



Constraining the internal variability of the stable isotopes of carbon and nitrogen within mantle diamonds



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ABSTRACT

The carbon and nitrogen isotope values of mantle xenoliths and xenocrysts are used to trace the cycling of volatiles in the deep Earth, for example, to place empirical constraints on the origin of diamond-forming carbon in the mantle. The global database for diamond shows that the $\delta^{13}\text{C}$ value of peridotitic diamonds is very narrow, typically around -5‰ , whereas eclogitic diamonds can show positive and very negative $\delta^{13}\text{C}$ values resembling crustal carbonates and crustal organic carbon (< -40 to $> +2\text{‰}$); commonly interpreted to reflect a relationship between eclogitic diamond formation and subduction zone planet tectonics. Curiously, diamonds from both parageneses can show positive (crust-like) and negative (mantle-like) $\delta^{15}\text{N}$ values (from < -40 to $> +20\text{‰}$). Most of these data are derived from single stage combustion gas sourced mass spectrometry, which produces simplistic datasets. By fragmenting single diamonds or using in-situ ion-beam techniques it is known that single diamonds can show large-scale heterogeneity for their carbon isotope values and nitrogen abundances, sometimes as large as entire populations of diamond across a few hundred micrometres. What is less well known is the scale of nitrogen isotope heterogeneity within single diamonds, and if the nitrogen isotope heterogeneity of single diamonds can provide an insight into why diamonds that show very restricted $\delta^{13}\text{C}$ values show a much large range of $\delta^{15}\text{N}$ values.

To investigate the scale, and to determine the origin of the nitrogen isotope heterogeneity (source vs. fractionation during diamond-formation) shown for populations of mantle diamonds we have determined multiple $\delta^{13}\text{C}$ – $\delta^{15}\text{N}$ values and nitrogen abundances from 14 monocrystalline (MCDs) and 25 polycrystalline diamonds (PCDs) using step-wise oxidation gas sourced mass spectrometry. These data show that the heterogeneity shown for carbon and nitrogen isotope values from single diamond samples presented here is typically $<5\text{‰}$ and $<8\text{‰}$ respectively, both of which are comparable to the standard deviation for the mean mantle $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values (± 3 and $\pm 4\text{‰}$). However, there are samples that show much larger heterogeneities for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values ($\leq 23\text{‰}$ and $\leq 33\text{‰}$ respectively), which cannot be generated by equilibrium stable isotope fractionation during, or prior to diamond-formation. These data suggest that isotopic heterogeneity may be present within the diamond-forming fluid on sub-mm scale, or that these diamonds formed during multiple diamond-formation events from isotopically distinct sources. From these 39 samples there are only 5 PCDs that show a larger range of carbon isotopes relative to nitrogen isotopes, but of these 5 samples only 2 show a range of $\delta^{13}\text{C}$ values outside of analytical uncertainty. The remaining 34 samples show a greater isotopic heterogeneity for $\delta^{15}\text{N}$ relative to $\delta^{13}\text{C}$ values. The samples with the largest carbon and nitrogen isotopic heterogeneity are also the samples with low-bulk $\delta^{13}\text{C}$ values ($< -10\text{‰}$), whilst there is no relationship between the ranges of nitrogen isotope values for a given sample and the corresponding bulk $\delta^{15}\text{N}$ value or nitrogen content.

These data show that $\delta^{15}\text{N}$ values recorded in mantle diamonds are relatively heterogeneous, and can show both mantle-like (negative) and crustal (sedimentary)-like (positive) $\delta^{15}\text{N}$ values within the same sample. We conclude that the large range of nitrogen isotope values seen within individual diamonds means that the observation of negative, mantle-like, nitrogen in mantle diamonds acquired by single-stage bulk combustion isotope ratio mass spectrometry cannot be used as a conclusive indicator for a mantle origin for the entirety of the diamond-forming carbon, and vice versa. Also, the behaviour of $^{15}\text{N}/^{14}\text{N}$ is not coupled with the behaviour of $^{14}\text{N}/^{12}\text{C}$ during diamond-formation. Instead, it appears that diamond-forming fluids can have positive and negative $\delta^{15}\text{N}$ values,

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irrespective of their $\delta^{13}\text{C}$ value(s). These data suggest that subduction induced nitrogen isotope heterogeneity may not be coupled with subduction induced carbon isotope heterogeneity in diamond-forming fluids.

