



Comparative analysis of nitrogen and carbon isotopic fractionation during diamond formation based on β -factor determination

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Abstract

First quantitative estimates are presented for nitrogen isotopic fractionation during diamond crystallization with respect to nitrogen-bearing fluid components using quantum-mechanical (DFT) calculations on the defect (with the substitutional nitrogen) diamond lattice. Provided equilibrium isotopic fractionation, $^{15}\text{N}/^{14}\text{N}$ ratio decreases within the sequence of compounds $\text{NH}_4^+ > \text{N}_2 > (\text{diamond}, \text{NH}_3) > \text{CH}_3\text{N} > \text{CN}^- > \text{NH}_2$. At temperatures of 1,100 to 1,200 °C fractionation among diamond and fluid N-compounds are estimated at $-2.23, -0.77, 0.01, 0.44, 1.31$ and 2.85 ‰ and substantially (over 1 ‰) exceed the already available estimates based on the modeling diamond C-N bonds by analogy with HCN or CN^- molecules. Depending on the dominant nitrogen and carbon substance in the mineral-forming fluid, diamond formation can be accompanied by different isotope compositional trends, as expressed either by zoned patterns within individual diamond grains or by isotopic $\delta^{15}\text{N}$ vs $\delta^{13}\text{C}$ covariations during successive crystallization. Provided the dominance of NH_3 component (the reduced conditions, high pressures and the cold geotherm) nitrogen isotope fractionation between diamond and fluid does not exceed 0.1-0.2 ‰ and the isotope shifts at temperature ca. 1100 °C $\Delta^{15}\text{N} \ll \Delta^{13}\text{C}$. In nitrogen depleted reduced mantle fluids possible existence of compounds with low heavy isotope affinity at temperature of diamond formation (especially NH_2) implies high isotope fractionation between diamond and the fluid and hence, evolved $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratios. Oxidized fluids dominated by CO_2 or CO_3 coupled with N_2 component are characterized by close to zero $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratios as inferred by prevailing carbon isotope fractionation with respect to nitrogen isotopes, the latter change considerably with nitrogen distribution coefficient among diamond and the growth media.

Keywords

diamond; isotope fractionation factors; $^{15}\text{N}/^{14}\text{N}$; $^{13}\text{C}/^{12}\text{C}$

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Introduction

The conditions of diamond growth and transformation are reflected by the morphological properties, spectroscopic features, impurity compositions [1-3], and inclusions [4, 5]. One of the most important indicators of the formation conditions – isotopic composition of carbon in diamond – characterize both the initial substrate (eclogites, peridotites, websterites, with different proportions of sedimentary and mantle components) as well as a mineral-forming fluid (oxidized, reduced, mantle, surface) [6]. Diamond can represent the most ancient isolated parts of the mantle [7] and thus retains carbon isotopic labels from the early stages of the Earth formation. In addition to carbon, diamond is characterized by significant amounts of nitrogen (up to thousands and even tens of thousands ppm in subduction-related microdiamonds), the occurrence of which is driven by mineral-forming fluids [8]. The combination of isotopic systems ^{12}C - ^{13}C and ^{14}N - ^{15}N is widely used not only to reveal the conditions of formation, but also to characterize the cycles of carbon and nitrogen in deep conditions. Very high retention of carbon and nitrogen in diamonds [9] encourages preservation of isotopic systems both in conditions of formation at great depths (>110 km) and during rise to the surface.



Hence, the two elements in diamond taken together provide a unique opportunity to study the Earth's mantle down to depths of about 800 km and ages up to 3.5 billion years [10]. Considering generally low nitrogen content in the upper mantle, diamond $^{15}\text{N}/^{14}\text{N}$ isotopic ratio could be a sensitive indicator of mantle and sedimentary reservoirs mixing [11].

The observed large variations of diamond isotopic composition can be explained by both isotopic heterogeneity (including mixing) of the initial substrate and by fractionation of isotopes during crystallization. Quantitative characterization for processes related to diamond genesis primarily requires estimated isotope fractionation factors between diamond and the crystallization medium. Carbon isotopic fractionation factors depending on temperature have been determined for many systems related to diamond formation, including diamond- CO_2 , diamond- CaCO_3 , diamond- CH_4 , and a number of others [12-14]. Unlike carbon isotopes, fractionation of nitrogen isotopes with diamond are barely studied. There are still no experimental data on the distribution of nitrogen isotopes between diamond and possible nitrogen-containing substances in diamond growth media. The available calculated (theoretical) nitrogen isotopic fractionation factors are restricted to individual molecules (NH_4^+ , NH_3 , N_2) in equilibrium with arbitrary molecular analogues of the C-N bond of diamond, such as HCN or CN^- [9]. In the absence of more or less reliable determinations of nitrogen fractionation factors between diamond and mantle fluids, it is impossible for example, to distinguish the processes of mixing nitrogen of fluid from different sources, to assess the evolution of the isotopic composition under various mechanisms of interaction between fluids and the nascent diamond, etc.

The present work aims to provide first quantitative estimates of equilibrium isotope fractionation of nitrogen during diamond crystallization relative to nitrogen-containing fluid compounds using quantum-mechanical calculations (within the framework of the density functional theory DFT) for the defective (N-containing) lattice of diamond and N-containing molecules of the mineral-forming fluid. For comparison, calculations were also carried out for diamond without nitrogen (fractionation of carbon isotopes) and the carbon-containing fluid molecules.

