Revision 2:

In-situ measurements of fluorine and chlorine speciation and partitioning between melts and aqueous fluids in the Na$_2$O-Al$_2$O$_3$-SiO$_2$-H$_2$O system

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ABSTRACT

The effect of pressure and temperature on the structure of silicate melts coexisting with silica-saturated aqueous electrolyte fluids enriched in fluorine or chlorine in the Na$_2$O–Al$_2$O$_3$–SiO$_2$–H$_2$O system has been described. In-situ measurements were conducted with the samples at desired temperatures and pressures in a hydrothermal diamond anvil cell (HDAC) by using microRaman and FTIR spectroscopy techniques. The data were acquired at temperatures and pressures up to 800°C and 1264 MPa, respectively.

In silicate melts, the intensity of the infrared bands assigned to the stretch...
vibration of OH-groups is smaller than those of coexisting molecular H₂O when F and Cl are present in the melt structure. This difference reflects the interaction of F or Cl with H₂O in the melts. With decreasing pressure and temperature (P-T) conditions, SiF complexes are favored in the melt over that in coexisting fluid, perhaps because of decreasing silicate concentration in fluids with decreasing temperature and pressure. In these melts, the solubility of Cl, likely in the form of NaCl, increases with decreasing P-T conditions, whereas the abundance of such complexes in coexisting fluids decreases in favor of HCl.

Our experimental data were employed to model the ascent of a fluid-saturated magma from the upper mantle to the shallow crust. This modeling offers insights into F and Cl partitioning between and the speciation of F and Cl in melts and magmatic fluids. We suggest that the formation of stable SiF and NaCl complexes and their increasing solubilities in silicate melts during magma ascent may explain the late volcanic degassing of F and Cl compared with the degassing behavior of other volatile species.

**Keywords:** Fluorine, chlorine, speciation, aqueous fluids, hydrous melts, structure, spectroscopy, hydrothermal diamond anvil cell.
INTRODUCTION

Characterization of the behavior of volatile elements during magma ascent is central to constraining the cycling of volatiles from the Earth’s interior to the surface. Volatile species are released into the atmosphere mainly through magma degassing and their abundance in the emitted gases and fluids is controlled by their speciation and solubility in melts and magmatic fluids.

Previous studies have focused on the characterization of volatile species (H₂O, CO₂, S, Cl and F) and their solubility in magmas of various compositions (e.g., Mysen et al. 1975; Mysen 1977; Egger et al. 1979; Dixon et al. 1995; Webster et al. 1999; Brooker et al. 2001; Tamic et al. 2001; King and Holloway 2002; Signorelli and Carroll 2002; Botcharnikov et al. 2004). The solubility of volatile halogens and the depth of their exsolution depend not only on magma composition but also on the concentration of other volatiles, especially H₂O and CO₂, which affects the solubility and fractionation of halogen-bearing species in and between minerals, melts and fluids (e.g., Holloway 1976; Carroll and Webster 1994; Dixon et al. 1995; Burgisser et al. 2008; Dalou and Mysen 2013). The partitioning of F and Cl between fluid and melt has been of special interest because these volatiles tend to degas during the latest stages of magmatic evolution (Carroll and Webster 1994; Spilliaert et al. 2006). While both F and Cl solubility in magmas can be quite high, their behavior in magmatic systems differs. For example, it is often concluded that Cl is dissolved preferentially in aqueous fluids, whereas F favors melts (Carroll and Webster 1994). However, comparative studies of F and Cl partitioning between fluid and melt with similar melt compositions, temperatures and pressures are rare as data on degassing in volcanic systems (e.g. Pennisi and Le Cloarec 1998;
Earlier experiments measured species concentrations in quenched glasses and calculated the composition of coexisting fluid after equilibration at high temperature and pressure (Webster 1992; Métrich and Rutherford 1992, Lowenstern 1994; Shinohara 1994; Webster 1997; Signorelli and Carroll 2000; Chevychelov et al. 2008; Alleti et al. 2009). However, the structure of a silicate glass is different from that of its high-temperature melt (e.g., Moynihan et al. 1976; Dingwell and Webb 1990), because silicate speciation in the melt/glass structure is temperature (and pressure) dependent (e.g. Mysen et al. 2003). Furthermore, the speciation of volatiles dissolved in melt is temperature-dependent as observed, for instance, in the OH/H$_2$O (e.g., Nowak and Behrens 1995; Sowerby and Keppler 1999) and CO$_3$/CO$_2$ ratios (Nowak et al., 2003). The speciation of volatiles in fluid also changes with pressure and temperature, affecting estimates of elemental solubility and speciation, for example those of C-O-H-N volatile components (e.g. Mysen and Yamashita 2010; Mysen 2013a).

To circumvent barriers raised by examining melts and fluids quenched to ambient pressure and temperature conditions, the in-situ experimental characterization of the melt and fluid structure and composition at high pressure and high temperature is key. Recently, experimental protocols employed have involved the integration of hydrothermal diamond anvil cell (HDAC) techniques (e.g., Bassett et al. 1994; 1996) with in-situ Raman and infrared spectroscopy (Shen and Keppler 1995; Nowak and Behrens 1995; Zotov and Keppler 2000; 2002; Mysen 2010, 2011, 2012, 2013a). In this paper, we present a series of HDAC experiments where such protocols are used to constrain the effect of cooling and associated decompression on the Cl and F speciation
of a SiO₂-rich aqueous fluid and a coexisting H₂O-rich aluminosilicate melt. The experiments were conducted at upper mantle/deep crustal pressure and temperature conditions.

EXPERIMENTAL METHODS

A Si₈Al₆Na₂O₂₀ (NS3A5: 65wt% SiO₂, 7.8wt% Al₂O₃ and 28wt% Na₂O) composition glass was the silicate starting material (see Dalou et al. in review for analytical details of the glass). The glass was prepared by mixing spectroscopically pure Na₂CO₃, SiO₂ and Al₂O₃ powders, which were then decarbonated by slow step heating (50 °C/15 minutes), and then melted for 2 hours at 1000 °C. The aqueous fluids were pure deionized H₂O, 0.5 M of NaF and 0.5 M of NaCl.

