Earth's Early Atmosphere

James Kasting
Evan Pugh Professor
of Geosciences
Penn State University

Talk outline

1. Strongly and weakly reducing atmospheres
2. The faint young Sun problem
3. The origin of life: Thermo-dynamic free energy considerations

Strongly reduced atmospheres

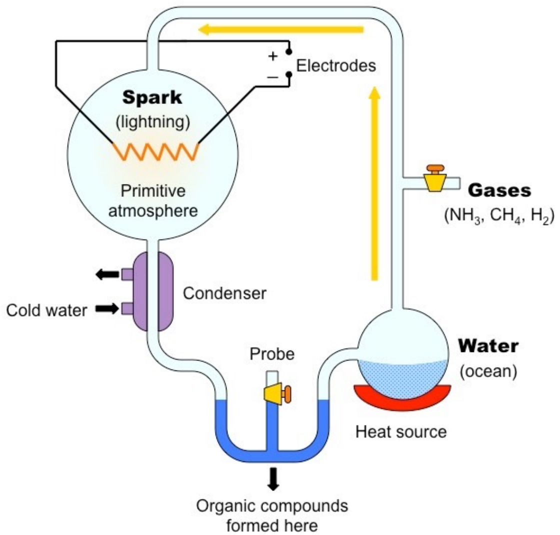
- Alexander Oparin proposed in his 1924 book (in Russian), reprinted in English in 1938, that Earth's early atmosphere was a mixture of highly reduced gases, like methane (CH_4) and ammonia (NH_3)
- This is similar to how carbon and nitrogen appear in the atmospheres of Jupiter and Saturn

Jupiter (from Galileo)

Strongly reduced atmospheres

- In 1953, Stanley Miller, working in Harold Urey's lab at Univ. of Chicago, showed that plausible prebiotic precursor compounds (e.g., amino acids) could be formed by spark discharge (simulating lightning) in a highly reduced atmosphere

⇒ A paradigm was born!



https://ib.bioninja.com.au/standard-level/topic-1-cell-biology/15-the-origin-of-cells/non-living-synthesis.html

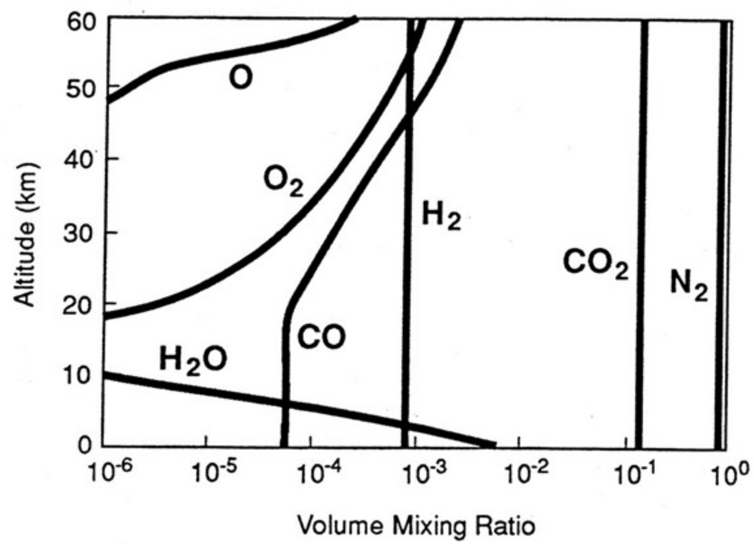
Weakly reduced atmospheres

- But William Rubey, working at the same time as Miller and Urey, noted that the gases being emitted by modern volcanoes are not CH_4 and NH_3, but rather CO_2, H_2O, N_2, and SO_2, along with minor amounts of H_2 and CO
- These gases are relatively oxidized, although free O_2 is absent
- The reason is that Earth's mantle is partially oxidized: it contains some ferric iron (Fe^{+3}) in addition to ferrous iron (Fe^{+2}). Metallic iron (Fe^0) has migrated to the core (Wade and Wood, 2005)

