Aluminum speciation in aqueous fluids at deep crustal pressure and temperature

Mainak Mookherjee a,*, Hans Keppler b, Craig E. Manning c

a Department of Earth and Atmospheric Sciences, Cornell University, Ithaca, NY 14853, USA
b Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany
c Department of Earth and Space Sciences, University of California Los Angeles, Los Angeles, CA 90095-1567, USA

Received 10 September 2013; accepted in revised form 6 February 2014; Available online 1 March 2014

Abstract

We investigated aluminum speciation in aqueous fluids in equilibrium with corundum using in situ Raman spectroscopy in hydrothermal diamond anvil cells to 20 kbar and 1000 °C. We have studied aluminum species in (a) pure H2O, (b) 5.3 m KOH solution, and (c) 1 m KOH solution. In order to better understand the spectral features of the aqueous fluids, we used ab initio simulations based on density functional theory to calculate and predict the energetics and vibrational spectra for various aluminum species that are likely to be present in aqueous solutions. The Raman spectra of pure water in equilibrium with Al2O3 are devoid of any characteristic spectral features. In contrast, aqueous fluids with 5.3 m and 1 m KOH solution in equilibrium with Al2O3 show a sharp band at ~620 cm⁻¹ which could be attributed to the [Al(OH)4]³⁻ species. The band grows in intensity with temperature along an isochore. A shoulder on the high-frequency side of this band may be due to a hydrated, charge neutral Al(OH)3H2O species. In the limited pressure, temperature and density explored in the present study, we do not find any evidence for the polymerization of the [Al(OH)4]³⁻ species to dimers [(OH)2-Al-(OH)2-Al(OH)2] or [(OH)3-Al-O-Al(OH)3]²⁻. This is likely due to the relatively low concentration of Al in the solutions and does not rule out significant polymerization at higher pressures and temperatures. Upon cooling of Al-bearing solutions to room temperatures, Raman bands indicating the precipitation of diaspore (AlOOH) were observed in some experiments. The Raman spectra of the KOH solutions (with or without dissolved alumina) showed a sharp OH stretching band at ~3614 cm⁻¹ and an in-plane OH bending vibration at ~1068 cm⁻¹, likely related to an OH⁻ ion with the oxygen atom attached to a water molecule by hydrogen bonding. A weak feature at ~935 cm⁻¹ may be related to the out-of-plane bending vibration of the same species or to an OH species with a different environment.

1. INTRODUCTION

Alumina is the second most abundant oxide in most crustal rocks, but its behavior in crustal metamorphic fluids has long been uncertain. While SiO2 is quite soluble in H2O at metamorphic conditions (e.g., Wasserburg, 1958; Anderson and Burnham, 1967; Manning, 1994; Zotov and Keppler, 2002; Newton and Manning, 2002, 2003), Al2O3 is dramatically less so (Ragnarsdottir and Walther, 1985; Walther, 1997; Tropper and Manning, 2007). This makes it difficult to explain the common occurrence of quartz with aluminous minerals such as Al2SiO5 polymorphs in metamorphic veins (e.g., Kerrick, 1990). One possible explanation is the amphoteric nature of alumina, which leads to enhanced Al solubility in acidic and alkaline solutions (Barns et al., 1963; Azaroual et al., 1996; Wohlers and Manning, 2009). Another possible explanation is Al complexing with other components of the fluid such as salts.

http://dx.doi.org/10.1016/j.gca.2014.02.016
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(Anderson and Burnham, 1967, 1983; Korzhinskiy, 1987; Sanjuan and Michael, 1987; Pascal and Anderson, 1989; Pokrovskii and Helgeson, 1995, 1997; Azaroual et al., 1996; Diakonov et al., 1996; Tagirov and Schott, 2001; Walther, 2001; Newton and Manning, 2006) or silica (Pokrovskii et al., 1996; Salvi et al., 1998; Manning, 2007).

One limitation preventing better understanding of the aqueous geochemistry of aluminum at high pressures and temperatures is fundamental uncertainty about the stabilities of various possible species. For example, it is debated whether the dominant aluminate species in alkaline solutions is $[\text{Al(OH)}_4]^{\text{3}}^1$, $\text{NaAl(OH)}_4$, or $\text{KAl(OH)}_4$ (e.g., Anderson, 1995; Azaroual et al., 1996; Tagirov and Schott, 2001). In addition, it is unknown whether dissolved alumina can exist at metamorphic conditions as polymeric species. While the polymerization of silica observed at low pressure and temperature (e.g., Iler, 1979) has now been inferred to occur in metamorphic conditions as well (Zotov and Keppler, 2000, 2002; Newton and Manning, 2002), the analogous search for the large, polymerized aqueous aluminum hydroxide clusters common at surficial conditions (e.g., Casey, 2005; Casey and Rustad, 2007) has not been conducted.

