Short communication

Microscale variations of δ^{13}C and N content within a natural diamond with mixed-habit growth

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Abstract

The variations of carbon isotope composition and nitrogen content in a natural diamond with mixed octahedral and cuboid habit have been studied with the ion microprobe technique (SIMS). The systematic variations of δ^{13}C and Nppm in continuous growth zones belonging to both octahedral and cubic sectors have been measured. In general the octahedral growth sector in comparison with the cuboid one is richer in nitrogen by 90–300 ppm and has a slightly heavier δ^{13}C by 0.3–1.5‰. These data show that simultaneous mixed growth of cuboid and octahedral sectors in natural diamond entails little fractionation of carbon isotopes. The observed variations are most likely due to the different nature and kinetics of growth of natural cuboid and octahedral diamonds.
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1. Introduction

Natural diamonds from kimberlites are known to occur worldwide with a varying set of chemical and physical properties and growth morphologies. These variations reflect a wide range of conditions of diamond formation in the mantle and of chemical composition of the C–O–H–N-bearing fluids/melts from which the diamonds grow. Diamonds show a wide range of carbon isotope composition ($+3‰$ to $-35‰$ in δ^{13}C), and these variations have been attributed to both fractionation processes during diamond crystallization in the mantle and the heterogeneity of the C–O–H–N source that possibly includes subducted crustal material (e.g., Deines, 1980; Galimov, 1991). The main impurity in natural diamonds is nitrogen, and large variations in N content and aggregation state are used to classify diamonds into several types (e.g. Harris, 1987).

The typical growth morphologies of diamonds are the octahedron and the cuboid (typically a fibrous crystal usually with overall cubic habit). The mechanisms of growth of these two varieties are different in their kinetics (Moore and Lang, 1972; Sunagawa, 1990), and a change in growth conditions may result in a change of the growth mechanisms and reshaping of crystals. Diamonds with signs of different growth mechanisms are found in many kimberlite pipes worldwide, but the extent to which carbon isotope composition and nitrogen content change

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with growth mechanisms is very variable. Swart et al. (1983) and Boyd et al. (1987) showed considerable variations in δ^{13}C and N abundance between laser-cut individual parts of single crystals of so-called "coated" diamonds (crystals with octahedral core and fibrous coat). It was also shown that the content and isotopic composition of nitrogen within a synthetic diamond may be controlled by its growth kinetics (Boyd et al., 1988). However, these studies used combustion techniques on laser cut segments of diamonds showing different growth zones and sectors, and in the case of the "coated" stones it was clear that the octahedral and fibrous cuboid parts had grown at different times and therefore from possibly different sources (with different C−O−H−N composition). The aim of the present study was to examine a natural diamond with evidence of simultaneously growing octahedral and cuboid sectors. The use of the ion microprobe provides much better monitoring of isotopic composition and nitrogen concentration within detailed growth structure (Harte et al., 1999; Fitzsimons et al., 1999; Hauri et al., 2002; Bulanova et al., 2002). In this study the high spatial resolution capacity of the ion microprobe was used to analyze material from each type of sector at a number of definite growth stages.

2. Methods

The measurements of chemical–physical properties made on diamonds themselves have been predominantly for carbon isotope composition, nitrogen content and aggregation state. Until recently, the C isotope composition of diamonds has been measured by gas source mass spectrometry with combustion of the samples. Nitrogen content may also be determined by combustion techniques, but more usually both N content and aggregation state are determined by FTIR spectroscopy. In this study we take advantage of relatively new approaches using an ion microprobe (SIMS). This technique allows quantitative investigation of local variations in C isotopic composition and N content within individual diamonds without their destruction. Nitrogen abundance and C isotope composition in the sample were measured relative to synthetic diamond standards using a CAMECA ims-4f ion microprobe, with a Charles Evans and Associates control system for magnetic peak switching, at the NERC Facility in the School of Geosciences, University of Edinburgh. The general procedure of measurements and standards used are given in detail in Harte et al. (1999) and Fitzsimons et al. (1999, 2000). The present measurements involved using a high-energy offset of 300 v for carbon but not for nitrogen. In all cases the primary beam diameter was $20-30$ μm. In the case of nitrogen a field aperture was used to restrict the collected beam diameter to 8 μm. The accuracy of measurements for δ^{13}C is presented in Table 1, and the reproducibility of standard measurements was always within 1.0 ‰. Calculated errors for N analyses are small ($< 5\%$).

