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Methane-related diamond crystallization in the Earth's mantle: Stable isotope evidences from a single diamond-bearing xenolith

E. Thomassot [a,b,*], P. Cartigny [a], J.W. Harris [c], K.S. (Fanus) Viljoen [d]

[a] Laboratoire de Géochimie des Isotopes Stables de l'Institut de Physique du Globe de Paris, Université Paris 7, UMR CNRS 7154, 2 Place Jussieu, T54-64 E1, 75251 Paris, Cedex 05, France
[b] Department of Earth and Planetary Sciences, McGill University, 3450 University Street, Montreal, Quebec, Canada H3A 2A7
[c] Department of Geographical and Earth Science, Gregory Building, University of Glasgow, G12 8QQ, UK
[d] Group Exploration Macrodiamond Laboratory, De Beers Consolidated Mines Ltd., Southdale, 2135, South Africa

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Abstract

Mineralogical studies of deep-seated xenoliths and mineral inclusions in diamonds indicate that there is significant variability in oxygen fugacity within the Earth's upper mantle. This variability is consistent both with the occurrence of reduced (methane-bearing) or oxidized (CO_2/carbonate-bearing) fluids. Invariably, direct sampling of reduced deep fluids is not possible as they are unquenchable and re-equilibrate with either the surrounding mantle or are affected by degassing. Key information about the nature of such fluids might be found in diamond if it were possible to study a population related to a single source. Usually, diamonds within a kimberlite pipe have different parageneses and can be shown to have formed at different times and depths.

We studied 59 diamonds extracted from a single diamondiferous peridotite xenolith (with a volume of only 27 cm^3), from the Cullinan mine (formerly called the Premier mine) in South Africa. Diamond sizes range from 0.0005 to 0.169 carats (0.1 to 33.8 mg). A correlation between the nitrogen contents of the diamonds (range 40 to 1430 ppm) and their nitrogen aggregation state (varying from 10 to 85% of IaB defects) is compatible with a single growth event. $\delta^{13}C$-values range from −4.2‰ to −0.1‰, with slight internal variability measured in the largest diamonds. Nitrogen isotope measurements show $\delta^{15}N$ ranging from −1.2‰ to +7.2‰. On the centimeter scale of this upper mantle rock, the variations for nitrogen content, nitrogen aggregation state, carbon and nitrogen isotopic compositions, respectively, cover 64%, 75%, 15% and 23% of the ranges known for peridotitic diamonds.

In spite of such large ranges, N-content, $\delta^{13}C$ and $\delta^{15}N$ within this diamond population are distinctly coupled. These relationships do not support a mixing of carbon sources, but are best explained by a Rayleigh distillation within the sub-continental mantle at depths > 150 km and $T > 1200$ °C, which precipitates diamonds from methane-bearing fluid(s). The involvement of this reduced metasomatic agent also suggests that the heterogeneous redox state of Archean cratons may mostly result from the heterogeneous nature of percolating fluids.

The striking variability of the four determined parameters at cm scale may also account for the difficulty in interpreting these parameters in larger productions, such as those from a mine, because in these cases, the diamonds are mixed and sub-populations cannot be disentangled.

Keywords: diamonds; peridotite xenolith; stable isotopes; methane; cratonic lithosphere

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[*] Corresponding author. Laboratoire de Géochimie des Isotopes Stables de l'Institut de Physique du Globe de Paris, Université Paris 7, UMR CNRS 7154, 2 Place Jussieu, T54-64 E1, 75251 Paris, Cedex 05, France.
E-mail address: thomassot@eps.mcgill.ca (E. Thomassot).

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1. Introduction

Diamonds and their encapsulated inclusions reach the Earth's surface from great depths (from 150 to >700 km [1,2]) with minimum modification. Due to alteration or disaggregation of their original host rocks during transport by the kimberlite, most diamond studies are undertaken on samples initially recovered directly from kimberlite. Chemical compositions of their inclusions indicate the presence of several diamond populations and as these may be both unrelated in time and/or temperature (Fig. 3 in [3]), the significance and genesis of these populations have sometimes proven difficult to unravel.

