

Nitrogen and hydrogen isotope compositions and solubility in silicate melts in equilibrium with reduced (N+H)-bearing fluids at high pressure and temperature: Effects of melt structure

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ABSTRACT

Solubility and solution mechanism(s) of reduced (N+H)- and H-containing N-O-H volatile components in Na₂O-SiO₂ composition melts in equilibrium with NH₃+H₂+N₂ and H₂O+H₂ fluid and H- and N-isotope concentrations in these melts were determined experimentally at 1.5 GPa and 1400 °C as a function of hydrogen fugacity, f_{H_2} , and melt polymerization (composition), NBO/Si (NBO/Si = 0.4–1.18). This NBO/Si-range is similar to that between dacite and olivine tholeiite melt (NBO/Si ~0.4–1). The f_{H_2} was controlled between that of the iron-wüstite + H₂O [$\log f_{\text{H}_2}(\text{IW}) \sim 3.42$ (bar)] and that of the magnetite-hematite + H₂O [$\log f_{\text{H}_2}(\text{MH}) \sim -0.91$ (bar)] buffer.

The N solubility decreases from 0.98 to 0.28 wt% in the melt NBO/Si-range from 0.4 to 1.18 at $f_{\text{H}_2}(\text{IW})$ and decreases by about 50% between $f_{\text{H}_2}(\text{IW})$ and $f_{\text{H}_2}(\text{MH})$. The H solubility at $f_{\text{H}_2}(\text{IW})$ is insensitive to NBO/Si and averages 0.76±0.28 wt% and 0.48±0.07 wt% H in (N+H)-saturated and in N-free and H-saturated melts, respectively. The H solubility in the melts decreases by at least ~70% between $f_{\text{H}_2}(\text{IW})$ and $f_{\text{H}_2}(\text{MH})$. Their N and H isotope ratios are systematic functions of the abundance ratio of structurally bound N and H (as NH₂⁻ and OH⁻-groups bonded to Si⁴⁺) relative to molecular H₂, N₂, and NH₃ in the melts. Molecular H₂O plays a subordinate role in these melts, the bulk H₂O content of which is <5 wt%. The NH₂⁻/NH₃ and OH⁻/H₂ abundance ratios vary by ~55 and ~500% between NBO/Si = 1.18 and 0.4 relative to the values at NBO/Si = 0.4. In this same NH₂⁻/NH₃ abundance ratio range, the $\delta^{15}\text{N}$ of (N+H)-saturated melts, relative to that of melts with NBO/Si = 0.4, varies by ~2‰, whereas the δD varies by ~87‰. In N-free melts, the δD varies by ~12‰. Changing abundance of volatiles dissolved in silicate melts in molecular form and as structural complexes that form bonds with the silicate melt structure is an important factor that can affect stable isotope fractionation during melting and crystallization at high pressure and temperature.

Keywords: Melt structure, spectroscopy, nitrogen solubility, isotope fractionation, solution mechanisms