The experiments were conducted with the samples in an externally heated hydrothermal diamond anvil cell (HDAC; Bassett et al. 1994, 1996) with 1 mm diamond culets. Samples comprised a small piece of NS3A5 glass, a small chip of synthetic ¹³C diamond, and a < 1 μl drop of H₂O (Fig. 1 and 2). Reactants were contained in a 500 μm central hole of a 125 μm thick iridium gasket. The temperature in the HDAC was controlled to within 1 °C with chromel-alumel thermocouples in contact with the surface of the upper and lower diamond anvils, however the accuracy of the temperature measurements is less than 3°C (Bassett et al., 2000). The pressure was calculated from the pressure-/temperature-dependent one-phonon Raman shift of diamond (Bassett et al. 1996; Hanfland et al. 1985). To distinguish this shift from the Raman spectra of diamond anvils, we used synthetic ¹³C diamond. Because of the mass difference between ¹²C and ¹³C diamonds (mass ratio, ν₁₂C/ν₁₃C), their frequency difference is about 80 cm⁻¹ at
ambient pressure and temperature ($P$-$T$) conditions but changes with $P$-$T$ (Table 1, Fig. 3a). The one phonon Raman shift of $^{13}$C diamond was calibrated in the 0.1 - 1300 MPa and 25° - 800 °C ranges, as described in Mysen and Yamashita (2010).

Raman spectra were obtained with a JASCO model IRS-3100 confocal microRaman spectrometer with holographic gratings. A 50X objective lens was employed for both visual microscopic examination and spectroscopic analysis. Signals were detected with an Andor Model DV401-F1 1024x128 pixel Peltier-cooled CCD (25 µm² pixels). To record spectra of melt and fluid, the 490.2 nm line of a solid-state laser was used. This laser operates at 33.3 mW on the sample. In these measurements, acquisition was performed with grating settings of 600 grooves/mm to cover the 178-4469 cm⁻¹ frequency range within a single CCD window. The frequency resolution was ±3 cm⁻¹. Acquisition time was typically 4 min per spectrum.

Spectra used to monitor pressure from the Raman shift of $^{13}$C diamond were acquired with 2400 grooves/mm to cover the 1218–1753 cm⁻¹ frequency range (covering the $^{12}$C and $^{13}$C diamond peaks and a Neon reference line) within a single CCD window. Here, a 532 nm laser line was used for sample excitation, operating at about 6.4 mW. By optimizing spectrometer frequency resolution to the 584.72 nm Ne emission line, the pressure precision is ±40 MPa (±0.1 cm⁻¹ uncertainty on the Raman shift, Fig. 3). This precision combined with the uncertainty in the pressure calibration of the one-phonon shift of the $^{13}$C diamond (±100 MPa; Mysen and Yamashita, 2010) yields a pressure uncertainty of about ±110 MPa.

Baseline correction of Raman spectra was performed on the JASCO® package spectra analysis software, as illustrated in Mysen et al. (2013). Curve-fitting of Raman
spectra was carried out using the IGOR™ software package from Wavemetrics™. In this procedure, location (Raman shift), bandwidth, and band intensity were treated as independent variables and minimization of $\chi^2$ was used as the convergence criterion. Bandwidths were first fixed, and the number of bands and their locations were chosen according to Mysen et al. (2003) for NS3A5 composition melt and according to Mysen et al. (2010b) for fluids. Location and bandwidth were then restricted to vary within 40 cm$^{-1}$ with minimization of $\chi^2$ as the convergence criterion.

We also investigated the speciation of H$_2$O dissolved in the silicate melts by Fourier transform infrared spectroscopy (FTIR). Measurements were performed with a Jasco model IMV4000 FTIR microscope system with 10X objective and condenser cassegraine lenses, an InSb detector, CaF$_2$ beam splitter, and a halogen light source. Sixteen cm$^{-1}$ resolution scans over the 750-7800 cm$^{-1}$ frequency range were accumulated over 2048 scans when the aperture was $\geq$50x50 µm, and 4096 scans when smaller aperture was used.

In the halogen-free experiment, the size of each phase (melt globule, aqueous fluid) was smaller than the distance between diamond culets. Under such circumstances, the transmitted infrared signal at the point of interest will include contributions from both phases, and thus introduce interferences (Mysen, 2011). Therefore, no FTIR data on halogen-free fluids or melts are presented. Fluid or melt small volumes (<25x25 µm) in this experiment, however, were suitable for Raman spectroscopic measurements, which exploit a 1µm diameter laser beam and a focal depth near 10 µm. The F- and Cl-bearing aqueous fluids and melts were analyzed with both Raman and FTIR spectroscopy.
Procedure

These experiments describe melt and fluid equilibrium relationships at 800°C. For silicate glasses to melt and not dissolve into the fluid at this temperature, the density of a coexisting fluid at $P$-$T$ conditions needs to be sufficiently low so that fluid and melt can coexist (Mysen 2013b) (Table 1). Control of the fluid density is accomplished by bleeding air into the sample chamber during several heating-cooling stages. The final experiment, analyzed by Raman and FTIR spectroscopy, is performed once the right proportion of solid-fluid and gas are reached (Fig. 2, photomicrograph 1).

Iridium gaskets tend to deform at high $P$-$T$ conditions (Fig. 2). Phase segregation occurs, therefore, at slightly different $P$-$T$ conditions during each cooling process because of the variable internal volume between experiments (Table 1). The homogenization temperatures reported in Table 1 reflect the point of gas-fluid separation during cooling. Experimental $P$-$T$ conditions (shown in Fig. 3b) and observed phases are summarized in Table 1.

RESULTS

Raman spectroscopy

The 3000-4000 cm$^{-1}$ and 700-1200 cm$^{-1}$ frequency ranges (Fig 4A) include Raman bands changing with $P$-$T$ conditions (Fig. 4B and C) and the presence of Cl and F in both melt and fluid. Therefore, these frequency ranges appear to be relevant to the characterization of the structural roles of Cl and F in coexisting fluid and melt

3000-4000 cm$^{-1}$ frequency range. This frequency range is dominated by an asymmetric envelope with an intensity maximum near 3540 cm$^{-1}$ together with a tail that
extends to lower frequencies. The low-frequency component of this intensity envelope is considered to reflect hydrogen bonding between the O-H groups in the melt and fluid phase (e.g., Ratcliffe and Irish 1982; Walrafen et al. 1986; Frantz et al. 1993; Kawamoto et al. 2004; Mysen and Yamashita 2010; Mysen 2013a). With increasing temperature, the band becomes more symmetric (Fig. 4) as the role of hydrogen bonding becomes less important with increasing temperature (Walrafen et al., 1986; Frantz et al., 1993). At any given temperature, the band is sharper in the fluid than in melt phase (Fig. 4).

