



# Diffusive relaxation of carbon and nitrogen isotope heterogeneity in diamond: a new thermochronometer

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Received 25 November 2002; received in revised form 17 March 2003; accepted 18 March 2003

## Abstract

The spatial distribution of carbon and nitrogen isotopes in diamonds provides information on mantle residence time. Diamonds with long residence at high temperature will gradually lose their initial zoning patterns due to diffusion. Using experimentally determined carbon self-diffusion coefficients and nitrogen diffusion coefficients derived from aggregation experiments, we have modeled the diffusive relaxation of zoning profiles with a spectrum of wavelengths. Carbon isotope heterogeneity will be preserved on wavelengths greater than  $\sim 1 \mu\text{m}$  after 1 billion years' residence at 1400 K, and on wavelengths greater than  $\sim 200 \mu\text{m}$  after 1 million years' residence at 2000 K. Nitrogen isotope zoning is relaxed much more slowly, with  $0.1 \mu\text{m}$  zoning preserved over the age of the Earth at 1400 K and  $1 \mu\text{m}$  zoning preserved after 1 million years at 2000 K. The large difference in diffusive relaxation times between carbon and nitrogen isotopes means that initially correlated carbon and nitrogen profiles will lose their correlation after sufficient diffusion of carbon has taken place. This could be used as a thermochronometer. Carbon isotope heterogeneity in diamonds associated with lower mantle mineral assemblages has significantly smaller amplitude than nitrogen isotope heterogeneity, consistent with diffusive relaxation at high temperatures in the lower mantle.

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**Keywords:** Diffusion; Carbon; Nitrogen; Diamond; Zoning; Residence time; Age; Thermochronometer

## 1. Introduction

Advances in micro-beam analytical techniques have made it possible to perform in situ, high-resolution (approximately  $10 \mu\text{m}$ ) measurements of carbon and nitrogen isotopic ratios in diamond (Harte and Otter, 1992; Harte et al., 1999; Hauri et al., 2002).

Fine-scale heterogeneity in isotopic composition and nitrogen concentration has been discovered in several diamonds (e.g., lithospheric diamonds from Mir kimberlite, Hauri et al., 2002; Bulanova et al., 2002), and shown to be broadly correlated with crystal growth features observed by cathodoluminescence. These observations suggest that the growth history of diamond is complex and that the residence time in continental lithosphere has to be shorter than the time required to homogenize such growth features by diffusion.

In this paper, we present a new thermochronometer for diamond that is based on the relaxation of carbon and nitrogen isotopic zoning profiles by diffusion. We use forward modeling calculations to examine the time

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required for discrete wavelengths of isotopic heterogeneity to be blurred or erased by diffusion at a given temperature. The results of the forward models allow us to predict the minimum length scale of isotopic heterogeneity that can be preserved in diamond as a function of residence time and temperature in the continental lithosphere or deeper mantle, and to estimate the maximum lithospheric residence time of natural diamonds that preserve isotopic zoning with a certain distribution of wavelengths.

This thermochronometer differs from previous dating methods, which primarily rely on the composition and isotopic systematics of inclusions in diamond. These do not provide direct information on the formation age of the diamond itself, but do provide an upper limit if the isotopic system has remained closed since diamond formation. For instance, Sm–Nd model ages from garnet inclusions in diamond (Richardson et al., 1984), and Re–Os (Pearson et al., 1999) and Pb–Pb (Rudnick et al., 1993) model ages from sulfide inclusions, yield old ages (1–3 billion years) that correspond to the age of the host craton of the diamond-bearing kimberlite. Conversely, an Ar isotope study reports an age synchronous to the kimberlite eruption (~400 Ma, Burgess et al., 2002), and trace element zoning found in garnet inclusions suggests young ages as well (Shimizu et al., 1997). All these ages are indirectly determined using inclusion phases in diamond, and therefore are subject to interpretation.

