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FTIR thermochronometry of natural diamonds: a closer look

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Abstract

FTIR is a commonly-used technique for investigating diamonds, but much of the most useful information is lost if spatially resolved measurements are not used. In this study we show examples of FTIR core-to-rim line scans, maps with high spatial resolution and maps with high spectral resolution that are fitted to extract the spatial variation of different nitrogen and hydrogen defects. Model residence temperatures are calculated from the concentration of A and B centres using known times of annealing in the mantle, and a new, two-stage aggregation model is presented that better constrains the thermal history of the diamond and that of the mantle lithosphere in which the diamond resided. The effect of heterogeneity within the analyzed FTIR volume is quantitatively assessed and errors in model temperatures that can be introduced by studying whole diamonds instead of thin plates are discussed. The spatial distribution of hydrogen associated with the 3107 cm^{-1} vibration does not follow the same pattern as nitrogen, and an enrichment of hydrogen at the boundary between pre-existing diamond and diamond overgrowths is observed. There are several possible explanations for this observation including a change in chemical composition of diamond forming fluid during growth or kinetically controlled uptake of hydrogen.

1. Introduction

Diamonds and their inclusions are some of the most valuable samples for elucidating the large scale geological history of our planet because they are the deepest sourced samples available for study, and in many cases, amongst the oldest. They form a key part of Earth's deep carbon cycle (Shirey et al., 2013). The very slow chemical diffusion rates in diamond combined with high resistance to changes in external physical and chemical environments result in diamonds behaving like time capsules over much of Earth history. Individual diamond crystals can therefore preserve a wealth of information on the nature of their growth conditions and subsequent storage in the mantle. While there have been significant developments in the study and interpretation of mineral and fluid

inclusions in diamonds in recent years (e.g. Stachel and Harris, 2008; Weiss et al. 2015; Thomson et al., 2016), there is still much to be learned from closer examination of the diamonds themselves.

Diamonds usually show zoned internal growth structures that can be complex with octahedral, cuboid or sectorial growth, multiple growth centres, dissolution and overgrowth features. These features can be detected with techniques such as photoluminescence, cathodoluminescence and optical birefringence and spatial discontinuities in isotopic compositions and infrared absorption features can commonly be observed. These zoning patterns provide an opportunity to extract a unique history of the nature of diamond forming fluids and can play an important part in understanding mantle processes such as metasomatism, input of subducted materials and changes in mantle conditions over geological time.

One measurement that is simple to perform and is therefore an essential part of nearly all systematic studies of suites of diamonds is Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectra are used mainly to determine the nitrogen concentration and the distribution of N between different defect centres, although several other parameters can also be measured. In many cases measurements are taken through whole diamonds, the assumption being that some sort of average or representative numbers are obtained. Of course, in the case of valuable gemstones this is the only option, as destruction of the diamond by slicing or breaking into smaller pieces is too costly. However, as we will show in this paper, reducing the available information to a single set of parameters not only misses the opportunities offered by more detailed sampling, but may in fact produce misleading information. The data presented in this study are from a range of spectra collected in our laboratory over the last five years and are selected to illustrate the opportunities and pitfalls of FTIR of diamond. The aims of this paper are: (i) to illustrate the heterogeneity that is common in natural diamonds; (ii) to provide guidance on the methods to extract the maximum information from the spatial distribution of N in diamonds; (iii) to describe a method for modeling the thermal histories of heterogeneous diamonds; (iv) to discuss the errors introduced by conventional FTIR methods on diamonds; (v) to show how the spatial distribution of the major hydrogen defect in natural diamonds provides important evidence for diamond growth conditions and (vi) to stimulate further developments in the use of spatially resolved FTIR spectroscopy of diamond.

2. Previous work on nitrogen defects and aggregation rates

Various absorption peaks in infrared spectra of diamonds were recognized as N-related as far back as the 1950s (e.g. Kaiser and Bond, 1959). A huge amount of work subsequently went into establishing the absorption envelope for each of the possible N-related defects, the quantitative relationships between the area of the peaks in the infrared spectra and the concentrations of the different N defects (e.g. Boyd et al., 1994, 1995) and determining the rate of conversion of single nitrogen centres (C-centres) to pairs of nitrogens (A centres) and subsequently to four nitrogens around a vacancy (B centres) (e.g. Chrenko et al., 1977; Allen and Evans, 1981; Evans and Qi, 1982). An important contribution to the literature, as far as geological applications are concerned, was the work of Taylor et al (1990) who established the activation energy and pre-exponential factor that controlled the rate of the 2nd order kinetic process of conversion of A to B defects. In a later paper on the kinetics of C to A aggregation (Taylor et al., 1996) slightly revised values of the constants for A to B aggregation based on unpublished work by Cooper (1990) were quoted. It is these latter values that are incorporated into a widely used, but unpublished, Excel spreadsheet distributed by Dr Judith Milledge. We will also use them here. In summary the nature of the kinetics as outlined by Taylor et al. (1990) is as follows: The rate of conversion of A to B is given by

