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

[Revision 1]

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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

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, $D/H = 1.5576 \times 10^{-4}$, 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; Dobsen 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 (Dobsen 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 between 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 H$_2$O and D$_2$O) 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 $^1$H 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 $^1$H solid state NMR
The 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, $^1$H 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 $^1$H, $^2$H and $^{29}$Si solid-state Nuclear Magnetic Resonance (NMR) spectroscopy was performed on hydrated sodium tretrasilicate glasses quenched from melt, at various water contents and variable D/H content. $^1$H and $^2$H solid state NMR were also performed on a hydrous glass with a model basalt composition. We show that large differences in intramolecular H-D partitioning are evident in all of the glasses studied.

Methods and Analytical Techniques

Sample preparation

This study employed two types of glasses: a hydrated sodium tetrasilicate (Na$_2$O·4SiO$_2$, hereafter referred to as NS4) glass, which is a classic model system investigated by multiple techniques (e.g. Schaller and Sebald 1995; Kummerlin et al 1992; Zotov and Keppler, 1998) and a synthetic, iron-free, hydrated glass of basalt-like composition (10CaO·20MgO·5Na$_2$O·15Al$_2$O$_3$·50SiO$_2$, hereafter referred to as CMNAS). The starting dry NS4 glass was made by mixing spectroscopically pure Na$_2$CO$_3$ and SiO$_2$, ground under alcohol for ~ 1 h, and then decarbonated during slow heating.
(-1.5°C/min). The resultant mixture was melted at ambient pressure in a Deltech furnace in open Pt crucibles at 1500°C for 60 min and then quenched to glass. The dry CMNAS glass was similarly synthesized with a melting temperature of 1400°C. These anhydrous starting glasses were crushed to $\geq 20 \, \mu m$ grains and stored at 110°C when not used.

To prepare for the synthesis of hydrous glasses, pure D$_2$O (99.5%) was mixed with isotopically unlabeled distilled deionized water at desired ratios to produce a series of solutions with D abundance varying from 0 to 100% (Table 1). Water was injected into Pt capsules, approximately 5 mm O.D. $\times$ 10 mm long, using a 10-μL microsyringe. The anhydrous glasses were then added to the same Pt capsules which were welded shut using a tungsten inert gas high frequency pulsed arc welder (Lampert PUK 3S). The use of a pulsed arc welder greatly reduces the heating and potential for water loss during welding. The exact amount of H$_2$O added was determined by weight. The average total sample mass (water + anhydrous glass) was around ~ 200 mg. The weighing accuracy was ± 0.02 mg, which gives accuracy $< \pm 0.1\%$ in the reported water contents. Table 1 summarizes the water content and hydrogen isotopic composition of all the glasses synthesized in this study.

The sealed Pt capsules containing the starting glass and water were loaded in 0.75-diameter furnace assemblies and then subjected to high-pressure (1.5 GPa) and high-temperature (1400°C) experiments in a solid-media, high-pressure apparatus. Temperatures were measured with Pt-Pt$_{90}$Rh$_{10}$ thermocouples. The estimated uncertainties are ±10°C and ± 0.1 GPa, respectively. The experimental temperature was programmed to initially rise from room temperature to 1400 °C at 300 °C /sec. The duration of each run was 3+ hrs, followed by quenching to glass at a rate of 100°C/s.
In order to test for potential kinetic isotope effects, one sample was also subjected to prolonged heating at 1.5 GPa for 48 hours to test for the attainment of D-H equilibrium (Table 1). This run was then quenched slowly at 1 °C/min in order to see whether H and D partitioning changed relative to the standard experiment, as a test for potential mass-derived kinetic isotope effects that might occur during any re-equilibration upon cooling to the glass transition temperature (see discussion in section 3.3). For comparison with hydrogen speciation in various glasses and minerals, we also prepared two hydrous SiO₂ glasses containing either 14 mol% H₂O or D₂O for ¹H and ²H NMR analysis. Also included for comparison is a sample of natural gypsum (CaSO₄•2H₂O).

²⁹Si, ¹H, and ²H solid state NMR spectroscopy

NMR experiments were performed with a Varian-Chemagnetics Infinity 300 solid-state NMR spectrometer with a static field of ~7.05 T. The resonance frequencies of ¹H, ²H, and ²⁹Si nuclei are 300, 46, and 59 mHz, respectively. ¹H and ²⁹Si spectra were referenced to tetramethylsilane (TMS), while ²H spectra were referenced to perdeuterated-tetramethylsilane (TMS-²H₁₂, 99%, from C/D/N Isotopes).

