# Nitrogen isotope fractionation during terrestrial core-mantle separation

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## Abstract

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The origin and evolution of the terrestrial nitrogen remains largely unresolved. In order to understand the potential influence of core-mantle separation on terrestrial nitrogen evolution, experiments were performed at 1.5 to 7.0 GPa and 1600 to 1800 °C to study nitrogen isotope fractionation between coexisting liquid Fe-rich metal and silicate melt. The results show that the metal/silicate partition coefficient of nitrogen $D_N^{metal/silicate}$ ranges from 1 to 150 and the nitrogen isotope fractionation $\delta^{15}N^{metal-silicate}$ is −3.5 ± 1.7 ‰. Calculations show that the bulk Earth is more depleted in $\delta^{15}N$ than the present-day mantle, and that the present-day mantle $\delta^{15}N$ of −5 ‰ could be derived from an enstatite chondrite composition via terrestrial core-mantle separation, with or without the addition of carbonaceous chondrites. These results strongly support the notion that enstatite chondrites may be a main component from which the Earth formed and a main source of the terrestrial nitrogen. Moreover, in the deep reduced mantle, the Fe-rich metal phase may store most of the nitrogen, and partial melting of the coexisting silicates may generate oceanic island basalts (OIBs) with slightly positive $\delta^{15}N$ values.

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## Introduction

Nitrogen isotopes may constrain the origin of terrestrial volatiles (Javoy, 1997; Marty, 2012), as well as the evolution and interaction of different terrestrial reservoirs (Marty and Dauphas, 2003). However, the origin and evolution of terrestrial nitrogen isotopes remains poorly understood. The present-day upper mantle $\delta^{15}N$, inferred from fibrous diamonds and mid-ocean ridge basalts (MORBs) is −12 to 0 ‰ and converges towards a globally uniform value of −5 ‰ (Marty and Dauphas, 2003; Cartigny and Marty, 2013). The $\delta^{15}N$ value of the organic matter and metasediments is overall positive, and the $\delta^{15}N$ value of Earth's surface (crust + atmosphere) is approximately +2 ‰ (Cartigny and Marty, 2013; Thomazo and Papineau, 2013). The oceanic island basalts (OIBs), thought to be derived from the lower mantle (*e.g.*, Shen *et al.*, 1998; Stuart *et al.*, 2003), have $\delta^{15}N$ of −2 to +8 ‰, with a mean value of about +3 ‰ (Dauphas and Marty, 1999; Marty and Dauphas, 2003). However, diamonds derived from the mantle transition zone and lower mantle show similar $\delta^{15}N$ values to the upper mantle (Palot *et al.*, 2012). Therefore the positive $\delta^{15}N$ values of OIBs were interpreted to be results of addition of recycled sediments to the OIB source region (Dauphas and Marty, 1999; Marty and Dauphas, 2003). Nevertheless, most diamond populations with Archean ages define a $\delta^{15}N$ range of −12 to +5 ‰, with a mode around −5 ‰ (Cartigny *et al.*, 2009), indicating no obvious secular change in mantle $\delta^{15}N$ and thus limited nitrogen recycling compared to the nitrogen abundance in the mantle. Li *et al.* (2013) show that the silicate mantle may still contain an amount of nitrogen one to two orders of magnitude larger than the present atmospheric reservoir. Accordingly, the uniform $\delta^{15}N$ value of −5 ‰ of Earth's mantle may have been established before Archean. Because enstatite chondrites have $\delta^{15}N$ of −45 to −15 ‰ (Grady *et al.*, 1986), while carbonaceous chondrites have $\delta^{15}N$ of +15 to +55 ‰ (Kerridge, 1985), the extremely negative $\delta^{15}N$ values down to −25 ‰ and −40 ‰ observed in a few mantle diamonds are interpreted to be relicts of primordial nitrogen and are used to argue for an enstatite chondrite origin of Earth's nitrogen (Javoy, 1997; Palot *et al.*, 2012; Cartigny and Marty, 2013). If this is correct, then one open question is how the Earth's nitrogen isotopes evolved from the initial $\delta^{15}N$ values of enstatite chondrites to the present-day mantle value of −5 ‰ and the positive values observed for OIBs.

