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

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26 **Abstract**
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28 In order to advance our knowledge of speciation among volatiles during melting and
29 crystallization in the Earth's interior, the nature of carbon-, nitrogen-, and hydrogen-bearing
30 species was determined in COHN fluids and dissolved in coexisting aluminosilicate melts.
31 Micro-Raman characterization of fluids and melts were conducted in-situ while samples were at
32 temperature up to 825˚C and pressure up to ~1400 MPa under redox conditions controlled with
33 the Ti-TiO_2-H_2O hydrogen fugacity buffer. The fluid species are H_2O, H_2, NH_3, and CH_4. In
34 contrast, under oxidizing conditions the species are H_2O, N_2 and CO_2.

35   The equilibria among silicate structures (Q-species) and reduced carbon and nitrogen
36 species are, $2NH_3 + 4Q^n \leftrightharpoons 2Q^{n-1}(NH_2) + 2Q^{n-1}(OH)$, and $2CH_4 + 4Q^n \leftrightharpoons 2Q^{n-1}(CH_3) + 2Q^{n-1}(OH)$.
37 $^{1}(OH)$. The Q^n- and Q^{n-1} denote silicate species with, respectively, n and n-1 bridging oxygens.
38 The formulation in parentheses, (NH_2), (CH_3), and (OH), is meant to indicate that those
39 functional groups replace one or more oxygen in the silicate tetrahedra. There is no evidence for
40 O-NH_2 or O-CH_3 bonding. Therefore, solution of reduced C- and N-species species in the COHN
41 system results in depolymerization of silicate melts. The ΔH-values derived from the X_{NH2}/X_{NH3}
42 and X_{CH3}/X_{CH4} evolution with temperature, respectively, were 8.1 ± 2.3 kJ/mol and between -
43 4.9 ± 1.0 and -6.2 ± 2.2 kJ/mol.

44   The fluid/melt partition coefficients, $K^{fluid/melt}$, of the reduced species, H_2O, H_2, NH_3, and
45 CH_4, remain above unity at all temperatures. For example, for carbon it is in the 6-15 range with
46 a $\Delta H = -13.4\pm2.4$ KJ/mol. These values compare with a 0.8-3 range with $\Delta H = -19\pm2.4$ kJ/mol
47 in N-free silicate-COH systems. The $K^{fluid/melt}$-values for reduced nitrogen and molelcular
48 hydrogen are in the 6-10 and 6-12 range with ΔH-values of -5.9 ± 0.9 kJ/mol and $=8\pm6$ kJ/mol,
49 respectively.

50   A change in redox conditions during melting and crystallization in the Earth sufficient to
51 alter oxidized to reduced carbon- and nitrogen-bearing species will affect all melt properties that
52 depend on melt polymerization. This implies that changing redox conditions during melting of a
53 COHN-bearing mantle can have profound effect on physical and chemical properties of melts
54 and on melting and melt aggregation processes.
55

Introduction

56 An understanding of the behavior of COHN volatiles in magatic systems at high temperature and

58 pressure is central to characterization of processes that describe formation and evolution of the

59 solid Earth, recycling of volatiles, and interaction between the solid Earth and its oceans and

60 atmosphere (Zhang and Zindler, 1993; Miyazaki et al., 2004; Adler and Williams, 2005; Sata et

61 al., 2010). These processes and the underlying materials properties needed for modeling are

62 governed by temperature, pressure, redox conditions, and bulk chemistry. Redox conditions can

63 affect the carbon and nitrogen distribution and recycling because they can exist in different

64 oxidation states within the range of redox conditions in the Earth's interior (Miyazaki et al.,

65 2004; Mysen et al., 2008; Mysen and Fogel, 2010; Kadik et al., 2011, 2015). Under highly

66 reducing conditions, molecular H_2 also becomes an important species.

67 Under reducing conditions, distribution of nitrogen in the Earth is governed in part by its

68 solubility in crystalline phases where NH_4^+ functional groups can substitute for K^+ in the crystal

69 structure of mica and amphibole, for example (Duit et al., 1986; Watenpuhl et al., 2009) and in

70 part by solubility of (N...H) complexes in melts and fluids. The nitrogen partitioning behavior

71 between and solubility in minerals, melts, and fluids at high pressure and temperature also is

72 important, and depends on the oxidation state of nitrogen (Libourel et al., 2003; Miayzaki et al.,

73 2004; Bebout et al., 2013).

74 Redox-dependent speciation of C-bearing volatile components also affects properties of

75 magmatic systems. For example, melting of oxidized CO_2- and CO_3^{2-}-bearing upper mantle

76 yields silica-undersaturated melts such as alkali olivine basalt and nephelinite and perhaps even

77 carbonatite (Hirose, 1997; Dalton and Wood, 1993). However, with the hydrogen fugacity

78 conditions greater than that of the MW (Fe_3O_4/FeO/H_2O) buffer, the stable C-species in COH-

79   bearing melts at high pressure and temperatures are CH_4 and CH_3^- groups (Mysen et al., 2011).

80   Such redox conditions are not unusual in the mantle of the present Earth (Carmichael and

81   Ghiorso, 1990). The potential importance of reduced C-bearing species in the modern Earth

82   notwithstanding, only a handful of experimental studies aimed to characterize the melting

83   behavior of methane-bearing silicate systems at high pressure has been reported. What is known

84   suggests that methane lowers activity coefficients of silica, which would drive composition of

85   partial melt towards silica enrichment, for example (Eggler and Baker, 1982; Taylor and Green,

86   1989).

87   Molecular H_2 is a major component under hydrogen fugacity conditions equivalent to the IW

88   (Fe/FeO)+H_2O buffer and above. It may, therefore, have been an important fluid component at

89   the redox conditions of the early Earth. Significant concentrations of molecular H_2 is less

90   important in the modern Earth (O'Neill, 1991) where the necessary high f_{H2}-conditions are rare.

91   An understanding of the role of COHN volatiles during the formation and evolution of the

92   Earth requires experimentally-determined speciation (structure) of volatiles in and their

93   partitioning between fluids and melts under conditions of the Earth's interior. Recently developed

94   methods that rely on externally-heated diamond anvil cell technology coupled with vibrational

95   spectroscopy have made it possible to obtain such data (Bassett et al., 1994; Zotov and Keppler,

96   2002; Mibe et al., 2008). In the present report, fluid and melt structure and fluid/melt partitioning

97   of volatile components silicate- COHN systems have been carried out with such techniques.

98

99   **Experimental Methods**

100   Experiments were carried out with the samples contained in a 500 µm diameter central hole of a

101   125 µm thick Ir gasket placed between the diamonds culets in the hydrothermal diamond anvil

102   cell (Bassett et al., 1994). Starting materials were glass chips of the alkali aluminosilicate

103   composition $(Na_2Si_4O_9)_{90}(Na_2(NaAl)_4O_9)_{10}$ that were mixed with $Ag_2C_2O_4$ and AgN_3 and loaded

104   into the hydrothermal diamond anvil cell together with double-distilled, dionized H_2O and small

105   pieces of Ti metal. Carbon dioxide and N_2 were formed from decomposition of the silver oxalate

106    $(Ag_2C_2O_4)$ and silver azide (AgN_3), which takes place near 200˚C. Condensed materials (silicate

107   + $Ag_2C_2O_4$ + AgN_3+Ti metal) represented about 50% of the starting composition together with

108   about 50% liquid H_2O. However, these proportions could not be determined with precision

109   because of the small sample volume (<0.0x μm^3).

