REVIEW **Open Access**

Redox-controlled mechanisms of C and H isotope fractionation between silicate melt and COH fluid in the Earth's interior

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Abstract

The behavior of COH fluids, their isotopes (hydrogen and carbon), and their interaction with magmatic liquids are at the core of understanding formation and evolution of the Earth. Experimental data are needed to aid our understanding of how COH volatiles affect rock-forming processes in the Earth's interior. Here, I present a review of experimental data on structure of fluids and melts and an assessment of how structural factors govern hydrogen and carbon isotope partitioning within and between melts and fluids as a function of redox conditions, temperature, and pressure.

The solubility of individual COH components in silicate melts can differ by several orders of magnitude and ranges from several hundred ppm to several wt%. Silicate solubility in fluid can reach several molecular at mantle temperatures and pressures. Different solubility of oxidized and reduced C-bearing species in melts reflects different solution equilibria. These equilibria are $2CH_4 + Q^n = 2CH_3^- + H_2O + Q^{n+1}$ and $2CO_3^{2-} + H_2O + 2Q^{n+1} = HCO_3^- + 2Q^n$, under reducing and oxidizing conditions, respectively. In the Q^n-notations, the superscript, n, denotes the number of bridging oxygen in the silicate species (Q-species).

The structural changes of carbon and silicate in magmatic systems (melts and fluids) with variable redox conditions result in hydrogen and carbon isotope fractionation factors between melt, fluid, and crystalline materials that depend on redox conditions and can differ significantly from 1 even at magmatic temperatures. The ΔH of D/H fractionation between aqueous fluid and magma in silicate–COH systems is between -5 and 25 kJ/mol depending on redox conditions. The ΔH values for $^{13}C/^{12}C$ fractionation factors are near -3.2 and 1 kJ/mol under oxidizing and reducing conditions, respectively. These differences are because energetics of $O–D$, $O–H$, $O–^{13}C$, and $O–^{12}C$ bonding environments are governed by different solution mechanisms in melts and fluids.

From the above data, it is suggested that (COH)-saturated partial melts in the upper mantle can have δD values 100%, or more, lighter than coexisting silicate-saturated fluid. This effect is greater under oxidizing than under reducing conditions. Analogous relationships exist for $^{13}C/^{12}C$. At magmatic temperatures in the Earth's upper mantle, $^{13}C/^{12}C$ of melt in equilibrium with COH-bearing mantle in the -7 to -30‰ range increases with temperature from about 40 to >100‰ and 80–120‰ under oxidizing and reducing conditions, respectively.

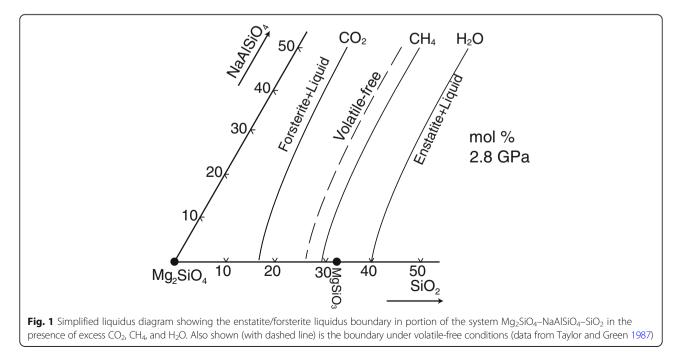**Keywords:** Fluid, Solubility, Structure, Spectroscopy, Redox, Stable isotopes

Introduction

The budget, recycling, and evolution of COH volatiles are central to our understanding of many geochemical and geophysical properties of the interior of the Earth. The behavior of COH volatiles, therefore, is a very important factor in the processes that governed the formation and evolution of the solid Earth and perhaps other terrestrial planets (Ardia et al. 2013; Armstrong et al. 2015).

The speciation and activity/concentration of volatiles are particularly relevant to melting and crystallization. For carbon-bearing species, for example, reduced and oxidized C behaves quite differently (Saxena and Fei 1988; Ulmer and Luth 1991). These factors can govern melt composition (see also Kushiro 1974, 1998; Eggler 1975; Eggler and Baker 1982; Gaetani and Grove 1998; Foley et al. 2009). For example, the clearly different effects of CO_2 and CH_4 on melting and crystallization of model magma systems are evident in the example in Fig. 1. The response of the liquidus boundary between forsterite and enstatite in the $NaAlSiO_4$–Mg_2SiO_4–SiO_2–COH system to changing volatile species at high pressure illustrates such effects (Taylor and Green 1987). This boundary defines the activity of SiO_2 in the system and moves from SiO_2 deficient to SiO_2-enriched when carbon is reduced from CO_2 to CH_4 (Fig. 1). In fact, the effect of CH_4 is not that different from the effect of H_2O. This difference is also the underlying explanation for redox melting in the mantle (Song et al. 2009).

The stable isotope behavior is critical to monitor budgets and recycling of volatiles (Van Soest et al. 1998; Dixon et al. 2002; Kingsley et al. 2002; Javoy 2004). Volatile components in the COH system, when dissolved in magmatic liquids, can affect stable isotope fractionation between the melt and coexisting fluids and crystalline materials (Dobson et al. 1989; Mattey et al. 1990; Deines 2002). Moreover, the redox state of the volatile components such as hydrogen, carbon, and perhaps sulfur can affect their influence on stable isotope fractionation in magmatic systems (Poulson 1996; Deines 2002).

In order to employ stable isotope behavior such as those of hydrogen and carbon to deduce processes of formation and evolution of the Earth's interior, experimental data are necessary. With such tools, we can address how, in particular, COH volatiles and their isotopes fractionate between magmatic liquids, fluids, and crystallizing materials as a function of redox conditions temperature and pressure. Data from samples analyzed after quenching to ambient conditions have been reported (Dobson et al. 1988; Mattey et al. 1990; Mattey 1991). However, extrapolation of such data to conditions during equilibration of magmatic liquids with fluids and crystals at high temperature and pressure is quite challenging because both fluids and melts commonly alter their structure, and sometimes their composition, during quenching to ambient temperature and pressure conditions (Kuroda et al. 1982; Baker and Stolper 1994; Zhang and Frantz 2000; Mysen and Yamashita 2010). That nature of those alterations can vary depending on the temperature–pressure quenching path. It is, therefore, better to determine the isotope fractionation while the samples are at the high temperature and pressure under controlled redox conditions relevant to magmatic processes in the Earth's interior. In this report, I will present

Fig. 1 Simplified liquidus diagram showing the enstatite/forsterite liquidus boundary in portion of the system Mg_2SiO_4–$NaAlSiO_4$–SiO_2 in the presence of excess CO_2, CH_4, and H_2O. Also shown (with dashed line) is the boundary under volatile-free conditions (data from Taylor and Green 1987)

and discuss recent experimental data relevant to these questions and illustrate with a few examples how the composition and redox state of COH volatiles affect carbon and hydrogen stable isotope fractionation between melts and fluids under conditions corresponding to those of the deep crust and upper mantle.

