Redox control on nitrogen isotope fractionation during planetary core formation

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The present-day nitrogen isotopic compositions of Earth’s surficial (15N-enriched) and deep reservoirs (15N-depleted) differ significantly. This distribution can neither be explained by modern mantle degassing nor recycling via subduction zones. As the effect of planetary differentiation on the behavior of N isotopes is poorly understood, we experimentally determined N-isotopic fractionations during metal–silicate partitioning (analogous to planetary core formation) over a large range of oxygen fugacities (ΔIW −3.1 < log10fO2 < ΔIW −0.5, where ΔIW is the logarithmic difference between experimental oxygen fugacity [fO2] conditions and that imposed by the coexistence of iron and wüstite) at 1 GPa and 1,400 °C. We developed an in situ analytical method to measure the N-elemental and -isotopic compositions of experimental run products composed of Fe–C–N metal alloys and basaltic melts. Our results show substantial N-isotopic fractionations between metal alloys and silicate glasses, i.e., from −257 ± 22‰ to −49 ± 1‰ over 3 log units of fO2. These large fractionations under reduced conditions can be explained by the large difference between N bonding in metal alloys (Fe–N) and in silicate glasses (as molecular N2 and NH complexes). We show that the 15N% value of the silicate mantle could have increased by ~20‰ during core formation due to N segregation into the core.

The bulk silicate Earth is the largest nitrogen reservoir on Earth, containing 3 to 11 times more N (27 ± 16 × 1018 kg N) than the present-day atmosphere (4 × 1018 kg N or the present atmospheric nitrogen abundance [PAN]) (1). In particular, Earth’s mantle is estimated to contain 6 PAN (up to 24 × 1018 kg N) (1), which is 12 times more than the continental crust (0.5 PAN) (1). The 2 stable isotopes of nitrogen, 14N and 15N (99.6% and ~0.4% of present atmospheric N2, respectively), are used to trace fluxes between surface and deep-Earth reservoirs. N stable isotopic compositions are conventionally normalized to the present atmospheric value and reported as follows:

\[ \delta^{15}N[^{\text{per}}] = 1,000 \times \left( \frac{^{15}N/^{14}N_{\text{sample}}}{^{15}N/^{14}N_{\text{air}}} - 1 \right) \]  

The current N-isotopic distribution among terrestrial reservoirs shows an unexplained difference (2) between the 15N-depleted mantle [δ15N = −5 ± 2‰ in diamonds and midocean ridge basalts (MORBs) (3)] and the 15N-enriched surface [δ15N = +6‰ in sediments, and 0‰ (by definition) in the present-day atmosphere (4)]. Contrary to these observations, diffusion-controlled N2 degassing (5) of the mantle is expected to preferentially segregate 14N into the atmosphere (Graham’s law), which would enrich the mantle in 15N. Equilibrium degassing of MORBs modeled by Rayleigh distillation (5, 6) enriches the residual melt in 15N, but this fractionation is limited to 1 to 1.5‰ (7). Recycling (subduction) of surficial material is expected to increase the δ15N value of the mantle because sediments and altered continental crust are enriched in 15N (3) by biological processes (i.e., N fixation pathways and N cycling within microbial communities (e.g., refs. 8 and 9)) and metamorphism-related devolatilization of N (4), respectively. Marty and Dauphas (7) proposed that the mantle’s N-isotopic signature corresponds to that of recycled Archean sediments; this hypothesis has been actively debated (10) because the δ15N values of ancient sediments are highly variable [−6.2 to +13‰ (8)]. Hence, neither degassing processes nor recycling can explain the mantle’s N-isotopic signature relative to the atmosphere (3).

An alternative explanation of the mantle’s N-isotopic signature is the heterogeneous accretion of the Earth from materials with δ15N values as low as −40‰ (11), the lowest value measured on Earth in deep diamonds (12). Indeed, the low δ15N values of enstatite chondrites [−45 to −15‰ (13)] compared with carbonaceous chondrites [+15 to +55‰ (14)] suggest an enstatite chondrite origin of Earth’s nitrogen (11, 12). After accretion, planetary differentiation processes could have modified the initial N budget and isotopic signature of the mantle. Core–mantle differentiation, magma ocean solidification/crystallization, and magma ocean degassing are key stages of early planetary evolution. These 3 processes could potentially result in N-isotopic fractionations.

Significance

The origin and evolution of Earth’s nitrogen is often discussed by comparing the large variation of N-isotopic compositions among Earth’s building blocks (chondrites) to the signatures of various terrestrial reservoirs. Here, we demonstrate that planetary differentiation processes, such as core formation, may have significantly modified the N-isotopic composition of the proto-Earth. During core–mantle differentiation, a significant amount of isotopically light N entered Earth’s core, producing an isotopic fractionation much larger than has been observed for other geochemo-tracers of core formation. The magnitude of N-isotopic fractionation varies significantly as a function of the redox history of the early Earth. Therefore, distinct N-isotopic ratios among Earth’s reservoirs or between planetary bodies may reflect different planetary evolution processes as opposed to different N sources.

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fractionations sufficient to explain the large differences in current $\delta^{15}$N values among the distinct terrestrial reservoirs (3).

Recent studies have revealed that a significant fraction of N could have been segregated into the core during the late stages of core formation (15–22). Investigation of the effect of core formation on the evolution of the bulk mantle $\delta^{15}$N value requires knowledge of the N-isotopic fractionation factors between metal and silicate phases. Li et al. (16) measured the $\delta^{14}$N/$\delta^{15}$N fractionation between metal and basaltic glasses ($\delta^{15}$N$_{\text{metal-silicate}} = 6^{15}$N$_{\text{metal}} - 6^{15}$N$_{\text{silicate}}$) at 1.5 to 7 GPa and 1,600 to 1,800 °C. They showed that during metal–silicate segregation, the silicate melt is enriched in $^{15}$N by 3.5 ± 2.5‰ relative to the coexisting liquid Fe–C–N metal alloy. These experimental results are consistent with an equilibrium isotopic fractionation, which causes the lighter isotope to be enriched in the reduced phase (23). However, the large uncertainties on their isotopic fractionation factors (typically 2.5‰) preclude any definitive conclusion on the effect of metal–silicate N segregation. Additionally, the relatively narrow range of oxygen fugacities (FO$_2$ reported as the logarithmic difference between experimental FO$_2$ conditions and the iron–wüstite buffer [IW]) explored by Li et al. [ΔIW = −0.11 to −0.35 (16)] presumably corresponds only to the latest stage of core–mantle differentiation (24). Although the FO$_2$ conditions in Earth's core formation are still debated (e.g., refs. 25–27), recent modeling acknowledges that the Earth accreted from highly reduced materials (typically around ΔIW ≈ 5) and that its FO$_2$ increased throughout the late stages of accretion and core–mantle differentiation (reaching ΔIW = 2 to ΔIW during the late stages of the magma ocean; refs. 24, 26, and 28).