The state of nitrogen impurities in diamond evolves with time to form more aggregated clusters from dispersed nitrogen atoms. Experimentally determined rates of nitrogen aggregation (e.g., Chrenko et al., 1977; Evans and Qi, 1982; Taylor et al., 1996) can be applied to infer the residence time for a given temperature condition (e.g., Taylor et al., 1990). Aggregation of nitrogen impurities requires diffusion on a relatively short length scale, in the order of ~30–100 nm depending on the nitrogen concentration. Many lithospheric diamonds have fully aggregated nitrogen, and the aggregation kinetics data can only give a minimum estimate of the residence time in this case.

Because diffusive relaxation of isotope zoning profiles requires diffusion on a range of length scales extending well beyond the sub-micron scale relevant to nitrogen aggregation, the method introduced in this paper can be used to extract temperature–time infor-

mation from diamonds with very long residence times at high temperature. It provides information that is complementary to nitrogen aggregation studies and extends to longer times and higher temperatures.

## 2. Model

The governing equation for diffusional homogenization is the continuity equation, which can be expressed as:

$$\frac{\partial[C]}{\partial t} = D_c \nabla^2[C],$$

where  $[C]$  is the concentration of carbon,  $D_c$  the self-diffusion coefficient of carbon and  $t$  the time. Because the model is for homogenization of isotopic species,  $[C] = [^{12}\text{C}] + [^{13}\text{C}]$ . Diffusion of the individual isotopes  $^{12}\text{C}$  and  $^{13}\text{C}$  can be calculated by independent continuity equations, one for each isotope.

In contrast to the simple case of carbon self-diffusion, homogenization of nitrogen isotopes requires us to consider the diffusion of more than one species—individual nitrogen atoms as well as several species of nitrogen clusters. Single atom nitrogen that is detected by spectroscopy is called a C-center (denoted as N hereafter), whereas an A-center is a nitrogen–nitrogen pair (denoted as N–N hereafter) and a B-center is a tetrahedral cluster of nitrogen surrounding a vacancy (Evans, 1992). The diffusivity of nitrogen decreases in the order  $D_N > D_{N-N} > D_{NB}$ ; as nitrogen atoms aggregate into larger clusters, the mobility decreases. For simplicity we developed a model of nitrogen homogenization that considers N and N–N only because the B-center can be considered to be effectively immobile compared to N and N–N at the conditions of Earth's crust and mantle. The equation of nitrogen diffusion was thus modeled as

$$\frac{\partial[N_N]}{\partial t} = D_{N_N} \nabla^2[N_N] - 2k[N_N]^2$$

for single nitrogen atoms, and

$$\frac{\partial[N_{N-N}]}{\partial t} = D_{N_{N-N}} \nabla^2[N_{N-N}] + 2k[N_N]^2$$

for N–N pairs, where  $D$  is the diffusion coefficient of the subscripted species and  $k$  the second-order reaction rate constant for  $N_N + N_N = N_{N-N}$ .

The initial conditions were selected to mimic carbon and nitrogen isotopic heterogeneity at various length scales using the formula

$$[^{13}\text{C}, ^{12}\text{C}, ^{15}\text{N}, \text{ and } ^{14}\text{N}] = \sum_1^n a_i \sin(b_i x) + c_i \cos(d_i x)$$

where  $a$ ,  $b$ ,  $c$ , and  $d$  are arbitrary constants. Depending on the choice of  $b$  and  $d$ , oscillatory variations with various frequency components are created. We have chosen this mathematical form because it demonstrates clearly the decay of discrete wavelengths of heterogeneity.

The geometry of the model is infinite in one dimension. The concentration of carbon is constant throughout while the isotopic abundance varies. For nitrogen, both the total concentration and the isotopic composition vary. The continuity equation for each species was solved by an implicit finite difference method using the Crank–Nicolson scheme (e.g., Smith, 1965).

### 3. Diffusion data

#### 3.1. Carbon self-diffusion

Self-diffusion rates of carbon atoms have been measured at a pressure of 10 GPa and temperatures of 1800–2100 °C (Koga et al., 2001, Fig. 1). The self-diffusion coefficient varies with temperature according to the following equation:

$$D \text{ (m}^2\text{/s)} = 4.1 \times 10^{-5} \exp\left(\frac{-6.8 \text{ eV}}{kT}\right) \quad (1)$$

The diffusion coefficient  $D$  is given in  $\text{m}^2/\text{s}$ ,  $k$  the Boltzmann's constant, and  $T$  the temperature in K. As discussed below, the measured rate of carbon diffusion is similar to the nitrogen diffusivity that is inferred from recent nitrogen aggregation experiments.

