H/D methane isotopologues dissolved in magmatic fluids: Stable hydrogen isotope fractionations in the Earth’s interior

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ABSTRACT

A series of hydrothermal diamond anvil cell experiments was conducted to evaluate the role of supercritical water on the isotopic equilibrium between H/D methane isotopologues at 600 – 800 °C and 409 – 1622 MPa. Raman spectroscopy was deployed to investigate the distribution of H/D isotopic molecules formed during hydrothermal decomposition of Si$_3$C$_{12}$H$_{36}$ in H$_2$O-D$_2$O aqueous solutions. To this end, the intensities of the fundamental vibrational C-H and C-D modes of deuteromethanes were employed to determine the thermodynamic properties of isotope exchange reactions between H/D isotopologues and to constrain the methane D/H molar ratios. By adjusting the initial volume ratios of silane/H$_2$O-D$_2$O, reactions in the CH$_4$-D$_2$O-H$_2$O system were monitored for gaseous and supercritical-water phases. Discreet differences of the equilibrium constants describing the relationship between the CH$_3$D-CH$_2$D$_2$-CHD$_3$-CH$_4$ species dissolved in supercritical water or present as a homogeneous gas phase are revealed. The bulk D/H methane composition in the liquid-system is also twice that of the D/H molar ratios recorded in the gas-bearing system. Accordingly, condensed-phase isotope effects are inferred to play a key role on the evolution of H/D isotopologues, likely induced by...
differences in the solubility of the isotopic molecules driven by the excess energy/entropy
developed during mixing of non-polar species in the H$_2$O-D$_2$O structure. Our experiments
show that isotope fractionation effects need to account for the presence of condensed
matter (e.g. melts, magmatic fluids), even at conditions at which theoretical models
suggest minimal (or nonexistent) isotope exchange, but comparable to those of the
Earth’s interior.
INTRODUCTION

Theoretical studies on the distribution between and the equilibrium relationships of isotopic molecules are commonly based on statistical mechanics models that calculate the partition functions (rotational, translational, vibrational) of the molecules by adopting a Wigner-Kirkwood free energy expansion (Kirkwood, 1934; Wigner, 1932) and by assuming simple harmonic oscillators (Bigeleisen and Mayer, 1947; Bottinga, 1969). These methods adopt ideal gas behavior between species with zero intermolecular forces, and thus, do not account for solubility, molar volume, and vapor pressure induced fractionations imposed by intermolecular interactions with condensed phases such as, for example, supercritical water (Bacsik et al., 2002; Chialvo and Horita, 2003; Gomes and Grolier, 2001; Jancso et al., 1993; Muccitelli and Wen, 1978; Van Hook, 2006). Condensed-phase isotope effects are attributed to the free energy differences between the condensed and gas phase (Van Hook, 2006) as reflected, for example, in differences on the solution properties (e.g. Henry’s/Raoult’s law) and/or the temperature and pressure dependence of isotopologues’s vapor pressure and partial molar volumes (Bigeleisen, 2006; Herzfeld and Teller, 1938).

Silicate melts and coexisting magmatic fluids represent the condensed phases present in the Earth’s interior. Determining the solubility and solution mechanisms of volatiles (e.g. H$_2$O, H$_2$, CO$_2$, CH$_4$,) in these phases is essential to constrain the melting and crystallization processes. Advances in our current understanding of stable isotope fractionations (e.g. $^{18}$O/$^{16}$O, $^{13}$C/$^{12}$C, D/H, $^{15}$N/$^{14}$N) under temperature and pressure conditions corresponding to lower crustal-/upper mantle conditions, and how this behavior can be related to structural roles of C-O-H-N-bearing volatiles in fluids and...
melts have significant implications for the development of isotope proxies to describe the water cycle and to model elemental fluxes between different sources and sinks in the Earth’s interior.

To investigate the role played by the condensed state on the isotope exchange reactions between deuterated and protonated molecules, Raman vibrational spectroscopy is an effective probe because of the large frequency separation of the D- and H- bearing functional groups [a factor of $1/\sqrt{2}$ (reduced mass effect)]. Accordingly, by combining Raman vibrational spectroscopy with experimental designs that allow in-situ monitoring of chemical processes at high temperatures and pressures (>600 °C, >300 MPa) (Bassett et al., 1996), D/H exchange between functional groups can be determined as a function of temperature and pressure. Thus, volume, enthalpy and entropy effects on isotopic distribution can be examined while the samples are at the desired temperature and pressure. For example, recent studies have shed light on the role of hydrogen bonding on the distribution of deuterated hydrogen dissolved in (D$_2$O+H$_2$O) aqueous solutions (Foustoukos and Mysen, 2012). These latter experiments were conducted at 300 – 800 °C and pressures between ~ 0.3 and 1.3 GPa and show significant deviation of the H$_2$-D$_2$-HD equilibrium relationship from the theoretical values predicted for gas phases (Bigeleisen and Mayer, 1947; Richet et al., 1977). There was also an apparent negative temperature effect possibly triggered by enthalpy contributions due to mixing of these species in supercritical water. This behavior has been attributed to differences in the strength of hydrogen bonding in the O-H···O relative to the O-D···O environment that could promote species solubility in dense and polar H$_2$O clusters. In turn, this affects the thermodynamic
properties of exchange reactions between the H/D hydrogen isotopologues and the coexisting H₂O-D₂O aqueous solutions.

