

Communication

The Carbon and Nitrogen Isotope Characteristics of Type Ib-IaA Cuboid Diamonds from Alluvial Placers in the Northeastern Siberian Platform

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Abstract: Cuboid diamonds are particularly common in the placers of the northeastern Siberian platform but their origin remains unclear. These crystals usually range in color from dark yellow to orange and more interestingly, are characterized by unusual low aggregated nitrogen impurities (non-aggregated C-center) suggesting a short residence time and/or low temperatures at which they have been stored in the mantle. In order to track possible isotopic signature that could help deciphering cuboid diamond's crystallization processes, $\delta^{13}\text{C}$ values, $\delta^{15}\text{N}$ values and nitrogen contents have been determined in-situ in three samples using secondary ion mass spectrometry (SIMS), whereas nitrogen aggregation state have been determined by FTIR spectroscopy. The samples fall out the $\delta^{13}\text{C}$ vs. $\delta^{15}\text{N}$ field of canonical mantle composition. Different scale of carbon and nitrogen fractionation may produce the observed variations. Alternatively, mixing of mantle and crustal material would obscure initial co-variations of $\delta^{13}\text{C}$ values with $\delta^{15}\text{N}$ or nitrogen content.

Keywords: cuboid diamond; carbon; nitrogen; SIMS

1. Introduction

Natural diamonds are the subject of extensive research because they provide unique information on the geochemistry, mineralogy and P-T-fO₂ regimes of the mantle. Most of such studies use inclusions trapped during diamond growth, providing important information about diamond-forming processes. Previous investigations of crystalline inclusions in diamonds from the subcontinental lithospheric mantle have shown that diamonds originated in a range of peridotitic (P-type) and eclogitic (E-type) host-rocks [1]. Diamonds from both parageneses occur with diverse morphological and physical properties which are widely interpreted as reflecting variations in the conditions of diamond formation, within the Earth's upper mantle, providing important information about growth conditions and subsequent diamond post-growth histories. Carbon and nitrogen isotopic systems are useful indicators for constraining the crustal and mantle sources and their interactions during subduction [2]. The carbon and nitrogen isotopic compositions of diamonds formed in the mantle have been widely used as a tool for investigating the origin of diamond-forming carbon in the mantle [3 and references therein]. The worldwide database 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 $+2\text{‰}$). Curiously, diamonds from both parageneses can show positive (crust-like) and negative (mantle-like) $\delta^{15}\text{N}$ values (from -40 to $+20\text{‰}$).

The alluvial placers of the northeastern Siberian Platform are characterized by specific diamond populations [4]. In particular, diamonds of cubic morphology (cuboids), forming a continuous color series from yellowish-green to yellow and dark orange, are commonly found in such placers. These

diamonds have been designated as variety II in the mineralogical classification [5]. Previously described characteristics of the diamonds of variety II, i.e. cuboid morphology, light carbon isotope composition and low aggregated nitrogen (type Ib – causing specific yellow coloration), suggest an unusual primary source [6,7]. Here we report variations of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ in several cuboid diamonds and investigate their nature and origin. This paper is part of a wider study of alluvial diamonds from the northeastern Siberian platform.

2. Materials and Methods

The three cuboid diamonds studied here have been chosen in an alluvial diamond collection originating from the placers of the northeastern Siberian Platform. Thirty-six samples from the same collection have been previously analyzed for carbon and nitrogen isotopes, nitrogen content and aggregation state. The results have been published previously [7]. The millimeter-size samples (2–3 mm) studied here, range in color from dark yellow (HL-3) to orange (MTII-27). In order to proceed in-situ geochemical measurements, we polished the samples along either (100) or (110) planes on a conventional diamond scaife (a special metal polishing wheel operating at a rotation speed of 3000 rpm), thereby producing a central plate. Growth patterns of polished plates were observed on polarized microscope Zeiss Axioscop 40 (Figure 1). All diamonds have concentric cuboid growth zones which can be distinguished from their orientation and different colors.