110   During an experiment, the Ti metal reacted with H_2O to control the hydrogen fugacity via the

111   reaction:

112

113    $Ti + 2H_2O \Leftrightarrow TiO_2 + 2H_2.$ (1)

114

115   This CO_2 and N_2 were transformed to CH_4 and NH_3 by reaction with H_2 from the f_{H2} buffer

116   reaction [eqn. (1)] (Mysen and Fogel, 2010; Foustoukos and Mysen, 2013);

117

118    $CO_2 + 3H_2 \Leftrightarrow CH_4 + H_2O,$ (2)

119

120    $N_2 + 4N_2 \Leftrightarrow 2NH_3 + H_2O.$ (3)

121

122   Molybdenum wire wrapped around each of two SiC diamond seats was used to form heaters.

123   Temperature was monitored with two K-type thermocouples touching the diamonds about 1-1.5

124   mm from the sample. Temperature variations, determined with the melting point of NaCl

125   (800.5˚C at ambient pressure), is ~±2˚C. Pressure, generated by the fluid at essentially constant

126   volume in the sample chamber, changed with temperature. It was monitored with the one-phonon

127   Raman shift of synthetic ^{13}C diamond added as small chips to the sample volume (Schiferl et al.,

128   1997). Pressure was, therefore, a temperature-dependent variable (Table 1). The ^{13}C diamond

129   was used in order to avoid interference from the Raman spectra from the natural diamonds in the

130   diamond anvil cell itself. Pressure/temperature-dependence of the one-phonon Raman shift was

131   calibrated against the equation-of-state of pure H_2O by Mysen and Yamashita (2010). The

132   pressure uncertainty, which includes both spectrometer precision and fitting errors in the

133   calibration, is about ±110 MPa. The spectrometer precision alone translates to a pressure

134   precision of ±40 MPa. Pressure does not decrease monotonously with decreasing temperature

135   because there was some deformation of the Ir gasket hole, which, therefore, resulted in sample

136   volume changes and, therefore, pressure variations.

137   Fluid and melt structure was evaluated from Raman spectra recorded with a JASCO model

138   NRS-3100 confocal microRaman spectrometer. With this system, a 2.5 cm working-distance

139   50X by 0.42 N.A. objective lens was used. The samples were excited with the 490 nm line of a

140   solid-state laser operating at ~ 30 mW at the sample. With this spectrometer set-up, the optical

141   resolution was 2-3 μm across by about 30 μm depth. The spectrometer is equipped with a single

142   monochromator, holographic notch filter, and holographic gratings. Gratings with 1200 and 2400

143   grooves/mm were employed. The 2400 grooves/mm gratings were used together with Ne

144   emission lines for frequency reference to collect high-precision carbon-13 diamond spectra with

145   ±0.1 cm^{-1} uncertainty. Measurements of the melt and fluid samples were carried out with 1200

146   grooves/mm and 2-3 cm^{-1} frequency uncertainty. The data were recorded with an Andor Model

147   DV401-F1 Peltier-cooled CCD.

148   Several temperature/pressure series of measurements were carried out. For each series, the

149   sample was first brought to the highest planned temperature and pressure and kept at this

150   condition (825˚C and ~1400 MPa in the present case) for ~60 minutes, which is sufficient to

151   attain equilibrium for which only several minutes are needed (Horita, 2014). Spectroscopic

152   measurements of the sample (fluid, melt, and/or supercritical fluid) and the ^{13}C diamond were

153   carried out at the highest planned temperature and pressure before the temperature was reduced

154   at 1˚C/s cooling rate to the next temperature. Pressure decreased accordingly (Table 1). The

155   measurement protocol was then repeated. Each experimental data point was 75˚C apart with the

156   last measurements at 525˚C and 634 MPa. Ambient conditions Raman measurements of the ^{13}C

157   diamond were carried before and after a series of high-temperature and -pressure experiments.

158

Results

160   For each temperature and pressure, spectra were recorded from about 400 cm^{-1} to 4200 cm^{-1} in

161   order to include frequencies of most (Si,Al)-O vibrations and vibrations in species involving

162   COHN components (Fig. 1). The band assignments in this and subsequent figures are based

163   predominantly on Nakamoto (1997). The peaks marked 1st and 2nd order diamond are from the

164   diamonds in the diamond anvil cell itself. There are no ^{13}C diamond signals the Raman spectra of

165   fluids and melts because carbon-13 diamond spectra were recorded separately.

8

166   The individual Raman band intensities differ significantly (Fig. 1). Therefore, in order to

167   make the topology of the peaks and their variations with temperature and pressure more visible,

168   the spectra have been divided into 4 segments, marked A, B, C, and D as indicated in Fig. 1, and

169   expanded in separate figures.

170   The frequency region, A, is from about 400 cm^{-1} to the strong one-phonon band from

171   diamond located near 1300 cm^{-1} (Figs. 1 and 2). It comprises signals assigned to (Si,Al)-O

172   vibrations as well as some of the bending modes of COHN species. In the spectra of fluids (Fig.

173   2A), this frequency regime is dominated by three bands, near 600, 800, and 1030 cm^{-1}. At the

174   highest temperatures, there is also a weak shoulder near 770 cm^{-1}. The integrated intensities of

175   the three main bands decrease with decreasing temperature and pressure while their frequencies

176   remain essentially constant (average frequencies: 591 ± 2, 813 ± 3, and 1030.4 ± 0.5 cm^{-1},

177   respectively). The 591 cm^{-1} band is assigned to Si-CH$_3$ stretching, and the other two to bending

178   vibrations in NH$_2$ functional groups (Fig. 2A). Additional support for Si-CH$_3$ bonds can be found

179   in recent ^{13}C MAS NMR data from quenched aluminosilicate melts equilibrated with

180   CH$_4$+H$_2$O+H$_2$ fluid at 1.5 GPa and 1400°C under reducing conditions (Mysen et al., 2011). The

181   770 cm^{-1} shoulder is assigned to Si-O$^-$ stretching in isolated SiO$_4$ entities (also denoted Q^0).

182   The spectra of melt are dominated by a broad band (FWHH ~80 cm^{-1}) at 885 cm^{-1} and

183   weaker and broad bands near 485, 570, and 1035 cm^{-1} (Fig. 2B). The 885 cm^{-1} band is assigned

184   to Ti-O vibrations from Ti^{4+} dissolved formed by oxidation of Ti metal [eqn. (1)].

185   The 485 cm^{-1} band is assigned to Si-O-Si rocking in Q^4 species and the 570 cm^{-1} band to Si-

186   O-Si bending most likely in Q^3 species (Furukawa et al., 1981; McMillan et al., 1992). The

187   existence of polymerized silicate species in the melts also is indicated by the broad band above

188   1000 cm^{-1} (FWHH near 100 cm^{-1}), which is assigned to Si-O stretching in polymerized species in

189   melts, most likely dominated by Q^3 type (McMillan et al., 1992). A more detailed review of the

190   band assignments assigned to (Si,Al)-O vibrations can be found in chapters 7 and 12 of Mysen

191   and Richet (2005).

192   The region between the 1st and 2nd order Raman peaks from the diamond cell diamonds

193   (near 1330 and 2600 cm^{-1}, respectively) is denoted segment B (Figs. 1 and 3). The spectra of

194   fluid are dominated by a sharp peak (FWHH: 10-15 cm^{-1}) near 1440 cm^{-1} (Fig. 3A). Its intensity

195   decreases with decreasing temperature. In melt spectra, this peak is only seen in those from the

196   highest temperature and pressure (825˚C/1400 MPa; see Fig. 3B). It is assigned NHN bending in

197   NH$_3$ molecules (Nakamoto, 1997). The fluid spectra also show a sharp peak near 1640 cm^{-1},

198   which could be assigned to HNH bending vibrations in NH$_3$ molecules (Colthup et al., 1990;

199   Nakamoto, 1997). The fluid spectra at 825˚ and 750˚C also show a sharp peak slightly above

200   1800 cm^{-1}. Although an assignment is quite uncertain, it cannot be ruled out that this is from C-O

201   vibrations in CO groups perhaps from carboxylic acid (Colthup et al., 1990). The only other peak

202   common to spectra of both fluids and melts in the B-region occurs near 1550 cm^{-1} (Figs. 3A, B),

203   which is assigned HOH bending in H$_2$O molecules (Nakamoto, 1997; Efimov and Pogareva,

204   2006).