Calculation methodology

Isotope fractionation factor between phases A and B , α_{AB} (R_A/R_B , R being the ratio of the atomic concentrations of the heavier and lighter isotopes in a given compound) at isotopic equilibrium is expressed by

$$1,000 \ln \alpha_{AB} = 1,000 \ln \beta_A - 1,000 \ln \beta_B, \quad (1)$$

in which β – values (the reduced partition function ratios of the isotopologues under consideration, or so-called β -factors) without accounting for anharmonicity are calculated from the frequencies of oscillations (phonon spectra) of isotopologues depending on temperature [15],

$$\beta = \prod_i \left(\frac{u_i^*}{u_i} \right) \left(\frac{e^{-u_i^*/2}}{e^{-u_i/2}} \right) \left(\frac{1 - e^{-u_i}}{1 - e^{-u_i^*}} \right),$$

or, in logarithmic form:

$$\ln \beta = \sum_i \ln \frac{\sinh(0,5u_i)}{\sinh(0,5u_i^*)} - \sum_i \ln \frac{u_i}{u_i^*}, \quad (2)$$

u – the dimensionless frequency, $u = hv/kT$; v – the frequency of the harmonic oscillator; T – temperature, K; h and k – are the Planck and Boltzmann constants; superscript * refers to the heavier isotope; the subscript i numbers independent harmonic vibrational frequencies for a compound. Summation is carried out for all vibrational states ($3N-6$ for nonlinear molecules, $3N-5$ for linear molecules, $3N-3$ for crystals); N – number of atoms of a compound. Hyperbolic sinus $\sinh(x) \equiv (\exp(x) - \exp(-x))/2$.

Experimental vibrational frequencies are mostly known only for the prevalent isotopologues (or for their natural mixtures) of individual substances. Therefore, to determine the values of v for the expression above, calculations “from the first principles” (ab initio) are currently used based on the

position of nuclei and the electronic properties of elements. In the present work, the vibrational frequencies of isotopologues are determined by the “frozen phonons” approach of the density functional theory as implemented in the CRYSTAL code (current version CRYSTAL23 [16]) with a set of Gaussian all-electron bases 6-311G(d). The basis sets for carbon and nitrogen are presented at the program site (https://www.crystal.unito.it/Basis_Sets/). Before calculating the phonon spectra, the parameters of the outer orbitals of the basic functions were optimized and the values of the vibration frequencies for the crystal lattice of pure diamond and diamond with different nitrogen impurity contents were compared, as well as structural optimization. Among the tested functionals of interaction between atoms (including LDA, GGA, hybrid), the minimum discrepancy with the experimental values of the calculated vibrational frequencies of pure diamond was obtained for the WC1LYP functional. The energy convergence threshold for self-matched field (SCF) calculations was chosen at the level of 10^{-11} amu. (Hartree) both during the optimization of the structure and calculation of vibrational frequencies, and the truncation of the summation series was controlled by the parameters of the CRYSTAL (TOLINTEG) program at values of (9; 9; 9; 9; 25).

Nitrogen in diamond occurs at various positions, including in place of carbon (substitutional nitrogen) and is present in various forms of aggregation [17]. Aggregated forms of nitrogen (A and B centers) usually are not associated with the initial defect formation, but are considered as secondary products during a long-term, of the order of billions of years residence (natural annealing) at high temperatures. The aggregation is restricted to the displacement of atoms within separate grains and does not affect the bulk isotope balance of diamond crystals. The present work deals with isotope effects associated with the primary (during diamond growth) entry of nitrogen into carbon sites with the appearance of substitutional nitrogen (C-centers). The possibility of nitrogen atoms being outside the C-center (dislocations, between lattice nodes, etc.) is not considered, as well as the entry of nitrogen in the form of A-center during crystallization [18]. Thus, carbon atoms were replaced by nitrogen atoms during calculations and the most energetically advantageous configurations of atoms in the diamond structure with C-centers have been determined, followed by the phonon spectra determination for nitrogen isotopologues and calculation of β -factors for substituted nitrogen. To adequately display real nitrogen concentrations, the method of expanded cells (super cells) with the number of carbon atoms $n = 16; 32; 54; 128$ (replacing one carbon atom with nitrogen atom in the cubic lattice) was used. The convergence of the results is achieved at $n = 32-54$ (corresponding to 20,000-30,000 ppm and exceeds maximum nitrogen concentrations in natural diamonds). Further volume increase of expanded cells leads to large costs of computing resources without any significant improvement of the results (including values of β -factors).

Calculations of β -factors for molecules representing possible fluid components during diamond formation (the set of molecules such as NH_3 , NH_4^+ , and N_2 has been accomplished by NH_2 , CH_3N , C_2H_6 in the work) included a sequence of nuclei coordinate optimization followed by vibrational level determination and calculation of β values. The B3LYP hybrid functional and basis vector sets of the TVZP quality in conjunction with the D3 dispersion correction [19], which minimized the discrepancy between calculated and experimentally determined frequencies, were used for molecular calculations. A more accurate presentation of the experimental spectra was achieved using the scaling factor, SF [20], with the reduction of the calculated frequencies of the main isotopologues to the experimental data together with the corresponding change of the frequencies of the heavier isotopologues.

