Solution mechanisms of COHN fluids in melts to upper mantle temperature, pressure, and redox conditions

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Abstract

In order to advance our knowledge of speciation among volatiles during melting and crystallization in the Earth's interior, the nature of carbon-, nitrogen-, and hydrogen-bearing species was determined in COHN fluids and dissolved in coexisting aluminosilicate melts. Micro-Raman characterization of fluids and melts were conducted in-situ while samples were at temperature up to 825°C and pressure up to ~1400 MPa under redox conditions controlled with the Ti-TiO$_2$-H$_2$O hydrogen fugacity buffer. The fluid species are H$_2$O, H$_2$, NH$_3$, and CH$_4$. In contrast, under oxidizing conditions the species are H$_2$O, N$_2$ and CO$_2$.

The equilibria among silicate structures (Q-species) and reduced carbon and nitrogen species are, $2\text{NH}_3 + 4\text{Q}^n \rightleftharpoons 2\text{Q}^{n-1}(\text{NH}_2) + 2\text{Q}^{n-1}(\text{OH})$, and $2\text{CH}_4 + 4\text{Q}^n \rightleftharpoons 2\text{Q}^{n-1}(\text{CH}_3) + 2\text{Q}^{n-1}(\text{OH})$. The Q$^n$- and Q$^{n-1}$ denote silicate species with, respectively, n and n-1 bridging oxygens. The formulation in parentheses, (NH$_2$), (CH$_3$), and (OH), is meant to indicate that those functional groups replace one or more oxygen in the silicate tetrahedra. There is no evidence for O-NH$_2$ or O-CH$_3$ bonding. Therefore, solution of reduced C- and N-species species in the COHN system results in depolymerization of silicate melts. The ΔH-values derived from the $X_{\text{NH}_2}/X_{\text{NH}_3}$ and $X_{\text{CH}_3}/X_{\text{CH}_4}$ evolution with temperature, respectively, were 8.1±2.3 kJ/mol and between -4.9±1.0 and -6.2±2.2 kJ/mol.

The fluid/melt partition coefficients, $K_{\text{fluid/melt}}$, of the reduced species, H$_2$O, H$_2$, NH$_3$, and CH$_4$, remain above unity at all temperatures. For example, for carbon it is in the 6-15 range with a ΔH = -13.4±2.4 KJ/mol. These values compare with a 0.8-3 range with ΔH = -19±2.4 kJ/mol in N-free silicate-COH systems. The $K_{\text{fluid/melt}}$ -values for reduced nitrogen and molecular hydrogen are in the 6-10 and 6-12 range with ΔH-values of -5.9±0.9 kJ/mol and =8±6 kJ/mol, respectively.

A change in redox conditions during melting and crystallization in the Earth sufficient to alter oxidized to reduced carbon- and nitrogen-bearing species will affect all melt properties that depend on melt polymerization. This implies that changing redox conditions during melting of a COHN-bearing mantle can have profound effect on physical and chemical properties of melts and on melting and melt aggregation processes.
Introduction

An understanding of the behavior of COHN volatiles in magmatic systems at high temperature and pressure is central to characterization of processes that describe formation and evolution of the solid Earth, recycling of volatiles, and interaction between the solid Earth and its oceans and atmosphere (Zhang and Zindler, 1993; Miyazaki et al., 2004; Adler and Williams, 2005; Sata et al., 2010). These processes and the underlying materials properties needed for modeling are governed by temperature, pressure, redox conditions, and bulk chemistry. Redox conditions can affect the carbon and nitrogen distribution and recycling because they can exist in different oxidation states within the range of redox conditions in the Earth's interior (Miyazaki et al., 2004; Mysen et al., 2008; Mysen and Fogel, 2010; Kadik et al., 2011, 2015). Under highly reducing conditions, molecular H$_2$ also becomes an important species.

Under reducing conditions, distribution of nitrogen in the Earth is governed in part by its solubility in crystalline phases where NH$_4^+$ functional groups can substitute for K$^+$ in the crystal structure of mica and amphibole, for example (Duit et al., 1986; Watenpuhl et al., 2009) and in part by solubility of (N...H) complexes in melts and fluids. The nitrogen partitioning behavior between and solubility in minerals, melts, and fluids at high pressure and temperature also is important, and depends on the oxidation state of nitrogen (Libourel et al., 2003; Miyazaki et al., 2004; Bebout et al., 2013).

