1 Experimentally-determined carbon isotope fractionation in and between
2 methane-bearing melt and fluid to upper mantle temperatures and pressures
3

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6

7 **Abstract**
8

9 The behavior of melts and fluids is at the core of understanding formation and evolution
10 of the Earth. To advance our understanding of their role, high-pressure/-temperature
11 experiments were employed to determine melt and fluid structure together with carbon
12 isotope partitioning within and between (CH₄ + H₂O + H₂)-saturated aluminosilicate
13 melts and (CH₄ + H₂O + H₂)-fluids. The samples were characterized with vibrational
14 spectroscopy while at temperatures and pressures from 475° to 850°C and 92 to 1158
15 MPa, respectively.

16 The solution equilibrium is $2\text{CH}_4 + \text{Q}^n = 2\text{CH}_3 + \text{H}_2\text{O} + \text{Q}^{n+1}$ where the superscript, n, in
17 the Qⁿ-notation describes silicate species where n denotes the number of bridging oxygen.
18 The solution equilibrium affects the carbon isotope fractionation factor between melt and
19 fluid, $\alpha^{\text{melt/fluid}}$. Moreover, it is significantly temperature-dependent. The $\alpha^{\text{melt/fluid}} < 1$ with
20 temperatures less than about 1050°C, and is greater than 1 at higher temperature.

21 Methane-bearing melts can exist in the upper mantle at $f_{\text{O}_2} \leq f_{\text{O}_2}(\text{MW})$ (Mysen et al.,
22 2011). Reduced (C-H)-species in present-day upper mantle magma, therefore, are likely.
23 During melting and crystallization in this environment, the $\delta^{13}\text{C}$ of melts increases with
24 temperature at a rate of ~0.6 ‰/°C. From the simple-system data presented here, at
25 $T \leq 1050^\circ\text{C}$, melt in equilibrium with a peridotite-(CH₄+H₂O+H₂)-bearing mantle source
26 will be isotopically lighter than fluid. At higher temperatures, melts will be isotopically
27 heavier. Degassing at $T \leq 1050^\circ\text{C}$ will shift $\delta^{13}\text{C}$ of degassed magma to more positive
28 values, whereas degassing at $T \geq 1050^\circ\text{C}$, will reduce the $\delta^{13}\text{C}$ of the degassed magma.
29

1. Introduction

The budget and recycling of volatile components in the Earth's interior govern the formation and evolution of the solid Earth, its oceans, and atmosphere (e.g., Kasting et al., 1993; Tolstikhin and Marty, 1998). Tracing the role of volatile components often relies on understanding the behavior of isotopes such as those of hydrogen, carbon, nitrogen, and sulfur (Dixon et al., 1997; Van Soest et al., 1998). As these elements can exist in different oxidation states in the range of redox conditions of the Earth's interior (e. g., Saxena and Fei, 1987; Luth et al., 1990), their redox state can affect their isotope fractionation behavior (Ohmoto, 1972; Richet et al., 1977). An understanding stable isotope behavior during magmatic processes, therefore, requires characterization of the redox conditions as well as temperature and pressure.

In the C-O-H system of volatiles, methane (CH_4) is a principal carbon-bearing species under redox conditions such as those existing during separation of iron-rich metal from an extensively melted Earth to form its core (below that described by the iron-wustite oxygen buffer; Ohmoto and Kerrick, 1977; O'Neill, 1991; Righter and Drake, 1999). It has been reported recently, however, that even under less reducing conditions such as those of the magnetite-wustite (MW) oxygen buffer, CH_4 is the dominant C-bearing species in silicate melts (Mysen et al., 2011). Such redox conditions are near those typical of the present day upper mantle (e.g., Bryndzia and Wood, 1990; McCammon, 2005).

