

# Microanalysis of $\delta^{13}\text{C}$ , $\delta^{15}\text{N}$ , and N abundances in diamonds by secondary ion mass spectrometry

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Received 12 January 2001; accepted 22 October 2001

## Abstract

This paper describes in situ analysis methods for determination of nitrogen abundance,  $\delta^{13}\text{C}$ , and  $\delta^{15}\text{N}$  in diamond by secondary ion mass spectrometry (SIMS). The simple chemical composition of diamond results in the absence of matrix effects on instrumental mass fractionation (IMF) of carbon and nitrogen. Carbon isotopes are analyzed using extreme energy filtering (EEF), while nitrogen abundance and isotope ratios are measured at high mass resolution (HMR) without energy filtering. Because the variable surface properties of different sample mounts can result in variable measurements of IMF, especially using HMR techniques, precise application of IMF values derived from standard measurements requires the co-location of standards and samples on the same probe mount. With care given to instrument alignment and standardization,  $\delta^{13}\text{C}$  in diamond can be determined to  $\pm 0.3\text{‰}$  ( $1\sigma$ ) total uncertainty (precision + accuracy). Reproducibility of  $\delta^{15}\text{N}$  measurements can be as good as  $\pm 1\text{‰}$  ( $1\sigma$ ) depending on N abundance, but standard heterogeneity currently limits the accuracy of  $\delta^{15}\text{N}$  data to  $\pm 3\text{‰}$  ( $1\sigma$ ). Nitrogen abundance measurements, obtained during  $\delta^{15}\text{N}$  measurements, have an accuracy of  $\pm 10\%$  and a detection limit of 0.5 ppm. The 25- $\mu\text{m}$  spatial resolution of this technique permits isotopic measurements at the scale of diamond growth zoning observed by cathodoluminescence (CL) imaging. Measurements on a central polished section of a Siberian diamond show variations in  $\delta^{13}\text{C}$  ( $-8.8\text{‰}$  to  $+1.7\text{‰}$ ),  $\delta^{15}\text{N}$  ( $-17.1\text{‰}$  to  $+5.3\text{‰}$ ) and N abundance (14–1390 ppm) associated with CL-imaged growth zones, which span a significant fraction of the total isotopic variability observed in bulk analyses of individual diamonds. In situ  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and N abundance measurements, in conjunction with CL imaging and FTIR N aggregation measurements, hold promise for determining the extent of isotopic variability which can be attributed to diamond formation processes, and the significance of isotopic variability in diamonds to large-scale mantle heterogeneity and the origin of terrestrial volatiles. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Diamond; Mantle; Carbon; Nitrogen; Stable isotopes; Ion probe

## 1. Introduction

By the nature of their exceedingly simple bulk composition, few chemical tracers exist to study the

origins, ages, and growth environments of natural diamonds. The variable carbon isotopic composition of diamond has been of interest since the first measurements by Craig (1953), but in the absence of other supporting chemical or isotopic data, a large number of hypotheses have persisted to explain the range of  $\delta^{13}\text{C}$  values among natural diamonds. Mineral inclusions

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trapped in diamond have yielded important conclusions on the antiquity of mantle-derived diamonds and their cratonic environs (e.g., Harris and Gurney, 1979; Richardson et al., 1984; Richardson, 1986; Pearson and Shirey, 1999), but because carbon is highly incompatible in silicate minerals, studies of inclusions provide only indirect information about the origin and growth history of the diamonds themselves. Studies of fluid inclusions in diamonds provide a useful record of the environments and conditions of the very rapid diamond growth required to trap fluids (e.g., Guthrie et al., 1991; Navon et al., 1988; Navon, 1991), but say little about the inclusion-free diamonds that make up the bulk of natural stones. For these reasons, complete chemical studies of natural diamonds must make use not only of inclusions but also the host diamonds themselves, and so techniques to study diamond must continue to improve and evolve in parallel with methods of inclusion-based studies.

The isotopic composition of carbon in diamonds has been investigated for nearly 50 years (Craig, 1953; Wickman, 1956; Vinogradov et al., 1966; Koval'skii and Cherskii, 1972; Galimov et al., 1978; Galimov, 1984, 1991; Smirnov et al., 1979; Milledge et al., 1983; Ozima et al., 1983; Deines, 1980; Deines et al., 1984, 1987, 1989, 1991, 1993, 1997), with measurements of over 3000 individual diamonds revealing a range of  $\delta^{13}\text{C}$  values from +3‰ to –35‰, but with a distribution strongly peaked at –5‰. The preponderance of diamonds with  $\delta^{13}\text{C}$  values near –5‰ has been used as evidence for an identical value for the Earth's upper mantle (Craig, 1953; Deines, 1980; Galimov et al., 1978; Boyd et al., 1994), yet constraints on the  $\delta^{13}\text{C}$  value of the bulk Earth contain considerable uncertainty (Javoy et al., 1986). Significant carbon isotope variations exist within single diamonds, as determined by bulk analysis of millimeter-sized diamond fragments (Swart et al., 1983; Boyd et al., 1987, 1988, 1992; Boyd and Pillinger, 1994), but this internal variability only occasionally exceeds 3‰ in  $\delta^{13}\text{C}$ .

Of the wide variety of trace elemental impurities found within the diamond lattice, only nitrogen is widespread and common (Kaiser and Bond, 1959; Melton et al., 1972; Melton and Giardini, 1974; Harris, 1987). As a result, most chemical studies of diamond have concentrated on the abundance of nitrogen and the isotopic composition of both carbon and nitrogen, either separately or together in the same

diamonds (Javoy et al., 1984; Boyd et al., 1987, 1988, 1992; Deines et al., 1987, 1989, 1991, 1993, 1997; Van Heerden et al., 1995; Cartigny et al., 1998a,b). Nitrogen isotopes have been measured in over 700 diamonds, with  $\delta^{15}\text{N}$  values ranging from +13‰ to –23‰. The distribution of  $\delta^{15}\text{N}$  values is rather broadly peaked around a value of –6‰, with about 90% of diamonds between 0‰ and –12‰. Variability in  $\delta^{15}\text{N}$  has been reported within single diamonds, with bulk analyses of fragments showing a range of 10–15‰ in natural diamonds (Boyd et al., 1987, 1992; Boyd and Pillinger, 1994), and an exceptional range of 45‰ between growth sectors of a synthetic diamond grown at high pressure and temperature (Boyd et al., 1988). Most of the information on N isotope geochemistry in the mantle come from the above data, and the variability results in significant uncertainties around the estimated  $\delta^{15}\text{N}$  values of the upper mantle and bulk silicate Earth (Javoy et al., 1986; Cartigny et al., 1998a,b).

The variability of carbon and nitrogen isotopes between and within diamonds has been attributed to large-scale mantle heterogeneity arising from three possible mechanisms; mixing between primordial variations remaining since accretion (Javoy et al., 1986; Deines et al., 1993), recycling of biogenic material during plate subduction (Chaussidon et al., 1987, 1989; Kirkley et al., 1991); or unidentified isotopic fractionation processes during fluid migration in the mantle (Galimov, 1991; Boyd and Pillinger, 1994; Cartigny et al., 1998a,b). However, few studies on whole diamonds have considered in depth the possibility of C and N isotope fractionation during diamond growth, which can occur at equilibrium under variable redox conditions and isotopic fractionation factors (Deines, 1980; Deines et al., 1987), or as a result of kinetic effects at variable growth rates (Boyd et al., 1994). Endemic to all of the studies cited above is the large scale of sampling of diamond material (millimeter-sized fragments) relative to the micron-scale growth zoning revealed by cathodoluminescence (CL) and infrared (IR) studies of natural diamonds (Boyd et al., 1987, 1988; Bulanova, 1995; Navon et al., 1988; Otter et al., 1991; Guthrie et al., 1991; Griffin et al., 1995; Pearson et al., 1999). Given the presence of small-scale variability of N concentrations, bulk analyses of even millimeter-sized fragments will sample nitrogen and carbon from different volumes of

material, and the resulting data will represent mixtures of material from distinct diamond growth zones.