https://www.britannica.com/science/volcano

Weakly reduced atmospheres

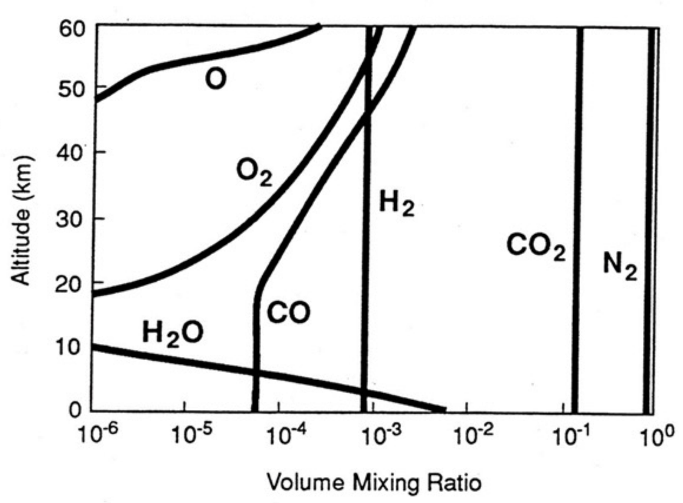
- One can simulate the resulting atmosphere using a one-dimensional (globally averaged) photochemical model
- A 1-bar atmosphere is assumed, although this need not be the case
- CO and O are formed by photolysis of CO_2. O atoms then recombine to form O_2
- The H_2 concentration is determined, to first order, by balancing volcanic outgassing with escape to space



J.F. Kasting (1993)

The faint young Sun problem

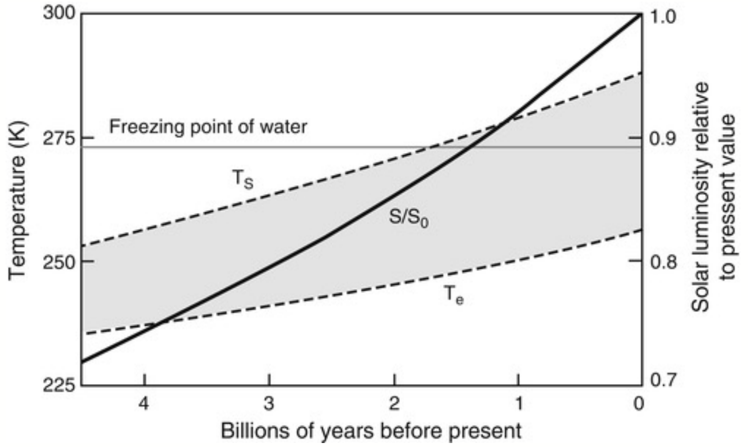
- The CO_2 content of this atmosphere is 0.2 bar. This is just enough to compensate for reduced solar luminosity
- The Sun is thought to have been ~30% dimmer when it formed 4.6 b.y. ago (Gough, 1981)



J.F. Kasting, Science (1993)

The faint young Sun problem

- Question: Why was the young Sun less bright?
- Answer: It fuses H into He in its core. The core becomes denser, causing it to contract and heat up. This makes the fusion reactions proceed faster.
- If Earth's atmospheric composition had not changed with time, the oceans would have been frozen over prior to ~2 b.y. ago, as first pointed out by Sagan and Mullen (1972)



J.F. Kasting (1988)

The origin of life

What does all this imply about the origin of life? Origin of life theories fall into three basic categories

1. Information first (sometimes called ‘RNA first)
2. Metabolism first
3. Vesicles first

In reality, all three things need to come together

Environments are also important. Two possibilities are a surface environment, like the one shown at the right, or alkaline (off-axis) midocean ridge hydrothermal vents

Darwin’s ‘warm little pond’
[Image from Air & Space magazine]

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The origin of life

- Proponents of the ‘Metabolism first’ hypothesis (e.g., Russell and Hall, 2006) have focused on the alkaline hydrothermal vent environment
- Free energy can be obtained by using H_2 to reduce CO_2 to acetate (shown here as acetic acid)

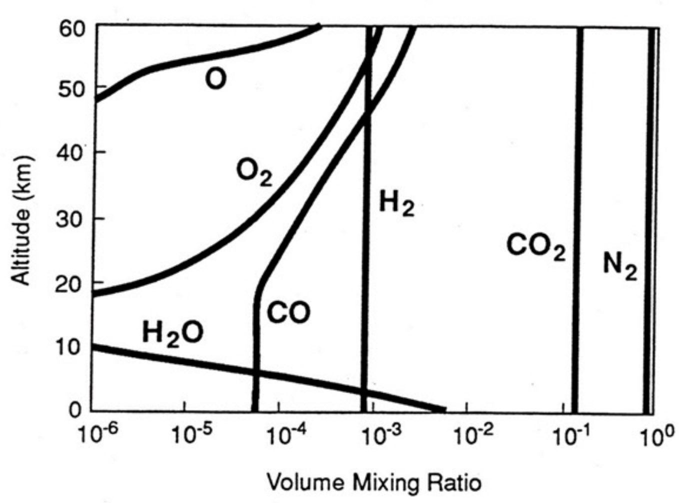
  $2\ CO_2 + 4\ H_2 \rightarrow CH_3COOH + 2\ H_2O$
- Additional free energy is available from pH gradients
- Quoted free energy gradients are in the range of –40 to –80 kJ/mol

The Lost City vent field on the Midatlantic Ridge [Courtesy: Woods Hole *Oceanus*]

