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# Diamond origin and genesis: a C and N stable isotope study on diamonds from a single eclogitic xenolith (Kaalvallei, South Africa)

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## Introduction

In order to better constrain diamond origin and genesis, diamond-bearing xenoliths represent a unique piece of mantle, with several diamonds being a priori related by similar growth conditions. However, despite the scarce abundance of this type of sample, Kaalvallei kimberlite in South Africa provides an unusual amount of diamond-bearing xenoliths (Viljoen, 2005). This work focuses on 35 diamonds extracted from a single eclogite nodule (K8/109) from Kaalvallei. We examined the relationships between carbon and nitrogen isotopic compositions and diamond growth to focus on (a) the origin of eclogitic diamonds and their relationships with their eclogitic host rock (b) the diamond genesis related to metasomatic process and (c) the implication for worldwide diamond formation.

## Analytical techniques

Diamonds were analyzed by micro-Fourier transform infrared (FTIR) spectroscopy to determine both nitrogen content ($N_{FTIR}$) and nitrogen aggregation state. The thirsty five diamonds have been analysed for $\delta^{15}N$. These analyses follow the experimental procedure given by Boyd at al. (1995) with accuracies of 0.5‰, 5% and 0.1‰ (all 2σ) for $\delta^{15}N$, total nitrogen content and $\delta^{13}C$ respectively.

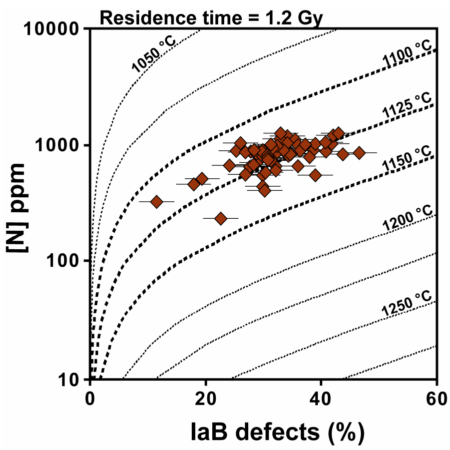


Fig. 1 N-%B diagram of diamonds from K8/109 xenolith. A residence time of 1.2 b.y was assumed. Diamonds show a small range of nitrogen aggregation.

## Results

As illustrated in Figure 1 nitrogen contents in diamonds range from 239 to 1272 ppm, which is in average higher (N-content of 839 ppm) compared to worldwide eclogitic diamond sources (about 300 ppm). Nitrogen aggregation states vary from 11.5% to 43.7% of IaB defects. Nitrogen content is positively correlated with N-aggregation state. Note that FTIR diamond characteristics of K8/109 xenolith are similar to that described for diamonds from other Kaalvallei xenoliths (i.e. N-content range from 366 to 1387 ppm and aggregation states from IaA to IaAB [10]).

Diamond carbon isotope data cover a narrow range of $\delta^{13}C$ values from −5.96‰ to −4.22‰ (see Fig. 2) with an average of $\delta^{13}C$= −5.22‰, it only represents 5% of the worldwide diamond isotopic range. These diamonds are in the range of the large majority of mantle-related samples which have $\delta^{13}C$ value about −4 ± 2‰. The nitrogen isotopic compositions vary little among negative values from $\delta^{15}N$= −8.95‰ to −4.14‰ (see Fig. 2) with an average of $\delta^{15}N$= −6.86‰. The range of $\delta^{15}N$ covers only 15% of the worldwide eclogitic diamonds and falls in the so-called mantle range (i.e. most of mantle-derived samples have negative $\delta^{15}N$ value with an average of $\delta^{15}N_{mantle}$= −5 ± 2‰, e.g. Javoy et al., 1984).