205   In the spectra of fluid, the C-region extends from the high-frequency side of the 2nd-order

206   peak of diamond cell diamonds near 2600 cm^{-1} to the beginning of the low-frequency tail of the

207   strong peak centered between 3500 and 3600 cm^{-1} (Figs. 1 and 4). There are two peaks, near

208   2900 cm^{-1} and 3320 cm^1, in the spectra of melts and fluids (Figs. 4A and B). There is also a

209   weak and broad band centered near 3240 cm^{-1} in the spectra of fluids (Fig. 4A). The 2900 cm^{-1}

210   band is asymmetric toward lower frequency. This asymmetry can be accommodated by fitting

211   two Gaussian lines, near 2895 cm^{-1} and 2910 cm^{-1} (Fig. 6). These two peaks are assigned to C-H

212   stretching in, respectively, CH_3 groups and CH_4 molecules (Nakamoto, 1997), similar to that

213   reported from Raman spectra of Al-free melts by Mysen and Yamashita (2010) and in the Raman

214   and ^{13}C MAS NMR spectra of aluminosilicate glasses equilibrated as melts under reducing

215   conditions and temperature-quenched to glass (Mysen et al., 2011).

216   The two peaks near 3300 cm^{-1} are expanded with Gaussian lines fitted to spectra in the

217   example in Fig. 6. The strongest band, at 3325 cm^{-1}, is assigned to N-H stretching in NH_3

218   molecules, whereas the weaker and broader band, near 3230 cm^{-1}, is assigned to N-H stretching

219   in NH_2 groups (Yeo and Ford, 1994; Nakamoto, 1997; Mysen et al., 2008). There is no evidence

220   for NH_4^+ because the N-H stretch frequencies from this functional group is in the 3000-3200 cm^{-}

221   ^{1} frequency range (Socrates, 2001; Mysen et al., 2008), in which range there are no Raman bands

222   in the present spectra.

223   Frequency region D extends from the intense band centered between 3500 and 3600 cm^{-1} and

224   a group of bands of lesser intensities near 4100-4150 cm^{-1} (Fig. 7). This latter group is assigned

225   the Q-branch of H_2 reflecting vibrational to rotational transitions (Veirs and Rosenblatt, 1987;

226   Schmidt et al., 1998). The 3500-3600 cm^{-1} peak is assigned to OH stretching in OH groups

227   bonded to cations such as Si^{4+}, Al^{3+}, and Na^+ as well as OH groups in molecular H_2O (see also

228   Nowak and Behrens, 1994; Kawamoto et al., 2004).

229

230

Discussion

231

Solution mechanisms of reduced COHN species

232

233 The solution mechanisms of reduced carbon and nitrogen in silicate-COH melts and silicate-

234 NOH melts, respectively, involve various combinations of C..H and N..H complexes (Kadik et

235 al., 2004; Mysen et al., 2008, 2011; Ni and Keppler, 2013; Armstrong et al., 2015). For melts and

236 fluids in silicate-COHN systems, little is known except for some recent data obtained in-situ

237 under oxidizing conditions (Mysen, 2018). In the latter case, the sole nitrogen species was N_2 so

238 that nitrogen simply acted as a diluent of the other gas species. Carbon existed as CO_2 and as

239 CO_3^{2-} groups.

240 The solution behavior of reduced carbon-bearing species has been developed with the aid of

241 the simple expressions based on the interpretation of ^{13}C MAS NMR spectra of quenched silicate

242 melt-COH (e. g., Mysen et al., 2011);

243

244 $2CH_4 + O^{2-} \Leftrightarrow 2CH_3^- + H_2O,$ (4)

245

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

247

248 $2NH_3 + O^{2-} \Leftrightarrow 2NH_2^- + H_2O.$ (5)

249

250   In equations (4) and (5), O^{2-} represents oxygen in the silicate structural network. It is linked to

251   silicate speciation via the expression,

252

253    $$2Q^n + O^{2-} \Leftrightarrow 2Q^{n-1},\qquad\qquad(6)$$

254

255   where Q^n and Q^{n-1} denote silicate species with, respectively *n* and *n-1* bridging oxygen, and,

256   therefore, *4-n* and *3-n* nonbridging oxygen.

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

258

259    $$2CH_4 + 4Q^n \Leftrightarrow 2Q^{n-1}(CH_3) + 2Q^{n-1}(OH),\qquad\qquad(7)$$

260

261   which describes the relations between dissolved CH_3groups and the silicate structure. From the

262   carbon-13 MAS NMR and Raman spectroscopic data of quenched melts, Mysen et al., (2011)

263   concluded that CH_3 groups thus formed substitute for oxygen in the silicate tetrahedra because

264   there was evidence of CH_3 and CH_4 groups, but no evidence for Si-O-C bonding environments.

265   Therefore, $2Q^{n-1}(CH_3)$ and $2Q^{n-1}(OH)$ denote depolymerized silicate tetrahedra with at least one

266   of the oxygens replaced by CH_3 and OH groups, respectively. This interpretation is also

267   consistent with the assignment of the Raman band near 600 cm^{-1}(Fig. 2).

13

268   For reduced nitrogen-bearing components, by combining equations (5) and (6), we have;

269

270    $2NH_3 + 4Q^n \Leftrightarrow 2Q^{n-1}(NH_2) + 2Q^{n-1}(OH).$ (8)

271

272   The Si-NH_2 interpretation relies on the assignment of the ~800 cm^{-1} band in Fig. 2 to be an NH_2

273   bending mode (Nakamoto, 1997). In other words, the exchange of NH_2 groups for oxygen in

274   silicate tetrahedra cleaves oxygen bridges to form Si-NH_2 and Si-OH bonds, which results in

275   silicate depolymerization.

276   There is also the equilibrium between molecular H_2O and OH^- groups that describes a

277   principal solution mechanism of H_2O in melts (e.g., Stolper, 1982);

278

279    $H_2O + O^{2-} \Leftrightarrow 2OH^-.$ (9)

280

281   Equation (9) combined with equation (6), yields the equilibria involving silicate (Q-species)

282   H_2O, and OH groups;

283

284    $H_2O + 4Q^n \Leftrightarrow 4Q^{n-1}(OH).$ (10)

285

14

286   By combining equations (7) and (8), the solution equilibrium among COHN species in

287   silicate fluids (and probably melts) under reducing conditions becomes;

288

289    $CH_4 + NH_3 + 4Q^n \Leftrightarrow Q^{n-1}(CH_3) + Q^{n-1}(NH_2) + 2Q^{n-1}(OH).$ (11)
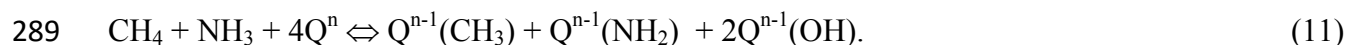
290

291   Equation (11) does not take into account interaction of H_2 with the silicate network. Such

292   interaction, through formation of Si-H and Si-OH bonds, is possible via a schematic formulation

293   such as (Van der Steen and Van den Boom, 1977);

294

295    $Si\text{-}O\text{-}Si + H_2 \Leftrightarrow Si\text{-}OH + Si\text{-}H.$ (12)

296

297   Si-H stretch vibrations would result in Raman bands in the 2100-2200 cm^{-1} region (Schmidt et

298   al., 1998) in addition to the OH fundamental stretch vibrations giving rise to the 3500-3600 cm^{-1}

299   envelope. The former frequency is within the frequency range of 2nd-order Raman scattering of

300   diamonds from the diamond cell, whereas the OH vibrations yield the same signal as OH

301   vibrations from the other H_2O in the system. Whether or not there are contributions from Si-H

302   and Si-OH from eqn. (12) cannot, therefore, be ascertained. Given this lack of information,

303   further speculation and adjustments to eqn. (11) does not seem justified.