Review

A description and discussion of how carbon and hydrogen isotopes fractionate between fluids and melts at high temperature and pressure and with variable redox conditions is the focus of this presentation. Most of the experimental work on this subject have been carried out by using externally heated hydrothermal anvil cell method (Bassett et al. 1996) where the samples can be probed by vibrational spectroscopy while at the desired conditions. It should be noted that in these diamond cell experiments, temperature is an independent variable. Pressure is generated by the fluid in sample chambers of approximately constant volume and measured with probes such as the one-phonon shift of carbon-13 diamond embedded in the sample (Schiferl et al. 1997). It is for this reason that pressure is included as an upper horizontal axis in some of the figures in this presentation.

Vibrational spectroscopies, such as Raman and infrared not only can be used to probe structure but may also be employed to determine isotope ratios. Most of the experimental data discussed in this report were obtained by such methods. This technique can be used because the frequency ratio of vibrations of two oscillators that differ only in their mass (e.g., two isotopes) ν_1/ν_2, is proportional to the square root of their mass ratio, $\sqrt{m_1/m_2}$. Provided that the cross section for a given vibration is not dependent on the type of isotope, 1 and 2, the ratio of integrated areas of the vibrational spectra, A_1/A_2, equals their abundance ratio, X_1/X_2. Data in support of this conclusion exist for the oxygen isotopes, ^{16}O and ^{18}O, (McKay et al. 2013) and hydrogen isotopes (Dalou et al. 2015).

With those caveats in mind, isotope ratios can be obtained by both transmission infrared absorption and by Raman spectroscopy. Moreover, the samples can be probed with those methods while at the desired conditions. Raman spectroscopy has an advantage over infrared spectroscopy in that Raman spectroscopic intensities do not depend on sample density, whereas infrared absorption intensity does. Densities of coexisting phases at high temperature and pressure often are not available. Laser beams used in microRaman measurements typically are 1–2 μm across and with confocal optics penetrate less than 30 μm into the sample (depending on optical transparency). Measurements with transmission microinfrared absorption have less spatial resolution with a minimum aperture of approximately 30 × 30 μm.

In addition, in infrared transmission spectroscopy, one has to ensure that only the sample of interest is in the optical path.

In addition to isotope ratios, it is also possible to ascertain the speciation and abundance ratio of the volatiles and the silicate components in silicate–COH systems from Raman and infrared spectroscopic data. Sometimes, it has also been possible to determine isotope fractionation between individual volatile species such as CO_3 and HCO_3 groups in silicate melts and coexisting, silicate-saturated melts, while these phases were at the temperature, pressure, and redox conditions of interest (Mysen 2015a, 2016, 2017). Further details of the experimental and analytical methods used for this purpose can be found in those papers and Dalou et al. (2015).

Although solubility of volatile components in silicate melts is not the focus of this report, solubility information is necessary in order to characterize the isotope behavior. Solubility of COH components can also be determined spectroscopically, using either infrared or Raman spectroscopy (Scholze 1960; Behrens et al. 2004, 2006). Traditionally, analyses have been conducted on quenched materials, but recent technical advances now allow infrared and Raman spectroscopy to be used to determine the concentration of at least some volatiles while the samples are at the desired temperatures and pressures (Behrens and Yamashita 2008; Le Losq et al. 2015).
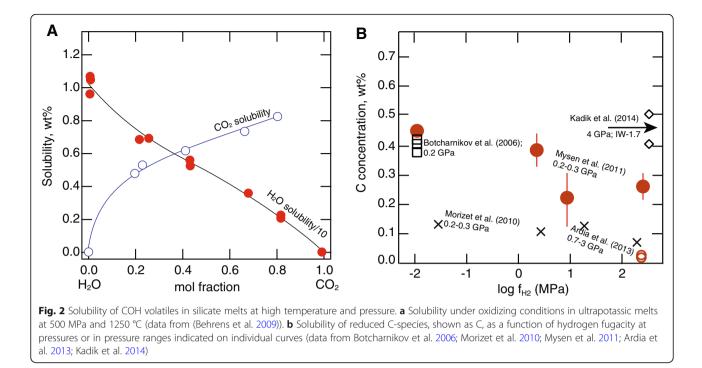
Solubility and solution mechanisms

Fractionation of stable isotopes between coexisting melts and fluids can be linked to solubility and solution mechanisms of volatiles in melts and of silicate in coexisting COH fluids. The principles that govern solubility in coexisting melts and fluids have been reviewed extensively elsewhere (Paillat et al. 1992; Newton and Manning 2008) and will not be discussed further here.

COH volatiles in melts

Determination of the solubility of H_2O and CO_2 in silicate–COH melts requires sufficiently oxidizing conditions so that carbon-bearing species more reduced than that of carbon in CO_2 are unimportant. Those conditions correspond to oxygen fugacities at or above that somewhere between that defined by the NNO (nickel-nickel oxide) and QFM (quartz-magnetite-fayalite) buffer (Mysen et al. 2011). In other words, CO_2–H_2O mixtures will be the principal species in environments such as those of subduction zone melting, for example (Wood et al. 1990; Arculus 1994).

The solubilities of neither H_2O nor CO_2 are simple linear functions of the CO_2/H_2O abundance ratio of the system (Fig. 2a; see also Behrens et al. 2009). This

Fig. 2 Solubility of COH volatiles in silicate melts at high temperature and pressure. **a** Solubility under oxidizing conditions in ultrapotassic melts at 500 MPa and 1250 °C (data from (Behrens et al. 2009)). **b** Solubility of reduced C-species, shown as C, as a function of hydrogen fugacity at pressures or in pressure ranges indicated on individual curves (data from Botcharnikov et al. 2006; Morizet et al. 2010; Mysen et al. 2011; Ardia et al. 2013; Kadik et al. 2014)

non-linear solubility behavior is at least in part because of non-deal mixing behavior of CO_2–H_2O fluids (Eggler et al. 1979; Aranovich and Newton 1999). In addition, silicate melt–CO_2–H_2O mixtures also are non-ideal (Papale et al. 2006) which adds to the non-linear behavior of CO_2 and H_2O solubility in Fig. 2a.

Reduced carbon species may be encountered in the deep Earth where redox conditions approach those described by the IW (iron-wüstite) buffer and below (Frost and McCammon 2008; Rohrbach et al. 2011). Even lower oxygen fugacity appears to have existed during the early core-forming stages of the Earth (O'Neill 1991; Righter and Drake 1999). Under such conditions, the dominant C-bearing species in the COH system likely is methane, CH_4. Molecular H_2 can also play a significant role and contribute more than 10% of the volatile species under such very reducing conditions (Kadik et al. 2014). Its solubility in silicate at high temperature and pressure is greater than that which would be expected if hydrogen simply existed as molecular H_2. There is some evidence to suggest that H_2 interacts chemically with the silicate melt to form OH-groups (Luth and Boettcher 1986; Luth et al. 1987).

More experimental solubility data exist for carbon in melts as a function of redox conditions (Morizet et al. 2010; Mysen et al. 2011; Ardia et al. 2013). Some of the data are summarized for various melt and magma compositions in Fig. 2b. It is evident that as carbon undergoes reduction, its solubility in silicate melt decreases. However, there is considerable variation in available solubility data so that, for example, even the solubility of CH_4 in basalt composition melt at several GPa pressure

and upper mantle temperatures has been reported between about a hundred ppm C (Fig. 2b; see also Ardia et al. 2013; Armstrong et al. 2015) to several thousand ppm (Kadik et al. 2004, 2014). The reasons for this wide solubility range are not clear, but may be related to experimental difficulties controlling the speciation of COH volatiles under extremely reducing conditions.

