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Nitrogen incorporation in silicates and metals: Results from SIMS, EPMA, FTIR, and laser-extraction mass spectrometry

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Abstract

A quantitative understanding of nitrogen incorporation in Earth materials is important for constraining volatile evolution in planetary bodies. We used a combination of chemical (SIMS, EPMA, and laser-extraction mass spectrometry) and spectroscopic (FTIR) observations to study nitrogen contents and speciation mechanisms in silicate glasses, metal alloys, and an N-bearing silicate mineral (hyalophane). One suite of Fe-free basaltic glasses was studied by all four methods. Concentrations of N in these glasses determined by EPMA are systematically higher than those measured by laser extraction but agree within mutual 2*s* uncertainties, demonstrating the general veracity of the EPMA method. SIMS working curves based on measurement of $^{14}N^+$ and $^{14}N^{16}O^-$ as a function of N content determined by EPMA (or laser extraction) are best fit with exponential functions rather than the linear regressions that are most commonly applied to SIMS data. On the other hand, the relationship based on $^{12}C^{14}N^-$ for C-poor, Fe-free glasses is exceptionally well fit to a linear regression ($r^2 = 1$, $p < 0.001$), in contrast to expectations from previous work on glasses with lower N contents. Matrix effects on the SIMS signals associated with Fe or H_2O content are not justified by the data, but volatile data (both N and H) for hyalophane, which contains 20 wt% BaO, reveal matrix effects possibly induced by its high average molar mass. A combination of FTIR and chemical data, together with a thorough review of the literature, was used to determine incorporation mechanisms for N in the Fe-free glasses. We infer that under reducing conditions at high pressure and temperature N is dissolved in basaltic melts chiefly as NH_2^- and NH^{2-}, with N_2 and/or nitride (X-N^{3-}) complexes becoming increasingly important at low f_{O_2}, increasing N content, and decreasing H content. Our results have implications for future studies seeking to accurately measure N by SIMS and for studies of N partitioning at high pressure relevant to planetary accretion and differentiation.

Keywords: SIMS, nitrogen, speciation, FTIR, EPMA, bonding, carbon