Carbon and nitrogen isotope systematics in diamond: Different sensitivities to isotopic fractionation or a decoupled origin?

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ABSTRACT

Using stable isotope data obtained on multiple aliquots of diamonds from worldwide sources, it has been argued that carbon and nitrogen in diamond are decoupled. Here we re-investigate the carbon–nitrogen relationship based on the most comprehensive microbeam data set to date of stable isotopes and nitrogen concentrations in diamonds (n = 94) from a single locality. Our diamond samples, derived from two kimberlites in the Chidliak Field (NE Canada), show large variability in $\delta^{13}C$ (-28.4 ‰ to -1.1‰, mode at -5.8‰), $\delta^{15}N$ (-5.8 to $+18.8$‰, mode at -3.0‰) and nitrogen contents ([N]; 3800 to less than 1 at.ppm). In combination, cathodoluminescence imaging and microbeam analyses reveal that the diamonds grew from multiple fluid pulses, with at least one major hiatus documented in some samples that was associated with a resorption event and an abrupt change from low $\delta^{13}C$ and [N] to mantle-like $\delta^{13}C$ and high [N]. Overall, $\delta^{13}C$ appears to be uncorrelated to $\delta^{15}N$ and [N] on both the inter- and intra-diamond levels. Co-variations of $\delta^{15}N$–log[N], however, result in at least two parallel, negatively correlated linear arrays, which are also present on the level of the individual diamonds falling on these two trends. These arrays emerge from the two principal data clusters, are characterized by slightly negative and slightly positive $\delta^{15}N$ (about -3 and $+2$‰, respectively) and variable but overall high [N].

Using published values for the diamond-fluid nitrogen isotope fractionation factor and nitrogen partition coefficient, these trends are perfectly reproduced by a Rayleigh fractionation model.

Overall, three key elements are identified in the formation of the diamond suite studied: (1.) a low $\delta^{13}C$ and low [N] component that possibly is directly associated with an eclogitic diamond substrate or introduced during an early stage fluid event. (2.) Repeated influx of a variably nitrogen-rich mantle fluid (mildly negative $\delta^{13}C$ and $\delta^{15}N$). (3.) In waning stages of influx, availability of the mantle-type fluid at the site of diamond growth became limited, leading to Rayleigh fractionation. These fractionation trends are clearly depicted by $\delta^{15}N$–[N] but are not detected when examining co-variation diagrams involving $\delta^{13}C$. Also on the level of individual diamonds, large (≥ 5‰) variations in $\delta^{15}N$ are associated with $\delta^{13}C$ values that typically are constant within analytical uncertainty. The much smaller isotope fractionation factor for carbon (considering carbonate- or methane-rich fluids as possible carbon sources) compared to nitrogen leads to an approximately one order of magnitude lower sensitivity of $\delta^{13}C$ values to Rayleigh fractionation processes (i.e. during fractionation, a 1‰ change in $\delta^{13}C$ is associated with a 10‰ change in $\delta^{15}N$). As a consequence, even minor heterogeneity in the primary isotopic composition of diamond forming carbon (e.g., due to addition of minor subducted carbon) will completely blur any possible co-variations with $\delta^{15}N$ or [N]. We suggest this strong difference in isotope effects for C and N to be the likely cause of observations of an apparently decoupled behaviour of carbon and nitrogen isotopes in diamond.

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1. Introduction

The recycling of crustal carbon and nitrogen into the deep mantle and the role of mantle-derived versus subducted carbon and nitrogen in diamond genesis have long been a subject of intense scientific debate (Cartigny et al., 1998; Deines, 2002; Javoy et al., 1986; Mikhail et al., 2014a, 2014b; Sobolev and Sobolev, 1980). In particular, the absence

of a correlation between ^{13}C depletion (the signature of original organic matter) and ^{15}N enrichment (characteristic for sediments) in diamonds has been used as an argument against an involvement of subducted carbon and nitrogen (see review in Cartigny, 2005). This argument, however, critically hinges on a common origin of carbon and nitrogen in diamond; this supposition was recently challenged by Mikhail et al. (2014a, 2014b), principally based on the much larger heterogeneity of $\delta^{15}N$ compared to $\delta^{13}C$ in their sample suite. A recent empirical determination of a nitrogen isotope fractionation factor for diamond-fluid (Petts et al., 2015) now allows us to re-examine the relationship of carbon and

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nitrogen in diamond. For this purpose, we undertook the first micro-beam $\delta^{13}C$–$\delta^{15}N$–[N] study based on a representative number (n = 94) of diamond samples from a single occurrence; this comprehensive data set allows us to re-evaluate the two conflicting proposals regarding coupled (Cartigny et al., 1998) or decoupled (Mikhail et al., 2014a, 2014b) carbon and nitrogen isotope systematics in diamond.

