The Origin of Earth's Mantle Nitrogen: Primordial or Early Biogeochemical Cycling?

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Abstract Earth's mantle nitrogen (N) content is comparable to that found in its N-rich atmosphere. Mantle N has been proposed to be primordial or sourced by later subduction, yet its origin has not been elucidated. Here we model N partitioning during the magma ocean stage following planet formation and the subsequent cycling between the surface and mantle over Earth history using argon (Ar) and N isotopes as tracers. The partitioning model, constrained by Ar, shows that only about 10% of the total N content can be trapped in the solidified mantle due to N's low solubility in magma and low partitioning coefficients in minerals in oxidized conditions supported from geophysical and geochemical studies. A possible solution for the primordial origin is that Earth had about 10 times more N at the time of magma ocean solidification. We show that the excess N could be removed by impact erosion during late accretion. The cycling model, constrained by N isotopes, shows that mantle N can originate from efficient N subduction, if the sedimentary N burial rate on early Earth is comparable to that of modern Earth. Such a high N burial rate requires biotic processing. Finally, our model provides a methodology to distinguish the two possible origins with future analysis of the surface and mantle N isotope record.

Plain Language Summary Nitrogen (N) is the main component of Earth's atmosphere, and essential for life. The atmospheric N content influences Earth's climate and capability to retain its surface water. Primary biological production is limited by bio-available N as well as phosphorous on modern Earth. It has been recently recognized that Earth's interior contains N comparable to that found in its atmosphere, and thus its origin is important for our understanding of Earth-life co-evolution. We modeled N partitioning in Earth's molten stage and long-term cycling after Earth's solidification. Two scenarios are proposed from our modeling, One is that Earth's mantle acquired its modern N content in the earlier stage due to an excess amount of N Earth accreted, which was later lost to space following asteroid impacts. Another is that Earth's mantle acquired N via subduction of N-rich sediments, which requires the sedimentary N burial rate on early Earth comparable to the modern value sustained by biological activity. The two scenarios can be tested with future analysis of the geochemical record of surface and mantle N.

1. Introduction

Nitrogen (N) is the main component of Earth's atmosphere and essential for the biosphere as it is an integral part of the building blocks of life. Though molecular nitrogen (N₂) is transparent in the infrared, its presence in the atmosphere increases the warming effect of existing greenhouse gases by pressure broadening of their absorption lines (Goldblatt et al., 2009). The N inventory in the atmosphere is also important for sustaining water on planets by the cold-trap mechanism (Wordsworth & Pierrehumbert, 2014). Primary biological production in modern aquatic environments is mostly limited by either fixed N or phosphorus (Zerkle, 2018). Though deficits in biologically available N can be mitigated by microbial N fixation on modern Earth, it might have been a limiting factor for early life on Earth.

Though N was once thought to predominantly reside in the atmosphere and biosphere, it can indeed become incorporated into the geosphere: minerals and rocks (e.g., Johnson & Goldblatt, 2015). Combined sample analyses with N-40 Argon (Ar) geochemistry (Marty, 1995) suggest that present Earth's mantle contains a comparable mass of N as the atmosphere (Bergin et al., 2015; Halliday, 2013; Johnson & Goldblatt, 2015; Marty &
Dauphas, 2003). A mantle which hosts N at a similar level as found in the atmosphere has great potential for influencing the surface environment through ingassing and outgassing of this mantle reservoir. Determining whether mantle N is a primordial feature set during the magma ocean stage or evolved with the subduction of sediments by plate tectonics is essential to our understanding of Earth’s formation and early biogeochemical cycling.

Mantle N has been proposed to be sourced by subduction of N-bearing sediments and the altered oceanic lithosphere (Barry & Hilton, 2016; Johnson & Goldblatt, 2018; Marty & Dauphas, 2003; Stüeken et al., 2021), which would also lead to secular evolution of atmospheric N partial pressure ($p_{N_2}$) (Laneuville et al., 2018; Zerkle & Mikhail, 2017). Notably, such subducting N on modern Earth has $\delta^{15}N \sim +6\%o$ (Cartigny & Marty, 2013; Halama et al., 2014; Johnson & Goldblatt, 2018), where $\delta^{15}N = \left[\frac{^{15}N/^{14}N}_{\text{sample}} / \frac{^{15}N/^{14}N}_{\text{standard}} - 1\right] \times 1000$. Thus, efficient subduction should lead to $^{15}N$ enrichment in the mantle. Carbon-bearing deep mantle diamonds have been found to host N with almost exclusively positive $\delta^{15}N$ values (Regier et al., 2020), which might be consistent with an origin from subducted oceanic sediments.

However, mantle N sampled from mid-ocean ridge basalt (MORB) is rather depleted in $^{15}N$ ($\delta^{15}N \sim -5\%o$), which is known as N isotopic disequilibrium (Cartigny & Marty, 2013; Marty, 1995). In this regard, several previous studies hypothesized that mantle N is predominantly a remnant of planet formation (Cartigny & Marty, 2013; Labidi et al., 2020; Mallik et al., 2018). In this primordial origin scenario, the isotopic disequilibrium is attributed to atmospheric escape, which enriches the residual atmosphere in $^{15}N$. Another study focusing on N isotopes proposed a recycling origin scenario in which the N isotope composition of sediments has changed over time (Marty & Dauphas, 2003). We note that here the prefix “re” is given because, in this scenario, the modern mantle N is a component once degassed to the atmosphere in the magma ocean stage.

Ar is another tracer of N partitioning and cycling (Marty, 1995). In oxidized magma, where N exists in the form of $N_2$, N and Ar behave similarly (e.g., Marty & Dauphas, 2003). However, under reducing conditions N exists as NH$_4^+$, which can substitute for K$^+$ in mineral phases, allowing for more efficient recycling of N than Ar. The large difference in $^{40}$Ar/$^{36}$Ar ratios between the modern atmosphere and mantle implies that the two reservoirs have largely stopped exchanging Ar with each other since early catastrophic degassing, and radiogenic $^{40}$Ar derived from $^{40}$K has continued to accumulate in the mantle (Ozima & Podosek, 2002, and references therein).

Previous studies which argued either primordial or recycling scenarios have greatly contributed to our understanding of the origin of mantle N, but they have missed some important behavior. N partitioning between the atmosphere and magma ocean has been experimentally investigated by several studies (Boulliung et al., 2020; Libourel et al., 2003), which concluded that mantle N could be primordial. However, these studies have not considered N degassing upon magma ocean solidification, which might limit N partitioning into the solidified magma significantly (Hier-Majumder & Hirschmann, 2017). Models which treated long-term N cycling after the magma ocean solidification did not trace N isotopic exchange between different reservoirs (Johnson & Goldblatt, 2018; Stüeken, Kipp, Koehler, Schwieterman, et al., 2016) or introduced a simplified assumption on the N isotopic ratio of the upper mantle (Tolstikhin & Marty, 1998) or sediments (Labidi et al., 2020). These points are covered by this study to further test the two scenarios (see Section 4.4 for more detailed comparison with these previous studies).

Here we test the primordial and recycling origin scenarios using numerical models for N partitioning and cycling coupled with Ar and N isotopes. Section 2 presents our models. Section 3 shows the model results. We discuss the origin of N in the mantle and the implications for the future analysis of N isotope record of early Earth and for other rocky planets in Section 4, and conclude in Section 5.

2. Methods

2.1. Model Overview and Constraints

We modeled N partitioning in the magma ocean stage and N cycling after magma ocean solidification separately (Figure 1). Our first model tested whether N in the modern mantle could be primordial by computing the N content trapped in the mantle upon solidification. Partitioning was also computed for $^{36}$Ar because the discrepancy in N/$^{36}$Ar ratios between the present atmosphere and mantle has been used to discuss the origin of mantle N (Marty & Dauphas, 2003). Our second model tested whether mantle N can originate from secular subduction.
This cycling model explicitly calculates $^{15}\text{N}/^{14}\text{N}$ ratios in the surface reservoirs (the atmosphere and continental and oceanic crust) and mantle, which can be used as another constraint.

Table 1 summarizes the constraints on model results: N contents, $\delta^{15}\text{N}$ values, and $^{36}\text{Ar}$ contents in the four largest reservoirs: the atmosphere, continental and oceanic crust, and mantle. We adapted a N content estimate for the modern mantle derived from N-$^{40}\text{Ar}$ geochemistry by Bergin et al. (2015): 0.41–2.53 times present atmospheric N $4.0 \times 10^{18}$ kg (hereafter PAN, Johnson & Goldblatt, 2015). This range brackets independent estimates by Marty and Dauphas (2003) (0.41–1.27 PAN) and Halliday (2013) (0.42–1.12 PAN). We adapted the N isotopic composition of the modern mantle of $\delta^{15}\text{N} = -10$ to $-2$‰ as informed from MORB (Marty & Dauphas, 2003). We note that Johnson and Goldblatt (2015) derived a higher estimate (2–10 PAN) by assuming the existence of the “high-N mantle,” which is associated with some oceanic island basalts (OIB) and OIB-related xenoliths. This proposed component is isotopically distinct ($\delta^{15}\text{N} = +5\%$, Johnson & Goldblatt, 2015). The high-N estimate was not used in our main results as its presence is not assumed in the other studies, but we discuss it further in Section 4.3. The $^{36}\text{Ar}$ amounts of modern atmosphere and mantle were adapted from the estimate of Bekaert et al. (2021).

### 2.2. Partitioning Model

Our partitioning model calculated the N and $^{36}\text{Ar}$ amounts trapped in the solidified mantle upon magma ocean cooling after core-mantle separation (Figure 1). Our model assumes bottom-up solidification, but the case for a basal magma ocean is discussed in Section 4.3. In contrast to previous studies which modeled N partitioning (Boulliung et al., 2020; Gaillard et al., 2022; Libourel et al., 2003), degassing caused by magma solidification, which limits N trapping into the mantle, was considered. We did not calculate N isotopes in this first model. Equilibrium degassing enriches the residual melt in $^{15}\text{N}$ by $\sim+1\%$ (e.g., Dalou et al., 2019). As we discuss quantitatively in Section 4.1, however, atmospheric escape processes enrich atmospheric $^{15}\text{N}$ easily and should be responsible for the observed isotopic disequilibrium between the current atmosphere and mantle in the primordial origin scenario.