304   The equilibrium among silicate melt and COHN volatiles under reducing conditions differs

305   significantly from that under oxidizing conditions where nitrogen simply dissolves as molecular

306   N_2 and acts as a diluent (Mysen, 2018). The H_2O equilibrium remains same, and molecular CO_2

307   is in equilibrium with carbonate groups, CO_3^{2-} (Morizet et al., 2015);

308

309     $CO_2 + O^{2-} \Leftrightarrow CO_3^{2-}$,   (13)

310

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

312

313     $CO_2 + H_2O + N_2 + 4Q^{n-1} \Leftrightarrow 2CO_3^{2-} + 2Q^{n-1}(OH) + N_2 + 2Q^n$.   (14)

314

315   Here, nitrogen as N_2 is shown on both sides of the equation simply to indicate that it behaves as

316   an inert component. It follows that under oxidizing conditions even in the presence of H_2O, in

317   silicate-COHN systems CO_2 dissolves to form CO_3^{2-}, which results in silicate polymerization.

318   The proportion of molecular and structurally bound species such as discussed above can be

319   determined from the Raman spectra with the assumption that for a specific vibration (e.g.,

320   stretching or bending etc.), the Raman cross sections are the same for vibrations in the molecule

321   and structurally bound functional groups (CH_4/CH_3 and NH_3/NH_2) and that the C-H and N-H

322   vibrations in these groups are localized thus not being significantly affected by the neighboring

323   electronic environments. Ratios of integrated Raman intensity ratios from a given type of

324   vibration in the two species then equals their abundance ratio. For X_{CH3}/X_{CH4} [eqn (4)], for

325   example, this intensity ratio is that of the C-H stretch vibrations near 2900 cm^{-1} (2895 and 2910

326   cm^{-1});

327

328   $X_{CH3}/X_{CH4} = A_{2895}/A_{2910}.$ (15)

329

330   In spectra of fluids, the X_{CH3}/X_{CH4} ratio increases with increasing temperature (Fig. 8), from

331   which an enthalpy of 8.1±2.3 kJ/mol can be extracted. In other words, in COHN fluids in

332   equilibrium with aluminosilicate melts, equation (4) shifts to the right with increasing

333   temperature. The spectra of melts are insufficiently resolved to extract such information.

334   The X_{NH2}/X_{NH3} in fluid was calculated from a similar treatment of the Raman data (Fig. 9).

335   Two sets of X_{NH2}/X_{NH3} data were extracted from the spectra of fluid from bands assigned to NH_2

336   and NH_3 bending motions in the low-frequency region and from those assigned to N-H stretching

337   in NH_3 and NH_2 near 3300 cm^{-1} (Fig. 2A). These slopes result in ΔH-values of -4.9±1.9 and -

338   6.2±2.2 kJ/mol. We note here that the temperature evolution of the X_{NH2}/X_{NH3} abundance ratio is

339   opposite of X_{CH3}/X_{CH4}. In other words, whereas equation (4) shifts to the right with temperature

340   thus enhancing the abundance of molecular CH_4, equation (5) shifts to the left so that molecular

341   NH_3 becomes increasingly abundant. Interestingly, under oxidizing conditions, the CO_2/CO_3

342   equilibrium [eqn. (13)] also shifts toward increasing abundance of molecular CO_2 with

343   increasing temperature (Nowak et al., 2003).

344

345   *Fluid/melt partitioning*

346   <u>Water.</u> The partition coefficient for H_2O between fluid and melt, when calculated from integrated

347   intensity of the 3600 cm^{-1} band (O-H stretching) in coexisting fluids and melts, is a non-linear

348   function of 1/T and less than unity (Fig. 10). This behavior contrasts with the H_2O partitioning in

349   silicate-COHN under oxidizing conditions where $K^{fluid/melt}_{H2O}$ >1 and is a linear function of 1/T

350   (Mysen, 2018). This difference likely is because under reducing conditions TiO_2 from the redox

351   reaction (1) dissolves in significant amounts in melts (but not in fluid), which results in the very

352   broad and asymmetric 3600 cm^{-1} band (Figs. 1 and 10). The TiO_2 concentration in the melt likely

353   changes with temperature and pressure. This results in a non-linear temperature-dependent

354     $K^{fluid/melt}_{H2O}$.

355

356   <u>Methane</u>. The partition coefficients for methane between coexisting fluid and melt are expressed

357   in terms as, $\Sigma C = CH_3 + CH_4$ (Fig. 11) because separate contributions from CH_4 and CH_3 cannot

358   be quantified from the spectra of melt. Methane partitions into fluid relative to melt. The

359   partition coefficients for the $CH_3 + CH_4$ components are not necessarily the same as total carbon

360   because of the suggested CO groups in the highest-temperature fluids (Fig. 3). However, given

361   the lack of relevant Raman signals in spectra of melts as well as in the low-temperature fluid

362   spectra, contributions from such carbon was not considered. This also means that the $K_{\Sigma C}^{fluid/melt}$-

363   values (Fig. 11) may be minimum values.

364   The partition coefficient decreases with increasing temperature (and pressure), which results

365   in ΔH= - 13.4±2.3 kJ/mol by assuming no pressure effect. This value compares with a ΔH-value

366   of -19±2.9 for the fluid/melt partition coefficient with the same bulk silicate, but without

367   nitrogen in the system (Mysen, 2015). The offset between the two data sets likely reflects the

368   different pressure/temperature paths in the two experimental series as well as the absence of

369   nitrogen species in fluids and melts in the silicate-COH system by Mysen (2015).

370

371   Ammonia. Qualitatively, the fluid/melt partition coefficient for total reduced nitrogen ($\Sigma N =$

372   NH_3+NH_2) decreases with increasing temperature. This behavior is similar to the temperature-

373   ·dependent $K_{\Sigma C}^{fluid/melt}$ (Figs. 11 and 12). The enthalpy value extracted from the temperature-

374   dependence with the assumption of no detectable pressure dependence is -5.9±0.9 kJ/mol.

375

376   Hydrogen. The H_2 fluid/melt partition coefficient ranges between ~6 and ~10 in the temperature

377   and pressure range examined (Fig. 13). There is a slight decrease with increasing temperature

378   and pressure, but the data scatter is significant thus leading to an enthalpy value with large

379   uncertainty, -8±6 kJ/mol.

380

381   **Implications**

382   Reduction of carbon and nitrogen in silicate-COHN melts at high temperature and pressure

383   occurs under conditions near and more reducing those defined by the MW+H_2O buffer (Mysen et

384   al., 2008, 2011). Under such conditions the dominant fluid species are H_2O, H_2, NH_3, and CH_4.

385   That behavior differs from oxidizing conditions where H_2O, N_2 and CO_2 are the principal

386   species. and where CO_2 may be in equilibrium with CO_3^{2-} and HCO_3^- groups, or both.

387   A change in redox conditions sufficient to alter oxidized to reduced carbon- and nitrogen-

388   bearing species during melting and crystallization in the Earth will affect all melt properties that

389   depend on melt polymerization [see solution mechanisms illustrated with equations (9) and (12)].

390   Examples of such melt properties are viscosity, diffusion, and density (Baker et al., 2005;

391   Behrens, 2010; Seifert et al., 2013). Crystal/melt element partitioning also is linked to melt

392   polymerization (Jaeger and Drake, 2000) and, therefore, the redox conditions during melting and

393   crystallization in the presence of COHN fluids. Melt polymerization is also linked to activity of

394   silicate, which means a change in redox conditions will lead to a change in melting and

395   crystallization phase relations (Moretti and Papale, 2004). This latter feature sometimes is termed

396   redox melting.

