

RESEARCH COMMUNICATIONS

Nitrogen isotopes in mantle-derived diamonds: indications of a multi-component structure

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Mantle nitrogen trapped in diamonds is commonly defined by an isotopic composition ($d^{15}\text{N}$) of $\sim -5\%$ based on the central tendency of total combustion diamond data that vary from -25 to $+18\%$. We present here the nitrogen isotopic data from stepped combustion of diamonds, which together with data from other mantle-derived materials suggest a multi-component structure of diamond-nitrogen. Mantle nitrogen sampled in diamonds apparently has $d^{15}\text{N} \sim -15\%$, similar to that observed in mantle xenoliths and mid-oceanic ridge basalts (MORBs), while nitrogen in a minor population of diamonds from China is consistent with contributions from an ocean island basalt like mantle source.

DIAMONDS contain up to ~ 1000 ppm of nitrogen and are potential samples in the search for the isotopic composition of nitrogen ($d^{15}\text{N}$; Table 1) in the earth's mantle, which bears clues for the precursor(s) of the earth¹. But a wide variation in $d^{15}\text{N}$ (from -25 to $+19\%$)^{2,3}, observed in diamonds presents a complicated picture of diamond-nitrogen, which is explained (for a brief review see Cartigny *et al.*² by: (a) mixing between mantle ($d^{15}\text{N} \sim -5\%$)⁴ and recycled nitrogen ($d^{15}\text{N} > +15\%$)⁵, (b) effects of kinetic isotopic fractionation processes and (c) contributions from 'primordial heterogeneities' inside the mantle.

Diamonds often contain inclusions of eclogite (commonly linked to metamorphism of subducted materials) and peridotite (believed to constitute the bulk of upper mantle). The observation of heavy $d^{15}\text{N}$ comparable to that of metamorphic sediments⁵ and the inclusions of eclogite in diamonds inspire the idea of the involvement a 'recycled component' in their geochemical evolution. But diamonds containing inclusions of both (eclogite and peridotite) kinds⁷ and 'mantle-like' $d^{15}\text{N}$ signatures⁴ observed in some of the 'eclogitic diamonds' are not consistent with the traditional genetic interpretation of diamond inclusions. Further, it has been shown that eclogites may have formed in the Archean mantle as part of normal 'crustal extraction processes', and not necessarily be related to subduction⁸. Thus, Cartigny *et al.*^{3,4,9} explain the observed variation in diamond $d^{15}\text{N}$ by a (poorly understood) kinetic fractionation process involving 'yet to be found' phases⁴ (mostly nitriles) of nitrogen in the earth's mantle.

None of the above explanations, however, is able to account for the extreme $d^{15}\text{N}$ signatures (-25 and/or $+19\%$) observed in diamonds. For example, with a mantle nitrogen

Table 1. Stepped combustion nitrogen data^a for the present diamond samples

Sample (wt, X) ^b	Temperature (°C)	N (ppm)	$d^{15}\text{N}$ (‰)
ARG-1 (9.4, F, B)	700	6	5.7 (9)
	1050	134	0.3 (1.0)
	Total	140	0.5 (1.0)
ARG-2 (8.7, F, B)	700	5	9.9 (9)
	900	33	2.6 (1.0)
	1050	148	-0.4 (1.0)
	Total	186	0.4 (1.0)
AUS-1 (8.5, F, C, I)	700	19	13.8 (1.5)
	1000	10	14.8 (8)
	1050	5	14.5 (6)
	Total	34	14.2 (1.2)
CDM-4 (8.7, P, A)	700	6	15.2 (1.0)
	900	26	16.1 (8)
	1000	33	2.7 (6)
	Total	64	9.2 (7)
CDM-5 (8.5, P, A)	700	7	11.4 (1.1)
	900	10	7.4 (6)
	1050	30	7.6 (5)
	Total	47	8.1 (6)
LJC-1 (6.2, P)	700	51	3.6 (4)
	900	66	-8.1 (1.2)
	1000	~Blank	
	Total	117	-3.0 (9)
LJD-1 (8.0, P, A)	700	38	9.3 (3)
	900	226	6.6 (9)
	1050	1023	8.1 (1.4)
	Total	1287	7.8 (1.3)
FNS-1 (7.1, K, C)	700	9	-1.5 (9)
	900	122	-8.5 (1.0)
	1050	107	-8.5 (9)
	Total	238	-8.2 (1.0)
FNS-2 (7.8, K, C)	700	7	14.2 (1.1)
	900	57	3.6 (5)
	1050	19	-2.4 (1.1)
	Total	83	3.2 (7)
PRM-1 (9.3, F, C)	700	2	8.5 (9)
	900	13	-2.3 (9)
	1050	202	-1.4 (1.0)
	Total	217	-1.3 (1.0)
PRM-2 (7.5, F, C)	700	2	2.2 (1.5)
	900	79	-7.1 (1.0)
	1050	28	-4.0 (1.0)
	Total	109	-6.2 (1.0)
ZA-1 (8.9, F, I)	700	24	-2.4 (1.0)
	900	175	-3.0 (1.0)
	1050	194	-9.4 (1.2)
	Total	393	-6.1 (1.1)

