Lecture 22

Continue with evolution of Earth’s atmosphere
(oxidation and reduction reactions on blackboard)

Start on “Snowball Earth”

Evidence for an oxic transition

Before the oxic transition: Reduced minerals (before 2.4 Ga)

1. Banded Iron Formations.

2. Detrital Reduced minerals in riverbeds.

3. Paleosols (ancient soils) show Fe loss.

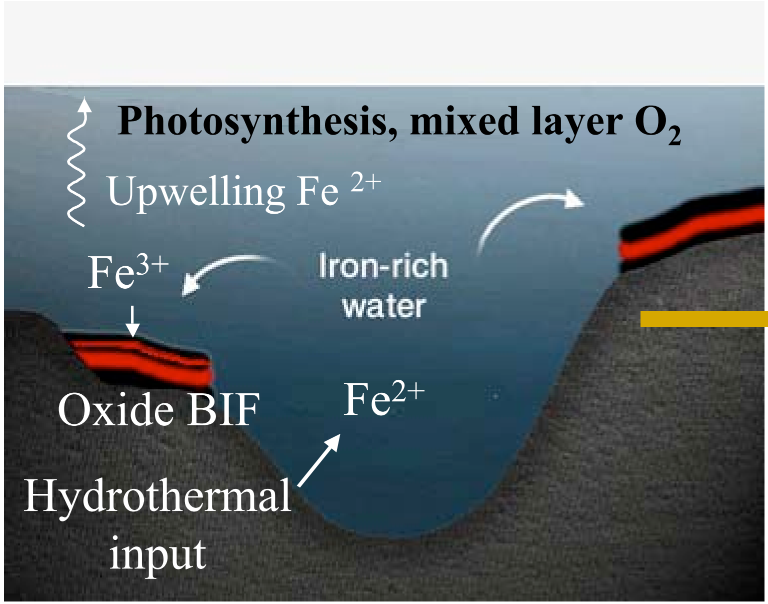
After the transition: Oxidized minerals.

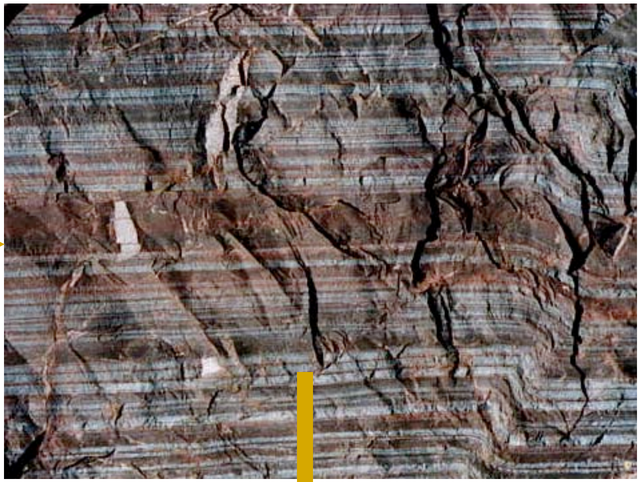
1. Red beds.

2. Decline of reduced indicators (BIFs, detrital) paleosols, Fe retained.

(Isotopic indicators are ‘smoking gun’ evidence (e.g. sulfur isotopes described in the textbook, p.217-218). But the chemistry is complex and we will skip this).

Banded Iron Formations (BIFs)





Laminated chemical sediments ≥15 wt% Fe.

Photo: A. Knoll, Harvard

Japanese cars

Litte change in the O_2 source

Remember that net O_2 input into the “atmosphere-ocean-surface” system comes from the burial of organic carbon.

When we look at average sedimentary rock from 3.8 Ga to present, apart from a few relatively brief periods, remarkably we find:

