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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 δ^{13}C value of peridotitic diamonds is very narrow, typically around −5‰, whereas eclogitic diamonds can show positive and very negative δ^{13}C values resembling crustal carbonates and crustal organic carbon (<−40 to >+2‰); 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) δ^{15}N values (from <−40 to >+20‰). 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 δ^{13}C values show a much large range of δ^{15}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 δ^{13}C–δ^{15}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‰ and <8‰ respectively, both of which are comparable to the standard deviation for the mean mantle δ^{13}C and δ^{15}N values (±3 and ±4‰). However, there are samples that show much larger heterogeneities for δ^{13}C and δ^{15}N values (≤23‰ and ≤33‰ 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 δ^{13}C values outside of analytical uncertainty. The remaining 34 samples show a greater isotopic heterogeneity for δ^{15}N relative to δ^{13}C values. The samples with the largest carbon and nitrogen isotopic heterogeneity are also the samples with low-bulk δ^{13}C values (<−10‰), whilst there is no relationship between the ranges of nitrogen isotope values for a given sample and the corresponding bulk δ^{15}N value or nitrogen content.

These data show that δ^{15}N values recorded in mantle diamonds are relatively heterogeneous, and can show both mantle-like (negative) and crustal (sedimentary)-like (positive) δ^{15}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 $^{15}N/^{14}N$ is not coupled with the behaviour of $^{14}N/^{12}C$ during diamond-formation. Instead, it appears that diamond-forming fluids can have positive and negative δ^{15}N values,

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irrespective of their δ^{13}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.

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 δ^{13}C of −5 ± 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 ± 4‰ (Fig. 1c) (Cartigny, 2005) and the mean δ^{15}N value for pre-Cambrian crustal organic nitrogen is +6 ± 4‰ (Fig. 1d) (Thomazo et al., 2009). This has lead several studies to argue that negative δ^{15}N values coupled with low δ^{13}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.

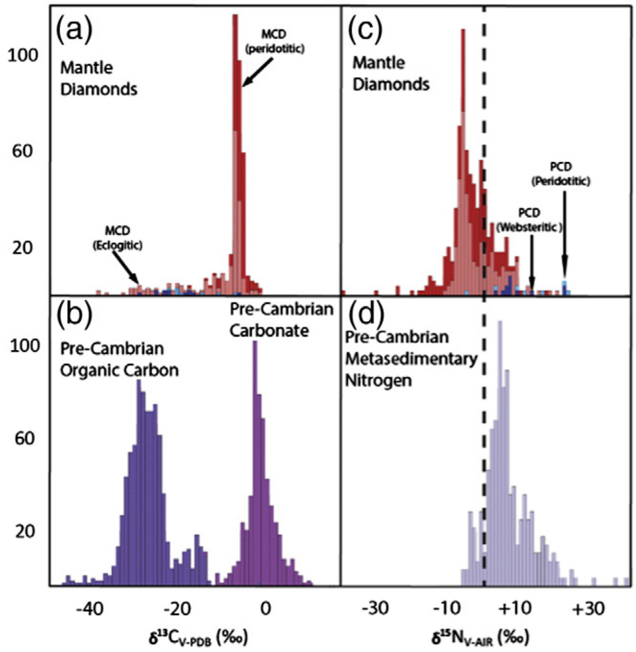

Fig. 1. Histograms showing the distribution for the carbon isotopes from (a) mantle diamonds, pre-Cambrian crustal organic carbon (b) and the same for nitrogen isotopes (c–d). Note, only data from diamonds where both carbon and nitrogen isotopes were determined are shown for an accurate comparison. The 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).

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}N/^{14}N relative to ^{13}C/^{12}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

The MCD samples are diamond fragments and laser sectioned off-cuts, not 'whole samples'. They are fluid-poor MCD, assumed to have grown under octahedral diamond growth conditions, as opposed to fibrous and cubic diamond growth. They come from Cullinan, South Africa ($n = 3$); Mir, Siberia ($n = 1$); West Africa ($n = 2$) and from two localities in Juina (Brazil), Sao Luiz and Collier 4 (with a total of 8 samples) (Table 1). These samples were mostly inclusion-free; therefore the paragenesis to some of these samples is unknown. Only the MCD samples from Juina contained inclusions and they are listed here: BZ270 contained an inclusion with a composition similar to olivine and three XRD-confirmed ferropericlase inclusions (peridotitic paragenesis); JUc4: contained ferropericlase; JUc7: contained an unknown inclusion (Hutchison et al., 1997). The following samples have been studied previously by Bulanova et al. (2010) and defined as eclogitic: J6 and J7 contained sulphide; J17 contained SiO_2; J18 contained Fe^0 + FeO and J19 contained SiO_2 + kyanite. The fragments analysed here were not the same polished sections analysed in Bulanova et al. (2010), but are instead off-cuts from the sample preparation procedure undertaken in that study.

3. Analytical technique

The $\delta^{13}C$-, $\delta^{15}N$-values and N-concentrations were obtained simultaneously using the custom made Finesse machine, housed at the Open University, UK (Boyd et al., 1997; Verchovsky et al., 1998). This facility operates with three fully automated static-mode mass spectrometers fed from a common extraction system under high vacuum (Verchovsky et al., 1998). The diamonds were crushed into pieces of around 0.19–1.022 mg and inclusion-free fragments were placed into a clean glass beaker and filled with propanol and incubated in an ultrasonic bath for 30 min then wrapped in clean Pt-foil. Samples were weighed using a Sartorius microbalance (precision of ~1 μg) to ensure that 100% yield is achieved during combustion by measuring the amount of combusted carbon using a high-precision baratron (precision better than 0.5% of the measurement). The main combustion sequence was performed repeatedly at 1100 °C for 30 min with as many steps as required to exhaust the whole sample and return the system to blank levels. The gas produced during the oxidation of diamond is mostly a mixture of $CO_2 + H_2O + N_2 + CO$. The CO is oxidised to CO_2 in the clean-up unit by heating CuO to >800 °C and the total $CO_2 + H_2O$ is trapped on a cryotrap at ca. −190 °C. The N_2 is then trapped on a molecular sieve at liquid nitrogen temperature and subsequently the molecular sieve is isolated from the cryotrap (by closing the valve between the sections) after both sections are pumped to remove the non-condensable gases (i.e. noble gases). The CO_2 is removed to the carbon analysis section by heating the liquid nitrogen cold finger to ca. −50 °C. The amount of CO_2 is then quantified using the high-precision baratron, and the isotopic composition of carbon is determined on a separate static mode mass spectrometer. Once the CO_2 is removed and stored within the baratron section the cold finger is heated to ca.120 °C and pumped to remove the H_2O. After that N_2 is desorbed from molecular sieves, additionally cleaned on CuO and analysed on a separate static mode mass spectrometer. All the procedures are fully automated (Verchovsky et al., 1998). Carbon and nitrogen stable isotope compositions ($^{13}C/^{12}C$ and $^{15}N/^{14}N$) are expressed in delta notation relative to the Pee Dee belemnite and air standards respectively (using carbon as an example); $\delta^{13}C = (^{13}C/^{12}C \text{ sample} / {}^{13}C/^{12}C \text{ standard} - 1) * 1000$. The N/C ratio is expressed as N ppm $= (N/C) * 1 \times 10^6$. The accuracy based on the analysis of international standards is $\pm<0.5‰$ for both $\delta^{13}C$ and $\delta^{15}N$ values and <10% for the N concentrations (2σ).

