IaB diamond and its geological implications

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Introduction

Nitrogen is one of the most common impurities in diamonds, and its aggregation styles in diamonds have been used as criteria for diamond classification. Among all diamond types, Ia is the most common type in nature, including type IaA, IaAB and IaB. However, pure IaB (with 100% B aggregation) diamonds are rather rare. Some of them are found in diamond suites that are related with super deep origin (Buffalo Hills, Eurelia, Sao Luis, Rio Soriso, Kankan, Jagersfontein Kimberlite, etc.) or oldest diamondiferous rocks (Wawa), others can be found occasionally in alluvial diamonds (Arenapolis, Boa Vista, Namibia) or at the base of lithosphere with deformation features (Argyle). The origin and formation of those diamonds are mainly mysterious. The nitrogen concentration of those diamonds can be very low (less than 200 ppm, i.g., Eurelia, Sao Luis, Buffalo Hills), and they can mix with type IIa diamonds in the same stone with large size. Experimental data shown that C center in diamonds can be gradually changed to A center and to B center (Evans & Qi, 1982) by high-temperature annealing, with parallel formation of the platelet in {001} planes. Therefore, the occurrence of B center and low nitrogen concentration has often been interpreted as a sign of high temperature and probably longer geological time for the host diamond. However, for many pure IaB diamonds, the platelet defects can be degraded completely (Buffalo Hills), which have been termed as irregular diamonds (Woods & Collins, 1986), indicating that they could have undergone unusual geological event during the diamond forming process. Previous studies proposed that platelet degradation in these diamonds results in formation of octahedral voidites and dislocation loops lying in the {001} planes (Evans et al., 1995). Those voidites could provide a milky/hazy appearance to the IaB diamonds and contain mantle-derived fluids but their physical and chemical properties are still controversial.

To understand the formation and geological implications of type IaB diamonds, we systematically studied their defects and deformation features by FTIR, cathodoluminesence, photo-luminescence spectroscopy, and examined their inclusions by Raman spectroscopy. We obtained evidence of the sublithospheric origin of a majority of IaB diamonds, and their interaction with deep hydrocarbon and carbonate fluids, which might be important to interpret the recycling of nitrogen in deep Earth.

Results

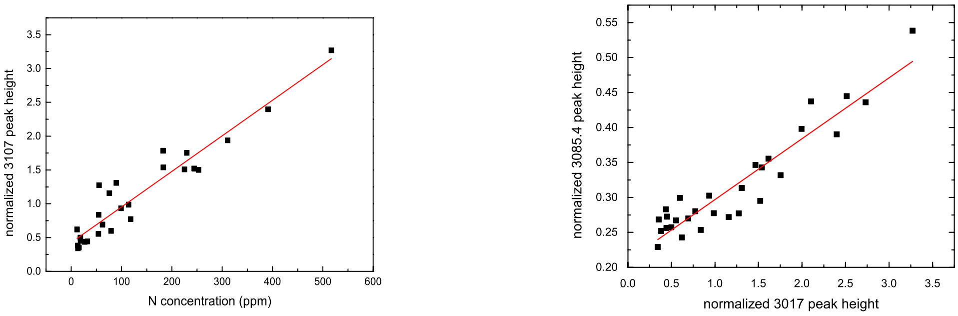

Figure 1 (Left) Nitrogen concentration determined by FTIR as a function of hydrogen concentration constrained by normalized 3107 peak height. (Right) Normalized 3107 peak height as a function of 3085.4 peak height. (Peak height at 3107 cm^{-1} and 3085.4 cm^{-1} have been normalized by diamonds peak at 2460 cm^{-1})

We examined about 69 IaB diamonds ranging from 0.2 ct to ~100 ct, and most of them (97%) shown the degradation of the platelet peaks, while 38 diamonds show micro inclusions detectable by Raman spectroscopy. Nitrogen concentration ranges from 4 ppm to 516 ppm determined by FTIR spectra. Hydrogen peaks at 3107 cm^{-1} have been detected, which shows a linear correlation with nitrogen concentration (Fig. 1). We observed the peak at 3085.4 cm^{-1} featured by IaB diamonds with milky appearance or cloudy inclusions; in contrast, this peak is missing among more than 90% of IaB diamonds without detectable cloudy inclusions. We normalized the peak height at 3107 cm^{-1} and 3085.4 cm^{-1} to diamond peak at 2460 cm^{-1}, and observed a linear correlation of the two peaks (Fig. 1). However, no correlation of the peak height at 3085.4 cm^{-1} and 3107 cm^{-1} has been observed for the greyish or violet type IaAB diamonds. Therefore, the peak at 3085.4 cm^{-1} could be a typical optical feature for the milky IaB diamond, which might be related with the VN3H defects (Goss et al., 2014) and B aggregation.

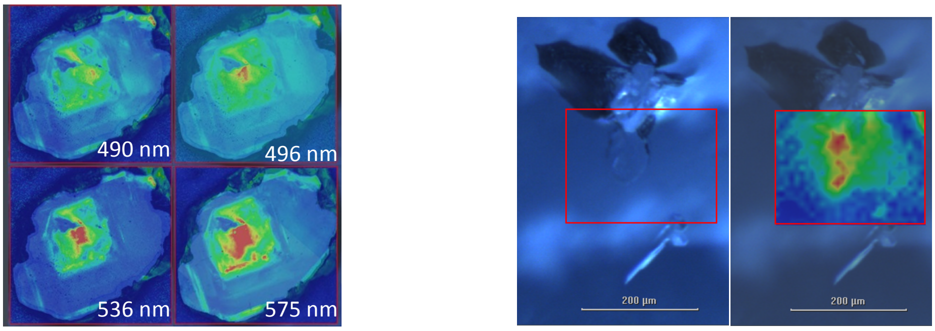

Figure 2 (Left) Diamond defect maps of photo-luminescence (PL) spectra taken with 455 and 532 nm excitations at liquid-nitrogen temperature. (Right) PL mapping of the 536 nm defect around the fracture area alongside a walstromite inclusion.