700-1200 cm\(^{-1}\) frequency range. This frequency range provides structural information relevant to the aluminosilicate species referred to as Q-species, in melts and silicate-saturated fluids (e.g., Brawer and White 1975; Furukawa et al. 1981; McMillan 1984; Maekawa and Yokokawa 1997; Zotov and Keppler 1998; Mysen et al. 2003 or Mysen 2012 for review). There are two maxima in this frequency range: one between 700 and 800 cm\(^{-1}\) and one between 1000 and 1100 cm\(^{-1}\) (Fig. 4). The latter is more intense in the melt, whereas the maximum at 700-800 cm\(^{-1}\) is more prominent in fluids. Moreover, the integrated area of the 700-800 cm\(^{-1}\) region in the spectra of aqueous fluid decreases with increasing \(P-T\), whereas it increases in the spectra of melt. The Raman band assigned to the Si-F stretching also resides in this frequency range near 990 cm\(^{-1}\) (Dalou and Mysen 2013).

Infrared spectroscopy

In the 4000-8000 cm\(^{-1}\) portion of the IR spectrum, there could be three bands near 4500, 5200 and 7200 cm\(^{-1}\) present in FTIR spectra of both H\(_2\)O-rich melt and silicate-rich fluid (Mysen 2009; 2011). In this study, the 4500 cm\(^{-1}\) band could not be discerned in the fluid
spectra. Furthermore, because we cannot unambiguously assess the extent of signal
interferences by fluid in the melt IR spectra because the melt globules often do not fill
entirely the volume between the two diamonds, these bands are treated qualitatively only.
In detail, the ratio of the integrated area of the 4500 and 5200 cm\(^{-1}\) bands (\(A_{4500}/A_{5200}\)) in
spectra of melt increases with increasing \(P-T\) conditions (Fig. 5). The dependence of the
\(A_{4500}/A_{5200}\) ratio on temperature is lower in F- and Cl- bearing melts than in melts of the
Na\(_2\)O-SiO\(_2\)-H\(_2\)O (Mysen 2009) and Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\)-H\(_2\)O systems (Mysen 2011) (Fig.
5b). This could be because of possible interference of aqueous fluid on the spectra of melt
(no OH-signal detected in spectra of fluids). Alternatively, the \(P-T\) paths in the
experiments in the Na\(_2\)O-SiO\(_2\)-H\(_2\)O (Mysen 2009) and Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\)-H\(_2\)O system
(Mysen 2011) are different from those in the present experiments. These differences
notwithstanding, the evolution of the \(A_{4500}/A_{5200}\) ratio with temperature is similar in the
Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\)-H\(_2\)O-F and Na\(_2\)O-Al\(_2\)O\(_3\)-SiO\(_2\)-H\(_2\)O-Cl systems. The temperature-
dependent \(A_{4500}/A_{5200}\) ratios, whether in halogen-bearing or halogen-free systems (Mysen
2009, 2011) are comparable, even though the experiments were carried out along quite
different pressure paths (Fig. 2b). This leads to the suggestion that pressure is not the
main control on the \(A_{4500}/A_{5200}\) ratio.

The 4500 cm\(^{-1}\) and 5200 cm\(^{-1}\) bands often are used to identify structurally bonded
OH groups and molecular H\(_2\)O, respectively, in aluminosilicate melts (Scholze 1956;
Bartholomew and Schreurs 1980; Withers et al. 1999; Malfait 2009). Although the
\(A_{4500}/A_{5200}\) ratio cannot be used to extract abundance of water species and total water
content in these melts, because of the possible interference from fluid and insufficient
information on molar absorption coefficients, it is worth noticing that the ratio of the
integrated peak areas of OH and H$_2$O increases with increasing temperature. In general, this ratio is lower in the halogen-bearing melt relative to the halogen-free aluminosilicate melt.

DISCUSSION

The structure of the melt and fluid phase

O-H bonding environment in aluminosilicate melts and aqueous fluids

The 3000-4000 cm$^{-1}$ frequency envelope is assigned to OH stretch vibrations (e.g., Van Thiel et al. 1957; Velde 1983; McMillan and Remmele 1986; Frantz et al. 1993; Kawamoto et al. 2004; Mysen, 2011). Two Gaussian bands were fitted with one centered near 3530 cm$^{-1}$ and the other near 3450 cm$^{-1}$ (Fig. 6a); assigned to isolated and hydrogen-bonded OH groups, respectively (Foustoukos and Mysen 2012). The relative distribution of the integrated peak areas is used to constrain the stability of the O…H-O bonding in the H$_2$O component of the melt and fluid phase (Walrafen 1968; Walrafen et al. 1996). By assuming that the relative normalized differential Raman scattering cross sections ($\sigma$) of the O-H and O…H-O $\nu_1$ vibrations are the same, the mole fraction ratio of isolated and hydrogen-bonded OH groups, $X_{HYDR}/X_{ISOL}$, equals the integrated intensities ratio:

$$K_{ISOL/HYDR} = X_{HYDR}/X_{ISOL} = A_{HYDR}/A_{ISOL}$$

(1)

From the correlation of $K_{ISOL/HYDR}$ with $1/T.10^3$, we estimate the enthalpy of rupture ($\Delta H$) of the O…H-O intermolecular bond in aqueous fluids and H$_2$O-rich melts (Fig. 5; Walrafen 1968; Foustoukos and Mysen 2012). In halogen-free fluids, $\Delta H$ of 18 kJ/mol for hydrogen-bond formation was estimated, consistent with the value reported for
supercritical H₂O solution (21±1 kJ/mol) (Foustoukos and Mysen 2012). As observed in Mysen (2013a), the ΔH is significantly weaker in melts than in fluids: 10±2 kJ/mol in Na₂O-SiO₂-H₂O melts and 11 kJ/mol in Na₂O-Al₂O₃-SiO₂-H₂O melts. Note that the ΔH reported in Mysen (2013a) and this study are similar (within the error bar) even though they are from different pressures (to 800ºC - 1250 MPa and to 800ºC - 829 MPa, respectively). This suggests that pressure is not an important factor controlling ΔH. The reason for this difference remains unclear, but an initial hypothesis suggests that molecular H₂O might be partly isolated in cavities in the silicate melt structure (Mysen 2013a). Notably, the ΔH values for the hydrogen bonding in the halogen-free aqueous phase (Fig. 6b) are lower than those calculated for the Na₂O-Al₂O₃-SiO₂-H₂O-Cl system (Fig. 6d), but higher than the estimations in the Na₂O-Al₂O₃-SiO₂-H₂O-F system (Fig. 6c).