Similar use of Raman spectroscopy can also be applied to study the D/H fractionation of (C-H)-bearing volatiles dissolved in supercritical fluids. For example, the multiple C-H bonds in methane allow for partial deuterium substitutions and result in the formation of deuterated isotopologues such as CH₃D, CH₂D₂, CHD₃, and CD₄. To the knowledge of the authors, only one theoretical study has been published to predict the equilibrium relationships between the different H/D isotopologues of methane and to model the stable hydrogen isotope fractionation of CH₄ with H₂O and H₂ over a range of temperatures (Bottinga, 1969). Experimental investigation of these isotopic molecules while a sample is at high temperature/-pressure, therefore, can provide ways to describe exchange reactions at conditions beyond those described in theoretical models. Such experiments lead to improved understanding of D/H fractionation effects in condensed matter (e.g. melts, fluids) at conditions relevant to the Earth’s mantle.

Here, we examine the equilibrium relationships of the several H/D isotopologues of methane (i.e. CH₃D, CHD₃, CH₂D₂, CD₄) and evaluate the D/H molar ratios of methane developed under gas and condensed-phase (supercritical water) conditions, through a series of hydrothermal diamond anvil cell experiments conducted at 600 – 800 °C and 409 - 1622 MPa, while employing Raman vibrational spectroscopy as the analytical tool to trace reaction kinetics and pathways in-situ at elevated temperatures and pressures.
EXPERIMENTAL SECTION

Hydrothermal Diamond Anvil Cell. Experiments were performed with an externally-heated hydrothermal diamond anvil cell (HDAC) (Bassett et al., 1996). The cell was equipped with low-fluorescence 1-mm culet diamonds. Samples were held between the anvil faces with a 125 µm thick rhenium gasket (500 µm diameter sample chamber). Prior to the actual experiments, a series of runs was conducted at 800 °C and 0.5 - 0.8 GPa with only H₂O in the cell to treat the gaskets hydrothermally. This procedure leads to the formation of a layer of inert Re oxide on the surface of the Re metal. Temperature was monitored and adjusted with chromel-alumel thermocouples in contact with the upper and lower diamonds. External heating was provided by Mo wire heaters placed around the tungsten carbide seats, and it was distributed homogeneously across and through the whole sample chamber (±1 °C accuracy). Pressure was derived by measuring the temperature/pressure dependent Raman frequency shift of synthetic ¹³C diamond (Schiferl et al., 1997), with an uncertainty of about ±40 MPa (Mysen and Yamashita, 2010). This level of accuracy is achieved by performing acquisitions at 2400 grooves/mm and then normalizing to the 584.72 nm Ne emission line; a protocol that yields a ± 0.1 cm⁻¹ frequency uncertainty on the fundamental band of the ¹³C diamond (Mysen and Yamashita, 2010).

Raman Spectroscopy Instrumentation. A Jasco model IRS-3100 confocal microRaman spectrometer was used with a λₑₓ = 532 nm continuous wave laser line operating at ~7 mW at the sample. The beam diameter is nearly 1 µm. Signal detection was through 50X/0.42 numerical aperture (N.A.) and 10X/0.28 N.A. long-working distance.
Mitutoyo™ objective lenses. Raman signal was dispersed using 1200 grooves/mm and
with the spectral window centered at 1150 cm⁻¹, 2400 cm⁻¹ and 3600 cm⁻¹; and collected
with a Peltier-cooled CCD (Andor™ Model DV401-F1 1024x128 pixel with 25 μm pixel
size) with a frequency resolution of 1-2 cm⁻¹. The system is equipped with a holographic
notch filter. Acquisition time ranged from 150 (in-situ measurements) to 300 (quenched
samples) sec/CCD window, and 2 acquisitions per window were collected.

Curve-fitting and background subtraction of the Raman spectra were orchestrated
using the commercial software Igor from Wavemetrics™. Background subtraction was
conducted prior to peak integration by fitting a third-order polynomial function through
portions of the spectra with baseline signal intensity only. To constrain further the extent
of uncertainty on spectra analysis and processing, replicate acquisitions (2-4) were
performed at the same beam spot and with the same instrumental parameters. The
standard deviation between the fitted Raman spectra reflects a 5% level of uncertainty,
which is larger than the uncertainty estimated for the integrated area of each individual
Raman peak. In the Raman spectra shown, the second-order Raman signal of the \(^{12}\text{C}\)
diamond anvils (~ 2300 - 2800 cm⁻¹) was removed by subtracting the background
spectrum measured on the lower diamond and outside the sample gasket-chamber at the
corresponding temperature and pressure.