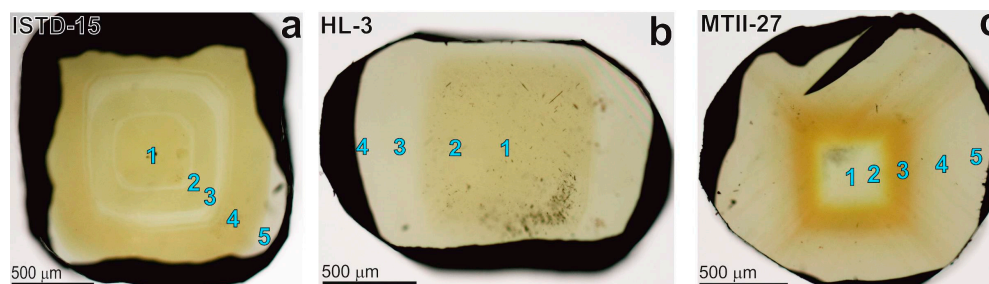


Figure 1. Polished plates of yellow cuboid diamonds from alluvial placers in the northeastern Siberian platform (transmitted light); (a) presents cubic section, (b) and (c) display dodecahedron polished sections. Zoning growth structures are visible. Analyzed points in different growth zones.

The infrared spectra of the diamonds were recorded using an FTIR Bruker VERTEX 70 equipped with a HYPERION 2000 microscope. Local spectra were measured in different growth zones at an aperture of $60 \times 60 \mu\text{m}$ over a range of $370\text{--}7000 \text{ cm}^{-1}$, with 32 scans at a resolution of 2 cm^{-1} . The deconvolution of the experimental spectra between 1100 and 1350 cm^{-1} made it possible to determine the relative contributions of different N-defects with characteristic spectral lines having known specified shape.

We used the CAMECA 1280-HR SIMS instrument in Deutsches GeoForschungsZentrum in Potsdam (GFZ Potsdam) for determining carbon and nitrogen isotope compositions in small domains in traverses across the diamonds from core to rim. Prior to the analyses, the three diamond plates together with reference materials of known compositions were put in indium using a hand operated press. The surface of the 1-inch sample mounts were then cleaned using high-purity ethanol prior to being argon sputter coated with high-purity gold. Carbon and nitrogen data were collected in June 2015 and March 2016, respectively. The analytical details were presented in [8].

Our analyses employed a $^{133}\text{Cs}^+$ primary beam with a total impact energy of 20 keV. The analyses used a 250 pA probe current for nitrogen and 2.5 nA current for carbon. The beam was focused to a $\sim 4\text{--}8 \mu\text{m}$ diameter with a Gaussian distribution at the sample surface. Secondary ions were extracted using a -10 kV potential applied to the sample holder. Charge compensation involved circa 250 pA low energy electron cloud provide by a normal incidence electron flood gun. The instrument was operated with a circa $80 \mu\text{m}$ field-of-view, with a 50 eV wide energy window. In the case of the carbon isotope measurements, we used static multi-collection mode operating at a mass resolution of $M/\text{dM} \approx 3200$, which fully resolve the ^{13}C mass station from the nearby $^{12}\text{C}^{1}\text{H}$

molecular isobar. For determining nitrogen contents and nitrogen isotope ratios our mass spectrometer was operated in mono-collection mode at a mass resolution of $M/dM \approx 6900$ using the peak-stepping sequence $^{12}\text{C}_2$, $^{12}\text{C}^{14}\text{N}$ and $^{12}\text{C}^{15}\text{N}$ signals.

Each carbon isotope analysis was preceded by a 60 second pre-sputter using a 25 μm raster, so as to remove the 35 nm thick gold coat and also to implant Cs^+ in order to establish equilibrium sputtering conditions. An analysis used a 15 μm raster, together with the tool's dynamic transfer capability, thereby generating a square, flat-bottom sputter crater. Prior to initiating data collection we conducted automatic beam centering routines in both X and Y for the field aperture. A single carbon analysis involved 20 cycles of 4 seconds integration each and the data were filtered at the 3std level. Thus, a single analysis required around 3 minutes of analysis time, including the pre-sputtering. All data were collected in fully automated data acquisition mode.

Prior to initiating nitrogen data collection on a selected target, the diamond region was sputter cleaned for 80 s using a 3 nA Cs^+ primary beam rastered over a $20 \times 20 \mu\text{m}$ area. Prior to initiating data collection the primary beam current was reduced to 250 pA and the rastered area was reduced to $10 \times 10 \mu\text{m}$, which was compensated using the dynamic transfer function tool. Automatic centering routines were then conducted for X and Y for the field aperture. Our data acquisition involved the peak-stepping sequence: $^{12}\text{C}_2$ (2 s integration time per cycle), $^{12}\text{C}^{14}\text{N}$ (4 s) and $^{12}\text{C}^{15}\text{N}$ (15 s). A single nitrogen isotope analysis consisted of 50 cycles of this peak-stepping sequence, leading to a total analysis time of ~20 minutes per acquisition.