**Table 1** Constraints on Our Model Results

| Reservoir        | N content [PAN] | $\delta^{15}\text{N}$ [%] | $^{36}\text{Ar}$ content [PA36Ar] |
|------------------|----------------|---------------------------|-----------------------------------|
| Atmosphere       | 1              | 0                         | 1                                 |
| Mantle           | 0.41–2.53$^a$  | -10 to -2$^b$             | 2.8–5.7 $\times 10^{-3}$          |
| Continental crust| 0.25–0.43$^d$  | +1 to +10$^e$             | –                                 |
| Oceanic crust     | 0.038–0.15$^f$ | +4 to +10$^g$             | –                                 |

*Note.* Present Atmospheric N (PAN) = $4.0 \times 10^{18}$ kg. 1 PA36Ar = $2.1 \times 10^{14}$ kg.

$^a$Marty and Dauphas (2003); Halliday (2013); Bergin et al. (2015). $^b$Marty and Dauphas (2003). $^c$Bekaert et al. (2021). $^d$Rudnick et al. (2003); Johnson and Goldblatt (2015, 2017). $^e$Busigny and Bebout (2013). $^f$Johnson and Goldblatt (2015). $^g$Cartigny and Marty (2013).
2.2.1. N Partitioning Between Reservoirs

Our method is based on the melt-trapping model of Hier-Majumder and Hirschmann (2017). The relevant parameters are summarized in Table 2. Dissolution equilibrium was assumed between the atmosphere and magma ocean for each time step, given as (see Appendix B for derivation),

$$ M'_{\text{atm}} = \frac{M'_i \cdot s_i \cdot M_{\text{mo}} / A_E}{1 + (\tilde{m} / m_i) \cdot S_i} \tag{1} $$

$$ M'^i = M'_{\text{atm+mo}} - M'_{\text{atm}} \tag{2} $$

where $M'_i$ is the mass of element $i$ (N or $^{36}$Ar) in the reservoir $j$ (atm = atmosphere, mo = magma ocean, and sm = solidified mantle), $m_i$ is the molecular mass in the atmosphere (28 and 36 amu for N and $^{36}$Ar), $\tilde{m}$ is the mean molecular mass of atmospheric gases, $S_i$ is the solubility, and $g$ is the gravitational acceleration at the surface, and $A_E$ is the total surface area of Earth. The value without a superscript $i$ is the mass of the reservoir itself (e.g., the mass of magma ocean $M'_{\text{mo}}$). Here we assumed that the volatile abundances in the magma ocean are constant in depth to derive Equation 1. This assumption is justified because the viscosity of the magma ocean is so low that the mixing timescale is much shorter than the cooling timescale (the orders of days to weeks vs. Myrs, Solomatov, 2015; Nikolaou et al., 2019; Sossi et al., 2020). The mean molecular mass $\tilde{m}$ was assumed to be 28 amu, assuming CO as the dominant gas. This assumption is valid for Earth's magma ocean (Sossi et al., 2020). While $S_{\text{atm}}$ was assumed to be constant, $S_j$ is dependent on N partial pressure, $p_N (= \tilde{m} / m_N) \cdot M_{\text{atm}} / A_E$, Equation A1. Thus, Equations 1 and A1 were iteratively solved to obtain $S_j$ and $M'_{\text{mo}}$. Our N solubility model, based on Boulliung et al. (2020), assumed atmospheric N is in the form of N$_2$ (Appendix A), which is expected for the oxygen fugacity range considered here (e.g., that of Schaefer & Fegley, 2017). As magma solidifies at the bottom of magma ocean, the volatile content in the solidified mantle increases as,

$$ \frac{d M'_{\text{sm}}}{dt} = [F_i + D_i (1 - F_i)] C_i \frac{d M'_{\text{atm}}}{dt} \tag{3} $$

where $t$ is the time, $F_i$ is the trapped melt fraction, $D_i$ is the partitioning coefficient between minerals and silicate melt, and $C_i$ is the concentration of the element $i$ in the magma ocean ($C_i \equiv M'_{\text{atm}} / M'_{\text{mo}}$). The first and second terms in the bracket of Equation 3 correspond to melt trapping and partitioning into minerals, respectively. The trapped mass is subtracted from the rest of the system, as,

$$ \frac{d M'_{\text{atm+mo}}}{dt} = - \frac{d M'_{\text{sm}}}{dt} \tag{4} $$

The trapped melt fraction as a function of cooling rate is defined as the fraction of the solidified mass trapped as interstitial melt relative to the total solidified mass (solidified interstitial melt plus crystallized minerals), and given by (Hier-Majumder & Hirschmann, 2017),

$$ F_i = \frac{\phi_i \cdot \tau \cdot T_p}{\Delta T} \tag{5} $$

where $\phi_i$ is the disaggregation melt fraction, $T_p$ is the mantle potential temperature, $\Delta T$ is the difference between the solidus and the liquidus temperatures at the bottom of magma ocean, and $\tau$ is the compaction time of the mushy layer at the bottom of magma ocean. The upper limit of $F_i = 0.3$ is given by the melt fraction for rheological transition (Hier-Majumder & Hirschmann, 2017).

2.2.2. Thermal Evolution

The thermal evolution of Earth was solved to compute $dT_p / dt$ in Equation 5, as given by (Hier-Majumder & Hirschmann, 2017).

Table 2

| Parameter Values Used in Our Partitioning Model | Density | Difference between solidus and liquidus | Heat Capacity | Entropy change on melting | Disaggregation melt fraction | Compaction time | Solidification time | Solubility of N | Partitioning coefficient of N | Solubility of Ar | Partitioning coefficient of Ar |
|-----------------------------------------------|--------|--------------------------------------|--------------|--------------------------|-----------------------------|----------------|------------------|-----------------|----------------------------|----------------|-----------------------------|
| Density                                       | $\rho$ | $\Delta T$                            | $C_p$        | $\Delta S$               | $\phi_c$                   | $\tau$         | $\tau$           | $S_N$           | $D_N$                     | $S_{Ar}$        | $D_{Ar}$                    |
| PREM                                          |        | F-peridotitic model                   | 1,000 [J kg$^{-1}$ K$^{-1}$]$^f$| 300 [J kg$^{-1}$ K$^{-1}$]$^f$| 0.3$^c$                | 4.35 Myr$^e$   | 0.2–7 Myr$^d$   | Equation A1$^e$ | 0.0073, 0.020, 0.0030$^f$ | 0.2 [ppm/MPa]$^g$ | 0.0011 $^b$                 |

$^a$Dziewonski and Anderson (1981). $^b$Monteux et al. (2016). $^c$Hier-Majumder and Hirschmann (2017). $^d$Hamano et al. (2013); Salvador et al. (2017); Nikolaou et al. (2019). $^e$Used Boulliung et al. (2020) data (see Appendix A). $^f$For upper mantle, transition zone, and lower mantle from Yoshikawa et al. (2018). $^g$Model of Iacono-Marziano et al. (2010), assuming a bulk silicate Earth (pyrolite) magma composition (McDonough & Sun, 1995) and 1,700 K. $^h$Heber et al. (2007).
\[
\frac{dT_p}{dt} = -L_{\text{int}} \left[ C_p \left( M_E - M_r(a) \right) - 4\pi \rho T_p a^2 \frac{da}{dt} \right]^{-1},
\]

where \( L_{\text{int}} \) is the intrinsic luminosity, \( M_e \) is Earth’s mass, \( M_r \) is the enclosed mass, \( \rho \) and \( C_p \) are the density and the heat capacity of the magma, and \( a \) is the radius of the solidification front. We derived a fitting formula for \( a \) to reproduce Figure 2 of Hier-Majumder and Hirschmann (2017) as,

\[
a(T_p) = \begin{cases} 
R_E \ (T_p < 1810 \text{ K}) , \\
-1.587 \times 10^{-1} T_p^3 + 8.83571 \times 10^{-2} T_p^2 - 1.641 \times 10^5 T_p + 1.0234 \times 10^9 [\text{m}] \\
(1810 \text{ K} < T_p < 2100 \text{ K}) , \\
R_{\text{core}} \ (2100 \text{ K} < T_p) , 
\end{cases}
\]

where \( R_E \) and \( R_{\text{core}} \) are the radii of Earth and the core, respectively. Computing the intrinsic luminosity \( L_{\text{int}} \) requires a radiative-convective model for the atmospheric structure with complete description of molecular composition, cloud properties, etc. (e.g., Nikolaou et al., 2019; Salvador et al., 2017). Instead, we assumed a constant value for \( L_{\text{int}} \) estimated from the given solidification time \( t_s \).

### 2.2.3. Initial Conditions and Parameters

The redox state of the mantle influences N solubility and, consequently, the trapped N content. Earth’s magma ocean in its final stage is thought to be more oxidized than \( \log_{10} f_{O2}, \Delta IW = -1 \) (Armstrong et al., 2019; Badro et al., 2015; Sossi et al., 2020), where \( f_{O2} \), \( \Delta IW \) is the oxygen fugacity relative to that of the iron-wüstite buffer. Following Dalou et al. (2017), we considered three cases – oxidized \((\log_{10} f_{O2}, \Delta IW = -1)\), intermediate \((\log_{10} f_{O2}, \Delta IW = -2)\), and reduced \((\log_{10} f_{O2}, \Delta IW = -3.5)\) cases (Table 2), where the latter two are shown for comparison with the realistic, oxidized model.

We considered \( t_s = 0.2–7 \text{ Myr} \), which covers the range of estimates in previous studies which simulated the magma ocean solidification (Hamano et al., 2013; Nikolaou et al., 2019; Salvador et al., 2017).

A fully molten magma ocean \( (T_p = 2100 \text{ K}) \) was assumed for the initial condition. The assumption maximizes the amount of trapped N. Initially the total N content (Table 1) was assumed to be in the atmosphere and magma ocean with the dissolution equilibrium. As we focus on the evolution after the major accretion and core-mantle separation, we did not model partitioning into alloy which would determine the total N content in concert with atmospheric loss during the major accretion stage (Grewal et al., 2019, 2021; Hirschmann, 2016; Sakuraba et al., 2021) before the magma ocean solidification stage we considered here.

### 2.3. Cycling Model

To test the recycling origin scenario, our N cycling model simulated the secular evolution of N masses and isotope ratios in the four major reservoirs: the atmosphere, continental and oceanic crust, and mantle (Figure 2). Our model explicitly treats more reservoirs than a recent study considering isotopic evolution (Labidi et al., 2020) but is simplified compared to the N cycling models that were developed based on geophysics and (bio-)geochemistry (Johnson & Goldblatt, 2018; Laneuville et al., 2018; Stüeken, Kipp, Koehler, & Buick, 2016). Our model was designed to understand (a) the requirement for realizing the recycling origin, and (b) its isotopic signatures as explained below.