In situ analysis by secondary ion mass spectrometry (SIMS) using an ion microprobe is capable of resolving chemical and isotopic variations on the scale of microns (Shimizu et al., 1978; Chaussidon et al., 1987; Valley et al., 1997). Spatially resolved  $\delta^{13}\text{C}$  SIMS measurements in diamond were first made by Harte and Otter (1992) on polished diamond plates, but no obvious relationship between  $\delta^{13}\text{C}$  and CL-imaged growth zoning in the diamond examined in this study was evident. More recently, SIMS measurements of N abundances have been made in conjunction with  $\delta^{13}\text{C}$ , and these studies have revealed clear relationships between growth zonation, CL color, and nitrogen abundance within diamonds (Fitzsimons et al., 1999; Harte et al., 1999; Hutchison et al., 1999). These SIMS studies have also revealed significant  $\delta^{13}\text{C}$  variability associated with identifiable growth zones within diamonds. Fitzsimons et al. (1999) reported extremes of  $\delta^{13}\text{C}$  from 0‰ to  $-20\%$  between

distinct CL-imaged growth zones in a diamond from Colorado; Harte et al. (1999) report a variation from  $-1.5\%$  to  $-8.1\%$  in diamonds from Kaapvaal, South Africa; and Hutchison et al. (1999) report  $\delta^{13}\text{C}$  variation from  $-1.3\%$  to  $-10.2\%$  in diamonds from Sao Luiz, Brazil. Although there appears to be no simple relationship between CL color and  $\delta^{13}\text{C}$ , all these studies have revealed variations in  $\delta^{13}\text{C}$  whose extremes equal or exceed the variations between diamonds from these locales as measured by bulk carbon isotope analyses. This observation makes clear the advantages of the spatial selectivity offered by SIMS in the study of diamond, and shows that internal variations in CL, N abundance and C isotopes are a ubiquitous feature of diamonds from many locales (Fitzsimons et al., 1999; Harte et al., 1999; Hutchison et al., 1999; Kinny et al., 1999).

Despite these detailed in situ studies, no simple or consistent relationships have emerged between  $\delta^{13}\text{C}$  and N abundance either within single stones or between stones, and this is true of the bulk data on

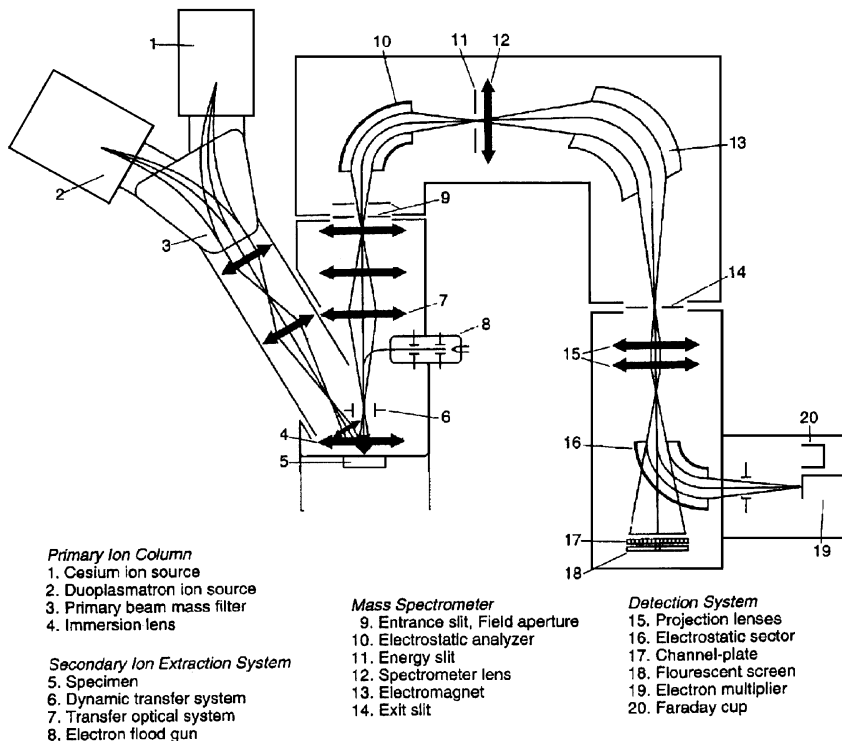


Fig. 1. Schematic layout of the Cameca 6f ion microprobe (from Valley et al., 1997).

whole diamonds as well (cf. Deines et al., 1987, 1989, 1991, 1993, 1997; Cartigny et al., 1998a,b). Variations in N abundance within single diamonds routinely span orders of magnitude, yet a vast majority of the SIMS  $\delta^{13}\text{C}$  data within any single diamond rarely show a variation of more than 3–4‰ (Hauri et al., 1999; Fitzsimons et al., 1999; Harte et al., 1999; Hutchison et al., 1999). It is possible that improved precision on  $\delta^{13}\text{C}$  might reveal relationships with N abundances or N isotopes within this limited variability.

The purpose of this paper is to provide a detailed report of methods for high-precision measurements of  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , and N abundance in diamond using a Cameca 6f ion microprobe (Fig. 1), and to demonstrate the ability of the technique to provide spatially resolved isotopic data on the scale of observed growth zoning in diamonds. Particular attention is paid here to experimental factors which can improve the reproducibility and accuracy of in situ  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  measurements in diamond, which is of prime importance in light of the limited variations (3‰ in  $\delta^{13}\text{C}$ , 10‰ in  $\delta^{15}\text{N}$ ) thus far revealed by most bulk analysis of diamond fragments. An example of isotopic variability in a diamond from the Mir kimberlite (Siberia) will be presented and briefly discussed.

## 2. Instrumental configuration

Carbon isotope ratios were measured using the technique of extreme energy filtering (EEF), first discussed by Hervig et al. (1992) and used extensively for SIMS isotope analysis of oxygen (Valley et al., 1997) and sulfur (Riciputi, 1996; Patterson et al., 1997). A primary beam of  $\text{Cs}^+$  ions with an impact energy of 15 keV was focussed to a spot of 20  $\mu\text{m}$  diameter using Kohler illumination, resulting in a homogeneous beam density and a flat-bottomed sputter crater. The Cameca 6f mass spectrometer is designed as an ion microscope, and the transfer optics were tuned to image a field of view of 75–100  $\mu\text{m}$  in diameter at  $-5$  kV extraction voltage. This tuning results in an ion optical crossover of  $<1800$   $\mu\text{m}$  diameter, permitting full transmission through the 1800- $\mu\text{m}$  contrast aperture and flat-topped peaks at a mass resolving power ( $\Delta M/M$ ) of 300. EEF techniques (Hervig et al., 1992; Riciputi, 1996; Patterson et al., 1997) were used with an extraction voltage offset and energy bandpass set to admit ions with

excess kinetic energies of 300–400 eV. Under these conditions,  $^{12}\text{CH}$  is completely eliminated and does not interfere on  $^{13}\text{C}$ . Secondary ions were counted with an ETP electron multiplier (EM) connected to an ECL-based counting system with 4 ns pulse-pair resolution. Before each analytical session, the efficiency of the EM (relative to the Faraday cup) was adjusted to 90% for  $^{12}\text{C}^-$  ions, which resulted in a routine counting system deadtime of 12 ns, and the background count rate was determined (always  $<6$  counts per minute). Count rates were kept close to  $10^6$  counts per second ( $\pm 10\%$ ) for  $^{12}\text{C}^-$ , and after a 300-s presputter period, the instrument was set to measure 200 cycles counting for 6 s on  $^{13}\text{C}$  and 1 s on  $^{12}\text{C}$ , respectively. Carbon isotope ratios ( $^{13}\text{C}/^{12}\text{C}$ ) were calculated using single linear interpolation and corrected for system deadtime. The standard error of each measurement (consisting of 200 ratios collected over 35 min) was always nearly identical to