Silicate solubility in fluid
Less is known about silicate solubility in COH composition fluids than about solubility of COH volatiles in silicate melts at high temperatures and pressures. Quantitative experimental data have been reported for silicates and aluminosilicates in pure H_2O (Manning et al. 2010; Hunt et al. 2011; Manning and Aranovich 2014). The silicate solubility can reach several molecular (Newton and Manning 2008). There is, in fact, a second critical endpoint in the SiO_2–H_2 system between 0.9 and 1 GPa (Kennedy et al. 1962). Solubility of silica and other oxide components also depends on the presence of other components such as, in particular, alkalies and alumina, which when occurring together, can cause major solubility enhancements because of formation of multicomponent complexes in the fluid (Pascal and Anderson 1989; Mysen and Armstrong 2002; Manning 2004; Mysen 2012).

Solution mechanisms
Water in melts and fluids
It has been known for some time that solution of water in silicate melts is in the form of molecular H_2O and as

OH-groups that form bonding to cations such as Si^{4+}, Al^{3+}, alkalis, and alkaline earths (Stolper 1982; Cody et al. 2005; Xue and Kanzaki 2008). The extent to which network-modifying cations such as alkalis and alkaline earths form bonds with OH-groups in aluminosilicate–H_2O systems appears somewhat sensitive to the electronic properties of the cations as well as their proportion relative to network-forming Si^{4+} and Al^{3+} (Xue and Kanzaki 2008). Little is known about this latter feature in aluminosilicate–COH systems.

In silicate–H_2O systems, water in aqueous fluids at high temperature and pressure does dissolve silicate components (Manning 2004) in which at least some of the oxygen in silicate tetrahedra are replaced by OH-groups (Zotov and Keppler 2002; Mibe and Bassett 2008; Mysen 2009). Such structural features recently also have been observed in Raman and infrared spectra of silicate-saturated COH fluid (Mysen, unpublished data). However, whether in silicate–H_2O or silicate–COH systems at high temperature and pressure, the abundance ratio, OH/H_2O, in melts always is greater than that in fluid (Mysen 2010). This difference is greater in silicate–COH fluids than in silicate–H_2O fluids.

Carbon species

Under oxidizing conditions, carbon-bearing species in melts and fluids at high temperature and pressure are dominated by CO_2, CO_3, and HCO_3. In hydrous C-bearing systems such as silicate-COH, the dominant species are of HCO_3 and CO_3 type with limited evidence for molecular CO_2. The limited existence of CO_2 is in part because it has been found that molecular CO_2 becomes decreasingly important with increasing H_2O content of silicate melts (King and Holloway 2002). The latter conclusion is also consistent with the general observation that abundance of molecular CO_2 species diminishes as a silicate melt becomes depolymerized, which does, indeed happen with solution of H_2O (Cody et al. 2005). It follows, therefore, that CO_2 might be an unimportant species in silicate–COH melt, which is consistent with the lack of observed signals from molecular CO_2 in such melts (Mysen 2015a, 2015b).

The relationship between carbonate stability (CO_3^{2-} and HCO_3^{-}) and molecular CO_2 in silicate melts and perhaps silicate-rich COH fluids in principle can be written as:

$$H^+ + 2CO_2 + 2Q^n = 2Q^{n+1} + HCO_3^- + CO_3^{2-}. \qquad (1)$$

In Eq. (1) the Q^n and Q^{n+1} formalism expresses silicate species with in this case n and $n+1$ bridging oxygen, respectively. Recent NMR-based evidence

suggest that the carbonate groups form isolated clusters (Morizet et al. 2017) whereas other experimental data have been interpreted to suggest that oxygen in the CO_3^{2-} complex is shared with the silicate network (Brooker et al. 2001).

Equation (1) obviously is a simplification. For example, this equation does not account for the observation that the HCO_3/CO_3 abundance ratio in both melts and fluids is temperature dependent (Fig. 3a) From the temperature dependence of the HCO_3/CO_3 abundance ratio in melts and in fluids and under the assumption of ideal mixing, the enthalpy change is 17 ± 3 and 29 ± 9 kJ/mol for melt and fluid, respectively. Equilibrium (1) likely also depends on temperature, and definitely on the activity of CO_2 and protons (pH) but experimental data with which to address such questions have not been reported.

Methane is a stable species in COH fluid under reducing conditions (Kadik et al. 2004). In silicate-COH, this oxidation state was detected with carbon-13 MAS NMR in glasses formed by quenching of melts from 1450 °C and 2 GPa and with f_{H2} controlled by the magnetite-wüstite-H_2O and more reducing conditions (Mysen et al. 2011). It was, furthermore, noted in the latter study that molecular CH_4 coexists with methyl groups (CH_3) in the melt similar to that more recently also reported by Ardia et al. (2013). Mysen et al. (2011) reported ^{13}C NMR-based evidence that these CH_3 groups were not linked to oxygen (methoxy groups). That conclusion may imply that the methyl groups actually replace oxygen in silicate tetrahedral with an equilibrium between CH_4, CH_3 and silicate species that in principle can be expressed as:

$$H_2O + Q^n(CH_3)_2 = Q^{n+1} + 2CH_4. \qquad (2)$$

In this equation, the $Q^n(CH_3)_2$ notation indicates that two of the n oxygens have been replaced by CH_3 groups.
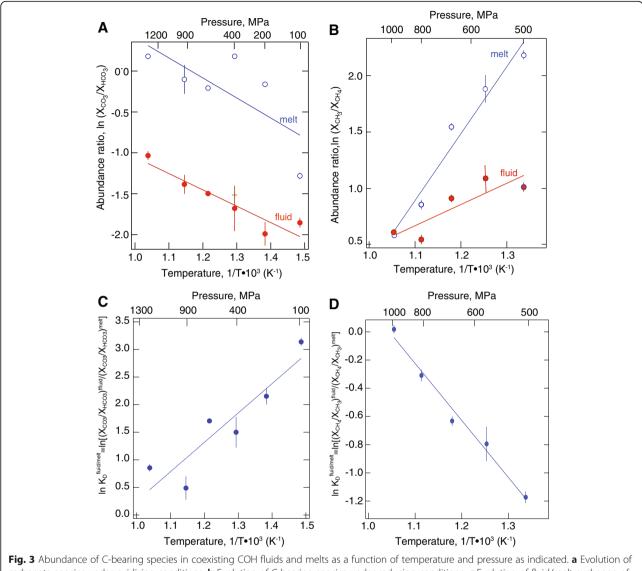
Even though in silicate–COH systems both HCO_3/CO_3 and CH_3/CH_4 abundance ratios vary in both melts and coexisting fluids, the exchange equilibria for oxidizing conditions (Fig. 3c);

$$CO_3^{2-}(\text{melt}) + HCO_3^-(\text{fluid})$$
$$= CO_3^{2-}(\text{fluid}) + HCO_3^-(\text{melt}), \qquad (3)$$

and reducing conditions (Fig. 3d);

$$CH_4(\text{melt}) + CH_3(\text{fluid})$$
$$= CH_4(\text{fluid}) + CH_3(\text{melt}), \qquad (4)$$