Redox-dependent speciation of C-bearing volatile components also affects properties of magmatic systems. For example, melting of oxidized CO$_2$- and CO$_3^{2-}$-bearing upper mantle yields silica-undersaturated melts such as alkali olivine basalt and nephelinite and perhaps even carbonatite (Hirose, 1997; Dalton and Wood, 1993). However, with the hydrogen fugacity conditions greater than that of the MW (Fe$_5$O$_{y}$/FeO/H$_2$O) buffer, the stable C-species in COH-
bearing melts at high pressure and temperatures are CH$_4$ and CH$_3$- groups (Mysen et al., 2011). Such redox conditions are not unusual in the mantle of the present Earth (Carmichael and Ghiorso, 1990). The potential importance of reduced C-bearing species in the modern Earth notwithstanding, only a handful of experimental studies aimed to characterize the melting behavior of methane-bearing silicate systems at high pressure has been reported. What is known suggests that methane lowers activity coefficients of silica, which would drive composition of partial melt towards silica enrichment, for example (Eggler and Baker, 1982; Taylor and Green, 1989).

Molecular H$_2$ is a major component under hydrogen fugacity conditions equivalent to the IW (Fe/FeO)+H$_2$O buffer and above. It may, therefore, have been an important fluid component at the redox conditions of the early Earth. Significant concentrations of molecular H$_2$ is less important in the modern Earth (O'Neill, 1991) where the necessary high f$_{H2}$-conditions are rare.

An understanding of the role of COHN volatiles during the formation and evolution of the Earth requires experimentally-determined speciation (structure) of volatiles in and their partitioning between fluids and melts under conditions of the Earth's interior. Recently developed methods that rely on externally-heated diamond anvil cell technology coupled with vibrational spectroscopy have made it possible to obtain such data (Bassett et al., 1994; Zotov and Keppler, 2002; Mibe et al., 2008). In the present report, fluid and melt structure and fluid/melt partitioning of volatile components silicate- COHN systems have been carried out with such techniques.

**Experimental Methods**

Experiments were carried out with the samples contained in a 500 µm diameter central hole of a 125 µm thick Ir gasket placed between the diamonds culets in the hydrothermal diamond anvil...
cell (Bassett et al., 1994). Starting materials were glass chips of the alkali aluminosilicate composition \((Na_2Si_4O_9)_{90}(Na_2(AlSiO_9))_{10}\) that were mixed with \(Ag_2C_2O_4\) and \(AgN_3\) and loaded into the hydrothermal diamond anvil cell together with double-distilled, dionized \(H_2O\) and small pieces of Ti metal. Carbon dioxide and \(N_2\) were formed from decomposition of the silver oxalate \((Ag_2C_2O_4)\) and silver azide \((AgN_3)\), which takes place near 200°C. Condensed materials (silicate + \(Ag_2C_2O_4\) + \(AgN_3\)+Ti metal) represented about 50% of the starting composition together with about 50% liquid \(H_2O\). However, these proportions could not be determined with precision because of the small sample volume (<0.0x \(\mu m^3\)).

During an experiment, the Ti metal reacted with \(H_2O\) to control the hydrogen fugacity via the reaction:

\[
Ti + 2H_2O \leftrightarrow TiO_2 + 2H_2. \tag{1}
\]

This \(CO_2\) and \(N_2\) were transformed to \(CH_4\) and \(NH_3\) by reaction with \(H_2\) from the \(f_H2\) buffer reaction [eqn. (1)] (Mysen and Fogel, 2010; Foustoukos and Mysen, 2013);

\[
CO_2 + 3H_2 \leftrightarrow CH_4 + H_2O, \tag{2}
\]

\[
N_2 + 4N_2 \leftrightarrow 2NH_3 + H_2O. \tag{3}
\]
Molybdenum wire wrapped around each of two SiC diamond seats was used to form heaters. Temperature was monitored with two K-type thermocouples touching the diamonds about 1-1.5 mm from the sample. Temperature variations, determined with the melting point of NaCl (800.5°C at ambient pressure), is ~±2°C. Pressure, generated by the fluid at essentially constant volume in the sample chamber, changed with temperature. It was monitored with the one-phonon Raman shift of synthetic $^{13}$C diamond added as small chips to the sample volume (Schiferl et al., 1997). Pressure was, therefore, a temperature-dependent variable (Table 1). The $^{13}$C diamond was used in order to avoid interference from the Raman spectra from the natural diamonds in the diamond anvil cell itself. Pressure/temperature-dependence of the one-phonon Raman shift was calibrated against the equation-of-state of pure H$_2$O by Mysen and Yamashita (2010). The pressure uncertainty, which includes both spectrometer precision and fitting errors in the calibration, is about ±110 MPa. The spectrometer precision alone translates to a pressure precision of ±40 MPa. Pressure does not decrease monotonously with decreasing temperature because there was some deformation of the Ir gasket hole, which, therefore, resulted in sample volume changes and, therefore, pressure variations.