The ¹H NMR spectra were obtained by ¹H single-pulse magic-angle-spinning (MAS) experiments employing a 2.5 mm rotor and fast MAS probe with spinning frequency (ω₀/2π) of 22 kHz. The DEPTH four pulse sequence was employed to suppress background ¹H signal where phase cycling (n=16) removes any signal from background protons (outside the RF coil) that experience a nutation angle of less than 45 °. The acquisition parameters include a ¹H 90° RF pulse length of 3 μs, a recycle delay
of 100 s (the spin-lattice relaxation time, $T_1$, for $^1$H in these glasses was determined by experiment to be 20 s) and a spectral width of 200 kHz. A total of 1600 acquisitions were acquired per sample.

The $^2$H NMR spectra were obtained by $^2$H single pulse experiments at MAS frequency of 8 kHz (controlled to $\pm$ 1 Hz). The $^2$H excitation pulse width was 1.5 $\mu$s ($\omega_1/2\pi = 55.5$ kHz) corresponding to a 30 °C nutation angle. Spinning at this rate is sufficient to induce complete homonuclear decoupling and significantly average out much of the $^1$H-$^2$H coupling. In order to ensure complete $^1$H-$^2$H decoupling, high power $^1$H decoupling was performed during signal acquisition with $\omega_1/2\pi = 62.5$ KHz. A pulse delay of 10 s was employed to minimize interference due to longitudinal (spin-lattice) relaxation effects [previous estimates of $^2$H’s $T_1$ in silicate glasses was less than 1 s (Ekert et al. 1987)]. A total of 16000 acquisitions were acquired per sample.

$^2$H is a spin-1 quadrupole and static NMR spectra of $^2$H in a rigid solid yields a classic Pake powder pattern spectrum spanning a spectral width that is dependent on the strength of the quadrupolar interaction, in some cases in excess of 200 kHz for $^2$H in rigid environments (Eckert et al. 1987). Under fast MAS rotation the quadrupolar powder pattern is defined by multiple spinning sidebands that spread out over the frequency range of quadrupole interaction. While it is possible to fit all of the sidebands in order to obtain the site specific powder patterns to quantify the standard $^2$H MAS NMR spectra, an alternative approach provides purely isotropic $^2$H MAS NMR spectra that are more directly comparable to $^1$H MAS NMR spectra. Isotropic spectra were obtained by rotor synchronized acquisition, where the spectral width is exactly equal to the MAS frequency (8 KHz $\pm$ 1 Hz), thus the dwell is equal to the rotor period.
The receiver bandwidth was set at 600 KHz, thus all of the sidebands detected outside of the spectral window are perfectly aliased into the central band, greatly increasing the signal-to-noise ratio and yielding a purely isotropic spectrum (see for example Eckman, 1982; Ashbrook and Wimperis, 2005).

Given that the $^2$H quadrupolar interaction may be 200 kHz or larger and given that the maximum power of the RF pulse is 55.5 kHz suggests that off resonance effects may be expected (Ernst et al. 1991). In the case where $^2$H in different environments have significantly different quadrupolar interaction strengths, $^2$H with larger quadrupolar interactions could have suppressed signal intensity in the rotationally resonant isotropic spectrum (Eckman, 1982). Consideration of the potential of such artifacts are addressed in the discussion below. In one case, wide line $^2$H MAS NMR was acquired, where the spectral width was 600 kHz and the nutation time was 500 ns to minimize off resonance effects.

Single pulse $^{29}$Si NMR spectra were obtained with MAS frequency of 8 kHz, $^{29}$Si pulse widths corresponding to 30° tip angles, a recycle delay of 100 s, and co-addition of 1000 acquisitions. Proton decoupling was performed with continuous RF irradiation at 62.5 kHz. More details on the $^{29}$Si Single pulse NMR experiments can be found in (Cody et al., 2005).