397

398   **Acknowledgments**

400

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555

556   Table 1. Temperature/pressure conditions of experiments
557
558

Temperature, ˚C	Pressure, MPa
25	0.1
525	634
600	594
675	554
750	1011
825	1414

558   Temperature, ˚C   Pressure, MPa
559   25   0.1
560   525   634
561   600   594
562   675   554
563   750   1011
564   825   1414
565
566

567   **Figure Captions**

568   Figure 1 - Example of Raman spectra of coexisting melt and fluid at 525°C/634 MPa in the entire

569   spectral range studied. Intensity is normalized to cts/s. Band assignments are discussed in the

570   text. The frequency ranges marked A, B, C, and D show ranges that are expanded in subsequent

571   figures (and discussed in the text) to show better the spectral evolution.

572   Figure 2 - Raman spectra of coexisting fluid (A) and melt (B) in the frequency regime A (see

573   Fig. 1) as a function of temperature as seen on individual spectra and pressure as shown in Table

574   1. Band assignments are discussed in the text.

575   Figure 3 - Raman spectra of coexisting fluid (A) and melt (B) in the frequency regime B (see

576   Fig. 1) as a function of temperature as seen on individual spectra and pressure as shown in Table

577   1. Band assignments are discussed in the text.

578   Figure 4 - Raman spectra of coexisting fluid (A) and melt (B) in the frequency regime C (see

579   Fig. 1) as a function of temperature as seen on individual spectra and pressure as shown in Table

580   1. Band assignments are discussed in the text.

581   Figure 5 - Example of curve-fitted Raman spectrum of fluid in frequency regime C near 2900

582   cm^{-1} recorded at 825°C/1414 MPa.

583   Figure 6 - Example of curve-fitted Raman spectrum of fluid in frequency regime C near 3300

584   cm^{-1} recorded at 600°C/594 MPa.

585   Figure 7 - Raman spectra of coexisting fluid (A) and melt (B) in the frequency regime D (see

586   Fig. 1) as a function of temperature as seen on individual spectra and pressure as shown in Table

587   1. Band assignments are discussed in the text.

588   Fig. 8 - Evolution of abundance ratio, CH_3/CH_4, in fluid as a function of temperature from fits to

589   the 2900 cm^{-1} region (see Table 1 for corresponding pressures). The straight line fit is described

590   with the expression, $\log(CH_3/CH_4) = -977\pm276/T(K)+0.5\pm0.3$, $r^2=0.81$.

591   Fig. 9 - Evolution of abundance ratio, NH_2/NH_3, in fluid as a function of temperature from fits

592   NHN stretching region between 3300 and 3200cm^{-1} and NHN bending region between 600 and

593   1000 cm^{-1} (see Table 1 for corresponding pressures). The straight line fits are described with the

594   expressions: For NHN stretching $\log(NH_2/NH_3) = 595\pm230/T(K)-1.1\pm1.2$, $r^2=0.69$, NHN

595   bending $\log(NH_2/NH_3) = 744\pm265/T(K)-1.2\pm0.3$, $r^2=0.72$.

596   Fig. 10 - Fluid/melt partition coefficient for H_2O as a function of temperature (closed circles)

597   compared with results under oxidizing conditions

598   Fig. 11 - Fluid/melt partition coefficient for total carbon, $\sum C$, under reducing conditions

599   ($K^{fluid/melt} = 1617\pm281/T-0.6\pm0.3$, $r^2=0.92$), under reducing conditions in silicate-COH ($K^{fluid/melt}$

600    $= 2283\pm347/T-2.6\pm0.4$, $r^2=0.94$) (open circles; Mysen, 2015), and under oxidizing conditions in

601   silicate-COH ($K^{fluid/melt} = -3628\pm1630/T+3.3\pm1.6$, $r^2=0.71$) (open diamonds; Mysen, 2015).

602   Fig. 12 - Fluid/melt partition coefficient for total nitrogen, $\sum N$, under reducing conditions

603   ($K^{fluid/melt} =709\pm111+0.2\pm0.1$, $r^2=0.93$).