A few experimental data exist for quenched silicate melts equilibrated with $(\text{CH}_4 + \text{H}_2\text{O} + \text{H}_2)$ -fluid at magmatic temperatures and upper mantle pressures. Those data indicate that silicate melt structure can have profound effect on $^{13}\text{C}/^{12}\text{C}$ fractionation between melt and fluid (Mysen et al., 2009). This conclusion relies, however, on the

assumption that temperature-quenching of high-temperature melt to form a glass for analysis at ambient conditions does not change its composition and structure. Silicate melt structure is, however, temperature-dependent (see, for example, review of such structural information by Mysen and Richet, 2005). Melt composition also can change because minerals sometimes crystallize from melt during temperature-quenching thus altering their composition. This can be a particular problem when quenching volatile-rich melt from high temperature at high pressure (e.g., Mysen et al., 1974; Baker and Stolper, 1994). Moreover, quench precipitation of oxide materials from fluids equilibrated at high temperatures and pressures is common (Mysen and Acton, 1999; Kessel et al., 2004). This material must be separated from quenched melts before analysis. Such separation is often challenging. Incomplete separation of quench precipitates from quenched melts will affect melt analytical data.

In order to avoid the complications that often arise from temperature-quenching of high-temperature/-pressure experimentally-equilibrated samples, structural and isotopic characterization of coexisting fluids and melts while at the temperatures and pressures of interest is desirable. The data in the present report were obtained in this manner. Carbon speciation and carbon isotope ratio of melts and fluids were determined by vibrational spectroscopic methods. These measurements were carried out while the samples, contained in hydrothermal diamond anvil cells, were at the temperatures, pressures, and redox conditions of interest. A compositionally simple ternary alkali aluminosilicate melt was used in the study in order to facilitate interpretation of vibrational spectra. It is emphasized, therefore, that the reported data serve to illustrate principles that describe carbon isotope fractionation in and between coexisting melt and

fluid to upper mantle temperatures and pressures. However, given the chemical simplicity compared with natural magmatic melts, quantitative application of the experimental results to natural magmatic processes should be carried out with caution.

2. Experimental Methods

High-temperature/-pressure experiments were carried out with externally-heated hydrothermal diamond cells (HDAC) of the type described by Bassett et al. (1996). The upper and lower diamonds were surrounded by Mo-wound heaters. Aluminosilicate glass, C-O-H fluid, a reducing agent (Ti metal), and a pressure sensor (synthetic ^{13}C diamond) starting materials were contained in a 500 μm -diameter central hole of 125 μm thick, polished Ir gaskets. Before an experimental measurement series, the gaskets were work-hardened to the highest temperatures and pressures to minimize sample volume changes during experiments.

The silicate portion of the starting material consisted of several $\leq 100\mu\text{m}$ chips of a Na aluminosilicate glass $[(\text{Na}_2\text{Si}_4\text{O}_9)_{90} \bullet (\text{Na}_2(\text{NaAl})_4\text{O}_9)_{10}]$, also used in previously for high-temperature/pressure examination of water solution mechanisms in silicate melts (Mysen, 2007, 2015). The carbon component of the fluid was added as $\text{Ag}_2\text{C}_2\text{O}_4$ followed by double-distilled, deionized and filtered H_2O . The starting $\text{Ag}_2\text{C}_2\text{O}_4$ was a 50:50 mixture of ^{13}C and ^{12}C . It was synthesized from an aqueous solution of a 50:50 mixture of $\text{H}_2^{13}\text{C}_2\text{O}_4$ and $\text{H}_2^{12}\text{C}_2\text{O}_4$ by reaction with AgNO_3 in aqueous solution. The $\text{Ag}_2\text{C}_2\text{O}_4$ breaks down to CO_2 and metallic Ag near 150°C . Powdered Ti metal was added to serve as reducing agent to convert $\text{CO}_2 + \text{H}_2\text{O}$ to $\text{CH}_4 + \text{H}_2$ (Foustoukos and Mysen, 2012) via the reaction,

The oxygen fugacity (f_{O_2}) of the $\text{Ti} + \text{O}_2 = \text{TiO}_2$ reaction at the temperatures of the present experiments is about 15 orders of magnitude lower than that required for CH_4 to dominate the C-O-H species (Robie et al., 1968; Ohmoto and Kerric, 1977). Metallic Ti in the presence of H_2O is, therefore, a very efficient means by which to produce CH_4 from $\text{CO}_2 + \text{H}_2\text{O} + \text{Ti}$.