To gain insight into aluminum species identities and possible polymerization at high pressure and temperature conditions, we conducted in situ Raman spectroscopy on aluminum-bearing solutions in hydrothermal diamond anvil cells. We carried out distinct sets of experiments by varying the chemistry and density of the aqueous fluids. The results provide new constraints on the stabilities of aluminate species at high temperature and pressure.

2. METHODS

2.1. Hydrothermal diamond anvil cell

Experiments were carried out with an externally heated Bassett-type diamond anvil cell (Bassett et al., 1993a,b; Bassett, 2003). The cell consisted of two low-fluorescence type I diamonds of 0.21 carat with 1 mm culet faces cut parallel to (100). Corrosion resistant iridium gaskets (Zotov and Keppler, 2000, 2002) with 250 µm initial thickness and 400 µm hole were used to contain the sample. Rhenium gaskets were avoided, since at high pressures and temperatures traces of rhenium dissolve into the fluid causing strong fluorescence (Zotov and Keppler, 2002). The cell was heated by coils of molybdenum wire around the tungsten carbide seats supporting the diamonds. Temperature was measured with two K-type thermocouples attached to the diamonds. The power of the upper and the lower heaters were controlled separately. This allowed the temperature of each diamond to be kept constant to ±5 °C during the heating and cooling cycles. A temperature calibration was carried out by visual observation of the melting point of NaCl inside the diamond cell. During operation, the cell was flushed with an argon (98%)-hydrogen (2%) mixture to prevent the oxidation of the diamonds and the molybdenum heaters. The maximum temperatures in the present set of experiments were limited to 1000 °C (Table 1).

The sample chamber was loaded with 1–2 pieces of synthetic corundum of high purity. The pressure was determined from the observed homogenization temperature ($T_H$) of the vapour bubble together with the equation of state of water (Saul and Wagner, 1989). The pressure determination is based on the assumption that the sample chamber behaves as an isochoric system and that the equation of state of the fluid is similar to that of pure water (Bassett et al., 1993b). While the latter assumption is certainly valid for the Al$_2$O$_3$–H$_2$O system, systematic deviations from the equation of state are possible for the KOH solutions and uncertainties in estimated pressures may reach 10–20%. Moreover, in the KOH-bearing systems, alumina solubility at high temperature is so large that precipitation of AlOOH may occur upon cooling (see below). This precluded repeated pressure–temperature cycling of the cell before the Raman measurement, so that significant deformation of the sample occurred.

<table>
<thead>
<tr>
<th>Exp name #</th>
<th>Chemical System</th>
<th>Cell used</th>
<th>Heating $T_H$ (°C)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>Cooling $T_H$ (°C)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$T_{\text{max}}$ (°C)</th>
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<tr>
<td>H</td>
<td>Pure H$_2$O</td>
<td>HDAC-2</td>
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<td>0.99</td>
<td>177.0</td>
<td>0.89</td>
<td>809.0</td>
</tr>
<tr>
<td>KH5</td>
<td>5.3 m KOH</td>
<td>HDAC-2</td>
<td>40.0</td>
<td>0.99</td>
<td>370.0</td>
<td>0.45</td>
<td>812.7</td>
</tr>
<tr>
<td>ALH-I</td>
<td>Al$_2$O$_3$ + pure H$_2$O</td>
<td>HDAC-3</td>
<td>–</td>
<td>1.09</td>
<td>–</td>
<td>1.09</td>
<td>718.4</td>
</tr>
<tr>
<td>ALH-II</td>
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<td>HDAC-3</td>
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<td>1.08$^1$</td>
<td>300.0</td>
<td>0.71</td>
<td>1000.0</td>
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<tr>
<td>ALKHK5-I$^1$</td>
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<td>237.0</td>
<td>0.79</td>
<td>–</td>
<td>–</td>
<td>801.5</td>
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<td>HDAC-3</td>
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<td>230.0</td>
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<td>HDAC-3</td>
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<td>1.01</td>
<td>–</td>
<td>–</td>
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<tr>
<td>ALKHK5-IV$^2$</td>
<td>Al$_2$O$_3$ + 5.3 m KOH</td>
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<td>1.00</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>ALKHI-II$^1$</td>
<td>Al$_2$O$_3$ + 1 m KOH</td>
<td>HDAC-2</td>
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<tr>
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<td>HDAC-2</td>
<td>–</td>
<td>1.24</td>
<td>–</td>
<td>–</td>
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<tr>
<td>ALKHI-IV$^3$</td>
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<td>HDAC-3</td>
<td>25.0</td>
<td>1.00</td>
<td>250.0</td>
<td>0.79</td>
<td>714.4</td>
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</tbody>
</table>

$\rho$ are equivalent densities for pure water as determined from the observed homogenization temperatures; the actual densities of the KOH solutions are higher.

$^1$ Data were not collected during cooling path, either due to leak, gasket collapse, or dissolution of crystal.

$^2$ Initial density is based on ruby fluorescence at ambient condition.

