

Carbonatitic melts in cuboid diamonds from Udachnaya kimberlite pipe (Yakutia): evidence from vibrational spectroscopy

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ABSTRACT

Micro-inclusions (1–10 µm) in 55 diamonds of cubic habit from the Udachnaya kimberlite pipe have been studied using vibrational spectroscopy. This has revealed a multiphase assemblage in cuboid diamonds from the Udachnaya kimberlite pipe. This assemblage includes carbonates, olivine, apatite, graphite, water and silicate glasses. The micro-inclusions preserve the high internal pressure and give confidence that the original materials were trapped during growth of the host diamond. The internal pressures, extrapolated to mantle temperatures, lie within the stability field of diamond and the relatively low temperatures are typical for the formation of cuboid diamonds. In contrast to previously reported data for African diamonds, the micro-inclusions in the cuboids from Udachnaya are extremely carbonatitic in composition ($H_2O/(H_2O+CO_2) \approx 5-20\%$) with the observed assemblage of micro-inclusions similar to some types of carbonatites. The low water and silica content testify that the material in the micro-inclusions of the Udachnaya diamonds was near-solidus carbonatitic melt. Vibrational spectroscopy has provided the evidence of carbonatitic melts in cuboid diamonds.

KEYWORDS: carbonatitic melt, diamonds, Udachnaya kimberlite pipe, vibrational spectroscopy, inclusions.

Introduction

INCLUSIONS in crystals provide important information about their formation. Previous investigations of crystalline inclusions in diamonds have revealed either peridotitic or eclogitic mineral paragenesis (Sobolev, 1974; Meyer, 1987). Most concepts of diamond genesis are based on this observation. Although many scientists supposed diamond genesis to be associated with the presence of fluids or volatile-rich melts, direct evidence for deep mantle fluids is scarce. From this point of view, diamonds of cubic habit are one of most attractive diamond populations. Relatively large inclusions in such diamonds are rarely found, but most of them usually contain numerous tiny inclusions with a size of less than several µm. The first infrared (IR) spectroscopic

study on such diamonds revealed the presence of water and carbonates (Chrenko *et al.*, 1967), and later silicates, apatite, quartz and CO₂ were identified among micro-inclusions using the same technique (Navon *et al.*, 1988). Transmission and analytical electron microscopy (TEM and AEM) have also been used to identify the presence of apatite, carbonates, mica and quartz (Lang and Walmsley, 1983; Guthrie *et al.*, 1991; Walmsley and Lang, 1992*a,b*). It was suggested that the assemblage of micro-inclusions represents a mantle-derived fluid or volatile-rich melt, which was trapped in the diamonds as they grew.

X-ray topographic studies have shown that the majority of diamonds with cubic habit have a fibrous internal structure and these diamonds were distinguished as a special group of cuboids (Sunagawa, 1990). In the earlier classification proposed by Orlov (1977), cuboid diamonds were distinguished as varieties of diamonds II and III. In many cases, so-called 'coated' diamonds have a fibrous coat and cubic habit. According to

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Orlov's classification, coated diamonds represent variety IV. Sunagawa (1990) proposed that fibrous diamonds are formed by a different growth mechanism from that of the predominant octahedral diamonds, and are believed to have crystallized fast as a result of a high degree of supersaturation. This rapid growth favours the entrapment of inclusions of the diamond-forming medium, and it has been shown that micro-inclusions in cuboids preserve a high residual pressure of 1.5–2.1 GPa (Navon, 1991; Kagi *et al.*, 2000). The extrapolation to mantle temperatures (1000–1300°C) yields pressures of 4–7 GPa. Micro-inclusions can therefore provide evidence about the deepest available fluids. Their characterization is very important in the understanding of the role of fluids in mantle metasomatism and diamond genesis.

In fibrous diamonds from Jwaneng (Botswana), the bulk composition of fluid trapped in micro-inclusions varies continuously between two endmembers: carbonatitic and hydrous (Schrauder and Navon, 1994); the methods used were electron-probe microanalysis (EPMA) and IR spectroscopy, because vibrational spectroscopy typically provides a unique signature of a given mineral structure. The measurement of such spectra is therefore extremely useful for identifying the phases included in diamonds. Here, we report new results from *in situ* observations of

micro-inclusions in diamonds from Udachnaya kimberlite pipe using IR and Raman spectroscopy. The Udachnaya pipe, located in the central part of the Yakutian diamondiferous province, Siberia, Russia, was chosen because cuboids with micro-inclusions form a comparatively high proportion of the diamond population.

Samples and methods

The 55 crystals of cubic habit with abundant micro-inclusions (Fig. 1a) were selected from the diamond collections of the Udachnaya kimberlite pipe. The selected diamonds were colourless to yellow and greenish-yellow crystals of 1–3 mm in size. The samples were polished into thin slabs of 100–200 μm thick. The size of individual micro-inclusions observed in the samples is usually less than several μm , but in rare cases some of them may reach 10–15 μm (Fig. 1b). Previous X-ray topography of some samples showed that their internal structure consisted of sub-parallel fibres, which expand throughout the crystal along the direction of octahedral growth (Zedgenizov *et al.*, 1999); the growth direction of fibres is also traced by numerous tiny inclusions (see Fig. 1a). Between individual fibres there are small angular differences, the largest differences being between different growth sectors of the cuboid. These differences in orientation, along

