

Water-related IR characteristics in natural fibrous diamonds

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ABSTRACT

Water-related features were studied using infrared absorption spectroscopy in fibrous diamonds with micro-inclusions. Both OH-stretching and HOH-bending vibrations were observed. The lack of correlation between the intensities of HOH and OH bands in different samples and the complexity of the OH-stretching band indicate that a large fraction of water is present as hydroxyl groups in minerals.

Heating and cooling experiments were performed to elucidate the properties of fluids in micro-inclusions in diamonds. The results of experiments at various temperatures support the presence of several water-related components in individual diamonds. These spectroscopic investigations of fibrous diamonds revealed two or more interrelated water-related components preserved in micro-inclusions. The existence of several water phases or water solutions with different salinity and solutes within one diamond crystal is possible.

KEYWORDS: diamond, fluid inclusions, supercritical water, vibrational spectroscopy.

Introduction

HYDROUS fluids are important for melting and elemental transport among mantle reservoirs, the crust and the atmosphere. Questions associated with water in the mantle remain a matter of great interest and considerable debate. Phases in the Earth's mantle that are capable of hosting water in the form of H₂O or OH span the range from liquids (Andersen and Neumann, 2001) to nominally anhydrous silicate minerals (Bell and Rossman, 1992). Water creates changes of different mantle properties: phase relationships, rheology, and kinetics of phase transitions, and others. Information related to chemical and physical properties of hydrous components in natural samples from the mantle is important in helping to solve these problems. Diamonds are physically and chemically stable capsules and can carry hydrous components directly from the mantle.

Studies of infrared (IR) absorption spectra (e.g. Chrenko *et al.*, 1967; Galimov *et al.*, 1979) of

diamonds with numerous micro-inclusions have shown the presence of water, carbonates and other minerals. Some inclusions preserve high internal pressure (e.g. Navon, 1991), indicating that the original fluids and minerals were trapped during growth of the host diamond. Evidence for high-pressure water polymorph-ice VI as an inclusion in cuboid diamonds also suggests the presence of hydrous fluid in the upper mantle (Kagi *et al.*, 2000). Observations of water species in diamond inclusions provide a unique opportunity for the direct study of mantle-derived fluids involved in mantle metasomatism of the sub-continental lithosphere and in diamond formation.

For detection of minor and trace amounts of water in minerals, glasses and melts, IR spectroscopy is a sensitive tool (Rossman, 1988). It is also a powerful means of investigating diamond lattice defects and micro-inclusions. The present study used IR absorption spectroscopy to investigate cuboid and coated diamonds with abundant micro-inclusions, thereby identifying water-containing species trapped in micro-inclusions in diamonds. A detailed study of the temperature behaviour of water-related absorption bands was performed to pursue that goal. Unless

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otherwise stated, we use the term ‘water’ synonymously for H₂O molecules and hydroxyl groups in minerals or glasses.

Samples

Fibrous diamond crystals of cubic habit with abundant micro-inclusions (Fig. 1) were selected, representing samples from different localities (Yakutia (24 crystals), Democratic Republic of Congo (1), and Canada (10)). Individual micro-inclusions are usually no more than several micrometers wide. The samples were polished into 100–200 µm-thick plates. According to IR spectroscopy, most samples were classified as type IaA (the nitrogen is present as a substitutional pair), but nitrogen-free type IIa diamonds were also studied. In some cases, traces of platelets and B-defects (four nitrogens arranged tetrahedrally around a carbon vacancy) were found. The nitrogen concentration reaches 1100 atomic ppm and is not constant within individual crystals. Hydrogen-related lattice defects (peaks at 3107 and 1405 cm⁻¹ and some others) are always detected in infrared spectra.

Methods

The IR absorption spectra were measured using a Fourier-transform infrared (FTIR) spectrometer (Spectra 2000; PerkinElmer Inc.) equipped with

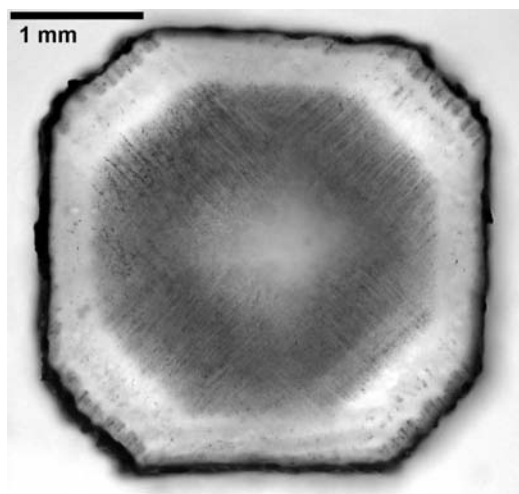


FIG. 1. Polished section of cuboid diamond from Udachnaya kimberlite pipe in transmitted light. Numerous micro-inclusions indicate the fibrous internal structure of the crystal.

an IR microscope. Measurements with a 60 µm × 60 µm beam were conducted in the mid-IR range using a global light source, MCT detector and KBr beam splitter. The resolution of the measurements was 4 cm⁻¹; data were recorded at every 1 cm⁻¹.

