Revision 1: *In situ* study of the fractionation of hydrogen isotopes between aluminosilicate melts and coexisting aqueous fluids at high pressure and high temperature - Implications for the δD in magmatic processes.

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Abstract

The hydrogen isotopic composition of melt inclusions trapped in phenocrysts during their crystallization and growth in a magma may contribute to a better understanding of the water cycle between the atmosphere, the hydrosphere and the lithosphere. Such understanding relies on the knowledge of the hydrogen isotopic fractionation factors between aqueous fluids, silicate melts, and minerals at temperature and pressure conditions relevant to the Earth's interior. Significant D/H fractionation between silicate melts and aqueous fluids was reported at hundreds of MPa and °C by using *in situ* measurements in hydrothermal diamond anvil cell (HDAC) experiments (Mysen, 2013, American Mineralogist 98, 376-386 and 1754-1764). However, the available dataset is focused on fluids and melts with D/H ratios close to unity. The relevance of such data for natural processes that involve per mil variations of δD -values may not always be clear. To address such concerns, the effect of the bulk D/H ratio on hydrogen isotope partitioning between water-saturated silicate melts and coexisting silicate-saturated aqueous fluids has been determined in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}-\text{D}_2\text{O}$ system. To this end, *in situ* Raman spectroscopic measurements were performed on fluids and melts with bulk D/H ratios from 0.05 to 2.67 by using an externally-heated diamond anvil cell in the 300 - 800°C and 200 - 1500 MPa temperature and pressure range, respectively.

In these pressure/temperature ranges, the D/H ratios of fluids in equilibrium with melt barely change with temperature (in average $\Delta H_{\text{fluid}} = 0.47 \pm 1.15$ kJ/mol), In contrast, the D/H ratios of coexisting melts display strong dependence on temperature (average

46 $\Delta H_{\text{melt}} = 7.18 \pm 1.27$ kJ/mol). The temperature-dependence of the D/H fractionation factor
47 between melt and fluid ($\alpha_{\text{fluid-melt}} = D/H_{\text{fluid}} / D/H_{\text{melt}}$) is comparable in all the experiments
48 and can be written: $1000 \cdot \ln(\alpha_{\text{fluid-melt}}) = 263 (\pm 26) \cdot T^{-2} - 126 (\pm 48)$. Therefore, the $\alpha_{\text{fluid-melt}}$
49 is independent of the bulk D/H ratio of the melt + fluid system.

50 Experimentally determined $\alpha_{\text{fluid-melt}}$ using D-enriched fluids, therefore, can be
51 applied to natural systems. It follows that for water-saturated magma strong isotopic
52 fractionation of D and H between water dissolved in magmas and deep aqueous fluids
53 may occur. The δD -values in melt inclusions in phenocrysts in such water-saturated
54 magma will reflect such fluid/melt fractionation effects. A likely result is underestimation
55 of the δD isotopic composition of slab fluids based on δD -values in melt inclusions. The
56 temperature-dependent hydrogen isotope fractionation must be taken into account in the
57 modeling of slab fluid – magma interaction in the mantle wedge.

58
59 **Keywords:** Hydrogen isotopes, fractionation, temperature, in-situ, subduction.

1. Introduction

The hydrogen isotopic composition of aqueous fluid or water dissolved in minerals/glasses is important for the assessment of the origin and exchange of fluids in and between geochemical reservoirs in the Earth and terrestrial planets. For instance, the δD -value of water in lunar glasses and olivine-hosted melt inclusions was used to suggest that water on Earth and the Moon has the same carbonaceous chondritic origin (Saal et al., 2013). The δD -values of water in melt inclusions and in minerals also have been used to track the exchange of water between the various geochemical reservoirs in subduction zones (Shaw et al., 2008), to provide evidence of older subduction (e.g. Kingsley et al., 2002), and to characterize the cycle of water in water-bearing reservoirs such as those of the Earth's uppermost crust and atmosphere (Gat, 1996).

Use of the hydrogen isotopic composition to address possible origins and cycling of water in and between various reservoirs relies on knowledge of the hydrogen isotopic fractionation factors (α_{A-B}) between fluids, minerals, silicate melts and glasses. The α_{A-B} factors quantify the fractionation that occurs between two different hydrogen-bearing components A and B at given temperature and pressure conditions:

$$\alpha_{A-B} = \frac{(DH)_A}{(DH)_B} \quad (1)$$

For gaseous substances, fractionation factors have been determined experimentally and also have been calculated by using the partition functions of the molecules (e.g. Richet et al., 1977, and references therein). Such a calculation assumes no interaction between functional groups in the material. This assumption is not valid for water dissolved in minerals, water-rich silicate melts (magma) and silicate-rich aqueous fluids because of

strong intermolecular bonding that may influence the exchange of hydrogen isotopes during chemical reactions. For instance, pressure and the chemical composition of minerals influence the hydrogen isotopic fractionation in mineral-water systems (Chacko et al., 2001, and references therein). There is also a strong influence of bond strength of H₂O-D₂O fluids on the partition function of D and H between H₂-D₂ gas and H₂O-D₂O fluid at high temperature (T) and high pressure (P ; Foustoukos and Mysen, 2012).

Fractionation of D and H between H₂O vapor and natural aluminosilicate melts or glasses in equilibrium with vapor has been reported (e.g. Richet et al., 1986; Pineau et al., 1998), and has been used to infer volcanic degassing processes (e.g., Dobson et al., 1989; De Hoog et al., 2009). However, such studies relied on isotopic characterization of quenched silicate and vapor phases, for which high temperature/pressure isotopic equilibrium was assumed. These studies also relied on perfect or near-perfect separation of fluids and melts after the experiments. This separation is not straightforward for aqueous fluids that are strongly enriched in silica and alkali metals at P - T conditions relevant to the Earth's interior (e.g., Manning, 2004) because of the high solubility of silicate components aqueous fluid at such conditions (Manning, 1998; Mysen and Armstrong, 2002). The silicate dissolved in the fluid at high temperature and pressure often precipitates during the quench so that the chemical composition of the fluid phase evolves during quenching. Furthermore, a significant fraction of water dissolved in the silicate melt can also be exsolved from the melt during quenching (e.g., Mysen and Wheeler, 2000) thus changing the composition of the resulting glass. Finally, platinum capsules that are used for high pressure and temperature experiments in externally-heated pressure vessels or piston-cylinder apparatuses have different permeability of H and D,

115 which can affect the D/H ratios of quenched silicate materials (Richet et al., 1986). All
116 those difficulties can be circumvented by studying the equilibrium between a silicate melt
117 and an aqueous fluid *in situ* while the sample is at the high temperature/pressure. This can
118 be accomplished using hydrothermal diamond anvil cell (HDAC) techniques (e.g.,
119 Bassett et al., 1994; 1996) with *in situ* Raman spectroscopy as a tool for isotope
120 spectroscopic analyses (Foustoukos and Mysen, 2012; Mysen, 2013a,b).

