Nitrogen solubility in the deep mantle and the origin of Earth's primordial nitrogen budget

Takahiro Yoshioka [a], Michael Wiedenbeck [b], Svyatoslav Shcheka [a], Hans Keppler [a],[*]

[a] *Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany*
[b] *GFZ German Research Centre for Geosciences, 14473 Potsdam, Germany*

A B S T R A C T

The solubility of nitrogen in the major minerals of the Earth's transition zone and lower mantle (wadsleyite, ringwoodite, bridgmanite, and Ca-silicate perovskite) coexisting with a reduced, nitrogen-rich fluid phase was measured. Experiments were carried out in multi-anvil presses at 14 to 24 GPa and 1100 to 1800 °C close to the Fe–FeO buffer. Starting materials were enriched in ^{15}N and the nitrogen concentrations in run products were measured by secondary ion mass spectrometry. Observed nitrogen (^{15}N) solubilities in wadsleyite and ringwoodite typically range from 10 to 250 µg/g and strongly increase with temperature. Nitrogen solubility in bridgmanite is about 20 µg/g, while Ca-silicate perovskite incorporates about 30 µg/g under comparable conditions. Partition coefficients of nitrogen derived from coexisting phases are $D_N^{wadsleyite/olivine} = 5.1 \pm 2.1$, $D_N^{ringwoodite/wadsleyite} = 0.49 \pm 0.29$, and $D_N^{bridgmanite/ringwoodite} = 0.24 \, (+0.30/-0.19)$. Nitrogen solubility in the solid, iron-rich metal phase coexisting with the silicates was also measured and reached a maximum of nearly 1 wt.% ^{15}N at 23 GPa and 1400 °C. These data yield a partition coefficient of nitrogen between iron metal and bridgmanite of $D_N^{metal/bridgmanite} \sim 98$, implying that in a lower mantle containing about 1% of iron metal, about half of the nitrogen still resides in the silicates. The high nitrogen solubility in wadsleyite and ringwoodite may be responsible for the low nitrogen concentrations often observed in ultradeep diamonds from the transition zone. Overall, the solubility data suggest that the transition zone and the lower mantle have the capacity to store at least 33 times the mass of nitrogen presently residing in the atmosphere. By combining the nitrogen solubility data in minerals with data on nitrogen solubility in silicate melts, mineral/melt partition coefficients of nitrogen can be estimated, from which the behavior of nitrogen during magma ocean crystallization can be modeled. Such models show that if the magma ocean coexisted with a primordial atmosphere having a nitrogen partial pressure of just a few bars, several times the current atmospheric mass of nitrogen must have been trapped in the deep mantle. It is therefore plausible that the apparent depletion of nitrogen relative to other volatiles in the near-surface reservoirs reflects the storage of a larger reservoir of nitrogen in the solid Earth. Dynamic exchange between these reservoirs may have induced major fluctuations of bulk atmospheric pressure over Earth's history.

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1. Introduction

Earth's atmosphere consists mostly of nitrogen (78 vol.%, equivalent to $3.87 \cdot 10^{18}$ kg N_2) and traditionally, the atmosphere has been regarded as the main nitrogen reservoir on our planet (e.g. Hall, 1999). However, for Venus, which in many aspects is similar to Earth, the mass of nitrogen in the atmosphere is about three times larger (Johnson and Goldblatt, 2015). This is one of several

lines of evidence suggesting that either nitrogen is anomalously depleted on Earth (Marty, 2012), or a major nitrogen reservoir may reside somewhere within Earth's interior (Johnson and Goldblatt, 2015). The existence of such a deep nitrogen reservoir would imply that bulk atmospheric pressure may have fluctuated significantly in the geologic past, with important implications for climate and habitability. High nitrogen partial pressures may enhance the greenhouse effect by broadening the infrared absorption bands of greenhouse gases (Goldblatt et al., 2009). Evidence for a dynamic exchange between the atmosphere and Earth's interior comes from data on nitrogen fluxes in subduction zones. The present day ni-