4. Results

The data presented in this study will be referred to as either 'bulk' or 'stepped'. Bulk data are derived from the weighted mean $\delta^{13}C$–$\delta^{15}N$ values and nitrogen concentrations for a given sample. The stepped data are the individual $\delta^{13}C$–$\delta^{15}N$ values and nitrogen concentrations released during each stage of oxidation. The bulk data reflect the average composition for the whole diamond placed in the furnace, whereas the stepped data reveal variations within the sample. The method employed here provides no spatial or temporal information, nor can this method accurately convey the relative proportions of each isotopic and elemental component within a sample because diamond growth sectors are not perfect spheres (Boyd et al., 1997). However, these data do provide new information for the multiple analyses and the range of $\delta^{13}C$–$\delta^{15}N$ values and nitrogen concentrations from individual mantle MCD and PCD.

4.1. Uncertainties and data validity

The total uncertainties for $\delta^{15}N$ values presented here takes into account the effects of the blank correction that therefore increases with decreasing nitrogen abundance for a given sample (as a function of increasing blank contribution). The measured $\delta^{15}N$ value and nitrogen mass are inclusive of the blank ($^{15}N/^{14}N$ for the sample + blank N_2). Therefore, we must correct the data for blank contribution to quantify the $\delta^{15}N$ value of the sample, i.e. the precision for $\delta^{15}N$ calculated using the reference gas correction is not applicable post-blank correction because those errors are inclusive of the blank ($^{15}N/^{14}N$ for the sample + blank). The removal of a known blank $^{15}N/^{14}N$ ratio where the blank mass is comparable or less than the sample mass is not a problematic task, as long as the blank is monitored regularly; i.e. the blank being a well constrained variable/parameter. Likewise, to calculate the uncertainties post-blank correction one must know the blank levels, isotopic composition and both the abundance and isotopic variability of the blank over the time period of data acquisition. The precision on the measured $\delta^{13}C$ value is determined using the reference gas measurements after each sample analysis because no blank correction is required. The precision of the measured $\delta^{15}N$ determined using the reference gas, is typically 0.5‰. The blank corrected error (referred to herein as the uncertainty) of the sample $\delta^{15}N$ value is greater post-blank correction. The blank corrected values and the associated uncertainty are calculated using the following equations:

$$\text{Mass of nitrogen in the sample} = N_m - N_b \tag{1}$$

$$\delta^{15}N_c = \frac{\left(\delta^{15}N_m \cdot N_m\right) - \left(\delta^{15}N_b \cdot N_b\right)}{N_m - N_b} \tag{2}$$

$$\Delta\delta^{15}\mathrm{N_c} = \frac{1}{(\mathrm{N_m}-\mathrm{N_b})^2}\cdot\sqrt{\left[(1-\delta^{15}\mathrm{N_m})^2\cdot(\Delta\mathrm{N_m})^2+(1-\delta^{15}\mathrm{N_b})^2\cdot(\Delta\mathrm{N_b})^2+(\mathrm{N_m}-\mathrm{N_b})^2\cdot\left((\Delta\mathrm{N_m})^2\cdot(\Delta\delta^{15}\mathrm{N_m})^2+(\Delta\mathrm{N_b})^2(\Delta\delta^{15}\mathrm{N_b})^2\right)\right]} \quad (3)$$

where N_m and N_b refer to the mass of nitrogen in the measured gas and blank, $\delta^{15}N_m$ and $\delta^{15}N_b$ refer to the $\delta^{15}N$ value of the measured gas and blank, $\Delta\delta^{15}N_m$ refers to the measured error in per mil, $\Delta\delta^{15}N_b$ and ΔN_b refer to the standard deviation for the multiple blank analyses and $\Delta\delta^{15}N_c$ is the blank corrected precision on the $\delta^{15}N$ value of the sample.

The Pt-foil used to load the sample is twice cleaned prior to sample wrapping. Pt-foil is first placed into a quartz tube attached to an O_2-source (CuO powder), evacuated and heated to ~900 °C for 24 h to oxidise any contaminants. The Pt-foil is removed and placed in a pure ozone environment and treated under UV-light for 24 h. Despite the care taken to clean the sample and Pt-foil before loading into the furnace, there will still be several nanograms of nitrogen present as an unavoidable contaminant. This is a relevant factor when determining the $^{15}N/^{14}N$ of samples with nitrogen concentrations of circa < 2 ng. Therefore, the first step in determining the nitrogen concentration and $^{15}N/^{14}N$ composition in diamonds is to remove the contaminants from both the diamond and the Pt-foil within the quartz combustion furnace under high-vacuum. This is achieved by employing a pyrolysis step at 1100 °C for 1 h (Shelkov, 1997). Once pyrolysis is completed, the furnace temperature is reduced to 500 °C and the sample is combusted in order to oxidise any reduced-species of nitrogen which were not removed in the 1100 °C pyrolysis step. Blank levels for nitrogen obtained are better than 1 ng per combustion step above 800 °C respectively (Fig. 2a) (carbon blanks are routinely <50 ng). Sample analysis was bracketed every two runs with blank determinations, and the blank subtraction and calculations for the error propagation for a given sample account for two blank runs during the same analytical session. Our blank corrected total uncertainties are directly comparable with the data from other laboratories working on the nitrogen isotope values from diamond (Cartigny et al., 2009; Cartigny, 2010; Palot et al., 2012). The error bars shown for $\Delta(\delta^{15}N)$ are the combined blank-corrected total uncertainties for the end-members used to determine the range. For example, the blank-corrected uncertainty of the end-members (maximum and minimum $\delta^{15}N$ value) for sample Dia020 was both ± 0.5‰, therefore the uncertainty on the $\Delta(\delta^{15}N)$ value for sample Dia020 shown here is ±1‰. Conversely, the blank-corrected uncertainty for the end-members of sample Dia018 was ±1.8 and 2.3‰, therefore the uncertainty on the $\Delta(\delta^{15}N)$ value for sample Dia018 shown here is ±4.1‰ (see Table 2).