Values of the β -factors were estimated from the expression (2) for temperatures from 0 to 2,500 °C with a step of 10 °C, the corresponding dependencies were approximated by polynomials $x = 10^6/T^2$ (K^{-2}): $1,000 \ln \beta = \sum a_i x^i$. The results (Table 1) for diamond and molecular species are presented in the form of the 5th degree polynomials ($i = 6$ for CO_2 and NH_2). The approximation error in all cases does not exceed 0.02 % at temperatures above 100 °C and 0.04 % at temperatures above 0 °C (coefficient of determination $r^2 > 0.999$).

Results

Table 1 shows the obtained temperature dependencies for determinations of diamond $^{15}\text{N}/^{14}\text{N}$ β -factors. Estimates are based on calculations for an expanded cell of 54 atoms. As noted above, further increase of the cell volume (with a corresponding decrease in the concentration of nitrogen in diamond)



with the substitution of one atom C \Rightarrow N does not yield any noticeable change in isotopic fractionation factors. The Table 1 also lists newly calculated (NH_2 , CH_3N) as well as previously known (N_2 , NH_3 , NH_4^+) results for probable nitrogen-containing components of mantle fluids, together with the results for carbon β -factors of diamond without nitrogen impurities as well as β -factors of fluid-carbon compounds. The presented data can be used to deduce (see expression (1)) isotopic fractionation factors for nitrogen ($\alpha^{15/14}$) and carbon ($\alpha^{13/12}$) between diamond and fluid components possible during crystallization. Hereafter, isotopic fractionation factors are presented in the form of the conventional values $\Delta = 1,000 \ln(\alpha)$.

Table 1

Temperature dependences of $1000 \ln \beta$ to calculate nitrogen and carbon fractionation between diamond and fluid

Compound	a_1	a_2	a_3	a_4	a_5	a_6	Source
$^{15}\text{N}/^{14}\text{N}$							
Diamond	13.13525 +0.05589P	-0.454961 -0.00471P	0.023558 +0.00038P	-0.000965 -1.9619E-5P	1.92024E-5 +4.3816E-7P	—	This work
N_2	15.27791	-2.088265	0.248047	-0.015932	0.0004036	—	[21]
NH_3	13.91689	-2.437494	0.339134	-0.023827	0.0006369	—	[21]
NH_4^+	18.40726	-3.003117	0.397865	-0.027115	0.0007104	—	[21]
Diamond (CN^-)	10.97264	-1.275805	0.138451	-0.008467	0.0002086	—	[21]
NH_2	8.293659	-1.827601	0.351646	-0.038804	0.0021684	-4.751E-5	This work
CH_3N	12.69071	-1.384621	0.155546	-0.009723	0.0002388	—	This work
$^{13}\text{C}/^{12}\text{C}$							
Diamond	20.931829 +0.10803P	-0.859144 -0.010389P	0.048253 +9.129E-4P	-0.0020401 -4.8886E-5P	4.09635E-5 +1.115E-6P	—	This work
Diamond	21.649 0.10768P	-0.9790 -0.0097P	0.052834 0.00079P	-0.001879 -3.7385E-5P	0.30747E-4 7.6468E-7P	—	[22]
Diamond	19.856	-0.4086	—	—	—	—	[23]
Diamond	20.398968	-0.858690	0.050281	-0.002209	4.56732E-5	—	[24]
Diamond	19.949068 +0.08177P	-0.622300 -0.00609P	0.014645 +0.00024P	—	—	—	[6]
CO_3^{2-}	24.74146	-1.08996	0.03178	—	—	—	This work
CO_2	31.32194	-3.969173	0.485570	-0.032037	0.0008268	—	This work
CO_2	30.48662	-4.092939	0.620806	-0.061011	0.0032451	-7.027E-5	[13]
CH_4	20.23303	-2.915760	0.371371	-0.024974	0.0006513	—	[9]
CH_4	18.81124	-1.818667	0.136254	-0.005159	0.0000743	—	[25]
CO	17.00663	-1.647067	0.122574	-0.004226	3.76328E-5	—	[26]
C_2H_6	20.71712	-2.397034	0.275367	-0.017105	0.0004143	—	This work
C_2H_6	19.84650	-1.631380	0.115636	-0.004252	0.0000601	—	[25]
CH_3N	22.33125	-2.555513	0.291656	-0.018280	0.0004487	—	This work

Notes. The results recalculated in the form of x polynomials [9, 21]; P, GPa dependence is estimated according to [22, (9)]; determinations based on the density of states (DOS) obtained from inelastic neutron scattering [24]; DFT calculations at $0 < P < 80$ GPa [6]; experimental data [26]; temperature range: $0 < T < 1,000$ °C [23]; $300 < T < 1,200$ °C [26]; $0 < T < 800$ °C [25]. Hyphen — not calculated.