121 Prior exploratory HDAC experiments were performed using mixtures of liquid
122 D₂O and H₂O and silicate and aluminosilicate melts (Mysen, 2013a,b). Those
123 experiments revealed that the D/H fractionation factors ($\alpha_{\text{melt-fluid}}$) can reach values on the
124 order of a few hundreds, at temperatures between 300 and 800°C, with corresponding
125 pressures from 100 to 1300 MPa. Such results may raise questions about the
126 interpretation of δD -values of water in magmas. For instance, Shaw et al. (2008) used the
127 δD -value of melt inclusions from arc volcanism of the Mariana trench to assess the δD -
128 value of the aqueous fluids released by the subducting slab. Their interpretations were
129 based on the assumption that no D/H fractionation occurred between slab aqueous fluids
130 and the magma, from which the melt inclusions originated. If the magma was saturated in
131 slab components transported to the melting region by aqueous fluids, the preliminary
132 results of Mysen (2013a,b) may suggest that the dissolved slab components themselves
133 affected the δD -value of the slab aqueous fluids.

134 The HDAC experiments of Mysen (2013a,b) involved fluids with high D/H ratios,
135 typically on the order of 1, which is far from geochemical δD -values that typically are on
136 the order of tens of ‰. This raises the question whether the isotope fractionation factors
137 are independent of the D/H ratio itself.

To evaluate whether D/H fractionation depends on bulk D/H ratio, we performed HDAC experiments with a $\text{Na}_6\text{AlSi}_8\text{O}_{20}$ melt in equilibrium with a fluid initially composed of different mixtures of liquid H_2O and D_2O (with D/H ratios ranging from 0.05 to 2.67). The anhydrous melt composition has the proportion of non-bridging oxygen per tetrahedrally coordination cations (NBO/T) of 0.6. This NBO/T-value is within the range of andesite melts (NBO/T from 0.2 to 0.7) and some tholeiitic basalt melts (NBO/T from 0.6 to 1.2). Therefore, this composition may be relevant to processes affecting arc magma genesis.

2. Methods

The $\text{Na}_6\text{AlSi}_8\text{O}_{20}$ (NS3A5: 64wt% SiO_2 , 8.2wt% Al_2O_3 and 28wt% Na_2O ; NBO/T= 0.6) starting material glass was prepared by mixing reagent-grade Na_2CO_3 , SiO_2 and Al_2O_3 powders, which were then decarbonated by slow step heating (50°C/15 minutes), and melted for 2 hours at 1000°C. Seven fluid compositions were prepared by mixing double-distilled deionized H_2O and D_2O fluids in desired volume proportions.

In situ experiments with the sample at the temperature and pressure of interest were carried out in an externally heated hydrothermal diamond anvil cell (HDAC) (Bassett et al. 1994, 1996) with 1 mm diamond cutlets. Chips of NS3A5 glass, ^{13}C diamond chips, and a 70 μm diameter by 100-200 μm long rod of Pt metal (to enhance isotopic equilibration rate; Horita 1988) were loaded together with the aqueous fluid solution into the sample chamber. Iridium gaskets of 125 μm thickness with a central 500 μm diameter hole were used to contain the samples (Fig. 1). The temperature in the

HDAC was controlled to within 1°C with chromel-alumel thermocouples that were in contact with the surface of the upper and lower diamond anvils. The accuracy of the temperature measurements is better than 3°C (Bassett et al. 2000). The pressure inside the cell is governed by the PVT relationship of the aqueous fluid at imposed temperature. The sample chamber volume being fixed, increasing temperature results in increasing pressure. Pressure was determined from the pressure-/temperature-dependent one-phonon Raman shift of the synthetic ¹³C diamond. This shift has been calibrated in the 0.1-1500 MPa and 25-800°C ranges by Mysen and Yamashita (2010).

Seven experimental series through a range of temperatures and pressures, each with a different bulk D/H ratio, were conducted by first increasing temperature and pressure up to the conditions at which the melt + fluid mixture was in a supercritical state. Then, temperature (and thus pressure) was decreased to *P-T* conditions where melt and fluid coexist (Fig. 1). Supercritical conditions are different for each experiment (Table 1). The temperature was decreased from the initial supercritical conditions (Table 1) to 350°C (lowest temperature where Raman spectroscopy measurements were carried out) in 50°C decrements (cooling at 1°C/s). The *P-T* trajectories of the seven series of experiments differ (Table 1) because of different fluid densities, which were governed by the initial amounts of glass and fluid introduced in the cell as well as by the initial starting pressure applied after closure of the cell. The temperature-dependent pressure trajectory for each experiment is shown in Fig. 2. Raman spectroscopic measurements were made at each temperature and pressure.

