Nitrogen isotope fractionation during magma ocean degassing: tracing the composition of early Earth's atmosphere

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Abstract

798 ± 4 ppm at IW, controlled by N speciation (as determined by Raman spectroscopy), which changed from nitride (±N-H complexes) to molecular N₂ with increasing *f*O₂. Nitrogen occurs solely as N₂ in the degassed gas, regardless of *f*O₂. Nitrogen isotopic compositions (as determined by secondary ion mass spectroscopy) became significantly lighter in the degassed melt (quenched glass), down to −41 ± 13 ‰ relative to the initial composition (measured in an undegassed sample), following open system degassing trends (variable with *f*O₂ conditions), indicative of Rayleigh fractionation. These findings imply that an atmosphere in equilibrium with a reduced magma ocean would be N-depleted, whereas with increasing magma ocean *f*O₂ conditions, the primitive atmosphere would have become more enriched in N₂ gas.

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Introduction

The accretion of reduced building blocks during Earth's formation released enough energy to at least partially melt the Earth, forming one or more magma oceans (Elkins-Tanton, 2012). The evolving nitrogen abundance in the degassing magma ocean, and thus in Earth's early atmosphere, was fundamental to the development of habitable conditions and the maintenance of the terrestrial atmosphere and biosphere (Goldblatt *et al.*, 2009). Yet, the composition of Earth's early atmosphere remains debated: it is thought to have been either *i*) neutral to oxidising and composed of H₂O, CO₂, and N₂ if it resembled modern volcanic gases (Kasting, 1993), or *ii*) reducing and CH₄- and NH₃-rich if it degassed from the reduced materials that formed the Earth (Zahnle *et al.*, 2020), based on geochemical evidence that magma ocean degassing contributed to the formation of the Hadean atmosphere (see review by Gaillard *et al.*, 2021). Therefore, reconstructing nitrogen degassing during Earth's magma ocean stage(s) is critical to constraining the composition of the early atmosphere.

Nitrogen is often considered to be an inert molecule (N₂) and expected to behave somewhat like noble gases. However, recent works have shown that nitrogen is not always chemically inert and occurs as various species (N³⁻, NH₃, NH₂⁻, NH₂⁻ and N₂) in silicate melts (Mikhail and Sverjensky, 2014; Dalou *et al.*, 2019a; Mosenfelder *et al.*, 2019; Boulliang *et al.*, 2020; Grewal

et al., 2020) and fluids (Li and Keppler, 2014). The speciation and solubility of nitrogen primarily depend on oxygen fugacity (Libourel *et al.*, 2003; Boulliang *et al.*, 2020; Bernadou *et al.*, 2021), which increased during the evolution of Earth's magma ocean (Frost *et al.*, 2008). Thus, the rate of nitrogen degassing and the reactions involved must have evolved similarly over geological time.

Nitrogen isotopic compositions, conventionally normalised to the present atmospheric value and reported as δ¹⁵N[‰] = $\left[\left(\frac{^{15}\text{N}/^{14}\text{N}_{\text{sample}}}{^{15}\text{N}/^{14}\text{N}_{\text{atm N}_2}} \right) - 1 \right] \cdot 1,000$, are useful for reconstructing Earth's N degassing history. For instance, the range of δ¹⁵N values observed in Archean diamonds corresponds to that in present day diamonds and mid-ocean ridge basalts (MORBs), implying that the mantle δ¹⁵N value has not evolved since the Archean (Cartigny and Marty, 2013). This is consistent with the observation that diffusion controlled N₂ degassing from the present day mantle, which is expected to preferentially segregate ¹⁴N into the atmosphere following Graham's law (*i.e.* the rate of diffusion/effusion of a gas is inversely proportional to the square root of its molecular weight; Javoy *et al.*, 1986), is limited to isotopic fractionations of 1–1.5 ‰ (Marty and Dauphas, 2003). However, Rayleigh models of equilibrium MORB degassing (Javoy *et al.*, 1986; Cartigny *et al.*, 2001) only consider the reaction N₂(magma) ↔ N₂(gas). This reaction has been experimentally determined at oxygen fugacity conditions (*f*O₂) > IW (Libourel