Working on diamonds released from a single xenolith provides a unique opportunity to study a population originating from a very restricted volume of the mantle and ensures similar growth conditions. Most diamond-bearing xenoliths are eclogites, which represent a very minor proportion of the rocks in the Earth's lithospheric mantle. Surprisingly, diamond-bearing peridotitic xenoliths are also uncommon, with only 13 samples reported so far on the Kaapvaal craton [4–7]. The work presented here focuses on 59 diamonds extracted from a single peridotite nodule (DO40) [7] recovered from the Cullinan kimberlite, South Africa.

2. Geological context and analytical techniques

The Cullinan mine is located in the central terrain of the Archean Kaapvaal craton in South Africa 25 km northeast of Pretoria [8]. It is the most important pipe in a cluster of twelve Group I kimberlites, with a preferred emplacement age of 1180±30 My [9]. The diamonds for this study were extracted from a 27 cm^3 xenolith, previously described as a harzburgite, but now totally overprinted by metasomatism, to give a fertile lherzolite [7]. Diamond crystals from this nodule are colourless with shape varying from octahedra to octahedral aggregates and range in weight from 0.0005 to 0.169 carats (0.1 to 33.8 mg). Inclusions, where present, are predominantly sulfides [7].

The nitrogen content and aggregation state were obtained by Fourier Transform Infrared spectroscopy (FTIR). Nitrogen spectra were deconvoluted with a precision of ±20% in N-content and ±5% on aggregation state, using an absorption coefficient of 16.5 at.ppm cm^{-1} for A-defect [10] and of 79.4 at.ppm cm^{-1} for B-defect [11] (see below for these definitions). Carbon and nitrogen isotopic compositions were measured after combustion of pure diamond (no inclusions) in an oxygen atmosphere and a temperature of 1100 °C [12]. Each measurement required about 1 mg of diamond, which allowed, in some cases, duplicate analyses. The isotopic compositions are expressed in classic delta notation (defined as $\delta^{13}C=[(^{13}C/^{12}C_{sample})/(^{13}C/^{12}C_{PDB})-1]\times 1000$ for carbon and $\delta^{15}N=[(^{15}N/^{14}N_{sample})/(^{15}N/^{14}N_{air})-1]\times 1000$ for nitrogen). CO_2 produced by the combustion was analyzed for carbon isotopes with a conventional dual-inlet gas source mass spectrometer [12].

Nitrogen was separated from carbon dioxide and any nitrogen oxides reduced to N_2 using a CaO/Cu mixture [13]. Nitrogen concentrations were measured with a capacitance manometer with a precision better than 5% [14]. Nitrogen isotopic composition was analyzed with a specially constructed triple collector static vacuum mass spectrometer directly connected to the extraction line. In addition to blank determinations, ^{40}Ar ($m/z=40$) was also monitored in the mass spectrometer as an indicator of potential atmospheric pollution for both sample and blank. The blank contribution was below 3 ng of nitrogen with $\delta^{15}N$ of −11±3‰. The accuracy of the measurements, as established on the basis of standard analyses, is better than ±0.1‰ and ±0.5‰ (2σ) for $\delta^{13}C$ and $\delta^{15}N$, respectively [12].

3. Results

The large range in N-contents, from 26 to 1226 at. ppm (Table 1), corresponds to 64% of the global variation observed among diamonds (n ~3000). Nitrogen concentration is positively correlated with the N-aggregation state (Fig. 1), which ranges from 10% to 85% of the Type IaB defects (Table 1). Twenty-four of the 59 diamonds covering the full range of N-content were analyzed for coupled C- and N-stable isotope measurements. The $\delta^{13}C$-values average −2.8‰, over a range from −4.2‰ to −0.1‰ (Table 1) and agree well with previous data reported for Cullinan peridotitic diamonds [15]. This range covers 15% of the global variation for $\delta^{13}C$ in peridotite diamonds (−26.4 to +0.2‰) [16]. Compared to the range defined by the population, two duplicate measurements on five samples show little internal variability (from 0 to 1.2‰) and were positively correlated to the original sample weights (the largest diamond showing the largest internal variability). Nitrogen isotope measurements show a $\delta^{15}N$ range from −1.2‰ to +7.2‰ (with an average of +3.9‰), which represents 23% of the total $\delta^{15}N$ range determined for peridotitic diamonds worldwide [16]. For each sample combusted, nitrogen was quantified by manometry and shows a reasonable correlation with the FTIR measurements (see Table 1).