In the temperature range within 1,000 and 1,400 °C (probable conditions of the lithospheric diamond formation) isotopic fractionation factors estimated from the calculated values of β are shown in Fig.1 in comparison with previously obtained results of the theoretical calculations. Such calculations of diamond nitrogen isotopic fractionation have been based so far on β -factors of molecules, which are assumed to represent C-N bonds in diamond. The molecules of HCN and CN^- are considered as the analogues [9]. At 1,127 °C, $\Delta^{15}\text{N}$ between HCN molecule (diamond) and fluid is -2.3 (for NH_3) and -1.1 ‰ (for N_2). According to the results of the DFT calculations, isotopic fractionation between diamond and NH_3

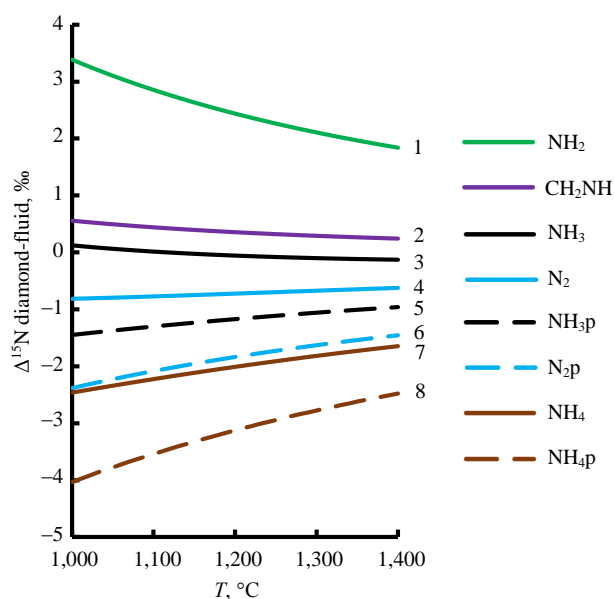


Fig.1. Isotopic fractionation of nitrogen between diamond and fluid
1-4, 7 – isotope fractionation factors, determined by DFT; 5, 6, 8 – isotope fractionation when modelling CN diamond bonds by CN^- molecule

molecule is nearly absent (-0.01 ‰ at 1127 °C), and between diamond and N_2 equals, given the same temperature -0.76 ‰ . The results differ by -2.3 and -0.3 ‰ . A decrease of $^{15}\text{N}/^{14}\text{N}$ occurs in the series of compounds $\text{NH}_4^+ > \text{N}_2 > (\text{diamond}, \text{NH}_3) > \text{CH}_3\text{N} > \text{CN}^- > \text{NH}_2$. At temperature of $1,100\text{ °C}$, fractionation between diamond and the above N-containing fluid compounds is estimated at $-2.23, -0.77, 0.01, 0.44, 1.31$ and 2.85 ‰ , respectively, and significantly (over 1 ‰) exceeds estimates based on C-N bond in diamond by analogy with CN^- molecule.

Significant discrepancies in the substitution of nitrogen bonds in diamond with the molecular bonds are due to substantially different strength and nature of the bonds (which is manifested, for example, in the parameters of vibrational spectra). Isotopic fractionation with condensed phases is different from that of gases with the same composition [27], so that nitrogen in diamond can concentrate the heavy isotope

more than gas molecules HCN or CN^- . Considering CN^- molecule as a model of nitrogen isotopic fractionation, the positive value of $\Delta^{15}\text{N}$ between diamond and fluid corresponds to N-containing fluid compounds which are common for upper mantle, but have not yet been identified by either experimental or theoretical studies. Thus, calculated β -factors of HCN and CN^- molecules can be considered at best only as very rough approximations for estimating diamond isotopic fractionation [9]. For a number of nitrogen and carbon compounds that may be specific to the sublithospheric mantle, the values of β -factors are already known (Table 1). Our calculations show that nitrogen β -factors of NH_2 are significantly smaller than those of other molecules under consideration, so that even at temperatures exceeding the lithospheric values, there is a noticeable enrichment of diamond by ^{15}N isotope relative to the equilibrium fluid (about 2 ‰ at equilibrium fractionation diamond- NH_2 , $T = 1,400\text{ °C}$). Isotopic fractionation of carbon between diamond and C_2H_6 molecule roughly corresponds to the fractionation with CH_4 (differ by $\approx 0.2\text{ ‰}$, $T = 1,400\text{ °C}$). These compounds can be considered as possible fluid components provided sublithospheric diamond origin.

Isotopic fractionation of nitrogen between diamond and fluid under mantle conditions is considered to exceed significantly carbon isotopic fractionation with most of the known carbon-containing diamond forming fluids [21]. Our results demonstrate that at a temperature of $1,200\text{ °C}$, diamond nitrogen β -factors are reduced relative to the molecules of N_2 and NH_4^+ by 0.8 and 1.0 ‰ , respectively, but exceed β -factors of CH_3N and especially, NH_2 by 0.3 and 2.4 ‰ . Fractionation of carbon isotopes between diamond and fluid species at the same temperature increases from negative values of -3.5 (CO_2), -1.8 (CO_3^{2-}) and -0.4 ‰ (CH_3N) to positive 1.1 ‰ (CH_4).

