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## On the possibility of a kinetic fractionation of nitrogen stable isotopes during natural diamond growth

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**Abstract**—In a diamond from New South Wales (Australia), cubic and octahedral growth sectors, as identified by cathodoluminescence (CL), show slight differences in N-contents of 29 and 42 ppm respectively but no significant differences in either  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  and nitrogen aggregation state with values at +1.96‰, +19.4‰, and 25% Type IaAB aggregation, respectively.

Two gem cubes from the Orapa kimberlite (Botswana) were studied by CL revealing a nonfaceted cubic growth. Accordingly, nine other gem cubes were combusted and yielded  $\delta^{13}\text{C}$ -values from -5.33‰ to -6.63‰,  $\delta^{15}\text{N}$  from -1.0‰ to -5.5‰, and nitrogen contents from 914 to 1168 ppm, with nitrogen aggregation state being only Type IaA (zero % B). The gem cubes show striking similarities to fibrous/coated diamonds, not only in both  $\delta^{13}\text{C}$  ranges (less than 3‰ from -5 to -8‰), but also in the high levels of nitrogen ( $\approx 1000$  ppm), suggesting that the two diamond types are related. Additionally, no  $\delta^{15}\text{N}$  variation was detected between the cube and octahedral growth sectors of the Australian diamond, in the cube sectors of the nine gem cubes from Botswana, nor in fibrous/coated diamonds previously studied. These analyses contrast with an earlier study on a synthetic diamond, which reported a strong kinetic fractionation of N-isotopes of about 40% between cube and octahedral growth. The present evidence, therefore, suggests that kinetic fractionation of N-isotopes does not operate during natural diamond formation. Copyright © 2003 Elsevier Science Ltd

### 1. INTRODUCTION

Within diamonds, nitrogen is the main atomic impurity substituting for and being strongly bonded to carbon atoms (Kaiser and Bond, 1959). As opposed to other mantle-derived materials, nitrogen is present in diamonds in rather high concentrations, averaging 300 ppm (Deines et al., 1993). Diamond is thus a very valuable sample in mantle geochemistry and has been used to infer mantle nitrogen isotopic composition. It is now well established that the sublithospheric mantle is depleted in  $^{15}\text{N}$  isotopes relative to the external reservoirs of the Earth (Javoy et al., 1984; Boyd et al., 1987, 1992; Cartigny et al., 1997), a result confirmed by subsequent studies of nitrogen isotopes in mid-ocean ridge basalts (Javoy and Pineau, 1991; Marty and Humbert, 1997). Because the deep (i.e., upper mantle) and external (i.e., sediment, metasediment, and crust) reservoirs of the Earth have different stable isotopic compositions, characterized by negative and positive  $\delta^{15}\text{N}$ -values [where  $\delta^{15}\text{N} = (^{15}\text{N}/^{14}\text{N}_{\text{sample}}/^{15}\text{N}/^{14}\text{N}_{\text{Air}} - 1) \times 1000$ ] respectively, this difference has been used to discuss the origin of carbon in supposedly subduction-related eclogitic diamonds. Given that eclogitic diamonds are mostly characterized by negative  $\delta^{15}\text{N}$ -values, it has been argued that the carbon of eclogitic diamonds is mantle-related (Cartigny et al., 1998).

However, in almost all these studies is the tacit assumption that the measured  $\delta^{15}\text{N}$ -values are representative of the medium from which the diamond grew. This assumption has however never been seriously tested and is not supported by a first-order observation. For a synthetic diamond of mixed crystal habit, Boyd et al., (1988) demonstrated a surface control in both the uptake of nitrogen and its isotopes in different growth sectors. The variations in  $\delta^{15}\text{N}$  were  $\sim 40\%$  between the cubic and octahedral growth sectors. This result led Boyd and Pillinger (1994) to emphasize that diamonds with stable isotopic signatures differing from the mantle value could reflect variations of the source itself or, alternatively, the occurrence of a kinetic fractionation of both carbon and nitrogen isotopes. According to the kinetic fractionation hypothesis, this would imply that diamond  $\delta^{15}\text{N}$ -values could, in some instances, be unrepresentative of the diamond growth medium. The aim of the present article is to consider such a possibility.

