Nitrogen solubility in upper mantle minerals

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ABSTRACT

Nitrogen solubility in the upper mantle minerals forsterite, diopside, enstatite and pyrope has been quantified by SIMS measurements of nitrogen-saturated, synthetic samples. The crystals were grown in a ^{15}N–H–O fluid buffered by Ni–NiO, Co–CoO, and Fe–FeO, at 1000–1300 °C and 15–35 kbar in a piston cylinder apparatus. Nitrogen solubility in minerals is significantly affected by temperature, pressure, mineral composition and, in particular, by oxygen fugacity. Nitrogen in all crystals buffered by Ni–NiO or Co–CoO is below detection limit or at most a few µg/g at very high pressures. Concentrations of 5–24 µg/g nitrogen have been quantified in diopside, enstatite and pyrope buffered by Fe–FeO at 1100 °C/15 kbar. Very high nitrogen solubility up to 100 µg/g is observed at the Fe–FeO buffer in enstatite at high-temperature or in Al-bearing enstatite and diopside. The nitrogen solubility in forsterite at the Fe–FeO buffer also clearly increases with temperature and pressure; a maximum solubility of 10 ppm is obtained at 1300 °C/35 kbar. The strong enhancement of nitrogen solubility under reducing conditions may be related to nitrogen dissolution as either NH_4^+ or as N^{3-} directly replacing O^{2-}. Both mechanisms require some charge compensation, consistent with the enhancement of nitrogen solubility with Al content in enstatite. Our results demonstrate that the reduced lower part of the upper mantle has a large nitrogen storage capacity, and may store ~20–50 times more nitrogen than the present atmosphere. Therefore, some 'missing' nitrogen may still be retained in the Earth's deep, reduced mantle. The calculated nitrogen partition coefficients between upper mantle minerals and silicate melt reveal that an oxidized mantle source would lose almost its entire nitrogen during partial melting, whereas under reducing conditions a considerable fraction of nitrogen could be retained in the residual solids. The high nitrogen solubility in upper mantle minerals at reducing conditions also suggests that solidification of the magma ocean on the early Earth should have retained significant nitrogen, yielding higher N/Ar and N/C ratios in the young upper mantle as compared to the young atmosphere.

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1. Introduction

Nitrogen is a volatile element that may record key information about the evolution and interaction of Earth's different reservoirs (Marty and Dauphas, 2003). Nitrogen geochemistry is closely linked to atmospheric evolution and may have had a strong effect on the climate of the early Earth and on the formation of the first biomolecules (Miller, 1953; Sagan and Mullen, 1972; Goldblatt et al., 2009; Wolf and Toon, 2010). Molecular N_2, the main component in the Earth's present atmosphere, is generally thought to have been derived from degassing of the Earth's interior. If one assumes a chondritic composition for the bulk Earth, most of the nitrogen might still be stored in Earth's mantle or core (Marty, 2012). However, little is known about how much nitrogen could have been retained in mantle minerals during the solidification of the magma ocean in the Earth's early history or in the residual mantle minerals after partial melting. Consequently, it is not known how efficiently nitrogen could have been degassed into the Earth's atmosphere, leaving the nitrogen abundance in the bulk silicate Earth poorly constrained. Using the relatively constant $N_2/^{40}$Ar ratio in midocean ridge basalts (MORB) and assuming that nitrogen and Ar have similar geochemical behavior during mantle melting, Marty (1995) estimated ~3 parts per million by weight (referred as ppm in the following) for the nitrogen abundance in the silicate Earth. Based on his layered model of Earth's accretion, Javoy (1997) estimated ~36 ppm nitrogen for the upper mantle. After a systematic study of δ^{13}C–N concentration in diamonds, Cartigny et al. (2001) suggested that mantle nitrogen contents in the range of 2–40 ppm are plausible.