Pressure effect

Available calculations of β -factor on pressure dependencies [28, 23] demonstrate significant (about $0, n\text{ ‰}$) increase in diamond $\beta^{13}\text{C}$ at $T \approx 1,000\text{--}1,200\text{ °C}$ and $P > 10\text{ GPa}$. Within the framework of the DFT method, pressure effect can be determined by β -factor variations with the lattice volume (within the quasi-harmonic approximation – QHA), including dependence of the volume V on polynomial coefficients $1,000 \ln \beta$ with variable $x = 10^6/T^2$. All polynomial coefficients linearly ($r^2 > 0.99$) depend on diamond volume with a decrease of V/V_0 to 0.88 (which approximately corresponds to a pressure up to 110 GPa):



$$\begin{aligned}\Delta a_1 V / \Delta V &\approx -24.701; & \Delta a_2 V / \Delta V &\approx 2.08287; & \Delta a_3 V / \Delta V &\approx -0.16878; \\ \Delta a_4 V / \Delta V &\approx 0.00867; & \Delta a_5 V / \Delta V &\approx -0.00019 \text{ (}^{15}\text{N} / ^{14}\text{N)};\end{aligned}\quad (3)$$

$$\begin{aligned}\Delta a_1 V / \Delta V &\approx -47.795; & \Delta a_2 V / \Delta V &\approx 4.5919; & \Delta a_3 V / \Delta V &\approx -0.40351; \\ \Delta a_4 V / \Delta V &\approx 0.021607; & \Delta a_5 V / \Delta V &\approx -0.0004926 \text{ (}^{13}\text{C} / ^{12}\text{C)}.\end{aligned}\quad (4)$$

Thus, the following decomposition is valid

$$\Delta(a_i) \cong \frac{\Delta(a_i)}{\Delta V} \left\{ \left[\left(\frac{\partial V}{\partial P} \right) \Delta P \right] + \frac{1}{2} \left[\left(\frac{\partial^2 V}{\partial P^2} \right) \Delta P^2 \right] \right\} + \dots \quad (5)$$

Using the definition of the isothermal bulk modulus of elasticity $K_T = -V \partial P / \partial V$ and confining to the second-order members, the relation (5) can be represented as

$$\Delta(a_i) \cong \frac{\Delta(a_i)V}{\Delta V} \left\{ -\frac{1}{K} \Delta P + \frac{1}{2} \frac{1}{K^2} \left(\left(\frac{\partial K}{\partial P} \right) + 1 \right) \Delta P^2 \right\} + \dots$$

For diamond, $V_0 = 3.416 \text{ cm}^3$, $K = 442 \text{ GPa}$, $\partial K / \partial P = 3.61$ (our QHA calculation results, which are almost identical to the experimental data [29]: $K = 445 \text{ GPa}$, with $\partial K / \partial P = 4$). In general, change in the coefficients a_i as a function of pressure (Table 1) is determined by the expression

$$\Delta a_i(P) \approx V(\Delta a_i) / \Delta V \{ -0.00226 \Delta P + 1.1799 \cdot 10^{-5} \Delta P^2 \}.$$

At $T = 1,000 \text{ }^\circ\text{C}$, carbon β -factor increases by 0.6 (given $P = 10 \text{ GPa}$), and the nitrogen factor increases by 0.33 ‰. At $T = 1,700 \text{ }^\circ\text{C}$, the change in carbon β -factor is 0.25 (10 GPa), and that of nitrogen 0.14 ‰. Thus, the dependence of β -factors on pressure for nitrogen isotopes is approximately 2 times lower than that for carbon. For control, the data on the change in the lattice constant of diamond during the substitution of carbon isotopes can be used. In particular, at $T = 25 \text{ }^\circ\text{C}$ $(\partial \beta / \partial P)_T = 0.619 \text{ (GPa}^{-1})$, and the calculated value of the change in the coefficient of thermal expansion, α at isotopic substitution $(\Delta \alpha) / \alpha = \Delta V / 3V = -(\partial \beta / \partial P)_T R T / (3V)$ is 1.50E^{-4} , which is equal to the experimental value [23]. The obtained diamond $\beta^{13}\text{C}$ or $\beta^{15}\text{N}$ dependencies on pressure are insufficient however, to determine the isotope fractionation between diamond and fluid, since for high-density fluids the assessment of the effect of P on β -factors of mineral-forming solutions is still a challenge.

β -factors considered determine the values of isotope fractionation during diamond formation for the volume (bulk) properties of the crystal lattice under conditions of equilibrium with the growth medium. The values of β can decrease significantly (up to several permille) in natural nanocrystalline diamonds (the size effect). For example, based on phonon density of states (PDOS) from the results of inelastic neutron scattering on diamonds with different size, isotopic shifts of carbon β -factors $10^3 \ln \beta_{\text{bulk}} - 10^3 \ln \beta_{\text{nano}}$ relative to the bulk values were estimated [24, Fig.6]. For nanodiamonds, the change of the coefficient Δa_1 was estimated from the approximate digitization of the lines [24, Fig.6], corrected for the deviation of the phonon DOS from the parabolic ratio due to surface inclusions. Interpolation of Δa_1 value for nanodiamonds by linear dependence on size: $\Delta a_1 \approx 1.7768 - 0.0092 \times \text{size, nm}$ with the coefficient of determination $r^2 \approx 0.99$. Shifts of $1,000 \ln \beta^{13}\text{C}$ for nanodiamonds at 5 nm $\Delta a_1 = 1.799$; at 40 nm $\Delta a_1 = 1.321$; at 170 nm $\Delta a_1 = 0.227$ ‰. Given the diamond size of 5 nm, isotopic ratio shifts due to surface effects can reach -1 ‰.