Experimental Procedures. The experiments were designed to yield deuteromethane
species through decomposition of \(\text{Si}_2\text{C}_{12}\text{H}_{36}\) (tetrakis(trimethylsilyl) silane (Alfa Aesar
98% - natural D/H abundance) under both supercritical water and gas phase conditions.
The study was carried out at temperatures of 600-800 °C and pressures of 409-1622 MPa.
The sample consisted of H$_2$O:D$_2$O (1:1 by volume) aqueous solutions with either metallic Ni (Alfa Aesar, Puratronic 99.996%, <100 μm diameter grain) or metallic Pt (100 μm x 70μm OD rod) with no specific in-plane crystal orientation (e.g. Ni(111), Pt(111)) (Table 1) (Fig. 1). Complete decomposition of Si$_5$C$_{12}$H$_{36}$ resulting in the formation of volatiles such as H$_2$, D$_2$, HD, CH$_4$, CH$_3$D, CHD$_3$, CH$_2$D$_2$ and CD$_4$ along with the precipitation of quartz (SiO$_2(s)$), occurs within 5 min at 600 °C (Si$_5$C$_{12}$H$_{36}$ + 10H$_2$O/D$_2$O = 5SiO$_2$ + 12CH$_x$D$_y$ + 4H$_x$D$_y$). In effect, decomposition of Si$_5$C$_{12}$H$_{36}$ with the use of highly enriched in D$_2$O aqueous solutions allows for the synthesis of deuterated methane species at abundances that permit quantification with spectroscopic methods. During this initial, short stage of silane decomposition and deuterated isomers formation by methyl radical reaction with the aqueous solution, kinetic isotope effects can be introduced. However, time series measurements, in-situ at high temperature/-pressure, indicate that chemical/isotopic equilibrium was reached within nearly 2 hours (at 600 and 800 °C) (see more detail later in discussion), due to the enhanced kinetics of the exchange reactions that proceed at the surface of either Ni or Pt (Beck et al., 2003; Horita, 1988; McKee and Norton, 1964).

An important component of the experimental design is the abundance of starting Si$_5$C$_{12}$H$_{36}$ relative to the volume of H$_2$O-D$_2$O solution encapsulated between the Re gasket and the diamond culets. Two distinctly different sets of experiments (“gas phase” and “liquid phase”) were conducted by adjusting the silane/water proportions based on volumetric approximations. For example, use of elevated silane/water initial ratios resulted in the removal of H$_2$O through SiO$_2(s)$ precipitation at high temperature and the establishment of gas phase conditions. When smaller amounts of silane were used, less...
H/D-bearing methane species were produced and remained dissolved in the supercritical aqueous solution. These processes were documented by *in-situ* visual observation of the reaction progress (and the extent of quartz precipitation) (Fig. 1), and by monitoring the relative abundance of the coexisting fluid through the evolution of the O-H stretching band (~3600 cm⁻¹).

The Raman spectra of aqueous and gaseous species were recorded at the desired temperature/-pressure conditions and also in samples quenched to ambient conditions ("ex-situ"). Quenching was orchestrated at a rate of ~600 °C/min until the temperature reached 100 °C, and then at 25 °C /min to room temperature. During quenching and for the "liquid phase" experiments, phase separation (degassing) occurred leaving the H/D isotopologues of CH₄ and H₂ trapped in the gaseous phase ("bubble") (Fig. 2). The absence of the Raman lines assigned to the fundamental vibrational modes of HDO and D₂O at ~2400 – 2600 cm⁻¹ (Foustoukos and Mysen, 2012; Walrafen et al., 1996) (revealed after subtracting the v₂ lines of diamond) is consistent with spectroscopic measurements on an *ex-situ* bubble. Slower rates of quenching (10 °C/min) were also applied to determine accurately the temperature and pressure of gas-liquid phase separation. At these conditions, the partial pressure of volatiles is equal to the confined pressure in the HDAC, and thus, total dissolved methane concentrations (ΣCH₄ = CH₄ + CD₄ + CH₃D + CH₂D₂ + CHD₃) (Table 1) can be retrieved from the solubility relationship: ΣCH₄(g) ↔ ΣCH₄(aq). The equilibrium constant of this reaction is calculated at high temperature/-pressure by using the Helgeson-Kirkham-Flowers equation of state and the SUPCRT92 code that are applicable to 1000 °C and 500 MPa, effectively extrapolated to 1 GPa (Johnson et al., 1992b; Manning, 1998; Shock and Helgeson,
The concentrations of the dissolved H/D hydrogen isotopologues appear to be minimal (but present) relative to methane (Fig. 2b) because of the relatively oxidizing redox conditions imposed by hydrothermal oxidation of Ni and Pt metals in H₂O-D₂O solutions. Manifestation of oxidizing conditions was also demonstrated by the formation of CO₂(aq) and the precipitation of amorphous graphitic carbon at 800 °C (Table 1).

Solution density is calculated following the PVT data of pure H₂O (Wagner and Pruss, 2002) applied to the homogenization conditions, while assuming minimal solubility for the crystalline phases (Ni, Pt, SiO₂(s)) (Johnson et al., 1992b; Robie and Hemingway, 1995).

RESULTS AND DISCUSSION

Spectroscopic data were collected mainly from the two frequency regions of 1560 – 3140 cm⁻¹ and 2900 – 4220 cm⁻¹ (1200 grooves/mm) where several vibration modes of the D- containing isotope molecules of CH₄ and H₂ are captured (Fig. 2). These species were identified both in-situ and in the quenched samples. The Raman spectra acquired from quenched bubbles allowed a detailed estimation of the relative abundances of the deuterated methane isotopologues (Fig. 2a). The bands assigned to stretch vibrations in these species are narrow (5-10 cm⁻¹ FWHH) and well defined, relative to those registered during spectral acquisition at high-temperature/-pressure conditions.