Recent studies have shown FO$_2$ to be the main control on N partitioning during metal–silicate segregation (15–22) because it determines the N speciation in the silicate phase (17, 29). N speciation, in turn, is expected to dictates $\Delta^{15}$N$_{\text{metal-silicate}}$ (29). The magnitude of isotopic fractionations is proportional to the difference in bond stiffness and vibration modes between equilibrated phases (30, 31), i.e., $\Delta^{15}$N$_{\text{metal-silicate}}$ is determined by the bonding of N in the metal (as Fe–N) and silicate melt [as N–N vs. N–H complexes depending on FO$_2$ conditions (29)]. Therefore, FO$_2$ is expected to play a fundamental role in the evolution of the $^{15}$N value of Earth’s mantle, and thus in the establishment of the observed difference between surficial and deep N-isotopic signatures.

In this study, we investigated the redox effect on N-isotopic fractionation during metal–silicate N partitioning in samples quenched at 1 GPa and 1,400 °C in a piston-cylinder (Laboratoire Magmas et Volcans, Clermont-Ferrand, France). We explored FO$_2$ conditions ranging from Fe–FeO equilibrium (IW) to ΔIW = –3 (i.e., 3 orders of magnitude more reducing), consistent with the inferred conditions of core formation (32). The duration of the experiments was 6 h, which is sufficient to reach compositional equilibrium (17). The starting material compositions comprised a Fe-rich haplo-basalt [similar to the Humphrey basalt composition of Dalou et al. (17) and Armstrong et al. (33)] to promote the segregation of large metal blobs under reducing conditions, and a haplo-andesite composition similar to that used by Zhang et al. (34). These mafic to intermediate compositions were chosen as analogs of planetary magma ocean compositions (35). The FO$_2$ of the samples was changed (not controlled) by adding 0.5 to 4 wt% SiO$_2$ [a reducing agent (17)] to the starting compositions. To “spike” the samples in $^{15}$N, we used mixtures of Si$_3$N$_4$ and Si$_5$$^{15}$N$_4$ as the N source. Si$_{14}$N$_4$ was synthesized by Si nitridation using flowing N$_2$ in a Nabertherm 1-atm furnace, whereas isotopically enriched Si$_{14}$N$_4$ (~95% $^{15}$N) was prepared as described by Leonova et al. (36). Mixtures of Si$_3$N$_4$ and Si$_5$$^{15}$N$_4$ were used to obtain variable initial $\Delta^{14}$N/$\Delta^{15}$N ratios (between 0.1 and 8; Table 1) in the starting materials to assess the effect of $^{15}$N spiking. Experimental procedures are described in SI Appendix, section S1.

Silicate- and Metal-Phase Nitrogen Analyses

Previous studies of N partitioning between metal and silicate phases (15, 17–22, 38) presented N abundance data obtained by electron probe microanalysis (EPMA). This in situ analytical method allows measuring N contents in metal alloys and silicate glasses in a polished section of an experimental charge with a detection limit as low as 0.03 wt% (17, 29) but is not adapted to isotopic measurements. Noble gas mass spectrometry enables bulk N-isotopic analyses (16) but, in our case, can only provide phase-specific isotopic compositions if the silicate glass and metal blobs are physically separated and measured independently, a challenging task depending on the sample texture (SI Appendix, Fig. S1).

We thus developed a method for in situ measurement of the N concentrations and isotopic compositions of quenched silicate and metal alloy phases by secondary ion mass spectrometry (SIMS) using the CAMECA IMS 1280 HR2 and 1270 at the Centre de Recherches Pétrographiques et Géochimiques (Nancy, France). Following the analytical protocol of Füri et al. (40), nitrogen isotopes in silicate glasses were measured with the IMS 1280 HR2 by spot analyses of $^{14}$N$_{\text{O}}$ and $^{15}$N$_{\text{O}}$ secondary molecular ions at mass numbers 30 and 31, respectively, at a nominal mass resolution m/Δm = 14,000 using a Cs+ primary ion beam with a current of ~10 nA. A suite of reference glasses with known $^{14}$N contents (40, 41) was used to determine the nitrogen concentration of each sample based on the $^{14}$N/$^{15}$N count rate normalized by the $^{14}$O$_2$ signal (SI Appendix, section S1).

The nitrogen and carbon abundances and $^{14}$N/$^{15}$N and $^{12}$C/$^{13}$C ratios of metal phases were measured on the IMS 1270 using a Cs+ primary ion beam with a current of ~2.4 nA. The size of the primary beam was set to ~5 μm to analyze metal blobs 10 to 65 μm in diameter. Carbon concentrations were measured as $^{12}$C$^{12}$C+ ions, whereas nitrogen isotopes were measured as $^{14}$N$^{14}$N+ at mass numbers 26 and 27, respectively, with a mass resolution of 8,000. Nitrogen elemental abundances were determined using the $^{12}$C$^{14}$N/$^{12}$C$^{12}$C ratio (42, 43). Owing to the low Si solubility in metals at the studied pressure–temperature (P–T) and FO$_2$ conditions (17), $^{28}$Si$^{16}$ was analyzed to monitor for potential silicate contamination during analyses. In parallel to the SIMS measurements, the nitrogen contents and $^{15}$N/$^{14}$N ratios of reference silicate glasses (40) and metal reference materials were determined independently by noble gas mass spectrometry (SI Appendix, section S1). The use of $^{14}$N-spiked samples allowed us to determine the $^{14}$N/$^{15}$N ratios in the silicate and metal phases with average analytical uncertainties of 0.1‰ and 5.5‰, respectively. However, this uncertainty reached 91‰ for metal alloys in sample HB01, likely due to its highly heterogeneous C distribution.

Raman spectroscopic analyses were performed to determine N speciation in silicate glasses and metal alloy blobs (SI Appendix, section S1).

Sample Description

Experimental run products were composed of graphite-saturated mafic glass close to the melt composition expected during a magma ocean stage (35), coexisting with variable amounts of an iron carbide metallic phase (SI Appendix, section S1 and Fig. S1). Among the experiments run, 6 samples had metal blobs of sufficient diameter (>7 μm) to permit SIMS analysis (SI Appendix, Fig. S1 and Table 1): only the data from these samples are presented herein. Silicate melts quenched to form large glass pools that were well separated from metal domains. Both silicate glasses and Fe–C–N alloys were compositionally homogeneous at the scale of EPMA analyses (~2 μm for metals; SI Appendix, section S1 and Tables S1 and S2). Along with Fe, the Pt and Si concentrations in the metal phases of all samples were measured by EPMA, which revealed Si contents below the detection limit.
and low amounts of Pt (<0.7 wt%). The major element compositions of silicate glasses and metal alloys determined by EPMA are presented in SI Appendix, Tables S1 and S2, respectively.

