

Determination of $^{15}\text{N}/^{14}\text{N}$ ratios in reduced silicate glasses using Raman spectroscopy.

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Although nitrogen is fundamental to the evolution and persistence of Earth's atmosphere and biosphere, many open questions are still pending about the present-day isotope distribution of its two stable isotopes ^{14}N and ^{15}N (~99.6% and ~0.4%, respectively) between the different deep geochemical reservoirs. Terrestrial reservoirs show a strongly heterogeneous distribution between the ^{15}N -depleted mantle and the ^{15}N -enriched surface. The use of N isotopes to address possible origins of characteristic N isotope signatures in deep Earth reservoirs requires constraints on the magnitude of fractionation between minerals, melts and fluids within the mantle. Because the determination of N isotope fractionation during magmatic processes involving aqueous fluids rely on experiments, we have developed the analytical protocol for measuring N isotopes by Raman spectroscopy, to be subsequently applied to *in-situ* hydrothermal diamond anvil cell experiments.

We present Raman spectra acquired in compositionally simple silicate glasses (NS4, an anorthite-diopside eutectic glass in CMAS) and in a haplobasalt, a haploandesite and a haplorhyolite, enriched in variable proportions of $\text{Si}_3^{15}\text{N}_4$ and $\text{Si}_3^{14}\text{N}_4$ ($^{15}\text{N}/^{14}\text{N}$: 0.004, 0.08, 0.2, 0.44 and 5.4). We added variable amounts of Si_3N_4 (a strongly reducing agent) to vary the oxygen fugacity among haplobasaltic glasses. Glasses were synthesized at 1.5 GPa and 1600°C for 4 hours in graphite capsules (to ensure reducing and graphite saturated conditions). Complementary to Raman, glasses were analyzed by secondary ion mass spectrometry (SIMS) to check the N content and $^{15}\text{N}/^{14}\text{N}$ molar ratios.

Raman spectra were acquired using the 457.9 nm (blue) excitation source with 13mW on samples, allowing us to detect CN, CO, CH_3 , CH_4 , NH_3 , NH_2 , OH and H_2 species in all glasses. We show that Raman spectroscopy has sufficient resolution to separate the ^{14}N -H vibration peaks from the ^{15}N -H peaks in NH_3 and NH_2 . At this stage, more data are being acquired to discuss the effect of the $f\text{O}_2$ and melt composition on the $^{15}\text{N}/^{14}\text{N}$ ratio between different N species.

Keywords: Nitrogen isotopes, Raman, reduced glasses