trogen flux into the mantle at subduction zones has been estimated to be about three times larger than nitrogen outgassing at midocean ridges, arc and intraplate volcanoes (Busigny et al., 2011), although there is some controversy about the efficiency of nitrogen subduction into the deep mantle (Busigny et al., 2003; Elkins et al., 2006; Halama et al., 2010, 2014; Mikhail et al., 2017; Mallik et al., 2018). Nitrogen transfer rates into the mantle are probably high enough to allow a complete recycling of all atmospheric nitrogen into the mantle over the history of the Earth (Busigny et al., 2011), perhaps even several times (Johnson and Goldblatt, 2015). Direct evidence for possible fluctuations in atmospheric pressure over geologic time is sparse and contradictory (e.g. Marty et al., 2013; Som et al., 2016).

In general, data on current-day nitrogen abundances become increasingly uncertain with depth in the solid Earth. Sediments may contain several 100 µg/g of nitrogen, which is mostly ammonium (NH_4^+) of biological origin (e.g. Karl et al., 1997). The average nitrogen concentration of about 120 µg/g in the continental crust is constrained by direct sampling, mostly of the upper crust, and translates into $1.7 \cdot 10^{18}$ kg N (Johnson and Goldblatt, 2015). However, the nitrogen budget of Earth's mantle is rather uncertain and the amount of nitrogen residing in the core is largely unknown. Virtually all available mantle samples (xenoliths and mantle derived magmas) are likely degassed and may have lost a significant part of their initial volatile budgets. Estimates of nitrogen abundances are therefore often based on observed $N_2/^{40}Ar$ ratios (Marty, 1995). The overall mantle abundance of ^{40}Ar, a decay product of ^{40}K, can be relatively well estimated from the abundance of K in the mantle, corrected for losses to the atmosphere. Estimated nitrogen abundances for the upper mantle range from fractions of a µg/g (e.g. 0.27 ± 0.16 µg/g, Marty and Dauphas, 2003) to a few µg/g (e.g. Cartigny et al., 2001; Johnson and Goldblatt, 2015). While these numbers appear low, it is important to note that 1 µg/g of N in the entire mantle would already be equivalent to one atmospheric mass of nitrogen. Direct data on nitrogen contents in the transition zone and the lower mantle are lacking. Overall, the available evidence suggests that either nitrogen is depleted on Earth relative to other volatiles, such as carbon or water (Marty, 2012), or most of the nitrogen presently resides within the solid Earth (Johnson and Goldblatt, 2015). Partitioning of some nitrogen into the core appears feasible based on a number of experimental studies that suggest a siderophile behavior of nitrogen during core formation (Kadik et al., 2013; Roskosz et al., 2013; Li et al., 2016). However, under all conditions studied, the observed metal/silicate partition coefficient for N is much smaller than for C. Therefore, if core formation had significantly affected the nitrogen budget, it would have depleted C relative to N (Dalou et al., 2017), which is not consistent with observation. While there may be a significant reservoir of N in the core, it is likely much smaller than what is estimated from a bulk core–mantle equilibrium model (Johnson and Goldblatt, 2015) due to the lack of equilibration between metal and silicate in the late stages of core formation (Rubie et al., 2015). It therefore appears plausible that the mantle could represent the largest reservoir of N in the solid Earth.

Early experimental studies have shown that a variety of ammonium-bearing silicates can be synthesized at high pressures (Watenphul et al., 2009, 2010). These data imply that the NH_4^+ ion readily replaces K^+ in many silicates (see also Honma and Itihara, 1981; Bebout and Fogel, 1992). Stabilizing NH_4^+ in the mantle, however, requires quite reducing conditions, with oxygen fugacities near or below the Fe–FeO buffer. Li et al. (2013) reported the first study of nitrogen solubility in the upper mantle minerals olivine, pyroxenes, and garnet in equilibrium with a nitrogen-rich fluid phase. Nitrogen solubilities generally increase with pressure and under more reducing conditions, reaching values near 100 µg/g in

aluminous orthopyroxenes at 1.5 GPa and at the Fe–FeO oxygen fugacity buffer. Compared to pyroxenes, solubilities in forsterite are lower. According to Li and Keppler (2014), ammonia NH_3 is the main nitrogen species in aqueous fluids coexisting with mantle minerals under Fe–FeO buffer conditions. The data of Li et al. (2013) suggest that the upper mantle alone has the capacity to store 20–50 times more nitrogen than presently resides in the atmosphere.