Table 1 presents sample oxygen fugacities, expressed as log \( f_{O_2} \), estimated from the equilibrium reaction:

\[
\text{FeO}_{\text{silicate melt}} = \text{Fe}_{\text{liquid metal}} + 1/2 \text{O}_2. \tag{2}
\]

Following this equilibrium, the \( f_{O_2} \) of each sample was calculated according to the method described in Dalou et al. (17), i.e., using the relationship between the mole fractions of FeO in the silicate melt (\( X_{\text{FeO}}^{\text{melt}} \)) and Fe in the liquid metal (\( X_{\text{Fe}}^{\text{melt}} \)), the associated activity coefficients of FeO in the metal phase (\( \gamma_{\text{FeO}}^{\text{metal}} \)), and the equilibrium constant, \( K \), of the reaction (44):

\[
\log_{10} f_{O_2} = \frac{2}{\ln(10)} \left( \ln \left( \frac{X_{\text{FeO}}^{\text{melt}}}{X_{\text{Fe}}^{\text{melt}}} \right) - \ln \left( \gamma_{\text{FeO}}^{\text{metal}} \right) + \ln \left( \gamma_{\text{Fe}}^{\text{metal}} \right) - \ln K \right). \tag{3}
\]

As described by Dalou et al. (17) and Grewal et al. (21, 22), we accounted for the effect of N and C on \( \gamma_{\text{FeO}}^{\text{metal}} \) by extending the Wagner ε formalism (45) for nonideal interactions in liquid Fe alloys (46) via the MetalAct metal activity calculator (47), and we assumed \( \gamma_{\text{Fe}}^{\text{metal}} = 1.2 \) (48). Moreover, to permit direct comparison with the IW buffer, which is referenced to solid Fe metal, the activity coefficient of Fe was adjusted following the method of Stanley et al. (49). Finally, the resulting \( f_{O_2} \) was compared with the IW buffer as determined by Zhang et al. (50). This calculation was applied to our samples and all literature data presented for comparison in the figures. The \( f_{O_2} \) of our samples spanned from \( \Delta IW \approx -0.45 \) to \( -3.13 \).

We observed a significant loss of N (up to 75%) between the N added to the starting material and the total N measured in our experimental products. Speelmanns et al. (19, 20) observed a similar N loss during their experiments and suggested that N was lost to the graphite capsules enclosing their samples. Nonetheless, no significant difference in N loss is observed in N-partitioning experiments using single graphite (this study) or double platinum–graphite capsules (22). The samples showed no signs of vapor bubbles in the silicate glasses or metal alloy blobs. Although we cannot rule out the possible presence of submicroscopic bubbles in these phases, we assume that our experiments were N-vapor saturated and that N was lost to pores in the graphite capsules during the experiments. Therefore, the measured elemental and isotopic N fractions between the metal and silicate phases occurred in an open system. The effect of N loss on N-isotopic fractionation is discussed in the following section.

The reported N and C contents and N-isotopic ratios and their associated SDs (2σ) were averaged from 2 to 6 analyses per sample (SI Appendix, Tables S2 and S3). Nitrogen and carbon contents in metal alloys are homogeneous within most samples, with SDs below 22% and 2% (2σ), respectively. The N contents of silicate glasses in each sample were homogeneous with a SD below 9%. As observed by Dalou et al. (17) and Füri et al. (40), the glasses contained micrometer-sized graphite inclusions, causing highly variable C signals over the course of an analysis and between distinct areas. Given that silicate glass N contents and isotopic compositions were measured as \( ^{14}N_{\text{SI}}/^{16}O_{\text{SI}} \) and \( ^{15}N_{\text{SI}}/^{14}O_{\text{SI}} \) instead of \( ^{14}C_{\text{SI}}/^{12}C_{\text{SI}} \) and \( ^{13}C_{\text{SI}}/^{12}C_{\text{SI}} \), this variability does not affect our N-elemental- and -isotopic analyses (40). In samples for which metal blobs were large enough to perform multiple measurements (up to 4 analyses in HB05 and HB3, and 6 in HB4), homogeneous N-isotopic ratios were observed across the metal blobs, with SDs below 2% (2σ; SI Appendix, Table S3). Nitrogen contents in silicate glasses and metal alloy blobs are presented in Table 1, and carbon contents in metal phases in SI Appendix, Table S2.

It is very difficult to ensure that isotopic equilibrium is attained during isotope fractionation experiments that do not allow application of the "3-isotope method" (51). At temperatures from 1,600 °C to 1,800 °C, Li et al. (16) performed a series of experiments with increasing equilibration times between 30 and 120 min to ensure that isotopic equilibrium was attained. To promote isotopic equilibrium at 1,400 °C, we extended the run periods of our experiments to 6 h. Moreover, the homogeneity of N contents and \( ^{15}N/^{14}N \) ratios of the metal blocks and silicate glasses (SI Appendix, Table S3) strongly suggests that both chemical and isotopic equilibria were attained during our experiments.

### f\(_{O_2}\) Control on N Partitioning Between Metal and Silicate Phases

Nitrogen partition coefficients between the metal and silicate phases, \( D_{\text{metal-silicate}} \), were calculated as \( D_{\text{metal-silicate}} = C_N^{\text{metal}} / C_N^{\text{silicate}} \), where \( C_N^{\text{metal}} \) and \( C_N^{\text{silicate}} \) are the average N contents (wt%) of the metal alloys and silicate glasses, respectively (Table 1).

With decreasing \( f_{O_2} \) from \( \Delta IW \approx -0.45 \) to \( -3.13 \), \( D_{\text{metal-silicate}} \) decreases from 7 ± 2 to 0.2 ± 0.2, consistent with previous experimentally determined partition coefficients (15–22, 52, 53) (Fig. 1). Despite highly variable experimental parameters between studies (melt composition, \( P \), and \( T \)), which produce scatter in the data trend (22), \( f_{O_2} \) remains the key parameter controlling N partitioning between the metal and silicate phases.
has 2 effects: it increases both melt polymerization and NH complexes (Fig. 2).

\[ \text{D}_{\text{metal-silicate}} \text{ decreases with decreasing } f_\text{O}_2 \text{ due to the stabilization of N species in more reduced silicate melts.} \]

In glasses, Raman spectroscopic analysis revealed that nitrogen is dissolved as \( \text{N}_2 \) and NH complexes (Fe-rich basalt and andesite) are in agreement with previously published data (15). All \( f_\text{O}_2 \) values were recalculated following the procedure described in the text. Following this calculation, only 2 of the 4 samples from Li et al. (16) have log \( f_\text{O}_2 < -1 \). Error bars represent \( 2 \\text{SDs}. \) P-T conditions have only a small effect on \( D_{\text{metal-silicate}} \) and explain the scatter among the overall decreasing trend with decreasing \( f_\text{O}_2 \). Our data measured using SIMS (Fe-rich basalt and andesite) are in agreement with previously published \( D_{\text{metal-silicate}} \) values measured by EPMA.

(17). \( D_{\text{metal-silicate}} \) decreases with decreasing \( f_\text{O}_2 \) due to the stabilization of N species in more reduced silicate melts (17).

