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

C. Dalou1*, C. Deligny1, E. Füri1

Abstract

The evolution of the nitrogen concentration and isotopic composition during the degassing of Earth’s magma ocean, and thus in the primitive atmosphere, is key to understanding how habitable conditions developed on Earth. To constrain nitrogen degassing from the magma ocean, we determined the variations of the N content in N2 gas saturation, N speciation, and N isotopic composition of a magma ocean analogue (basaltic komatiite) at oxygen fugacities (fO2) from IW−4.2 to IW (where IW is the logarithmic difference between experimental fO2 and that at Fe–FeO equilibration). We performed a series of N degassing experiments in a piston cylinder at 1.5 GPa and 1550 °C in pure forsterite capsules. N concentrations in the mafic silicate melts decreased from 13,481 ± 735 ppm under the most reducing conditions to 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 fO2. Nitrogen occurs solely as N2 in the degassed gas, regardless of fO2. 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 fO2 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 fO2 conditions, the primitive atmosphere would have become more enriched in N2 gas.

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+, NH4+, NH3–, NHF+ and N2) in silicate melts (Mikhail and Sverjensky, 2014; Dalou et al., 2019a; Mosenfelder et al., 2019; Boulliung et al., 2020; Grewal et al., 2020) and fluids (Li and Keppeler, 2014). The speciation and solubility of nitrogen primarily depend on oxygen fugacity (Libourel et al., 2003; Boulliung 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 815N/814N = (815N/814Nsample−1) · 1,000, are useful for reconstructing Earth’s N degassing history. For instance, the range of 815N values observed in Archean diamonds corresponds to that in present day diamonds and mid-ocean ridge basalts (MORBs), implying that the mantle 815N 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 (fO2) > IW (Libourel et al., 2020) and fluids (Li and Keppeler, 2014). The speciation and solubility of nitrogen primarily depend on oxygen fugacity (Libourel et al., 2003; Boulliung 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.
Degassing Experiments and Results

To establish the effect of O₂ 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 O₂ conditions ranging from IW to IW−4.2 (Table 1). These O₂ 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 ¹⁵N/¹⁴N 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 ¹⁵N/¹⁴N 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 ¹⁴N²⁰O− and ¹⁵N²⁰O+ 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 ± 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 ± 735 ppm (at IW−4.2) to 3,084 ± 377 ppm (at IW−1). This decrease of N solubility with increasing O₂ is consistent with observations in silicate melts (with low uncertainties of 0.1 ‰ between the glass and the forsterite capsule. The dissolved forsterite contains negligible amounts of N (2 ± 2 ppm).

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

<table>
<thead>
<tr>
<th>Exp ID</th>
<th>Estimated fO₂ (ΔIW)</th>
<th>Initial N content (ppm)</th>
<th>Measured N content (ppm)</th>
<th>F (remaining N fraction)</th>
<th>Measured ¹⁵N/¹⁴N ratios</th>
<th>Calculated δ¹⁵N normalised (%)</th>
<th>Bubbles present</th>
</tr>
</thead>
<tbody>
<tr>
<td>V152-PB05N</td>
<td>0.0</td>
<td>910</td>
<td>798 ± 4</td>
<td>0.88 ± 0.01</td>
<td>0.871 ± 0.005</td>
<td>−79 ± 8</td>
<td>✓</td>
</tr>
<tr>
<td>V149-PB1N</td>
<td>−0.3</td>
<td>1945</td>
<td>1316 ± 16</td>
<td>0.68 ± 0.01</td>
<td>0.845 ± 0.028</td>
<td>−107 ± 34</td>
<td>✓</td>
</tr>
<tr>
<td>V129-PB2N</td>
<td>−1.0</td>
<td>5075</td>
<td>3084 ± 377</td>
<td>0.61 ± 0.07</td>
<td>0.916 ± 0.003</td>
<td>−32 ± 6</td>
<td>✓</td>
</tr>
<tr>
<td>V148-PB4N</td>
<td>−2.3</td>
<td>10435</td>
<td>4914 ± 102</td>
<td>0.47 ± 0.01</td>
<td>0.907 ± 0.011</td>
<td>−41 ± 13</td>
<td>✓</td>
</tr>
<tr>
<td>V133-PB2N2Si</td>
<td>−2.6</td>
<td>8371</td>
<td>8335 ± 194</td>
<td>1.00 ± 0.02</td>
<td>0.946 ± 0.003</td>
<td>0 ± 6</td>
<td>✓</td>
</tr>
<tr>
<td>V125-PB8N</td>
<td>−3.5</td>
<td>16076</td>
<td>13342 ± 841</td>
<td>0.83 ± 0.05</td>
<td>0.925 ± 0.004</td>
<td>−5 ± 7</td>
<td>✓</td>
</tr>
<tr>
<td>V151-PB2N3Si</td>
<td>−3.4</td>
<td>11353</td>
<td>7534 ± 526</td>
<td>0.66 ± 0.05</td>
<td>0.926 ± 0.007</td>
<td>−21 ± 10</td>
<td>✓</td>
</tr>
<tr>
<td>V150-PB8N6Si</td>
<td>−4.2</td>
<td>14609</td>
<td>13481 ± 735</td>
<td>0.93 ± 0.05</td>
<td>0.941 ± 0.006</td>
<td>−5 ± 9</td>
<td>✓</td>
</tr>
</tbody>
</table>

