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Nitrogen and carbon isotopic composition in the diamonds of Mbuji Mayi (Zaire)

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The concentration and isotopic composition of nitrogen, measured in large diamonds (gram size) from the Mbuji Mayi kimberlite district (Zaire) show a large range of variation ($100 < N < 2100$ ppm, $-11.2 < \delta^{15}\text{N} < +6.0$). The ^{15}N -depleted nitrogen is associated with the higher nitrogen concentrations. The large diamonds are individually rather homogeneous in ^{13}C (range of $\delta^{13}\text{C} < 0.9\text{‰}$) while variations occur within small octahedral diamonds from the same district (range up to 5.8‰). The total range of $\delta^{13}\text{C}$ variations is about the same for the large diamonds ($-10.5 < \delta^{13}\text{C} < -5.5$), the small octahedral diamonds ($-10 < \delta^{13}\text{C} < -4.6$), and the carbonates from local kimberlites ($-11.8 < \delta^{13}\text{C} < -5.5$). The diamond carbon isotopic data could indicate a complex story of crystallization within a deep-seated system fractionating its carbon isotopes.

The nitrogen results indicate that nitrogen in diamonds is, on the average, markedly depleted in ^{15}N (weighted average -5.15‰) relative to atmosphere, sediments and upper mantle.

1. Introduction

Nitrogen is one of the terrestrial constituents for which the estimate of primary amounts and isotopic compositions is the least constrained because of the presumably large outgassing suffered by the proto-Earth constituents, before accretion [1,2]. The simplest assumption that terrestrial nitrogen resides mainly in the atmosphere [3], would result in a low concentration when related to the whole Earth. Recent estimates of the bulk Earth's concentration [4], of a few parts per million, are closer to the concentration in various types of chondrites [5,6], which are likely analogues to primordial terrestrial material. However, the only detailed study of the isotopic composition of nitrogen in meteorites failed to give even an approximate answer to the problem of the isotopic composition of terrestrial nitrogen, since the range

of $\delta^{15}\text{N}$ * values measured is very large. The situation is even worse than in the case of carbon, presumably because nitrogen is less abundant than carbon in meteorites and is likely to be in a much more advanced state of fractionation in meteorites with low nitrogen concentrations. The situation is further complicated by various effects (extra solar component, spallation produced ^{15}N , etc.) [7–9]. The nitrogen of ocean and sediments, which has been studied most up to now, shows a majority of positive $\delta^{15}\text{N}$ deviations relative to the atmosphere, understandable in terms of low-temperature fractionations [10]. If the system ocean-atmosphere-sediments were taken as representative of

* The δ notation is defined by $\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$ where $R = ^{15}\text{N}/^{14}\text{N}$, $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$, etc., and standards are atmosphere for nitrogen, PDB for carbon, SMOW for oxygen.

the whole Earth, which is not proven, this would place the earth in the large field of ordinary chondrites (Fig. 1). However, the isotopic composition of the major element oxygen [11] more likely relates Earth to the enstatite chondrites, whose isotopic signature in nitrogen is characteristically very negative (-20 to -40%) [6]. The very few data on deep-seated terrestrial nitrogen [12], [13], point rather to a positive $\delta^{15}\text{N}$. Becker and Clayton [12] have found $\delta^{15}\text{N}$ of $+17$ to $+20\%$ in mid-ocean ridge basalts (MORB) and peridotites. Wand et al. [14] and Becker [15] recently found slightly positive $\delta^{15}\text{N}$ in diamonds. However, Wand et al. [14] give only an average value for 15 Namibia diamonds, no concentration and no estimate of analytical uncertainty. Becker's analyses relate to diamonds with no indication of origin. This last characteristic is frequent in diamond studies. We took the advantage of a collection of large diamonds from the Mbuji Mayi area (Zaire) to shed some light on the problem of the isotopic composition of deep seated nitrogen in a given area.

2. Geology

The Mbuji Mayi kimberlite field (East Kasai province, Zaire; Fig. 2) of late Cretaceous age (71 m.y) [16] consists of 14 pipes and/or eluvial deposits: 10 of them—the northern group (5–10 km²)—are aligned on an east-west fracture of the Archean Kasai craton; the southern group has only 4 irregularly distributed pipes.

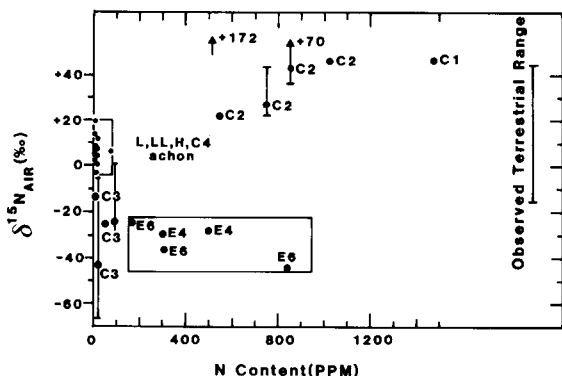


Fig. 1. $\delta^{15}\text{N}$ -nitrogen concentration relationship in meteorites (after Kung and Clayton [6]).

