The origin of hydrocarbons in fluid inclusions in diamonds

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Introduction

Fibrous cuboid diamonds with fluid inclusions and carbonado diamonds have been reported to contain hydrocarbons. They were detected by characteristic C-H peaks between 2800 and 3000 cm^{-1} using the Fourier-Transform Infrared (FTIR) spectroscopy. The presence of hydrocarbons in these diamonds were interpreted as artifacts of grease or acryl paint contamination (Klein-BenDavid et al., 2006) or a sign of hydrogen-rich interstellar origin (Garai et al., 2006). We report the presence of hydrocarbons in 15 fibrous cuboid diamonds, prove an association of hydrocarbons with carbonates in the diamond fluid inclusions, and propose a model of the hydrocarbon formation. We suggest a low-temperature deuteric origin of hydrocarbons from CO_2 and hydrogen formed as a result of serpentinization of minerals crystallized from the fluid trapped by the diamonds.

Methods

Micro-inclusions (<1 micron) in diamonds were detected using back-scattered imaging on a JEOL JXA 8600 electron probe (Institute of Earth Sciences, the Hebrew University, Jerusalem). Inclusions were analyzed using a 1 micron focused electron beam at 15 keV, 10 nA. All other analytical work was done at the Bayreuth Geoinstitut, Germany. Diamonds were studied on a Bruker IFS 120 HR spectrometer equipped with a Bruker IR microscope, Globar source, CaF_2 beam-splitter and a narrow-band MCT detectorXRD analysis was carried out using the system consisting of three major components, RIGAKU FR-D high-brilliance source, OSMIC Inc. Confocal Max-Flux optics, and SMART APEX 4K CCD area detector. We employed MoKα radiation and collimated beam with FWHM 40 μm.

Samples

Twenty fibrous cuboid and cuboctahedron diamonds from the Democratic Republic of Congo (4 to 9 mm) with matte grey, yellow and green colours contain multiple sub-micron fluid inclusions between fibers of cubic multiple concentric growth layers. Total N contents of the fibrous regions are 112-1650 ppm, whereas octahedral cores contain 80-1070 ppm N. In general, octahedral cores may be either lower or higher in N than the outer fibrous coats, but always contain more aggregated N (up to 55%) The majority of nitrogen in the diamonds exists as A-centers. Further quantification of the spectra is difficult as absorption of inclusions interferes with absorption of nitrogen impurities in diamond. Fluid inclusions in the DRC diamonds range in composition from silicic to Ca-carbonatitic and are typical of other fluid inclusions worldwide.

Daughter minerals crystallizing from fluid inclusions

The submicron inclusions in fibrous diamonds were historically called "fluid" to emphasize their distinct nature as compared to larger, 3-5000 μm, mineral inclusions also found in diamond. Fluid inclusions are composed of intergrown nanometer-sized solid phases with minor amount of hydrous solution (Guthrie et al., 1991) and gas bubbles (Logvinova et al., 2008). The low proportions of gas and liquid phases suggest that the inclusions are crystallized melt (Navon et al., 1988; Zedgenizov et al., 2004), which may have originated well above the second critical point of the lherzolite- H_2O-CO_2 system (75 Kb, Wyllie and Ryabchikov, 2000) where melt and aqueous fluid are indistinguishable.

We identified minerals and non-crystalline components of the inclusions using their compositional trends in the electron microprobe analyses of inclusions, an innovative bulk X-ray diffraction analysis and characteristic FTIR peaks. Thirty minerals were detected by these methods in the diamonds. Among the minerals, only 3 were found essential and common precipitates from the diamond-forming fluid, high-Si Cl-bearing mica, complex carbonates and apatite (Kopylova et al., in press). Other major components of the fluid are saline and carbonate-bearing hydrous solution and gaseous CO_2. The majority of daughter minerals crystallized from the fluid are natural silicates containing structural and coordinated H_2O. The accessory and deuteric minerals detected in the inclusions using XRD and FTIR analyses are serpentine, amesite, quartz, chlorite-vermiculite-montmorillonite, hectorite, halloysite glauconite, zircon, a hydrous carbonate and an unidentified zeolite.