In short, the relative stability of the intermolecular hydrogen bond between OH groups in both melt and fluid can be expressed as ΔHCl>ΔHO>ΔHF. While hydrogen bonding typically occurs where the partially positively charged hydrogen atom lies between partially negatively charged oxygen atoms, it has been shown experimentally at temperature up to 500ºC and pressure up to 500 MPa (Mayanovic et al. 2001) that hydrogen can form bonds with F⁻, Cl⁻ (and Br⁻) in fluids, such as HO-H˙˙˙˙F⁻ and HO-H˙˙˙˙Cl⁻ (see Collins et al. 2007 for review). The strength of hydrogen bonding is reduced as the halide radius increases (Collins et al. 2007). Statistical mechanics models have also suggested that charge densities control the ion-water interaction by affecting the two competing forces of electrostatic interaction (water’s dipole interacting with ions) and the hydrogen bonding (water interacting with neighboring waters) in water structure (Hribar...
et al. 2002). Based on this model, small ions (e.g. F\(^-\)) exhibit large charge densities that cause strong electrostatic ordering within water molecules and disrupt the water-water hydrogen bonds in the first solvation shell. To this end, the HO-H\(\cdots\)F\(^-\) bond appears to be weak (\(\Delta H\)-value: 2.2 kJ/mol at temperatures ranging from 300 to 800°C and pressures between 143 to 606 MPa, Table 1). In contrast, the HO-H\(\cdots\)Cl\(^-\) bond is stronger in fluid (\(\Delta H\)-value: 37.5 kJ/mol; at 300 to 800 °C and between 246 to 1264 MPa, Table 1) than the hydrogen bond in water HO-H\(\cdots\)OH\(_2\) at high P-T (\(\Delta H\)-value: 21±1 kJ/mol, at 300-800 °C, 330-1340 MPa, Foustoukos and Mysen 2012). This is consistent with Bondarenko et al. (2006) who show that at 100 MPa, <500°C in the H\(_2\)O-NaCl system the Cl\(^-\)H electrostatic attraction is stronger than O\(\cdots\)H bonds between H\(_2\)O molecules (O\(_{\text{H}_2\text{O}}\) partial charge is \(-0.82|e|\) in the SPC water model, while Cl\(_{\text{H}_2\text{O}}\) full formal charge is \(-1|e|\)).

In the case of the melt phase, charge density differences appear to impose less of an effect on the stability of the hydrogen intermolecular bonds. For example, the \(\Delta H\)-value of hydrogen bonding measured in F-bearing NS3A5 melts (3.1 kJ/mol; at 300 to 800°C – 143 to 606MPa) compares well with C\(\cdots\)H-OH\(_2\) (theoretically predicted ~ 4 kJ/mol; Li et al. 2007; Scheiner 2010), a structural behavior attributed to their comparable atomic radii, 0.072 and 0.077 nm, respectively.

The effect of fluorine and chlorine on the structure of H\(_2\)O-rich aluminosilicate melts

The 700-1200 cm\(^{-1}\) frequency range of Raman spectra is assigned to the stretch vibrations of Si-O and Al-O in aluminosilicate melts and fluids (see, for example, Mysen and Richet 2005), supported by \(^{29}\)Si and \(^{27}\)Al NMR spectroscopy in silicate glasses and
silicate-rich aqueous fluids (e.g. Stebbins 1987; Kinrade and Swaddle 1988; Buckermann et al. 1992; Kinrade 1996; Mysen and Cody 2005; Mysen 2007; Mysen et al. 2011).

Examples of curve-fitting results, deconvolved following Gaussian distributions, from the 700-1200 cm\(^{-1}\) frequency range are presented in Figure 7. There are 4 main bands near 750-820, 820-860, 870-910 and 1070-1090 cm\(^{-1}\) associated with aluminosilicate structural units with 4, 3, 2 and 1 non-bridging atoms for the Q\(^0\), Q\(^1\), Q\(^2\) and Q\(^3\) structural units, respectively. A band around 1050 cm\(^{-1}\) is observed in all spectra (Fig. 7). This band likely corresponds to (Si,Al)–O° vibrations in any structural units with bridging oxygen (Mysen et al., 1982; Lasaga, 1982). However, its assignment is still debatable (Mysen, 2007; Mysen and Cody, 2005) and will not be discussed any further.

Bandwidth and location of Q\(^n\) species’ bands are constant among spectra (within 10 cm\(^{-1}\) and 40 cm\(^{-1}\), respectively).

By assuming that the ratio of Raman cross-sections for the Si-O vibrations of the Q\(^0\), Q\(^1\), Q\(^2\) and Q\(^3\) are similar, the ratio of integrated intensities is the same as the ratio of mole fractions (Mysen et al. 2013). The abundance of Q\(^n\) species in melts and fluids, derived in this manner, are presented in Table 2. The location and bandwidth of the band around 1050 cm\(^{-1}\) strongly depends on the noise in the 960-1000 cm\(^{-1}\) area, which can reach up to 25% of the spectra intensity. Although the 1050 cm\(^{-1}\) band was not taken into account in the calculation of Q\(^n\) species mole fraction, its area can induce an uncertainty, in particular regarding Q\(^3\) mole fraction. This uncertainty is difficult to estimate but we consider that it cannot account for the whole variation of Q\(^n\) mole fractions derived from the spectra (Figures 7 and 8).

Differences between the relative abundances of silicate species in the hydrous
melt and aqueous fluid are immediately evident (Fig. 7). The abundance of the more polymerized species, $Q^2$ and $Q^3$, is greater in melts than in fluids, whereas the most depolymerized species, $Q^0$, is found to be more abundant in fluids (Fig. 7). The most polymerized $Q^n$ species, $Q^3$, is less abundant in F- and Cl-bearing aqueous fluids than in the halogen-free fluid (Table 2). This suggests that F and Cl presence in fluids disrupts the fluid structure, perhaps by depolymerizing the silicate network. Our experimental data suggest that such an effect might be greater in F-bearing relative to Cl-bearing fluids.

From the integrated peak area of bands assigned to Si-O stretch vibrations in the individual $Q^n$ species normalized to the sum of all $Q^n$ species areas, we calculated fluid/melt partition coefficients, $D_{\text{fluid/melt}}$ (Fig. 8). The $D_{\text{fluid/melt}}$ of the most depolymerized $Q^n$ species, $Q^0$, decreases rapidly with increasing temperature, and therefore pressure (as increasing temperature drives increased pressure, Fig. 3b), in all experiments. In contrast, the partition coefficients of more polymerized species, $Q^2$ and $Q^3$, increase with increasing temperature/-pressure in the halogen-free experiment (Fig. 8).

Interestingly, the dependence of $Q^n$ abundance on $P$-$T$ conditions is modified by the presence of F and Cl in the system (Fig. 8). In the F-bearing system, with increasing $P$-$T$, the partition coefficients of the most depolymerized species, $Q^0$, and $Q^1$ decrease whereas that of the most polymerized species, $Q^3$, increases but remains lower than in the halogen-free system. A small effect is observed in the case of the Cl-bearing system. Moreover, $D_{\text{fluid/melt}}^{Q3}$ initially decreases from 400 to 600$^\circ$C and then increases at higher temperature, ergo higher pressure. These trends tend to suggest that the depolymerization
The effect of H₂O in highly alkaline aluminosilicate melts is less effective in the presence of Cl.