Finally, there is no evidence of nitrogen isotope fractionation induced by the technique employed nor does the data show evidence of a strong influence from the blank. The variability for the sample $\delta^{15}N$ value does not show any systematic variability, i.e. the data do not show an increase or decrease for $\delta^{15}N$ value progressively subsequent stages of combustion (Table A1). The platinum foil blanks during the two analytical sessions were characterised by ^{15}N-depleted $\delta^{15}N$ values with average $\delta^{15}N$ values of -9 ± 6 ($n = 54$) and -4 ± 7‰ ($n = 30$) for March–April and August 2010 respectively (Fig. 2b). The blank-corrected sample data show a range of $\delta^{15}N$ values from +36 to −14.8‰ (Fig. 3) with no relationship for the bulk or stepped $\delta^{15}N$ or $\delta^{13}C$ value vs. the nitrogen concentration for these samples (Fig. 3a–b). Importantly, samples with >50% blank contributions were omitted from this study (the average blank percentage in this study for March–April 2010 is 26% $\sigma = 19$‰ where $n = 54$ and for August 2010 is 30% $\sigma = 20$‰ where $n = 20$).

4.2. Bulk combustion data

The PCD samples show a large range of nitrogen contents from <10 to >3600 ppm (Table 2 and Fig. 4). The range of the 25 PCDs used in this study is comparable to the range for monocrystalline diamonds of peridotitic and eclogitic paragenesis globally (where the sample set is 2 orders of magnitude larger ($n = > 2500$) (reviewed by Cartigny, 2005)). The bulk C- and N-stable isotope data for the PCD-Or samples are very similar to the PCD-P and PCD-W samples. The range for the $\delta^{13}C$ values for PCD in this study is collectively −4.6 to −28.5‰ (Fig. 5) with an overall mode at −18‰ for carbon (mean = −18.1 ± 6.1‰) and +8.6‰ for nitrogen (mean = +9.2 ± 7.3‰). The MCDs are from 4 geographical localities (Table 1) and have a large range of nitrogen concentrations from 3 to 624 ppm ($n = 9$) (Table 2). The majority of these diamonds show $\delta^{13}C$ values within the range commonly seen for mantle diamonds (termed mean mantle value) (Fig. 5). The exceptions are samples J6, J18 and J19 that show ^{13}C-depletion relative to the mean mantle value (Fig. 5). The $\delta^{15}N$ values for the MCD mostly plot within the range shown for peridotitic MCD from −8.5 to +12.3‰ (mean = +1.7 ± 6‰; $n = 14$) (Fig. 5).

4.3. Stepped combustion data

The stepped data for each sample are shown in the Supplementary material (Table A1), presented in Fig. 5 and the ranges for each sample are shown alongside the bulk data in Table 2. To express the stepwise oxidation data we use the parameters $\Delta(\delta^{13}C)$, $\Delta(\delta^{15}N)$ and $\Delta(N/C)$, defined as the maximum–minimum carbon and nitrogen isotope value and nitrogen concentration for an individual diamond produced by stepwise oxidation respectively. The range of nitrogen concentrations is loosely related to the bulk nitrogen concentration of a given sample (Fig. 4; $R^2 = 0.66$). However, specifically the samples show heterogeneous nitrogen abundances. For example, sample ORF23 has a bulk nitrogen concentration of 678 ppm with a much larger total range of nitrogen contents (1280 ppm; $n = 3$) whereas sample Dia061 has bulk nitrogen concentration of 1428 ppm with a much smaller total range of nitrogen contents (107 ppm; $n = 3$), both of which are heterogeneous outside of analytical uncertainty (which is ±10%) yet the scale of heterogeneity for samples ORF23 and Dia061 is not related to their bulk nitrogen abundances.

Stepped data for the stable isotope values show an almost constant relationship where $\Delta(\delta^{15}N) > \Delta(\delta^{13}C)$ (Fig. 6). There are only 5 PCDs that show a $\Delta(\delta^{13}C) > \Delta(\delta^{15}N)$, but of these 5 samples, only 2 are beyond analytical uncertainty. The samples with the highest $\Delta(\delta^{13}C)$ values are from the PCD-Or samples (ORF3 and ORF4) where both show the same $\Delta(\delta^{13}C)$ value of 23.5‰ with $\Delta(\delta^{15}N)$ values of 4.9 and 6.1‰ respectively (Fig. 6). The highest $\Delta(\delta^{15}N)$ values (>15‰) are seen for 5 of the PCD-W samples and 2 MCD samples from Juina (one of an eclogitic and one of an unknown paragenesis). The majority of the samples shown here plot with $\Delta(\delta^{15}N)$ values <10‰ (Fig. 6). The samples with the largest $\Delta(\delta^{15}N)$ and $\Delta(\delta^{13}C)$ values are also samples with low-$\delta^{13}C$ values (Fig. 7a, c). However, there is no correlation for $\Delta(\delta^{15}N)$ vs. $\delta^{13}C$ or $\delta^{15}N$ (Fig. 7c–d) or for the bulk nitrogen content of the diamond, $\Delta(N/C)$ (Fig. 8a, b). With the exception of samples ORF3 and ORF4, there is a steady increase for $\Delta(\delta^{13}C)$ with an increasing $\Delta(N/C)$, however this relationship is not true for all of the samples with a high $\Delta(N/C)$ (Fig. 8b).

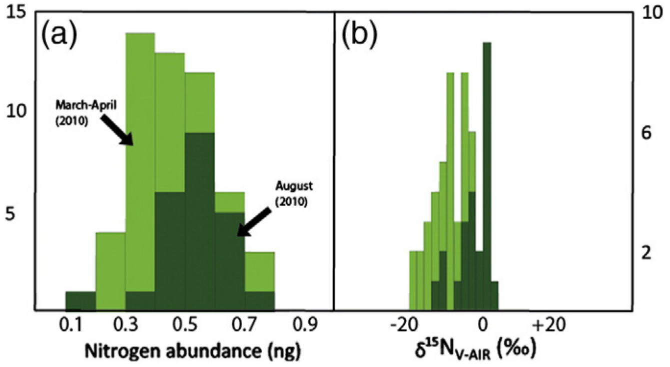

Fig. 2. Histograms showing the distribution for the nitrogen abundance (a) and isotopic composition (b) for the platinum foil blanks analysed during the two analytical sessions.