Fluid and melt structure was evaluated from Raman spectra recorded with a JASCO model NRS-3100 confocal microRaman spectrometer. With this system, a 2.5 cm working-distance 50X by 0.42 N.A. objective lens was used. The samples were excited with the 490 nm line of a solid-state laser operating at ~ 30 mW at the sample. With this spectrometer set-up, the optical resolution was 2-3 µm across by about 30 µm depth. The spectrometer is equipped with a single monochromator, holographic notch filter, and holographic gratings. Gratings with 1200 and 2400 grooves/mm were employed. The 2400 grooves/mm gratings were used together with Ne
emission lines for frequency reference to collect high-precision carbon-13 diamond spectra with  
±0.1 cm\(^{-1}\) uncertainty. Measurements of the melt and fluid samples were carried out with 1200 
grooves/mm and 2-3 cm\(^{-1}\) frequency uncertainty. The data were recorded with an Andor Model  
DV401-F1 Peltier-cooled CCD.

Several temperature/pressure series of measurements were carried out. For each series, the 
sample was first brought to the highest planned temperature and pressure and kept at this 
condition (825°C and ~1400 MPa in the present case) for ~60 minutes, which is sufficient to 
attain equilibrium for which only several minutes are needed (Horita, 2014). Spectroscopic 
measurements of the sample (fluid, melt, and/or supercritical fluid) and the \(^{13}\)C diamond were 
carried out at the highest planned temperature and pressure before the temperature was reduced 
at 1°C/s cooling rate to the next temperature. Pressure decreased accordingly (Table 1). The 
measurement protocol was then repeated. Each experimental data point was 75°C apart with the 
last measurements at 525°C and 634 MPa. Ambient conditions Raman measurements of the \(^{13}\)C 
diamond were carried before and after a series of high-temperature and -pressure experiments.

Results

For each temperature and pressure, spectra were recorded from about 400 cm\(^{-1}\) to 4200 cm\(^{-1}\) in 
order to include frequencies of most (Si,Al)-O vibrations and vibrations in species involving 
COHN components (Fig. 1). The band assignments in this and subsequent figures are based 
predominantly on Nakamoto (1997). The peaks marked 1\(^{st}\) and 2\(^{nd}\) order diamond are from the 
diamonds in the diamond anvil cell itself. There are no \(^{13}\)C diamond signals the Raman spectra of 
fluids and melts because carbon-13 diamond spectra were recorded separately.
The individual Raman band intensities differ significantly (Fig. 1). Therefore, in order to make the topology of the peaks and their variations with temperature and pressure more visible, the spectra have been divided into 4 segments, marked A, B, C, and D as indicated in Fig. 1, and expanded in separate figures.

The frequency region, A, is from about 400 cm\(^{-1}\) to the strong one-phonon band from diamond located near 1300 cm\(^{-1}\) (Figs. 1 and 2). It comprises signals assigned to (Si,Al)-O vibrations as well as some of the bending modes of COHN species. In the spectra of fluids (Fig. 2A), this frequency regime is dominated by three bands, near 600, 800, and 1030 cm\(^{-1}\). At the highest temperatures, there is also a weak shoulder near 770 cm\(^{-1}\). The integrated intensities of the three main bands decrease with decreasing temperature and pressure while their frequencies remain essentially constant (average frequencies: 591±2, 813±3, and 1030.4±0.5 cm\(^{-1}\), respectively). The 591 cm\(^{-1}\) band is assigned to Si-CH\(_3\) stretching, and the other two to bending vibrations in NH\(_2\) functional groups (Fig. 2A). Additional support for Si-CH\(_3\) bonds can be found in recent \(^{13}\)C MAS NMR data from quenched aluminosilicate melts equilibrated with CH\(_4\)+H\(_2\)O+H\(_2\) fluid at 1.5 GPa and 1400°C under reducing conditions (Mysen et al., 2011). The 770 cm\(^{-1}\) shoulder is assigned to Si-O\(^{-}\) stretching in isolated SiO\(_4\) entities (also denoted Q\(^0\)).