are such that under all conditions in Fig. 3, with increasing temperature under oxidizing conditions the CO_3/HCO_3 abundance ratio increases faster in melts than in
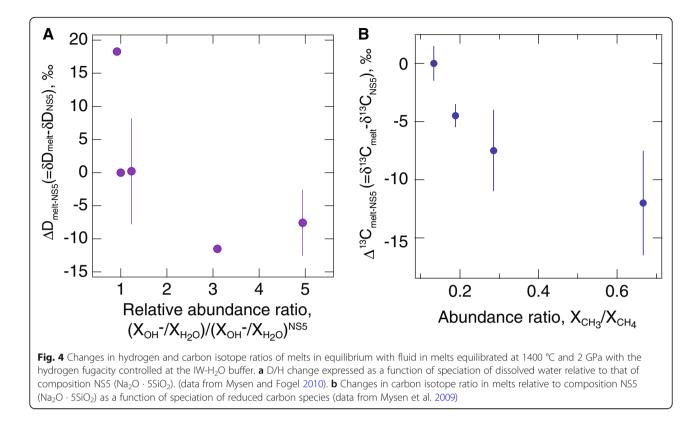
Fig. 3 Abundance of C-bearing species in coexisting COH fluids and melts as a function of temperature and pressure as indicated. **a** Evolution of carbonate species under oxidizing conditions. **b** Evolution of C-bearing species under reducing conditions. **c** Evolution of fluid/melt exchange of carbonate species under oxidizing conditions. **d** Evolution of fluid/melt exchange of C-bearing reduced species under reducing conditions. Note that temperature is the independent variable with pressure evolving as a function of temperature as described briefly in the text and in more detail in the original sources (modified after Mysen 2015a, 2015b). The ΔH values derived from the linear regression of the data are discussed in the text. In calculated these ΔH values, it was assumed that there is no pressure effect on these equilibria

coexisting fluid. The enthalpy change, ΔH, for reaction (3) is − 44 ± 9 kJ/mol with the assumption of ideal mixing (Mysen 2015a). Under reducing conditions, the CH_4/CH_3 abundance ratio in fluid increases faster than in coexisting melt with a ΔH for reaction (4) of 34 ± 3 kJ/mol (Mysen 2015b).

Hydrogen and carbon isotope behavior

In a situation where there is no interaction between the molecules, isotope fractionation factors can be calculated (Bigeleisen and Mayer 1947; Bottinga 1968). However, in most magmatic environments, there are indeed interactions between various silicate and COH complexes

(Chacko et al. 2001). Changes in structural complexes in fluids and brines are known to affect isotope behavior (Horita 1988; O'Neil and Truesdell 1993; Horita et al. 1995; O'Neil et al. 2004). Isotope substitution also can affect materials properties (Horita et al. 2010). It should not be surprising, therefore, that significant isotope fractionation can be observed between melts or fluids with variable structural complexes. For example, hydrogen and carbon isotope ratios in melts in equilibrium with fluid of fixed composition vary as a function of changes on solution mechanisms of COH species in the melt (Fig. 4). The data in Fig. 4 were obtained by analyzing glasses along the join $Na_2O–SiO_2$ after quenching from

Fig. 4 Changes in hydrogen and carbon isotope ratios of melts in equilibrium with fluid in melts equilibrated at 1400 °C and 2 GPa with the hydrogen fugacity controlled at the IW-H_2O buffer. **a** D/H change expressed as a function of speciation of dissolved water relative to that of composition NS5 ($Na_2O \cdot 5SiO_2$). (data from Mysen and Fogel 2010). **b** Changes in carbon isotope ratio in melts relative to composition NS5 ($Na_2O \cdot 5SiO_2$) as a function of speciation of reduced carbon species (data from Mysen et al. 2009)

equilibration with a COH fluid at 1400 °C and 2 GPa and with the hydrogen fugacity buffered with the iron-wüstite-H_2O buffer. Isotope variations are expressed relative to composition, NS5 ($Na_2O \cdot 5SiO_2$). Subsequent spectroscopic examination of the fluid, which remained of constant composition in all experiments, was a mixture of CH_4, H_2, and H_2O. It can be seen quite clearly that the D/H and $^{13}C/^{12}C$ ratios respond to changes in water and methane speciation in the melt, respectively. Similar effects have been reported for D/H fractionation in melts formed in the silicate–H_2O–D_2O systems determined with proton and deuteron MAS NMR (Wang et al. 2015). Analogous experimental data were reported by Dobson et al. (1989) for D/H fractionation between fluid and rhyolite and feldspar melts and Mattey et al. (1990) and Mattey (1991) for carbon isotope fractionation between fluid, basalt, and sodamelilite melt. In light of the more recent data such as summarized in Fig. 4, those earlier data likely reflected variations in speciation of the volatiles in the synthetic and natural melts.

In studies such as those described in the previous paragraph, mass spectrometric measurements were made on glasses and fluids subsequent to quenching from high temperature and pressure. However, fluids quenched from pressures in the GPa pressure range and high temperature such as was the case with those experiments often comprise several molecular silicate components. These silicate-rich fluids are prone to precipitation of solid

materials during quenching. There are also the problems that derive from exsolution of fluid from melts as these are cooled during quenching thus changing the content and possibly proportion of volatile components.

In order to circumvent quenching problems, more recent experiments have combined high-temperature/high-pressure experiments conducted in diamond anvil cells with vibrational spectroscopy as a means to obtain isotope ratios of elements whose isotopic mass differences are relatively large (e.g., D and H, ^{13} and ^{12}C; see (Foustoukos and Mysen 2012; Mysen 2013; Dalou et al. 2015).

With this method, it is taken advantage of the fact that vibrational frequencies are discreet functions of oscillator mass:

$$\nu_1 = \nu_2 \cdot \sqrt{\frac{m_1}{m_2}}, \qquad (5)$$

where ν_1 and ν_2 are vibrational frequencies of a specific mode for isotopes 1 and 2. The m_1 and m_2 are the atomic masses of the ^{12}C and ^{13}C oscillator. In the case of an elemental phase such as graphite or diamond, m_1 and m_2 could be ^{12}C and ^{13}C.

We emphasize that the frequency difference between vibrations with two different isotopes does not change with abundance, but the vibrational intensity, expressed

as integrated areas, A_1 and A_2, does. From vibrational spectra, the isotope ratio, X_1/X_2, of a sample then becomes

$$A_1/A_2 = X_1/X_2. \tag{6}$$

Such vibrational spectroscopic methods have been used to determine hydrogen and carbon isotope ratios in coexisting silicate melts and fluids in silicate–COH systems contained in hydrothermal diamond anvil cells at pressures and temperatures up to those of the Earth's upper mantle. In some of these experiments, redox conditions were controlled with metal/oxide buffers (Re/ReO_2, Ti/TiO_2).

The method has the significant advantage that the analyses are conducted in situ while the samples are the conditions of interest, the method is non-destructive and with spatial resolution on the micrometer scale (see above). There is, therefore, no concern for sample changes during quenching because quenching is not involved. It can also probe quite small samples without interference from adjacent phases. Moreover, in this experimental environment, pressure/temperature conditions can be changed quickly (on the time scale of minutes) without changing the sample. A potential limitation is the sensitivity of the method to isotope abundances relevant to natural conditions. In an effort to assess whether or not this could be a problem, Dalou et al. (2015) conducted experiments with several series of fluid/melt D/H fractionation with different bulk D/H ratios in silicate–H_2O–D_2O systems, but did not find any concentration-dependent variations (Fig. 5).