Figure 1 Optical microscope photograph of sample V125-PB8N, which contains 13,342 ± 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).
average). With increasing fraction of degassed N, $^{15}$N/$^{14}$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 $^{15}$N/$^{14}$N ratios were normalised to the initial $^{15}$N/$^{14}$N ratio of the undegassed glass V133-PB4N2Si (0.946 ± 0.003) and expressed as $\delta^{15}$N$_{\text{norm}}$ as:

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

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

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

where $\delta^{15}$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 $\alpha$ 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 N$_2$, even in very reduced samples in which N was dissolved as N-H complexes (V148-PB4N) and/or nitriles (V125-PB8N).

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

$$N_2(\text{magma}) \leftrightarrow N_2(\text{gas}) \quad \text{Eq. 3}$$

Had the least reduced samples (V152-PB05N and V149-PB1N) not been affected by diffusion through cracks, they would be expected to degas following Equation 3, since N$_2$ is the only N species dissolved in those melts. In contrast, under more reduced conditions, N degassed as (e.g., Dalou et al., 2019a):

$$2NH_3(\text{magma}) \leftrightarrow N_2(\text{gas}) + 3H_2(\text{gas}) \quad \text{Eq. 4}$$

$$2SiN(\text{magma}) + 4OH(\text{melt}) \leftrightarrow 2SiO_2(\text{magma}) + N_2(\text{gas}) + 2H_2(\text{gas}) \quad \text{Eq. 5}$$

These equilibrium 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):

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

$$\alpha = \exp(\Delta^{15}\text{N}_{\text{gas-melt}}/1000), \text{ Eq. 7}$$

where $h$ is Planck’s constant (J·K$^{-1}$), $k_b$ is the Boltzmann constant (J·K$^{-1}$), $T$ is temperature (K), $\rho$ and $\mu$ denote the Raman vibration modes (Hz) of N species in the gas and silicate phases, respectively, and $\rho_N$ is the reduced mass of the N-bearing molecule. Using this expression, we calculated that the N isotopic fractionation factor at 1550 ℃ 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 $\delta^{15}$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
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 $f_O_2$ conditions. The magnitude of diffusive N isotopic fractionation during degassing is similar to that observed in natural high pressure-high temperature peridotitic systems (>25 ‰; 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 ($m$): 

$$\frac{D_{^{15}N}}{D_{^{14}N}} = \left(\frac{m_{^{15}N}}{m_{^{14}N}}\right)^\beta,$$

where $\beta$ 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 ($high \beta$), whereas $N_3^-$, which is bonded to Si, diffuses slowly (Boulliung et al., 2021) and has a smaller isotopic effect ($low \beta$). Good fits to our data are $\beta = 0.2$ for $N_2$ diffusing as $N_2$, 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 $f_O_2$ 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 $f_O_2$ 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 ($δ^{15}N = -5 \pm 2$ ‰ in diamonds and MORBs) and the $^{15}$N-enriched surface ($δ^{15}N = +6$ ‰ in
sediments and δ15N = 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 δ15N 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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References


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Supplementary Information

The Supplementary Information includes:

1. Methods
2. Supplementary Discussion
Tables S-1 and S-2
Figures S-1 to S-3
Supplementary Information References

1. Methods

Synthesis of starting material

Two series of mafic glasses were prepared:

- a series of Fe-free glasses, noted PB, for the degassing experiments presented in the main text was designed to equilibrate magma-ocean-like melts with a N-rich gas; and to avoid N partitioning into Fe metal blobs at low fO2 conditions (Dalou et al., 2017; Speelmanns et al., 2019; Grewal et al., 2019).
- a series of Fe-bearing glasses, noted PBF, was designed to equilibrate magma-ocean-like melts and a Fe-N or Fe-Si-N alloy (± N-rich gas) under reducing conditions to allow the calculation of fO2 conditions.