The spectra of melt are dominated by a broad band (FWHH \(\sim\)80 cm\(^{-1}\)) at 885 cm\(^{-1}\) and weaker and broad bands near 485, 570, and 1035 cm\(^{-1}\) (Fig. 2B). The 885 cm\(^{-1}\) band is assigned to Ti-O vibrations from Ti\(^{4+}\) dissolved formed by oxidation of Ti metal [eqn. (1)].

The 485 cm\(^{-1}\) band is assigned to Si-O-Si rocking in Q\(^4\) species and the 570 cm\(^{-1}\) band to Si-O-Si bending most likely in Q\(^3\) species (Furukawa et al., 1981; McMillan et al., 1992). The existence of polymerized silicate species in the melts also is indicated by the broad band above...
1000 cm\(^{-1}\) (FWHH near 100 cm\(^{-1}\)), which is assigned to Si-O stretching in polymerized species in melts, most likely dominated by Q\(^3\) type (McMillan et al., 1992). A more detailed review of the band assignments assigned to (Si,Al)-O vibrations can be found in chapters 7 and 12 of Mysen and Richet (2005).

The region between the 1st and 2nd order Raman peaks from the diamond cell diamonds (near 1330 and 2600 cm\(^{-1}\), respectively) is denoted segment B (Figs. 1 and 3). The spectra of fluid are dominated by a sharp peak (FWHH: 10-15 cm\(^{-1}\)) near 1440 cm\(^{-1}\) (Fig. 3A). Its intensity decreases with decreasing temperature. In melt spectra, this peak is only seen in those from the highest temperature and pressure (825°C/1400 MPa; see Fig. 3B). It is assigned NHN bending in NH\(_3\) molecules (Nakamoto, 1997). The fluid spectra also show a sharp peak near 1640 cm\(^{-1}\), which could be assigned to HNH bending vibrations in NH\(_3\) molecules (Colthup et al., 1990; Nakamoto, 1997). The fluid spectra at 825°C and 750°C also show a sharp peak slightly above 1800 cm\(^{-1}\). Although an assignment is quite uncertain, it cannot be ruled out that this is from C-O vibrations in CO groups perhaps from carboxylic acid (Colthup et al., 1990). The only other peak common to spectra of both fluids and melts in the B-region occurs near 1550 cm\(^{-1}\) (Figs. 3A, B), which is assigned HOH bending in H\(_2\)O molecules (Nakamoto, 1997; Efimov and Pogareva, 2006).

In the spectra of fluid, the C-region extends from the high-frequency side of the 2\(^{nd}\)-order peak of diamond cell diamonds near 2600 cm\(^{-1}\) to the beginning of the low-frequency tail of the strong peak centered between 3500 and 3600 cm\(^{-1}\) (Figs. 1 and 4). There are two peaks, near 2900 cm\(^{-1}\) and 3320 cm\(^{-1}\), in the spectra of melts and fluids (Figs. 4A and B). There is also a weak and broad band centered near 3240 cm\(^{-1}\) in the spectra of fluids (Fig. 4A). The 2900 cm\(^{-1}\) band is asymmetric toward lower frequency. This asymmetry can be accommodated by fitting
two Gaussian lines, near 2895 cm\(^{-1}\) and 2910 cm\(^{-1}\) (Fig. 6). These two peaks are assigned to C-H stretching in, respectively, CH\(_3\) groups and CH\(_4\) molecules (Nakamoto, 1997), similar to that reported from Raman spectra of Al-free melts by Mysen and Yamashita (2010) and in the Raman and \(^{13}\)C MAS NMR spectra of aluminosilicate glasses equilibrated as melts under reducing conditions and temperature-quenched to glass (Mysen et al., 2011).

The two peaks near 3300 cm\(^{-1}\) are expanded with Gaussian lines fitted to spectra in the example in Fig. 6. The strongest band, at 3325 cm\(^{-1}\), is assigned to N-H stretching in NH\(_3\) molecules, whereas the weaker and broader band, near 3230 cm\(^{-1}\), is assigned to N-H stretching in NH\(_2\) groups (Yeo and Ford, 1994; Nakamoto, 1997; Mysen et al., 2008). There is no evidence for NH\(_4^+\) because the N-H stretch frequencies from this functional group is in the 3000-3200 cm\(^{-1}\) frequency range (Socrates, 2001; Mysen et al., 2008), in which range there are no Raman bands in the present spectra.