Carbon isotopic analysis is a standard tool for monocrystalline diamond studies and may be employed to fingerprint the original diamond substrate in Earth's mantle (peridotitic versus eclogitic or websteritic paragenesis; Kirkley et al., 1991; Stachel et al., 2009). The frequency distributions of diamonds of peridotitic and eclogitic (-websteritic) paragenesis both share a common mode in $\delta^{13}C_{VPDB}$ at -5 ± 1‰ ("mantle value" of carbon; Cartigny, 2005; Deines, 1980a, 1980b). Diamonds of peridotitic paragenesis, however, have a much narrower range in carbon isotopic composition (with rare exceptions, they generally fall between about -10 and 0‰) than eclogitic diamonds (-41 to $+5$‰) (e.g., Cartigny, 2005; Kirkley et al., 1991; Stachel et al., 2009), and consequently $\delta^{13}C$ values that extend past the range of peridotitic diamonds can be attributed with fairly high confidence to eclogitic (-websteritic) substrates.

As carbon and nitrogen have a similar ionic radius and charge, nitrogen substitutes for and bonds strongly with carbon in the diamond lattice (Cartigny, 2005); as a consequence, nitrogen is by far the most abundant molecular impurity in diamond, with concentrations as high as 0.55 wt.% (Sellschop et al., 1980). This enables utilizing the content and isotopic composition of nitrogen as an additional tool to obtain broad constraints on the mantle substrate(s) of a suite of diamonds. For example, globally, peridotitic diamonds are typically much lower in nitrogen content (median of 82 at.ppm) than eclogitic diamonds (median of 494 at.ppm; Stachel, 2014). The nitrogen content of the mantle is much lower than the carbon content; estimates for primitive upper mantle N fall between 2 ppm (Marty, 1995) and 36 ppm (Javoy, 1997), with the latter value likely representing an extreme upper limit (Cartigny and Marty, 2013). Depleted mantle (MORB source) contains about 0.3 ppm nitrogen (Johnson and Goldblatt, 2015; Marty and Dauphas, 2003). Due to the low quantities of nitrogen in the upper mantle, coupled with a large extent of nitrogen recycling in the course of subduction (Cartigny and Marty, 2013), $\delta^{15}N$ is a sensitive recorder of mixing between isotopically highly distinctive mantle and crustal reservoirs. The mantle value for $\delta^{15}N$ is -5 ± 3‰ (Cartigny, 2005; Nadeau et al., 1990), whereas crustal reservoirs are characterized by positive $\delta^{15}N$ values (e.g., Cartigny and Marty, 2013; Peters et al., 1978). Therefore, a subducted crustal nitrogen component is traceable in mantle plume-related magmas and some mantle xenoliths (Marty and Dauphas, 2003) and may reflect the presence of an important additional, high-nitrogen mantle reservoir with a nitrogen isotopic composition of about $+5$‰ (Johnson and Goldblatt, 2015).

Here we present the first study on diamonds from the recently discovered Chidliak kimberlite field (Pell et al., 2012, 2013) in NE Canada. The Chidliak kimberlites are located on the Hall Peninsula, southern Baffin Island, an area that was originally considered part of the Churchill Province but is now recognized as an independent Archean cratonic block, possibly representing a fragment of the North Atlantic Craton (Pell et al., 2013 and references therein). To date, 74 kimberlites have been discovered and of the 51 kimberlites tested, 21 contain "commercial-sized" (>850 μm) diamonds (J. Pell, pers. comm., 2015). In this study we focus on diamonds from two kimberlite bodies, CH-7 (kimberlite sample P5500) and CH-6 (kimberlite sample P6807).

