Near-Infrared Spectroscopic Determination of Salinity and Internal Pressure of Fluid Inclusions in Minerals

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INTRODUCTION

The determination of the salinity of aqueous solutions of fluid inclusions in natural minerals is crucial for establishing the physical and chemical environment in which fluids were trapped within the minerals. The salinity of fluid inclusions is determined using microthermometry, which measures the final melting point of the last solid remaining upon heating a frozen sample. The appropriate phase diagram is then consulted for assessing the salt solution. However, metastability of fluid phases for inclusions of low vapor/liquid ratios, stretching of inclusions due to increasing internal pressure from ice formation, and clathrate formation often make it difficult to determine melting points precisely using microthermometry. Furthermore, visual observation of the contents of inclusions themselves can be difficult, especially for inclusions of less than several micrometers’ diameter. The phase diagrams of mixed systems are also required for natural fluid samples with complex chemical compositions. To overcome these difficulties, Mernagh and Wilde proposed the use of the Raman microprobe as an alternative method for determining the total chloride concentrations (salinity) of fluid inclusions in mineral samples. They observed Raman spectra of fluids in the region of OH stretching at 2800–3800 cm\(^{-1}\). Subsequently, they calibrated the results based on the salinity of the fluid inclusions and the effect of NaCl concentration on the intensity and profile of the OH band. The Raman microprobe offers excellent spatial resolution (1 \(\mu\)m), which is advantageous for determining the fluid composition. Nevertheless, strong luminescence from minerals often interferes with weak Raman bands. Furthermore, Raman scattering from liquid water is extremely weak. It is often difficult to obtain meaningful Raman signals.

Measurements of infrared (IR) absorption spectra using an IR microscope have limited spatial resolution, typically of about 30 \(\mu\)m. Notwithstanding, IR spectroscopy is a powerful tool for studying the associated state of liquid water because the frequency of the OH stretching vibration is strongly dependent on the strength of the hydrogen bond. The high absorption of water simplifies the detection of the water spectra in trace amounts. Unfortunately, the high absorption coefficient engenders saturation of the intensity for fluid samples with a thickness of a few micrometers.

This study specifically examines the anti-symmetric stretching + bending (\(v_2 + v_3\)) combination band of water at about 5180 cm\(^{-1}\). The use of near-infrared (NIR) absorption spectroscopy for determination of fluid inclusions in minerals provides several advantages. First, NIR light is transparent to various minerals, including opaque minerals such as sulfide minerals. This transparency allows measurement of the band shape of water appearing in the NIR region without interference from matrix minerals. No absorption is observed in the region of 4500–5500 cm\(^{-1}\) for the glass slide or glue used to mount the sample; the polished thin section can be analyzed as it is. Recent progress in NIR spectroscopy also gives enough information for analysis of data. In contrast, Raman spectra of polished thin sections sometimes suffer from fluorescence from chemical glue. Second, the combination band of water arises exclusively from molecular water. It is therefore unnecessary to consider interference from OH ions contained in the samples and from the glass slide. Development of NIR spectroscopy for the determination of salinity in mineral samples is therefore complementary to micro Raman analysis.

In addition to the salinity determination, the residual pressure of the fluid inclusions was intended to be determined from the spectral shape independent of the salinity determination. The residual pressure in fluid inclusions is fundamental information. In particular, the residual pressure in fluid inclusions in minerals derived from the mantle can serve as a useful pressure marker, giving information related to the depth origin of the minerals and rocks. According to Kagi et al., the peak position of the combination band of molecular water is sensitive to pressure. The method is applicable for the determination of the pressure of ice inclusions in the high-pressure form of a diamond. How much water is stored and how hydrous components are

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TABLE I. Parameters of standard salt solutions.