^aUncertainties in concentrations are $\pm 10\%$; errors in isotopic data, in the least significant figures, are at 95% confidence level.

$d^{15}\text{N} = \{[(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{air}}] - 1\} \times 1000$.

^bSample weights in mg, X: A, Alluvial; B, Bort quality; C, Clear; F, Fragments (~ 1 mm size); I, Inclusions present³⁷; K, Recovered from host kimberlite; P, Powdered (50–100 μm).

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(end-member) with $d^{15}\text{N} \sim -5\%$, it is not possible to explain the much lighter $d^{15}\text{N}$ signatures observed in diamonds by mixing with recycled nitrogen⁴. While taking into account the isotopic composition of diamond-carbon ($d^{13}\text{C}$) hardly reduces the controversy concerning nitrogen, results from the studies of a number of geochemical tracers such as Nd, Pb, S and Sr (in diamond-inclusions) suggest the presence of contributions from recycled materials in diamonds¹⁰⁻¹².

Nitrogen data available in the literature have been obtained from total combustion experiments (mostly) on bulk samples of diamonds (Figure 1). But a small fraction of data, obtained from physically separated (using laser) sub-samples (e.g. ladder-sections, coats and cores) of diamonds reveals large variations in $d^{15}\text{N}$ (Figure 2) within diamonds. However, no attempt has so far been made to study nitrogen by stepped combustion of diamond. We have studied diamond samples from Africa and Australia simultaneously for nitrogen and argon isotopes by stepped combustion using static mass spectrometry. Low amounts of argon in the studied samples (weighing 9 mg), however, did not yield meaningful isotopic data. In this communication we present the nitrogen isotopic data obtained by stepped combustion of mantle-derived diamonds, and discuss their implications for the source of diamond-nitrogen in light of data from other mantle-derived materials.

Samples under the present study include ~1 mm size particles obtained by crushing single or fragmental diamonds in a hardened-steel mortar and/or already powdered diamonds (Table 1), where the smaller sample size (corresponding to higher surface area) was intended to facilitate combustion. After cleaning in ethanol and acetone (in an ultrasonic bath), the samples were thoroughly examined under a binocular microscope to ensure the absence of any extraneous materials. Up to 9 mg of the samples packed in gold foils was loaded into a Pyrex sample tree and baked overnight at 150°C. The stepped combustion experiments were performed in a double-vacuum quartz finger with ultra-pure oxygen generated in line from a copper-oxide finger. Prior to the main combustion steps (in ~8 torr of oxygen), the samples were cleaned by a 'routine' combustion step at 400°C in 2 torr of oxygen (to remove any surficial contamination). Nitrogen in each step was 'cleaned' by (up to three) 'copper oxide cycles', isolating the condensable gases in each cycle by a liquid nitrogen trap on a Pyrex finger and was analysed by a VG1200 noble gas mass spectrometer using standard procedures¹³. A typical 1050°C blank gave $^{28}\text{N}_2 \sim 100$ pg, negligible (<2%) compared to the sample signals. Mass spectrometric sensitivity and mass discrimination (favouring the lighter mass) for nitrogen (on Faraday cup, 10^{10} ohms), measured in samples of air (standard) during the period of the experiment, are 5.84 ng/volt and $2.50 \pm 0.02\%$ /amu respectively¹⁴.

The present experiment has certain shortcomings. Detailed information regarding the paragenesis of diamonds and their age could not be obtained as many of the diamonds were transparent fragments or already powdered

materials (CDM-4 and 5) and were not of sufficient amounts to allow pre-characterization. Similarly, little was known about their geological history. While they restrict the scope of forceful interpretation, these drawbacks do not undermine the quality of the data, which on the other hand have interesting implications for diamond-nitrogen.

