



## MULTIPLE GROWTH EVENTS, PROCESSES AND FLUID SOURCES INVOLVED IN THE GROWTH OF DIAMONDS FROM FINSCH MINE, RSA: A MICRO-ANALYTICAL STUDY

Palot\* M<sup>1</sup>, Pearson DG<sup>1</sup>, Stern R<sup>1</sup>, Stachel T<sup>1</sup>, Harris JW<sup>2</sup>

\* corresponding author: palot@ualberta.ca

<sup>1</sup> Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada.

<sup>2</sup> School of Geographical and Earth Sciences, University of Glasgow, Glasgow, United Kingdom.

### INTRODUCTION

Over the last five decades, studies of diamond from worldwide occurrences have yielded important constraints on the deep carbon isotopic cycle (Craig, 1957; Deines, 1980; Cartigny 2005; Stachel et al. 2009). The  $\delta^{13}\text{C}$  distribution of diamond worldwide ranges from 41.4 to +5.0‰ with approximately three quarters of analyses falling within a narrow range from -8 to -2‰ (Cartigny et al, 2005, Stachel et al., 2009; de Stephano et al., 2009). Peridotitic diamonds are commonly described as mantle-related, the origin of eclogitic diamonds and the source of their carbon are more controversial because of the fairly common observation of very negative  $\delta^{13}\text{C}$  values (Deines, 1980; Cartigny, 2005; Stachel and Harris, 2008). Deines (1980) suggested that the carbon isotopic variability of diamonds is primordial, acquired during Earth accretion. Others suggested that eclogitic diamonds formed from sedimentary carbon recycled into the mantle (Sobolev and Sobolev, 1980; Kirkley et al., 1991; Navon, 1999). Another possibility is open-system isotopic fractionation at high temperature (Javoy et al., 1986; Galimov, 1991; Cartigny et al., 2001, Stachel et al, 2009).

In the past, such types of studies focussed on inter-diamond variability, where diamonds were usually recovered as mixed xenocryst populations from the host kimberlite, and

therefore, may represent a large variety of growth environments. Previous stable isotope studies have shown, however that significant isotopic variation may exist within single stones (Swart et al., 1983; Fitzsimons et al. 1999). Only few studies have focused on intra-diamond carbon isotopic variability using in-situ measurement techniques by secondary ion mass spectrometry (SIMS) (Harte and Otter, 1992; Harte et al. 1999; Fitzsimons et al., 1999; Bulanova et al., 2002; Hauri et al., 2002, Smart et al., 2011). Knowledge of zonation patterns in single diamonds provides a means for improving our understanding of diamond genesis and the deep carbon cycle as reflected in diamonds.

Diamonds from Finsch (South Africa) commonly believed to have a typical mantle like signature, based on their narrow range of  $\delta^{13}\text{C}$  with a mode at -6‰ (using bulk analysis), (Deines et al., 1984, 1989). However complex internal growth patterns (characterised by cathodoluminescence), and distinct infrared characteristics within single diamonds have been recorded in a recent study of Finsch diamonds of mainly eclogitic paragenesis (Appleyard et al., 2004). This suggests that Finsch kimberlite sampled multiple source regions either of similar age but differing temperature, or different ages. In order to evaluate the concept of a single diamond growth episode from a single chemical



reservoir, we have undertaken a geochemical study of 21 sulphide-bearing diamonds from Finsch. Sulphides are among the most common inclusions in diamonds (Efimova et al., 1983, Pearson et al., 1998, Stachel and Harris, 2008, Taylor and Liu, 2009). Our sample suite contains mostly eclogitic sulphides (on the basis of their Ni contents) with one additional diamond containing a single P-type garnet inclusion (sample F215). Nitrogen content and aggregation state were measured by infrared spectroscopy (FTIR). For selected diamonds,  $\delta^{13}\text{C}$  and N abundances were mapped at high spatial resolution by SIMS.

#### ANALYTICAL TECHNIQUE

Nitrogen aggregation states and nitrogen contents ( $N_{\text{FTIR}}$ ) were obtained by micro Fourier Transform Infrared Spectroscopy (FTIR). Diamond fragments used mainly consisted of {111} cleavage planes. Spectra ( $650\text{--}4000\text{cm}^{-1}$ ) were acquired in transmission mode for 200s with a resolution of  $4\text{ cm}^{-1}$  and an aperture size of 100  $\mu\text{m}$  using a Thermo Nicolet Nexus 470 FT-IR. Using the absorption coefficients for the A- and B-centers at  $1282\text{cm}^{-1}$  of 16.5 and 79.4 at.ppm/cm, respectively (Boyd et al., 1994, 1995), nitrogen concentrations were calculated after spectral decomposition using the Excel program CAXBD97, developed by David Fischer (The Diamond Trading Company, Maidenhead, UK). Detection limits and errors typically range from 5 to 15 ppm and about 10% respectively. The error of the aggregation state of nitrogen is estimated to be better than  $\pm 3\%$ .