Samples (supercritical fluid, or coexisting melt and fluid) were examined while at high temperature and pressure with a JASCO model NRS-3100 confocal microRaman

single monochromator spectrometer using a holographic notch filter and holographic gratings. Measurements were carried out in melt and fluid with 1200 grooves/mm centered at 3000 cm^{-1} . A 50X Mitutoyo long working-distance objective lens was employed for both visual microscopic examination and spectroscopic analysis. An Andor Model DV401-F1 1024×128 pixel (25×25 μm pixel size) Peltier-cooled CCD was used for signal detection. To record spectra of melt and fluid, the 490.2 nm line of a solid-state laser was used. The laser power on the sample was $\sim 33\text{ mW}$. Acquisition time was between 45 and 80 s, with two accumulations per analysis. The Raman spectra of the ^{13}C diamonds, used for pressure estimates, together with a Ne reference line were performed by exciting the sample with a 532 nm laser line and using 2400 grooves/mm to ensure the best spectral resolution. By using the Ne reference lines, spectrometer accuracy was $\pm 0.1\text{ cm}^{-1}$, which introduces a $\pm 40\text{ MPa}$ pressure uncertainty. The error in the calibration of the one-phonon Raman shift of ^{13}C diamond is about $\pm 100\text{ MPa}$, so that the total pressure uncertainty was $\pm 110\text{ MPa}$. The pressure precision, which depends only on the uncertainty Raman signal ($\pm 0.1\text{ cm}^{-1}$), is $\pm 40\text{ MPa}$.

The $2000\text{--}4000\text{ cm}^{-1}$ portion of Raman spectra of samples is dominated by the second-order diamond signal from the diamond cell (Fig. 3a). To remove interference from this signal, we recorded two spectra during measurements at given P - T conditions: one from the sample (Fig. 3a, in red) and one from the upper diamond (Fig. 3a, in black). Before subtracting the spectrum of the diamond from that of the sample, the background was first removed by fitting a generalized, cross-validators (GCV) spline function (Woltring, 1986) to portions of spectrum devoid of signals (Fig. 3a). The GCV spline function is then subtracted from the spectrum (Fig. 3b). The background-subtracted

spectra of the diamond and the sample present small differences in intensities. We assumed that this difference is linear, such that the second-order diamond signal in the diamond and sample spectra are proportional via a proportionality constant, K . The K constant was determined by fitting the 2140-2250 cm^{-1} portion of the sample and diamond spectra by linear least-squares, because no signal from the sample is expected in this spectral region. After adjusting the intensity of the spectra, the diamond signal was subtracted from the sample signal, so that the Raman spectrum of the analyzed phase was obtained (Fig. 3c). Areas of the observed peaks were measured by trapezoidal integration.

3. Results and discussion

3.1. D/H fractionation between melt and fluid

Seven different D/H ratios were measured in supercritical fluids: 0.05 ± 0.02 , 0.13 ± 0.04 , 0.42 ± 0.01 , 0.50 ± 0.01 , 0.93 ± 0.01 , 2.47 ± 0.04 and 2.68 ± 0.06 . The error on those average values represents one standard deviation from the 2 to 5 measurements (Table 1). The D/H measurements of the supercritical fluid provide the bulk D/H ratio of an experimental series. The three experimental series with D/H ratios in their supercritical fluid equal to 0.13 ± 0.04 , 0.50 ± 0.01 and 2.68 ± 0.06 followed similar P - T trajectories ($T = 350$ - 550 °C with P in the 322-484, 248-490 and 313-445 MPa ranges, respectively). The three experimental series with D/H ratios of their supercritical fluid equal to 0.42 ± 0.01 , 0.93 ± 0.01 and 2.47 ± 0.04 followed higher, but also similar, P - T trajectories ($T = 350$ - 600 °C and $P = 431$ - 899 , 430 - 790 , 403 - 819 MPa, respectively). The experiment with

a supercritical fluid D/H ratio of 0.05 ± 0.02 followed a lower P - T trajectory than the other experimental series (400-680 °C/187-496 MPa). The different P - T trajectories between the various experiments result from both different ratios of melt and fluid in the cell (such parameter being difficult to control) as previously noted, and different deformation of the Ir gasket hole during experimental P - T increase.

To determine the time needed for isotopic equilibration following a change of temperature and pressure, time series experiments were performed at both 550°C (779 MPa) and 350°C (431 MPa). Within error, the D/H ratio of melt does not vary after a few minutes (Fig. 4). This indicates that isotopic equilibrium is achieved within minutes, consistent with preliminary results from Mysen (2013a). Therefore, in order to ensure perfect isotopic equilibrium in all experimental series, Raman measurements were conducted after an equilibration time of 20 minutes in supercritical fluids, 40 minutes in fluids, and 50 minutes in melts at each temperature and respective pressure.

Two broad bands, centered near 2600 and 3500 cm^{-1} , are visible in the 2000-4000 cm^{-1} portion of Raman spectra of fluids and melts (Fig. 5a and b). The band near 3500 cm^{-1} is asymmetric at low temperature in spectra of both the aqueous fluid and the hydrous melt. It becomes more symmetric with increasing temperature (and pressure), as previously reported for aqueous fluids or silicate melts (e.g., Frantz et al., 1993; Kawamoto et al., 2004; Foustoukos and Mysen, 2012). That band is assigned to O-H stretching vibrations from H_2O molecules and OH^- groups in silicate-saturated fluids (Walrafen et al., 1986, Foustoukos and Mysen, 2012) and water-saturated silicate melt (e.g. Walrafen and Abede, 1978; Mysen et al. 1980). The 2500-2800 cm^{-1} band also becomes narrower with increasing temperature. It is assigned to O-D stretching vibrations

in molecular D₂O and OD⁻ groups (e.g. Walrafen et al., 1986; 1996; Foustoukos and Mysen, 2012). For both bands, the narrowing reflects the decrease of hydrogen bonding with increasing temperature (Walrafen et al., 1986; Frantz et al., 1993; Foustoukos and Mysen, 2012). A small (< 10% in normalized intensity) and narrow peak (< 15cm⁻¹ FWHH) near 2950 cm⁻¹ is also observed mainly in fluids, and in some melts at high temperature. This band is assigned to the D₂ vibron (Foustoukos and Mysen, 2012) and was not taken into account in the integration of the intensity of O-H and O-D band.