604   Fig. 13 - Fluid/melt partition coefficient for H_2 under reducing conditions ($K^{fluid/melt} = 1007\pm815-$
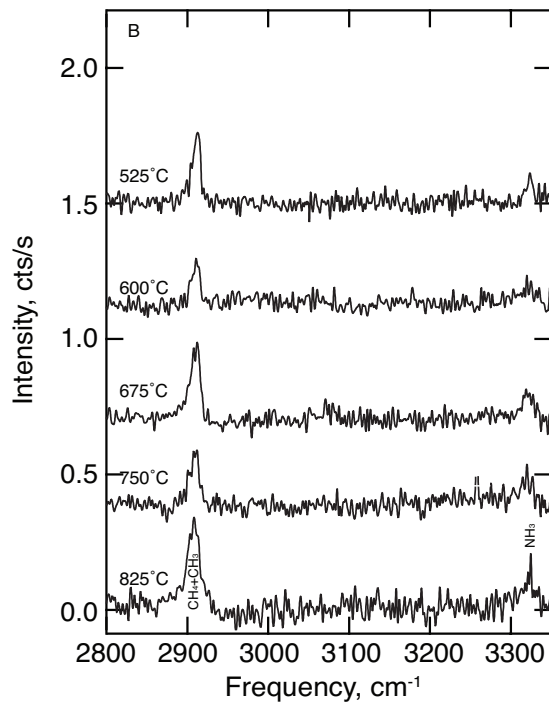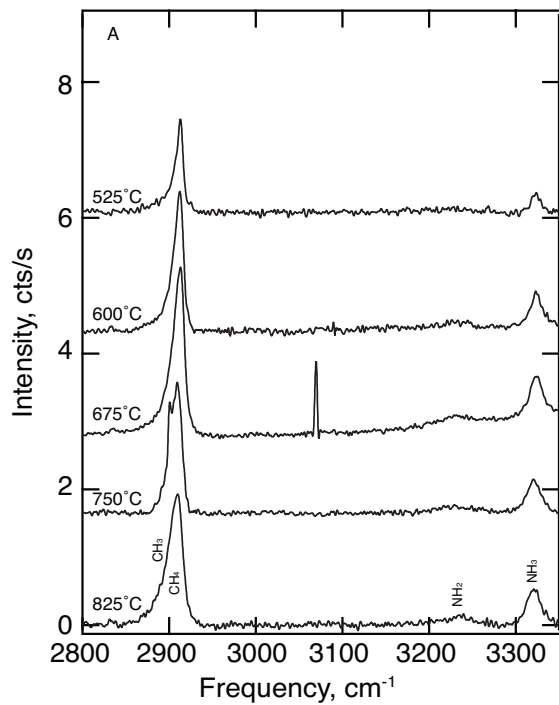
605   0.1 ± 0.8, $r^2=0.34$).
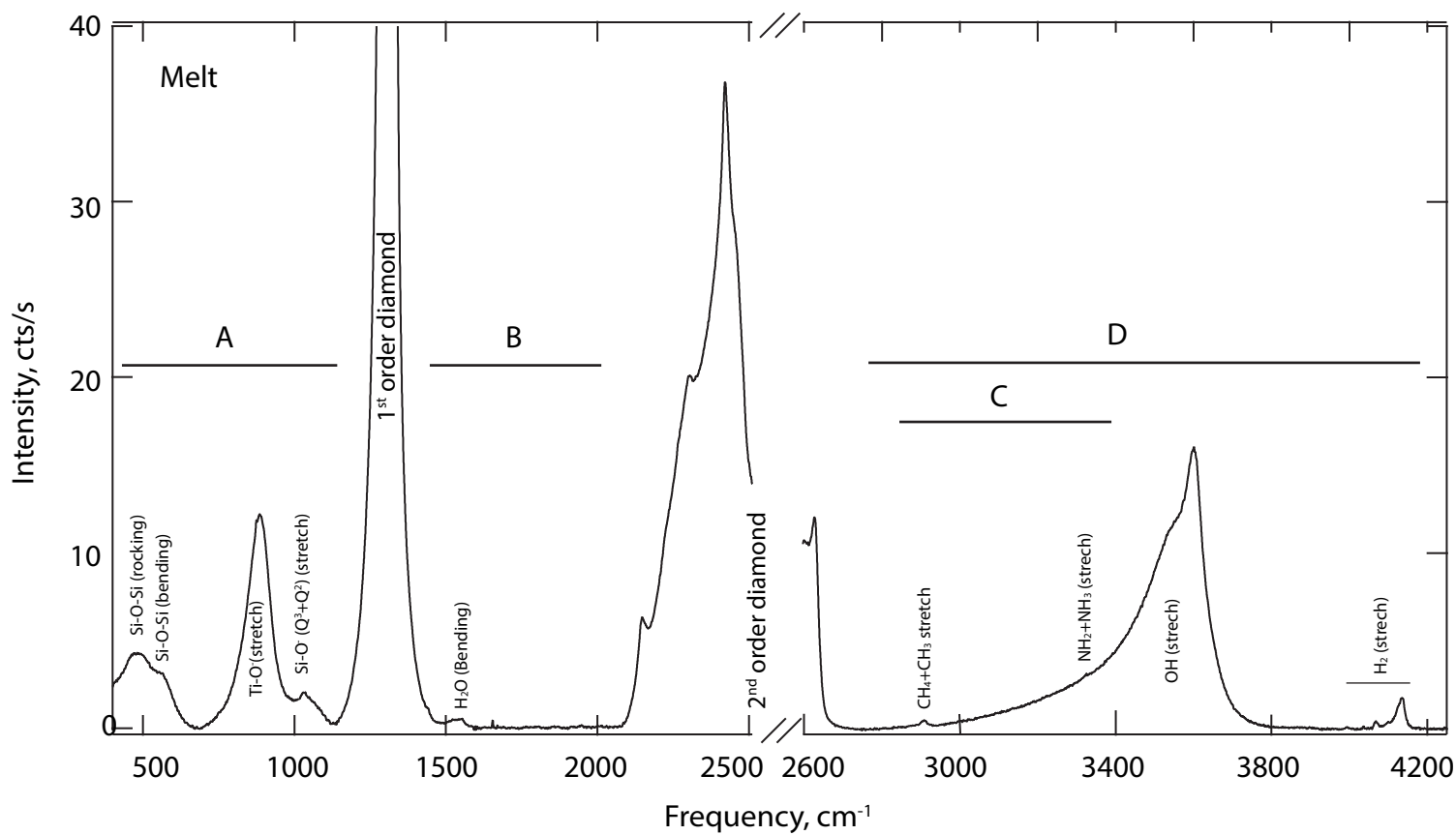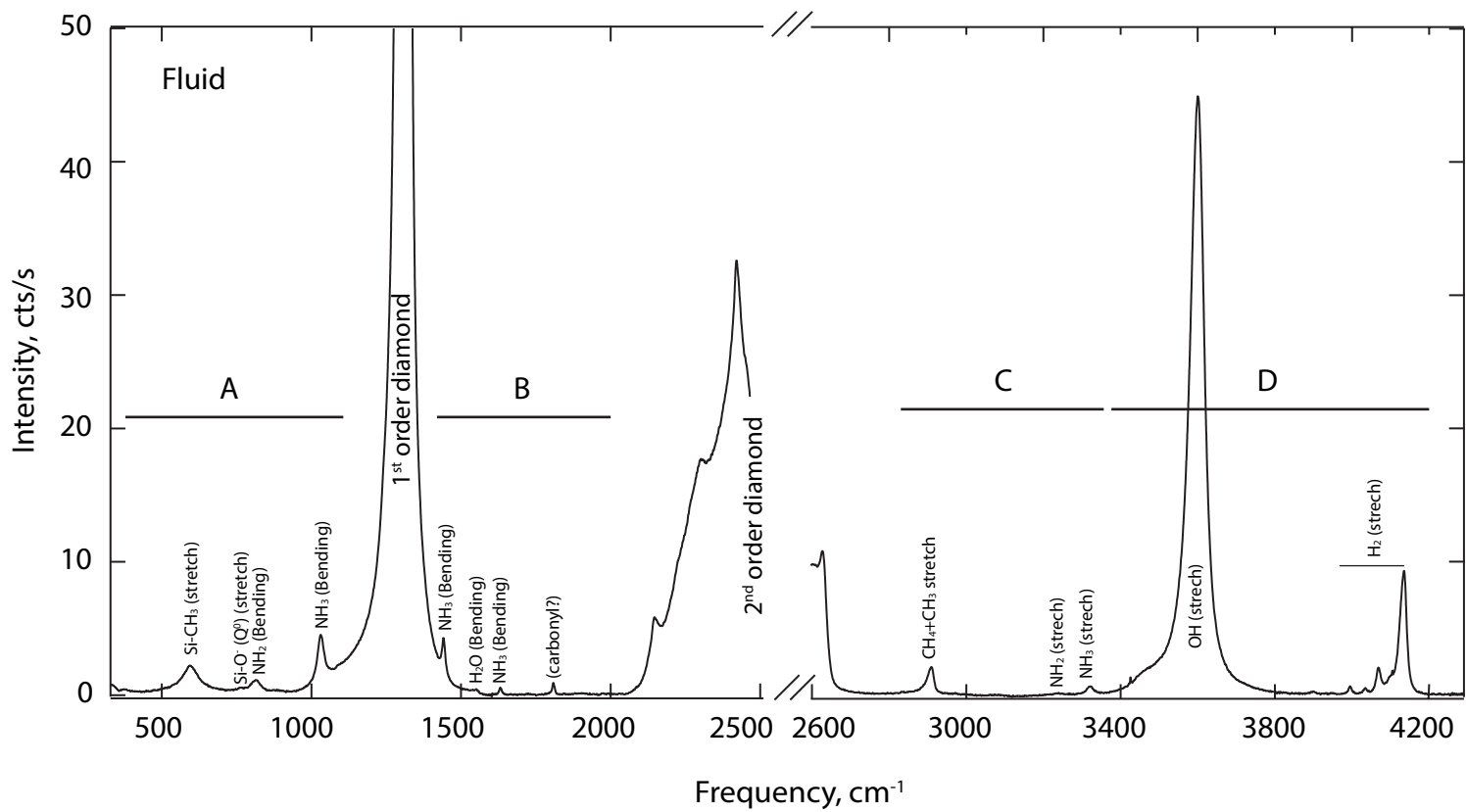
Figure 1
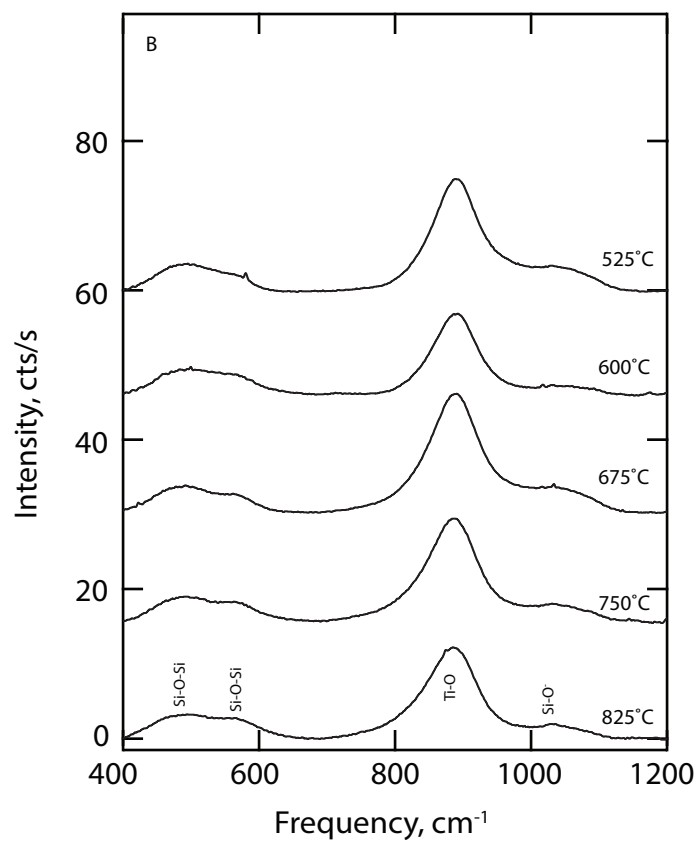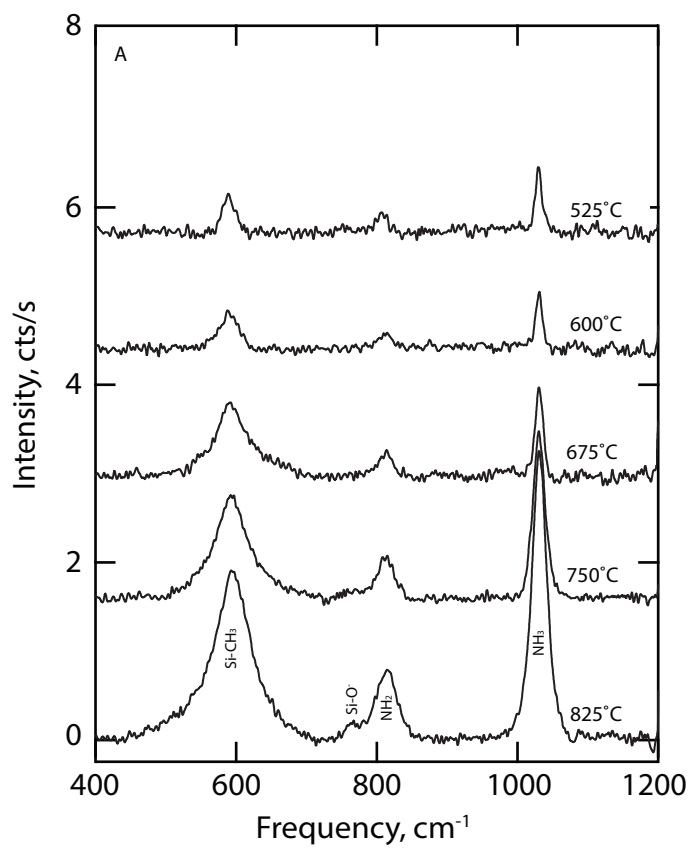
Figure 2