Results

$^{29}$Si MAS NMR of hydrous (H$_2$O and D$_2$O) Sodium tetrasilicate glasses
Chemically, D₂O and H₂O are expected to interact with the sodium silicate melt similarly, i.e., both D₂O and H₂O should depolymerize the silicate network to essentially the same extent. This is confirmed with $^{29}$Si solid state NMR of sodium silicate glass with 9 wt % water (Fig. 1), from which it is determined that hydrogen exists nearly equally as (H,D)$_2$O and as silanol OH,D independent of the D-H content of water. The only means for determining the proportion of Si-OH and H₂O in NS4 glass quenched from melt via NMR is through the determination of the proportion of Q species via $^{29}$Si NMR. Individual Q⁰ species Q⁴-⁰ in simple sodium tetrasilicate glasses are resolvable using $^{29}$Si NMR (Maekawa et al. 1991, Kümerlin et al. 1992, Zotov and Keppler 1998, Cody et al. 2005). Compositionaly, Q⁴ = SiO₂, Q³ = NaSiO₂.₅, and anhydrous NS4 glass = Na₀.₅SiO₂.₂₅; therefore, NS4 glass is expected to be composed of equal concentrations of Q⁴ and Q³, with the number of non-bridging oxygens per tetrahedron (NBO/T) being 0.5. The accuracy of determination of the proportion of Q species is clearly subject to the choice of fitting parameters, i.e., peak shape characteristics (Zotov and Keppler, 1998). In the present case the $^{29}$Si spectra were fit with purely Gaussian bands with fixed peak widths where Q⁴ is centered at -103 ppm, Q³ at -95 ppm, and Q² at -90 ppm. The resulting percentages of Q⁴, Q³, and Q² are presented in Table 2. Whereas anhydrous NS4 glass has an NBO/T of 0.5, NS4 glass with 9 wt % water in the form of H₂O, D₂O or mixed H₂O-D₂O has an NBO/T of 0.88-0.92 that is expectedly independent of the D-H composition of the water. The increase in NBO/T with water addition reflects the additional depolymerization of the silicate oxide network by water, where Na₂O is expected to act only as a depolymerizing agent, and the speciation of water between Si-OH and H₂O is readily attained (Table 2). This degree of depolymerization
is in accord with other data at this water content (Stolper, 1982, Zotov and Keppler, 1998); where differences are ascribed to the approach to fitting (Kümmerlen et al. 1992; Zotov and Keppler 1998; Cody et al. 2005).

1H and 2H MAS NMR of hydrous sodium tetrasilicate glasses

The 1H MAS NMR spectrum of sodium tetrasilicate glass (NS4) is complex (Fig. 1, center), spanning a wide range of frequencies, but with intensity concentrated in a low to intermediate-frequency band spanning from 0 up to 7 ppm and an asymmetric high-frequency band extending out to 16 ppm. These bands are clearly composite bands of numerous overlapping resonances based on their asymmetric peak shapes. For comparison, 1H NMR of CaSO₄•2H₂O (gypsum) and water containing SiO₂ glass, quenched from melt are also shown. The molecular H₂O in gypsum gives rise to a broad symmetric resonance at 5.5 ppm, whereas hydrated SiO₂ melt quenched to glass exhibits a sharp resonance nearly coincident with a broader peak, at 4.9 and 5.6 ppm, respectively. Focusing on the hydrous NS4 glass (Fig. 1, center), the high-frequency 1H resonance band at 16 ppm corresponds to a particularly short O-H•••O distances (Eckert et al. 1988, Xue and Kanzaki 2001). The low to intermediate frequency resonance band at ~ 5 ppm corresponds to water and silanol residing in sites with longer O-H•••O distances (Fig. 1, center). Evidently one result of network depolymerization upon Na₂O addition to SiO₂ is the creation of sites for OH and H₂O with short O-H•••O distances.

The isotropic 2H solid state NMR spectra is expected to be very similar to that of the 1H solid state NMR spectra. Thus, in the case of 2H in hydrated NS4 glass (Fig. 1,
right) we observe resonance intensity spanning a wide frequency range, concentrated in low and high frequency resonance bands as is observed in the $^1$H NMR spectra of hydrated NS4 (Fig. 1, center). What is immediately obvious is that the spectral intensity distribution in the $^1$H and $^2$H spectra of the hydrated NS4 glasses is very different. Deuterium ($^2$H) preferentially resides in high spectral frequency sites with short O-D•••O distances, whereas hydrogen ($^1$H) populates the intermediate and high frequency regions of the spectrum nearly equally (Fig 1, center). In comparison, in the case of a pure SiO$_2$ melt with D$_2$O, quenched to glass, the $^2$H NMR spectrum extends only to the intermediate frequency resonance bands, similar to the $^1$H NMR spectrum of SiO$_2$ glass with H$_2$O.

