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

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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 silicate melts (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 equilibrium). 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 Ω neutral to oxidising and composed of H2O, CO2, and N2 if it resembled modern volcanic gases (Kasting, 1993), or Ω 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−, 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[%o] = (15N/15N atm) − 1 · 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(gas) ↔ N2(gas). This reaction has been experimentally determined at oxygen fugacity conditions (fO2 > IW (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.

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increasing to 3,084 ± 377 ppm (at IW conditions 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 15N16O and 16N18O 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 ± 841 ppm (at IW) to 798 ± 4 ppm (at IW−4.2) (Table 1). 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 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 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 Bernardou et al. (2021). The variation of N solubilities with O2 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 (O2 > IW−4), N is mostly dissolved as N-H complexes (Fig. 2c), and above IW−2, N is also dissolved as molecular N2 (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 O2 conditions. Depending on initial N content and O2, the fraction of N degassed varied from 7 to 53 %. Samples V152−P80N 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 15N spiked samples permits us to obtain precise 15N/14N ratios in the silicate (with low uncertainties of 0.1 %) on
average). With increasing fraction of degassed N, $^{15}$N/$^{14}$N ratios decreased from 0.946 ± 0.003 in the degassed 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 degassed glass V133-PB4N2Si (0.946 ± 0.003) and expressed as $\delta^{15}$N$_{norm}$ as:

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

Eq. 1

These normalised values are not calculated relative to the atmospheric N isotopic composition ($^{15}$N/$^{14}$N$_{air}$ = 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 degassed 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 evolved 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):

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

Eq. 2

where $\delta^{15}$N$_{initial}$ 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 nitrides (V125-PB8N).

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

$$N_2(magma) \leftrightarrow N_2(gas)$$  

Eq. 3

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 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):

$$2NH_3(magma) \leftrightarrow N_2(gas) + 3H_2(gas)$$  

Eq. 4

$$2SiN(magma) + 4OH−(magma) \leftrightarrow 2SiO_2(magma) + N_2(gas) + 2H_2(gas).$$  

Eq. 5

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):

$$\Delta^{15}$N$^{gas-melt} = \frac{1,000}{24} \left( \frac{h}{k} \right)^{\Delta m} \left( \frac{m_{^{15}N}}{m_{^{14}N}} \right)^{\Delta \nu_{gas-melt}} \exp(\Delta \nu_{gas-melt} / 1,000),$$  

Eq. 6

where $h$ is Planck’s constant (J·K$^{-1}$), $k$ is the Boltzmann constant (J·K$^{-1}$), $T$ is temperature (K), $\Delta \nu_{gas}$ and $\Delta \nu_{melt}$ are the Raman vibration modes (Hz) of N species in the gas and silicate phases, respectively, and $\mu_N$ 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 $\delta^{15}$N$_{norm}$ 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 ($m$): $D_{^{15}N}/D_{^{14}N} = (m_{^{15}N}/m_{^{14}N})^{\beta}$, 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 $N_3^-$ 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.

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 $^{14}$N. This could have produced the currently observed isotopic differences between the $^{15}$N-depleted mantle ($\delta^{15}$N = −5 ± 2 ‰ in diamonds and MORBs) and the $^{15}$N-enriched surface ($\delta^{15}$N = +6 ‰ in

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**Figure 3** (a) $^{15}$N/$^{14}$N ratios as a function of N content in glass, and (b) $^{15}$N/$^{14}$N ratios, and (c) $\delta^{15}$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 $^{15}$N/$^{14}$N ratios were the same in all starting materials. The degassing models are described in the text.
sediments and $\delta^{15}N = 0 \permil$, by definition, in the atmosphere (Cartigny and Marty, 2013). Other explanations of the N isotopic distribution among terrestrial reservoirs include i) recycling (sub-
duction) 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 $\delta^{15}N$ 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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