Revision 1

Speciation of and D/H partitioning between fluids and melts in silicate - D-O-H-C-N systems determined in-situ at upper mantle temperatures, pressures, and redox conditions

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Abstract

Speciation of D-O-H-C-N volatiles in alkali aluminosilicate melts and of silicate in D-O-H-C-N fluid has been determined in-situ to 800°C and >2 GPa under reducing and oxidizing redox conditions by using an externally-heated hydrothermal diamond cell with Raman spectroscopy as the structural probe. Reducing conditions were near those of the IW oxygen buffer, whereas oxidizing conditions were obtained by conducting the experiments with oxidized components only and with Pt as a catalyst.

Raman bands assigned to C-H stretching in CH₃D₂ isotopologues and CH₄ groups (including CH₃) were employed to determine the CH₄/CH₃D₂ ratio in fluids and melts. This ratio decreases from 1.5-2 at 500°C to between 1.2 and 1 with 800°C with ΔH-values of 13.6±2.1 and 5.5±1.1 kJ/mol for melt and fluid, respectively. The CH₄/CH₃D₂ fluid/melt partition coefficient ranges between ~16 and ~3 with ΔH=33±6 kJ/mol assuming no pressure effect. This behavior of deuterated and protonated complexes is ascribed to speciation of volatile and silicate components in fluids and melts in a manner that is conceptually similar to D/H partitioning among complexes and phases in brines and hydrous silicate systems.

Molecular N₂ is the N-bearing species in fluids and melts under oxidizing conditions. Under reducing conditions, the dominant species are molecular NH₃ and ammine groups, NH₂-⁺. The NH₃/NH₂ ratio varies between 0.15 and 0.75 in the 425°-800°C temperature range. The enthalpy change of the ammonia/ammine equilibrium, ΔH, derived from the temperature and assuming no pressure effect on the equilibrium, is 19±8 kJ/mol and 61±9 kJ/mol for melt and fluid, respectively. The fluid/melt partition coefficient, (NH₃ + NH₂⁺)fluid/(NH₃ + NH₂⁺)melt, ranges from 8 to 3 with ΔH=45±12 kJ/mol. For oxidized nitrogen, the fluid/melt partition coefficient is twice or more of
those values for reduced nitrogen. Hydrogen bonding can be detected at 500°C and below. This behavior resembles that of H$_2$O. Deuterium-containing analogues of the (N+H)-species could not be detected with precision because these were in the frequency-range of the 2.-order Raman shift of diamond in the diamond anvil cell itself and could not be isolated from the strong background generated by the Raman intensity from the diamond.

**Introduction**

Characterization of the processes that govern the budget and recycling of volatile components in the Earth’s interior is central to our understanding of the formation and evolution of the solid Earth, its ocean and its atmosphere (e.g., Kasting et al., 1993; Tolstikhin and Marty, 1998; Cartigny and Ader, 2003; Kadik et al., 2013). The speciation and solubility of volatiles (H$_2$O, CO$_2$, CO, CH$_4$, N$_2$, NH$_3$, noble gases, etc.) in magmatic melts and fluids are integral parts of this understanding.

Oxygen fugacity affects the behavior of volatile-bearing magmatic systems because oxidized and reduced volatile species can behave quite differently (e.g., Saxena and Fei, 1987; Ulmer and Luth, 1991; Mysen et al., 2011). In the present silicate mantle $f\text{O}_2$ commonly is considered to be near redox conditions similar to QFM±1-2 (Wood et al., 1990; Luth et al., 1990; Canil, 2002). Under these conditions, the dominant C-O-H-N volatiles species are H$_2$O, CO$_2$, and N$_2$ with smaller amounts of CH$_4$ and NH$_3$ (Ulmer and Luth, 1991; Kasting et al., 1993; Holloway and Blank, 1994; Mysen et al., 2008, 2011). Under reducing conditions similar to those during the Earth’s core-forming stage (perhaps 1-2 order of magnitude lower than that of the IW oxygen buffer) the main species were likely CH$_4$, H$_2$O, H$_2$, and NH$_3$ (Holland, 1984; Kasting et al., 1993; Mysen et al., 2011; Kadik et al., 2011). This redox-
dependent speciation has profound effects because interaction between dissolved volatiles and the silicate melt solvent depends on their oxidation state. Melt properties vary with melt polymerization (for review, see for example, Mysen, 2012).

Most current experimental data on solubility and solution mechanisms of C-O-H-N volatiles in silicate melts are from analysis of glasses that were formed by quenching volatile-containing melts to ambient temperature at high pressure. Reliance on glass structure to establish melt structure/property relations requires that glass is, in fact, a quantitative proxy for melt. This is not the case because the glass structure records that of the liquid at its glass transition temperature. The glass transition temperature is hundreds of degrees lower than the liquidus temperature (Moynihan et al., 1976; Dingwell and Webb, 1990).