Temperature was measured with two K-type thermocouples in contact with the upper and lower diamonds, respectively, and located less than 1 mm from the sample area. Temperature precision was $\pm 1^\circ\text{C}$ and uncertainty $\pm 3^\circ\text{C}$ from calibration against the NaCl melting temperature (800.5°C) at ambient pressure. Pressure, generated with changes in temperature in a near-fixed volume sample chamber, was monitored with the 1st-order Raman shift of synthetic ^{13}C diamond from 10-20 μm diamond pieces mixed in with the sample (Schiferl et al., 1997). With this arrangement, precision was ± 40 MPa, whereas uncertainty is ± 110 MPa (Mysen and Yamashita, 2010).

Aluminosilicate-saturated ($\text{CH}_4 + \text{H}_2\text{O} + \text{H}_2$)-fluid and coexisting ($\text{CH}_4 + \text{H}_2\text{O} + \text{H}_2$)-saturated aluminosilicate melts were monitored optically with optical microscopy at 500X magnification and characterized with Raman spectroscopy while in the HDAC at the temperature and pressure conditions of interest. Melt and fluid structure and the carbon isotope ratios were determined with a JASCO model NSR3100 confocal micro-Raman system equipped with an Olympus microscope, a single monochromator, holographic notch filter, and holographic gratings. A 2.5 cm working distance, Mitotoyo, 50X/0.42 N.A. objective lens was attached to the Olympus microscope for the optical observations

and backscatter Raman measurements. Spectra were recorded with an Andor Model DV401-F1 1024x128 pixel, Peltier-cooled CCD operating at $\sim -70^{\circ}\text{C}$. The samples were excited with 30-35 mW power of the 490.2 nm line of a solid state CoherentTM laser. The beam diameter at the sample was 2-3 μm . Confocal optics limits to $\sim 30 \mu\text{m}$ the depth of excitation of optically clear samples (Mysen, 2015). Groove density of the holographic gratings for sample measurements was 1200 grooves/mm, which resulted in $\pm 3 \text{ cm}^{-1}$ frequency uncertainty. To determine the Raman shift of the ^{13}C diamond for pressure determination, 2400 grooves/mm were used ($\pm 1 \text{ cm}^{-1}$ frequency uncertainty). The frequency uncertainty of these latter measurements was reduced to $\pm 0.1 \text{ cm}^{-1}$ by using Ne emission lines as internal frequency standard.

Raman spectra of each melt+fluid sample were recorded at a series of pressure and temperature conditions. The temperature separation between each condition was $50^{\circ} - 75^{\circ}\text{C}$. The measurements were carried out following about 60 minutes dwell time at each temperature, which is sufficient to reach equilibrium in experiments under conditions such as those employed here (Horita, 1988). That conclusion also is consistent with HFSE solubility measurements in aqueous fluid equilibrating with crystalline oxides (Wilke et al., 2012).

3. Results

Fluid and melt coexisted over the entire temperature- and pressure range of the experiments. A straight-line fit through the pressure/temperature data points (Fig. 1) was used to obtain an approximate pressure corresponding to a temperature and used in the

figures where temperature is an independent variable as a reminder that unless otherwise stated, there is a temperature-dependent pressure for each temperature.

3.1. Raman spectra

Fluid and melt spectra in the 300-1200 cm^{-1} frequency range are different (Fig. 2). Those of fluids have a sharp peak, marked R_1 , near 600 cm^{-1} , one or two peaks between 800 and 850 cm^{-1} (marked Q and R_2), and a sharp peak near 1050 cm^{-1} (R_3). The R_1 , R_2 , and R_3 are the rotational bands from molecular H_2 (Taylor and Strauss, 1989). At temperatures and pressures above 700°C/768 MPa, there is an additional weak peak near 770 cm^{-1} (marked Q). This peak is assigned to Si-O stretching in Q^0 structural units in the fluid (Zotov and Keppler, 2000; Mibe et al., 2008). This signal reflects, therefore, silicate dissolved in the fluid. At and above similar temperature and pressure, there is also a broad peak near 900 cm^{-1} (marked c) that is assigned to Ti-O vibrations in oxidized Ti-bearing complexes dissolved in the fluid.

