

Metasomatic Processes in the Cratonic Lithosphere: the case of Polycrystalline Diamonds

E. Thomassot^(1,2), P. Cartigny⁽²⁾, J.W.Harris⁽³⁾

¹*Stable Isotope Lab, Dept. of Earth and Planetary Sciences, McGill University, Montréal, Qc, Canada*

²*LGIS, Institut de physique du Globe de Paris, France*

³*Dept. of Geographical and Earth Sciences, University of Glasgow, UK*

Introduction

The composition of cratonic lithosphere, and more particularly of fluids and melts that circulate through it, is a subject that has been partly investigated through the study of natural diamonds. Integrated work, compiling carbon and nitrogen isotopic data, nitrogen content and speciation in diamonds, as well as the chemistry of their mineral inclusions, lead to a better understanding of continental lithosphere evolution (Shirey et al., 2003). But in spite of a large dataset concerning diamonds, some basic questions related to (i) the nature of the carbon source(s) from which diamonds crystallize, and (ii) the crystallization process itself remain partially unresolved. However, most studies carried out on diamonds only consider monocrystalline (i.e., gem) diamonds. But natural diamonds formed in the Earth's mantle do not only occur as a single "gem" crystals but also are found with a large variety of polycrystalline forms (i.e., diamond aggregates).

This second type of diamond consists of fine-grained diamond aggregates thought to represent a rapid crystallization in localized areas of carbon oversaturation, which allow high nucleation rates. To date, these crystallization conditions have always been associated with "abnormal" geological contexts like large impact events, decompression environments in shallow-seated explosion structures, or abnormal mantle domains oversaturated by carbon-bearing fluids because of their peculiar geodynamical context (e.g., environments of kimberlite eruption or regions rich in crustally derived fluids in subduction zones). Nevertheless, excepting the evidence for more rapid crystallization, differences between polycrystalline diamonds and gem crystals remain poorly discussed.

In order to establish what makes the polycrystalline diamonds special (or not) we undertook a coupled study (C and N isotopic compositions, N-content and N-speciation, chemistry of mineral inclusions) and compared them to gem diamonds from same kimberlite pipes.

Sample description

For the present study, nineteen samples of cryptocrystalline diamond aggregates originated from Orapa and Jwaneng kimberlite pipes (Botswana) have been provided. For these two pipes, gem diamonds have previously been studied, which revealed distinct $\delta^{13}\text{C}$ distributions as well as $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ trends characteristic of these localities.

The samples are dense and are formed by grey to black interlocking crystallites (from 100 to 500 μm in size). They have a bright to glassy lustre and are commonly identified as Framesites (see figure 1a). Orapa framesites ($n=9$) range from 1 to 2.5 cm in length and are characterized by crack, euhedral microdiamonds (Fig 1b) and mineral inclusions (garnet and clinopyroxene) on their surface (Fig 1a). Jwaneng framesites ($n=10$) are smaller ($< 1 \text{ cm}^3$). Following to the definition of McCandless et al. (1989), they occur either as rounded coarse aggregates (typical glassy lustre), or as fine grained aggregates with angular shape and bright sugary surfaces.

Mineral Inclusions

Garnet (Gt) and clinopyroxene (Cpx) are present in Orapa specimens. We analysed their chemical composition in order to reconstruct the paragenetic association from which these diamonds grew.

Gt parageneses have been determined using their CaO and Cr_2O_3 content (according to Sobolev et al., 1973). We identified three types of Gt. Cr-rich specimens ($\text{Cr}_2\text{O}_3 = 6.3 \pm 0.1 \text{ wt\%}$), with iron content lower than 7.5 wt% Cr are taken to be associated with highly residual peridotite. Transitional compositions with intermediate Cr content ($\text{Cr}_2\text{O}_3 = 1.7 \text{ wt\%}$) correspond potentially to a less residual peridotite (i.e. lherzolite). Finally, Cr-depleted garnet ($\text{Cr} \leq 0.3 \text{ wt\%}$), which likely resulted from the partial melting of a protolith containing orthopyroxenes as attested by the low Ca content ($\text{Ca} \leq 4 \text{ wt\%}$), resemble a websteritic paragenesis rather than a simple eclogite.