Table 1
Weight, N-contents (determined by Fourier Transform Infrared Spectroscopy, FTIR, and capacitance manometer after bulk combustion, Mano), percentage of the nitrogen B-defect, δ^{13}C and δ^{15}N of diamonds from DO40 xenolith

Sample	Weight (mg)	[N] IR (ppm)	[N] IR (at.ppm)	%B defects	[N] Mano (ppm)	[N] Mano (at.ppm)	δ^{13}C (‰)	δ^{15}N (‰)
1	13.8	76	65	30				
2	3.7	70	60	13				
3	33.8							
4	11.8	487	418	81	299	256	−2.78	4.0
–	11.8	487	418	81	93	80	−2.82	3.2
5	27.0	207	178	49				
6	18.9	79	67	47				
7	19.3	234	201	71				
8	20.8	262	225	68				
9	25.4	345	296	80				
10	23.1	1430	1226	85	1221	1046	−1.39	3.2
10	23.1	1430	1226	85	1265	1084	−0.75	0.78
11	7.8							
12	10.9	69	59	28				
13	9.0	268	229	72				
14	9.0	60	51	30	50	43	−4.26	−1.1
15	14.4	244	209	58	553	474	−1.19	7.2
16	6.5							
17	7.3	55	47	13				
18	5.6	196	168	55	150	128	−2.12	6.8
19	18.5	274	235	65	288	247	−2.87	6.2
–	18.5	274	235	65	397	340	−1.70	6.6
20	1.1							
21	?	41	35	13	70	60	−3.68	2.5
22	11.2	54	47	32	87	75	−3.29	5.2
–	11.2	54	47	32	185	158	−3.59	
23	7.0	473	405	85	272	233	−3.79	−1.2
–	7.0	473	405	85	111	95	−4.01	0.7
24	7.6	30	26	22	48	41	−4.06	4.3
25	9.0	75	64	38				
26	9.5	107	91	34				
27	7.7	98	84	38	120	103	−1.83	5.6
28	7.6	41	35	10	48	41	−4.03	2.0
29	3.2							
30	6.5	177	152	46				
31	5.4	273	234	57	148	127	−2.73	5.9
32	7.2	92	79	30				
33	7.8	165	141	50				
34	3.5	94	80	34	127	109	−2.33	5.6
35	5.4	192	164	50				
36	5.1	69	59	46	60	51	−3.83	2.4
37	5.3	262	225	57	237	203	−2.04	6.4
38	3.8	120	103	53	105	90	−2.82	3.1
39	2.1							
40	2.1	302	259	59	655	562	−0.84	2.1
41	4.7	122	105	56				
42	3.7	75	65	58	59	50	−3.57	2.3
43	3.8	77	66	39				
44	4.9	117	100	58				
45	2.4	81	69	51				
46	1.4	89	76	58				
47	0.1	198	170	50				
48	4.7	82	70	39				
49	1.5	154	132	55				
50	2.0	242	207	52	187	160	−2.42	6.1

Table 1 (*continued*)

Sample	Weight (mg)	[N] IR (ppm)	[N] IR (at.ppm)	%B defects	[N] Mano (ppm)	[N] Mano (at.ppm)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
51	0.1	96	82	37				
52	0.1	152	136	40				
53	1.6	329	282	80				
54	3.5	115	99	58	67	57	−3.89	2.6
55	3.7	65	56	43	55	47	−3.87	3.0
56	2.6	88	76	42				
57	4.0	311	266	61	410	352	−1.58	7.1
58	2.3	61	53	63	82	70	−3.97	3.8
59	4.5	96	83	39				

Note that nitrogen content ([N]) is expressed both in ppm (µg/g) and at.ppm (µmol/mol). The conversion factor is: [N] ppm = 14/12 × [N] at.ppm.

The wide ranges in chemical and isotopic compositions displayed by DO40 diamonds are remarkable, given the small size of the xenolith. There is, for the first time, positive co-variance between $\delta^{13}C$, $\delta^{15}N$ and N-content on a centimetre scale in the Earth's mantle (Figs. 2–4). Present trends differ from previous studies based on either a worldwide diamond analysis [17], or a single zoned diamond [18] which show increasing $\delta^{15}N$ with decreasing $\delta^{13}C$ and/or N-content.