The kimberlites have been described as xeno-tuff breccias which contain numerous fragments of all sizes of the country rocks, abundant eclogitic nodules and the typical “discrete nodule associations” [18] or “megacryst suite” [19]; that is, pyrope, Cr-diopside and magnesian ilmenite. The breccia, which is in fact a blueground, also contains rounded nodules (12–15 cm) of what has been called “primary kimberlites” [17]. This implies that at least two phases of kimberlite emplacement may be defined: the nodules represent an earlier kimberlitic episode corresponding perhaps to dykes or sills. Detailed petrographic, geochemical and Sr isotopic data on these nodules have been published elsewhere [20–22]. Only a brief summary is given below.

Although often very altered, the kimberlite nodules display the typical porphyritic texture with two generations of euhedral (serpentinized) olivine phenocrysts, set in a fine-grained groundmass consisting of idiomorphic chlorite, saponite and

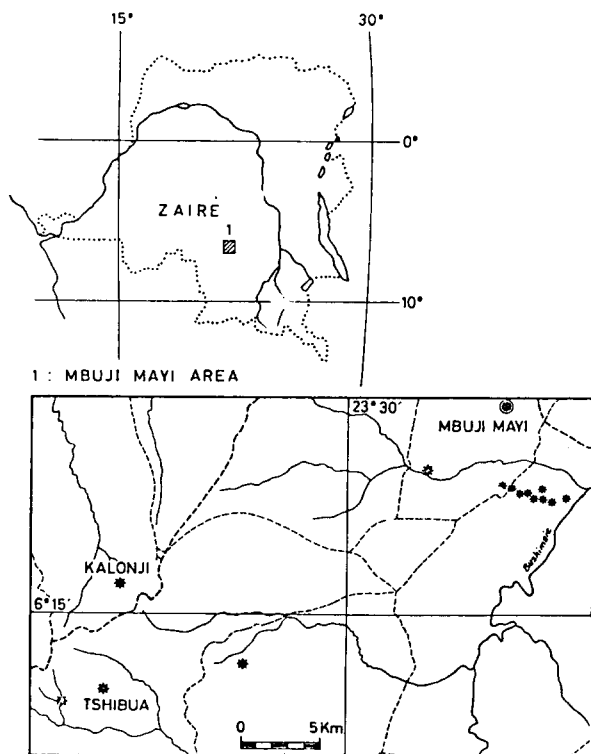


Fig. 2. Geographical situation of the Mbuji-Mayi kimberlitic field.

carbonates with subordinate amounts of magnetite, apatite and rutile. The carbonate, mainly calcite, appears either in the groundmass as isolated grains with amoeboid outlines and poikilitic crystals enclosing the silicates, or as carbonate inclusions (up to 4 cm) which consist of randomly oriented or dendritically arranged lath-shaped crystals. Chemically, the Mbuji Mayi kimberlites (fresh nodules) are comparable to the typical kimberlites of South Africa, Lesotho, and Yakutia. They nevertheless appear significantly enriched in volatiles (up to 15% CO₂ as carbonates and 10% H₂O) when compared to average kimberlite [8], as reflected by the high carbonate and mica content of the matrix.

The Sr isotopic initial compositions for the fresh kimberlite nodules fall in a narrow range: (⁸⁷Sr/⁸⁶Sr)₀ = 0.7041–0.7045 (8 values) [21]. These data are comparable to those reported by Barrett and Berg [23] for fresh South African kimberlites and to the present isotopic ratio of the whole Earth as deduced from the Nd-Sr correlation [24,25]. This suggests that the kimberlites are derived from an undifferentiated chondritic mantle source, as was also proposed by Basu and Tatsumoto [26], on the basis of Nd isotopic data (ϵ_{Nd} close to zero). The carbonate inclusions have ⁸⁷Sr/⁸⁶Sr ratios undistinguishable from that of the enclosing kimberlites [21], which points to a genetic relation between these two rocks: the carbonate could correspond to late-stage segregation from a CO₂-rich fluid or to an immiscible carbonatitic liquid.

The Mbuji Mayi kimberlitic field is one of the biggest diamond mining centers in the world with a mean annual production of 12,000,000 carats.

Detailed investigations of the physical properties of the diamonds (crystal form, twinning, colour, transparency, etc.) have been made [27]. Three classes of diamond from Mbuji Mayi have been described:

(1) *The gem quality diamonds* are transparent, colorless stones, generally well-crystallized (mainly octahedra; less abundant rhombododecahedra). This class represents only 2–3% of the diamond population.

(2) *The industrial diamonds* (10–15%) are translucent, or opaque, generally colored stones oc-

curing as single crystals (cubic form) or crystal aggregates.

(3) *The crushing boarts* represent 80% or more of the diamond population; usually they are crystal aggregates or have irregular forms with very few, if any, crystalline faces.

Mvuemba et al. [28] have examined about two hundred diamond crystals (1–2 mm) to study the mineral inclusions. Contrary to what is frequently observed [29,30] olivine is very rare in the Kasai diamonds and enstatite is completely lacking. Garnet and clinopyroxene are the most common inclusions while sulfides, kyanite, Mg-ilmenite, chromite and diamond are also recorded.

3. Description of the samples

Isotopic data have been obtained on two series of diamonds:

(1) Fragments of clear octahedral crystals broken by Mvuemba et al. [28] to study the mineral inclusions. These fragments, a few milligrams in weight, have been analyzed only for carbon.