The pressure dependence of carbon self-diffusion has not been determined but is considered to be small compared to the variation with temperature along a subcontinental geotherm. The maximum estimate of the activation volume for diffusion is  $3 \text{ cm}^3/\text{mol}$  (Koga et al., 2001) using an elastic model discussed by Sammis et al. (1981). For this activation volume, a 1 GPa change in pressure leads to a change in diffusion coefficient of only about 30%. In contrast a

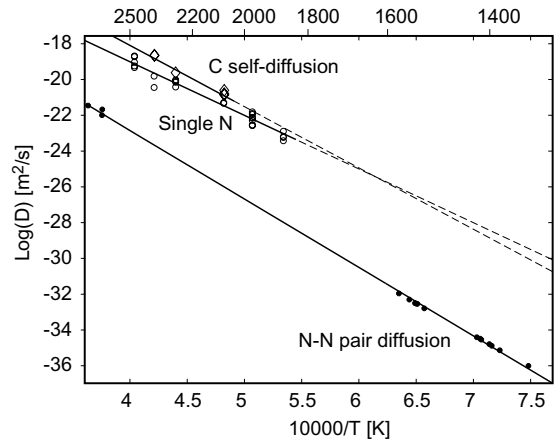


Fig. 1. Arrhenius relationships for carbon, single N, and N–N pair diffusion. The dotted segment of the Arrhenius line for carbon shows the region of data extrapolation. Open diamonds are C self-diffusion data (Koga et al., 2001), open circles are diffusion coefficients derived from single N aggregation data (Evans and Qi, 1982; Taylor et al., 1996), and closed circles are diffusion coefficients derived from paired N–N aggregation data (Evans and Qi, 1982; Taylor et al., 1990).

100 K increment in temperature leads to a factor of  $\sim 50$  increase in diffusivity.

Because diffusion coefficients could only be measured over a relatively small temperature interval in the study of Koga et al. (2001), there is a significant uncertainty in extrapolating Eq. (1) to the lower temperatures of the subcontinental lithosphere. It should also be noted that the nitrogen content of the type Ia diamonds studied by Koga et al. (2001) was  $\sim 200$  ppm, while over 90% of natural diamonds contain greater than 1000 ppm nitrogen. Because nitrogen impurities may be charge-balanced by introducing vacancies into the diamond lattice, and carbon is thought to diffuse by a vacancy mechanism, the results of Koga et al. (2001) may underestimate the diffusivity of carbon in diamonds with greater than 200 ppm nitrogen. However, because we lack information on the influence of nitrogen impurities on carbon self-diffusion (it is unclear whether C self-diffusion is intrinsic or extrinsic), we use the Koga et al. data without correcting for possible compositional effects to estimate the relaxation time for carbon isotopic heterogeneity. If diffusion is extrinsic and there is a linear relation between nitrogen concentration diffusivity, the

carbon diffusion coefficient in natural diamonds may be underestimated here by up to an order of magnitude.

### 3.2. Nitrogen diffusion

Although there have been no direct measurements of nitrogen diffusivity in diamond, estimates of the N diffusion coefficient can be obtained from kinetic studies of nitrogen aggregation. The formation of N–N pairs from the reaction of two nitrogen impurity atoms in diamond is analogous to diffusion-controlled chemical reactions in aqueous solvents (with diamond being the solvent in the present case). In order for the nitrogen atoms to form a pair, they must hop through the lattice until two nitrogen atoms meet on adjacent sites, and then they must bind together to form an attached pair. The rate of formation of N–N pairs is diffusion-limited if a bound pair is formed at every encounter between N atoms, and reaction-limited if many encounters are required before the N atoms react to form a pair. Given the large binding energy ( $\sim 2$  eV) of N–N pairs (Mainwood, 1994), a reaction to form N–N pairs is likely at every encounter between N atoms and the reaction is therefore almost certainly diffusion-limited.