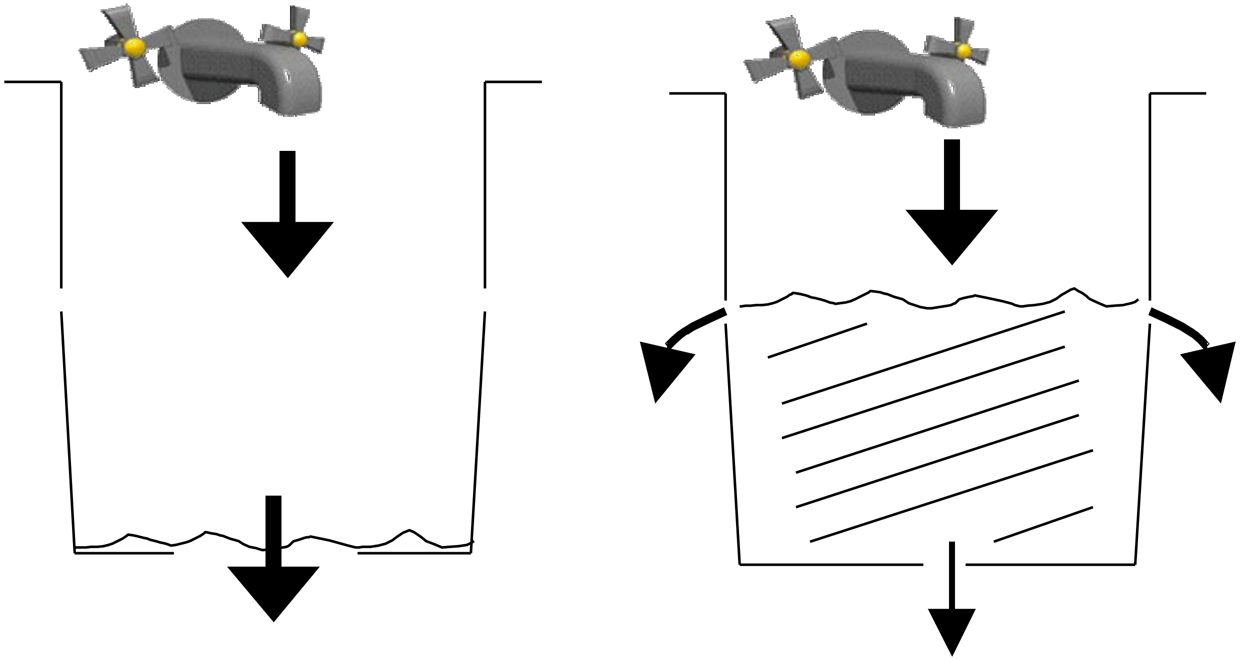
1) roughly constant 0.5% by weight organic carbon (no change)

2) Isotopic evidence for litte change in organic carbon burial rates

If the source of O_2 has not changed, then what else could have caused a rise of O_2?

Answer: the sink (i.e. mechanism for removal of O_2).

Leaky bucket analogy for growth in O_2 atmospheric levels



In each case: flux in = total flux out, but the water level is different.

Water level	- analogous to the O_2 amount in the atmosphere
Hole size in base	- analogous to amount of volcanic & metamorphic reducing gases (H_2, CO) that react rapidly with O_2
Holes in sides	- analogous to oxidation of continents (e.g. loss to red beds) that kicks in only at higher O_2 amounts.