Machine calibration used two diamond reference materials contained in the same indium-based sample mount. The samples were cut out from isotopically homogenous "steady state" parts of up-octahedral sectors in synthetic crystals 140/4 and 150/3 [9]. The synthetic crystals had been characterized for their $\delta^{13}\text{C}_{\text{VPDB}}$ values and nitrogen contents refer to "SynAT" reference material [10] at Edinburgh ion-microprobe facility. Minor pieces of the specific chips used in this study were additionally checked for their $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and nitrogen content using static vacuum gas source mass-spectrometry by Dr. A. Verchovsky at Open University (Milton Keynes, UK). The established characteristics are as follow: Crystal 140/4 with $\delta^{13}\text{C}_{\text{VPDB}} = -26.5\text{‰}$, 460 $\mu\text{g/g}$ nitrogen and $\delta^{15}\text{N}_{\text{AIR}} = 0\text{‰}$; Crystal 150/3 with $\delta^{13}\text{C}_{\text{VPDB}} = -24.5\text{‰}$, 215 $\mu\text{g/g}$ nitrogen and $\delta^{15}\text{N}_{\text{AIR}} = -5\text{‰}$.

Our raw isotope data were tested for the presence of a time dependent linear drift, which was corrected for when needed. Such drifts, which we attribute to changes in sensitivity of the amplifiers in our detector system, were 0.3 ‰ per hour or less. After correcting for such drift the repeatability of our $^{12}\text{C}^{15}\text{N}/^{12}\text{C}^{14}\text{N}$ determinations on the two reference materials was in the range of 1.1 to 1.5 ‰ (1std), which is our best estimate for the random component that might be present in our nitrogen data. Hence, we can conclude that the overall reliability of our $\delta^{15}\text{N}$ values is better than $\pm 1.5 \text{‰}$ (1std). Using the same approach for $^{13}\text{C}/^{12}\text{C}$ determinations, the overall reliability of our $\delta^{13}\text{C}$ values is better than $\pm 0.24 \text{‰}$.

3. Results

3.1. Nitrogen content and aggregation state

According to FTIR data the three cuboid diamonds are of mixed type IaA/Ib caused by the presence of A-center (pair of N atoms [11]) and C-center (single N atom [12]) with additional lines of unknown centers described as X (sharp peak at 1332 cm^{-1}) and Y (superposition with a maximum at $1140\text{--}1150 \text{ cm}^{-1}$) [13,14]. The nitrogen content ($N = N_A + N_C$) in studied diamonds shows little variations from 24 to 133 ppm and is commonly higher in the central zones (Table 1). The nitrogen aggregation (relative abundance of A-centers) in diamonds ISTD-15 and MTII-27 is higher in central zones and nearly constant in diamond HL-3. The nitrogen content determined by SIMS in these diamonds varies in the range 28–217 ppm (Table 1). The higher nitrogen contents as determined by SIMS relative to those measured from FTIR are in the central zones. We suppose this discrepancy may be explained by the presence of additional nitrogen beyond that contained in the IR-active A- and C-centers. Additionally, SIMS measurements give results for the surface area, but FTIR for the

whole width of the plate, where input of the other zones is inevitable [15]. Notably, all the areas with low nitrogen content show precise agreement between FTIR and SIMS results.

Table 1. Isotopic compositions of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) and nitrogen contents (N) in cuboid diamonds from alluvial placers in the northeastern Siberian platform. Also indicated are the nitrogen contents as measured by SIMS and FTIR.

sample		$\delta^{13}\text{C}$, ‰	$\delta^{15}\text{N}$, ‰	N _{SIMS} , ppm	N _{FTIR} , ppm	N _A , ppm	N _C , ppm
ISTD-15							
1	core	-3.9	-5	144	83	33	50
2		-3.9	-22	55	54	12	42
3	↓	-3.8	-18	55	52	12	40
4		-4.1	-19	28	26	7	19
5	rim	-3.8	-11	56	57	12	45
HL-3							
1	core	-9.3	-12	109	91	36	55
2		-9.1			75	30	45
3	↓	-9.0	-20	58	59	22	37
4	rim	-8.9			24	9	15
MTII-27							
1	core	-15.1	-11	165	123	48	75
2		-14.8	-14	217	133	53	80
3	↓	-15.4			115	23	92
4		-15.8	-10	55	46	8	38
5	rim	-16.1			35	6	29