**Fluorine speciation and fluid/melt partitioning**

Curve fitting of the Raman spectra of F-bearing melts and fluids requires the presence of a band near 990 cm⁻¹. This is attributed to the Si-F in Q³, noted Q³(F), assuming that the replacement of O²⁻ by F⁻ likely causes a reduced vibrational frequency and that the 990 cm⁻¹ band is just lower than the frequency of Si-O vibrations in Q³. Furthermore, this frequency is near the Si-F stretching vibration of SiO₃-F complexes (~ 945 cm⁻¹; Dumas et al., 1982; Yamamoto et al., 1983) in silicate glasses.

The integrated area of the 990 cm⁻¹ peak (normalized to the sum of all Qⁿ species areas) was used to calculate the partition coefficient of Si-F between fluids and melts, because the cross section for Si-F stretching is similar in fluids and melts assuming that the (Si+F)-species are the same in fluids and melts. With increasing P-T conditions, the D_{fluid/melt}^{Si-F} increases (Fig. 9a). The linear regression of the relationship between ln(D_{fluid/melt}^{Si-F}) and 1/T, results in a ΔH = -15.2 ±0.6 kJ/mol (Fig. 9b) for the equilibrium exchange of Si-F between fluid and melt. This value is comparable to the ΔH we find for Q³ (~16 ±2 kJ/mol, Fig. 9c), suggesting that F does not significantly disturb the silicate structure.

Water solubility in melts increases and progressively depolymerizes melts with increasing P-T in our P-T condition range (Table 2). During melt depolymerization, the relative abundance of Q³ and, therefore, of Q³(F) decreases (Table 2), while there is no evidence of Si-F vibrations in more depolymerized species Q² or Q¹ (no shoulders on the
lower frequency parts of Q\(^2\) or Q\(^1\) bands are observed). Results, therefore, indicate that
the Si-F concentration in melts decreases with increasing \(P-T\) (Table 2). In silicate–rich
aqueous fluids at low \(P-T\) conditions (200-400 °C and 50-150 MPa), F and OH
complexes with Si may form SiF\(_4\), SiF\(_5\)\(^-\), SiF\(_6\)\(^2-\), Si(OH)\(_2\)F\(_2\), H\(_3\)SiO\(_4\)\(^-\) and H\(_4\)SiO\(_4\)
(Konyshev and Aksyuk 2008). Konyshev and Aksyuk (2008) observe that, with
increasing \(P-T\), the abundance of the F-bearing complexes in fluids increases, while the
abundance of Si-OH complexes decreases. Consistently, we observe that the solubility of
these Si-F complexes in the fluid phases increases with increasing \(P-T\) (Table 2),
regardless of complex speciation.

As \(P-T\) increases, FTIR \(\text{in-situ}\) measurements indicate that the OH/H\(_2\)O
proportion increases in melts (Figure 5b). The OH/H\(_2\)O ratio increase in the halogen-free
systems is similar although the two sets of data in the NS4 (Mysen 2009) and NA10
(Mysen 2011) systems are from different pressures (up to 1033 and 791 MPa,
respectively) than the present experiments. The OH/H\(_2\)O increase with temperature is
smaller in F-bearing melts than halogen-free melts (Fig. 5b). This suggests that F
suppresses the formation of OH bonds with silicate, which is consistent with the reaction,
found in F-bearing hydrous glasses, quenched at 1400°C – 1.5 GPa (Dalou and Mysen
2013):

\[
2\text{AlSi}_2\text{O}_4\text{F}_3 + 2Q^3(\text{OH}) \leftrightarrow 3Q^3(\text{F}) + Q^4 + Q^2 + 2\text{Al}^{3+} + \text{H}_2\text{O}, \quad (2)
\]

where Q\(^3\)(OH) refers to Q\(^3\) species with 2H\(^+\) per Si and AlSi\(_2\)O\(_4\)F\(_3\) refers to a possible F-
bearing aluminosilicate complex formed by F\(_2\) solution mechanism in anhydrous glass
(Dalou et al. in revision).
In effect, by forming Si-F bonds, F reduces the formation of Si-OH bonds in aluminosilicate melts and promotes the formation of molecular H$_2$O.

As shown in previous studies (Schaller et al. 1992; Mysen et al. 2004), F preferentially bonds with Al in some aluminosilicate glasses. The presence of F in four- and six-fold coordination around Al is recorded by the variation of Raman spectra intensity near 800 and 600 cm$^{-1}$, respectively. The resolution of our spectra in those frequencies is insufficient to resolve the variation of Al-F complexes. Therefore, changes of Al-F bonding with P-T conditions cannot be discussed in more detail.

**Chlorine speciation and fluid/melt partitioning**

Previous work on chloride solubility in melts and fluids has shown that it preferentially bonds with alkali network-modifiers (Ca, Na or K; e.g. Stebbins and Du, 2002; Sandland et al. 2004; Zimova and Webb 2006; Evans et al. 2008; Baasner et al. 2013). For example, Dalou and Mysen (2013), proposed that Cl dissolves in hydrous silicate melts following the equilibrium reaction:

$$2\text{NaOH} + Q^4 + \text{Cl}_2 \leftrightarrow 2\text{NaCl} + Q^2 + \text{H}_2\text{O}. \quad (3)$$

This reaction suggests that the formation of NaCl species in the melt structure releases molecular H$_2$O and implies that the presence of Cl reduces the formation of OH bonds with sodium. This likely explains the lower OH/H$_2$O ratio in Cl-bearing melts than in halogen-free melts (Fig. 4b). To this end, increased H$_2$O solubility in silicate melts along the P-T path shifts the equilibrium reaction (3) to the right.

It also has been proposed that Cl can be dissolved in melts as HCl, an abundant species in magmatic gases:
HCl$_{\text{fluid}}$ + O$_2^{-}_{\text{melt}}$ ↔ Cl$^{-}_{\text{melt}}$ + OH$^{-}_{\text{melt}}$  \hspace{1cm} (4)

(Kogarko 1974; Burnham 1979). The Cl solubility, however, decreases as water content increases in aluminosilicate melts (Dalou and Mysen 2013). Therefore, as $P$-$T$ and H$_2$O solubility increases in aluminosilicate melt, Cl and Na activity decreases. If HCl was the dominant speciation of Cl in hydrous silicate melts, it would be expected than an H$_2$O content increase in the melt would increase Cl solubility as:

2NaCl + H$_2$O ↔ 2HCl + Na$_2$O,  \hspace{1cm} (5)

which is not observed in silicate melts. This would suggest that NaCl bonds in hydrous aluminosilicate melts are more important than HCl.