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et al., 2003; Boulliung *et al.*, 2020), which applies to present day conditions of upper mantle degassing. However, because the integrated fO_2 during core formation was closer to IW–2 (Frost *et al.*, 2008), this reaction does not hold for the more reduced N species present in the magma ocean. Larger N isotopic fractionations are expected under reducing conditions at which N does not behave inertly. Therefore, quantifying N isotopic fractionations under conditions at which N dissolves in magmas as nitride or N–H complexes is prerequisite to quantitatively modelling the evolution of N concentrations and isotopic compositions during the formation of the Hadean atmosphere.

Degassing Experiments and Results

To establish the effect of fO_2 on the N degassing rate and identify N degassing reactions that may have occurred in the Earth's magma ocean, we determined the N concentration, speciation, and isotopic fractionation of a basaltic komatiite (used as magma ocean analogue melt) during degassing at 1.5 GPa and 1550 °C in pure forsterite capsules. Degassing experiments were performed using a series of Fe-free primitive basalts in which we explored fO_2 conditions ranging from IW to IW–4.2 (Table 1). These fO_2 conditions were not determined in the Fe-free experiments, but only estimated afterwards from the IW reaction in equivalent Fe-bearing runs (see Supplementary Information). The initial $^{15}N/^{14}N$ ratio of the starting material was 0.946 ± 0.003 , as determined in sample V133-PB4N2Si (Table 1), in which the initial N content was equal, within errors, to that measured after the experiment. Nitrogen was saturated in five experiments, as evidenced by bubbles in the quenched glass and/or surrounding forsterite (Fig. 1, Table 1).

The major element compositions of the silicate glasses were measured by electron microprobe (Table S-1). Nitrogen concentrations and $^{15}N/^{14}N$ ratios were determined by secondary ion mass spectrometry (SIMS) using the CAMECA IMS 1280-HR2 at the CRPG (Table 1). On each sample, four to six spot analyses of $^{14}N^{16}O^-$ and $^{15}N^{16}O^-$ were performed (see Supplementary Information). Measured N concentrations were homogeneous (*i.e.* with standard deviations below 10 %). N concentrations at 1.5 GPa and 1550 °C decreased from $13,481 \pm 735$ ppm (at IW–4.2) to 798 ± 4 ppm (at IW; Fig. 2a). In N saturated samples (as attested by the presence of bubbles), N concentrations decreased from $13,481 \pm 735$ ppm (at IW–4.2) to $3,084 \pm 377$ ppm (at IW–1). This decrease of N solubility with increasing fO_2 is consistent with observations in silicate melts at 1 atm (Libourel *et al.*, 2003; Boulliung *et al.*, 2020) and modelled at pressures up to 1 GPa (Bernadou *et al.*, 2021). Yet, the N solubilities observed herein are up to three orders of magnitude higher than those in a similar melt composition and at similar

Figure 1 Optical microscope photograph of sample V125-PB8N, which contains $13,342 \pm 841$ ppm N and lost 15 % of its initial N content by degassing. The reduced glasses contain aligned microscopic bubbles, likely produced during quenching. Large bubbles, produced by degassing at high pressure and high temperature, are located within a rim of dissolved forsterite (Fo) at the border between the glass and the forsterite capsule. The dissolved forsterite contains negligible amounts of N (2 ± 2 ppm).