In glasses, Raman spectroscopic analysis revealed that nitrogen is dissolved as \( \text{N}_2 \) and NH complexes (Fig. 2 A and B). At near-constant water content (Table 1), the ratio of NH to OH complexes (NH/OH, as determined from the Raman peak areas) increases with decreasing \( f_\text{O}_2 \) (54), reflecting the increased N solubility in silicate glasses at more reducing conditions (17, 53). We note that vibrations associated with NH complexes are more intense in the Raman spectra of Fe-rich basalt samples (noted HB) than in the andesite A05 (Fig. 2B). Increased melt polymerization is known to increase N solubility and decrease the proportion of NH relative to \( \text{N}_2 \), i.e., the NH/\( \text{N}_2 \) ratio (29, 55). Therefore, the melt structure of sample A05 (more polymerized than the Fe-rich basalt glasses) favors N dissolution in the form of \( \text{N}_2 \) rather than NH complexes (Fig. 2 A and B). Overall, decreasing \( f_\text{O}_2 \) has 2 effects: it increases both melt polymerization (due to increasing metal precipitation; SI Appendix, section S2) and the NH/\( \text{N}_2 \) ratio. Among the HB samples, we observe that the change of \( f_\text{O}_2 \) primarily controls the NH/\( \text{N}_2 \) ratio, whereas at constant \( f_\text{O}_2 \), melt polymerization governs the NH/\( \text{N}_2 \) ratio in silicate glasses (29).

Under nominally anhydrous conditions, N is assumed to chemically dissolve as nitride ions (N\textsuperscript{3-}) in reduced melts (below \( \Delta \text{IW} = 1 \)) at 1 atm (56). The vibration mode of Si-N (near 800 cm\textsuperscript{-1}) is in the range of the dominant Si-O vibrations in silicate glasses. We therefore cannot ascertain the presence or absence of nitride species in our glasses by Raman spectroscopy.

**Metal-Silicate N Isotopic Fractionation (\( \Delta^{15}\text{N}_{\text{metal-silicate}} \))**

The N-isotopic compositions of metal alloys (\( ^{15}\text{N}/^{14}\text{N}_{\text{metal}} \)) and silicate glasses (\( ^{15}\text{N}/^{14}\text{N}_{\text{silicate}} \)) in the Fe-rich basalts and haploandesites were determined via SIMS. The N-isotopic ratios, \( ^{15}\text{N}/^{14}\text{N}_p \), where \( p \) denotes the phase, were normalized to the initial \( N \)-isotopic composition of the starting material, \( ^{15}\text{N}/^{14}\text{N}_{\text{Initial}} \), which ranged from 0.09 ± 0.01 to 8.0 ± 0.1 (Table 1).

The normalized isotopic compositions are represented as follows:

\[
\delta^{15}\text{N}_{\text{norm}} \text{[‰]} = 1,000 \left( \frac{^{15}\text{N}/^{14}\text{N}_\text{norm}}{^{15}\text{N}/^{14}\text{N}_{\text{Initial}}} - 1 \right) \tag{4}
\]

Although these normalized values were not calculated relative to the atmospheric N-isotopic composition and are not directly comparable to \( \delta^{15}\text{N} \) values measured in natural samples (40), they represent the magnitude of the observed change in the isotopic composition of each phase during the experiments. Fig. 3A reveals that N loss (in the form of \( \text{N}_2 \), NH\textsubscript{3}, or both) by Rayleigh distillation during the experiments could increase the \( \delta^{15}\text{N}_{\text{silicate}} \) values of the melt and may explain the positive \( \delta^{15}\text{N}_{\text{silicate}} \) values measured in the silicate glasses (Fig. 3B). In contrast, \( \delta^{15}\text{N}_{\text{metal norm}} \) is clearly negative compared with the initial \( \delta^{15}\text{N} \) value (i.e., \( \delta^{15}\text{N}_{\text{norm}} = 0 \text{‰} \)), suggesting that the metal phase becomes

**Fig. 1.** \( D_{\text{metal-silicate}} \) as a function of \( f_\text{O}_2 \). Large symbols represent \( D_{\text{metal-silicate}} \) values from this study, and small symbols are results from several previous studies: diamonds and red x’s (17), blue x’s (16), black x’s (21), gray circles (20), empty circles (22), triangles (18, 37, 50, 51), and blue crosses (15). All \( f_\text{O}_2 \) values were recalculated following the procedure described in the text. Following this calculation, only 2 of the 4 samples from Li et al. (16) have log \( f_\text{O}_2 < -1 \). Error bars represent \( 2 \text{SDs}. \) P-T conditions have only a small effect on \( D_{\text{metal-silicate}} \) and explain the scatter among the overall decreasing trend with decreasing \( f_\text{O}_2 \). Our data measured using SIMS (Fe-rich basalt and andesite) are in agreement with previously published \( D_{\text{metal-silicate}} \) values measured by EPMA.

**Fig. 2.** Representative normalized Raman spectra of N species in silicate glasses and metal alloys of samples HB01, HB3, and A05: (A) \( \text{N}_2 \) isotopomers in silicate glasses, (B) NH complexes in silicate glasses, and (C) Fe-N bonds in metal alloys. The Raman shifts of N species are significantly different depending on speciation (\( \text{N}_2 \) versus NH complexes) and whether N is dissolved in metal alloy or silicate glass. Details of our Raman analysis are presented in SI Appendix, section S1.
Fig. 3. Effect of N loss (A and B) and fO₂ (C and D) on N-isotopic fractionation Δ₁⁵Nmetal-silicate. (A) Modeled effect of N loss by Rayleigh distillation on the Δ₁⁵Nnorm values of silicate glasses as a function of fO₂, the fraction of N remaining in the sample at the end of the experiments compared with the initial N content of the starting materials. The Δ₁⁵Nnorm values represent measured Δ₁⁵Nsilicate ratios normalized to the initial ₁⁴N/₁⁵N ratio of the starting material (see text and Table 1). Rayleigh distillation was modeled for N₂ loss (green curve) and NH₃ loss (red curve) as Δ₁⁵Ncalc = 1,000 · (fN/fN₀−1), where f is the fractionation factor approximated here by \(\sqrt{[m(₁⁴N) + m(₁⁵N)]/[m(₁⁴N)]} = 1.02\) for N₂ loss and by \(\sqrt{[m(₁⁴N)]/m(₁⁵N)] + 3 \cdot m(₁⁴N)] + 3 \cdot m(₁⁵N)] = 1.03\) for NH₃ loss. The positive Δ₁⁵N values measured in our silicate glasses can be explained by the Rayleigh distillation model, suggesting that N loss may have increased the Δ₁⁵N values of the silicate glasses. (B) Evolution of Δ₁⁵N in the silicate glasses (closed symbols) and in the metal strips (open symbols) as a function of fO₂. The Δ₁⁵Nnorm values represent measured Δ₁⁵N/₁⁴N ratios (p representing the metallic or silicate phase) normalized to the initial ₁⁴N/₁⁵N ratio of the starting material (see text and Table 1), and the gray line at 0‰ represents the initial Δ₁⁵N norm value. The difference between the Δ₁⁵N values measured in the metal and the silicate phases (Δ₁⁵Nmetal-silicate) approximates the calculated Δ₁⁵Nmetal-silicate values. Considering that positive Δ₁⁵Nmetal-silicate values may have been produced by N loss, the difference between the initial Δ₁⁵N norm (0‰) and the Δ₁⁵Nmetal-silicate values corresponds to Δ₁⁵N*, the N-isotopic fractionation corrected for N loss. (C) Δ₁⁵Nmetal-silicate as a function of fO₂, showing both calculated Δ₁⁵Nmetal-silicate (blue symbols) and Δ₁⁵N* (purple symbols). The small blue x’s are reproduced from Li et al. (16), with fO₂ values recalculated following the procedure described in the text. Error bars represent 2σ SDs. Whereas the uncertainties on Δ₁⁵Nmetal-silicate are determined from the SDs on ₁⁴N/₁⁵N ratios measured by SIMS, the larger uncertainties on fO₂, Δ₁⁵N norm values, and Δ₁⁵N* are derived from the weighing uncertainties associated with the addition of Si₁₂N₄ and Si₁₂N₈ to the starting material. The dashed line represents a linear regression \((r^2 > 0.9)\) on the Δ₁⁵Nmetal-silicate values measured in Fe-rich basalt. Δ₁⁵Nmetal-silicate data describe 2 trends that can be explained by compositionally dependent differences in N speciation in the silicate glasses (see text). (D) Evolution of Δ₁⁵N norm in the silicate glasses and metal strips as a function of fO₂. This plot shows that positive Δ₁⁵Nnorm values can also be produced by N-isotopic fractionation during metal segregation from the melt via the formation of ₁⁴N–Fe bonds in the metal from ₁⁵N in NH complexes in the melt. This process becomes more important as the fO₂ decreases due to the increasing stabilization of NH complexes in the melt under more reducing conditions.

