Nitrogen speciation in silicate melts by nuclear magnetic resonance spectroscopy

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Nitrogen makes up 78% of the present-day atmosphere, but debate continues regarding how this reservoir has developed through time (i.e. through surface-interior tectonic fluxes) [1]. A key unknown is the high-temperature speciation—and thus the geochemical behaviour—of nitrogen in silicate mineral–melt–fluid systems.

Previous work has shown that nitrogen can be incorporated in silicate minerals and melts in a variety of forms, including physical dissolution of interstitial N_2 or NH_3, ions such as NH_4^+, NH_2^-, NH_2^+, NH^{2-} or CN^-, nitrosyl complexes and N^{3-} substituting for oxygen in oxides/silicates (or for carbon in diamond) [2]. These species have been identified from Fourier transform infrared (FTIR) and Raman spectroscopy, but in some cases the species assignments are ambiguous.

^{15}N nuclear magnetic resonance (NMR) spectroscopy can also be used to determine N speciation in glasses and minerals, but so far only a single study has used this technique [3]. NMR is a bulk technique, but has the advantage of being element-specific (i.e. no overlapping interferences), and NMR spectra are therefore easier to interpret than FTIR or Raman spectra.

We have applied solid-state ^{15}N NMR spectroscopy to ^{15}N-bearing $CaO–MgO–Al_2O_3–SiO_2$ glasses synthesised over a range of oxygen fugacities. We show that ^{15}N NMR can be used to identify the speciation of N in these glasses even at low concentrations (< 1 wt%). The spectra indicate the presence of N_2 at high oxygen fugacities and both N_2 and NH_4^+ at lower oxygen fugacities. We are continuing our experiments to constrain the ratio of molecular to ammonic nitrogen as a function of oxygen fugacity. These data are applied to understanding tectonic cycling of nitrogen between the mantle and the atmosphere over geological time.

References: [1] Zerkle & Mikhail, 2017. Geobiology 15, 343–352. [2] Mosenfelder, et al., 2019. Am. Mineral. 104, 31–46. [3] Roskosz et al., 2006. Geochim. Cosmochim. Acta 70, 2902–2918.