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1. Introduction

The carbon and nitrogen isotopic compositions for crustal and mantle derived samples are, on average, distinct (Hoefs, 2009 and references therein) (Fig. 1a–d). This means that the carbon and nitrogen isotopic systems are potentially useful indicators for the interactions between crustal and mantle volatile during subduction zone plate tectonics, and associated magmatism/volcanism (Wallace, 2005). Based on this premise, the carbon and nitrogen isotopic compositions of diamonds formed in the mantle have been widely used as a tool for investigating the origins of diamond-forming carbon in the terrestrial mantle (Javoy et al., 1984; Boyd et al., 1987, 1992; Boyd and Pillinger, 1994; Cartigny et al., 1997, 1998a, 1998b, 1999, 2003, 2004, 2009; Shelkov 1997; Bulanova et al., 2002; Hauri et al., 2002; Gautheron et al., 2005; Harte et al., 1999; Shiryaev et al., 2005; Thomassot et al., 2007, 2009; Palot et al., 2009, 2013; Cartigny, 2010; Klein-BenDavid et al., 2010; Mikhail et al., 2013). Monocrystalline diamonds (MCDs) from the upper and lower mantle, containing both peridotitic and eclogitic silicate and sulphide inclusions, show a strong mean $\delta^{13}\text{C}$ of $-5 \pm 3\%$ (Cartigny, 2005 and references therein) (Fig. 1a). However, a subset of eclogitic and websteritic monocrystalline diamonds (Stachel and Harris, 2009) alongside peridotitic and websteritic polycrystalline diamonds (PCDs) (Mikhail et al., 2013) show ^{13}C -depletion akin to crustal organic carbon (Fig. 1a). Interpreting these data is not straightforward, because the stable isotopes of carbon can be fractionated under mantle conditions, ergo, conclusions based solely on carbon isotope data can be readily contested (Galimov, 1991; Kirkley et al., 1991). The use of nitrogen isotopes alongside carbon can theoretically provide a more accurate insight into the origin(s) of diamond-forming carbon, because the mean nitrogen isotope value for

peridotitic diamonds is $-5 \pm 4\%$ (Fig. 1c) (Cartigny, 2005) and the mean $\delta^{15}\text{N}$ value for pre-Cambrian crustal organic nitrogen is $+6 \pm 4\%$ (Fig. 1d) (Thomazo et al., 2009). This has lead several studies to argue that negative $\delta^{15}\text{N}$ values coupled with low $\delta^{13}\text{C}$ values are evidence against the subduction of crustal organic carbon as a source of diamond-forming fluids (Cartigny et al., 1998a, 1998b, 1999, 2009; Cartigny, 2010). However, the data presented in Fig. 1 are derived from bulk stable isotope determinations achieved by oxidation of single diamonds followed by isotopic analyses of the resulting gas (i.e. Boyd et al., 1987). This method provides information about the bulk of the diamond-forming carbon and nitrogen for a given sample, but does not provide information for the internal isotopic variability of a given sample (unless a single sample is fragmented prior to combustion and each fragment analysed separately). This is important to note because single diamonds can show internal geochemical and isotopic heterogeneity (Harte and Otter, 1992; Fitzsimons et al., 1999; Hutchison et al., 1999; Bulanova et al., 2002, 2010; Hauri et al., 2002; Zedgenizov and Harte, 2004; Shiryaev et al., 2005; Smart et al., 2011; Walter et al., 2011; Palot et al., 2012; Howell et al., 2013; Wiggers de Vries et al., 2013), meaning the bulk isotope value for a given sample may not reflect all of the components that contributed to the formation of the sample, i.e. single diamonds can show evidence of growth from volatiles derived from both the mantle and the Earth's surface which are not visible using data acquired with single stage combustion mass spectrometry.

The main aim of this study is to present data that quantifies the carbon and nitrogen isotopic heterogeneity of 14 monocrystalline and 25 polycrystalline diamonds using stepwise oxidation gas sourced mass spectrometry (see Boyd et al., 1997 for a discussion). We use these data to discuss the behaviour of $^{15}\text{N}/^{14}\text{N}$ relative to $^{13}\text{C}/^{12}\text{C}$ and total nitrogen content during diamond-formation in the mantle. We also outline several important implications for how best to extract geological information from diamond.