In a diffusion-limited reaction there is a simple relationship between the diffusion coefficient and the second-order rate constant for the reaction, which can be written (e.g., Steinfeld et al., 1989; Schmalzried, 1995) as:

$$D_N = \frac{k_{N-N}}{8\pi r_{N-N}^2} \quad (2)$$

Here,  $r_{N-N}$  is the contact distance between bound nitrogen atoms, approximately 0.20 nm (Mainwood, 1994), and  $k_{N-N}$  is the rate constant for nitrogen aggregation. In writing this equation, it is assumed that there are no long-range interactions between nitrogen atoms (i.e., no interactions unless the N atoms are nearest neighbors) and that nitrogen aggregation is controlled by steady-state diffusion. The steady-state condition requires that  $D_N t / r_{N-N}^2 > 1$ , where  $t$  is the duration of the annealing experiment. Only experiments that met this condition were used to estimate nitrogen diffusivities. Diffusion coefficients were calculated from the experimental nitrogen aggregation results of Evans and Qi (1982) and Taylor et al. (1996)

using Eq. (2), and yielded the following Arrhenius relationship:

$$D_N \text{ (m}^2\text{/s)} = 9.7 \times 10^{-8} \exp\left(\frac{-6.0 \text{ eV}}{kT}\right) \quad (3)$$

Diffusion of single nitrogen atoms is slower than carbon by about a factor of 5 at the high temperatures of the diffusion and aggregation experiments. At temperatures of the subcontinental mantle, carbon and single nitrogen atoms are predicted to diffuse at similar rates.

The process by which B-centers form is probably similar to that for nitrogen pairs, but is thought to involve diffusion of nitrogen pairs themselves rather than single nitrogen atoms. Two nitrogen pairs react to form a B-center, with the kinetics controlled by diffusion of the nitrogen pairs if a reaction occurs at each meeting. The energy of a B-center is about 8.2 eV lower than that of two isolated nitrogen pairs and a vacancy (Mainwood, 1994). This very large binding energy implies that a reaction will take place each time two A-centers meet on adjacent sites, and therefore, as in the case of nitrogen pair formation, the kinetics are expected to be diffusion-controlled. The kinetics of B-center formation have been studied experimentally at high temperatures and pressures (9.5 GPa, 2400–2600 °C; Evans and Qi, 1982) and in natural samples for which the temperature history is reasonably well known (Taylor et al., 1990). We used an equation with the same form and value of  $r_{N-N}$  as Eq. (2) to calculate diffusion coefficients from the kinetic data of Evans and Qi (1982) and Taylor et al. (1990), with the resulting Arrhenius relationship:

$$D_{N-N} \text{ (m}^2\text{/s)} = 2.8 \times 10^{-8} \exp\left(\frac{-7.6 \text{ eV}}{kT}\right) \quad (4)$$

Diffusion of nitrogen pairs is many orders of magnitude slower than carbon or single nitrogen atoms (Fig. 1). Diamonds in which nitrogen has fully aggregated into A- or B-centers will lose nitrogen isotopic zoning patterns much more slowly than carbon isotopic zoning.

Chrenko et al. (1977) also present the diffusivity of single N atoms estimated by “a rule of thumb” equation,  $x^2 = Dt$ . However, we prefer the present model formulation (Eq. (2)) over that of Chrenko et al. (1977), since the “rule of thumb” method significantly overestimates diffusion coefficients. Furthermore, other recent N aggregation studies (Evans and Qi,

1982; Evans, 1992; Taylor et al., 1996) reported significantly slower rates of N aggregation than Chrenko et al. (1977). As a result of these factors, the diffusion coefficients estimated by Chrenko et al. (1977) are three to six orders of magnitude higher than those of Eq. (3); we excluded the data of Chrenko et al. (1977) from our model calculations.

