Changes in the geologic nitrogen cycle coupled to redox evolution on the early Earth

DAVID C. CATLING[1]

[1]Earth & Space Sciences/ Astrobiology Program, Univ. of Washington, Seattle WA 98195, USA (dcatling@uw.edu)

How the nitrogen cycle changed and affected pN_2 in the Precambrian atmosphere is uncertain. Although pN_2 changed little in the Phanerozoic, invariant pN_2 is doubtful for the Precambrian because the N cycle is coupled to redox. Importantly, pN_2 affects the pressure broadening of absorption lines of greenhouse gases and so influences climate. Some hypothesize that Archean pN_2 was high [1], but data suggest lower pN_2 than today [2] [4]. In anoxic Archean seawater, N dominantly existed as NH_4^+ [5] (c.f. ~40 μM in the deep Black Sea). A long-term sink for NH_4^+ was incorporation into silicates, replacing K^+. Silicate NH_4^+ is stable under metamorphic and igneous conditions. Thus, it is reasonable to hypothesize that Archean subduction of N was important. I explore its consequences. Support for Archean subduction is in diamond $\delta^{15}N$. Some subsequent subduction can also be inferred from Ar^{40}/N_2 and $\delta^{15}N$ systematics.

The geologic N cycle is modeled as time change in the atmosphere-ocean reservoir, *dN/dt*. Sources of N include volcanism and metamorphism, continental weathering of organics, and a small flux from continental silicate weathering; the main sink is organic burial. For an NH_4^+-rich Archean ocean, N in subducted silicates cannot be ignored.

Such a model can result in lower Archean pN_2 than today, while subsequent increase in pN_2 is linked to oxygenation. In particular, the Great Oxidation Event (GOE) throttles the loss of N out of the atmosphere-ocean system via ammonium sequestration into clays. Once the water column has ~15 μM O_2, nitrifying chemoautotrophs oxidize NH_4^+ to nitrite and then NO_3^- [6]. In turn, in anaerobic settings, denitrifiers return N_2 to the atmosphere. Imbalance with geologic sources can result in a rise in pN_2 after the GOE, albeit on a timescale comparable to the interval between 2.4-2.2 Ga.

This view of evolving, redox-coupled Precambrian pN_2 is testable using paleobarometric proxies [e.g., 2-4].

[1] Goldblatt C. et al. (2009) *Nature Geosci.* 2, 891-896. [2] Som S. M. et al. (2012) *Nature* 484, 359-362. [3] Som S. M. et al. (2015), in prep. [4] Marty B. et al. (2013) *Science* 342, 101-104. [5] Holland H. D. (2002) *Geochim. Cosmochim. Acta* 66, 3811-3826. [6] Falkowski P. G. (1997) *Nature* 387, 272-275.