The position of ion microprobe analysis points was determined on black and white cathodoluminescence (CL) images collected on a Phillips XL30CP SEM in the ion microprobe laboratories at Edinburgh Univer-

Table 1
C isotope and N content data for sector-growth diamond

| Cuboid					Octahedron					$\Delta\delta^{13}$C	ΔN wt. ppm	
CL zone	δ^{13}C		N wt. ppm		CL zone	δ^{13}C		N wt. ppm				
	‰PDB	1s (±)	SIMS	FTIR		‰PDB	1s (±)	SIMS	FTIR		SIMS	FTIR
1	− 4.1	0.35	1589	1510	1	− 2.8	0.15	1859	1803	1.3	270	293
2	− 4.7	0.44	1611	1525	2	− 3.3	0.28	1780	1769	1.4	169	244
						− 3.8	0.32	1819		0.9	208	
3	− 3.7	0.29	1631	n/a	3	− 3.4	0.28	1935	n/a	0.3	304	n/d
4	− 5.5	0.42	1718	n/a	4	− 4	0.3	1997	n/a	1.5	279	n/d
5	− 4.8	0.38	1662	n/a	5	− 3.7	0.25	1898	n/a	1.1	236	n/d
6	− 4.5	0.29	1605	1590	6	− 3.4	0.21	1695	1704	1.2	90	114
7	− 3.4	0.34	1570	n/a	7	− 3	0.25	1769	n/a	1.4	199	n/d
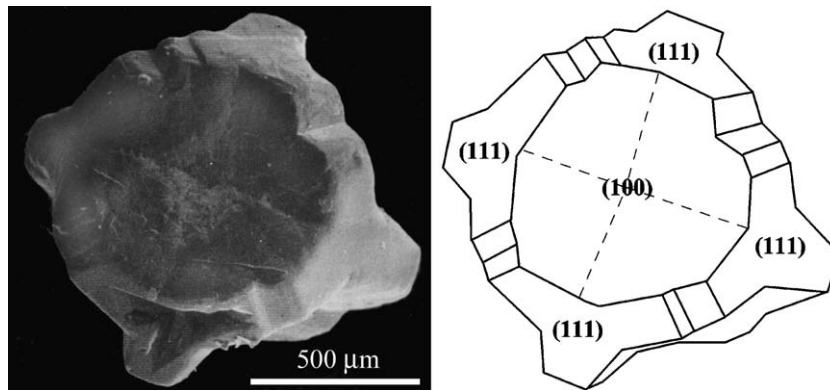
Fig. 1. SEM image of a mixed-habit diamond and schematic representation of its crystallography.

sity. FTIR spectroscopy at the Institute of Mineralogy and Petrography, Novosibirsk, was also used to monitor N content and aggregation state.

3. Morphology and growth structure

A diamond in which cuboid and octahedral faces are present together (Fig. 1) was selected from a collection from the Udachnaya kimberlite pipe (Yakutia). The octahedral faces of the diamond are flat and smooth, and have trigonally symmetric trilete-shape. The cuboid surfaces of the crystal are hollowed and have a frosted appearance. Tiny tetragonal etch-pits decorate the bottom and diagonals of cuboid surfaces. The diamond is a representative example of mixed-habit growth in which crystallization proceeded simultaneously on octahedral plane faces and on cuboid hummocky (not single face) surfaces (Suzuki and Lang, 1976; Welbourn et al., 1989).