$$-\frac{d[A]}{dt} = k_2[A]^2 \quad \text{equation 1}$$

where $[A]$ is the concentration of A at time t and k_2 is the second order rate constant. The integrated form of equation 1 is

$$[A]_t = \frac{[A]_0}{1 + k_2 t [A]_0} \quad \text{equation 2}$$

where $[A]_t$ is the concentration of A at time t , $[A]_0$ is the initial concentration of A (equivalent to total nitrogen concentration as it is assumed that all C aggregates to A before any A aggregates to B) and k_2 is given by

$$k_2 = A. e^{-\frac{E_a}{RT}} \quad \text{equation 3}$$

where T is temperature (in kelvin), $\mathbf{A}$ (note the boldface) is the pre-exponential factor and E_a is the activation energy for the A centre to B centre transformation. The values used here are $E_a = 7.0 \text{ eV}$ and $\ln \mathbf{A} = 12.59$ (Taylor, 1996).

As pointed out by many authors the final measured aggregation state is much more sensitive to temperature than time, so given a known diamond age and exhumation age, nitrogen aggregation can be used as a geothermometer. It is important to note that the temperature recorded reflects the temperature history of the diamond during its residence in the mantle (*after growth*) and is therefore different from temperatures derived from mineral geothermometers based on inclusion chemistry which record the inclusion trapping temperature (*during growth*). Further, if the temperature varies during the period of mantle residence, the temperature recorded by nitrogen aggregation is not simply an average over the period of residence. A short period of elevated temperature would have a disproportionately large effect on aggregation; we therefore refer to the temperatures derived from nitrogen aggregation as *model temperatures*. In this paper we will only consider examples of diamonds containing A and B defects and the rate of A to B aggregation, as this is the most common situation for natural diamonds. However exactly analogous discussion could be made for diamonds containing C and A centres and the kinetics of C to A aggregation.

3. Experimental methods

3.1 Sample preparation

Infrared spectroscopy, as implemented here, is a transmission technique that involves focusing an infrared beam using a parabolic mirror. If the sample is very thin, the spatial resolution can be on the order of a few microns (the diffraction limit). However, in practice there is an optimum thickness for a slice of diamond. If the slice is too thin the signal-to-noise ratio becomes problematic for fast acquisition of maps with many pixels, and interference fringes resulting from multiple scattering between top and bottom of the plate obscure important absorption information. If the slice is too thick, spatial resolution is compromised because of the cone-shaped sampling of the slice that results from the focussing geometry. The optimum thickness for diamond seems to be around 300 microns. Diamond plates were prepared in the conventional way by polishing using a diamond impregnated scaife and orienting the diamond parallel to the $[110]$ direction (Bulanova et al., 2005).

3.2 Collection of infrared spectra. Single points vs. line scans vs. maps

Infrared spectra, line scans and maps were collected using a Thermo Nicolet iN10MX infrared microscope. The diamond plates were suspended between two razor blades, and attached to the blades at two corners using double-sided adhesive tape. Using this arrangement, some parts of the diamond are not available for infrared transmission measurements, but in many cases the parts that were obscured were the unpolished octahedral apices of the diamonds, that would not have been suitable for measurements. The alternative possibility of placing the diamond plates on infrared-transparent BaF₂ discs was less successful because of the frequent appearance of interference fringes in the spectra, presumably related to the air gap between the diamond and the plate.