$^3$ Trouble with heater and thermocouple wires.
the cell may have occurred during heating, as indicated by major changes in homogenization temperature after the experiment. In such cases, measurements were carried out during the cooling path and it was assumed that the cell had remained isochoric during cooling (i.e., all deformation had happened during heating). For the experiments with initial fluid density >1 g/cm³, i.e., without a vapor bubble at room temperature conditions, the initial density is determined by comparing the shifts in the fluorescence spectra of a ruby chip at ambient condition and the piece of corundum within the HDAC. The initial density is calculated by converting the $D_m$ to pressure based on existing calibration on variation of ruby fluorescence under compression (Mao et al., 1986). The estimated error in the determination of the pressure is of the order of ±1.0 kbar (Wei et al., 2011) and the resulting error in the estimation of the fluid density is of the order of ±0.3 g/cm³.

### 2.2. In-situ Raman spectroscopy

Raman spectra were collected with a Horiba Jobin-Yvon Labram HR 800 UV spectrometer using the 514 nm line of an argon laser at 2 Watt output power for excitation. The spectrometer was equipped with a 1800 gr/mm grating and a Peltier-cooled CCD detector. Measurements were made in backscattering geometry with an Olympus microscope using an objective SLMP LAN N 50/0.35 (numerical aperture = 0.35) in conjunction with confocal optics. In order to obtain a reasonable signal to noise ratio, the measuring times were relatively long (2 accumulations of 60 s per

<table>
<thead>
<tr>
<th>Species</th>
<th>Energy (a.u.)</th>
<th>Frequency [activity] [cm⁻¹ (A²/AMU)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-399</td>
<td>400-499</td>
</tr>
<tr>
<td>(OH)⁺⁻</td>
<td>-75.80</td>
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</tr>
<tr>
<td>H₂O</td>
<td>-76.43</td>
<td></td>
</tr>
<tr>
<td>H₂O-OH⁺⁻</td>
<td>-152.29</td>
<td>197.1 (1.3)</td>
</tr>
<tr>
<td>Al-≈-H₂O</td>
<td>-700.82</td>
<td>347.8 (0.6)</td>
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<tr>
<td>Al(OH)₃</td>
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<td>215.9 (1.1)</td>
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<tr>
<td>Al(OH)₂·H₂O</td>
<td>-546.57</td>
<td>209.1 (1.3)</td>
</tr>
<tr>
<td>[Al(OH)₄]⁻</td>
<td>-546.05</td>
<td>355.3 (1.0)</td>
</tr>
<tr>
<td>K[Al(OH)₄]</td>
<td>-1145.96</td>
<td>244.7 (1.1)</td>
</tr>
<tr>
<td>Al-dimers</td>
<td></td>
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<tr>
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<td>232.7 (1.2)</td>
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<tr>
<td>[(OH)₂-Al(OH)₂-Al(OH)₂]⁻</td>
<td>-940.29</td>
<td>88.94 (1.5)</td>
</tr>
<tr>
<td>Al-trimer</td>
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<td></td>
</tr>
<tr>
<td>[(OH)₂-O-Al-O⁻]⁻</td>
<td>-1408.49</td>
<td>114.5 (1.2)</td>
</tr>
<tr>
<td>[4(OH)₃-Al-O⁻]⁻</td>
<td>223.1 (1.6)</td>
<td>535.4 (1.7)</td>
</tr>
<tr>
<td>244.4 (3.7)</td>
<td>543.8 (1.3)</td>
<td>647.2 (4.0)</td>
</tr>
<tr>
<td>291.4 (1.6)</td>
<td>566.5 (3.3)</td>
<td>651.3 (3.6)</td>
</tr>
<tr>
<td>352.0 (1.8)</td>
<td>577.7 (2.4)</td>
<td>651.3 (3.6)</td>
</tr>
<tr>
<td>373.6 (9.5)</td>
<td>382.2 (3.6)</td>
<td>389.9 (10.4)</td>
</tr>
</tbody>
</table>
spectral window). A confocal aperture of 300 µm was used to limit the sampling volume; spectral resolution was 2.5 cm⁻¹.

The blackbody contribution measured at high temperatures of 800 °C is only few percent of the Raman signal from the solution and is nearly independent of frequency over the spectral window of the present study. Hence, no correction for the black body radiation was made.

The Horiba Jobin-Yvon Labram HR Raman spectrometer has confocal microscopy capabilities; however, the spectra collected often contained minor contributions from diamond fluorescence. This is because the signal collected from the volume of aqueous fluid travels through the upper diamond. We selected diamonds with minimum fluorescence. In order to remove minor features related to diamond fluorescence, we corrected the spectra of the solution by subtracting the spectrum of the upper diamond measured at the same temperature.

