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AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†

Solubility and solution mechanisms of NOH volatiles in silicate melts at high pressure and temperature—amine groups and hydrogen fugacity

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ABSTRACT

The solubility and solution mechanisms of nitrogen in silicate melts have been examined via nitrogen analyses and vibrational spectroscopy (Raman and FTIR). Pressure (P), temperature (T), hydrogen fugacity (f_{H_2}), and silicate melt composition (degree of melt polymerization) were independent variables in experiments in the 1–2.5 GPa pressure and 1300–1500 °C temperature ranges. The f_{H_2} was controlled at values defined by the magnetite-hematite (MH), Mn_3O_4-MnO (MM), NiO-Ni (NNO), magnetite-wustite (MW), and iron-wustite (IW) buffers together with H_2O.

The nitrogen solubility ranges from about 1 to about 5 mol%, calculated as N, with $\partial X_N/\partial P > 0$ and $\partial X_N/\partial f_{H_2} > 0$. The $\partial/\partial f_{H_2}(\partial X_N/\partial P)$ is also positive. Raman and FTIR spectroscopic data are consistent with solution mechanisms that involve reduction of nitrogen with increasing f_{H_2}. At low f_{H_2} [f_{H_2}(MH) and f_{H_2}(MM)], nitrogen is dissolved in melts only as molecular N_2. At f_{H_2}(NNO) and f_{H_2}(MW), there is partial reduction of nitrogen to form N_2, NH_2^+ complexes and molecular NH_3 in the melts, whereas at the highest f_{H_2}(IW), only molecular NH_3 and NH_2^- groups can be identified. OH groups are also formed whenever there is reduction of nitrogen from N_2. Solution in silicate melts of reduced, NH-bearing species results in silicate melt depolymerization. At f_{H_2}(NNO) and f_{H_2}(MW), depolymerization occurs via H^+ interaction with oxygen and NH_2^+ groups serving as network-modifier. Under more reducing conditions, oxygen is replaced by NH_2^- groups. Solution of reduced nitrogen in silicate melts causes depolymerization of their structure. This implies that melt properties that depend on silicate structure depend on redox conditions.

Keywords: NOH volatiles, melt, structure, spectroscopy