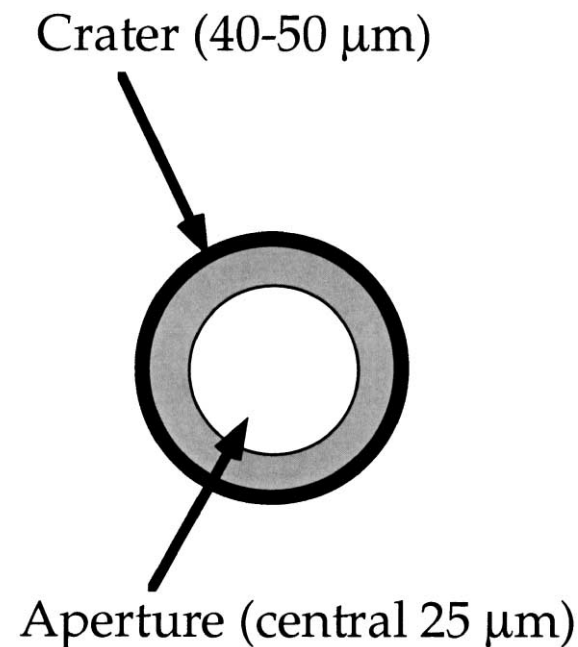


Fig. 2. Schematic outline of the spatial relationships between the diamond sample surface (light gray), sputter crater (dark gray with thick black rim, 40–50  $\mu\text{m}$  diameter), and the portion of the crater open to the mass spectrometer through the field aperture (white circular area 25  $\mu\text{m}$  diameter) during measurements for N abundances and isotope ratios. Use of a small field aperture limits the transmission of ions to only the central part of the flat-bottomed crater, effectively masking ions originating from the sample surface and crater rim (heavy black circle).

that estimated from Poisson statistics (0.22%). The accuracy and reproducibility of the  $\delta^{13}\text{C}$  measurements are described in the section on instrumental mass fractionation (IMF, see below).

Nitrogen abundances and isotopes were measured using a  $\text{Cs}^+$  beam (20–80 nA) and collection of negatively charged CN molecular ions at high mass resolving power with no energy filtering (50 eV bandpass). Nitrogen itself does not readily form stable ions, but an intense  $\text{CN}^-$  signal is formed in the presence of carbon (Zinner et al., 1989). The instru-

ment was tuned to image a field of view of  $150\ \mu\text{m}$  in diameter at  $-5\ \text{kV}$  extraction voltage. The primary beam was defocused to  $40\text{--}50\ \mu\text{m}$  diameter using Kohler illumination, and a field aperture inserted in the secondary ion optics to admit ions from the central  $25\ \mu\text{m}$  of the sputter crater. As a result, the spatial resolution of the technique is  $25\ \mu\text{m}$ , but the center of adjacent craters can usually be no closer than  $40\text{--}50\ \mu\text{m}$ . The insertion of a small field aperture is crucial to the nitrogen analyses, as it effectively prohibits transmission of  $\text{CN}^-$  ions originating from the sample

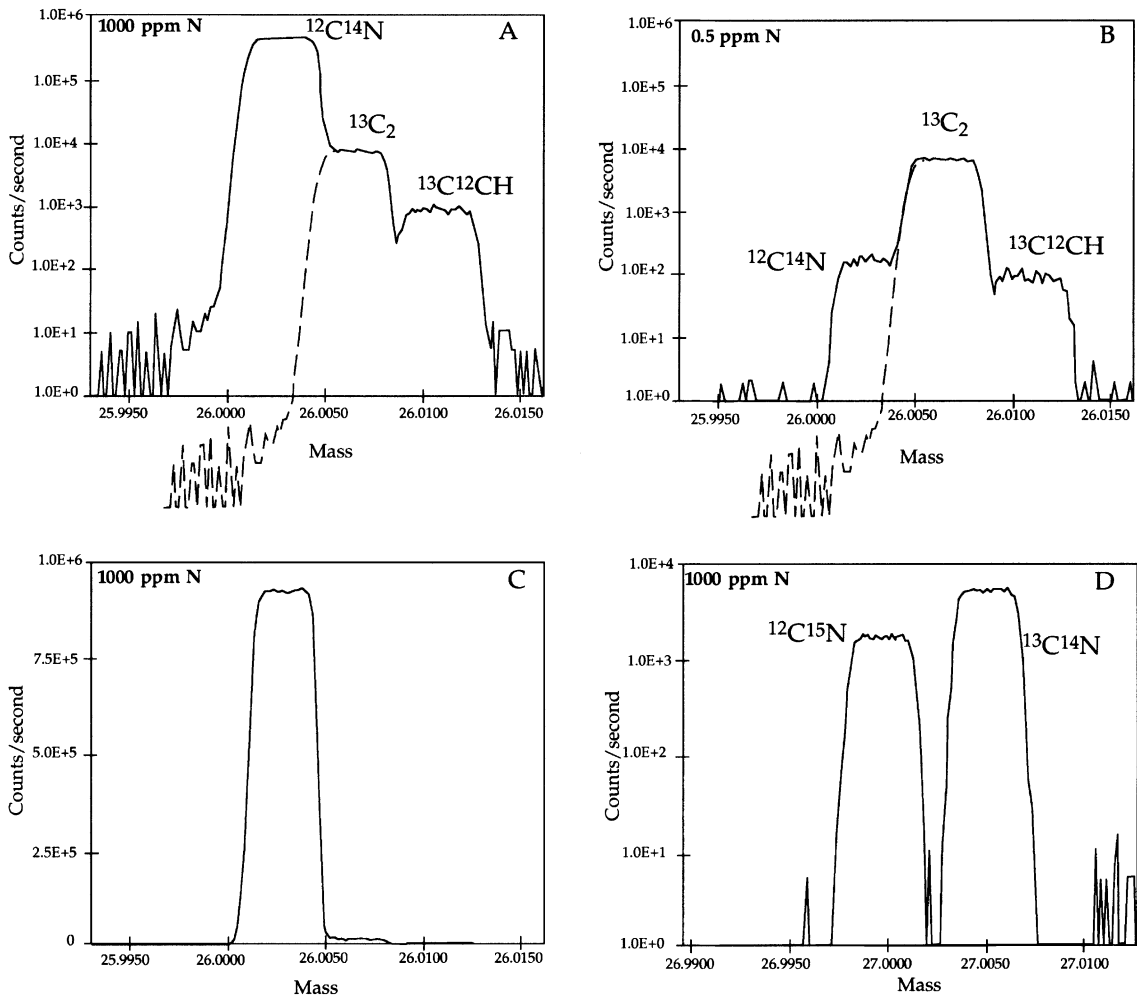


Fig. 3. Mass scans of peaks of interest for N isotope measurements, obtained at mass resolving power of 6500. (A) Separation of  $^{12}\text{C}^{14}\text{N}$  from  $^{13}\text{C}_2$  is obtained with estimated tailing of  $^{13}\text{C}_2$  reduced to near background levels. (B) N detection limit of 0.5 ppm, estimated from analysis of a Type II diamond, is limited by contributions of scattered CN ions from the crater rim. (C) Peak scan on linear scale shows flat-topped peak at  $\text{MRP}=6500$ . (D) Separation of  $^{12}\text{C}^{15}\text{N}$  from  $^{13}\text{C}^{14}\text{N}$ .