2.3. Ab initio simulations

In order to gain insights into the various aluminate species, the geometry optimizations of the species were performed with the Becke’s three-parameter combination of Hartee-Fock and gradient-corrected density functional exchange combined with the non local correlational functional of Lee-Yang-Parr (B3LYP) (Lee et al., 1988; Becke, 1993). The B3LYP hybrid functional has been quite reliable in optimizing the geometry and prediction of vibrational spectrum of the alumino-silicate species (Gale et al., 1998; Tossell, 1999; Mibe et al., 2008). All the calculations were performed using the 6-31G**(d, p), a triple split valence basis sets with polarized p and d orbitals and diffuse functions (**)(Hehre et al., 1986) as implemented in Gaussian 09 (Frisch et al., 2009). We considered several species including

(a) Monomers – (i) Al(H₂O)₆³⁺, where Al³⁺ is surrounded by six water molecule in octahedral configuration, (ii) Al(OH)₃ with a planar trigonal configuration; (iii) Al(OH)₃·H₂O with a distorted tetrahedral arrangement and overall neutral charge, (iv) [Al(OH)₄]⁻ with the Al³⁺ ion in the center of a tetrahedron formed by OH⁻ ions, and (v) K[Al(OH)₄], where a potassium ion is attached to the tetrahedral [Al(OH)₄]⁻ unit, thus rendering it charge neutral.

(b) Dimers and trimers – (vi) [OH₂-Al-O-Al(OH)₃]²⁻ with alumina tetrahedral units sharing a bridging oxygen atom and (vii) [OH₂-Al-O-Al(OH)₃] with edge-sharing alumina tetrahedral units with two fully protonated bridging oxygen atoms; (viii) alumina tetrahedral units forming a cyclic trimer [(–Al(OH)₂-O–)₃, (ix) interaction between H₂O molecules and excess OH⁻ arising due to addition of KOH into the aqueous solution (Table 2, Fig. 1).

All calculations for energetics and vibrational frequency were done in the gas-phase and as a result, the theoretically predicted vibrational frequencies for the gas-phase molecule are often lower than the experimentally observed frequencies (Pople et al., 1993). Hence, for the individual aluminate species, the theoretically predicted vibrational frequencies need to be multiplied with a scaling factor of 1.04 as noted in previous studies on alumino-silicate clusters (Mibe et al., 2008). Hence for instance, our predicted vibrational frequency for K[Al(OH)₄] will be 615 cm⁻¹, i.e., 1.04 × 591 cm⁻¹ (Table 2).

Fig. 1. Raman spectra for aluminum species in aqueous fluids calculated using density functional theory, (a) monomers and (b) dimers and trimers, and H₂O–OH⁻ interactions. Also shown are the optimized geometries of the aluminum species (i) Al³⁺–6H₂O, (ii) Al(OH)₃, (iii) Al(OH)₃·H₂O, (iv) [Al(OH)₄]⁻, (v) K[Al(OH)₄], (vi) [OH₂-Al-O-Al(OH)₃]²⁻, (vii) [OH₂-Al-O-Al(OH)₃] with edge-sharing alumina tetrahedral units with two fully protonated bridging oxygen atoms; (viii) alumina tetrahedral units forming a cyclic trimer [(–Al(OH)₂-O–)₃, (ix) interaction between H₂O molecules and excess OH⁻ arising due to addition of KOH into the aqueous solution (Table 2, Fig. 1).
Fig. 2. Raman spectra of pure H$_2$O and 5.3 m KOH aqueous solution as measured along an isochore: (a) The 100–1200 cm$^{-1}$ region for the pure water is devoid of any vibrational features, (b) the 2800–4000 cm$^{-1}$ region for the pure water is characterized by three distinct bands at 3256 cm$^{-1}$, 3452 cm$^{-1}$, and 3606 cm$^{-1}$. In addition, there are features at 2913 cm$^{-1}$ due to methane produced by interaction of the diamond and water at high temperatures, (c) the 100–1200 cm$^{-1}$ region for the 5.3 m KOH solution contains a feature at 1068 cm$^{-1}$ due to the $\delta$(OH) mode, and (d) the 2800–4000 cm$^{-1}$ region for the 5.3 m KOH solution contains intramolecular water bands at 3348, 3542, and 3564 cm$^{-1}$ and a sharp feature at 3614 cm$^{-1}$ probably related to the stretching vibration of the dissolved OH$^{1-}$ ion.
3. RESULTS

3.1. Blank experiments

Reference Raman spectra of Al-free systems were collected for (i) pure water and (ii) 5.3 m KOH solution. It has been noted that the rhenium gaskets used for hydrothermal diamond anvil cell experiment often reacts with the aqueous fluids (Chellappa et al., 2009). However, we have used iridium gaskets to avoid strong fluorescence (Zotov and Keppler, 2002) and we do not observe features in the Raman spectra that could be attributed to the formation of iridium oxides. Hence, there is no evidence of reaction of the iridium gasket with the aqueous fluid.