A standard procedure for calculating the nitrogen content and determining N-related defects was used. Absorption by the diamond lattice at 2030 cm⁻¹ is used as an internal standard (absorption is 12.3 cm⁻¹, e.g. Zaitsev, 2001). Deconvolution of the spectral envelope in the 1100–1350 cm⁻¹ region gave absorption by nitrogen-related point defects. The concentration of nitrogen in point defects was obtained using a calibration by Woods *et al.* (1990).

A series of heating and cooling experiments was performed to further constrain the properties of fluids in micro-inclusions in diamonds: IR spectra of three samples were measured in the temperature range from -150 to 450°C using a heating/cooling stage (HCCS-1; S.T. Japan, Inc.). The stage was evacuated during measurements to prevent frost formation and sample oxidation. The heating and cooling rates were 5–10°C/min. Reference spectra were obtained on a type IIa diamond crystal at every temperature point corresponding to the sample temperatures. However, no significant change in the reference spectra was observed.

To assign the IR spectra of fluid in natural diamonds, which might be still under pressure, IR spectra of water at high pressure were measured using a diamond anvil cell consisting of a pair of type Ia diamonds with 600 µm flat culets. Because water is a strong IR absorber, a trace amount of H₂O contained in commercial 99.9% D₂O (Sigma-Aldrich Corp.) was used to study pressure-induced changes in stretching and bending vibrations of H₂O. Pressure was calibrated using the ruby-fluorescence method.

Results

Water species in diamond micro-inclusions

Room-temperature observations

Because IR absorption spectroscopy probes the entire thickness of a sample, data obtained here reflect the bulk content of all species in a given volume, including absorption from the host diamond and its lattice impurities (Fig. 2). The presence of the hydrous components is indicated by wide absorption bands between 2800 and 3600 cm⁻¹ and near 1650 cm⁻¹ in IR spectra.

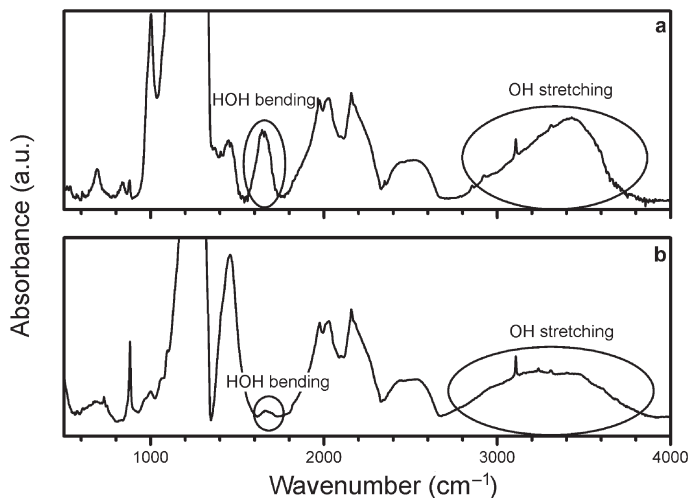


FIG. 2. MIR spectra of cuboid diamonds: (a) sample from Zaire; (b) sample from Udachnaya pipe (Siberia). The IR spectra show features of diamond absorption, impurity defects (N, H), and minerals in inclusions. Water-related absorption is considerable.

These are overlapping OH-stretching (e.g. symmetric and asymmetric) and HOH-bending vibrations, respectively. In addition, H₂O-related absorption bands occur in a very broad spectral range, including the 600–1400 cm⁻¹ region, which was studied in this work. However, it is difficult to assign bands observed in this region to specific water vibrations because they strongly overlap with absorption by abundant silicate and carbonate inclusions in the samples analysed.

The intensities of absorption bands were normalized to diamond lattice modes in the two-phonon region as an internal standard. A technical hurdle in finding intensities is the selection of adequate baselines. The absorption spectrum of an inclusion-free type IIa (nitrogen-free) diamond was used as a reference spectrum. However, the strength of diamond lattice absorption in the three-phonon region is not very well constrained (e.g. Zaitsev 2001). Three-phonon diamond absorption overlaps with OH-stretching vibrations. Therefore, subtractions of nitrogen-free diamond spectra might sometimes introduce an error to the determined intensities of OH components. A similar problem complicates quantitative measurements at high temperatures: the strength of diamond lattice absorption increases slightly with increasing temperature (Davies *et al.*, 2002). However, such errors will not influence peak positions of the OH components. Because the quantitative calibration of

absorption by water and carbonates is strongly sample-dependent, we primarily present absorption in units of cm⁻¹.