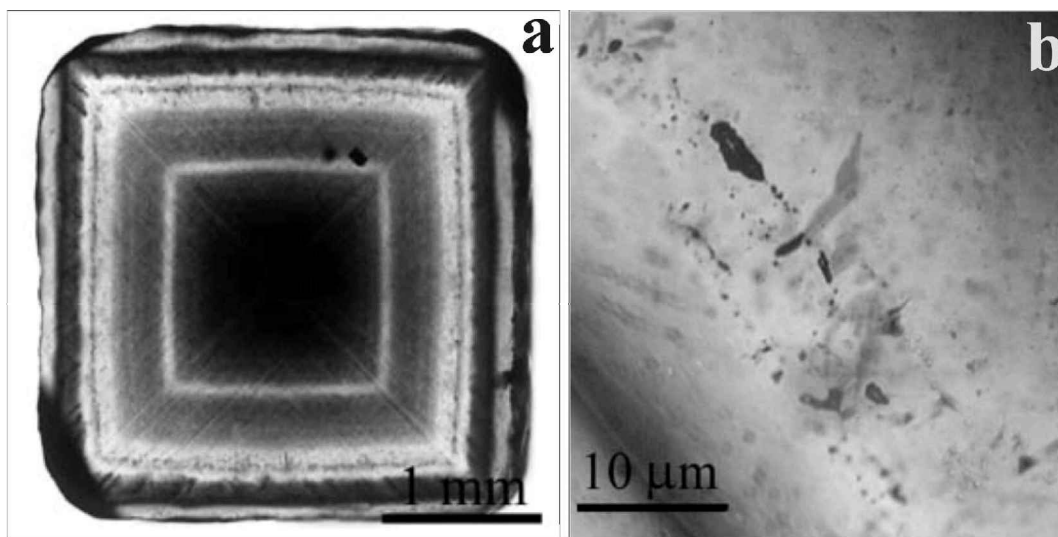


FIG. 1. Micro-inclusions in cuboid diamonds from Udachnaya kimberlite pipe. (a) A polished section of sample Ud-02-107, showing zonal structure. Micro-inclusions trace the fibrous internal structure. (b) Higher magnification micrograph of sample Ud-02-107. Individual micro-inclusions reach several μm in size. Transmitted light.

with the presence of numerous micro-inclusions, lead to strong strain inside the crystals which is recognized from birefringence patterns. According to IR spectroscopy, all the samples studied are classified as type IaA. An impurity of hydrogen (peaks at 3107 and 1405 cm^{-1} (Woods and Collins, 1983)) is always present. The absorption intensity of the main hydrogen peak at 3107 cm^{-1} in the studied cuboids varied from 1 to 5 cm^{-1} in the absorption coefficient. The concentration of nitrogen was estimated to be in the range 400–1100 ppm; the nitrogen abundance is not constant within individual crystals and may vary within the above limits.

The IR absorption spectra were measured using a Perkin Elmer Spectra 2000 Fourier-transform infrared (FTIR) spectrometer equipped with an IR microscope. With an aperture of $60 \times 60 \mu\text{m}$, IR measurements were performed using a combination of a globar light source, MCT detector and KBr beam splitter. Infrared spectra of bulk samples were collected with a combination of the globar light source, TGS detector and KBr beam splitter in the mid-IR region, and with a halogen light source, InSb detector and quartz beam splitter in the near-IR region. The absorption coefficient was determined with correction for lattice modes in the 2-phonon region. The nitrogen defect abundance was calculated from the ratios proposed by Woods *et al.* (1990).

Raman spectra were obtained on a 30 cm single polychromator (Chromex, 250is), equipped with an optical microscope (Olympus, BX60), Ar⁺ Laser (514.5 nm; Ion laser technology, 5500 A), a CCD camera with 1024×256 pixels (Andor, DU420-OE) installed at the Laboratory for Earthquake Chemistry, University of Tokyo. The Rayleigh line was removed by using a holographic supernotch plus filter (Kaiser, HSPF-514.5-1.0). The excitation laser beam was focused on a spheroidal spot of $\sim 1 \times 1 \times 5 \mu\text{m}$ in volume using an Olympus $\times 100$ objective lens (N.A. = 0.95) with a confocal arrangement that allows us to pick up signals exclusively from fluid inclusions. Raman shift is calibrated using Raman lines of naphthalene at 513.6, 763.5, 1021.3, 1147.3, 1382.3, 1464.3 and 1576.3 cm^{-1} . Typical analytical uncertainty in the range of olivine bands is $\sim 1 \text{ cm}^{-1}$.

Several selected samples were investigated by energy-dispersive spectroscopy (EDS). This study was carried out using an Hitachi S-530 scanning electron microscope equipped with EDX Kevex-ray 3200-0380.

Results

In the present study, IR spectra were recorded both from whole crystals and from individual zones saturated with micro-inclusions. The amount of trapped material is variable even in individual samples but the average composition in different zones is quite uniform. Since IR absorption spectroscopy samples the optical signals from the entire thickness of the sample, the data obtained here reflect the bulk content of all species in a given volume, including absorption from diamond and its lattice impurities (i.e. nitrogen and hydrogen). To complement this, micro-Raman spectroscopy has been used for phase identification in the individual micro-inclusions because of its high spatial resolution ($\sim 1 \mu\text{m}$). The integrated IR and Raman spectroscopic investigations have permitted the characterization of a multiphase assemblage of micro-inclusions. In cuboids from Udachnaya this assemblage includes carbonates, olivine, apatite, graphite, water and silicate glasses.