Frequency region D extends from the intense band centered between 3500 and 3600 cm\(^{-1}\) and a group of bands of lesser intensities near 4100-4150 cm\(^{-1}\) (Fig. 7). This latter group is assigned the Q-branch of H\(_2\) reflecting vibrational to rotational transitions (Veirs and Rosenblatt, 1987; Schmidt et al., 1998). The 3500-3600 cm\(^{-1}\) peak is assigned to OH stretching in OH groups bonded to cations such as Si\(^{4+}\), Al\(^{3+}\), and Na\(^+\) as well as OH groups in molecular H\(_2\)O (see also Nowak and Behrens, 1994; Kawamoto et al., 2004).
Discussion

Solution mechanisms of reduced COHN species

The solution mechanisms of reduced carbon and nitrogen in silicate-COH melts and silicate-NOH melts, respectively, involve various combinations of C..H and N..H complexes (Kadik et al., 2004; Mysen et al., 2008, 2011; Ni and Keppler, 2013; Armstrong et al., 2015). For melts and fluids in silicate-COHN systems, little is known except for some recent data obtained in-situ under oxidizing conditions (Mysen, 2018). In the latter case, the sole nitrogen species was $N_2$ so that nitrogen simply acted as a diluent of the other gas species. Carbon existed as $CO_2$ and as $CO_3^{2-}$ groups.

The solution behavior of reduced carbon-bearing species has been developed with the aid of the simple expressions based on the interpretation of $^{13}C$ MAS NMR spectra of quenched silicate melt-COH (e.g., Mysen et al., 2011);

\[ 2CH_4 + O^{2-} \rightleftharpoons 2CH_3^- + H_2O, \]  \hspace{1cm} (4)

and for reduced nitrogen in silicate melt-NOH systems (Mysen et al., 2008);

\[ 2NH_3 + O^{2-} \rightleftharpoons 2NH_2^- + H_2O. \]  \hspace{1cm} (5)
In equations (4) and (5), $O^{2-}$ represents oxygen in the silicate structural network. It is linked to silicate speciation via the expression,

$$2Q^n + O^{2-} \leftrightarrow 2Q^{n-1},$$

where $Q^n$ and $Q^{n-1}$ denote silicate species with, respectively $n$ and $n-1$ bridging oxygen, and, therefore, $4-n$ and $3-n$ nonbridging oxygen.

By combining equations (4) and (6), we have;

$$2CH_4 + 4Q^n \leftrightarrow 2Q^{n-1}(CH_3) + 2Q^{n-1}(OH),$$

which describes the relations between dissolved CH$_3$ groups and the silicate structure. From the carbon-13 MAS NMR and Raman spectroscopic data of quenched melts, Mysen et al., (2011) concluded that CH$_3$ groups thus formed substitute for oxygen in the silicate tetrahedra because there was evidence of CH$_3$ and CH$_4$ groups, but no evidence for Si-O-C bonding environments. Therefore, $2Q^{n-1}(CH_3)$ and $2Q^{n-1}(OH)$ denote depolymerized silicate tetrahedra with at least one of the oxygens replaced by CH$_3$ and OH groups, respectively. This interpretation is also consistent with the assignment of the Raman band near 600 cm$^{-1}$ (Fig. 2).
For reduced nitrogen-bearing components, by combining equations (5) and (6), we have;

\[ 2\text{NH}_3 + 4Q^n \leftrightarrow 2Q^{n-1}(\text{NH}_2) + 2Q^{n-1}(\text{OH}). \]  

The Si-NH\textsubscript{2} interpretation relies on the assignment of the \(\sim800\) cm\(^{-1}\) band in Fig. 2 to be an NH\textsubscript{2} bending mode (Nakamoto, 1997). In other words, the exchange of NH\textsubscript{2} groups for oxygen in silicate tetrahedra cleaves oxygen bridges to form Si-NH\textsubscript{2} and Si-OH bonds, which results in silicate depolymerization.

There is also the equilibrium between molecular H\textsubscript{2}O and OH\textsuperscript{-} groups that describes a principal solution mechanism of H\textsubscript{2}O in melts (e.g., Stolper, 1982);

\[ \text{H}_2\text{O} + \text{O}^{2-} \leftrightarrow 2\text{OH}^{-}. \]  

Equation (9) combined with equation (6), yields the equilibria involving silicate (Q-species) H\textsubscript{2}O, and OH groups;

\[ \text{H}_2\text{O} + 4Q^n \leftrightarrow 4Q^{n-1}(\text{OH}). \]
By combining equations (7) and (8), the solution equilibrium among COHN species in silicate fluids (and probably melts) under reducing conditions becomes:

\[ \text{CH}_4 + \text{NH}_3 + 4Q^n \Leftrightarrow Q^{n-1}(\text{CH}_3) + Q^{n-1}(\text{NH}_2) + 2Q^{n-1}(\text{OH}). \]  

