The nitrogen budget of Earth

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We comprehensively compile and review N content in geologic materials to calculate a new N budget for Earth. Using analyses of rocks and minerals in conjunction with N–Ar geochemistry demonstrates that the Bulk Silicate Earth (BSE) contains ~7 ± 4 times present atmospheric N (4 × 10^18 kg N, or PAN), with 27 ± 16 × 10^18 kg N. Comparison to chondritic composition, after subtracting N sequestered into the core, yields a consistent result, with BSE N between 17 ± 13 × 10^18 kg to 31 ± 24 × 10^18 kg N. Embedded in the chondritic comparison we calculate a N mass in Earth’s core (180 ± 110 to 30 ± 180 × 10^18 kg) as well as present discussion of the Moon as a proxy for the early mantle.

Significantly, our study indicates that the majority of the planetary budget of N is in the solid Earth. We suggest that the N estimate here precludes the need for a "missing N" reservoir. Nitrogen–Ar systematics in mantle rocks and primary melts identify the presence of two mantle reservoirs: MORB-source like (MSL) and high-N. High-N mantle is composed of young, N-rich material subducted from the surface and identified in OIB and some xenoliths. In contrast, MSL appears to be made of old material, though a component of subducted material is evident in this reservoir as well.

Taking into account N mass and isotopic character of the atmosphere and BSE, we calculate a δ15N of ~2%.

This value should be used when discussing bulk Earth N isotope evolution. Additionally, our work indicates that all surface N could pass through the mantle over Earth history, and in fact the mantle may act as a long-term sink for N. Since N acts as a tracer of exchange between the atmosphere, oceans, and mantle over time, clarifying its distribution in the Earth is critical for evolutionary models concerned with Earth system evolution. We suggest that N be viewed in the same light as carbon: it has a fast, biologically mediated cycle which connects it to a slow, tectonically-controlled geologic cycle.

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1. Introduction

Nitrogen, the fifth most common element in the solar system, is the main component of the atmosphere, a key nutrient for life, and has potential to be a tracer of processes linking the surface Earth to different reservoirs in the solid planet. Though N has long been known to exist geologically in fluid inclusions or as NH4+ in mineral lattices (e.g., Mayne, 1957), it was thought to predominantly reside in the atmosphere and biosphere (Baur and Wlotzka, 1969). It is now clear that N can indeed become incorporated into minerals and rocks in significant amounts and cycles over long time scales through the atmosphere, oceans, crust, and mantle. While the absolute concentration of N in rocks is low (often ~1 ppm, but up to ~100 or 1000 ppm), the great mass of the solid Earth compared to the atmosphere means that it has the potential to sequester large amounts of N. A picture of the behaviour of N in the Bulk Silicate Earth (BSE) has begun to emerge, but necessitates a new review and synthesis of available data (Fig. 1).

Similar to C (e.g., Holland, 1984), N is cycled in the Earth system in two ways: a fast, biologic cycle; and a slow, geologic cycle. Descriptions of biologic (e.g., Kelly, 2000) and geologic (e.g., Boyd, 2001; Holloway and Dahlgren, 2002; Kerrich et al., 2006) N cycles exist, but no adequate Earth system-wide picture of the fast and slow N cycles together is currently available. Briefly, the biologic cycle (for the modern Earth) is as follows: N2 in the atmosphere dissolves in the ocean and is converted to a biologically available form by N-fixing bacteria. This process is termed N-fixation. Nitrogen-fixing bacteria are either consumed by other organisms, or release N in waste, primarily as NH4+, which is quickly oxidized to NO3− in a bacterially-mediated process called nitrification. The primary return flux of N to the atmosphere is via denitrification, where NO3− is used by certain bacteria as the terminal acceptor in the electron transport chain and converted to either N2 or N2O. Recently, the importance of an additional reaction, anaerobic ammonium oxidation or anammox has been recognized as a return flux of N to the atmosphere (Thamdrup, 2012, and references therein). This is another bacterially mediated process whereby NH4+ reacts with NO2− to produce N2 and two H2O molecules.

The slow geologic cycle begins when dead organic matter sinks and settles in oceanic sediment. Organic N breaks down in the sediment via hydrolysis reactions, and converts to NH4+ (Hall, 1999). Since NH4+ has the same charge and a similar ionic radius as K+, it substitutes into mineral lattice sites that are normally occupied by K+. Clay minerals, micas, and K-feldspars are important mineral hosts of N. Once entrained in oceanic sediments and crust, N is carried into subduction zones, where it is either volatilized and removed from the down-going plate or carried into the mantle past the subduction barrier. In general, subduction zones with high geothermal gradients favour volatilization (e.g., Elkins et al., 2006), while cooler subduction zones favour N retention (e.g., Mitchell et al., 2010). Volatilized N either oxidizes to N2 and escapes via arc volcanism or is incorporated into intrusive igneous rocks. Nitrogen that is not returned to the surface becomes entrained in mantle circulation. Basalts at both mid-ocean ridges (MORB) (Marty, 1995) and ocean islands (OIB) (Mohapatra et al., 2009) show evidence for this surface-derived N, through either positive δ15N values.

While the general outline of the geologic N cycle is known, in order to more fully quantify this cycle and describe changes in it over Earth history, we calculate a thorough inventory of the N on Earth. This is a necessary step to accurately portray the Earth-system nature of the N cycle. To achieve this goal we present two approaches: “top-down” and “bottom-up” budget estimates. The “top-down” approach uses the composition of planetary building blocks and analogues to bracket total Earth N content. We then subtract the amount of N in the core to estimate BSE N content. For the “bottom-up” approach, we compile analyses of N in terrestrial rocks and minerals. We use these to estimate N concentration in various reservoirs: oceanic and continental sediments, oceanic and continental crust, and the mantle. We also use observed relationships between N and Ar from basalts to estimate mantle N content. In addition, we briefly discuss the behaviour of N in specific reservoirs. Our approach differs from past attempts (e.g., Table 1) by utilizing an extensive literature compilation in conjunction

![Number of Studies measuring N in geologic materials since 1975. The number of studies has increased as detection capability improves. Data produced after the mid-1990s have not been incorporated into a broad, Earth system perspective on the N cycle.](image-url)
with new experimental results to provide a thorough, comprehensive assessment of the N in all reservoirs of the Earth.

The structure of the paper is to first present description of the speciation and behaviour of N in the solid Earth, then a brief discussion of the data compilation used herein; this is followed by the two budget approaches, and finally a discussion of the implications of results. We present a discussion of N speciation and solubility first to serve as orientation, as N can exist as different species in the Earth depending on physical and chemical conditions. A flurry of recent experiments have elucidated many aspects of N solubility in silicate minerals (e.g., Li et al., 2013), metal alloys (Roskosz et al., 2013), and fluids (Li and Keppler, 2014).

Ultimately, we find that both approaches are mutually consistent. Chondritic comparison suggests between 17 ± 13 × 10^{18} kg and 31 ± 2410^{18} kg N in the BSE; terrestrial compilation suggests 27 ± 16 × 10^{18} kg N in the BSE. Our work not only suggests a higher N mass in the BSE than previous work (Goldblatt et al., 2009), but also arrives at approximately the same value from two independent tactics. A higher N content may have important implications for the geochemical history of N on the Earth. In addition, our budget allows for a reassessment of the overall N-isotopic composition of the planet, which is used to track interaction between various reservoirs on the Earth. These implications are detailed in our discussion (Sec. 5).

2. Nitrogen speciation in geologic materials, experimental results, and budget tools

In this section, we first summarize which N species are found in geologic materials, highlighting silicate rocks and minerals, fluids, and Fe-metal. Secondly, we incorporate recent experimental work to attempt to quantitatively describe N behaviour in geologic materials in response to changes in pressure, temperature, and oxygen fugacity. Thirdly, we describe the database used for subsequent budget calculation. Details pertinent to specific reservoirs will be discussed in the appropriate sections.

2.1. Nitrogen speciation in the solid Earth

Nitrogen is present as a number of species in the solid Earth. The primary control on speciation is redox, with temperature, pressure, and even pH playing roles in stability and solubility. Oxygen fugacity (fO\textsubscript{2}) is presented relative to some mineralogically controlled buffer (Frost, 1991). Buffers used in this study, in order of decreasing pertinence to speciation is redox, with temperature, pressure, and oxygen fugacity.

The third important reservoir for N is Fe-metal. Nitrogen is quite soluble in Fe-metal alloys at a variety of depths in the Earth (Kadik et al., 2011; Roskosz et al., 2013). It likely either dissolves as NH\textsubscript{3} or forms Fe–N (nitride) compounds. This has important ramifications for the N distribution in the Earth. Not only could significant N be found in Earth’s core, Fe–Ni metal may be present in the mantle transition zone and lower mantle (Frost and McCammon, 2008). There might be ≤ 10 wt.% N in FeNi-metal and ≤ 0.5 wt.% N in silicates in the transition zone and lower mantle (Roskosz et al., 2013). These concentrations indicate that an enormous quantity of N is theoretically plausible in the deeper domains of the mantle. This is discussed in more detail later.

Since N concentrations in geologic materials are usually quite low, analytical techniques present a non-trivial obstacle. A thorough discussion on this subject is provided by both Holloway and Dahlgren (2002) and Brauer and Hahne (2005). Briefly, N can be measured by dissolution/combustion and analysis on a mass spectrometer, spectral methods, Kjeldahl extraction, or colorimetric methods. These techniques continue to evolve and improve (Yokochi and Marty, 2006; Barry et al., 2012), and the availability of quality N data from rocks will continue to grow.

2.2. Experimental results

We have compiled experimental results to augment the discussion in the previous section and to quantitatively describe the N solubility of geologic materials (Figs. 2–3). Measurements have been made for N in minerals (Li et al., 2013), silicate melt (Libourel et al., 2003; Myssen et al., 2008; Myssen and Fogel, 2010; Myssen et al., 2014), Fe-metal (Kadik et al., 2011; Roskosz et al., 2013), and aqueous fluids (Li and Keppler, 2014; Li et al., 2015). Experimental conditions are variable (e.g., different starting materials, presence of alkalis), so at times trends are only visible when discussing single studies. Most studies use a basaltic composition for experimental rocks, with new experimental results to provide a thorough, comprehensive assessment of the N in all reservoirs of the Earth.

Pressure, temperature, and fO\textsubscript{2} all have an effect on N solubility in silicate melts, Fe–metal, and aqueous fluids. A first order observation is that N concentration appears to always be higher in fluids, melts, and
Fe-metal than in coexisting silicate minerals (Fig. 2). This is especially clear when the distribution coefficients ($D_{\text{metal/fuid}} = [N_{\text{metal/fuid}}]/[N_{\text{silicate}}]$) are calculated (Fig. 3). At all measured conditions, N prefers metal or fluid over silicates. Increasing pressure has noticeable effects on N solubility in silicates and metals, while the effect is less clear in fluids. Silicate N concentration increases with pressure, and, at least in the presence of Fe-metal, saturates at 0.64 wt.% at pressures above about 5 GPa (Roskosz et al.,).

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At lower pressures, solubility appears to follow a Henry’s law relationship, given by:

$$[N]_S = k_i p \quad (2)$$

where $[N]_S$ is in wt.%, $k_i$ is 0.128 wt.% GPa$^{-1}$, and $p$ is pressure (GPa). Concentration in Fe-metal also increases with pressure, and appears to be described by a Sievert’s law equation:

$$[N]_M = k_s \sqrt{p} \quad (3)$$

where $[N]_M$ is in wt.%, $k_s$ is an experimentally determined constant (3.06 wt. % GPa$^{-1/2}$), and $p$ is pressure (GPa). The pressure effect in aqueous fluids appears to be equivalent to silicates and metal, but experiments have been done only at lower pressures (Li et al., 2015).

Increasing temperature results in a decrease in N content in silicate melts (Fig. 2). The effect is most clearly seen in data from individual studies (Libourel et al., 2003; Mysen et al., 2008). Higher temperatures favour formation of N$_2$, which is more easily removed from silicate melts via extraction in fluids. Fig. 3 shows this well: higher temperature is associated with a higher $D_{\text{H}2O}$. This is partially due to the instability of N–H bonds at high temperature. Experiments done at the highest temperatures have Fe-metal in equilibrium with silicates, and since N-solubility in metal increases with increasing temperature, it is likely that N was lost from the silicates and taken up by the Fe-metal in these experiments (Roskosz et al., 2013).