surface and the rim of the sputter crater (Fig. 2). The mass spectrometer entrance and exit slits were closed to achieve a mass resolving power ( $M/M$ ) of 6500 while maintaining a high-quality surface image. This mass resolution provides adequate separation of  $^{13}\text{C}_2$  from  $^{12}\text{C}^{14}\text{N}$  while maintaining good transmission and flat-topped peaks (Fig. 3). Particular attention is paid during tuning to the low-mass tail of the peak, which is usually sufficiently small to permit N isotope measurements at  $^{12}\text{C}^{14}\text{N}$  signals similar to the  $^{13}\text{C}_2$  signal with  $<1\%$  tailing of  $^{13}\text{C}_2$ . This instrument tuning achieves a typical useful ion yield for  $^{12}\text{C}^{14}\text{N}$  of 10–20 counts per second/ppm N/nA.

Nitrogen isotope ratios ( $^{12}\text{C}^{15}\text{N}/^{12}\text{C}^{14}\text{N}$ ) are measured by counting for 10 s on  $^{12}\text{C}^{15}\text{N}$  and 1 s on  $^{12}\text{C}^{14}\text{N}$ , with  $^{12}\text{C}^{14}\text{N}$  count rates up to  $10^6$  counts per second. For N abundance measurements,  $^{13}\text{C}$  is also counted for 1 s and the ratio  $^{12}\text{C}^{14}\text{N}/^{13}\text{C}$  is used for quantitative N abundance measurements. At each analysis point, before data collection, care is taken in instrument alignment to ensure that (1) the sputter crater ( $\text{CN}^-$  ion image) is centered in the optic axis of the mass spectrometer magnet (which defines the optic axis of the instrument), (2) the field aperture is then centered in the sputter crater, and (3) the cross-over slit image is then centered in the detector. The number of cycles per analysis is set to achieve an estimated precision of  $<1\%$  ( $1\sigma_M$ ) when possible. The standard error of the mean ( $\sigma_M$ ) of each analysis is normally very close to that predicted from Poisson statistics, and is limited by the total number of counts of  $^{12}\text{C}^{15}\text{N}$ . Precision of the N isotope measurements in homogeneous areas is typically  $\pm 1\text{--}2\%$  ( $1\sigma_M$ ) for  $\text{N} \geq 200$  ppm, and from 2% to 10% from 200 ppm down to 10 ppm. The detection limit for N abundance is estimated at 0.5 ppm, as determined by analysis of nitrogen-free (Type II) diamond (Fig. 3B); the detected N is still well above the background estimate from the tail on  $^{13}\text{C}_2$ . The detection limit for N by FTIR is only 20 ppm, so the detected nitrogen in our “nitrogen-free” diamond may actually be present in the diamond, or may originate from stray CN ions originating from the crater rim and entering the mass spectrometer through the field aperture at oblique angles. Sample charging in excess of 2–3 eV is not observed when sputtering gold-coated diamond with  $\text{Cs}^+$  beam intensities up to 100 nA. The accuracy and reproducibility of the  $\delta^{15}\text{N}$  measurements is described in the next section.

### 3. Correction for IMF

Isotope ratios of light elements measured by SIMS are always shifted from their true ratios due to IMF, with the measured ratios usually depleted in the heavy isotopes relative to the true isotopic abundances. Measurement of the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of unknowns requires that the IMF for C and N be measured accurately, which can only be done by repeat measurements of homogeneous standards with known C and N isotopic composition interspersed with analyses of unknowns. As a result, the quality and homogeneity of standards is crucial for precise and accurate stable isotope analyses by SIMS. Fortunately, the very simple chemistry of diamond results in a total lack of matrix effects on carbon and nitrogen IMF, so that the precision and reproducibility of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  measurements is typically limited only by counting statistics and by the quality of standardization (see also Fitzsimons et al., 2000).

High-quality standardization is made as accurate as possible only if the standards and unknowns are located on the same sample mount, a feature of SIMS standardization that is unfortunately not commonly cited in many published studies. The importance of standard-sample co-location is especially true when performing isotope ratio measurements at high mass resolution (HMR) without energy filtering, as described for diamond analyses by Harte and Otter (1992), Harte et al. (1999), and Fitzsimons et al. (2000). The importance of standard-sample co-location was examined in detail by Riciputi (1996) and Patterson et al. (1997). These workers found that  $\delta^{34}\text{S}$  measurements of Balmat pyrite grains at HMR could be very reproducible within a given probe mount, but that measurements of different grains located in different probe mounts gave values of IMF which differed in  $\delta^{34}\text{S}$  by up to 7.2%. Yet when these same mounts were analyzed by EEF, the different mounts gave the same IMF to within 0.5%, indicating that the standards were homogeneous (Riciputi, 1996; Patterson et al., 1997), as had been previously found by laser fluorination studies of the same Balmat pyrite standard (Crowe and Vaughan, 1996). The conclusion of these studies is that isotope analyses at HMR are less reproducible between sample mounts than within a given sample mount, even for conducting phases such as sulfides and diamond. Furthermore, it is clear that

proper application of IMF values to unknowns at the sub-permil level requires that standards and unknowns be located on the same sample mount when undertaking isotope measurements at HMR, and that SIMS data that do not meet this requirement should be viewed with caution. Isotope ratio techniques utilizing EEF appear to be much more stable, and do not require standard-unknown co-location (Farquhar et al., 1999; Riciputi, 1996; Patterson et al., 1997). Nevertheless, we have chosen to conduct our  $\delta^{13}\text{C}$  analyses (EEF) and  $\delta^{15}\text{N}$  analyses (HMR) with standards and unknowns located on the same sample mount with uniform sample height.