This very large difference in intensity between $^1$H and $^2$H NMR spectra in the high and medium frequency sites was not expected. A valid concern is that the difference in intensity may result from an artifact related to the deuteron’s quadrupolar interaction influencing the rotor synchronized isotropic $^2$H spectra. In general, an ideal NMR experiment employs RF excitation pulse strength greater than any of the internal NMR interactions, e.g., the chemical shielding interaction. In the case of deuterium solid state NMR, whereas the chemical shielding interaction is relatively weak, the quadrupolar interaction is not inconsequential and is typically larger than available RF pulse power. In cases where the NMR spectrum is wider than the available RF power, off resonance effects at some level are inevitable (Ernst et al. 1991) leading to phase and amplitude errors particularly with long pulse widths (e.g. 90° pulses with typical RF pulse power).
It is well established that $^1$H NMR frequency correlates with O-H•••O length (Eckert et al. 1988, Xue and Kanzaki 2001). There is also a strong correlation between O-D•••O length and the $^2$H quadrupolar coupling constant, $C_q$, for that site (Ekert et al. 1987). Thus, one can correlate $^1$H NMR frequency for a given site to $^2$H’s $C_q$. For the high frequency $^1$H peak at 16 ppm (Fig. 1) one predicts a $^2$H $C_q$ of 113 KHz and for the intermediate frequency peak at 5 ppm one predicts a $^2$H $C_q$ of 240 KHz (Eckert et al. 1987). Note that these predictions assume that the deuterium atom is immobile, however, Eckert et al. (1987) showed in their study of hydrated rhyolite glass that many deuterons are partially mobile at room temperature, where motion of the deuteron has a short correlation time ($\tau_c^{-1} > C_q$). Such motion strongly effects the $^2$H NMR spectrum by greatly reducing the spectral width (Schmidt-Rohr and Speiss, 1994). As will be shown below, non rigid deuterons are also present in these hydrated NS4 glasses.

The worse case scenario associated with off resonance effects would be spectral distortion in the isotropic $^2$H NMR spectrum assuming rigid deuterons with $C_q$’s of 113 and 240 KHz, corresponding to the 16 and 5 ppm sites, respectively. The net effect could be to potentially lose intensity at the 5 ppm site in the $^2$H NMR spectrum relative to that in the $^1$H NMR spectrum (fig. 1). The magnitude of this off resonance distortion will increase with excitation pulse width (Ernst et al. 1991). In the present experiments a pulse width of 1.5 µs, corresponding to 30 ° pulse, was employed. Such a short pulse width will help minimize off resonance distortion between $^2$H sites with significantly different $C_q$’s. In order to determine the magnitude, if any, of spectral distortion, assuming this worse case scenario, rotor synchronized $^2$H MAS NMR was simulated numerically using the SIMPSON code (Bak et al. 2000) with the experimental
parameters outlined in the methods section. These calculations reveal that off resonance effects can result in the large C_q site (low frequency) exhibiting a reduction in intensity of 8% relative to the low C_q site (high frequency). Therefore, this worse case scenario involving off resonance effects is not sufficient to explain the very large observed differences in spectral intensity distribution between ^1H and ^2H in hydrated NS4 glasses (Fig 1).

Having established that the large differences in intramolecular D-H partitioning are real, hydrated NS4 glasses were synthesized from melts equilibrated with 3, 6, and 9 wt % water with pure H_2O, D_2O and mixed D-H water. From near IR studies (e.g. Stolper 1982; Nowak and Behrens 1995; Zotov and Keppler 1998) it is expected that at 3 wt % water content the dominant species is silanol (Si-OH,D), whereas at 6 wt % water, silanol and molecular water are near equal in abundance, and at 9 wt % molecular water is expected to be predominant. It is clear in Figs 2-4, that there are no systematic spectral trends attributable to water or D-H content. This means that whether hydrogen species are predominantly Si-OH (at 3 wt %) or majority H_2O (at 9 wt %) such speciation is not obvious in either the ^1H and ^2H MAS NMR spectra and the site affinity difference exhibited by D and H is independent of water content and D-H content. Recall that the H or D NMR frequency is not sensitive to whether either isotope is bonded to Si-OX or X_2O (X= H or D), but is sensitive to O-H•••O distance (Eckert at al. 1988, Xue and Kanzaki 2001).

In order to quantify a site affinity ratio for D and H in different regions of the ^1H and ^2H MAS NMR spectra, the relevant spectral regions need to be integrated. It is obvious from the line shapes in the ^1H and ^2H MAS NMR spectra that if one chose to fit
either spectra with Gaussian, Lorenztian, or mixed Gaussian/Lorenztian, many overlapping peaks would be required with minimal constraint on peak shape characteristics. As the point of this analysis is purely to see whether there was any trend in the partitioning ratio for D-H in between the high frequency and low frequency regions of the spectrum we chose to define the low frequency domain as the spectral area spanning from -30 ppm to 7.3 ppm (for $^2$H MAS NMR) and -15 to 10 ppm (for $^1$H MAS NMR) and the high frequency domain spanning the area from 7.3 ppm up to 40 ppm (for $^2$H MAS NMR) and 10 to 30 ppm ($^1$H MAS NMR). The small differences in frequency ranges reflect the more Lorenztian shape of the $^2$H NMR spectrum and the observation that the $^2$H NMR spectrum is consistently shifted by ~ 2 ppm to lower frequency, relative to the $^1$H NMR spectrum.