These mafic glasses were synthesised based on the magma ocean composition proposed by Fichtner et al. (2021). The starting composition was chosen to account for MgO dissolution from the forsterite capsule at 1550 °C, which here increased the MgO concentration of the melt from 9.7 to up to 22 wt. % (Table S-1). Using this composition, we obtained well-quenched MgO-rich glasses that were relatively depolymerised (i.e. NBO/T ≥ 1, where NBO/T is the ratio of non-bridging oxygens to tetrahedral cations).

The starting powders were prepared by mixing pre-dried, spectroscopically pure SiO2, Al2O3, MgO, CaCO3, Na2CO3, and K2CO3 reagents. The mixtures were decarbonated by slow heating (3 °C/min), then fused in air for 2 h at 1350 °C in platinum crucibles in a 1 atm furnace. Melts were quenched to glass in water, then crushed and hand ground.
in an agate mortar for 45 min. After decarbonating the glass powders, Fe was added to the PBF series as FeO powder, whereas the PB series remained Fe free. Nitrogen was added to both series using 0.5–8 wt. % Si$_3$N$_4$, noted ‘0.5N’ to ‘8N’ in the sample names. Both Si$_3^{14}$N$_4$ and Si$_3^{15}$N$_4$ powders (prepared as described in Dalou et al., 2019) were used to yield an initial $^{15}$N/$^{14}$N ratio of 0.946 ± 0.003. By varying the amount of Si$_3$N$_4$ added to the starting compositions and adding additional Si powder (2, 3 and 6 wt. %, noted ‘2Si’, ‘3Si’, and ‘6Si’ in the sample names), we were able to change (but not control) the sample $f$O$_{2}$ because Si$_3$N$_4$ and Si have a strong reducing effect (Dalou et al., 2017). The starting materials were loaded into pure forsterite capsules to ensure reducing conditions and prevent N loss. Glasses were originally anhydrous but were likely contaminated by atmospheric hydrogen, since N-H vibrations were observed in the experimental run products.

**Experimental procedure**

Experiments were performed in a 1/2-inch piston cylinder at 1.5 GPa and 1550 °C at the Centre de Recherches Pétrographiques et Géochimiques (CRPG, Nancy, France). Run temperatures were controlled to within ~1 °C of the set point using W$_{95}$Re$_{5}$/W$_{74}$Re$_{26}$ thermocouples. The duration of the experiments was 6 h, which is sufficient to reach compositional equilibrium (Dalou et al., 2017). Before decompression, the power to the furnace was cut and the experiment was quenched rapidly (~175 °C/s). During this stage of decompression, the forsterite capsules suffered cracking, which divided them into three to six lamallae 0.2–0.8 mm thick.

Hence, the final run product from each experiment consisted of various lamallae of glass embedded in forsterite, which were individually mounted in epoxy and polished with ethanol. For each experiment, the best sample was selected: the sample with the largest bubbles was selected for Raman spectroscopy (PB series) and that with the largest metal blobs for electron probe microanalysis (EPMA, all glasses). The selected lamellae were then removed from the resin, pressed into high-purity indium metal mounts, and gold coated for SIMS analysis. After re-polishing to remove any coating to avoid interference from Au vibrational bands, mounts from the PB series were analysed by Raman spectroscopy, and then all glasses were carbon coated for EPMA.

**SIMS analyses**

In-situ SIMS analyses of N concentrations and isotopic ratios in the silicate glasses were performed at the CRPG using the CAMECA 1280-HR2. Nitrogen ($^{14}$N + $^{15}$N) contents and isotopic ratios (Table 1) were measured by analysing the secondary molecular ions $^{14}$N$_2$O$^-$ and $^{15}$N$_2$O$^-$ at masses 30 and 31, respectively, at a nominal mass resolution of 14,000. A 10 kV Cs$^+$ primary ion beam was used with a ~10 nA current, resulting in a beam diameter of 15–20 μm, and a normal-incidence electron gun was used for charge compensation. To minimise surface contamination, glass surfaces were pre-sputtered for 180 s over a 10 × 10 μm area prior to signal acquisition. Further details on the SIMS N analysis procedure are available in Füri et al. (2018). The $^{14}$N$_2$O$^-$ and $^{15}$N$_2$O$^-$ ions were measured for 30 cycles in peak-jumping mode on an electron multiplier for 6 s, together with $^{27}$Al$^-$ (3 s), $^{30}$Si$^-$ (3 s), and $^{16}$O$_2^-$ (3 s) on a faraday cup. We used a suite of eight reference glasses with known N concentrations and isotopic compositions to determine the N contents in
the silicate glasses based on the $^{14}$N$^{16}$O$^{-}$ count rate normalised by the $^{16}$O$^{2-}$ signal (Füri et al., 2018). This method has been shown to yield N contents in excellent agreement with static mass spectrometry analyses for glasses of variable composition and containing ≤1 to 6,000 ppm N (Boulliung et al., 2020). Based on repeated isotopic ratio measurements of five reference glasses containing ≥136 ppm N ($\delta^{15}$N$_{true}$ = $-4 \pm 1 \%$), the instrumental mass fractionation (IMF) for glass analyses was determined to be $\alpha_{inst} = 1.0120 \pm 0.0015$ (2σ; Fig. S-1). Thus, the measured $^{15}$N/$^{14}$N ratios of the experimental glasses were corrected for IMF as $(^{15}$N/$^{14}$N)$_{corr} = (^{15}$N/$^{14}$N)$_{measured} / \alpha_{inst}$.