A significant fraction of nitrogen may have been segregated into the core during core-mantle separation (Roskosz *et al.*, 2013). However, so far the potential influence of core-mantle separation on Earth's mantle nitrogen isotope evolution has never been investigated. Here we experimentally show that a significant nitrogen isotope fractionation occurs between liquid Fe-rich metal and coexisting silicate melt, and terrestrial core-mantle separation may have greatly enriched the silicate mantle in $\delta^{15}N$.

## Results and Discussion

Experimental results obtained at 1.5 to 7.0 GPa and 1600 to 1800 °C are given in Table 1. The nitrogen metal/silicate melt partition coefficient $D_N^{metal/silicate}$ ranges from 1 to 150. Figure 1 shows that regardless of pressure or temperature, $D_N^{metal/silicate}$ increases with increasing oxygen fugacity, as calculated from the composition of the coexisting quenched metal and silicate (Table S-1). The trend in Figure 1 can be rationalised if one assumes that under these very reducing conditions below the iron-wüstite buffer, nitrogen is mostly dissolved as $N^{3-}$ ion

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in the silicate melt (Kadik *et al.*, 2011, 2013; Li *et al.*, 2015), while it dissolves as interstitial N atoms in the metal (Häglund *et al.*, 1993). This would imply that the exchange reaction between silicate melt and metal may be written as

$$2\ N^{3-}\ (\text{silicate}) + 3/2\ O_2 = 2\ N\ (\text{metal}) + 3\ O^{2-}\ (\text{silicate}) \qquad (\text{Eq. 1})$$

This equation would imply that $\log D_N^{metal/silicate}$ should increase with 0.75 $\log fO_2$, in very good agreement with the overall trend in Figure 1. We noticed that the silicates recovered from the multi-anvil experiments performed at 5.0 to 7.0 GPa were not completely glassy, but contained fine-grained quench crystals. Since nitrogen solubility in silicate minerals is much lower than in silicate melts, we cannot completely rule out that some nitrogen might have been lost from the silicate melt during quench, so that the measured partition coefficients from these experiments may be too high. However, considering that nitrogen solubility in reduced silicate melt ranges up to a few wt. % (Kadik *et al.*, 2011, 2013; Roskosz *et al.*, 2013) and only a few hundred ppm nitrogen was present in our silicate melt, partial crystallisation during quench may not have caused exsolution of nitrogen. The observed systematic dependence of $D_N^{metal/silicate}$ on oxygen fugacity (Fig. 1) also precludes any significant exsolution of nitrogen during quench.