<table>
<thead>
<tr>
<th>Conc. (wt.%)</th>
<th>Conc. (mol/kg)</th>
<th>Position</th>
<th>Height</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>0</td>
<td>5231</td>
<td>0.479</td>
<td>120.9</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.1</td>
<td>5231</td>
<td>0.724</td>
<td>121.1</td>
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<tr>
<td></td>
<td>4.9</td>
<td>5229</td>
<td>0.470</td>
<td>122.6</td>
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<tr>
<td></td>
<td>10.0</td>
<td>5227</td>
<td>0.491</td>
<td>121.7</td>
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<td></td>
<td>17.9</td>
<td>5224</td>
<td>0.502</td>
<td>122.1</td>
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<tr>
<td></td>
<td>19.8</td>
<td>5220</td>
<td>0.506</td>
<td>122.6</td>
</tr>
<tr>
<td>KCl</td>
<td>2.53</td>
<td>5231</td>
<td>0.482</td>
<td>120.6</td>
</tr>
<tr>
<td></td>
<td>4.9</td>
<td>5230</td>
<td>0.485</td>
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<tr>
<td>MgCl₂</td>
<td>20.7</td>
<td>5222</td>
<td>0.499</td>
<td>119.2</td>
</tr>
<tr>
<td></td>
<td>5.1</td>
<td>5229</td>
<td>0.474</td>
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<tr>
<td></td>
<td>10.0</td>
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<tr>
<td>CaCl₂</td>
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<td>5225</td>
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<td></td>
<td>26.3</td>
<td>5219</td>
<td>0.483</td>
<td>123.3</td>
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</table>

Inclusions in Natural Samples. After calibrating the salt concentration from the band shape of the combination band as described in the Results and Discussion section, mineral samples containing well-characterized fluid inclusions were analyzed to test the present analytical method on natural samples. Natural mineral samples investigated in this study were three pegmatite quartz (SiO₂) samples from Naegi granite, Gifu Prefecture (TS-NG-1); from Hiroshima granite, Hiroshima Prefecture; and from Uchiyama granite, Tsushima, Nagasaki Prefecture (TS94120302), Japan. One fluorite (CaF₂) sample was from a Hansonburg Mississippi-Valley-Type deposit, New Mexico. Fluid inclusions from Tsushima (TS97031904) contained halite (NaCl) as a daughter mineral over-saturated with NaCl (26.4 wt. %). In the following sections, the samples are described according to their locations as Naegi, Hiroshima, Hansonburg, and Tsushima. Figure 1 shows representative photographs of the fluid inclusions in these mineral samples. The salinities in the fluid inclusions were estimated using microthermometry. The final respective melting points of ice in the fluid inclusions were −4.6 to −4.0 °C, −1.8 to 0.2 °C, and −7 °C for Naegi, Hiroshima, and Hansonburg, respectively. In general, the major dissolved chemical component of crustal fluids at a shallow level is NaCl; the salinities of fluid inclusions are expressed by NaCl-equivalent values. Corresponding concentrations in NaCl-equivalent values are 6.0–7.0 wt. % for Naegi, 0.4–3.0 wt. % for Hiroshima, and 10–11 wt. % for Hansonburg. The average size of the fluid inclusions was 60–70 μm. We also observed NIR spectra of small inclusions with 30 μm diameter.

These mineral samples were doubly polished. Their thickness was 0.5–2.0 mm. NIR absorption spectra of fluid inclusions were measured using an IR microprobe equipped with the FT-IR spectrophotometer. A halogen lamp was used as a light source and the incident light was focused into one fluid inclusion with a pair of optical apertures. Pure N₂ gas was...
pumped continuously into the microscope to minimize the effect of atmospheric water vapor. A combination of a quartz beam splitter and an MCT detector was used to observe natural fluid inclusions. At least 500 scans were averaged to obtain one absorption spectrum. Results indicate that 1000 scans were averaged for fluid inclusions as small as 30 \( \mu m \) to obtain sufficient sensitivity for the subsequent spectral analysis.

Application of Near-Infrared Spectroscopy to Fluid Inclusions in a Natural Diamond. Near-infrared absorption spectra of fluid inclusions in natural cuboid diamonds were measured. The sample size was about 5 mm. These diamonds are known to be rich in fluid inclusions derived from mantle. As reported in the literature, fluid inclusions in cuboid diamonds are less than 1 \( \mu m \) in diameter. For that reason, it is impossible to focus the incident NIR light on one fluid inclusion; we decided to use a large NIR beam to illuminate an entire sample, and the absorption spectrum was observed using the same instrumental conditions as applied to the measurements of standard aqueous solutions. The incident light was approximately 10 mm in diameter and four orders of magnitude larger than the fluid inclusions. The spectrum of the unpolished diamond sample was obtained from an interferogram averaged from 1000 scans because transmitted light through the sample is insufficient to give a reasonable signal-to-noise (S/N) ratio from 100 scans.