The C-O-H-N fluids in equilibrium with silicate at high temperature and pressure relevant to the deep crust and upper mantle cannot be quenched to ambient conditions for quantitative study because oxides dissolved in fluids commonly precipitate during quenching to ambient conditions. This is so because oxide solubility is greatly different at high temperature and pressure (Pascal and Anderson, 1989; Mysen and Armstrong, 2002; Kessel et al., 2004). It is very difficult, therefore, to extract compositional, isotopic, and structural information of high-temperature/pressure fluids from examination of their quench products.

The experimental complications can be overcome by compositional and structural characterization of coexisting melts and fluids at the temperature and pressure of interest. This is the objective of the present report. Here, structure and D/H isotopic behavior of
silicate - D-O-H-N-C fluids and melts in equilibrium in an externally-heated
hydrothermal diamond anvil cell have been determined in-situ by vibrational
spectroscopic methods with the samples at the desired high temperature, pressure, and
redox conditions.

Experimental Methods

The silicate starting material was the same Na₂O-Al₂O₃-SiO₂ NA10 glass {NA10:
[(Na₂Si₄O₁₀)(Na₂(NaAl)₄O₉)]₁₀} as that used by Mysen (2007). In its molten form at
pressures less than that where Al- or Si-coordination transformation in aluminosilicate
melts occur, the degree of polymerization of NA10, expressed as NBO/T, is near 0.5. The
Al/(Al+Si) is near 0.2. In these respects, the composition resembles basaltic andesite. The
NA10 composition also is advantageous from a practical perspective because its liquidus
and glass transition temperatures are so low (Richet and Bottinga, 1984; Knoche et al.,
1994; Del Gaudio et al., 2007) that the melt is thermodynamically relaxed (supercooled
liquid) over a temperature interval of at least 500°C below the maximum sustainable
temperature in the Bassett diamond cell (≤1000°C; Bassett et al., 1996). These
circumstances provide a wide temperature interval over which to examine the interaction
of C-O-H-N volatile components with aluminosilicate melt.

Water was added as a H₂O:D₂O mixture of 50 vol% of each component. We will
refer to this as water throughout this report. Nitrogen was added as AgN₃. The silver azide
decomposes to metallic Ag and N₂ below 350°C (Roskosz et al., 2006). Carbon was from
residue after cleaning of residual glue (Crystal Bond™ with acetone as cleaning agent)
employed during polishing of the gaskets before use.
High-temperature-pressure experiments were carried out in an externally-heated diamond anvil cell device (HDAC) (Bassett et al., 1994, 1996) with a 125 μm thick Ir gaskets with a 500 μm diameter central hole used for sample containment. During an experimental series, these dimensions shrank to about 80 μm thickness in the region of contact with the 1-mm diamond culets and to a hole diameter near 400 μm. In the HDAC, external wire heaters surrounding each diamond aids in homogeneous temperature distribution (±2°C) over the entire sample.

The temperature was measured with two K-type thermocouples (in contact with the upper and lower diamonds) that are calibrated against the melting temperature of NaCl (800.5°C). Pressure was generated by the fluid because increasing temperature in a constant volume sample compartment increases the pressure. The presence of a C-O-H-N fluid phase also ensures hydrostatic pressure conditions. Pressure at high temperature was determined from the Raman shift of 13C synthetic diamond (Bassett et al., 1996; Schiferl et al., 1997; Mysen and Yamashita, 2010). Spectrometer precision during the measurements of the 13C diamond (±0.1 cm⁻¹) was optimized by using 2400 gratings/mm and Ne emission lines as internal frequency reference. The pressure/temperature effect on this Raman shift has been calibrated to an uncertainty of ±100 MPa with a ±40 MPa precision (Mysen and Yamashita, 2010). By combining this uncertainty with that of the Raman shift of the 13C diamond at experimental conditions, overall pressure uncertainty of an experiment is ±110 MPa.

The experiments were carried out with two different redox conditions. Reducing conditions were obtained with the redox equilibrium, Mo + H₂O = MoO₂ + H₂, where Mo was added to the sample and was oxidized to MoO₂ via reaction of water at high
temperature and pressure. The \( f_{O_2} \) of this reaction in the presence of pure \( H_2O \) is about an order of magnitude below that of the common redox buffer, \( Fe/FeO \) (iron-wustite). In mixed C-O-H-N fluids, the \( f_{H2O} \) is less than for pure \( H_2O \) thus leading to higher \( f_{O2} \). Another series of experiments was carried out under what is referred to as "oxidizing conditions". In these experiments, small pieces of Pt metal was added to Mo-free starting materials. This Pt was employed to enhance isotope equilibration rate. There is no evidence that Pt reacts with water to form hydrogen and platinum oxide (Mysen, 2013a). The \( f_{O2} \) was not buffered in these experiments.