In contrast, $f_{O_2}$ has a fairly strong effect on N solubility, and especially N partitioning between silicates and fluids (Fig. 3). In each experiment shown here, decreasing $f_{O_2}$ results in higher N content in silicates. This effect is less clear in metal, though these experiments were carried out at a narrower $f_{O_2}$ range, and $f_{O_2}$ must be at or below the IW buffer (\(=\Delta N\text{NO}_2 - 4\)) to even have Fe-metal stable in the experiment. Since oxidizing conditions promote N speciation as more fluid-mobile N$_2$, as opposed to NH$_3$, $D_{\text{H}2O}$ tends to decrease with decreasing $f_{O_2}$, as well. While the magnitude of the $f_{O_2}$ effect is different between different studies, the direction is the same throughout: lower $f_{O_2}$ results in higher N contents in silicates.

There are also some measurements of N-contents in minerals directly. We utilize equations, described by Li et al. (2013), of N solubility experimental results for olivine, pyroxene, and melt (in the absence of Fe-metal) to guide both estimates of N concentration and distribution coefficients (described below) between minerals and melt in poorly sampled reservoirs:

Olivine: $\log_{10} [N] = 2.15 - \frac{6.8 \times 10^7}{T} + 0.27p - 0.43\Delta\text{NiNiO}; \quad r^2 = 0.79 \quad (4)$

Pyroxene: $\log_{10} [N] = 6.48 - \frac{8.7 \times 10^7}{T} + 0.086p - 0.122\Delta\text{NiNiO}; \quad r^2 = 0.64 \quad (5)$

Melt: $\log_{10} [N] = 0.92 - \frac{3.50 \times 10^7}{T} + 0.4p - 0.083\Delta\text{IW}; \quad r^2 = 0.70 \quad (6)$

The above equations have temperature ($T$) in K, pressure ($p$) in GPa, $\Delta\text{NiNiO}$ or $\Delta\text{IW}$ is the $f_{O_2}$ relative to the NiNiO or IW buffer, and $[N]$ is in ppm. At appropriate conditions, concentrations of up to 100 ppm may be possible in the lowest metamorphosed upper mantle (Li et al., 2013), which means the upper mantle may have the capacity to sequester between $80 \times 10^{14}$ and $200 \times 10^{18}$ kg N, which is 20–50 times PAN.

The last tool based on experiments we utilize is measured or inferred partition coefficients ($K_0 = [\text{Element}]_{\text{mineral}}/[\text{Element}]_{\text{metal}}$); these are often used in conjunction with an equation linking partition coefficients to degree of partial melting (Rollinson, 1993):

$$\frac{[C_i]}{[C_0]} = \frac{1}{K_0 + F(1-K_0)} \quad (7)$$

$[C_0]$ is element concentration in source and $[C_i]$ is concentration in melt, and $F$ is degree of partial melting. Note that this equation is for batch (equilibrium) melting, which means that melt formed equilibrates with residual solids. We assume that any melt much reach a critical threshold (~1–10%) before extraction from the source rock, and prior to extraction it would have time to equilibrate fully with residual solids.

2.3. Database of geologic N measurements

We have compiled all of the available, published measurements of N concentration and $\delta^{15}$N values of geologic materials. Where they exist, we also include in the database $\delta^{13}$C, age of sample, Ar-isotope ratios and abundance, and concentrations of elements that behave similarly to NH$_4^+$, including K$_2$O, Rb, Lu, and Yb. The complete database is available in the supplementary material, which is organized by both rock names, as given in the original publications, and our interpreted geologic settings.

While rock names follow standard naming procedure, we also categorize data based on geologic setting. Unmetamorphosed samples are labelled as oceanic sediments (OS), oceanic lithosphere (OL), continental sediments (CS), and continental lithosphere (CL). Altered reservoirs (i.e., metamorphosed at $T < 300 \, ^\circ\text{C}$) are prefixed with ‘A’; those metamorphosed at $T > 300 \, ^\circ\text{C}$ are prefixed with ‘M’. Data for the mantle are from diamonds (D) and xenoliths (X). We also discuss mid-ocean ridge basalts (MORB) and ocean island basalts (OIB). These reservoirs will be addressed individually in the following sections.

Nitrogen concentration from most reservoirs is log-normally distributed. To calculate N mass in a given reservoir, we will generally use the product of the log-normal mean of N concentration and mass of that reservoir. As sample size is often low, we calculate maximum likelihood estimator parameters $\mu$ and $\sigma^2$, which are the mean and variance of the natural log of concentration, respectively (Limpert et al., 2001).

$$\bar{\mu} = \frac{\sum_i \ln [N_i]}{n} \quad (8)$$

$$\sigma^2 = \frac{\sum_i (\ln [N_i] - \bar{\mu})^2}{n} \quad (9)$$

Where $n$ is the number of samples. These parameters are then used to estimate the mean ($\mu$) and standard deviation ($\sigma$) of the total population:

$$\mu = x = e^{\bar{\mu} + \frac{\sigma^2}{2}} \quad (10)$$

$$\sigma = \sqrt{(e^{\sigma^2} - 1)} e^{\bar{\mu} + \frac{\sigma^2}{2}} \quad (11)$$

Unless otherwise specified, all errors given are standard error of the mean:

$$\text{SE}_{\bar{x}} = \frac{\sigma}{\sqrt{n}} \quad (12)$$

3. "Top-down" budget: accretion through core formation

In this section, we estimate the N budget of the BSE by comparing the Earth to other inner solar system bodies. The atmosphere of Venus hints that there is more N in the Earth than is found in its atmosphere alone. We bracket mass of N delivered to Earth during accretion by...
comparison to chondritic compositions. From this, we subtract N sequestered into the core to estimate the remainder in the BSE and atmosphere. While this model is dependent on the N content of accretionary material, we find that it is in reasonable agreement with our terrestrial-based budget, presented in Section 4. In addition, the N content of the Moon is calculated, as this may provide some constraints on the composition of the early, but post-core formation, mantle.

3.1. Initial N composition and planetary comparison: missing N?

Some motivation for this study comes from comparison of the Earth to extraterrestrial bodies: meteorites and Venus. Undifferentiated meteorites are leftover remnants from the early history of the Solar System, and are often used as proxies for the bulk composition of the protoplanetary disk. Venus is thought to have had a similar initial volatile composition as the Earth (Ringwood and Anderson, 1977; Lécyer et al., 2000; Chassefière et al., 2012). Comparison to both meteorites and Venus suggest that the Earth should have much more N than is found in the present atmosphere; by extension, we posit that the atmosphere is not the major N reservoir on Earth.

We address Venus first. The Venustian atmosphere contains $3.5 \pm 0.8\%N_2$, with the remainder composed of predominately (95.5%) CO$_2$ (von Zahn et al., 1983). We calculate the mass of N ($M_{N_2}$) in the atmosphere by using the following equation:

$$M_{N_2} = \frac{m_{N_2}}{m_o} N_2 \frac{4n^2p}{g} \quad (13)$$

where $m_{N_2}$ and $m_o$ are molar masses of $N_2$ (0.028 kg mol$^{-1}$) and Venus' atmosphere (0.04344 kg mol$^{-1}$); $N_2$ is the mixing ratio of $N_2$ (0.035); $r$ is the radius of Venus (6.052 $\times 10^7$ m); $p$ is the surface pressure ($9.2 \times 10^6$ Pa); and $g$ is the acceleration due to gravity (8.87 m s$^{-2}$).

The resulting N content of Venus' atmosphere is $11 \times 10^{18}$ kg N. When normalized to planetary mass, Venus' atmosphere has 3.4 times the mass of N in Earth's atmosphere. Given similar initial volatile composition, Earth should have substantial N in non-atmospheric reservoirs. Curiously, the amount of C in the Venustian atmosphere (as CO$_2$) is nearly identical to the amount of C in carbonate rocks on Earth (Taylor, 1992; Berner, 1998; Lécyer et al., 2000). If a similar mass balance exists for N, then a substantial amount of N must be in geologic reservoirs on Earth.

While the exact nature and composition of planetary accretionary bodies are a matter of debate, (e.g., Marty, 2012; Halliday, 2013), some combination of chondrite-like material accreted to form the rocky planets, including Earth. The volatile content of these bodies is thought to have decreased with distance from the Sun, though the feeding zones of growing planets may be substantial (Kaid and Cowan, 2015). We bracket terrestrial N content by using volatile-poor enstatite chondrites (EC) and volatile-rich carbonaceous chondrites (CC) as analogues for possible volatile delivery material. Note that we are not attempting to find a "perfect fit’’ meteorite to explain terrestrial volatiles, but simply providing some context for how much N should be present in the planet.

To utilize N contents of chondrite proxies, we follow the approach of Marty (2012) for both CC and EC. Marty compared two chondrites (Orgueil and Murchison) volatile abundances to a calculated volatile budget for the Bulk Earth (BE). These specific meteorites were chosen as they are primitive in composition and have experienced low grades of metamorphism. We include both a broader suite of CC and EC analyses. Both chondrite types have substantial N content: EC have an average N concentration of $605 \pm 206$ ppm and CC have $1235 \pm 440$ ppm N (Fig. 4).

Non-N volatile elements (e.g., C, H$_2$O, halogens) appear to be depleted in the Earth relative to chondritic concentration (Marty, 2012). These volatiles are expected to have negligible concentrations in the core, which is likely not the case for N, as discussed in the next section. Therefore, we assume that the abundance calculated by Marty for the BSE plus atmosphere accounts for the total abundance, and differences from chondritic values are due to processes during accretion/delivery. Note that we exclude Xe from this comparison, as it is more depleted than other volatiles, and requires explanation beyond the scope of this paper (e.g., Pujol et al., 2011).

Overall, we show that the Earth appears to be depleted by about an order of magnitude compared to chondritic values (Table 2), which is consistent with Marty (2012). Using only Orgueil (CI-chondrite) and Murchison (CM-chondrite) suggests that terrestrial volatiles are 2.48 $\pm$ 0.3% as abundant as they are in CI/CM-chondrites. Incorporating analyses of a broader suite of CC gives an indistinguishable volatile abundance pattern, with terrestrial volatiles 2.75 $\pm$ 0.2% as abundant as CC. The latter is adopted here. Enstatite comparison yields less