The purpose of the present study is to provide the first experimental constraints on the nitrogen storage capacity of the transition zone and the lower mantle. Nitrogen solubility in wadsleyite, ringwoodite, bridgmanite, and Ca-silicate perovskite, the most abundant phases of the deep mantle, was experimentally quantified. Due to the generally reduced nature of the transition zone and the lower mantle (Frost and McCammon, 2008), all experiments were carried out at oxygen fugacities close to the Fe–FeO buffer. While the solubility data cannot give actual nitrogen concentrations in the mantle, they provide upper limits and can constrain the equilibrium partitioning of nitrogen between different mantle domains as well as the behavior of nitrogen upon partial melting and magma ocean crystallization.

2. Experimental and analytical methods

2.1. Starting materials and preparation of sample capsules

For the synthesis of wadsleyite, ringwoodite, and bridgmanite, stoichiometric mixtures were prepared from analytical grade SiO_2 and MgO. Moreover, an additional 20 wt.% Na_2CO_3 powder was added as a fluxing agent to enhance crystal growth during the experiment. The mixtures were homogenized for 1 h in a mortar under ethanol and then dried at 140 °C for one night. For Ca-silicate perovskite, we used a glass as starting material. A mixture with molar ratio of Ca:Si:Ti = 1:0.75:0.25 was prepared from analytical grade $CaCO_3$, SiO_2 and TiO_2. Titanium was added to avoid complete amorphization of the Ca-silicate perovskite upon decompression (Kubo et al., 1997). After decarbonation at 1100 °C, the mixture was converted into a glass by melting at 1700 °C for 30 min, followed by quenching in water.

Upon loading into sample capsules, about 10–20 wt.% ^{15}N-labeled $^{15}NH_4^{15}NO_3$ (>95% ^{15}N) was added to the starting materials (silicate mixture or glass) as a nitrogen source. The labeling with ^{15}N was used so as to distinguish nitrogen dissolved in the sample from atmospheric contamination in the subsequent SIMS analysis. Moreover, iron metal powder (more than five times the weight of $^{15}NH_4^{15}NO_3$) was loaded into one end of the capsules to maintain reducing conditions close to the Fe–FeO buffer. Samples were sealed by arc welding into $Pt_{95}Rh_5$ capsules with sizes of $1.6 \times 1.1 \times 3.0$ mm (outer diameter × inner diameter × length) or $1.2 \times 1.0 \times 2.4$ mm.

2.2. High-pressure experiments

We conducted a series of experiments at 14–24 GPa and 1100–1800 °C using Kawai-type multi-anvil presses with tungsten carbide cubes as secondary anvils (Supplementary Table 1). Pressure calibration curves reported by Keppler and Frost (2005) were used. Experiments at 14–15, 17–19 and 21–24 GPa were carried out in a 1000-ton press with 14/8, 10/5 and 10/4 assemblies (octahedral edge length/truncation edge length in mm), respectively. Only the runs Z1383 and Z1405 were done in a 5000-ton press using a 18/11 octahedral sample assembly. The octahedral assemblies consisted of an outer octahedral MgO pressure medium, a ZrO_2 sleeve, a $LaCrO_3$ heater and an inner MgO sleeve. Inside the MgO inner sleeve and below the sample, an MgO spacer was inserted for the 18/11 and 14/8 assemblies, while an Al_2O_3 spacer