Experimental data on the evolution of the HCl/NaCl ratio in melts and fluids have been determined at lower pressure than in this study (below 150MPa) and with natural composition melts (from basalt to rhyolite, e.g Williams et al. 1997; Shinohara, 2009). In these experiments, it has been shown that the HCl/NaCl ratio increases with decreasing Na/Al in silicate melts and with decreasing pressure (Shinohara 1987; Candela 1990). Shinohara (2009) also illustrates that, below ~65MPa, HCl becomes more abundant than NaCl in the aqueous fluid, regardless of the composition of the melt in equilibrium with the fluid. In other words, the equilibrium reaction (5) shifts to the right (Sourirajan and Kennedy 1962) probably because of the large difference in partial volumes of HCl and NaCl in low-density phases at high temperature and low pressure conditions (Shinohara and Fujimoto 1994). Therefore, we can assume that in the range of pressure studied here (246-1264 MPa), the abundance of HCl in the melt, compared to NaCl, is too low to be detected spectroscopically. Moreover, as pressure decrease, the HCl/NaCl increasingly partitioned from the melt into the aqueous fluid (Williams et al. 1997). This implies that
HCl solubility increases more rapidly in fluids than in silicate melts during decompression.

Frank et al. (2003) found a positive correlation between the $\text{NaCl}_{\text{fluid}}/\text{NaOH}_{\text{melt}}$ ratio and the HCl concentration in the aqueous fluid. Their observation suggests exchange equilibrium of Cl between fluid and melt written as:

$$\text{NaOH}_{\text{melt}} + 2\text{NaCl}_{\text{fluid}} \leftrightarrow \text{NaCl}_{\text{fluid}} + \text{HCl}_{\text{fluid}} + \text{Na}_2\text{O}_{\text{melt}} \quad (6)$$

As pressure decreases, the equilibrium 6 is shifted to the right. This solution mechanism allows more Na$^+$ to be released in the melt as a network modifier. Because Na prefers to bond with non-bridging oxygen in $Q^3$ species, this likely explains the decrease of the abundance of $Q^3$ in the melt (Table 2) from 600°C – 790 MPa to 400°C – 358 MPa, and leads to the decreases of the $D_{\text{fluid}/\text{melt}}^{\text{Q3}}$ at low $P$-$T$ (Fig. 8d). In summary, the Cl exchanges between melt and fluid, as pressure and temperature decrease, favors the formation of HCl and NaCl in fluids and reduces Cl solubility in melts. Nevertheless, this exchange reaction cannot be detected at elevated $P$-$T$ conditions ($> 600°C – 790$ MPa).

**IMPLICATIONS**

The cooling and decompression of NaF- and NaCl-bearing magmatic liquids in a chemically closed environment was considered to model the ascent of a magma-fluid system. Although this model is restricted to alkaline systems in the 143-1264 MPa pressure range (i.e. from upper mantle or deep crustal pressures (50 – 25 km) to shallow crustal depths (10 to 5 km)), it significantly contributes to explain why F and Cl are the last volatiles to be degassed by magmatic systems (Spilliaert et al. 2006). Our data on solubility, speciation and partitioning, during magma ascent and cooling can also explain
the difference in degassing between F and Cl.

Fluorine solubility during magma ascent is discussed using Si-F complex as a proxy since we found no evidence of HF\textsubscript{aq} (weak bonds in fluids), while dissolved NaF\textsubscript{aq} species are in trace amounts in aqueous fluids (Weber et al. 2000) and in depolymerized melts (Mysen and Virgo, 1985). The positive correlation of $D_{\text{fluid/melt}}^{\text{Si-F}}$ with temperature (Fig 9a) suggests that during cooling and ascension, (Si-F) complexes increasingly partitions from the fluid into the melt. This is consistent with the decreasing solubility of Si-F complexes like Si(OH)$_2$F$_2$\textsubscript{aq} observed in low pressure and temperature fluids (50 -150 MPa and 200 – 400ºC) as the solubility of quartz decreases (Konyshev and Aksyuk, 2008). The solubility of (Si-F) complexes increases in melt with decreasing pressure and temperature (Fig. 9d), i.e. as the magma cools and ascends. Below 600ºC and 790 MPa, Si-F partition coefficients between melt and fluid becomes >1, e.g. Si-F becomes more concentrated in melts than in fluids. Our data supports the enrichment of fluorine in the melt during ascent and cooling continues even after exsolution of the fluid phase from the magmatic liquid at the late stages of magmatic history.

The Cl-bearing magma-fluid system is characterized by the high solubility of NaCl-bearing complexes in fluids. Such fluids or brines transported in the crust by various volcanic systems can be observed in inclusions either as fluid inclusions trapped in host crystals or in silicate melt inclusions (e.g. Lowenstern 1994; Zajacz et al. 2008), or as part of hydrothermal systems in high-temperature reservoirs (e.g. Hedenquist and Lowenstern 1994; Chiodini et al. 2001). The Cl solution mechanism in hydrous aluminosilicate melts suggests that Cl solubility in melts increases during magma ascent, as H$_2$O solubility decreases in the form of NaCl-melt complexes (Dalou and Mysen...
2012) at pressures < 790 MPa. The exchange reaction (6) suggests that the NaCl concentration in melts starts to decrease, forming dissolved HCl in fluid at conditions below 600°C – 790 MPa. During shallower decompression, the abundance of HCl may also become significant and, perhaps, exceed that of NaCl at shallow crustal pressures (< 65 MPa, Shinohara 2009) particularly in fluids. Once saline fluids are separated from the magma to ascent in crustal veins, Cl degassing (i.e. HCl vapor) from the residual magma is controlled by the extent of Cl solubility in melts determined by the magma composition, e.g. alkalinity (Frank 2003; Shinohara 2009). For instance, HCl solubility in basaltic melts is larger than in rhyolitic melts, while HCl exsolution from basalt occurs at lower pressure than from rhyolite (Shinohara 2009).

To this end, it appears that during ascent, F and Cl speciation favors their solution in melts (perhaps only up to 790 MPa for Cl). Therefore, their solubility remains high to shallow depth in the Earth, consistent with F and Cl being the last degassed volatiles from magmas (Spilliaert et al. 2006). We pose that such behavior explains why F and Cl are often undersaturated in magmas (Carroll and Webster 1994) and, therefore, do not degas significantly. As less than 15% of initial F content is degassed, Cl can be degassed to 50% of its initial content (Métrich and Wallace 2008), suggesting that F solubility in magmas remains higher than Cl likely due the increasing formation of HCl in the last ~ 5 - 25 km of decompression.

