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## Evidence for ice VI as an inclusion in cuboid diamonds from high $P$ - $T$ near infrared spectroscopy

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### ABSTRACT

Near infrared absorption (NIR) spectra of natural morphologically cubic polycrystalline diamonds (cuboid) were obtained at room temperature, and the stretching plus bending combination band of molecular water was observed. The spectrum consisted of the main band at  $5180\text{ cm}^{-1}$  due to liquid water and a shoulder at  $5000\text{ cm}^{-1}$ . The  $5000\text{ cm}^{-1}$  band suggests the presence of a phase with stronger hydrogen bonding in inclusions in the diamond. This shoulder absorption decreased on heating to  $120^\circ\text{C}$ . The combination band of  $\text{H}_2\text{O}$  at high pressure and temperature was measured using a resistively heated diamond cell and the pressure dependence of the peak position was obtained. Comparison with the present experimental results indicates that the spectral changes induced by heating of the cuboid corresponded to melting of a high-pressure form of ice, and the shoulder absorption at  $5000\text{ cm}^{-1}$  arises from ice VI at 1.9 GPa. On the other hand, the liquid water, a main component of the fluid inclusions in the cuboid, was not under high pressure judging from the frequency of the combination band. This contrast might relate to the texture of the cuboid diamond. The spectral observation enables us to estimate the residual pressure of mantle fluid encapsulated in these diamonds. The diamond-cell data also provide high- $P$ - $T$  NIR fingerprint spectra that could be useful for identifying  $\text{H}_2\text{O}$  phases and confining pressures in other samples.

**KEYWORDS:** ice VI, cuboid diamond, near-IR spectroscopy.

### Introduction

NATURAL minerals of high-pressure origin with high strength have the potential to retain high internal pressures on material trapped within these crystals. Previously reported infrared and Raman spectra have revealed that high internal pressures can be retained in some diamond inclusions. Frequency shifts in IR spectra showed that the residual internal pressures for quartz inclusions in cuboid diamonds were 1.5–2.1 GPa (Navon, 1991). Using micro-Raman spectroscopy, pressures of 0.13 to 0.65 GPa were measured inside olivine inclusions in Siberian diamonds (Izraeli *et*

*al.*, 1999). Furthermore, solid carbon dioxide was observed by IR spectroscopy in a natural diamond, and the blue shift seen in the  $\text{CO}_2$  absorption bands suggested that the solid  $\text{CO}_2$  was present at pressures as high as 5 GPa (Schrauder and Navon, 1993). More recently, the combination of micro-Raman spectroscopy and single-crystal X-ray diffraction (XRD) has been used to obtain pressures of 5.5 GPa for coesite inclusions in Venezeulan diamonds (Sobolev *et al.*, 2000). These experimental results showed that the diamond is strong enough to encapsulate high pressure on the order of gigapascals.

Some natural diamonds are rich in mantle-derived fluid inclusions (Chrenko *et al.*, 1967; Guthrie *et al.*, 1991; Navon, 1991; Navon *et al.*, 1988; Schrauder and Navon, 1993, 1994). The phase diagram of water (Bridgman, 1935;

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Pistorius *et al.*, 1963; Fei *et al.*, 1993) illustrated in Fig. 1 shows that the high internal pressure retained in diamonds is high enough to crystallize liquid water into ice VI or VII at room temperature. Thus one may expect that water can exist as ice inclusions in diamonds at ambient temperature, but ice inclusions have not been reported although there are numerous reports of liquid water. Navon (1991) demonstrated that water contained in cuboid diamonds did not freeze to ice even at liquid nitrogen temperature, and he suggested that the high surface-to-volume ratio of the micro-inclusions and/or the high solute content of the residual fluid resulted in the supercooled fluid. It was presumed that the size and chemical composition of the inclusions caused supercooling even at high pressure and room temperature in which ices are the stable form of water. Most of the water in cuboid diamonds is contained in liquid form as reported previously, but the possibility of the presence of ice as an inclusion in diamonds cannot be ruled out given the  $P$ - $T$  condition of present inclusions in diamonds. In this study, we searched for ice as a solid inclusion in natural diamonds using NIR spectroscopy.