Theory for the rise of O_2

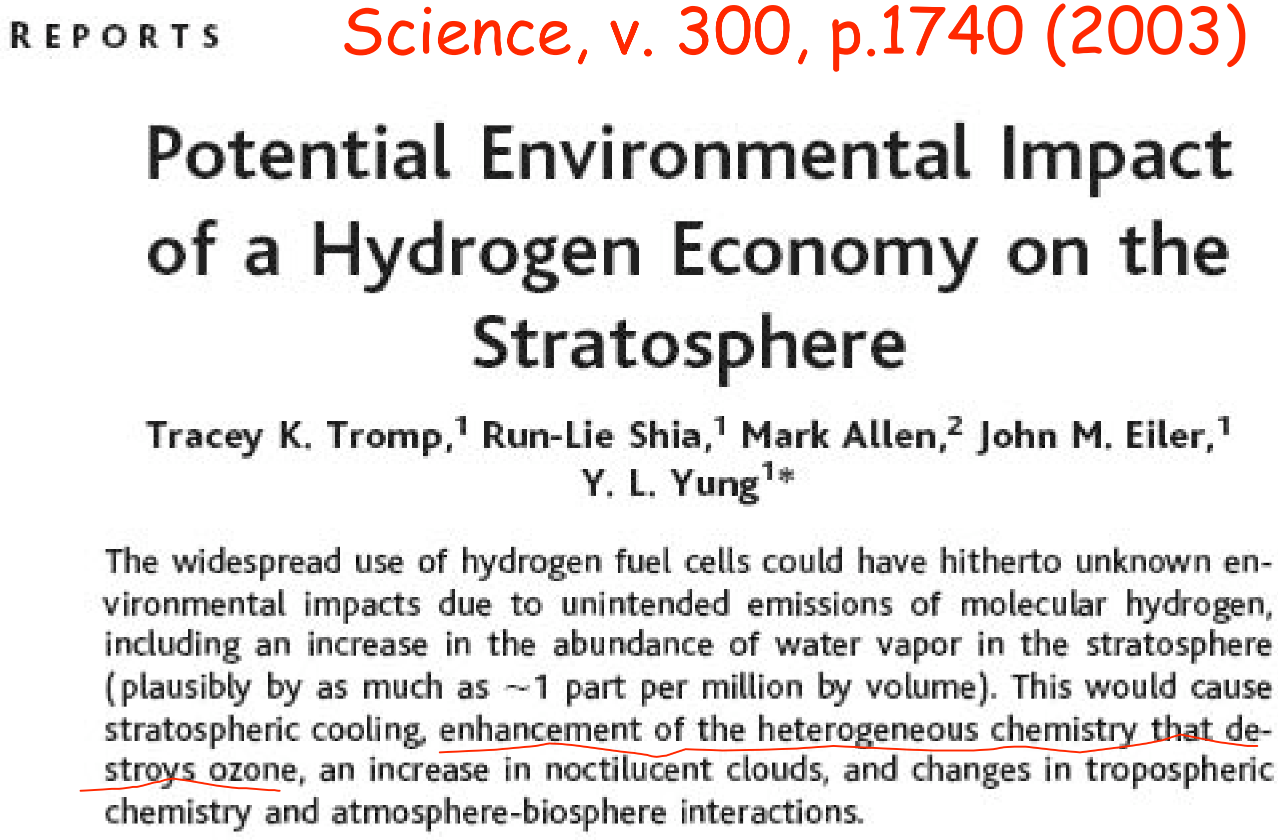
It is thought that the Earth's rocky crust (and mantle) became more oxidized because of the loss of hydrogen to outer space.

A more oxidized crust and mantle produces more oxidized outgassed gases, and the amount of outgassed oxygen-consuming gases (H_2, CO, etc.) diminish. Implies more O_2.

The set of reactions in the atmosphere that remove O_2 are highly **nonlinear**. We do not get a steady increase in O_2 with a steady decrease of reducing gases.
Instead, O_2 reaches a critical point after which it leaps up in abundance.

Aside: H_2 emissions in today's environment

Science, v. 300, p.1740 (2003)



REPORTS

Potential Environmental Impact of a Hydrogen Economy on the Stratosphere

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The widespread use of hydrogen fuel cells could have hitherto unknown environmental impacts due to unintended emissions of molecular hydrogen, including an increase in the abundance of water vapor in the stratosphere (plausibly by as much as ~1 part per million by volume). This would cause stratospheric cooling, enhancement of the heterogeneous chemistry that destroys ozone, an increase in noctilucent clouds, and changes in tropospheric chemistry and atmosphere-biosphere interactions.

2000 Presidential election:
George W. Bush mocks
Al Gore as an
environmental extremist
for wanting to eradicate
the combustion
engine in the future

January 2002:
Pres. George W. Bush
announces a $1.2b program
to research hydrogen fuel
….to eradicate
the combustion
engine in the future