Figure 3
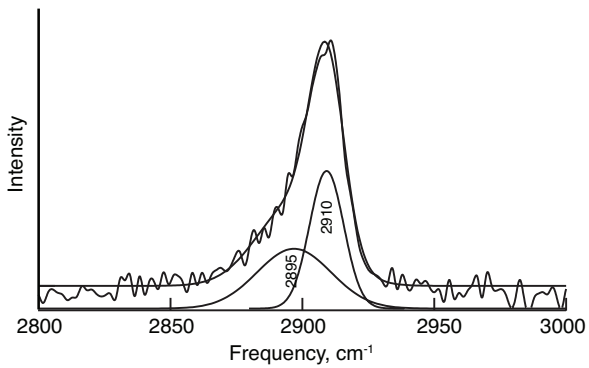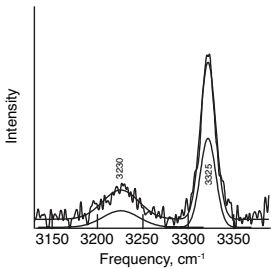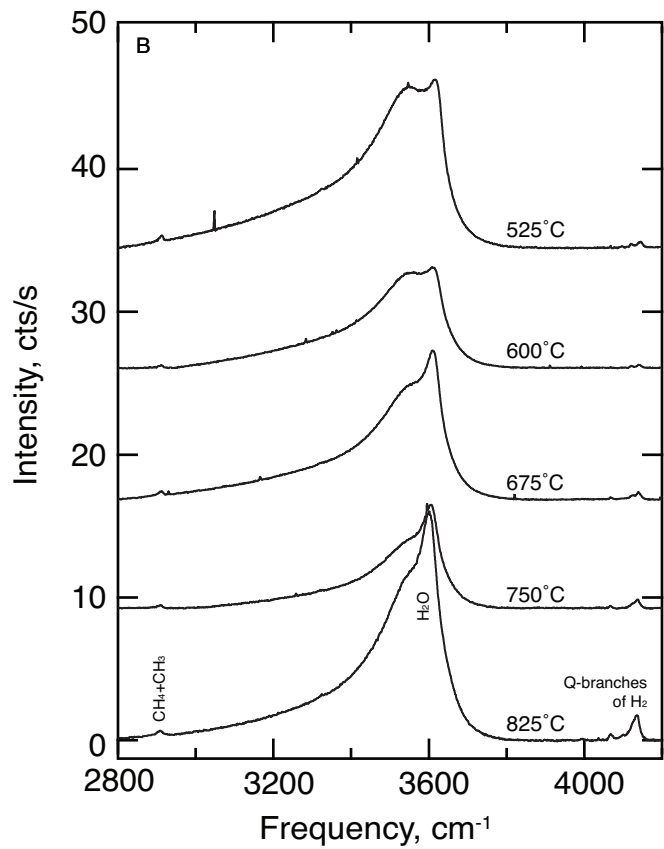
Figure 4

Intensity

2895
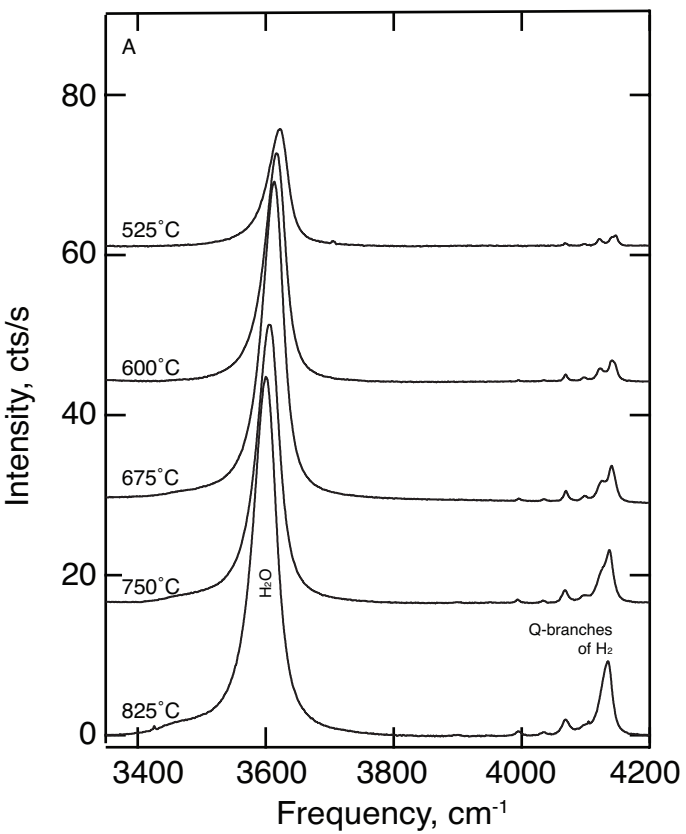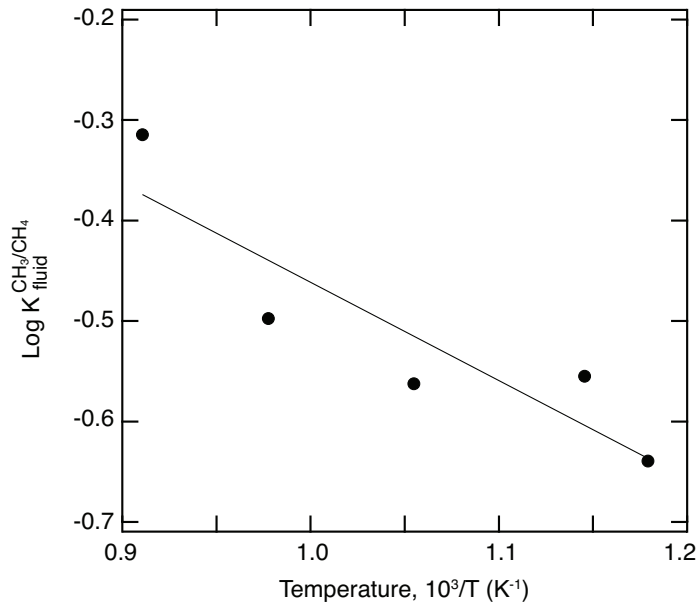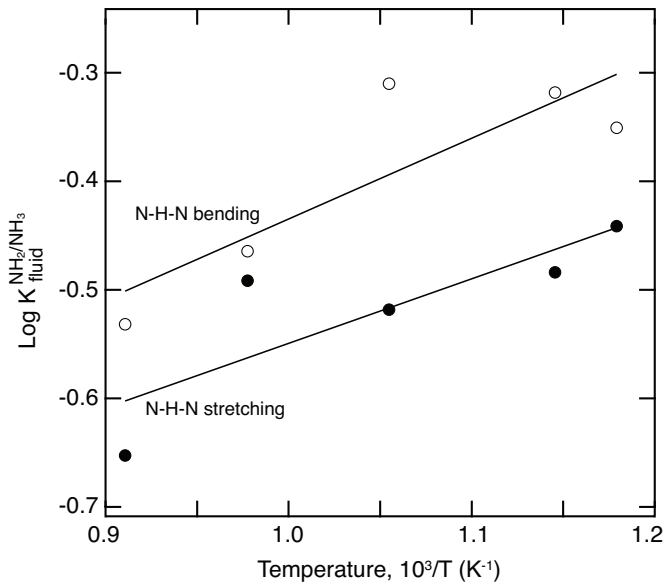
2910