The 2000 - 2400 cm⁻¹ frequency envelope accommodates the bands of the asymmetric stretching and bending vibrations of the CHD₃ (2134 cm⁻¹, 2305 cm⁻¹), CH₃D - CH₂D₂ (~2190 cm⁻¹) and the C-D fundamental mode of the CD₄ molecule (2098 cm⁻¹) (Fig. 2a). However, because of the strong baseline correction introduced by subtracting
the complex group of bands assigned to the second-order vibration of the diamond anvils (~ 2300-2800 cm\(^{-1}\)) from sample signal(s), the integrated peak areas of these bands have large uncertainties. Their intensities cannot be used, therefore, to describe equilibrium relationships between the isotopologues. For this purpose, we employ the fundamental harmonics at the slightly higher frequencies of 2905 cm\(^{-1}\) (CH\(_4\)), 2961 cm\(^{-1}\) (CH\(_3\)D), 2966 cm\(^{-1}\) (CH\(_2\)D\(_2\)) and 2984 cm\(^{-1}\) (CHD\(_3\)). Vibrational assignments are in agreement with the values reported in the experimental study of Kagel (1964) and the review article of Schötter and Klöckner (1979) at room-temperature conditions, and internally consistent with the correlation between peak intensities and the Raman scattering cross sections for the different vibrational modes of the molecules of interest (Table 2) (Kagel, 1964; Schrotter and Klockner, 1979). Within the same spectral window, the fundamental vibrations of C\(_2\)H\(_6\) and C\(_3\)H\(_8\) also reside. These carbon-bearing species could possibly be formed by polymerization of the methyl radicals at high temperature (Spanu et al., 2011).

However, in preliminary experiments involving Si\(_5\)C\(_{12}\)H\(_{36}\) decomposition in H\(_2\)O solution at 600 °C, we did not observe their symmetric C-H and C-C vibrational bands at 2950-2990 cm\(^{-1}\) and 870-995 cm\(^{-1}\), respectively (Atamas et al., 2004; Shimanouchi, 1972), concluding, therefore, that long chain hydrocarbons (< 100 μmolal (Foustoukos, 2010)) were undetectable in our experimental setup.

From the overall intensity relationships, the distribution of the deuteromethanes suggests that deuterium enrichment was enhanced when dissolved in supercritical water than when present as gas phase components (Fig. 2a). This could be attributed to the D/H fractionation between methane and the coexisting H\(_2\) or H\(_2\)O, however, the former is highly improbable due to the significantly lower concentrations of hydrogen relative to...
methane (Fig. 2b). Another hypothesis involves the introduction of kinetic isotopic
effects during high temperature/-pressure quenching and the subsequent phase
segregation of volatiles from the supercritical fluid (liquid-phase experiments). To assess
the contribution from such processes, a series of Pt- supercritical water- bearing
experiments were quenched to room temperature after being equilibrated at 600 °C –
1093 MPa and 800 °C – 1050 MPa for 480 and 540 minutes, respectively. The samples
were then immediately exposed to a second heating cycle that lasted for two hours. The
second series of temperature-quenching was at 55 °C/min as compared with the initial of
600 °C/min. Comparison between the Raman spectra of the quenched bubbles from two
individual liquid-phase bearing HDAC experiments that underwent two heating cycles
reveals no differences on the relative distribution of CHxDy species (Fig. 3). There is,
therefore, no evidence for retrograde reactions and kinetic isotope effects associated with
phase segregation during quenching of the high temperature/-pressure chemical
equilibrium to room temperature conditions.

Distribution of deuterated methane isotopologues

Ex-situ Samples: The spectral region between ~2800 – 3100 cm⁻¹ that includes the
fundamental frequencies of CH₄, CH₃D, CH₂D₂ and CHD₃ (Fig. 4), allows for a detailed
examination of the equilibrium relationships between the isotopologues. In spectra of the
quenched bubbles, for example, there are well-defined peaks that can be de-convoluted
following Lorentzian (CH₄, CH₃D) and Gaussian (CH₂D₂) functions. Peak integration for
the tri-deuterated methane was carried out with both Gaussian and Lorentzian peak
shapes. Thus, subsequent comparison between the integrated intensities of the ν₁-CHₓDₓ
includes the average values of the \( v_1 \)-CHD\(_3 \) peak area following these two fitting
distributions. Attempts to introduce the stretching vibrational mode of D\(_2 \) in the
frequency spectrum of the \( v_1 \)-CHD\(_3 \) (\( \sim 2970\text{-}2985 \text{ cm}^{-1} \)) failed, largely because the \( v_1 \)-D\(_2 \)
intensity is inferred to be very small due to the low abundance of H\(_2 \) and HD (Fig. 2)
combined with the small Raman scattering cross section of the D\(_2 \) relative to the other
hydrogen species (Bischel and Black, 1983; Polavarapu, 1990; Schrotter and Klockner,
1979).

The distribution of the H/D methane isotopologues calculated from the integrated
peak areas follows a general abundance order of CH\(_4\)>CH\(_3\)D>CH\(_2\)D\(_2\)>CHD\(_3\). This trend
is consistent with other experimental results of Pt-supported H-D exchange reaction
between methane and deuterium at elevated temperatures (McKee and Norton, 1964),
and also is in accord with the overall kinetic isotope effect expected from the higher
activation energy required for C-D bond formation relative to the C-H bond (Anslyn and
Dougherty, 2006).