The sample was polished parallel to {110}, and examined and photographed in cathodoluminescence (CL) to show the complex growth history of both cuboid and octahedral sectors (Fig. 2). The crystal clearly exhibits two main sequential growth phases: core and outer regions. The core region shows much more varied intensity of luminescence and has a typical "central cross" structure (e.g. Lang, 1974; Bulanova et al., 2002). This structure reflects the case of mixed-habit growth in which a gradual diminution of cuboid surfaces occur leading up to formation of a regular octahedron. The outer region of the diamond

also shows mixed-habit growth but with quite constant development of cuboid surfaces and octahedral faces throughout the whole region. The external surfaces tend to follow underlying growth horizons which are weakly revealed by CL; thus the octahedral sectors reveal growth horizons with straight linear boundaries, whereas cuboid sectors have curved growth horizons. Although the contrasts in CL are small it is possible to
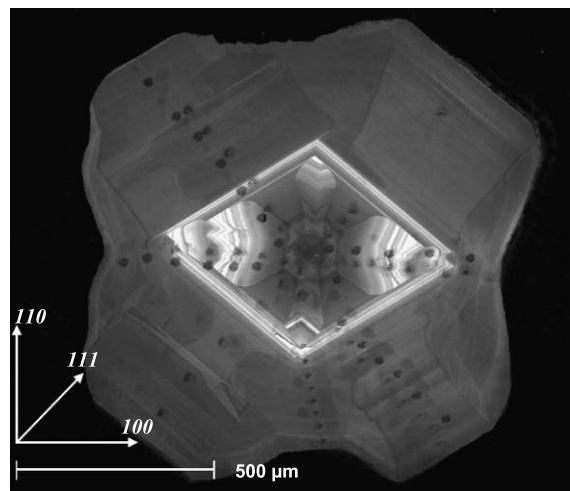

Fig. 2. Cathodoluminescence image of a polished plate of the mixed-habit diamond of Fig. 1. The polished face is parallel to (110) and shows the internal sector growth structure. Mixed-habit growth is seen both in the central growth zones (with higher luminescence and "central cross" structure) and in the outer growth zones. Cuboid sectors have curved growth structure and octahedral sectors have flat growth horizon boundaries and faces. Dark roundish spots are ion microprobe pits.

trace individual growth horizons from octahedral growth sectors into cuboid ones. This is very important in enabling the analysis of the same growth horizons in both octahedral and cuboid sectors.

4. C isotope composition and N content in relation to growth structure

Some preliminary measurements across the whole diamond were made (Fig. 2), followed by two detailed traverses across the octahedral and cuboid sectors in the outer region (Fig. 3). These two detailed traverses were used to compare values of $\delta^{13}C$ and Nppm in simultaneous growth horizons belonging to the two growth sectors. Since the growth structure revealed by CL is not visible during SIMS analysis, a close spacing of points was made in the traverses in order to be sure of analyzing the growth horizons formed at the same time in the two different sectors. The complete data set is presented in the Table 1 and Fig. 3.

The separate analysis of cuboid and octahedral sectors has shown some differences both in C isotope composition and N content. The differences of $\delta^{13}C$ in the same growth horizons between adjacent cuboid and octahedral sectors fall within the range from

0.3‰ to 1.5‰. Although the lowest values are within the error limits of the method, the observed differences are quite systematic and the octahedral sectors are always slightly enriched in ^{13}C in comparison with cuboid ones (see Fig. 3 and Table 1). Similarly the N content is systematically higher in octahedral sectors than in cuboid ones with differences in adjacent sectors of 90–300 ppm (approximately 5–20% of the total concentration). The differences between octahedral and cuboid growth sectors in N content agree with those found using FTIR spectroscopy (see Table 1). The nitrogen aggregation state in both sectors corresponds to diamond spectral type IaA (nitrogen pair). No additional defects have been shown by the FTIR spectroscopy.