(2) Large crystal aggregates of gram size provided by the SIBEKA, some of them with well-defined crystal habits.

After the results of Mvuemba et al., the first category would contain mainly the eclogite type of inclusions [19]. Few silicate inclusions exist in the large diamonds of the second category. A study in progress [31] has shown the existence of Cr-poor diopside and plagioclase (~An₅₀) and possibly calcite.

Optical spectra in the UV and the visible range have been studied on two samples: sample D₃ exhibits a sharply increasing absorption towards UV which may be correlated to type IB diamonds [32] with very well defined N₃ centers. Sample D₅ may be classified as a type IA diamond [32], according to its absorption slope towards UV. The absence of narrow absorption bands may be attributed to the lack of discrete centers. Two very broad absorption bands near 460 and 380 nm may be attributed to nitrogen clusters under H₃ and N₃ forms, respectively*.

* H₃ is a vacancy or an interstitial trapped on A-type defect. N₃ is a group of 3 nitrogen atoms lying in a (111) plane.

As will be discussed below, the nitrogen concentrations measured in the present study seem to place most of our diamonds in type IA as is normal. Sample D₃ is indeed much poorer in nitrogen and its $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values are distinctly different.

It must be stressed that, although the documentation is much better than for the previous studies [14,15], we cannot assign a sample to a given pipe or to a given kimberlite. Hence, if some heterogeneity appears in the results it is possibly due to the fact that several pipes are involved. We cannot assign a given trend to a given pipe.

4. Experimental procedure

The diamond fragments used for both carbon and nitrogen were obtained by cleavage of the samples. However, due to the very poor crystal quality of the large diamonds it was seldom possible to attribute a precise location to the fragments. When it was possible, such as for samples D₃ and D₅, there was no apparent correlation between either concentration or $\delta^{15}\text{N}$ or $\delta^{13}\text{C}$.

The carbon analyses have been done on CO₂ obtained by combustion of the diamonds at 1000°C in oxygen liberated by CuO. For nitrogen analyses, some attempts had been made to liberate the nitrogen by graphitization at high temperatures [14,32]. However, we did not have the necessary apparatus to obtain 2000°C which would have insured a quick graphitization and the attempts revealed that very high levels of blank nitrogen were released by the molybdenum or tantalum crucibles. So the nitrogen was released by combusting the diamonds in an oxygen atmosphere ($p \sim 100$ mm Hg) released by decomposition of copper oxide, which, under cooling, takes back the excess oxygen.

The diamonds and the copper oxide are heated in coaxial platinum crucibles with an induction furnace at about 1000°C and the resulting CO₂ is continuously trapped just below the platinum crucible in liquid nitrogen. For an average sample of 75 mg, the combustion is complete in about 15–20 minutes as can be followed visually through the top of the glass container since the optical

contrast between the platinum crucible and the diamond is very sharp. The diamond disappears completely and this is confirmed to better than 0.1 mg by weighing both the platinum crucible after combustion and the CO₂ produced (by double weighing of the CO₂ sample tube).

The nitrogen amounts are measured by toeplering the sample into a known volume (0.25 or 1 cm³) after treatment over “reduced” copper (see below). The nitrogen blanks are comparable to those quoted by Thiemens and Clayton [33] (< 0.03 μmole), with $\delta^{15}\text{N}$ varying between +10 and +13‰. Those blanks have been measured both in vacuum and with reagent-grade graphite producing the same amount of CO₂ as the diamond samples. Hence, the circulation of CO₂ in the extraction line and its contact with the glass walls, stopcocks and grease produced no extra nitrogen blank. We have also checked by putting 2.5 μmole of N₂ (average size of our samples) into the combustion apparatus before combustion of reagent-grade graphite that no N₂ is trapped with the CO₂ ($< 0.1\mu\text{mole}$) and that its $\delta^{15}\text{N}$ does not vary (less than 0.2‰).

For nitrogen analyses we used large samples (32–280 mg of diamond), which, given the nitrogen concentration, released 0.3–5 μmole of nitrogen. The blank corrections for $\delta^{15}\text{N}$ varied from 0.6‰ down to 0.1‰ and where less than 0.3‰ for most of the samples. The corrections for nitrogen concentrations were less than 40 ppm and close to 10 ppm for most of the samples.

For some samples rich in nitrogen (e.g. sample D₉) condensible nitrogen oxide species were produced which had to be reduced over “reduced copper”, at 660°C, which is the classical Dumas method. The proportion of oxidized nitrogen was around one third of the total, which may possibly be related to the presence of N₃ groups. These groups, under oxidation of the diamond, may release a nitrogen molecule N₂ and a nitrogen atom N, much more sensitive to oxidation under a rather large oxygen pressure. The failure to recover this oxidized nitrogen resulted in higher $\delta^{15}\text{N}$, probably due to a kinetic effect during the oxidation of the nitrogen, as was shown by recovering the nitrogen complement by reduction.