**Raman spectroscopy analyses**

Raman spectroscopy was performed using a LabRAM HR microspectrometer (Horiba Jobin Yvon) at GeoRessources (Nancy, France) using the 457.9 nm radiations of an Ar$^+$ laser (Stabilite 2017, Spectra-Physics) with 154 mW output. The laser intensity was focused to a ~2 µm spot-size with 7 mW on-sample through a 50× long-working-distance Olympus objective with a 0.5 numerical aperture. The spectrometer was equipped with a 1,800 grooves/mm grating. Acquisition times were 10 s, with 20 acquisitions collected per spectrum. To observe Si-N vibrations, molecular N$_2$ vibrations, and N-H vibrations in the degassed silicate glasses, spectra were acquired in the 700–1200, 2000–2400, and 3060–3560 cm$^{-1}$ spectral windows, respectively. No baseline corrections were applied to the spectra presented in Figure 3.

To analyse gas bubble contents, the laser was focused into the largest bubbles (>30 µm in diameter) and spectra were acquired for 15 s with 30 acquisitions, centred on the 2200 and 3160 cm$^{-1}$ spectral windows. In these bubbles, the N triple bond vibration of molecular N$_2$, and the C-H vibration in CH$_4$ were observed at 2331 and 2917 cm$^{-1}$, respectively (Fig. S-2). We note the absence of N-H vibrations in the range 3200–3450 cm$^{-1}$.

**EPMA**

Major element compositions of glasses and metal blobs (in Fe-bearing samples) were determined using a CAMECA SXFive-Tactics at the Laboratoire Magmas et Volcans (Clermont-Ferrand, France). For glass analyses, we used an accelerating voltage of 15 kV and a 8 nA beam defocused to 10 µm. Wollastonite (Si, Ca), basaltic glass VG2 (Al), Fe$_2$O$_3$ (Fe), MgO (Mg), and albite (Na) were used as standards. For metal alloys, we used a 15 kV accelerating voltage and a 15 nA focused beam. Along with Fe, the Pt and Si concentrations in the metal phases of all samples were measured, and pure Fe, Si, and Pt were used as metal standards. Aluminium was analysed to check for silicate contamination during metal analyses, using VG2 as a standard. The major element compositions of silicate glasses determined by EPMA are presented in Table S-1 and those of metal blobs in Table S-2.
Oxygen fugacity calculation

Oxygen fugacities, expressed as log \( f_O^2 \) (IW), were estimated from the equilibrium reaction \( \text{FeO}_{\text{silicate melt}} = \text{Fe}_{\text{liquid metal}} + 1/2 \text{O}_2 \) for Fe-bearing samples. Following this equilibrium, \( f_O^2 \) was calculated using the relationship between the mole fractions of FeO in silicate melt (\( X_{\text{FeO}}^{\text{melt}} \)) and Fe in liquid metal (\( X_{\text{Fe}}^{\text{alloy}} \)), their associated activity coefficients (\( \gamma_{\text{FeO}}^{\text{melt}} \) and \( \gamma_{\text{Fe}}^{\text{alloy}} \), respectively), and the equilibrium constant (\( K \)) of the reaction (Médard et al., 2008) as described in Dalou et al. (2017):

\[
\log_{10} f_O^2 = \frac{2}{\ln(10)} \left[ \ln \left( \frac{X_{\text{FeO}}^{\text{melt}}}{X_{\text{Fe}}^{\text{alloy}}} \right) - \ln \left( \gamma_{\text{Fe}}^{\text{alloy}} \right) + \ln \left( \gamma_{\text{FeO}}^{\text{melt}} \right) - \ln K \right]
\]

Eq. S-1

\( \gamma_{\text{Fe}}^{\text{alloy}} \) was derived via the MetalAct metal activity calculator (Wade and Wood, 2005) for each sample and \( \gamma_{\text{FeO}}^{\text{melt}} \) was assumed to be 1.2 (Dalou et al., 2017, 2019). We used the method of Stanley et al. (2014) and Zhang et al. (2016) to directly compare the resulting \( f_O^2 \) to the IW buffer, which is referenced to solid Fe metal. The \( f_O^2 \) conditions of the PBF series could only be determined in 5 samples (Fig. S-3a and Table S-2), in which the metal blobs were >5 µm in diameter (Fig. S-3b); the \( f_O^2 \) values of these samples range from IW −2.3 to IW −4.2. The \( f_O^2 \) conditions in samples PBF05N and PBF2N, in which metal blobs were too small to be analysed, were roughly estimated by extrapolation of the trend in Figure S-3a.