The integrated $^1$H and $^2$H NMR spectra allow quantification of the percentage of H or D residing in low and high frequency regions of the spectra, as is presented as histograms in Figure 5. While there is some variation in speciation amongst various environments exhibited by both protium and deuterium, there is no correlation with water abundance. Furthermore, the environmental partitioning of deuterons and protons within the quenched melts is independent of D/H ratio and water content.

The site affinities of deuterons and protons for the different environments responsible for the high and low frequency resonances may be quantified through a D-H partitioning factor, R, defined as $R = (D/H)_{HF}/(D/H)_{LF}$, where “HF” is the ratio of $^2$H signal intensity in the high frequency region of the spectrum relative to $^1$H and where “LF” is the ratio of intensity of $^2$H intensity in the low to middle frequency region of the spectrum relative to $^1$H. R, so defined, is determined to be very large with an average of
3.1 (± 0.5) reflecting the strong association of deuterium to sites with short O-D•••O distances in the silicate melt (fig. 5). There is no correlation between R and the water or D-H content of the glass.

Testing for kinetic isotope effects during quenching

The structure of these glasses is that of their melt at the glass transition where the glass transition temperature is on the order of 550 to 600 °C (Mysen and Richet 2005). It is known that the speciation of Si-OH and H₂O are dependent on water content (Stolper, 1982; Zotov and Keppler, 1998) and temperature (Nowak and Behrens, 1995). Although no evidence was found for water speciation affecting the affinity ratio (Figs 2-5), there remains the possibility that kinetic isotope effects during quenching may result in the observed differential partitioning. During a typical experiment, run times were on the order of 3 hours and the quench rate following the run was 100 °C/second. As the glass transition of hydrous NS4 melt (quenched at these rates) is on the order of 500 to 600 °C, 8 to 9 seconds are available for kinetic isotope effects to potentially arise from mass differences in isotope diffusion rates.

For example, if at high temperatures, both H and D equally favor the high frequency sites (shorter O-H•••O distance) but at lower temperatures favored environments with longer O-H•••O distances, then if H diffusion rates were greater than D, then it is possible that the apparent partitioning observed in Figs 1-5 could be due to a kinetic isotope effect. To test this possibility a run was performed where the melt was held at 1400 °C and 1.5 GPa for 48 hours and then quenched at a rate of 1 °C/second.
(providing ca. 800 seconds for any site exchange that might occur during cooling). No change in the observed intramolecular H-D partitioning was observed (Fig. 6) relative to the fast quench samples (Fig 1-4). Integration of the $^1$H and $^2$H MAS NMR spectra from the slow quenched sample yielded an $R$ of 3.1 (consistent with the fast quench samples, Fig. 5). This experiment indicates that the very large intramolecular partitioning observed with hydrated NS4 glass quenched from melts is not due to a kinetic isotope effect associated with quench rate.

Wide line $^2$H NMR of hydrated NS4 glass: insight from quadrupolar powder patterns

Whereas the rotor synchronized $^2$H MAS NMR spectra provide isotropic spectra directly comparable to $^1$H MAS NMR spectra, information derived from the quadrupolar interaction is lost. Acquisition of the wide line $^2$H MAS NMR spectrum (spectral width 600 kHz at 8 kHz MAS) reveals a broad spectrum spanning just over 200 kHz composed of 30 peaks that are spinning sidebands derived by the quadrupolar interaction, where the intensity of the sidebands trace out the static quadrupolar line shape. In Fig. 7 A & B the center band (Fig. 7A) and the most intense high frequency echo (Fig. 7B) are extracted from the wide line $^2$H NMR spectrum and presented separately. In the center band (Fig. 7A) one clearly observes a high (H), middle (M), and low (L) frequency peaks at 13, 3, and 0 ppm. In the high frequency side band (Fig. 7B) one observes the prominent high frequency peak with significantly diminished intensity for the middle and low frequency peaks. The quadrupolar line shapes are obtained by plotting the
intensities of the H, M, and L peaks for each side band (Fig. 7C). There are two important pieces of information in Fig. 7C. First, the total area of the high frequency peak is far greater than that of the middle and low frequency peaks, further confirming what is observed in the rotor synchronized isotropic $^2$H NMR spectra. Second, in the case of the high frequency peak (H) one observes a classic, albeit broadened, double peaked Pake powder pattern (Fig. 7C) consistent with deuterium in a rigid environment. The frequency spread between the pair of peaks is indicative of a $C_q$ of ca. 110 KHz. This magnitude of $C_q$ is consistent with an immobile deuteron in a site with an O-D•••O distance that would yield a corresponding $^1$H NMR frequency of ca. 16 ppm (Eckert et al. 1987, Eckert et al. 1988, Xue and Kanzaki 2001). In the case of the middle and low frequency peaks, however, one observes a very different quadrupolar line shape, each with a single maxima centered near 0 frequency. Such line shapes are typical of partial motional (dynamical) averaging of the $^2$H quadrupolar interaction, e.g., through O-D wagging or flipping motion (Eckert et al. 1987, Schmidt-Rohr and Speiss 1994). Such motional averaging leads to considerable reduction in the $^2$H spectral width and greatly reduces concerns of off-resonance effects, i.e., where as the worse case scenario predicts a potential 8 % intensity artifact (see discussion above) assuming rigid deuterons, the observation that the deuterons in the low frequency sites are not rigid further reduces any potential artifact related to off-resonance effects.