3.2. Carbon isotope composition

Carbon isotope compositions were analyzed in four to five growth zones of the cuboid diamonds (See Figure 1 and Table 1). $\delta^{13}\text{C}$ values of the diamonds vary substantially from sample to sample but show very small intra-crystal variations (-3.8 to -4.1 ‰ in ISTD-15, -8.9 to -9.3 ‰ in HL-3, and -15.1 to -16.1 ‰ in MTII-27). These values fall within the previously described carbon isotope range of cuboid diamonds of this variety from this locality [7], that are commonly off-set from the main mantle mode of $\delta^{13}\text{C}$ at -5.5 ‰ towards lighter carbon isotope compositions (Figure 2). Nonetheless, the studied cuboid diamonds plot in the field of most known diamonds from the worldwide dataset by Stachel and Harris, 1997 [16] and are outlined by Cartigny et al., 2001 [17] (Figure 2). Despite observed wide variations we did not found any straightforward correlation between carbon isotope compositions and nitrogen content of studied diamonds.

3.2. Nitrogen isotope composition

The nitrogen isotope composition of our cuboid diamonds show a broad range in $\delta^{15}\text{N}$ values (-5 to -22 ‰ in ISTD-15, -12 to -20 ‰ in HL-3, and -10 to -14 ‰ in MTII-27). We found no correlation between $\delta^{15}\text{N}$ values and nitrogen contents of the diamonds (Table 1). The measured $\delta^{15}\text{N}$ values are lighter than the average modern mantle value [18]. Compared to diamonds worldwide, the observed range of $\delta^{15}\text{N}$ in our diamonds is more typical of diamonds from a peridotitic lithology (Figure 3). Diamond ISTD-15 shows wide $\delta^{15}\text{N}$ variations within the field of peridotitic diamonds against a background of minute variations of carbon isotope composition (Figure 3). Diamonds HL-3 and

MTII-27 have lighter carbon isotope composition which is rare in peridotitic diamonds, whereas the range of $\delta^{15}\text{N}$ is close to that seen in ISTD-15 with pronounced shift to lighter compositions (Figure 3).

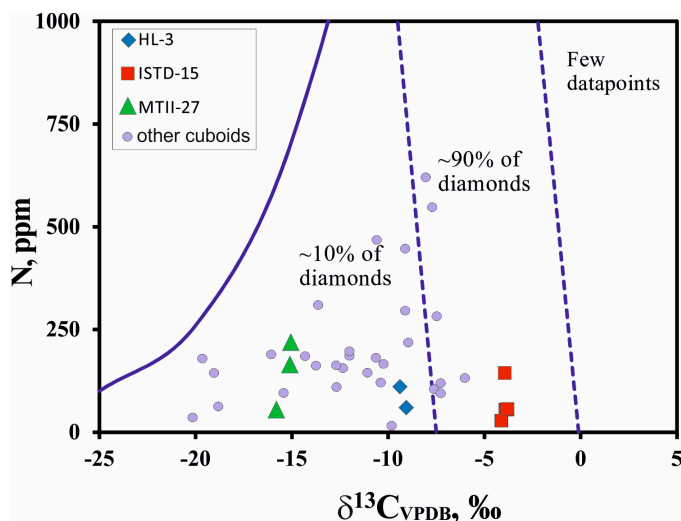


Figure 2. Carbon isotope values ($\delta^{13}\text{C}_{\text{VPDB}}$) and nitrogen abundance (N, ppm) in yellow cuboid diamonds from alluvial placers in the northeastern Siberian platform compared to worldwide data summarized by Cartigny et al., 2001 [17].