Fig. 3. Deconvolution of the 2700 to 4000 cm\(^{-1}\) region of the Raman spectrum of pure H\(_2\)O (a, b) and of 5.3 m KOH solution (c, d). There are three panels, top indicates the residual (pink dots), the middle panel indicates the data (pink crosses), the fit (black line), and the baseline (dashed line) and the lower panel shows the deconvoluted peaks. The bands for pure water occur at (a) 3255 cm\(^{-1}\), 3452 cm\(^{-1}\), and 3606 cm\(^{-1}\) at 42 °C, 0 kbar, and the bands shift to (b) 3266 cm\(^{-1}\), 3517 cm\(^{-1}\), and 3545 cm\(^{-1}\) at 696 °C, 8.6 kbar. We also observe the band at 2914 cm\(^{-1}\) due to methane produced by the interaction of diamond and pure water upon heating. The band may persist even when the hydrothermal diamond anvil cell is cooled. The spectral region of 2800–4000 cm\(^{-1}\) for the 5.3 m KOH aqueous solution, consists of distinct bands at (c) 3023 cm\(^{-1}\), 3304 cm\(^{-1}\), 3497 cm\(^{-1}\), and 3613 cm\(^{-1}\) at 34.5 °C, 0 kbar; upon heating along an isochore (d), the bands shift to 3348 cm\(^{-1}\), 3542 cm\(^{-1}\), 3564 cm\(^{-1}\), and 3625 cm\(^{-1}\) at 812.7 °C, 2.2 kbar system. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
In the blank experiment with pure water, we do see evidence for the interaction of diamond and aqueous fluids at higher temperature with the formation of a band at 2913 cm\(^{-1}\) (Fig. 2b). This is likely related to the presence of methane (CH\(_4\)), as documented by bands at 2918 cm\(^{-1}\) (Chou and Anderson, 2009). The band at 2913 cm\(^{-1}\) is typically observed in the Raman Spectra collected during the cooling (Fig. 2b). However, this band could also be seen for the Raman spectra collected during the heating paths, if the cell was subjected to repeated heating and cooling prior to the Raman measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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The spectral region between 2700 and 4000 cm\(^{-1}\) of pure water near ambient conditions is dominated by the vibrations related to H\(_2\)O and consisted of three distinct bands at 3256 cm\(^{-1}\) (\(2\nu_2\), overtone of bending mode), 3452 cm\(^{-1}\) (\(\nu_1\), symmetric stretch) and 3606 cm\(^{-1}\) (\(\nu_3\), asymmetric stretch) (Fig. 3). These three bands are very similar to the bands previously reported for pure water- 3225 cm\(^{-1}\), 3450 cm\(^{-1}\), and 3630 cm\(^{-1}\) (Walrafen, 1964). At a temperature of \(~696^\circ\text{C}\) and 8.6 kbar, these bands shift to 3265, 3518, and 3544 cm\(^{-1}\), respectively. For the 5.3 m KOH aqueous solution near ambient conditions, the spectral region between 2700 and 4000 cm\(^{-1}\) is characterized by three distinct bands, which occur at 3023 cm\(^{-1}\), 3304 cm\(^{-1}\), and 3497 cm\(^{-1}\) respectively (Fig. 3). In addition, a sharp feature at 3614 cm\(^{-1}\) is also observed for the 5.3 m KOH solution. It is likely due to the excess hydroxyl groups from the dissolved KOH. It could be attributed to a free or “quasifree” (OH\(^-\)) group i.e., a proton that is not hydrogen bonded (Busing and Hornig, 1961). This band is also attributed to the H–O–H interactions, i.e., H\(_2\)O\(^2-\) ions (Walrafen and Douglas, 2006). The oxygen of the hydroxyl group is hydrogen bonded to the other water molecules but the proton attached to the hydroxyl could remains isolated and therefore has a high stretching frequencies as explained from theoretical studies (Hermansson et al., 2011).

In the region 100–1200 cm\(^{-1}\), the “pure water” blank experiment is devoid of any vibrational bands. In 5.3 m KOH blank experiment, a vibrational band is identified at 1068 cm\(^{-1}\) (full width at half maximum, FWHM \(~6\) cm\(^{-1}\)). This is likely related to the in-plane deformation of hydroxyl group attached to a water molecule, which causes the sharp
3.2. Al$_2$O$_3$–H$_2$O system

Raman spectra of pure water in equilibrium with corundum were recorded at various temperatures along a high-density isochore (~1.09 g/cm$^3$) (Fig. 4). Solubility of Al$_2$O$_3$ in pure H$_2$O at low pressure and temperatures is low and below the detection limit of the Raman spectrometer, hence the spectra in the region of 100–1200 cm$^{-1}$ are devoid of any features (Fig. 4). We estimate that the detection capabilities of the Raman spectrometer is for solubilities greater than 2.70 ± 0.15 millimolal based on the estimated concentration of alumina (Tropper and Manning, 2007) at pressure temperatures conditions of 700 °C, and ~20 kbar (Fig. 4a). In particular, there is no peak at ~620 cm$^{-1}$, the symmetric stretching mode of [Al(OH)$_4$]$^{3-}$. The vibrational bands at 438 cm$^{-1}$ (the symmetric stretching mode for Al–OH$_2$) (Tossell, 1999) and the bending modes at 656 cm$^{-1}$ due to Al(OH)$_3$·H$_2$O are also missing. The absence of these features indicates that monomeric aluminate species are below detection limit (Fig. 4). Our observation is consistent with a previous study on the Al$_2$O$_3$–H$_2$O system, where monomers were not detected (Davis, 2005).