Data Analysis. As can be seen from Fig. 2, the combination band of liquid water has a highly asymmetrical shape. For a numerical analysis of the band shape, curve fitting was applied to the broad combination band obtained from fluid samples. After subtracting the linear baseline from the raw spectrum, three Gaussian curves with approximate peak heights, peak positions, and peak widths were initially given. The reason for selecting three as the number of curves will be described later. These parameters were optimized using the least squares method with a commercially available software package (GRAMS, Thermo Electron Corp.). Gaussian, Lorentzian, Gaussian–Lorentzian, and Voigt curves were employed during the peak fitting procedure; the Gaussian curve was found to give the best function to reproduce the experimental data.

RESULTS AND DISCUSSION

Salinity-Dependent Changes in the Band Shape of the Combination Band. Figure 2 shows representative NIR absorption spectra of NaCl standard solutions. The antisymmetric stretching + bending \((v_2 + v_3)\) combination band exhibits an asymmetrical band shape that tails toward the lower frequency side. It is noteworthy that increasing salinity weakens absorption at the lower frequency side (see also Fig. 3). Similar changes in band shape were also observed for the other salt solutions (KCl, CaCl\(_2\), and MgCl\(_2\)). On the other hand, the peak position shows no marked change with salt concentration (see also Table I). It was necessary to analyze the effect of salinity on the band shape of the \(v_2 + v_3\) combination band by means of a numerical method. Bujis and Choppin\(^{16}\) studied the combination band around 8000 cm\(^{-1}\) and

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Fig. 1. Representative transmitted-light photographs of fluid inclusions: (a) Naegi, (b) Tsushima, (c) Hansonburg, and (d) Hiroshima.
demonstrated that the absorption band can be resolved into three components that are assignable to free water molecules \((S_0)\), to molecules with one OH involved in hydrogen bonds \((S_1)\), and to molecules with two OH involved in H bonds \((S_2)\). A similar method was used on the \(\nu_2 + \nu_3\) combination band of water in the range of \(-50^\circ C\) to \(50^\circ C\).\(^{17}\) They determined the energy \(\Delta H^\circ\) involved in the transition of molecules between the three energy states \((S_0, S_1,\) and \(S_2)\). NIR absorption spectra in the \(7000-10000\ cm^{-1}\) region have been studied and the average sizes of water clusters were calculated.\(^{18}\) Furthermore, Kato et al. applied the “three-band model” to liquid water under pressure and the high-pressure form of ice.\(^{19}\) Their study successfully showed that the \(\nu_2 + \nu_3\) combination band can be resolved into the same three components \(S_0, S_1,\) and \(S_2\). A recent review paper also mentioned the availability of the peak analysis method.\(^{20}\) In this study, each spectrum was resolved into three components—\(S_0, S_1,\) and \(S_2\)—according to the procedures reported in the previous studies.\(^{18,19}\) Representative results of curve-fitting on salt solutions and pure water are illustrated in Fig. 3. The obtained peak parameters for the fitted curves are listed in Table I. It has to be emphasized here that the method of analyzing the asymmetrical band shape of the combination band of water is not unique. We have just chosen the method proposed by Bujis and Choppin and later confirmed by Kato et al. as a possible numerical method. Another analytical procedure would also be applicable to evaluate the subtle change in peak shape.

With increasing salt concentration, the peak positions of the combination bands are shifted slightly toward lower frequencies. Among the spectral parameters listed in Table I, the most sensitive parameter to the change in the band shape in response to the change of salinity was the intensity ratio of \(S_2\) to \(S_1\). The intensity ratio \((S_2/S_1)\) substantially decreased with increasing salt concentration. This change is attributable to the change in the association of water molecules in the solutions induced by the dissolution of ions. The intensity ratios \((S_2/S_1)\) versus salt concentrations are plotted in Fig. 4 for each salt. We adopted the plots as a calibration curve for determining the solutions’ salinity. NaCl and KCl display a similar trend. CaCl\(_2\) and MgCl\(_2\) display a different trend, showing a steeper gradient. These differences are attributable to the difference in charges and ionic radii of the cations; both can affect the dissociation of water molecules in the fluid.

**Application to Fluid Inclusions in Natural Minerals.**
Fluid inclusions whose salinities had been characterized by microthermometry were examined to test the spectroscopic method on fluid inclusions in natural samples. NIR spectra of...
Fluid inclusions with diameters greater than 30 μm were obtained using an IR microscope equipped with FT-IR. Incident NIR light was focused on a single fluid inclusion. We obtained well-resolved NIR absorption spectra from inclusions as small as 30 μm. The absorbance values were 0.01–0.1 at the peak position of the combination band at about 5170 cm⁻¹. The number of scans for obtaining Fourier transformed spectra changed with respect to the obtained absorbance depending on the size of the fluid inclusions. Fluid inclusions larger than 100 μm required up to 100 scans, whereas those as small as 30 μm required 1000 scans to achieve a good S/N ratio.