**Structural Analysis**

Raman spectroscopy was used for structural examination. Spectroscopy was carried out with a JASCO model NRS-2000 microRaman spectrometer with a triple monochromator and a 400 mm focal distance. Spectra were recorded through a Mitutoyo 20X magnification/0.42 N.A. long-working distance objective lens. The samples were excited with the 488 nm line of a Spectra Physics, Stabilite 2017 Argon Ion Laser operating at 50 mW at the sample. A Princeton Instruments, LN/CCD-1100PF LN\(_2\)-cooled CCD is used for signal detection.

The measurements were conducted by subjecting a given sample in the HDAC to a series of temperatures and pressures. The sample was first brought to the highest temperature and pressure for a planned series of experiments (800°C and 843 or 2165 MPa, for reduced and oxidized samples, respectively). After acquisition Raman spectra for carbon-13 diamond, fluid, and melt, the sample was brought to the next lower
temperature. The temperature decrement per measurement was 75°C with 1°C/s cooling rate. Acquisition times ranged from 180 to 900 s/CCD window.

The spectra were first corrected for instrumental background followed by temperature- and frequency-dependent correction of Raman intensities (Long, 1977). The background correction was carried about by subtracting a spline function fitted through spectral regions without Raman signals from the raw Raman spectra. Segments of the spectral range of the resulting temperature-, frequency-, and background-corrected Raman spectra were fitted to Gaussian lines by using the commercial software package IGOR™ from Wavemetrics.

The Raman spectra were used to characterize speciation of volatiles and of silicate components in melts and fluids and also to determine fluid/melt partition coefficients. Partition coefficients could be determined in this manner because for the same vibration of the same bond in the same structural species in coexisting fluid and melt, the Raman cross-section is the same in spectra of coexisting fluid and melt. These cancel out in a ratio of integrated Raman intensities. The partition coefficient then is the ratio of integrated areas of the Raman signals assigned to given vibration,

\[ K_{\text{fluid/melt}}^M-X = \frac{A^\text{fluid}_V(M-X)}{A^\text{melt}_V(M-X)} \]  

(1)

In this expression, \( v_{M-X} \) refers to the vibration of the M-X species of interest and A the integrated area of the Raman band in the spectra of coexisting fluid and melt.
The D/H ratios in individual species in coexisting fluids and melts were
determined by using the same principles. To determine D/H ratio, it is also assumed that
the Raman cross-sections of D- and H-containing species are the same. In a recent study
of D/H partitioning between silicate melt and aqueous fluid in a similar system, Mysen (2013b) found this to be so within the errors associated with determination of area ratios
typically 5-10% relative to actual value).

Equilibrium Considerations

Platinum and molybdenum can serve to enhance isotopic (and chemical) equilibration
rates. For example, Horita (1988) found that D/H equilibrium between H₂O and D₂O at
25°C is reached in 1-2 hours in the presence of metallic Pt. In the current experiments at
much higher temperature, the samples remained at each temperature for more than 1 hour.
Further, previous time studies during in-situ experiments with Na10+H₂O+D₂O in
similar temperature and pressure ranges indicated that D/H equilibrium was reached in
minutes (Mysen, 2013b). We conclude, therefore, that equilibrium was reached in the
present experiments.

Results

The temperature paths were similar for the two series of experiments (Fig. 1). The
pressures during the experiment under oxidizing conditions were 30 - >100% higher than
those under reducing conditions. The different pressure paths reflect different proportions
of fluid and melt, different fluid proportions, and different types of fluid species.
Raman Spectra

The low-frequency region, below about 1200 cm$^{-1}$, comprises signals from the structural environments of silicate components (Fig. 2). In the frequency range between ~2000 and ~2800 cm$^{-1}$, in addition to second-order diamond vibrations from the diamond in the diamond cell, this is where Raman bands from pure N$_2$ and deuterated nitrogen complexes would be found (Fig. 3). The 2800-4200 cm$^{-1}$ range comprises bands assigned to N-H and C-H stretching together with O-H and H-H stretching (Fig. 4).

