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Nitrogen evolution within the Earth's atmosphere–mantle system assessed by recycling in subduction zones

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ABSTRACT

Understanding the evolution of nitrogen (N) across Earth's history requires a comprehensive understanding of N's behaviour in the Earth's mantle – a massive reservoir of this volatile element. Investigation of terrestrial N systematics also requires assessment of its evolution in the Earth's atmosphere, especially to constrain the N content of the Archaean atmosphere, which potentially impacted water retention on the post-accretion Earth, potentially causing enough warming of surface temperatures for liquid water to exist. We estimated the proportion of recycled N in the Earth's mantle today, the isotopic composition of the primitive mantle, and the N content of the Archaean atmosphere based on the recycling rates of N in modern-day subduction zones. We have constrained recycling rates in modern-day subduction zones by focusing on the mechanism and efficiency of N transfer from the subducting slab to the sub-arc mantle by both aqueous fluids and slab partial melts. We also address the transfer of N by aqueous fluids as per the model of Li and Keppler (2014). For slab partial melts, we constrained the transfer of N in two ways – firstly, by an experimental study of the solubility limit of N in melt (which provides an upper estimate of N uptake by slab partial melts) and, secondly, by the partitioning of N between the slab and its partial melt. Globally, 45–74% of N introduced into the mantle by subduction enters the deep mantle past the arc magmatism filter, after taking into account the loss of N from the mantle by degassing at mid-ocean ridges, ocean islands and back-arcs. Although the majority of the N in the present-day mantle remains of primordial origin, our results point to a significant, albeit minor proportion of mantle N that is of recycled origin (17 ± 8% or 12 ± 5% of N in the present-day mantle has undergone recycling assuming that modern-style subduction was initiated 4 or 3 billion years ago, respectively). This proportion of recycled N is enough to cause a departure of N isotopic composition of the primitive mantle from today's δ^{15}N of −5‰ to −6.8 ± 0.9‰ or −6.3 ± 1.2‰. Future studies of Earth's parent bodies based on the bulk Earth N isotopic signature should take into account these revised values for the δ^{15}N composition of the primitive mantle. Also, the Archaean atmosphere had a N partial pressure of 1.4–1.6 times higher than today, which may have warmed the Earth's surface above freezing despite a faint young Sun.

1. Introduction

Nitrogen (N) is the most abundant element in the Earth's present atmosphere; nonetheless, given recent estimates, the most massive reservoir for N is likely the mantle, which contains between 2 and 10 times the atmosphere's N mass (Johnson and Goldblatt, 2015). Therefore, understanding Earth's N systematics requires a thorough investigation of N cycling between Earth's various reservoirs, including N transfer from the atmosphere to the mantle and vice-versa (Barry and Hilton, 2016; Busigny et al., 2011; Goldblatt et al., 2009; Mikhail and Sverjensky, 2014). A fundamental question about N in the Earth's mantle is whether it is of primordial or of recycled origin (Marty and Dauphas, 2003). The answer to this question has two key implications. Firstly, N content and isotopic composition of the primitive mantle (i.e., during the first billion years of Earth history) is key for estimating the nature and proportion of the parent bodies that accreted to form the Earth (Cartigny and Marty, 2013; Li et al., 2016). Isotopic compositions of fibrous diamonds and mid-ocean ridge basalts show that the present-day mantle (mostly the upper mantle) has a $\delta^{15}N\ [({}^{15}N/{}^{14}N)_{sample}/({}^{15}N/{}^{14}N)_{air}-1)\times 1000]$ value of −5 ± 2‰

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(Cartigny and Marty, 2013). Given that both Archaean as well as younger sediments are enriched in ^{15}N (Cartigny and Marty, 2013), presence of recycled crustal material in the mantle would imply that the primitive mantle was depleted in ^{15}N as compared to the present-day mantle. If such is the case, it would imply that the Earth might have dominantly accreted from reduced enstatite chondrites, rather than oxidized carbonaceous chondrites (Javoy, 1997; Li et al., 2016). Secondly, if it can be shown that there has been a drawdown of N from the atmosphere to the mantle via subduction, then estimating the mass of subduction-derived N in the present-day mantle can be used to constrain the partial pressure of N in the Archaean atmosphere. A high partial pressure of N in the Archaean atmosphere could have caused warming in the early Earth in spite of a faint young Sun (Goldblatt et al., 2009), because it would enhance the potency of greenhouse gases by pressure broadening their absorption lines. Also, a N-rich Archaean atmosphere is purported to help retain water which could be a key requirement for development of the Earth into a wet planet, as we know it today (Wordsworth and Pierrehumbert, 2014).

The isotopic composition of N in the primitive mantle remains largely unknown and the partial pressure of N in the Archaean atmosphere is debated. A recent model based on the isotopes of N–He–Ne–Ar in oceanic basalts predicts a 50% higher N partial pressure in the Archaean atmosphere than that at present (Barry and Hilton, 2016). This, however, contradicts results obtained from analysing fluid inclusions from Archaean hydrothermal quartz (Marty et al., 2013), raindrop size distribution (Som et al., 2012) and vesicle size distribution (Som et al., 2016) preserved in Archaean rocks, all of which yielded an Archaean atmospheric N partial pressure of $\sim$0.5 bar (which is lower than today). Here, to constrain the mass and isotopic composition of N in the primitive mantle, from which we can derive the N partial pressure in the Archaean atmosphere, we performed a systematic study on N recycling efficiency (or the proportion of the subducted nitrogen that escapes slab dehydration and/or melting and enters the deep Earth) in modern subduction zones.