Figure 6 presents a summary of data obtained from fluid inclusions in natural mineral samples. The horizontal axis represents the salinity expressed in the equivalent value of NaCl determined by microthermometry. The error bars in the horizontal axis are derived from the distribution of temperatures (except for the Tsushima sample, whose salinity was uniquely estimated from solubility of NaCl at room temperature). The vertical axis displays the intensity ratio of S₂/S₁ obtained from the NIR spectroscopic measurements. The error bars in the vertical axis represent the distribution of the obtained values based on about 10–15 data points for each sample. Variability in results obtained by the NIR spectroscopic method was greater than that for microthermometry. The dotted line in Fig. 6 is a parabolic curve fitted to the relationship between the S₂/S₁ ratio and the concentration of NaCl obtained from the standard NaCl solutions (see Fig. 4). The obtained plots fall on the curve within error bars, implying that the present NIR spectroscopic method is consistent with results obtained using conventional microthermometry. The significantly large error on the Tsushima sample presumably results from the low S/N ratio due to small (≤10 μm) inclusion sizes. The detection limit in the present spectroscopic method depends on the spectral resolution (4 cm⁻¹ in this study) and the size of the fluid inclusions.

As shown in Fig. 6, the precision in the NIR spectroscopic method for determination of the salinity in fluid inclusions is inferior to that of microthermometry, but NIR spectroscopy acquires objective data without the need for skilled specialists. Furthermore, its analysis time is short: NIR spectroscopy takes approximately 2 minutes for 100 scans. In contrast, microthermometry requires a skilled operator and takes at least one hour to study one fluid inclusion with decreasing and increasing temperature. As an analytical tool, NIR spectroscopy presents many benefits.

**Pressure-Induced Changes in Near-Infrared Spectra of Saline Fluids.** Some inclusions in natural diamond samples are under pressures of up to several gigapascals due to the mechanical strength and deep origin of diamond.9,21–24 It would be a tremendous advantage for the application of NIR spectroscopy to fluid inclusions if the internal pressure of fluids could be estimated from the fluids’ NIR spectra. NIR absorption spectra of saline fluids were measured using a diamond anvil cell. Hydrogen bonds in liquid water decrease with increasing pressure.25,26 Therefore, the frequency of the internal OH stretching vibration of molecular water decreases. The frequency of the combination band appearing in the NIR region also decreases with increasing pressure.9,19 However, the pressure-response of the combination band of saline fluid is not well established at present. Figure 7 portrays the pressure dependence of peak positions in the combination band of pure water and KCl aqueous solutions. Pure water undergoes a phase transition at a pressure of less than 1 GPa and forms a high-pressure form of ice. The number of plots for pure water is therefore limited. Saline fluid can be compressed to higher pressures without freezing under supercooled conditions. With increasing pressure, the combination band shifts linearly toward lower frequencies. The pressure dependence of the S₂/S₁ ratio and the data scatter should be considered as a broad band rather than a straight line. The range of shifts in the pressure range of 0–2 GPa is much larger than that resulting from changes in the salt concentration. The difference in peak positions between pure water and 15 wt. % KCl solution is approximately 5 cm⁻¹, but the pressure-induced peak shift from ambient pressure to 2 GPa was as large as 30 cm⁻¹. Presumably, the uncertainty in determining peak position arises from the resolution of the FT-IR measurements (4 cm⁻¹) and the broadness of the combination band. The uncertainty in determining the pressure of fluid is approximately 0.2 GPa, taking into account the precision in determining the peak position (described below again). In this...
sense, the peak position of the combination band is more sensitive to pressure determination of fluid inclusions in natural diamonds and is insensitive to salinity. Strictly speaking, however, the change in the peak position is not independent between changes of pressure and salinity.

Simultaneous determination of salinity and pressure of aqueous fluids requires a parameter that is independent of pressure and salinity. The curve-fitting procedure was applied for data for 15 wt. % KCl solution at high pressures. Plots of the $S_2/S_1$ ratio versus pressure are shown in Fig. 8. No systematic decrease or increase is detectable with increasing pressure. This fact implies that the $S_2/S_1$ ratio is constant for pressures between 0 and 2 GPa. On the other hand, the $S_2/S_1$ ratio shows strong salinity dependence. We therefore infer that the $S_2/S_1$ ratio parameter is independent of pressure and salinity.

