9th International Kimberlite Conference Extended Abstract No. 9IKC-A-00190, 2008

Mineralogy of natural diamond-forming fluids

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A suite of 20 cubic fibrous diamonds from placers of the Democratic Republic of Congo was studied to determine mineral phases crystallized from diamondforming fluids or trapped as solids together with the fluid. We identified minerals using their compositional trends in electron microprobe (EMP) analyses of bulk inclusions, X-ray diffraction patterns and characteristic FTIR and Raman peaks. The emphasis of the study was on techniques that provide an integral, representative analysis of the entire volume of the diamond rather than point analyses of selected single microinclusions. Such an approach allowed us to identify most common minerals in fluid inclusions and to significantly expand a list of minerals occurring in fibrous diamonds.

The diamonds contain numerous sub-micron fluid inclusions that range in composition from silicic to carbonatitic (Fig. 1). One diamond is zoned, with silicic inclusions in the inner part and carbonatitic in the outer. Observed chemical trends show the presence



Fig. 1. Ternary diagram of SiO₂+Al₂O₃ (silicic end-member) vs CaO+MgO+FeO+Na₂O+P₂O₅ (carbonatitic end-member) vs. K₂O+Cl (saline end-member) for fluid inclusions in 7 randomly selected DRC diamonds. Compositions of minerals are from diamond fluid inclusions elsewhere (Klein BenDavid et al., 2004, 2006, 2007, Izraeli et al., 2004). Dashed lines show inclusions in carbonatitic and silicic areas in the zoned diamond.



of several common minerals. A slope of the SiO₂-Al₂O₃ correlation suggests their presence in high-Si mica, similar to mica found in fluid inclusions in diamonds elsewhere, rather then in phlogopite (Fig. 2A). A strong apatite trend of correlated Ca and P is evident in 18 out of 20 diamonds. Positive and variable intercepts of this trend with the Ca axis (Fig. 2B) suggest that while apatite is the main depository for P, not all Ca is sequestered in apatite. An apatite trend is absent in the silicic part of the zoned diamond,



Fig. 2. Fluid inclusions compositions in 10 randomly selected DRC diamonds. Analyses of minerals are from diamond fluid inclusions elsewhere (Klein Ben David et al., 2004, 2006, 2007, Izraeli et al., 2004). On plot B, symbols of different colours correspond to inclusions in different stones.

but is strong in an outer carbonatitic zone. A broad negative correlation between Na and K, and correlations of Ca with Na, Mg, and Fe suggest that all these elements are present in complex carbonates. Potassium, in contrast to Na, correlates with Cl. The approximate 3:1 ratio (Fig. 2C) of this correlation indicates that the mineralogy of Cl-bearing phases in diamond-forming fluids is complex and include Clbearing mica (Izraeli et al., 2004) and KCl. The presence of a K-bearing, Cl-free phase in addition to mica in implied by a position of most analyses above the mica-KCl tie-line on Fig. 2C. Overall, compositions of fluid inclusions can be described as a mixture of 3 components, 1) a silicic end-member composed of Cl-bearing mica, 2) a carbonatitic endmember composed of Na-Mg-Fe-Ca carbonates and apatite, and 3) K-Cl bearing minerals or solutions (Fig. 1). Analyses that plot away from the majority of fluid inclusions and sometimes outside of the confining Mica - Carbonate+Apatite - KCl triangle (Fig. 1) represent microinclusions trapped as solids. In the studied diamonds, these are apatite, chromite, rutile, quartz and Ni-Zn-Cu sulfides.

XRD analysis was carried out on the system that consist 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 MoK α radiation and collimated beam with FWHM 40 µm. Data processing included subtraction of diffraction pattern spots produced by small diamond crystallites that host inclusions. Multiple mineral peaks sufficient for phase identification were detected in 8 out of 20 diamonds (Fig. 3). We observed XRD patterns of 2 distinct micas with crystal lattices of phlogopite-ferri-annite solid solution and muscovite, chlorite-vermiculitemontmorillonite, Na2Mg3Si6O16*8H2O (loughlinite, 2 samples), Na_{0.2}Mg₃Si₄O₁₀(OH)₂*4H₂O (hectorite, 2 samples), goethite, pyrope, (Mg₈Al)(Si₇Al)₂₀(OH)₁₀ (kulkeite), $Al_2Si_2O_5(OH)_4$ (halloysite), Mg(OH)F, NaClO₄*H₂O, a carbonate hydroxide hydrate mineral containing large cations, and Mg₃SiAlO₅(OH)₄ (amesite). Interestingly, carbonate peaks are absent.



Fig. 3. Observed XRD pattern of a sample (black line) compared with peak positions and amplitudes of ferri-annite (red) and loughlinite (green).

Raman spectroscopy was carried out using a Jobin Yvon Labram spectrometer with a 632.8 nm He–Ne excitation line and laser output power of 8 mW (Bayreuth Geoinstitut, Germany). The laser beam was focused using a 50× objective on a confocal microscope, resulting in a ~5 μ m spot. A non-unique identification of peaks showed the presence of serpentine, pyrope, olivine, apatite, Ca₂Fe(PO₄)₂*4H₂O (anapaite), biotite, carbonate, (Mg,Fe)CO₃ (breunnerite), NaHCO₃ (nahcolite), halite, graphite, brucite, fluorite, chromite, orthopyroxene, and molecular H₂O and CO₂.