It is possible to assess the surface effects due to the preferential development of certain facets during diamond growth and the formation of sectorial (including isotopic) zoning [30]. The composition of the growing crystal is a consequence of the competition of growth and diffusion at the surface (for example, GEM is a model of growth capture [31]). The crystal inherits the composition of the growth surface at low diffusion at the surface, which can be characterized by the Peclet number:

$$\text{Pe} = r \cdot 0.5L/D,$$

where r – is the growth rate, mm/s; L – is the thickness of the surface layer, nm; D is the diffusion coefficient of the element (or isotope) under consideration. The growth face is represented by a periodic plate with the number of layers LS . The inner layer is determined by the structure of the gross diamond, the outer $LS-1$ layers are reconstructed [32]. The parameters of the CRYSTAL calculation and sets of basis vectors are the same as during calculations on the bulk (gross) structure. Change of $1,000 \ln \beta$ relative to the gross values of $\sum_i (a_i^0 - a_i) x_i^0$; a_i^0 – are given in Table 1.

Table 2

1000 lnβ for diamond growth facets						
Edge Index*	LS	a_1	a_2	a_3	a_4	a_5
¹⁵ N/ ¹⁴ N						
{111}	2	12.14579	−0.59010	0.03920	−0.00176	4.190E ^{−5}
	4	12.93791	−0.60624	0.04139	−0.00204	4.621E ^{−5}
{110}	2	10.99022	−0.52717	0.02365	−0.00097	1.948E ^{−5}
	4	12.70019	−0.69832	0.04544	−0.00304	3.966E ^{−5}
{100}	2	8.66005	−0.20426	0.01380	−0.00129	9.954E ^{−7}
	4	11.30632	−0.41044	0.02322	−0.00102	2.129E ^{−5}
	6	12.67306	−0.44731	0.02390	−0.00100	2.015E ^{−5}
¹³ C/ ¹² C						
{111}	2	19.98622	−1.11557	0.08240	−0.00415	9.234E ^{−5}
	4	20.50007	−1.17320	0.08803	−0.00447	9.997E ^{−5}
	6	20.82774	−1.18265	0.08748	−0.00432	9.623E ^{−5}
{110}	2	18.23049	−0.93891	0.05031	−0.00205	4.197E ^{−5}
	4	20.55262	−1.14874	0.08495	−0.00428	9.542E ^{−5}
{100}	2	14.19463	−0.44483	0.02006	−0.00074	1.364E ^{−5}
	4	18.91818	−0.81383	0.04992	−0.00227	4.770E ^{−5}
	6	20.02506	−0.85221	0.04975	−0.00216	4.402E ^{−5}

* Miller's index.

The key parameters of the model can be controlled by experimental observations but in most cases, they are not determined under natural conditions [32]. Since the volume β -factors characterize growth at equilibrium ($Pe \ll 1$), the values of β -factors for individual faces (Table 2) provide possibilities to estimate deviations from ideal conditions.

Comparison with natural ¹⁵N/¹⁴N fractionation

In the conditions of isotopic equilibrium between growth medium (homogeneous fluid) and the surface of the produced diamond (according to the Rayleigh mechanism), linear relationships can arise between ratios ¹³C/¹²C, ¹⁵N/¹⁴N and the logarithm of nitrogen concentration ln(N) which are noted in numerous works [21, 33, 34]. The observed covariances both within individual diamond grains and among genetically related diamonds enable estimates “natural” isotopic nitrogen fractionation. The regression slope between genetically related diamonds in coordinates is determined by the equality

$$\delta^{13}\text{C}_{\text{vs}} \delta^{15}\text{N} = \Delta^{13}\text{C}/(\Delta^{15}\text{N}K_{\text{N}}),$$

where K_{N} – is the nitrogen partition coefficient between diamond and fluid; $\Delta = 1,000 \ln \alpha$, α – being factors of equilibrium isotope fractionation of carbon ¹³C/¹²C or nitrogen ¹⁵N/¹⁴N between diamond surface and growth medium [21]:

$$\delta^{15}\text{N} - \delta^{15}\text{N}_0 = \Delta^{15} \ln f_{\text{N}} = \Delta^{15} K_{\text{N}} \ln f,$$

f – fraction of fluid consumed; f_{N} – fraction of fluid nitrogen species consumed.