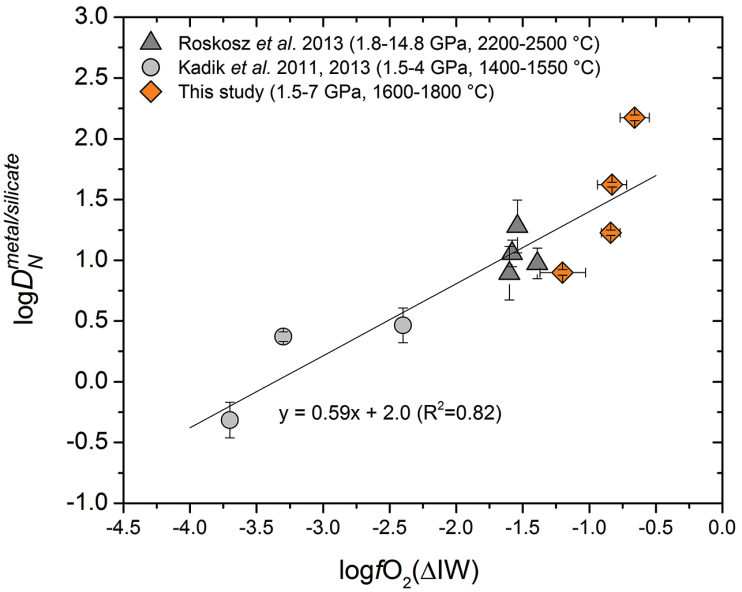


**Figure 1** Nitrogen partition coefficients between liquid Fe-rich metal and silicate melt ($D_N^{metal/silicate}$). The published $D_N^{metal/silicate}$ data (Kadik *et al.*, 2011, 2013; Roskosz *et al.*, 2013) are plotted for comparison. $D_N^{metal/silicate}$ is a function of oxygen fugacity, regardless of pressure or temperature. The slope of the trend line is moderately lower than 0.75 expected based on Eq. 1, which could be due to a small fraction of nitrogen present as $N_2$ in the silicate melt. Errors of $D_N^{metal/silicate}$ in this study are at 95 % confidence interval.





**Table 1** Experimental results on nitrogen partitioning and isotope fractionation between liquid Fe-rich metal and silicate melt.

| Exp. ID | P GPa | T °C | Run duration mins | [a]$\log fO_2$ (ΔIW) | N con. in metal mol/g | N con. in silicate mol/g | $\delta^{15}$N of metal | $\delta^{15}$N of silicate | $D_N^{metal/silicate}$ | $\Delta^{15}N^{metal-silicate}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Piston Cylinder Experiments | | | | | | | | | | |
| Y-1 | 2.0 | 1600 | 120 | -0.84 ± 0.07 | 3.7E-04 ± 1.3E-05 | 2.2E-05 ± 7.9E-07 | 9.2 ± 1.6 | 13.3 ± 1.8 | 17 ± 1 | -4.1 ± 2.4 |
| A-659 | 1.5 | 1600 | 90 | -1.2 ± 0.17 | 4.9E-04 ± 1.8E-05 | 6.2E-05 ± 2.3E-06 | -1.1 ± 2.0 | 2.6 ± 1.6 | 8 ± 0.4 | -3.8 ± 2.5 |
| A-666 | 2.5 | 1700 | 30 | n.d. | 2.6E-06 ± 9.4E-08 | 3.4E-06 ± 1.3E-07 | -3.3 ± 2.4 | -2.2 ± 1.4 | 1 ± 0.04 | -1.1 ± 2.8 |
| Multi-Anvil Experiments | | | | | | | | | | |
| YS-5 | 5.0 | 1700 | 90 | -0.66 ± 0.11 | 2.4E-03 ± 8.7E-05 | 1.6E-05 ± 5.8E-07 | 1.7 ± 1.5 | 7.2 ± 1.7 | 149 ± 8 | -5.5 ± 2.3 |
| YS-1 | 7.0 | 1700 | 90 | n.d. | 7.2E-04 ± 2.6E-05 | 3.6E-05 ± 1.3E-06 | -0.6 ± 1.9 | 1.4 ± 1.7 | 20 ± 1 | -2.0 ± 2.5 |
| YS-2 | 7.0 | 1800 | 90 | -0.83 ± 0.11 | 1.0E-03 ± 3.8E-05 | 2.5E-05 ± 6.8E-07 | -2.0 ± 2.1 | 2.6 ± 1.5 | 42 ± 2 | -4.6 ± 2.6 |

a: The $\log fO_2$(ΔIW) was calcualted using this equilibrium: FeO (silicate melt) = Fe (liquid metal) + 1/2$O_2$, from which the $fO_2$ of the experiment relative to $fO_2$ of the iron-wüstite buffer (IW) can be defined as: ΔIW = 2 log ($X_{FeO}\gamma_{FeO}/X_{Fe}\gamma_{Fe}$), $X_{FeO}$ and $X_{Fe}$ are the mole fractions of FeO in silicate melt and Fe in liquid metal, respectively; $\gamma_{FeO}$ and $\gamma_{Fe}$ are the activity coefficients of FeO in silicate melt and Fe in liquid metal, respectively. Calculation of $\log fO_2$(ΔIW) was performed assuming $\gamma_{FeO}$ = 1.2 in the silicate melt (O'Neill and Eggins, 2002) and ideal solution of liquid Fe-C-Pt-N metal ($\gamma_{Fe}$ = 1).
For major element compositions of silicate melt and liquid metal, see Supplementary Table 1.
n.d.: not determined.
Errors for $D_N^{metal/silicate}$ and $\Delta^{15}N^{metal-silicate}$ are at 95 % confidence interval.