Hydrogen isotopes

In silicate–COH melt and fluid systems, the principal hydrogen-bearing species are H_2O, OH, H_2, CH_4, CH_3, and HCO_3 where redox conditions and chemical composition of the fluids govern which species will dominate. The molecular species, H_2O and H_2, when present likely occupy 3-dimensional cavities in glass and melts much like that reported for noble gases, for example (Carroll and Stolper 1993; Zhang et al. 2010; Guillot and Sator 2012). Hydrogen isotopes in those molecular species likely will not show significant fractionation effects. As to bicarbonate, HCO_3, no clear isotopic effects in either infrared or Raman spectra (Mysen 2015a) which may suggest that the C–O bond is not affected detectably whether H^+ or D^+ forms the bicarbonate complex.

For the exchange equilibrium,
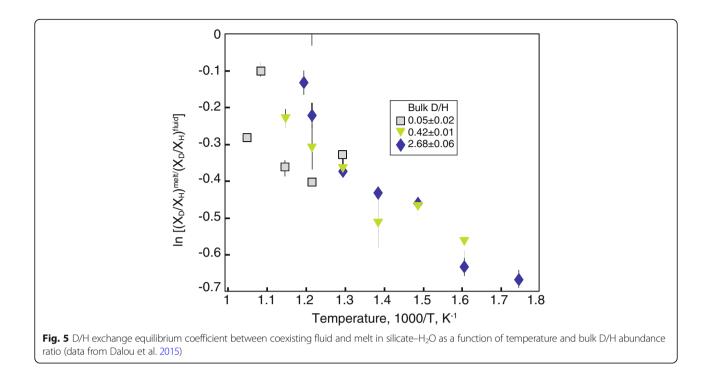
$$H(fluid) + D(melt) = D(fluid) + H(melt), \tag{7}$$

under both oxidizing and reducing conditions, the dominant contribution is via OD/OH fractionation. The

appearance of the vibrational modes assigned to O–D and O–H stretch vibrations is shown in the insert in Fig. 6, where the exchange equilibrium coefficient, $K_{D/H}^{fluid/melt}$, is defined as;
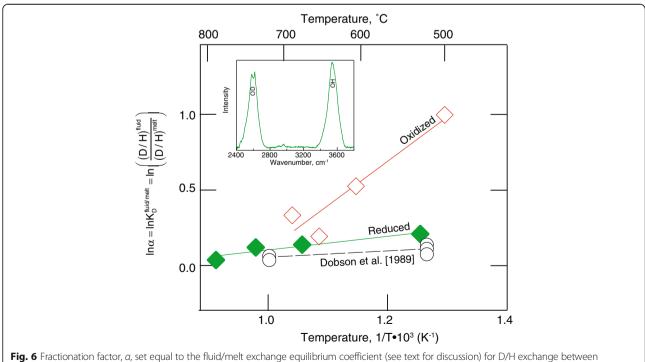
$$K_{D/H}^{fluid/melt} = \left[\frac{(D/H)(fluid)}{(D/H)(melt)} \right], \tag{8}$$

where D/H denotes abundance ratio. From experiments conducted under oxidizing conditions, the D/H ratio simply is the ratio of integrated intensity such as indicated in the insert in Fig. 6, whereas for reducing conditions, information from deuterated methane and methyl complexes also is incorporated.

The D/H evolution with temperature in fluids and melts under oxidizing and reducing conditions differ significantly (Table 1). In general, under oxidizing conditions the ΔH is greater, whether in melts or coexisting fluids. The D/H abundance ratio in fluid always is greater than that in melt. This behavior leads to a D/H exchange coefficient that not only differs at given temperature and pressure, but the rate of change with temperature is different under oxidizing and reducing conditions (Fig. 6; see also Table 1). Notably, experimentally determined D/H fractionation data for rhyolite–H_2O and feldspar composition–H_2O (Dobson et al. 1989) are quite similar to those of silicate–COH under reducing conditions (Fig. 6). Furthermore, the temperature-dependent D/H fractionation in silicate–H_2O–D_2O, using the same silicate composition and working in similar temperature and pressure ranges, result in $\Delta H = 6.5 \pm 0.7$ kJ/mol (Mysen 2013). These groups have somewhat similar structural behavior (see discussion above—Eq. (2)) so a closer similarity between silicate–COH under reducing conditions and silicate–H_2O than between silicate–COH under oxidizing conditions and silicate–H_2O may not be so surprising.

The variations of D/H ratios in fluids and melts and, therefore, in the D/H exchange coefficient are because of changing silicate and COH speciation with changing redox conditions (Kadik et al. 2004; Mysen et al. 2011; Ardia et al. 2013). Additionally, speciation change as a function of temperature and pressure takes place partly because silicate solute concentration in the fluid increases and partly because of changing C-bearing species abundance in the melt (Manning 2004; Newton and Manning 2008; Mysen et al. 2009; Mibe and Bassett 2008; Mysen et al. 2013). Network-modifying cations, which include H^+ and D^+ (which form bonding with nonbridging oxygen), will show preference for specific silicate species depending on the ionization potential of the metal cation as has been demonstrated with ^1H and ^2H MAS NMR spectroscopy (Wang et al. 2015). These

Fig. 5 D/H exchange equilibrium coefficient between coexisting fluid and melt in silicate–H_2O as a function of temperature and bulk D/H abundance ratio (data from Dalou et al. 2015)

Fig. 6 Fractionation factor, α, set equal to the fluid/melt exchange equilibrium coefficient (see text for discussion) for D/H exchange between coexisting fluid and melt as a function of temperature in silicate–COH systems under reducing and oxidizing conditions. Insert shows typical Raman spectrum (here from fluid) to illustrate the appearance of the Raman bands assigned to OD and OH stretch vibrations and used to extract the data themselves. The ΔH values from the two fits are given in Table 1. Also shown are the experimental data for rhyolite–H_2O and feldspar–D_2O glass and melt composition in the 5–20 MPa pressure range from Dobson et al. (1989) (data otherwise from Mysen 2015a)

Table 1 Enthalpy of D/H fractionation in coexisting fluid and melt in silicate-COH under oxidizing and reducing conditions (data from Mysen 2015a)

	Oxidizing	Reducing
$\Delta H(fluid)^*$	9.7 ± 2.0 kJ/mol	− 4.9 ± 1.1 kJ/mol
$\Delta H(melt)^*$	34 ± 4 kJ/mol	− 1.2 ± 0.2 kJ/mol
$\Delta H(Eq. 8)^{**}$	24.8 ± 6 kJ/mol	− 4.5 ± 0.5 kJ/mol

In all cases, ideal mixing is assumed

[*]Enthalpy change from temperature-dependent D/H abundance ratio, $\ln(X_{OD}/X_{OH})$ vs. $1/T$ (K^{-1}), in fluid and melt

[**] Enthalpy change from temperature-dependent exchange equilibrium coefficient between fluid and melt, $\ln[(X_{OD}/X_{OH})^{fluid}/[(X_{OD}/X_{OH})^{melt}]$ vs. $1/T$ (K^{-1})

effects govern H^+- and D^+-oxygen bonding, with the temperature (and pressure)-dependent D/H ratio summarized in Fig. 6 as the result.