## Experimental methods

A morphologically cubic diamond (cuboid diamond) with a size of  $\sim 2$  mm, containing water inclusions, from the Democratic Republic of Congo, was investigated. The NIR absorption spectra of the cuboid diamond were recorded using an FTIR spectrometer (Perkin Elmer, Spectrum 2000) with a halogen lamp, quartz beam splitter and InSb detector. Spectral measurements were carried out at  $4\text{ cm}^{-1}$  resolution, and interferograms from 1000 scans were averaged to obtain one spectrum. Mid-IR measurements were performed with the combination of a Globar light source, TGS detector and KBr beam splitter operating at a spectral resolution of  $4\text{ cm}^{-1}$ . The cuboid diamond was set in a holder made from copper plate of 2 mm thickness with a square hole of  $\sim 2$  mm to fit the cuboid diamond. A small space between diamond and the copper holder was sealed with aluminium foil to get high heat conduction. The beam size of the IR incident light ( $10\text{ mm}\phi$ ) was larger than the diamond specimens. The sample holder was heated with a belt heater up to  $120^\circ\text{C}$  and the temperature of the diamond sample surface was monitored by a

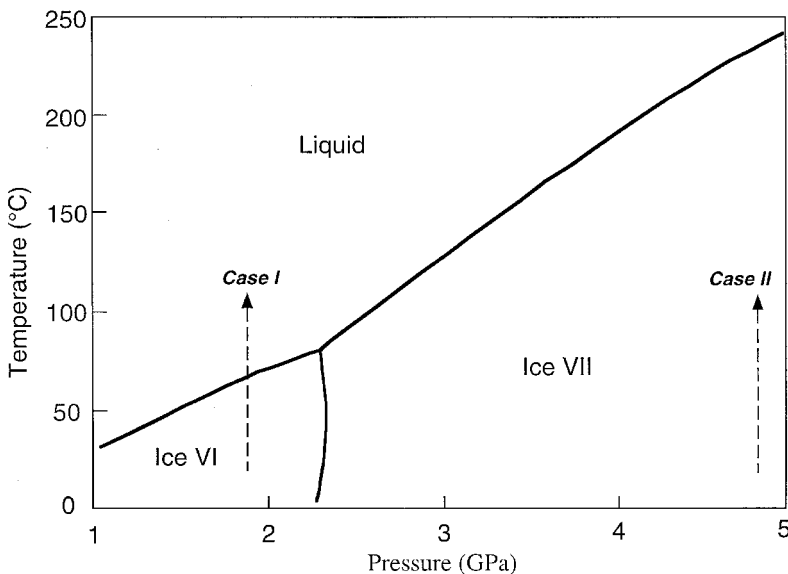


FIG. 1. Schematic phase diagram of water at high pressure (after Bridgman, 1935; Pistorius *et al.*, 1963; Fei *et al.*, 1993). The arrows show two possible heating sequences for natural cuboid diamond samples at the pressures estimated exclusively from the frequency of the combination band of water. Case I corresponds to the ice VI at 1.9 GPa and Case II corresponds to ice VII at 5 GPa.

thermocouple. For comparison, NIR spectra of liquid water sandwiched between two  $\text{CaF}_2$  disks were also measured.

The NIR spectra of water at high pressure were measured in a diamond anvil cell consisting of a pair of type IIa diamonds with 500  $\mu\text{m}$  flat culets. Spectra were recorded using a Bruker IFS66v/s FTIR spectrometer equipped with a Bruker II IR microscope (Irscope II) with KBr beam splitter, globar source and MCT detector. Pressure was calibrated by the ruby fluorescence method. Measurements were carried out at room temperature and as a function of temperature to 120°C at high pressure, with heating coils placed around the entire diamond cell.

## Results and discussion

Figure 2 shows the mid-IR absorption spectrum of a natural diamond sample. As previously reported, our sample contained water, silicates, etc. as inclusions. Water concentration in this sample was estimated to be 65 ppm using a molar absorptivity value for the OH-stretching mode of liquid water (81 liter  $\text{mol}^{-1} \text{cm}^{-1}$ ) reported by Thompson (1965). Generally, in order to identify

the phase of water, attention must be paid to the shape of fundamental OH-stretching absorption band around  $3400 \text{ cm}^{-1}$  which is sensitive to the extent of hydrogen bonding of water. However, the intrinsic absorption of diamond, the first overtone of the  $\text{H}_2\text{O}$  bending mode, and the fundamental stretching mode due to the OH ion from possible hydrous minerals can overlap the OH-stretching band derived from molecular water.