Carbonates

Both IR and Raman spectra have revealed that carbonates are the most abundant phase in the micro-inclusions of the Udachnaya diamonds. The presence of carbonates has been determined by their distinctive absorption in the IR spectra, a wide band at $1420\text{--}1450 \text{ cm}^{-1}$ due to asymmetric stretch (ν) and sharp peaks at $860\text{--}890 \text{ cm}^{-1}$ caused by out-of-plane bending (ν) (McMillan and Hofmester, 1988). The intensities of these two characteristic carbonate bands are always correlated in spite of the variation in the concentration of micro-inclusions within single crystals. In some cases, the band at $1420\text{--}1450 \text{ cm}^{-1}$ has an asymmetric structure with several modes (Fig. 2a). There are usually two peaks in the wavenumber range $860\text{--}890 \text{ cm}^{-1}$ as well. This appears to be due to the pressure effect as was shown experimentally for carbonates (Biellmann and Gillet, 1992). However, this observation was shown to be correct only when the whole crystal spectra were recorded ignoring sample heterogeneity. The IR spectra recorded from separate zones of the same crystals are usually different. We have not observed signs of pressure effects on carbonates in the spectra of separate zones of individual crystals. In these instances, carbonates in micro-inclusions in some cuboids are of

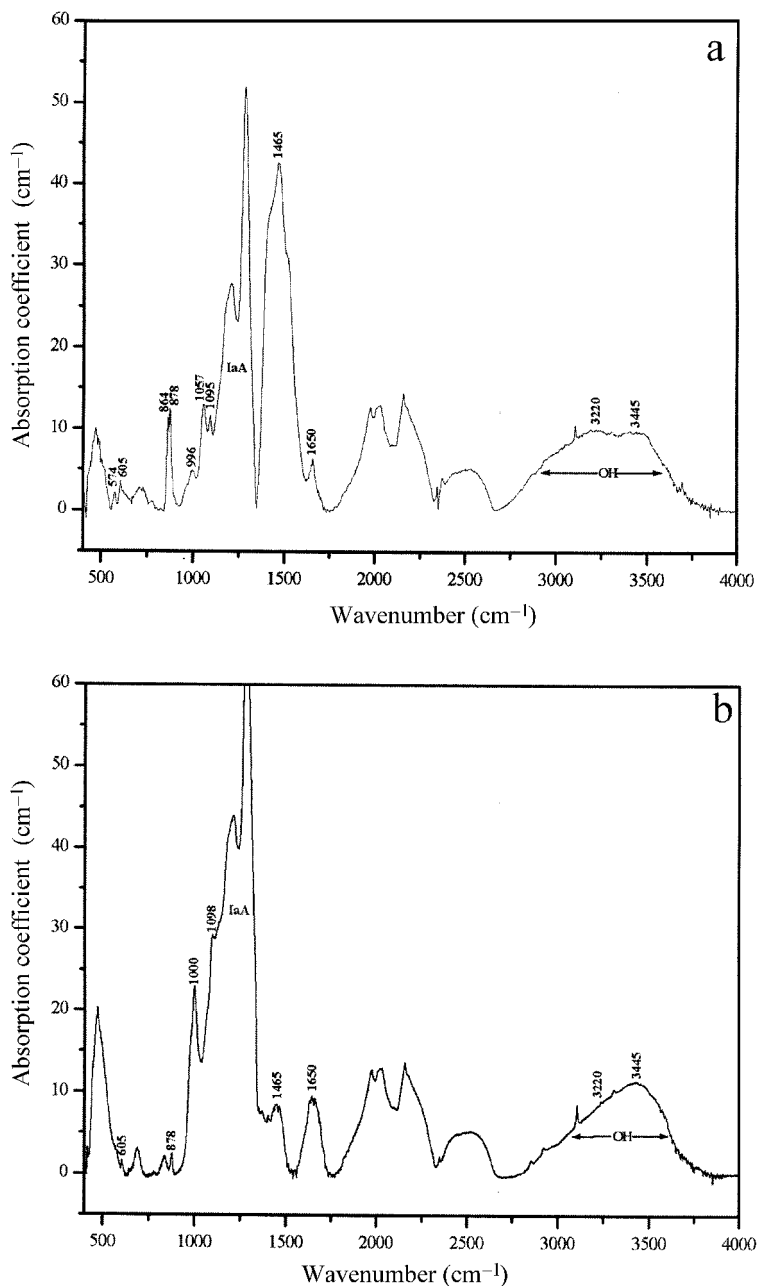


FIG. 2. Mid-IR spectra of cuboid diamonds: (a) sample UD-02-160 from Udachnaya pipe; (b) sample SL-3-9 from Snap Lake, Slave craton (for comparison). The IR spectra reflect all the species including diamond absorption and impurity defects such as nitrogen and hydrogen. For more details see the text.

variable composition compared with those under high residual pressure.