Provided $f = f_{\text{C}}$ (the fraction of fluid consumed equals the fraction of carbon species in the fluid), the following expression is valid



$$\delta^{13}\text{C} = (\delta^{15}\text{N} - \delta^{15}\text{N}_0) \Delta^{13} / (\Delta^{15} K_N)^* + \delta^{13}\text{C}_0,$$

where $\delta^{13}\text{C}_0$ or $\delta^{15}\text{N}$ – diamond isotope composition at the initial growth stage. The value of K_N is defined by the dependence of $\delta^{13}\text{C}$ on nitrogen content in diamond $\ln(\text{N})$,

$$\delta^{13}\text{C} = [(\ln(\text{N}) - \ln(\text{N}_0))] \Delta^{13} / (K_N - 1) + \delta^{13}\text{C}_0.$$

The above expressions are restricted to fluids dominated by carbon species although can be generalized for fluids of mixed composition. For example, $^{15}\text{N}/^{14}\text{N}$ fractionation between diamond and growth media was estimated at -4.0‰ (given $T = 1,100\text{ °C}$ for a fluid dominated by CO_3^{2-} carbonate ion, $\Delta^{13}\text{C} \approx -1.7\text{‰}$, $K_N = 4.4$, Jericho kimberlite [33]). Data on the bulk isotopic composition of carbon and nitrogen in diamonds from a lherzolite xenolith (representing the lithospheric mantle) were used to estimate $\Delta^{15}\text{N}$ value at $+1.2\text{‰}$ ($T = 1,200\text{ °C}$, provided the methane-rich fluid [35]). Data on ultra-deep diamonds from Guinea, with a crystallization temperature of about $1,725\text{ °C}$, were applied to determine $\Delta^{15}\text{N}$ between diamond and fluid (-4.5‰) in the conditions of crystallization from a fluid dominated by CO_3^{2-} , $\Delta^{13}\text{C} = -0.9\text{‰}$ [36].

Isotopic fractionation factors of nitrogen in diamonds, $\Delta^{15}\text{N}$ estimated from natural covariances $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ - $\ln(\text{N})$ depend, in addition to the choice of $\Delta^{13}\text{C}$ values, on the balance of fluid components as well as other parameters, including the fractionation model and the accepted crystallization temperature. Despite numerous assumptions and speculations especially regarding the values of K_N , in the absence of other calibrations, this method has so far been practically the only way to estimate $\Delta^{15}\text{N}$ between diamond and fluid.

The results of $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ estimates by covariances from the natural genetically related samples can be compared with empirical dependencies and fractionation factors determined within the work. 64 series of conventionally cogenetic diamonds have been identified among the available dataset [9, 37] with the significant correlation $\Delta^{15}\text{N}$ vs $\Delta^{13}\text{C}$ (at a confidence level of 1σ), with the derived distribution of $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratio (Fig.2, solid red line). At 2σ confidence level, the number of the series decreases (57 series), with no significant change in the distribution (the main maximum of Δ^{15}/Δ^{13} of about 0 and local peaks around 1 and 2). The representativeness of each series was assessed using the Student's t -distribution. The lines represent theoretical (see Table 1) $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ values among diamond and fluid of different composition calculated at temperatures of 800 to $1,800\text{ °C}$. Composition

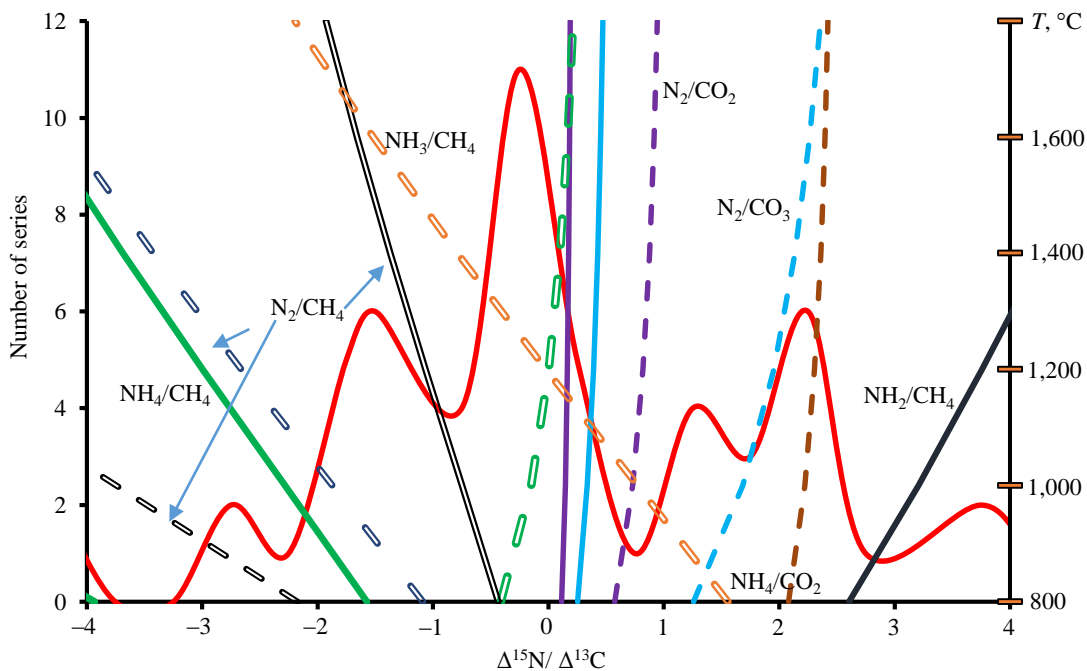


Fig.2. Frequency distribution of $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratio in a series analysis of natural diamonds