In order to overcome these difficulties, especially acute for natural samples, it is necessary to observe a vibrational mode of water that is free from interference of other modes related to hydrous species and is sensitive to the extent of hydrogen bonding of water molecule. In this study, we focused on the combination stretching plus bending mode of the  $\text{H}_2\text{O}$  molecule in the condensed phases. In Figure 3, the combination band is shown for the cuboid diamond (Fig. 3a) and pure liquid water (Fig. 3b), respectively. The large rise at the right end on the spectrum of cuboid diamond in Fig. 3a is a tail from a sharp absorption at  $4500 \text{ cm}^{-1}$  derived from a combination of CH vibrations typical of natural diamonds (Davies, 1977; Davies *et al.*, 1984) at  $1405 \text{ cm}^{-1}$

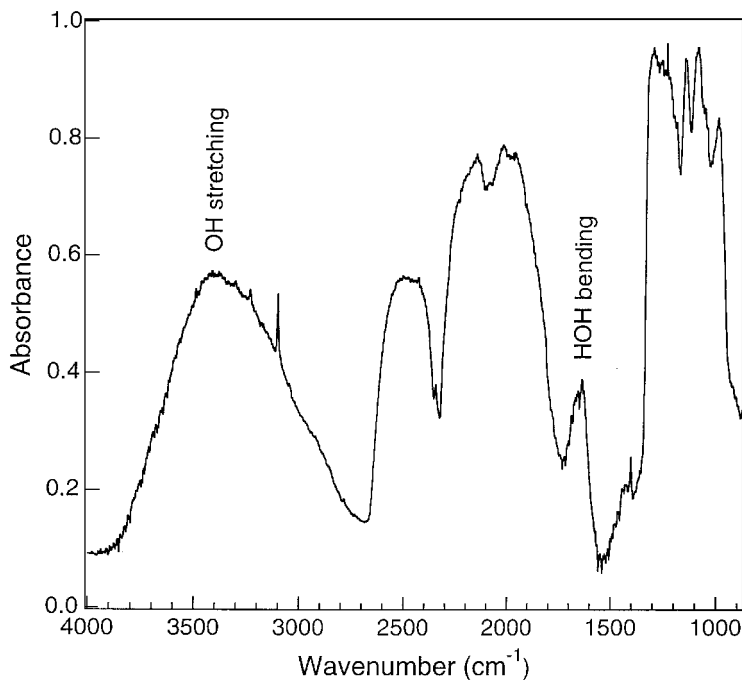


FIG. 2. Mid-IR absorption spectra of the cuboid diamond.

and  $3107\text{ cm}^{-1}$ . These two spectra in Fig. 3*a,b* reveal the same peak position at  $\sim 5180\text{ cm}^{-1}$ . It suggests that most of the water in the diamond is liquid water. In contrast to the similarity in these

peak positions, the band shapes differ sharply from each other between the diamond and liquid water. Figure 3 also shows these two spectra superimposed in order to highlight the difference