#### 4. Results

Zoning profiles for carbon and nitrogen isotopes were calculated for times up to 1 billion years at a typical lithospheric mantle temperature of 1400 K (Figs. 2 and 3). Short wavelength features present in the initial profiles dissipate to smooth broader peaks as time progresses (Fig. 2a). For carbon, the decay of discrete wavelengths of heterogeneity can be seen in Fig. 2b and c. Only heterogeneity on the scale of  $\sim 1.6 \mu\text{m}$  or less is lost after a residence time of 1 billion years (defining “loss” as a 95% decrease in the initial amplitude at that wavelength). “Blurring” of carbon zoning profiles (defined as a 10% decrease in initial amplitude) is restricted to wavelengths less than  $\sim 8.0 \mu\text{m}$ . Nitrogen isotopic heterogeneity is even more resistant to diffusive relaxation (Fig. 3), due to the formation of very slowly diffusing N–N pairs. Nitrogen is converted to nearly 100% N–N pairs within the first 2 million years (for a diamond with 800 ppm total nitrogen). Within this time heterogeneity on the scale of  $\sim 0.1 \mu\text{m}$  or less is erased, and  $0.2 \mu\text{m}$  features are “blurred”. All features remaining after 1 million years are kept over 1 billion years, because N–N pairs are effectively immobile at 1400 K.

Because of the sluggish diffusivity of carbon and nitrogen in diamond at 1400 K, little disturbance of C and N isotope zoning profiles is expected under the conditions of the subcontinental lithospheric mantle. At higher temperatures significant annealing of isotopic heterogeneity may take place. Compiling homogenization length scales determined from calculations over a range of temperatures, we constructed contour plots that summarize a simple relationship between the wavelength of heterogeneity, annealing-time and temperature (Figs. 4 and 5). At 2000 K, annealing for 1 million years leads to the homogenization of carbon isotope zoning with  $\sim 200 \mu\text{m}$  wavelength (Fig. 4). Under the same conditions nitrogen isotope

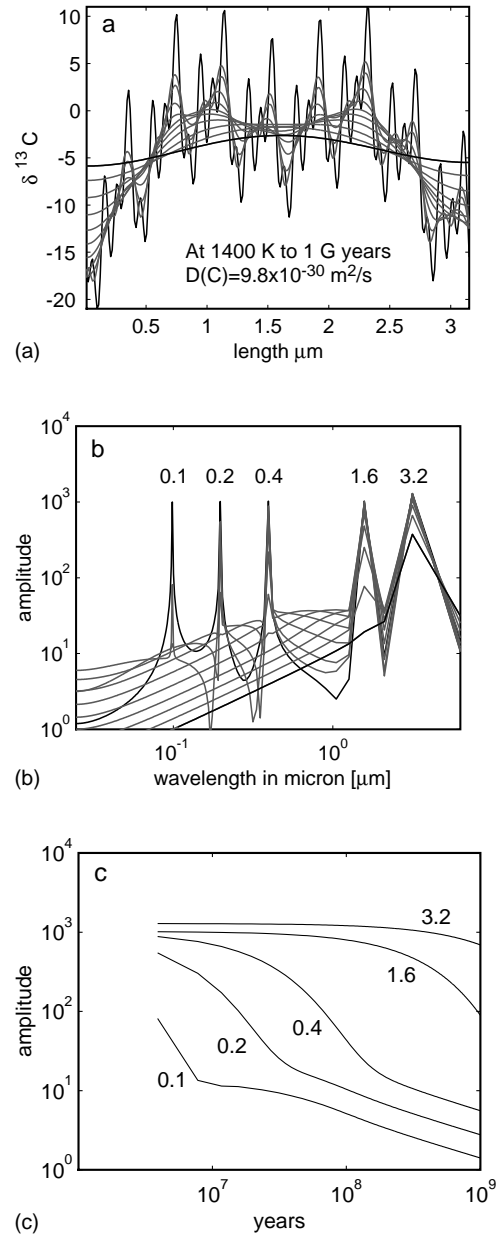


Fig. 2. (a) Diffusive relaxation of carbon isotope heterogeneity across a one-dimensional section of diamond. Each line shows the time progression of the concentration profiles, at time steps of 0, 2, 4, 10, 21, 43, 80, 152, 285, 533 and 1000 million years. (b) The isotopic variation with respect to distance (a) is converted to a periodogram of wavelength against amplitude by fast Fourier transform (FFT). The decay of short wavelengths with time is demonstrated as the disappearance of peaks. (c) The decay of characteristic wavelength peaks (determined by FFT) is shown with respect to time.