Nitrogen solubility in mantle minerals is crucial for understanding the dynamic exchange of nitrogen between Earth's mantle and atmosphere. If nitrogen has a very small solubility in upper mantle minerals, behaving as an atmophile element such as Ar (Marty and Dauphas, 2003; Libourel et al., 2003), most of the nitrogen might have been efficiently degassed into the Earth's very

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early atmosphere; therefore the present mantle nitrogen might be of atmospheric origin and may have been recycled by subduction (Goldblatt et al., 2009). However, if under certain conditions nitrogen could be dissolved in mantle minerals, behaving as a lithophile element such as K and Rb (Bebout et al., 1999; Yokochi et al., 2009; Halama et al., 2010), an average mantle nitrogen content of just 10 ppm would constitute a reservoir ten times larger than the present atmosphere. The two orders of magnitude higher $N_2/^{36}Ar$ ratio in MORB as compared to the atmosphere (Marty and Dauphas, 2003) and the relative depletion of nitrogen compared to other volatiles (e.g., H_2O, Ar, Kr, and Ne) in both atmosphere and the depleted MORB source (Marty, 2012) may indeed indicate that a significant amount of nitrogen is being retained in the Earth's deep interior. Moreover, about 80% of the presently subducted nitrogen does not appear to return to the Earth's surface (Busigny et al., 2011). This imbalance of fluxes, which is associated with a contrasting isotope composition of subducted and degassing nitrogen, implies that a mechanism for storing significant amounts of nitrogen in the mantle must exist.

Ar and other noble gases have been shown to be quite insoluble in upper mantle minerals (Parman et al., 2005; Heber et al., 2007). However the potential role of upper mantle minerals in retaining nitrogen and producing the depleted nitrogen signature has received little attention. One previous experimental study showed that nitrogen in the form of NH_4^+ could be incorporated in diopside in a concentration up to 1000 ppm at 750 °C and 11.5 GPa (Watenphul et al., 2010), which suggests that clinopyroxene might be a potential candidate for storing nitrogen in Earth's upper mantle. The study of Watenphul et al. (2010), however, was carried out without buffering of oxygen fugacity and nitrogen was detected only by infrared spectroscopy, which is sensitive for ammonium, but not for other possible nitrogen species (e.g., the direct substitution of N for O as in synthetic nitridosilicates; Huppertz and Schnick, 1997). In this article, we present the first secondary ion mass spectrometer (SIMS) data on nitrogen solubility in upper mantle minerals including olivine, clinopyroxene, orthopyroxene and garnet synthesized at various temperatures, pressures, mineral compositions and redox conditions, which constrain the nitrogen storage capacity of the upper mantle and nitrogen partitioning between minerals and silicate melts.

2. Experimental methods

Stoichiometric mixtures with the composition of forsterite, diopside, enstatite and pyrope were prepared from high purity oxides and hydroxides (SiO_2, $Al(OH)_3$, $Ca(OH)_2$ and $Mg(OH)_2$). To synthesize relatively large crystals, about 10 wt% Na_2CO_3 was added as a fluxing agent, except to the diopside and enstatite runs that contained aluminum. To avoid any contamination or isotopic interference in the following SIMS analysis, about 5 wt% ^{15}N-labeled $^{15}NH_4^{15}NO_3$ (>95% ^{15}N) was added to the starting material as the nitrogen source. $^{15}NH_4^{15}NO_3$ decomposes mostly into $^{15}N_2O$ and H_2O upon heating, thereby producing a nitrogen enriched fluid phase coexisting with the starting material in the inner capsule (see below).