The integrated intensity of a Raman peak assigned to a specific vibration of bonding within a molecule or functional group is proportional to the molecule concentration in the studied matter (Long, 1977). However, a direct calculation requires knowledge of the Raman cross sections, which are unknown at high temperature in the case of the stretching vibrations of O-D and O-H bonds in silicate melts and in aqueous fluids. However, by assuming that the Raman cross-section for the stretching vibration of O-D bonds equals that for O-H bonds at a given temperature and pressure, the ratios of the areas A_{OD} and A_{OH} of the peaks assigned to the O-D and O-H stretching vibrations directly provide the D/H concentration ratios in the investigated fluid or melt (Mysen, 2013a):

$$DH = A_{OD} / A_{OH} . \quad (2)$$

The assumption of equal cross section was verified for aqueous fluids at room temperature where we determined that equation (2) provides the same ratio of mol fractions of H₂O and D₂O as the prepared fluid. The A_{OD} / A_{OH} ratio of the starting fluid in the HDAC cell prior to heating also was similar, within error ($\leq \sim 0.05$), to that of the supercritical fluid at high temperature and high pressure. Furthermore, within error, the

A_{OD} / A_{OH} ratios of supercritical fluids do not change with P and T (Fig. 5). Another indication that the A_{OD} / A_{OH} ratio provides a good estimate of the D/H molar ratio is that, at high T near the critical point, the D/H ratios of the melt and the fluid approach that of the supercritical fluid (Fig. 5). These observations indicate that the O-D and O-H Raman cross sections can be considered similar at a given temperature and pressure in fluid or in melt and that Equation (2) provides reliable D/H molar ratios of coexisting fluid and melt during HDAC experiments.

The D/H values in aluminosilicate melts and coexisting aqueous fluids show different variations with P - T conditions (Fig. 5c and d). For melts, there is a positive temperature-dependence. In contrast, the D/H ratio in the fluid does not significantly vary with temperature (Fig. 5c and d). The enthalpy of the D/H exchange (denoted ΔH , Table 2) is derived from the slope of the linear regression of the D/H ratio variation with temperature (Fig. 5c and d). The errors on ΔH -values are representative of data scatter. Except for the experiment with $D/H_{\text{supercritical}} = 0.13 \pm 0.04$, for which only 3 D/H ratio measurements were obtained, the ΔH_{melt} (on average 7.18 ± 1.27 kJ/mol) and ΔH_{fluid} (on average 0.47 ± 1.15 kJ/mol) barely vary (close to or within the error bars) between different experiments, i.e. with different bulk D/H ratios (Table 2).

The $\alpha_{\text{fluid-melt}}$ values of all the experiments show a strong dependence on temperature (Fig. 6). This dependence is similar among all the experiments within error, and can be expressed as:

$$1000 \cdot \ln \alpha_{\text{fluid-melt}} = b + m \cdot T - 2, \quad (3)$$

with $m = 263 \pm 26$, $b = -126 \pm 48$ and T in Kelvin. Considering the errors affecting the different $\alpha_{\text{fluid-melt}}$ values, the hydrogen isotopic fractionation factor does not depend on

the D/H of the supercritical fluid composition. Furthermore, pressure can change of a factor 2 between different experiments (Fig. 3). This does not seem to affect strongly the $\alpha_{\text{fluid-melt}}$ at first order.

The greater variation of ΔH_{melt} compared with ΔH_{fluid} suggests that the variations of $\alpha_{\text{melt-fluid}}$ with temperature are mainly controlled by the melt. Nevertheless, the fact that D/H values for melt and fluid approach each other near supercritical conditions also indicates a fluid effect on the $\alpha_{\text{melt-fluid}}$. The dependence of Mysen (2013b)'s ΔH_{melt} and ΔH_{fluid} on P - T conditions differs from that of the present results. In Mysen (2013a;b) spectra, sharp peaks near 2650 cm^{-1} are superimposed on the broad band that is assigned to O-D stretching vibrations, and the signals assigned to O-H and O-D stretching vibrations are noisier than the ones retrieved in this study. The present study uses generalized cross-validated cubic-spline functions for background removal below the spectra, whereas Mysen (2013a;b) used a linear function. This translates in an improvement of the signal to noise ratio of the retrieved signals assigned to O-H and O-D stretching vibrations. Mysen (2013a;b) data were reprocessed using our new processing procedure. Results show that the sharp peaks in spectra of Mysen (2013a,b) arise from residues of the second-order vibration of diamond, not from the samples and therefore, it affected the D/H ratios. With use of the new procedure on the same raw data, results show comparable variations of ΔH_{melt} and ΔH_{fluid} (see Table 2).

Compared to fractionation factors and their temperature dependence determined for vapor-glass systems (Dobson et al. 1989; Pineau et al. 1998) and vapor-melt (Richet et al. 1986), our hydrogen isotopic fractionation values are significantly higher (one order of magnitude; Fig. 7). Hydrogen (and hence, D) can form Si-OH bonds or metal-OH

bonds (e.g. Cody et al. 2005; Xue and Kanzaki, 2009) or present as H₂O. Its speciation and environments are strongly dependent on temperature (e.g. see Stolper, 1982; Nowak and Behrens, 1995; Sowerby and Keppler, 1999; Behrens and Yamashita, 2008, Moretti et al., 2014) and chemical composition (e.g. see Robert et al., 2001; Behrens and Yamashita, 2008, Xue and Kanzaki, 2009, Le Losq et al., 2015). In addition, H environments have a broad distribution of oxygen-oxygen distances, as testified by the large signals assigned to O-H stretching vibrations, observed in Raman or IR spectra of glasses (Le Losq et al. 2012) or in ¹H NMR spectra (Eckert, 1988; Robert et al., 2001, Cody et al., 2005, Le Losq et al., 2015). Recent data highlight differences between the distribution of H and D in given structural environments in sodium silicate glasses (Wang et al. 2015), suggesting the occurrence of intramolecular fractionation of D and H in silicate melts. Because of such complexities, H and D cannot be treated as they are in minerals, where they occupy specific structural sites. The variability of those environments associated with their temperature and compositional dependence probably results in enhancing isotopic effects, because they are characterized by different length and strength for the O-H and O-D bonds, and hence, present different zero point energy (Bottinga, 1969; Richet, 1977). Those variables may explain the differences in the results of Pineau et al. (1998) and the present results.