Extending the results obtained from synthetic diamonds to natural diamonds is however difficult. As summarized by Frank (1987), “The cubo-octahedral morphology of synthetic diamonds grown from solution in molten transition metal tells us one thing for certain, that this was not the medium in which the natural diamonds grew.” Relatively large sized synthetic diamonds (like those studied by Boyd et al., 1988 and Burns et al., 1990, but for which no growth conditions were provided), are normally made under extremely reducing conditions, in a metal alloy matrix, a system quite unlike the silicate-dominated growth environments of natural diamonds (Harris, 1992). Also, syntheses occur at higher pressures and temperatures ( $>65$

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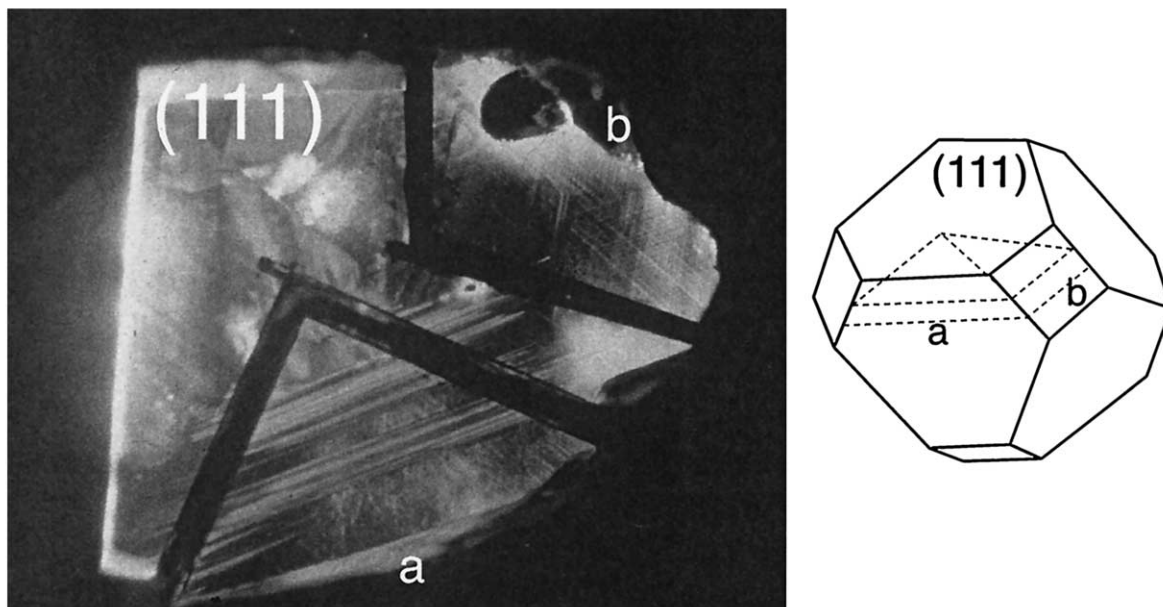


Fig. 1. Cathodoluminescence picture of alluvial diamond sample W13 from New South Wales (SE Australia) showing the octahedral (a) and cubic (b) growth sectors. On an adjacent cubo-octahedron, these sectors are schematically illustrated. The black “V” lines on the cathodoluminescent image are cuts made by a laser.

kbars, 1300°C) relative to the formation of most lithospheric diamonds ( $\approx 50$  kbars,  $\approx 1100^\circ\text{C}$ ; Harris, 1992). These pressure–temperature differences may not be truly significant, as most synthetic diamonds do not have the opportunity of slow growth. The rate of growth of synthetic diamonds is known to be very fast, and such diamonds grow by macro-steps, usually in the order of few thousand nanometers as opposed to slow growth conditions for octahedral-shaped natural diamonds achieved by monolayer steps (Sunagawa, 1990).

## 2. SAMPLE SELECTION

The majority of natural diamond cubes (like those belonging to varieties III and part of varieties IV in the classification of Orlov, 1977) are not of gem or near gem quality, but are rounded, opaque and consist of an array of diamond fibres. These diamonds can either be totally fibrous, or form as fibrous coats over a gem quality core. Hereafter they will be referred to as fibrous/coated diamonds. In both cases, a distinct cubic morphology can result, but the individual fibres have an octahedral orientation (Kamiya and Lang, 1964; Orlov et al., 1982; Moore, 1985; Welbourn et al., 1989; Boyd et al., 1994).