4. Discussion

4.1. Nitrogen paleothermometry

Nitrogen is diamond's main crystallographic lattice impurity [19], strongly bonded with carbon atoms initially through one-to-one substitution. At the My scale in the upper mantle, a diffusion on the atomic scale results in clustering of singly-substitutional nitrogen to form atomic pairs (A-defects, IaA diamond). Ultimately, at the Gy scale, aggregation proceeds further to groups of 4 atoms surrounding a vacancy (B defects, IaB diamond) [20–22]). This progression in defect formation (usually expressed as the %IaB) follows a second-order kinetic law, which reflects the time/temperature history of diamonds [20].

$$1/[\mathrm{IaA}] - 1/[N] = (A.\mathrm{Exp}^{-\mathrm{Ea}/Rt}).t$$

In the formula, A and R are constants (A = 674.8 kJ/mol, and R = 8.314 kJ/mol/°K), Ea = the activation energy in eV, N = the total amount of nitrogen ([IaA] + [IaB] = [N]), t = time in seconds, and T = temperature in Kelvin [23]. For these calculations, a value of 7.0 eV was used to determine the proportion of the B aggregation state. Assuming a mantle residence of 0.75 billion years (Gy), inferred from diamonds of the same locality and paragenesis [9], an isotherm of 1200 ± 25 °C is obtained (Fig. 1). Even if a longer residence time was considered, for example 2 Gy (diamond genesis age of 3.2 Gy), this temperature is still robust because it would only change by about 40 °C (see [24]). The reliability of this isotherm is further reinforced by the large ranges in N-contents and aggregation states of the present data set and by the fact that diamond productions from the Cullinan kimberlite, clearly show a much greater scatter of these same parameters [15].

Because of the poor dependence of the nitrogen aggregation with time, there is the possibility that the present data set represents more than one diamond population. For example, two (or more) populations could form over a short interval of time (say about 50 My) giving the isotherm in Fig. 1. However, multiple generations of diamonds are unlikely to lead to the observed single C and N isotope trend that is discussed

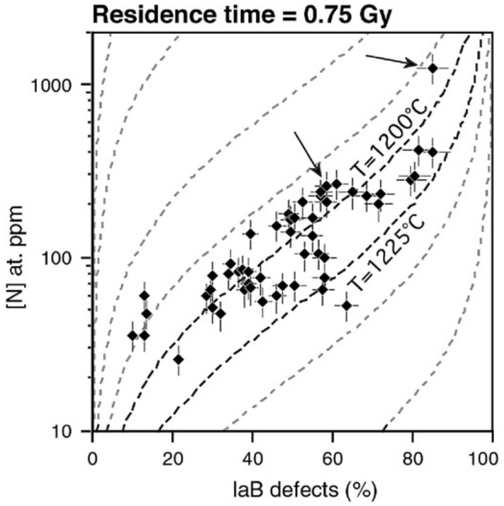

Fig. 1. Nitrogen contents and aggregation states for diamonds from DO40 xenolith. Error bars for Type IaB defects and N-contents are ±5% and ±20% (2σ), respectively. Isotherms are from the equation of nitrogen diffusion for a specific residence time of 0.75 Gy. These times are not significantly affected by temperature (see text). Two anomalous data points are arrowed (see text).

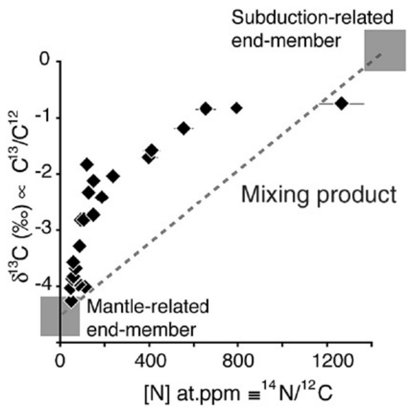

Fig. 2. The dashed line represents the predicted compositions of hypothetical diamonds crystallized from a mixing between two distinct carbon sources (represented by the grey boxes) as a function of $\delta^{13}C$ (‰) vs. N-contents (at.ppm). This model (straight line) does not fit these data, as the relationship is one which is clearly curved.

below (Section 4.2). Thus, these data indicate that DO40 diamonds belong to a single (time related) population.

Considering the geothermal gradient of the continental lithosphere under Premier [25–27] the temperature inferred from the present study corresponds to a depth of about 160 km. This depth places the crystallization of Premier DO40 xenolith diamonds in the sub-continental conductive lithosphere.

