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Nitrogen abundance and isotope analysis of silicate glasses by secondary ionization mass spectrometry

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ABSTRACT

Chondritic meteorites preserve extreme intra-sample $^{15}N/^{14}N$ variations, which exceed, in some cases, the range of nitrogen isotope ratios observed at the Solar System scale. These observations are based on in situ analyses of CN^- molecular ions by secondary ionization mass spectrometry (SIMS) in carbon-rich phases. The distribution of nitrogen and its isotopes in silicate minerals and glasses has not been investigated to this date due to the lack of an appropriate analytical protocol, as well as of suitable N-bearing standards. In order to improve our knowledge of the nitrogen signature of both extraterrestrial and terrestrial silicate samples, we have developed a protocol for determining precise and accurate nitrogen abundances (and isotope ratios) in basaltic glasses using high mass resolution SIMS. Twelve (C-)N-bearing synthetic basaltic glasses, containing between < 1 and 18,443 ± 966 ppm N, form the suite of reference materials for this study. By targeting the CN^-, NO^-, AlN^-, and SiN^- secondary molecular ions, nitrogen abundances can be detected down to the ppm level in both carbon-bearing and carbon-free glasses. The analytical precision and reproducibility of isotope ratios in the form of $^{15}N^{16}O^-/^{14}N^{16}O^-$ is on the order of 11‰ and 10 to 17‰ (2σ), respectively, for reference glasses containing ≥ 100 ppm N. Thus, nitrogen isotope ratios can be determined with an uncertainty that is small enough to resolve nitrogen isotope variations in extraterrestrial silicates. The study of four chondrules of the ordinary chondrite Semarkona (LL3.0) reveals that the nitrogen distribution in the mesostasis is highly heterogeneous, with concentrations ranging from 0 to 1099 ± 168 ppm. The $\delta^{15}N$ values in mesostasis, olivine, and pyroxene vary between −36 ± 50‰ and +55 ± 72‰, indicating that silicate phases in chondrules do not host particularly ^{15}N-poor nitrogen.

1. Introduction

Nitrogen isotopes provide a powerful tool for tracing the origin of volatile elements on planetary bodies because the relative proportion of ^{14}N and ^{15}N shows outstanding variability among different Solar System objects and reservoirs (Füri and Marty, 2015). Although turbulent mixing regionally homogenized the material available for planet formation – resulting in similar nitrogen isotope compositions for Earth and the Moon, the interior of Mars, and most chondrite groups ($\delta^{15}N \approx 0 \pm 50$‰; e.g., Füri et al., 2015a; Kerridge, 1985; Kung and Clayton, 1978; Mathew and Marti, 2001; Pearson et al., 2006) –, micron-sized zones with extreme nitrogen isotopic anomalies remain preserved in some chondritic meteorites. So-called ^{15}N-hotspots have been detected in the insoluble organic matter of carbonaceous chondrites ($\delta^{15}N = 3200 \pm 700$‰; Busemann et al., 2006) and in lithic clasts of the Isheyevo meteorite ($\delta^{15}N = 4200 \pm 1500$‰ to 4900 ± 300‰; Bonal et al., 2010; Briani et al., 2009). In contrast, osbornite (TiN) within a calcium-aluminum-rich inclusion of Isheyevo records an exceptionally ^{15}N-poor, solar-like nitrogen isotope signature ($\delta^{15}N = -364 \pm 12$‰; Meibom et al., 2007). Bulk chondrules, millimeter-sized silicate spheres in chondrites, also display a significant range of $^{15}N/^{14}N$ ratios ($\delta^{15}N \approx -100$ to $+170$‰; Das and Murty, 2009; Fredriksson et al., 1985; Kung and Clayton, 1978; Mahajan and Murty, 2003; Murty and Marti, 1985) which lead previous authors to suggest that chondrule precursors carried various nitrogen components with distinct isotopic compositions, and that this heterogeneity was preserved during the high-temperature chondrule forming process(es). Silicates are inferred to be the carriers of isotopically light nitrogen in chondrules, whereas organics and metals or metal sulfides are thought to represent the ^{15}N-enriched endmember (Fredriksson et al., 1985; Murty and Marti, 1985). However, previous data were obtained through bulk analyses, and the nitrogen isotopic signature of distinct chondrule phases (mesostasis, silicate minerals, melt inclusions, metals, sulfides) has not been investigated to this date. Since chondrules have

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recently been shown to contain relict olivine grains inherited from chondrule precursors (Marrocchi et al., 2018), and to preserve significant hydrogen and oxygen isotopic heterogeneities (Deloule and Robert, 1995; Marrocchi et al., 2016, 2018), in situ analyses are crucial for better understanding the origin and distribution of nitrogen in chondrules.