Experimentally observed absorption bands of some samples were decomposed into several Gaussian peaks using a commercially available software package to extract information about water phases that are present in micro-inclusions. The number of components was determined from the number of inflection points of each band. An example of those decompositions is shown in Fig. 3. In all the diamonds, the observed absorption bands in the region of HOH-bending vibrations consisted of at least two components: a lower-frequency component (LC) at 1620–1640 cm⁻¹ and a higher-frequency mode (HC) at 1660–1680 cm⁻¹. In one sample, a weak shoulder at ~1705 cm⁻¹ was observed. The ratios of intensities (LC/HC) were in the range 0.2–6; they varied from sample to sample. The ratios of the full-width at half maximum (FWHM, LC/HC) were 0.3–2. The broad absorption band in the 2800–3600 cm⁻¹ region apparently consists of several components. Inflection points were used to estimate the number of these components. At least three distinguishable broad components were observed in each spectrum: 3250–3300 cm⁻¹, 3450–3500 cm⁻¹, ~3600 cm⁻¹. In some cases, weaker absorption was observed at 3100–3140 cm⁻¹ and 3780–3800 cm⁻¹. These bands represent fundamental symmetric and

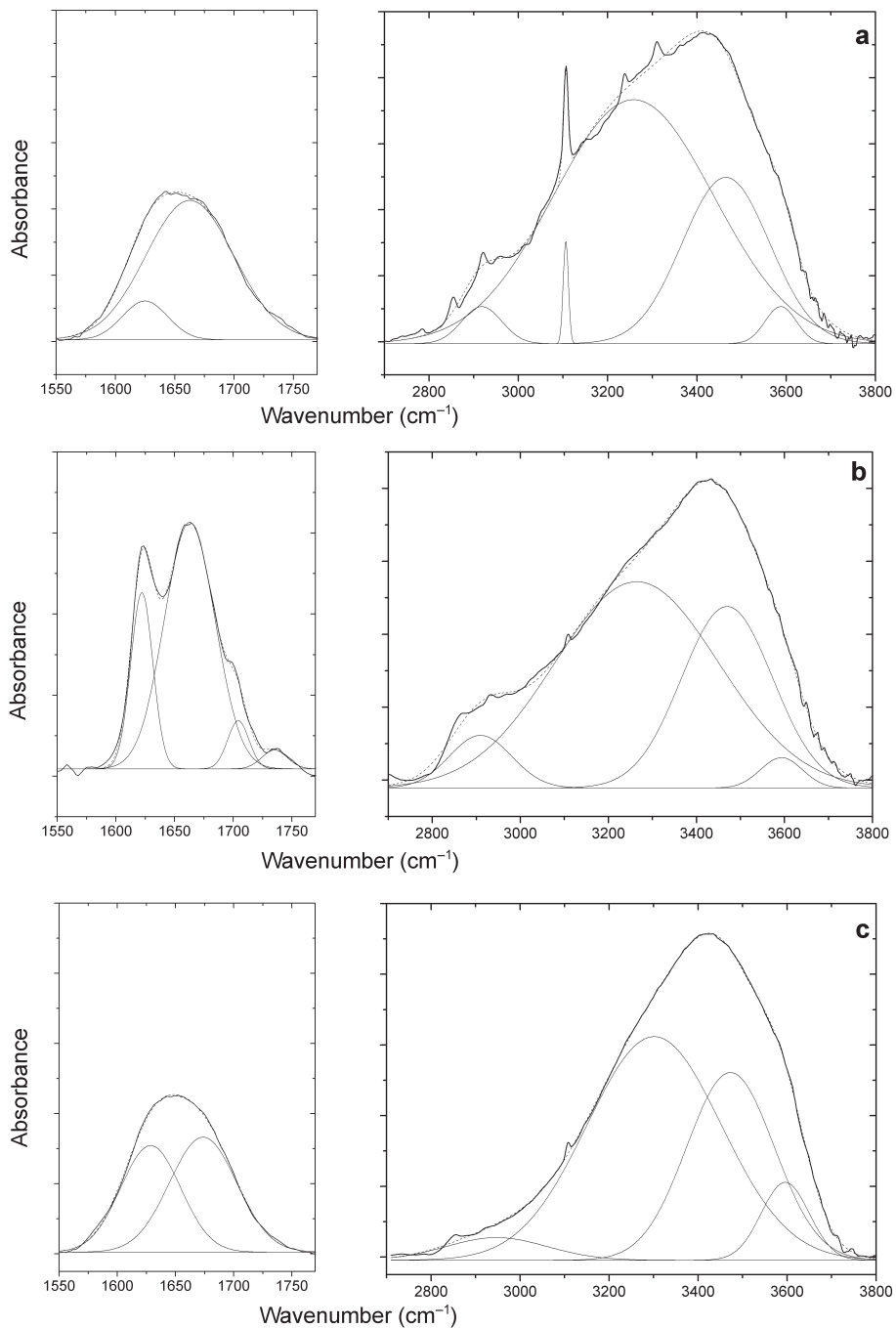


FIG. 3. Examples of decomposition of HOH-bending and OH-stretching bands of cuboid diamonds (*a, b* – Ebelyakh (Siberia); *c* – Zaire). Two or three main components in the bending region and up to seven components were obtained from the least-squares fitting method.

asymmetric OH-stretching modes, as well as overtones and combinations of bending vibrations of water molecules in different aggregate states. In some cases, weaker absorption was observed at $\sim 2860\text{ cm}^{-1}$ and $2900\text{--}2920\text{ cm}^{-1}$. The FTIR spectrometer revealed a pair of peaks near 2855 and 2922 cm^{-1} attributable to some organic coating materials on the optical parts. Usually those two bands are cancelled out by taking a ratio to the reference spectrum. However, when we observe very subtle absorption spectra, those peaks are not canceled out because of the lack of linearity in the MCT detector.

Observations at non-ambient temperatures

Figure 3 shows that the shape of the OH-stretching band is highly variable, even in diamonds from a single locality. Such changes indicate the presence of a variable, sample-dependent hydrous species in the micro-inclusions. To constrain the behaviour of fluids in diamonds, we performed a spectroscopic study of some representative samples in a broad temperature range. Figure 4 shows some spectra at different temperatures (from -150 to 450°C). For consistency, these observations are described by representing the results as a continuous heating from the lowest to the highest temperature.