Below 1200 cm$^{-1}$. At 800°C and 2165 MPa under oxidizing conditions the spectrum of fluid below 1200 cm$^{-1}$ characteristically shows a strong band near 780 cm$^{-1}$ and a weaker band near 600 cm$^{-1}$ (Fig. 2). There may also be slight intensity above 780 cm$^{-1}$, but this cannot be observed at any temperature less than 800°C. The intensity of both bands diminishes rapidly with decreasing temperature and pressure. These features resemble those of silicate-saturated fluids in hydrous alkali aluminosilicate, silicate, and silica systems under similar pressure and temperature conditions (Zotov and Keppler, 2000; Mibe et al., 2008; Mysen, 2010). The band near 600 cm$^{-1}$ is a bending vibration involving bridging oxygen thus implying silicate polymerization. It follows that the silicate species are dominantly of Q$^0$ and Q$^1$ type at least at the highest temperature and pressure. At lower temperatures and pressures, there is no evidence for silicate species that are more polymerized than Q$^0$.

The spectra of fluid under reducing conditions (Mo-MoO$_2$) differ from those of oxidized fluids in that there are additional strong bands centered near 880 and 920 cm$^{-1}$ (Fig. 2). The 780 cm$^{-1}$ band, present in spectra of oxidized fluids, remains, but no Raman
intensity can be seen at lower frequencies. The 880 and 920 cm\(^{-1}\) bands probably cannot
be assigned to vibrations associated with silicate (e.g., Si-OH or Si-OD, with symmetric
stretching resulting in Raman intensity near 900-970 cm\(^{-1}\); see also Stolen and Walrafen,
1976; McMillan and Holloway, 1987) because there is no Raman intensity in this
frequency region in the spectra recorded under oxidizing conditions even though H\(_2\)O
was also a major component on those experiments. Rather, these bands should be
assigned to vibrations involving reduced nitrogen, such as, for example, Si-NH\(_2\)
stretching. Such Raman bands occur in this frequency region (Ishida et al., 1982; Dillon
et al., 1991).

The absence of Raman bands below 780 cm\(^{-1}\) likely means that there are no
silicate species with bridging oxygen because that would result in Raman intensity
between about 550 and 700 cm\(^{-1}\) (Si-O-Si bending; see, for example, Furukawa et al.,
1981; Hemley et al., 1987). In other words, the silicate dissolved in fluid under reducing
conditions exists only as completely depolymerized Q\(^0\) species even at the highest
temperatures and pressures used in the illustration of Raman spectra of fluid in Fig. 2.

The Raman spectra of melt are significantly more complex than those of fluids
whether under oxidizing or reducing conditions (Fig. 2). There are Raman bands centered
near 500, 570, and 600 cm\(^{-1}\). Under oxidizing conditions, the spectra show a strong band
at and above 780 cm\(^{-1}\). The three lowest frequency bands are assigned to rocking and
bending motions in Si-O bonding in polymerized silicate structures (Matson et al., 1986;
McMillan et al., 1992). The 780 cm\(^{-1}\) band is assigned to Si-O stretching in Q\(^0\) as for
other samples, whereas the broad and strong maximum near 850 and additional bands
toward higher frequency (900 cm\(^{-1}\) and higher) in spectra of melts recorded under
oxidizing conditions are assigned to stretch vibrations of Si-O bonds in increasingly polymerized silicate species as the frequency increases (e.g., Furukawa et al., 1981; Mysen et al., 1982 McMillan et al., 1992). The intensity in this spectral region of melts under reducing conditions differs from those of melts formed from oxidizing conditions. The bands are narrower, with a maximum near 880 cm\(^{-1}\) and a shoulder near 920 cm\(^{-1}\). These frequencies are nearly identical to those of the spectra of fluid under reducing conditions. It is probable, therefore, that the structural features that give rise to these intensities in coexisting fluids and melts formed under reducing conditions may resemble one another.

2000-2800 cm\(^{-1}\). This is the spectral range where Raman bands occur that are assigned to N-D, OD, and N-N vibrations (Loutellier and Percha, 1989; Walrafen et al., 1996; Schäfer et al., 2012). These could be from molecular N\(_2\), from ND\(_2\), NHD and OD groups. However, this is also spectral range where the 2.-order Raman spectrum of diamond from the diamond cell itself occurs. This is a very intense group of bands (Fig. 3). This diamond signal imposes, therefore, a strong and complex background on spectra of the fluids and melts. Two examples with fluid under oxidizing and reducing conditions at the highest temperature (800°C) are shown in Fig. 3. Spectra recorded at lower temperature and pressure show the same features.

The spectral range where bands assigned to OD vibrations from D\(_2\)O would be expected (e.g., Walrafen et al., 1996) is indicated with double arrows in Fig. 3. The presence of molecular N\(_2\) is manifested by a Fermi doublet 2300 cm\(^{-1}\) (e.g., Loutellier and Percha, 1989). These can be seen as sharp peaks in spectra of fluids under both
oxidizing and reducing conditions (Fig. 3). They are weak or cannot be detected in
spectra of melts. Deuterium-substituted (N-D)-complexes would be indicated by Raman
bands assigned N-D stretching around 2400 cm\(^{-1}\) (Schäfer et al., 2012). These positions
are marked by arrows in Fig. 3B. However, whether or not these are present cannot be
discerned above the strong intensity from the 2.-order diamond intensity in this frequency
region.