The R_1 , R_2 , and R_3 peaks were not observed in the melt spectra. In those, there are two peaks near 450 and 550 cm^{-1} (marked a and b in Fig. 2), respectively, which closely resemble those in spectra of Na-aluminosilicate melt+ H_2O (upper right spectrum in Fig. 2; see also Mysen, 2010). There is also a very strong peak at 900 cm^{-1} (marked c) and a less pronounced peak or shoulder between 1050 and 1100 cm^{-1} (marked d). The 900 cm^{-1} signal is assigned to Ti-O stretching (Reynard and Webb, 1998) from Ti metal that was oxidized to Ti^{4+} [see eqn. (1)]. As Ti-O bonds are very efficient Raman scatterers, much less intense bands in this region from the aluminosilicate network are partially buried beneath this intensity. The weaker peak or shoulder near 1050-1100 cm^{-1} is the only

signal not affected by the strong Raman intensity from Ti-O vibrations. This portion of the spectrum resembles that of hydrous Na-aluminosilicate melt spectra of similar chemical composition (Fig. 2). Likely it reflects the presence of Q^3 units. The two lower-frequency bands, a and b, are assigned to bending and rocking motions in the aluminosilicate network (see, for example, McMillan et al., 1982)

The higher-frequency Raman spectra of fluids and melts (Fig. 3) have an asymmetric sharp band centered near 2910 cm^{-1} (marked a) and a multiple of up to 4 bands near 4150 cm^{-1} (marked b) in addition to a much stronger, asymmetric intensity envelope centered near 3600 cm^{-1} . The latter intensity region is assigned to O-H stretch vibrations in H_2O molecules and in OH-groups with chemical bonding to other cations in the system (ie, Na^+ , Al^{3+} , Si^{4+} , and perhaps C) (Walrafen, 1964; Ratcliffe and Irish, 1982; Kawamoto et al., 2004). Their exact frequencies are affected by the type of such cation or cations (Le Losq et al., 2012).

The number of bands near 4150 cm^{-1} decreases from 4 at the lowest temperatures to only 1 or perhaps 2 at the highest temperature and pressure conditions ($850^\circ\text{C}/\geq 1158\text{ MPa}$) (Fig. 3). These bands, similar to those seen in spectra of H_2 - H_2O fluids under similar temperature and pressure conditions by Foustoukos and Mysen (2012), are the rotational components of the Q-branch of the H_2 molecule (Holzer et al., 1973). The decreasing number of bands with increasing temperature and pressure is because of the increased density of the fluid.

The 2910 cm^{-1} peak is asymmetric toward lower frequency. It broadens with increasing temperature and pressure (by as much as 100% between 475° and 850°C) (Figs. 3, 4). This is the frequency region of C-H stretching in C_nH_{2n+2} alkanes (Snyder et al.,

1984). For $n=1$ (methane, CH_4) with natural carbon (98.93 % ^{12}C), the symmetric C-H stretch results in a band near 2918 cm^{-1} at ambient temperature and pressure (e.g., Dubessy et al., 1999). The 50:50 mixture of $^{13}\text{C}:^{12}\text{C}$ used in the present experiments results in pairs of bands from vibrations in $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ molecules because the frequency of a given vibration depends on the square root of mass ratio of the oscillators. For a pure C-vibration such as in diamond or graphite, the $\sqrt{m_{^{13}\text{C}} / m_{^{12}\text{C}}} = 1.04$. The observed frequency ratio for diamond is 1.039 (e.g., Mysen and Yamashita, 2010). For vibrational environments involving more complex oscillators such as, for example, C-H bonds, this difference will be less because of contributions from components other than C to the oscillator mass. For the methane molecule, the extent of the contribution from H may be estimated from the CH_4 frequency shift from C- ^1H to C- ^2H substitution. That shift is $\sim 800\text{ cm}^{-1}$ (Anderson and Savoie, 1965). This shift is about 85% of that expected from the relationship to the mass ratio of the hydrogen isotopes alone (Teal and MacWood, 1935; Foustkoukos and Mysen, 2012). The 85% contribution implies that the C-H vibrations in CH_4 are dominated by hydrogen motion, and that the contribution to frequency shifts from ^{13}C substitution of ^{12}C is less than indicated by the $\sqrt{m_{^{13}\text{C}} / m_{^{12}\text{C}}}$ - ratio. If we assume that the hydrogen contribution to the C-H stretch vibrations is, in fact 85% as suggested by frequency effect of the D/H substitution, the expected Raman shift resulting from ^{13}C substitution for ^{12}C in the methane molecule would be $\leq 15\text{ cm}^{-1}$. In fitting these spectra, the average frequency difference of these two peaks in fluid and melt spectra was found to be near 10 cm^{-1} (Fig. 5; see also Table 2).