Bending vibrations

As a general observation, all components in the region of water-bending vibration shifted to higher wavenumbers with heating (the difference was up to 15 cm^{-1}). The exact behaviour of these bands is sample-dependent, indicating that fluids differ from sample to sample. In some diamonds, the effect of heating on the band position can be described as a sequence of increase–plateau–increase; but in other samples, we observed plateau–increase–plateau (see Fig. 5*a,b*). Three important temperature points in the evolution of the bands are $-50\text{--}60^\circ\text{C}$, $150\text{--}160^\circ\text{C}$ and $225\text{--}250^\circ\text{C}$. At these temperatures, a transition from increase to plateau, or *vice versa*, occurs. Changes in band intensities and half-widths occur at those temperatures. All spectral changes were reversible.

Stretching vibrations

The positions of most components observed in the stretching region (as described above) remain relatively constant with heating, although some exceptions exist. The intensities of the bands

change considerably with cooling to -150°C . Decomposition of stretching is not straightforward, mostly because of the band complexity, because of the presence of very different phases with variable thermal evolution. During heating, the shape of the stretching band changes considerably. For example, in some samples, the shoulder at 3560 cm^{-1} , which becomes visible at 200°C , appears as a distinct band at temperatures $>250^\circ\text{C}$. In addition, the absorbance of this band decreases as temperature increases from 25 to 450°C . No change that indicates freezing was observed from the stretching mode of water, even at temperatures as low as -150°C . This observation is consistent with the results of Navon *et al.* (1988), suggesting super-cooled fluids in diamonds.

Other phases

Strong absorption bands attributed to carbonates, at $\sim 800\text{--}900$ and $1430\text{--}1480\text{ cm}^{-1}$, are observed in many diamonds. The relative amounts of carbonates and water depend on sample provenance: samples from the Udachnaya pipe usually contain larger amounts of carbonates (estimated from the absorption band at $1430\text{--}1480\text{ cm}^{-1}$) and smaller amounts of water-related phases than for other sample localities (Zedgenizov *et al.*, 2004). It is important to note that the presence of carbonates does not always imply the presence of hydrous phases. Similar to fibrous diamonds described from other localities (e.g. Navon *et al.*, 1988), our samples also show absorption by silicates (e.g. quartz) and phosphates (e.g. apatite). Rarely, weak absorption by CO_2 molecules is observed.

