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/Hw,Melt ≠ D/Hw,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

INTRODUCTION

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‰) than the standard mean ocean water (SMOW, D/H = 1.5576 × 10–4, defined as 0‰) (Bell and Ihinger 2000). Experiments have revealed significant hydrogen isotope partitioning between melts and fluids or vapors at magmatic temperatures (e.g., Kuroda et al. 1982; Richet et al. 1986; Dobson et al. 1989; Pineau et al. 1998; Mysen 2013). The origin of such fractionation, given the high temperatures of magmatic processes, is not likely due to equilibrium isotope effects as described by statistical mechanics (Urey 1947; Bigeleisen and Mayer 1947).

Near infrared (NIR) spectroscopy reveals that water exists in quenched melts as hydroxyl (silanol) and molecular water (Stolper 1982); where the proportion of these species is a function of water concentration and temperature (Nowak and Behrens 1995). The possibility that fractionation of hydrogen isotopes exists between silanol and molecular water within melts has been considered (Dobson et al. 1989). Whereas NIR spectroscopy reveals distinct bands for silanol and molecular water, the primary O-H vibrational structure in the mid-infrared region cannot distinguish these primary species (Zotov and Keppler 1998). What is observed in the mid-infrared region with hydrous glasses at room temperature is very complex vibrational structure spanning a very wide frequency range. Interestingly, a FTIR study comparing primary O-H and O-D vibrational structure in a hydrated (with H2O and D2O) sodium tetrasilicate glasses, does suggest differences in the intensities of various OH and OD vibrational modes (Zotov and Keppler 1998), possibly indicating differences in intramolecular D-H partitioning between different molecular sites within the hydrated silicate glass. However, in the study of Zotov and Keppler (1998) the deuterated and hydrated glasses were separately prepared samples, thus the apparent differences in vibrational intensities across the mid-infrared could be attributed to slight differences in water composition or synthesis conditions across the two samples.

Solid-state 1H nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for the study of water in hydrous silicate glasses quenched from melts. Previous studies have shown that water resides in wide range of molecular environments within glasses formed in this manner (e.g., Eckert et al. 1987, 1988; Kohn et al. 1989; Schaller and Sebald 1995; Cody et al. 2005; Xue and Kanzaki 2009). The 1H solid-state NMR spectrum of silanol and water in hydrous glasses is understood to be predominantly controlled by O-H···O distance (Eckert et al. 1988; Xue and Kanzaki 2001). Similar to mid-IR vibrational spectroscopy, 1H solid-state NMR cannot readily distinguish between silanol and molecular water, i.e., hydrogen’s chemical shift is unaffected by whether the oxygen it is bonded to is water or a siloxy group.

Solid-state NMR does have the advantage that it is an isotope specific emission spectroscopy, therefore, signal interference between different isotopes is very rarely a problem and one can investigate mixed isotopic systems without interference. In the present study 1H, 2H, and 29Si solid-state nuclear magnetic