The measured nitrogen metal/silicate melt isotope fractionation $\Delta^{15}D_N^{metal-silicate}$ ranges from –1.1 to –5.5 ‰ (Table 1; Fig. 2), with a mean value of –3.5 ± 1.7 ‰, indicating $^{15}$N-enrichment in the silicate melt relative to the coexisting liquid Fe-rich metal. Within the analytical uncertainties, there is no apparent temperature dependence of $\Delta^{15}N^{metal-silicate}$ over the interval of 1600-1800 °C, which might be partially due to the covariation of pressure and temperature. The consistent $\Delta^{15}N^{metal-silicate}$ values from piston cylinder and multi-anvil experiments (Table 1) rule out the possibility that a significant change in $\Delta^{15}N^{metal-silicate}$ occurred during quench of the multi-anvil experiments. The nearly constant $\Delta^{15}N^{metal-silicate}$ values, independent on the run duration (30 to 120 mins; Table 1), also demonstrate that isotopic equilibrium was reached during the run and any kinetic fractionation should be within the analytical error.

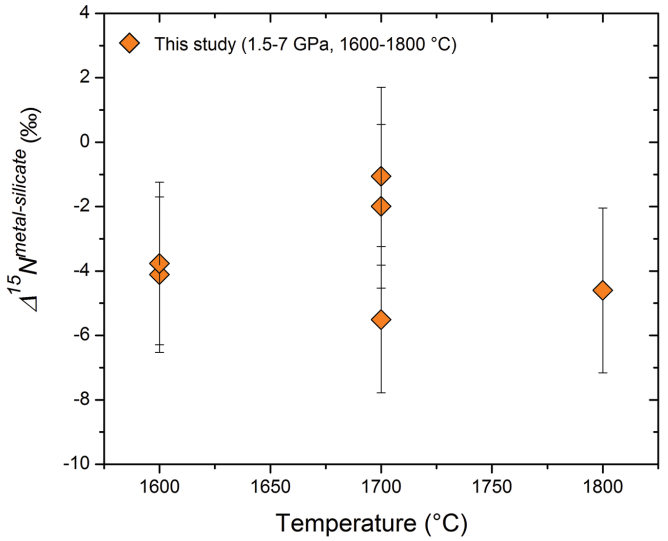


**Figure 2** Nitrogen isotope fractionation between liquid Fe-rich metal and silicate melt ($\Delta^{15}N^{metal\text{-}silicate}$). Temperature has a very limited effect on $\Delta^{15}N^{metal\text{-}silicate}$ in the *P-T* range studied. Errors of $\Delta^{15}N^{metal\text{-}silicate}$ are at 95 % confidence interval.

## Implications

The $D_N^{metal/silicate}$ and $\Delta^{15}N^{metal-silicate}$ obtained here have important implications for the origin and evolution of Earth's nitrogen. The $D_N^{metal/silicate}$ values of 1 to 150 demonstrate that a large fraction of nitrogen in the magma ocean may have segregated into the core, while the $\Delta^{15}N^{metal-silicate}$ values of –1.1 to –5.5 ‰ imply that terrestrial core-mantle separation may have enriched the silicate mantle in $^{15}N$. There are two endmember models for terrestrial core formation. The first one is the single stage model or equilibrium model, in which chemical equilibrium between the core and the mantle is thought to be achieved at certain *P-T* conditions at the base of the magma ocean (Li and Agee, 1996; Righter, 2011). This equilibrium model leads to the below mass balance for the segregation of nitrogen in the core

$$\delta^{15}N^{mantle} \times X_N^{mantle} + \delta^{15}N^{core} \times X_N^{core} = \delta^{15}N^{BE} \quad \text{(Eq. 2)}$$

$$D_N^{metal/silicate} \times C_N^{mantle} = C_N^{core} \quad \text{(Eq. 3)}$$

$$\delta^{15}N^{core} - \delta^{15}N^{mantle} = \Delta^{15}N^{metal-silicate} \quad \text{(Eq. 4)}$$