In the in situ studies with corundum in equilibrium with pure water, the spectral region between wavenumber 2700 and 4000 cm$^{-1}$ is unaffected and is dominated by the vibrations related to H$_2$O (Fig. 4). The vibrations related to H$_2$O are characterized by three distinct peaks ($v_1$, $2v_2$, and $v_3$), which vary as a function of temperature and density (Fig. 5) as shown in Eq. (1).

$$v_i = v_i^0 + \frac{\partial v_i}{\partial T}(T - T_0) + \frac{\partial^2 v_i}{\partial T^2}(T - T_0)^2 + \frac{\partial v_i}{\partial \rho}(\rho - \rho_0) + \frac{\partial^2 v_i}{\partial \rho \partial T}(T - T_0)(\rho - \rho_0)$$

(1)

where, subscript “i” refers to 1, 2, and 3 for the three vibrational bands; $v_i^0$ refers to a reference frequency at temperature ($T_0$) and density ($\rho_0$). A least square regression analysis of the data from the Al$_2$O$_3$–H$_2$O system and from the pure H$_2$O system along two different isochores with $\rho = 0.89$ and 1.09 g/cm$^3$ indicates that the band $v_2$ increases with both temperature and density, with $\frac{\partial v_2}{\partial T} \approx 0.35$ cm$^{-1}$/°C and $\frac{\partial v_2}{\partial \rho} \approx 9.4$ cm$^{-1}$/g, respectively. In contrast to the band $v_3$, the band $v_2$ remains insensitive to temperature and decreases upon compression. The band $v_3$ decreases with both temperature and under compression (Fig. 5). The results of the regression are listed in Table 3.

3.3. Al$_2$O$_3$–KOH–H$_2$O system

Raman spectra of 5.3 m KOH solution in equilibrium with corundum up to 800 °C and 7.2 kbar along an isochore with equivalent density of ~0.79 g/cm$^3$ are shown in Fig. 6. The dominant spectral feature between 200 and 1200 cm$^{-1}$ is the 620 cm$^{-1}$ mode. This is attributed to the symmetric stretching mode of [Al(OH)$_4$]$^{3-}$ based on previous Raman spectroscopic studies at low pressure and temperature (620–625 cm$^{-1}$) (Moolenaar et al., 1970;
Watling, 1998; Sipos et al., 2006), as well as our quantum mechanical simulations and previous theoretical studies (Fig. 2; Table 2). The \( \text{\text{Al}}(\text{OH})_4 \) stretching mode appears first at \( 319 \text{ cm}^{-1} \) and \( 0.95 \text{ kbar} \) respectively and shifts gradually to \( 618 \text{ cm}^{-1} \) upon heating to \( 800 \text{ °C} \). The integral intensity of the \( \text{\text{Al}}(\text{OH})_4 \) stretching mode also increases with temperature (Fig. 6) due to enhanced alumina solubility in the KOH solution. In the pressure and temperature range explored in the present study (Table 1), we do not find any evidence for polymerization or formation of higher aluminate species such as dimers \( [(\text{OH})_3\text{Al}-(\text{OH})_2]_2^{-} \) and \( [(\text{OH})_2\text{Al}-(\text{OH})_2]_2^{-} \) or trimers. This is very different from silica, which readily polymerizes at these conditions (Zotov and Keppler, 2002). In experiments with corundum in equilibrium with \( 1 \text{ m KOH} \) solution along a cooling isochore of \( 0.79 \text{ g/cm}^3 \), the major feature remains the \( \text{\text{Al}}(\text{OH})_4 \) stretching mode, however, upon cooling the solution is likely supersaturated with the dissolved alumina and the stretching mode remains observable until room temperature. Additional features appear at higher wavenumbers that are likely related to the deformation modes of OH due to KOH.

According to our ab initio simulation (Fig. 1, Table 2), it is difficult to tell whether the \( \text{\text{Al}}(\text{OH})_4 \) ion is isolated in solution or whether it forms an ion pair with \( \text{K}^+ \), as there is only a very slight difference \( \Delta v \text{ cm}^{-1} \) in the predicted frequency of the main peak for \( \text{\text{Al}}(\text{OH})_4 \) and \( \text{K}[\text{Al(OH)}_4] \).

