

From N₂ to NH_x groups in silicate melts governed by f_{H2} at high pressure and temperature

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Characterization of the processes that govern the behavior and budget of volatiles in the Earth's interior is fundamental to our understanding of the formation and evolution of the solid Earth, its oceans, and atmosphere. To this end the behavior of volatiles in the NOH system in magmatic liquids is of central importance. The solubility and solution mechanisms of N-bearing species in silicate melts have been, therefore, examined via nitrogen analyses and vibrational spectroscopy with pressure (P=102.5 GPa), temperature (T=1300°-1500°C), hydrogen fugacity (f_{H2}=MH-IW+H₂O), and silicate melt composition as independent variables.

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. Two f_{H2} ranges are identified within which the solubility relations with f_{H2} differ. Under oxidizing conditions, the solubility can be fit to a straight line that passes through the origin (Henry's Law). However, at higher f_{H2} such linear extrapolation through the origin is not feasible.

Raman and FTIR spectroscopic data are consistent with solution mechanisms that involve gradual reduction of nitrogen with increasing f_{H2}. In the low f_{H2} range [near f_{H2}(MH) – Fe₂O₃/Fe₃O₄+H₂O] there is evidence only for molecular N₂ in the melts. At f_{H2}(NNO) (Ni/NiO+H₂O) and f_{H2}(MW) (FeO/Fe₃O₄+H₂O), there is partial reduction of nitrogen to form N₂, NH₂⁺ complexes and molecular NH₃ in the melts. At the highest f_{H2}(IW) (Fe/FeO+H₂O), only molecular NH₃ and NH₂⁻ groups can be identified in the melts. OH groups are also formed whenever there is reduction of nitrogen from N₂. Solution in silicate melts of reduced, (NH)-bearing species results in silicate melt depolymerization. At f_{H2}(NNO) and f_{H2}(MW), depolymerization occurs via H⁺ interaction with oxygen and NH₂⁺ groups serving as network-modifier. Under more reducing conditions, oxygen is replaced by NH₂⁻ groups.

Degassing models of the Earth depend rely on solubility and solution behavior of volatiles (including nitrogen) in magmatic liquids in the Earth's interior. The f_{H2}-dependent behavior of nitrogen species in melts implies the redox conditions in the Earth also affect these processes.

Excess interfacial force induced by oxide nanostructures on rhodochrosite

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Rhodochrosite (MnCO₃) is an important component of anoxic soils and sediments. At the oxic-anoxic interface, a rhodochrosite surface can be oxidized by dissolved oxygen and form oxide structures of a few nanometers high. The patchwork of exposed rhodochrosite surface and oxide nanostructures results in a map of surface-potential heterogeneity, as previously demonstrated, and suggests that differences in chemical composition and structure at nanoscale can induce dramatic local variations in surface properties and consequently remarkable local variations in the interaction with the surrounding environment. In aqueous solution, the interaction of a surface with ions, molecules, and cells is often manifested as the interfacial force between them, which strongly influence surface adsorption. Nanoscale heterogeneity of the interfacial force is therefore an important regulator of the immobilization of metal contaminants and bacterial attachment.

In this study, we map out the interfacial-force heterogeneity of reacted rhodochrosite to demonstrate that the formation of oxide nanostructures can potentially induce significant changes in surface adsorption in aqueous solution. Using a miniature probe to represent an adsorbate, the interfacial force over reacted rhodochrosite was characterized using force-volume microscopy.

The interfacial force of oxide nanostructures is dominated by electrostatic repulsion at probe-surface distances greater than ca. 2 nm and overtaken by van der Waals attraction at shorter distances. Across the investigated pH range of 5.0 to 9.7, the interfacial force of oxide nanostructures has a repulsive maximum that occur at a separation distance of 2.4(±1.1) nm. The pH dependence of nanostructure interfacial force indicates that oxide nanostructures have a point of zero charge around pH 6.5. In comparison to oxide nanostructures, the rhodochrosite substrate exerts little interfacial force to the probe in the same pH range, indicating that the substrate has minimal surface charge. Mapping interfacial-force heterogeneity provides a basis for more sophisticated and accurate modeling of processes affecting contaminant immobilization and bacterial attachment on mineral surfaces under natural conditions.