where $\delta^{15}N^{mantle}$, $\delta^{15}N^{core}$, $\delta^{15}N^{BE}$ are the isotopic composition of the silicate mantle, the core, and the bulk Earth, respectively; $X_N^{mantle}$ and $X_N^{core}$ are the fraction of carbon in Earth's mantle and core, respectively; $C_N^{mantle}$ and $C_N^{core}$ are the nitrogen concentration in the silicate mantle and core, respectively. As $\Delta^{15}N^{metal-silicate}$ is between –1.1 ‰ and –5.5 ‰, the $\delta^{15}N^{core}$ should be –1.1 ‰ to –5.5 ‰ lower than the $\delta^{15}N^{mantle}$ (Eq. 4). If a $D_N^{metal/silicate}$ of 5-20 is used in Equation 3, the $\delta^{15}N^{BE}$ needs to be between –6 ‰ and –10 ‰ in order to achieve a $\delta^{15}N^{mantle}$ value of –5 ‰ (Eq. 2). In this case, if the $C_N^{mantle}$ of 0.8 ppm constrained by Marty (2012) is used, then the $C_N^{core}$ would be 4-16 ppm.

The second endmember mode is the continuous core formation model (Wood *et al.*, 2006, 2013). In this model, Earth accretion and the delivery of core-forming metal occur in small steps of 1 % mass with constant metal/silicate ratio. In each step the metal equilibrates with the silicate magma ocean, and it remains chemically isolated once it segregates in the core. The fractionation of light element isotopes in this model can best be described by the Rayleigh distillation model (Wood *et al.*, 2013; Horita and Polyakov, 2015)

$$\delta^{15}N^{mantle} = \delta^{15}N^{BE} + \Delta^{15}N^{metal-silicate} \times lnf_N^{mantle} \quad \text{(Eq. 5)}$$

where $f_N^{mantle}$ is the remaining fraction of nitrogen in the silicate mantle just after complete core-mantle separation. By combining $D_N^{metal/silicate}$ and mass balance, $f_N^{mantle}$ can be determined using the equations

$$f_N^{mantle} = (C_N^{mantle} \times M^{mantle}) / (C_N^{BE} \times M^{BE}) \quad \text{(Eq. 6)}$$

$$C_N^{mantle} = C_N^{BE} \times (M^{mantle} / M^{BE})^{(D_N^{metal/silicate} - 1)} \quad \text{(Eq. 7)}$$

where $C_N^{BE}$ is the nitrogen concentration in the bulk Earth; $M^{mantle}$ and $M^{BE}$ are the mass of the silicate mantle and bulk Earth, respectively. For different $\delta^{15}N^{BE}$ values that represent the $\delta^{15}N$ range of enstatite chondrites (Grady *et al.*, 1986), this model implies that core-mantle separation may cause a significant increase in $\delta^{15}N^{mantle}$ and may reproduce the $\delta^{15}N^{mantle}$ range, if $D_N^{metal/silicate}$ is between 5 and 20 (Fig. 3). Using the $C_N^{mantle}$ of 0.8 ppm by Marty (2012) and a $D_N^{metal/silicate}$ of 5-15, the calculated $C_N^{BE}$ is 4-220 ppm (excluding surface nitrogen) and the $C_N^{core}$ is 10-660 ppm. However, if a $D_N^{metal/silicate}$ of 15-20 is used, the calculated $C_N^{BE}$ is 220-1600 ppm and the $C_N^{core}$ is 660-5000 ppm. The high end of these $C_N^{BE}$ values may be higher than the nitrogen concentration in any known chondrites (Krot *et al.*, 2014), which thus indicates that a hybrid Rayleigh-equilibrium model may be more realistic for the segregation of nitrogen in Earth's core if $D_N^{metal/silicate}$ is 15-20. Such a hybrid model (Rubie *et al.*, 2015) assumes that during the early stages of accretion, the impacting objects are relatively small and their metal phase sequentially extracts nitrogen from the magma ocean according to a Rayleigh model; however, towards the end of accretion, large, differentiated planetesimals collide with the growing Earth. The cores of these large objects are in bulk equilibrium with their mantles, but due to their large size, they do not exchange nitrogen with the silicate magma ocean anymore.