As a consequence of very different growth conditions (Su-

nagawa, 1990), the abundance of gem or near gem primary growth cubes or cubo-octahedra is very low relative to gem quality octahedral-shaped diamonds (Harris et al., 1979). Gem cubes or those with cubic growth sectors within gem diamonds of mixed habit are not faceted-growth surfaces like octahedral growth sectors (Hartmann and Perdok, 1955), but are non-faceted and hummocky, with only a mean cubic (i.e.,  $\{100\}$ ) orientation. Diamond cubes, therefore, are often referred to as having a cuboid shape.

The approach used here to test the possibility of a kinetic fractionation of nitrogen isotopes during natural diamond growth consists of replicating the type of work initially completed on a synthetic diamond, but this time, on natural stones. A comparison of  $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ -values, between cubic and octahedral growth zones, would only be appropriate, if these two growth zones are synchronous. Diamonds characterized by mixed habit crystals have been described by Lang (1974), Moore (1985), and Welbourn et al. (1989). Two diamonds from the alluvial deposits from Wellington (New South Wales) were found to be of this type (Davies et al., 1999), and as only one of these, (W13), contained nitrogen, it was selected for the present study. In addition, for comparative purposes, 11 gem cube diamonds from the Orapa kimberlite in Botswana were analyzed.

## 3. EXPERIMENTAL TECHNIQUES

Nitrogen aggregation states were determined using micro infrared spectroscopy (Fourier Transform Infrared [FTIR]) (Cartigny et al., 1997). Nitrogen-bearing diamonds can be subdivided as a function of the nitrogen speciation. During diamond growth, single nitrogen atoms substitute for single carbon atoms (Type Ib diamond). The nitrogen then migrates to form pairs of atoms (Type IaA) and eventually, clusters of four atoms and a vacancy (Type IaB) (Woods, 1986). These different defects are linked by a diffusion process (Chrenko et al., 1977; Evans and Qi, 1982), the percentage of the B species depending upon

Table 1.  $\delta^{13}\text{C}$ - and  $\delta^{15}\text{N}$ -values, nitrogen contents—determined by both bulk combustion and infrared spectroscopy (FTIR)—and aggregation state (%B) of cubic and octahedral growth sectors of a single natural stone from Wellington (New South Wales, Australia).

Ref	Mass (mg)	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	N (ppm) Combustion	N (ppm) FTIR	%B
W13 - cubic (B)	3.2754	+1,90	+19.4	29	$\approx 23$	25
W13 - octa (A)	4.6383	+1,98	+19.5	42	57	28

Table 2.  $\delta^{13}\text{C}$ - and  $\delta^{15}\text{N}$ -values, nitrogen contents, and aggregation state of natural gem cubes from Orapa (Botswana).

Ref	Mass (mg)	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	N (ppm) Combustion	N (ppm) FTIR	%B
OR 380	1.5016	-6.28	-2.3	1168	1072	0
OR 381	1.5617	-5.33	-2.4	1060	1123	0
OR 382	1.4590	-5.85	-2.3	914	1023	0
OR 383	2.7924	-6.31	-1.0	1142	1225	0
OR 384	1.7490	-5.68	-2.4	1061	1251	0
OR 385	0.5105	-6.56	-5.5	1015	1052	0
OR 386	2.8042	-6.34	-4.9	1090	937	0
OR 387	0.5692	-6.45	-4.8	1007	1124	0
OR 388	1.0793	-6.63	-5.0	1039	1075	0

initial nitrogen concentration and the integrated time–temperature history of the diamond. Errors on the nitrogen aggregation are better than 5%. Cathodoluminescence (CL) of diamond reveals growth modes and patterns. After spectroscopic analyses, samples were combusted for  $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ -N measurements following the experimental procedure given by Boyd et al., (1995). The accuracies are 0.1‰, 0.5‰, and 5% (all  $2\sigma$ ) for  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and N-contents respectively.