The nitrogen samples were analyzed on a dou-

ble collector mass spectrometer Micromass 602C equipped with a cold finger into which the samples were frozen with liquid helium and compared to tank nitrogen of $\delta^{15}\text{N} = -3.5\text{‰}$. The necessary 28 and 29 background corrections (the latter monitored by the height of peak 27), as well as valve mixing corrections, were made. Scanning up to mass 44 checked for the absence of CO_2 and undue levels of ^{40}Ar (i.e. larger than those given by the blanks $\approx 6 \times 10^{-13}$ A), which would reveal the existence of atmospheric contamination. In fact, those levels corresponded to the blanks within error limits, although the 40/36 ratio was different, which may reflect the influence of argon from the diamond, of low 40/36 ratio [34]. The samples were then frozen back into the sample tubes and chemically analyzed on a 24-collector Cameca mass spectrometer to check for the absence of H_2 , CO (measured on mass 12) and CH_4 , which would give rise to spuriously high $\delta^{15}\text{N}$ by interference from N_2H^+ , $^{13}\text{CO}^+$ and C_2H_5^+ respectively. The 2σ deviations on mass spectrometric measurements were $< 0.1\text{‰}$. Given the size of the CO_2 samples, the $\delta^{13}\text{C}$ of the diamonds were measured with an excellent reproducibility, which, for different samples of the same diamond was frequently the same as the 2σ deviation of the mass spectrometric analysis (0.01–0.03‰). Finally the carbonates were analyzed after attack by 100% H_3PO_4 on either powdered whole rock or separated carbonate inclusions.

5. Results and discussion

5.1. Carbon

The $\delta^{13}\text{C}$ in diamonds varies from -4.6 to -10.5‰ whereas those in carbonates from “primary” kimberlite nodules varies from -5.5 to -11.8‰ (Tables 1–3). This is in the range of most diamonds and kimberlitic carbonates analyzed to date [35–37]. As already shown by the ^{87}Sr results, there is thus little doubt that the carbonate carbon is of the same origin as the diamonds and essentially free from any contamination from sedimentary carbonates. The $\delta^{18}\text{O}$ has been modified to some extent by deuteric alteration [36–38] as it

frequently happens in kimberlites and carbonates. Hence, at the time of emplacement of the pipes, the kimberlitic magma provided an almost infinite reservoir of carbon since the carbonates constitute 9–34% of the unaltered kimberlites. Accordingly, there is little difference to be expected overall between the $^{13}\text{C}/^{12}\text{C}$ ratio in carbonates and diamonds, that is a relatively small isotope evolution of the carbon reservoir during the formation of the carbon species.

However, when we look at the homogeneity of the results among individual diamonds, we see some striking differences: although the bulk composition of small, well crystallized, octahedral diamonds, calculated by mass balance, is less variable from one diamond to another, they are individually more heterogeneous isotopically than the large, poorly crystallized diamonds (Fig. 3). The maximum variation within a small diamond is 5.8‰ whereas it is only 0.9‰ in the large diamonds.

Of course, it is well possible that there is a sampling effect since samples from the large diamonds are themselves very large (on the average fifty times larger than those from the small diamonds). Hence their $\delta^{13}\text{C}$ value may represent an average of values as variable as in the small diamonds. It shows, however, that there is no large-scale isotope effect during the growth of large diamonds. The results for the small octahedral diamonds are very similar to those reported by Swart et al. [39].

Consequently, it looks like, within a rather nor-

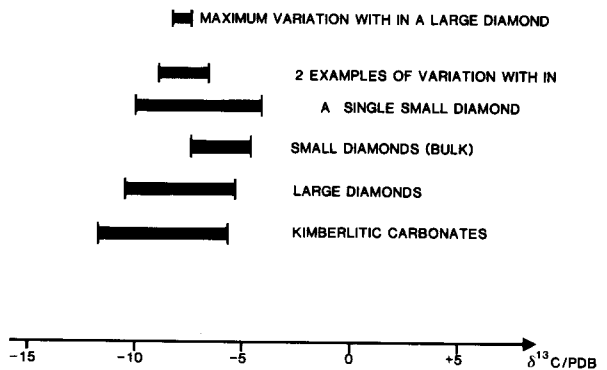


Fig. 3. $\delta^{13}\text{C}$ range of diamonds and kimberlitic carbonates of the Mbuji-Mayi field.

TABLE 1

 $\delta^{13}\text{C}$ variations in small octahedral diamonds

Sample	Mass of fragment (mg)		$\delta^{13}\text{C}$ (‰ vs. PDB)	Maximum range and standard deviation ^a within a single diamond
D 2P	1.04		-4.63	1.63
	1.50		-5.06	0.21
	0.70		-3.99	
	0.13		-3.43	
	0.87		-4.39	
	0.36		-4.98	
	0.38		-4.75	
	1.44		-4.45	
Total	6.42	weighted average	-4.59	
D 3P	1.26		-6.62	2.25
	2.18		-8.87	0.27
	1.98		-7.72	
	2.88		-6.80	
	3.84		-6.68	
	0.35		-7.84	
	0.66		-6.85	
	0.73		-6.66	
1.30		-6.81		
Total	15.20	weighted average	-7.20	
D 16P	1.14		-5.83	0.62
	1.54		-6.06	0.10
	1.12		-5.87	
	0.46		-5.77	
	0.37		-6.02	
	0.54		-6.24	
	0.10		-6.45	
Total	5.3	weighted average	-5.92	
D 19P	2.35		-6.57	1.89
	1.10		-8.40	0.29
	3.00		-6.69	
	1.98		-6.79	
	1.26		-8.46	
	0.74		-6.80	
	0.49		-7.01	
	1.20		-6.97	
Total	11.8	weighted average	-7.26	
D 20P	1.22		-7.05	1.62
	1.92		-8.31	0.17
	4.56		-7.50	
	1.32		-6.75	
	2.04		-7.09	
	1.26		-6.94	
	2.82		-7.14	
	0.31		-6.93	
	3.42		-6.68	
Total	18.5	weighted average	-7.35	