In a hybrid Rayleigh-equilibrium model, the $\delta^{15}N^{mantle}$ after complete core-mantle separation should be between the $\delta^{15}N^{mantle}$ constrained by the Rayleigh model and the $\delta^{15}N^{mantle}$ constrained by the equilibrium model. For example, in a 90 % Rayleigh and 10 % equilibrium model, the resulting $\delta^{15}N^{mantle}$ would be –17 ‰ at a $D_N^{metal/silicate}$ of 15, a $\Delta^{15}N^{metal-silicate}$ of –5 ‰, and the average enstatite

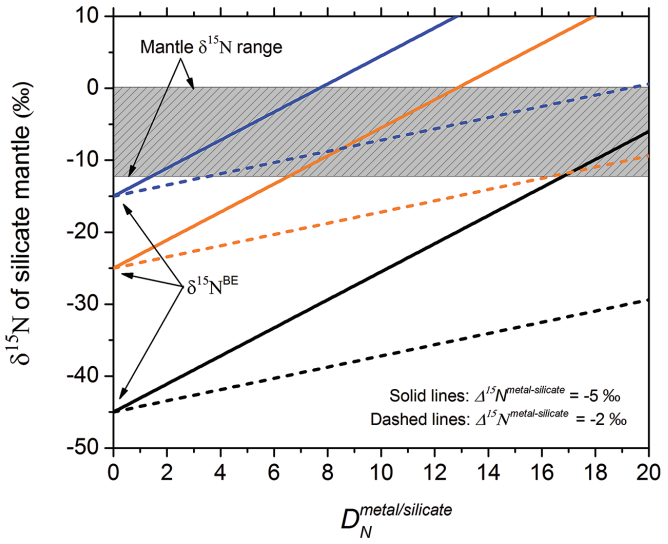


**Figure 3** The modelled $\delta^{15}N$ value of the silicate mantle as a function of $D_N^{metal/silicate}$, just after complete core-mantle separation, using the Rayleigh distillation model (Eq. 5) and the relationship between $f_N^{mantle}$ and $D_N^{metal/silicate}$ (Eqs. 6 and 7). Three different $\delta^{15}N^{BE}$ values are used: the lowest value (–45 ‰) is the lowest value observed so far for Earth's mantle and enstatite chondrites (Grady *et al.*, 1986; Palot *et al.*, 2012); the values of –25 ‰ and –15 ‰ correspond to the average and highest $\delta^{15}N$ values of enstatite chondrites (Grady *et al.*, 1986), respectively. Two different $\Delta^{15}N^{metal-silicate}$ values of –2 ‰ and –5 ‰ are used for the dashed lines and solid lines, respectively. The gray box represents the main range of $\delta^{15}N$ values observed for the silicate mantle (Marty and Dauphas, 2003; Palot *et al.*, 2012; Cartigny and Marty, 2013), which may be produced from the average nitrogen isotopic composition of enstatite chondrites by core-mantle separation with $D_N^{metal/silicate}$ between 5 and 20.

chondrite $\delta^{15}N$ value of –25 ‰. The $C_N^{BE}$ required to achieve the $C_N^{mantle}$ of 0.8 ppm by Marty (2012) would be about 40 ppm. According to Rubie *et al.* (2015), 80-100 % of the core-forming metal may have equilibrated with the silicate magma ocean according to the Rayleigh model. However, it should be noted that the resulting $\delta^{15}N^{mantle}$ of –17 ‰ in the hybrid model above is still significantly lower than the present-day mantle $\delta^{15}N$ of –5 ‰, which indicates a much reduced efficiency of the hybrid Rayleigh-equilibrium model in increasing $\delta^{15}N^{mantle}$ compared to the pure Rayleigh model.