Because each PB sample has an equivalent PBF sample in terms of initial Si\( _3 \)N\( _4 \) and Si metal concentrations (e.g., PB4N2Si and PBF4N2Si), we assumed that the \( f_O^2 \) determined for each PBF sample corresponds to that of its equivalent in the PB series. Although this is a very rough approximation (±0.5 log units), this indirect method of estimating \( f_O^2 \) in the degassed Fe-free glasses enabled us to discuss the effect of \( f_O^2 \) conditions on N solubility in the main text.

\( P(N_2) \) calculation

Determining the partial pressure of nitrogen \( P(N_2) \) or nitrogen fugacity \( f_{N_2} \) in the gas phase (i.e., bubbles) of the samples from this study could provide more quantitative information on the effect of the gas composition on the solubility and isotopic fractionation of N. Indeed, it could be used to calculate the equilibrium constant \( K \) of the different N degassing reactions. Bernadou et al. (2021) calculated \( P(N_2) \) in the fluid phase of their experiments by quantifying the partial pressure of other species within the fluid phase: H\( _2 \)O, CO\( _2 \), CO, and H\( _2 \). They determined the pressure of H\( _2 \)O and CO\( _2 \) by converting the measured IR band intensities into concentrations following Shishkina et al. (2010), and then into partial pressures using the numerical model of Iacono-Marziano et al. (2012). The partial pressures of CO and H\( _2 \) were determined using the activities of C (graphite) and water and \( f_O^2 \) by using the equilibrium reaction presented in Bernadou et al. (2021). They then calculated \( P(N_2) \) by subtracting the fugacities of the other species from the “total
pressure” of the experiment and converted \( P(N_2) \) to \( fN_2 \) by applying different coefficients depending on the pressure conditions of their experiments.

Unfortunately, we cannot apply this method to our experiments because only two bubbles in two experiments performed at the same pressure and temperature conditions were analysed by Raman spectroscopy. As previously mentioned, \( N_2 \) and \( CH_4 \) were detected in the bubbles by Raman spectroscopy, but, unlike IR band intensities, Raman band intensities cannot be converted into concentrations, which are necessary to follow the methods of Bernadou et al. (2021) or Hirschmann et al. (2012) for \( H_2 \). Moreover, because \( N_2 \) is not the only gas species in the bubbles, its pressure cannot be considered as equivalent to the confining pressure. Even considering the mixed gases species in the bubbles, Zhang and Duan (2009) do not provide the equations of state to calculate the fugacities of \( N_2 \) and \( CH_4 \) at pressure conditions relevant to our study (>1 GPa). Therefore, calculating \( P(N_2) \) in the samples from this study would require numerous assumptions and generate meaningless values.

### 2. Supplementary Discussion

**H, C, and S isotopic variations observed during basaltic magma degassing**

Studies of degassed basalts, whether terrestrial mid-ocean ridge basalts (Pineau and Javoy, 1994; Cartigny et al., 2001), ocean island basalts (Gerlach and Taylor, 1990; Aubaud et al., 2006), arc basalts (De Hoog et al., 2001; Hauri, 2002), or lunar basalts (Saal and Hauri, 2021) have shown H, C, and S isotopic variations consistent with our observations for N isotopes during degassing.

In natural degassed basaltic glasses, H and C become isotopically lighter with increased degassing (e.g., Taylor et al., 1986; Gerlach and Taylor, 1990; Pineau and Javoy, 1994; Cartigny et al., 2001; Hauri, 2002). For instance, melt inclusions from a single Hawaiian volcano display \( \delta D \) values from \(-61 \pm 4 \, % \) to \(-165 \pm 4 \, % \) (Hauri, 2002). Whereas the heavier \( \delta D \) values (> \(-70 \, % \)) can be explained by a kinetic isotopic fractionation due to H diffusion from the melt inclusions, the most negative values (\(-103 \pm 4 \, % \) to \(-165 \pm 4 \, % \)) negatively correlate with their water contents. This variation of \( \delta D \) values was modelled by the shallow open-system degassing of \( H_2O \) vapour with a vapour-melt hydrogen isotopic fractionation factor of 1.024 (Hauri, 2002). Thus, increased equilibrium degassing of H produces isotopically lighter silicate melts. This applies for the degassing of H as \( H_2O \) under present-day volcanic degassing conditions. Under more reduced conditions, such as a lunar or martian magmatic degassing, H degasses as \( H_2 \) or \( CH_4 \), producing isotopically heavier silicate melts as degassing increases (Taylor et al., 1986).