2800-4200 cm\(^{-1}\). The most intense feature in this region, observed in all spectra, is the
broad (>100 cm\(^{-1}\)) slightly asymmetric band centered near 3600 cm\(^{-1}\) (Fig. 4). This band –
actually a composite of several Raman bands – resembles that reported for water-
saturated Na-silicate and aluminosilicate melt+fluid systems (Mysen, 2009, 2010) as well
as that of pure H\(_2\)O (Walrafen et al., 1986; Frantz et al., 1993). These Raman bands are
assigned to O-H stretching in OH-groups in H\(_2\)O and HDO (Walrafen et al., 1986; Veirs
and Rosenblatt, 1987; Frantz et al., 1993).

There are two groups of bands below the 3600 cm\(^{-1}\) maximum in spectra of melts and
fluids formed under reducing conditions. There is an asymmetric band near 3320 cm\(^{-1}\)
with a shoulder near 3350 cm\(^{-1}\) (Fig. 4). In spectra of fluids, these can be separated into
two distinct bands, whereas in spectra of melts, the bands are so weak that separation into
two bands is not statistically meaningful (see also Fig. 4). These bands are assigned to N-
H stretching in amine groups (NH\(_2\)) and likely ammonia (NH\(_3\)) (Yeo and Ford, 1994;
Kowal, 2002). Ammonium (NH\(_4^+\)) groups are unlikely because the N-H stretch bands for
NH\(_4^+\) groups are between 3000 and 3200 cm\(^{-1}\) (Socrates, 2001). Mysen et al. (2008)
noted that in Raman spectra of ammonium salts, there were no Raman bands at frequencies greater than 3200 cm\(^{-1}\).

In Raman spectra of melts and fluids equilibrated under reducing conditions there is also a doublet of bands near 2920 and 2960 cm\(^{-1}\). These bands do not exist in spectra of samples equilibrated under oxidizing conditions (Fig. 4). Their assignment is somewhat complex. One possibility is N-H stretching in NH\(_2\)\(^+\) functional groups, which would result in a Raman band near 2960 cm\(^{-1}\) (Socrates, 2001). However, this interpretation does not explain the 2920 cm\(^{-1}\) band. The band cannot be assigned to N-D stretching in ND\(_2\) or NHD complexes because such a Raman band would occur near 2500 cm\(^{-1}\) (Schäfer et al., 2012). It seems, therefore, that the two bands in this doublet should not be assigned to vibrations in N-bearing functional groups. A band near 2920 cm\(^{-1}\) has been reported, however, in high-temperature/-pressure in-situ Raman spectra of nominally pure H\(_2\)O in the hydrothermal diamond anvil cell. A Raman band near 2900 cm\(^{-1}\) was originally ascribed to CH\(_4\) formed by interaction between H\(_2\)O and carbon from the diamond in the diamond cell itself to form CH\(_4\) (Chou and Anderson, 2009). Mysen and Yamashita (2010) noted, however, that a more likely source of the carbon is from incomplete cleaning of gaskets after polishing (held in place by Crystal Bond\textsuperscript{TM}, an organic adhesive) and/or incomplete removal of organic solvents (acetone) during the same processes. This possibility certainly also exists in the present experiments. If so, the band near 2920 cm\(^{-1}\) could be assigned to C-H stretching in CH\(_4\) or methyl (CH\(_3\)) groups and the 2960 cm\(^{-1}\) band to C-H stretching in CH\(_3\)D\(_2\) isotopologues as has been reported in spectra of high-temperature/-pressure H\(_2\)O-D\(_2\)O-CH\(_4\) fluids (Foustoukos and Mysen, 2013). The frequencies of the bands from the present study are identical, within
uncertainty, to those in that study (Fig. 5). The isotopologues were formed by D/H exchange between CH$_4$ and D$_2$O in the fluid.

Spectra of fluids and melts formed under reducing conditions at the highest temperature and pressure have a weak band near 4140 cm$^{-1}$ (see insert in Fig. 4), which is not observed in spectra of fluids and melts formed under oxidizing conditions. This band has a frequency and a width similar to those of the peak arising from H-H vibration in molecular H$_2$ in H$_2$-saturated NaAlSi$_3$O$_8$ melts (e.g., Luth et al., 1987).