Previous studies have estimated modern-day N recycling efficiency based on the difference between ingassing rates in subduction zones and degassing rates at arcs, mid-ocean ridges, ocean islands and back arc spreading centres. Such studies have estimated that 0% (Fischer et al., 2002) to 80–92% (e.g. Barry and Hilton, 2016; Busigny et al., 2011) of slab N is transported to mantle depths beyond sub-arc conditions. Key to estimating recycling rates of an element using such an approach is the assumption that the entire mass of the element carried away from the subducted slab is degassed at arcs; this assumption is not necessarily valid for N. For example, xenoliths from the mantle-wedge, the lithosphere and the lower crust of overriding plates contain abundant amphibole and/or mica (e.g. Kawamoto et al., 2013), which can incorporate significant amounts of N in the form of NH_4^+ substituting for K^+. The shallow upper mantle, such as the sub-arc mantle, can also store 5–20% of present day atmospheric N (Li et al., 2013) during its metasomatism by siliceous slab-derived flux. Hence, the assumption that the flux of N degassed at arcs represents the entire flux released from the subducted slab results in an overestimation of the rates of N sent past the "arc filter" into the deep mantle. Furthermore, while the outflux/degassing rate of N at arcs is constrained (Hilton et al., 2002), differences in the estimates of the influx of N can yield very different estimates of deep mantle injection rates, as has been observed in previous studies (e.g. Busigny et al., 2011; Fischer et al., 2002).

Here, we used an innovative forward approach for determining recycling efficiency in subduction zones, by focusing on the extraction of N from the slab to the overlying mantle-wedge via aqueous fluids and slab partial melts, for which we have investigated a broad range of subduction thermal regimes (Syracuse et al., 2010). We estimated the N ingassing rate for each of the Earth's 55 subduction zones (Supplementary Table 1). Then we determined the rate of N transfer by aqueous fluids in each subduction zone taking into account pressure (P), temperature (T) and oxygen fugacity (fO_2) along the slab-top while also considering the likely N speciation in subduction zone fluids (Li and Keppler, 2014) (Supplementary Information). For subduction zones where slabs are hot enough to partially melt, we quantified the rate of N transported by slab partial melts (referred to as slab-melts) using two approaches, assuming – (i) N is dissolved in the slab-melt at its solubility limit, which anchors the highest rate of N removal from the slab, and (ii) N partitioning between the slab and slab-melt is controlled by NH_4^+, and NH_4^+ behaves similarly as Rb^+ due to the same charge and similar ionic radii; hence, the behaviour of Rb^+ was used as a guide to the partitioning of N between the key N hosting minerals in the slab and any associated partial melt.

We determined the solubility limit of N in slab-melts experimentally. The breakdown of NH_4^+-bearing minerals in the slab, such as phengite and amphibole, controls N release from the subducted slab to any resulting partial melt. N concentrations in the sediments range from 424 μg/g (Busigny et al., 2011) to 2382 μg/g (Li and Bebout, 2005). Assuming a partitioning behaviour of NH_4^+ that is similar to Rb^+ (also assuming a phengite modal abundance in sediments and modal proportion during partial melting), low degree slab partial melts should carry 0.2 to 1.1 wt.% (g/100 g) of N. We deemed it necessary to assess whether such high concentrations of N being dissolved in slab-melts are realistic, leading us to determine experimentally the solubility limit of N in slab partial melts. We also required a knowledge of (i) speciation of N at the relevant conditions, as this determines the solubility mechanism, and (ii) the effect of solubility on variable H_2O concentrations in the slab-melt (as H_2O is the principle volatile species in slab-melts whose contents can vary depending on the degree of melting, and amount of H_2O present in the slab). Considering the aforementioned factors, we experimentally determined the solubility limit of N (the concentration of N dissolved in the melt in the presence of a N-rich fluid phase) in rhyolitic slab partial melts with two different H_2O concentrations (referred to as "low H_2O" and "high H_2O" slab melts, respectively) at fO_2 and pressure conditions applicable for subduction zones (Supplementary Table 2).

2. Methods

2.1. Experimental determination of N dissolved in slab-melt at its solubility limit and analysis of experimental products

We experimentally determined N solubility limit in slab-derived partial melts. The experiments were performed at 1050–1300 °C, 2–4 GPa, fO_2 varying from ΔNNO -0.6 to -4 log units, with slab partial melts (hydrous rhyolites) containing 2.5–6.2 wt.% added N and 4 wt.% ('low H_2O slab melt') and 8 wt.% ('high H_2O slab melt') added H_2O (Table 1). These P–T conditions are appropriate for the hot core of the mantle-wedge in the sub-arc region (Syracuse et al., 2010), where the slab-melt retains its chemistry from the slab-top to the mantle-wedge by channelized flow (Pirard and Hermann, 2015), or slab-melts are produced in the mantle-wedge by the partial melting of slab lithologies in a diaper (e.g. Nielsen and Marschall, 2017). Further details about synthesis of starting materials are provided in the Supplementary Information.

We performed the experiments using a modified double capsule geometry, with $Pt_{95}Rh_5$ capsules (2.5 mm OD, 2.0 mm ID, 5.0 mm length) placed inside nickel outer capsules (5.0 mm OD, 3.0 mm ID, 10.0 mm length). Nickel oxide and distilled water were then added to the space between the inner and outer capsules. Details about the modified double capsule geometry are described in the Supplementary Information. Also, most of our experiments