temperatures at 1 atm (Boulliung *et al.*, 2020) and one order of magnitude higher than those at 0.08 GPa (Bernadou *et al.*, 2021), consistent with the effect of pressure on N solubility described by Bernadou *et al.* (2021). The variation of N solubilities with fO_2 is directly related to changes of N speciation in the silicate melts, which were determined by Raman spectroscopy (see Supplementary Information). Around IW–4 and below, N is very soluble because it is dissolved as nitride, forming Si–N bonds with the silicate network; indeed, in very N-rich samples (>1 wt. % N), Si–N vibrations around 800 cm^{-1} were observed (Fig. 2b). In less reduced samples ($fO_2 > \text{IW}–4$), N is mostly dissolved as N–H complexes (Fig. 2c), and above IW–2, N is also dissolved as molecular N_2 (Fig. 2d). Consistent with previous studies (Mosenfelder *et al.*, 2019; Grewal *et al.*, 2020), N speciation in the silicate glasses controls N solubility variations with fO_2 conditions. Depending on initial N content and fO_2 , the fraction of N degassed varied from 7 to 53 %. Samples V152-PB0.5N and V149-PB1N did not show any evidence of degassing, *i.e.* no bubbles were observed in the glass or the forsterite rim, but lost 12 and 32 % of their initial N, respectively, likely due to diffusion through cracks formed in the forsterite capsule during compression.

The use of ^{15}N spiked samples permits us to obtain precise $^{15}N/^{14}N$ ratios in the silicate (with low uncertainties of 0.1 ‰ on

Table 1 Experimental results on nitrogen contents and isotope fractionation in silicate glasses.

Exp ID	Estimated fO_2 (Δ IW)	Initial N content (ppm)	Measured N content (ppm)	F (remaining N fraction)	Measured $^{15}N/^{14}N$ ratios	Calculated $\delta^{15}N$ normalised (‰)	Bubbles present
V152-PB05N	0.0	910	798 ± 4	0.88 ± 0.01	0.871 ± 0.005	-79 ± 8	
V149-PB1N	–0.3	1945	1316 ± 16	0.68 ± 0.01	0.845 ± 0.028	-107 ± 34	
V129-PB2N	–1.0	5075	3084 ± 377	0.61 ± 0.07	0.916 ± 0.003	-32 ± 6	✓
V148-PB4N	–2.3	10435	4914 ± 102	0.47 ± 0.01	0.907 ± 0.011	-41 ± 13	✓
V133-PB4N2Si	–2.6	8371	8335 ± 194	1.00 ± 0.02	0.946 ± 0.003	0 ± 6	✓
V125-PB8N	–3.3	16076	13342 ± 841	0.83 ± 0.05	0.925 ± 0.004	-5 ± 7	✓
V151-PB6N3Si	–3.4	11353	7534 ± 526	0.66 ± 0.05	0.926 ± 0.007	-21 ± 10	✓
V150-PB8N6Si	–4.2	14609	13481 ± 735	0.93 ± 0.05	0.941 ± 0.006	-5 ± 9	✓

Figure 2 (a) N concentrations measured by SIMS in reduced glasses synthesised at variable fO_2 conditions, as represented by the colour scale. Open symbols represent samples that did not reach saturation. Raman spectra show (b) Si-N vibrations in sample V125-PB8N and also observed in sample V150-PB8N6Si, (c) N-H vibrations in sample V148-PB4N and also observed in all samples between IW-4 and IW-1 (pink shaded area in (a)), and (d) N₂ vibrations in sample V141-PB1N, corrected for air contamination, and also observed in samples V152-PB05N and V129-PB2N.

average). With increasing fraction of degassed N, $^{15}\text{N}/^{14}\text{N}$ ratios decreased from 0.946 ± 0.003 in the undegassed sample to 0.907 ± 0.011 in the most degassed sample (53 % of initial N lost). The $^{15}\text{N}/^{14}\text{N}$ ratios were normalised to the initial $^{15}\text{N}/^{14}\text{N}$ ratio of the undegassed glass V133-PB4N2Si (0.946 ± 0.003) and expressed as $\delta^{15}\text{N}_{\text{norm}}$ as:

$$\delta^{15}\text{N}_{\text{norm}}[\text{‰}] = \left[\left(\frac{^{15}\text{N}/^{14}\text{N}_{\text{melt}}}{^{15}\text{N}/^{14}\text{N}_{\text{initial}}} \right) - 1 \right] \cdot 1,000. \quad \text{Eq. 1}$$

These normalised values are not calculated relative to the atmospheric N isotopic composition ($^{15}\text{N}/^{14}\text{N}_{\text{air}} = 0.003676$) and cannot be directly compared to the $\delta^{15}\text{N}$ values of natural samples.