ACKNOWLEDGEMENTS
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doi:10.1007/s00410-001-0320-y


FIGURE CAPTIONS

**Figure 1:** Photomicrographs of the sample chamber in the HDAC at ambient temperature and 1 atm pressure. Starting materials include a grain of NS3A5 glass, a 0.5M NaF aqueous fluid and a $^{13}$C diamond chip.

**Figure 2:** Photomicrographs of the sample in Fig. 1, before the heating process noted initial state (1), after heating process at 800ºC (2) and during cooling stages to ambient conditions (3 to 6).

**Figure 3:** A. Example of Raman spectrum of $^{13}$C diamond inside the HDAC at ambient temperature and pressure conditions (solid line), at 400ºC and 358 MPa (dashed line) and at 800ºC and 1264 MPa (dotted line), as indicated. The peak marked “natural diamond” is the peak of $^{12}$C from the diamond of the diamond cell itself. The Neon reference line is also shown here. B. Pressure-temperature relationships among our experiments: diamonds are for the experiment without halogens, the crosses are for the experiment with the addition of NaF and the circles are for the experiment with the addition of NaCl. Pressure-temperature relationships in aluminum-free Na$_2$O.4SiO$_2$ (NS4) and with 10mol% Al (NS4A10) (Mysen, 2010; 2011) are also shown.

**Figure 4:** Example of Raman spectra collected at high temperature and pressure in F-bearing melts and fluids. The frequency range highlighted in grey (A) refers to the second-order vibrations of the diamond anvils. The intensity of peaks shown in B and C
changes with $P$-$T$ conditions and with the presence of either F or Cl in both melt and fluid.

**Figure 5:** A. FTIR spectrum of a Cl-bearing H$_2$O-rich melt at 700 ºC in the 4200-5600 cm$^{-1}$ region. B. Relationship between the ratio of integrated areas, $A_{4500}/A_{5200}$, vs. temperature, for F-bearing (crosses) and Cl-bearing (circles) H$_2$O-rich melts. Experimental data are compared with HDAC studies of halogen-free water-saturated Na$_2$Si$_4$O$_9$ (NS4) and Na$_2$AlSi$_3$O$_9$ (NA10) melts (Mysen 2009, 2011). Melt spectra were obtained at different pressures up to: 1033 MPa for NS4, 791 MPa for NA10, 606 MPa for F-bearing experiment and 1264 MPa for Cl-bearing experiment (Fig. 3b).

**Figure 6:** Raman spectra used to describe the extent of hydrogen bonding in H$_2$O-rich NS3A5 melt and aqueous fluid. A. Example of a curve-fitted Raman spectrum in the frequency range 3000-4000 cm$^{-1}$ of a silicate-rich fluid recorded in-situ at elevated temperature and pressure. Modified Van’t Hoff expression of ln K vs. 1/T were employed to calculate the stability hydrogen bonding in coexisting water-saturated aluminosilicate melt (full symbols) and silicate-saturated aqueous fluid (empty symbols), for the halogen-free experiment, B; the F-bearing experiment, C; and the Cl-bearing experiment, D. Note that $\Delta H$-values are derived from the lnK vs. 1/T slope with no correction for pressure.

**Figure 7:** Examples of Raman spectra in the frequency range of first-order (Si,Al)-O vibrations from the halogen-free H$_2$O-rich melt (A); the F-bearing hydrous (B), and the Cl-bearing fluid (C), at the pressure-temperature conditions indicated on individual
spectra. Grey lines are the Raman spectra and the black lines are the result of the curve fitting. Spectra are normalized to 100% intensity, where 100% represents the highest intensity of each spectrum. Residues of the curve-fittings are also presented.

**Figure 8:** Partition coefficients between fluid and melt, $D_{\text{fluid/melt}}$, for $Q^0$, $Q^1$, $Q^2$, and $Q^3$ species as a function of temperature. The $D_{\text{fluid/melt}}$ were calculated from each $Q^\alpha$ species area normalized to the sum of all $Q^\alpha$ areas. Diamonds are data from the halogen-free experiment, crosses from the F-bearing experiment and circles from the Cl-bearing experiment.

**Figure 9:** Partition coefficients of Si-F between fluid and melt, $D_{\text{fluid/melt}}$ as a function of temperature (A); ln$D_{\text{fluid/melt}}$ as function of $1/T \cdot 10^3$ (B); ln$D_{Q3, \text{fluid/melt}}$ as function of $1/T \cdot 10^3$ in NS3A5 + H$_2$O + NaF experiment (C) and integrated Si-F band area of F-bearing melts (D). The $D_{\text{fluid/melt}}$ and the Si-F$_{\text{melt}}$ were calculated from the 990 cm$^{-1}$ band area normalized to the sum of all $Q^\alpha$ integrated peak areas.
### Table 1. Run data

<table>
<thead>
<tr>
<th>Temp (ºC)</th>
<th>Raman shift $^{13}$C diamond (cm$^{-1}$)</th>
<th>$^{a}$Pressure $^{13}$C diamond (MPa)</th>
<th>Phase present</th>
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<tr>
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<td>829</td>
<td>Melt (R$^b$), Fluid (R),$^{13}$C</td>
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<td>1268.7</td>
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<td>575</td>
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<tr>
<td>500</td>
<td>1274</td>
<td>423</td>
<td>Melt (R), Fluid (R),$^{13}$C</td>
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<tr>
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<td>Quartz, Melt (R), Fluid (R),$^{13}$C</td>
</tr>
<tr>
<td>300</td>
<td>1278.2</td>
<td>143</td>
<td>Quartz, Melt (R), Fluid (R),$^{13}$C</td>
</tr>
</tbody>
</table>

**Experiment NS3A5 + pure H$_2$O fluid**  
$T_h = 210$ºC- Fluid density = 0.853 g.cm$^{-3}$

| 800       | 1264                                  | 606                                   | Melt (R,$^b$), Fluid (R, IR),$^{13}$C |
| 700       | 1264                                  | 448                                   | Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 600       | 1268                                  | 365                                   | Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 500       | 1271.8                                | 313                                   | Salt$^c$, Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 400       | 1274.4                                | 218                                   | Salt, Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 300       | 1277.2                                | 143                                   | Salt, Melt (R, IR), Fluid (R, IR),$^{13}$C |