5. Discussion

5.1. Nitrogen concentration variability in mantle diamonds

The majority of the samples in this study show heterogeneous nitrogen concentrations (Fig. 4). These observations suggest that the initial N/C ratio for the diamond-forming fluid(s) is highly heterogeneous, or the partition coefficient of nitrogen between diamond and C–O–H fluid is not a constant during diamond formation. Our data cannot make a distinction between these two models. We instead direct the reader to previous studies who provide contrasting conclusions for nitrogen to be compatible (Stachel and Harris, 2009) and incompatible (Cartigny et al., 2001) during diamond-formation relative to the diamond-forming fluid(s).

5.2. Carbon and nitrogen isotope variability in mantle diamonds

These data show a clear relationship whereby the variability for nitrogen isotope values is typically larger than the variability for carbon isotope values within individual diamonds (Fig. 6), as is the case for the distribution of nitrogen isotopes vs. the distribution for carbon isotopes from mantle diamonds on a global scale (Fig. 1a & c). The heterogeneity shown for carbon and nitrogen isotope values from single diamond samples presented here is typically <5‰ and <8‰ respectively (Fig. 6), both of which are comparable to the standard deviation for the mean mantle δ^{13}C and δ^{15}N values (±3 and ±4‰; Cartigny, 2005). Such small variations can be explained by stable isotope fractionation during diamond-formation in an open system (Cartigny et al., 2001 for carbon and (Thomassot et al., 2007) for nitrogen).

However, there are samples that require a different explanation. PCD-Or samples ORF3 and ORF4 show $\Delta(\delta^{13}$C) values of 23.5‰ (Table 2) which is comparable to the range of δ^{13}C values shown for the bulk analysis of 11 separate PCD-Or samples from Orapa, Botswana (Deines et al., 1993). These data can be explained by

Table 2
This table shows the bulk carbon and nitrogen isotope values for the samples in this study and the parameters $\Delta(\delta^{15}$N), $\Delta(\delta^{13}$C) and Δ(N/C). The latter parameters are defined as the maximum–minimum carbon and nitrogen isotope value and nitrogen concentration for an individual diamond produced by stepwise oxidation. The uncertainty shown for δ^{15}N (±) is blank corrected (see Section 4.1) and the combined uncertainty (combined ±) for the $\Delta(\delta^{15}$N) is the combined blank-corrected uncertainty for the end-members used to determine the range. The precision for the δ^{13}C values is ±0.5‰ and 10% for the nitrogen contents, therefore the combined uncertainty for $\Delta(\delta^{13}$C) is ±1‰.

Morphology	Paragenesis	Weight (mg)	Sample	Locality	N ppm	ΔN/C	δ^{13}C	Δ (δ^{13}C)	n	δ^{15}N	±	$\Delta(\delta^{15}$N)	Combined ±	n
Monocrystalline	Unknown	0.670	WA5	West Africa	19	13	−2.8	3.5	5	−6.5	1.4	5.6	3.6	5
Monocrystalline	Unknown	0.620	WA3	West Africa	20	42	−4.4	0.5	3	−8.5	1.5	7.6	3.0	3
Monocrystalline	Unknown	0.260	Mir3	Mir, Siberia	35	14	−8.6	0.7	2	6.3	0.5	10.8	1.0	2
Monocrystalline	Unknown	0.480	Prem22d	Cullinan, SA	3	4	−6.2	2.4	3	0.1	3.5	1.1	10.3	2
Monocrystalline	Unknown	0.310	Prem22c	Cullinan, SA	36	57	−7.1	2.6	4	3.7	1.5	9.6	5.1	3
Monocrystalline	Unknown	0.250	Prem173a	Cullinan, SA	23	36	−3.4	4.4	4	2.0	1.0	2.2	3.7	2
Monocrystalline	Unknown	0.190	JUc4	Sao Luiz, Brazil	17	27	−6.5	1.6	2	3.4	0.6	0.8	1.4	2
Monocrystalline	Peridotitic	0.470	BZ270	Sao Luiz, Brazil	7	58	−7.7	1.4	3	4.8	2.2	8.6	3.4	3
Monocrystalline	Unknown	0.190	JUc7	Sao Luiz, Brazil	12	2	−6.5	0.1	2	−6.4	2.6	2.2	9.4	2
Monocrystalline	Unknown	0.204	J-7	Collier-4, Brazil	34	3	−5.6	1.0	2	6.1	1.5	9.0	4.4	2
Monocrystalline	Eclogitic	0.336	J-17	Collier-4, Brazil	463	76	−7.6	3.0	3	2.3	0.5	9.3	1.0	3
Monocrystalline	Eclogitic	0.201	J-19	Collier-4, Brazil	56	60	−19.9	0.8	2	−2.8	1.1	15.8	4.6	2
Monocrystalline	Unknown	0.405	J-18	Collier-4, Brazil	48	80	−23.8	3.4	4	7.5	1.2	20.9	1.5	4
Monocrystalline	Unknown	0.541	J-6	Collier-4, Brazil	624	169	−10.6	1.4	5	12.3	0.8	8.9	1.9	5
Polycrystalline	Unknown	0.390	ORF3	Botswana	44	51	−27.0	23.5	3	14.0	1.2	4.9	1.0	3
Polycrystalline	Unknown	0.380	ORF4	Botswana	9	2	−23.3	23.5	3	14.7	3.6	6.1	4.1	3
Polycrystalline	Unknown	0.290	ORF7	Botswana	92	19	−24.0	2.8	2	7.6	0.5	1.2	2.2	2
Polycrystalline	Unknown	0.330	ORF23	Botswana	678	1280	−22.9	9.1	3	6.7	0.5	9.1	2.1	3
Polycrystalline	Unknown	0.360	ORF27	Botswana	173	199	−24.2	1.3	3	4.2	0.5	7.0	1.9	3
Polycrystalline	Peridotitic	0.334	Dia050	Southern Africa[*]	314	97	−24.1	2.0	4	21.5	0.8	6.1	1.0	4
Polycrystalline	Peridotitic	0.248	Dia074	Southern Africa[*]	59	49	−4.6	1.0	3	5.2	1.4	3.1	1.9	3
Polycrystalline	Peridotitic	0.891	Dia066	Southern Africa[*]	412	562	−24.6	7.7	10	21.7	0.6	13.2	1.0	10
Polycrystalline	Peridotitic	0.334	Dia005	Southern Africa[*]	449	228	−21.6	6.4	14	21.8	1.3	5.5	1.0	14
Polycrystalline	Peridotitic	0.523	Dia054	Southern Africa[*]	130	137	−16.5	1.3	4	12.0	0.5	1.8	1.6	4
Polycrystalline	Peridotitic	0.480	Dia078	Southern Africa[*]	76	30	−28.5	1.5	3	6.6	0.5	1.7	1.0	3
Polycrystalline	Peridotitic	0.400	Dia006	Southern Africa[*]	28	13	−19.3	0.2	4	−0.2	2.0	8.3	1.2	4
Polycrystalline	Peridotitic	0.307	Dia019	Southern Africa[*]	207	83	−19.1	2.6	4	8.6	0.5	2.4	3.4	4
Polycrystalline	Websteritic	0.278	Dia052	Southern Africa[*]	34	69	−15.9	0.8	4	4.8	2.5	20.1	5.8	4
Polycrystalline	Websteritic	0.260	Dia059	Southern Africa[*]	13	12	−22.9	1.9	4	5.3	6.1	33.3	9.5	4
Polycrystalline	Websteritic	0.369	Dia018	Southern Africa[*]	15	6	−22.2	1.6	3	6.4	2.8	9.3	4.1	3
Polycrystalline	Websteritic	0.360	Dia030	Southern Africa[*]	8	55	−16.3	6.2	3	6.4	3.9	21.9	3.2	3
Polycrystalline	Websteritic	0.270	Dia073	Southern Africa[*]	3635	1905	−17.6	1.4	4	6.9	0.5	4.3	1.0	4
Polycrystalline	Websteritic	0.341	Dia022	Southern Africa[*]	1635	2074	−21.3	4.3	4	8.6	0.5	24.7	1.6	4
Polycrystalline	Websteritic	0.250	Dia053	Southern Africa[*]	56	17	−21.1	0.9	2	2.0	0.7	1.9	1.0	2
Polycrystalline	Websteritic	0.296	Dia061	Southern Africa[*]	1428	107	−13.9	1.7	3	15.3	0.5	1.0	1.0	3
Polycrystalline	Websteritic	0.208	Dia063	Southern Africa[*]	462	102	−19.1	1.4	3	22.5	0.5	3.9	1.0	3
Polycrystalline	Websteritic	0.227	Dia068	Southern Africa[*]	266	167	−5.5	3.3	3	2.7	0.5	6.3	1.0	3
Polycrystalline	Websteritic	0.260	Dia001	Southern Africa[*]	54	52	−18.9	1.9	4	−5.7	2.8	10.7	1.0	4
Polycrystalline	Websteritic	1.022	Dia020	Southern Africa[*]	437	676	−9.8	2.6	21	10.7	0.7	30.6	1.0	21