Table 1

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Amount (mol g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSE</td>
<td>2.78</td>
<td>Halliday (2013)</td>
</tr>
<tr>
<td>Mantle</td>
<td>5</td>
<td>Marty (2012)</td>
</tr>
<tr>
<td>$\geq 8.4 \pm 5.2$</td>
<td>Goldblatt et al. (2009)</td>
<td></td>
</tr>
<tr>
<td>Continental crust</td>
<td>$2.1 \pm 1.1$</td>
<td>Goldblatt et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>Rubnick and Gao (2003, 2014)</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>Wedepohl (1995)</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>Delwiche (1970)</td>
</tr>
<tr>
<td>Continental sediments</td>
<td>4</td>
<td>Delwiche (1970)</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Species</th>
<th>CI/CM (mol g$^{-1}$)</th>
<th>CC (mol g$^{-1}$)</th>
<th>BE$^{17}$ (mol g$^{-1}$)</th>
<th>BE/C (CI/CM) (%)</th>
<th>BE/CC (%)</th>
<th>BE/EC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$C</td>
<td>2.00 $\pm 0.2 \times 10^{-3}$</td>
<td>2.23 $\pm 0.2 \times 10^{-3}$</td>
<td>3.75 $\pm 0.4 \times 10^{-4}$</td>
<td>4.38 $\pm 1.7 \times 10^{-5}$</td>
<td>2.19 $\pm 0.5 (1.4)$</td>
<td>1.96 $\pm 0.2 (2.0)$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>5.50 $\pm 0.9 \times 10^{-3}$</td>
<td>7.50 $\pm 1.8 \times 10^{-3}$</td>
<td>--</td>
<td>1.50 $\pm 0.7 \times 10^{-4}$</td>
<td>2.74 $\pm 0.7 (1.9)$</td>
<td>2.00 $\pm 0.3 (1.4)$</td>
</tr>
<tr>
<td>$^{22}$Ne</td>
<td>2.68 $\pm 0.2 \times 10^{-3}$</td>
<td>3.49 $\pm 0.5 \times 10^{-3}$</td>
<td>4.28 $\pm 0.2 \times 10^{-12}$</td>
<td>2.66 $\pm 0.2 \times 10^{-14}$</td>
<td>0.99 $\pm 0.2 (0.5)$</td>
<td>0.76 $\pm 0.1 (0.8)$</td>
</tr>
<tr>
<td>$^{36}$Ar</td>
<td>4.51 $\pm 0.1 \times 10^{-11}$</td>
<td>3.36 $\pm 0.8 \times 10^{-11}$</td>
<td>2.22 $\pm 0.9 \times 10^{-11}$</td>
<td>1.01 $\pm 0.3 \times 10^{-12}$</td>
<td>2.24 $\pm 0.7 (0.18)$</td>
<td>3.01 $\pm 0.5 (4.4)$</td>
</tr>
<tr>
<td>$^{84}$Kr</td>
<td>4.98 $\pm 0.1 \times 10^{-13}$</td>
<td>1.23 $\pm 0.3 \times 10^{-13}$</td>
<td>1.06 $\pm 0.2 \times 10^{-12}$</td>
<td>2.10 $\pm 0.07 \times 10^{-14}$</td>
<td>4.23 $\pm 1.3 (3.4)$</td>
<td>6.03 $\pm 1.0 (8.3)$</td>
</tr>
<tr>
<td>Average abundance</td>
<td>2.48 $\pm 0.3 (1.0)$</td>
<td>2.75 $\pm 0.2 (2.0)$</td>
<td>9.2 $\pm 0.1 (5.3)$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

consistent results, though are within an order of magnitude (9.2 ± 0.1%). This value was calculated without Ne-abundance, as this appears to be distinct from other volatiles (Table 2).

If N behaved similarly to other volatiles during accretion/delivery, the abundance values can be used in concert with N concentrations of CC and EC to calculate BE N. Multiplying CC N content (1235 ± 440 ppm) by BE/CC abundance (2.75 ± 0.2%) gives BE N mass of 204 ± 75 × 10^18 kg N; the same calculation with EC N content (605 ± 206 ppm) and EC/BE abundance of 9.2 ± 0.1% gives BE N mass of 330 ± 12 × 10^18 kg N. These masses are equivalent to a BE N concentration of 34 ± 12 ppm and 55 ± 20 ppm, respectively. For comparison, both N mass estimates are two orders of magnitude greater than the mass of N in the present atmosphere (4 × 10^18 kg).

While the preceding approach is appropriate if N had similar behaviour to noble gases, water, and C during accretion, it is possible that N may have existed in reduced forms in the protoplanetary disk. Ammonia in comets is well known (Oró, 1961), and recent identification of NH₃ as inclusions in primitive chondrites indicates that reduced N was also present in the chondrite-forming region of the solar system (Harries et al., 2015). If N was found as NH₄⁺ in significant quantities in the Earth-forming region, it may have behaved more like K or Rb than noble gases. We note that NH₄+ was likely found mostly in ices, and its behaviour would be quite different than NH₃ substituting into silicate lattices or Fe-metal. The following discussion assumes that N was found as NH₄⁺ in the Earth-forming region.

Estimates of BE N based on K and Rb content of CC and EC are higher than noble gas constraints (Table 3). EC have higher K (770 ppm) and Rb (2.5 ppm) concentrations than CC ([K] = 400 ppm, [Rb] = 1.7 ppm) (Wasson and Kallemeyn, 1988). The Bulk Earth (BE) has 280 ppm K (Arevalo et al., 2009) and 0.6 ppm Rb (Palme and O’Neill, 2014). These abundances suggest that the Earth has about 1/3 as much K or Rb as chondrites. If N behaved like K or Rb, it would have a

<table>
<thead>
<tr>
<th>Proxy</th>
<th>Bulk Earth N</th>
<th>Bulk Earth N (ppm)</th>
<th>Core N mass</th>
<th>Core N (ppm)</th>
<th>BSE + Atm</th>
<th>BSE only</th>
<th>BSE only concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC-volatile</td>
<td>204 ± 75</td>
<td>34 ± 12</td>
<td>180 ± 110</td>
<td>102 ± 63</td>
<td>21 ± 17</td>
<td>17 ± 13</td>
<td>4.1 ± 3.1</td>
</tr>
<tr>
<td>EC-volatile</td>
<td>330 ± 120</td>
<td>55 ± 20</td>
<td>300 ± 180</td>
<td>165 ± 100</td>
<td>35 ± 28</td>
<td>31 ± 24</td>
<td>7.3 ± 5.6</td>
</tr>
<tr>
<td>K-CC</td>
<td>5200 ± 1850</td>
<td>864 ± 310</td>
<td>4600 ± 3500</td>
<td>2580 ± 2000</td>
<td>530 ± 400</td>
<td>526 ± 396</td>
<td>128 ± 116</td>
</tr>
<tr>
<td>Rb-CC</td>
<td>2600 ± 880</td>
<td>430 ± 150</td>
<td>2300 ± 1800</td>
<td>1300 ± 1000</td>
<td>270 ± 250</td>
<td>255 ± 246</td>
<td>64 ± 58</td>
</tr>
<tr>
<td>K-EC</td>
<td>1300 ± 500</td>
<td>220 ± 74</td>
<td>1100 ± 900</td>
<td>650 ± 500</td>
<td>140 ± 125</td>
<td>136 ± 121</td>
<td>32 ± 29</td>
</tr>
<tr>
<td>Rb-EC</td>
<td>870 ± 300</td>
<td>145 ± 50</td>
<td>780 ± 600</td>
<td>430 ± 330</td>
<td>90 ± 80</td>
<td>86 ± 76</td>
<td>19 ± 0.8</td>
</tr>
<tr>
<td>Iron meteorite</td>
<td>250 ± 20</td>
<td></td>
<td>140 ± 10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermodynamic calculation</td>
<td>1.8 ± 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**Fig. 4.** Nitrogen concentration in carbonaceous chondrites (CC), enstatite chondrites (EC), and iron meteorites. Nitrogen content of both CC (1235 ± 440 ppm) and EC (605 ± 2 – 6 ppm) is significant, and suggests that many atmospheric masses of N were delivered to the Earth during accretion. Iron meteorites are presented as a proxy for N content of the core (140 ± 10 ppm, Section 3.2 See supplemental information for data table).
very large mass in the BE of between 870 and 5200 × 10^{18} \text{ kg N} (Table 4). Since N is likely more volatile than K and Rb, this provides a strict upper limit on N abundance in the Earth. For the remainder of the paper we adopt the CC- and EC-volatile based proxy, but do not exclude N behaving somewhere in between more volatile elements and K or Rb during planetary formation.

It should be noted that neither class of chondrite appears to fully satisfy the isotope composition of volatile elements on Earth. Both EC (Grady et al., 1986) and CC (Pearson et al., 2006) have δ^{15}N values similar to the mantle value of −5‰. A significant problem with EC as proxy for volatile delivery is that they have negligible water content, and therefore very low H. In contrast, CC are more water-rich and have δD values that are more or less consistent with at least the surface reservoirs of Earth (Marty, 2012). The δ^{15}N values of the mantle (−35‰ to −5‰) match more closely with EC, −35‰ (Grady et al., 1986), than with CC, which are variable, but consistently positive (Pearson et al., 2006).

3.2. Core formation, N sequestration, and remaining BSE N content

Now that we have established some estimates for initial N content, the next step is to model N behaviour during core formation; some N was likely incorporated into the core. Core formation occurred as gravitationally separating Fe, Ni, and additional elements from silicates during accretion. Nitrogen is siderophile (soluble in metal-Fe) under reducing conditions, allowing large quantities of N to be scavenged during accretion. Nitrogen is siderophile under reducing conditions, allowing large quantities of N to be scavenged during core formation. Because the core is geochemically isolated from the BSE (Halliday, 2004), any scavenged N is effectively removed from the BSE during core formation. Nitrogen is siderophile (soluble in metal-Fe) under reducing conditions, allowing large quantities of N to be scavenged during core formation. Because the core is geochemically isolated from the BSE (Halliday, 2004), any scavenged N is effectively removed from the rest of the planet. It is therefore important to constrain how much N is in the core, which will be subtracted from a chondritic starting composition.

There are several types of constraints provided (Table 4). The first is N measurements from iron meteorites, which are derived from cores of planetesimals formed early in the solar system's history (Grady and Wright, 2003). While variable, these meteorites have an average N content of 138 ± 12 ppm (Fig. 4), mostly contained in the mineral taenite (Fe_{0.8}Ni_{0.2}). If iron meteorites are a good proxy for the core, it contains 250 ± 20 × 10^{18} \text{ kg}. Secondly, there are calculations, based on thermodynamic properties, indicating the partition coefficient between liquid iron and silicate melt ($K_D = [N]_{\text{metal}}/[N]_{\text{silicate}}$) is 1.8 ± 0.2. This suggests 0.001 wt.% N in the core, for a N content of 1.8 ± 0.2 × 10^{18} kg (Zhang and Yin, 2012). This estimate matches experimental work done at low pressures (e.g., Kadik et al., 2011), but does not agree with experimental work done at higher pressures appropriate for core formation conditions.

The third, and preferred, type of constraint uses our calculated CC- or EC-volatile proxies for BE N content in concert with experimental measurements of $K_D$ under high pressure (5–20 GPa). Measured $K_D$ is 20 ± 10 (Roskosz et al., 2013). The N concentration of the core can be calculated by using the following two relationships:

\[
N_t = N_c + N_b \quad (14)
\]

\[
N_t = |N_t|/|M_c| + |N_b|/|M_b| \quad (15)
\]

where M is mass, N without brackets is N mass, N in brackets is concentration, and subscripts are t for total Earth, c for core, and b for BSE. Mass of the core is 1.8 × 10^{24} kg and mass of the BSE is 4.2 × 10^{24} kg. Taking $K_D = [N]_t/[N]_b$, we find

\[
[N_c] = \frac{N_t}{M_c + N_b/K_D} \quad (16)
\]

A partition coefficient of 20 ± 10 and bulk Earth N mass that is either CC-like (204 ± 75 × 10^{18} kg) or EC-like (330 ± 120 × 10^{18} kg) suggests 180 ± 110 × 10^{18} or 300 ± 180 × 10^{18} \text{ kg N} is in the core. These values are very similar to iron meteorites, suggesting that they are a good proxy for core composition. Were the volatile concentration based on K–Rb, not noble gases, the core N inventory would be 780–4600 × 10^{18} kg. Importantly, all proxies indicate that if N were present in the Earth during core formation, the majority of it is sequestered into the core. This may have had an isotopic effect on the N remaining in the BSE, though it may have been minimal due to the high temperature. No measurements of this fractionation have been made, to our knowledge.

We can estimate N remaining in the BSE and atmosphere by subtracting core N mass from the total Earth. This leaves N masses of 21 ± 17 × 10^{18} kg and 35 ± 28 × 10^{18} kg remaining in the BSE and atmosphere for CC-like and EC-like models, respectively. Further subtracting the amount in the modern atmosphere (4 × 10^{18} kg N), suggests that between 17 ± 13 × 10^{18} kg and 31 ± 24 × 10^{18} kg N (4.1 ± 3.1 to 7.3 ± 5.6 ppm) reside in the BSE. These estimates are higher than previous work for BSE N content, and serve as a useful comparison for the terrestrial-based, literature compilation budget presented in Section 4.

3.3. A lunar analogue for the early mantle?

The Moon formed after a Mars-size proto-planet (Theia) collided obliquely with a Venus-size proto-Earth (Tellus) at the end of planetary accretion (Hartmann and Davis, 1975), marking the end of the so-called Chaotic Eon and the start of “Earth” history sensu stricto (Goldblatt et al., 2010). The density and composition of the Moon indicate that it formed after core–mantle differentiation on Earth. In addition, the identical O-isotope composition (Wiechert et al., 2001) of the Earth–Moon system indicates that the Moon-forming impact was energetic enough to homogenize the Earth and its impactor, Theia. Hence, Lunar rocks may sample the very early Earth mantle.

