



Atmospheric nitrogen evolution on Earth and Venus



R.D. Wordsworth ^{a, b, *}

^a Harvard Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, United States

^b Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138, United States

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ABSTRACT

Nitrogen is the most common element in Earth's atmosphere and also appears to be present in significant amounts in the mantle. However, its long-term cycling between these two reservoirs remains poorly understood. Here a range of biotic and abiotic mechanisms are evaluated that could have caused nitrogen exchange between Earth's surface and interior over time. In the Archean, biological nitrogen fixation was likely strongly limited by nutrient and/or electron acceptor constraints. Abiotic fixation of dinitrogen becomes efficient in strongly reducing atmospheres, but only once temperatures exceed around 1000 K. Hence if atmospheric N₂ levels really were as low as they are today 3.0–3.5 Ga, the bulk of Earth's mantle nitrogen must have been emplaced in the Hadean, most likely at a time when the surface was molten. The elevated atmospheric N content on Venus compared to Earth can be explained abiotically by a water loss redox pump mechanism, where oxygen liberated from H₂O photolysis and subsequent H loss to space oxidises the mantle, causing enhanced outgassing of nitrogen. This mechanism has implications for understanding the partitioning of other Venusian volatiles and atmospheric evolution on exoplanets.

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Despite the fact that it makes up over 78% of our atmosphere and is essential to all known life, nitrogen remains a poorly understood element on Earth. In comparison to other major non-metal elements such as oxygen and carbon, the mechanisms responsible for its initial delivery, isotopic evolution and partitioning between the surface and mantle are all still subject to great uncertainty. As a result, one of the most basic features of our planet's climate – the atmospheric pressure – remains unexplained by Earth science.

Nitrogen is an important player in climate because it causes pressure broadening of the absorption lines of greenhouse gases like CO₂ and H₂O (Goldblatt et al., 2009), and can also cause intense warming in combination with H₂ in reducing atmospheres via collision-induced absorption in the 800–1200 cm⁻¹ H₂O 'window' region of the infrared spectrum (Wordsworth and Pierrehumbert, 2013). The atmospheric nitrogen inventory also affects the latitudinal temperature gradient (in general denser atmospheres transport heat from equator to poles more effectively). All these effects are particularly relevant in the context of the faint young Sun problem, which arises because solar luminosity was 20–25% lower 3–4 Ga, but Earth was not permanently glaciated in the Archean

(Sagan and Mullen, 1972). Furthermore, planets with very low atmospheric N₂ will no longer cold trap H₂O and hence will irreversibly oxidise via hydrogen loss, which can lead to the buildup of abiotic O₂-dominated atmospheres in extreme cases (Wordsworth and Pierrehumbert, 2014). Understanding Earth's nitrogen is hence important both as a fundamental problem, and for addressing wider questions of planetary climate evolution.

Thanks to its strong triple bond and lack of a permanent dipole moment, molecular nitrogen (N₂) is both chemically unreactive and highly volatile, and hence was once thought of as similar to the noble gases in terms of its incompatibility in the solid Earth. However, this simple view of N₂ has been eroded over the last few decades by a number of studies suggesting that a significant fraction of the present-day atmospheric inventory (between around 0.4 and 7 times) is currently stored in the crust and mantle (Marty, 1995; Marty and Dauphas, 2003; Halliday, 2013; Johnson and Goldblatt, 2015). The main evidence for this comes from the N₂/⁴⁰Ar ratios measured in mid-ocean ridge basalts (MORBs) and rocks of mantle plume origin, which allow the mantle N inventory to be estimated when combined with bulk silicate Earth (BSE) estimates of radiogenic K abundance. Earth's atmosphere is also depleted in ¹⁴N relative to chondritic C and noble gas abundance ratios (Marty, 2012) (the 'missing N' problem), which can be explained by the presence of a substantial mantle N component (Johnson and Goldblatt, 2015). The correlation of N with ⁴⁰Ar in MORBs and the large-ion lithophile elements

* Correspondence to: Harvard Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, United States.

E-mail address: rwordsworth@seas.harvard.edu.

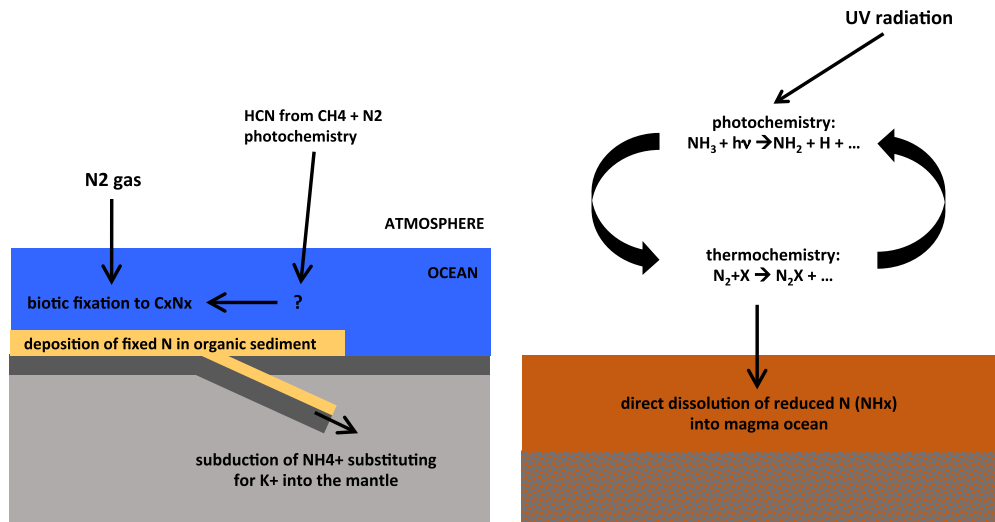


Fig. 1. (left) Biological and (right) abiotic mechanisms capable of transferring atmospheric nitrogen to early Earth's mantle. Biological mechanisms are possible from the origin of nitrogen fixation and methanogenesis metabolisms onwards, while the abiotic mechanism shown would have operated in the early Hadean, during and just after accretion.