The C isotope standards consist of polished fragments of larger diamonds that have been analyzed repeatedly by conventional gas-source mass spectrometry (Table 1). Five gas-source measurements of 1-mm fragments of the Mao diamond gave a  $\delta^{13}\text{C}$  value of  $-6.51\text{‰} \pm 0.10\text{‰}$  (P. Deines, pers. comm.). Repeat SIMS measurements over a single analytical session in 1997 determined the spatial isotopic homogeneity of the Mao diamond to within 0.2‰ (Fig. 4A). The combined standard errors of the SIMS ( $0.064\text{‰ } 1\sigma_{\text{M}}$ ) and gas-source measurements ( $0.022\text{‰ } 1\sigma_{\text{M}}$ , Table 1) result in an IMF measurement accurate to better than 0.1‰. A similarly good SIMS reproducibility is routinely achieved for  $\delta^{34}\text{S}$  analyses of sulfide standards using EEF (E. Hauri, unpublished data). The other diamond standards (DP333, DP351, DP348, P. Cartigny, pers. comm.) show a slight degree of hetero-

geneity in  $\delta^{13}\text{C}$  (about 1–2‰) when analyzed by SIMS, consistent with the presence of growth zoning imaged by CL. IMF values for EEF  $\delta^{13}\text{C}$  analyses range from  $-48.5\text{‰}$  to  $-58.5\text{‰}$  (Fig. 5), and vary mainly with the efficiency and age of the EM. The IMF values for  $\delta^{13}\text{C}$  in diamond and graphite using EEF have previously been shown to be identical within 1‰, and to be independent of crystallographic orientation, surface topographic relief ( $< 50 \mu\text{m}$ ), and distance of the sample to the extraction plate (Farquhar et al., 1999). IMF values for  $\delta^{13}\text{C}$  rarely vary by more than 1‰ during a single day. For analytical sessions lasting more than 1 day, we occasionally observe downward drift in the measured ratios of the Mao standard diamond, which are correlated with small changes in the efficiency of the EM. Since this drift is normally small (never more than 1‰ per day), we have chosen to use the standard values to correct for this instrumental drift by interspersing sample and standard measurements and interpolating the drift of IMF between standard measurements (Fig. 5). After correction for IMF and any EM drift, the  $\delta^{13}\text{C}$  values are calculated assuming a  $^{13}\text{C}/^{12}\text{C}$  ratio of 0.0112246 for Pee Dee Belemnite (PDB). Combining the uncertainties in the  $\delta^{13}\text{C}$  value of the Mao standard with the instrumental reproducibility, each point analysis of  $\delta^{13}\text{C}$  in unknowns is assigned an error of 0.3‰ ( $1\sigma$ ). This uncertainty is a factor of 2–3 better than the HMR technique used by Harte et al. (1999) and Fitzsimons et al. (2000), due mainly to longer count times and the improved stability of EEF analyses over HMR analyses.

Nitrogen isotopic measurements are not as reproducible as those for carbon isotopes; mitigating factors include lower count rates, the requirement of HMR, and heterogeneity of the standard diamonds DP333 and DP351 (Table 1; Fig. 4B). Both of these diamonds show evidence of growth banding in CL images, and ion imaging of CN emission shows wide bands of N-rich diamond (90% of the diamond) surrounded by thin bands (10% of the diamond) with very low N abundance. Early  $\delta^{15}\text{N}$  measurements in diamonds (Hauri et al., 1999) were standardized using a microdiamond powder deposited on a separate Al metal mount, but these analyses were compromised by a contribution of atmospheric N from grain surfaces; no such data are reported in this paper. The polished diamond DP333 (located on the same probe mount as samples) proved far superior, and is our main N isotope standard despite

Table 1  
Gas-source data for SIMS diamond standards

	N (ppm)	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)
Mao diamond (P. Deines)	–	–	– 6.56
	–	–	– 6.52
	–	–	– 6.44
	–	–	– 6.49
	–	–	– 6.56
DP333 (P. Cartigny)	993	– 10.9	– 5.41
	1037	– 8.3	– 5.87
DP351 (P. Cartigny)	918	– 0.7	– 4.67
	910	– 1.8	– 4.85
DP348 (P. Cartigny)	<20	–	– 5.57
	<20	–	– 5.54
#1013 rim	1100	–	–
#3648 core	200	–	–
#3648 int.	110	–	–
#3648 rim	<20	–	–
T2 plate	<20	–	–

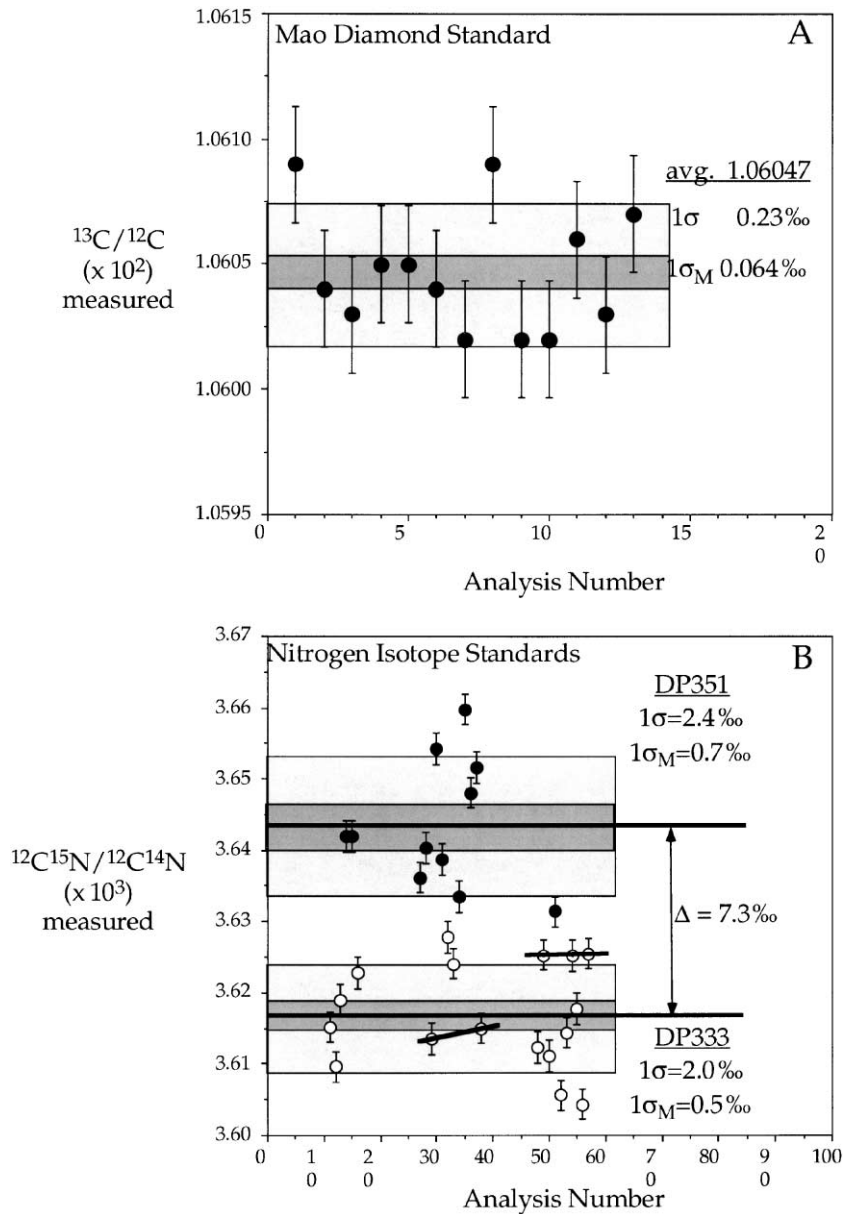


Fig. 4. (A) Measured C isotope ratios from multiple analyses of the Mao diamond standard in a single 1997 session, obtained from points widely dispersed around the 2 mm<sup>2</sup> surface. Error bars are  $\pm 0.2\%$  ( $1\sigma_M$  of 200 ratios per analysis) representing analytical precision. (B) Measured N isotope ratios from multiple points on the DP333 and DP351 diamond standards. Analyses from the same crater (connected by short tie lines) are more reproducible than analyses of different points on DP333, yet the  $\sim 8\%$  difference between DP333 and DP351 is easily resolved.

