, which exchange gases every six years or so. Planctonic organisms called phytoplankton play four critical roles in this cycle. These microscopic ocean dwellers annually incorporate about 50 billion metric tons of carbon into their cells during photosynthesis, which is often stimulated by iron via windblown dust (1). Phytoplankton also temporarily store CO₂ in the deep ocean via the biological pump; about 15 percent of the carbon they assimilate settles into the deep sea, where it is released as CO₂ as the dead cells decay (2). Over hundreds of years, upwelling currents transport the dissolved gas and other nutrients back to surface waters. A tiny fraction of the dead cells avoids being recycled by becoming part of petroleum deposits or sedimentary rocks in the seafloor. Some of the rock-bound carbon escapes as CO₂ gas and reenters the atmosphere during volcanic eruptions after millions of years of subduction and metamorphism in the planet’s interior (3).

Burning of fossil fuels, in contrast, returns CO₂ to the atmosphere about a million times faster (4). Marine phytoplankton and terrestrial forests cannot naturally incorporate CO₂ quickly enough to mitigate this increase; as a consequence, the global carbon cycle has fallen out of balance, warming the planet. Some people have considered correcting this disparity by fertilizing the oceans with dilute iron solutions to artificially enhance phytoplankton photosynthesis and the biological pump. —P.B.P.