Discussion

Interaction of water molecules with surrounding ions (proton solvation) leads to a change of the force constant of bending and stretching vibrations. Consequently, the positions of absorption bands and their evolution with temperature and pressure depend on solution chemistry and on the aggregate state of water. Observations of several water-related components in absorption spectra of fibrous diamonds do not necessarily imply that all these phases are present in every micro-inclusion. The probing beam samples the overall thickness of the diamond plate, thereby giving an averaged picture of all compositionally different inclusions present in the beam path. An explanation of the spectra obtained in the present study and tentative

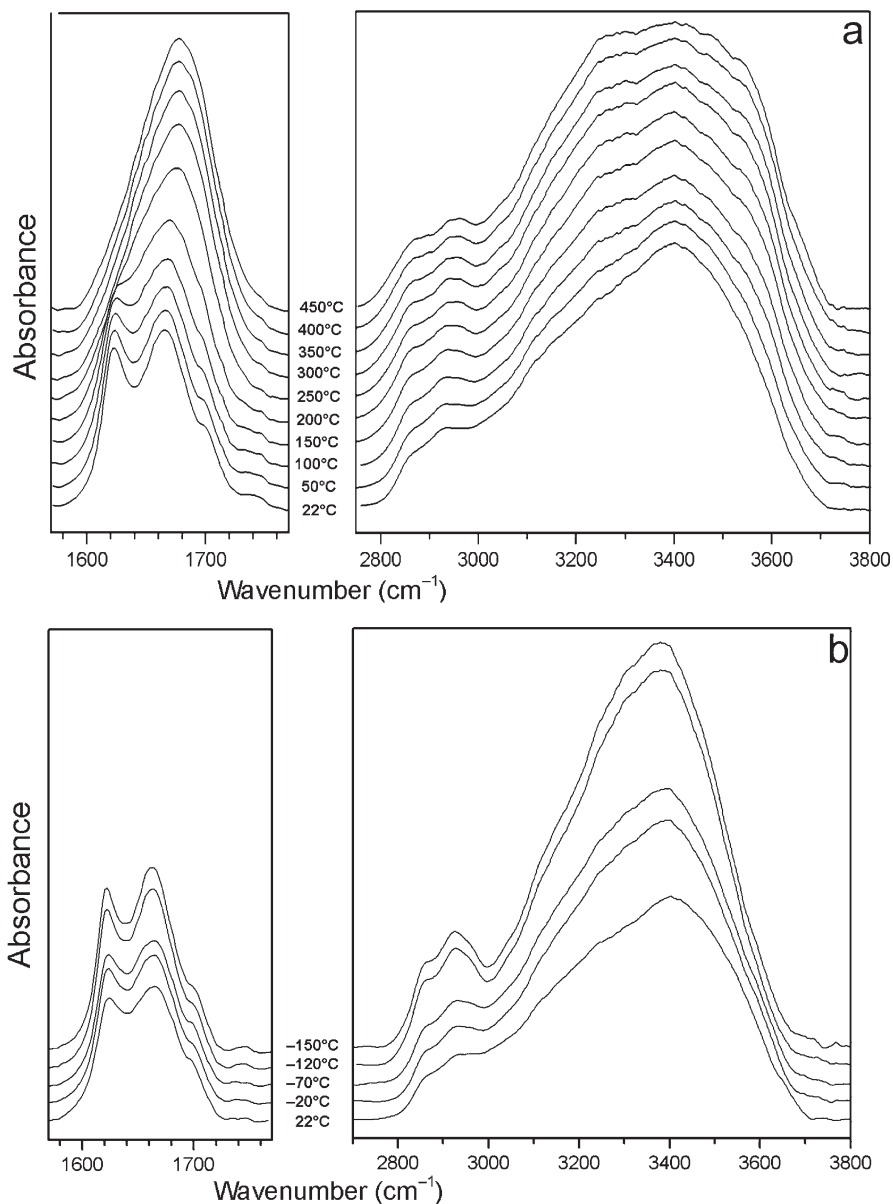


FIG. 4. (a,b) Absorption spectra of HOH-bending and OH-stretching vibrations in Siberian cuboid diamond at different temperatures.

identification of hydrous phases that are present in inclusions are presented here.

Which water phases do we observe?

Analyses of the spectrochemical literature (e.g. Nakamoto, 1970; Yuhnevich *et al.*, 1973; Lutz

1988; Chang *et al.*, 2000) and our own research at high pressures suggest several main candidates for phases of inclusions: (1) high-pressure ice polymorphs; (2) solutions with different chemical compositions; and (3) hydrates. Different types of the compounds mentioned are present in inclusions in a single diamond.