Total nitrogen in the present samples varies in concentration from ~30 to 1280 ppm (Table 1), and in $\delta^{15}\text{N}$ from ~-8 to ~+14%. Nitrogen (N ppm and $\delta^{15}\text{N}$) data from the present study and the literature are compared in Figure 1. The concentrations of nitrogen in the present samples, which are orders of magnitude smaller in weight than those in the literature data (up to a couple of grams in weight), are at the lower end of the compositional field of diamonds. This may be explained by the heterogeneous distribution of nitrogen in diamonds as revealed by spectroscopic studies^{2-4,6,9,15-17}. An important aspect of the present data, however, is the large (up to ~15%) variation in $\delta^{15}\text{N}$ observed in the different combustion steps (Figure 2 a). A majority (8 out of 12; Table 1) of the present samples show heavy $\delta^{15}\text{N}$ at low temperatures (700°C) and light $\delta^{15}\text{N}$ at high (> 700°C) temperatures, while a few show either uniform heavy (e.g. AUS-1) or light (e.g. FNS-1, except for the minor release at 700°C) $\delta^{15}\text{N}$. While variation in the 'totals' (Figure 1 a) is comparable to that observed in the literature data, the intra-sample variation confirms the isotopic heterogeneity in a single diamond, although on a much smaller sample scale, as revealed by the studies on different sub-samples of single diamond grains (Figure 2 b).

One may attribute the variation in $d^{15}\text{N}$ in the present data partly to contributions from organic contamination. Such possibility is, however, ruled out by our sample preparation and experimental approach outlined earlier. The efficiency of the 'routine' 400°C combustion in removing surficial contamination is testified by our previous experiments on terrestrial and meteoritic samples^{13,18-21}. Nitrogen in contemporary organic materials ($d^{15}\text{N} \sim +5\%$ ²²) cannot explain the observed spectrum of $d^{15}\text{N}$ data in Table 1. It may be tempting to attribute the observed variation in $d^{15}\text{N}$ in the stepped combustion data to isotopic fractionation intrinsic to stepped temperature extraction. This however is inconsistent with the present stepped temperature data, which do not follow the release trend (low temperature light and high temperature heavy $d^{15}\text{N}$) expected in isotopic fractionation. Diamond growth probably does not fractionate nitrogen isotopes³. Therefore, it is reasonable to consider the observed variation in $d^{15}\text{N}$ as a reflection of that which existed in the diamond forming-fluid.

One may invoke isotopic fractionation of a mantle source with ~500 ppm of nitrogen and a $d^{15}\text{N} \sim -5\%$ to explain the present data, which fails to account for the outlier data (Figure 1) however. It is now well understood that diamond formation took place over a period of time during which the supply of volatiles varied²³. This is difficult to reconcile with an end-member with fixed nitrogen concentra-

tion and occurring in widely separated localities (Table 1) from which the present samples have been collected. The global nature of any such fractionation process is hard to reconcile also with the scatter of data in Figure 1.

At present it is not possible to either prove or reject the existence of 'primordial heterogeneity' in the earth's mantle, which apparently went through large-scale 'processing' (e.g., magma ocean)²⁴ early in its history. Alternatively, we examine diamond-nitrogen data in the light of inferences drawn from nitrogen and noble gas isotopic data on mantle xenoliths and mid-oceanic ridge basalts (MORBs) which apparently have common source mantle-volatiles²⁵.

Diamonds form in the sub-continental mantle (SCM), which also provides mantle xenoliths. Nitrogen and noble gas data on worldwide xenolith samples indicate an intri-

cate mixture of mantle and recycled volatiles at their mantle sources^{13,21,26-28}. The importance of metasomatic fluids (related to subduction recycling) in the geochemical evolution of SCM is well understood from data (also) involving a host of solid trace elements^{10-12,29,30}. Considering the possibility of the presence both of 'mantle' and 'recycled' volatiles and trace elements in SCM, as indicated by the above studies, it is difficult to rule out a multi-component structure for diamond volatiles.