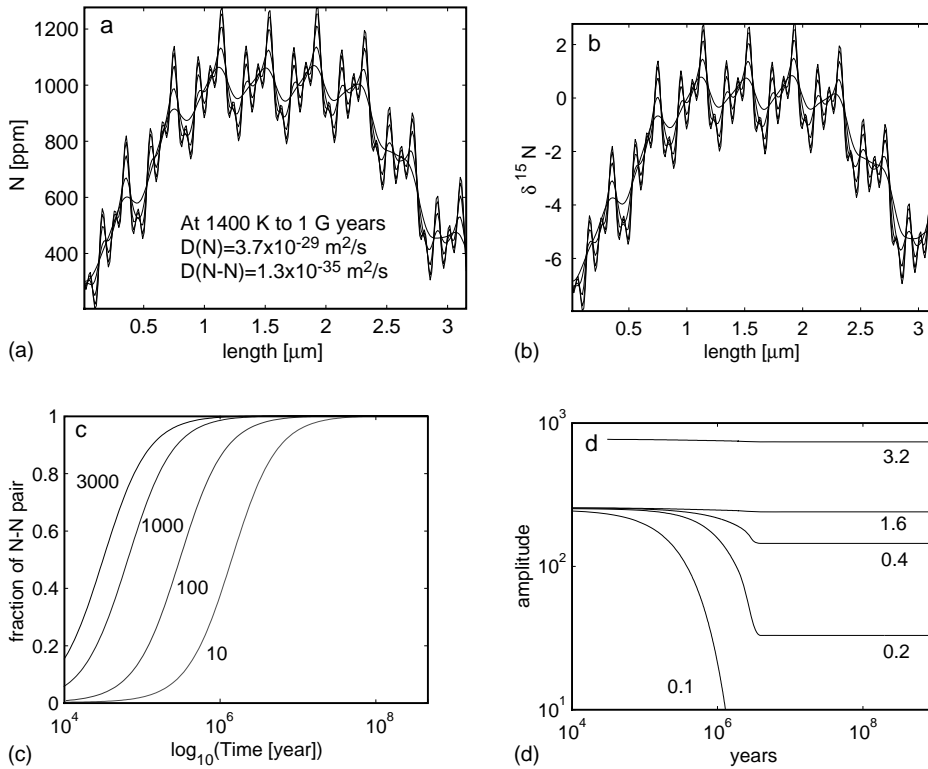


Fig. 3. (a) Heterogeneity of nitrogen concentration, and (b) nitrogen isotope ratio in diamond with 800 ppm total N. Time steps are the same as in Fig. 2. (c) Fraction of aggregated N–N pairs formed as a function of time. The function is [% aggregation of N–N] =  $1/(1 + kt[C_0])$ , where  $k$  is reaction rate constant, and  $[C_0]$  is initial concentration of nitrogen. The family of curves show 10, 100, 1000, and 3000 ppm of initial nitrogen abundance. Aggregation is nearly complete after 2 million years. (d) The decay of characteristic peaks determined by FFT is shown with respect to time.

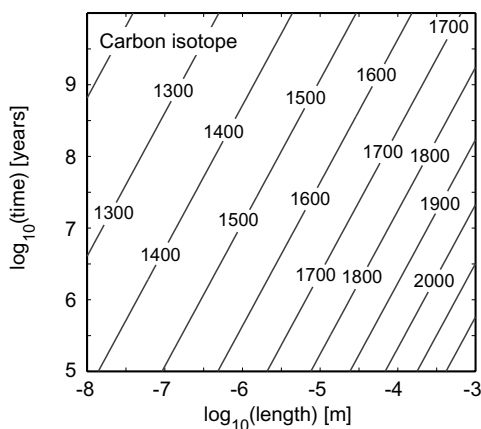


Fig. 4. Temperature contour plot showing the time required for relaxation of carbon isotope heterogeneity of different length scales. For example, at 2000 K, heterogeneity on a 650  $\mu\text{m}$  length scale is homogenized in 10 million years.

heterogeneity with  $\sim 0.8 \mu\text{m}$  wavelength is homogenized (Fig. 5).