TABLE 1 (continued)

Sample	Mass of fragment (mg)	$\delta^{13}\text{C}$ (‰ vs. PDB)	Maximum range and standard deviation ^a within a single diamond
D 68P	0.048	-9.96	5.8
	3.06	-7.30	1.10
	1.02	-6.15	
	0.37	-5.45	
	0.12	-4.16	
Total	<u>4.60</u>	weighted average	-6.84

^a $\sigma/\sqrt{n-1}$.

mal range of isotopic compositions, the well-crystallized diamonds originate from a rather heterogeneous medium, whereas the large diamonds seem to have grown each in a homogeneous medium or a medium with only small isotopic oscillations around a constant mean composition. Again there is an almost perfect overlapping between the whole range of $\delta^{13}\text{C}$ for the Mbuji Mayi field and the maximum range of variation inside a single small diamond (Fig. 3).

If, as is usually accepted, crystal quality is closely linked to the rate of growth, we can assume that this rate has been faster for the large, poorly crystallized diamonds than for the small, well crystallized diamonds. The explanation of the iso-

topic differences between the two could then be that small and large diamonds have grown from an isotopically similar carbon but under very different conditions: the large diamonds could have grown in a medium rich in carbon which provided both the conditions of rapid kinetics and an unlimited reservoir while the small diamonds grew from an environment where the carbon was scarce or dispersed, which means a slow growth. Hence they have either sampled different locations of varying $\delta^{13}\text{C}$ values or they have somewhat exhausted the carbon of their environment, leading to some kind of isotopic distillation of the carbon reservoir by fractionation during diamond formation.

TABLE 2

$\delta^{13}\text{C}$ variations in large crystal aggregates

Sample	Number of analyses ^a	Mass (mg)	$\delta^{13}\text{C}$ (‰ vs. PDB)	Maximum range observed in a single diamond	Standard deviation
D ₁	2	161	-5.75	0.2	0.2
D ₂	6	472	-5.47	0.5	0.09
D ₃	5	589	-10.52	0.35	0.05
D ₅	12	620	-7.01	0.4	0.06
D ₆	4	268	-7.46	0.2	0.06
D ₇	4	368	-6.74	0.9	0.20
D ₈	3	272	-6.36	0.2	0.07
D ₉	6	399	-6.90	0.26	0.04
D ₁₀	5	433	-5.94	0.19	0.08

^a On different parts of the same diamond.

TABLE 3

Isotope composition of kimberlitic carbonate

Sample	Description	CaCO ₃ (%)	$\delta^{13}\text{C}$ (‰ vs. PDB)	$\delta^{18}\text{O}$ (‰ vs. SMOW)
K1	carbonate inclusion	78	-5.6	+23.0
K2	carbonate inclusion	76	-5.5	+23.5
K1/41	kimberlite nodule	8.7	-7.7	+19.6
K4	kimberlite nodule	26.5	-11.8	+18.8
K6	kimberlite nodule	21.6	-7.6	+19.55
K4/41	kimberlite nodule	34.2	-6.1	+13.3
K5/2	kimberlite nodule	17.9	-10.4	+20.0

Such a model implies that the carbon in the vicinity of Mbuji Mayi pipes' source region need not have been heterogeneous, since this heterogeneity could well have been produced by the above distillation processes [38]. Regarding the large diamonds, the present results suggest that their formation is linked to the concentration of large quantities of carbon at a given place. This concentration could correspond to the formation and ascent of the kimberlitic magma itself. This would give some support to the ideas of Mitchell and Crockett [41] on the metastable growth of at least some diamonds. It also means that those imperfect diamonds, while perhaps not reflecting very characteristic conditions of the deep mantle, are a major sampling of carbon material from the source region of kimberlites together with the carbonates. This fact is reflected also by their overwhelming abundance over any other type of diamond.

If small-scale heterogeneity in the large diamonds is concealed by the scale of sampling there is of course another explanation: that large diamonds grow by steps similar to those of the small diamonds, during which isotopic distillation occurs by exhaustion of the carbon source. Hence, their growth should be discontinuous, but the large-scale homogeneity shows that the growing

medium is regularly supplied with new carbon of constant isotopic composition.

Finally, as will be seen also from the nitrogen results, sample D₃ is very distinct from all the other large diamonds, which are, otherwise, rather tightly grouped ($-7.46 < \delta^{13}\text{C} < -5.47\text{‰}$). This is possibly linked to the fact that D₃ is a type IB diamond, of very rare occurrence in natural samples. This fact can be explained in two ways:

—either type IB diamonds originate from a mantle region or a material with a carbon isotope signature very different from the average. This is less than evident when placing this analysis in the general distribution of diamonds' isotope compositions [35]: a value of -10‰ is not very rare although it corresponds to a kink in the general histogram.