In addition to the C-H doublet reflecting the isotope substitution of carbon, there is a band between 2880 and 2890 cm^{-1} (Fig. 5). This band is assigned to C-H stretching in

C_nH_{2n+2} ($n>1$) because the frequency of bands assigned to symmetric C-H stretching in C_nH_{2n+2} compounds decreases by about 14.5 cm^{-1} /unit change of n (Snyder et al., 1984). Given that this band occurs near 2890 cm^{-1} , whereas the average frequency of the two CH_4 bands is near 2905 cm^{-1} (Fig. 5), it seems reasonable to conclude that $n=2$ in the C_nH_{2n+2} compound (ethane) that gives rise to the 2890 cm^{-1} Raman intensity.

4. Discussion

Carbon-13 MAS NMR spectra of glasses quenched from similar composition melt equilibrated with $(CH_4+H_2O+H_2)$ -fluid at 1400°C at 1.5 GPa pressure indicate that molecular CH_4 and methyl groups, CH_3 , coexist in melts (Mysen et al., 2011). However, in the in-situ, high-temperature/-pressure Raman spectra presented here (Fig. 5), signals from CH_3 and CH_4 groups could not be isolated. In the following discussion, this entity is simply referred to as ΣCH_4 .

The two bands assigned to $^{12}\text{C-H}$ and $^{13}\text{C-H}$ stretching in ΣCH_4 comprise 85-95 % of the integrated area of 2910 cm^{-1} envelope. The remaining intensity is contained in the 2890 cm^{-1} band (Fig. 5). If we assume that the relative abundance of C_nH_{2n+2} equals the area ratio of the 2890 cm^{-1} band relative to the total area under the 2910 cm^{-1} intensity envelope, the abundance of C_2H_{2n+2} ranges from less than 5 % of the total hydrocarbon abundance at the lowest temperatures and pressures and up to about 10% of the total in the fluid and as much as 15% of the total in melt at the highest temperature and pressure (Fig. 6).

The integrated intensity ratio of the 2900 and 2910 cm^{-1} bands (Fig. 5) approximates the carbon isotope ratio abundance, $^{13}\text{C}/^{12}\text{C}$, of ΣCH_4 in the fluids and melts,

$$A_{2900} / A_{2910} = X_{\Sigma^{13}\text{CH}_4} / X_{\Sigma^{12}\text{CH}_4}, \quad (2)$$

where A_{2900} and A_{2910} are the integrated intensities of these bands, and $X_{\Sigma\text{CH}_4}$ -values are the corresponding mol fractions of $\Sigma^{13}\text{CH}_4$ and $\Sigma^{12}\text{CH}_4$. Temperature is not a factor in this relationships because the measurements of fluids and melts are carried out at the same temperature. Density is not a factor in relations between Raman signal intensity and species concentration (e.g., Long, 1977).

The carbon isotope evolution in ΣCH_4 with temperature incorporates possible $^{13}/^{12}\text{C}$ fractionation between coexisting CH_3 and CH_4 groups. However, the Raman spectra are insufficiently sensitive to resolve C-H vibrations in $^{12}\text{CH}_3$, $^{13}\text{CH}_3$, $^{12}\text{CH}_4$, and $^{13}\text{CH}_4$. This simplification must be kept in mind when the concepts developed in this study are applied to characterization of natural processes.