#### 4. SAMPLE DESCRIPTION AND RESULTS

The single natural macrodiamond of mixed cubo-octahedral crystal habit (W13) was  $\sim 1$  cm in octahedral edge. The sample had already been doubly polished (nearly parallel to a 111 face) and examined by CL (Davies et al., 1999). For the present study, both sides of the diamond slab were further polished to ensure that an identical CL growth pattern was observed on both sides. The sample was then laser sectioned to separate octahedral and cubic sectors, and these are shown in Figure 1 as parts “a” and “b” respectively. Crystallographic orientations were verified using X-ray diffraction before infrared spectroscopy analysis. Finally, part of this sample was weighed and combusted for the  $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ -N determinations. Results obtained on this diamond are reported in Table 1. Note that, for N-contents, the combustion techniques agree well with FTIR determinations. Cubic and octahedral growth sectors have slightly different nitrogen contents, 29 ppm and 42 ppm, respectively.  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ -values are however identical within experimental error, mean values being  $+1.94\text{‰}$  and  $+19.4\text{‰}$  respectively. Both stable isotope ratios are unusually enriched in heavy isotopes relative to other mantle-derived diamonds (Cartigny et al., 1998) but are very similar to other diamonds from SE Australia (P. Cartigny and R. Davies, unpublished data).

Table 3. Summary of N-contents and  $\delta^{15}\text{N}$  N-values, measured in cubic and octahedral growth zone of synthetic diamonds (i.e. of mixed cubo-octahedral shape). Data from the literature.

Growth sector	N content (ppm)	$\delta^{15}\text{N}$	Reference
(111)	$\approx 100$	—	Strong and Chrenko (1971)
(100)	5–7	—	
(111)	$\approx 100$	—	Burns et al., (1990)
(100)	$\approx 50$	—	
(113)	$\approx 10$	—	
(110)	$\approx 1$	—	
(111)	$\approx 100$	$\approx +40\text{‰}$	Boyd et al., (1988)
(100)	$\approx 50$	$\approx 0\text{‰}$	

The 11 gem cubes from Orapa, were colorless, their surfaces being nearly flat. From these specimens, two samples,  $\sim 4$  mm in size, were polished on one side and examined in CL. For both diamonds, the growth patterns observed showed a similar green-CL core surrounded by a large fairly homogeneous blue-CL rim, the latter accounting for more than 80% of the crystal volume. Crystal growth, therefore, was in the cube directions there being no significant octahedral growth. With cube-shaped diamonds, it should be noted that there is a continuum of shapes from gem cubes, which have almost no octahedral growth sectors (the two above mentioned cubes from Botswana), to the so-called truncated cuboids (“truncated” being used to account for some octahedral facets truncating the cube corners Moore, 1985); to more mixed-habit cubo-octahedral diamonds (Welbourn et al., 1989). The two gem cubes were kept as reference material. Because of the similarity of the CL patterns, it was assumed that all the remaining cubes grew in the same way. Accordingly, the other nine specimens, all  $\sim 2$  mm in size, were individually crushed and one fragment from the outermost part of each selected for FTIR,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and N measurements. The results are reported in Table 2. Nitrogen aggregation is constant, being pure Type IaA (i.e., zero Type IaB).  $\delta^{13}\text{C}$ -values vary from  $-6.63\text{‰}$  to  $-5.33\text{‰}$ ,  $\delta^{15}\text{N}$ -values from  $-5.5\text{‰}$  to  $-1.0\text{‰}$ , and nitrogen contents measured by combustion (914 to 1168 ppm) agree well with the results obtained by FTIR (937 to 1251 ppm) (see Table 2). Also the present  $\delta^{13}\text{C}$ -values and N-contents agree well with previous gem cube diamond analyses from Orapa (Deines et al., 1993). However, the aggregation state data differ from those reported by Deines et al., (1993) as some diamonds had up to 36% of nitrogen in the B aggregation. This discrepancy could be the result of the fact that they performed FTIR analyses through the core of the diamond, whereas we analyzed chips from the outermost part of the crystal.

#### 5. DISCUSSION

Chemical sector zoning consists of the development of distinct compositions behind the crystallographically distinct faces of a growing crystal (Hollister, 1970). Such chemical variations have been recorded for many natural and synthetic minerals (Northrup and Reeder, 1994; Henry et al., 1999) and have been extended to include the fractionation of light stable isotopes, such as carbon and oxygen isotopes in carbonates (Dickson, 1991, 1996), or oxygen isotopes in quartz (Onasch and Venemann, 1995). The dependence of N-content with growth sector in synthetic diamonds is also widely recognized (Strong and Chrenko, 1971; Boyd et al., 1988; Burns et al., 1990) (Table 3). In the most detailed study by Burns et al., (1990) on synthetic diamonds grown from metal alloys, they showed that nitrogen content was sector-dependent, with the highest value in the (111) planes ( $\sim 100$  ppm), and the least in the (110) growth sectors ( $\sim 1$  ppm). The fractionation of N-isotopes was also clearly demonstrated in large synthetic diamonds (Boyd et al., 1988; Table 3), with cubic sectors enriched by  $\sim 40\text{‰}$ , but also lower in nitrogen relative to octahedral growth sectors. According to Northrup and Reeder (1994), chemical or isotopic growth sector zoning is likely to occur in rapidly growing crystals, reflecting the different geometries of the protosites on every nonequivalent growth surface.