Figure 1 *b* presents the statistical distribution of the literature diamond $d^{15}\text{N}$ data, which shows a mode at $\sim -5\%$ that is commonly believed to represent the isotopic composition of mantle nitrogen trapped in diamonds⁴. But a multi-component structure of diamond-nitrogen would suggest that the above statistical central tendency of the diamond $d^{15}\text{N}$ data actually defines a mixture rather than any particular nitrogen end-members present in the diamond-forming fluid. Diamonds apparently have trapped volatiles from a MORB-like mantle reservoir, as indicated by their noble gas isotopic signatures²⁵, which is also true for mantle xenoliths. The nitrogen isotopic signature of MORB source mantle³¹ (based on statistical central tendency) was long believed to be $\sim -5\%$ (e.g. M 1 in Figure 1 *b*), which was more or less used as a 'mutual support' for the traditional view of mantle nitrogen trapped in these two kinds of mantle samples. But we have recently shown that the true $d^{15}\text{N}$ of the MORB source mantle should¹⁸ be $\sim -15\%$ (e.g. M 2 in Figure 1 *b*), similar to what has also been found in mantle xenoliths^{13,21}. Therefore, we feel that mantle nitrogen trapped in diamonds should have $d^{15}\text{N}$ much lighter than -5% , which is also supported by light $d^{15}\text{N}$ signatures ($\sim -9\%$) observed in the present and in the earlier studies ($\sim -12\%$)⁶. The much lighter ($\sim -25\%$)² signature found in particular diamond samples from China, however, requires contributions from a mantle end-member of the type inferred from recent data on Ocean Island Basalts (OIB)³² and carbonatites³³. This is also supported by the observations of OIB like noble gas signatures in samples from SCM^{13,34,35}.

We have presented here the nitrogen isotopic data from a stepped combustion experiment on mantle-derived diamonds. Together with inferences from the nitrogen and noble gas isotopic data from mantle xenoliths (samples from the diamond-forming mantle region) and MORBs (whose mantle source was the ultimate source of mantle-volatiles for the above two kinds of samples), these data are consistent with a 'two-component mixing' between nitrogen from mantle and recycled materials. Based on the multi-component structure of diamond-nitrogen, we suggest that isotopic composition of mantle nitrogen trapped in diamonds should be much lighter than -5% (the commonly believed signature). While a signature of $\sim -15\%$ appears consistent with contributions from a MORB-like mantle source, the observation of much lighter $\sim -25\%$ in certain diamonds suggests contributions also from an OIB-like mantle source.

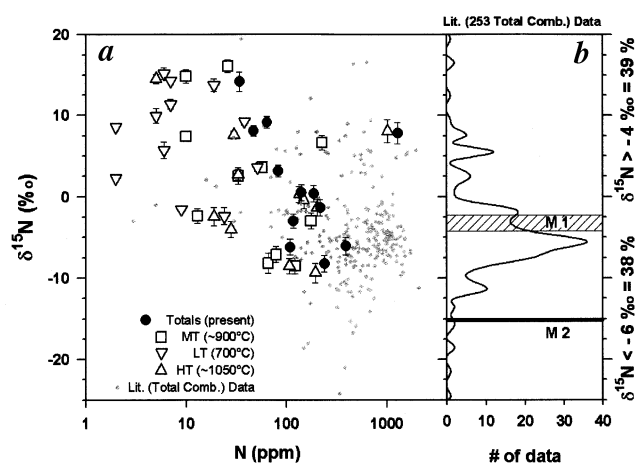


Figure 1. Variation of $d^{15}\text{N}$ in bulk samples of diamonds. *a*, With N (ppm) for the present (both totals and stepped temperature; LT, MT and HT respectively, refer to low, medium and high temperature extractions) and the literature (*total combustion)^{2-4,6,9,15-17} data. *b*, In the above literature data (77% of which fall beyond the peak at -5% $\pm 1\%$). Also shown are two different signatures for the MORB mantle $d^{15}\text{N}$ (see text for discussion)¹⁸.

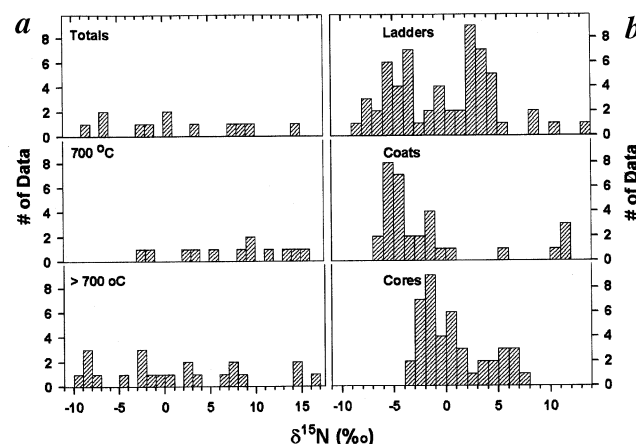


Figure 2. Variations in $d^{15}\text{N}$ observed in (*a*) the present (totals, low and high temperature extractions) and (*b*) literature data^{15,36} for ladders, cores and coats of diamonds.

We believe that controversies regarding the source of nitrogen (carbon and probably other trace elements) in diamonds may be addressed by simultaneous nitrogen and noble gas isotopic data on worldwide diamonds, which should form a future effort in the study of volatiles in diamonds.

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