enriched in ₁⁴N during its segregation (Fig. 3B). Therefore, the observed positive Δ₁⁵Nnorm values may result from N loss from the experiments and/or ₁⁴N depletion during N partitioning into the metal phase.

The N-isotopic fractionations between metal and silicate in the samples (Table 1 and Fig. 3C) were calculated from the ₁⁵N/₁⁴N metal and ₁⁵N/₁⁴N silicate ratios measured by ion probe as follows:

\[
Δ₁⁵Nmetal-silicate \approx 1,000 \cdot \ln \left( \frac{₁⁵N_{metal}}{₁⁴N_{metal}} \cdot \frac{₁⁴N_{silicate}}{₁⁵N_{silicate}} \right) .
\]  

They decrease from −49 ± 1‰ to −257 ± 22‰ with decreasing fO₂ from ΔIW −0.45 to −3.13. Such negative N-isotopic fractionations are in accord with equilibrium fractionation, during which the lightest isotopes favor bonds in the most reduced phase (23, 56), here as Fe–N (Fig. 2C). As the metal segregates from the silicate melt at isotope equilibrium, it more favorably forms ₁⁴N–Fe bonds than ₁⁵N–Fe bonds, thereby depleting the silicate melt in ₁⁴N; this process may increase the Δ₁⁵N norm values. Alternatively, assuming that Rayleigh distillation alone produced the positive Δ₁⁵Nnorm values observed in Fig. 3A and B, then, when corrected for this process, Δ₁⁵N norm can be assumed to remain at 0‰ during N partitioning into the metal phase. In this scenario, N-isotopic fractionations corrected for N loss, expressed as Δ₁⁵N* = Δ₁⁵N metal−Δ₁⁵N silicate with Δ₁⁵N metal−Δ₁⁵N silicate corrected to 0‰ (Fig. 3B), decrease from −27 ± 4‰ to −171 ± 28‰ with decreasing fO₂ from ΔIW −0.45 to −3.13 (Fig. 3C). Following this reasoning, Δ₁⁵N metal−silicate and Δ₁⁵N* represent the maximum and minimum bounds on metal–silicate N-isotopic fractionation in our experiments, respectively.

The Δ₁⁵N metal−silicate and Δ₁⁵N* values from this study are significantly lower than those obtained by Li et al. [Δ₁⁵N metal−silicate between 1.1 ± 2.8‰ and −5.5 ± 2.3‰ (16)]. This difference may be explained by the different P–T conditions of the 2 studies, although the results of Li et al. (16) show no pressure or temperature dependence over 1.5 to 7 GPa and 1,600 to 1,800 °C. It is,
However, questionable that they do not observe any temperature effect on $\Delta^{15}\text{N}_{\text{metal-silicate}}$ since, by definition, fractionation factors are inversely proportional to temperature (e.g., refs. 23 and 58). In addition, our large N-isotopic fractionations cannot be explained by $^{15}\text{N}$ spiking of our samples. As has been shown for H isotopic fractionation (59), $\Delta^{15}\text{H}_{\text{metal-silicate}}$ values are not dependent on the initial $^{15}\text{N}^{14}\text{N}$ ratio of the experiments (Table 1). Instead, $\text{O}_2$ is the key parameter differing between the 2 studies. The $\text{O}_2$ of the samples of Li et al. (16) were between $\Delta\text{IW} = -0.11$ and $-0.35$, whereas the $\text{O}_2$ of our samples varies from $\Delta\text{IW} = -0.45$ to $-3.13$. This observation implies an effect of $\text{O}_2$ on $\Delta^{15}\text{N}_{\text{metal-silicate}}$.

These large N-isotopic fractionation values are comparable to estimates of H metal–silicate isotopic fractionation [between $-55$ and $-285\%$, modeled based on chondritic and mantle-like D/H values and H solubility in metal and silicate phases (60)], although, to our knowledge, no experimental data on metal-silicate fractionation are available for hydrogen or carbon isotopes. There are, however, experimental data available on H- and C- isotopic fractionations during other high-temperature magmatic processes. For instance, hydration or dehydration of silicate melts and nominally anhydrous minerals produces 6D variations of up to $550\%$ at 1,000 °C (61). During aqueous fluid–silicate melt interaction, H- and C-isotopic fractionations can reach $150\%$ at 750 °C (56, 62–64). Among other isotopic tracers of core formation, i.e., isotopes of heavier siderophile elements such as Si, Fe, Mo, Cr, Cu, and Ni (65), sulfur is the most comparable to N in terms of mass, solubility in reduced melts (66), and volatile behavior. However, experimentally determined metal–silicate S isotopic fractionation factors, $\Delta^{34}\text{S}_{\text{metal-silicate}}$ are only on the order of 0.1 to $1.2\%$ between $\Delta\text{IW} = -0.6$ and $-4.1$ (67). Although the mass difference between N isotopes is 2.5 times larger than that between S isotopes, this difference is insufficient to explain the vast difference between the metal–silicate isotopic fractionations of N and S.