[*] denotes the exact locality is unknown (see Kurat and Dobosi, 2000)

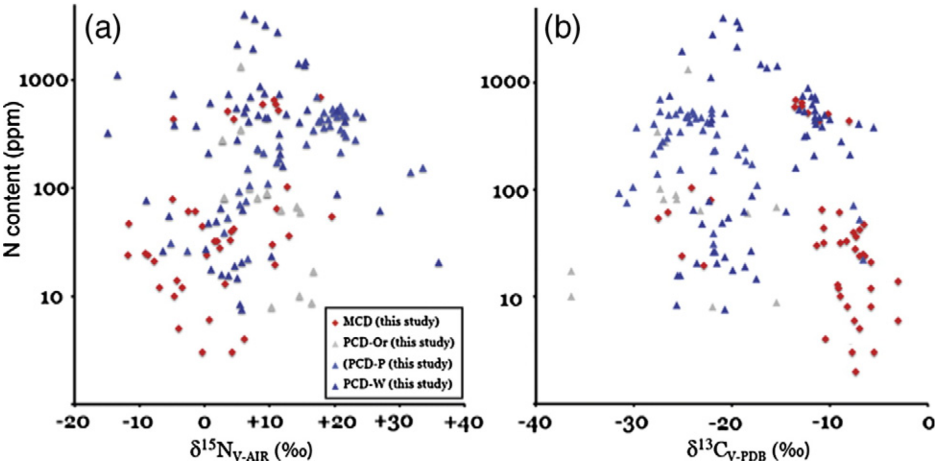

Fig. 3. Variation diagrams for the nitrogen isotope composition vs. the nitrogen content of each step during analysis (a) and for the carbon isotope composition vs. the nitrogen content of each step (b) for the samples in this study. Note the lack of any co-variations.

incomplete mixing of mantle and crustal end-member components (Mikhail et al., 2013), but importantly these data suggest that isotopic heterogeneity may be present within the diamond-forming fluid on very localised scales. The extreme $\Delta(\delta^{15}\text{N})$ values of >8‰ cannot be explained by equilibrium stable isotope fractionation during diamond formation because nitrogen isotope fractionation between diamond and molecular or ammonic nitrogen is too small under mantle temperatures (Richet et al., 1977). But we do acknowledge that these data are not well constrained (see Busigny and Bebout, 2013 for a review), therefore more theoretical and experimental data are required. However, the possibility of large kinetic fractionation of $^{15}\text{N}/^{14}\text{N}$ at mantle temperatures, both between different phases and between different growth sectors within a single diamonds needs to be considered. Yokochi et al. (2009) presented evidence of kinetic isotope fractionation between ferromagnesian minerals and phlogopite can be very large, where the assumed reaction molecular-ammonic nitrogen can result in a large δ^{15}N fractionation of 25.4‰, whilst also being accompanied by a large fractionation for the total nitrogen abundance between the two components (≥order of magnitude). Also, Boyd et al. (1988) and Reutsky et al. (2008) show a large kinetic Δ^{15}N of up to ca.40‰ between octahedral and cubic growth sectors found in synthetic diamonds grown from metal (Fe–Ni) solvents and also show that the kinetic isotopic effect is accompanied by a large difference for the nitrogen contents between the components. To date, data from only one sample has been presented in the literature that investigates this fractionation in a natural sample and found no evidence for kinetic nitrogen-isotope fractionation during diamond-formation in the mantle (Cartigny et al., 2003). Also, the lack of a relationship for Δ(N ppm) vs. $\Delta(\delta^{15}\text{N})$ (Fig. 8d) suggests that kinetic isotope fractionation is not the cause for the extreme $\Delta(\delta^{15}\text{N})$ values of >8‰ shown here. We propose that the large range of δ^{15}N values, with both ^{15}N-enriched and ^{15}N-depleted values for peridotitic diamonds globally (Fig. 1c) and for the samples in this study (Fig. 6) reflects mantle heterogeneity induced by the subduction of ^{15}N-enriched crustal nitrogen into a ^{15}N-depleted mantle (akin to the conclusion in Fischer et al., 2005 for mantle derived silicates).