5. Discussion

Variations of nitrogen concentration between different growth sectors have been defined in synthetic diamonds of mixed habit: cubic sectors are always relatively depleted in nitrogen (Boyd et al., 1988; Burns et al., 1990). Boyd et al. (1988) also demonstrated a sector-related variation in N isotopes in synthetic diamond (~ 40‰ of ^{15}N more in octahe-
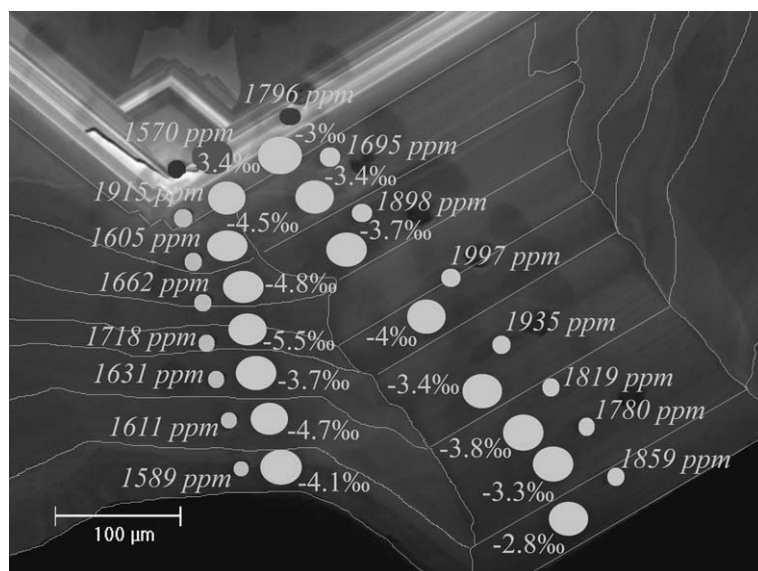

Fig. 3. Enhanced CL image of a portion of the diamond of Fig. 2 showing continuous zones of simultaneous growth belonging to cuboid and octahedral growth sectors. The measurement points and relevant data are also shown for both $\delta^{13}C$‰ and Nppm.

dral sectors), but with only slight differences in $^{13}C/^{12}C$ ratio. In natural mixed-habit diamonds Cartigny et al. (2003) reported the absence of such kinetic fractionation of N and C isotopes between cuboid and octahedral sectors. However, in the Boyd et al. (1988) and Cartigny et al. (2003) studies the samples were obtained by laser cutting and were therefore usually composites of several growth horizons. Such bulk sampling means that information on individual growth horizons in the diamonds are lost or at least blurred.

The use of ion microprobe analysis with a primary beam of 20–30 μm has now confirmed that simultaneous growth of cuboid and octahedron may occur in natural diamond with little variation in $\delta^{13}C$ (Figs. 3 and 4). Although small, the systematic differences between cubic and octahedral sectors found in this study are larger than those found by Bulanova et al. (2002) in a sector-growth diamond from Mir kimberlite pipe (Yakutia). The high spatial resolution of each analysis point, coupled with the close spacing of analysis points in our study, shows the systematic nature of the differences between the sectors, and gives confidence that the small differences between the sectors are real and not merely within the measurement error. The differences in Nppm (with higher values in octahedral sectors) found here have the same

tendency as was found in synthetic diamonds (Boyd et al., 1988). However the differences in Nppm values in our natural diamond are much smaller than those of the synthetic stone studied by Boyd et al. (1988).

At high temperatures the C isotope equilibrium fractionation between diamond and many co-existing solid or fluid C-bearing phases is small and of the order of 1‰ (Deines, 1980). Larger differences of 3–4‰ are expected for equilibrium fractionation between diamond and CO_2 or carbonate (Bottinga, 1969). Although these fractionations are of limited extent, it has been suggested that the wide range of $\delta^{13}C$ found in natural diamonds from $-35‰$ to $+3‰$ may be produced in a process of Rayleigh fractionation between growing diamonds and their carbon-source phase (Javoy et al., 1986; Galimov, 1991). The question arises of whether kinetic growth factors linked to different growth conditions (Sunagawa, 1990; see also Fig. 4) may also play a role in enhancing equilibrium fractionation effects.