All experiments were conducted in an end-loaded, solid media piston cylinder apparatus using 0.5 inch diameter MgO–NaCl assemblies with stepped graphite heaters. The temperatures and pressures ranged from 1000 to 1300 °C and from 15 to 35 kbar, to simulate conditions typical of the upper mantle. A modified double capsule technique, similar to that described by Bali et al. (2010) and Li and Audétat (2012), was used to buffer oxygen fugacity by three different oxygen buffers (Fe–FeO, Co–CoO, Ni–NiO). This method employs a small inner $Pt_{95}Rh_{05}$ capsule containing about 35 mg starting mixture loaded into an outer capsule made of Ni, Co, or Fe where the space between was packed with corre-

sponding oxides (NiO, CoO, or FeO) and water. The outer capsule was sealed mechanically under high pressures. Note that in equilibrium under run conditions, hydrogen fugacity in the inner and outer capsule will be equal, due to the high permeability of platinum for hydrogen. This means that hydrogen fugacity in all of our experiments is exactly the same as that of pure water coexisting with the corresponding oxygen buffer. The hot piston-in method was used to pressurize the assembly. Temperature was monitored by Pt–$Pt_{90}Rh_{10}$ (S-type) thermocouples with an estimated temperature uncertainty of ± 10 °C. A friction correction of 5% was applied to the nominal pressure based on bracketing of the quartz–coesite transition at 790 °C and using the data of Bose and Ganguly (1995) as reference. The experiments were quenched within 10–20 s to below 100 °C by switching off the electrical power to the heater.

The recovered capsules were punctured and opened. In experiments without Na_2CO_3 in the starting material the sample capsules contained loose aggregates of crystals together with a quenched fluid phase, whereas in experiments with Na_2CO_3 crystals were embedded in a quenched, fine-grained carbonate matrix, which was removed by soaking in a 1 mol/l HCl solution. The synthetic crystals were identified using Raman spectroscopy and are similar to those synthesized by Shcheka et al. (2006), which are euhedral or subhedral with grain size varying from 30 to hundreds µm (Fig. 1). The odor of NH_3 was often detected upon opening of capsules buffered by the Fe–FeO buffer. Alloying of Fe and PtRh at high temperatures appears to render the $Pt_{95}Rh_{05}$ inner capsule brittle so that it was often broken upon quench. Buddingtonite ($^{15}NH_4AlSi_3O_8$ or $^{14}NH_4AlSi_3O_8$) was synthesized and used for identifying useful nitrogen ion species during SIMS analysis. Buddingtonite with grain size varying from 20 to 60 µm (with one single crystal of 250 µm) was synthesized at 600 °C, 8 kbar, and Fe–FeO oxygen buffer for 12 days, using the setup described above for piston cylinder experiments and starting with an excess 20 wt% $^{15}NH_3$ or $^{14}NH_3$ solutions together with a stoichiometric $Al(OH)_3$ and SiO_2 mixture.

3. SIMS analytical procedure

SIMS is one of the few techniques which provides the necessary spatial resolution and which is also able to detect the presence of nitrogen. A further reason for favoring the SIMS technique is that, being a mass spectrometric method, it is able to distinguish between the two naturally occurring isotopes of nitrogen. Thus, we could base our experiments on the rare isotope ^{15}N, and by detecting the presence of this isotope in the absence of the more abundant ^{14}N, we could be assured that any signal was not due to the presence of atmospheric or instrumental contamination. In the presence of carbon as a matrix element, the signals at mass stations $^{12}C^{14}N^-$ or $^{12}C^{15}N^-$ can have quite high count rates. Thus, SIMS has been used for both the quantification and isotopic characterization of nitrogen in diamonds, graphite and organic-rich samples (Smart et al., 2011; De Gregorio et al., 2011). In contrast, the use of SIMS for the analysis of nitrogen in silicates is effectively unknown. As the present study is one of the first to attempt this approach, we will describe our analytical method in detail.

The first requirement for SIMS quantification of nitrogen is that one identifies a matrix matched reference material with known nitrogen concentration. As our work reports the first SIMS-based data on nitrogen, no suitable reference material was available from any previous study. We therefore decided to produce two suites of ion implant reference materials which consisted of co-implanted samples of near end-member forsterite (synthetic), diopside (Jaipur, India), enstatite (Sri Lanka) and pyrope (Dora Maira, Alps). Two cm-sized, highly polished pieces of each phase were sent to the Institute of Ion Beam Physics and Materials Re-