Carbon isotope ratio and nitrogen abundance were measured in situ using a Cameca IMS 1280 multi-collector ion microprobe at the Canadian Centre for Isotopic Microanalysis, University of Alberta, Canada. Carbon isotope composition is expressed as per mil deviation relative to the composition of Vienna Pee Dee Belemnite (V-PDB). All measurements were performed with

samples and standard mounted in the same analytical block. All measurements for  $\delta^{13}\text{C}$  were referenced to two small blocks cut out of an isotopically homogenous slab through a {100} growth sector of an hP-hT synthetic diamond having a value of  $^{13}\text{C}/^{12}\text{C} = 0.0109276$  or  $\text{d}^{13}\text{C} = -22.576\text{‰}$  (2 $\sigma$ ). Another slab has been used as reference material for N abundance. The {100} sector in the inner part of this standard was determined to contain 420 at.ppm nitrogen by FTIR at the University of Alberta. A mass resolution of  $m/\Delta m \sim 1860$  and 2650 for cups  $^{12}\text{C}$  and  $^{13}\text{C}$ , respectively, ( $m$  is the molar mass of the molecule and  $\Delta m$  is the mass difference between two molecules) gave a clear separation of the principal molecular interference between  $^{13}\text{C}^-$  and  $^{12}\text{CH}^-$ . Secondary ions for all N-abundance measurements were acquired using Faraday cups. Characterisation of samples prior to analysis was performed using a Zeiss EVO 15 scanning electron microscope equipped with secondary electron and backscattered electron detectors, a Robinson wide spectrum cathodoluminescence detector, and a Gatan Chroma CL detector.

#### FTIR AND SIMS RESULTS

Nitrogen abundances determined by FTIR on 58 diamond fragments (from 21 whole diamonds) range from 21 to 1093 at.ppm.N with a mean value of  $559 \pm 291$  at.ppm.N (1 $\sigma$ , figure 1). Diamond F203 shows the largest N-abundance heterogeneity, ranging from 21 to 770 at.ppm.N. Nitrogen aggregation states (expressed as % of B defects) vary from 0 to 83% (figure 1). Diamond F203 shows the largest variation in the aggregation state of nitrogen heterogeneity ranging from 0 to 60%. Note that diamond F215 (containing a P-type garnet inclusion) is within the range of [N]-%B of the other diamonds from our set.

Nineteen fragments from nine diamonds were selected for carbon isotopes and N abundance analyses by SIMS for a total of 141 spots. Carbon isotopic compositions range from

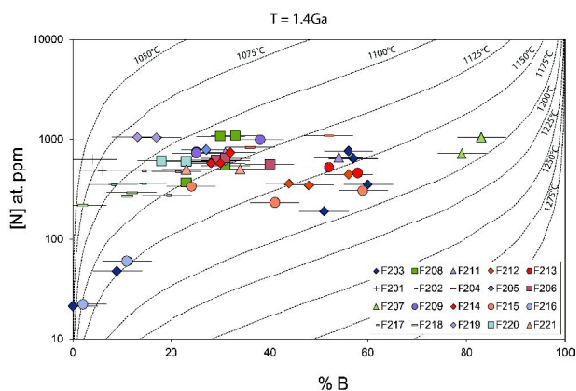


Figure 1. Nitrogen content (atomic.ppm in a log. scale) and aggregation state of nitrogen (%B) of diamonds from Finsch. Isotherms are based on the second order kinetic law for the nitrogen diffusion (Chrenko et al., 1977) assuming a mantle residence of 1.4Ga. Total errors of N-abundance and aggregation state of nitrogen is within the size of the symbol and better than  $\pm 3\%$ , respectively.