—or type IB diamonds form in a given region when the carbon reservoir is in a very advanced state of evolution, that is, for example, nearly exhausted. This would correspond to the fact that, as a typical type IB diamond, sample D₃ is also poor in nitrogen (see below).

5.2. Nitrogen

The results are displayed in Table 4. The concentrations vary from 100 to 2100 ppm and the

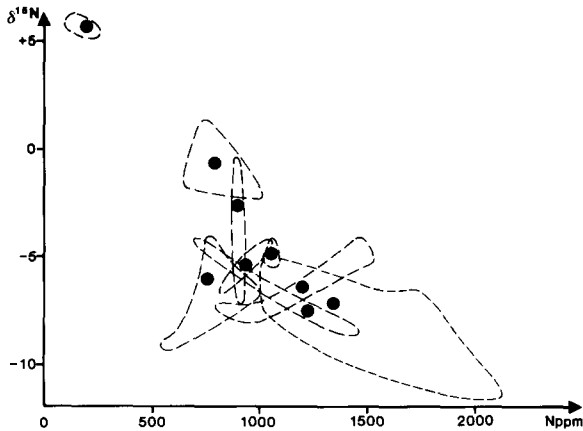


Fig. 4. $\delta^{15}\text{N}$ -nitrogen concentration relationship. The numbers used are the mass balanced values for each individual diamond. The dotted lines represent the range of variation of each diamond.

$\delta^{15}\text{N}$ from +6.0 to -11.2‰. All average concentrations but one are greater than 750 ppm, which places those diamonds into type IA, the largest category. Sample D_5 , which was recognized as a IA diamond after its optical characteristics, is indeed one of the samples richest in nitrogen. Sample D_3 which was classified as IB on the same basis is indeed the poorest sample and its $\delta^{15}\text{N}$ is

the only one to be distinctly positive. There are rather large variations within a given sample, which may reflect a complex growth history, in a similar but more contrasted way than the carbon isotopes. It would be normal, since nitrogen is less abundant, hence more sensitive to perturbations such as isotopic distillation of a limited reservoir, contamination or local heterogeneities. However, if we plot the weighted mean concentrations and isotopic compositions for each individual diamond, they are clearly anticorrelated (correlation coefficient = -0.92) (Fig. 4). The weighted averages are 950 ppm, for the nitrogen concentration and -5.15‰ for the $\delta^{15}\text{N}$, with a total variation of -7.5 to +5.5‰: the mean $\delta^{15}\text{N}$ is well below zero, and more than 90% of the diamonds' nitrogen has negative $\delta^{15}\text{N}$. The positive $\delta^{15}\text{N}$ could be a signature of distinct origin for IB type diamonds, but it is equally likely that a process which would have lowered the nitrogen concentration to the level corresponding to IB diamonds, would have also increased the $\delta^{15}\text{N}$ by isotopic fractionation from an initial value similar to those of the other diamonds.

The preliminary result of Becker [15] who finds $\delta^{15}\text{N}$ between 0 and +5‰ agrees partially with these results but he does not find any negative

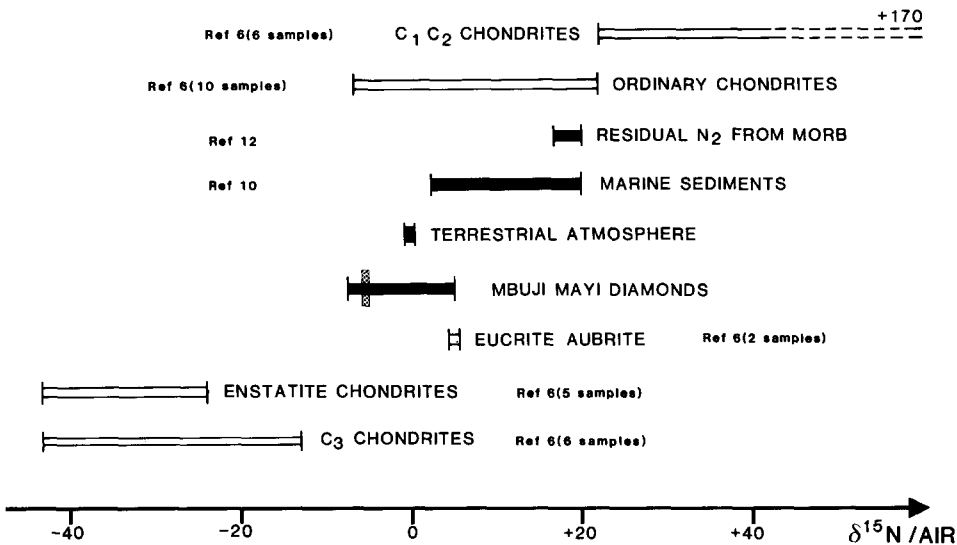


Fig. 5. Comparison of $\delta^{15}\text{N}$ range in Mbuji-Mayi diamonds with terrestrial and extraterrestrial references. The dotted bar shows the mass balance average of Mbuji-Mayi diamonds. The data for other reservoirs are from Kung and Clayton [6] (meteorites), Sweeney et al. [10] (sediments), and Becker and Clayton [12] (MORB).