Evidently, the degrees of such fractionations are expected to be smaller for C and S than for H due to the smaller relative mass differences between their isotopes. However, large C isotopic fractionations produced by C degassing have also been observed in degassed MORBs. For instance, \( \delta^{13}C \) values range between \(-11.4 \) and \(-4.3 \, % \) in MORBs from the South Indian Ridge and positively correlate with sample vesicularity, confirming the influence of degassing on C isotopic fractionation (Cartigny et al., 2001). In melt inclusions from Koolau volcano, Hawaii, Hauri (2002) also observed large \( \delta^{13}C \) variations (\(-12 \) to \(-21 \, % \)), again explained by C degassing. In both cases, these wide ranges of \( \delta^{13}C \)
values were explained by open-system (Rayleigh) rather than closed-system degassing. Yet, in the South Indian Ridge MORBs, the observed N isotopic fractionation during degassing is opposite to that of C isotopes, i.e. δ15N values increase from −5.9 to +2.1 ‰ in the residual melt with increased degassing (Cartigny et al., 2001). The opposite fractionation trends of C and N isotopes during degassing can be explained by their equilibrium degassing reactions. Carbon degasses as:

\[
\text{CO}_3^{2−} \text{ (silicate melt)} \rightarrow \text{CO}_2 \text{ (gas)} + \text{O}^{2−} \text{ (silicate melt)}, \quad \text{Eq. S-2}
\]

\[
\text{CH}_4 \text{ (silicate melt)} + 2\text{O}_2 \text{ (silicate melt)} \rightarrow \text{CO}_2 \text{ (gas)} + 2\text{H}_2\text{O }\text{(vapour)}, \quad \text{Eq. S-3}
\]

depending on whether it dissolves as carbonate or its more reduced form. Both degassing reactions produce a gas-melt isotopic fractionation factor >1 as determined by Javoy et al. (1976), and thus isotopically lighter silicate melts with increased C degassing. In contrast, in MORBs and OIBs, N is dissolved under its molecular form and degasses as:

\[
\text{N}_2 \text{ (silicate melt)} \rightarrow \text{N}_2 \text{ (gas)}, \quad \text{Eq. S-4}
\]

which, as modelled in Figure 3, produces a gas-melt isotopic fractionation factor of 0.999, and thus isotopically heavier silicate melts with increased degassing. Under the more reduced conditions investigated in this study to simulate magma ocean degassing, this N degassing reaction no longer holds, as shown by Equations 4 and 5.

Sulfur degassing is more complex because sulfur is dissolved and degassed as multiple gaseous species depending on fO2 conditions. Under reducing conditions comparable to those investigated herein, S dissolves into silicate melts as S2− (Jugo et al., 2010) and can degas as H2S, COS, and S2 in various proportions depending on pressure, temperature, and fO2 conditions (Renggli et al., 2017). Simplifying the issue by taking an average gas-melt sulfur isotopic fractionation factor of 1.003, Saal and Hauri (2021) successfully modelled the large variation of δ34S values measured in lunar volcanic glasses (+1.3 to −14 ‰) as equilibrium open-system degassing. Therefore, increased degassing of sulfur under reduced conditions decreases the δ34S values of silicate melts. However, at higher fO2 conditions, S is dissolved as SO42− in the silicate melt and degasses either as SO2 or H2S, and the δ34S values of the silicate melt increase with increasing degassing (de Moor et al., 2013).

Large kinetic nitrogen isotopic effects observed in natural mantle samples

Large variations have been observed among the nitrogen isotopic compositions of diverse mantle samples including diamonds (e.g., Mikhail et al., 2014) and xenoliths (Yokochi et al., 2009; Banerjee et al. 2015; Yamamoto et al., 2020). For instance, Yokochi et al. (2009) reported large isotopic disequilibria up to 25.4 ‰ between ferromagnesian minerals (olivine and pyroxene with positive δ15N values) and phlogopite (with δ15N as low as −17.3 ‰) in single peridotite xenoliths. Furthermore, both peridotitic and eclogitic diamonds show δ15N values varying from <−40 ‰ to >+20 ‰ (Mikhail et al., 2014). Whereas some of these variations can be explained by source variability, others cannot,
particularly $\delta^{15}$N heterogeneities observed in single diamond samples (≤33‰; Mikhail et al., 2014). Very interestingly, $\delta^{15}$N variations in both xenoliths and diamonds are of the same order of magnitude as those measured in the degassed glasses from this study and are, therefore, too large to be explained by equilibrium N isotopic fractionations. Whereas Mikhail et al. (2014) could not conclude with certainty that kinetic isotopic fractionation was the only cause for the large range of $\delta^{15}$N values they measured, Yokochi et al. (2009) presented evidence for kinetic isotopic fractionation during the substitution of NH$_4^+$ for N$_2$ in phlogopite during N uptake from the host magma. Therefore, as discussed in the main text, large kinetic N isotopic fractionations (≥25‰) resulting from a diffusive process at magmatic temperatures can be observed in natural settings and reproduced experimentally at high pressure and high temperature.