The $^{13}\text{C}/^{12}\text{C}$ of ΣCH_4 equals the total carbon isotope ratio provided that the small proportion of higher-order alkanes (5-15 %) does not have a significant effect on the total carbon isotope budget. At ambient temperature and pressure, the carbon isotope ratio of C_2H_6 is 10 ‰ or so lighter than that of CH_4 (McCollum et al., 2010). This means that in the 5-15% abundance range of $\text{C}_{2n}\text{H}_{2n+2}$ (n=2) indicated by the experimental data (Fig. 6), an error in total $^{13}\text{C}/^{12}\text{C}$ resulting from ignoring its contribution is near 2 %. This error decreases with temperature because the n-dependent carbon isotope ratio difference decreases with increasing temperature (McCollum et al., 2010).

4.1. Carbon isotope distribution

The $^{13}\text{C}/^{12}\text{C}$ -values of fluid and melt approach one another with increasing temperature (and pressure (Fig. 7; see also Table 1). The two curves will meet at the temperature/pressure conditions of the boundary between those where fluid + melt coexist and those of a single supercritical fluid. From extrapolation of the least-squares fitted straight lines to higher temperature (Fig. 7B) and using the straight line fit through the temperature/pressure points in Fig. 1, this boundary is near 1090°C and 1.7 GPa at $^{13}\text{C}/^{12}\text{C}=0.996$.

The carbon isotope exchange equilibrium between melt and fluid is:

with the exchange equilibrium coefficient:

$$K_D^{\text{melt}/\text{fluid}} = \frac{\frac{X_{\Sigma^{13}\text{CH}_4(\text{melt})}}{X_{\Sigma^{12}\text{CH}_4(\text{melt})}}}{\frac{X_{\Sigma^{13}\text{CH}_4(\text{fluid})}}{X_{\Sigma^{12}\text{CH}_4(\text{fluid})}}}. \quad (4)$$

In Fig. 8, expression (4) is simplified to:

$$K_D^{melt/fluid} = \frac{\left(\frac{\sum {}^{13}C}{\sum {}^{12}C} \right)^{melt}}{\left(\frac{\sum {}^{13}C}{\sum {}^{12}C} \right)^{fluid}} . \quad (5)$$

279

280 The temperature-dependent $K_D^{melt/fluid}$ (Fig. 8) likely incorporates the fact that both
 281 CH_4 and CH_3 groups are involved in the equilibrium. For reasons discussed above, the
 282 individual contributions from $^{13}C-H$ and $^{12}C-H$ stretch vibrations in CH_3 and CH_4 groups
 283 cannot be separated in the present Raman spectra.

284

285 5. Implications

286 Carbon isotope composition has been used to deduce the carbon isotope composition of a
 287 mantle source of a magmatic liquid (Nishio et al., 1998). It also can be used to
 288 characterize degassing and contamination processes during magmatic evolution (e.g.,
 289 Dixon et al., 1997; Van Soest et al., 1998; Aubaud et al., 2005). In studies such as those,
 290 it was assumed that at temperatures of melting, crystallization, and degassing carbon
 291 isotope fractionation factors, α , do not differ significantly from unity at the temperature
 292 of these processes.

293 The present data (Fig. 8) suggest, however, that the assumption of $\alpha=1$ needs to be
 294 revisited. To address consequences of this possibility, it is assumed that the $K_D^{melt/fluid}$ is
 295 independent of isotope concentration, which means that the carbon isotope fractionation
 296 factor, $\alpha^{melt/fluid} = K_D^{melt/fluid}$. That assumption has been found valid for D/H fractionation
 297 between melt and fluid determined under similar conditions with methods analogous to

those of the present report (Dalou et al., 2015). Similar data do not exist for carbon isotopes. That notwithstanding, we will assume that the $\alpha^{melt/fluid} = K_D^{melt/fluid}$ relationship also holds for carbon isotopes. When applying these principles to natural processes, it is also assumed that they may be applied to discuss major principles governing carbon isotope evolution in natural magmatic systems. Differences in composition (and structure) of magmatic melts likely will not affect the principles. This is because even though the structural variations of natural magmatic liquid differ from those in simple systems in quantitative detail, their principal structural features are the same (see, for example, discussion by Mysen and Richet, 2005; ch. 17).

With the above caveats, the results in Fig. 8 are employed to illustrate how carbon isotopes evolution in (CH₄+H₂O+H₂)-bearing magmatic systems can vary with temperature during melting, crystallization, and degassing. In doing so, it is assumed that there is no pressure effect on the carbon isotope exchange equilibrium. In other words, it is assumed that for equilibrium (3), $\Delta V=0$. ..