Frequency, cm⁻¹

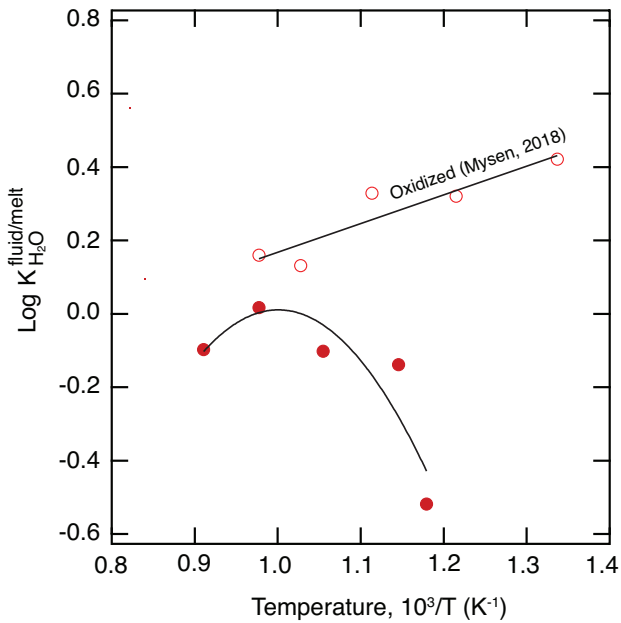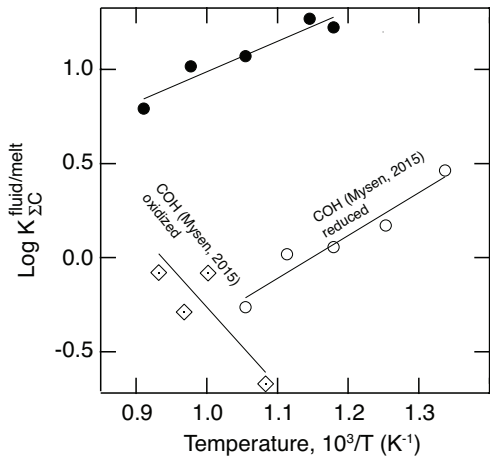2800   2850   2900   2950   3000
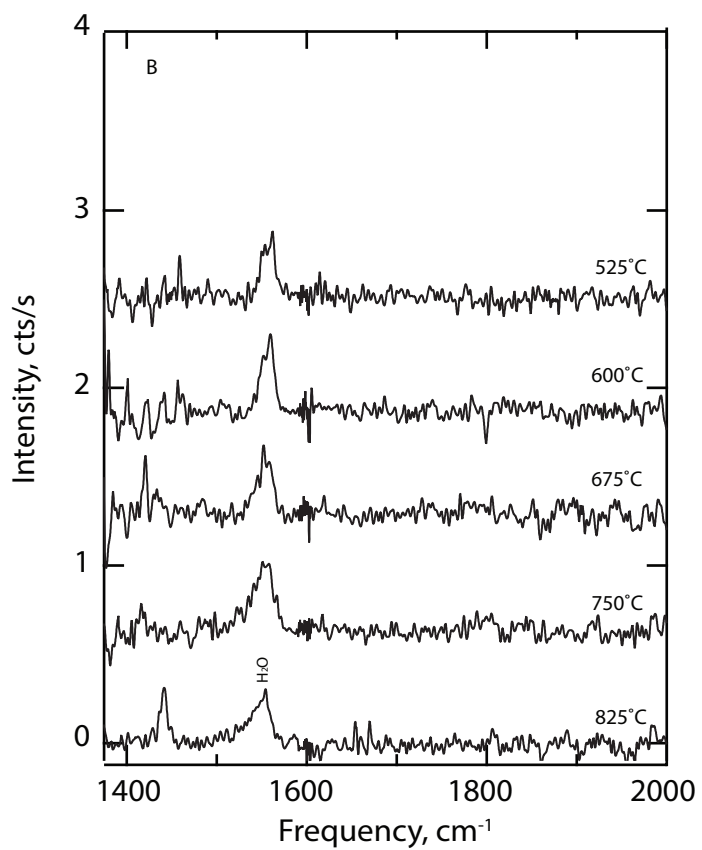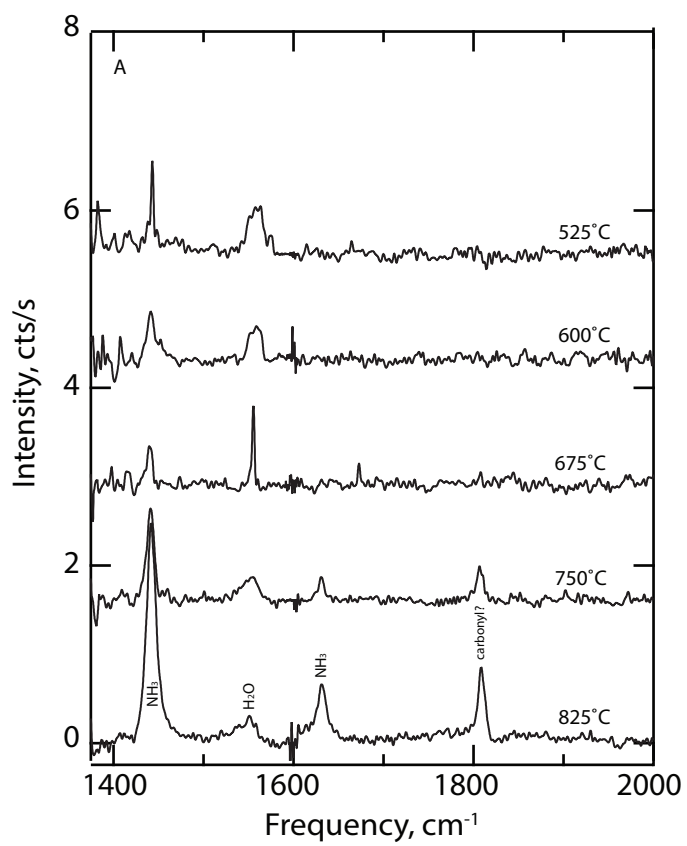
Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13