$\delta^{13}\text{C} = 9.1\text{‰}$  to  $2.6\text{‰}$  ( $n=141$ ) with a mean value of  $5.2 \pm 1.2\text{‰}$  ( $1\sigma$ , figure 2). The range of  $\delta^{13}\text{C}$  for our diamonds is within the typical range of worldwide diamond (Kirkley et al., 1991, Pearson et al., 2003, Cartigny et al., 2005, Stachel et al., 2009) where 72% of diamonds range from  $\delta^{13}\text{C} = 8\text{‰}$  to  $2\text{‰}$ . Nitrogen abundances measured by SIMS range from 3 to 2221at.ppm.N with a median value of 819at.ppm.N ( $1\sigma$ , figure 2). These data are slightly different from N-abundances

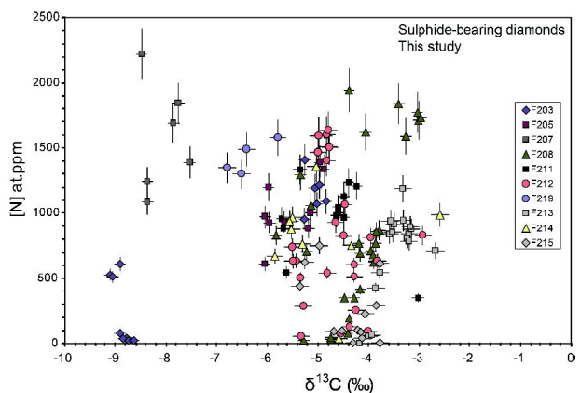


Figure 2. Carbon isotopic composition analysed by SIMS (‰) as a function of nitrogen abundance (atomic.ppm) of 10 sulphide inclusion-bearing diamonds from Finsch. N-abundance and  $\delta^{13}\text{C}$  were acquired on the same spots. Total errors of  $\delta^{13}\text{C}$  and [N] are better than  $\pm 0.18\text{‰}$  ( $2\sigma$ ) and  $\pm 10\%$  ( $2\sigma$ ), respectively.

determined by FTIR and are consistent with a heterogeneous distribution of nitrogen within Finsch diamonds.

The carbon isotopic variability ranges from 1.0 (F219) to 4.2‰ (F203) with an average variability of  $2.6 \pm 1.1\text{‰}$  ( $1\sigma$ ). Most of the studied diamonds have carbon isotopic variations  $< 4\text{‰}$ , consistent with worldwide diamond characteristics (Harte et al., 1999, Bulanova et al., 2002).

The parts of diamond fragments which contain the lowest nitrogen abundances in general have the darkest CL response. No clear correlation is observed between carbon isotopic composition and CL response. Since the analyses were conducted on diamond fragments core-rim relationships cannot be derived.



formation ages) for different diamond portions. Both possibilities are compatible with multiple diamond growth episodes.

### **Multiple metasomatism events and associated diamond growth inferred from variations of $\delta^{13}\text{C}$ and nitrogen abundance**

Finsch diamonds clearly show complex growth events which may be constrained through modelling of co variations in the  $\delta^{13}\text{C}$  and N-abundance (Thomassot et al., 2007, Palot et al., 2009, Stachel et al, 2009, Smart et al., 2011). Two groups of diamonds appear to be dominated by either isotopic fractionation or mixing processes.

Diamonds from the first group (F205, F207, F208 and F219) are dominated by isotopic fractionation from either a  $\text{CO}_2$  or  $\text{CH}_4$ -bearing fluid. Four diamonds have  $\delta^{13}\text{C}$  N systematics that can be explained by models involving a single or two distinct C-H-O rich fluids as metasomatic agents during open system isotopic fractionation.

Diamonds from the second group (F203, F213, F214) are better explained by models involving mixing of distinct fluids coupled with isotopic fractionation. Mixing could occur prior to, or following isotopic fractionation processes. Calculation of  $\delta^{13}\text{C}$  and [N] in precursor fluids is consistent with a typical mantle origin from either  $\text{CH}_4$  or  $\text{CO}_2$ -bearing fluids.

### **Summary and implication for diamond genesis**

Previous studies, based on bulk methods have concluded that Finsch diamonds originated from a common and homogeneous mantle-related reservoir (Deines et al., 1989). Our new in-situ data, however, reveal a more complex growth history involving several different fluids, with diamond growth possibly extending over a significant time period. This is supported by strongly variable  $\delta^{13}\text{C}$ -[N] systematics, even within a single diamond. Such systematics are

compatible with diamond growth occurring during ingress of metasomatic fluids of both oxidised ( $\text{CO}_2$ ) and reduced ( $\text{CH}_4$ ) compositions and require mixing of isotopically different fluids. In some cases, bulk analyses may have averaged out internal heterogeneities and evidence for multiple diamond growth episodes, resulting in non-coherent  $\delta^{13}\text{C}$ -[N] co variations.

Our observation of multiple growth episodes involving different reservoirs/fluids documents that several generations of diamonds are present in a single kimberlite, implying that great care must be taken in selecting diamonds for dating studies using an isochron approach.

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