3.2. Geochemical implications

The D/H ratios used for HDAC experiments do not influence the $\alpha_{\text{fluid-melt}}$ values. Therefore, the present *in-situ* experimental $\alpha_{\text{fluid-melt}}$ data may be applied to natural

processes that involve D/H ratios at the ‰ level.

The variation of $\alpha_{\text{fluid-melt}}$ with temperature and pressure (Fig. 6) in the present experiments suggests that, for equilibrium conditions, large hydrogen isotopic fractionation may occur between water-saturated magmas and fluid within the Earth's interior. For example, experimental hydrogen isotopic fractionation data between minerals and fluid (e.g., Vennemann and O'Neil, 1996; Saccocia et al., 2009) lead to the suggestion that slab dehydration processes in subduction zones may release fluids enriched in D (Shaw et al. 2008). Once released into the mantle wedge, those fluids may enrich the mantle wedge lithology and magma genesis zone in deuterium relative to ^1H .

The δD -values of melt inclusions in phenocrysts from subduction settings (Shaw et al., 2008; Bouvier et al., 2010; Métrich et al., 2014) might be used to constrain the δD -value of slab-derived fluids provided that the D/H fractionation factor, $\alpha_{\text{fluid-melt}}$, is known. For example Shaw et al. (2008) suggested that the average δD -value of melt inclusions from the Mariana arc (-34‰) reflects the δD -value of the aqueous fluids released by the subducting slab, and thus might be used to determine the extent of slab dehydration. This would be possible provided that $\alpha_{\text{fluid-melt}} = 1$. In other words, for fluid-saturated magmas (not uncommon in subduction zone contexts), it is assumed that there is no D/H fractionation between the magma from which the melt inclusions originate and the slab-derived aqueous fluids in the source region of partial melting. Provided that the magma is fluid-saturated, the D/H fractionation is:

$$\delta\text{DMI} = \text{DHMI} / \text{DHSMOW} - 1.1000 \quad , \quad (4)$$

$$\delta\text{DSF} = \text{DHSF} / \text{DHSMOW} - 1.1000 \quad , \quad (5)$$

where MI stands for melt inclusions and SF stands for slab fluids. Combining equations

(4) and (5) with equation (1), the slab fluid isotopic signature can be expressed as:

$$\delta D_{SF} = \alpha_{fluid-melt} \cdot \delta D_{MI} 1000 + 1 - 1 \cdot 1000$$

(6)

and therefore can be deduced from the hydrogen isotopic composition of melt inclusions.

The $\alpha_{fluid-melt}$ data demonstrate, however, that the $\alpha_{fluid-melt}$ -values are not unity. As the $\alpha_{fluid-melt}$ may depend on melt chemical composition, a first-order estimation with $\alpha_{fluid-melt} \neq 1$ can be made to highlight the possible impact of the D/H fractionation between melt and fluid of the δD -value of the slab fluids. By extrapolating $\alpha_{fluid-melt}$ to between 600 to 800°C (i.e. fluid-saturated basalt solidus around 1 GPa; Lambert and Wyllie, 1972; Schmidt and Poli, 1998), $\alpha_{fluid-melt}$ values would be about 1.11-1.24 ($1000 \cdot \ln \alpha_{fluid-melt} = 102$ to 218). These values result in a slab-fluid with δD_{SF} of about 202 to 70‰, using equation (6) and the Mariana melt inclusion data from Shaw et al. (2008). This value, although deduced from a simple composition not directly representative of that involved in natural processes, indicates that the δD -values of slab fluids are most likely higher than previously inferred.

Although δD -values from fluid inclusions trapped in subduction contexts are lacking to compare with our calculated slab δD_{SF} -values, Johnson and Harlow (1999) recalculated the δD -values of serpentinizing fluids reacting at high pressure with the slab ultramafic rocks. The δD -values of these fluids, later released in the mantle wedge, range from -10 to 5‰. These data also suggest that δD_{SF} -values are higher than δD -values measured in melt inclusions. As a consequence, fractionation occurring during slab dehydration may have been underestimated. This conclusion, in turn, impacts on estimates of H₂O fluxes between the slab and the mantle wedge and, therefore, our

understanding of the water cycle between the hydrosphere and the mantle.

4. Conclusions

The *in-situ* experimental determination of D/H fractionation between aluminosilicate melt and aqueous fluid reveals strong fractionation of D and H between melts and coexisting fluids. We demonstrated that $\alpha_{\text{fluid-melt}}$ data determined using fluids with high D/H ratios during *in situ* experiments are relevant to geochemical processes involving D/H ratios generally on the order of tens to hundred. The fractionation factors, expressed as $1000 \cdot \ln(\alpha_{\text{fluid-melt}})$, can reach values of ~ 550 at temperatures near 350°C and pressures near 0.2 GPa, and ~ 150 at near 700°C and 1 GPa.

The experimental results lead to the suggestion that D/H fractionation may occur during the interaction of magmas and fluids in natural environments. In particular, this probably occurs in subduction zones where magmas can be fluid oversaturated. Therefore, δD -values measured in melt inclusions from arc magmas may not reflect the δD -value of the slab fluids. Taking into account $\alpha_{\text{fluid-melt}}$ at mantle wedge temperatures, the present results suggest that the δD -value of fluids is likely higher than previously assumed. This implies that δD -values measured in arc magmas must be used with caution to deduce the source δD .

Acknowledgements

The authors thank George D. Cody, Dionysis Foustoukos and Marion Le Voyer for inspiring discussions about the project. This research was conducted with support from

NSF grants EAR1212754 and EAR12504491 (BOM) and Dalou's Jackson School of Geosciences Distinguished post-doctoral Fellowship. We also thank Robert L. Dennen for his English edits on the manuscript.

References

Bassett, W.A., Shen, A.H., Bucknum, M., Chou, I.M., 1994. A new diamond cell for hydrothermal studies to 2.5 GPa and from -190 °C to 1200 °C. *Rev. Sci. Instrum.*, 64, 2340-2345.