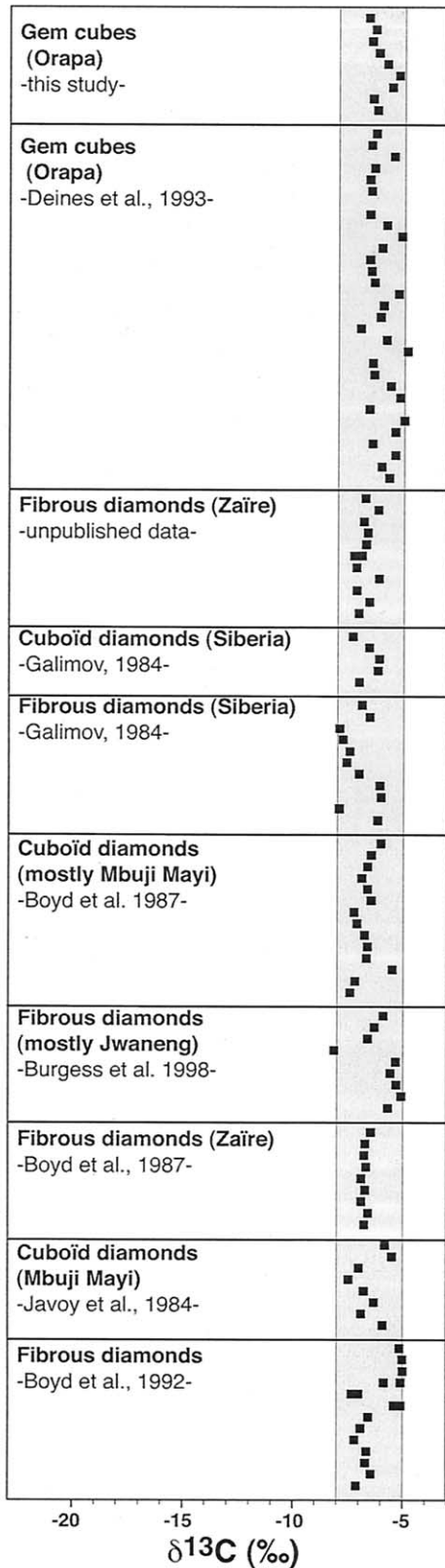


Fig. 2. Comparison of  $\delta^{13}\text{C}$ -values of gem cubes (only data from Orapa are available) and fibrous/coated diamonds from worldwide localities. Note that gem cubes have  $\delta^{13}\text{C}$ -values typically between  $-7$  and  $-5\%$ .