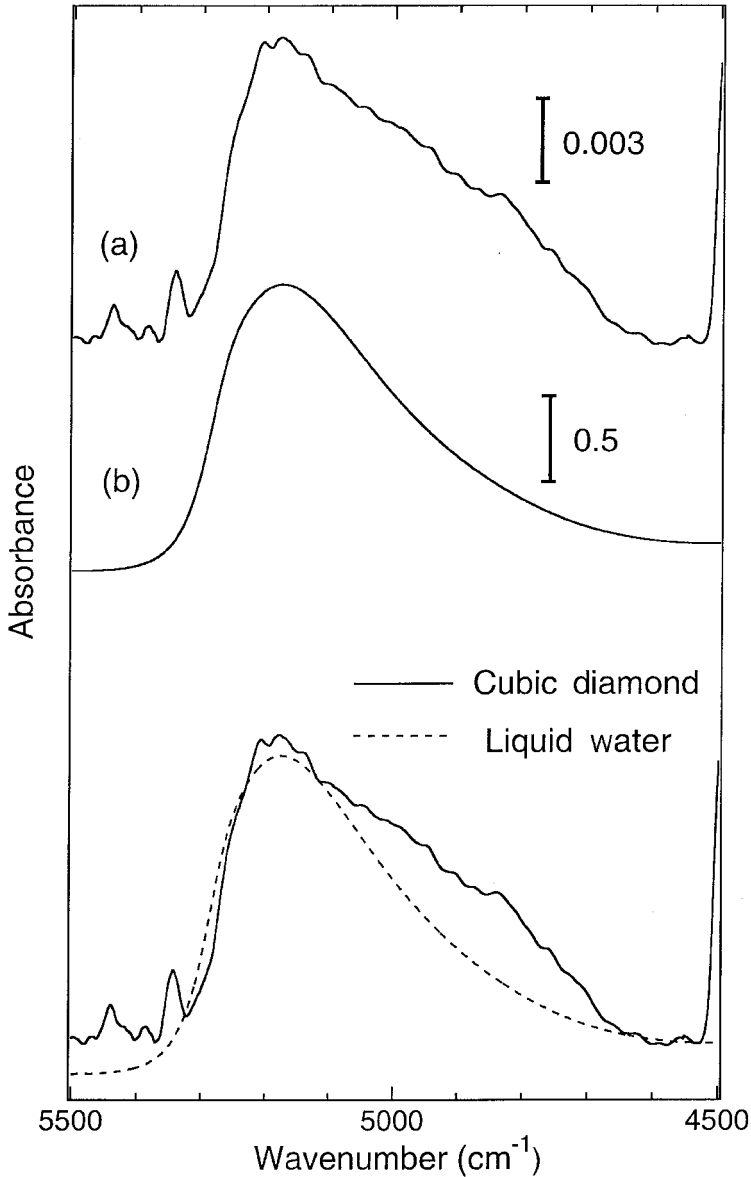


FIG. 3. NIR absorption spectra of water involving the stretching plus bending combination band at room temperature. The upper spectrum (a) is from the cuboid diamond, and lower spectrum (b) from liquid water. Both spectra show a peak at  $\sim 5200\text{ cm}^{-1}$ , but the upper spectrum shows a convex upward feature on the low wavenumber side of the band in contrast to the concave upward feature for the lower spectrum. The two spectra are superimposed in the lower part of the figure in order to clarify the difference in band shapes between them.

in the band shapes. A spectrum of the cuboid diamond shows convex upward features in the lower wavenumber side of the combination band, while liquid water shows concave upward features in the lower wavenumber side. This convex upward band shape observed for the diamond (Fig. 3a) suggests that the water in the latter contains some additional components giving rise to the absorption at lower wavenumbers other than liquid water.

The frequency of the OH-stretching vibration decreases with increasing strength of hydrogen bond (e.g. Nakamoto *et al.*, 1955; Lutz, 1995; Goncharov *et al.*, 1996). The presence of a component in the lower wavenumber side (Fig. 3a) suggests that water in the diamond contained some additional phase of water with stronger hydrogen bonding. This might be ice inclusions under pressure. Water molecules in ice are strongly hydrogen bonded and typically show lower OH-stretching frequencies than liquid water (e.g. Bertie and Whalley, 1964; Marckmann and Whalley, 1964; Bertie *et al.*, 1968; Engelhardt and Whalley, 1979; Wong and Moffat, 1987; Aoki *et al.*, 1996). Therefore, the combination band of ice should be observed at a lower frequency compared with that of liquid water.

If the material contained in the diamond associated with a stronger hydrogen bond is ice, a high pressure polymorph of water, it should melt on increasing temperature, as indicated by the phase diagram of water shown in Fig. 1. In this study, the diamond sample was heated to 120°C and a change in shape of the combination band was observed. In Fig. 4 combination bands measured for the diamond at room temperature (20°C) and high temperature (120°C) are shown. We can clearly see that the convex upward feature, denoted by the arrow in the room temperature spectrum, (Fig. 4a) disappeared in the spectrum obtained at 120°C (Fig. 4b). Figure 4c shows the difference spectrum. The concave upward shape of the spectrum in Fig. 4b is similar to that of liquid water taken at room temperature (Fig. 3b). The decreased component suggests that a high-pressure phase of water (an ice phase) melts to liquid water and had almost disappeared at 120°C. The peak position of the decreasing component was at  $\sim 5000\text{ cm}^{-1}$  as shown in Fig. 4c, which was lower by  $200\text{ cm}^{-1}$  when compared with the combination band of liquid water at room temperature. This observation suggests that a portion of the water in the diamond exists as ice and it melts with increasing

temperature. Furthermore, by cooling to room temperature, the combination mode band reverted to the convex upward feature in the lower wavenumber side, the same as the spectrum obtained before heating. This demonstrates that the spectral changes were reversible.

