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

*Celia Dalou$^1$, Evelyb Füri$^1$, Marie-Camille Caumon$^2$, Mickael Laumonier$^3$

1. CRPG, UMR 7358, CNRS-UL, 15 rue Notre Dame des Pauvres, 54501 Vandœuvre-lès-Nancy, France, 2. Université de Lorraine, CNRS, CREGU, GeoRessources Laboratory, BP 70239, F-54506 Vandœuvre-lès-Nancy, France, 3. Laboratoire Magmas et Volcans, Université Blaise Pascal-CNRS-IRD, Clermont Universite, 63178 Aubière, France

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 $^{135}$N$_4$ and $^{134}$N$_4$ ($^{15}$N/$^{14}$N: 0.004, 0.08, 0.2, 0.44 and 5.4). We added variable amounts of $^{315}$N$_4$ (a strongly reducing agent) to vary the oxygen fugacity among haplobasaltic glasses. Glasses were synthetized 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 $^{15}$N/$^{14}$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 fO$_2$ and melt composition on the $^{15}$N/$^{14}$N ratio between different N species.

Keywords: Nitrogen isotopes, Raman, reduced glasses