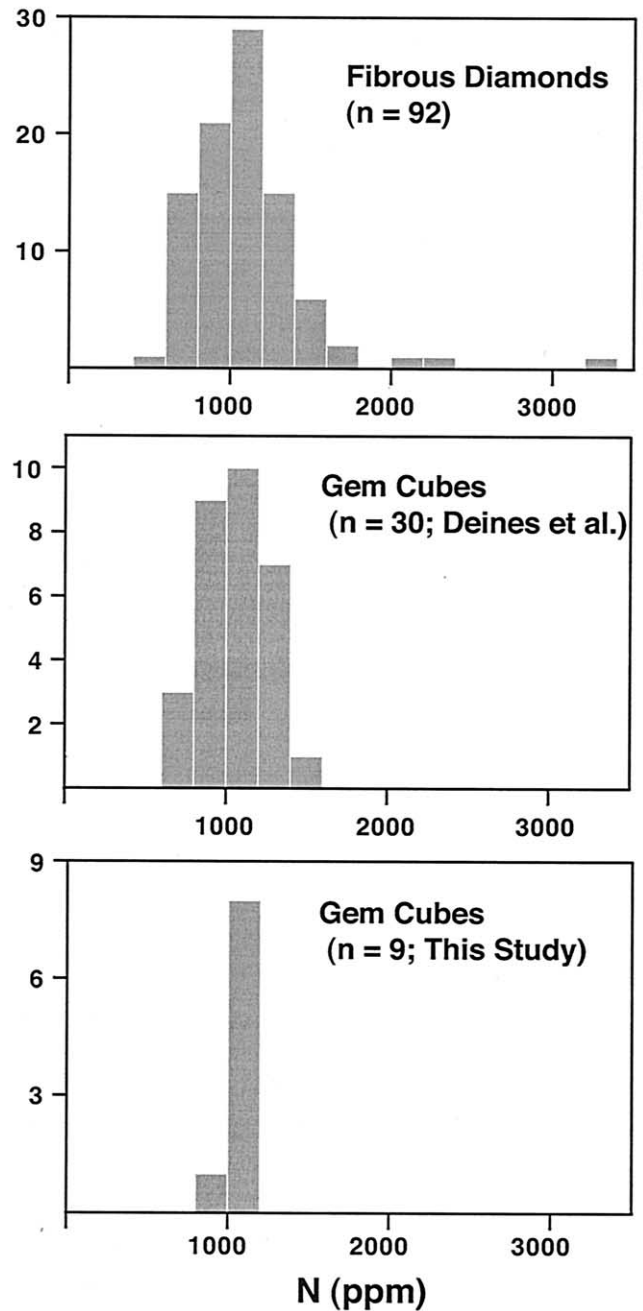


Fig. 3. N-contents of gem cubes, Orapa (cubic growth zones) and worldwide fibrous/coated diamonds (octahedral growth zones).

Boyd et al., (1988) suggested that the sector variations in  $\delta^{15}\text{N}$ -N seen in their single mixed crystal habit synthetic diamond might similarly occur between the core and coat of natural diamond. With this type of natural diamond, there is no synchronicity between the core and coat as these parts represent two distinct growth periods. Furthermore, it is well established that both core and coat of coated stones are of octahedral growth (Orlov et al., 1982; Moore, 1985; Boyd et al., 1994). Thus kinetic fractionation of N-isotopes appears to be confined only to the growth sectors in synthetic diamonds.

With the present study, we have shown that the  $\delta^{15}\text{N}$ -values

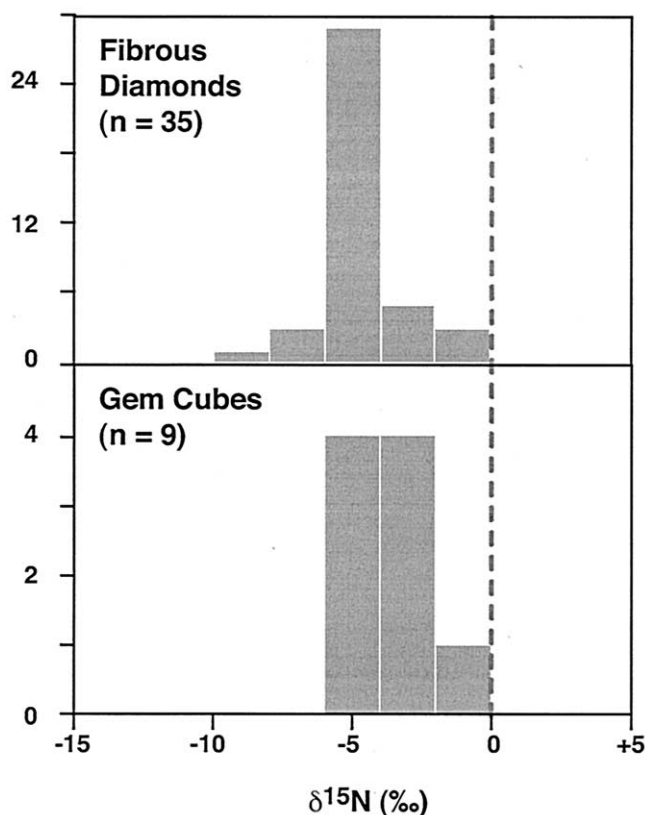


Fig. 4.  $\delta^{15}\text{N}$ -values of gem cubes, Orapa (cubic growth zones) and worldwide fibrous diamonds (octahedral growth zones).

between the two synchronous growth sectors are identical within experimental error. Additional evidence for minimal kinetic fractionation of nitrogen isotopes comes from the fibrous/coated diamonds and their relationship to the gem cubes.