Our above calculations demonstrate that: (1) the bulk Earth $\delta^{15}N$ value has to be significantly negative to produce the present-day mantle $\delta^{15}N$ of –5 ‰; (2) core-mantle separation alone may be sufficient to cause the present-day mantle $\delta^{15}N$ of –5 ‰ even if the Earth accreted only from the enstatite chondrites, if the Rayleigh model is used for describing the segregation of nitrogen in Earth's core; (3) as has been suggested previously (Javoy, 1997), a small fraction of carbonaceous chondrites with $\delta^{15}N$ of +15 to +55 ‰ may have to be added to the Earth to





achieve the present-day mantle $\delta^{15}N$ of –5 ‰, if the Earth accreted mainly from enstatite chondrites and if the equilibrium or the hybrid Rayleigh-equilibrium model is used for describing the segregation of nitrogen in Earth's core. These results support previous models (Javoy, 1997; Palot *et al.*, 2012; Cartigny and Marty, 2013) that assumed enstatite chondrites to be the main source of Earth's nitrogen. These results are also consistent with several other isotopic systems that point towards enstatite chondrites as a main source of the material from which the Earth formed (Javoy, 1997; Trinquier *et al.*, 2007; Regelous *et al.*, 2008; Javoy *et al.*, 2010).

The Earth's deep mantle below 250 km is reducing with oxygen fugacity lower than the iron-wüstite buffer (Frost and McCammon, 2008). Recent experimental studies (Frost *et al.*, 2004; Rohrbach and Schmidt, 2011) suggest that about 1 wt. % Fe-rich metal may be stable in the mantle below this depth, because of the incorporation of significant $Fe^{3+}$ in majoritic garnet and bridgmanite according to the disproportion reaction $3Fe^{2+} = 2Fe^{3+} + Fe^0$, which produces metallic Fe. The moderately siderophile nature of nitrogen together with the relatively low nitrogen solubility in mantle minerals (Li *et al.*, 2013) implies that 1 wt. % Fe-rich metal may store more than 99 % of the nitrogen in the deep mantle. If one assumes negligible nitrogen isotope fractionation between silicate minerals and silicate melt at temperatures corresponding to the deep mantle, the silicate minerals should be enriched in $\delta^{15}N$ by +1 to +5.5 ‰ relative to the Fe-rich metal. Partial melting of the deep mantle with $\delta^{15}N$ of –5 ‰, in the presence of 0.5 to 1.5 wt. % Fe-rich metal (Rohrbach *et al.*, 2014), may therefore generate OIBs with very slightly positive $\delta^{15}N$ values; however, generating OIBs with $\delta^{15}N$ up to +8 ‰ may need the source region $\delta^{15}N > +0$ ‰.

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## Additional Information

**Supplementary Information** accompanies this letter at www.geochemicalperspectivesletters.org/article1614

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# Nitrogen isotope fractionation during terrestrial core-mantle separation

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## Supplementary Information

The Supplementary Information includes:

- Methods
- Table S-1
- Supplementary Information References

### *Methods*

Starting materials for high-pressure experiments included high-purity iron powder, ammonium nitrate ($NH_4NO_3$), and a synthetic silicate glass with a chemical composition similar to that of the global MORB. A mixture of iron powder and finely-ground silicate glass was loaded together with about 0.1 to 1.5 wt. % ammonium nitrate into a graphite-lined platinum capsule. Experiments were conducted at 1.5 to 7.0 GPa and 1600 to 1800 °C in a piston cylinder or multi-anvil high-pressure apparatus, such that only liquid Fe-rich metal and basaltic melt were coexisting in the sample charge. Experiments were quenched to room temperature within a few seconds after about 90 mins. The coexisting Fe-rich metal and silicate of the recovered samples were carefully separated for analyses of nitrogen concentration and isotopic composition, using a static gas mass spectrometer.

