

# Microscale variations in C and N isotopes within mantle diamonds revealed by SIMS

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## Introduction

Very few chemical or isotopic techniques exist to investigate the history and formation conditions of natural diamonds. Natural diamonds themselves contain few chemical impurities (N, B, H, fluid inclusions), but often contain silicate and sulfide mineral inclusions which are usually considered to be syngenetic. Detailed studies on natural diamonds have utilized a variety of strategies to infer the age systematics and formation conditions of natural diamonds; these include examining large numbers of diamonds from individual locales (Deines, 1980), the isotopic systematics of pooled silicate inclusions (Richardson et al., 1984), isotopic work on fragments of individual diamonds (Boyd et al., 1987, 1994), optical, CL and FTIR N-aggregation studies of individual diamonds (Bulanova and Milledge, 1995), and trace element systematics in individual silicate inclusions (Shimizu and Sobolev, 1995). Despite a large number of studies, there remains much debate on two central issues in diamond genesis, namely (1) the timing of diamond formation (e.g. old or young) relative to emplacement by kimberlite magmatism, and (2) whether isotopic variability among mantle diamonds and their inclusions relates to source variability or isotopic fractionation during diamond growth. In part, this continued debate may be the result of inclusion studies and diamond studies being decoupled from each other, with few individual inclusion-bearing diamonds getting the complete analysis available by modern techniques. Recent studies examining the Re-Os (Pearson et al., 1998) and Pb-Pb (Rudnick et al., 1993) isotope systematics of individual diamond inclusions have begun unravel some of these questions, and our objective is to add to these studies by investigating the micro-scale geochemistry of C and N isotopes within the individual diamonds themselves.

## Ion Probe Methods

A technique has been developed using secondary ion mass spectrometry (SIMS) to investigate variations in N abundance,  $\delta^{15}\text{N}$ , and  $\delta^{13}\text{C}$  within a number of inclusion-bearing natural diamonds from locations in Siberia and southern Africa. Carbon isotopes are measured using a  $\text{Cs}^+$  ion beam (0.5-2 nA) and collecting negatively-charged  $\text{C}^-$  ions at low-mass resolution and high energy offset ( $+250 \pm 100$  eV), with a reproducibility and accuracy of  $\pm 0.3\%$  on  $\delta^{13}\text{C}$ . Nitrogen isotopes are measured using a  $\text{Cs}^+$  ion beam (5-40 nA, depending on N concentration) and collecting negatively-charged  $\text{CN}^-$  molecules at high mass resolution (MRP=9000); such high mass resolution is required in order to completely eliminate  $^{13}\text{C}_2$  interference on  $^{12}\text{C}^{14}\text{N}$  at the lowest N abundances. Reproducibility of  $\delta^{15}\text{N}$  is  $\pm 1-3\%$  depending on N concentration; N abundances are measured from the ratio  $^{12}\text{C}^{14}\text{N}/^{13}\text{C}$  calibrated against FTIR measurements on homogeneous octahedral growth zones of natural diamonds. Analysis of Type-II diamond plates demonstrates a detection limit of better than 5-10 ppm for N abundance. These analyses are made with a spatial resolution of 40  $\mu\text{m}$ , limited by the spot sizes necessary for precise N isotope data.

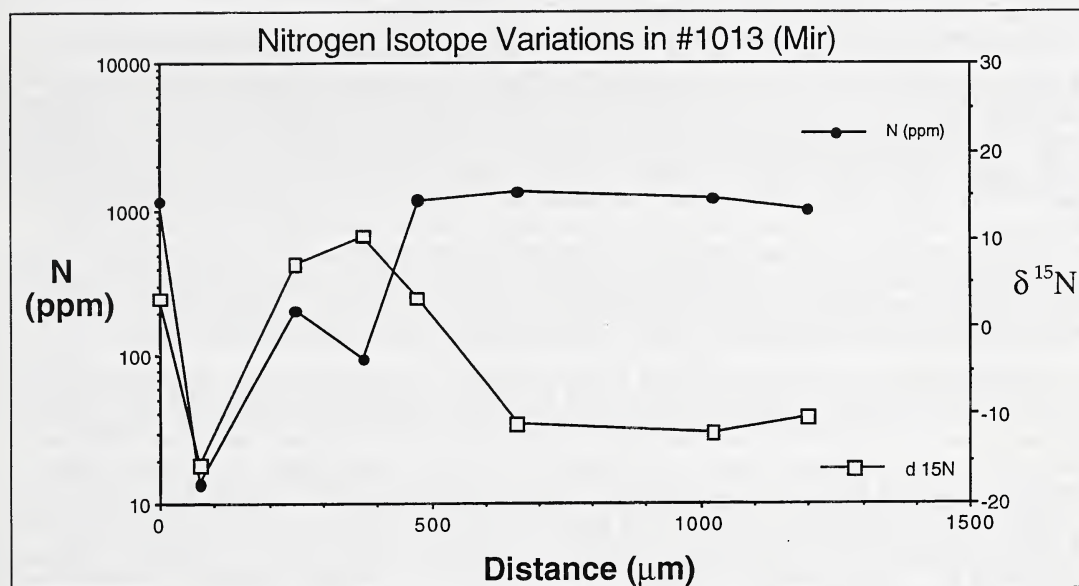
## Isotopic Variations in Siberian Diamonds