Degassing Models of N Isotopic Fractionation under Reduced Conditions

The normalised N isotopic composition of the glasses decreases from 0 ‰ in the undegassed glass to -41 ± 13 ‰ in the most degassed glass (Fig. 3). Although this $\delta^{15}\text{N}$ variation is opposite to that observed during MORB degassing (Cartigny *et al.*, 2001), it is consistent with glasses becoming isotopically lighter with increased degassing as observed for H, C, and S in natural settings (Supplementary Information). An open system degassing model, in which the exsolved vapour is immediately removed from contact with the melt during degassing, is suitable with the presence of gas bubbles within the dissolved forsterite rims (Fig. 1):

$$\delta^{15}\text{N}_{\text{glass}} = \delta^{15}\text{N}_{\text{initial}} + (F - 1)1,000 \ln \alpha, \quad \text{Eq. 2}$$

where $\delta^{15}\text{N}_{\text{initial}}$ is the “normalised initial” isotopic composition of the melt (here 0 ‰; sample V133-PB4N2Si), F is the fraction of N remaining in the melt, and α is the isotopic fractionation factor. In this case, open system degassing occurs in a finite N budget, conforming to a Rayleigh process (Equation 2).

In bubbles for which the gas pressure was sufficient to obtain a Raman signal above the noise, N was observed only as N₂, even in very reduced samples in which N was dissolved as N-H complexes (V148-PB4N) and/or nitrides (V125-PB8N).

Therefore, we propose that at IW to IW-1, the N degassing reaction is:

Had the least reduced samples (V152-PB0.5N and V149-PB1N) not been affected by diffusion through cracks, they would be expected to degas following Equation 3, since N₂ is the only N species dissolved in those melts. In contrast, under more reduced conditions, N degassed as (*e.g.*, Dalou *et al.*, 2019a):

The fugacities of the relevant N species cannot be calculated at present due to a lack of thermodynamic data (see Supplementary Information).

To understand how N speciation can affect gas-melt N isotopic fractionation, we derived the basic equation for equilibrium isotopic fractionation for stable isotopes (Young *et al.*, 2015):

$$\Delta^{15}\text{N}_{\text{gas-melt}} = \frac{1,000}{24} \cdot \left(\frac{h}{k_b T} \right)^2 \left(\frac{\Delta m}{m_{14} m_{15}} \right) \times [(\nu_{\text{N}}^{\text{gas}^2} - \nu_{\text{N}}^{\text{melt}^2})(\mu_{\text{N}}^{\text{gas}} - \mu_{\text{N}}^{\text{melt}})], \quad \text{Eq. 6}$$

$$\alpha = \exp(\Delta^{15}\text{N}_{\text{gas-melt}}/1,000), \quad \text{Eq. 7}$$

where h is Planck's constant (J.K^{-1}), k_b is the Boltzmann constant (J.Hz^{-1}), T is temperature (K), $\nu_{\text{N}}^{\text{gas}}$ and $\nu_{\text{N}}^{\text{melt}}$ denote the Raman vibration modes (Hz) of N species in the gas and silicate phases, respectively, and μ_{N} is the reduced mass of the N-bearing molecule. Using this expression, we calculated that the N isotopic fractionation factor at 1550 °C is 0.999 for degassing by Equation 3, and, under more reduced conditions, 1.005 for Equation 4, both in agreement with Hanschmann (1981), and 0.998 for Equation 5. These equilibrium fractionation factors cannot explain the variation of $\delta^{15}\text{N}_{\text{norm}}$ values observed in the degassed samples; the high isotopic fractionation undergone by these degassed melts rather suggests a kinetic process. Indeed, such large kinetic nitrogen isotopic effects have also