The spectral region between \( 2700 \) and \( 4000 \text{ cm}^{-1} \) is dominated by the hydroxyl \( (\text{OH}) \) stretching vibrations related to \( \text{H}_2\text{O} \). In the solution with \( 5.3 \text{ m KOH} \) solution the high frequency stretching vibration of the “quasifree” \( (\text{OH})^+ \) group is more intense (Fig. 6) compared to the \( 1 \text{ m KOH} \) solution (Fig. 7).

In an experiment along a high-density isochore (equivalent density of \( 1.0 \text{ g/cm}^3 \)), with corundum and \( 5.3 \text{ m KOH} \) solution, we noticed that in addition to the stretching mode at \( 620 \text{ cm}^{-1} \), a broad shoulder appeared at \( 570 \text{ cm}^{-1} \) and shifted as a function of temperature with a stronger temperature dependence (Fig. 8). This could be related to the formation of a neutral \( \text{Al(OH)}_3\text{H}_2\text{O} \) species (compare Fig. 1). However, the additional band is unlikely to be related to a
higher order polymer since it co-exists with the monomer at 300 °C. An alternative possibility could be that at higher fluid density the K[Al(OH)₄]⁻ species starts to dissociate into K⁺ and [Al(OH)₄]⁻, as this may also produce an additional band on the high-frequency side of the main Raman peak (Fig. 1). This interpretation, however, is not consistent with observations from studies at room temperature (e.g., Watling, 1998; Sipos et al., 2006), where the high...
dielectric constant of water should favor dissociation. Indeed, at room temperature, the nature of the cation in the solution (e.g., K$^+$ or Na$^+$) has very little effect on the main band of [Al(OH)$_4$]$^{1-}$. The room temperature spectra do not show the shoulder at 670 cm$^{-1}$ and accordingly, it is likely not related to the dissociation of an ion pair, but to another species, possibly Al(OH)$_3$·H$_2$O.

### 3.4. Precipitates

Unlike silica, which does not form stable hydroxides at pressures and temperatures conditions relevant for crustal and subduction zone settings, there are several stable hydroxides of alumina (e.g., Ervine and Osborn, 1951; Verdes et al., 1992). The aluminum oxide hydroxide AlOOH, diaspor, is stable at least up to 400 °C (Haas, 1972). In many experiments, we noticed additional sharp peaks occurring at 338 cm$^{-1}$, 454 cm$^{-1}$, and 797 cm$^{-1}$ upon cooling of Al$_2$O$_3$-saturated solutions to room temperature. These bands correspond to diaspor crystals, which apparently precipitated throughout the sample chamber. Raman spectra of the fluid show the [Al(OH)$_4$]$^{1-}$ stretching mode in addition to some of the vibrational bands of diaspor (Fig. 9).

![Phase diagram of H$_2$O. Solid ice phases (I, III, V, VI and VIII) and the liquid H$_2$O boundary are shown in different shades of blue (Bridgman, 1912; Guildner et al., 1976; IAPWS, 1996; Wagner and Prüß, 2002). The boundary between liquid and vapor phase of H$_2$O is also shown with the critical point denoted by an grey filled circle. Also shown are the stability fields of various aluminum hydroxide phases (Ervine and Osborn, 1951). As a function of temperature, gibbsite transforms to bohemite and eventually to diaspore. Diaspore is stable until ~400 °C. At temperature greater than 400 °C, corundum is the stable solid. Representative P–T paths are shown for experiments from this study. All these paths traverse the aluminum hydroxide stability fields. (b) Gasket and sample chamber, with 1 m KOH solution and a 400 °C/1 m KOH solution (e.g., K$^+$-saturated solutions to room temperature.  

![Raman spectra from region 1 has the monomer, [Al(OH)$_4$]$^{1-}$ dominated by aqueous fluids. (e) The Raman spectra corresponding to region 1 has sharp peaks that correlate with the Raman spectrum for corundum crystal. (c) The corundum crystal has transformed to diaspore. (d) Region 1 – dominated by diaspore (AlOOH), region 2 – dominated by aqueous fluids. (e) The Raman spectra corresponding to region 1 has sharp peaks that correlate with the Raman spectrum for diaspore (natural sample from Turkey, RRUF database- Downs, 2006). Raman spectrum from region 1 has the monomer, [Al(OH)$_4$]$^{1-}$ mode at 620 cm$^{-1}$, and in addition has sharp features due to formation of diaspore (AlOOH). (f) The intensity of the intramolecular bands are greatly reduced when thin films of diaspore are formed in the cooler region of the sample chamber. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

### 4. DISCUSSION

The similarity of the Raman spectra obtained from the experiments conducted at different bulk densities in KOH–H$_2$O aqueous solution indicates that apart from the anharmonic effects, the [Al(OH)$_4$]$^{1-}$ molecule exists as a well defined entity without significant distribution of bond length, bond angles and polarizability parameters. The relatively high concentration of this anionic species is...
consistent with the alkaline conditions (Wohlers and Manning, 2009). In experiments with high fluid density, we have observed bands that might be attributed to Al(OH)₃·H₂O.