**Experiment NS3A5 + H$_2$O + 0.5M NaF fluid**  
$T_h = 340$ºC- Fluid density = 0.611 g.cm$^{-3}$

| 800       | 1266                                  | 1264                                  | Melt (R), Fluid (R),$^{13}$C |
| 780       | 1266.3                                | 1237                                  | Melt (R), Fluid (R),$^{13}$C |
| 720       |                                       |                                       | Melt (IR), Fluid (IR) |
| 700       | 1268.7                                | 1072                                  | Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 600       | 1271.9                                | 790                                   | Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 500       | 1274.8                                | 638                                   | Salt, Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 400       | 1276.4                                | 358                                   | Salt, Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 300       | 1278.4                                | 246                                   | Salt, Melt (R, IR), Fluid (R, IR),$^{13}$C |

**Experiment NS3A5 + H$_2$O + 0.5M NaCl fluid**  
$T_h = 340$ºC- Fluid density = 0.926 g.cm$^{-3}$

| 800       | 1266                                  | 1264                                  | Melt (R), Fluid (R),$^{13}$C |
| 780       | 1266.3                                | 1237                                  | Melt (R), Fluid (R),$^{13}$C |
| 720       |                                       |                                       | Melt (IR), Fluid (IR) |
| 700       | 1268.7                                | 1072                                  | Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 600       | 1271.9                                | 790                                   | Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 500       | 1274.8                                | 638                                   | Salt, Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 400       | 1276.4                                | 358                                   | Salt, Melt (R, IR), Fluid (R, IR),$^{13}$C |
| 300       | 1278.4                                | 246                                   | Salt, Melt (R, IR), Fluid (R, IR),$^{13}$C |

$^a$Pressure calculated from the $^{13}$C diamond shift normalized to the 584.72 nm Ne line (see text for further discussion).

$^b$R – Raman spectra recorded. IR – infrared spectra recorded.

$^c$Salt refers to salt precipitation.
Table 2. Silicate species, $Q^n$, abundance in melt and fluid of each experiment.

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<th>Temp (ºC)</th>
<th>$Q^0$</th>
<th>$Q^1$</th>
<th>$Q^2$</th>
<th>$Q^3$</th>
<th>$Q^3(F)$</th>
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<td></td>
<td></td>
<td></td>
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<td><strong>Melt</strong></td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>700</td>
<td>0.127(3)</td>
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<td>0.209(3)</td>
<td>0.409(6)</td>
<td>0.351(6)</td>
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</tr>
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<td><strong>Fluid</strong></td>
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<tr>
<td><strong>Melt</strong></td>
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<td><strong>Fluid</strong></td>
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<td>0.432(4)</td>
<td>0.108(2)</td>
<td>0.179(3)</td>
<td>0.280(4)</td>
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<td>780</td>
<td>0.458(3)</td>
<td>0.094(1)</td>
<td>0.217(2)</td>
<td>0.230(2)</td>
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<tr>
<td>700</td>
<td>0.564(6)</td>
<td>0.067(0.5)</td>
<td>0.154(1)</td>
<td>0.215(1)</td>
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<tr>
<td>600</td>
<td>0.583(8)</td>
<td>0.064(1)</td>
<td>0.148(2)</td>
<td>0.204(3)</td>
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<tr>
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<td>0.037(1)</td>
<td>0.135(2)</td>
<td>0.207(3)</td>
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<tr>
<td>400</td>
<td>0.611(9)</td>
<td>0.045(1)</td>
<td>0.134(1)</td>
<td>0.209(3)</td>
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</tr>
</tbody>
</table>

Numbers in parentheses represents one standard deviation in terms of least units cited.
FIGURES

Figure 1

Before experiment
0.1 MPa - 25°C

Ir gasket

0.5M NaF aqueous solution

Starting glass ¹²C diamond

NS3A5

100 μm
Figure 2

INITIAL STATE

25°C
0.1 MPa

 Ir gasket
 NaF crystal
 Glass
 Gas bubble
 Fluid

Heating

12C diamond

800°C
606 MPa

 Melt
 Fluid


600°C
365 MPa

 Melt
 Fluid

50 µm


500°C
313 MPa

 Melt
 NaF crystal
 Fluid


400°C
218 MPa

 Melt
 NaF crystal
 Gas bubbles

400°C
218 MPa

 Melt
 Gas bubble
Figure 3

(A) Raman spectra

Intensity

800°C - 1264 MPa
400°C - 358 MPa
25°C - 0.1 MPa

Frequency (cm⁻¹)

(B) Pressure (MPa) vs. Temperature (ºC)

- NS4 + H₂O (Mysen 2009)
- NA10 + H₂O (Mysen 2011)
- NS3AS + H₂O
- NS3AS + H₂O + NaF
- NS3AS + H₂O + NaCl

13C diamond
12C diamond
"natural" diamond
Neon line
1400 1200 1000
NA10 + H₂O (Mysen 2011)
NS4 + H₂O (Mysen 2009)
NS3AS + H₂O
NS3AS + H₂O + NaF
NS3AS + H₂O + NaCl

Always consult and cite the final, published document. See http://www.minsocam.org or GeoscienceWorld
Figure 4

Raman spectra

A

Melt

800°C - 606 MPa

B

Melt

Fluid

C

Melt

Fluid

Always consult and cite the final, published document. See http://www.minsocam.org or GeoscienceWorld
Figure 5

A

FTIR spectrum

Absorbance

Frequency (cm⁻¹)

B

\( \frac{A_{4500}}{A_{5200}} \) vs. Temperature (ºC)

\( \Delta \) NS4 + H₂O (Mysen 2009)
\( \Delta \) NA10 + H₂O (Mysen 2011)
\( \times \) NS3AS + H₂O + NaF
\( \bigcirc \) NS3AS + H₂O + NaCl
Figure 6

A Raman spectrum

B pure H₂O

C H₂O + NaF

D H₂O + NaCl

ΔH = 37.5 kJ/mol

ΔH = 14.4 kJ/mol

ΔH = 3.1 kJ/mol

ΔH = 18.9 kJ/mol

ΔH = 11.1 kJ/mol

ΔH = 2.2 kJ/mol

ΔH = 2.2 kJ/mol

ΔH = 3.1 kJ/mol
Figure 7

A. Melt: NS3A5 + H₂O

B. Melt: NS3A5 + H₂O + NaF

C. Fluid: NS3A5 + H₂O + NaCl

Frequency (cm⁻¹)

Normalized intensity, %
Figure 8

A

B

C

D

Temperature (ºC)

Temperature (ºC)

\[ D_{\text{fluid/melt}} \]

\[ D_{\text{Q}_i} \]
Figure 9

A

\[ D_{\text{fluid/melt}}^{\text{Si-F}} \]

\[ \ln D_{\text{fluid/melt}}^{\text{Si-F}} \]

B

\[ \Delta H = 15.2 \pm 0.6 \text{ kJ/mol} \]

C

\[ \Delta H = 15.9 \pm 2 \text{ kJ/mol} \]