The N content of Lunar rocks can be used to estimate Lunar mantle, and therefore early Earth mantle, N concentrations. There are a few measurements of N in Lunar rocks, including basaltic glasses (3 ppm), basalts (0.7 ppm), and anorthosites (1.5 ppm) (Mathew and Marti, 2001). We use the concentration from basalt glasses as is done for terrestrial basalts (Section 4.5), as these are most quickly quenched and have experienced the least amount of degassing. Lunar glasses appear to be petrogenetically related to Lunar mare basalts (Mathew and Marti, 2001), which have relatively well constrained melting conditions. These basalts are the result of partial melting of 1–10% at a depth of 100 km (2.85 GPa, lower pressure than the equivalent depth on Earth due to the smaller Lunar mass) (Shearer and Papicky, 1999) and temperatures of 1125 °C (Marty et al., 2003). Oxygen fugacity is between IW-2 and IW-4 (Marty et al., 2003). By comparison, terrestrial mid-ocean ridge basalts (MORB) formed at much more oxidizing conditions of IW + 6 (Frost and McCammon, 2008).

To use these data to calculate N concentration in the Lunar mantle, we calculate a hypothetical $K_D$ based on a basalt-source rock (peridotite) at the given T (1125 °C), P (2.85 GPa), and $f_{O_2}$ (IW-2 to IW-4) conditions (Table 5). First, N solubility in olivine, pyroxene, and melt is calculated using Eqs. (4), (5), and (6). Next, bulk $K_D$ is calculated for a source rock is assumed to be 60% olivine and 40% pyroxene. These $K_D$ values, along with percent partial melt, are used in Eq. (7) to calculate N concentration in basalt glass source region, given glass concentration of 3 ppm (Table 5). Thus we determine that the average source N concentration for the Lunar mantle is 0.18 ± 0.15 ppm.

This calculated concentration is lower than what is predicted from the chondritic model, but is similar to analyses of terrestrial xenoliths (0.28 ± 0.25 ppm, Section 4.5). The lunar value is interpreted as a lower limit for the N concentration of the early Earth mantle, as there may well have been substantial N loss during moon formation. Some N was likely volatilized and lost to space during the moon-forming
These are used to calculate $\textit{K}_d$ for a source rock that is 60% olivine and 40% pyroxene. Source concentration based on measurements of glass (3 ppm) are calculated with Eq.(7).

$\textit{K}_d = \frac{C_{\text{source}}}{C_{\text{melt}}}$

where $C_{\text{source}}$ is the source concentration and $C_{\text{melt}}$ is the melt concentration.

Eqs. (4), (5), and (6) are used in concert with estimated N concentrations to calculate N mass in poorly characterized reservoirs (Table 13). A more complete picture of the current state of N on Earth should provide a more solid springboard from which to leap into interpretations of past processes.

### 4.1. Atmosphere

$N_2$ is the dominant form of N in the atmosphere; its mass ($4 \times 10^{16}$ kg) is calculated via Eq. (13); using $m_n$ as molar mass dry air (0.02897 kg mol$^{-1}$); $r = 6.4 \times 10^6$ m; $p = 1.014 \times 10^5$ Pa; and $g = 9.8$ m s$^{-2}$. Other N species in the atmosphere include $N_2O$, $NH_3$ ($NH_3$), and $NO_2$ ($NO$, $NO_2$, $NO_3$). These are minor species, with abundances of $1.5 \times 10^{12}$, $1.7 \times 10^9$, and $7 \times 10^8$ kg N, respectively (Ussiri and Lal, 2013).

### 4.2. Oceans

The N content of the oceans is small compared to the atmosphere. Dissolved $N_2$ is the main N species in the ocean, with a mass of about $2.4 \times 10^{16}$ kg (Ussiri and Lal, 2013). Concentrations of minor species ($NO_3^-$, $NH_4^+$, $N_2O$) can vary over the year, spatially, and with depth. Surface $NO_3^-$ concentration is typically higher in the winter, due to lower productivity, but varies throughout the year at concentrations of 0–30 µM (Garcia et al., 2010). $NO_3^-$ at depth is more constant spatially and is found at higher concentrations, between 10 and 35 µM. Total $NO_3^-$ in the ocean has a mass of $5.7 \times 10^{14}$ kg N (Ussiri and Lal, 2013). On average, the $NH_4^+$ is found at a concentration of 0.4 µM, and $N_2O$ at a concentration of 11 nM. These concentrations yield masses of $7 \times 10^{12}$ and $2 \times 10^{13}$ kg N, respectively.

Concentrations of N species also depend on redox conditions. In deep waters of the Black Sea, which are anoxic, $NH_4^+$ is the dominant N species, with concentrations of up to 40 µM, while $NO_3^-$ concentration is negligible (Fuchsman et al., 2008). A similar relationship is seen during the winter in Saanich Inlet on Vancouver Island, with deep anoxic waters dominated by $NH_4^+$ (10 µM) instead of $NO_3^-$ (~0.2 µM) (Velinsky et al., 1991).

### 4.3. Biomass

The mass of N in living biomass is small compared with dissolved $N_2$ (above) and inorganic N species. Living biomass in the ocean contains about $5 \times 10^{11}$ kg N. Marine dead organic matter is a much more substantial reservoir, comparable to inorganic fixed N, with $8 \times 10^{14}$ kg N (Ussiri and Lal, 2013).

Soil and terrestrial biomass constitute a reservoir of N comparable to oceanic biomass. Soil has a N content of $1.62 \times 10^{14}$ kg and living biomass has a N mass of $1.1 \times 10^{13}$ kg (Ussiri and Lal, 2013).

Despite its low mass in biomass, we emphasize the importance of biology in fixing N. This process is responsible for transferring N from the atmosphere into other reservoirs in the Earth.

### Table 5

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Source concentration (ppm)</th>
<th>Melt N concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceanic sediments</td>
<td>4.0</td>
<td>$4 \times 10^{-6}$</td>
</tr>
<tr>
<td>Oceanic lithosphere</td>
<td>$1.7 \times 10^{-6}$</td>
<td>$1.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>Continental crust</td>
<td>$7 \times 10^{-10}$</td>
<td>$7 \times 10^{-10}$</td>
</tr>
<tr>
<td>MORB-source mantle</td>
<td>$2.4 \times 10^{-2}$</td>
<td>$2.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>Off-cratonic mantle</td>
<td>$2 \times 10^{-7}$</td>
<td>$2 \times 10^{-7}$</td>
</tr>
<tr>
<td>Cratonic mantle</td>
<td>$7 \times 10^{-7}$</td>
<td>$7 \times 10^{-7}$</td>
</tr>
<tr>
<td>Transition zone</td>
<td>$1 \times 10^{-5}$</td>
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</tr>
<tr>
<td>Lower mantle</td>
<td>$1 \times 10^{-4}$</td>
<td>$1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

### Table 6

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Form</th>
<th>Size ($10^{18}$ kg N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>$N_2$</td>
<td>4.0</td>
</tr>
<tr>
<td>Oceans</td>
<td>$N_2$O</td>
<td>$1.5 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$NH_3$</td>
<td>$1.7 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$NO_3$</td>
<td>$5.7 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>$NH_3$</td>
<td>$7 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$N_2O$</td>
<td>$2 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Ocean living</td>
<td>$5 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Ocean dead organic matter</td>
<td>$8 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Continental living</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>Soil organics</td>
<td>$1 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

### Table 7

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Density (g/cm³)</th>
<th>Thickness (km)</th>
<th>Area (km²)</th>
<th>Mass (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceanic sediments</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>$7.4 \times 10^{20}$</td>
</tr>
<tr>
<td>Oceanic lithosphere</td>
<td>3</td>
<td>50</td>
<td>$3.61 \times 10^{8}$</td>
<td>$5.4 \times 10^{22}$</td>
</tr>
<tr>
<td>Continental crust</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>$1.9 \times 10^{22}$</td>
</tr>
<tr>
<td>MORB-source upper mantle</td>
<td>4</td>
<td>400</td>
<td>$3.61 \times 10^{4}$</td>
<td>$5.8 \times 10^{23}$</td>
</tr>
<tr>
<td>Off-cratonic upper mantle</td>
<td>4</td>
<td>400</td>
<td>$6 \times 10^{2}$</td>
<td>$9.6 \times 10^{22}$</td>
</tr>
<tr>
<td>Cratonic upper mantle</td>
<td>4</td>
<td>400</td>
<td>$9 \times 10^{3}$</td>
<td>$1.4 \times 10^{23}$</td>
</tr>
<tr>
<td>Transition zone</td>
<td>4.4</td>
<td>240</td>
<td>Volume = $1.1 \times 10^{11}$ km³</td>
<td>$4.8 \times 10^{23}$</td>
</tr>
<tr>
<td>Lower mantle</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>$2.93 \times 10^{24}$</td>
</tr>
</tbody>
</table>

4.4. The crust

4.4.1. Oceanic sediments

Nitrogen concentration in oceanic sediments is ultimately controlled by local biologic activity. In the modern ocean, primary productivity is higher near continental margins. Proximity to continental margins increases the available nutrient pool via river/weathering input and upwelling nutrient-rich deep waters (Gruber and Sarmiento, 1997). Consequently, primary productivity is higher near continental margins. Higher productivity leads to greater organic matter concentration, and the potential for more N to be deposited in sediments. Indeed, concentrations of N in sediments off the Central American margin have >1000 ppm N in some locations, with an average of about 770 ppm (Li and Bebout, 2005). This is notably higher than sediments from the Izu–Bonin–Mariana arc (IBM) in the western Pacific, which is further from continental margins, has lower primary productivity, and an average N content of about 280 ppm (Sadofsky and Bebout, 2004).

Our N abundance estimate in oceanic sediments is based on the proportion of three sediment types covering the seafloor. All samples that are younger than 250 Ma are used, since this is the maximum age of oceanic basins. Current sedimentary cover on the seafloor is composed of carbonate (47.1%), clastic (38.1%), and biogenic (14.8%) sediments (Davies and Gorsline, 1976; Brown et al., 1989). Biogenic sediments include organic materials, kerogen, graphite, microbialite, and chert and have a mean N concentration of 1930 ± 1540 ppm (Fig. 5, Table 8). Clastic sediments include siltstone, mudstone, clay, shale, sandstone, and pelite and have a mean N concentration of 570 ± 17 ppm. Carbonates, limestone, and dolostone, have a mean N concentration of 130 ± 17 ppm. The resulting weighted average is 560 ± 230 ppm, which yields a N content for oceanic sediments of 0.41 ± 0.2 × 10¹⁸ kg (Table 13).

An important consideration when attempting to estimate N contents in the past is the redox conditions of the overlying water column, as sediments deposited under anoxic water conditions may be more N-rich. A sediment core from the Black Sea shows that sediments deposited under an anoxic water column have twice the N content (1800 ppm) as sediments deposited under an oxic water column (900 ppm) (Quan et al., 2013b). Changes in redox sensitive metal (Fe, Mo) concentrations and lack of significant changes in total organic carbon and δ¹³C values corroborate redox control over N concentration, as opposed to a purely biological control. The increase of N content with reducing conditions may not be universal, as some shale units do not show N enrichment under anoxic conditions. They do, however, show distinct δ¹⁵N values that appear to reflect redox conditions (Quan et al., 2013a).

![Fig. 5](image-url) Nitrogen concentrations in oceanic crust less than 250 Ma. Sediments are separated into biogenic (organic materials, kerogen, graphite, microbialite, chert), clastic (siltstone, mudstone, clay, shale, sandstone, and pelite), and carbonates (limestone, dolostone). Oceanic lithosphere samples are labelled as OL and AOL.
4.4.2. Oceanic crust and upper lithosphere

Fresh gabbros and basalts at mid-ocean ridges inherit N from their mantle source (Marty, 1995). Since these magmas are oxidized, N present in fresh MORB is typically found as N\textsubscript{2} locked in fluid inclusions in glassy rims. Concentrations in fresh crust are low, with an average of 1.4 ± 1.3 ppm. Concentration in unaltered lithospheric mantle (defined here as harzburgite and undifferentiated peridotite) is also low, at 0.24 ± 0.33 ppm (Fig. 6, Table 8).