**In-situ Samples:** For the spectra collected at high temperature/-pressure conditions, the
rapid broadening of the Raman lines and the decrease of spectral resolution with
increasing temperature (due to black body radiation) resulted in an extensive overlapping
and interference between the isotopologues. Black body radiation is transmitted from the
furnace and sample when at temperature higher than 600 °C, causing signal deterioration
and an increase of the background intensity. In addition, an overall decrease on the
intensities of the CH\(_x\)D\(_y\) (i.e. deuteromethanes) vibrations is expected when species are
dissolved in the supercritical H\(_2\)O-D\(_2\)O fluid.
To this end, peak de-convolution was performed by fitting Lorentzian curves assigned to the symmetric C-H stretching vibration of methane and to the frequency envelope that encloses the stretching vibrations of the other CHₓDₙ species (Fig. 4). These in-situ measurements permit monitoring of reaction progress towards establishing chemical/isotopic equilibrium in the H₂O-D₂O-CH₄ system, while providing information regarding the condensed-phase isotope effects associated with the solvation of the H/D isotopologues in supercritical aqueous solutions.

To probe isotopic fractionations at experimental conditions, we employed the ratio between the integrated intensities of the Raman bands assigned to the H/D-isotopologue frequency envelope (v₁-CHₓDₙ) and the C-H stretching of non-deuterated methane (v₁-CH₄) as a function of time (Fig. 5). From these results, we conclude that chemical/isotopic equilibrium was achieved within 2 hours, largely induced by the catalytic activities of Ni and Pt, which are enhanced at elevated surface thermal energy (Harris et al., 1991; Lutz and Bethune, 1989). There are also abundant concentrations of deuterated species in the liquid-phase system with the retrieved CHₓDₙ/CH₄ intensity area ratios being nearly twice that in the gas-bearing system. Furthermore, platinum is shown to more efficiently promote the H/D exchange between C-H and C-D bonds than Ni. This observation is in agreement with previously published experimental and theoretical studies that support the greater probability of hydrogen/deuterium atoms to exchange when methyl groups bind on the Pt surface relative to when chemisorption occurs on Ni substrate (McKee and Norton, 1964; Nave et al., 2010). Experimental methodologies adopted, however, cannot provide further information regarding the CH₃- dissociative absorption on catalyst’s surface nor the mechanism of isotope exchange reactions/
diffusion (Wonchoba and Truhlar, 1996) associated with H and D atoms embedded in the metal lattice (Johnson et al., 1992a; Killelea et al., 2008; Wonchoba and Truhlar, 1998).

**Condensed Phase Isotope Effects**

Results indicative of increased deuteration of methane when dissolved in supercritical water were also obtained from interpreting Raman vibrational spectra collected ex-situ at 25 °C (Fig. 6a). This was accomplished by combining the integrated peak areas (Fig. 4) with the well-constrained relative normalized differential Raman scattering cross sections ($\sigma_j$) of the stretch vibrations (Table 2). Species concentrations are then considered proportional to the quotient of the integrated Raman peak areas ($A_j$) with ($\sigma_j$) assuming that the force constants are the same for the fundamental vibrational modes of $\text{CH}_x\text{D}_y$ when instrumental parameters are constant (Kagel, 1964). Accordingly, the D/H molar composition of methane can be defined as such:

$$
\frac{D}{H} = \frac{\sum_{n=3}^{3} \frac{A_j \text{CH}_4-n\text{D}_n}{\sigma_j} + \frac{A_{\text{CD}_4}}{\sigma_{\text{CD}_4}}}{A_{\text{CH}_4} / \sigma_{\text{CH}_4}}
$$

Integrated area contributions from the Lorentzian peak shape of $v_1\text{-CD}_4$ (2098 cm$^{-1}$) are included because D/H molar ratios estimated with or without this factor exhibit the same mean values and range of uncertainties.

Experimental results demonstrate that the D/H molar composition of methane is increased by a factor of 2 in the liquid-bearing experiments compared with the gas-bearing system (Fig. 6a) (Table 3). Obvious also is the effectiveness of Pt over Ni as catalyst for the reconstruction of the C-H and C-D bonds, and for possible tunneling of hydrogen during chemisorption of methyl radical on hot metal surfaces (Harris et al.,...
Thermal vibrational energy provided by excitation of the fundamental stretch of the C-H/D bonds could also promote the reaction between H- and deuterated methyl radicals through bond cleavage (Beck et al., 2003; Crim, 2008). However, a decrease in activation barriers with increasing temperature of coexisting compounds (methane, metal) is expected to drive the process (Lutz and Bethune, 1989), especially for the low-power laser beam (7 mW) deployed. The effect of externally imposed thermal energy on D/H exchange reactions can also be inferred from the slight increase of the methane D/H molar ratios when shifting thermal conditions from 600 to 800 °C (Fig. 6a).