## Diamonds and xenolith-related geothermometry

Nitrogen aggregation thermometry is based on the fact that the different nitrogen-bearing defects are related by second order kinetic diffusion processes (Chrenko et al., 1977). Nitrogen aggregation state depends chiefly on nitrogen content and temperature and little on time (Evans and Harris, 1989). Diamonds show a very good positive correlation between N-content and IaB defects and are plotted along a unique isotherm. That suggest they belong to a unique population with growth under similar physical conditions. We assume a residence time of 1.2 Gy based on data and on the Proterozoic Sm-Nd ages for most of eclogitic diamonds in Kaapvaal craton. Note that a difference for mantle residence times of 1 Gy to 3 Gy corresponds to a difference of 25 °C in mantle temperature. Although the poor dependence of the nitrogen aggregation with time could imply a multiplepopulation origin (i.e. several diamonds formed through discrete events separated by several million years), that is not consistent with $\delta^{15}N$ and $\delta^{13}C$ small ranges that is discussed below.

Ellis and Green garnet-clinopyroxene geothermometer gives temperature of 1180 °C and 1240 °C at 50 and 65 kbar respectively. This consistently higher $T_{Ellis\&Green}$ compared to $T_{FTIR}$ may be attributing to relatively large uncertainty on the activation energy Ea of the nitrogen thermometer.

**On a diamond genesis by metasomatic stage**

Because of small ranges of $\delta^{13}C$ and $\delta^{15}N$, no clear trends could be identified as illustrated in figure 2. However isotopic data are more compatible with diamond formation by a metasomatic process from a single homogeneous fluid than a solid by diffusion. In the latter case we should measured isotopic diffusion fractionations, and also a positive correlation between $\delta^{13}C$ and $\delta^{15}N$, this is not the case.

The evolution of oxidised ($CO_2$ or carbonate-bearing) and reduced fluids can be modelled in a $\delta^{15}N$-$\delta^{13}C$-N space according to previous studies (e.g. Cartigny et al., 2001a; Thomassot et al. 2007). However because the range in isotopes compositions (Fig. 2) is small, we cannot so far reject/identify any type of fluid.

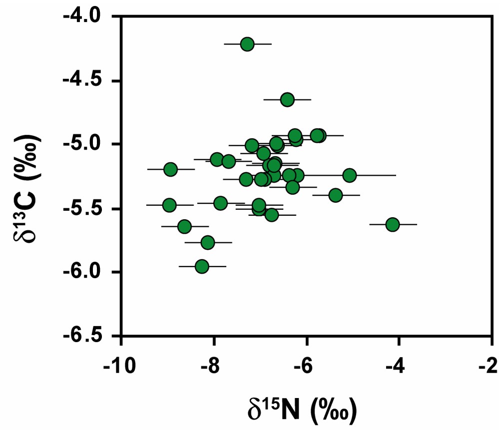


Fig. 2 Nitrogen and carbon isotopic compositions for 35 diamonds from the K8/109 xenolith.

**Evidence for a mantle-related origin of Kaalvallei diamonds**

The slight positive Eu anomaly in garnets from Kaalvallei eclogite xenoliths is consistent with oceanic crust material origin with the transformation of plagioclase into garnet. The range of oxygen isotopes in the K8/109 eclogite garnets varies from +5.8‰ to +7.1‰ and belongs to a larger range of $\delta^{18}O_{grt}$ for Kaalvallei diamond-bearing xenoliths (i.e range from +4.30‰ to +7.2‰). These values deviate from the oxygen isotopes mantle-range typically $\delta^{18}O_{grt}$= +5 to +6‰. The fractionation of oxygen isotopes requires sea-water interaction process at low temperature close to Earth surface. However trace element and oxygen isotope data cannot be used to constrain the source of carbon from which the diamond growth because of the potential metasomatic diamond growth.

Based on the $\delta^{13}C$ analyses only, it is not possible to distinguish carbon contributions from subducted materials or mantle because the Earth isotopic carbon cycle is in equilibrium. Inner reservoirs defined by MORB, peridotitic and eclogitic diamonds exhibit typical $\delta^{13}C$ centred on −5 ± 2‰, while external reservoir show the same $\delta^{13}C$ value of −5‰ if it is defined by a oceanic crust summarised to a mixture of 20% of organic matter (average $\delta^{13}C$ value of about −25‰) and 80% of carbonates (average $\delta^{13}C$ value of about 0‰). Yet the carbon isotopic compositions fall within the range of unmodified mantle.