For the purpose of assigning the component at  $5000\text{ cm}^{-1}$  in the spectra, the stretching plus bending combination band of ices were measured at high pressure using a diamond anvil cell. Representative spectra measured at room temperature are shown in Fig. 5. The pressure dependences of the peak positions of the combination band are illustrated in Fig. 6. The frequency of the band decreases with increasing pressure, and the phase transitions from liquid water through ice VII are reflected in the clear discontinuity of frequency. Pressure derivatives of frequency estimated from the present results were negative for liquid water, ice VI and ice VII ( $-34.0\text{ cm}^{-1}/\text{GPa}$ ,  $-106\text{ cm}^{-1}/\text{GPa}$  and  $-36.3\text{ cm}^{-1}/\text{GPa}$ , respectively). The pressure derivative for ice VII at 100°C gave a value ( $-35.1\text{ cm}^{-1}/\text{GPa}$ ) similar to that taken at 20°C. Larsen and Williams (1998) reported that the pressure derivative of the frequency for ice VII was  $-13 \pm 4\text{ cm}^{-1}/\text{GPa}$  in the wide pressure range extended to 30 GPa. The difference implies the decrease of the pressure derivative in the higher pressure region. This indicates that the frequency of the combination band can serve as a pressure marker of fluid inclusions in diamonds especially within the range of internal pressure inside of natural diamonds (<10 GPa). The decreasing component at  $5000\text{ cm}^{-1}$  for the diamond sample on heating corresponds to ice VI at 1.9 GPa (Case I in Fig. 1) or ice VII at 5 GPa (Case II in Fig. 1) at room temperature for the NIR frequencies, respectively. However, ice VII can be excluded by consideration of the phase diagram (see Fig. 1), assuming that the phase relations in the sample correspond to those of bulk H<sub>2</sub>O. Since ice VII near 5 GPa melts at temperatures far above 120°C, we can conclude that the cuboid diamond studied here contained inclusions of ice VI at 1.9 GPa. The residual internal pressure of such diamonds previously estimated from quartz inclusions was 1.5–2.1 GPa (Schrauder and Navon, 1994). The consistency of the present results with those obtained for quartz inclusions further indicates that the inclusions in cuboid diamonds are under hydrostatic conditions and the effects of solutes on melting relations are minimal. Furthermore,