D/H behavior in COH-fluid-saturated magmatic systems

Variations in COH speciation in silicate–COH systems at high temperature and pressure affect melt polymerization. Silicate speciation and melt polymerization affect all physical and chemical properties of magmatic liquids, including D/H fractionation among species in the phases (Wang et al. 2015) which, in turn, will affect melt/mineral/fluid D/H fractionation behavior. This feature is evident in Fig. 6. Both redox conditions and abundance of COH volatiles are important.

Experimental data such as summarized in Fig. 6 (see also Table 1) can be employed to illustrate how temperature and redox conditions affect D/H fractionation factors, $\alpha_{D/H}^{fluid/melt}$, and how the fractionation factors, in turn, influence D/H evolution of melts and fluids in magmatic silicate–COH systems in the upper mantle and the deep crust. In doing this, I emphasize, however, that the data to be used are from model compositions in the Na_2O–Al_2O_3–SiO_2–COH system and should, therefore, not be applied quantitatively to natural magmatic processes. The behavior does, however, illustrate principles that should be kept in mind when applying hydrogen isotope data to deduce petrogenetic processes in the Earth's interior.

The exchange equilibrium coefficient, $K_{D/H}^{fluid/melt}$, in Eq. (8) equals the D/H fraction factor, of $\alpha_{D/H}^{fluid/melt}$, provided that the $K_{D/H}^{fluid/melt}$ is independent of bulk composition. According to the results in Fig. 5, this seems a reasonable assumption. Then, we can write its temperature-dependence;

$$\ln K_{D/H}^{fluid/melt} = \ln \alpha_{D/H}^{fluid/melt} = a/T + b, \qquad (9)$$

where T is temperature (kelvin) and a and b are the regression coefficients in a plot such in Fig. 6. The fractionation factor is a strong non-linear function of temperature and is more sensitive to temperature under

oxidizing conditions than under reducing conditions (Fig. 7). That fact that these curves do indeed pass through 1 as the result of changing silicate content in the fluid and COH fluid content in the melt with increasing temperature.

As an example of how the D/H relationships may affect the D/H evolution of magmatic liquids in (COH)--bearing mantle environments, let us start with the assumption that the COH fluid retains a fixed D/H = ratio, δD, of − 100‰. This value was chosen because it is reasonable near the δD value range of the Earth's upper mantle (Bell and Ihinger 2000). The δD values of the melt in equilibrium with such a fluid is

$$\delta D^{melt} = \frac{\delta D^{fluid}}{a_{D/H}^{fluid/melt}} + 1000 \cdot \frac{1-a_{D/H}^{fluid/melt}}{a_{D/H}^{fluid/melt}}. \qquad (10)$$

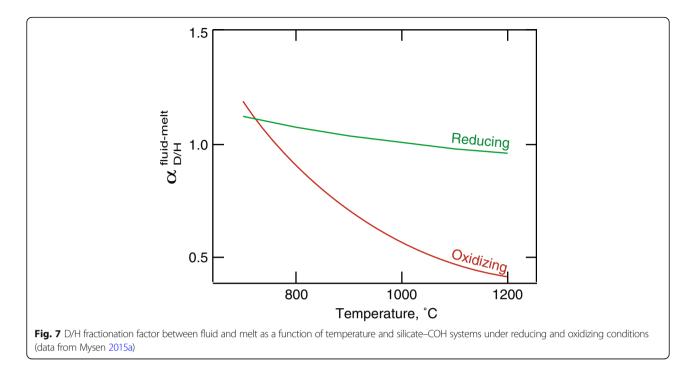In Eq. (10), $\alpha_{D/H}^{fluid/melt}$ is defined in Eq. (9).

As can be seen from the calculated results (Fig. 8), this leads to the suggestion that a magmatic liquid in equilibrium with COH fluid under oxidizing conditions can be as much as 100% heavier than a melt equilibrated with COH under reducing conditions. The δD^{melt} difference is not significantly dependent on temperature of equilibration.

Carbon isotopes

For carbon isotopes, ^{13}C and ^{12}C, the relationship between vibrational frequency and oscillator mass in Eq. (5) would suggest a frequency difference near 4% if the masses simply were those of the carbon isotopes. However, this is not the case. For oxidized carbon, the frequency shift of C–O stretch vibrations, which for natural carbon (nearly pure ^{12}C) occur near 1070 cm^{-1} in the Raman spectra (Frantz 1998) is only about 1.5%. Under reducing conditions, that of C–H stretch vibrations is less than 1% (see inserts in Fig. 9). This happens because oxygen and hydrogen vibrations, respectively, contribute to the oscillator mass.
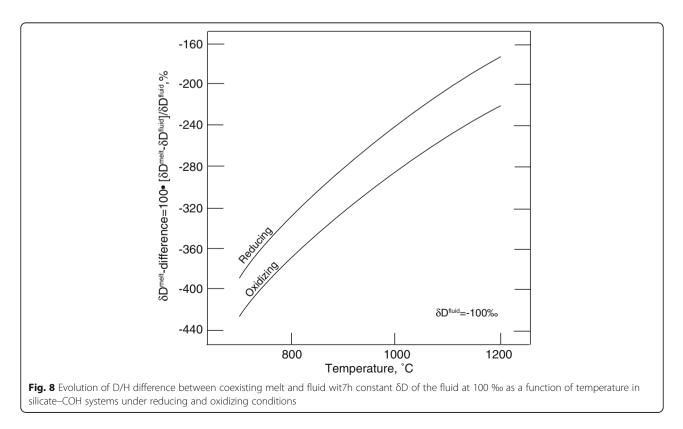
In an examination of carbon isotope behavior in silicate–COH systems under oxidizing conditions, the behavior of both CO_3^{2-} and HCO_3^- complexes and their linkage to the silicate structure in fluids and melts need to be addressed (see Eq. (1)). This is so because the $^{13}C/^{12}C$ ratio and its temperature-dependence in coexisting CO_3^{2-} and HCO_3^- differ (Table 2).
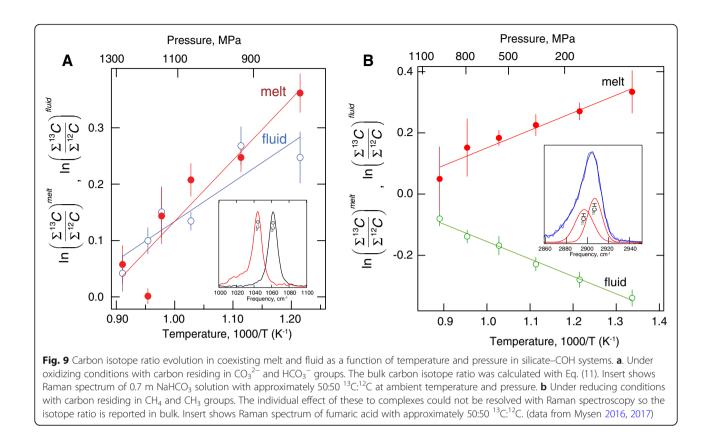
The variations with temperature of the $^{13}C/^{12}C$ ratios in the CO_3 and HCO_3 species also differ in fluids and melts (Table 2). In fluid, the $^{13}C/^{12}C$ ratio in HCO_3 species decreases with temperature (and pressure) whereas for the CO_3 groups, the opposite temperature trend is observed (Table 2). For (C–O–H)-saturated melt coexisting with fluid, on the other

Fig. 7 D/H fractionation factor between fluid and melt as a function of temperature and silicate–COH systems under reducing and oxidizing conditions (data from Mysen 2015a)

hand, the $^{13}C/^{12}C$ ratio of HCO_3 complexes increases and that of CO_3 complexes decreases with increasing temperature and pressure (Table 2). The absolute ΔH values for carbonate complex variations in melts is greater than for fluids, but do, of course, approach one another as the temperature (825 °C) and pressure (1303 MPa) conditions of supercritical phase stability field are reached (Mysen 2017).