The concentration of [Al(OH)₄]⁻ in KOH–H₂O solutions should be directly proportional to the integral intensity of the ~620 cm⁻¹ band. The integral intensities were calculated for the monomer peak at ~620 cm⁻¹ and were corrected for thermal effects by the thermal population factor, R (Zotov and Keppler, 2002)

\[ R = v \left( 1 - \exp \left( -\frac{h\nu}{k_BT} \right) \right) \]  

(2)

where, ν is the frequency, h is the Planck’s constant, c is the speed of light, k_B is the Boltzmann constant and T is the absolute temperature in Kelvin.

In the in situ studies with corundum in equilibrium with 5.3 m KOH and 1 m KOH solutions, the variation of the frequency and integral intensity of the [Al(OH)₄]⁻ stretching band can be described by the equations

\[ v_{[Al(OH)_4]^-} = v_0 + \frac{\partial v_{[Al(OH)_4]^-}}{\partial T}(T - T_0) + \frac{\partial v_{[Al(OH)_4]^-}}{\partial \rho}(\rho - \rho_0) \]  

(3)

and,

\[ A_{[Al(OH)_4]^-} = A_0 + \frac{\partial A_{[Al(OH)_4]^-}}{\partial T}(T - T_0) + \frac{\partial A_{[Al(OH)_4]^-}}{\partial \rho}(\rho - \rho_0) \]  

(4)

The thermally corrected integral intensities were converted to concentrations (mol/kg of H₂O) units using the reported alumina solubility in 1 m KOH solution as calibration point (Wohlers and Manning, 2009). We calibrate the intensity of the monomer as

\[ C_{[Al(OH)_4]^-} = k_{[Al(OH)_4]^-} \times A_{[Al(OH)_4]^-} \]  

(5)

where, the concentration of the monomer, C_{[Al(OH)_4]^-} is from the solution experiments (Wohlers and Manning, 2009), the intensity of the monomer, A_{[Al(OH)_4]^-} is derived from the in situ experiments and the integral intensity of the 620 cm⁻¹ bands (Fig. 10) and k_{[Al(OH)_4]^-} contains the scattering cross section at various instrument parameters. We used k_{[Al(OH)_4]^-} and the intensity of the monomer for a range of isochores and with varying temperatures to predict the monomer concentrations, which should be equivalent to bulk alumina solubilities in these alkaline solutions. Results are shown in Fig. 10 (see Table 4 for the regression parameters).

5. CONCLUSION

This study demonstrates that in situ Raman Spectroscopy in externally heated diamond anvil-cells allows identification of the major aluminate species dissolved in alkaline aqueous solution with 5.3 m and 1 m KOH solution in equilibrium with corundum. The dominant species is the monomer [Al(OH)₃]⁻ species at all temperatures greater than ~300 °C. Within the temperature, pressure, and density explored in the present study, there is no evidence for polymerization via formation of e.g., [OH]₂·Al(OH)_n·Al(OH)_3] dimer species. In pure H₂O, the monomer species is beyond the detection limit of the Raman spectrometer as the solubility of corundum is very low. Our data therefore show that for typical crustal P, T conditions, thermodynamic models of alumina in aqueous solutions may safely ignore polymerization effects, in particular when the bulk alumina solubilities are low. This does not, however, rule out the potential importance of polymeric species at deeper mantle with P (>20 kbar), T (>1000 °C) conditions where higher bulk alumina solubilities may enhance polymerization.

![Fig. 10](image-url) Dependence of frequency and intensity of the [Al(OH)₄]⁻ stretching mode on temperature and density for (a, b) 5.3 m KOH aqueous solution and (c, d) 1 m KOH solution. The integral intensities were corrected with the thermal population factor (Eq. (2), see text). The deviation of the data for the 1.25 g/cm³ isochore from the initial trend are likely due to a leak of the sample chamber (e) Variation of Al concentration in 1 m KOH in equilibrium with corundum as a function of temperature and density. Data below 400 °C represent metastable equilibria.
ACKNOWLEDGEMENTS

MM acknowledges the support staff- Sven Linhardt, Stefan Übelhack, Hubert Schulze, Heinz Fischer, and Gertrud Gollner at Bayerisches Geoinstitut, Bayreuth, Germany for their support during the experiments. MM acknowledges the research discussions with Prof. William Bassett. MM acknowledges computing resources (request # EAR130015) from the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number OCI-1053575. MM is currently supported by US NSF EAR 1250477. CEM was supported by a Humboldt Fellowship and US NSF EAR 1049901. Authors thank constructive reviews from Dr. I-Ming Chou, two anonymous reviewers, and associate editor.

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