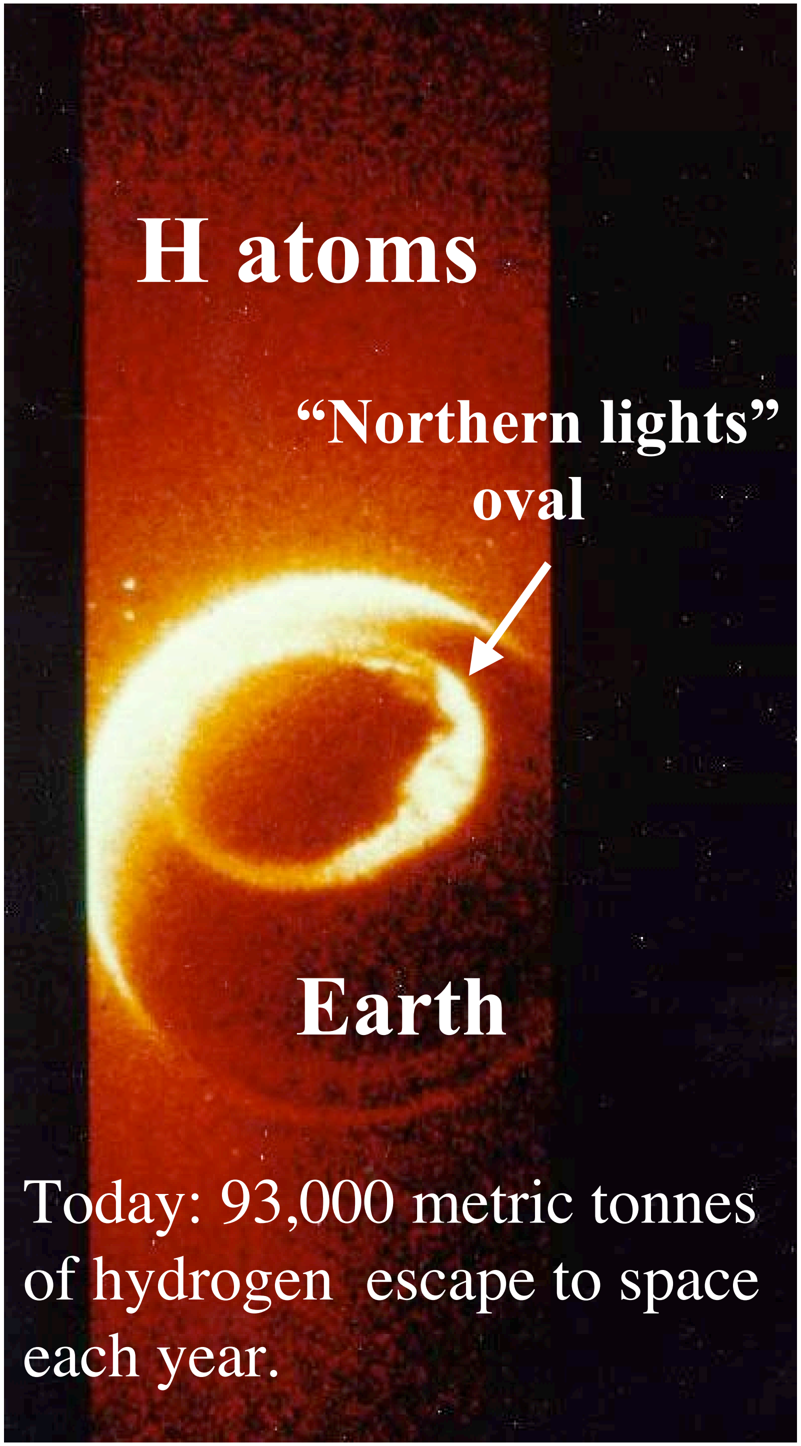
However, this paper took an extreme "worst case" view that 10% of hydrogen would leak from the future production/fueling system. This is probably a huge overestimate; more like 1%.

Back to the Archean Earth: Enhanced H escape via methane, CH_4

Today vast amounts of methane are consumed in reaction with oxygen in the atmosphere, leaving CH_4 at a trace abundance of only 1.7 ppmv.

In the low O_2 Archean atmosphere, biogenic methane would be abundant, at about ~1000 ppmv.

But what ultimately happens to such methane in the upper atmosphere? Answer: It gets photolyzed and hydrogen escapes away.



Today: 93,000 metric tonnes of hydrogen escape to space each year.

H atom geocorona in red: UV (121 nm) image of Earth.

- **Today, half of these H atoms originate from microbial CH_4 ; the other half from H_2O that makes it into the stratosphere.**

- **With greater CH_4, H escape would be significant and oxidize the Earth**

- **In the low-O_2 Archean, CH_4 would be ~1000 ppmv (compare 1.7 ppmv today).**

H escape rates were few hunderd times greater.

Methane’s H escape causes O_2 gain

$$\underbrace{CO_2+2H_2O \rightarrow CH_4+2O_2} \rightarrow CO_2 + O_2 + 4H(\uparrow \text{space})$$

Photosynthesis + methanogenesis:

$$\begin{array}{ll}
\cancel{2}CO_2+2H_2O = 2O_2 + \cancel{2CH_2O} & \text{photosynthesis} \\
\cancel{2CH_2O} = CH_4 + \cancel{CO_2} & \text{+ methanogenesis} \\
\hline
CO_2 +2H_2O = CH_4 + 2O_2 & \text{net}
\end{array}$$