Discussion

The band near 2920 cm$^{-1}$ was assigned to C-H stretching in CH$_4$ or methyl (CH$_3$) groups and the 2960 cm$^{-1}$ band to C-H stretching in CH$_4$D$_2$ isotopologues. There are multiple CH$_4$D$_2$ isotopologues from which C-H stretching will be slightly different (Foustoukos and Mysen, 2013). However, these the frequency of these individual bands is quite close together and with such extensive overlap at high temperature the individual Raman bands cannot be separated in the spectra. So only two bands are considered. These are also compared with a spectrum of fluid from the system H$_2$O-D$_2$O-CH$_4$-CD$_4$ recorded in-situ at 600°C/1053 MPa (Fig. 5). The essentially identical frequencies of the two bands (within spectrometer uncertainty; 3-4 cm$^{-1}$) lends further support to these being assigned to symmetric C-H of in CH$_4$ and CH$_4$D$_2$ groups in the fluid and melt. From the intensity ratio of these two bands we calculate the abundance ratio of CH$_4$ relative to the group of CH$_4$D$_2$ isotopologues reflected in the 2960 cm$^{-1}$ band, $A_{2920}/A_{2960}$, in fluid and coexisting melt. This abundance ratio is temperature-dependent and approaches 1 with increasing temperature (Fig. 6). The rate of change, however, differs for melt and fluid. In this
regard, these data resemble the temperature-dependent D/H behavior in coexisting aqueous fluid and water-saturated silicate melts (Mysen, 2013b). In this latter case, silicate-speciation considered the controlling factor for the D/H evolution in fluids and melts. Furthermore, in a study methane-saturated melt quenched to a glass from melts equilibrated with CH₄+H₂O+H₂ fluid at similar pressures and temperature carbon isotope fractionation was found significantly dependent on melt compositions (Mysen et al., 2009). Carbon-13 MAS NMR data of these melts indicate that CH₃ (methyl) and CH₄ (molecular methane) coexist in melt in equilibrium with a CH₄+H₂O+H₂ fluid. The proportion of those functional groups in melts were composition- and temperature-dependent. Carbon isotope fractionation was considered driven, therefore, by these structural effects (Mysen, 2012). It is considered reasonable to assume that both species coexist even though the Raman spectra of the fluids and melts in the present system are insufficiently well resolved to distinguish between methyl groups and methane. These features could explain the temperature-dependent isotope ratios in fluids in melts (Fig. 6).

The different temperature-dependent D/H evolution in fluids and melts leads to the D/H partitioning between (C-O-H-D-N)-saturated melt and silicate-saturated (C-O-H-D-N) fluid (Fig. 7). The ΔH-value is several times higher (33±6 kJ/mol) in the present system than in the simpler (O-H-D)-saturated melt + silicate-saturated (O-H-D) fluid (ΔH=6.5±0.7 kJ/mol) (Mysen, 2013b). The temperature-dependence in Fig. 7 incorporates different (D,H)-bearing species, changes in pressure (from 387 to 843 MPa in the 500°-800°C temperature range of Fig. 7), changes in silicate speciation in the C-O-H-N fluid, and changes in the (C-O-H-N)-saturated silicate melt with temperature and
pressure. These factors likely account for the different ΔH-values in Fig. 7 compared
with those of Mysen (2013b).

The nitrogen speciation in oxidized and reduced fluids and melts differs greatly.
Nitrogen solubility in silicate melts also varies by more than a factor of 2 depending on
nitrogen oxidation state. Reduced nitrogen is the most soluble (Mysen et al., 2008; Kadik
et al., 2013). Under oxidizing conditions, there is spectroscopic evidence for N₂ in
molecular form only in fluid and melt (Fig. 3). Other possible forms of oxidized nitrogen,
whether in the form of a nitrosyl group or as nitrate, cannot be discerned as the strongest
Raman bands from such groups are near 2100 and 1050 cm⁻¹, respectively (Kloprogge et
al., 2002; Roskosz et al., 2006). There is no evidence for new Raman bands in these
regions of the spectra of fluid and melt formed under oxidizing conditions.

The speciation of reduced nitrogen comprises (N-H)-bearing functional groups. The
two bands near 3300-3350 cm⁻¹ (Fig. 4) likely is because there exist two types of N-H
groups, as molecular NH₃ and as ammine groups, NH₂ (Yeo and Ford, 1994; Kowal,
2002; Mysen et al., 2008). In a study of quenched nitrogen-saturated quenched Na₂SiO₃
– N-O-H melt equilibrated with N-O-H fluid under reducing conditions at 1.5
GPa/1400°C Mysen et al. (2008) suggested that these groups are associated with Si. This
suggestion is also supported by the bands near 880 and 920 cm⁻¹, respectively (Figs. 3
and 8). In a study of amino-coupled silane this frequency range, Ishida et al. (1982) also
suggested that Raman bands in this this frequency range should be assigned to vibrations
in Si-NH₂ and Si-NH₃. As also noted above, an alternative assignment may be to Si-OH
stretching as these vibrations can also result in Raman bands >900 cm⁻¹ (Stolen and
Walrafen, 1976; McMillan and Holloway, 1987). However, if this assignment is correct,
one would also expect Raman bands in this region in spectra of melts equilibrated under oxidizing conditions. However, no such band can be observed.