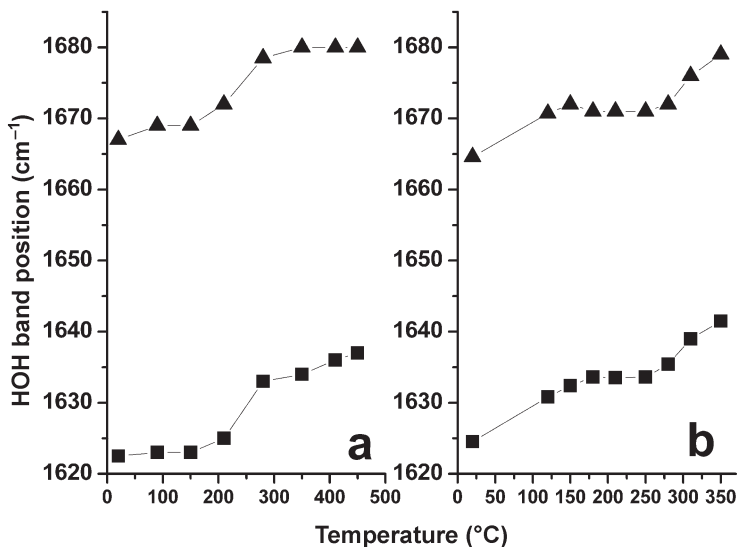


FIG. 5. (a,b) Positions of low-frequency and high-frequency bending components (see text) illustrating two different types of evolution with temperature: (a) sample EK1, (b) sample EK3 (both from the Ebelyakh alluvial deposit, Northern Siberia).

High-pressure polymorphs of water

It is also well known that, in many cases, micro-inclusions in diamonds preserve high residual pressures up to 5 GPa, but usually not greater than 2 GPa (Navon, 1991; Schrauder and Navon, 1993). The phase diagram of water at pressures lower than 4 GPa is very complex. At room temperature, pure water undergoes a phase transition to form ice VI at ~ 0.6 GPa, and to ice VII at ~ 1.8 GPa. Liquid water might be in equilibrium with ices Ih, III, V, VI and VII. Ice polymorphs have slightly different structures. For that reason, their vibration bands are polymorph-dependent. To assign the absorption components in bending and stretching regions, IR absorption spectra of H₂O phases were measured at high pressure (up to 5.02 GPa) and room temperature. Representative spectra are shown in Fig. 6. The present study shows that the bending vibration of liquid water is observed at ~ 1650 cm⁻¹. It shifts to 1690 cm⁻¹ and to 1620 cm⁻¹ in ice VI and ice VII, respectively. It is noteworthy that the considerable half-width of the bending mode does not allow unique identification of water phases because, for different ice polymorphs, this band could be narrower (e.g. ice VII) or broader (e.g. Ice VI) than the band in liquid water. In our study, the ratio of FWHM of low-frequency to high-frequency bending components in natural diamond samples varies among samples. It is

usually in the range 0.2–0.4, but values up to 2 were observed.

The main fraction of water in cuboids exists in liquid form (Navon *et al.*, 1988). In a previous study, the authors suggested that the high surface-to-volume ratio of the micro-inclusions or high solute content of the residual fluid engendered supercooling, even at high pressure, where high-pressure ice phases are the stable forms of water. The evidence for ice VI as an inclusion in a cuboid diamond from Democratic Republic of Congo was obtained from the observed shoulder absorption at 5000 cm⁻¹ arising from ice VI at 1.9 GPa in near-IR spectroscopy (Kagi *et al.*, 2000). The majority of fluid inclusions, however, consist of liquid water in the diamonds; the ice VI was a minor component. Some components observed in this work at ~ 3230 cm⁻¹ might be related to ice. However, this assignment is not unique: hydrous species with strong hydrogen bonds might also be responsible for this band (Aines and Rossman, 1984; Lutz, 1988). The complexity of the stretching band that we observed (e.g. Fig. 2b) indicates that different species might be present in the samples.

Aqueous solutions

Each solute disturbs the structure of the liquid water leading to changes in vibrations of the H₂O