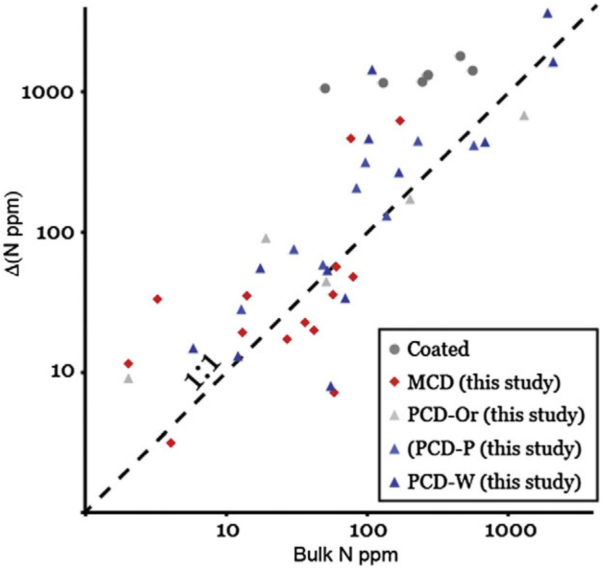

Fig. 4. Variation diagrams for the range of nitrogen concentrations within single samples vs. the bulk nitrogen concentration for the samples. Data for coated diamonds are from Boyd et al. (1987).

5.3. Implications for understanding diamond-formation in the mantle

Studies that employ single stage (bulk) combustion methods to determine the carbon and nitrogen isotope values of mantle diamond provide useful information about the origin of the bulk of diamond-forming carbon. However, this method will produce data that cannot resolve dynamic information within single samples, unless they are first fragmented into separate smaller grains. Therefore, bulk combustion methods may have produced overly simplistic models for diamond-formation. For example, the occurrence of negative δ^{15}N values determined by bulk combustion mass spectrometry for some eclogitic MCD in conjunction with moderate- to low-δ^{13}C values has been used as an argument against the subduction of crustal organic carbon as the source of eclogitic diamond-forming fluids (Cartigny et al., 1998a, 1998b, 1999, 2009; Cartigny, 2010). This counter argument is founded on crustal nitrogen being dominated by positive δ^{15}N values (Thomazo et al., 2009) and mantle nitrogen being dominated by negative δ^{15}N values (see the discussion in Cartigny et al., 2009 and Fig. 1c–d). Here we have shown the variability for $^{15}\text{N}/^{14}\text{N}$ within individual mantle diamond can be large (Fig. 5b). Importantly, single diamonds can record both negative and positive δ^{15}N values, irrespective of the bulk δ^{13}C values; i.e. samples Dia020, Dia022, Dia006, Dia001, Dia068, J-17, J-18 and BZ270 (Fig. 5a–b). This observation complicates the use of bulk nitrogen isotope values as a source identification for diamond-forming carbon (using bulk combustion isotope ratio mass spectrometry). For example, samples Dia022 (PCD) and J18 (MCD) show definitively low (bulk) δ^{13}C values (−21.3 and −19.9‰) and positive bulk δ^{15}N values (+8.6 and +7.5‰). Using only the bulk stable isotope data these diamonds would appear to have formed from crustal organic carbon and nitrogen with no evidence of a mantle component. However, when observing the stepwise oxidation data, both samples also show a component with 'mantle-like' δ^{15}N values

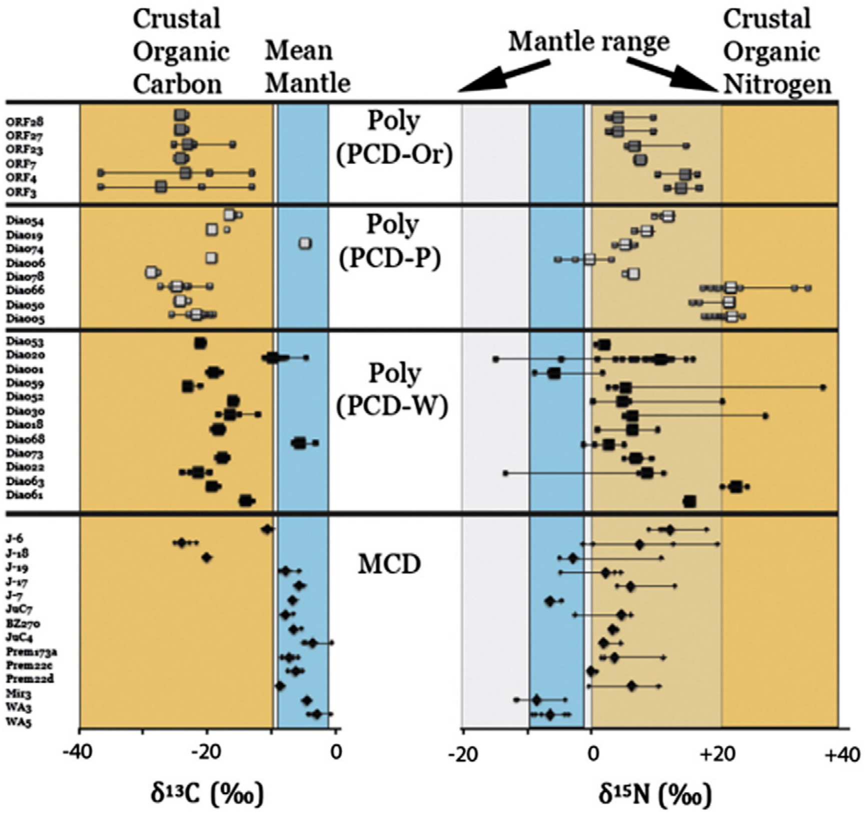

Fig. 5. The range of carbon (left) and nitrogen (right) stable isotope values from single MCD and PCD in this study. The orange areas represent the typical ranges shown for crustal organic materials (Thomazo et al., 2009) and the blue areas represent average mantle $\delta^{13}C$ and $\delta^{15}N$ values (Cartigny, 2005). The range shown for the mantle $\delta^{15}N$ value is smaller than the range in Fig. 1 for clarity (extends down to ca. −40‰). The large symbols show the bulk (weighted mean) stable isotope values and the smaller symbols are the individual stable isotope values recorded during the different stages of oxidation (see Table A1).