Kinetic isotope effects associated with hydrogen isotope fractionation between methane and water fluid could also explain the higher D/H ratio of the methane when dissolved in supercritical D₂O-H₂O aqueous solutions compared with the D/H ratio of the methane in the gas phase system. In addition, kinetic isotope effects can be introduced by the reforming of deuterated isomers on the catalyst surface. To evaluate such possible effects, the equilibrium relationship between the methane isotopologues was studied through the following reaction:

$$\text{CH}_3\text{D} + \text{CH}_2\text{D}_2 \rightarrow \text{CHD}_3 + \text{CH}_4 \quad (2)$$

By utilizing the vibrational characteristics of the different species (i.e. $A_j$ and $\sigma_j$) and by assuming that the activity of neutral species is equal to their concentration under homogeneous gas phase conditions and for a non-electrolyte mixture of H₂O-D₂O, the equilibrium constant of this reaction is expressed as:

$$K_{eq}(\text{CH}_4y\text{D}_y - \text{CH}_4) = \frac{A_{\text{CH}_4}^* A_{\text{CH}_3\text{D}_y}^*}{A_{\text{CH}_4\text{D}_y}^* A_{\text{CH}_3\text{D}_2}^*} \frac{\sigma_{\text{CH}_3\text{D}_y}^* \sigma_{\text{CH}_3\text{D}_2}^*}{\sigma_{\text{CH}_4}^* \sigma_{\text{CHD}_3}^*} \quad (3)$$

For the C-H-D system in supercritical H₂O+D₂O at 873-1073 K (Fig. 6b), estimated $K_{eq}$ values range from 0.42 ± 0.07 (Ni) to 0.59 ± 0.12 (Pt), corresponding to $\Delta G_{\text{rxn}}$ of 7.1 ±
1.4 and 4.3 ± 1.7 kJ/mol, respectively (Table 3). Differences on the estimated $K_{eq}$ are within analytical uncertainties, and likely reflect the greater efficiency of Pt over Ni in promoting D/H isotope exchange reactions (Beck et al., 2003; Horita, 1988; McKee and Norton, 1964; Nave et al., 2010). This observation does not preclude the establishment of equilibrium conditions supported by the *in-situ* time series measurements conducted at the course of the Pt-bearing experiments (Fig. 4). It also appears to be an exothermic reaction, however, the possible temperature dependence of the equilibrium constant may be somewhat obscured by the analytical errors introduced after adopting the combination of Lorentzian and Gaussian functions (Fig. 4) and the vigorous analytical/peak integration protocols discussed earlier.

When these values are compared to those derived for the gas-bearing system, the role of supercritical water in affecting the equilibrium between H/D methane isotopologues is evident (Fig. 6b). In effect, $K_{eq}$ is shifted to 0.27 ± 0.04, reflecting a $\Delta G_{\text{rxn}}$ of 10.7 ± 1.1 kJ/mol and minimal differences between the Ni- and Pt-catalyzed experiments. Interestingly, these values are in close agreement with theoretical calculations ($K_{eq} = 0.16$) conducted following standard state canonical partition functions and conditions of ideal gas mixing (Bottinga, 1969); a conclusion that furthers supports the establishment of chemical/isotopic equilibrium in these experiments. Most importantly, the different thermodynamic properties of the equilibrium relationship between H/D methane isotopologues attained for the gas- and liquid- phase system, allow us to decouple possible kinetic isotope effects linked to the D/H fractionation between CH$_4$ and H$_2$O with the extensive deuteration of methane observed in the liquid-bearing
experiments, and thus, focus on solvation effects in the condensed supercritical-fluid phase.

Considering all of the above, the differences on the extent of D/H exchange and the H/D isotopologues’ distribution between the gas- and supercritical-fluid bearing systems are attributed to condensed-phase isotope effects. Such processes can involve changes in solubility induced by differences in Henry’s law constants of the deuterium-substituted isotopologues reflecting different standard-state free energies of solvation for infinite dilution in the H₂O-D₂O cage (Bacsik et al., 2002; Chamberlin et al., 2006; Gomes and Grolier, 2001). These effects are, in general, introduced when excess Gibbs free energy of mixing is developed due to the presence of intermolecular interactions between C-H-D species and the hydrogen bonded to H₂O/D₂O molecules (Jancso et al., 1993; Van Hook, 2006). Here, differences in the strength of the O-D···D and O-H···H bonds can influence the solvent properties of the D₂O-H₂O mixtures. In essence, titration of H₂O-D₂O solutions and the formation of HDO through the endothermic reaction between H₂O-D₂O has been proposed to rearrange the H and D bonding environment (Graziano, 2000; Katsir et al., 2010), resulting in excess entropy costs for the solvation of non-polar molecules in D₂O-H₂O. Furthermore, evidence exists for a temperature dependent distribution of O-D···D and O-H···H bonds in supercritical fluids driven by the increasingly stronger hydrogen bonding in H₂O relative to D₂O with temperature increase (Erickson et al., 2011; Foustoukos and Mysen, 2012). Accordingly, contributions from isotope effects governed by the solvent because of the employment of D₂O-enriched aqueous solutions cannot be excluded.
D/H FRACTIONATIONS IN THE EARTH’S INTERIOR