in metamorphic rocks also suggests that its primary form in the crust and upper mantle is NH_4^+ , where it generally substitutes for K^+ (Busigny and Bebout, 2013). Finally, measurements of the content of nitrogen and other volatiles in Alpine metasediments suggest that today, there is a net flux of N to the mantle of order 1×10^{12} g/yr (Busigny and Bebout, 2013).

Based on these observations, it has been proposed that biological N fixation has caused atmospheric nitrogen levels to decrease over geological time, and hence that surface pressure on the early Earth was two times or more the present-day value (Goldblatt et al., 2009). However, this apparently logical conclusion has not been supported by recent observational constraints on the ancient atmospheric pressure. First, measurements of the radii of putative fossil raindrops have been argued to constrain the atmospheric density 2.7 Ga to no more than double the present-day value (Som et al., 2012). Independently, recent measurements of N_2 to ^{36}Ar ratios in the fluid inclusions in Archean hydrothermal quartz have suggested that as long ago as 3.0–3.5 Ga, the partial pressure of N_2 in the atmosphere was 0.5–1.1 bar (Marty et al., 2013). Hence Earth's mantle N inventory was apparently in place by the mid-Archean or earlier. If these measurements are correct, nitrogen exchange between the mantle and interior must have been very effective at some earlier point in Earth's early history.

Further clues to terrestrial nitrogen's origins and evolution come from isotopic measurements. Of nitrogen's two stable isotopes, the rarer ^{15}N is enhanced in the atmosphere and in crustal rocks relative to the mantle [$\delta^{15}\text{N}$ of approx. -5% vs. the atmosphere in the upper mantle and perhaps as low as -40% in the lower mantle; Cartigny and Marty, 2013].¹ This has been interpreted previously as an indication of biological processes. Earth's atmospheric $^{15}\text{N}/^{14}\text{N}$ ratio ($\sim 3.7 \times 10^{-3}$) is close to the values found in ordinary and carbonaceous chondrites (Marty, 2012), but the solar and gas giant N reservoirs are lighter ($\sim 2.3 \times 10^{-3}$; Owen et al., 2001). This has led to the prevailing view that most of Earth's N was delivered by bodies with composition close to that of the carbonaceous chondrites. At which stage of accretion, and in what form this nitrogen was delivered is still uncertain, but a reasonable interpretation is of volatile-rich bodies of chondritic composition impacting the Earth during the later stages of accre-

tion, with much of the nitrogen in the form of ammonia ices or simple organic compounds such as HCN.

Clearly, our current understanding of the long-term atmosphere-interior exchange of nitrogen on Earth is lacking in many respects. Most previous research has focused on improving the (vital) geochemical constraints on the deep-time N cycle. To date, however, far less attention has been paid to the theoretical aspects of the problem. Here the importance of several key processes to Earth's earliest nitrogen cycle are analysed (see Fig. 1). First, it is noted that nitrogen delivered to Earth in fixed form would have initially degassed into the atmosphere and that it therefore must have entered the mantle at some point after this. Based on primary productivity constraints and other arguments, it is then argued that drawdown of bars of nitrogen before 3.0–3.5 Ga via biological fixation is highly unlikely. An atmospheric chemistry model is used to show that abiotic reduction of atmospheric nitrogen can be effective, but only under conditions where the atmosphere is strongly reducing and the surface temperature is extremely hot. Based on this, a new explanation involving a magma ocean redox pump driven by water loss is proposed for the differing atmospheric N inventories of Earth and Venus.

1. Nitrogen delivery by impacts

The first stage of Earth's nitrogen cycle is delivery of the element during accretion. As discussed in the introduction, most of this incoming nitrogen was likely fixed in the form of ammonia ices or organics. However, the temperatures and peak shock pressures on impact for the majority of accreting bodies mean that it would have initially thermalised and degassed into the atmosphere. Impact shock experiments on carbonaceous chondrites (Tyburczy et al., 1986) indicate that for accretion occurring after Earth has reached around 30% of its final radius, mineral devolatilisation is effective. As the majority of Earth's nitrogen was probably delivered late, this implies the immediate post-impact location of delivered nitrogen would have been the atmosphere. Note that as well as depositing their own nitrogen to the atmosphere, impactors would also devolatilise any crustal and sedimentary nitrogen that was already present in the region of impact. We do not attempt to model this process here, but it would act to reduce the efficiency of the slow drawdown mechanisms discussed in the next two sections.

¹ Here for a given sample i , $\delta^{15}\text{N} = 1000[(^{15}\text{N}/^{14}\text{N})_i / (^{15}\text{N}/^{14}\text{N})_{\text{atm}} - 1]$ and $(^{15}\text{N}/^{14}\text{N})_{\text{atm}} = 3.7 \times 10^{-3}$ is the Earth atmospheric value.

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