of nitrogen species shown as the numerator, carbon species – as the denominator. Solid lines – assuming independent fractionation from $K_N = 1$, dashed $K_N = 5$, double dashed line $K_N = 2.5$. Double dashed green line – NH_3/CO_2 , purple – N_2/CO_2 , blue – N_2/CO_3 . The figure was constructed with no use of the “empirical” fractionation factors estimated from natural nitrogen and carbon isotopic distributions. Most of the $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratios fall within the values of -1.5 to 0.5 (with a maximum of about -0.3). Close to zero $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratios may reflect the predominance of NH_3 as nitrogen-containing fluid compound during diamond genesis ($\Delta^{15}\text{N}$ close to zero) and/or the dominance of carbon-containing component with relatively high fractionation of $^{13}\text{C}/^{12}\text{C}$ during diamond growth (CO_2 , CO_3). CO_2+N_2 or CO_3+N_2 dominated fluids have positive $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratios. Provided two-component carbon source, the maximum distribution of $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ may represent isotopic exchange of diamond with CO_2 or carbonate ion mixed with CH_4 , with N_2 dominating as the nitrogen source. Evolved $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratios (local maxima of the $\Delta^{15}\text{N}/\Delta^{13}\text{C} \approx$ ratio at 1.5 and 2.3) may correspond to diamond crystallization from a fluid dominated by NH_4/CO_2 , N_2/CO_3 or NH_2/CH_4 . C_2H_6 or CH_3N species are possible as a source. Negative $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ correspond to a combination of such components as NH_4/CH_4 , N_2/CH_4 or NH_3/CH_4 (the latter, at temperatures above $1,250$ - $1,300$ °C). It should be noted that temperature increase shifts the equilibrium isotopic ratios of $^{15}\text{N}/^{13}\text{C}$. Empirically estimated values of the $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratio beyond the range of -4 to $+4$ may indicate extreme nitrogen partitions between diamond and the growth medium, or the presence of some unconsidered fluid components enriched in either ^{15}N or ^{13}C relative to diamond. Depending on the $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratio, the Rayleigh crystallization within the cogenetic series of diamond may be accompanied by the increase of $\delta^{15}\text{N}$, by the decrease of this value or by the lack of any trend.

Conclusion

Isotopic fractionation factors have been relatively well established for carbon in many systems related to diamond genesis. The distribution of nitrogen isotopes between diamond and the mineral-forming fluid is, however much less studied and is mainly based on empirically observed trends from natural diamonds, yielding significant uncertainties in estimates and the need for more rigorous constraints [11]. The reliable values of nitrogen isotope fractionation factors should be a prerequisite for revealing the causes of the observed isotopic heterogeneity of diamond, the nature of covariances in $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ -N values, the composition of fluids and, possibly, other conditions during diamond formation. In this paper, an attempt is made to quantify the fractionation of nitrogen isotopes “from first principles” based on crystallo-chemical properties of diamond with nitrogen substitution and nitrogen-containing fluid species.

In particular, the “frozen phonon” method within the density functional theory using the full-electron bases was adopted to determine the sets of β -factors ($^{15}\text{N}/^{14}\text{N}$, $^{13}\text{C}/^{12}\text{C}$) of diamond in harmonic and quasi-harmonic approximations at temperatures from 0 to $2,500$ °C. To achieve representativeness of the calculations, the method of expanded cells (with an increase in volume by 8, 16, 27 times) was utilized. In addition, some β -factors of fluid components (including carbon C_2H_6 , CH_2NH and nitrogen CH_2NH) have been deduced to estimate isotopic fractionations during diamond formation. The results of the *ab initio* calculations differ significantly from the previously obtained theoretical results based on the representation of the CN bonds of diamond by the molecular compounds HCN or CN^- . In the conditions of diamond formation, with a volume decrease under pressure, factors of isotopic fractionation of nitrogen and carbon can increase by tenths of permille for carbon. Pressure effects diamond nitrogen isotope fractionation more than carbon isotope fractionation, which in extreme conditions (super cold subduction) can lead to an increase in fractionation factors up to significant values. The volume increase in diamond lattice due to thermal expansion however, partially reduces the effect of pressure, so that the shifts in isotopic ratios are generally determined by the value of the $\Delta P/\Delta T$ gradient. In the “standard” lithospheric conditions of diamond genesis (about 6 GPa and $1,100$ °C), factors of carbon and nitrogen isotopic fractionation do not change significantly.



Depending on the dominant nitrogen and carbon substances, fractionation of isotopes during diamond formation can result either in various zonation of isotopic composition within individual grains and different variations within cogenetic series. In most cases (maximum in the $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ distribution, Fig.2), nitrogen isotope fractionation is negligible ($\Delta^{15}\text{N} \ll \Delta^{13}\text{C}$), which is consistent with calculations of the fractionation factors between diamond and $\text{NH}_3\text{-CO}_2$ or $\text{N}_2\text{-CO}_2$ fluids. Shifts in the $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ ratio to the negative values may indicate reduced conditions at high pressures and the “cold” geotherm [38]. In nitrogen-poor reduced mantle fluids [39], amines (NH_2) or methanimine (CH_3N) may play an important role and their dominance may also correspond to the occurrence of local maxima within the $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ distribution. Oxidized fluids dominated by CO_2 or CO_3 in combination with the N_2 component yield positive $\Delta^{15}\text{N}/\Delta^{13}\text{C}$ between diamond and fluid and significantly depend on the nitrogen partition coefficient ratio.

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