Evolution of N masses and isotopic ratios \((^{15}\text{N}/^{14}\text{N})\) in the reservoirs was calculated by using the following equations (Kurokawa, Foriel, et al., 2018),

\[
\frac{dM_r}{dt} = \sum_{\text{sources}} F_s - \sum_{\text{sinks}} F_s,
\]
\[
\frac{d}{dt} (M, I) = \sum_{\text{sources}} (F_s a_s I_s) - \sum_{\text{sinks}} (F_s a_s I_s),
\]

where \( M \) and \( I \) are the mass and isotopic ratio of N in the reservoir \( i \) (atm: atmosphere, cc: continental crust, oc: oceanic crust, and ma: mantle), and \( F_s \) and \( a_s \) are the flux of the process \( k \) and its isotopic fractionation factor. We considered net isotopic fractionation in sediment deposition (the atmosphere to sediments on the crust, through fixed N in the oceans). The other processes are known to induce relatively small isotopic fractionation only (typically \( \approx 1\% \)). Busigny & Bebout, 2013; Cartigny & Marty, 2013). A potential caveat here is that N isotopic fractionation in the subduction zones and in the mantle has not been fully understood, which is discussed in Section 4.3.

### 2.3.1. Sediment Burial

Surface N cycling evolved through time (e.g., Ader et al., 2016; Shen et al., 2006; Stüeken, Kipp, Koehler, & Buick, 2016). On modern Earth, biology mediates primary N fixation from N\(_2\), and dissolved nitrate in the ocean is the main form of bio-available N. In contrast, abiotic N fixation might have been a dominant source of fixed N on early Earth (Navarro-González et al., 2001), especially before the development of biological N fixation (Stüeken et al., 2015), and nitrate would be limited because of limited biological oxidative nitrification in anaerobic environments. A fraction of fixed N is continuously removed from the N pool as sedimentary deposits, which is ultimately transported to the mantle via subduction through time (Figure 2).

Because how the sedimentary N deposition rate changed through time is poorly constrained, we simply parameterized the flux as,

\[
F_{\text{sed}}(t) = F_{\text{sed},0} \times 10^{C_{\text{sed}} (t - t_0)/0},
\]

where \( t_0 = 4.5 \) Gyr, \( F_{\text{g}} \) is the sediment deposition (N burial) flux on modern Earth (0.455 PAN/Gyr, Stüeken, Kipp, Koehler, Schwieterman, et al., 2016) and \( C_{\text{sed}} \) is the power-law parameter and can be either positive or negative. This parameterization does not require explicit modeling of the size of biosphere, which influences surficial N cycling, but we discuss the implications for the early biosphere by utilizing the obtained values of \( C_{\text{sed}} \) (Section 4.2). The majority of sediments is deposited onto continental shelves (modeled as a part of the continental crust), and the rest onto the oceanic crust as pelagic sediments. We assumed the fraction of pelagic sediments, \( f_{\text{pel}} \), to be 0.038 (Berner, 1982; Stüeken, Kipp, Koehler, Schwieterman, et al., 2016).

Sedimentary N can be incorporated into rocks after deposition. This process was not explicitly included in our model as the crust and overlying sediments are treated as a single reservoir, but it was implicitly considered as an internal process.

Because there exists an isotopic disequilibrium within the N cycle (Cartigny & Marty, 2013), a successful recycling model should take into account the evolution of the surficial N cycle which controls the net fractionation factor between atmospheric and sedimentary N. The net isotopic fractionation factor from the atmosphere to the sediments was modeled as occurring over four stages.

In Period 1 (>3.2 Ga), \( \Delta^{15}N = -9\%e \) was assumed (by definition, \( 10^3 \ln a_{\text{sed}} = \Delta^{15}N \)). This was motivated by lower mean \( \delta^{15}N \) values (\( -3.6\%e \)) of organic matter in the Eo-paleoarchean (e.g., Marty & Dauphas, 2003; Shen et al., 2006). The adapted factor (\( \sim -9\%e \)) is the lowest value of the sedimentary record (assuming \( \delta^{15}N = 0\%e \) for the atmosphere) as well as the value typically expected for abiotic N-fixation via lightning or photochemistry (Kuga et al., 2014; Moore, 1977; Navarro-González et al., 2001; Stüeken et al., 2021). Anaerobic processing after N fixation (and thus absence of nitrate) was implicitly assumed in this stage, as we did not consider \( ^{15}N \) enrichment due to denitrification. Abiotically fixed, \( ^{15}N \)-depleted ammonia (Moore, 1977; Navarro-González et al., 2001) would have been consumed by chemosynthetic bacteria in hydrothermal systems under anaerobic conditions in this period (Shen et al., 2006).

In Period 2 (3.2–2.75 Ga), \( \Delta^{15}N = 0\%e \). The environment is still anaerobic, but biotic N fixation (diazotrophy) began and became the major source of bio available N in this period (Stüeken et al., 2015).

During Period 3 (2.75–2.4 Ga), \( \Delta^{15}N = +10.8\%e \). Aerobic N cycling (coupled nitrification, denitrification, and assimilation) started in this period (Garvin et al., 2009). Dissimilatory denitrification leads to residual nitrate being kinetically enriched in \( ^{15}N \), and the isotopically enriched nitrate is then reduced to ammonium and converted
to organic matter and finally trapped in sediments (e.g., Stüeken, Kipp, Koehler, & Buick, 2016). Larger N fractionation as recorded in organic matter compared to the modern value can be explained by limited amounts of nitrate (Shen et al., 2006). In Period 4 (<2.4 Ga), Δ\(^{15}\)N = +6‰. The isotopic shift during nitrification-denitrification-assimilation would have decreased to the modern average value due to the formation of a sizable global nitrate pool (Shen et al., 2006).

### 2.3.2. Continental Weathering

Continental N is gradually transported to the oceanic crust via weathering. The weathering flux is assumed to be proportional to \( M_{cc} \) as,

\[
F_{\text{wea}} = \frac{M_{cc}}{\tau_{\text{wea}}},
\]

where \( \tau_{\text{wea}} \) is the timescale of weathering. The timescale depends on atmospheric O\(_2\) partial pressure, and here modeled as (Johnson & Goldblatt, 2018),

\[
\tau_{\text{wea}} = \tau_{\text{wea,0}} \cdot \left[ a_{\text{wea}} + (1 - a_{\text{wea}}) \frac{P_{\text{PAL}O_2}}{P_{\text{PAL}O_2} + k_{\text{wea}}} \right]^{-1},
\]

where \( \tau_{\text{wea,0}} \) is the weathering timescale on modern Earth (\( \tau_{\text{wea,0}} = 0.3 \) Gyr), \( P_{\text{PAL}O_2} \) is the atmospheric O\(_2\) partial pressure scaled to present atmospheric levels for which we used the model of Johnson and Goldblatt (2018) developed based on geochemical reconstruction (e.g., Lyons et al., 2014), \( a_{\text{wea}} \) is the fraction of available material weathered under anoxic conditions (\( a_{\text{wea}} = 0.1 \)), and \( k_{\text{wea}} \) is the weathering constant (\( k_{\text{wea}} = 10^{-3} \)), respectively (Johnson & Goldblatt, 2018). The dependence on \( P_{\text{PAL}O_2} \) is not critical for the surface-mantle N exchange, but it is important to reproduce the Archean low \( P_{N_2} \) record (Marty et al., 2013; Som et al., 2012, 2016, see Section 3.2).

### 2.3.3. Subduction, Arc Volcanism, and Continental Growth

Sedimentary N on the oceanic crust is eventually conveyed to subduction zones. N is then either returned to the atmosphere via arc volcanism (\( F_{\text{arc}} \)), incorporated into the continental crust (\( F_{\text{ccg}} \)), or transported to the mantle (\( F_{\text{sub}} \)). We modeled these fluxes as,

\[
F_{\text{sub, tot}} \equiv F_{\text{sub}} + F_{\text{arc}} + F_{\text{ccg}} = \frac{M_{cc}}{\tau_{\text{sub}}},
\]

where \( \tau_{\text{sub}} \) is the subduction timescale. We assumed \( \tau_{\text{sub}} = 0.1 \) Gyr, following Stüeken, Kipp, Koehler, Schwieterman, et al. (2016). Fast plate tectonics on early Earth, which leads to the short \( \tau_{\text{sub}} \), was assumed in the past, but recent studies suggest that the plate speed is nearly constant through time (Bradley, 2008; Condie et al., 2015; Korenaga, 2003, 2018; Pehrsson et al., 2016).

We note that hydrothermal addition of N to the oceanic crust is not explicitly included in our cycling model. In reality, N in the altered crust can also transport N to the mantle (Halama et al., 2014; Johnson & Goldblatt, 2018; Mitchell et al., 2010). However, this N in the altered crust is likely sourced from sedimentary organic material deposited to the crust (Halama et al., 2014), and thus the conversion does not change the global N balance.

The ratio \( F_{\text{sub}} : F_{\text{arc}} : F_{\text{ccg}} \) (\( 1 - f_{\text{arc}} - f_{\text{ccg}} : f_{\text{arc}} : f_{\text{ccg}} \)) is highly uncertain (Catling & Zahnle, 2020; Johnson & Goldblatt, 2018). We evaluated \( f_{\text{arc}} \) and \( f_{\text{ccg}} \) as follows. First, we assumed \( f_{\text{arc}} = f_{\text{ccg}} \), following Johnson and Goldblatt (2018). Then, We evaluated \( f_{\text{ccg}} \) by considering the mass balance. Assuming a steady state for \( M_{cc} \) and \( M_{oc} \) leads to,

\[
M_{cc} = F_{\text{sed}} \tau_{\text{wea}} \left( \frac{1}{1 - f_{\text{ccg}}} - f_{\text{pel}} \right), \quad M_{oc} = \frac{F_{\text{sed}} \tau_{\text{sub}}}{1 - f_{\text{ccg}}},
\]

provided the short \( \tau_{\text{wea}} \) after the GOE and \( \tau_{\text{sub}} \) the steady state assumed here to evaluate \( f_{\text{ccg}} \) is shown to be valid with our cycling model where the time evolution is explicitly solved (Section 3.2). In order to reproduce the
modern $M_{cc}$ and $M_{oa}$ (Table 1) with Equation 13, $f_{ccg}$ needs to be $\approx 0.5$. Thus, we assumed $f_{ccg} = f_{ac} = 0.45$, and the rest, $1 - f_{ccg} - f_{ac} = 0.1$, is transported to the mantle.