In the Raman spectra of individual micro-inclusions, we observed two different sets of

carbonate peaks: 1088, 713, 283 cm^{-1} and 1098, 727, 308 cm^{-1} (Fig. 3a,b) which can be attributed to two internal modes (ν_1 , ν_4) and libration mode (L). Disregarding the significant pressure influ-

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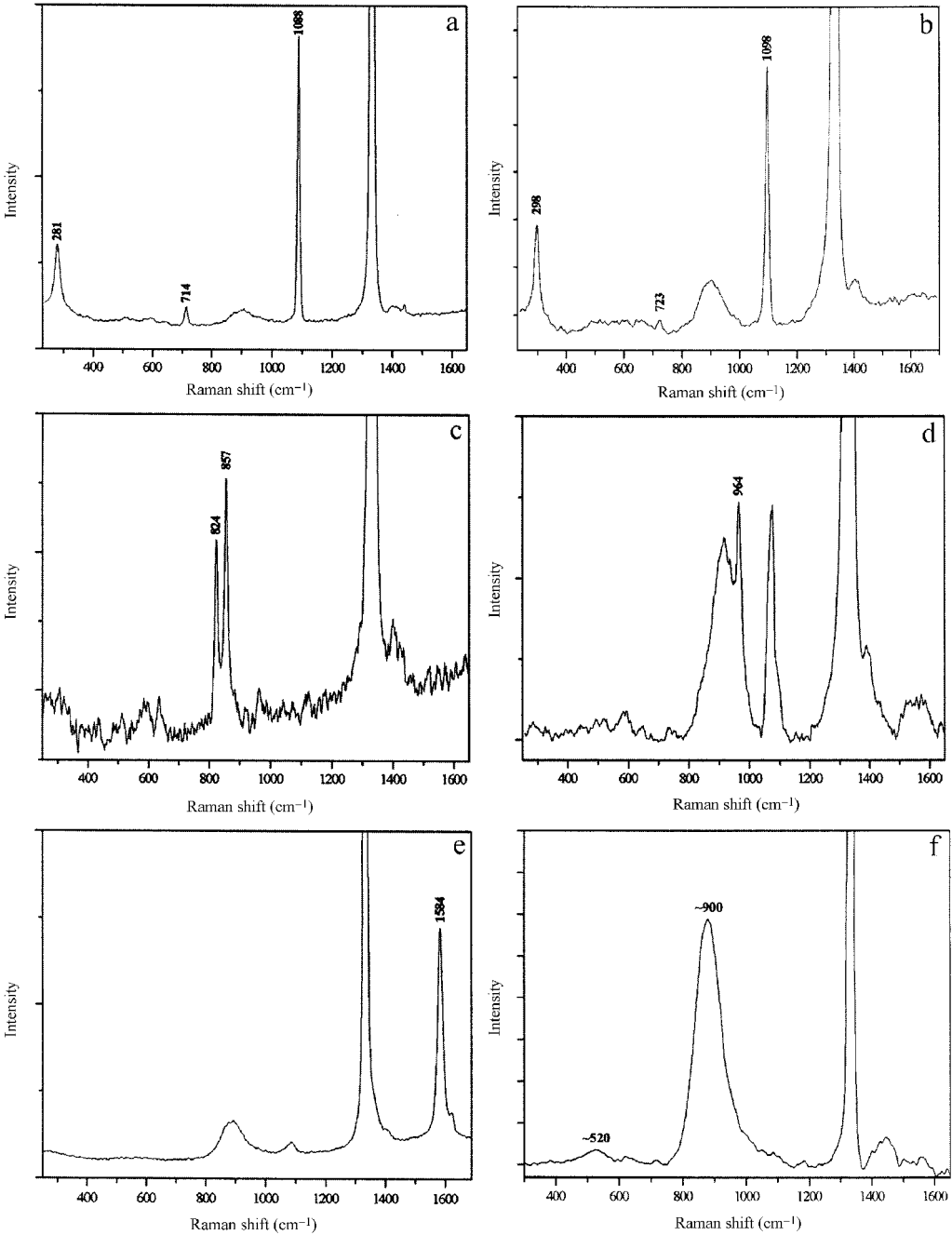


FIG. 3. Raman spectra of an individual micro-inclusion indicating multi-phase assemblage: (a,b) Ca-carbonate (calcite) and Ca-Mg-carbonate (dolomite) in the same sample; (c) olivine; (d) apatite, in association with carbonate and silicate glass; (e) graphite; (f) silicate glass.

ence, these two series generally correspond to Ca and Ca-Mg carbonates: calcite and dolomite. It

should be noted that dolomite is a more abundant phase in the micro-inclusions than calcite. The

presence of both carbonates together was observed in only a few samples. Micro-inclusions containing calcite are usually located in the outer part of crystals while inclusions with dolomite occur in the centre. The same distribution of carbonates within the samples is also supported by the results of IR mapping.

Olivine

Olivine is the most abundant diamond inclusion and also the main mineral of peridotitic mantle xenoliths. Here, we report the first find of olivine as a micro-inclusion phase in fibrous diamonds. In comparison with carbonates, however, olivine is a less common phase in fibrous diamonds. Raman study indicates that the olivine usually accounts for <10% of the individual micro-inclusions. In Raman spectra, olivine generally has two sharp peaks, at 822 and 854 cm^{-1} , both corresponding to vibrational modes of SiO_4 tetrahedra of the structure of olivine (α -phase). However, we always observed the shift of these two characteristic olivine peaks to higher frequencies, up to 831 and 859 cm^{-1} , respectively, in the studied cuboid diamonds (Fig. 3c). According to the experimental data, these shifts result from a pressure effect: Besson *et al.* (1982) and later Wang *et al.* (1993) measured the pressure dependence of high-frequency Raman bands of forsterite, and showed that peak positions are linearly correlated with pressure up to 70 GPa. The observed shifts of olivine peaks in Raman spectra are therefore likely to be due to the high residual pressure of micro-inclusions encapsulated in cavities in cuboid diamonds.