In contrast the nitrogen isotopic tracer can be used to better constrain diamond origin. Compared to carbon isotopic composition, nitrogen isotopic composition of inner and outer earth reservoirs show distinct distribution (Fig. 3). MORB and diamonds show negative value of $\delta^{15}N$ with an average of −5 ± 2‰, while metasediments show clearly positive value of $\delta^{15}N$. Diamond is a good recorder of carbon and nitrogen source, the example of Kokchetav metamorphic diamonds (Cartigny et al., 2001b) shows positive $\delta^{15}N$ values as expected for a subducted material source. K8/109 Kaalvallei diamonds show negative $\delta^{15}N$ values centred on −6.86‰ which is symptomatic of a mantle origin, confirming the decoupled origin of diamond and the xenolith.

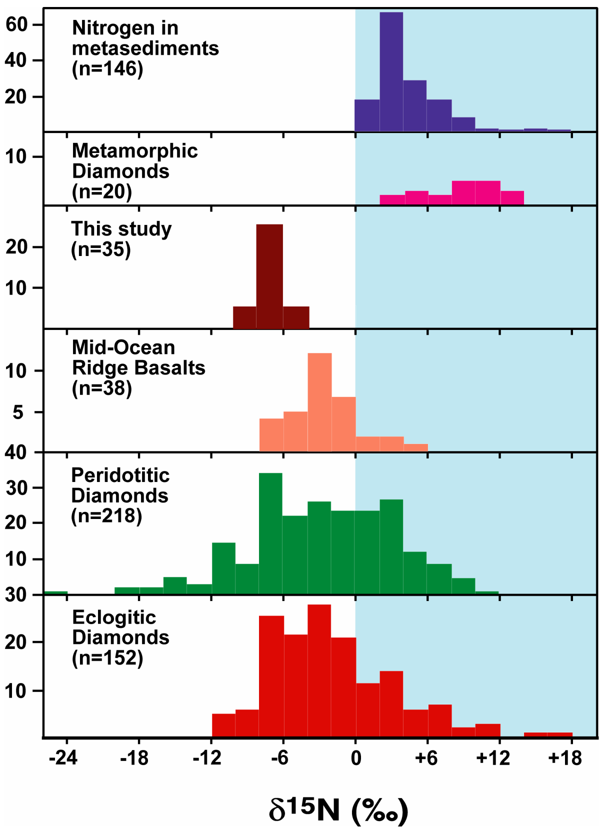


Fig. 3 Comparative histograms of $\delta^{15}N$ values for metasedimentary nitrogen, metamorphic diamonds from Akluilâk (Canada), K8/109 Kaalvallei diamonds, MORB, peridotitic and eclogitic diamonds.

**Implications for Kaalvallei and worldwide diamonds genesis**

The eclogitic diamond-bearing xenoliths recovered from the Kaalvallei kimberlite all exhibit similar main constituents and belong to the Group I variety (Kiviet, 2000). Their $\delta^{18}O$ range, trace element patterns and Ellis&Green temperatures are in the same order than K8/109 eclogite. Thus, we would expect a unique recycled subducted material for Kaalvallei diamond-bearing eclogite formation.

Kaalvallei diamonds show similar $\delta^{13}C$ and $T_{FTIR}$ (Kiviet, 2000), except for one diamond in xenolith KV5 which exhibit $\delta^{13}C = -11.45‰$ and higher $T_{FTIR}$ suggesting another carbon source. Based on these striking similarities we speculate that most of Kaalvallei diamonds has crystallized from a unique mantle-related fluid. This study gives additional evidence in favour of a metasomatic mantle-related origin for eclogitic diamonds.

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