The origin of life

- But free energy can also be obtained in the surface environment, given a weakly reducing atmosphere
- CO is abundant in such an atmosphere due to photolysis of CO_2. H_2 is relatively scarce due to escape of hydrogen to space. Thus, the *water-gas shift reaction* is energetically favorable by ~20 kJ/mol (Kasting, 2014)

$$CO + H_2O(\ell) \rightarrow CO_2 + H_2$$



J.F. Kasting (1993)

The origin of life

- Consider the reaction

$$CO + H_2O(\ell) \rightarrow CO_2 + H_2$$

- The Gibbs free energy change for this reaction can be written as

$$\Delta G_R = \Delta G_R^0 + RT \ln Q$$

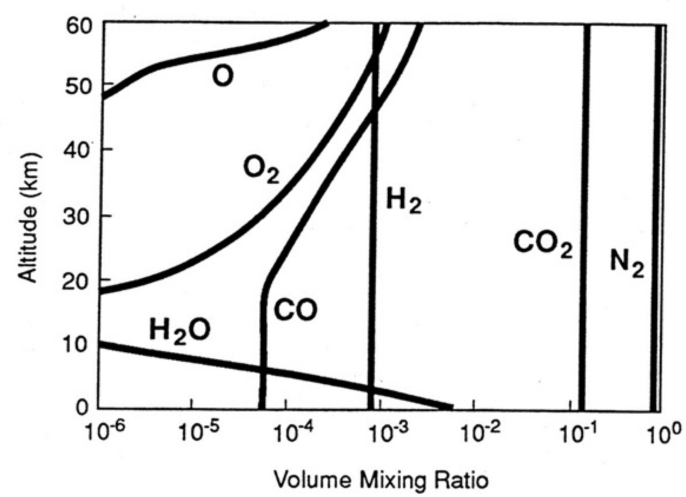
$$\text{where } Q = \frac{pH_2 \cdot pCO_2}{pCO}$$

- Here, $\Delta G_R^0 = 20 \text{ kJ/mol}$ is the free energy change at standard state, Q is the reaction quotient, and pX represents the partial pressure of gas X in bar

- For the atmosphere shown here, at 25°C

$$RT \ln Q \cong 3 \text{ kJ/mol}$$

- Thus, $\Delta G_R \cong -17$ kJ/mol



J.F. Kasting (1993)

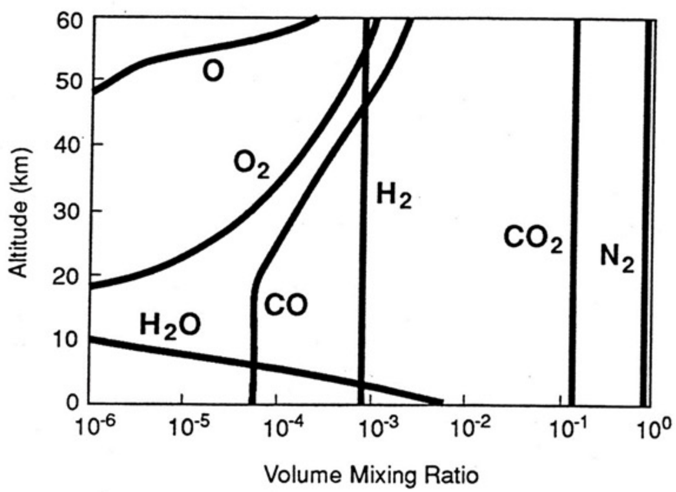
The origin of life

- But the atmosphere shown here is a hypothetical early Archean atmosphere, appropriate for, say, 3.8 Ga Hadean atmospheres could have been much more CO-rich as a result of impacts (Kasting, 1990) or charged particle bombardment from the young Sun (work in progress)
- Under these Hadean conditions, *p*CO could have been equal to *p*CO_2, yielding

$$RT \ln Q \cong -20 \text{ kJ/mol}$$

and $\Delta G_R \cong -40$ kJ/mol

- This is comparable to free energy gradients suggested for the hydrothermal vent environment



J.F. Kasting (1993)

The origin of life

Possible advantages of originating life in a surface environment:

1. Temperatures *may* have been cooler, at least in some regions, thereby promoting the stability of nucleic and amino acids
2. Vesicles composed of simple lipids (as opposed to today's complex phospholipids) would have been more stable in a freshwater environment

A cooler version of Darwin's warm little pond [Newsweek, Sept. 16, 2021]

Summary

- Earth's early atmosphere was probably a weakly reduced mixture of CO_2, H_2O, and N_2 with lesser amounts of H_2
- High CO_2 levels are needed to resolve the faint young Sun problem
- CO levels could have been high during the Hadean as a consequence of impacts and charged particle bombardment
- The surface environment could have provided substantial free energy gradients to drive the origin of life, along with relatively cool temperatures and freshwater environments in which simple lipid vesicles could have been stable

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