Apatite

Most IR spectra of cuboids from the Udachnaya pipe show bands at 575 and 606 cm^{-1} , which can be attributed to IR absorption of phosphate. These two bands are similar in position and shape to the doublet of apatite. The presence of apatite in Zairean diamonds was reported by Navon *et al.* (1988) based on IR spectroscopy. Apatite has also been found in a TEM and AEM study of micro-inclusions in coated diamonds (Lang and Walmsley, 1983; Guthrie *et al.*, 1991).

The presence of apatite in individual cavities has been also identified by an intense line at 964 cm^{-1} in the Raman spectra (Fig. 3d). The weaker characteristic modes of apatite are usually not so obvious because of the low signal/noise

ratio. Based on Raman spectroscopy, apatite in individual cavities is almost always associated with carbonates. The apatite line was observed in 5–10% of the micro-inclusions examined.

Graphite

The Raman spectroscopic observations revealed that many of the micro-inclusions contain graphite (50–90% of inclusions depending on samples). In individual cavities, graphite is usually associated with other phases. Graphite was identified by the band near 1582 cm^{-1} in the Raman spectra (Fig. 3e). The position and shape of this band varies significantly from sample to sample (Fig. 4). The disorder of the graphite structure has a marked effect on the Raman spectrum; with increasing disorder, the main Raman band of graphite broadens, and moves to higher frequency, while a new broad band appears at 1350 cm^{-1} and increases in intensity (Lespade *et al.*, 1984). In the present study, the upshifts (shifts to higher wavenumber) of the main band observed in the graphite inclusions are larger than those expected from structural disordering (Kagi *et al.*, 1994). This disorder may result from deformation under high pressure (Zhenxian, 1990). We therefore suggest that the upshift and broadening of the graphite band observed in the present study may also be due to pressure. The residual pressure will be estimated in the discussion section.

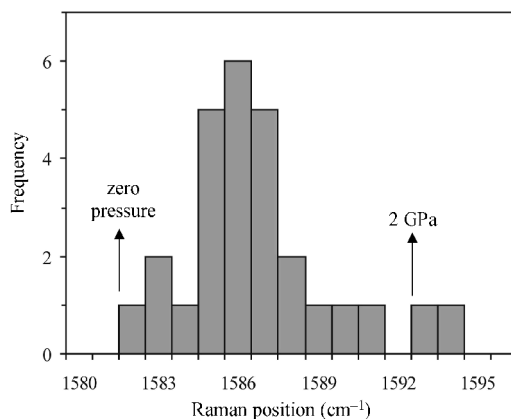


FIG. 4. Distribution of Raman frequencies of graphite at near 1582 cm^{-1} . The upshift of this band corresponds to residual pressure up to 2 GPa and higher.

Water

Present and previous studies (Chrenko *et al.*, 1967; Navon *et al.*, 1988) have shown that almost all samples with numerous micro-inclusions have water-absorption characteristics. The presence of hydrous components is determined by wide absorption bands at $3200\text{--}3400\text{ cm}^{-1}$ and 1630 cm^{-1} in the IR spectra. As such, it consists of two overlapping fundamental OH-stretching motions (symmetric 3220 cm^{-1} and antisymmetric 3445 cm^{-1}) and one H_2O -bending (1630 cm^{-1}) motion (Rossman, 1988). The prominent OH and H_2O absorption positions in the IR spectra are host dependent.

We find that there are two distinctive features of water absorption for cuboids from the Udachnaya kimberlite pipe, compared with those from Central Africa and Canada (Fig. 2). Firstly, the higher intensity of OH-stretching occurs at 3220 cm^{-1} rather than at 3445 cm^{-1} . Secondly, (possibly as a result of the first), there is a discrepancy between the OH-stretching modes and the H_2O bending mode (Fig. 5). The lack of hydrous components is typical of the more carbonate-rich samples from Udachnaya, and suggests that water is dissolved in other phases mainly as the hydroxyl-group and not as molecular water.

Silicate glass

The IR spectra of cuboids saturated with micro-inclusions show several strong absorption bands in the region $1000\text{--}1200\text{ cm}^{-1}$, which are attributed to silicates (Navon *et al.*, 1988). Raman spectroscopy has revealed only one silicate – olivine, but the characteristic lines of olivine were not clear in the IR spectra of our samples. One or more other silicate phases may, therefore, also be present in these cuboids. Raman spectra of individual micro-inclusions have a wide band at 900 cm^{-1} (Fig. 3f). This band is accompanied by much less intense bands at lower frequencies. In position and configuration of the bands, the spectra are almost identical to Raman spectra of Ca-Mg silicate glasses with low silica concentration (the ratio $(\text{Ca}+\text{Mg})/\text{Si} > 1.8$) (McMillan and Wolf, 1996). Moreover, in the same micro-inclusions, we found a band at 3500 cm^{-1} showing the presence of water species as observed in glass phases.