The principal equilibrium between the two (N+H)-species and the silicate components silicate melts is (Mysen et al., 2008):

\[ Q^{n-1}(\text{NH}_2) + Q^{n+1}(\text{OH}) = 2Q^n + \text{NH}_3 \]  

(2)

We suggest a similar solution mechanism for the (NH$_3$-NH$_2$-H$_2$O-H$_2$)-bearing fluid phase in equilibrium with silicate melt because silicate components in water-bearing fluids in equilibrium with sodium aluminosilicate melts can reach several mol % under the conditions of these experiments. In eqn. (2) the superscript \( n \) denotes the number of bridging oxygen in the Q-species, \( Q^{n-1}(\text{NH}_2) \) indicates a Q-species where an oxygen bridge is replaced by an ammine group (NH$_2$) and \( Q^{n+1}(\text{OH}) \) a Q-species where an oxygen bridge has been replaced by an OH group. In other words, solution of reduced nitrogen, NH$_3$, in silicate melts to form Si-NH$_2$ bonding results in depolymerization of the silicate melt structure.

With the assumption that the Si-NH$_2$ and Si-NH$_3$ vibrations assigned to the 880 and 920 cm$^{-1}$ Raman bands have similar force constants, the ratio of integrated areas of these bands, \( A_{880} \) and \( A_{920} \), equals the ratio of mol fraction of these species,

\[ \frac{X_{\text{SiNH3}}}{X_{\text{SiNH2}}} = \frac{A_{880}}{A_{920}} \]  

(3)
Notably the NH$_2$/NH$_3$ ratio in fluid is much more sensitive to temperature (and pressure) than in melt (Fig. 8). In other words, the equilibrium constant for equilibrium (2);

$$K = \frac{(Q^n)^2 \cdot X_{NH_2}}{Q^{n-1}(NH_3) \cdot Q^{n+1}(OH)}.$$  \hspace{1cm} (4)

shifts to the right with temperature and pressure perhaps because the abundance of hydroxylated silicate, Q$^{n+1}$(OH), increases with increasing pressure. The greater temperature-sensitivity of equilibrium (2) in fluid likely is because the overall abundance of silicate in the fluid is also temperature and pressure-dependent (Zhang and Frantz, 2000; Newton and Manning, 2003).

In addition to the two bands in the 3300-3350 cm$^{-1}$ range, there is an additional band near 3300 cm$^{-1}$ in the 425$^\circ$ - 650$^\circ$C temperature range. This band likely is because of hydrogen bonding in the NH$_3$ or NH$_2^+$ groups, or both (Fig. 9; see also Yeo and Ford, 1994).

The Raman spectra of fluids and melts equilibrated under reducing conditions are interpreted to be consistent with similar (N-H) species in both phases (molecular NH$_3$ and NH$_2$-groups forming bonds with Si$^{4+}$). The relationship between integrated areas of Raman bands and mol fraction of coexisting species [eqn. (1)] can, therefore be used to extract fluid/melt partition coefficients for the total (N+H)-species (NH$_3$-+NH$_2$) (Fig. 11).

Its temperature-dependence yields $\Delta H = 45\pm 12$ kJ/mol. This treatment is, however, an oversimplification because pressure increases with temperature (Fig. 1) and the solubility of reduced nitrogen species in silicate melts is positively correlated with pressure (Mysen...
The fluid/melt partition coefficients in Fig. 11 arc, therefore, maximum values. The ΔH-value is also a maximum.

Applications

The pressure-/temperature-dependence of fluid/melt partition coefficients imply that degassing of N-bearing magmatic liquids in the earth’s interior is more efficient the lower the temperature pressure (shallower depth). Furthermore, the degassing process also depends on redox conditions because nitrogen solubility in melts depends on the redox state of nitrogen (Mysen et al., 2008). The solubility of oxidized nitrogen in silicate melts of similar composition and at the same pressure and temperature is less than 50% of that of reduced N-O-H species (Mysen et al., 2008). This means that fluid/melt partition coefficients must be at least 100% greater for oxidized nitrogen than for reduced nitrogen. It follows from this conclusion that the extent to which nitrogen will be scavenged from the earth’s interior is also redox dependent. Nitrogen may not, for example, be treated in a manner analogous to noble gases, where solubility behavior and depletion are simply functions of atomic/molecular ratio. Furthermore, given that nitrogen isotope partitioning between fluids and melts under reducing conditions is melt composition and (N-H)-speciation dependent (Mysen and Fogel, 2010), the redox conditions during melting and degassing of the Earth’s interior must take redox conditions into considerations.