4.2. Origin of $\delta^{13}C$, $\delta^{15}N$ and N-content co-variations

Isotope variations within and among diamonds could result from a mixing between distinct carbon sources [28]. In the present case, the lowest and highest N-contents of the diamond set (41 and 1084 at.ppm) were used to constrain two end-member N/C ratios of $<41\times10^{-6}$ and $>1084\times10^{-6}$, respectively. In the same way, the carbon isotopic values of these two specimens become the maximum ($\delta^{13}C\leq-4.1$‰) and minimum ($\delta^{13}C\geq-0.8$‰) values of the two mixing end members.

The end-member with the lowest N/C ratio and with $\delta^{13}C\leq-4.1$‰, is compatible with a mantle-related origin [17,29,30]. The second N-enriched source ($N/C>1500$ ppm, with $\delta^{13}C\geq-0.8$) could be related to subducted carbonates [28,31]. Mixing of these end-members produces a linear relationship between $\delta^{13}C$ ($\propto{}^{13}C/^{12}C$) and N/C ($\propto{}^{14}N/^{12}C$), which is represented in Fig. 2 by a dashed line. With the present data, mixing might account for the $\delta^{13}C$-$\delta^{15}N$ co-variations, but would be definitely incompatible with the curved variation noted between $\delta^{13}C$ and N-content shown in Fig. 2. The above mixing model neglects potential isotopic fractionation between diamond and its growth medium. This additional consideration, however, would only correspond to a shift of the true C- and N-isotope compositions of the two mixing end-members (by ΔC and ΔN, see below), but would not affect their relative C/N-ratios. Hence, the observed isotopic variations cannot result from mixing between two heterogeneous carbon sources. In our view, the large variations in N-contents, $\delta^{13}C$ and $\delta^{15}N$ within a few cubic centimeters in the Earth's mantle more likely point to stable-isotope fractionation related to diamond growth.

3D X-ray tomography of an eclogitic xenolith [32,33], the trace element chemistry of inclusions in diamonds [2], investigations on fibrous [34–36] or gem diamonds [16,17,37,38], all consider a metasomatic agent in diamond formation. If diamond crystallization occurred from a single homogeneous fluid in an open system (Rayleigh distillation), where minute amounts of diamond formed under isotopic equilibrium and remained isolated from their growth medium, then significant chemical and isotopic fractionation can be expected [39–41]. Only limited diffusion within diamond is supported by both recent experimental work [42] and the large isotope variations/correlations among the DO40 population. During Rayleigh distillation, the C isotopic composition is related to N-content by the following equation, which predicts a positive linear relationship between $\delta^{13}C$ and ln [N] [17]:

$$\ln(N/C) = \ln(N/C)_0 + [(\delta^{13}C - \delta^{13}C_0)/\Delta_C] \times (K_N - 1)$$

For the first time, such a relationship is clearly observed among a diamond population and is displayed in Figs. 3 and 4a.

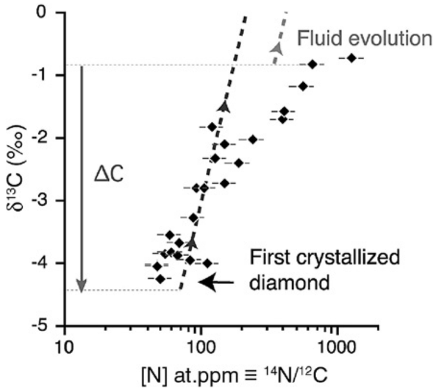

Fig. 3. A plot of the expected variations in $\delta^{13}C$ (‰) vs. N-content (at. ppm, in logarithmic scale) during diamond crystallization via a Rayleigh distillation from an oxidized carbon fluid. The grey dashed line represents the evolution of the fluid and the black one, the evolution of the diamond crystallized in equilibrium with this fluid. The nitrogen enrichment produced in diamonds by this model is not significant enough to fit the present data.