its heterogeneous distribution of N. Measured  $^{12}\text{C}^{15}\text{N}/^{12}\text{C}^{14}\text{N}$  ratios of the N-rich bands tends to reproduce the 8‰ difference in  $\delta^{15}\text{N}$  between DP333 and DP351 indicated by the bulk analyses (Table 1), but with a

reproducibility of only 3‰ ( $1\sigma$ ) for analyses within one standard. However, the reproducibility of repeat measurements of the same sputter crater, or along the same growth band, appear to be reproducible to  $\pm 1\%$  ( $1\sigma$ )



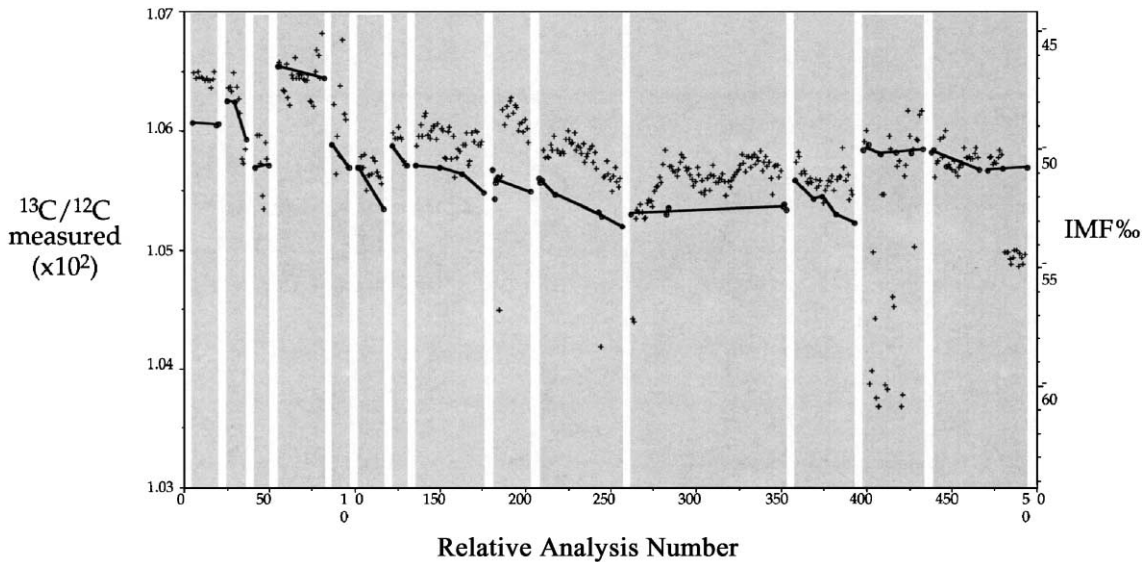


Fig. 5. Raw measured  $^{13}\text{C}/^{12}\text{C}$  ratios of 442 individual spot measurements in diamonds from 14 separate analytical sessions during 1997–2000. Analytical sessions are highlighted in gray, and are separated by sample changes or instrumental tuning. Individual analytical uncertainties are indicated by the size of the symbols ( $\pm 0.3\%$   $1\sigma$ ). Filled circles indicate analyses of the Mao diamond standard; solid lines connect standard analyses within individual analytical sessions. Most recent standard analyses indicate drift in IMF of  $\leq 1\%$  per day and  $\leq 3\%$  per session, correlated with gradual shifts in the efficiency of the EM detector (see text). Length of time of analytical sessions can be estimated by the number of analyses per session (approx. 30 min per analysis); the longest analytical session covered 50 h. Total variation of IMF is 6‰ over 3 years (3‰ over the past two years).

(Figs. 4 and 6). Thus, while we judge the reproducibility of the technique to be around 1‰, the accuracy is no better than 3‰ in the absence of demonstrably homogeneous standards. The SIMS N isotope analyses seem also to be insensitive to surface topographic effects (at least at the 3‰ level), as estimated from repeat analyses of prior sputter craters and analyses of the edges of diamond plates. After correction of the measured  $^{12}\text{C}^{15}\text{N}/^{12}\text{C}^{14}\text{N}$  ratios for IMF and any observed EM drift, values of  $\delta^{15}\text{N}$  are calculated assuming an atmospheric  $^{15}\text{N}/^{14}\text{N}$  ratio of 0.003676. Combining the uncertainties in the  $\delta^{15}\text{N}$  values of the standards with the instrumental reproducibility, each point analysis of  $\delta^{15}\text{N}$  in unknowns is assigned an analytical error equivalent to either the in-run analytical precision or 1‰, whichever is larger, but with the data from individual sessions subject to an uncertainty of  $\pm 3\%$  in accuracy based on the observed  $\delta^{15}\text{N}$  heterogeneity of the DP333 and DP351 standards (Fig. 6).

The calibration curve for N abundance measurements was calibrated by measuring the ratio  $^{12}\text{C}^{14}\text{N}/^{13}\text{C}$  in homogeneous growth zones of Siberian dia-

mond plates previously analyzed by FTIR, and the N-rich growth bands in the DP333 and DP351 N isotope standards which were analyzed in bulk by gas-source mass spectrometry (P. Cartigny, pers. comm.). The results are consistent, and give an average scatter of standards of 10% about the calibration line (Fig. 7). Because analysis of Type II diamond routinely gives an estimated detection limit of 0.5 ppm N, the slope of the calibration line was fit by linear least squares and forced through the origin. The slope of the calibration line has been found to vary systematically with  $\text{Cs}^+$  beam density (i.e., beam current at a fixed beam diameter), so all N abundance measurements are made with a 40- $\mu\text{m}$  diameter beam and a beam current of 10 nA. Although the analytical uncertainty on each  $^{12}\text{C}^{14}\text{N}/^{13}\text{C}$  measurement is  $< 1\%$ , the error in the slope of the calibration line is 10%, which is the  $1\sigma$  uncertainty assigned to each N abundance determination.

A typical analysis routine involves consecutive measurement of N and  $\delta^{15}\text{N}$  in the same crater over many locations on diamond samples and standards,