Figure 3 (a) $^{15}\text{N}/^{14}\text{N}$ ratios as a function of N content in glass, and (b) $^{15}\text{N}/^{14}\text{N}$ ratios, and (c) $\delta^{15}\text{N}$ values normalised to the initial value (see text) in reduced glasses as a function of F , the fraction of N remaining. F was calculated by dividing the measured N content in the glass by the estimated N content added to the starting material. Because all starting compositions were prepared from the same initial N-rich powder by variable mixes with a N-free powder, the initial $^{15}\text{N}/^{14}\text{N}$ ratios were the same in all starting materials. The degassing models are described in the text.

been observed in mantle-derived samples (Yokochi *et al.*, 2009). However, kinetic fractionation *via* evaporation results in increasingly heavy isotopic values (Saal and Hauri, 2021), opposite to our observations (Fig. 3c). The observed large isotopic fractionation may thus be explained by a variable diffusion process depending on N speciation, and therefore on $f\text{O}_2$ conditions. The magnitude of diffusive N isotopic fractionation during degassing is similar to that observed in natural high pressure-high temperature peridotitic systems ($>25 \text{ ‰}$; Yokochi *et al.*, 2009; see Supplementary Information). Such a fractionation effect can be estimated from the ratio of the diffusion coefficients (D) of ^{14}N and ^{15}N , expressed as a function of their mass (m): $\frac{D_{^{14}\text{N}}}{D_{^{15}\text{N}}} = \left(\frac{m_{^{15}\text{N}}}{m_{^{14}\text{N}}}\right)^\beta$, where β is an empirical parameter with values between 0 and 0.5 that positively correlates with the diffusivity of the ion in silicate melts (Van Orman and Krawczynski, 2015). Hence, N_2 and NH_3 , which diffuse rapidly through silicate melts relative to Si, have a large isotopic effect (high β), whereas N^{3-} , which is bonded to Si, diffuses slowly (Boulliung *et al.*, 2021) and has a smaller isotopic effect (low β). Good fits to our data are $\beta = 0.2$ for N diffusing as N^{3-} and $\beta = 0.5$ for N as NH_3 (Fig. 3c). A simple diffusion process cannot explain the extremely large fractionation in undegassed samples (V152-PB0.5N and V149-PB1N), unless the diffusion of ^{14}N and ^{15}N is decoupled,

with ^{15}N favouring the stiffest bonds (N_2) and diffusing significantly faster than ^{14}N , favouring weaker N-H bonds in NH_3 . It is possible that N_2 diffusion in these melts is faster than degassing and controls the isotopic fractionation mechanism in these undegassed samples.

Evolution of the N Composition of Earth's Primitive Atmosphere

Figure 3 shows that $f\text{O}_2$ conditions determine N solubility and, therefore, the fraction of N degassed and the isotopic fractionation trends. Our results suggest that the upper layer of Earth's magma ocean degassed N as N_2 , regardless of $f\text{O}_2$ conditions, but that the intensity of N_2 degassing increased as the magma ocean became less reduced. This is in agreement with the recent model of Sossi *et al.* (2020), which predicts that Earth's prebiotic atmosphere was dominated by CO_2 and N_2 gases.

Whether N was dissolved in the magma ocean as nitride, ammonia, or both, N loss depleted the surface or upper parts of the magma ocean in ^{15}N relative to the atmosphere. This could have produced the currently observed isotopic differences between the ^{15}N -depleted mantle ($\delta^{15}\text{N} = -5 \pm 2 \text{ ‰}$ in diamonds and MORBs) and the ^{15}N -enriched surface ($\delta^{15}\text{N} = +6 \text{ ‰}$ in

sediments and $\delta^{15}\text{N} = 0$ ‰, by definition, in the atmosphere) (Cartigny and Marty, 2013). Other explanations of the N isotopic distribution among terrestrial reservoirs include *i*) recycling (subduction) of surficial materials, and *ii*) core–mantle differentiation (Li et al., 2016; Dalou et al., 2019b). However, Labidi et al. (2020) recently showed that N recycling is inefficient. How core–mantle differentiation would have affected the upper layer of the magma ocean and thus the present day depleted mantle, would have depended on the depth of the magma ocean and the efficiency of post-magma ocean convection to homogenise the $\delta^{15}\text{N}$ value of the mantle; thus this process remains disputable.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2204>.

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