2. Samples

The diamonds investigated here were sourced from various localities as listed in Table 1. The PCDs are sub-divided into 3 groups. The first two groups are from an unknown Southern African origin (8 peridotitic and 12 websteritic samples; herein referred to as the PCD-P and PCD-W) (Kurat and Dobosi, 2000, 2010). The third group is a suit of 5 PCDs of unknown paragenesis originating from the Orapa kimberlite cluster, Botswana (PCD-Or) (Table 1). Note, the weighted mean values for the samples, which were analysed by stepwise oxidation (i.e. bulk carbon and nitrogen stable isotope values) for the PCD-P and PCD-W have been previously published in Mikhail et al. (2013). However, the stepped data presented here for the PCD-P and PCD-W samples were not previously published in Mikhail et al. (2013).

Table 1

List of the samples used in this study according to morphology, geographical origin, paragenesis and the amount of samples for each locality. * denotes the exact locality is unknown (see Kurat and Dobosi, 2000).

Morphology	Locality	Paragenesis	n
Monocrystalline	West Africa	Unknown	2
Monocrystalline	Mir, Siberia	Unknown	1
Monocrystalline	Cullinan, SA	Unknown	3
Monocrystalline	Sao Luiz, Brazil	Unknown	2
Monocrystalline	Sao Luiz, Brazil	Peridotitic	1
Monocrystalline	Collier-4, Brazil	Unknown	3
Monocrystalline	Collier-4, Brazil	Eclogitic	2
Polycrystalline	Botswana	Unknown	5
Polycrystalline	Southern Africa*	Peridotitic	8
Polycrystalline	Southern Africa*	Websteritic	12

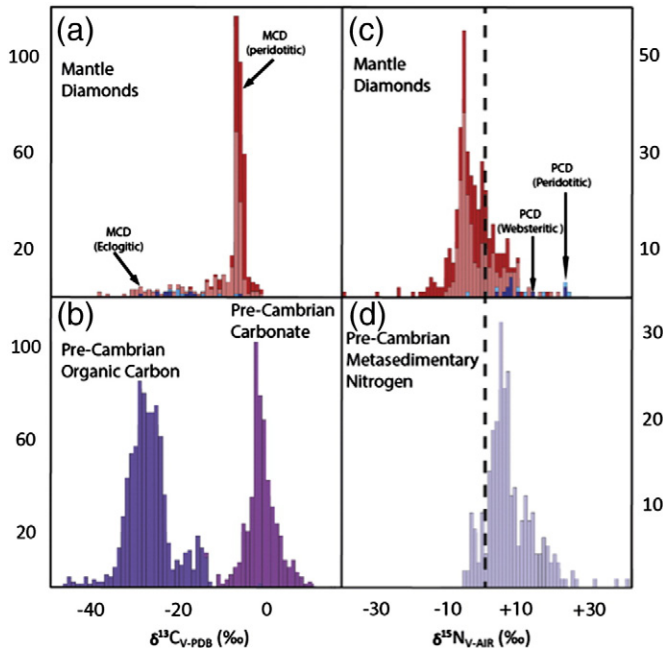


Fig. 1. Histograms showing the distribution for the carbon isotopes from (a) mantle diamonds, pre-Cambrian crustal organic carbon (b) and the same for nitrogen isotopes (c–d). Note, only data from diamonds where both carbon and nitrogen isotopes were determined are shown for an accurate comparison. The data are sourced from the following: Data for monocrystalline diamonds are from Boyd and Pillinger (1994), Cartigny et al. (1997, 1998a, 1998b, 1999, 2003, 2004, 2009), Cartigny (2010), Javoy et al. (1984), Palot et al. (2009, 2012) and Thomassot et al. (2007, 2009). The data for polycrystalline diamond are from Shelkov (1997), Gautheron et al. (2005) and Mikhail et al. (2013). The carbon and nitrogen isotope compositions for crustal organic carbon are from Thomazo et al. (2009) and Shields and Veizer (2002).

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