Bassett, W.A., Wu, T.C., Chou, I.M., Haselton, T., Frantz, J.D., Mysen, B.O., ... Schiferl, D., 1996. The hydrothermal diamond anvil cell (HDAC) and its applications. *Mineral spectroscopy: A tribute to Roger G. Burns*, 5, 261-272.

Bassett, W.A., Anderson, A.J., Mayanovic, R.A., Chou, T., 2000. Hydrothermal diamond anvil cell for XAFS studies of first-row transition elements in aqueous solution up to supercritical conditions. *Chem. Geol.*, 167(1), 3-10.

Behrens, H., Yamashita, S., 2008. Water speciation in hydrous sodium tetrasilicate and hexasilicate melts: Constraint from high temperature NIR spectroscopy. *Chem. Geol.*, 256(3), 306-315.

Bottinga, Y., 1969. Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite-carbon dioxide-graphite-methane-hydrogen-water vapor. *Geoch. Cosmoch. Acta*, 33(1), 49-64.

Bouvier, A.S., Métrich, N., Deloule, E., 2010. Light elements, volatiles, and stable isotopes in basaltic melt inclusions from Grenada, Lesser Antilles: Inferences for magma genesis. *Geochem. Geophys. Geosyst.*, 11(9).

437 Chacko, T., Cole, D.R., Horita, J., 2001. Equilibrium oxygen, hydrogen and carbon
438 isotope fractionation factors applicable to geologic systems. *Rev. Mineral.*
439 *Geochem.*, 43(1), 1-81.

440 Cody, G.D., Mysen, B.O., Lee, S.K., 2005. Structure vs. composition: A solid- state ^1H
441 and ^{29}Si NMR study of quenched glasses along the $\text{Na}_2\text{O-SiO}_2\text{-H}_2\text{O}$ join. *Geochim.*
442 *Cosmochim. Acta*, 69, 2373-2384.

443 De Hoog, J.C., Taylor, B.E., Van Bergen, M.J., 2009. Hydrogen-isotope systematics in
444 degassing basaltic magma and application to Indonesian arc basalts. *Chem.*
445 *Geol.*, 266(3), 256-266.

446 Dobson, P.F., Epstein, S., Stolper, E.M., 1989. Hydrogen isotope fractionation between
447 coexisting vapor and silicate glasses and melts at low pressure. *Geochim.*
448 *Cosmochim. Acta*, 53, 2723-2731.

449 Eckert, H., Yesinowski, J.P., Silver, L.A., Stolper, E.M., 1988. Water in silicate glasses:
450 quantitation and structural studies by proton solid echo and magic angle spinning
451 NMR methods. *J. Phys. Chem.*, 92(7), 2055-2064.

452 Foustoukos, D.I., Mysen, B.O., 2012. D/H isotopic fractionation in the $\text{H}_2\text{-H}_2\text{O}$ system at
453 supercritical water conditions: Composition and hydrogen bonding effects. *Geochim.*
454 *Cosmochim. Acta*, 86, 88-102.

455 Frantz, J.D., Dubessy, J., Mysen, B.O., 1993. An optical cell for Raman spectroscopic
456 studies of supercritical fluids and its applications to the study of water to 500 °C and
457 2000 bar. *Chem. Geol.*, 106, 9-26.

458 Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. *Annu. Rev. Earth*
459 *Planet. Sci.*, 24(1), 225-262.

460 Horita, J., 1988., Hydrogen isotope analyses of natural waters using an H₂-water
461 equilibration method: a special implication to brines. *Chem. Geol.*, 72, 89-94.

462 Johnson, C.A., Harlow, G.E., 1999. Guatemala jadeitites and albitites were formed by
463 deuterium-rich serpentinizing fluids deep within a subduction zone. *Geology*, 27(7),
464 629-632.

465 Kawamoto, T., Ochiai, S., Kagi, H., 2004. Changes in the structure of water deduced
466 from the pressure dependence of the Raman OH frequency. *J. Chem. Phys.*, 120,
467 5867-5870.

468 Kingsley, R.H., Schilling, J.G., Dixon, J.E., Swart, P., Poreda, R., Simons, K., 2002. D/H
469 ratios in basalt glasses from the Salas y Gomez mantle plume interacting with the
470 East Pacific Rise: water from old D-rich recycled crust or primordial water from the
471 lower mantle? *Geochem. Geophys. Geosyst.*, 3, U23-U48.

472 Lambert, I.B., Wyllie, P.J., 1972. Melting of gabbro (quartz eclogite) with excess water
473 to 35 kilobars, with geological applications. *J. Geol.*, 693-708.

474 Losq, C.L., Neuville, D.R., Moretti, R., Roux, J., 2012. Amorphous Materials:
475 Determination of water content in silicate glasses using Raman spectrometry:
476 Implications for the study of explosive volcanism. *Amer. Mineral.*, 97(5-6), 779-790.

477 Le Losq, C., Cody, G.D., Mysen, B.O., 2015. Alkali influence on the water speciation
478 and the environment of protons in silicate glasses revealed by ¹H MAS NMR
479 spectroscopy. *Amer. Mineral.*, 100(2-3), 466-473.

480 Long, D.A, 1977. Raman spectroscopy.

481 Manning, C.E., 1998. Fluid composition at the blueschist-eclogite transition in the model
482 system $\text{Na}_2\text{O-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-HCl}$. Schweiz. Mineral. Petrogr. Mitt., 78(2),
483 225-242.

484 Manning, C.E., 2004. The chemistry of subduction-zone fluids. Earth Planet. Sci. Lett.,
485 223, 1-16.

486 Métrich, N., Deloule, E., 2014. Water content, δD and ^{11}B tracking in the Vanuatu arc
487 magmas (Aoba Island): Insights from olivine-hosted melt inclusions. Lithos, 206,
488 400-408.

489 Moretti, R., Le Losq, C., Neuville, D.R., 2014. The amphoteric behavior of water in
490 silicate melts from the point of view of their ionic-polymeric constitution. Chem.
491 Geol., 367, 23-33.

492 Mysen, B.O., 2013a. Hydrogen isotope fractionation between coexisting hydrous melt
493 and silicate-saturated aqueous fluid: An experimental study in situ at high pressure
494 and temperature. Amer. Mineral., 98, 376-386.