### The Effects of $\text{O}_2$ and N Speciation on $\Delta^{15}\text{N}_{\text{metal-silicate}}$

Following Bigeleisen and Mayer (30) and Urey (31), mass-dependent N-isotopic fractionation can be expressed as follows:

$$\Delta^{15}\text{N}_{\text{metal-silicate}} = \alpha, 1000 \times \frac{(\Delta m)_{\text{metal}}}{(\Delta m)_{\text{metal-silicate}}} \times \frac{T^2}{(m_{14}m_{15})}, \tag{6}$$

where $m_{14}$ and $m_{15}$ are the atomic masses of $^{14}\text{N}$ and $^{15}\text{N}$, respectively, $\Delta m$ is their mass difference, $\Delta^{15}\text{N}_{\text{metal-silicate}}$ is the difference between the force constants acting on the isotopes in the metallic phase and the silicate melt ($\Delta F_{\text{metal-silicate}} = F_{\text{N}} - F_{\text{N}}$), with $F_{\text{metal}}$ and $F_{\text{silicate}}$ the effective force constants that depend on the chemical bond stiffness of N bonds in the metallic phase and silicate glass, respectively, and $T$ is temperature in kelvin. In this study, at constant $T$, $\Delta F_{\text{metal-silicate}}$ is the only variable in the above equation acting on the N-isotopic fractionation between metal alloy and silicate melt, along with $\text{O}_2$ variations. This parameter is related to vibrational frequency, $v_{\text{N}}$, (30, 51), following:

$$v_{\text{N}}^2 = \frac{1}{\pi} \left( \frac{h}{k_bT} \right)^2 \frac{\Delta m}{(m_{14}m_{15})}, \tag{7}$$

where $v_{\text{N}}$ was determined from the Raman vibration modes of N species in the metallic phases and the silicate glasses (Fig. 2) and $\mu_{\text{N}}$ is the reduced mass of the N-bearing molecule, calculated for N–H as $µ_{\text{N}} = (m_{14} + m_{15})/ (m_{14} + m_{15} + m_{\text{H}})$, with $m_{14}$ and $m_{15}$ being the atomic masses of N and H, respectively. More details on the principles and factors controlling stable isotopic fractionations can be found in Schauble (23) and Young et al. (51). Nitrogen dissolves in silicate glasses as molecular nitrogen ($N_2$) and NH complexes, and as Fe–N in metal alloys. $N_2$ has 3 isotopomers, $^{15}\text{N}=^{15}\text{N}$, $^{15}\text{N}=^{14}\text{N}$, and $^{14}\text{N}=^{14}\text{N}$, with vibration modes in silicate glasses at 2,251, 2,287, and 2,326 cm$^{-1}$, respectively (Fig. 24) (55), whereas the vibration mode of gaseous $^{15}\text{N}=^{14}\text{N}$ is at 2,351 cm$^{-1}$ (68). The vibration modes of NH complexes are between 3,180 and 3,350 cm$^{-1}$ (Fig. 2B) (e.g., refs. 41 and 69). Fe–N vibrations in metal alloys are distinctly different, occurring at 338 cm$^{-1}$ (Fig. 2C) (70). In comparison, S dissolves in metal alloys as Fe–S with vibration modes at 310 and 360 cm$^{-1}$, and in silicate melts as Fe–S, Mg–S, and Ca–S with vibration modes between 285 and 350 cm$^{-1}$ (66). Although the vibration modes of complexes involving N or S have been determined for quenched silicate and metal, their equivalents in silicate melts and liquid metals at HP–HT are expected to vary only by a few cm$^{-1}$, as shown by Myssen (71) for the $N_2$ vibration mode in silicate melts and aqueous fluids. The observed vibration modes are directly related to the reduced masses $\mu_{\text{N}}$ and $\mu_{\text{S}}$ of the bonds formed by N and S, respectively, in the metal and silicate phases. As the relevant N bonds have very different reduced masses $[\mu(N–H) = 1$ a.m.u., $\mu(N\equiv N) = 7$ a.m.u., and $\mu(Fe–N) = 11$ a.m.u.], the bonding of N with ions of very different masses directly produces large differences in the force constants (i.e., $\Delta F_{\text{metal-silicate}}$) acting on N isotopes in the 2 phases.

In comparison, the smaller $\Delta^{15}\text{N}_{\text{metal-silicate}}$ values for S isotopes should result from the similar reduced masses of S bonds $[\mu(Mg–S) = 14$ a.m.u., $\mu(Ca–S) = 18$ a.m.u., and $\mu(Fe–S) = 20$ a.m.u.]. Therefore, we conclude that the observed large N-isotopic fractionations relative to those of S are a consequence of the distinct N speciation between the metallic phase and the silicate melt.

The difference in vibrational frequencies and reduced masses between the metal and silicate phases is higher when N is dissolved as N–H complexes (e.g., NH$_3$) than as molecular $N_2$. The basic equation for equilibrium isotopic fractionation for stable isotopes, derived from Bigeleisen and Mayer (30), Urey (31), and Young et al. (51), can be expressed as follows:

$$\Delta^{15}\text{N}_{\text{metal-silicate}} = \frac{1,000}{24} \left( \frac{h}{k_bT} \right)^2 \frac{\Delta m}{(m_{14}m_{15})} \times \left( \frac{\mu_{\text{metal}}^{15} - \mu_{\text{metal}}^{14}}{\mu_{\text{metal}}^{15} - \mu_{\text{silicate}}^{15}} \right), \tag{8}$$

where $h$ is Planck’s constant (in joules per kelvin), $k_b$ is the Boltzmann constant (in joules per hertz), $T$ is temperature in kelvin, and $\mu_{\text{metal}}$ and $\mu_{\text{silicate}}$ denote the Raman vibration modes (in hertz) for the metal and silicate phases, respectively. From Eq. 8, we estimate $\Delta^{15}\text{N}_{\text{metal-silicate}}$ to be $-4$ to $-24\%$ for N dissolved as $N_2$ or NH$_3$ in the silicate glass, respectively. Eq. 8 only considers N speciation differences between phases and assumes the absence of N interactions between molecular groups within each metal or silicate phase (e.g., different structural units). In general, however, this assumption is not valid for silicate melts because strong intermolecular bonds influence isotopic exchanges, thereby leading to a significant underestimation of the isotopic fractionation between distinct phases (e.g., refs. 59, 67, 72, and 73). However, this calculation shows that larger N-isotopic fractionations between the metal and silicate phases are produced depending on whether N is dissolved as N–H complexes or as molecular $N_2$. Accordingly, we can assume that higher NH/N$_2$ ratios in the melt produce larger metal–silicate N-isotopic fractionations than when N is present in the melt mainly as N$_2$. The increasing stabilization of NH complexes with decreasing $\text{O}_2$ (Fig. 2B) therefore increases the observed metal–silicate N-isotopic fractionation among HB samples (Fig. 3C and SI Appendix, Fig. S5). In contrast, the $\Delta^{15}\text{N}_{\text{metal-silicate}}$ value of A05, $-25 \pm 1\%$, is significantly smaller than those of the Fe-rich
basalts at equal fO2 values (Fig. 3). This discrepancy may be explained by the lower NH/N2 ratio of the anesite compared with that of the Fe-rich basalts.