$^1$H and $^2$H MAS NMR of model basalt composition glass
The large intramolecular partitioning of H and D is readily observed in Figs 1-6 because of the relatively simple structure of NS4 glass. An important question is whether intramolecular hydrogen isotope partitioning would also occur in glasses and melts with more geochemically relevant compositions. To test this, a quenched silicate melt designed to model basaltic melt composed of Ca, Na, Mg, Al, Si oxides (CNMAS) was synthesized with 6 wt % water D:H 1:1. The $^1$H and $^2$H solid state NMR spectra of the CNMAS glass quenched from melt are presented (overlayed) in fig. 8. Significant differences in deuteron and proton speciation are evident. There is much more electronic diversity in the CNMAS glass compared with the NS4 glass leading to a more complex NMR spectrum. Notwithstanding the resulting increased spectral complexity, the $^1$H and $^2$H NMR spectra are quite different indicating preferential affinity of deuterons and protons for different molecular sites within the hydrous model basalt structure of the CNMAS glass. As in the case of the simpler hydrated NS4 glass, $^2$H prefers sites with shorter O-D•••O distances, hence higher NMR frequency.

Discussion

Given that these glasses are synthesized and quenched at such high temperatures classical equilibrium fractionation, i.e., due to differences in zero-point energies (Bigeleisen and Mayer 1947; Urey 1947), is not expected. A lack of any spectroscopic evidence of broadening of OH stretching vibrations at 500 to 600 °C would appear to rule out isotope fractionation associated with hydrogen bonding effects (Mysen 2010).
The fact that $^2$H prefers sites with shorter O-D•••O distances suggests deuterium favors sites with small molar volume and the observed large intramolecular partitioning is likely derived from density or molar volume isotope effects (e.g. Driessner 1997; Horita et al. 2002; Polyakov et al. 2006). Molar volume isotope effects (MVIE) have been invoked to explain a pressure-dependence of isotopic fractionation between water and Mg(OH)$_2$, attributed to differences in the molar volume of D$_2$O and H$_2$O (Horita et al. 2002). Also, recent high pressure neutron diffraction experiments on Mg(OD)$_2$ indicate greater compressibility than Mg(OH)$_2$ (Horita et al. 2010). For supercritical fluids at elevated pressures, theoretical calculations and experimental studies have supported the significant effect of D$_2$O and H$_2$O molar volume differences on isotope exchange reactions between D-H bearing dissolved volatiles (Polyakov et al. 2006; Foustoukos and Mysen 2012, 2013).

Molar volume isotope effects have been identified in aqueous ionic solutions containing sodium acetate and sodium hydroxide, where at elevated temperatures and pressures (up to the critical point of aqueous solutions) the Na$^+$ solvation volume with D$_2$O differs significantly than that with H$_2$O (Tevani et al. 2007; Erikson et al. 2011). In NS4 glasses, the extent to which water and Si-OH solvate Na$^+$ is equivocal (Zotov et al. 1996). Solvation isotope effects in aqueous solutions are predicted to diminish as temperature increases (Driesner and Seward 2000). How increased pressure might change such effects is not known.