Cpx inclusions are rich in Cr and Mg ($\text{Cr}_2\text{O}_3 = 0.33$ to 0.79 wt\% ; $\text{MgO} = 14.76$ to 18.29 wt\%), and their parageneses are determined using their Fe and Al

contents. Three framesites contained Al- and Fe-poor Cpx ($\text{Al}_2\text{O}_3 = 2.52 \text{ wt\%}$; $\text{FeO} = 0.35 \text{ wt\%}$) that displayed relatively high Mg numbers (Mg# range from 0.85 to 0.83) and were classified as diopsides, typical of peridotitic mineralogy. Two other samples contained inclusions with higher amounts of Al and Fe ($\text{Al}_2\text{O}_3 = 5.28 \text{ wt\%}$; $\text{FeO} = 1.49 \text{ wt\%}$) and were linked to a websterite as a protolith (Mg# = 0.77).

Chemical analysis of mineral inclusions reveals that framesites are formed in equilibrium with multiple parageneses. We clearly identified peridotitic to websteritic mineral assemblages in framesites, as mentioned by Deines et al. (1993) for gem diamonds from the same locality. In two samples, we found both peridotitic and eclogitic garnet. This result is unexpected because such heterogeneous association in a same gem diamond is extremely rare (see Gurney, 1989).

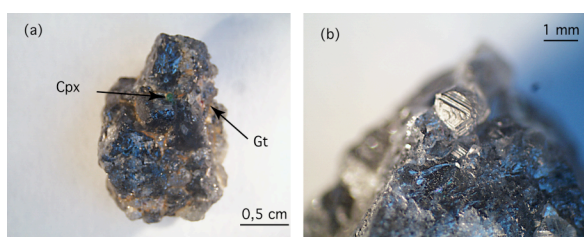


Figure 1: Photography of framesites from Orapa. (a) Cpx and Gt inclusions on the surface of Or 8, (b) Octahedral microdiamonds of sample Or 7.

Results

We measured carbon and nitrogen isotopic compositions, nitrogen content and aggregation state in multiple grains ($n=107$) from the whole sample set.

Carbon isotopic compositions of Orapa samples exhibit a bimodal distribution illustrated in Fig. 2, with $\delta^{13}\text{C}$ ranging from -23.5 to -4.2‰ w.r.t. PDB. Numerous measurements in each sample (from 10 to 28 grains analyzed in one specimen) allow us to conclude that the carbon isotopic compositions of framesites are surprisingly homogeneous ($\delta^{13}\text{C}$ standard deviation always smaller than 0.9‰). The Jwaneng sample set is also homogeneous in terms of C isotopes and displays an asymmetric Gaussian distribution with $\delta^{13}\text{C}$ values ranging from -17.8 to -0.75‰ (median = -4.93‰).

Carbon isotopic compositions presented here are similar to those published for gem diamonds from the same mines, from the point of view of both the total range and shape of the $\delta^{13}\text{C}$ distributions (Deines et al., 1993 and Cartigny et al., 1998)

Nitrogen isotopic compositions measured on multiple grains are enriched in light isotopes with $\delta^{15}\text{N}$ ranging from -6.5 to $+17\text{‰}$ w.r.t. Air, whereas Jwaneng samples display a narrow range in $\delta^{15}\text{N}$ (from -8.3 to $+5.2\text{‰}$) around a median value of -1.92‰ .

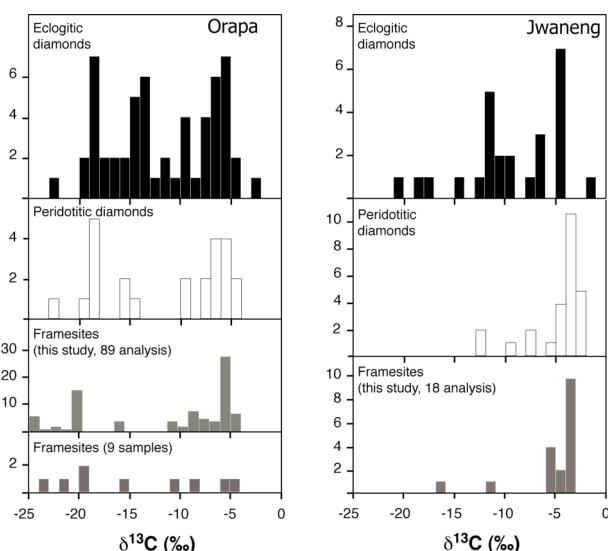


Figure 2: Histograms of $\delta^{13}\text{C}$ values for both gem peridotitic and eclogitic diamonds (Deines et al., 1993 and Cartigny et al., 1998) compared with framesite (this study), from Orapa and Jwaneng pipes.