2.3.4. Mantle Degassing

The flux of volcanic N degassing from the mantle with time depends on the mantle N content, $M_{ma}$, the thermal evolution (Keller & Schoene, 2018; Korenaga, 2018), and the redox state (Mikhail & Sverjensky, 2014; Zerkle & Mikhail, 2017) which might have become oxidized over time (Aulbach & Stagno, 2016; Aulbach et al., 2019; Nicklas et al., 2018, 2019).

We parameterized the volcanic degassing flux from the mantle as,

$$F_{vol} = \frac{M_{ma}}{\tau_{vol}},$$

where $\tau_{vol}$ is the degassing timescale, which was parameterized as,

$$\tau_{vol} = \tau_{vol,0} \times 10^{C_{vol}(t - t_0)/\gamma},$$

the power-law parameter, $C_{vol}$, can be either positive or negative. The mantle N degassing timescale, $\tau_{vol,0}$, on modern Earth was estimated from the mean value of the estimates of modern mantle N content 1.47 PAN (Table 1) divided by the modern N degassing flux (0.018 PAN/Gyr, Busigny et al., 2011).

2.3.5. Initial Conditions, Parameters, and Classification of Results

We performed Monte Carlo simulations to find parameter sets which satisfy the constraints on N masses and isotopic compositions of present reservoirs (Table 1). The model runs which are consistent with these observations are hereafter called “accepted runs.” The Monte Carlo simulations were repeated until 100 accepted runs were found; this typically required $10^6$ trials. In accepted runs, we classified those with $M_{ma}(t = 0 \text{ Ga}) \times 0.5 > M_{ma}(t = 4.5 \text{ Ga})$ as “accepted recycling-origin runs,” and the others as “accepted primordial-origin runs.”

There are five Monte Carlo parameters. The total N content is varied from 1.844 to 3.964 PAN (Table 1). The initial mantle N content is from 0 PAN to the total N content. The N isotopic ratio of initial mantle is from $-40$ to $0\%$ as found in enstatite chondrites (Piani et al., 2020, and references therein). We note that such low $\delta^{15}$N values have been reported for some rare diamonds from Earth’s mantle, which possibly record the signature of Earth’s N source (Palot et al., 2012). The subduction and degassing parameters $C_{sub}$ and $C_{vol}$ are both from $-5$ to $5$.

The other parameters were fixed during the Monte Carlo simulations, but their influences were investigated separately. (a) The onset time of biological N fixation. Our nominal case assumed that biological N fixation (Phase 2) started at 3.2 Ga. This is based on the N isotope record which suggests that biological N fixation had already started by that time (Stüeken et al., 2015). Phylogenetic data also suggests that the last universal common ancestor (LUCA) had this function (Weiss et al., 2016). Thus, we tested the case where Period 2 started 4.5 Ga as another endmember. (b) The onset time of the plate tectonics. The onset time of the plate tectonics on Earth is controversial (Korenaga, 2013). In the nominal case, we assumed the initiation time for plate tectonics, $t_{pt, init}$, to be 3.5 Ga, following Johnson and Goldblatt (2018). We also tested $t_{pt, init} = 4.5$ Ga. (c) The onset time of N subduction. Our nominal case assumed $f_{ccg} = f_{ac} = 0.45$ and, thus, 10% of N conveyed to subduction zones is transported to the mantle. Because a hot mantle might have inhibited N subduction prior to 2.5 Ga (Johnson & Goldblatt, 2018), we also tested a model where $f_{ccg} = f_{ac} = 0.5$ and $f_{ccg} = f_{ac} = 0.45$ before and after 2.5 Ga, respectively. However, we find that these model variants do not differ significantly (Section 3.2).

Paleo-atmospheric pressure and $N_2$ partial pressure, $p_{N_2}$, have been constrained from geochemical and geological record (Marty et al., 2013; Som et al., 2012, 2016). These studies suggest low $p_{N_2}$ values in the Archean, which corresponds to 0.64–1.4 PAN at 3.5–3.0 Ga (Marty et al., 2013) and <0.64 PAN (assuming that $N_2$ is the dominant atmospheric gas) at 2.7 Ga (Som et al., 2012, 2016). Our model did not adapt these constraints explicitly, but we compared the accepted runs with them. Overall, we find that these low $p_{N_2}$ values are satisfied in many, but not all, accepted runs by N sequestration in the crust (as proposed by Stüeken, Kipp, Koehler, Schwieterman, et al., 2016).
3. Results

3.1. Partitioning Model

First, we studied N partitioning in the magma ocean stage to test the primordial-origin scenario. Time evolution with $t_s = 0.2$ Myrs and the total N content = 2 PAN in the oxidized case is shown in Figure 3. N was chiefly partitioned into the atmosphere owing to its low solubility (Equation A1 in Appendix A). As the magma ocean solidified, a fraction of N in the magma ocean partitioned into the solidified mantle chiefly in the form of N in the trapped melt. Because of its incompatibility (low mineral-melt partitioning coefficients, $D_N$, Table 2), the contribution of N partitioned into minerals was small. As a consequence, the mantle right after magma ocean solidification is depleted in N (the mantle N content is only $\sim 0.1$ PAN). We note that the final mantle N content in this low solubility limit is well approximated by $\frac{A_{N\text{mantle}}}{A_{\text{mantle}}} \approx p_N S N F_{\text{tl}}$ (Equation 11 of Kurokawa et al., 2021) with $F_{\text{tl}} = 0.3$ in this rapid solidification case.

Figure 4 shows the atmospheric and mantle N contents after magma ocean solidification for a range of total N content and solidification times $t_s$ in the oxidized, intermediate, and reduced cases (see text) with increasing transparency. Dashed curves show constant total-N (1.698 and 4.110 PAN). The shaded areas are the N amounts in the modern surface (the atmosphere plus continental and oceanic crust, blue) and mantle (red).
to chemically bound N in the magma (Libourel et al., 2003). The mantle N amounts in all cases were mainly attributed to trapped interstitial melt (Figure 3). The contribution of N in minerals was smaller by an order of magnitude. A shorter solidification time $t_s$ leads to a higher trapped melt fraction $F_{tl}$ and thus more N in the solidified mantle. However, our result with the shortest solidification time ($t_s = 0.2 \text{ Myrs}$) already reached the maximum value ($F_{tl} = 0.3$).

In contrast, the partitioning model reproduced the $^{36}$Ar content of the modern mantle as well as the atmosphere (Figure 5). Ar behaves similarly to N in the oxidized magma (e.g., Marty & Dauphas, 2003), and ends up with a similar degree of depletion in the mantle. The agreement between the model and observations is due to the fact that the modern mantle is depleted in $^{36}$Ar by two orders of magnitude with respect to N/$^{36}$Ar ratios compared to the current atmosphere.

To summarize, our partitioning model suggests that the mantle received only $\sim 10\%$ of the total N when the magma ocean fully solidified, unless the magma was reducing. The reduced magma ocean at the time of solidification is not supported from geophysical and geochemical studies (Armstrong et al., 2019; Badro et al., 2015; Sossi et al., 2020).

We also performed model calculations with increased total N content and found that putting the modern N content into the solidified mantle in the oxidized case ended up with 7.7–150 PAN in the atmosphere (Figure 6). The range was derived from uncertainties in the modern mantle N content $M^N_{\text{mantle}}$ and the magma ocean solidification time $t_s$. In Section 4.1, we discuss a primordial-origin scenario for the mantle N by considering the excess amount of total N, which could have been removed later by atmospheric escape processes.
3.2. Cycling Model

3.2.1. Evolution of N Contents in Reservoirs

Next, we tested the recycling origin for mantle N with our cycling model. We note that, unless otherwise stated, we refer to the results of the nominal case where we assumed the onset times of biological N fixation, plate tectonics, and N subduction to be 3.2, 3.5, and 3.5 Ga, respectively (see Section 2.3.5 for details). The evolution of N masses and isotopic ratios in the atmosphere, continental and oceanic crust, and mantle after the solidification of magma ocean was simulated with the nominal parameter set (Figure 7). Rather than directly adopting the results of the magma-ocean partitioning model, initial conditions of the cycling model were treated as Monte Carlo parameters, and we looked for parameter sets which reproduce the modern N contents and isotopic ratios in the four reservoirs. We compare the results of the two models to discuss possible scenarios for N partitioning and cycling in Section 4.

The atmospheric N contents in the runs which started from a few PAN show decline with time to reach a minimum at 2.4 Ga (the top-left panel of Figure 7). The decline is caused by sediment deposition and sequestration in the continental and oceanic crust. Notably, the constraints on $p_{N_2}$ (Marty et al., 2013; Som et al., 2012, 2016) can be satisfied by many, but not all, accepted runs. The modeled evolution curves also agree with evidence for a stable atmospheric $p_{N_2}$ reservoir over the Phanerozoic (Berner, 2006). The initiation of plate tectonics can be seen as the decline of N contents in the oceanic crust after 3.5 Ga. In contrast, the influence of subduction on the mantle N contents in the recycling-origin runs is limited before 2.4 Ga. In some primordial-origin runs, the mantle N contents even decreased in this period due to degassing.

At 2.4 Ga, which corresponds to the GOE, the rate of continental weathering increased drastically, leading to the decline of N content in the continental crust. The continental N was first transported to the oceanic crust as sediments, and then to the mantle via subduction. Owing to the return N flux via arc volcanism, the atmospheric N contents start to increase due to subduction of relatively N-rich surface N. The rate of change increases after 2.4 Ga. This is caused by enhanced continental weathering after the GOE, which leads to more N transported onto the oceanic crust, and consequently, to the mantle.

3.2.2. Evolution of N Isotopic Ratios in Reservoirs

N cycling between the reservoirs is reflected to the evolution of isotopic ratio (the top-right panel of Figure 7). In the recycling-origin runs, the atmospheric $\delta^{15}N$ values increase by $\sim +5$‰ with time prior to 3.2 Ga. This is caused by deposition of $^{15}$N-depleted sediments in Period 1 (>3.2 Ga, Section 2.3). As the net fractionation factor between the atmosphere and sediments became zero (Period 2, 3.2–2.75 Ga) to positive (Periods 2 and 3, <2.75 Ga), the atmospheric $\delta^{15}N$ values change their trend to decline with time. The minimum values at 2.4 Ga correlate with the atmospheric N contents at that time. Following the recovery of $p_{N_2}$ after 2.4 Ga, the atmospheric $\delta^{15}N$ values approach asymptote of 0‰.