Experimental results presented support extensive hydrogen isotope fractionation at high temperatures/-pressures when methane is dissolved in the condensed supercritical water phase relative to systems adopting ideal gas behavior. At such thermal conditions, statistical thermodynamic models predict small isotope effects following vibrational zero point energy distributions and high temperature anharmonicity contributions for isotopic molecules in ideal-gas reference state (Bottinga, 1969). These models, however, do not account for solubility and solvent isotope effects associated with the solvation of H/D methane isotopologues in supercritical aqueous solutions and/or silicate melts. The theory of condensed-phase isotope effect follows the same Born-Oppenheimer approximation as the canonical approach for calculating the potential energy surface of the isotopic molecules, but also includes inputs from intermolecular forces developed in the condensed phase to the shape and the kinetic energy of the potential energy surface (Van Hook, 2006). In our study, the in-situ and ex-situ spectroscopic measurements of deuterated methane species coexisting with supercritical water suggest a significant contribution from condensed-phase isotope effects, rendering essential any further theoretical studies to assess the atomistic details of the D/H fractionation mechanisms in aqueous solutions (and silicate melts) at elevated temperature/-pressure conditions.

Condensed-phase isotope effects are expected to play a significant role on the distribution of deuterium and hydrogen species between C-O-H-N-saturated melts and coexisting fluids (Mysen, 2012), since this distribution can be affected by the abundance ratios of the different C, N and H-bearing structural complexes in the equilibrated phases (Hirschmann et al., 2012; Mysen and Fogel, 2010; Mysen et al., 2009). These structural
complexes in melt formed upon solution of H-bearing species likely contribute to the D/H budget of the mantle and the isotopic composition of evolved magmatic fluids (Kasting et al., 1993; Mattey et al., 1990).

For example, isotope fractionation effects between phases coexisting in Earth’s interior likely constrain the observed D/H disequilibrium between mantle and oceanic H2O reservoir, as well as the subduction zone contributions to the mantle-water cycle (Hauri, 2002; Shaw et al., 2008) (and references therein). The disequilibrium relationships between water reservoirs imply that cycling of water in the mantle is not extensive and/or hydrogen isotope fractionation effects are imposed between the oceanic water and the amorphous/crystalline phases of the Earth’s interior (Shaw et al., 2008).

Magmatic degassing of C-O-H-N volatiles during magma ascent and the subsolidus dehydration of hydrous minerals are also expected to induce hydrogen fractionation effects between fluids and mineral phases (Suzuoki and Epstein, 1976; Taylor et al., 1983). Molecular water appears to concentrate deuterium relative to silicate melts/minerals, while the dehydration of OH from minerals likely yields to a decrease in both D and water content (Suzuoki and Epstein, 1976). Degassing of CH4 and H2 from a magma that contains small amounts of H2O can also result in significant changes in the δD of melt (Kyser and Oneil, 1984), driven by the possible large D/H fractionation factors between CH4 and H2 with H2O at high temperatures. Accordingly, further studies are needed to constrain the fundamental mechanisms of stable isotope fractionation between C-O-H-N species and functional groups dissolved in phases and at conditions resembling those of the Earth’s interior.
ACKNOWLEDGMENTS

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Table 2. Relative normalized differential Raman scattering cross sections of the fundamental vibrational frequencies of D-H isotopologues normalized to the value of the CH$_4$ molecule (25 °C)

<table>
<thead>
<tr>
<th>Component</th>
<th>$\sigma_i$ ((\sigma_{\text{CH}_4} = 1))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$D</td>
<td>0.75</td>
<td>Schrötter and Klöckner (1979), Bermejo et al. (1977)</td>
</tr>
<tr>
<td>CH$_2$D$_2$</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>CHD$_3$</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>CD$_4$</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>CH$_3$D</td>
<td>0.78</td>
<td>Kagel (1964)</td>
</tr>
<tr>
<td>CH$_2$D$_2$</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>CHD$_3$</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>CD$_4$</td>
<td>0.71</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Temperature and pressure of the gas-liquid phase homogenization/separation. At these conditions, dissolved volatile species separate from the supercritical fluid forming a gas phase. $^b$ Precipitation of amorphous graphitic carbon was documented in the retrieved solid reaction products by the strong presence of the D (~ 1325 cm$^{-1}$) and G (~ 1570 cm$^{-1}$) bands accompanied by their second-order overtone and combination scattering at 2670 cm$^{-1}$ ($S_1$) and 2910 cm$^{-1}$ ($S_2$). $^c$ Spectroscopic evidence for the formation of CO$_2$ in both the high temperature/-pressure and quenched samples is the presence of frequency splitting of the $v_1$:2$v_2$ Fermi diad at 1275 cm$^{-1}$ and 1378 cm$^{-1}$.
Table 3. Thermodynamic properties estimated for the CH$_3$D + CH$_2$D$_2$ → CHD$_3$ + CH$_4$ reaction from ex-situ measurements