<table>
<thead>
<tr>
<th>Table 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimates for the amount of N in the continental crust, shown with standard error of the mean (with an arbitrary error of 50% for very poorly known rock types). Rock proportions are based on Wedepohl (1995), who based upper crustal rock abundances on mapped area and lower crustal abundance on xenoliths.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reservoir (% of crust)</th>
<th>Concentration (ppm)</th>
<th>Rock type (% of reservoir)</th>
<th>SE</th>
<th>No. samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper crust (53%)</td>
<td></td>
<td>Shale/silt (44%)</td>
<td>860</td>
<td>64</td>
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<td></td>
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<td>Sandstone (21%)</td>
<td>230</td>
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<td>Volcanics (20%)</td>
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<td>60</td>
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<td>Carbonates (14%)</td>
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<td>17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average</td>
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<td>Felsic intrusives (50%)</td>
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<td>Granitic (90%)</td>
<td>54</td>
<td>7</td>
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<tr>
<td></td>
<td></td>
<td>Tonalite (10%)</td>
<td>24</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td>52</td>
<td>6</td>
</tr>
<tr>
<td>Mafic intrusives (6%)</td>
<td></td>
<td>Gabbros (100%)</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Metamorphic rocks (30%)</td>
<td></td>
<td>Gneisses (64%)</td>
<td>135</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mica schist (16%)</td>
<td>500</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Amphibolites (18%)</td>
<td>22</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Marble (3%)</td>
<td>1000</td>
<td>500(?)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td>200</td>
<td>36</td>
</tr>
<tr>
<td>Felsic/mafic granulites (62%)</td>
<td></td>
<td>17</td>
<td>6</td>
<td>2\textsuperscript{2,22,27,32,37,47,51–56}</td>
</tr>
<tr>
<td>Mafic granulites (38%)</td>
<td></td>
<td>17</td>
<td>6</td>
<td>2\textsuperscript{22,27,32,37,47,51–55,57}</td>
</tr>
<tr>
<td>Lower crust (47%)</td>
<td></td>
<td>17</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Total crust average</td>
<td></td>
<td>17</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Continental crust N estimate</td>
<td>1.7 ± 0.1 × 10\textsuperscript{18} kg N</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6. Nitrogen concentrations in oceanic crust and lithospheric mantle. Hydrothermal alteration increases the N content of oceanic crust, and it retains high N even during metamorphism. The same increase is seen in the oceanic lithospheric mantle. Samples are as in Table 8.
Hydrothermal alteration tends to increase the N content of the rocks, to an average of 6.1 ± 0.7 ppm for crustal rocks (altered basalts and gabbros) and 3.7 ± 0.5 ppm for lithospheric mantle (harzburgite and serpentinite). The source of this N is from biologic activity in seawater, identified by positive δ¹⁵N values. As seawater enters a hydrothermal system, it carries NH₄⁺ from overlying sediments into the crust and mantle (e.g., Halama et al., 2010). NH₄⁺ substitutes into mineral lattices of hydrothermal minerals, most importantly K-bearing clays. It is possible that some N may be present as N₂ in cordierite (Palya et al., 2011).

Since hydrothermal alteration is the main control on geologically stable N in oceanic crust, estimates of N concentration in these rocks depend on the depth and extent of hydrothermal alteration into the lithosphere. The deepest cores show that alteration occurs at least to a depth of 470 m (Li et al., 2007). Metagabbros and serpentinitized mantle rocks in ophiolites show that alteration can reach even deeper, into the upper mantle. Hydrothermal origin of N is confirmed by enriched δ¹⁵N values, derived from oceanic biologic processes (Busigny et al., 2011; Halama et al., 2012). Some ophiolites experienced metamorphic pressures of up to 2.5 GPa (~80–90 km depth), yet still retain N derived from the ocean, indicating the durability of the NH₄⁺-silicate bond. Indeed, the concentration of N in metamorphosed oceanic crust (basalt, gabbro, blueschist, eclogite) is identical within error (7.1 ± 1.2 ppm) to altered crust.

A N budget estimate for the oceanic lithosphere can be calculated assuming shallow or deep alteration. Shallow alteration affecting the entire crust (6.1 ± 0.7 ppm), 0.5 km of mantle (3.7 ± 0.5 ppm), with the...
remainder of the mantle (9.5 km) at 0.24 ± 0.33 ppm N, yields a N concentration of 2.9 ± 0.3 ppm. This concentration gives N mass of 0.16 ± 0.02 × 10¹⁸ kg N. If alteration occurs on a lithospheric scale (8 km crust and 10 km mantle), we calculate an upper estimate of 4.8 ± 0.4 ppm N, which gives total N mass of 0.26 ± 0.02 × 10¹⁸ kg N. While these values are orders of magnitude less than the amount of N contained in the atmosphere, N in the oceanic crust is of critical importance as subduction over long time scales has the potential to transport a large amount of N into the mantle.

An average column of oceanic crust, sediments, and lithosphere can subduct substantial N over Earth history. A column with 500 m of sediment (560 ppm N, Table 8) and the conservative oceanic crust plus lithosphere concentration of 2.9 ± 0.3 ppm gives an average column concentration of 18 ppm. If we assume that all N gets subducted, which depends on temperature and varies by subduction zone, we can multiply this concentration times the mass of oceanic slab being subduction each year (~40,000 km trench length, 18.5 km thick crust, 5 cm/year convergence rate, and density of 3.5 g/cm³), and calculate that 2.3 × 10⁹ kg N are subducted every year. Over Earth history (4 Ga, for illustrative purposes), current subduction equates to 9.3 × 10¹⁸ kg N, which is twice the current mass of N in the atmosphere.

It therefore seems reasonable to suggest that the entire atmosphere may have passed through the mantle at least once, given current subduction efficiency, or more times if subduction of N was more efficient in the past (Section 5).

4.4.3. Continental crust

The continental crust is composed of two categories of rocks: (meta)sedimentary and (meta)igneous (Fig. 7). We base our estimate for the N budget of the continental crust on our literature compilation and the rock abundance estimates of Wedepohl (1995) (Table 9). These proportions are based on surface outcrop area for upper crustal rocks and xenolith data for lower crustal rocks.

Upper crustal rocks are, unsurprisingly, the most analyzed and well characterized. Clastic sediments (especially shales) are the most sampled, and these include both samples explicitly formed in continental settings and sediments that formed in oceanic settings and are older than 250 Ma. Samples with oceanic provenance older than 250 Ma must now be preserved on continents in order to be sampled, so are included in the continental N budget. Nitrogen in continental sedimentary
rocks is incorporated as organic matter, NH$_4$+ from the breakdown of organic matter (as described previously), or NH$_4$+ in minerals weathered from crystalline rocks.

Crystalline rocks, both igneous and metamorphic, form the majority of the upper continental crust. Nitrogen in both rock types is predominantly NH$_4$+ when compared to other K+-bearing minerals (Honma and Gao, 2014) based on older compilations (Wedepohl, 1995) and Gao and Goldblatt (2014) based on new compilations.

Our total continental crust estimate, 1.7 ± 0.1 × 10$^{18}$ kg N (Table 9), suggests that a substantial amount of N may be sequestered in the continental crust. This estimate is equivalent to a recent rough estimate (Goldblatt et al., 2009), but higher than another recent study (Rudnick and Gao, 2014) based on older compilations (Wedepohl, 1995) and measurements (Wlotzka, 1972).

4.5. The mantle

The large mass of the mantle, compared to the atmosphere, means that it contains substantial N, even at low concentration. For example, 1 ppm N in the mantle would give N mass of 4 × 10$^{18}$ kg, which is the same as the atmosphere. Determining the actual abundance of N in the mantle is difficult, as N analyses are rare. Most information concerning volatile elements is from noble gas geochemistry, which is augmented by diamond analyses, xenoliths, and direct mantle melts. We can estimate the N content of the mantle either as a whole or by

Table 12
Nitrogen concentration and total mass estimates in the off-cratonic mantle based on analysis of lamproite/lamprophyre (LL) and K$_2$O values of Yb and Lu (Table 11). Nitrogen behaviour is assumed to be similar to Yb and Lu (Fig. 12), and bulk K$_2$O values are then used to estimate N mass (10$^{18}$ kg) using Eq. (7). We present estimates for 1 and 10% melt.

<table>
<thead>
<tr>
<th>Melt</th>
<th>N concentration (ppm)</th>
<th>N mass (10$^{18}$ kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yb-based</td>
<td>Lu-based</td>
</tr>
<tr>
<td></td>
<td>Yb-based</td>
<td>Lu-based</td>
</tr>
<tr>
<td>10%</td>
<td>35 ± 7</td>
<td>33 ± 9</td>
</tr>
<tr>
<td>1%</td>
<td>18 ± 4</td>
<td>15 ± 5</td>
</tr>
</tbody>
</table>

N analyses from the deeper crust are sparse, but recent measurements suggest that this might be an important long-term reservoir for N (Palya et al., 2011). To calculate the mass of lower crust N, we use two well-studied outcrops to represent the average mineralogy of both mafic (Cone Peak, California) (Hansen and Stuk, 1993) and felsic (Gruf Complex, eastern Alps) (Galli et al., 2011) granulites. The majority of N in these rocks should be contained in biotite and potassium feldspar, with some in plagioclase in a ratio of 1:0.38:0.11 (Honma and Itihara, 1981). Mafic granulites have 17% biotite, 59% plagioclase, and negligible potassium feldspar; felsic granulites have 17% biotite, 17% plagioclase, and 10% potassium feldspar. Globally, average N content of biotite in metamorphosed continental igneous and sedimentary rocks is 87 ± 8 ppm, which in turn suggests plagioclase (in equilibrium) has 10 ± 2 ppm and potassium feldspar 33 ± 8 ppm. Thus, mafic and felsic granulites have similar N concentrations of 17 ± 6 ppm (Table 9).
breaking it into different domains. First we calculate a whole-mantle esti-
mated based on N–Ar geochemistry. Then, we discuss distinct domains
(MORB-source, OIB-source, off-cratonic, cratonic) individually, and base
N estimates on analyses of xenoliths where available, as well as detail
potential N capacity in unsampled domains (transition zone, lower
mantle).

4.5.1. Argon geochemistry-based estimate
Nitrogen and Ar behave similarly in basaltic melts under oxidizing
conditions (e.g., Libourel et al., 2003; Roskosz et al., 2006; Mysen
and Fogel, 2010; Li et al., 2014, 2015), so N–Ar systematics may be used
to calculate whole-mantle N budgets (Marty, 1995; Marty and Humbert,
1997; Dauphas and Marty, 1999; Marty and Zimmermann, 1999;
Goldblatt et al., 2009). This approach is valid for both MORB and OIB,
since they are generated from melting of oxidized upper mantle, even
though they are geochemically distinct (White, 2010). There are a num-
ber of measurements of N2 and Ar in both basalt types, which can be
used to estimate N concentration in their source. Calculating the
amount of N in MORB-source and OIB-source mantle depends on estab-
lishing three criteria: (a) the amount of Ar in MORB- and OIB-source
mantle, (b) the relationship between N and Ar in MORB and OIB, and
(c) the proportion of mantle that is MORB- and OIB-source.

Before calculating the N mantle budget, we highlight some aspects of
Ar geochemistry, as these are crucial to the following interpretation.
Argon has three isotopes: 36Ar, 38Ar, and 40Ar. The first two are primor-
dial (i.e., inherited during planetary formation), while the third is pro-
duced by radioactive decay of 40K, and has been increasing over time.
Both primordial isotopes are found almost exclusively in the atmos-
phere, though minor amounts are degassing from the mantle. The ra-
diogenic isotope, 40Ar, is present in both the atmosphere and the BSE,
since K is found in the solid Earth. Thus, we chose to compare N to
40Ar, as both elements are found in the atmosphere and BSE; these
data are normalized to primordial 36Ar (for chondritic values, please
see Table 10).