The $\delta^{15}N$ values of the continental and oceanic crust showed secular increase as a result of the change in $\Delta^{15}N$ between the atmosphere and sediments deposited. The rate-determining process of the continental $\delta^{15}N$ evolution is continental weathering whose timescale is 3 and 0.3 Gyrs before the GOE and at present, respectively (Equation 11). The timescale of the evolution of the oceanic crust $\delta^{15}N$ values is determined by the subduction (0.1 Gyrs) after the onset of the plate tectonics. Because this is much shorter than the timescale of continental weathering, the oceanic crust follows the continents in terms of $\delta^{15}N$ evolution.

Mantle $\delta^{15}N$ stays constant before 3.5 Ga because no subduction is assumed in the nominal case. After the onset of the plate tectonics, these values start to increase due to subduction of relatively $^{15}$N-rich surface N. The rate of change increases after 2.4 Ga. This is caused by enhanced continental weathering after the GOE, which leads to more N transported onto the oceanic crust, and consequently, to the mantle.

We note that several primordial origin runs showed high $\delta^{15}N$ values for the atmosphere and crust initially. These are runs where the Monte Carlo code chose high initial mantle N contents, so that the mass balance led to high atmospheric $\delta^{15}N$ values to keep the bulk $\delta^{15}N$ consistent with the modern value. Because the continental and oceanic crust receives atmospheric N as sediments, their $\delta^{15}N$ values were also high earlier on. The record of the initial state is eventually lost after $\sim 1$ Gyr.

3.2.3. Monte Carlo Parameters in Accepted Runs

Histograms of Monte Carlo parameters in accepted runs are shown in the bottom panels in Figure 7. Because our model is not fully physics-based but rather conceptual, all results should not necessarily be treated as realistic.
Figure 7. Cycling model results for the nominal case where we assumed the onset times of biological N fixation, plate tectonics, and N subduction to be 3.2, 3.5, and 3.5 Ga, respectively (see Section 2.3.5 for details). Top: Evolution of masses (left) and $^{15}$N/$^{14}$N ratios (right) in the atmosphere (blue), continental and oceanic crust (purple and green), and mantle (red). Curves show accepted runs whose outcomes are consistent with modern values (shown along the right y-axis). Thick and thin curves denote accepted recycling- and primordial-origin runs, respectively. Gray boxes indicate $p_{60}$ constraints from Som et al. (2016) and Marty et al. (2013). Bottom: Histograms of Monte Carlo parameters of all accepted runs. Recycling- and primordial-origin runs are shown in red and blue, respectively.
without discussion, but these should be considered as requirements to reproduce the N contents and isotopic ratios in the modern reservoirs (see Section 4.2 for discussion on possible scenarios).

In comparing the recycling- and primordial-origin runs, the former show lower total N masses and lower initial mantle $\delta^{15}$N values than the latter. This is caused by the finite ability of the system to transport surface N without increasing the mantle $^{15}$N value too much. The low initial mantle $\delta^{15}$N values in the recycling runs (typically $-40 \text{ to } -20\%$) mean that, even they were classified as the recycling origin, the initial mantle condition matters - in terms of the isotopic composition, mantle N cannot be fully of recycling origin.

The sediment deposition parameter, $C_{\text{sed}}$ (positive and negative values mean higher and lower fluxes in earlier time, respectively), was constrained around zero, which means that sediment N burial has been nearly constant, for both recycling- and primordial-origin runs. This is reasonable for the former. Given the modern N subduction flux, $\sim0.1$ PAN/Gyr assumed in our model, it takes $\sim4$ Gyrs to transport $\sim0.4$ PAN (the lowest estimate for the modern mantle N mass) to the mantle. Lower sediment N deposition flux on early Earth (negative $C_{\text{sed}}$) would lead to less N subduction, which would not satisfy the constraints of modern mantle N content.

Why $C_{\text{sed}}$ is highly constrained even for the primordial-origin runs is not so intuitive. In order to understand this behavior, we tested an additional case where we omitted the constraints on the N masses and $\delta^{15}$N values for the modern continental and oceanic crust (Figure C1). In this case, accepted primordial-origin runs include lower $C_{\text{sed}}$ values down to $-5$, but these runs show lower N contents in the continental and oceanic crust. This result indicates that modern crustal N masses rule out low $C_{\text{sed}}$ values from the primordial-origin runs. Importantly, even in this case where the constraints on crustal N masses are relaxed, the recycling-origin runs showed their $C_{\text{sed}}$ values constrained to be around zero, indicating that sediment N deposition flux on early Earth comparable to the modern value is a robust requirement for the recycling-origin scenario.

In contrast to $C_{\text{sed}}$, the accepted degassing parameter values, $C_{\text{vol}}$ (positive and negative values mean longer and shorter earlier degassing timescale, respectively), were distributed over a wider range. This is likely because mantle degassing has a relatively minor effect on overall N cycling. The modern degassing flux of mantle N was assumed to be 0.018 PAN/Gyr (Busigny et al., 2011), which is an order of magnitude lower than the N subduction flux.

### 3.2.4. Effects of the Onset Time of Biological N Fixation, Plate Tectonics, and N Subduction

The case where we assumed the onset of biological N fixation (Phase 2) at 4.5 Ga is shown in Figure 8. There was no significant difference with the nominal case (Figure 7) in the accepted Monte Carlo parameters. However, the difference of the evolution of $\delta^{15}$N values is notable. In contrast to the nominal case showing atmospheric $\delta^{15}$N values to be $\sim+5\%$ prior to 2.4 Ga in the recycling-origin runs, the atmospheric $\delta^{15}$N values stayed nearly constant at $1-4\%$ in the early biological-N-fixation case. Because there is no net-fractionation between the atmosphere and sediments, the crustal $\delta^{15}$N values stayed equal to the atmospheric values before 2.75 Ga.

Finally, we tested two cases where we assumed the onset of plate tectonics at 4.5 Ga (Figure C2) and all subducted N was returned to the atmosphere and continental crust before 2.5 Ga due to the hotter mantle of early Earth (Figure C3). Although there were differences in the evolution of N contents in the oceanic crust and mantle, no significant difference was found in the accepted Monte Carlo parameters. This is because the most important mechanisms to determine N cycling are N storage in the crust and efficient continental weathering to cause N subduction before and after the GOE, respectively, both of which were satisfied in these variants of the nominal case.

### 4. Discussion

#### 4.1. The Origin of Mantle N: The Primordial Excess-N Scenario

In Section 3.1, we suggested that magma ocean solidification led to depletion of N in the mantle, unless the magma ocean was reducing (Figure 4). Both high pressure experiments (Armstrong et al., 2019; Sossi et al., 2020) and coupled geochemical and geophysical constraints (Badro et al., 2015) point to Earth’s magma ocean at the time of solidification being close to or more oxidizing than IW-1. Therefore, we rule out a scenario that reducing conditions led to the primordial origin of N in the mantle, and focus on the oxidized magma ocean condition.
Figure 8. Cycling model results for the case where we assumed Phase 2 (biological N fixation) started 4.5 Ga, while the other settings are the same as in the nominal case (Figure 7). See Figure 7 caption for details.
A possibility we should consider is that primitive Earth right after core-mantle separation might have a higher bulk N content than it currently does, and thus even preferential partitioning into the atmosphere in the oxidized magma ocean condition could end up with an amount of N remaining in the mantle sufficient to match modern observed values. If this were the case, the early atmosphere would have an excess amount of N of 7.7–150 PAN in the oxidized case (Section 3.1 and Figure 6). We name this case the primordial “excess-N” scenario as a variant of the primordial origin and test whether atmospheric escape processes can remove the excess N in the atmosphere.

We estimated the $^{15}$N-enrichment effect due to extreme ultraviolet (EUV)-driven escape and solar wind-induced ion pickup to see how much atmospheric N should be removed to end up with $\sim +6\%e$ $^{15}$N-enrichment in the remnant 1 PAN atmosphere (Figure 9, see Appendix D for model details). We found that these processes can remove only 0.5 PAN at most even assuming an EUV level 500 times higher than at present, which is significantly smaller than the excess atmospheric N estimated above. This level of EUV corresponds to so-called fast-rotating young Sun model, but previous studies focusing on volatile contents on Venus (Lammer, Leitzinger, et al., 2020; Lammer, Scherf, et al., 2020) and the Moon (Saxena et al., 2019) concluded that the EUV level of the young Sun is likely to be less active than a moderate rotator, whose EUV level was $\approx 100$ times that of the current Sun. For this EUV level, neither $^{14}$N nor $^{15}$N can be removed by EUV-driven escape. Moreover, the contribution of solar wind-induced ion pickup should be limited to 0.01 PAN, otherwise the atmosphere would have excess $^{15}$N.

Next we estimated how much N can be removed by atmospheric erosion due to late accretion impacts, using the model of Sakuraba et al. (2019) (Figure 10, see Appendix E for model details). Impact erosion does not fractionate isotopes, as it removes the bulk atmosphere well below the homopause. However, we found that impact erosion cannot remove the excess N (7.7–150 PAN) with the minimum estimate of the late accretion mass (0.5 wt.% of Earth’s total mass) and N-containing impactors (such as enstatite chondrites) that have been suggested from the isotopic analysis of siderophile elements in Earth and the Moon (Dalou et al., 2017; Fischer-Gödde & Kleine, 2017; Fischer-Gödde et al., 2020; Worsham & Kleine, 2021). The excess N can be removed by completely N-depleted impactors or by a higher cumulative mass of late accreting material (Marchi et al., 2018). We note that here we assumed asteroid-belt-like impactor-size distribution which leads to efficient impact erosion. Assuming shallower size distribution (more large impactors, as proposed by Bottke et al., 2010) does not yield sufficient atmospheric loss (Sakuraba et al., 2019, 2021).
From these results shown above, we conclude that the primordial origin scenario for the mantle N is possible only if Earth at the time of magma ocean solidification had an excess amount of N (>7.7 PAN in the atmosphere), and if the N content, size distribution, and total mass of late accretion impactors allowed efficient loss of the excess N in the atmosphere to space by impact erosion. The feasibility of this model also depends on primitive Earth's total N content after major accretion and core-mantle separation. Grewal et al. (2021) modeled Earth's accretion and argued that the N content of the bulk silicate Earth (Earth minus the core, hereafter BSE) was determined by partitioning into the core and atmospheric loss during major accretion, which is incompatible with the excess-N scenario proposed here. In their model, the atmospheres on planetesimals in each stage of accretion were assumed to be lost completely. In contrast, Sakuraba et al. (2021) simulated Earth's accretion with an impact erosion model (Sakuraba et al., 2019). They showed that atmospheric loss in the main accretion stage before the late accretion is significant but not complete, and thus Earth formed with excess N, which was removed by late accretion impacts.