495 Mysen, B.O., 2013b. Effects of fluid and melt density and structure on high-pressure and
496 high-temperature experimental studies of hydrogen isotope partitioning between
497 coexisting melt and aqueous fluid. Amer. Mineral., 98, 1754-1764.

498 Mysen, B.O., Wheeler, K., 2000. Solubility behavior of water in haploandesitic melts at
499 high pressure and high temperature. Amer. Mineral., 85, 1128-1142.

500 Mysen, B.O., Armstrong, L., 2002. Solubility behavior of alkali aluminosilicate
501 components in aqueous fluids and silicate melts at high pressure and
502 temperature. Geochim. Cosmochim. Acta, 66(12), 2287-2297

503 Mysen, B.O., Yamashita, S., 2010. Speciation of reduced C-O-H volatiles in coexisting

504 fluids and silicate melts determined in-situ to ~1.4 GPa and 800°C. *Geochim.*
 505 *Cosmochim. Acta*, 74, 4577-4588.

506 Mysen, B.O., Virgo, D., Scarfe, C.M., 1980. Relations between the anionic structure and
 507 viscosity of silicate melts - a Raman spectroscopic study. *Am. Mineral*, 65, 690-710.

508 Nowak, M., Behrens, H., 1995. The speciation of water in haplogranitic glasses and melts
 509 determined by in situ near-infrared spectroscopy. *Geochim., Cosmochim.*
 510 *Acta*, 59(16), 3445-3450.

511 Pineau, F., Shilobreeva, S., Kadik, A., Javoy, M., 1998. Water solubility and D/H
 512 fractionation in the system basaltic andesite–H₂O at 1250 C and between 0.5 and 3
 513 kbars. *Chem. Geol.*, 147, 173-184.

514 Richet, P., Bottinga, Y., Javoy, M., 1977. A review of hydrogen, carbon, nitrogen,
 515 oxygen, sulphur, and chlorine stable isotope fractionation among gaseous molecules.
 516 *Annu. Rev. Earth Planet. Sci.*, 5, 65-110.

517 Richet, P., Roux, J., Pineau, F., 1986. Hydrogen isotope fractionation in the system H₂O-
 518 liquid NaAlSi₃O₈: New data and comments on D/H fractionation in hydrothermal
 519 experiments. *Earth Planet. Sci. Lett.*, 78, 115-120.

520 Robert, E., Whittington, A., Fayon, F., Pichavant, M., Massiot, D., 2001. Structural
 521 characterization of water-bearing silicate and aluminosilicate glasses by high-
 522 resolution solid-state NMR. *Chem. Geol.*, 174(1), 291-305.

523 Saal, A.E., Hauri, E.H., Van Orman, J.A., Rutherford, M.J., 2013. Hydrogen isotopes in
 524 lunar volcanic glasses and melt inclusions reveal a carbonaceous chondrite
 525 heritage. *Science*, 340(6138), 1317-1320.

526 Saccocia, P.J., Seewald, J.S., Shanks, III W.C., 2009. Oxygen and hydrogen isotope
 527 fractionation in serpentine–water and talc–water systems from 250 to 450° C,
 528 50MPa. *Geochim, Cosmochim, Acta*, 73(22), 6789-6804.

529 Shaw, A.M., Hauri, E.H., Fischer, T.P., Hilton, D.R., Kelley, K.A., 2008. Hydrogen
 530 isotopes in Mariana arc melt inclusions: Implications for subduction dehydration and
 531 the deep-Earth water cycle. *Earth Planet. Sci. Lett.*, 275(1), 138-145.

532 Schmidt, M.W., Poli, S., 1998. Experimentally based water budgets for dehydrating slabs
 533 and consequences for arc magma generation. *Earth Planet. Sci. Lett.*, 163(1), 361-
 534 379.

535 Sowerby, J.R., Keppler, H., 1999. Water speciation in rhyolitic melt determined by in-
 536 situ infrared spectroscopy. *Amer. Mineral.*, 84, 1843-1849.

537 Stolper, E., 1982. The speciation of water in silicate melts. *Geochim, Cosmochim,*
 538 *Acta*, 46(12), 2609-2620.

539 Vennemann, T.W., O'Neil, J.R., 1996. Hydrogen isotope exchange reactions between
 540 hydrous minerals and molecular hydrogen: I. A new approach for the determination
 541 of hydrogen isotope fractionation at moderate temperatures. *Geochim. Cosmochim.*
 542 *Acta*, 60(13), 2437-2451.

543 Walrafen, G.E., Abebe, M., 1978. Raman studies of the bending and vibrational bands
 544 from water and ice VI to ~ 12 kbar at 32° C. *J. Chem. Phys.*, 68(10), 4694-4695.

545 Walrafen, G.E., Fisher, M.R., Hokmabadi, M.S., Yang, W.H., 1986. Temperature
 546 dependence of the low frequency and high- frequency Raman scattering from liquid
 547 water. *J. Chem. Phys.*, 85, 6970-6982.

- Wang, Y., Cody, S.X., Foustoukos, D., Mysen, B.O., Cody, G.D., 2015. Very large differences in intramolecular DH partitioning in hydrated silicate melts synthesized at upper mantle pressures and temperatures. *Amer. Mineral.*, 100(5-6), 1182-1189.
- Woltring, H.J., 1986. A FORTRAN package for generalized, cross-validatory spline smoothing and differentiation. *Adv. Eng. Softw.*, 8(2), 104-113.
- Xue, X., Kanzaki, M., 2009. Proton Distributions and Hydrogen Bonding in Crystalline and Glassy Hydrous Silicates and Related Inorganic Materials: Insights from High-Resolution Solid-State Nuclear Magnetic Resonance Spectroscopy. *J. Am. Ceram. Soc.*, 92(12), 2803-2830.