2. Sample description and experimental methods

We inspected 210 Chidliak diamonds for their physical characteristics; the upper stone size is -850 μm $+650$ μm (aperture size of upper and lower sieves) and the lower stone size is -300 μm $+212$ μm. Half of the diamonds are from kimberlite CH-7, the other half from CH-6. The studied diamonds are predominantly irregular (a

common feature of very small diamonds), followed by octahedral fragments. Dodecahedroids, cuboids, macles, aggregates and mixed octahedral–dodecahedral morphologies are also present. The majority of the diamonds are colourless, followed by brown, yellow, and grey.

A subset of 94 diamonds, in the size range of 850 μm to 300 μm, was analysed via secondary ion mass spectrometry (SIMS) with high spatial resolution (15 μm spot size). All analytical data are summarized in Table 1. $\delta^{13}C$ (the $^{13}C/^{12}C$ ratio expressed as relative difference to the same value in the Vienna PeeDee Belemnite standard) and nitrogen contents ([N]) were analysed for all 94 diamonds, whereas $\delta^{15}N$ values (the $^{15}N/^{14}N$ ratio expressed as relative difference to the same value for standard atmosphere) could only be obtained for 85 diamonds having nitrogen contents > 40 at.ppm. Prior to SIMS analysis, the diamonds were mounted in epoxy, polished and then imaged by cathodoluminescence (CL). Due to mounting procedures, the imaged diamonds could not be oriented in specific crystallographic directions. In addition, as multiple diamonds were polished in single mounts, sections through crystal centres were only achieved in rare cases. The consequent random sections through mainly outer parts of diamond crystals introduce complexity to the CL images.

MC-SIMS (Cameca IMS-1280) analyses of diamond follow the procedures outlined in Stern et al. (2014); the reference materials used for $\delta^{13}C$ analysis were diamonds S0011Bd and S0011Cd, while the reference diamond used for $\delta^{15}N$ analyses was S0270. After $\delta^{13}C$ analysis, the nitrogen content was measured on the same spot location (N_C in Table 1); $\delta^{15}N$ was measured on adjacent spots but within the same diamond growth layer and a second nitrogen content value (N_N in Table 1) was obtained during these analyses. The error on the nitrogen content measurements is $\pm 10\%$, which is largely due to the uncertainty of the FTIR analysis of the reference material.

Following SIMS analysis, all analytical spots were verified using a light microscope and the CL and SE (secondary electron) images to ensure (1.) the absence of surface contamination (one analyses was removed due to possible epoxy contamination) and (2.) that analytical spots are located within single growth layers (three analyses were removed as they overlapped boundaries between distinct growth zones). Since nitrogen content was always measured on two adjacent spots, associated with the $\delta^{13}C$ and $\delta^{15}N$ analyses, all paired nitrogen values that did not agree within error prompted re-examination of correct placement of the adjacent spots within the same growth layer; this led to the recognition of two pairs of spots where $\delta^{13}C$ and $\delta^{15}N$ were obtained on different sides of important growth boundaries (associated with changes in $\delta^{13}C > 3$‰). The $\delta^{13}C$ and $\delta^{15}N$ values associated with these two pairs of spots are listed in Table 1 (highlighted by a *) as they are accurate analyses within individual layers but they are not used to examine co-variations in $\delta^{13}C$–$\delta^{15}N$.

3. Results

3.1. Carbon isotopic composition.

Multiple points (2–7, average of 3 points) per diamond were measured. Diamonds from the two kimberlites have subtly distinct principle modes (defined using probability density curves; Ludwig, 1999): -5.8‰ for CH-7 and -6.4‰ for CH-6. Combined, these diamonds show a range in $\delta^{13}C$ between -28.4 and -1.1‰, with a principle mode at -5.8‰, near the value of mantle carbon (-5 ± 1‰; Cartigny, 2005; Deines, 1980a, 1980b), and minor modes about -15.5‰ and -23.5‰ (Fig. 1A; Table 1).

3.2. Nitrogen content and isotopic composition

Nitrogen contents (N_C, i.e. measured on the same analytical spots as $\delta^{13}C$) for the diamonds studied range from <1 to 3833 at.ppm with a median value of 1112 at.ppm (Fig. 2). Compared to diamonds worldwide, median [N] values are high for diamonds from the two