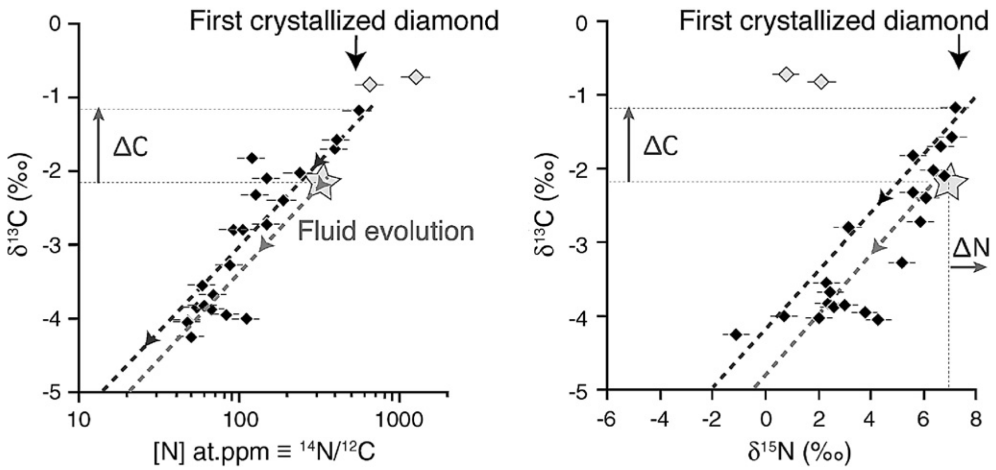

Fig. 4. Plots of the expected variations in $\delta^{13}C$ (‰)vs. N-content (at.ppm, in logarithmic scale) and $\delta^{15}N$ (‰) during diamond crystallization via a Rayleigh distillation from a methane-rich fluid. The grey dashed lines represent the evolution of the fluid and the black ones, the evolution of the diamond crystallized in equilibrium with this fluid. Stars identify the initial parent fluid of DO40 diamond population. Errors in $\delta^{13}C$, $\delta^{15}N$ and N-content are ±0.1‰, ±0.5‰ and ±20% (2σ), respectively. Two data points (open diamonds) are not included in the model (see text). ΔC and ΔN are the equilibrium isotope fractionations of carbon and nitrogen between diamond and methane. The positive ΔC implies that the $\delta^{13}C$ of the fluid diminishes as diamond crystallization proceeds. This evolution requires a positive nitrogen isotopic fractionation (b) estimated, from the data, to be equal to +1.2±0.2‰. The determination of the nitrogen partition coefficient between fluid and diamond in (a) gives a values of Kn=2.

Modelling $\delta^{13}C$–$\delta^{15}N$ and N-content co-variations during diamond crystallization from an oxidized carbon-bearing fluid (CO_2 or carbonate). Carbon monoxide is neglected here, because it is a minor species stable in the present P–T conditions. Fig. 3 shows that under isotopic equilibrium the diamonds will be depleted in ^{13}C isotopes [30,43–45] by about 3‰ relative to the original carbon source. This depletion reflects to the negative isotopic fractionation between diamond and fluid ($\Delta C = \delta^{13}C_{diamond} - \delta^{13}C_{carbonate} \sim -3.5$‰ for $T \sim 1200$ °C [45]). The residual fluid would thus evolve towards less negative $\delta^{13}C$ values with increasing diamond crystallization (Fig. 3). Under these circumstances, the first diamond to crystallize would be nitrogen depleted which implies an incompatible behavior of nitrogen in diamonds (nitrogen partition coefficient K_N being <1). With increasing diamond crystallization the present data also require that $\delta^{15}N$ increases significantly in the fluid (by at least 9‰). The formation therefore, from oxidized carbon is unlikely as the incompatible behavior of nitrogen cannot be reconciled with $\delta^{13}C$ and N-content co-variation, shown in Fig. 3.

In contrast to oxidized carbon-bearing fluids, diamond crystallizing from methane would be enriched in ^{13}C isotopes [30,44] according to $\Delta C = \delta^{13}C_{diamond} - \delta^{13}C_{methane} \sim +1$‰ for $T \sim 1200$ °C. The fractionation value is extrapolated both from thermodynamic calculations in the temperature range 0 to 700 °C [44] and from the anchor point of $\Delta C \equiv 0$‰ for an infinite temperature. For the following discussion, the important aspect regarding ΔC is not its value but its sign. Current available data always indicate a positive value. The first diamond to crystallize from a methane-rich fluid, therefore, must be enriched in both ^{13}C-isotopes and nitrogen (Fig. 4a) indicating that nitrogen behaves as a compatible element in diamond. In consequence, both the $\delta^{13}C$ and N-content of the fluid decreases as diamond crystallization proceeds (Fig. 4a). The slope of the $\delta^{13}C$ vs. ln [N] (Fig. 4a) depends upon $\Delta C \times (Kn - 1)$. With $\Delta C \sim +1$‰ (see above), K_N is determined as $\sim 2.0 \pm 0.1$, which means that diamonds are two times enriched in N compared to their growth medium.