Results

The majority of the diamonds contains IR peaks of varied intensity at ~2860 cm^{-1}, ~2930 and ~ 2960 cm^{-1}. In sample 16 (Fig. 1), the magnitude of these peaks even exceeds that of the main water band at 3300-3400 cm^{-1}.
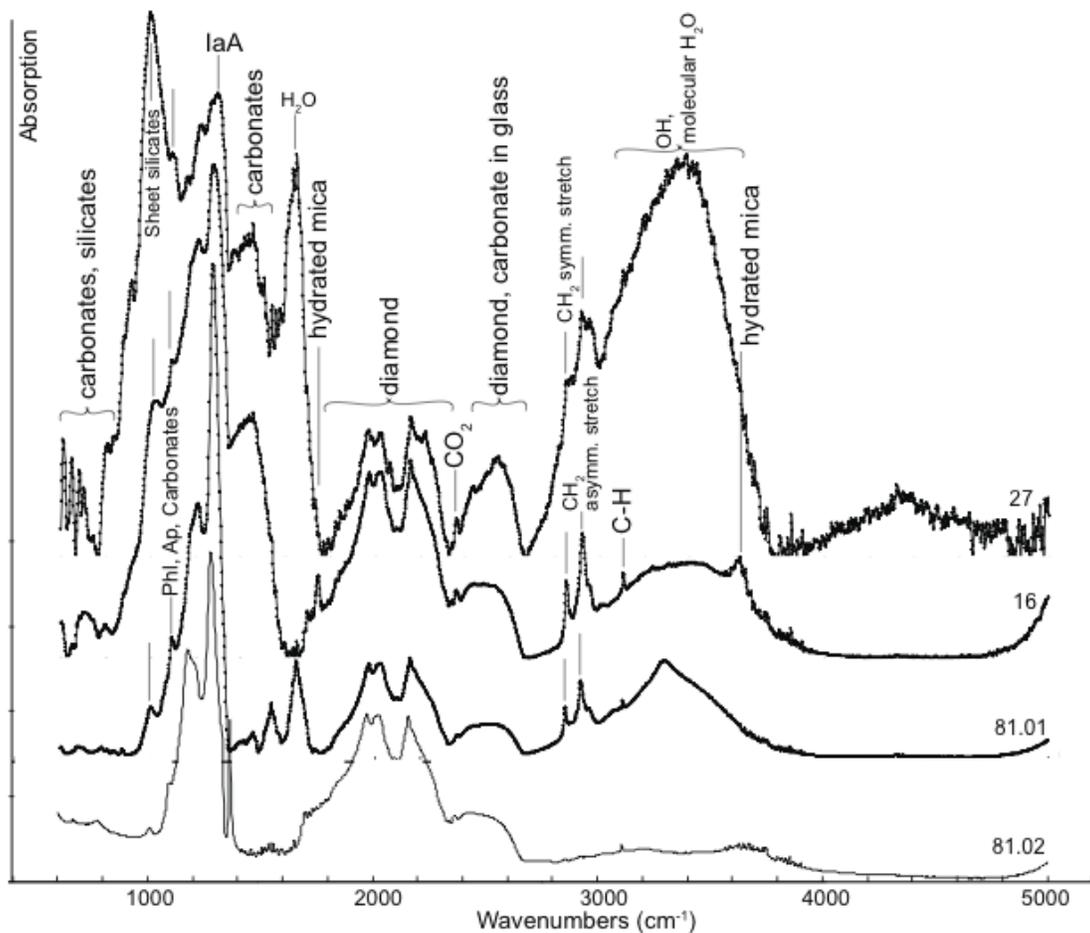
Figure 1: FTIR absorption spectra of 8 representative diamond samples compared with peak positions of diamond, N and H defects in diamond (Evans, 1992), various minerals, hydrocarbons (Titus et al., 2005) and CO_2 - and H_2O - bearing species (Guilhaumou et al., 2005). Spectra 81.01 and 81.02 were acquired from fluid inclusion-rich and fluid inclusion-poor areas of sample 81.

The peaks are assigned to absorption of CH_2 groups bonded to sp^3-hybridized carbon in hydrocarbons heavier than methane, i.e. symmetric (~2860 cm^{-1}) and asymmetric stretch of CH_2 (2930 and ~ 2960 cm^{-1}) (Titus et al., 2005). To eliminate a possibility that the peaks are artifacts of organic grease, ethanol or acryl paint, we carefully washed samples and repeated all FTIR measurements in different spots of the samples on the Specord M-80 spectrophotometer (Zeiss) at the Central Research Geological Prospecting Institute of Nonferrous and Noble metals (Moscow, Russia). The analyses confirmed that CH_2 groups are intrinsic to the diamonds as the intensity of CH_2 peaks correlate with the density of inclusions in the sample (compare spectra 81.01 and 81.02 in Fig. 1) and with the geochemistry and mineralogy of the fluid inclusions. Diamonds with high CH_2 peaks have lower $H_2O/(H_2O+CO_2)$ ratios. The $H_2O/(H_2O+CO_2)$ ratios of the bulk fluid were estimated by the relative intensities of H_2O and carbonate peaks in FTIR spectra as postulated by Navon et al. (1988). For example, diamonds with an entirely hydrous fluid ($H_2O/(H_2O+CO_2)$=1) show low CH_2 peaks at 2930 cm^{-1} (I_{2930}/I_{2160}=0-0.12). As the $H_2O/(H_2O+CO_2)$ ratio decreases to 0.65, the intensity of the 2930 cm^{-1} peak increases to 0-0.6. A single diamond with the most CO_2-rich fluid (($H_2O/(H_2O+CO_2)$=0.33) shows an extreme (0.8) height of the 2930 cm^{-1} peak. In zoned diamond 28, the intensity of the CH_2 peaks at 2930 cm^{-1} increases from 0.12 to 0.3 as the composition of the fluid changes from silicic to carbonatitic with higher Na_2O, CaO, MgO and FeO. In addition, diamonds with high CH_2 peaks are lower in SiO_2 and in the abundance of sheet silicates as indicated by intensities of the IR sheet silicate peaks.