These microanalytical techniques have allowed us to investigate the C and N isotope variations in previously well-characterized diamonds, concentrating on CL-defined growth zones and sectors within polished diamond plates. Our approach is exemplified by the variations within two Siberian diamonds, #1013 (E-type, Mir) and #3648 (P-type, Udachnaya). #1013 is most likely E-type based on the occurrence of adjacent zones with highly different N concentrations and aggregation states; such features are found only in E-type diamonds at Mir. The internal structure of #1013 is fairly typical of Siberian diamonds, with a core of poor-quality diamond surrounded by clear octahedral growth. The central region shows considerable birefringence, indicative of strain. 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. CL brightness correlates with N abundance, with the central region being highly variable (13-1300 ppm) and the octahedral rim being fairly uniform at 1200 ppm. Nitrogen in the central region is highly aggregated (avg 75% B), implying prolonged residence at lithospheric mantle temperatures (2.9 Ga at 1190°C); the octahedral rim N is much less aggregated (avg 10-20% B), and demonstrate very different thermal histories for the core and rim of this diamond. Isotopic variations in the zoned diamond core are large (total ranges of 10.5‰ in  $\delta^{13}\text{C}$  and 26‰ in  $\delta^{15}\text{N}$ ); two spots near the center of the diamond, separated by only 50  $\mu\text{m}$ , have very different  $\delta^{13}\text{C}$  (-8.8‰, -5.8‰),  $\delta^{15}\text{N}$  (+3.3‰, -15.6‰) and N abundance (1130 ppm, 14 ppm). The unzoned octahedral rim is uniform in both  $\delta^{13}\text{C}$  ( $-4.3 \pm 0.2\text{‰}$ ) and  $\delta^{15}\text{N}$  ( $-11.2 \pm 0.9\text{‰}$ ) to within the precision of the analyses.

P-type diamond #3648 from Udachnaya is structurally complex, with no good areas of octahedral growth. In CL images, the diamond shows three distinct growth zones. The central cubo-octahedral zone is CL-blue and contained a cluster inclusions of sulfide, wüstite and Mg-rich olivine (Fo<sub>93</sub>). The intermediate zone is a lighter CL-blue octahedral zone which also contains sulfides. Growth lines in this zone are truncated by the outer zone, which is non-luminescent but also contains sulfides which appear to be open to the diamond surface through fractures. The central and intermediate sulfides give unequivocally old Re-Os ages (3.1-3.5 Ga), while the rim sulfides may have exchanged with the surrounding mantle or host kimberlite (Pearson et al., 1998). Nitrogen is highly aggregated in the central zone (300-400 ppm N, 60-75% B), while the rim is lower in N and is less aggregated (<100 ppm, 3-30% B). Despite its complex internal zonation, carbon and nitrogen isotope variations in #3648 are less extreme, with  $\delta^{13}\text{C}$  ranging from -8.9‰ to -4.6‰ and  $\delta^{15}\text{N}$  from -3.6‰ to -7.7‰. The lowest  $\delta^{13}\text{C}$  value in particular is rather depleted in  $^{13}\text{C}$  for a P-type diamond, but still within the range observed for bulk P-type diamond analyses.

Given some of the uncertainties surrounding ages determined by N aggregation, #3648 is the only one of these two diamonds which we can definitively say is ancient. The Mir diamond #1013 may be younger, and young age estimates have been previously reported for a Mir diamond (Shimizu and Sobolev, 1995), but the highly aggregated N would seem to suggest that it cannot be much younger than #3648. Diamond #1013 shows more fine-scale zonation in CL intensity, N abundance,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  than #3648; is this due to some diffusive homogenization in the (perhaps) older #3648? If the ca. 3 Ga nitrogen aggregation ages are correct, then the fine-scale and large-amplitude isotopic zonation in the core of #1013 must have persisted for a similar length of time. This is perhaps not surprising for  $\delta^{13}\text{C}$  given that C diffusion in diamond is thought to be extremely sluggish even at very high temperatures. Such zonation was not initially expected for N isotopes, which we thought might be much more mobile. However, from kinetic studies of N aggregation (Taylor et al., 1996), it appears that the aggregation process is one in which N atoms move only very small distances, on the order of tens to hundreds of unit cells (much smaller than the spatial resolution of the ion probe). As a result, the kinetics of N aggregation are not the same as the kinetics of N self-diffusion through the diamond lattice, and there is no data on the latter phenomenon which might constrain the time scale for preservation of the large-amplitude  $\delta^{15}\text{N}$  zonation seen in #1013. If the N aggregation ages for

#1013 are taken at face value, then the kinetics of "aggregated" N diffusion would appear to be extremely slow, but the diffusivity of other forms of N (e.g. single atoms) is unknown. Work is currently underway to evaluate possible  $\delta^{15}\text{N}$  fractionation during N aggregation (though we expect this to be minor), and the kinetics of N self diffusion in diamond, in order to understand better the origin and preservation of small-scale  $\delta^{15}\text{N}$  variability.



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