We infer that the fluid had a $\delta^{13}C_0$ of ~ -2.2‰ and a $(N/C)_0 = 0.4 \times 10^3$ before precipitating the first diamond with $\delta^{13}C = -1.2$‰ (see Fig. 4a). Modelling the positive correlation between $\delta^{13}C$ and $\delta^{15}N$ (Fig. 4b) gives ΔN of $\sim +1.2$‰, and an initial $\delta^{15}N_0$ of $\sim +7$‰. Two samples (with the highest $\delta^{13}C$ values) depart from the correlation (Fig. 4b) and are not considered in this model. They could either result from another growth event closely related in time to the main one (as shown in Fig. 1) or be due to an isotope disequilibrium effect related to a nucleation barrier at the beginning of the process. Therefore, diamond crystallization from a methane-bearing fluid perfectly matches the observed trends among the C and N isotopic values as well as the N-contents of the diamonds from xenolith DO40. Open system precipitation of diamonds can also account for internal N-content and carbon isotopic composition variability (maximum $\delta^{13}C$ heterogeneity = 1.2‰, see Table 1). Such mutual variations in geochemical signatures during diamond growth are consistent with precipitation from a fluid, reflecting the evolution of the source during the diamond formation event. This conclusion is supported by a positive correlation between sample size and the internal geochemical variability (see Table 1). Nitrogen speciation and isotope fractionation in mantle fluids, melts, or minerals, remain poorly constrained at temperatures, pressures and oxygen fugacities under which methane is stable (see [46]). In particular, no nitrogen isotopic fractionation coefficient is available between diamond and any other molecular species. However, if we assume NH_3 to be the closest analogue of nitrogen in diamond (nitrogen being incorporated in diamond as a single N-atom bonded to three carbons), the ΔN value of 1.2‰ reported in this study is consistent with the theoretical value of 1.4‰ determined at 1200 °C for the N_2/NH_3 equilibrium [45].

The approach presented above differs from some previously published works [40,47,48] which emphasize that isotopically heterogeneous diamond forming fluids result from a series of mantle fractionation(s) prior to diamond formation. In our view, the record of such process(es) in a single xenolith would be fortuitous. The present model links the chemical and isotopic variations in these diamonds to a crystallization from an initially homogeneous fluid, resulting in a striking relationship between N-contents, N-aggregation, $\delta^{13}C$ and $\delta^{15}N$, which is considered to be very real.

4.3. Implication for worldwide diamond studies

Whilst previous studies on specific aspects of diamond geochemistry usually infer their formation from oxidized carbon [17,18,34,36,40,47,49,50], the present results strongly indicate diamond crystallization from a methane-bearing metasomatic fluid, a result suggested earlier by [41,51–53].

For many years, possible relationships between N-contents, N-speciation, $\delta^{13}C$ and $\delta^{15}N$ of diamonds and the chemical compositions of their inclusions have been suggested and tested in attempts to define a general pattern for diamond formation (see for example [15,41]). The profound variability in these parameters identified here and occurring at the centimeter scale in the Earth's mantle may provide an explanation for the lack of global geochemical correlations among studied diamond populations.

The initial $\delta^{13}C$ value of −2.2‰ for the parent fluid determined in this study (Fig. 4a) corresponds to the highest value within the commonly accepted unfractionated mantle range ($\delta^{13}C$ from −8 to −2‰ with a median value of −4.5 ‰±0.5‰ as determined from peridotitic diamonds, fibrous diamonds and other mantle related samples [17,29,38,54]). This value however is incompatible with derivation from subducted biogenic (reduced) carbon where $\delta^{13}C < -10$‰, average ~−26‰ [28,31]. In addition, the relative abundance of N to C of the parent fluid ($N/C = 0.4 \times 10^3$) is also low compared to the values reported elsewhere for mantle samples (N/C ~ from 1×10^3 to $5 \times 10^3 3 \pm 2$) [29,55]. Furthermore, an initial $\delta^{15}N \geq +7$‰ of this fluid differs from mantle-related samples ($\delta^{15}N = -5 \pm 3$‰ [29,38,54] and overlaps with subduction-related materials. The relatively low N/C ratio and the $\delta^{15}N$ of the diamond source could result from fluid evolution prior to diamond crystallization. However, these results may also suggest, that under reduced conditions, nitrogen behaves as a compatible element leading to fluid(s) with low N/C ratios and ^{15}N-enrichment. The origin of the fluid remains unclear, but given the overlap of the isotopic signatures of DO40 diamonds with worldwide diamonds, we suggest that methane rich fluids could contribute to peridotitic diamonds genesis.