The excess-N and impact erosion scenario need to reproduce $^{36}$Ar/N ratios in Earth's atmosphere and mantle. The agreement of the $^{36}$Ar partitioning model results with $^{36}$Ar in the modern atmosphere and mantle (Figure 5) suggests that, in contrast to N, there was no significant excess atmospheric $^{36}$Ar at the time of solidification, requiring preferential N removal. However, impact erosion itself is not a fractionation process. A possibility to reconcile the excess-N scenario with the observed $^{36}$Ar/N ratios is late accretion of bodies having a high $^{36}$Ar/N ratio on average, as proposed for the cometary contribution to Earth's atmospheric noble gases (but not to major volatile elements: H, C, and N, Marty et al., 2016; Marty et al., 2017), while the majority of impactors would be chondritic or more dry bodies. If this was the case, even though impact atmospheric erosion itself is not a selective process, the erosion combined with the replenishment of Ar would lead to a net loss of N preferentially to Ar. This gives another constraint on the impactor composition in the primordial scenario.

4.2. The Origin of Mantle N: The Early Biogeochemical Cycling Scenario

In Section 3.2, we showed that the recycling origin scenario requires sediment N deposition rates on early Earth being comparable to that of modern Earth. The high sediment N deposition flux is, as discussed below, likely to be sustained by biotic activity.

Figure 10. Evolution of atmospheric N content during the late accretion in the primordial N-excess scenario. Green: Enstatite chondrite-like impactors. Yellow: N-depleted "dry" impactors. Initial N contents are 7.7 PAN (thin curves) and 150 PAN (thick curves), which corresponds to the atmospheric N content required to put N into the mantle comparable to the current mantle in the oxidized magma-ocean scenario (Section 3.1 and Figure 6). The horizontal blue line is the modern surface N content (the atmosphere and crust). The vertical dashed line is the minimum estimate for the cumulative mass of the late accretion. Note. that the thick green and yellow curves are largely overlapping.
A simple solution is that high sediment deposition flux at earlier times has been sustained by biological N fixation similar to as on modern Earth (as assumed in Figure 8). This scenario might be consistent with the phylogenetic study which suggests that LUCA was able to fix N (Weiss et al., 2016).

Alternatively, even if N fixation on early Earth was being sustained by abiotic processes (as assumed in the nominal case, Figure 7), biotic activity is needed to keep high N concentration in sediments. Considering the reasonable range of abiotic N fixation fluxes, adsorbed N content in sediments was estimated to be smaller by more than an order of magnitude in abiotic conditions than in modern Earth condition (~10 ppm vs. ~400 ppm, Stüeken, 2016; Busigny et al., 2011). This is the maximum estimate as it assumes that all NOx is reduced to NH$_4^+$ during hydrothermal circulation or by reaction with ferrous iron. Another study found that abiotic chemistry significantly limits the NOx abundance in the oceans (Hu & Diaz, 2019) and thus NH$_4^+$ as well. On modern Earth, the efficient NH$_4^+$ adsorption is caused by a high NH$_4^+$ concentration in pore water of anoxic sediments due to the degradation of organic matter (e.g., Stüeken, 2016). Therefore, here we suggest a scenario that the same mechanism also contributed to the high NH$_4^+$ abundance in sediments and thus efficient cycling, and that the modern mantle N was sourced by biogeochemical cycling (either biotic or abiotic N fixation and subsequent biotic processing) developed on early Earth.

4.3. Model Uncertainties and Limitation

As discussed in Section 2, Johnson and Goldblatt (2015) estimated a higher modern mantle N content (2–10 PAN) than the range assumed in our study (0.41–2.53 PAN). The higher N content is more difficult to reconcile with partitioning in the magma ocean stage. In contrast, because the proposed high-N mantle has high δ$^{15}$N values (~+5‰) comparable to modern sediments (Johnson & Goldblatt, 2015), it can be sourced by subduction of sediments after the development of the modern aerobic N cycle, if high sedimentary deposition flux is considered (as modeled by Johnson & Goldblatt, 2018). Therefore, the high-N mantle component, if confirmed, supports the recycling origin for mantle N.

Our cycling model assumes monotonic increase or decrease for the sediment deposition flux and the mantle degassing timescale for simplicity, but Earth might have experienced continuous inversions of N subduction and degassing fluxes (Zerkle & Mikhail, 2017). For instance, the N subduction flux has likely been lower and higher before and after the emergence of life as it enhances NH$_4^+$ adsorption efficiency (Section 4.2). Nevertheless, our conclusion for the requirement for the high sediment N burial rate would be valid as an averaged condition before the onset of aerobic N cycling.

Following Stüeken, Kipp, Koehler, Schwieterman, et al. (2016), we assumed that the effects of continental growth (e.g., Korenaga, 2018) on the offshore to onshore ratio of sediment burial ($f_{pel}/(1 - f_{pel})$) and on the continental weathering timescale (τ$_{wec}$) were minor. The reader is referred to Stüeken, Kipp, Koehler, Schwieterman, et al. (2016) for detailed discussion. Key assumptions of our model were that sediments are mainly deposited to the continental crust (shelves) through Earth's history ($f_{pel} ≪ 1$ and is assumed to be constant through time) and the long residence time of sediments on the continental crust before the GOE (τ$_{wec}$~1 Gyr). Thus, unless the continental fraction was extremely small in the Archean to lead $f_{pel} ~ 1$, the continental growth curve would not influence our model results and conclusions significantly. If these assumptions did not hold, the low $p_{o2}$ constraints might not be satisfied in the recycling scenario.

Our modeling followed the generally accepted inference that $^{15}$N-enriched sedimentary rocks are dominant in subduction flux of N (e.g., Bekaert et al., 2021), and thus there exists N isotopic disequilibrium between the atmosphere and mantle (Marty & Dauphas, 2003). However, Mitchell et al. (2010) argued that hydrothermally altered oceanic crust is the dominant cause of this, and it has a negative δ$^{15}$N value (~1.8‰) on average. The negative δ$^{15}$N value assumed is the case for Mariana trench (Li et al., 2007), and may not necessarily represent the mean value of the whole oceanic crust. Estimates in other studies have shown positive δ$^{15}$N values for the average oceanic crust (Bekaert et al., 2021; Busigny et al., 2011).

N isotopic fractionation in the subduction zones and in the mantle has not been fully understood, and thus not considered in our cycling model. Devolatilization during subduction leads to an increase in residual $^{15}$N of meta- morphic rocks (Haendel et al., 1986). The effect is limited on present-day Earth (Cartigny & Marty, 2013), yet its influence on N cycling through Earth's history remains to be resolved. Additionally, it is not yet known whether N
isotopes are fractionated during partial melting reactions in the mantle (Busigny & Bebout, 2013). Better understanding of N isotopic fractionation in these processes is needed to further test the recycling scenario.

Atmospheric loss processes (EUV-driven escape, ion pickup, and impact erosion) and replenishment by impactors were not coupled in our model. This would require complete modeling of atmospheric composition and of how escape rates are dependent on it, the latter of which is not available for ion pickup. A possible scenario to support the primordial origin scenario by combining those processes is that, EUV-driven escape or ion pickup first removed the large amount of excess N in the atmosphere, and then impact erosion and replenishment later erased the excess $^{15}$N signature. Though the comparable timescales of those processes (≥100 Myrs) implies that this is not the case, a future modeling study is needed to fully test this scenario.

Mineral-melt partitioning of N in the magma ocean solidification stage has not been fully understood. We used the partitioning coefficients estimated by Yoshioka et al. (2018). This estimation was based on solubility experiments involving minerals and melts coexisting with a discrete fluid phase, and it is not guaranteed whether the partitioning coefficients are applicable for lower levels of N concentration. However, our partitioning model showed that the contribution of minerals as N hosts is smaller than that of melt trapping in the cumulate by two orders of magnitude (Figure 3). Thus, unless the actual mineral-melt partitioning coefficients were more than two orders of magnitude higher, the influence of their uncertainties would be minor.

Our cycling model does not consider possible N supply from the core, but its contribution for the mantle N content seems to be limited from the following reasons. First, the N abundance in the core is too low to cause N exsolution from the outer core due to N saturation induced by cooling and inner core solidification. The N solubility in the core condition is the order of ~10 wt.% (Speelmanns et al., 2018). In contrast, geophysical constraints limit the N abundance in the core to be < 2.0 wt.% (Bajgain et al., 2019) and modeling of Earth's accretion and volatile partitioning has estimated the core N abundance to be ~10–100 ppm (Sakuraba et al., 2021), both of which are much smaller than the saturation level. Second, the N exchange at the core-mantle boundary (CMB) would be insufficient to supply N from the core to explain the modern mantle N abundance. Occasional observations of core signatures in surface lavas suggest the fraction of silicate Earth which interacted with the core at the CMB may be the order of ~1 wt.% (Hernlund et al., 2015; Lim et al., 2021). In order to estimate the maximum contribution of the core, here we assume that this fraction of silicate Earth received core N through the interaction at the CMB and released all N to the entire mantle. To explain the modern mantle N abundance (~1 ppm), the mantle portion which interacted with the core needs to contain ~100 ppm of N. Although mantle mineral-metal melt partition coefficients have not been directly measured, adapting an estimated value (~100, Speelmanns et al., 2018) leads to the required N abundance in the core side to be ~1 wt.%, which is much higher than the above-mentioned estimates (Bajgain et al., 2019; Sakuraba et al., 2021).