Equation (11) does not take into account interaction of H\(_2\) with the silicate network. Such interaction, through formation of Si-H and Si-OH bonds, is possible via a schematic formulation such as (Van der Steen and Van den Boom, 1977):

\[ \text{Si-O-Si} + \text{H}_2 \Leftrightarrow \text{Si-OH} + \text{Si-H}. \]  

Si-H stretch vibrations would result in Raman bands in the 2100-2200 cm\(^{-1}\) region (Schmidt et al., 1998) in addition to the OH fundamental stretch vibrations giving rise to the 3500-3600 cm\(^{-1}\) envelope. The former frequency is within the frequency range of 2nd-order Raman scattering of diamonds from the diamond cell, whereas the OH vibrations yield the same signal as OH vibrations from the other H\(_2\)O in the system. Whether or not there are contributions from Si-H and Si-OH from eqn. (12) cannot, therefore, be ascertained. Given this lack of information, further speculation and adjustments to eqn. (11) does not seem justified.
The equilibrium among silicate melt and COHN volatiles under reducing conditions differs significantly from that under oxidizing conditions where nitrogen simply dissolves as molecular N$_2$ and acts as a diluent (Mysen, 2018). The H$_2$O equilibrium remains same, and molecular CO$_2$ is in equilibrium with carbonate groups, CO$_3^{2-}$ (Morizet et al., 2015);

$$\text{CO}_2 + \text{O}^{2-} \leftrightarrow \text{CO}_3^{2-}, \quad (13)$$

so that by combining equations (9, 10, 13), we have;

$$\text{CO}_2 + \text{H}_2\text{O} + \text{N}_2 + 4\text{Q}^{n-1} \leftrightarrow 2\text{CO}_3^{2-} + 2\text{Q}^{n-1}(\text{OH}) + \text{N}_2 + 2\text{Q}^n. \quad (14)$$

Here, nitrogen as N$_2$ is shown on both sides of the equation simply to indicate that it behaves as an inert component. It follows that under oxidizing conditions even in the presence of H$_2$O, in silicate-COHN systems CO$_2$ dissolves to form CO$_3^{2-}$, which results in silicate polymerization.

The proportion of molecular and structurally bound species such as discussed above can be determined from the Raman spectra with the assumption that for a specific vibration (e.g., stretching or bending etc.), the Raman cross sections are the same for vibrations in the molecule and structurally bound functional groups (CH$_4$/CH$_3$ and NH$_3$/NH$_2$) and that the C-H and N-H vibrations in these groups are localized thus not being significantly affected by the neighboring
electronic environments. Ratios of integrated Raman intensity ratios from a given type of vibration in the two species then equals their abundance ratio. For $X_{\text{CH}_3}/X_{\text{CH}_4}$ [eqn (4)], for example, this intensity ratio is that of the C-H stretch vibrations near 2900 cm$^{-1}$ (2895 and 2910 cm$^{-1}$);

$$X_{\text{CH}_3}/X_{\text{CH}_4} = A_{2895}/A_{2910}. \tag{15}$$

In spectra of fluids, the $X_{\text{CH}_3}/X_{\text{CH}_4}$ ratio increases with increasing temperature (Fig. 8), from which an enthalpy of 8.1±2.3 kJ/mol can be extracted. In other words, in COHN fluids in equilibrium with aluminosilicate melts, equation (4) shifts to the right with increasing temperature. The spectra of melts are insufficiently resolved to extract such information.

The $X_{\text{NH}_2}/X_{\text{NH}_3}$ in fluid was calculated from a similar treatment of the Raman data (Fig. 9). Two sets of $X_{\text{NH}_2}/X_{\text{NH}_3}$ data were extracted from the spectra of fluid from bands assigned to NH$_2$ and NH$_3$ bending motions in the low-frequency region and from those assigned to N-H stretching in NH$_3$ and NH$_2$ near 3300 cm$^{-1}$ (Fig. 2A). These slopes result in $\Delta H$-values of -4.9±1.9 and -6.2±2.2 kJ/mol. We note here that the temperature evolution of the $X_{\text{NH}_2}/X_{\text{NH}_3}$ abundance ratio is opposite of $X_{\text{CH}_3}/X_{\text{CH}_4}$. In other words, whereas equation (4) shifts to the right with temperature thus enhancing the abundance of molecular CH$_4$, equation (5) shifts to the left so that molecular NH$_3$ becomes increasingly abundant. Interestingly, under oxidizing conditions, the CO$_2$/CO$_3$ equilibrium [eqn. (13)] also shifts toward increasing abundance of molecular CO$_2$ with increasing temperature (Nowak et al., 2003).
**Fluid/melt partitioning**