(−13.3 and −1.3‰ respectively), demonstrating that a mantle component likely contributed to the formation of these diamonds (Fig. 5b). Conversely, should the bulk $\delta^{15}N$ data have been negative, then a solely mantle origin for the diamond-forming carbon might have been wrongly assigned (i.e. sample J-19; Fig. 5b). We find that the large range of nitrogen isotope values seen within individual diamonds means that the stable isotopes of nitrogen acquired by bulk combustion methods cannot be used as a conclusive indicator for a mantle origin of diamond-forming carbon, and vice versa. However, conclusions regarding the origin of diamond-forming carbon using bulk C–N stable isotope determinations should be viewed in light of assigning an origin to the 'bulk', and not the entirety, of the diamond-forming carbon and nitrogen.

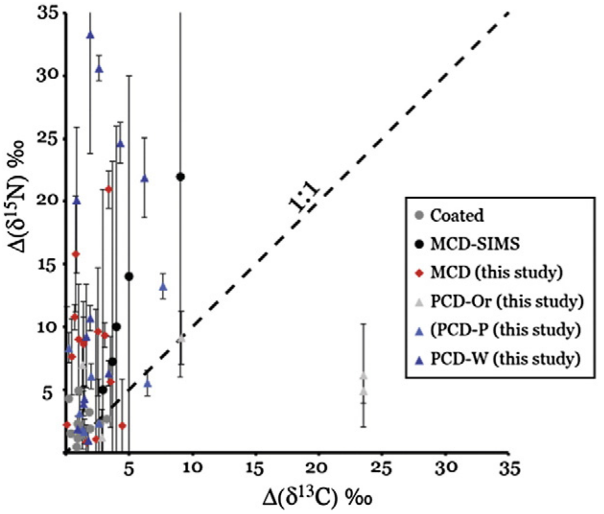

Fig. 6. The range of carbon isotope values vs. the range nitrogen isotope values from the samples in this study. Data for the coated samples are from Boyd et al. (1987) and MCD data from the literature are from Hauri et al. (2002), Bulanova et al. (2002) and Shiryaev et al. (2005). Note the much reduced total uncertainties for $\Delta(\delta^{15}N)$ between the data from this study (diamond and triangle symbols) vs. the SIMS data (filled circles).

The fact that the range of $\delta^{15}N$ values is typically larger than the range of $\delta^{13}C$ values within individual diamonds (Fig. 6) is viewed here as evidence for nitrogen isotope heterogeneity in diamond-forming fluids, and the mantle in general. Likewise, nitrogen isotope heterogeneity has also been recorded in basaltic samples (Fischer et al., 2005; Barry et al., 2012) and mantle xenoliths (Fischer et al., 2005; Yokochi et al., 2009), with typical $\delta^{15}N$ values from ca. +8 to ca. −8‰ (noteworthy, the basaltic and xenolith $\delta^{15}N$ data show no evidence of being produced through degassing; see Fischer et al., 2005). The data in Fig. 1c suggests that the nitrogen isotope heterogeneity is a global phenomenon, however, when combined with the data from our study, these results collectively suggest that nitrogen isotope heterogeneity is also present on very localised scales (Fig. 5b).

The data presented here suggest that the stable nitrogen isotopes are either (a) not homogenised within diamond-forming fluids prior to and during diamond formation, thus recording the observed nitrogen isotope heterogeneities within individual PCD and MCD, or (b) sourced from isotopically distinct sources during multiple, distinct, growth events. A viable mechanism to preserve isotopic heterogeneity of nitrogen whilst allowing carbon isotope homogeneity in diamond-forming fluids (for fluids with both 'mean mantle' and 'low-$\delta^{13}C$' values) would require a stark difference in the mobility of nitrogen and carbon in mantle fluids, melts and/or minerals (where carbon mobility ≫ nitrogen mobility). One explanation could be that carbon is a very incompatible element in mantle silicate phases (Shcheka et al., 2006), whereas ammonic nitrogen is a moderately incompatible element, being compatible in K-bearing phases and highly incompatible in other phases (Watenphul et al., 2010). To infer the behaviour of

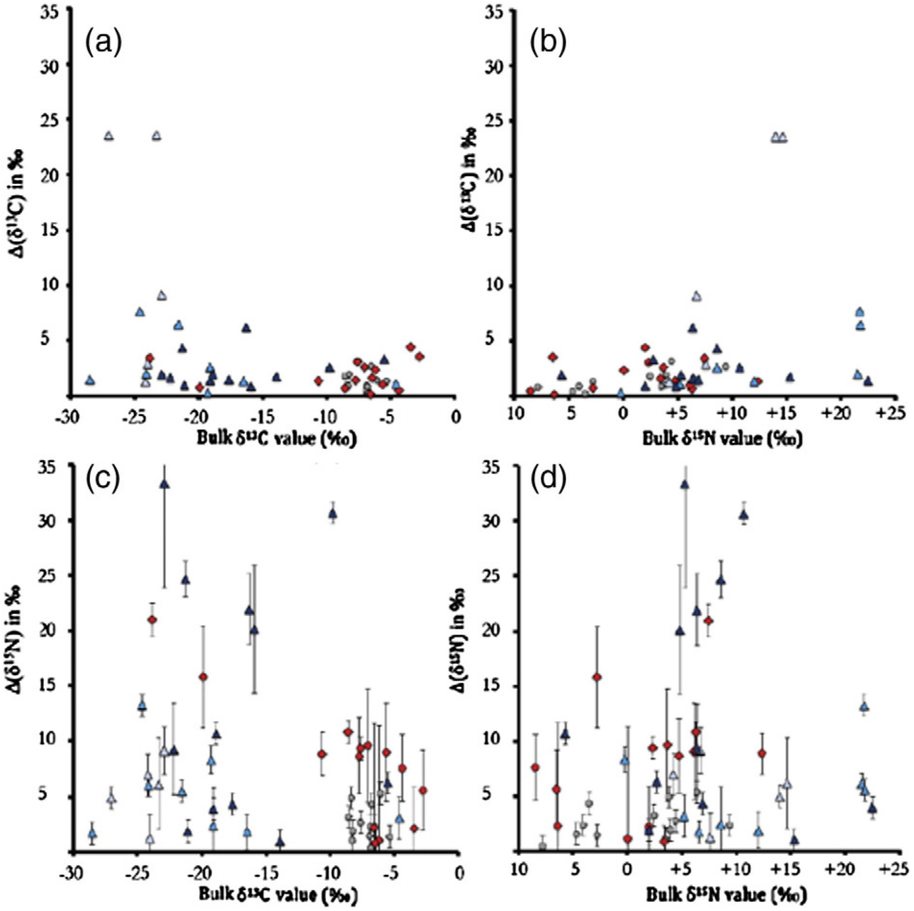

Fig. 7. Variation diagrams for the bulk carbon and nitrogen isotope values for MCD and PCD vs. the internal range of carbon isotope values (a, b) and nitrogen isotope values (c, d) for the MCD and PCD samples. Symbols are the same as Fig. 6.