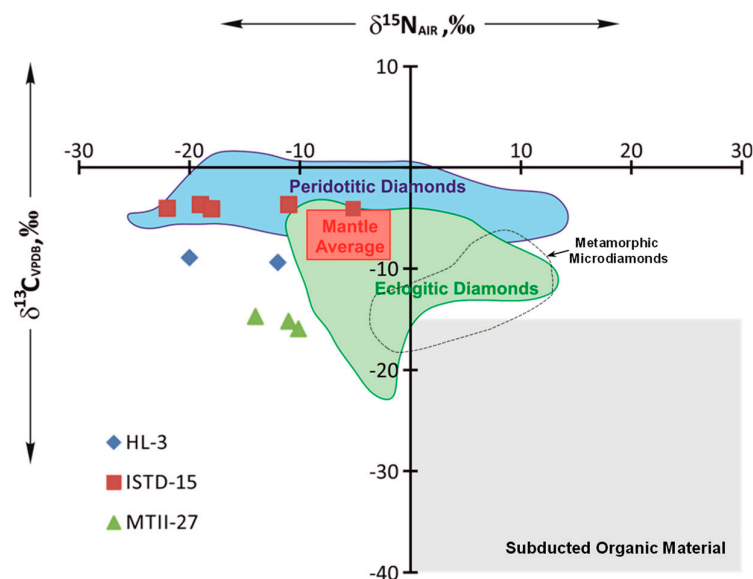


Figure 3. Carbon ($\delta^{13}\text{C}_{\text{VPDB}}$) and nitrogen ($\delta^{15}\text{N}_{\text{AIR}}$) isotope compositions of yellow cuboid diamonds from alluvial placers in the northeastern Siberian platform and comparison with peridotitic and eclogitic diamond data worldwide [3] and metamorphic microdiamonds [31]. Average mantle range and range of subducted organic material for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are also shown [3].

4. Discussion

Diamonds worldwide exhibit a large range of carbon isotope compositions. These variations have been attributed to several factors: (i) isotopic fractionation during fluid/melt migration [17,19] and directly during diamond crystallization [e.g. 20,23]; (ii) primordial heterogeneities in mantle carbon [e.g. 20,24]; (iii) addition of isotopically heterogeneous carbon sources incorporated into the mantle by subduction processes [25–27]. In the last scenario, the low $\delta^{13}\text{C}$ values would imply that

the carbon originated not as carbonate but as organic carbon. It is supposed that diamonds of eclogitic parageneses were formed from metasedimentary carbon preserved in deeply subducted oceanic crust, whereas diamonds of peridotitic parageneses were formed from primordial mantle carbon source ($\delta^{13}\text{C} \sim -5 \text{ ‰}$). It was also suggested that during progressive partial melting of subducted material the relative proportion of the organic and carbonate carbon contribution changes in time/space, thereby generating a wide range of $\delta^{13}\text{C}$ values [28]. The shift from average mantle $\delta^{13}\text{C}$ values towards lighter compositions in our studied cuboid diamonds, seems typical for diamonds of eclogitic parageneses and their wide range of carbon isotope compositions suggests formation from distinct mantle and crustal carbon sources [7].

Diamonds with extremely light and heavy nitrogen isotope compositions may reflect sources from an isolated, ^{15}N -depleted primordial mantle reservoir and from a ^{15}N -enriched mantle reservoir that contains recycled crustal components, respectively [29-31]. Significant general variations in the nitrogen isotope composition of peridotitic diamonds (Figure 3) may be related to primordial mantle heterogeneity. Very low $\delta^{15}\text{N}$ values of rare lithospheric and sublithospheric diamonds suggest that the Archaean mantle was more isotopically depleted in ^{15}N than is the case today [18]. However, some evidence for lowering of $\delta^{15}\text{N}$ values down to -40 ‰ were recently suggested as a result of nitrogen isotope fractionation during diamond crystallization [32]. Importantly, metasedimentary nitrogen is characterized by $\delta^{15}\text{N}$ values that are invariably positive for throughout the Archean to recent geological periods [33] (Fig. 3). It is recognised that eclogitic diamonds with low $\delta^{13}\text{C}$ values and positive $\delta^{15}\text{N}$ signatures were formed from crustal material [30,31]. Alternatively, Cartigny et al., 2001 [17] suggested that the very negative $\delta^{13}\text{C}$ values associated with positive $\delta^{15}\text{N}$ values can result from an open-system fractionation of metasomatic fluids.