The rate of nitrogen aggregation varies inversely with concentration, and therefore blurring of oscillatory features is slightly more extensive for lower nitrogen concentrations. More time is available before nitrogen atoms are effectively immobilized by N–N pair formation in low-N diamonds, and diffusive relaxation is therefore more extensive than in diamonds with higher N contents. This is important, however, only for very fine-scale features. Once the diffusion length scale approaches the average distance between N atoms, aggregation occurs and further diffusion effectively ceases. Thus, significant relaxation of N isotope zoning can only occur on length scales comparable to or less than the average distance between single nitrogen atoms in the diamond. This distance is generally in the range 30–100 nm for natural diamonds.

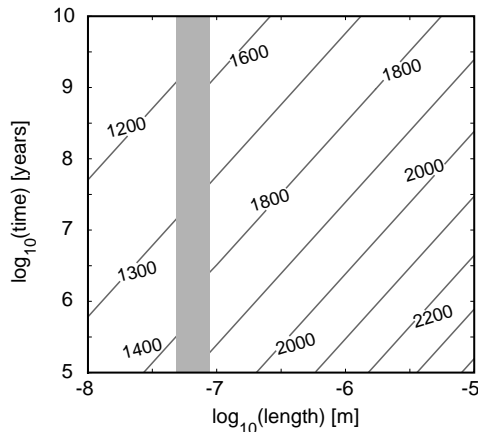


Fig. 5. Contour plot of nitrogen isotopic homogenization. The gray band marks a transition between relaxation controlled by diffusion of single N atoms on the left, and by slowly diffusing N–N pairs on the right. For applications of geological interest, the right-hand side of the figure is sufficient.

## 5. Discussion

Homogenization length scales of isotopic variation in a diamond from the subcontinental lithosphere are smaller than the current analytical resolution of the ion probe, even if the residence time is as long as the age of the Earth. In 1 billion years at 1400 K, carbon isotope heterogeneity of more than  $1.6 \mu\text{m}$  wavelength is preserved while nitrogen isotope and concentration heterogeneities are preserved on wavelengths greater than  $\sim 0.1 \mu\text{m}$  (Fig. 3). Deciphering the age of diamonds that have resided in the subcontinental lithosphere at temperatures of 1300–1600 K requires analytical resolution from 0.1 to  $16 \mu\text{m}$  for carbon isotopes and  $\sim 0.1 \mu\text{m}$  for nitrogen heterogeneity (Figs. 4 and 5). Spectroscopy may provide sub-micron spatial resolution, however, it does not allow the determination of isotopic abundance. The combination of spectroscopy and ion probe analyses provides the possibility of age determination, which will be better constrained for diamonds that have resided at very high temperatures for a considerable length of time.

Forward models of isotopic homogenization in diamond can provide strong constraints on the residence time for diamonds that have experienced temperatures of  $\sim 2000 \text{ K}$  or greater, corresponding to temperatures near the 670 km seismic discontinuity (Ito and

Katsura, 1989). Diamonds from Brazil have been reported to contain inclusions of the lower mantle minerals Mg- and Ca-perovskite, which would indicate residence in the lower mantle (e.g., Harris et al., 1997). If such diamonds reside in the lower mantle for 100,000 years, their carbon isotopic heterogeneity should be restricted to length scales of  $100 \mu\text{m}$  or greater (Fig. 4); any fine-scale zoning initially present would be erased at these conditions. These length scales are within the present resolution of the ion probe technique. Unfortunately, comprehensive isotopic data to which the forward modeling approach might be applied do not yet exist. However, it has been reported that the variation of  $\delta^{13}\text{C}$  within and among lower mantle diamond crystals is smaller than the variation observed in lithospheric diamonds (Hutchison et al., 1999). This is consistent with our prediction that carbon isotope heterogeneity will be significantly relaxed during any substantial residence at lower mantle conditions.