FT Infrared spectroscopy was performed on a Bruker IFS 120 HR spectrometer equipped with a Bruker IR microscope, Globar source, CaF_2 beam-splitter and a narrow-band MCT detector (Bayreuth Geoinstitut, Germany). Deconvolution of FTIR spectra determined that most diamonds contain 110-1400 ppm of nitrogen in A and C centers (up to 23% of type Ib component). The spectra also suggest the presence of carbonates, sheet silicates, apatite, OH⁻ and CH₂ groups, molecular H₂O and CO₂ (Fig. 4).



Fig. 4. FTIR absorption spectra of 3 diamond samples compared with peak positions of diamond, N and H defects in diamond (Evans, 1992), various minerals (Farmer, 1974; Plusnina, 1977), hydrocarbons (Titus et al., 2005) and CO₂- and H₂O- bearing species (Guilhaumou et al., 2005).

The $H_2O/(H_2O+CO_2)$ ratio of the bulk fluid estimated by the relative intensities of H_2O and carbonate peaks in FTIR spectra (Fig. 5) varies between 0.3 and 1, typical of other suites of fibrous diamonds from DRC and Jwaneng (0.16-0.86, Zedgenizov et al., 2004).

The majority of the diamonds contains IR peaks related to absorption of CH₂ groups bonded to sp³-hybridized carbon in heavy hydrocarbons, i.e. peaks at ~2860 cm⁻¹ (symmetric stretch of CH₂), ~2930 and ~ 2960 cm⁻¹ (asymmetric stretch of CH₂) (Titus et al., 2005). These peaks were found previously in fibrous diamonds (Klein Ben David et al., 2006) but assigned to organic compounds in the IR microscope or grease. To eliminate this possibility, we carefully washed samples and repeated all FTIR measurements in two different laboratories. IR analyses done on the Specord M-80 spectrophotometer (Zeiss) at the Central Research Geological Prospecting Institute of Nonferrous and Noble metals (Russia) confirmed that CH₂ groups are intrinsic to the included diamonds. The intensity of CH₂ peaks correlate with the geochemistry and



Fig. 5. Correlations between $H_2O/(H_2O+CO_2)$ ratio and intensity of the 2930 cm⁻¹ peak (A), Ca+Mg+Fe (B) and Na₂O (C). $H_2O = 64.1* I_{3420}$; CO₂ = 213.7* I_{1430} (Navon et al., 1988). Intensity of 2930 cm⁻¹ peak is normalized to the intensity of a diamond peak at 2160 cm⁻¹. Arrows connect compositions of inner silicic and outer carbonatitic growth zones in one diamond.

mineralogy of the fluid inclusions. Diamonds with high CH₂ peaks have lower H₂O/(H₂O+CO₂) ratios (Fig. 5), higher Na₂O, CaO, MgO and FeO. In addition, these diamonds are lower in SiO₂ and in the abundance of sheet silicates as indicated by intensities of IR sheet silicate peaks (Fig. 6).



Fig. 6. Histograms showing difference in fluid composition and mineral abundances in samples with various intensities of CH₂ peak at 2930 cm⁻¹. Amplitudes of FTIR peaks are normalized to the intensity of a diamond peak at 2160 cm⁻¹. High CH₂ peaks have amplitudes $I_{2930} > 0.18 I_{2160}$, whereas low CH₂ peaks have amplitudes $I_{2930} < 0.18 I_{2160}$.

The CH₂ peaks are 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). CH₂ groups may also reside in the imperfect diamond matrix, but the absence of correlation between CH₂ peaks and C-H peak at 3107 cm⁻¹ makes this unlikely.

As the CH_2 peaks are stronger in diamonds that include fluids with more carbonatitic compositions, we suggest the hydrocarbons are associated with carbonate minerals in inclusions. Similar to hydrocarbons in magmatic carbonatities (Nivin et al., 2005), CH_2 groups in the diamonds may be associated with Nabearing carbonates. Indeed, Na- and H-bearing carbonates are recorded in our diamonds and the Na content is higher in more carbonatitic diamonds. Our study found that aqueous and CO₂-rich fluids that deposited fibrous diamonds crystallize a variety of minerals with structural and coordinated H₂O and carbonates if high aH₂O and aCO₂ are preserved in inclusions by the host diamond. Most common phases of the fluid are found to be high-Si micas, complex Na-Ca-Mg-Fe carbonates, apatite, aqueous solution containing K and Cl ions and gaseous CO2; silicate glasses were not found. Bulk composition of the fluid is fully described by the presence of Cl-bearing mica (90-30%), carbonates and apatite (5-70%) and K- and Cl-bearing hydrous fluid (0-30%) (Fig.1). Overall, the mineralogy of the assemblage that crystallized from diamond-forming fluid resembles that of carbonatites and kimberlites rather than diamondiferous peridotites or eclogites.

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