FLUID-INCLUSIONS IN BRAZILIAN COATED DIAMONDS

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Fluids were found in micro-inclusions in diamond from Africa (Navon et al., 1988; Schrauder and Navon, 1994; Izraeli et al., 2001), Siberia (Logvinova et al., this volume), Canada (Klein-BenDavid et al., this volume) and India (Schrauder et al. unpublished data). The fluid composition varies between three end-members: carbonatitic melts, rich in carbonate, Ca, Fe, Mg, K and P; Hydrous-silicic melts, rich in Si, water, Al and K and brine rich in water, Cl and K.

Here we report new data from micro-inclusion bearing diamonds from Brazil. The micro-inclusions contain melts that span the range between carbonatitic and hydro-silicic compositions. The entire range between the two end members is observed in single diamonds. Thus, in two diamonds, it is possible to follow the evolution of the melt during diamond growth.

METHODS

The five Brazilian diamonds are 2-3 mm is size. BR-1, 2, 3 and 5 are cubes and BR-4 is a twin of two interpenetrating cubes. BR-3 and 4 are transparent, the others are dark green and opaque. Two parallel surfaces were polished and cleaned by HF (60%) HNO₃ (69%) and ethanol prior to analysis to remove all organic and inorganic contamination. The diamonds were analyzed using FTIR, Electron probe micro analyzer (EPMA), Cathodo-luminescens (CL) imaging and synchrotron-XRF (SYXRF).

OPTICAL MICROSCOPY AND CL IMAGING

Four diamonds (BR-1,2,3,5) have octahedral, inclusionfree cores surrounded by opaque fibrous rims. The rims carry many micro-inclusions that are less than one micron in size. Large cracks prevent identification of a core in diamond BR-4.

In BR-1 and BR-3 CL imaging reveals bright octahedral cores separated from the cubic fibrous coats by a dark thin ring. The cores exhibit internal, concentric zoning (Fig. 1a). CL in the coat is weaker but still reveals concentric zoning with development of cubic faces. BR-2 and BR-5 have bright, irregular, small cores surrounded by a darker fibrous mantle and a brighter, double-ring rim (Fig. 1b). The CL of BR-4 is dominated by the cracks, but still shows some

concentric growth-zones surrounding the center of the whole twin crystal.



Figure 1: CL image of BR-3 (a) and BR-5 (b). BR-3 exhibits bright octahedral core surrounded by rings of cubic habit. BR-5 shows a bright cubic inner core surrounded by homogenous darker zone of cubic habit and brighter rims. Micro-inclusions densly populate the dark zone and are present at lower concentartion in the rims.

FTIR SPECTRA

Nitrogen concentration in all samples is high; 910-1500 ppm. The aggregation state of most diamonds is IaA except for the core of BR-3 which is a mixed IaA-IaB. Three diamonds (BR-1, 2 and 5) indicate the presence of water (~1640 and ~3420 cm⁻¹) and carbonate (~1440 and ~885 cm⁻¹). Calculated $CO_2/(CO_2+H_2O)$ molar ratios vary between 0.07 and 0.24. Spectra collected along a profile in BR-2 and BR-5, show variation of the ratio from ~ 0.1 in the inner parts to ~ 0.2 in the rim. In BR-1 the ratio is ~0.2 in the center while at the rims the ratio is low enough so that only water is detected while carbonate concentration is at the detection limit. Two peaks at 1000 and 1100 cm⁻¹ are probably due to silicate absorption and show broad inverse correlation with the intensity of the carbonate bands. Ouartz lines are shifted from their 1 bar positions to 787 and 816 cm^{-1} in the spectra of BR-1. 2, and to 784 and 812 cm^{-1} in BR-5. These shifts correspond to internal pressures of 2.5 and 2 GPa, respectively, somewhat higher than pressures recorded for Zairian diamonds (Navon, 1991). In the two other diamonds, BR-3 and BR-4, the number density of inclusion is low and no IR absorption due to the inclusions was observed.

SYXRF AND EPMA ANALYSES

SYXRF analyses indicated the presence of K, Ca, Fe, Ti, Sr and Zr in all samples. Ba was detected in BR-1,2,4,5.

The major element composition of 149 microinclusions was analyzed using EPMA. The inclusions in BR-1, 3, 4 and 5 share similar characteristics. Those in BR-2 are of different compositions and are presented at the end of this section. The composition of the four diamonds falls on similar arrays between the hydroussilicic and carbonatitic end-members (Fig. 2). The first contains ~70 wt% SiO₂, 10% K₂O, 9% Al₂O₃, 6% FeO, minor amounts (under 3%) of Na₂O, Cl and P₂O₅ and no CaO. The second contains 10% SiO₂, 45 wt% CaO, 18% FeO, 11% P2O5, 6% MgO, minor amounts (under 3%) of Na₂O, TiO₂, BaO and Cl and no detectable K₂O and Al₂O₃. This compositional variation is broadly similar to that documented for diamonds from Zaire and Botswana (Navon et al., 1988; Schrauder and Navon, 1994). However, while the inclusions in each Zairian or Botswanan diamond spanned only a limited range of compositions, the inclusions in individual Brazilian diamond cover a wide range of composition, and sometimes the full range.