nitrogen in COH-fluids relative to carbon requires an understanding of the speciation of nitrogen in equilibrium with C – O – H and relevant mineral phases/melt compositions to the mantle. However, these data are inadequate at present to address this issue (see Busigny and Bebout, 2013 for a review). Therefore, we can only infer that a difference in the relative compatibilities and solubilities of carbon and nitrogen species could enable the homogenisation of carbon isotopes in an evolving fluid whilst preserving primordial and tectonic-induced δ^{15}N heterogeneities through geological time, thus explaining the larger $\Delta(\delta^{15}N)$ values for diamonds with much smaller $\Delta(\delta^{13}C)$ values. Our new data shows $\Delta(\delta^{15}N) \gg \Delta(\delta^{13}C)$ irrespective of the total nitrogen concentration (Fig. 8a & c) and Δ(N/C) (Fig. 8b & d). Thus, the stable isotopes of nitrogen and the elemental incorporation of nitrogen in diamond appear decoupled prior to, and during diamond-formation in the mantle.

6. Conclusions

We have determined multiple δ^{13}C–δ^{15}N values and nitrogen contents from 14 monocrystalline and 25 polycrystalline diamonds using step-wise oxidation. Our results show a variability of nitrogen concentrations within single diamonds consistent with previous studies. However, these data cannot distinguish between mantle heterogeneity, or a variable partition coefficient for nitrogen in diamond during diamond-formation to explain the heterogeneity. We therefore direct the reader to previous studies who provide contrasting conclusions for nitrogen to be compatible (Stachel and Harris, 2009) and incompatible (Cartigny et al., 2001) in diamond relative to the diamond-forming fluids.

The variability of stable isotopes of nitrogen within individual diamonds is typically larger than the variability for the stable isotopes of carbon. Some of these data show a large range of nitrogen and carbon isotope values from single samples that cannot be explained by equilibrium stable isotope fractionation during diamond formation. Our data also show that the fractionation of stable isotopes of nitrogen is decoupled from the behaviour of elemental nitrogen incorporation during diamond formation. This explains why correlations between the stable isotopes of nitrogen and elemental nitrogen abundances are not observed for populations of natural diamonds on both local and global scales. We find 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 bulk combustion mass spectrometry cannot be used as a conclusive indicator for a mantle origin of the entirety of diamond-forming carbon, and vice versa.

We strongly suggest that future determinations for the nitrogen concentration, δ^{13}C and δ^{15}N values for populations of mantle diamonds should consider the large $\Delta(\delta^{15}N)$, $\Delta(\delta^{13}C)$ and Δ(N/C) shown here for individual diamonds. We recommend that future analysis should be performed in a manner that allows the internal variability of these parameters to be determined. Analytical techniques would include stepwise oxidation (*this study*), fragmentation and the combustion of multiple fragments of a given sample (Boyd et al., 1987, or in situ SIMS measurements on polished samples (Bulanova et al., 2002) assuming the total uncertainties for $^{15}N/^{14}N$ determinations in diamond using SIMS have been improved upon.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2013.12.014.

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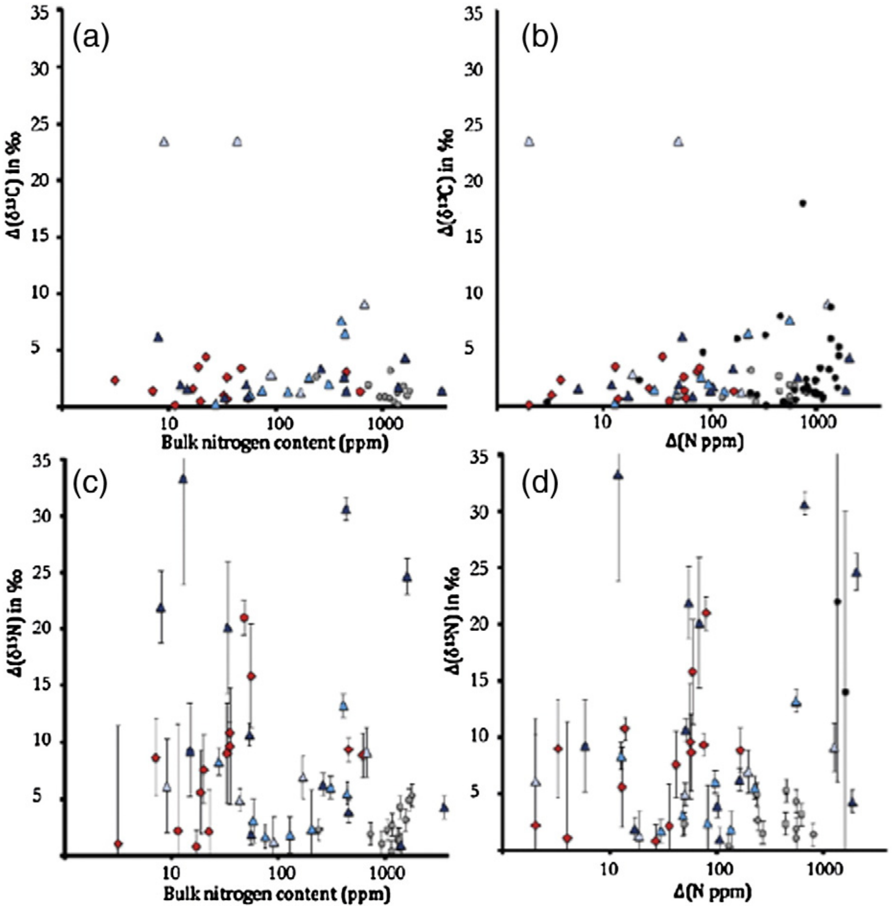

Fig. 8. Variation diagrams for the bulk nitrogen content and the internal range of nitrogen contents of MCDs and PCDs vs. the internal variability for the carbon isotope values (a, b) and nitrogen isotope values (c, d) for the same MCD and PCD samples. Symbols are the same as Fig. 6. Note the much reduced total uncertainties for $\Delta(\delta^{15}N)$ between the data from this study (diamond and triangle symbols) vs. the SIMS data (filled circles) in (d).

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