Carbon isotope abundance of a melt coexisting with fluid is related via the fractionation factor, $\alpha^{melt/fluid}$,

$$\delta^{13}D^{melt} = \alpha^{melt/fluid} \cdot \delta^{13}D^{fluid} + 1000 \cdot (\alpha^{melt/fluid} - 1). \quad (6)$$

The temperature-dependence of the fractionation factor, $\alpha^{melt/fluid}$, is described by the linear regression coefficients from the fit to the data in Fig. 8. This temperature-dependence results in the temperature-dependent $\delta^{13}C^{melt}$ -trajectories shown in Fig. 9.

The heavier lines, marked $\delta^{13}C^{melt} @ \delta^{13}C^{fluid} = -7\text{‰}$ and $\delta^{13}C^{melt} @ \delta^{13}C^{fluid} = -30\text{‰}$, are

those calculated for melt in equilibrium with a (CH₄+H₂+H₂O)-fluid with $\delta^{13}\text{C}^{\text{fluid}} = -7\text{‰}$ and -30‰ , respectively. Those two $\delta^{13}\text{C}^{\text{fluid}}$ -values correspond to maxima in $\delta^{13}\text{C}$ distribution of mantle-derived peridotite and eclogite nodules in basalt and kimberlite (see Deines, 2002, for review). Also shown In Fig. 9 in less heavy lines is the evolution of the temperature trajectories of $\delta^{13}\text{C}^{\text{melt}}$ with an increasingly isotopically light and increasingly heavy fluid.

The $\delta^{13}\text{C}^{\text{melt}}$ of melts in equilibrium with a (CH₄+H₂O+H₂)-bearing upper mantle of given carbon isotopic composition become isotopically heavier with increasing temperature at an average rate of $\sim 0.6\text{‰}/^\circ\text{C}$ (averaged between 900° and 1300°C). Such melts can be lighter or heavier than the source region depending on temperature (Fig. 9). The cross-over temperature from isotopically lighter to heavier than the fluid-bearing upper mantle source increases with increasing $\delta^{13}\text{C}$ of the source region. It is near 950°C for $\delta^{13}\text{C}^{\text{fluid}} = 100\text{‰}$ to near 1220°C for $\delta^{13}\text{C}^{\text{fluid}} = -100\text{‰}$. Partial melting in the 1200° - 1300°C , which is typical for upper mantle peridotite melting, would yield $\delta^{13}\text{C}^{\text{melt}} = 30$ - 100‰ based on the simple-system data in Fig. 9. Conversely, during degassing of a magmatic liquid at similar 1200° - 1300°C temperatures, the $\delta^{13}\text{C}$ of an evolving CH₄+H₂O+H₂-rich fluid will be depleted in carbon-13 relative to the melt, which will, of course, result in an increase $\delta^{13}\text{C}$ of the liquid itself. With degassing temperatures less than the 1050° - 1100°C of the cross-over, the fluid will be heavier than the magma. Lower-temperature degassing, in other words, would shift magma composition to become isotopically lighter.

The use of carbon isotopes of mantle-derived magma to derive isotopic composition of upper mantle source regions, therefore, is discouraged. This is because the carbon

isotope ratios are affected by temperature, bulk composition, and redox conditions during melting, crystallization, and degassing events.

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Table 1 Carbon isotope results[†]

Temp	Pressure, MPa	fluid ¹³ C/ ¹² C ^{††}	melt ¹³ C/ ¹² C ^{†††}
475	92	0.71±0.02	1.40±0.10
550	114	0.76±0.02	1.31±0.04
625	172	0.80±0.01	1.25±0.05
700	489	0.85±0.03	1.20±0.03
775	768	0.87±0.02	1.16±0.12
850	1158	0.92±0.02	1.05±0.12

[†] Derived from the integrated intensity ratio
of the 2900/2910 cm⁻¹

Raman bands.