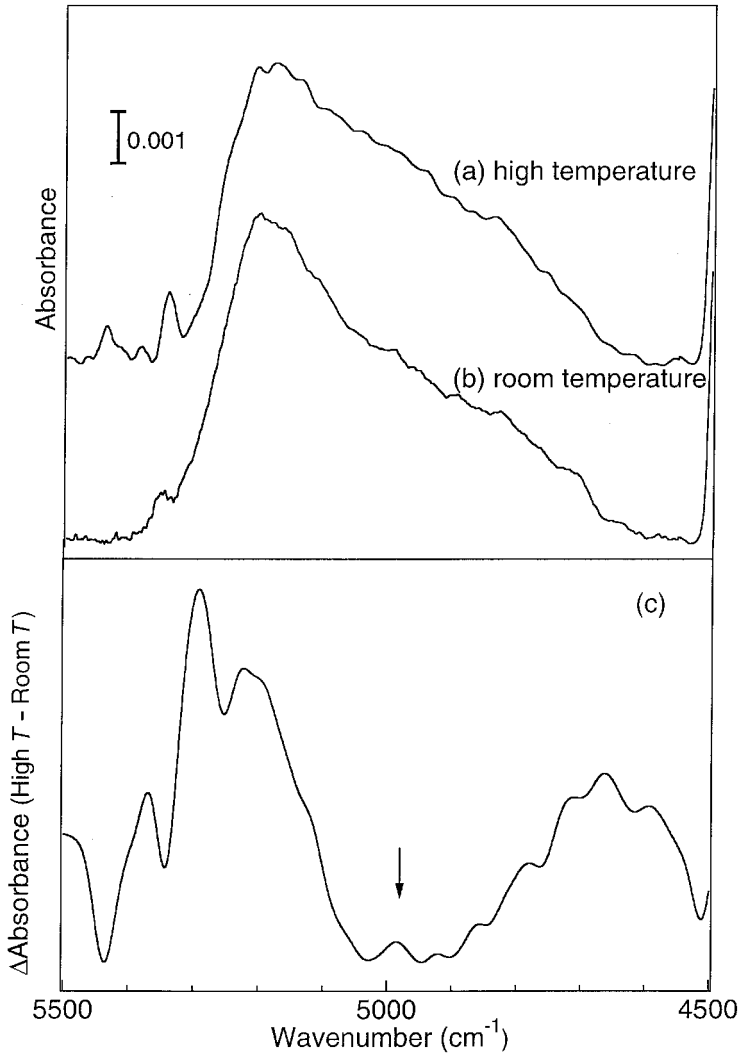


FIG. 4. NIR absorption spectra of the cuboid diamonds obtained (a) at 120°C and (b) at room temperature. The combination band of molecular water was observed in both spectra. While the band shape of the combination mode appeared to be convex upward before heating, it changed to concave upward at 120°C as well as liquid water (Fig. 2a). The spectral change is denoted by the arrow. The difference spectrum between (a) and (b) is displayed in part (c).

the inferred confining pressure in ice VI will result in the same fluid pressure value of 4–7 GPa as estimated from the residual internal pressure of quartz. Navon (1991) obtained this pressure value by an extrapolation to the mantle temperature with the assumption of constant volume due to the compensating thermal expansion and compressibility of diamond. The

pressure range showed that the physical conditions of mantle fluid fall within the thermodynamic stability field of diamond.

The relative intensity of the 5000  $\text{cm}^{-1}$  shoulder on the main absorption around 5200  $\text{cm}^{-1}$  can give us information on the relative abundance of ice in the cuboid diamond. A contribution from the shoulder absorption on the