Some investigators (e.g. Boyd et al., 1994; Cartigny et al., 2001) have suggested that carbon isotope fractionation due to the different nature and kinetics of the surface reactions leading to growth of natural cuboid and octahedral diamonds may play a significant part in generating $\delta^{13}C$ variation of diamonds. It was proposed that for a fluid phase supersaturated with carbon, such as would lead to rapid cuboid (rough) growth (Sunagawa, 1990; and Fig. 4), either ^{12}C- or ^{13}C-bearing species would react immediately to produce new diamond. In this case, the isotopic composition of the diamond would be controlled only by the isotopic composition of carbon arriving at the growing surface (Boyd et al., 1988), and thus for rapid cuboid growth it was suggested that there will be no difference in isotopic composition between fluid and diamond. On the other hand in steady and relatively slow octahedral growth the isotope fractionation theoretically predicted for diamond-fluid equilibrium will apply.

The difference of $\delta^{13}C$ between simultaneously grown cuboid and octahedral sectors found in this study is about 1‰ on average. This difference is similar to that predicted for equilibrium fractionation between diamond and many possible carbon-bearing phases and sources at mantle conditions. In the present case there is no evidence of a marked difference in growth rates between the different growth
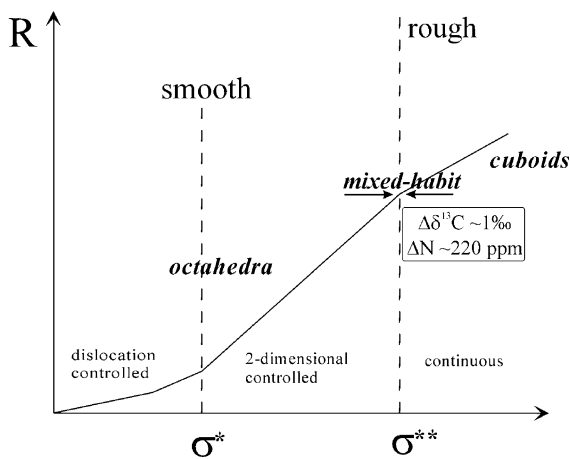

Fig. 4. Schematic drawing showing change of morphology of the diamonds as a function of growth rate (R) and supersaturation (σ) after Sunagawa (1990). The mixed-habit growth occurs on the boundary of different growth fields. The average fractionation in carbon isotopes and nitrogen content for the analysed sample are given.

sectors, and the isotopic composition and nature of the initial fluid reservoir are unknown. Nonetheless, the observed differences between octahedral and cuboid sectors of around 1‰ are very reasonable for a case where the cuboid growth inherits the isotope composition of the source medium, and the octahedral growth shows an equilibrium fractionation of 1‰. If the diamond-precipitating source had been CO_2 or carbonates then bigger differences (3–4‰) might have occurred between the sectors. Obviously, the different surface properties of the cuboid and octahedral diamond zones are apparent in the uptake of nitrogen (Figs. 3 and 4), although the precise cause of this sectorial fractionation is unknown.

6. Conclusions

Using ion microprobe techniques, we have measured in detail systematic variations both of C isotope composition and of N abundance in simultaneous growth horizons belonging to cubic and octahedral sectors in a natural mixed-habit diamond. It has been shown that simultaneous mixed growth of cuboid and octahedral sectors in natural diamond entails little fractionation of $^{13}C/^{12}C$ ratio, but there are significant differences in Nppm. The data show that the kinetic fractionation of carbon isotopes between cuboid and octahedral crystal forms of natural diamonds does not significantly enhance the equilibrium fractionation between diamond and its fluid sources. Thus it appears unlikely that kinetic fractionation is an important factor in widening the spread of $\delta^{13}C$ values in natural mantle diamonds. However, in the case of nitrogen abundance the growth sectors show significantly different fractionation factors. The further study of nitrogen isotopes in natural diamonds with mixed-habit growth is needed for understanding of this effect.

Acknowledgements

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