The range of  $\delta^{13}\text{C}$ -values for peridotitic diamonds is generally between  $-9$  and  $-1\%$ , whereas eclogitic diamonds cover an even larger range from  $-35$  to  $+3\%$  (Sobolev et al., 1979; Galimov, 1991; Deines et al., 1993). As illustrated by Figure 2, gem cube diamonds cover a very narrow range of  $\delta^{13}\text{C}$ -values of  $2\%$  from  $-7\%$  to  $-5\%$  (Deines et al., 1993; this study). Figure 2 also shows a restricted range of  $3\%$ , from  $-8\%$  to  $-5\%$ , (Boyd et al., 1994) for fibrous/coated diamonds from worldwide localities. These very narrow ranges of  $\delta^{13}\text{C}$ -values are unlikely to be a coincidence. Additionally, while 80% of peridotitic and eclogitic diamonds have N-contents lower than 1000 ppm (Deines et al., 1993), Figure 3 clearly shows that fibrous/coated diamonds from worldwide localities and gem cubes from Orapa are characterized by high N-contents of  $\sim 1000$  ppm and constant nitrogen aggregation states at 100% Type IaA. Nitrogen isotope data, shown in Figure 4, further emphasizes the genetic similarities between fibrous/coated and those specific gem cube diamonds (i.e., it is probably not the case for all cuboids). It might be expected, therefore, that kimberlite-related fluids like those identified with coated diamonds will be found in the gemcubes from Orapa and potentially, in some cube-shaped diamonds from other localities. The different shapes exhibited by these two types of diamonds are most likely the result of crystallization under a higher driving-

force for fibrous/coated diamonds than for gem cubes (Sunagawa, 1990). As fibrous/coated diamonds are octahedral-facet growth whereas gem cube growth is primarily in the cube direction, the similarity of their  $\delta^{15}\text{N}$ -values (see Fig. 4) further indicates the absence of kinetic fractionation on N-isotopes in natural diamonds.

Therefore in two different cases, no difference in  $\delta^{15}\text{N}$  exists between the cube and octahedral growth zones of natural diamonds (Table 1; Fig. 4). This result is also similar to a recent study on a diamond from the Mir kimberlite (Siberia) by Bulanova et al., (2002) who found no  $\delta^{15}\text{N}$  variation between cube and octahedral growth sectors in a diamond of mixed habit growth. The present conclusion is further supported by some additional observations. In their preliminary study, Boyd and Pillinger (1994) showed that natural octahedral-shaped diamonds have a large range of  $\delta^{15}\text{N}$ -values (about  $\approx 18\%$ ), yet a relatively restricted  $\delta^{13}\text{C}$  range of  $\approx 4\%$ . The authors argued that this relationship "is probably due to the more complicated conditions of growth, [...] isotopic fractionation (of nitrogen being) favored during slow growth." For peridotitic diamonds, the range of  $\delta^{15}\text{N}$ -values is also very large,  $\sim 45\%$ , for an associated  $\delta^{13}\text{C}$ -range of less than  $8\%$  (Cartigny et al., 1997). If the  $\delta^{15}\text{N}$  variability was related to more complicated conditions of growth, we might also expect eclogitic diamonds (which are known to cover a larger range of  $\delta^{13}\text{C}$ -values, from  $-35$  up to  $+3\%$ ; Sobolev et al., 1979; Galimov, 1991) to possess at least the same range of  $\delta^{15}\text{N}$ -values. On the contrary, observations made on eclogitic diamonds from the Jwaneng kimberlite (Botswana) revealed a rather small range of  $\delta^{15}\text{N}$ -values, of  $\approx 9\%$  associated with a  $\delta^{13}\text{C}$ -range of  $\approx 20\%$  (Cartigny et al., 1998). Therefore, the large range of  $\delta^{15}\text{N}$ -values is unlikely to be the result of more complicated growth conditions.

## 6. CONCLUSIONS

This study, on a mixed cubic and octahedral growth sector diamond from Wellington (SE Australia), has shown that the strong kinetic fractionation of N-isotopes of  $\sim 40\%$  between cubic and octahedral growth sectors seen in synthetic diamond is not present during the growth of natural diamonds, variation in  $\delta^{15}\text{N}$ -values being representative of the growth medium. A similar absence of kinetic fractionation of  $\delta^{15}\text{N}$  isotopes is also noted when fibrous/coated diamonds are compared with gem cubes.

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