Although not observed in our glasses, N dissolution as nitrides in the silicate melt would lead to smaller metal–silicate N-isotopic fractionation than for N dissolved as N2 or N–H complexes, given the small difference in vibration modes between Fe–N in metals and Si–N in silicates ($\delta^{15}\text{N}_{\text{metal}} - \delta^{15}\text{N}_{\text{silicate}} = 462 \text{ cm}^{-1}$).

Nitrogen Isotopic Fractionation during Core Formation

N partitioning data (this study; refs. 15–22, 38, 52, and 53) show that, during terrestrial core–mantle differentiation, a fraction of N must have been removed from the magma ocean into the core-forming metals (Fig. 1). This N segregation produced an isotopic fractionation that depleted the metallic phase and enriched the silicate mantle in $^{15}\text{N}$ and was fundamentally dependent on the fO2 conditions of the proto-mantle. Recent models (24, 28, 74) propose that the Earth accreted from small and highly reduced materials ($\Delta W \sim 5$) during the first stages of its formation (60 to 70% of its mass), then from larger and more oxidized bodies ($\Delta W \sim 2$) toward the end of accretion. Thus, the studied fO2 range ($\Delta W \sim 3.1$ to $\sim 0.5$) represents plausible conditions of metal–silicate equilibration during the later stages of accretion and core formation (24, 74). During progressive oxidation from $\Delta W \sim 3.1$ to $\sim 0.5$, while the fraction of Earth’s N increased in core-forming materials, the N-isotopic fractionation between the segregating metal and the silicate mantle would likely have decreased. These concurrent processes can be modeled using an equilibrium model of Earth’s core–mantle differentiation (16). We adapted an equilibrium model of core formation that assumes complete equilibration between the silicate mantle and the forming core (16) to account for progressive metal–silicate equilibration. This progressive equilibration is represented by the ratio of the masses of the silicate mantle and the bulk Earth (BE), $m_{\text{silicate}} / m_{\text{BE}}$, which varied between 1 (precore) and 0.67 (present-day Earth). The total mass $M_N$ of N in the silicate mantle or BE is calculated from the following:

$$M_N = c_{N_{\text{mantle, BE}}} \cdot \frac{m_{\text{silicate, BE}}}{m_{\text{BE}}},$$

where $c_{N_{\text{mantle, BE}}}$ is the N concentration in the mantle or BE, with

$$c_{N_{\text{mantle}}} = c_{N_{\text{BE}}} \cdot \left( \frac{m_{\text{mantle}} / m_{\text{BE}}}{(\text{mantle/silicate})_{\text{pre-core}}} \right).$$

The evolution of the N-isotopic composition of the mantle $\delta^{15}\text{N}_{\text{mantle}}$ during core formation is expressed as follows:

$$\delta^{15}\text{N}_{\text{mantle}} = \delta^{15}\text{N}_{\text{BE}} + \Delta^{15}\text{N}_{\text{metal–silicate}} \cdot \left( 1 - \frac{M_{\text{mantle}}}{M_N} \right).$$

This model is primarily dependent on the N-isotopic composition of the BE, $\delta^{15}\text{N}_{\text{BE}}$, and, to a lesser extent, $c_{N_{\text{BE}}}$, necessitating assumptions regarding the nature of the accreting bodies that formed the Earth. Considering an enstatite chondrite origin for Earth’s N (11) and assuming no N was lost during accretion, the $c_{N_{\text{BE}}}$ value of the proto-Earth was $10^5$ ppm (75). For $\delta^{15}\text{N}_{\text{BE}}$, we chose to explore the 2 most extreme $\delta^{15}\text{N}$ values measured in enstatite chondrites: $\sim 45$ and $\sim 15\%$ (13). Over the fO2 range $\Delta W \sim 3.1$ to $\sim 0.5$ (i.e., using the N partition coefficients and isotopic fractionation values derived from our experiments), a proto-Earth with a $\delta^{15}\text{N}_{\text{BE}}$ value of $\sim 45\%$ would result in a $\delta^{15}\text{N}_{\text{mantle}}$ value between $\sim 25$ and $\sim 11\%$ at the end of core formation depending on the fO2, whereas a $\delta^{15}\text{N}_{\text{BE}}$ value of $\sim 15\%$ would result in a $\delta^{15}\text{N}_{\text{mantle}}$ value between $\sim 5$ and $\sim 3\%$ (Fig. 4). The modeled trend is linear at $\Delta W \sim 3$ but logarithmic at IW, such that the difference between the 2 trends increases to a maximum of $\sim 27\%$ at $\sim 60\%$ metal–silicate equilibration, and then decreases to $\sim 20\%$ at 100% metal–silicate equilibration (Fig. 4). This simple model demonstrates that the present-day mantle’s $\delta^{15}\text{N}$ value of $\sim 5\%$ could have been produced by core–mantle differentiation, assuming that enstatite chondrites are Earth’s primary building blocks and the source of terrestrial N (or if $\delta^{15}\text{N}_{\text{BE}}$ was between $\sim 51$ and $\sim 25\%$; Fig. 4). Nevertheless, the outcome of this model is mainly controlled by the value of $\delta^{15}\text{N}_{\text{BE}}$ (Fig. 4) and therefore the source of Earth’s N, which remains a matter of debate (5, 76).

On the Origin(s) and Evolution of Terrestrial N

Because the N-isotopic signatures of solar system objects and reservoirs are highly variable (77), N isotopes are key tracers of the source of terrestrial volatiles. Among chondrites, only enstatite chondrites have negative $\delta^{15}\text{N}$ values ($\sim 45$ to $\sim 15\%$) (13)). This fact led Javoy et al. (5) to suggest that enstatite chondrites are the source of Earth’s N. An enstatite chondrite-like $\delta^{15}\text{N}$ value of the proto-Earth is consistent with the scenario presented by Li et al. (16) and herein: N segregation into the core during proto-Earth differentiation could have increased the $\delta^{15}\text{N}$ value of the silicate
mantle from very negative values (as low as $-45\%_e$) to $-5\%_e$. In addition, the range of $\delta^{15}N$ values in Archean diamonds is similar to that of present-day diamonds and MORBs (11), suggesting that the mantle acquired its $\delta^{15}N$ value of $-5\%_e$ before the Archean (19). This would support the idea of a very negative proto-Earth $\delta^{15}N$ signature, similar to that of enstatite chondrites, and the subsequent enrichment of the mantle in $\delta^{15}N$ by an early process, for instance core formation (16), possibly combined with magma ocean degassing and/or recycling (7).