Nitrogen isotope profiles in diamond should be undisturbed at the present resolution of the ion probe technique even after millions of years at lower mantle temperatures ( $\sim 2000 \text{ K}$ ), or billions of years at subcontinental lithospheric mantle conditions (1300–1600 K). Thus we might expect a detectable difference in the minimum wavelengths of carbon and nitrogen isotope heterogeneity in diamonds that have been annealed for sufficient time at a high enough temperature for carbon zoning to become significantly relaxed. Carbon and nitrogen profiles that are initially correlated will begin to lose their correlation once diffusion of carbon has become detectable. As a rule of thumb, a perfectly correlated nitrogen and carbon isotopic profile will lose its correlation (correlation coefficient  $\sim 0.1$ ) when the non-dimensional number  $D_c t/x^2$  is approximately 0.16, where  $x$  represents the longest wavelength of isotopic variation.

Bulanova et al. (2002) observed a lack of strong correlation between nitrogen and carbon isotopic zoning profiles within a diamond from the Mir kimberlite. The variation of carbon isotopes in the reported diamond spans approximately 10% of the carbon isotope variation of peridotitic diamonds, while the variation of nitrogen isotopic compositions in the same diamond spans over 40% of the peridotitic diamond range. This may suggest partial relaxation of carbon isotope heterogeneity in this sample.

Harte et al. (1999), in an extensive ion microprobe study of diamonds from the Kaapvaal Craton found correlated zoning patterns (with  $\sim 100\ \mu\text{m}$  wavelength) of  $\delta^{13}\text{C}$  and N abundance in a peridotitic diamond (K3) from Koffiefontein, but no resolvable variation in carbon isotopes within diamonds from Bultfontein despite strong N zoning. The lack of  $\delta^{13}\text{C}$  zoning in the Bultfontein samples could be a growth feature, or may indicate post-growth diffusional relaxation of carbon isotope heterogeneity (Harte et al., 1999). To erase carbon isotope zoning on the  $100\ \mu\text{m}$  length scale would require residence at  $\sim 1600\text{--}1800\ \text{K}$  for 1 billion years (Fig. 4). These temperatures are much higher than temperatures determined from mineral thermometers in these samples (Harte et al., 1999 and reference therein), and it therefore seems unlikely that diffusional relaxation could account for the lack of carbon isotope zoning in the Bultfontein samples.

Fitzsimons et al. (1999) performed an ion probe and cathodoluminescence study of eclogitic diamonds from George Creek, Colorado, USA, and observed carbon isotopic variation within single crystals to be 10–60% of the worldwide carbon isotopic variation. The well-coordinated information on ion probe analysis locations and CL imaging are valuable for the forward model discussed here. Sharp and erratic variations in  $\delta^{13}\text{C}$  over  $\sim 50\ \mu\text{m}$  length scales (with  $20\text{--}40\ \mu\text{m}$  resolution), which are apparent in the sample GC030, suggest that the diamond did not reside at temperature conditions above  $1600\ \text{K}$  on billion year timescales (Fig. 4).

Improvements in the spatial resolution of ion probe analyses of nitrogen and carbon isotopes would allow more conclusive forward modeling for thermochronometry of lithospheric diamonds. A gain in resolution of a factor of 5–10 would make it possible to measure carbon isotopic zoning on wavelengths short enough to be blurred by residence at lithospheric mantle temperatures. While waiting for these technical developments, the authors stress the effectiveness of the present approach for determining the residence time of diamonds with lower mantle affinity.

## Acknowledgements

We thank Erik Hauri, Ben Harte and Wim van Westrenen for discussions and reviews which im-

proved the manuscript. This work was supported by JSPS postdoctoral fellowship for foreign researchers (KK), JSPS grant-in-aid for scientific research (MW, KK), and NSF grant EAR0074189 (JV).

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