The NS4 glasses in the present study were synthesized from silicate melts at 1400 °C and 1.5 GPa (corresponding to a depth of 50 km). The partial molar volume of water in quenched silicate melts is low, ca. 12 cm$^3$/mol (Richet et al. 2000). This is far
denser than pure water at the same conditions, suggesting that partial molar volume isotope effects may be expected (Driessner 1997; Horita et al. 2002; Palyakov et al. 2006). The O-H•••O distances for the high frequency and low frequency sites correspond to 2.47 Å and 2.9 Å, respectively (Eckert et al. 1988, Xue and Kanzaki 2001); in terms of molar volume this could imply that the high frequency site has a molar volume that is 60% that of the low frequency site. This is consistent with deuterons in the high frequency site being rigid (immobile), whereas the deuterons in the low to medium frequency sites are at least partially mobile (Fig. 7). Such a large molar volume difference evidently has a strong influence on the affinity of H and D for different sites within NS4 melt quenched to glass (Fig. 1-8).

Implications

The fact that deuterons and protons have different affinities for different molecular sites in glasses and presumably melts based on molar volume differences potentially has important implications for understanding Earth’s deep hydrological cycle as well as the D/H composition of Earth’s first oceans and mantle. For example, during the magma ocean phase of Earth’s earliest history, shortly after accretion and, again, following the moon forming impact, much if not all of the Earth was molten. Devolatilization during crystallization of the magma ocean might have contributed the water from which Earth’s oceans ultimately formed (Drake and Righter 2002). Although the solubility of water in silicate melts at high pressure is relatively high (Richet et al. 2000), eventually during crystallization the water content will saturate the melt leading to exsolution of a silica saturated aqueous phase coexisting with the water-saturated
melt. Neither the cation-silicate ratio or NBO/T of silicate is expected to be the same for co-existing melt and silica saturated aqueous fluid (Mysen 2010, 2013), therefore significant D-H isotope partitioning between melt and aqueous fluid could be expected. Furthermore, it has been noted that complete extraction of volatiles from melt from a deep magma ocean even under moderate extents of crystallization becomes physically difficult and perhaps impossible (Elkins-Tanton 2011); implying that some water must have been retained in the mantle even after degassing that may have formed the Earth’s oceans.

In model hydrated NS4 melts saturated with water is has been shown that \( \frac{D}{H}_{\text{Water-Melt}} \neq \frac{D}{H}_{\text{Water-fluid}} \) (Mysen 2013). In effect, the D/H isotope exchange between silicate melts and fluids appears to be controlled mainly by the solubility and speciation of silicate species dissolved in the fluid phase. The present study provides further evidence that D-H partitioning between molecular and structural water is independent of the water content in the silicate melt, but largely constrained by the affinity of deuterium into sites with lower molar volume. While it is not possible at this stage to predict the magnitude or even the direction of D-H partitioning between fluid and melt during magma ocean crystallization for geochemically realistic hydrous melt compositions, these experimental data strongly suggest such an isotope partitioning process governed by different intermolecular site affinities of H and D in fluids and melts must be considered a distinct possibility early in Earth’s history.
Acknowledgments

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References


Figure Captions

**Figure 1**. *Left*, solid state $^{29}$Si MAS-NMR spectra of hydrated sodium tetrasilicate melt quenched to glass with 9 wt % water, variously deuterated from 100 %, 90 % and 0 %. Dashed lines highlight the silicate Q species, where for $Q^n$, $n$=the number of bridging oxygens: $Q^4$ (-103 ppm), $Q^3$ (-95 ppm), $Q^2$ (-90 ppm). These $^{29}$Si MAS-NMR spectra are statistically indistinguishable and reveal that D and H depolymerize the glass network similarly. *Center*, solid state $^1$H MAS-NMR spectra of hydrated NS4 glass (Center-Top)
(9 wt% water, 90 % D 10 % H), gypsum (Center-Middle), and hydrated SiO$_2$ glass (Center-Bottom). \textit{Right}, solid state $^2$H NMR spectra of deuterated NS4 glass (Right-Top) and deuterated SiO$_2$ glass (Right-Bottom).

\textbf{Figure 2}: $^1$H (left) and $^2$H NMR spectra of hydrated NS4 glasses with 3 wt. % water with varying D-H content.

\textbf{Figure 3}: $^1$H (left) and $^2$H NMR spectra of hydrated NS4 glasses with 6 wt. % water with varying D-H content.

\textbf{Figure 4}: $^1$H (left) and $^2$H NMR (right) spectra of hydrated NS4 glasses with 9 wt. % water with varying D-H content.

\textbf{Figure 5}: Quantitative analysis of D-H speciation in hydrated silicate melts quenched to glass with variation in total water content (3, 6 and 9 wt %) and D-H content of the water. High frequency (black) vs. low frequency (gray) abundances between $^1$H and $^2$H solid state NMR are different (bottom and middle). The partitioning ratio, R, between water in high frequency and low frequency environments is very large (R=3.1) (top).