## ICE VI INCLUDED IN CUBOID DIAMONDS

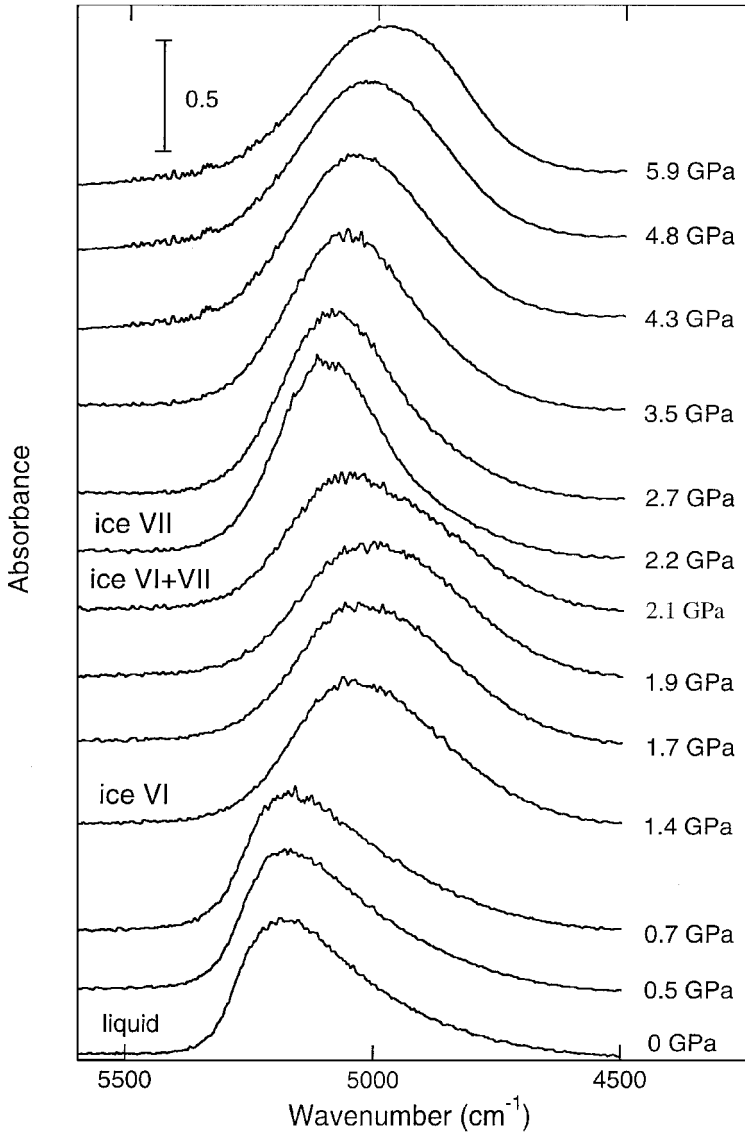


FIG. 5. Representative NIR spectra of water at high pressure and room temperature observed using a diamond anvil cell. Pressure-induced phase transitions (liquid water—ice VI—ice VII) were observed.

low wavenumber side of the combination band was 10–20% of the main peak as shown in the lower illustrations in Figs 3 and 4. The present result demonstrates that most of the water in the diamond sample exists as liquid, but a considerable amount (10–20%) of liquid water coexists as ice VI. The extent to which the fluid inclusions observed here are trapped in the inside of diamond crystals or in between the grain

boundary of diamond crystals is not clear, because cuboid diamonds have a polycrystalline texture, especially for the inclusion-rich outer portion of diamond grain. We can speculate that the grain boundaries were completely closed from outside during the crystal growth and the inside of the crystal and grain boundary would be indistinguishable. The majority of the water in the cuboid diamonds could be liquid in a



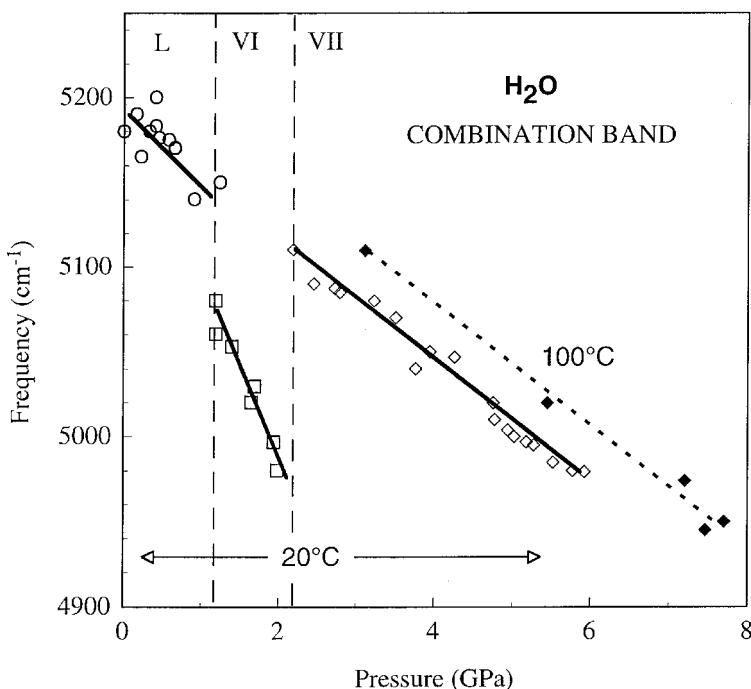


FIG. 6. Pressure dependence of the OH-stretching plus HOH bending combination band frequency for liquid water, ice VI and ice VII at room temperature (20°C; open squares) and 100°C (filled squares).

supercooled condition resulting from the small inclusion droplet size or high solute content. Here, we have to mention the physicochemical conditions of liquid water observed in the present study. As shown in Fig. 3, the combination band for the cuboid diamond measured at room temperature exhibited a peak at  $5180\text{ cm}^{-1}$ . This peak position is identical to that of pure water at ambient pressure within the experimental error (spectral resolution of  $4\text{ cm}^{-1}$ ). The pressure dependence of the combination band of liquid water (Fig. 6) demonstrates that the liquid water in the diamond is not under the same high pressure as the ice VI (1.9 GPa). This suggests two water phases being at two distinct residual pressures in the same diamond. One might speculate that the liquid phase is embedded in boundaries of diamond crystals and the ice VI is inside single crystals. This possibility will require intensive study by taking the salinity of the fluids into account (Navon, 1999). The speciation of water in natural diamonds is important for considering the geochemical stages of incorporation of mantle fluid during the formation of cuboid diamonds.

Further study by IR microscopy may provide additional insight into these issues.

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