Nitrogen abundances and isotope ratios of geologic samples have historically been analyzed using isotope ratio mass spectrometers operated in dynamic pumping mode or noble gas mass spectrometers operated under static vacuum conditions (e.g., Frick and Pepin, 1981; Hashizume and Marty, 2004; Javoy and Pineau, 1991; Thiemens and Clayton, 1983). Although the latter technique requires only a small amount of material (≤5 mg; e.g., Füri et al., 2015a), these bulk analytical methods are destructive and do not provide any information on the spatial distribution of nitrogen within the sample. Nuclear reaction (Mosbah et al., 1993; Varela et al., 2003) and electron microprobe analyses (EPMA; Kadik et al., 2011; Li et al., 2015; Roskosz et al., 2013; von der Handt and Dalou, 2016) allow for in situ measurements of nitrogen abundances in silicate glasses with detection limits on the order of 10 and 100 s–1000 s ppm, respectively. Since nitrogen nuclear microanalysis is based on the $^{14}N(d,p)^{15}N$ reaction, and EPMA cannot distinguish between isotopes of the same element, isotope ratio measurements are not feasible by these techniques.

Secondary ionization mass spectrometry (SIMS) analysis represents a quasi non-destructive method for determining chemical and isotopic variations with a high lateral resolution (at a scale as small as ≤10 μm) or a high depth resolution (≤10 nm). The measurement of nitrogen by SIMS is challenging because it does not form a stable elemental negative ion. However, an intense CN^- signal forms in the presence of carbon, when the sample surface is bombarded with a Cs^+ ion beam (Zinner et al., 1989). Thus, nitrogen isotope ratios have successfully been determined in the form of $^{12}C^{15}N^-/^{12}C^{14}N^-$ in a range of carbon-rich materials such as pollen (e.g., Lhuissier et al., 2000), organic matter (e.g., Aléon et al., 2003; Busemann et al., 2006; Thomen et al., 2014), graphite (e.g., Mostefaoui et al., 2005), diamond (e.g., Hauri et al., 2002), SiC (Marty et al., 2011; Zinner et al., 1989), osbornite (Meibom et al., 2007), and iron meteorites (e.g., Sugiura, 1998). As an alternative, for carbon-free samples such as silicate minerals and glasses, the NO^- signal can be targeted for nitrogen abundance measurements, as demonstrated by Li et al. (2013) and Regier et al. (2016). The lack of an appropriate analytical protocol, as well as of suitable N-bearing standards, has so far prevented the use of SIMS for nitrogen isotope analyses of silicates.

Here we present a novel protocol for in situ nitrogen abundance and isotope analyses in basaltic silicate glasses. The CAMECA IMS 1280 HR2 at the Centre de Recherches Pétrographiques et Géochimiques (CRPG, Nancy) can achieve a high mass resolution, i.e., MRP = m/Δm up to 18,000 in this study, allowing significant isobaric interferences from neighboring masses on the CN^-, NO^-, AlN^-, and SiN^- signals to be resolved. By targeting these secondary molecular ions, nitrogen abundances can be detected down to the ppm level in both carbon-bearing and carbon-free silicate samples. Furthermore, isotope ratios in the form of $^{15}NO^-/^{14}NO^-$ can be determined with an uncertainty of < 20‰ for reference glasses containing ≥100 ppm nitrogen. Hence, this technique is key for the study of nitrogen trapped within micron-sized silicate phases such as chondrule components (e.g., mesostasis).