The first step needed to estimate N content from 40Ar is to calculate
the amount of 40Ar present in the mantle. As mentioned, all 40Ar has
been produced from the decay of 40K over time. Based on U/K ratios, the
K concentration of the BSE is estimated at 280 ± 120 ppm (Arevalo
et al., 2009). Given a known decay rate of 40K (λ = 5.55 × 10−10 yr−1),
the proportion of this decay which produces 40Ar (10.72%), and the abun-
dance of 40K (0.0117%) (Haynes et al., 2014), we calculate that a total
of 4.2 ± 1.8 × 1018 mol 40Ar has been created over Earth history. Subtracting
40Ar in the atmosphere (1.65 × 1018 mol) and continental crust
(0.35 × 1018 mol, Arevalo et al. (2009)) gives the 40Ar content of the man-
tle to be 2.2 ± 1.8 × 1018 mol.

Next, we observe that the N2 and 40Ar data fall into two populations
(Fig. 8): one containing MORB, some OIB, and some xenoliths with
N2/40Ar values around 102, which we coin as MORB-source like (MSL);
and one containing some OIB and xenoliths with N2/40Ar around 103,
which we coin high-N. Interestingly, the MORB samples fall along a co-
herent trend with air at one end, as seen in previous work (Marty,
1995). Perhaps this indicates that the atmospheric N and Ar composi-
tion is the result of degassing the MORB-source mantle over time. In ad-
dition, the correlation between N2 and 40Ar in the MORB, with weak
relation between N2 and 36Ar over the same range, indicates that N
has been cycled through the mantle; by proxy, it correlates with K−,
which is concentrated in the continental crust, so observing a signal of
K-input suggests contribution of continental material (Marty, 1995).

In contrast, OIB and xenolith data appear to describe a three-
component mixture between air, a high-MSL end-member, and an
end-member composition with high N2 compared to 40Ar (Fig. 8).
Although the high-N field has only two OIB samples, we suggest it is a
robust feature of the mantle as it is also defined by OIB-associated
xenoliths and other xenoliths. OIB-associated xenoliths are thought to
represent OIB-source material on the basis of high 3He/4He (Mohapatra
et al., 2009, and references therein). High-N xenolith samples
are metasomatized, more fertile mantle lithologies (i.e., therozolite,
harzburgite, wehrlite) from locations in Oman and Europe (Yokochi
et al., 2009). In addition, MORB samples that fall off the MSL trend are
analyses from the East Pacific Rise, which is thought to have a plume-
like component (Marty and Zimmermann, 1999), so may represent an
intermediate between MSL and high-N mantle types.

To actually estimate N content in mantle source regions, we must
determine the N2/40Ar ratio for MSL and high-N mantle (Fig. 8). This is
straightforward for MSL, which is described by a well-defined trend,
and has a value of 120 ± 11. This value is consistent with previous
work (N2/Ar = 124 ± 6, from Marty and Zimmermann (1999)).
Determining the high-N ratio is less straightforward, as it defines a
more dispersed field. Since OIBs tend to record a somewhat more di-
verse set of mantle source types (White, 2010), we suggest that taking
the average N2/40Ar ratio from all samples with N2/40Ar > 103 is the
most appropriate approach to obtain a representative value. This ratio is
9.3 ± 3.3 × 102.

Now armed with 40Ar abundance for the total mantle and N2/40Ar for
MSL and high-N reservoirs, the last step required is to estimate the ac-
ual proportion of these types of mantle. This is the most difficult of
the three criteria. Trace element (e.g., U, Ta) mass balance suggests that
the mantle is approximately 80% MORB-source composition and the re-
mainder 20% is OIB-source composition (Workman and Hart, 2005;
Arevalo et al., 2009, 2013). Determining what proportion of OIB-
source mantle is high-N and what proportion is MSL is difficult, but cru-
ially important to the overall estimate of N in the mantle. As a first at-
tempt, we assume that analyzed OIB represent a statistical sampling of
the OIB-source mantle. There are 9 OIB samples with high N2/40Ar
(>103) out of 61 total OIB samples. This corresponds to high-N being
~15% of the OIB-source mantle, or 3% (15% × 20%) of the total mantle.
If we assume uniform distribution of 40Ar in the mantle, MSL (97% of
the total) has 2.13 ± 1.7 × 1018 mol 40Ar and the high-N mantle (3%
of the total) has 0.066 ± 0.0054 × 1018 mol 40Ar. Given N2/40Ar men-
tioned above (120 ± 11 for MSL and 9.3 ± 3.3 × 102 for high-N), we cal-
culate N mass in the MSL and high-N mantle to be 7.2 ± 5.9 × 1018 and
4.9 × 1018, respectively. Total mantle N is 24 ± 16 × 1018 kg, which is
 equivalent to 6 ± 4 ppm N. While there is uncertainty in this
estimate, primarily related to the K concentration estimate and distribu-
tion in the mantle, we suggest that our calculation represents a lower
estimate. A larger proportion of high-N mantle would significantly in-
crease a N mass estimate.

The most interesting and important aspect of our approach is the
identification of two distinct mantle N reservoirs. The origin of both

Fig. 10. Mantle reservoirs as defined for individual domain-based budget (Section 4.5.2). The transition
zone and lower mantle are defined by mineral phase changes. The mass of non-
cratonic and cratonic mantle is estimated by multiplying the area of Phanerzoic-aged crust and pre-Cambrian crust by the depth to the top of the transition zone.

The proportion of this decay which produces 40Ar (10.72%), and the abun-

MSL and high-N components present a fascinating geochemical quandry. MSL mantle has low N/40Ar, low N concentration, but its δ15N values describe two sub-populations: depleted δ15N in MORB and enriched δ15N in OIB (Fig. 9). Given the low N concentration (<1 ppm) in most samples, the low N/40Ar ratio should be caused by a high 40Ar content resulting from significant time since this material (and by proxy K) was at the surface of the Earth. Subducted material with variable N and K contents would require a long time to acquire enough 40Ar to push all samples towards a common trend. It therefore seems likely that MSL mantle is tapping a reservoir of older material derived from the surface. The δ15N values are interesting, as MORB values of −5‰ are distinct from modern subducted material, which is around +5 to +7‰. OIB that fall along the MSL trend, however, show enriched δ15N values, at −5‰. The difference either means that MORB and OIB in the MSL are tapping N reservoirs of subducted material that are different in space (Marty and Dauphas, 2003) but not in time (i.e., both tap old material) or that the way N is processed in the MORB-and OIB-source mantle or eruptions is different. It is difficult to discern between these options at this time, though future modelling and experimental work would aid in this pursuit.

The high-N mantle, in contrast, appears to be tapping relatively recently subducted surface material. This reservoir has high N/40Ar, high N concentration, and enriched δ15N values in OIB and xenoliths (Fig. 9). High N concentration associated with high N/40Ar implies this material is young, as it has not had sufficient time to accumulate 40Ar through radioactive decay (Marty and Dauphas, 2003). The δ15N values are also very close to modern, oceanic sedimentary values, at 7.1‰. Overall, the high-N mantle appears to be young, N-rich, and received its N from subduction of surficial materials.

In detail, there are differences between high-N OIB, OIB-xenoliths, and xenoliths. While both OIB basalts and OIB-xenoliths have relatively high N content (4.5 and 2.7 ppm), they have distinct δ15N values of 7.1‰ and −3.5‰, respectively. Recall that the OIB-associated xenoliths are thought to represent the source rocks of coexisting OIBs. The difference in N isotopes could mean that N fractionates during partial melting, enriching the melt compared to the source. To our knowledge, there are no studies that quantify isotopic fractionation of N between partial melt and residual material in OIB genesis. If melt preferentially incorporates the heavy isotope, perhaps this could explain the observed relationship between OIB and their source. The remainder of the high-N xenolith population has enriched δ15N values of 4.5 ± 2‰ and low N concentration of 0.35 ± 0.07 ppm.

An alternate approach to explain the high N/40Ar ratio of the high-N mantle would be some process whereby N is retained preferentially to K during subduction and recycling. Such a process would concentrate N more in the mantle than K, and therefore this material would have
that storage of \( N \) as \( \text{NH}_4 \) pyroxene is more stable at greater depth in the mantle, it is possible (Watenphul et al., 2010) that are stable to eclogite
\( \Rightarrow \text{K-hollandite} \) (Watenphul et al., 2009) and clinopyroxenes

...ing, and we use this observation as an estimate for the \( N \) content of the off-cratonic upper mantle. Empty symbols were not included in regression.

les \( ^{40}\text{Ar} \). It is possible that \( K \) is more mobile during subduction than \( N \).

...There are synthesized \( \text{NH}_4^+ \)-bearing micas (phengite), aluminosilicates
\( \Rightarrow \text{K-hollandite} \) (Watenphul et al., 2009) and clinopyroxenes
\( \Rightarrow \text{K-hollandite} \) (Watenphul et al., 2010) that are stable to eclogite-field conditions. As

"...pyroxene is more stable at greater depth in the mantle, it is possible that storage of \( N \) as \( \text{NH}_4^+ \) in pyroxene allows for it to be more effectively retained than \( K \), whose host minerals (feldspars, micas) break down. Further experimental work concerning \( N \) and \( K \) behaviour during subduction could help address this issue. Discussed in some detail later, other locations that could fractionate \( N \) from \( K \) are the transition zone and lower mantle. In these reservoirs, metallic Fe is stable and \( N \) may be retained in this metal, while \( K \) is not. This is highly speculative, but further investigation of this high-\( N \) reservoir could help characterize the fate of volatiles in the mantle.

4.5.2. Individual mantle domain estimates

An alternate approach to the \( \text{Ar} \)-based geochemistry is to attempt to break the mantle into different domains, and use measurements of xenoliths from those domains to estimate \( N \) mass. This approach may be more limited, due to relative paucity of analyzed samples as well as lack of material from the transition zone and lower mantle. Thus, we suggest the following be viewed as a minimum estimate. We will also only provide quantitative estimates for actual \( N \) content in domains that have been sampled, while for domains without direct analyses we will discuss the capacity for \( N \) storage.

We identify four sampled mantle reservoirs (Table 7): MORB-source, OIB-source, off-craton, and cratonic mantle. There are two reservoirs, the transition zone and lower mantle, that do not have \( N \) analyses from xenoliths (Fig. 10). Note this division is not intended to comment on chemical heterogeneity or stratification in the mantle, but merely to utilize different petrologic/geochemical proxies where appropriate to estimate the \( N \) content of the total mantle.

4.5.2.1. MORB-source mantle. The amount of \( N \) in the MORB mantle is largely a function of the efficiency of degassing during mantle partial melting and MORB genesis. Melting under oxic conditions seems to be efficient at removing \( N \) from source rocks into magma (Libourel et al., 2003). Our data compilation of MORB-source mantle rocks (peridotite, harzburgite) suggests \( N \) content of 0.28 ± 0.2 ppm (Fig. 11). Using the same MORB-source mass abundance from the previous section (80% of the mantle) yields a \( N \) content for the MORB-source mantle of 0.74 ± 0.1 \( \times 10^{18} \) kg. Note that experimental (Li et al., 2013) and theoretical (Mikhail and Sverjensky, 2014) work suggest that in the middle to lowermost upper mantle redox, pressure, and \( pH \) conditions may be consistent with the presence of \( \text{NH}_3 \) or \( \text{NH}_4^+ \). These molecules may be retained more effectively than \( N_2 \); thus this portion of the mantle may be more \( N \) rich than indicated by xenoliths alone.

4.5.2.2. OIB-source mantle. For this estimate, we turn to analyses of OIB as well as OIB-associated xenoliths as described in Section 4.5.1. These rocks have an average \( N \) concentration of 0.7 ± 0.5 and 2.7 ± 0.8 ppm. Note that we include all OIB in this estimate, whereas in Section 4.5.1 we identified two OIB-source reservoirs. In addition, OIB have likely experienced some degassing upon eruption, so this concentration should be viewed as a minimum. We assume that OIBs represent partial melts that melted under conditions conducive to quantitative \( N \) extraction from the source. Therefore, with 10% partial melt (Winter, 2001), source concentration would be 0.07 ± 0.04 ppm \( N \). This is much lower than the OIB-xenolith values, but again should be viewed as a minimum. Given an OIB-source proportion of 20% yields a \( N \) mass of 0.06 ± 0.04 \( \times 10^{18} \) kg for OIB-based \( N \) concentration and 2.2 ± 0.6 \( \times 10^{18} \) kg for OIB-xenolith based concentration.