The silicate glasses were observed in ~90% of the studied cavities in cuboids from the

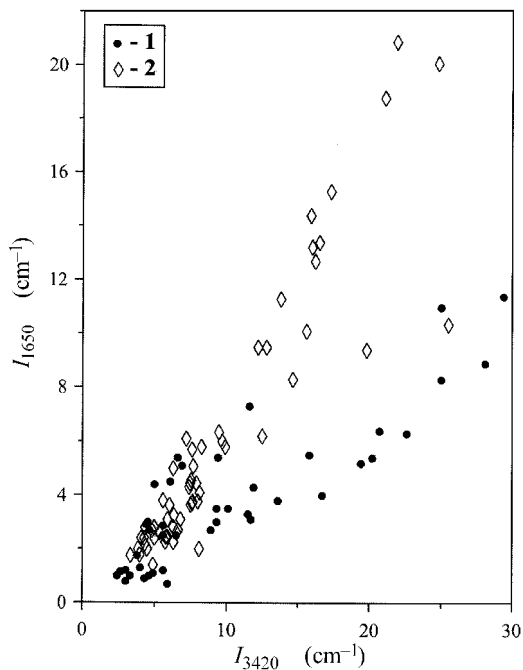


FIG. 5. The relation of intensities of H_2O (1650 cm^{-1}) and OH (3420 cm^{-1}) IR absorption modes for diamonds from Udachnaya (1) and other localities (2). The other localities include Central Africa (Zaire, Botswana, Congo) and Canada (Snap Lake, Slave craton) – data from Navon *et al.* (1988), Schrauder and Navon (1994) and the present authors.

Udachnaya kimberlites. They are often associated with one or more other minerals (carbonates, olivine, apatite, graphite). From the results of the micro-Raman study, it might be assumed that IR absorption of cuboids is mainly caused by the presence of silicate glasses. The position of the main Raman band corresponds to monomer and dimer silicate units (Rossman, 1988). This is in contrast with the results of Navon *et al.* (1988) for cuboids from Zaire and Botswana where the presence of sheet silicates was suggested, based on an analysis of IR spectra (Navon *et al.*, 1988). However, oriented biotite inclusions have been detected in fibrous diamond coat by TEM (Walmsley and Lang, 1992b). Micas have not been observed in the present study.

Discussion

Residual pressure of micro-inclusions

The present spectroscopic study of fibrous diamonds from the Udachnaya kimberlite pipe

has identified a multi-phase assemblage of micro-inclusions. Some phases show a shift of characteristic peaks possibly due to the high internal pressure preserved in cavities. Theoretically, these shifts enable us to determine the residual pressure in the micro-inclusions. Navon (1991) reported spectroscopic evidence for residual internal pressures of 1.5–2.1 GPa within micro-inclusions in the cuboids from Zaïre and Botswana. This result was based on a shift of the quartz absorption peaks in the IR region (779 and 798 cm^{-1}) and suggested that the pressure within the inclusions is hydrostatic and is exerted by the trapped volatiles (water and CO_2). Consequently, most of the water in cuboids was believed to be in liquid form. Subsequently, the evidence for ice VI as an inclusion in cuboid diamonds (Democratic Republic of Congo) has been obtained from near-IR spectroscopy (Kagi *et al.*, 2000). They observed shoulder absorption at 5000 cm^{-1} arising from ice VI at 1.9 GPa. Although the shoulder absorption at 5000 cm^{-1} has not been clearly identified in cuboid diamonds from the Udachnaya pipe, the observed higher intensity of the symmetric stretching absorption at 3220 wavenumbers is probably characteristic of ice or some hydrous species with strong hydrogen bonds (Aines and Rossman, 1984).

As noted above, the Raman spectra show the shift of two major olivine peaks. Using the calibration of Wang *et al.* (1993), 3.09 $\text{cm}^{-1}/\text{GPa}$, pressures of 0.13–0.65 GPa were measured inside olivine macro-inclusions in Siberian diamonds (Izraeli *et al.*, 1999). Besson *et al.* (1982) determined the Raman shift of olivine as a function of pressure: 0.34 (± 0.03) $\text{P cm}^{-1}/\text{kbar}$ for 854 cm^{-1} and 0.35 (± 0.06) $\text{P} - 0.3 \times 10^{-4} \text{P}^2 \text{ cm}^{-1}/\text{kbar}$ for 822 cm^{-1} . These dependencies are similar to those determined by other researchers (e.g. Wang *et al.*, 1993). Based on these, the pressure of olivines in micro-inclusions in our cuboids falls within the range 0.5–1.5 GPa (Fig. 6). These internal pressures are higher than those reported by Izraeli *et al.* (1999). However, it does not necessarily indicate a higher pressure of formation. If the presence of nitrogen only in A centres (pairs of nitrogen atoms) is taken as an indication of low temperatures at the source, the estimation of pressure (Izraeli *et al.*, 1999) at relatively low temperatures of 900°C indicates a reasonable range of 3.9–5.1 GPa. Alternatively, the hydrostatic effect of the liquid phase (see Navon, 1991) may be responsible for a higher residual pressure

of olivine in micro-inclusions than in macro-inclusions.

Graphite is a low-pressure polymorph of carbon and its association with diamond is unexpected. Based on the upshift of Raman spectra observed in the present study, the graphite contained in the individual micro-inclusions is distorted, possibly due to the high internal pressure. Estimates of residual pressure of graphite using the shift of the main Raman peak yield a wide range of values from zero up to 2 GPa (Fig. 4), which is within the graphite stability field. Crystallization of metastable graphite under P - T conditions of diamond stability has been observed in fluid-containing carbonate systems (Arima *et al.*, 2002; Pal'yanov *et al.*, 2002). However, the reasons for this phenomenon are uncertain. We found graphite only in individual micro-inclusions without visible cracks. The graphite was therefore probably formed as a daughter phase of the trapped fluids during cooling or as the product of reaction between volatile components of micro-inclusions with the host diamond or during decompression. When the pressure falls below the diamond-graphite equilibrium line, graphitization may occur on the walls of the micro-inclusion (Anthony, 1999). We cannot use graphite as an accurate barometer because the exact phase composition of individual micro-inclusions is unknown. However, the high internal pressure existing in most micro-inclusions testify that they