Figure 2: Composition of individual micro-inclusions in Brazilian diamonds and average composition of Botswanian diamonds.

In two diamonds (BR-1 and 5) enough inclusions were found so that compositional variation along radial profiles could be observed. In BR-1 three profiles indicated evolution from carbonatitic composition in the inner coat towards hydrous-silicic composition at the rims (Fig. 3 a and b). In BR-5 six profiles indicated an opposite compositional variation, from hydroussilicic in the inner coat to carbonatitic at the rim (Fig. 3c and d), these opposing directions conform with FTIR data.

The composition of the micro-inclusions in BR-2 fall in a tighter range, around 44 wt% SiO₂, 17% Na₂O, 15% FeO, 13% MgO and less than 3% each of CaO, Al₂O₃, K₂O, P₂O₅ and Cl. The presence of water and carbonate in the IR spectra imply that the inclusions carry fluids, but its major element composition is different compared with all previously reported analyses.



Figure 3: Composition of individual micro-inclusions in BR-1 (a and b) and BR-5 (c and d). Profiles of CaO and SiO_2 from the inner part of the diamond to the rims display the variation between CaO-rich, carbinatitic melt, , and SiO2-rich hydrous-silicic melt. The two diamonds show opposite behavior.

DISCUSSION

COMPARISON TO OTHER MICRO-INCLUSION BEARING DIAMONDS

The external and internal morphology of the Brazilian diamonds is similar to that of Zairian and Botswanan diamonds. A broad similarity was also found for the composition of the micro-inclusions found in all three localities. The compositions of all these diamonds fall between two end-members, one rich in silica and water, the other in carbonate. In detail, important differences can be recognized and are discussed below, but the broad similarity suggests that all inclusions belong to one family that traps melts that are rich in water and carbonate and are intermediate between the two endmembers. They are distinct from micro-inclusions that carry brine, e.g. those found in cloudy diamonds from Koffiefontein, South Africa (Izraeli et al., 2001) and in coated diamonds from Diavik, Canada (Klein-BenDavid et al., this volume).

The micro inclusions in each Brazilian diamond span a wide range of composition. This is in contrast to the inclusions in Botswanan diamonds that exhibit uniform composition in individual diamonds, in spite of the wide range spanned by all diamonds. The trends of the correlation lines in major element variation diagrams for Brazil, Botswana and Zaire are similar, except for the negative correlation between K_2O and SiO_2 in the Brazilian diamonds (Fig. 2). Other differences are mainly in the slope and broadness of the correlation lines.

The hydrous-silicic end-member is similar in the three localities. The only exception is Al₂O₃ which reaches 10-14 wt% in the silicic inclusions of BR-1 and BR-3, compares with 6-7 wt% in BR-4, BR-5 and the diamonds from Zaire and Botswana. (Note that the high Al₂O₃ content of BR-1 and 3, brings the composition of this end-member close to that of Kfeldspar). More variability exists in the composition of the carbonatitic melt. The most important difference is in the K_2O content. No K_2O is present in the carbonatitic end-member of all Brazilian diamonds, while it reaches 20-25 wt% in Zaire, Jwaneng (Botswana), Koffiefontein and Diavik. Other differences include: a. P_2O_5 content reaches 15 wt% in Brazilian carbonatitic end-member (and up to 30% in a few inclusions of BR-5), but is less than 3% in all other localities. b. The main cation in the Brazilian carbonatitic melt is CaO (~45-50 wt%) and the Mg/Ca molar ratio is 0.2. The carbonatitic melts from all other localities have molar Mg/Ca ratio that is higher than one. c. TiO₂ concentrations in BR-1 show clear enrichment towards the carbonatitic end-member. In other Brazilian diamonds and in diamonds from other localities TiO₂ variation between the two end members is small. d. Na₂O in the Brazilian carbonatitic melt is low (<5 wt%) and similar to that in Zaire and Botswana. Much higher sudium contents were found in the carbonatitic melts of Diavik and Coffiefontein).

CONCENTRATION PROFILES AND MELT EVOLUTION

Diamonds BR-1 and BR-5 exhibit wide range of compositions and span the whole range between the hydrous-silicic and the carbonatitic end-members. When plotted against distance from the diamond rims, SiO_2 and CaO concentrations reveal the evolution of melt composition during the growth of the diamond (Fig. 3). Different profiles in the same diamond are consistent and show the same direction of evolution. However, the two diamonds evolve in contrasting manner. BR-1 evolves from carbonatitic to hydrous-silicic melt, and BR-5 in the opposite direction.

It is hard to explain this contrasting behavior as originating from a single process, such as fractional crystallization during cooling or the separation of an immiscible fluid. It is not impossible for these processes to proceed in different directions, for example, crystallization during cooling and dissolution during heating. However, it looks like the simplest explanation for such contrasting evolution is mixing between the end-member melts or re-introduction of carbonatitic melt after the previous batch cooled, crystallized and evolved into a hydrous-silicic melt.

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