From cathodoluminesence (CL) images of the IaB diamonds, we found about half of them show dislocation networks and deformation features, indicating they have been brought up from deep Earth and experienced plastic deformation under high-pressure conditions. Photo-luminescence spectra have been taken at liquid-nitrogen temperature. Among 69 stones we examined, we observed ~90% IaB milky diamonds contain 536 nm defect, in contrast with IaB diamonds with no distinct cloudy features among which less than 30% showing 536 nm defects. In a IaB diamond with cloudy zone in the center, we observed 490 nm, 496 nm, 536 nm, and 575 nm defects in the cloudy center compared with the relatively clean surrounding area (Fig. 2). The 536 nm defect has also been observed in the discoid fracture alongside a walstromite inclusion, which might be caused by high temperature plastic deformation (Fig. 2). Therefore, presence of 536 nm defects in most milky IaB diamonds may indicate a certain dislocation style associated with high temperature.

By examining systematically the mineral inclusions in those diamonds, we found more than three quarters of them are from sublithosphere, indicated by inclusions that might be fragments of transition zone and lower mantle. Walstromite, larnite, titanite, coesite, Ca-perovskite assemblages have been found for more than half of the IaB diamonds, which indicates they originate as deep as the transition zone area. The equilibrium of the Ca-silicate inclusions imply that the initial Ca-silicate inclusions were trapped by diamond growth at conditions near to the $CaSiO_3$-walstromite → larnite (β-Ca_2SiO_4)+$CaSi_2O_5$-titanite equilibrium phase boundary, which begins above 10 GPa and 1773 K (Anzolini et al., 2016). Besides, we observed ferropericlase in several IaB diamonds, coexisting with walstromite and Ca-perovskite, indicating a superdeep origin of its host diamonds. We also found jeffbenite (TAPP) in three typical IaB diamonds, either as separate phase or coexisting with enstatite pyroxene and walstromite. The well preserved rhombus shape of the jeffbenite inclusion (Fig. 3) indicates that it could be a syngeneic inclusion with the host diamond forming in the lower mantle as bridgmanite while retrograde to current phase. In addition, spinel phase which has been considered as retrogressed calcium ferrite (CF) structured phases with high Al content at upper lower mantle (Walter et al., 2011) was observed coexisting with enstatite pyroxene phase in several milky IaB diamonds with relatively high hydrogen concentration. Interestingly, we found calcite and dolomite inclusions in six IaB diamonds coexisting with walstromite or as separate phases, with calcite phase in a well-crystallized rhombus shape suggesting their syngeneic character. The coexisting walstromite phase indicates their deep origin and implies that a carbonate-rich fluid has been involved during the diamond forming process in the transition zone. Moreover, methane has been detected coexisting with carbonate phases in a IaB diamond with low nitrogen concentration (4 ppm). In this typical diamond, calcite, dolomite, magnetite, ferropericlase, spinel, nepheline and corundum have been detected by Raman spectroscopy. Methane has been detected in the fluid jacket in several inclusions (Fig. 3). Coexisting of methane and carbonate phases could confirm the former experimental evidence of the production of methane through the reaction $CaCO_3+H_2O+FeO \rightarrow CH_4+CaO+Fe_3O_4$ under mantle conditions (Scott et al., 2004).

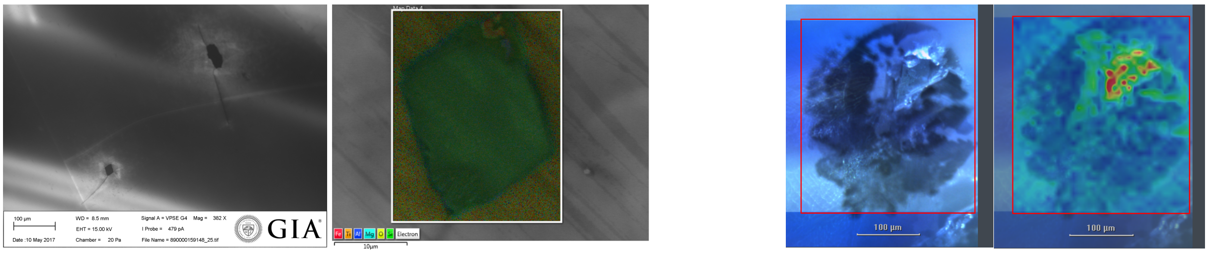

Figure 3 (Left) CL image of a diamond with jeffbenite (TAPP) phase on the surface and the chemical mapping of the smaller one with rhombus shape. (Right) Raman mapping of the methane peak at ~2913 cm^{-1} in a diamond inclusion with spinel and nepheline.

Discussions

Combined with FTIR, Raman spectroscopy and the luminescence optical features, formation of IaB diamonds may take place in the transition zone and lower mantle region where large size pure IaB diamonds (5 ct up to 100 ct) can form. Absence of the platelet peak and presence of the 536 nm defect for most milky IaB diamonds indicates they have experienced high temperature during their residence in the deep Earth, which could take a long geological time suggested by the full aggregation of B center. The FTIR features of the IaB diamonds suggests a N-H rich fluid has been involved during the diamond formation process, which could reach as deep as the lower mantle in ancient geological time. Compared with nitrogen free sublithospheric diamonds (such as IIa diamonds with metallic inclusions, Evan et al., 2016), inclusions in the pure IaB diamonds suggests they could form from C-O-H system that might be more compatible with nitrogen.

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