The different temperature trajectories of the $^{13}C/^{12}C$ in fluids and melts probably reflect the much

Fig. 8 Evolution of D/H difference between coexisting melt and fluid wit7h constant δD of the fluid at 100 ‰ as a function of temperature in silicate–COH systems under reducing and oxidizing conditions

Fig. 9 Carbon isotope ratio evolution in coexisting melt and fluid as a function of temperature and pressure in silicate–COH systems. **a**. Under oxidizing conditions with carbon residing in CO_3^{2-} and HCO_3^- groups. The bulk carbon isotope ratio was calculated with Eq. (11). Insert shows Raman spectrum of 0.7 m $NaHCO_3$ solution with approximately 50:50 ^{13}C:^{12}C at ambient temperature and pressure. **b** Under reducing conditions with carbon residing in CH_4 and CH_3 groups. The individual effect of these to complexes could not be resolved with Raman spectroscopy so the isotope ratio is reported in bulk. Insert shows Raman spectrum of fumaric acid with approximately 50:50 ^{13}C:^{12}C. (data from Mysen 2016, 2017)

higher silicate and aluminosilicate content of melts compared with fluid. This difference is responsible for the presence of essentially only Q^0 species in fluids compared with significant abundance of more polymerized aluminosilicate species in the melt (Mysen

Table 2 Enthalpy of ^{13}C/^{12}C fractionation in coexisting fluid and melt in silicate-COH under oxidizing and reducing conditions (data from Mysen 2016, 2017)

Oxidizing		Reducing	
$\Delta H_{CO3}(fluid)$[*]	11 ± 3 kJ/mol	$\Delta H_{CH4}(fluid)$[†]	4.7 ± 0.2 kJ/mol
$\Delta H_{HCO3}(fluid)$[**]	-12 ± 5 kJ/mol	$\Delta H_{CH4}(melt)$[†]	-4.8 ± 0.6 kJ/mol
$\Delta H_{CO3}(melt)$[*]	-30 ± 4 kJ/mol	$\Delta H_{Kmelt/fluid}$[b]	9.5 ± 0.8 kJ/mol
$\Delta H_{HCO3}(melt)$[**]	29 ± 6 kJ/mol		
$\Delta H_{\Sigma13C/\Sigma12C}(melt)$[a]	-9 ± 1.6 kJ/mol		
$\Delta H_{\Sigma13C/\Sigma12C}(fluid)$[a]	-5.8 ± 1.3 kJ/mol		
$\Delta H_{Kmelt/fluid}$[b]	3.2 ± 0.7 kJ/mol		

[*]$\Delta H_{CO3}(fluid)$ and $\Delta H_{CO3}(melt)$ were derived from the relationship, $\ln(^{13}C/^{12}C)$ vs. $1/T$ (K^{-1}) in fluid and melt under oxidizing conditions
[**]$\Delta H_{HCO3}(fluid)$ and $\Delta H_{HCO3}(melt)$ were derived from the relationship, $\ln(^{13}C/^{12}C)$ vs. $1/T$ (K^{-1}) in fluid and melt under oxidizing conditions
[†]$\Delta H_{CH4}(fluid)$ and $\Delta H_{CH4}(melt)$ were derived from the relationship, $\ln(^{13}C/^{12}C)$ vs. $1/T$ (K^{-1}) in fluid and melt under reducing conditions
[a]The same as for $\Delta H_{CO3}(fluid)$ and $\Delta H_{CO3}(melt)$ except that total carbonate ratio $\Sigma^{13}C/\Sigma^{12}C$, where total carbonate is $CO_3 + HCO_3$, is used
[b]$\Delta H_{Kmelt/fluid}$ under oxidizing and reducing conditions was derived from the relationship, $\ln[(\Sigma^{13}C/\Sigma^{12}C)^{melt}/[(\Sigma^{13}C/\Sigma^{12}C)^{fluid}]$ vs. $1/T$ (K^{-1})

2017). Given the interaction between the carbonate groups and oxygen in the Q-species in the melts and the fact that nonbridging oxygen in Q-species of different degree of polymerization likely are energetically diggerent (Kohn and Schofield 1994; Mysen 2007), it follows that the energetics of oxygen bonds associated with CO_3 and HCO_3 groups is also different. These difference, in turn, means that energetics of the C–O bonds in CO_3 and HCO_3 groups differ. As a result, the $^{13}C/^{12}C$ abundance evolution with temperature (and pressure) of these groups in silicate melt will differ from that in fluid. These differences in silicate speciation in fluid and melt change, however, with temperature and pressure. In particular, the silicate content of the fluid likely increases, which will cause changes in Q-speciation in the fluid (Mysen et al. 2013). As this occurs, the influence of fluid composition on its $^{13}C/^{12}C$ ratio will also become increasingly important, a conclusion which is similar to that made for temperature- and pressure-dependent changes D/H fractionation in silicate–H_2O and silicate–C–O–H systems (Wang et al. 2015; Dalou et al. 2015; Le Losq et al. 2016).

The bulk $^{13}C/^{12}C$, Σ $^{13}C/\Sigma^{12}C$, comprises the contributions from both the CO_3^{2-} and HCO_3^- groups, $^{13}CO_3^{2-}$, $^{12}CO_3^{2-}$, $^{13}HCO_3^{2-}$, and $^{12}HCO_3^{2-}$ together

with the molecular fraction of the species, X_{CO3} and X_{HCO3}, where $X_{HCO3} = 1 - X_{CO3}$, so that

$$K_D^{melt} = \left(\frac{\sum {}^{13}C}{\sum {}^{12}C}\right)^{melt}$$
$$= \left(\frac{X_{CO_3}g13CO_3^{2-} + (1-X_{CO_3})g13HCO_3^-}{X_{CO_3}g12CO_3^{2-} + (1-X_{CO_3})g12HCO_3^-}\right)^{melt},$$

(11)

and with a similar expression for fluid. The K_D^{melt} and K_D^{fluid} differ (Fig. 9a; Table 2) because the values and temperature-dependence of ${}^{13}C/{}^{12}C$ of fluid and melt differ.

Therefore, for the carbon isotope exchange equilibrium between melt and fluid under oxidizing conditions we have the exchange equilibrium

$$\sum 12C(melt) + \sum 13C(fluid)$$
$$= \sum 12C(fluid) + \sum 13C(melt).$$

(12)

for which,

$$K_D^{melt/fluid} = \frac{K_D^{melt}}{K_D^{fluid}},$$

(13)

where K_D^{melt} and K_D^{fluid} are defined in Eq. (11) for melt and fluid, respectively.

The temperature-dependence of this $K_D^{melt/fluid}$ (Fig. 10b) leads to $\Delta H = 9.5 \pm 0.8$ kJ/mol. Under the assumption that the carbon isotope ratio is not dependent on total carbon concentration, the $K_D^{fluid/melt}$ values equal the fractionation factors. The carbon isotope fractionation factor under reducing conditions is about three times as sensitive to temperature than under oxidizing conditions. This means the carbon isotope behavior also differs from the D/H fractionation behavior where oxidizing conditions are those under which the D/H fractionation factor is the most sensitive to temperature.