**Supplementary Tables**

**Table S-1** Major element contents (wt. %) of silicate glasses; bdl, below detection limit.

<table>
<thead>
<tr>
<th>Exp ID</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>FeO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-free degassed glasses</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V152-PB05N</td>
<td>52.9 ± 0.3</td>
<td>7.8 ± 0.1</td>
<td>bdl</td>
<td>19.9 ± 0.3</td>
<td>6.8 ± 0.1</td>
<td>7.7 ± 0.1</td>
<td>3.4 ± 0.1</td>
<td>98.4 ± 0.3</td>
</tr>
<tr>
<td>V149-PB1N</td>
<td>52.5 ± 0.2</td>
<td>7.8 ± 0.2</td>
<td>bdl</td>
<td>20.5 ± 0.4</td>
<td>7.1 ± 0.1</td>
<td>7.2 ± 0.1</td>
<td>3.3 ± 0.1</td>
<td>98.3 ± 0.3</td>
</tr>
<tr>
<td>V129-PB2N</td>
<td>53.0 ± 0.2</td>
<td>7.9 ± 0.1</td>
<td>bdl</td>
<td>20.0 ± 0.4</td>
<td>6.7 ± 0.1</td>
<td>7.6 ± 0.1</td>
<td>3.5 ± 0.1</td>
<td>98.6 ± 0.4</td>
</tr>
<tr>
<td>V148-PB4N</td>
<td>54.2 ± 0.2</td>
<td>7.0 ± 0.1</td>
<td>bdl</td>
<td>21.3 ± 0.3</td>
<td>6.6 ± 0.2</td>
<td>7.2 ± 0.1</td>
<td>3.1 ± 0.1</td>
<td>99.3 ± 0.5</td>
</tr>
<tr>
<td>V133-PB4N2Si</td>
<td>57.9 ± 0.3</td>
<td>8.7 ± 0.1</td>
<td>bdl</td>
<td>17.0 ± 0.1</td>
<td>6.2 ± 0.1</td>
<td>7.6 ± 0.1</td>
<td>3.4 ± 0.1</td>
<td>100.8 ± 0.5</td>
</tr>
<tr>
<td>V125-PB8N</td>
<td>52.2 ± 0.2</td>
<td>7.4 ± 0.1</td>
<td>bdl</td>
<td>19.7 ± 0.2</td>
<td>6.6 ± 0.1</td>
<td>7.2 ± 0.1</td>
<td>3.1 ± 0.1</td>
<td>101.2 ± 0.2</td>
</tr>
<tr>
<td>V151-PB6N3Si</td>
<td>58.1 ± 0.4</td>
<td>6.3 ± 0.1</td>
<td>bdl</td>
<td>21.9 ± 0.3</td>
<td>5.5 ± 0.1</td>
<td>6.3 ± 0.1</td>
<td>2.6 ± 0.1</td>
<td>99.7 ± 0.3</td>
</tr>
<tr>
<td>V150-PB8N6Si</td>
<td>61.6 ± 0.6</td>
<td>5.7 ± 0.2</td>
<td>bdl</td>
<td>19.8 ± 0.6</td>
<td>6.0 ± 0.1</td>
<td>5.5 ± 0.1</td>
<td>2.6 ± 0.1</td>
<td>101.2 ± 0.4</td>
</tr>
<tr>
<td>Fe-bearing glasses</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V153-PBF05N</td>
<td>47.2 ± 0.3</td>
<td>8.3 ± 0.2</td>
<td>2.8 ± 0.1</td>
<td>19.6 ± 0.6</td>
<td>6.8 ± 0.1</td>
<td>7.5 ± 0.2</td>
<td>3.4 ± 0.1</td>
<td>95.7 ± 0.4</td>
</tr>
<tr>
<td>V142-PBF2N</td>
<td>50.2 ± 0.4</td>
<td>7.7 ± 0.1</td>
<td>4.5 ± 0.1</td>
<td>18.4 ± 0.2</td>
<td>7.1 ± 0.1</td>
<td>7.3 ± 0.1</td>
<td>3.4 ± 0.1</td>
<td>98.7 ± 0.4</td>
</tr>
<tr>
<td>V141-PBF4N</td>
<td>50.9 ± 0.3</td>
<td>8.0 ± 0.1</td>
<td>2.0 ± 0.1</td>
<td>18.6 ± 0.3</td>
<td>7.5 ± 0.1</td>
<td>6.5 ± 0.1</td>
<td>3.3 ± 0.1</td>
<td>96.7 ± 0.4</td>
</tr>
<tr>
<td>V145-PBF4N2Si</td>
<td>53.4 ± 0.2</td>
<td>7.2 ± 0.1</td>
<td>1.8 ± 0.1</td>
<td>19.6 ± 0.4</td>
<td>6.4 ± 0.1</td>
<td>6.5 ± 0.1</td>
<td>3.2 ± 0.1</td>
<td>98.1 ± 0.5</td>
</tr>
<tr>
<td>V147-PBF8N</td>
<td>54.9 ± 0.4</td>
<td>7.0 ± 0.2</td>
<td>0.9 ± 0.1</td>
<td>20.2 ± 0.4</td>
<td>6.2 ± 0.1</td>
<td>7.0 ± 0.2</td>
<td>3.2 ± 0.1</td>
<td>99.3 ± 0.4</td>
</tr>
<tr>
<td>V154-PBF6N3Si</td>
<td>58.0 ± 0.5</td>
<td>6.9 ± 0.1</td>
<td>0.8 ± 0.4</td>
<td>19.4 ± 0.3</td>
<td>5.9 ± 0.1</td>
<td>6.3 ± 0.1</td>
<td>3.0 ± 0.1</td>
<td>100.3 ± 0.5</td>
</tr>
<tr>
<td>V155-PBF8N6Si</td>
<td>62.8 ± 0.5</td>
<td>5.9 ± 0.2</td>
<td>0.2 ± 0.2</td>
<td>19.6 ± 0.3</td>
<td>5.0 ± 0.1</td>
<td>5.5 ± 0.1</td>
<td>2.7 ± 0.1</td>
<td>101.6 ± 0.7</td>
</tr>
</tbody>
</table>
**Table S-2**  Fe, Pt, and Si contents (wt. %) of metal blobs and estimated $f$O$_2$ conditions.