**Water.** The partition coefficient for H$_2$O between fluid and melt, when calculated from integrated intensity of the 3600 cm$^{-1}$ band (O-H stretching) in coexisting fluids and melts, is a non-linear function of 1/T and less than unity (Fig. 10). This behavior contrasts with the H$_2$O partitioning in silicate-COHN under oxidizing conditions where $K_{\text{fluid/melt}}^{\text{H}_2\text{O}} > 1$ and is a linear function of 1/T (Mysen, 2018). This difference likely is because under reducing conditions TiO$_2$ from the redox reaction (1) dissolves in significant amounts in melts (but not in fluid), which results in the very broad and asymmetric 3600 cm$^{-1}$ band (Figs. 1 and 10). The TiO$_2$ concentration in the melt likely changes with temperature and pressure. This results in a non-linear temperature-dependent $K_{\text{fluid/melt}}^{\text{H}_2\text{O}}$.

**Methane.** The partition coefficients for methane between coexisting fluid and melt are expressed in terms as, $\Sigma C = \text{CH}_3 + \text{CH}_4$ (Fig. 11) because separate contributions from CH$_4$ and CH$_3$ cannot be quantified from the spectra of melt. Methane partitions into fluid relative to melt. The partition coefficients for the CH$_3$+CH$_4$ components are not necessarily the same as total carbon because of the suggested CO groups in the highest-temperature fluids (Fig. 3). However, given the lack of relevant Raman signals in spectra of melts as well as in the low-temperature fluid spectra, contributions from such carbon was not considered. This also means that the $K_{\Sigma C}^{\text{fluid/melt}}$ values (Fig. 11) may be minimum values.
The partition coefficient decreases with increasing temperature (and pressure), which results in $\Delta H = -13.4 \pm 2.3$ kJ/mol by assuming no pressure effect. This value compares with a $\Delta H$-value of $-19 \pm 2.9$ for the fluid/melt partition coefficient with the same bulk silicate, but without nitrogen in the system (Mysen, 2015). The offset between the two data sets likely reflects the different pressure/temperature paths in the two experimental series as well as the absence of nitrogen species in fluids and melts in the silicate-COH system by Mysen (2015).

Ammonia. Qualitatively, the fluid/melt partition coefficient for total reduced nitrogen ($\Sigma N = NH_3 + NH_2$) decreases with increasing temperature. This behavior is similar to the temperature-dependent $K_{\Sigma C}^{\text{fluid/melt}}$ (Figs. 11 and 12). The enthalpy value extracted from the temperature-dependence with the assumption of no detectable pressure dependence is $-5.9 \pm 0.9$ kJ/mol.

Hydrogen. The $H_2$ fluid/melt partition coefficient ranges between $\sim 6$ and $\sim 10$ in the temperature and pressure range examined (Fig. 13). There is a slight decrease with increasing temperature and pressure, but the data scatter is significant thus leading to an enthalpy value with large uncertainty, $-8 \pm 6$ kJ/mol.

Implications

Reduction of carbon and nitrogen in silicate-COHN melts at high temperature and pressure occurs under conditions near and more reducing those defined by the MW+$H_2O$ buffer (Mysen et
Under such conditions the dominant fluid species are H₂O, H₂, NH₃, and CH₄. That behavior differs from oxidizing conditions where H₂O, N₂ and CO₂ are the principal species. and where CO₂ may be in equilibrium with CO₃²⁻ and HCO₃⁻ groups, or both. A change in redox conditions sufficient to alter oxidized to reduced carbon- and nitrogen-bearing species during melting and crystallization in the Earth will affect all melt properties that depend on melt polymerization [see solution mechanisms illustrated with equations (9) and (12)]. Examples of such melt properties are viscosity, diffusion, and density (Baker et al., 2005; Behrens, 2010; Seifert et al., 2013). Crystal/melt element partitioning also is linked to melt polymerization (Jaeger and Drake, 2000) and, therefore, the redox conditions during melting and crystallization in the presence of COHN fluids. Melt polymerization is also linked to activity of silicate, which means a change in redox conditions will lead to a change in melting and crystallization phase relations (Moretti and Papale, 2004). This latter feature sometimes is termed redox melting.