^{††}: Average $\Delta v = 10 \pm 0.8$ cm⁻¹

^{†††}: Average $\Delta v = 9.4 \pm 0.6$ cm⁻¹

Figure Captions

Figure 1 – Pressure-temperature trajectory of the experiments. The straight-line fit through the data points does not include the ambient conditions pressure. The fitted curve $[\text{Pressure (MPa)} = 2.9 \pm 0.5 \cdot \text{Temperature (}^\circ\text{C)} - 1454 \pm 392, r^2 = 0.90]$ was used to derive the pressure axis in the figures.

Figure 2 – Examples of spectra of coexisting melt and fluid in the $350\text{--}1200\text{ cm}^{-1}$ frequency region. Temperature/pressure conditions for each spectrum are marked on each spectrum. Also shown is an example of a spectrum of from composition, NA10+H₂O (Mysen, 2010). Composition NA10 is the same as that of the present experimental study. See text for detailed discussion of topological features.

Figure 3 – Examples of spectra of coexisting melt and fluid in the $2850\text{--}4200\text{ cm}^{-1}$ frequency region. Temperature/pressure conditions for each spectrum are marked on each spectrum. Inserts in the left spectra show expanded versions near the 2910 (left) and 4150 cm^{-1} (right). See text for detailed discussion of topological features.

Figure 4 – Temperature vs. FWHH (full width at half height) of the 2910 cm^{-1} peak in coexisting melt and fluid. Pressure-axis (upper horizontal axis) was derived from the linear fit in Figure 1.

Figure 5 – Examples of curve-fitted spectra with those from $850^\circ\text{C}/1158\text{ MPa}$ as examples. These highest temperature/pressure condition spectra were chosen because those most clearly show the $\text{C}_n\text{H}_{2n+2}$ band near 2890 cm^{-1} . The band assignments shown on the individual fitted peaks are discussed in the text.

Figure 6 – Proportion of $\text{C}_n\text{H}_{2n+2}$ species in fluids and melts relative to the total hydrocarbon abundance. As discussed in the text, for this purpose, the scattering efficiency of the C-H symmetric stretching is assumed the same for CH₄ and $\text{C}_n\text{H}_{2n+2}$ ($n \geq 2$). Pressure-axis (upper horizontal axis) was derived from the linear fit in Figure 1.

Figure 7 – A. Evolution of $^{13}\text{C}/^{12}\text{C}$ in coexisting fluid and melt as a function of temperature ($^\circ\text{C}$). B. Linear least squares of $\ln(^{13}\text{C}/^{12}\text{C})$ with the temperature ($1/T$, kelvin). Regression lines were, melt: $\ln(^{13}\text{C}/^{12}\text{C}) = -0.42 \pm 0.08 + (576 \pm 70)/T$, $r^2 = 0.94$, and melt: $\ln(^{13}\text{C}/^{12}\text{C}) = 0.41 \pm 0.03 + (576 \pm 26)/T$, $r^2 = 1.00$. In this figure it is assumed the $^{13}\text{C}/^{12}\text{C} = ^{13}\text{CH}_4/^{12}\text{CH}_4$. Pressure-axis (upper horizontal axis) was derived from the linear fit in Figure 1.

547 Figure 8 – Linear of the $\ln K_D^{\text{melt/fluid}}$ vs. temperature ($1/T$, kelvin) for equilibrium (6).
 548 The regression line is: $\ln (K_D^{\text{melt/fluid}})=0.84\pm0.10-(1143\pm93)/T$, $r^2=0.99$. Pressure-axis
 549 (upper horizontal axis) was derived from the linear fit in Figure 1.
 550 Figure 9 – Calculated $\delta^{13}\text{C}$ of melt in equilibrium with a $\text{CH}_4+\text{H}_2\text{O}+\text{H}_2$ -bearing as a
 551 function of temperature. Horizontal dashed lines mark as a function of temperature. The
 552 dashed horizontal lines mark $\delta^{13}\text{C}^{\text{fluid}} = -7$ and -30‰ mark the position of a source with
 553 typical peridotite mantle values (see Deines, 2002). The corresponding melt curves are
 554 indicated with heavy lines. Additional, thinner, lines show $\delta^{13}\text{C}^{\text{melt}}$ -evolution with
 555 various other $\delta^{13}\text{C}^{\text{fluid}}$ -values as indicated.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9