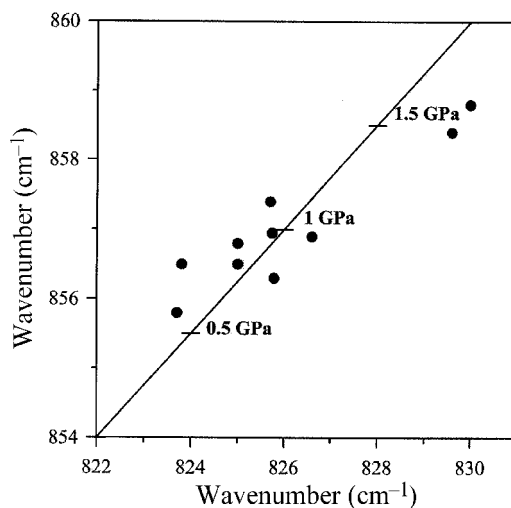


FIG. 6. Raman shift of olivine peaks. The pressure scale (from Besson *et al.*, 1982) indicates the residual pressure of olivines in the range 0.5–1.6 GPa.

are well sealed and still preserve the original fluids trapped during the growth of the host diamond. The extrapolation of pressure to mantle temperatures indicates the conditions of diamond stability. It appears that relatively low temperatures (900–1000°C) are required to explain the high internal pressure of olivines which might be typical for the formation of cuboid diamonds.

Phase composition and relationship

This study has discovered multi-phase assemblages of micro-inclusions in cuboid diamonds from Udachnaya, including carbonates, olivine, apatite, graphite, water and silicate glass; the carbonates are the most abundant phase. Carbonates in cuboids from the Udachnaya kimberlite pipe have a composition with Ca-Mg-Fe cations predominant. The dolomite-like carbonates are most common with Ca-carbonate sometimes present in the outer parts of the crystals. Two types of carbonates were previously identified in the turbid coats on two diamonds from Zaïre: a high-Ca variety (dolomite-like) and low-Ca variety (magnesite-like) (Guthrie *et al.*, 1991).

From IR spectroscopy, we can estimate the amount of CO₂ from carbonates as well as of water in the trapped fluids. Following Navon *et al.* (1988), the concentration of carbonates and water was calculated using $\text{CO}_2 = 213.7 \times I_{1430}$ ppm and $\text{H}_2\text{O} = 64.1 \times I_{3420}$ ppm, where I_{1430} and I_{3420} represent absorption coefficients at 1430 cm⁻¹ for carbonates and 3420 cm⁻¹ for water, respectively. This calibration differs from recent values, but we use it for consistency with previous studies. In a bulk analysis, the concentration of CO₂ of carbonates reached 14000 ppm, but it is strongly dependent on the saturation of samples with micro-inclusions. The content of molecular CO₂ is much less than that in carbonates (Navon *et al.*, 1988) so that it could be disregarded in our estimates. The water content varies from 100 to 1000 ppm. The concentration of water is usually correlated with that of CO₂, calculated from the carbonates (Fig. 7). Consequently, the H₂O/(H₂O+CO₂) ratio in most samples lies within the narrow range 5–20%. Based on this parameter, the cuboid diamonds from the Udachnaya kimberlite pipe are significantly different from cuboids and coated diamonds from other localities (Fig. 7). This observation suggests that extremely carbonatitic fluids are trapped in the cuboid diamonds from the Udachnaya pipe.

Schrauder and Navon (1994) reported that the H₂O/(H₂O+CO₂) ratio in Jwaneng cuboids is correlated with the SiO₂ content. We found that the intensities of IR absorption of water and silicates are usually positively correlated (see Fig. 2). The only observed silicate mineral – olivine – contains 39–42 wt.% of SiO₂. Analysis by energy-dispersive spectroscopy (EDS) has indicated two types of silicate inclusions in several selected samples from Udachnaya: (1) Mg-Fe-Si phases that are probably olivine; and (2) K-Na-Ca-Mg-Fe-Al-Si phases that are probably glasses. Compositions similar to these inferred glasses have been determined in fibrous diamonds from Zaïre and Botswana measured by electron-probe micro-analysis (EPMA) (Navon *et al.*, 1988; Schrauder and Navon, 1994), where it was believed that this composition represents a volatile-rich fluid or melt from the upper mantle. The SiO₂ content in this fluid or melt varied widely from 16 to 60 wt.%. The micro-inclusions from Udachnaya also fall within this range. At present, it is difficult to estimate the proportion of silicates from IR and Raman spectroscopy. Since the silicate absorption is much lower than that of carbonates in cuboids from Udachnaya, the micro-inclusions should contain significantly less silicate material than in cuboids from other localities.

The presence of apatite shows that the fluids were also rich in phosphorus. Unfortunately, we cannot estimate the exact apatite composition and its content from vibrational spectroscopy. However, previous compositional analysis has shown that most crystals were hydroxylapatite, although small amounts of chlorine were detected in some samples (Guthrie *et al.*, 1991). Brine species in micro-inclusions have also been reported for diamonds from Koffifontein (Izraeli *et al.*, 2001) and Canada (Johnson *et al.*, 1999).