Acknowledgments

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<tr>
<td>750</td>
<td>1011</td>
</tr>
<tr>
<td>825</td>
<td>1414</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1 - Example of Raman spectra of coexisting melt and fluid at 525°C/634 MPa in the entire spectral range studied. Intensity is normalized to cts/s. Band assignments are discussed in the text. The frequency ranges marked A, B, C, and D show ranges that are expanded in subsequent figures (and discussed in the text) to show better the spectral evolution.

Figure 2 - Raman spectra of coexisting fluid (A) and melt (B) in the frequency regime A (see Fig. 1) as a function of temperature as seen on individual spectra and pressure as shown in Table 1. Band assignments are discussed in the text.

Figure 3 - Raman spectra of coexisting fluid (A) and melt (B) in the frequency regime B (see Fig. 1) as a function of temperature as seen on individual spectra and pressure as shown in Table 1. Band assignments are discussed in the text.

Figure 4 - Raman spectra of coexisting fluid (A) and melt (B) in the frequency regime C (see Fig. 1) as a function of temperature as seen on individual spectra and pressure as shown in Table 1. Band assignments are discussed in the text.

Figure 5 - Example of curve-fitted Raman spectrum of fluid in frequency regime C near 2900 cm⁻¹ recorded at 825°C/1414 MPa.

Figure 6 - Example of curve-fitted Raman spectrum of fluid in frequency regime C near 3300 cm⁻¹ recorded at 600°C/594 MPa.
Figure 7 - Raman spectra of coexisting fluid (A) and melt (B) in the frequency regime D (see Fig. 1) as a function of temperature as seen on individual spectra and pressure as shown in Table 1. Band assignments are discussed in the text.

Fig. 8 - Evolution of abundance ratio, CH$_3$/CH$_4$, in fluid as a function of temperature from fits to the 2900 cm$^{-1}$ region (see Table 1 for corresponding pressures). The straight line fit is described with the expression, log(CH$_3$/CH$_4$) = -977±276/T(K)+0.5±0.3, r$^2$=0.81.

Fig. 9 - Evolution of abundance ratio, NH$_2$/NH$_3$, in fluid as a function of temperature from fits to NHN stretching region between 3300 and 3200 cm$^{-1}$ and NHN bending region between 600 and 1000 cm$^{-1}$ (see Table 1 for corresponding pressures). The straight line fits are described with the expressions: For NHN stretching log(NH$_2$/NH$_3$) = 595±230/T(K)-1.1±1.2, r$^2$=0.69, NHN bending log(NH$_2$/NH$_3$) = 744±265/T(K)-1.2±0.3, r$^2$=0.72.

Fig. 10 - Fluid/melt partition coefficient for H$_2$O as a function of temperature (closed circles) compared with results under oxidizing conditions.

Fig. 11 - Fluid/melt partition coefficient for total carbon, ΣC, under reducing conditions ($K_{\text{fluid/melt}}^{C} = 1617±281/T-0.6±0.3$, $r^2=0.92$), under reducing conditions in silicate-COH ($K_{\text{fluid/melt}}^{C} = 2283±347/T-2.6±0.4$, $r^2=0.94$) (open circles; Mysen, 2015), and under oxidizing conditions in silicate-COH ($K_{\text{fluid/melt}}^{C} = -3628±1630/T+3.3±1.6$, $r^2=0.71$) (open diamonds; Mysen, 2015).

Fig. 12 - Fluid/melt partition coefficient for total nitrogen, ΣN, under reducing conditions ($K_{\text{fluid/melt}}^{N} = 709±111+0.2±0.1$, $r^2=0.93$).

Fig. 13 - Fluid/melt partition coefficient for H$_2$ under reducing conditions ($K_{\text{fluid/melt}}^{H_2} = 1007±815-0.1±0.8$, $r^2=0.34$).
Figure 1
Figure 2
Figure 3
Figure 5
Figure 6
Figure 7
Figure 8

Temperature, $10^3/T$ (K$^{-1}$) vs. Log $K_{\text{fluid}}$.
Log $K_{\text{fluid}}^{\text{NH}_2/\text{NH}_3}$ vs. Temperature, $10^3/T$ (K$^{-1}$)

- N-H-N stretching
- N-H-N bending

Figure 9
Figure 10
Temperature, $10^3/T$ (K$^{-1}$)

$\log K_{\Sigma C}^{\text{fluid/melt}}$

COH (Mysen, 2015)

- oxidized
- reduced

Figure 11
Figure 12
Figure 13