

Very large differences in intramolecular D-H partitioning in hydrated silicate melts synthesized at upper mantle pressures and temperatures

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ABSTRACT

Hydrated (with D₂O and H₂O) sodium tetrasilicate glasses, quenched from melts at 1400 °C and 1.5 GPa, are studied using ¹H, ²H, and ²⁹Si solid-state nuclear magnetic resonance (NMR) spectroscopy. Whereas D₂O and H₂O depolymerize the silicate melt to similar degrees, protium and deuterium intramolecular partitioning between different molecular sites within the glasses is very different and exemplified by a strong preferential association of deuterons to sites with short O-D···O distances. This preference is independent of total water content and D/H ratio. Substantially different intramolecular D-H partitioning is also observed in a glass with a model hydrous basalt composition. Such large differences in isotope partitioning cannot result from classic equilibrium fractionation because of the high synthesis temperature. Potential kinetic isotope effects are excluded via a slow quench experiment. The apparent fractionation is likely governed by density/molar volume isotope effects, where deuterium prefers sites with smaller molar volume. Large differences in intramolecular site partitioning in melts could lead to significant differences in D-H partitioning between water-saturated melt and exsolved aqueous fluid (where $D/H_{W,Melt} \neq D/H_{W,Fluid}$) during crystallization of Earth's magma ocean, potentially controlling the D/H content of the Earth's oceans.

Keywords: Hydrogen isotopes, silicate melts, fractionation