2. Reference materials used for nitrogen analyses by SIMS

2.1. N-bearing basaltic glasses synthesized at atmospheric pressure

To investigate the nitrogen solubility in tholeiitic melt, Humbert (1998) experimentally produced basaltic glass samples with a range of nitrogen concentrations (< 1 to ≥5000 ppm). Nitrogen equilibration experiments were carried out for 36 to 48 h at a temperature of 1400 to 1425 °C and at atmospheric pressure in a GERO HTVR 70–250 vertical drop-quench furnace over a range of 18 log units of oxygen fugacity in a C-N-O vapor system (see Libourel et al. (2003) for details). Subsequently, the nitrogen content and isotopic composition of the quenched run products was determined by CO_2 laser extraction static mass spectrometry (Humbert et al., 2000). The solubility of nitrogen in basaltic melt was found to be highly sensitive to the oxygen fugacity, with a drastic increase of the nitrogen concentration by several orders of magnitude under reducing conditions (i.e., between $\log fO_2$–10.7 and −18). Libourel et al. (2003) proposed that this solubility increase can be related to changes in the mechanism of nitrogen dissolution in silicate melt: under oxidizing conditions, nitrogen dissolves physically as a N_2 molecule, whereas under reducing conditions, nitrogen is chemically bounded to the silicate melt network as N^{3-} species. Thus, basaltic glasses covering a wide range of nitrogen contents were obtained by simply varying the redox conditions of the equilibration experiments. Eight nitrogen-bearing glasses synthesized by Humbert (1998) are used in this study as reference materials for nitrogen abundance and isotope analyses by SIMS (Table 1). These glasses cover a concentration range between < 1 and 3906 ± 188 ppm N, and their $\delta^{15}N$ value (where $\delta^{15}N$ is the permil deviation from the atmospheric $^{15}N/^{14}N$ ratio of 0.003676) has been shown to be close to −4 ± 1‰ (Humbert, 1998), which corresponds to the isotopic composition of the N_2 gas used for the experiments.

2.2. C-N-bearing basaltic glasses synthesized at high pressure

Six C-N-rich glasses were synthesized from N-MORB-like (Presnall and Hoover, 1984) starting material, obtained by mixing pre-dried, spectroscopically pure oxides and carbonates. The starting composition was prepared Fe-free to prevent iron nitride crystallization. The mixture was decarbonated by heating, ground in ethanol in an agate mortar, and nitrogen was added by using between 0.3 and 5 wt% Si_3N_4, which has a strong reducing effect. Although in the absence of Fe, the fO_2 could not be measured, it is expected that the samples are reduced within the same range as those of Dalou et al. (2016), i.e., $-13 < \log fO_2 < -8.5$.

Nitrogen equilibration experiments were carried out for six hours in a ½-inch piston cylinder at 1.2 ± 0.1 GPa and 1400 °C at the University of Minnesota. From outside to inside, assemblies consisted of a CaF_2 sleeve surrounding a graphite furnace, and MgO cell parts, which were dried beforehand at 1000 °C for 4 h and stored in a drying oven at 110 °C. The starting material was loaded into a graphite capsule to prevent nitrogen diffusion into metal capsules, to ensure reducing conditions (thus promoting the nitrogen dissolution into the melt phase; e.g., Kadik et al., 2015; Libourel et al., 2003), and to provide a source of carbon. The graphite capsule was placed into an MgO sleeve and isolated from the thermocouple by a 1 mm MgO ring. The temperature was measured with a type B ($Pt_{70}Rh_{30}/Pt_{94}Rh_6$) thermocouple to within ± 2 °C of the set point (Zhang and Hirschmann, 2016). Experiments were temperature-quenched rapidly before decompression (at a rate of ~175 °C/s) by turning off the power to the furnace. The recovered capsules were cut lengthwise using a wire saw, and one half of each experimental charge was roughly ground into sub-millimetric fragments.

The clearest glass fragments (free of visible graphite, as observed under the microscope) are used as SIMS calibrants for this study, and a few chips of each sample were targeted for nitrogen concentration and isotope ratio analyses by CO_2 laser extraction static mass spectrometry (Appendix A). Total nitrogen abundances of the six glasses vary between 383 ± 33 and 18,443 ± 966 ppm, with $\delta^{15}N$ values of −9.9 to −0.7‰ (± 2.5‰) (Table 1 and Appendix A), and represent both N_2 and N-H species (Dalou et al., 2017). Complementary SIMS analyses revealed that the CO_2-equivalent carbon content of the glasses is highly variable and heterogeneous, likely due to the presence of micron-sized graphite inclusions (Table 1 and Appendix B). Furthermore, the glasses contain between 0.8 and 2.4 wt% H_2O, which is assumed to have been