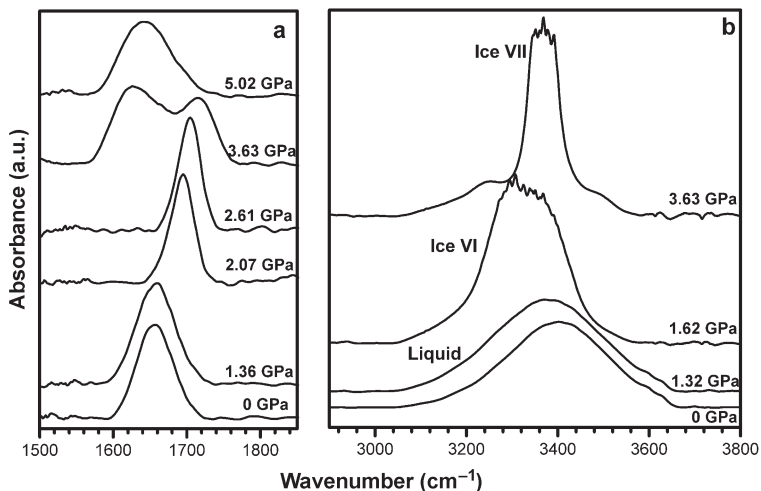


FIG. 6. Representative MIR spectra of water at high pressures and room temperature observed using a diamond anvil cell. Pressure-induced phase transitions (liquid water – ice VI – ice VII) were observed.

clusters. It therefore alters the spectra of solutions. In general, with increasing strength of hydrogen bonds or decreasing hydrogen bond distance, the frequency of OH-stretching decreases and that of HOH-bending vibration increases (Nakamoto, 1970). The change in hydrogen bond characteristics depends on the solutions' compositions. The HOH-bending vibration mode shifts to lower frequency in a chloride solution and to higher

frequency in a carbonate solution, whereas the OH-stretching mode moves to higher frequency in a chloride solution and to lower frequency in a carbonate solution (as illustrated in Fig. 7 for NaCl- and Na₂CO₃-saturated aqueous solutions). The magnitude of shifts in such fluids depends on the charge and ionic radii of the cations because both can affect the dissociation of the water molecules.

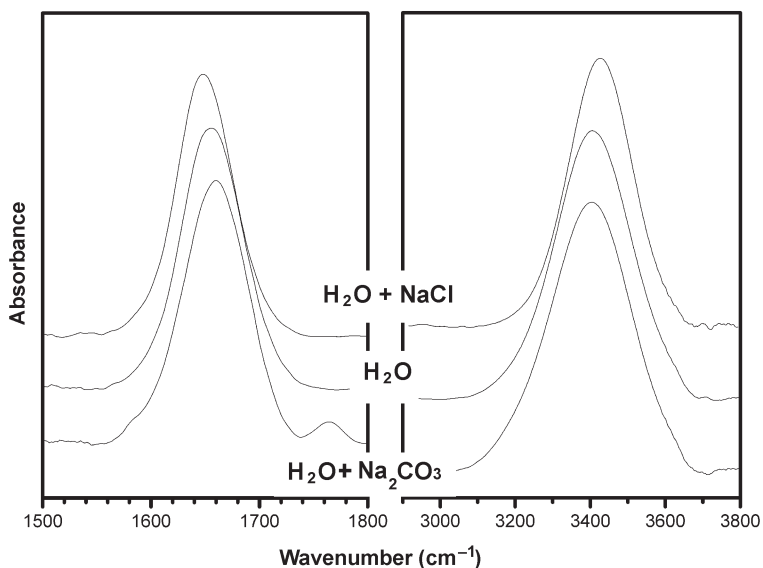


FIG. 7. IR absorption spectra of HOH bending and OH stretching of liquid water and NaCl and Na₂CO₃ oversaturated aqueous solutions.

The presence of pure water in natural diamonds is unlikely because water is quite an aggressive solvent at mantle conditions. A salinity of ~4.4 wt.% in NaCl-eq and residual pressures of 0.6–0.8 GPa were recently estimated in a cuboid diamond from the DRC (Kagi *et al.*, 2006). Usually, the IR spectra of a solute the compositions of which are geochemically reasonable are variable only in the fine structure. However, structures observed in diamonds in the present study vary widely (see Figs 2 and 3) implying that the differences in solute compositions alone cannot explain the variability of observed spectra.

This study revealed IR absorption bands at 1700 cm^{-1} in some samples. The high-frequency component disappeared at high temperature, as shown in Fig. 4a. The change was reversible and the high frequency component reappeared when the sample was cooled to room temperature, suggesting that this high-frequency component was derived from a phase that was soluble at high temperature. The phase cannot be determined exclusively from the spectra, but silicate gel with strongly bound water molecules, or complexes of H_xO_y^+ type (e.g. H_5O_2^+) are candidates.

OH groups in minerals and hydrates

Aside from molecular water, the presence of hydrated minerals in micro-inclusions is also possible. Water-containing minerals might be important reservoirs of hydrogen in fibrous diamonds. Because sharp lines that are unrelated to hydrogen in diamond are not observed in IR spectra of the studied samples, identification of these minerals from positions of their OH bands is difficult.