Before giving an example of fluid inclusions in a natural diamond in the next section, a general procedure to interpret NIR spectra of fluid inclusions is summarized here. Obtained spectra are curve-fitted to three Gaussian curves and the $S_2/S_1$ ratio is estimated. Salinity can be estimated from the relationship shown in Fig. 4. The residual pressure of fluid can be estimated from Fig. 7; the obtained value would contain an uncertainty of approximately $\pm 0.2$ GPa, taking into account the width of the band in the relationship between peak position and pressure (see Fig. 7).

**Application to the Measurement of Salinity of Fluid Inclusions in a Natural Diamond.** We have not mentioned that the present method can also be applied to samples in which fluid inclusions are smaller than 1 $\mu$m and dispersed in minerals. In such cases, it is extremely difficult to focus the incident laser beam of the Raman microprobe into a single inclusion even if a polished thin section is prepared with an excellent surface smoothness. On the other hand, a micro-infrared microscope has a spatial resolution of about 10 $\mu$m if the instrumental conditions are arranged properly, and it is not possible to focus NIR light into 1 $\mu$m fluid inclusions. However, it is possible to measure IR and NIR absorption spectra using an incident beam much larger than the size of a single fluid inclusion. In other words, using a large incident light, one can obtain average spectra containing information from numerous inclusions existing in the illuminated area.

We next present an example of the application of NIR spectroscopy to the measurement of fluid inclusions in a natural diamond with a cubic habit (cuboid). Fluid inclusions in natural diamonds were first discovered in cuboid diamonds using infrared spectroscopy. Subsequently, high contents of alkali ions were reported in the inclusions of cuboid diamonds based on electron microprobe analyses. However, direct analysis of the salinity of fluid inclusions in diamond has not been achieved because of the extremely hard and stable properties of diamond.

This study examined the NIR absorption spectrum of a cuboid diamond from the Congo using a 10 mm diameter beam, which is larger than the sample diamond (5 mm cube). The combination band of liquid water was observed and the obtained spectrum with three resolved Gaussian curves is displayed in Fig. 9. The intensity ratio ($S_2/S_1$) calculated from the resolved curves was 0.52. This value is markedly smaller than that of pure water (0.60); the fluid trapped in the diamond contains a small amount of salt. Salinity, as estimated from the relationship in Fig. 4, is approximately 1 M NaCl-eq or 4.4 wt.

**Fig. 7.** Plots of the pressure dependence of the peak position of the combination band for pure water, 5 wt. % KClaq, 10 wt. % KClaq, and 15 wt. % KClaq.

**Fig. 8.** Plots of the pressure dependence of the $S_2/S_1$ ratio for 15 wt. % KClaq. The $S_2/S_1$ ratio shows no systematic change with increasing pressure.

**Fig. 9.** NIR absorption spectra of fluids in a natural diamond with a cubic habit, cuboid. The $v_1 + v_3$ combination band was resolved into three Gaussian curves. The $S_2/S_1$ ratio was 0.52 and the peak position of the combination band is at 5162 cm$^{-1}$. 
% in NaCl-eq. The peak position is approximately 5162 cm\(^{-1}\), which is much lower than that of fluids at ambient pressure taking into account the salinity-induced decrease in frequency. Figure 7 shows that the fluid inclusions contained in the cuboid diamond have a residual pressure of 0.6–0.8 GPa. This value is in the range of previously reported residual pressures,\textsuperscript{22–24} NIR spectroscopy therefore allows characterization of fluids from deep in the Earth.

CONCLUSION

Observations of the OH stretching + HOH bending combination band from saline fluids with NIR absorption spectroscopy allows the determination of the salinity and pressure of fluid inclusions. The intensity ratio of the resolved components of the combination band is sensitive to salinity, and the peak position of the combination band is sensitive to the fluid’s pressure. The minimum spatial resolution for a single fluid inclusion is restricted by the optical resolution of IR microscopes to 10 \(\mu\)m or greater. However, average spectra are measurable for small fluid inclusions using a large incident beam. Using this technique, we investigated micro inclusions in a natural diamond; a salinity of 1 M in NaCl equivalent concentration and a pressure of 0.6–0.8 GPa were obtained from spectral analysis. This method’s analytical precision is not as good as that of conventional microthermometry, but it requires no skilled operator. Simultaneous determination of pressure and salinity can be achieved exclusively by this spectroscopic method.

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