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 2σ uncertainties, demonstrating the general veracity of the EPMA method. SIMS working curves based on measurement of 14N and 16O 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 12C14N for C-poor, Fe-free glasses is exceptionally well fit to a linear regression (r² = 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 H2O 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 NH3 and NH4+, with N2 and/or nitride (X-N3) complexes becoming increasingly important at low fO2, 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

INTRODUCTION

Recent experimental studies have shown that nitrogen can be a significant constituent in deep-seated silicate melts and minerals (Miyazaki et al. 2004; Roskosz et al. 2006, 2013; Watenphul et al. 2009, 2010; Yokochi et al. 2009; Kadik et al. 2011, 2013, 2015; Li et al. 2013, 2015, 2016b; Armstrong et al. 2015; Dalou et al. 2017a; Yoshioka et al. 2018), which has important consequences for planetary differentiation and subsequent evolution (e.g., Marty 2012; Johnson and Goldblatt 2015; Hirschmann 2016). This scientific advance raises the need to improve techniques for measuring N in geologic materials and to understand the mechanisms by which it is incorporated. Nitrogen can be difficult to quantify accurately—particularly at low concentration levels—with conventional, widely available microanalytical techniques such as electron probe microanalysis (EPMA) and secondary ion mass spectrometry (SIMS).

Measurement of nitrogen by EPMA has consistently been fraught with problems owing to its low fluorescence yield, resulting in low count rates and poor peak-to-background ratios (Bastin and Heijligers 1991; Raudsepp 1995). Furthermore, the curvature of the background on LDE monochromators as well as the presence of higher order metal interference lines can complicate analysis. Using a protocol that takes these factors into account, von der Handt and Dalou (2016; see also Dalou et al. 2017a and Supplementary Material) achieved a detection limit of 0.04 wt% N in silicate glasses. This method represents a significant improvement over previous studies using EPMA. For instance, Roskosz et al. (2013) reported a practical detection limit of 0.15 wt% N. Li et al. (2015) achieved a lower detection limit (~0.05 wt% N) using a calibration curve technique, but this approach is limited to simple systems because it does not explicitly take matrix corrections into account (as is normally done with major and minor element EPMA data).

For most elements, SIMS offers lower detection limits than EPMA. In the case of N, however, analysis is impeded by low