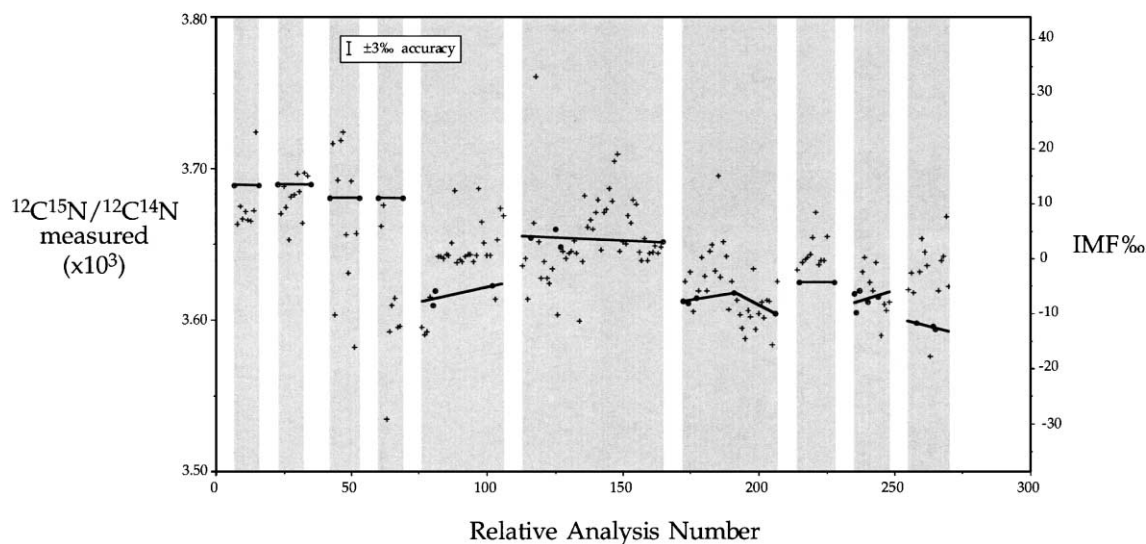


Fig. 6. Raw measured  $^{12}\text{C}^{14}\text{N}/^{12}\text{C}^{15}\text{N}$  ratios of 216 individual spot measurements in diamonds from 10 separate analytical sessions during 1998–2000. Analytical sessions are highlighted in gray, and are separated by sample changes or instrumental tuning. Typical individual analytical uncertainties are indicated by the size of the symbols ( $\pm 1\%$   $1\sigma$ ); estimated error in the accuracy of the analyses is indicated by the large error bar ( $\pm 3\%$   $1\sigma$ ). Filled circles indicate repeat analyses within single growth bands (or sometimes single craters) on the DP333 diamond standard; solid lines connect standard analyses within individual analytical sessions. Length of time of analytical sessions can be estimated by the number of analyses per session (approx. 40–60 min per analysis); the longest analytical session covered 50 h.

followed by a separate analytical session devoted to  $\delta^{13}\text{C}$  measurements in the same craters. Although the analyzed areas are 20–25  $\mu\text{m}$  in diameter, defining the

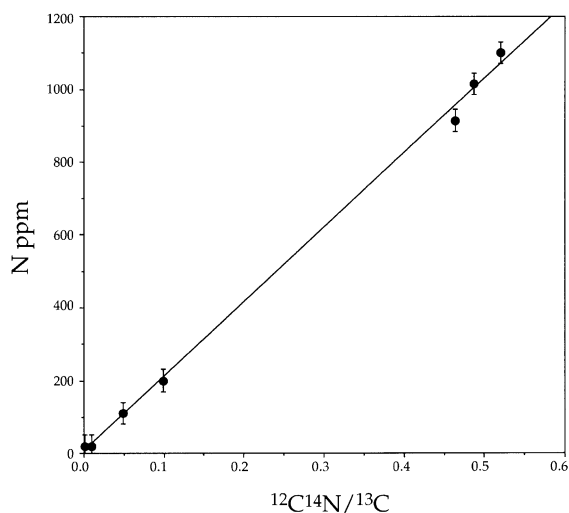


Fig. 7. Calibration line for nitrogen abundance measurements in diamond, from spot analyses of polished plates previously analyzed by FTIR.

spatial resolution of the technique, the spacing of adjacent craters can normally be no closer than 40–50  $\mu\text{m}$ , effectively defining the limit of adjacent growth features that can be examined with this technique. Spatial resolution should be better on SIMS instruments with improved ion transmission at HMR, such as the Cameca 1270.

#### 4. Application to analysis of natural diamonds

Precise  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  measurements are best made on flat diamond surfaces with a minimum of surface topography. Samples are typically pressed into indium metal contained within a 1-cm-diameter ring, which is then inserted into a 2.5-cm-diameter Al-metal mount containing the polished diamond standards (also pressed into indium metal). Care is taken to surround the diamond edges with indium, and to minimize the topography of the indium surrounding both standard and sample diamonds. By subsequently polishing the sample mount with dilute 1- $\mu\text{m}$  alumina paste, it is normally possible to reduce the topography between indium and diamond edges to within 20–30

$\mu\text{m}$ . Analyses are first made for N concentrations and  $\delta^{15}\text{N}$ , and these analysis craters are later re-analyzed for  $\delta^{13}\text{C}$  using EEF due to the demonstrated stability of this technique against topographic effects.

Fig. 8 shows a CL image of a central plate from diamond #1013, a stone of unknown paragenesis from the Mir kimberlite pipe (Hauri et al., 1999). CL imaging of the central plane shows an irregular core (50–60  $\mu\text{m}$  diameter) surrounded by 600  $\mu\text{m}$  of complex oscillatory zoning, followed by a 1200- $\mu\text{m}$  clear, sharp-edged octahedral rim with uniform CL brightness. A traverse made from the core of this diamond to the rim reveals large variations in N abundance,  $\delta^{15}\text{N}$ , and  $\delta^{13}\text{C}$  (Table 2). Previously reported  $\delta^{15}\text{N}$  data for this diamond (Hauri et al., 1999) were made with a different standard located on a separate sample mount; the new  $\delta^{15}\text{N}$  analyses reported here were standardized using the DP333 standard located on the same mount as the diamond sample. The new  $\delta^{15}\text{N}$  data thus supercede the data reported in Hauri et al. (1999).

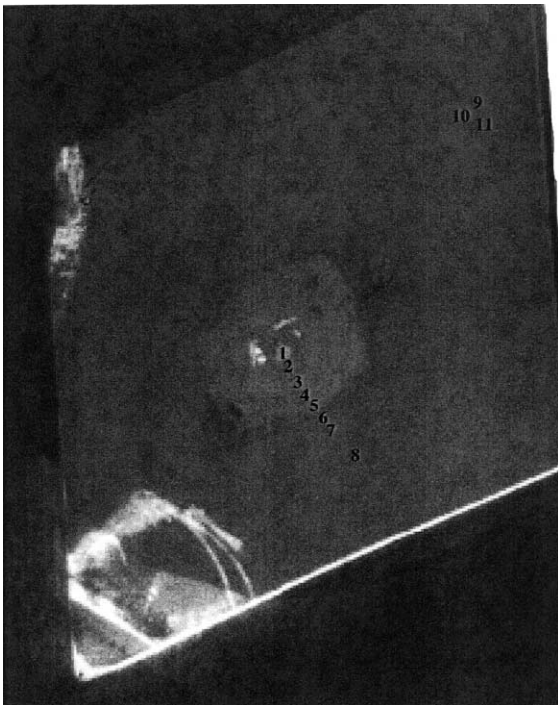


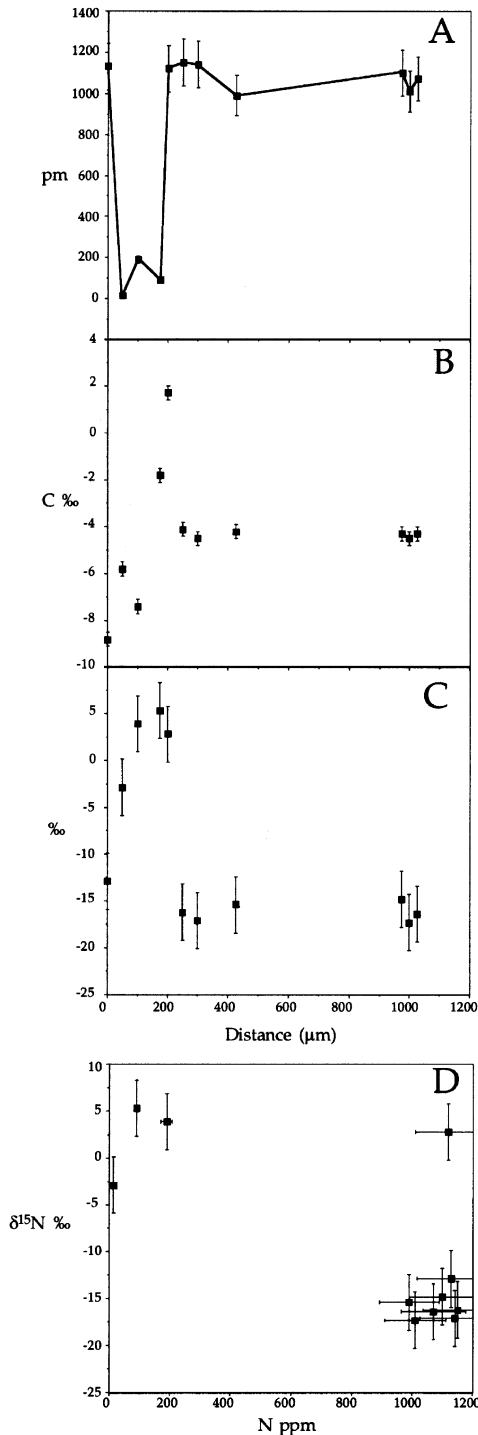
Fig. 8. CL image of Siberian diamond #1013 from the Mir kimberlite. Numbers indicate individual analysis locations listed in Table 2.