4.4. On the role of sulfide inclusions in diamond crystallization

If nitrogen behaves as a diamond-compatible element during methane-related growth, these diamonds should be, on average, N-enriched relative to those formed from oxidized carbon, because in this latter case, nitrogen would behave as an incompatible element [17,56]. With sulfide-bearing diamonds, a unique feature, yet unexplained is their high N-contents compared to that in silicate-bearing diamonds [57]. A genetic link between methane-related diamonds and sulfides therefore might account for the overabundance of inclusion-bearing diamonds containing sulfides (up to 70% [1]), minerals which are scarce in mantle xenoliths [58]. In the present diamond data set, 7 of the 18 inclusions observed from DO40 diamonds may be sulfides [7].

4.5. Implication for the redox state of the Archean sub-lithospheric mantle

The oxidation state of the Earth's upper mantle varies over at least four log units from FMQ-3 (i.e. three log units below the Fayalite-Magnetite-Quartz buffer) to FMQ+1, with rare samples of cratonic Archean lithosphere showing extremely reduced oxidation states (as low as FMQ-5) [59–62]. This variability in oxygen fugacity is observed at depths of >150 km in deep-seated xenoliths [63] as well as in inclusion-bearing diamonds which may contain either reduced (carbide [64]) or oxidized (CO_2/carbonate [34,35]) minerals. The present study extends mantle sampling to methane-rich fluid in the diamond stability field suggesting that these variable redox states within Archean cratons mostly reflect the heterogeneous nature of fluids interacting with mantle rocks (the fluids potentially buffering fO_2), rather than a secular and unidirectional evolution of the oxidation state of the lithospheric mantle.

Recent studies emphasize that the systematic (but non-monotonic) decrease in fO_2 with depth would imply that at 220 km, where $\Delta\log fO_2$ lies just below FMQ-4 [61,62], carbon-bearing fluid phases would be predominantly composed of CH_4. Due to methane buoyancy, such fluids could migrate upwards through cratonic peridotite into less reduced environments and generate multiple redox-fronts (as suggested by Arculus and Delano, 1987 [65]), which would facilitate diamond formation. DO40 diamonds from Cullinan mine indicate that these circumstances occurs at approximately 160 km. Whilst no fO_2 measurements have been obtained from either DO40 or other xenoliths at Cullinan, this depth could be anomalous with respect to the Kaapvaal craton. In this respect, the possible influence of the adjacent and similarly aged Bushveld Complex may be a factor on the oxidation state of this part of the cratonic lithosphere.

Finally, the presence of methane-related diamonds within the mantle may modify some concepts in diamond geology. Garnets in xenolith DO40 are chromium-rich [7]. As Cr is insensitive to fluid/melt enrichment(s), this element can quantify melt depletion. Experimental data for Cr-immobility, however, are based on oxidized systems, where chromium is Cr^{3+}. Thus, the possibility that Cr^{2+} might be fluid-mobile [66] ought to be investigated, as such studies may help in further understanding diamond origins.

5. Conclusions

We have examined a unique peridotite xenolith (DO40), containing 59 diamonds within a volume of only 27 cm^3. As nitrogen paleo-thermometry is consistent with diamond formation during a single growth event, these samples thus provide the first opportunity to study a single diamond population. Geochemical characteristics of these diamonds reveal that the nitrogen content and speciation cover 64% and 75% of the variation known for peridotitic diamonds worldwide. $\delta^{13}C$, $\delta^{15}N$ and N-content are correlated and their co-variations are consistent with stable isotopic and chemical fractionation related to diamond growth from a methane-rich fluid. The large ranges of nitrogen content, nitrogen speciation, $\delta^{13}C$ and $\delta^{15}N$ measured within this diamond population may provide an explanation for the lack of global geochemical correlations among diamond populations studied so far. Finally, the present study reinforces the model of metasomatic diamond crystallization in the Earth's mantle and provides evidence for the occurrence of highly reduced carbon fluids in the sub-continental lithospheric mantle.

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