Tables

Table 1: Run data

Supfluid D/H ^a	<i>T</i> (°C) range	<i>P</i> (MPa) range	Phases present
0.05 ±0.02	750-700	715-495	Supercritical fluid
	680-400	496-187	Melt + fluid
0.13 ±0.04	650	741	Supercritical fluid
	550-350	484-350	Melt + fluid
0.42 ±0.01	800-650	1347-972	Supercritical fluid
	600-350	899-431	Melt + fluid
0.50 ±0.01	800-650	1115-860	Supercritical fluid
	600-350	849-248	Melt + fluid
0.93 ±0.01	800-700	1167-942	Supercritical fluid
	650-350	860-430	Melt + fluid
2.47 ±0.04	800-600	1500-819	Supercritical fluid
	565-300	686-262	Melt + fluid
2.68 ±0.06	800-650	858-626	Supercritical fluid
	630-350	592-313	Melt + fluid

^a Average D/H ratio in supercritical fluid

Table 2: Derived enthalpy change, ΔH (kJ/mol) of D/H ratios in melts and coexisting fluids, and of D/H partition coefficients between melt and coexisting fluid.

Supfluid D/H ^a	Pressure range (MPa) ^b	Temperature range (°C) ^b	ΔH_{melt} (kJ/mol)	ΔH_{fluid} (kJ/mol)	$\ln \alpha_{D/H \text{ fluid-melt}}$ at 500°C
<i>This study (NS3A5 glass)</i>					
0.05 ±0.02	496-192	680-400	7.99 ±5.08	2.58 ±1.51	0.32 ±0.28
0.13 ±0.04	484-374	550-450	28.38 ±2.00*	14.26 ±1.91*	0.23 ±0.06
0.42 ±0.01	431-899	600-350	5.07 ±1.49	-0.74 ±1.15	0.36 ±0.04
0.50 ±0.01	849-248	700-350	6.55 ±1.93	-0.09 ±0.14	0.24 ±0.04
0.93 ±0.01	860-430	650-350	8.12 ±0.35	0.40 ±0.49	0.36 ±0.03
2.47 ±0.04	686-403	565-300	6.92 ±0.61	-0.12 ±0.58	0.27 ±0.01
2.68 ±0.06	592-313	630-350	8.45 ±0.86	0.80 ±0.78	0.37 ±0.01
<i>Mysen (2013a; NS4 glass)</i>					
0.55 ±0.02	420-101	750-450	6.40 ±1.67	2.77 ±1.36	0.45 ±0.03 ^c
<i>Mysen (2013b; low density NS4A10 glass)</i>					
0.65 ±0.01	754-156	750-450	4.50 ±1.37	0.88 ±0.33	0.40 ±0.02 ^d
<i>Mysen (2013b; high density NS4A10 glass)</i>					
0.38 ±0.01	1271-562	725-425	1.58 ±1.61	-0.55 ±0.25	0.43 ± 0.05

^a Average D/H ratio in supercritical fluid

^b From phase exsolution temperature (Table 1) to the end of the experiment.

^c at 550°C

^d at 525°C

* large error on data

Figure captions

Figure 1. Photomicrograph of experiment $D/H_{\text{Supfluid}} = 2.47 \pm 0.04$, at 350°C and 313 MPa.

Figure 2. Pressure/temperature trajectories (starting at high P and T) of the six series of experiments with different D/H ratios in supercritical fluids.

Figure 3. Examples of signal processing of Raman spectra in the frequency region that encompasses OD and OH stretching vibrations of a silicate melt from the experiment with $D/H = 2.06 \pm 0.04$. The spectrum was recorded with the sample at 550°C and 572 MPa (where silicate melt and aqueous fluid coexist). A) shows the baseline correction of Raman spectra of the melt, i.e. combined signal of the silicate met and the HDAC diamond (red spectrum) and of the HDAC diamond (black spectrum) at high pressure and high temperature, and their baselines (dashed spline lines). B) shows the Raman spectra of the melt (red spectrum) and of the HDAC diamond (black spectrum) after baseline correction. C) presents the Raman spectrum of the melt after subtraction of the HDAC diamond signal and shows the area of OD and OH stretching bands (marked “OD” and “OH”).

Figure 4. Results of a time study that shows the D/H ratio in hydrous silicate melt as a function of experimental run duration (time) from experiments conducted at 550 °C and 779 MPa (dark green triangles) and at 350 °C and 431 MPa (light green triangles), with an average $D/H = 0.42 \pm 0.01$ in the supercritical fluid.

Figure 5. Examples of processed spectra in the frequency region that encompasses OD and OH stretching (A and B) and the temperature dependence of the D/H molar ratio deduced from Raman data (C and D), in green for the supercritical fluid, in blue for the aqueous fluid and in red for the aluminosilicate melt. A and C show the data for the experiment with a supercritical fluid D/H ratio of 0.50 ± 0.1 , and B and D present the data for the experiment with a supercritical fluid D/H ratio of 2.68 ± 0.4 . The ΔH are the exchange enthalpy deduced from the slope of the linear correlation between fluid or melt D/H molar ratio and the temperature following: $\ln D/H = b + mT$, where m is $\Delta H/R$, and R the gas constant.

Figure 6. Relationship between D/H fractionation factor ($\alpha_{\text{fluid-melt}}$) and temperature for all the experiments. For clarity, data are presented as $1000 \cdot \ln(\alpha_{\text{fluid-melt}})$ versus $10^6 \cdot T^{-2}$ (with T in Kelvin). It shows that the $1000 \cdot \ln(\alpha_{\text{fluid-melt}})$ dependence on temperature is similar (within error) for all experiments, regardless of the D/H ratio of the supercritical fluid. The black line is the linear regression on the data points (Eq. 3).

Figure 7. Temperature dependence of hydrogen isotope fractionation factors between aqueous fluid and melt (red circles; Mysen, 2013a, b and this study), H₂O-vapor and melt

(grey diamonds are $\text{NaAlSi}_3\text{O}_8$ glass from Richet et al., 1986) and H_2O -vapor and glasses
(dashed lines are water-poor feldspathic and rhyolitic – obsidian – glasses from Dobson
et al., 1989; black circles are basaltic andesite including respective water contents from
Pineau et al., 1998;).

Figure 1

Figure 2

Figure 3

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Figure 6

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811 Figure 7

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