Discussion and conclusions

Peaks of the methylene group CH_2 in aliphatic hydrocarbons with IR absorption between 2800 and 3000 cm^{-1} are confirmed as a component of fluids in diamond inclusions for the first time. Hydrocarbons heavier than methane, however, have been reported in diamond fluids, kimberlite-derived xenolithic garnet (Tomilenko et al., 1997) and in magmatic carbonatites (Nivin et al., 2005). In all these materials, hydrocarbons are found not only using IR spectroscopy, but also by cryometric and chromatographic analyses. The CH_2 peaks are also found in CVD and nanodiamonds (e.g. Shiryaev et al., 2006) where their amplitudes are proportional to the abundance of sp^3-hybridized amorphous carbon, a common impurity in CVD diamonds (Tang et al., 2004) and in cavities of fibrous diamonds (Klein-BenDavid et al. 2007). Carbonado diamond was reported to contain methylene groups connected to surface diamond carbon; this was ascribed to a cuboid growth in hydrogen-rich environment (Garai et al., 2006).

The hydrocarbons in the studied diamonds is unlikely to be associated with the imperfect diamond matrix as there is no correlation between CH_2 peaks and a C-H diamond peak at 3107 cm^{-1}. Moreover, a comparison between fluid-rich and fluid–poor zones of a single diamond (spectra 81.01 and 81.02 on Fig. 1) demonstrate that CH_2 peaks are higher in fluid-rich zones with more intense H_2O, CO_2 and carbonate peaks. As the CH_2 peaks are stronger in diamonds that include fluids with more carbonatitic compositions, we suggest the hydrocarbons are associated with the carbonate and CO_2 phases in the inclusions. Similar to hydrocarbons in magmatic carbonatites (Nivin et al., 2005), CH_2 groups in the diamonds may be associated with Na-bearing carbonates. Indeed, Na- and H-bearing carbonates are recorded in our diamonds and the Na content is higher in more carbonatitic diamonds.

The presence of hydrocarbons suggests domains of locally reduced environment existing at the prevalent Enstatite-Magnesite-Olivine-Diamond fO_2 buffer defined by the diamond-carbonate equilibrium. The closest analogy to this mismatch is the complex mineralogy of the Khibiny massif known for its extremely high content of abiogenic hydrocarbons (CH_4 and its higher homologues) associated with magmatic carbonatites, apatite mineralization and hydrothermal veins of Na, Ba and REE carbonates. The Khibiny hydrocarbons were shown to form post-magmatically at P<2 kb, T=200-400°C as products of a reaction between magmatic CO_2 and H_2 generated by deuteric development of hydrous minerals (Nivin et al., 2005).

We propose that aliphatic hydrocarbons heavier than methane that occur in diamond inclusions form deuterically at low temperature from trapped CO_2 and secondary H_2. The fluid inclusions in diamonds have abundant CO_2, deuteric serpentine and other OH-bearing minerals. It is well known that formation of secondary OH-bearing minerals may release hydrogen (O'Henley, 1996; Kelley et al., 2005). In the H_2O-rich environment of the inclusions, we recorded a variety of hydrous minerals, from high-T hectorite ($1000-700^oC$), to serpentine and chlorite ($>700^oC$), halloysite ($<400^oC$) and low-T glauconite ($<250^oC$). Potentially, all reactions that form these OH-bearing minerals can produce hydrogen. The origin of hydrocarbons as byproducts of deuteric hydration of primary minerals in the CO_2-rich environment, furthermore, could explain the preferential formation of hydrocarbons in inclusions with carbonatitic compositions.

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