TABLE 4
Nitrogen concentrations and isotopic compositions in large diamonds

Sample	Total mass (g)	Mass analyzed (mg)	N(ppm)	$\delta^{15}\text{N}$ (‰ vs. air)
D ₁	1.371	80.0	836	-6.48
		80.6	1030	-4.32
Weighted average		160.6	930	-5.4
D ₂	1.264	102.8	765	-4.05
		116.7	756	-5.04
		63.9	662	-8.42
		51.8	553	-9.06
		61	989	-6.66
		76	750	-5.97
Weighted average		472.2	752	-6.0
D ₃	1.162	280	247	+5.53
		70.1	261	+5.33
		86.6	126	+6.04
		70.7	138	+5.24
		81.4	98	+5.67
Weighted average		589	197	+5.55
D ₅	1.427	51.2	1166	-6.58
		51.4	1115	-6.22
		51.3	1004	-5.61
		43.8	1055	-5.07
		49.5	1034	-7.15
		50.8	1155	-5.87
		40.0	1391	-9.68
		47.7	1501	-6.74
		54.7	1027	-7.18
		32.4	2109	-11.2
		84.7	1734	-6.58
		62.7	1730	-6.93
		Weighted average		620.2
D ₆	0.873	96	897	-0.6
		67.6	911	-7.0
		83.7	917	-4.1
Weighted average		247.3	908	2.56
D ₇	0.892	57.0	707	-4.26
		90.7	1435	-8.30
		104.0	1260	-7.26
		117.0	1253	-7.98
Weighted average		368.7	1220	-7.5
D ₈	1.010	78.3	1000	-2.06
		105.7	735	+1.2
		83.2	656	-1.6
Weighted average		267.2	788	-0.7

TABLE 4 (continued)

Sample	Total mass (g)	Mass analyzed (mg)	N(ppm)	$\delta^{15}\text{N}$ (‰ vs. air)
D ₉	1.549	46.5	814	-7.25
		57.0	937	-7.88
		82.4	1089	-7.33
		93.5	1253	-5.87
		74.0	1524	-5.14
		45.8	1461	-4.14
Weighted average		399.2	1185	-6.12
D ₁₀	1.136	100.3	1050	-4.31
		107.0	1030	-5.12
		67.0	1075	-5.26
		106.7	1072	-4.77
Weighted average		381	1055	-4.8
Average weighted on the 44 samples analyzed (44 analyses)		3.5054 g	921	-5.34
Average weighted on the total mass of each diamond		10.68 g	947	-5.15

value of $\delta^{15}\text{N}$ in five diamonds whose occurrence is not specified. The unique result of Wand et al. [14] does not conflict with our results since neither the concentration of nitrogen, nor the uncertainty of their evaluation of $\delta^{15}\text{N}$ (+1.5‰) is given. Our low-concentration result could correspond to that case.

The source region of Mbuji Mayi diamonds display nitrogen isotope characteristics which cannot be related to those of the outer reservoir (atmosphere, sediments and crust) in a simple manner, such as the very crude model developed by Wetzel and Winkler [42], that is, without significant fractionations or primary differences in isotopic composition between surficial and deep-seated nitrogen.

Indeed, large isotope variations (~15‰) are evident in a single kimberlite field. Moreover, the weighted average isotope composition is distinctly negative. If we compare the range of $\delta^{15}\text{N}$ of Mbuji Mayi diamonds to those of the atmosphere, sediments and residual nitrogen in MORB [10,12], (Fig. 5), we can thus conclude that:

(1) There is a significant difference in isotopic

composition between the Mbuji Mayi diamonds and the other reservoirs.

(2) More than 90% of the nitrogen contained in those diamonds has a $\delta^{15}\text{N}$ well outside the range defined by the residual MORB nitrogen around 20‰ [12] and the reservoir atmosphere-sediments whose calculated $\delta^{15}\text{N}$ can vary according to the weight given to the sediments but is in any case positive [10,42].

Hence it is not possible to derive *both* the surface reservoir as a whole (outgassed part) and the nitrogen in MORB (residual from outgassing) by the outgassing of a unique source like Mbuji Mayi diamonds, since the $\delta^{15}\text{N}$ of the latter is distinctly negative and the first two distinctly positive. We need at least two sources, one of negative $\delta^{15}\text{N}$, such as the one found in Mbuji Mayi diamonds and also in other mantle-derived products such as volcanic gases [43] and one of positive $\delta^{15}\text{N}$, so that the mixing of both sources in the outer layers of the Earth produces the positive $\delta^{15}\text{N}$ of the outer reservoir. Of course this model is very dependent on the ^{15}N content of nitrogen in MORB, for which we have only a few measure-

ments but the MORB's $\delta^{15}\text{N}$ would have to vary drastically (from +20‰ to negative values) to change the present conclusions. This problem will be developed in another paper.