Additionally, while degassing during eruption has likely occurred, it is worth noting that the concentration of \( N \) in OIBs is of the same order of magnitude as the concentration of \( N \) in carbonatites from the Kola peninsula, which are around 0.11 ppm (Dauphas and Marty, 1999). The carbonatites are thought to be sourced from fairly deep, crystalized at depth, and to have experienced minimal degassing during emplacement. Carbonatite magmas, however, are likely sourced from a mantle domain distinct from the OIB-source mantle.

4.5.2.3. Off-cratonic upper mantle. The sub-continental mantle can be broken into two domains: off-cratonic mantle, which has been influenced by Phanerozoic subduction and cratonic mantle, which is the stable mantle underneath cratons. We discuss the off-cratonic mantle first.

Off-cratonic mantle is roughly equivalent to the mantle wedge associated with subduction zones. Since mass balance studies suggest the majority of subducted \( N \) does not return to the atmosphere via arc magmatism (Mitchell et al., 2010; Busigny et al., 2011), it is possible that some of this \( N \) is retained in this reservoir. We invoke analyses of specific alkaline volcanic rocks, lamprophyres and lamproites (LL), as proxy for mantle influence by subduction. These rocks, though volumetrically small, are geographically widespread (Winter, 2001), which indicates their potential as a useful proxy.

Petrogenetic analysis of LL suggests that they are sourced from hydrated mantle composed of phlogopite (mica)-bearing harzburgite (Tainton and McKenzie, 1994; Mitchell, 1995), though some may be sourced from deeper in the mantle (Murphy et al., 2002). Phlogopite harzburgite may be produced via a two step process: an initial mantle melting event, and the subsequent addition of fluids sourced from subducted continental/marine sediments. Later partial melting (1–10%) of the harzburgite produces LL magmas.

A suite of LL from India have \( N \) concentrations that range from 21 to 394 ppm (Jia et al., 2003), with an average of 210 ± 60 ppm (Fig. 11). The corresponding \( N \) content of the mantle source of LL depends, then, on the behaviour of \( \text{NH}_3 \) during melting.

The Rare Earth Element (REE) profiles of the Indian LL may both constrain the compatibility of \( N \) in the source rock and could perhaps be used as a proxy for \( N \) in other samples where \( N \) was not measured explicitly. Ytterbium and Lu show a significant correlation with \( N \) (when disregarding a sample with high, 400 ppm, \( N \), with \( r^2 \) values of 0.70 and 0.79, respectively (Fig. 12). This suggests that \( N \), \( Yb \), and \( Lu \) behave similarly during LL formation.
The behaviour of Yb and Lu during LL formation is relatively well known, as K$_0$ values have been measured in minerals experimentally (Table 11). We use these mineral K$_0$ values to calculate a bulk K$_0$ value, which is a simple weighted average, for a phlogopite–harzburgite source rock with 60% olivine, 30% pyroxene, and 10% phlogopite. Bulk K$_0$ is 0.0505–0.0979 for Yb and 0.0636 for Lu (Fujimaki et al., 1984; Foley and Jenner, 2004). The K$_0$ of N has not been measured during LL formation, so as a first approximation we will assume that it is equal to the K$_0$ of Yb or Lu, based on the strong correlation shown in Fig. 12. Using Eq. (7), we calculate a N concentration in LL source of 35 ± 7 ppm on Yb and 33 ± 9 ppm on Lu for 10% partial melting. Assuming 1% partial melting gives N concentration of 18 ± 4 ppm based on Yb and 15 ± 5 ppm based on Lu. Correspondingly, the mass of N would be between 1.4 × 10$^{18}$ and 3.4 × 10$^{18}$ kg (Table 12).

4.5.2.4. Cratonic mantle. We draw upon three data sources to calculate the N content of the cratonic upper mantle: xenoliths, olivine and pyroxene are much lower (Table 12). If portions of the mantle are more fertile (i.e., higher pyroxene content) they would have correspondingly a higher N capacity. Analyses of N in natural olivine and pyroxene are much lower (<1 ppm, Yokochi et al. (2009)) than this calculated upper limit, implying that the actual content may be significantly lower than the capacity.

The capacity of upper mantle minerals is consistent with relatively high (~40 ppm) N contents. We suggest that N remaining in diamond-forming fluid after diamond formation may be effectively sequestered in the sub-cratonic lithosphere. In addition, N concentration in the 10s of ppm is corroborated by estimates of C/N based on diamond analyses (Cartigny et al., 2001). A N concentration of 40 ppm yields a N mass of ~5.6 × 10$^{18}$ kg. This is likely an upper estimate, as it assumes that all cratonic mantle was infiltrated by diamond-forming fluids and that all N not included in diamonds was retained in the host rock. Uncertainty in the extent of diamond-forming fluid (if this is the source of N) introduces error to this estimate, though if experimental relationships accurately describe the N solubility in upper mantle minerals there is no issue with storage capacity.

Additional uncertainty may result from disagreement concerning the compatibility of N during diamond growth. An extensive compilation by Cartigny et al. (2001) suggests that the incorporation of N into diamonds from diamond-forming fluids is a kinetic process: slow diamond growth results in low N content. Both measurements of Slave Craton diamonds (Smart et al., 2011) and synthetic diamonds suggest that N behaves compatibly (Stachel and Harris, 2009). The majority of diamonds with depleted $^{13}$C values that are indicative of a recycled crustal input do not have commensurate enriched $^{15}$N values (Cartigny, 2005), which would be expected if the source of N and C was subducted oceanic material. This either indicates that recycled material that was incorporated into diamond growth had different $^{15}$N values from modern surface reservoirs (Marty and Dauphas, 2003) or that C and N incorporation into diamonds is decoupled/depends only on growth rate (Cartigny et al., 2001).

4.5.2.5. Transition zone. The transition zone (TZ) is the region in the mantle below 660 km depth, and is defined by mineral phase changes. At 410 km, olivine changes its structure to the more tightly packed spinel-like crystal lattice of wadsleyite then ringwoodite. Below 660 km, another phase change occurs, and the spinel-structure mineral changes to bridgmanite, a high-pressure polymorph. These phase changes control redox chemistry, and the TZ is more reducing than the overlying upper mantle. The $f_0$$_2$ here is around IW–1, and both experiments and calculations suggest the presence of 0.1 wt. % metallic Fe (Frost and McCammon, 2008) in this region.

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Location</th>
<th>This study</th>
<th>Approach</th>
<th>CG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceanic lithosphere</td>
<td>Sediments</td>
<td>0.41 ± 0.2</td>
<td>LC</td>
<td>0.31 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>Crust + mantle</td>
<td>0.16 ± 0.01 to 0.26 ± 0.02</td>
<td>LC</td>
<td>0.012 ± 0.005</td>
</tr>
<tr>
<td>Continental crust</td>
<td>Igneous</td>
<td>0.55 ± 0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sedimentary</td>
<td>1.55 ± 0.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>1.7 ± 0.1</td>
<td>LC</td>
<td>2.1 ± 1.05</td>
</tr>
<tr>
<td>Mantle</td>
<td>MORB-source</td>
<td>1.2 ± 0.8</td>
<td>LC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>OIB-source</td>
<td>&gt;0.06 ± 0.04 to 2.2 ± 0.6</td>
<td>LC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Off-cratonic</td>
<td>1.4 ± 3.4</td>
<td>LC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cratonic</td>
<td>&lt;5.6</td>
<td>LC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Transition zone</td>
<td>&lt;100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>&gt;3.4 ± 1.3 – 5.8 ± 1.4</td>
<td>LC</td>
<td></td>
</tr>
<tr>
<td>Mantle</td>
<td>MORB-source-like mantle</td>
<td>7.2 ± 5.9</td>
<td>AR</td>
<td>≥8.4 ± 5.2</td>
</tr>
<tr>
<td></td>
<td>High-N</td>
<td>17 ± 15</td>
<td>AR</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>24.2 ± 16</td>
<td>AR</td>
<td></td>
</tr>
<tr>
<td>BSE total</td>
<td>LC crusts and LC mantle</td>
<td>&gt;5.7 ± 1.3 – 8.1 ± 1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BSE total</td>
<td>LC crusts and AR mantle</td>
<td>27 ± 16</td>
<td></td>
<td>10.8 ± 5.3</td>
</tr>
</tbody>
</table>
Therefore, with 0.1–2 wt.% N dissolved (Kadik et al., 2011; Roskosz et al., 2013) in 0.1 wt.% metallic Fe (Frost and McCammon, 2008), N concentration would be 100–2000 ppm. This represents the N capacity of the transition zone, with a strong upper bound between 48 × 10^{23} and 960 × 10^{23} kg N. The high N potential of the transition zone, and indeed the lower mantle, was recently suggested based on the observation that the more deeply diamonds form, the less N they contain (Smith et al., 2014). The authors suggest that the low-N diamonds grew in the presence of Fe-metal, which preferentially dissolved N. This is consistent with our literature review.

Sequestering N in the transition zone for significant periods of time may be difficult, however. Whole mantle circulation means that material in the transition zone does not stay there (e.g., Nakagawa and Tackley, 2012). Both the upper mantle and lower mantle are more oxidizing than the TZ (Frost and McCammon, 2008). Thus, when material moves out of the TZ, previously metal-bound N may be released into either fluids or minerals. This may preclude long-term N storage in the TZ. Without further evidence (petrologic or experimental), the transition zone remains a hypothetical reservoir for N. It is not considered in our total N estimates for the Earth.

4.5.2.6. Lower mantle. The lower mantle, which is defined by the phase transition at 660 km depth described above, is not represented by xenoliths or inclusions in our N database. We are unaware of any such analyses. As with the transition zone, we may only be able to speak to the storage capacity of this portion of the mantle.

There is speculation that 1 wt.% metallic Fe may exist in the lower mantle (Frost et al., 2004). High pressure/temperature experimental petrology demonstrates that N is quite soluble in metallic Fe at these conditions, with up to 8 wt.% (Roskosz et al., 2013). Given a mantle with these proportions of Fe-metal and N solubility suggests a N capacity of 2.3 × 10^{23} kg N. This value is orders of magnitude higher than any other reservoir in the planet, perhaps save the core. As with the transition zone, this is highly speculative, and would require further confirmation via geochemical or modelling studies.

If there are regions of the lower mantle that remain shielded from mantle convection and mixing, they may represent a location for storage of the Earth’s “missing N.” That is, the abundance of N compared to other volatiles in the BSE was previously estimated to be about an order of magnitude lower (Marty, 2012). The lower mantle has more than enough capacity to store additional N. If, however, our Ar-based estimate for N abundance in the mantle is correct, there is no need to invoke hidden reservoirs of N, as we calculate mantle N mass in line with other volatile abundances.

5. Discussion

We find that our two methods for calculating the N budget of the Bulk Silicate Earth (BSE) are consistent. Both comparison to chondrite N abundance (“top-down”) and compilation of terrestrial analyses (“bottom-up”) of rocks and minerals suggest the BSE contains many atmospheric masses (PAN = 4 × 10^{18} kg) of N. The chondritic comparison suggests between 17 ± 3.3 × 10^{18} and 31 ± 24 × 10^{18} kg N are in BSE while the terrestrial literature compilation suggests 27 ± 16 × 10^{18} kg N. Both estimates also have theoretical upper limits that are much higher (Table 4), due to increased solubility of N in silicates at depth. This close agreement shows that our budget is internally self-consistent. It may also remove the concept of “missing N” (e.g., Marty, 2012; Halliday, 2013), as the mantle appears to have ample capacity for N sequestration.

Importantly, our estimate is higher than previous estimates (e.g., Goldblatt et al., 2009). The mantle appears to have a significant portion of the planetary N budget. High N content in the BSE has significant ramifications in relation to Earth and atmospheric geochemistry.