Carbonatitic melt

The micro-inclusions in fibrous diamonds are believed to be present as either low-density supercritical fluids or as volatile-rich melt. Schrauder and Navon (1995) have reported that the composition of micro-inclusions in diamonds from Jwaneng (Botswana) varies between two end-members: hydrous fluids or melts rich in silica and alkalis and carbonatitic melts rich in Mg and Ca. Compared with reported data, micro-inclusions in the cuboids from the Udachnaya kimberlite pipe indicate that the trapped material

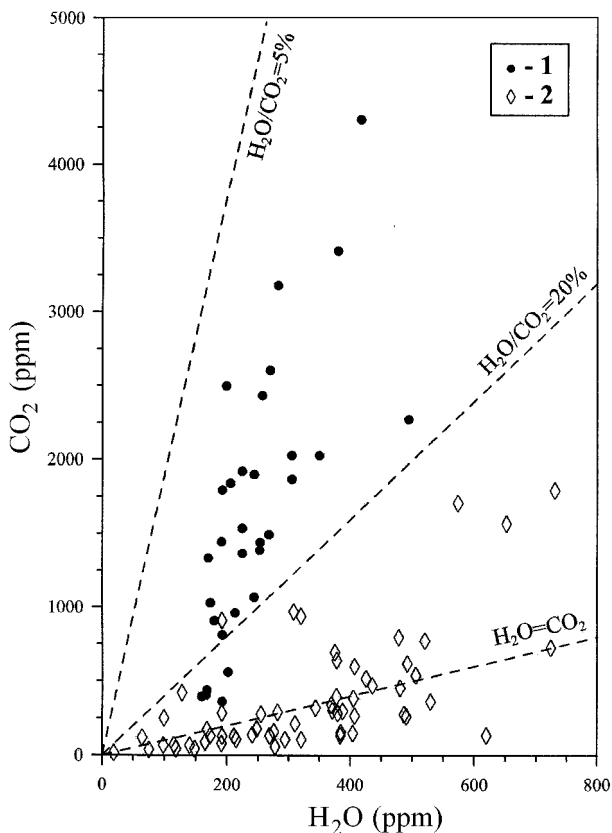


FIG. 7. The relationship between the water content and concentration of CO_2 (in carbonates) in micro-inclusions in cuboid diamonds from Udachnaya (1) and other localities (2). The material trapped in micro-inclusions in cuboids from Udachnaya has extreme carbonatitic compositions.

has an extremely carbonatitic composition. They contain an association of daughter phases which include Ca-Mg and Ca carbonates, olivine, apatite, water, graphite and silicate glasses. We have also found that a significant quantity of water is present in the form of hydroxyl ion dissolved in other phases, probably in melt glasses. The carbonatitic melts are poor in silica: the SiO_2 content of silicate glasses and olivines is <40 wt.%. The presence of apatite is well known to be typical in carbonatites worldwide.

The carbonatitic melts trapped in most cuboids from the Udachnaya kimberlite pipe have very similar compositions. No significant variations were found, suggesting that the cuboids in this mine possibly originate from one source. The carbon isotope composition of cuboids from Udachnaya also shows only small $\delta^{13}\text{C}$ variations from -2 to -6‰ (Zedgenizov *et al.*, 2002). This range corresponds to the average value of mantle

carbon (Galimov, 1991). The mantle origin of carbonatites has been discussed in numerous publications (e.g. *Journal of Petrology*, 39, No. 11–12).

Many studies have shown that near-solidus melts of carbonated peridotite in the mantle are carbonatitic (e.g. Green and Wallace, 1988; Wyllie *et al.*, 1990; Dalton and Presnall, 1998). Such low-degree carbonatitic melts are poor in water and silica. Taking reasonable estimates for the peridotite+ CO_2 + H_2O solidus and melt composition, an apatite-saturated carbonatitic melt will contain ~6.8 wt.% P_2O_5 (Baker and Wyllie, 1992). The near-solidus melts may result in diamond formation. Successful experiments on diamond growth from carbonate and carbonate-silicate melts in the last decade have supported the possibility of natural diamond formation from carbonatitic melts (e.g. Akaishi *et al.*, 1990; Pal'yanov *et al.*, 1999; Litvin and Zharikov,

2000). The nucleation and growth of diamond proceeded either via precipitation of free carbon dissolved in a carbonatitic melt or through carbonate-silicate interaction (reaction of decarbonation). The association in micro-inclusions described here in cuboid diamonds from the Udachnaya kimberlite pipe provides evidence of their crystallization from a carbonatitic melt. This result supports the suggestion that carbonatitic fluids or carbonate-rich melts may play a significant role in diamond formation. For this reason, more detailed characterization of carbonatitic melts included in diamonds would be helpful.

Conclusions

(1) Vibrational spectroscopy is very useful for characterizing micro-inclusions (1-10 μm) in fibrous diamonds. Infrared spectroscopy provides the bulk content of all species in a given volume, whilst micro-Raman gives the phase identification in individual micro-inclusions. Neither method requires complicated sample preparations, as for TEM.

(2) A spectroscopic study of micro-inclusions has revealed the multiphase assemblage in cuboid diamonds from the Udachnaya kimberlite pipe. This assemblage includes carbonates, olivine, apatite, graphite, water and silicate glasses. These micro-inclusions are under high internal pressure, which indicates that the original fluids were trapped during growth of the host diamond. The extrapolation to mantle conditions suggests an origin in the diamond stability field, but at relatively low temperatures.

(3) The micro-inclusions in cuboids from the Udachnaya kimberlite pipe are of extreme carbonatitic composition. The dominance of carbonatitic compositions and low water and silica demonstrate that the material forming micro-inclusions in the Udachnaya diamonds was a near-solidus carbonatitic melt. Vibrational spectroscopy techniques have therefore provided the evidence of carbonatitic melts in cuboid diamonds.

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