Nitrogen concentrations are markedly high in Orapa samples (from 0 to 2360 ppm, with an average value of 913 ppm) as well as in Jwaneng specimens (from 336 to 1263 ppm, with an average value of 800 ppm). N-content in framesites is clearly higher than in octahedral diamonds, whether peridotitic or eclogitic, as illustrated in Figure 3. We note that from a N-content point of view, framesites are similar to other polycrystalline diamond such as fibrous (i.e., kimberlite-related) diamonds (Fig. 3). The N-aggregation is advanced with a majority of IaB defects (79% and 31% of IaB defect at Orapa and Jwaneng respectively) and confirms the xenocrystic nature of these polycrystalline diamonds.

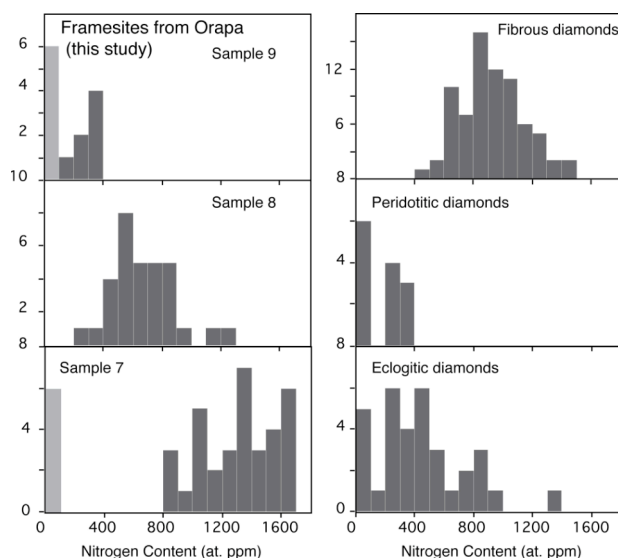


Figure 3: N-content (in atomic ppm) of framesites (this study). N-content of gem diamonds and fibrous diamonds are shown here for comparison (Deines et al., 1993 and Cartigny et al., 1999).

Discussion

From textural considerations, framesites are consistent with a rapid crystallization under carbon-oversaturated conditions that enable high nucleation rates (see Jaynes, 1978). This textural hypothesis is confirmed here by the striking homogeneity of carbon isotopic compositions, which are consistent with single-step formation from an effectively infinite carbon source. Similarly, the high and homogeneous nitrogen content reported in framesites is also typical of rapid growth, which would allow the incorporation of higher levels of impurities (as suggested by Boyd et al., 1994). This would suggest that the physical conditions of formation and, consequently, the crystallization process of polycrystalline diamonds have to differ in some way from those for gem diamonds.

For both mines, the framesite C- and N-isotopic compositions display the same range as gem diamonds. We also identified the trend of decreasing N content with decreasing $\delta^{13}\text{C}$ previously identified in gem diamonds from Orapa and Jwaneng, and interpreted as the result of diamond crystallization from a fluid. The present data set ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) does not support a relationship between framesites and fibrous diamonds as recently suggested (Heaney et al., 2005; Rege et al., 2008). *A contrario*, our study clearly point out similarities between gem diamonds and framesites and, from their C and N isotopic composition we propose that these two types of diamonds likely crystallize from similar type of fluids.

Finally, nitrogen speciation indicates crystallization in a temperature domain compatible with lithospheric mantle (1100 to 1150°C), and does not suggest a contemporaneous formation with respect to kimberlite eruption, as previously proposed on the basis of REE patterns in mineral inclusions in framesites (Gorshkov et al., 1998). We suggest that such a signature for REE may be an artifact of the high porosity of the aggregates.

Conclusion

Coupled isotopic study of framesites confirms that these diamonds crystallize in the Earth mantle during a metasomatic process that provided the C-rich fluid needed to induce a high nucleation rate. According to a series of similarities reported here between framesites and gem diamonds (same distribution of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, same N-content and $\delta^{13}\text{C}$ covariation, same paragenetic affinities) we conclude that the cryptic metasomatic processes responsible for framesite formation must be considered in the formation of octahedral monocrystalline diamonds as well.

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