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Figure Captions

Fig. 1 – Pressure-temperature trajectories of the two series of experiments (solid squares: oxidized. Solid dots: Reduced (Mo-MoO$_2$ buffer).

Fig. 2 – Raman spectra of coexisting melt (solid line) and fluid (dashed line) in the frequency range if Si,Al-O vibrations recorded under reducing and oxidizing conditions and temperatures and pressures as indicated.

Fig. 3 – Examples of Raman spectra in the 2000-2800 cm$^{-1}$ frequency region at 800°C and corresponding pressure as indicated. In left panel, central insert shows the spectrum in diamond in the diamond cell with no sample. Left insert shows the region between 2250 and 2350 cm$^{-1}$ greyed area on main spectrum. On the right spectrum (reducing conditions) is also indicated the approximate frequency of N-D and D$_2$O vibrations. At lower temperature, the Fermi doublet of N$_2$ between 2250 and 2350 cm$^{-1}$ becomes less intense. It is also less intense in spectra of melt compared with spectra of fluid.

Fig. 4 - Raman spectra of melt (solid line) and coexisting fluid (dashed line) under oxidizing and reducing conditions and at temperatures and pressures as indicated in the 2800-4200 cm$^{-1}$ region. Inserts show expanded view of spectra of fluid under reducing conditions between 2800 and 3400 cm$^{-1}$ and 4100 and 4160 cm$^{-1}$.

Fig. 5 – Example of curve-fitted portion (2800-3050 cm$^{-1}$) of spectrum of melt and fluid at 650°C and 760 MPa recorded under reducing conditions. Also shown is a curve-fitted spectrum in the same frequency region from H$_2$O-D$_2$O-CH$_4$-CD$_4$ supercritical fluid at 600°C/1053 MPa [data from Foustouskos and Mysen, 2013]. Note that in these three panels the exact frequencies from the fits are shown. These spectra were recorded with 600 mm/grating groove density, so the frequency uncertainty for each band is 3-4 cm$^{-1}$.

Fig. 6 – Temperature (and pressure - see Fig. 1) variations of the integrated intensity ratio of 2920 relative to 2960 cm$^{-1}$ band (mol fraction ratio, $X_{CH4}/X_{CH3CD3}$) for coexisting fluid and melt under reducing conditions.

Fig. 7 – Temperature (and pressure - see Fig. 1) dependence of fluid/melt partition coefficient of CH$_4$/CH$_3$Y$_2$ from the integrated area ratio of the 2920 cm$^{-1}$ and 2960 cm$^{-1}$ Raman bands. See text for additional details.

Fig. 8 – Temperature (and pressure - see Fig. 1) variations of the integrated intensity ratio of 800 relative to 920 cm$^{-1}$ band, considered equal to the abundance ration, $X_{SINH2}/X_{SINH3}$, for coexisting fluid and melt under reducing conditions. Inserts show fitted Raman spectra in the relevant frequency regions at temperatures and pressures indicated.

Fig. 9 - Example of curve-fitted portion (3260-3400 cm$^{-1}$) of spectrum of fluid at 575°C and 692 MPa recorded under reducing conditions.

Fig. 10 – Temperature (and pressure - see Fig. 1) dependence of ratios Raman bands assigned to N-H vibrations in fluid under reducing conditions (as illustrated in Fig. 6). Note that the temperature range is limited to that where both Raman bands can be observed in spectra of fluid.

Fig. 11 – Temperature (and pressure - see Fig. 1) dependence of fluid/melt partition coefficient of [N+H]-containing species ($\Sigma$NH=NH$_2$+NH$_3$).
Fig. 12 - Examples of Raman spectra of melt (solid line) and coexisting fluid (dashed line) under oxidizing and reducing conditions as indicated in the 2250-2350 cm$^{-1}$ region at 800°C and corresponding pressure as indicated with approximate background from 2$^{nd}$-order Raman intensity from diamond cell diamond subtracted.
Fig. 1
Reducing conditions

Intensity

2800 3200 3600 4000
Raman shift, cm$^{-1}$

800°C/843 MPa
725°C/835 MPa
650°C/760 MPa
575°C/692 MPa
500°C/617 MPa

Oxidizing conditions

Intensity

2800 3200 3600 4000
Raman shift, cm$^{-1}$

800°C/2163 MPa
650°C/1183 MPa
575°C/1000 MPa
500°C/902 MPa

Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 10
Fig. 11

\[ \Delta H = 45 \pm 12 \text{ kJ/mol} \]
Fig. 12