

## Early Earth's Atmospheric Evolution

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Atmospheric composition in the Hadean is barely constrained. Zircon data indicate continents, oceans, and maybe life. In models, mean Hadean-Archean climates are not hot because even without land, weathering of seafloor and impact ejecta moderates CO<sub>2</sub> levels and temperature [1, 2].

Rocks indicate oceans, an atmosphere, and land by 3.8 Ga [3], and then, in the Paleoarchean, widespread signs of life. A faint Sun, biospheric gas exchange, and effects of anoxia all bear consideration. Glacial rocks (3.5, 2.9, and 2.7 Ga) suggest global mean temperatures below ~20°C, which can be supported by a CO<sub>2</sub>-rich atmosphere (or CO<sub>2</sub>-rich with biogenic CH<sub>4</sub>). High Archean pCO<sub>2</sub> does not conflict with paleosol inferences with a range 0.02-0.75 bar [4]. Inferred pN<sub>2</sub> <0.5 bar at 2.7 Ga [5] causes a few °C loss of warming, but plausible CO<sub>2</sub> and CH<sub>4</sub> levels can compensate.

A geologic N cycle in an anoxic world may cause low pN<sub>2</sub>. Today, oxidative weathering of organics releases nitrate and nitrate denitrification to N<sub>2</sub> is almost half the long-term N<sub>2</sub> flux; the other half is outgassing [6, p.204]. Archean oxidative weathering was absent, so pN<sub>2</sub> was plausibly lower and would have risen at the Great Oxidation Event (GOE) [5].

What of Archean CH<sub>4</sub> levels? Mass-independently fractionated S isotopes require >20 ppmv [7]. But evidence of H escape to space (light ocean D/H [8] and Xe isotopes that lighten in time [9]), require 2H<sub>2</sub>+CH<sub>4</sub> levels >10<sup>3</sup> ppmv.

Finally, global redox is key to the GOE, which requires oxidation of the surface environment by reductant removal. H escape to space driven by CH<sub>4</sub>-enriched Archean air is by far the biggest net oxidation effect over time [10], so its effect of diminishing the pre-GOE O<sub>2</sub> sinks cannot be ignored.

[1] Krissansen-Totton et al. (2018) *PNAS*, in press. [2] Charnay et al. (2017) *EPSL* 474, 97-109. [3] Nutman (2006) *Elements* 2, 223-227. [4] Kanzaki, Murakami (2015) *GCA* 159, 190-219. [5] Som et al. (2016) *Nature Geosc.* 9, 448-451. [6] Catling & Kasting, *Atmospheric Evolution on Inhabited and Lifeless Worlds*, Cambridge Univ. Press, New York, 2017. [7] Zahnle et al. (2006) *Geobiol.* 4, 271-283. [8] Pope et al. (2012) *PNAS* 109, 4371-4376. [9] Bekaert et al. (2018) *Sci. Adv.* 4. [10] Catling et al. (2001) *Science* 293, 839-843.