

Very Large Intramolecular D-H Partitioning in Hydrated Silicate Melts Synthesized at Upper Mantle P and T

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Hydrogen isotope fractionation during magmatic processes is key to understanding the deep Earth hydrological cycle and may place constraints on the origin of Earth's oceans. It is well established that the D/H content of water in hydrated nominally anhydrous mantle minerals is systematically lower ($< -100\text{‰}$) than the standard mean ocean water (SMOW, $D/H = 1.5576 \times 10^{-4}$, defined as 0‰). Experiments have revealed significant hydrogen isotope partitioning between melts and fluids or vapors at magmatic temperatures. The origin of such fractionation, given the high temperatures of magmatic processes, is not likely due to classical isotope effects as described by bond energies via statistical mechanics.

It is well known that water has a very high affinity for silicate melts, it both dissolves in the melt as molecular water and hydrolyzes Si-O-Si linkages forming Si-OH. Whereas the molecular forms of water in melts are limited to H_2O and OH, the variety of environments available for water to reside in the melt structure is surprising large. In order to study water in silicate melts one is restricted to molecular spectroscopy, e.g. Raman spectroscopy in the mid infrared regime, in windowed high pressure devices, e.g. the hydrothermal diamond anvil cell. Alternatively, one can study melts quenched to glass, where the structure of the glass corresponds to the structure of the melt at the glass transition temperature. The advantage of glasses is that one can use Solid State Nuclear Magnetic Resonance (NMR) Spectroscopy. The hydrogen isotopes conveniently provide two stable nuclei with spin, 1H (H) and 2H (D), thus we can use D and H solid state NMR to analyze the nature of water in silicate melts quenched to glass. Given that glass transition temperatures for silicate melts are high ($500\text{--}600\text{°C}$), one does not expect H and D to behave differently. D-NMR can, however, be useful in characterizing the molecular dynamics of water in various sites in the glass.

We studied hydrated (with D_2O and H_2O) sodium tetrasilicate glasses, quenched from melts at 1400°C and 1.5 GPa , using 1H , 2H and ^{29}Si solid state NMR. Whereas D_2O and H_2O depolymerize the silicate melt to similar degrees, as would be expected, we surprisingly find that protium (H) and deuterium (D) intramolecular partitioning between different molecular sites within the glasses is very large and controlled 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. Substantial intramolecular D-H partitioning is also observed in a glass with a model hydrous basalt composition. Such large isotope partitioning cannot result from classic fractionation effects because of the high synthesis temperatures. Potential kinetic isotope effects are excluded via a slow quench experiment. The partitioning is likely governed by density/molar volume isotope effects, where deuterium prefers sites with smaller molar volume. Large intramolecular site partitioning in melts could lead to significant 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: Silicate Melt, D-H fractionation, NMR, Magma Ocean