<table>
<thead>
<tr>
<th>Exp ID</th>
<th>Fe</th>
<th>Pt</th>
<th>Si</th>
<th>$f$O$_2$ (IW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V141-PBF4N</td>
<td>92.0 ± 0.3</td>
<td>0.03 ± 0.03</td>
<td>0.04 ± 0.02</td>
<td>−2.3</td>
</tr>
<tr>
<td>V145-PBF4N2Si</td>
<td>94.0 ± 0.2</td>
<td>0.16 ± 0.04</td>
<td>0.007 ± 0.004</td>
<td>−2.6</td>
</tr>
<tr>
<td>V147-PBF8N</td>
<td>94.2 ± 0.4</td>
<td>0.30 ± 0.06</td>
<td>0.04 ± 0.01</td>
<td>−3.3</td>
</tr>
<tr>
<td>V154-PBF6N3Si</td>
<td>92.9 ± 0.3</td>
<td>0.4 ± 0.2</td>
<td>0.007 ± 0.002</td>
<td>−3.4</td>
</tr>
<tr>
<td>V155-PBF8N6Si</td>
<td>77.1 ± 0.9</td>
<td>1.8 ± 1.8</td>
<td>20.9 ± 1.1</td>
<td>−4.2</td>
</tr>
</tbody>
</table>

**Supplementary Figures**

![Graph](image)

**Figure S-1**  Measured $^{15}$N$^{16}$O$^-$/14$^{16}$O$^-$ ratios in five reference glasses used to calculate IMF. Each symbol corresponds to a reference glass whose N content was previously measured by static mass spectrometry (Füri *et al.*, 2018). The dashed line is the average of all standard analyses calculated using IsoplotR (Vermeesch, 2018) with 2σ uncertainties (shown by the grey shaded bar). The true $^{15}$N/$^{14}$N value of these reference glasses is shown by the black line (~0.003662). The ratio of the average to the true value (*i.e.* the dashed and solid lines, respectively) is $\alpha_{\text{inst}}$. 
Figure S-2  Raman spectra obtained in bubbles of sample V125-PB8N.

Figure S-3  (a) $fO_2$ conditions (relative to the IW buffer) calculated for samples containing sufficiently large metal blobs (b). The $fO_2$ conditions of samples in which metal blobs were too small to be analysed (<5 µm) were estimated by extrapolation of the trend, i.e., log $fO_2$ as a function of the amount of reducing agent (Si$_3$N$_4$ and Si metal) added (dashed line, log function).

Supplementary Information References