Our partitioning model assumed bottom-up solidification of an initially fully-molten magma ocean, but Earth might have had a long-lived (the order of ~1 Gyr) basal magma ocean (Labrosse et al., 2007), which could affect N partitioning and trapping in the mantle. Although quantitative modeling of the influence of the basal magma ocean is beyond the scope of our study, we expect that, because of the two-step processes discussed below, its primary effect is to reduce the amount of N trapped in the bulk mantle and, consequently, limit the possibility of the primordial scenario. First, the lower cooling rate of the basal magma ocean compared to that of the surficial magma ocean (the orders of Gyrs vs. Myrs) would reduce the trapped melt fraction $F_t$ (Equation 5) significantly. This effect would limit the trapped N content in the solidified mantle above the basal magma (We note that for the basal magma ocean its solidification proceeds in a top-down fashion) and the majority of N which was initially in the magma just solidified would be released into the residual basal magma ocean. In the slow-cooling limit, the trapped N content, which is determined by N partitioning into crystallized minerals, would be smaller than that in the fast-cooling limit by two orders of magnitude (see Figure 3 for comparison of N contents in minerals and in trapped melt). Second, N which concentrated in the residual basal magma ocean would ultimately be lost to the underlying core. Recent high-pressure experiments performed in graphite-undersaturated conditions (Grewal et al., 2021) have shown that the metal-silicate melt partitioning coefficient of N is ~20–30 for $\log_{10} f_t$; $\Delta IW = -2$ (the oxygen fugacity expected for the core-magma ocean boundary, Armstrong et al., 2019). As a result, the trapped N content in the bulk mantle would become smaller than that in the case of bottom-up solidification without the basal magma ocean.
4.4. Comparison With Previous Studies

Several studies on N partitioning in the magma ocean stage have concluded that Earth’s mantle N is primordial (Boulliung et al., 2020; Libourel et al., 2003), but these studies did not consider degassing upon solidification. The degassing process significantly limits N in the solidified mantle (Section 3.1), which led us to conclude that the primordial origin scenario is only possible if Earth had an excess amount of N (Section 4.1).

Labidi et al. (2020) simulated the evolution of N masses and isotopic ratios by using a two-reservoir model (the surface and mantle) where the atmosphere-sediment N isotopic fractionation factor was assumed to be constant through time. Their preferred model supported the primordial origin for mantle N. In contrast, our cycling model uses four reservoirs (the atmosphere, continental and oceanic crust, and mantle) and the isotopic fractionation factor varied with time following the evolution of surface N biogeochemical cycling, and found that the recycling origin was possible with high sedimentary N deposition rates on early Earth.

Although our N cycling model is simple compared to the two recent models (Johnson & Goldblatt, 2018; Stüeken, Kipp, Koehler, Schwieterman, et al., 2016), those most important results were reproduced: sequestration of N in the continental crust in the Archean (Stüeken, Kipp, Koehler, Schwieterman, et al., 2016) and efficient N subduction after the GOE (Johnson & Goldblatt, 2018). We note that the mechanisms are slightly different. In contrast to Stüeken, Kipp, Koehler, Schwieterman, et al. (2016) which modeled enhanced crustal weathering after the GOE as the release of N to the atmosphere, our model assumed the weathering as N-containing sediment transport to the oceanic crust, following Johnson and Goldblatt (2018). The latter treatment seems to be more consistent with the picture of global N balance which suggests high N flux from crustal rocks to sediments (Houlton et al., 2018). As a consequence, whereas weathering mainly led to increase of $p_{\text{N}_2}$ in Stüeken, Kipp, Koehler, Schwieterman, et al. (2016), our model showed efficient N subduction after the GOE. Moreover, efficient N subduction after the GOE in Johnson and Goldblatt (2018) was caused by an increase in primary biological production at the time, but in our case N transport to the mantle was the result of the release of the continental crust N, which was a product of N fixation before the GOE. This difference in the model assumption allowed our model to meet the low $p_{\text{N}_2}$ constraints (Marty et al., 2013; Som et al., 2012, 2016) in the Archean, while it was difficult with the nominal model of Johnson and Goldblatt (2018).

4.5. Implications for Sample Analysis

Our modeling of N isotopic exchange provides a methodology to distinguish primordial and recycling origins for mantle N. The recycling origin is characterized by large increase ($\geq$10‰) in the mantle $\delta^{15}$N values with time, while the primordial origin model showed more limited change (Figures 7 and 8, C1, C2, and C3). The surface (the atmosphere and crust) $\delta^{15}$N record is more complicated because they can vary owing also to N exchange between the surficial reservoirs, but combining them with the mantle trend would help constrain deep N cycling. Moreover, if the surface N cycle had already become slightly aerobic as assumed in our model (Period 3, Section 2.3), the possible minimum in $p_{\text{N}_2}$ around the time of the GOE can be informed from a kink in the surface $\delta^{15}$N values.

Given these results, constraining mantle isotopic evolution informed for example, from diamonds (e.g., Cartigny & Marty, 2013) would offer a more global picture of Earth’s N cycling and the origin of mantle N. In addition, better determination of the surface N isotopic composition and particularly more data around the time of the GOE will be useful.

4.6. Constraints From Other Volatile Elements and Isotopes

Comparison to cycling of other volatile elements is potentially useful, but care should be taken to the importance of redox control on N. Xenon (Xe) isotope studies suggest limited subduction before 2.5 Ga (Parai & Mukhopadhyay, 2018) and a higher degassing rate at the time (Marty et al., 2019). If N behaved similarly to Xe, these conditions might rule out the recycling-origin scenario. However, the crust is an additional reservoir for N to cause different evolution. Furthermore, because both the surficial and mantle redox states chiefly influence N (but not noble gases), the redox control, in addition to the different stability in their host phases, can lead decoupling of N from noble gases. Such decoupling between volatile elements has already been suggested for sulfur (S).
and Xe (Bekaert et al., 2021). Mass-independent S isotope signatures in the source of various hotspots indicate significant recycling occurred prior to 2.5 Ga (Bekaert et al., 2021; Cabral et al., 2013; Dottin III et al., 2020).

A classical interpretation for elementally depleted and isotopically fractionated Xe in Earth's atmosphere as a result of early hydrodynamic escape (e.g., Pepin, 1991) might suggest significant N loss due to the same process and support the presence of excess N. However, this interpretation is not supported by recent measurements of paleo-atmospheric Xe which revealed that Xe isotopic fractionation was progressive through time (Avice et al., 2017, 2018; Bekaert et al., 2018, 2020; Pujol et al., 2011). Rather, Xe fractionation was likely due to selective loss of Xe^+ ions caused by strong coupling with escaping H^+ ions with time (Avice & Marty, 2020; Zahnle et al., 2019).

The ^40K-^40Ar decay system gives another constraints on degassing history as well as continental growth (Guo & Korenaga, 2020; Johnson & Goldblatt, 2018; Ozima & Podosek, 2002; Pujol et al., 2013). Our cycling model showed that N masses and isotopic ratios in different major reservoirs on modern Earth can be reproduced with a wide range of the degassing parameter, C_0 (Section 3.2), but it can be constrained by ^40Ar data. Combining these volatile elements and their isotopes in a single model would be important for future studies.

4.7. Implications for Venus, Mars, and Exoplanets

Venus' atmosphere has about 3 PAN (Johnson & Goldblatt, 2015), which is comparable to BSE N content (Table 1). Whether Venus once possessed an habitable condition and an Earth-like volatile cycle is controversial (e.g., Krissansen-Totton et al., 2021; Way & Del Genio, 2020), but recent three-dimensional atmospheric simulations (Turbet et al., 2021) and accretion modeling focusing on the difference in hydrogen to carbon ratios between Earth and Venus (Sakuraba et al., 2021) suggest Venus never possessed oceans. This lack of oceans would lead to no N cycling between the surface and mantle. Because Venus' magma ocean was likely more oxidized than Earth's due to hydrogen loss to space (Wordsworth, 2016), we predict that its mantle right after magma ocean solidification was depleted in N similarly to Earth (Section 3.1). Provided that Venus and Earth have similar bulk N contents (namely that the atmosphere is the major reservoir of N for Venus), the comparison with Venus may suggest that N recycling operating only on Earth differed the distribution of N on the two planets. Alternatively, the different distribution might be caused by the cumulative effect of possible active volcanism on Venus. Constraining Venus' volcanic activity with future missions (e.g., ESA's EnVision and NASA's VERITAS and DAVINCI+, D'Incecco et al., 2021) may provide better understanding of the partitioning and cycling of N on Venus.

Prolonged N degassing on Mars has been suggested from the atmospheric ^15N/^14N ratio being close to the steady state between atmospheric escape and degassing (Kurokawa, Kurosawa, & Usui, 2018; Lammer, Scherf, et al., 2020). Mars' small size might have led to a more reducing condition than Earth during its magma ocean stage (Armstrong et al., 2019). Our partitioning model predicted ≥10% of bulk N can be partitioned into the mantle in the reduced case (Section 3.1). While N recycling driven by plate tectonics has been absent at least since ~4 Ga on Mars (e.g., Grott et al., 2013), the N-rich mantle might have contributed to prolonged degassing. The atmospheric neon abundance which is likely in balance between atmospheric escape and mantle degassing also suggests abundant volatile elements in Mars' mantle (Kurokawa et al., 2021).

Our study suggests that the p_N2 of extrasolar rocky planets in habitable zones may provide useful constraints not only on present climate (Vladilko et al., 2013; Wordsworth & Pierrehumbert, 2014) but also on the biogeochemical processes that have acted on such planets. The p_N2 of extrasolar rocky planets can in principle be constrained from future observations (e.g., Schwieterman et al., 2015; Stüeken, Kipp, Koehler, Schwieterman, et al., 2016) through for example, N2-N2 dimer absorption, collision-induced absorption involving N2, and/or Rayleigh scattering slope, although the last measurement is prone to the degeneracy with other parameters. Combined with the estimates for the amount of N that a planet initially accreted and the amount that has escaped to space, a low p_N2 value may indicate efficient subduction of N, which may be attributed to active tectonics (which may not necessarily Earth-like plate tectonics but can be mobile lid and episodic resurfacing e.g.,) with liquid water and perhaps biological N cycling. It would be interesting to look at the p_N2 of multiple rocky planets in the same system whose building blocks can be reasonably considered to be similar; they may show interesting diversity in the p_N2 depending on their evolution, similar to the case of Venus, Earth and Mars. Our model for the recycling origin scenario for mantle N implies that the p_N2 of planets with active tectonics and an anoxic atmosphere anti-correlates with...
their age, which can be tested with future observations. In this manner, understanding the origin of Earth’s mantle N and the surface environments of extrasolar rocky planets is linked with each other.