\textbf{Figure 6}: $^1$H (left) and $^2$H NMR (right) spectra of hydrated NS4 glasses with 6.3 wt. % water with D:H of the water being 50:50 synthesized at 1400 °C, 1.5 GPa for 48 hours, quenched to glass at a rate of 1 °C/sec. Large intramolecular partitioning is still observed (R=3.1)
Figure 7: Wide line $^2$H NMR spectrum of hydrated NS4 glass (9 wt % D$_2$O). A) The central band highlighting the high (H), medium (M), and low (L) frequency deuterium resonances. B) The forth (most intense) high frequency side band- note the diminished intensity of the M and L peaks. C) $^2$H quadrupolar line shapes for the H, M, and L deuterium resonances. Note that the high frequency peak exhibits a broadened classic Pake powder pattern indicative of deuterium in a rigid environment. The M and L powder patterns exhibit the characteristics of deuterons in more mobile environments, e.g., O-D wagging motion.

Figure 8: $^1$H (black) and $^2$H (gray) solid state NMR spectra of a hydrated Ca, Mg, Na, Al, Si oxide glass (a model basalt composition without Fe) with 6 wt % water (D:H 1:1). The lack of fine structure relative to the NS4 glasses is due to a much larger number of electronic environments available for H and D to reside with the glass structure. It is evident that large intramolecular D-H partitioning exists, where D tends to favor environments corresponding to the high frequency (shorter O-[H,D]•••O distance) resonances and H favors environments corresponding to the lower frequency (longer O-[H,D]•••O distance) resonances.
Table 1
Total water content and $^2\text{H}:^1\text{H}$ concentration of the synthesized glasses

<table>
<thead>
<tr>
<th>Composition of anhydrous glass</th>
<th>total water content (wt %)</th>
<th>$^2\text{H}/^1\text{H}$</th>
<th>H content (mol %)</th>
<th>D content (mol %)</th>
<th>run duration (hrs)</th>
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<tbody>
<tr>
<td>NS4</td>
<td>3.3</td>
<td>11.4</td>
<td>100 : 0</td>
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<td>NS4</td>
<td>3.3</td>
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<td>90 : 10</td>
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<td>20.6</td>
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<tr>
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<td>11.0</td>
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<tr>
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<td>21.1</td>
<td>50 : 50</td>
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<td>21.0</td>
</tr>
<tr>
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</tr>
<tr>
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<tr>
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Table 2

$^{29}$Si NMR Q-species determination and water speciation OH to H$_2$O calculations

<table>
<thead>
<tr>
<th>Run no.</th>
<th>D:H (9 wt % water)</th>
<th>Integration % (Hi, Mid, Low)</th>
<th>NBO/T</th>
<th>% as H$_2$O</th>
<th>% as Si-OH</th>
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<tr>
<td>6881</td>
<td>100% H</td>
<td>21.9 (-90 ppm) Q2</td>
<td></td>
<td>49.0</td>
<td>51.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>46.7 (-95 ppm) Q3</td>
<td></td>
<td></td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.4 (-103 ppm) Q4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6872</td>
<td>9:1</td>
<td>21.2 (-90 ppm) Q2</td>
<td></td>
<td>43.5</td>
<td>56.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.9 (-95 ppm) Q3</td>
<td></td>
<td></td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28.8 (-103 ppm) Q4</td>
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</tr>
<tr>
<td>6879</td>
<td>100% D</td>
<td>20.7 (-90 ppm) Q2</td>
<td></td>
<td>48.7</td>
<td>51.3</td>
</tr>
<tr>
<td></td>
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<td>46.7 (-95 ppm) Q3</td>
<td></td>
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<td>0.88</td>
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<td></td>
<td></td>
<td>32.7 (-103 ppm) Q4</td>
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</tbody>
</table>
Figure 1
Figure 3

$^1$H

6 wt % $X_2O$
D:H 1:1

6 wt % $X_2O$
100 % $H_2O$

$^2$H

6 wt % $X_2O$
100 % $D_2O$
D:H 1:1
Figure 4

$^{1}H$

- 9 wt% $X_{2}O$
- D:H 9:1

- 9 wt% $X_{2}O$
- D:H 1:1

- 9 wt% $X_{2}O$
- 100% $H_{2}O$

$^{2}H$

- 9 wt% $X_{2}O$
- 100% $D_{2}O$

- 9 wt% $X_{2}O$
- D:H 9:1

- 9 wt% $X_{2}O$
- D:H 1:1

$H$ Frequency (ppm) $^{2}H$ Frequency (ppm)
Figure 5
$^1$H NMR

$^2$H NMR

Figure 6