Individual chips of glass and metal weighting a few micrograms to a few milligrams were loaded in a laser heating cell consisting of a metal sample holder covered by a ZnSe window. The cell was baked at about 100 °C and pumped under high vacuum ($10^{-8}$-$10^{-9}$ mbar) for several days. Individual samples were then

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incrementally heated in static vacuum using a $CO_2$ laser (wavelength = 10.6 μm). Evolved gases including N compounds were purified for carbon and hydrogen bearing species using a combination of a CuO furnace, Pt catalyst and cold trap held just above the liquid $N_2$ temperature. Purified $N_2$ was then introduced in a static mass spectrometer where masses 28 and 29 were analysed on a Faraday cup detector and masses 29 and 30 were counted on an electron multiplier (Humbert *et al.*, 2000). Potential CO contamination, checked with the measured 29/30 ratio, was found to be always negligible. The abundances of nitrogen and the $^{15}N/^{14}N$ ratios were then computed from the data and from runs with our in-house $N_2$ standard (purified atmospheric $N_2$). Blanks were found to be less than 0.1 % of the signals for all runs. Errors on the isotopic ratios are computed from the standard deviation of in-house $N_2$ standard runs and from the internal precision of the respective sample runs.

Nitrogen metal/silicate partition coefficients $D_N^{metal/silicate}$ were calculated according to $D_N^{metal/silicate} = C_N^{metal}/C_N^{silicate}$, where $C_N^{metal}$ and $C_N^{silicate}$ are the nitrogen concentrations in the liquid Fe-rich metal and silicate melt, respectively. Nitrogen metal/silicate isotope fractionation $\Delta^{15}N^{metal-silicate}$ was calculated according to $\Delta^{15}N^{metal-silicate} = \Delta^{15}N^{metal} - \Delta^{15}N^{silicate}$, where $\Delta^{15}N^{metal}$ and $\Delta^{15}N^{silicate}$ are the nitrogen isotopic composition of the liquid Fe-rich metal and silicate melt, respectively.

**Table S-1** Major and minor element contents in silicate melt and liquid Fe-rich metal (in wt. %).

| | silicate | | | | | | | | | | metal | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exp. ID | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Cr_2O_3$ | FeO | MgO | CaO | $Na_2O$ | $K_2O$ | Total | Fe | Pt | C | O | Total |
| YS-1 | 43.4 | 1.3 | 12.9 | 0.0 | 25.4 | 6.4 | 9.3 | 2.2 | 0.2 | 101.1 | 79.7 | 14.2 | 6.2 | 0.1 | 100.2 |
| 1-σ | 0.7 | 0.1 | 0.2 | 0.0 | 1.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.4 | 1.7 | 2.1 | 0.6 | 0.1 | 0.6 |
| A-659 | 47.4 | 1.4 | 14.6 | 0.0 | 15.4 | 6.9 | 10.2 | 2.6 | 0.2 | 98.9 | 92.4 | 0.0 | 10.5 | 0.1 | 103.1 |
| 1-σ | 0.2 | 0.0 | 0.1 | 0.0 | 0.1 | 0.1 | 0.1 | 0.0 | 0.0 | 0.3 | 1.9 | 0.0 | 4.5 | 0.0 | 1.8 |
| YS-5 | 40.3 | 1.1 | 12.3 | 0.0 | 30.4 | 6.0 | 8.9 | 1.8 | 0.0 | 101.0 | 76.0 | 17.7 | 6.3 | 0.4 | 100.4 |
| 1-σ | 1.5 | 0.2 | 0.5 | 0.0 | 2.4 | 0.3 | 0.6 | 0.2 | 0.0 | 0.6 | 1.8 | 1.8 | 0.5 | 0.3 | 0.7 |
| YS-2 | 43.5 | 1.3 | 13.1 | 0.0 | 25.0 | 6.3 | 9.3 | 2.4 | 0.2 | 101.1 | 77.5 | 16.1 | 6.8 | 0.2 | 100.5 |
| 1-σ | 0.7 | 0.1 | 0.3 | 0.0 | 1.2 | 0.1 | 0.2 | 0.1 | 0.1 | 0.3 | 3.3 | 4.8 | 0.9 | 0.5 | 0.7 |

All the major and minor elements were measured by electron microprobe.
1-σ is the standard deviation based on replicate analyses of 10-20 spots.
The Pt in the metal is due to contamination by the Pt capsule used.

## *Supplementary Information References*

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