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>Metal</th>
<th>$K_{eq}$</th>
<th>$\Delta G_r$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gas phase experiments</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>577 ± 2</td>
<td>Ni</td>
<td>0.31 ± 0.05</td>
<td>8.6 ± 1.2</td>
</tr>
<tr>
<td>800</td>
<td>758 ± 99</td>
<td>Ni</td>
<td>0.26 ± 0.02</td>
<td>12.2 ± 0.7</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td>0.28 ± 0.04</td>
<td>10.4 ± 1.0</td>
</tr>
<tr>
<td>600</td>
<td>514 ± 18</td>
<td>Pt</td>
<td>0.27 ± 0.04</td>
<td>9.5 ± 1.2</td>
</tr>
<tr>
<td>800</td>
<td>1105 ± 182</td>
<td>Pt</td>
<td>0.25 ± 0.04</td>
<td>12.5 ± 1.3</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td>0.26 ± 0.04</td>
<td>11.0 ± 1.2</td>
</tr>
<tr>
<td><strong>Liquid phase experiments</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>409 ± 26</td>
<td>Ni</td>
<td>0.43 ± 0.08</td>
<td>6.1 ± 1.4</td>
</tr>
<tr>
<td>800</td>
<td>1622 ± 131</td>
<td>Ni</td>
<td>0.40 ± 0.06</td>
<td>8.2 ± 1.4</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td>0.42 ± 0.07</td>
<td>7.1 ± 1.4</td>
</tr>
<tr>
<td>600</td>
<td>1093 ± 157</td>
<td>Pt</td>
<td>0.60 ± 0.11</td>
<td>3.7 ± 1.3</td>
</tr>
<tr>
<td>800</td>
<td>1050 ± 157</td>
<td>Pt</td>
<td>0.58 ± 0.13</td>
<td>4.9 ± 2.0</td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td>0.59 ± 0.12</td>
<td>4.3 ± 1.7</td>
</tr>
</tbody>
</table>
Figure 1. Microphotographs depicting phases involved in the high temperature/-pressure HDAC experiments. Hydrothermal decomposition of Si$_2$C$_{12}$H$_{36}$ in D$_2$O-H$_2$O aqueous solution and in the presence of metal catalyst (Ni, Pt) resulted to the formation of H/D methane isotopologues, and the precipitation of SiO$_2$(s).
Figure 2. Examples of Raman spectra collected in samples quenched from high temperature/-pressure conditions. Degassing processes induced during quenching allow the formation of gas bubbles that contain H/D isotopologues of methane (a) and hydrogen (b).
Figure 3. Vibrational spectra collected in samples from two district liquid-phase (Pt) HDAC experiments at 600 °C and 800 °C that were subjected to two heating cycles and then quenched at two different rates. Peak assignments are comparable to those shown in figure 2a.
Figure 4. Examples of curved-fitted Raman spectra recorded within the 2800 – 3100 cm$^{-1}$ frequency region that encompasses the fundamental frequencies of CH$_4$, CH$_3$D, CH$_2$D$_2$ and CHD$_3$. 
Figure 5. Times series measurements conducted in-situ at high temperature/-pressure and in the presence of either Ni (a) or Pt (b) metal catalyst to describe the evolution of the ratio between the integrated peak areas of the frequency envelope that encompasses the $v_1$-CH$_3$D$_y$ and the stretching vibrational mode of CH$_4$. 
Figure 6. (a) The D/H molar ratios of methane measured in quenched samples as a function of the temperature, the metal catalyst and the phases present. Uncertainties shown reflect the standard deviation between ratios estimated with/without contributions from the ν₁-CD₄. (b) The relationship between isotopologues is examined through the equilibrium constant of the reaction: CH₃D + CH₂D₂ → CHD₃ + CH₄. Experimental data are compared to statistical models developed for ideal-gas reference state (Bottinga, 1969). Estimated errors correspond to the different integrated peak areas calculated through a combination of Lorentzian and Gaussian functions for the de-convolution of the CHₓDᵧ frequency envelope at 2900 - 2990 cm⁻¹.
REFERENCES SITED


Nave, S., Tiwari, K.A., and Jackson, B. (2010) Methane dissociation and adsorption on Ni(111), Pt(111), Ni(100), Pt(100) and Pt(100)-(1x2): Energetic study. The Journal of Chemical Physics, 132, 054705.


Fluid

Re

Qtz

Pt

50X/0.42 N.A.

600 °C - 1.1 GPa

10X/0.28 N.A.
a) 
Pt: 600 °C - 514/1093 MPa
quenched samples

Raman Shift (cm⁻¹)

Intensity

- $v_1$-CH₄
- $v_2$-CHD₃
- $v_1$-CHD₃
- $v_3$-(CH₃)

b) 
T = 600 °C
P = 409 - 1093 MPa
quenched samples

Raman Shift (cm⁻¹)

Intensity

- $v_1$-H₂
- $v_1$-HD
- $v_3$-CH₄

liquid phase (Pt)

gas phase (Pt)

liquid phase (Ni)

gas phase (Ni)
Raman Shift (cm$^{-1}$)

- $800 \, ^{\circ}C - 1050 \, MPa$
- $600 \, ^{\circ}C - 1093 \, MPa$

$liquid \ phase \ (Pt)\quenched \ samples$
600 °C 1093 MPa
liquid phase (Pt)

in-situ

v₁-CH₄

v₁-CH₃D

v₁-CH₂D₂

v₁-CHₓDᵧ

quenched sample

600 °C 1093 MPa liquid phase (Pt)
a) 

![Graph showing liquid and gas phase values over time]

- Liquid
- Gas
- Ni

Time (min)

b) 

![Graph showing liquid and gas phase values over time]

- Liquid
- Gas
- Pt

Time (min)