5. Conclusions

Two hypotheses for the origin of N in Earth’s mantle were tested with numerical models constrained by Ar and N isotopes. Our model results for N partitioning in the magma ocean stage constrained by Ar showed that low solubility and low partition coefficients between minerals and silicate melts leads to N depletion in the solidified mantle unless the magma ocean was reducing. The highly reducing magma ocean model may be relevant to Mars which shows indirect evidence of prolonged degassing of N, but it is not favored for Earth from high pressure experiments or geochemical and geophysical constraints. Modeling of impact erosion and isotopic fractionation via EUV-driven escape and ion pick up suggests that the excess atmospheric N, which is required to put sufficient N into the mantle as comparable as the minimum estimate for the modern mantle, can be removed only when efficient net removal is assumed. Our model results for N cycling between surface reservoirs and mantle constrained by N isotopes showed that sequestration of N into the crust before the GOE and subsequent efficient weathering and subduction after the period could have sourced N to the modern mantle. This recycling origin scenario requires high sedimentary N burial flux on early Earth, which was likely sustained by biotic N utilization. The two hypotheses can be tested by analyzing the surface and mantle N isotope record. Unveiling the origin of Earth’s mantle N is linked with understanding the difference in N contents with Venus and the evolution of surface environments of extrasolar rocky planets.

Appendix A: N Solubility Model

We developed a model for N solubility as a function of the oxygen fugacity and the N partial pressure. Solubility data measured by Boulliung et al. (2020) for the terrestrial magma ocean-like composition (MO2) were fitted by the sum of two terms following Libourel et al. (2003) as (Figure A1),

\[
S_N \text{[ppm \cdot atm}^{-1}] = 10^{-0.6934 \log_{10} f_{O_2,\Delta IW\text{-}1} + 1.7002 \left( \frac{p_{N_2}}{1 \text{ atm}} \right)^{\frac{1}{2}}} + 0.2. \tag{A1}
\]

the first and second terms denote chemical and physical solubilities dominant under reducing and oxidizing conditions, respectively (Bernadou et al., 2021; Libourel et al., 2003). The first term was given with the least squares method for \(\log_{10} f_{O_2,\Delta IW}< -1.5\) data, assuming \(p_{N_2}^{1/2}\) dependence (Boulliung et al., 2020). The second term was given to much the data point for the oxidized limit (\(\log_{10} f_{O_2,\Delta IW} = +4\)).

![Figure A1. N solubility model used in this study (Equation A1, purple curve). Two terms in the fitting formula are also shown (fitting curves 1 and 2, red and yellow lines). Original data are from Boulliung et al. (2020) (Blue points).](image-url)
Appendix B: Derivation of Equation 1

The equation for the solubility equilibrium between the atmosphere and the magma ocean (Equation 1) is derived from those for hydrostatic equilibrium, the ideal gas, and the definition of solubility, which are given by,

\[
\frac{dp}{dz} = -\rho_{atm} g, \tag{B1}
\]

\[p_i = n_i k_u T = \rho_i k_u T / m_i, \tag{B2}\]

and,

\[p_i = \frac{x_i}{S_i}, \tag{B3}\]

where \(z, \rho_{atm}, n_i\), and \(x_i\) are the height from the surface, the density of atmospheric gas, the number density of species \(i\), and the mass fraction of species \(i\) in the magma ocean, respectively. From Equations B1 and B2, we obtain,

\[
\frac{d}{dz} \left( \frac{n}{n_i} p_i \right) = -\frac{n}{n_i} \frac{\bar{m}}{m_i} \rho_i g. \tag{B4}\]

assuming the mixing ratio \(n/n_i\) to be constant in the atmosphere, Equation B4 can be integrated analytically to lead,

\[p_i(z = 0) = \frac{\bar{m}}{m_i} \frac{M_{atm}}{A} g. \tag{B5}\]

we can rewrite \(M_{\text{ino}}\) using Equations B3 and B5 and obtain,

\[M_{\text{ino}} = x_i M_{\text{ino}} = \frac{\bar{m}}{m_i} \frac{M_{\text{ino}}}{A} g \cdot S_i \cdot M_{\text{ino}}. \tag{B6}\]

finally, substituting Equation B6 into Equation 2 leads to Equation 1.

Appendix C: Supplementary Results of the Cycling Model

Figure C1 shows the result of the nominal model runs without the constraints on the crustal N masses and isotopic ratios. Figures C2 and C3 show the variants of the nominal model, where we assumed the onset time of plate tectonics to be 4.5 Ga (Figure C2) and the initiation of N subduction at 2.5 Ga (Figure C3), respectively.
Figure C1. Cycling model results for the case where we omitted the constraints on the N content and isotopic ratios of the modern continental and oceanic crust, while the other settings are the same as in the nominal case (Figure 7). See Figure 7 caption for details.
Figure C2. Cycling model results for the case where the plate tectonics started at 4.5 Ga, while the other settings are the same as in the nominal case (Figure 7). See Figure 7 caption for details.
Figure C3. Cycling model results for the case where N subduction started 2.5 Ga, while the other settings are the same as in the nominal case (Figure 7). See Figure 7 caption for details.
Appendix D: Atmospheric Escape Models

The isotopic fractionation factor, defined as,

\[ f \equiv \frac{F_{15N}/F_{14N}}{[15N]/[14N]}, \]  

was estimated for EUV-driven hydrodynamic escape and solar wind-induced ion pickup, where \( F_i \) is the escape flux. Then we estimated the amounts of N removed by the escape processes \( M_{\text{lost}} \) to enrich the remnant atmosphere (1 PAN) in \( \Delta^{15}N = +6\% \) (Figure 9), using the Rayleigh dissolution equation,

\[ M_{\text{lost}} = \left( \frac{1}{1 - 10^{-3} \times \Delta^{15}N} \right)^{1/3} - 1 \text{ [PAN]}. \]  

Escaping hydrogen drags \( ^{14}N^{14}N \) and \( ^{15}N^{14}N \) mass-dependently, and causes isotopic fractionation. The fractionation factor for hydrodynamic escape was estimated using a model of Lammer, Leitzinger, et al. (2020). In the model, the radii of visible- and EUV-photospheres are estimated with their Equations 5, 11 and 12. Then escape fluxes of hydrogen and other minor species are computed with their Equations 10, 14 and 15. For simplicity, we assumed that the model proto-Earth had a \( H_2 \) plus \( N_2 \) atmosphere, whose mass is \( 10^{-3} \) times Earth’s mass. The mixing ratio of \( N_2 \) was assumed to be \( 10^{-3} \) considering a primordial dense \( H_2 \) atmosphere. We assume skin and upper atmospheric temperatures to be 255 and 400 K (Watson et al., 1981), respectively. The binary diffusion coefficient between \( H \) and \( N \) was taken from Zahnle and Kasting (1986). EUV luminosity of the young Sun was taken to be a parameter, and is expected to be 30–500 times the present-day value during the first 100 Myrs, depending on its rotation rate (Tu et al., 2015).

Ion pickup by the solar wind removes N from the exobase level, where heavier \( ^{15}N \) is depleted due to diffusive separation. The fractionation factor was estimated by adapting an isothermal, hydrostatic structure for both \( ^{14}N^{14}N \) and \( ^{15}N^{14}N \), given as,

\[ f = \exp \left[ \frac{GM_s \Delta m}{k_s T_{\text{exo}} r_{\text{homo}}} \left( \frac{r_{\text{homo}}}{r_{\text{exo}}} - 1 \right) \right], \]  

where \( G \) is the gravitational constant, \( k_s \) is the Boltzmann constant, \( \Delta m \) is the mass difference between \( ^{14}N^{14}N \) and \( ^{15}N^{14}N \), \( T_{\text{exo}} \) is the exospheric temperature, and \( r_{\text{homo}} \) and \( r_{\text{exo}} \) is the radii of homopause and exobase, respectively. We assumed \( T_{\text{exo}} = 10^3 \) K, \( r_{\text{homo}} = R_E + 100 \) km, and \( r_{\text{exo}} = 12.7R_E \) (Lichtenegger et al., 2010; Tian et al., 2008).

Appendix E: Impact Erosion Model

Atmospheric loss by impact-induced atmospheric erosion during late accretion was calculated by using the model of Sakuraba et al. (2019) (Figure 10). The model setting is the same for the early Earth model of Sakuraba et al. (2019) except for the impactor composition and the initial N content, for the latter we assumed the estimate from our partitioning model for the oxidized magma-ocean case (7.7 PAN to 150 PAN).

Here we summarize the main feature of the impact erosion model (see Sakuraba et al., 2019, for details). The impact erosion model computes the loss and supply of volatile elements by statistically averaged impacts. Assuming the carbonate-silicate cycle, we fixed the background \( CO_2 \) partial pressure at 1 bar. A trace amount of water vapor (0.017 bar) was included assuming the saturated vapor pressure. We assumed the surface temperature to be 288 K. The results depend on the assumed temperature only weakly (Sakuraba et al., 2019, 2021).

We assumed two cases for the N content of impactors: enstatite chondrite-like impactors containing 400 ppm \( N_2 \) (Bergin et al., 2015; Hirschmann, 2016) and “dry” objects containing no N. The former is consistent with the N isotopic signatures of Earth and enstatite chondrites (Dalou et al., 2019; Piani et al., 2020). The latter is an extreme case to maximize the eroded N mass case. We did not compute the case of carbonaceous chondrite-like impactors, but they are richer in N than enstatite chondrites (e.g., Grady & Wright, 2003) so that the net effect to remove N from the atmosphere is weaker (Sakuraba et al., 2019, 2021). Isotopic signatures of siderophile elements in the mantle also point to the types of late accretion impactors containing a non-negligible amount of N, such as enstatite or carbonaceous chondrites (Dauphas, 2017; Fischer-Gödde et al., 2020).
The assumed size distribution of the impactors is \( dN(D)/dD \propto D^{-q} \) with \( q = 3 \), where \( N(D) \) is the number of objects of diameter smaller than \( D \). The minimum and maximum sizes are assumed to be \( D = 10^{-15} \) km and \( 10^3 \) km, respectively. A steeper size distribution (larger \( q \)) leads to more efficient impact erosion. The assumed size distribution is similar to that of the asteroid belt (Bottke et al., 2005), and is likely an upper limit for \( q \) (see, Sakuraba et al., 2021, for discussion).

The cumulative mass of late accretion is constrained by highly siderophile element concentrations in Earth’s mantle (Chou, 1978; Marchi et al., 2018). We assumed 0.5% of Earth’s mass as a minimum estimate, but calculated up to 1% to take a larger estimate into account.

**Data Availability Statement**

Data and codes to generate figures in this paper are available at https://doi.org/10.6084/m9.figshare.17128421.v1.

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