Our study reveals that $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ variations in two studied cuboid diamonds locate close to known the peridotitic (ISTD-15) and eclogitic (MTII-27) diamond isotopic fields (Fig. 3). The mixing between mantle and crustal source cannot properly explain the origin of cuboid diamonds with observed low $\delta^{13}\text{C}$ values and negative $\delta^{15}\text{N}$ values. The shift from average mantle $\delta^{13}\text{C}$ values towards lighter compositions observed for HL-1 and MTII-27 diamonds are typical for a series of diamonds from eclogitic parageneses. On the contrary, variation of nitrogen isotope composition towards light values is attributed to peridotite paragenesis (Fig.3) and results from isotopically light Archean mantle [18]. Using stable isotope data obtained on diamonds from worldwide sources, Hogberg et al., 2016 [23] argued that carbon and nitrogen in diamonds are decoupled. They suggested that even a minor heterogeneity in the primary composition of diamond forming carbon (e.g., due to addition of minor subducted carbon) will completely obscure any possible correlations between $\delta^{13}\text{C}$ values and either $\delta^{15}\text{N}$ or nitrogen content. Modeling for mixing between mantle-related and subduction-related carbon also illustrates the impossibility of its matching with associated nitrogen content in diamonds [34]. Thus, C and N isotopes data do not provide direct evidence of relationship between subducted carbon and formation of cuboid diamonds from alluvial placers of the northeastern Siberian platform. However, the lack of C-N co-variations in isotopically light diamonds can suggest a mixing of mantle and subducted crustal material. It also cannot rule out a possibility of significant nitrogen isotope fractionation against a background of moderate $\delta^{13}\text{C}$ changes during fluid crystallization [8].

Formation of cuboid diamonds was suggested to proceed through different growth modes: (i) a "fibrous" (columnar) growth in the $\langle 111 \rangle$ direction, and (ii) "cuboids" growth of the crystals which do not show a fibrous internal structure [35]. In both cases, the cuboid habit of diamonds may be a primary feature, reflecting rough growth under high degrees of carbon supersaturation which operates as the driving force for diamond growth [36]. Most cuboid diamonds worldwide are characterized by a restricted range of carbon and nitrogen isotope compositions, nitrogen contents and aggregation states, suggesting their formation from a common primary source [37,38]. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values in cuboid diamonds generally resemble the average mantle range with a low nitrogen aggregation state (99% of them are IaA diamonds) attributed to short residence times, which indicates a close relationship of their formation to kimberlite magmatism [39,40]. The presence of non-aggregated substitutional single nitrogen defects in our studied cuboid diamonds

(Type Ib-IaA) testifies to an even shorter mantle residence time. These features point to the formation of cuboid diamonds during metasomatic events prior to their ascent to the surface in kimberlite magmas. Alternatively, the low aggregation state of nitrogen defects in the cuboid diamonds may be related to their storage in the mantle at relatively low temperature and conditions where an active transformation of nitrogen defects is inhibited [41]. Thus, the observed isotopic and N composition variations in the studied diamonds may also record chemical and isotopic heterogeneities of the host rocks and thermal gradients up to several hundred degrees inside of subducted oceanic plates [42].

5. Conclusions

A population of yellow- to dark orange-colored cuboid diamonds from alluvial placers of the Northeastern Siberian Platform shows a specific set of morphological and chemical features, suggesting they were derived from a rare primary source. The overall presence of non-aggregated C centers in these diamonds requires their short mantle residence time or low temperatures where C- to A-centers conversion becomes exceedingly slow. In this study we have determined multiple $\delta^{13}\text{C}$ – $\delta^{15}\text{N}$ values and nitrogen contents in three cuboid diamonds using SIMS and FTIR. We found a wide range of $\delta^{15}\text{N}$ intracrystal variations with no significant fluctuations of carbon isotope values of diamonds. The isotope values of the cuboid diamonds fall out of the $\delta^{13}\text{C}$ vs. $\delta^{15}\text{N}$ field of average mantle compositions, which is also typical for most cuboid and fibrous diamonds worldwide. This might be evidence of mantle mixing with crustal material that would have obscured any initial $\delta^{13}\text{C}$ – $\delta^{15}\text{N}$ co-variations. Chemical heterogeneities of host rocks and different scale of carbon and nitrogen isotopic fractionation may also affect co-variations of $\delta^{13}\text{C}$ values with $\delta^{15}\text{N}$ or nitrogen content.

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Author Contributions: D.Z. studied samples by optical microscopy, made the polished plates and analyzed them by FTIR; V.R. analyzed C and N isotope composition in samples and discussed the results; M.W. contributed analysis tools and discussed the results; D.Z. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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