The IR data obtained indicate the existence of at least two water phases in the same diamond crystal. The liquid phase is probably embedded as a residual fluid between the solid phases in a micro-inclusion and the diamond matrix. It is tempting to use the temperature behaviour of water-related bands for better identification of phases in inclusions. The evolution of intensities of different bands observed in the stretching region is complicated. Some bands strengthen as a result of heating, probably reflecting the very inhomogeneous system being observed.

For pure liquid water, the stretching modes shift to higher wavenumbers with a decrease in intensity during heating. The bending band shifts to lower wavenumbers and becomes more intense. Our samples showed an almost complete absence

of a shift in the positions of stretching vibrations, whereas bending modes are shifted to higher wavenumbers. It is also known that an increase in temperature usually weakens hydrogen bonds; in the case of strongly bent and (asymmetrically) bifurcated hydrogen bonds, the bond might strengthen during heating (Lutz, 1988).

Inclusions with ‘pure’ water (i.e. diluted solutions with small amounts of solutes, modifying H_2O molecules) behave ‘normally’ and the intensity of stretching vibrations decreases, but ices and concentrated solutions might behave differently. Especially important is the different thermal evolution of different compounds. Another complication arises from the possible *in situ* formation of new ionic complexes caused by melting and mixing of inclusion components. The chemical variability of fluid compositions influences the thermodynamics of phase transitions. For example, the presence of carbonate ions considerably increases the pressures of water-ice VII transformation (Martinez *et al.*, 2004). All these processes together might result in sluggish changes of band position reflected in IR spectra. The frequency of bending vibrations of liquid water or of its high-pressure polymorphs is known to be rather insensitive to pressure if no phase transformation occurs. Therefore, the plateaux that we observed indicate fields of stability of a given water phase and temperature regions where band-position changes indicate ongoing phase transition.

To identify a water phase uniquely, an independent pressure calibrant is required, such as an inclusion containing water and quartz, with well-constrained spectral characteristics under high pressure.

Mantle fluids

Fluid inclusions in diamonds are the deepest available samples of mantle fluids. For that reason, they are important for studies of general mantle geochemistry. Supercritical water is an aggressive solvent at mantle conditions and might dissolve many components. For example, micro-inclusions in cloudy diamonds from Koffiefontein are reported to contain brines or highly saturated aqueous solutions with average mass proportions of ~30–42% water, 19–22% Cl, 14–17% Na and K, 22–25% Fe-Ca-Mg-carbonates, and 3–4% silica (Izraeli *et al.*, 2001). Previously, Schrauder and Navon (1994) proposed the existence of two main fluids that are responsible for diamond

formation: hydrous-silicic and carbonatitic. Such solutions might also mobilize sulphate and phosphate minerals and would have important consequences for redistribution of incompatible elements. Although the origin of diamond carbon and nitrogen remains unresolved, these fluids may serve as their carrier. Changes in water and oxygen fugacity influence the solubilities of these elements in surrounding rocks. Therefore, they might induce diamond precipitation or growth.

Micro-inclusions within a single diamond might carry different hydrous solutions. This heterogeneity probably reflects the presence of tiny growth zones that grew from slightly different fluids. This fine zoning might reflect an interrupted growth process, or be a consequence of thermal pulses. It has been shown (Vailati and Giglio, 1997) that when two immiscible fluids are rapidly heated to their miscibility point, huge fluctuations in their fluid composition can occur. Fluctuations in the chemical composition of micro-inclusions might therefore reflect the occurrence of distinct thermal events. The results of this study show that diamonds from a single kimberlite pipe have trapped various hydrous components. In some cases, even single diamonds contain fluids of various compositions. Presumably, such heterogeneity indicates that a single kimberlite pipe might collect fibrous diamonds that were formed in several growth events.

It is also important to mention that studies of fibrous diamonds are not necessarily applicable to 'normal' diamonds with silicate or sulphide inclusions. It is very likely that the majority of all diamonds grew in the presence of metasomatic fluids. However, fluid-bearing inclusions are found mostly in diamonds with a fibrous internal structure. The apparent lack of fluid or carbonate inclusions in common monocrystalline diamonds might indicate completely different growth media for diamonds without fibrous structures. More experimental work is required before a consistent model for diamond formation can be produced.

Conclusions

The present spectroscopic investigation of fibrous diamonds revealed two or more water-related components preserved in micro-inclusions. High residual pressures in inclusions suggest their syngenetic origin. The existence of several water phases or water solutions within a single diamond crystal is probably attributable to the difference in

the structure of water and high-pressure polymerization. The structure of water is not clear, but water in natural diamonds definitely contains hydrous phases, and not only as fluid inclusions. Differences in fluids in fibrous diamonds from a given kimberlite pipe presumably indicate that several diamond-forming events occurred.

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