Table 2  
SIMS data for Siberian diamond #1013

	N (ppm)	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)
@1-core	1130	-12.9	-8.8
@2	14	-2.9	-5.8
@3	204	+3.9	-7.4
@4	95	+5.3	-1.8
@5	1153	+2.8	+1.7
@6	1314	-16.2	-4.1
@7	1174	-17.1	-4.5
@8	993	-15.4	-4.2
@9-corner	1390	-16.4	-4.3
@10-corner	1310	-14.8	-4.3
@11-corner	1210	-17.3	-4.5

Regions of the diamond that luminesce brightly in CL are characterized by higher N abundances than the CL-dark zones, suggesting a relationship between N abundance, abundance of defects, and luminescence (Hauri et al., 1999). A similar correspondence has been observed in diamonds from South Africa (Harte et al., 1999), Colorado (Fitzsimons et al., 1999), Brazil (Hutchison et al., 1999), Siberia (Taylor et al., 2000; Bulanova et al., in press), and many other locales (Hauri, unpublished data). The nitrogen in the complex core of this diamond is highly aggregated (75% B-nitrogen) implying prolonged residence at cratonic mantle temperatures (2.9 Ga at 1190 °C), yet this long mantle residence time appears to have been insufficient to homogenize the extreme variations in N abundance among the central growth zones. This observation is consistent with the extremely slow diffusivity that is thought to characterize aggregated clusters of N atoms (see discussion in Harte et al., 1999). The octahedral rim nitrogen is much less aggregated (average 10–20% B-nitrogen), suggesting a later stage of more homogeneous growth around a pre-existing core.

Isotopic variations in the irregular core are large, displaying total ranges of 10.5‰ in  $\delta^{13}\text{C}$  and 22‰ in  $\delta^{15}\text{N}$  (Fig. 9). The unzoned octahedral rim is uniform in both  $\delta^{13}\text{C}$  ( $-4.3 \pm 0.2\text{‰}$ ) and  $\delta^{15}\text{N}$  ( $-16.2 \pm 0.9\text{‰}$ ) to within the precision of the analyses. Two spots near the center of the diamond, separated by only 50  $\mu\text{m}$ , have very different  $\delta^{13}\text{C}$  ( $-8.8\text{‰}$ ,  $-5.8\text{‰}$ ),  $\delta^{15}\text{N}$  ( $-12.9\text{‰}$ ,  $-2.9\text{‰}$ ), and N abundance (1130 ppm, 14 ppm), suggesting again that the prolonged mantle residence time of this part of the diamond did not permit diffusive equilibration of C or



N isotopes at the 50-μm scale. This observation can only be explained if either (1) the central growth features are young and N aggregation was much more rapid than can be explained by experimental studies of N aggregation kinetics (Evans and Qi, 1982; Taylor et al., 1996), or (2) C and N self-diffusion in diamond is exceedingly slow ( $< 3 \times 10^{-22}$  cm<sup>2</sup>/s). In particular, if the temperature–time history inferred by the highly aggregated nitrogen is correct, then carbon self-diffusion must be considerably slower than most previous estimates inferred from N aggregation kinetics (Chrenko et al., 1977; Evans and Qi, 1982; Taylor et al., 1996). This single 4-mm-wide plate preserves δ<sup>15</sup>N and δ<sup>13</sup>C values that span a large fraction of the isotopic range of bulk analyses of individual diamonds; whether these large variations are the rule or the exception awaits more work on a larger number of stones. This work points out a clear need for direct determinations of the diffusivity of carbon, nitrogen, and other elements in diamond.

## 5. Conclusions

Ion probe microanalysis of carbon and nitrogen isotopes in diamonds has been shown to provide very precise data for δ<sup>13</sup>C (±0.2‰) and δ<sup>15</sup>N (down to ±1‰) when special attention is paid to instrument tuning and alignment, and frequent analysis of standards interspersed with sample unknowns. The accuracy of SIMS determinations of IMF in diamond, which in turn limit the accuracy of analyses of samples, is entirely dependent on the spatial isotopic homogeneity of standard diamonds (currently ±0.1‰ for δ<sup>13</sup>C and ±3‰ for δ<sup>15</sup>N; our search for a more homogeneous N isotope standards is ongoing). The applicability of standard-based IMF measurements to analyses of samples, at the highest levels of accuracy, is dependent on co-location of samples and standards on the same probe mount, critically so if the isotope

Fig. 9. Data for Mir diamond #1013, showing zonation of (A) N abundance, (B) C isotopes, and (C) N isotopes as a function of distance from the growth center of the diamond (spot 1). (D) N isotopes show no systematic variation with N abundance. When the data are weighted by the area of growth zonation, the SIMS data indicate values of δ<sup>13</sup>C of -4.3‰, δ<sup>15</sup>N of -17‰, and 1100 ppm N for the diamond plate.

measurements are made at HMR. With care, total analytical uncertainties for SIMS diamond analyses can be reduced to  $\pm 0.3\%$  ( $1\sigma$ ) for  $\delta^{13}\text{C}$ , and as low as  $\pm 1\%$  ( $1\sigma$  precision, dependent on N content) with a  $\pm 3\%$  uncertainty on the accuracy for  $\delta^{15}\text{N}$ .

While the origin of the large isotopic variations in diamonds such as #1013 from the Mir pipe is as yet unclear, in situ  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  analyses, in conjunction with other spatially resolved data such as CL imaging and FTIR analysis, hold great potential for unraveling the complex growth histories of natural diamonds, and promise to constrain the extent of C and N isotope fractionation which can be attributed to the diamond growth process. Hopefully, with such information in hand, the significance of the variability in  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in mantle diamonds to large-scale Earth processes will become clearer.

## Acknowledgements

We thank the Carnegie Institution of Washington and National Science Foundation for capital and continuing support for the DTM ion microprobe laboratory, and the Yakutian Institute of Geosciences for providing diamond #1013. Thanks go also to Peter Deines and Pierre Cartigny for providing measured diamond standards, Judith Milledge for FTIR analyses of diamond plates, and Ed Vicenzi and Jim Rougvie for assistance with CL imaging. This paper has benefited from probe sessions and discussions with Al Brandon, Peter Deines, John Eiler, James Farquhar, Lee Ricupiti, Steve Shirey, Nobu Shimizu, and Ed Vicenzi, and from constructive reviews by Ben Harte and Stuart Boyd.

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