Nitrogen degassing (as $N_2$ or $NH_3$; Fig. 3A) from the magma ocean to the primitive atmosphere could also have increased the $\delta^{15}N_{\text{mantle}}$ value from an enstatite chondrite $N$-isotopic signature to the present-day value. Considering the highest reported $\delta^{15}N$ value for enstatite chondrites ($-15\%_e$), only $30\%$ of magma ocean degassing is required to increase $\delta^{15}N_{\text{mantle}}$ by $10\%_e$ to the present-day value of $-5\%_e$ assuming a Graham’s law relationship (Fig. 3A). On the other hand, from an enstatite chondrite $\delta^{15}N$ value of $-45\%_e$, more than $75\%$ of the initial $N$ of the Earth needs to be degassed to increase $\delta^{15}N_{\text{mantle}}$ by $40\%_e$ to the present-day value (Fig. 3A). Considering the low solubility of $N_2$ at low pressure under reduced conditions [<0.2 ppm at 1 atm between $\Delta IW$ $-$2 and 1W (56)], large fractions of the proto-Earth’s initial $N$ content could have been degassed from a reduced magma ocean (e.g., refs. 20 and 35). However, these considerations are dependent on $N$ solubility variations with $O_2$ and $fH_2$ (which control the stabilization of NH complexes and thus $N$ solubility) in mafic to ultramafic melts, for which data are sparse. In comparison, $N$ recycling via subduction is insufficient to increase $\delta^{15}N_{\text{mantle}}$ by more than $5\%_e$, even if subduction was initiated 4 Ga (78). As both magma ocean degassing and core formation may have increased the $\delta^{15}N$ value of the magma ocean, the source of terrestrial $N$ might have had a $N$-isotopic signature significantly more negative than $-45\%_e$.

The very low $\delta^{15}N$ values of some Archean diamonds [$-25$ to $-39\%_e$, compared with $-12$ to $+6\%_e$ in most other Archean diamonds (12, 79)] have been suggested to represent relics of primordial $N$ that have been preserved in an undegassed reservoir. The existence of such a primitive, undegassed mantle reservoir has been proposed to explain the low $\delta^{15}N$ values in ocean island basalts (OIBs) [see review by Moreira (80)], as well as the near-absence of a守达成能的 $N$ component in the deep mantle (81). However, OIBs, typically associated with mantle plumes, exhibit high $\delta^{15}N$ values (around $+2\%_e$) akin to surficial $N$-isotopic compositions (7), suggesting that at least some of the $N$ in OIBs is derived from recycled surficial $N$. The low $\delta^{15}N$ signature of the inferred undegassed reservoir responsible for Archean diamonds must have somehow been maintained during metal–silicate fractionation and core formation. The stable isotopic (i.e., $\delta^{15}N$) signature of diamonds can vary widely as a result of the redox state of the C–O–H–N fluids/melts from which they form (82, 83). Therefore, the extremely low $\delta^{15}N$ values of some Archean diamonds (12, 79) may similarly reflect $fO_2$ heterogeneities in the Archean mantle, although the effects of $fO_2$ on $N$ speciation and isotopic fractionation in diamonds remain unknown (82).

Another possible origin of terrestrial $N$ arises from the combined study of $N$ isotopes and noble gases among solar system bodies. Based on the solar-like $N$ isotopic composition of the mantle, Marty (76) discussed the possibility that the mantle has preserved some solar $N$. This scenario implies that precursor grains accreted during Earth’s formation were first irradiated by the solar wind and preserved their solar volatile isotopic signature during Earth’s accretion and differentiation [$\delta^{15}N_{\text{IFS}} \leq -240\%_e$; IFSW: implantation-fractionated solar wind (84, 85)]. Alternatively, a primordial solar atmosphere could have been captured by Earth’s gravity and dissolved into the early magma ocean [$\delta^{15}N_{\text{Solar}} = -383\%_e$ (e.g., ref. 86)]. Assuming a solar-like source of $N$ for the proto-Earth, the mantle’s $N$ must have been significantly enriched in $^{15}N$ by $N$-isotopic fractionation during core–mantle differentiation, during magma ocean degassing (as $N_2$ and/or $NH_3$; Fig. 3A), and/or by the delivery of carbonaceous chondrites [$\delta^{15}N_{\text{CC}} = +15$ to $+55\%_e$ (14)] during late accretion and the addition of the late veneer.

Conclusions

We studied metal–silicate $N$-isotopic fractionation over a $fO_2$ range consistent with the inferred conditions of Earth’s core formation. Our results reveal large $N$-isotopic fractionations over $fO_2$ conditions spanning 3 orders of magnitude. Such large fractionations can be explained by the vastly different $N$ bonds formed in metal and silicate phases. The particularity of $N$, compared with other isotope tracers of core formation, is that it forms $N_2$ molecules or $NH$ complexes in silicate melts, whereas it bonds as Fe–$N$ in metal alloys. The strong dependence of $N$-isotopic fractionation on $fO_2$ conditions is a consequence of the increased solubility of $NH$ complexes in silicate melts under increasingly reducing conditions. We also demonstrated that the $N$/$N_2$ ratio and the $N$-isotopic fractionation depend on melt composition. Planetary magma oceans are expected to be mafic (close to our Fe-rich basalts) to ultramafic. Ultramafic melts (SiO$_2$-poor and MgO-rich) are difficult to quench from HP–HT to ambient conditions. Therefore, to advance our understanding of the effect of melt composition on $N$ speciation and isotopic fractionation for extrapolation to such ultramafic melts at core-forming reduced conditions, experimental studies need to be performed using silicate melts spanning a large range of polymerization degrees.

Metal–silicate $N$ partitioning coefficients increase significantly with increasing $P$–$T$ conditions (22) because $N$ solubility in metal melts increases (15). How $P$–$T$ conditions affect $N_2$ and $NH$ solubility in silicate melts, and thereby metal–silicate $N$-isotopic fractionation, remains to be experimentally constrained over a wide range of $P$–$T$ conditions. Although isotopic fractionations decrease with increasing temperature [$\Delta\delta^{15}N \propto 1/T^2$ (20, 21)], an increase of pressure over tens of gigapascals should increase isotopic fractionations by increasing bond stiffness (51). However, how pressure affects bond stiffness in silicate glasses versus in metal alloys remains to be studied. At $P$–$T$ conditions more representative of core–mantle equilibration in the terrestrial mantle (0 to 40 GPa and 2,000 to 3,000 K (87)), the magnitude of $N$-isotopic fractionation is expected to be smaller than determined in this study since the effect of $T$ should dominate that of $P$. Thanks to our analytical developments, the $N$-content and -isotopic ratios of small phases (<15 \(\mu\)m in diameter) can now be measured in high-pressure (>10-GPa) experimental samples, which will allow the determination of $N$-isotopic compositions at $P$–$T$ conditions more representative of core–magma ocean equilibration conditions.

We have highlighted the fundamental effect of $fO_2$ on the evolution of the mantle’s $\delta^{15}N$ value during core formation. We showed that $fO_2$ variations of 3 log units can produce a $\delta^{15}N$ variation of $>20\%_e$ in the silicate mantle after only 30% metal–silicate equilibration (Fig. 4). The magnitude of the $N$-isotopic fractionation observed here during metal–silicate segregation, larger fractionations under more reducing conditions, suggests that large $N$-isotopic fractionations could have also occurred during other high-temperature stages of Earth’s formation, such as accretion and magma ocean crystallization and/or degassing.

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