Carbon isotope behavior in COH-fluid-saturated magmatic systems

Before addressing an example of how redox conditions during melting and crystallization may affect the carbon isotope behavior, the reader is reminded that the data to be used for this illustration were obtained in simple three component systems and with only one C/O/H ratio of the fluid component. We must also remember that the melts examined in this study were (C–O–H)-saturated and the coexisting (C–O–H) fluids were silicate-saturated. The speciation behavior is not, therefore, the same as in silicate-free carbonate–H_2O system

such as in the in situ studies of Facq et al. (2014) and Foustoukos and Mysen (2015).

The example below, therefore, is intended to illustrate principles, but not necessarily quantitative behavior. Calculated $\delta^{13}C$-evolutions in a melt in equilibrium with a (C–O–H)-bearing source with $\delta^{13}C$ of fixed at − 7 and − 30 ‰ and in a temperature corresponding to those of magmatic processes in the deep crust and upper mantle are shown in Fig. 11. The − 7 and − 30 ‰ $\delta^{13}C$ values correspond to the range in $\delta^{13}C$ of mantle-derived peridotite and eclogite nodules in basalt and kimberlite (see Deines 2002, for review).
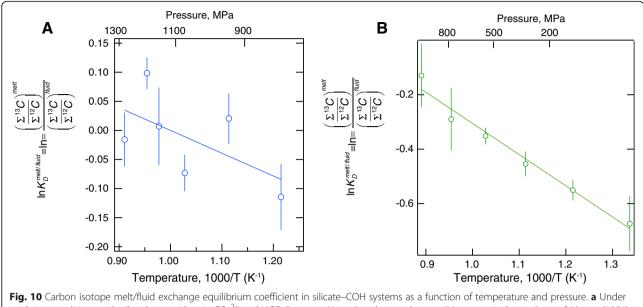
For a melt, its $\delta^{13}C$ value can differ from that of the source region by more than 100‰ and this difference increases with increasing temperature (Fig. 11). This also means that exsolution of C–O–H fluid from a melt in the upper mantle and deep crust, the $\delta^{13}C$ of an evolving CO_2-rich fluid can be equally enriched in carbon-13 relative to the magma. This isotope behavior is, however, quite different under reducing and oxidizing conditions regardless of the $\delta^{13}C$ value of the source rock (Fig. 11). Under reducing conditions, (COH)-saturated melts are isotopically heavier than silicate-saturated fluids. Under oxidizing conditions, the $\delta^{13}C$ of the magmatic liquid at lower temperature is also heavier than fluid, but the temperature effect shifts this value to become isotopically lighter at higher temperature. This different behavior under reducing and oxidizing conditions reflects the different structural roles and effects on melt and fluid structure depending on the oxidation state of carbon (Mysen 2015a) (see also Eqs. (1) and (2)). It follows that changing redox conditions during melting and crystallization of (C–O–H)-bearing deep crust and upper mantle can have profound effect on the carbon isotopic signature of the melt.
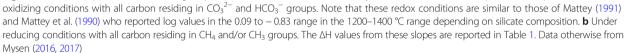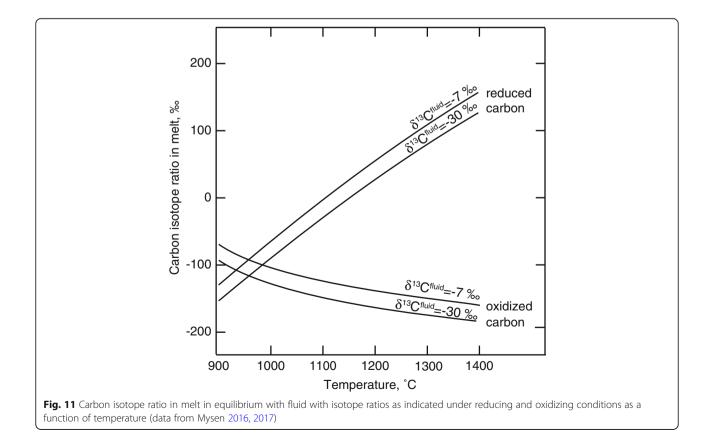
Conclusions

The behavior of COHN fluids, their isotopes, and their interaction with magmatic liquids are at the core of understanding formation and evolution of the Earth.

The solubility of individual COHN components in silicate melts can differ by several orders of magnitude and ranges from several hundred ppm to several wt% at upper mantle pressure and temperature. Silicate solubility in fluid can reach several molecular. Different solubility of oxidized and reduced C-bearing species in melts reflects different solution equilibria. The oxidized species are H_2O, OH^-, CO_3^{2-}, HCO_3^-, CO_2, and N_2, whereas reduced species are H_2O, OH^-, H_2, CH_4, CH_3, NH_3, and NH_2. The C-solubility decreases and N-solubility increases with f_{O_2} below the QFM oxygen buffer.

The structural changes with variable redox conditions of carbon and silicate in magmatic melts and fluids result in D/H, ${}^{13}C/{}^{12}C$, and ${}^{15}N/{}^{14}N$ fractionation between

Fig. 10 Carbon isotope melt/fluid exchange equilibrium coefficient in silicate–COH systems as a function of temperature and pressure. **a** Under oxidizing conditions with all carbon residing in CO_3^{2-} and HCO_3^{-} groups. Note that these redox conditions are similar to those of Mattey (1991) and Mattey et al. (1990) who reported log values in the 0.09 to − 0.83 range in the 1200–1400 °C range depending on silicate composition. **b** Under reducing conditions with all carbon residing in CH_4 and/or CH_3 groups. The ΔH values from these slopes are reported in Table 1. Data otherwise from Mysen (2016, 2017)

Fig. 11 Carbon isotope ratio in melt in equilibrium with fluid with isotope ratios as indicated under reducing and oxidizing conditions as a function of temperature (data from Mysen 2016, 2017)

melt, fluid, and crystalline materials that depend on redox conditions and can differ significantly from 1 even at magmatic temperatures. The D/H fractionation between aqueous fluid and magma yields ΔH between -5 and 25 kJ/mol depending on redox conditions. The ΔH values for $^{13}C/^{12}C$ fractionation factors are near -3.2 and 1 kJ/mol under oxidizing and reducing conditions, respectively. These differences are because energetics of O–D, O–H, O–^{13}C, and O–^{12}C bonding environments are governed by different solution mechanisms in melts and fluids.

It is suggested that (COH)-saturated partial melts in the upper mantle can have δD values of 100‰, or more, lighter than coexisting silicate-saturated fluid. This effect is greater under oxidizing than under reducing conditions. Analogous relationships exist for $^{13}C/^{12}C$. For example, at magmatic temperatures in the Earth's upper mantle, $^{13}C/^{12}C$ of melt in equilibrium with COH-bearing mantle in the -7 to $-30‰$ range increases with temperature from about 40 to > 100‰ and 80–120 ‰ under oxidizing and reducing conditions, respectively.

Availability of data and materials
This is a review paper. All data discussed here are in the original papers cited in the text.

Authors' contributions
All research of the manuscript was by the author. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

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