5.1. Key uncertainties

Before discussing geochemical implications of the new budget presented herein, we touch briefly on the main uncertainties in our estimate. First, sparsely analyzed reservoirs (specifically the mantle and lower continental crust) inherently limit accuracy in estimates. Further analysis of these important reservoirs should be a focus of future work. Second, though the behaviour and partitioning of N during melting in the mantle is beginning to be tested experimentally (e.g., Libourel et al., 2003; Mysen and Fogel, 2010; Li et al., 2013, 2015), the relative lack of studies necessarily introduces uncertainty. We suggest that N behaves similarly to Lu and Yb, though this relationship has not been assessed in all rock types. It is becoming clear that f_o2, temperature, and pressure all exert strong control over N contents in the mantle. More experimental petrology and modelling studies would be valuable in elucidating the behaviour of N at the range of conditions found in the solid Earth.

Thirdly, determining the geochemical character of the high-N mantle reservoir identified in Section 4.5.1 more accurately is of crucial importance. This reservoir, despite its small mass, may contain the majority of the N in the mantle. As it appears to be sampled by some OIB and xenoliths, more coupled N–Ar measurements of these rocks should help define this end member more completely. The stable isotopes are consistent with a recycled component, but the extent, residence time, and other geochemical properties are not fully constrained at this time.

5.2. Evolution of the atmosphere–mantle system

The atmosphere is not the main reservoir for N on Earth today. However, the processes responsible for the current distribution are not fully resolved. It remains ambiguous if the distribution between BSE and atmosphere has been the same as the current state, or if it has been different in the past. Nitrogen isotopic evidence and correlation with radiogenic 40Ar indicates that N derived from the surface of the Earth is subducted and cycled into the BSE (e.g., Marty, 1995; Marty and Dauphas, 2003; Palya et al., 2011), so exchange has clearly occurred. The setting where this input occurs is subduction zones. At current subduction rates, 9.3 × 10^{18} kg N could be subducted over 4 Ga of Earth history (Sec. 4.4.2). So at modern subduction rates, consistent since at least the Cretaceous (Busigny et al., 2011), the entire atmosphere could be potentially pass through the mantle if ~50% of subducted N is recycled to the mantle (i.e., not returned to the atmosphere). This retention efficiency at modern subduction zones is poorly constrained (Halama et al., 2012), with the Central American margin appearing to return significant sedimentary N (10%) to the atmosphere (Elkins et al., 2006), while the colder Izu–Bonin–Mariana Arc retains most of subducted N (~85%) to mantle depth (Mitchell et al., 2010). As such, there is no reason to rule out different efficiency in the past.

There are two reasons to suggest that N subduction was more efficient in the past. The first is that prior to the Great Oxidation Event, it is likely that the dominant N ion in the oceans was NH4+ (Garvin et al., 2009). Since NH4+ substitutes into sediments and oceanic lithosphere to enter the geologic cycle, a higher concentration might promote a greater N flux into subducting sediments and lithosphere. Indeed, an increase in N concentration is seen in Black Sea samples in the Quaternary, with sediments deposited under anoxic conditions having about twice as much N as sediments deposited under oxic conditions (Quan et al., 2013b). Additionally, higher mantle temperature in the Archean (e.g., Herzberg et al., 2010) has been interpreted to lead to more vigorous mantle convection. Hotter mantle is also thought to produce thicker oceanic crust, due to greater degree of partial melting. Higher heat flow should cause extensive hydrothermal alteration, which could act as a sink for NH4+ from the ocean. A hotter mantle, however, may also be a drier mantle (Korenaga, 2011; Sandu et al., 2011), which would tend...
to slow convection and subduction. The interplay between these two factors, increased \(\text{NH}_4\) in the ocean and crust and hotter mantle, and any effects on N subduction are not known.

Progressive N sequestration over time implies a more massive atmosphere in the Archean, which has potentially important effects on greenhouse warming (Goldblatt et al., 2009; Byrne and Goldblatt, 2014). Independent proxies for Archean paleopressure based on fossil raindrops (Som et al., 2012) and hydrothermal inclusions in quartz grains (Marty et al., 2013), however, suggest the Archean atmosphere had the same amount (or less) of N as the modern. The raindrop constraint has subsequently been found to be too low; a more realistic constraint here is up to ten times modern density (Kavanagh and Goldblatt, 2015). The \(N_2/^{36}{\text{Ar}}\) ratio from 3.0 Ga hydrothermal inclusions in quartz grains is approximately equal to the modern value (Marty et al., 2013); this is inferred to suggest that the atmosphere may have had the same pressure (and therefore N content) as the modern day Earth. An earlier study on the same grains suggests, however, an upper limit for the \(N_2/^{36}{\text{Ar}}\) of 3.3 times the modern value (Nishizawa et al., 2007). A robust empirical constraint on the amount of \(N_2\) in the Archean atmosphere is enigmatic at this time. Our work indicates substantial N in the mantle, at least some of which has been recycled from the surface, so it is possible that the atmosphere was more massive in the past. Whether this indicates a monatomic drawdown or some more dynamic evolution of the atmosphere–mantle system is unknown at this time.

The fate of subducted N has a direct effect on the \(\delta^{15}N\) value of the mantle. In fact, a significant missing piece of the N puzzle is the origin of the depleted \(\delta^{15}N\) signature of the MORB-source mantle, which exists in an apparent disequilibrium with isotopically enriched surface reservoirs. As briefly discussed in Section 4.5.1, there appear to be two classes of solutions to this dilemma: the MORB-source mantle records early subduction of depleted N (Marty and Dauphas, 2003) or that fractionations of N isotopes during deep Earth transport are responsible. A distinct MORB-only source mantle is not supported by our compilation herein, as many OIB have equivalent \(N_2/^{40}\text{Ar}\) values as MORB. However, MORB and OIB have different \(\delta^{15}N\) values at \([-5\%]\) and \([+0\%]\), respectively, so there must be some process to explain this distinction. Possibly they represent pools of different subducted material that has “aged” the same amount to yield equivalent \(N_2/^{40}\text{Ar}\). Preservation of distinct \(\delta^{15}N\) values implies incomplete mantle mixing over time. The existence of the high-N mantle supports the existence of different mantle domains, though we cannot rule out that the different \(N_2/^{40}\text{Ar}\) signature of the high-N reservoir could be caused by fractionation of N from during subduction or deeper mantle processing. Redox reactions and possible N sequestration in the transition zone and lower mantle may all affect N geochemical signatures of mantle and mantle melts.

It is becoming apparent experimentally (Li et al., 2013) and theoretically (Mikhail and Sverjensky, 2014) that \(\text{NH}_4\) is the predominant species of N in much of the mantle. The geochemical behaviour of \(\text{NH}_4\) in subduction zones and mantle reservoir materials (e.g., silicates, Fe-metal) should be a target for future research, as any isotopic fractionations are unknown to us at this time.

### 5.3. Bulk Earth \(\delta^{15}N\) and N delivery during accretion

A long-standing conundrum concerns the geochemistry and isotopic signature of N delivered to the planet during accretion. The budget estimate based on CC and EC compositions assumes that significant N was present in the Earth during its early history to ensure its participation in core formation. The implication is that N was not delivered in any late veneer, but instead was delivered during the main phase of accretion. It must have been in a reduced form, either \(\text{NH}_4\) or as nitride, and contained within either silicate lattices or Fe-metal, as \(N_2\) would be too volatile, and perhaps not present in significant quantity in the inner solar system. Existing isotopic data are inconclusive in identifying a single meteoritic analogue. The presence of very depleted \(\delta^{15}N\) values from the mantle has been suggested to reflect preservation of primordial EC-like material, though these are analyses from diamonds (Palot et al., 2012), and the behaviour and fractionation of N during diamond growth may not be fully understood. Additionally, CC have \(\delta^{15}N\) that is generally enriched. Our BSE + atmosphere bulk \(\delta^{15}N\), given masses in Table 13 and \(\delta^{15}N\) values for MORB-source mantle (\(-5\%\)), high-N mantle (\(+5\%\)), continental crust (\(7.3\%\)), and atmosphere (\(0\%\)), is \(2.1\%\).

This estimate is distinct from either CC (\(\sim+30\%\)) or EC (\(\sim-25\%\)), meaning either the Earth did not acquire its N from a single chondritic source or the process of core formation significantly fractionated N. The Bulk Earth \(\delta^{15}N\) value could be explained by a \(-50\%\) contribution of CC-like and a \(-50\%\) contribution of EC-like material during accretion, given no fractionation during core formation. If there was significant fractionation during core formation, it would have a large effect on residual N in the BSE. There is suggestion proposed that the dissolution of N into Fe-metal would preferentially fractionate light isotopes into the metal, following a Siever’s law-type reaction of \(N_2 = 2N\text{ dissolved}\) (Dauphas and Marty, 1999). This assumption suggests that breaking of the \(^{14}N–^{15}N\) bond is easier, so this iso-tope goes into the metal, leaving residual silicates enriched in \(\delta^N\). Were this the case, it would imply a higher contribution of EC to Earth’s N. In principle, the same effect would be seen in N-H in \(\text{NH}_4\), but to our knowledge, there are no experimental studies measuring N isotopes in coexisting metal and silicates.

A possible source of information concerning fractionation during core formation could be measurements of pallasites, which are meteorites thought to represent core–mantle boundaries of planetesimals. Measurements made by Prombo and Clayton (1993) on coexisting silicate and metal in pallasites show that the silicate phase is almost always isotopically enriched compared to the metal phase. The fractionation is up to \(-70\%\), which suggests fractionation during core formation could be quite large. Experimental work at pressures appropriate to Earth’s core formation could help corroborate or quantify this effect for the Earth.

### 6. Conclusions

We have compiled a nominal, self-consistent, whole-Earth N budget based on two independent approaches. Both a chondritic comparison and literature compilation of terrestrial analyses reveal that BSE contains many present atmospheric masses of N (PAN). Estimates are \(17 \pm 13 \times 10^{18}\) kg to \(31 \pm 24 \times 10^{18}\) kg N and \(27 \pm 16 \times 10^{18}\) kg N, respectively. Both estimates are higher than previous work, and suggests that we have found the supposed “missing N”. Additionally, several conclusions are apparent from each approach.

The chondritic comparison is consistent with the Earth receiving its N during the main phase of accretion. This indicates significant \((-10^{20}\) kg) N in the core, as N is siderophile under reducing conditions. If there is limited N-isotope fractionation during core formation, \(\delta^{15}N\) values for the BSE plus atmosphere suggest a mix of \(-50\%\) enstatite-like and \(-50\%\) carbonaceous-like chondritic material can explain the N content of Earth.

Our terrestrial literature compilation budget indicates that the continental crust \((-0.5\) PAN) and especially the mantle \((-6\) PAN) contain significant N. Interestingly, N–Ar and \(\delta^{15}N\) data from MORB, OIB, and xenoliths identifies the existence of two distinct N reservoirs: MORB-source like (MSL) and high-N. MSL, which is \(-98\%\) of the mantle by mass, contains \(-2\) atmospheric masses of N, has depleted \(\delta^{15}N\), and its N-isotopes suggest material was subducted deep in the geologic past. In contrast, high-N mantle has at least several atmospheric masses of N, enriched \(\delta^{15}N\), and appears to have been subducted more recently.

The presence of a large mass of subducted N in the mantle has important implications for the history of atmosphere–mantle communication over time. At present subduction rates, the entire atmospheric mass of N could be mixed into the mantle if only \(-50\%\) of down-going N is returned to the atmosphere via arc volcanism. Nitrogen–Ar systematics
indicate that the atmosphere and MSL are well mixed, and therefore that the mantle may serve to buffer the amount of N in the atmosphere. More reduced geochemical conditions at the surface and hotter mantle temperatures in the Archean may have led to more efficient N subduction in the past, perhaps indicating a more massive atmosphere early in Earth history that has been progressively sequestered into the mantle. This is an exciting time for research concerning the geologic N cycle. While the overall cycle is understood, there are areas for future research that are critical for more fully understanding N in the solid Earth. More analyses of N and Ar in OIB and xenoliths would help clarify the nature and extent of the high-N mantle. Experimental work investigating the behaviour of N, specifically as NH₃, during subduction and under mantle conditions should help reveal geochemical and isotopic fractionations during mantle transport. Modelling work, anchored to the budget presented herein, can elucidate the interchange of N and other surface materials through the solid Earth over geologic time.

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Appendix A. Supplementary data

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References