Another problem remains which is the large $\delta^{15}\text{N}$ range in diamonds and the anticorrelation to nitrogen concentrations. Basically two types of models are possible: fractionation models and mixing models with possible combinations between the two types:

(1) *Fractionation model.* The main objection is the large range of $\delta^{15}\text{N}$ ($\sim 13\%$) observed for a relatively small range of concentrations. Equilibrium fractionations at temperatures in excess of 1000°C should be small and it is indeed the case for simple molecules of nitrogen compounds [44]. For example, $\Delta(\text{N}_2\text{-NH}_3) = \delta_{\text{N}_2} - \delta_{\text{NH}_3}$ becomes negative for $T < 675^\circ\text{C}$ but never exceeds -1.5% . This could explain the direction of $\delta^{15}\text{N}$ evolution in depleted material such as MORB or the diamonds poorest in nitrogen but certainly not the range of variation. Given the range of nitrogen concentrations ($\sim 200\text{--}1370$ ppm that is a factor 7) distillation effects could not increase this range by more than a factor two ($\sim \ln 7$) since the most efficient process would be a Rayleigh distillation. The only way to obtain the observed variation by fractionation effects alone would be by large fractionations nearly independent of temperature, that is, possibly by diffusion effects. Simple molecular diffusion of nitrogen results in a fractionation factor of ~ 1.018 ($\sqrt{29/28}$), which would be the right order of magnitude. The difficulty will be to find a mantle process in which such a diffusion may operate. For kimberlites, a possible process would be the outgassing of the kimberlitic magma during the ascent to the surface, which would imply that large diamonds can grow significantly during that process, as already discussed in the carbon results' section.

(2) *Mixing model.* The other way to obtain a concentration-dependent $\delta^{15}\text{N}$ is to mix a nitrogen-rich source poor in ^{15}N with a nitrogen-poor source rich in ^{15}N . Because of previous results [12] on upper mantle material and of simple pressure-solubility relationships the ^{15}N -poor source is likely to be of deeper origin. A simple mixing model plots as a straight line in a $\delta^{15}\text{N}$ vs. $1/[\text{N}]$ dia-

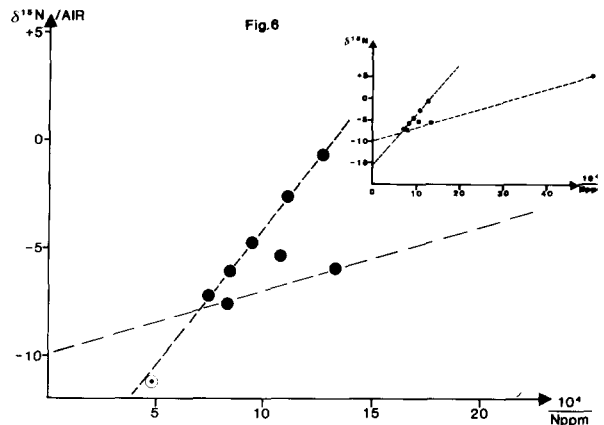


Fig. 6. $\delta^{15}\text{N}$ - $1/[\text{N}]$ relationship for a test of mixing model. Black dots correspond to the mean value for each diamond. The open circle corresponds to the lowest observed value for sample D_5 and is shown for comparison.

gram. The two end members plot anywhere on that line (outside the observed range) and the ordinate intercept gives the minimum $\delta^{15}\text{N}$ when the ^{15}N poor source can be considered of very large concentration in nitrogen. For example, a pure nitrogen fluid ($c = 10^6$ ppm) is close to that definition relative to any silicate system. The diagram of Fig. 6 shows that, if a mixing model applies, it is not a simple one and possibly involves more than two sources, but it can give us limits for the $\delta^{15}\text{N}$ of the deep-seated source namely -11.2% (lowest $\delta^{15}\text{N}$ found in a diamond chip) to -16% (lowest ordinate intercept).

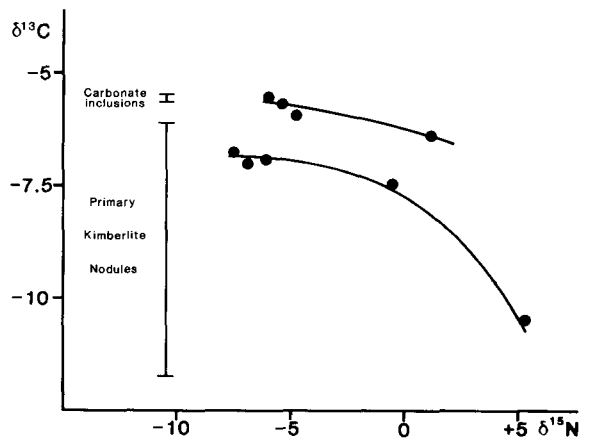


Fig. 7. $\delta^{15}\text{N}$ - $\delta^{13}\text{C}$ relationship in large diamonds.

We cannot choose between those two models but both imply the existence of a deep seated source with a $\delta^{15}\text{N} < -11\text{‰}$.

6. Nitrogen-carbon relationships

$\delta^{13}\text{C}$ is plotted versus $\delta^{15}\text{N}$ in Fig. 7. One can see that this diagram defines two groups and an inverse correlation ($\delta^{15}\text{N}$ increases when $\delta^{13}\text{C}$ decreases). This may represent two stages of distillation effects corresponding to the two episodes of kimberlitic activity postulated by the geologic study [20–22]. It seems indeed that the carbonates disseminated in the kimberlite nodules (“primary” nodules) are poorer in ^{13}C than those concentrated in the carbonate inclusions, with $\delta^{13}\text{C}$ ranges roughly corresponding to the two diamond groups. More information has to be collected about these trends.

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