When collecting FTIR data on diamonds there is a tradeoff between spectral resolution, spatial resolution and time. Some of the peaks in the spectra are rather narrow, so 2 cm⁻¹ spectral resolution is required for all but the roughest work. With 2 cm⁻¹ resolution, high quality spectra can be obtained in a matter of minutes even with a small sample aperture of 25 x 25 µm. Time of acquisition only becomes an issue with long line scans or maps. In the case of a map with 70 x 70 pixels, 15 s per spectrum would give an achievable acquisition time of 20 hours. For a diamond that is, for example 3 mm x 3 mm, this would give a step size of 43 µm which is larger than desirable. The iN10MX has a feature called ultrafast mapping that enables maps with low spectral resolution (16 cm⁻¹) to be collected at a rate of 0.1s per pixel. For the same 3 x 3 mm diamond, this allows a 3000 x 3000 micron grid with a 20 micron step size to be acquired in 40 minutes. These ultrafast maps are excellent for visualizing the internal structure of the diamond and for locating small features that may not be easy to observe with a larger pixel size, but the individual spectra are of low quality and not suitable for observing narrow peaks or for spectral decomposition and extraction of quantitative values for the concentrations of the different defects. Thus the best strategy is to first collect an ultrafast map for an overview of the sample, then to choose line scans (especially those that explore zoning from core to rim) and if necessary a high-quality map. To obtain maps where the individual spectra can be quantitatively fitted, a larger step size and a 2 cm⁻¹ resolution was used.

Single spectra can be processed using the widely used Excel spreadsheet, CAXBD97n written by D. Fisher (De Beers Technologies, Maidenhead), and line scans of up to perhaps 30-40 points could also be fitted individually using that method. For maps, which might contain several

thousand individual spectra, automated processing using software such as Diamap (Howell et al., 2012) is required. For consistency all the spectra presented here (linescans and maps) were processed using a Python program being developed in this laboratory by Laura Speich and Simon Kohn. In this program the baseline is fitted by subtracting a first order polynomial curve, the variable parameters of which are set such that the difference between the corrected spectrum and a reference type IIa diamond spectrum is minimized in the regions 1500-2312 cm^{-1} , 2391-3000 cm^{-1} and 3800-4000 cm^{-1} . The software has a range of functionalities, but in this paper we will focus on total nitrogen concentration, A and B defect concentrations, spatial distribution of the 3107 cm^{-1} defect and the calculated model temperature.

4. Results

4.1 Line scans of diamonds from the Murowa kimberlite, Zimbabwe.

Mur 70 is a diamond from Murowa, Zimbabwe that has an octahedral external morphology and contains a peridotitic garnet inclusion (Bulanova et al., in review). Figure 1 shows the results of a line scan across diamond Mur 70 plotted in the conventional way with log N vs %1aB. This style of presentation is the standard one used in the geological literature, and demonstrates that the annealing temperature implied by most points is about 1140°C, but it is of limited value as it contains no spatial information for the points. A better way to present the data is as a function of distance or point number across the transect, shown in figure 2. Panel (a) shows the intensity at the position of the main B peak in an ultrafast map data set. It shows the concentric zoning structure and the arrow shows the location of the core-rim high quality linescan used for (d)-(g). Panels (b) and (c) are cathodoluminescence images of the two sides of the plate. Panel (d)-(g) are based on rigorous fitting of high quality spectra. Panel (d) shows the variation in the concentrations of total N and A and B defects as a function of distance on a core-to-rim traverse. The total N increases smoothly from the core, then drops before rising rapidly to a plateau and finally dropping to a low value with a small increase right at the rim. The cause of the variation in N concentration is not yet fully understood but in some way reflects either the equilibrium N concentration of the diamond in response to changing composition of the fluid from which the diamond grew and/or disequilibrium effects such as growth rate. Panel (e) shows the %1aB which is used in the calculation of model temperature and panel (g) shows the calculated model temperature for each point based on a mantle residence time of 2.7 Ga (Smith, et al. 2009; Smith, et al. 2004). The real significance of these

numbers will be discussed in section 5.1. The area of the 3107 cm⁻¹ peak, which has recently been shown to arise from a vibration of the VN₃H group (Goss et al., 2014) is shown in panel (f). The significance of these data will be discussed in section 5.3.

Figures 3 and 4 show similar data to figures 1 and 2, but for a different diamond, Mur 33, another peridotitic diamond containing a chromite inclusion (Bulanova et al., in review). The conventional plot of log N vs %1aB again shows the majority of points close to the 1140°C isotherm, with some points at higher temperatures, but the lack of spatial context makes it difficult to extract much useful information. Figure 4 shows that (as for Mur 70 in Figure 2) there is a complex variation in N concentration from core to rim, with a corresponding variation in A, B and %1aB parameters. The main difference is that the model temperature at the rim is essentially the same as at the core. The most notable feature is the excursion to higher temperatures between points 30 and 40. It is not possible for the model temperature to be higher in a core or intermediate zone than in the rim, so this *must* be an artifact and the origin of the artifact will be explained in section 5.2.

4.2 Line scan of diamond from Machado River placer deposit, Brazil.

A comprehensive study of diamonds from Machado River, Brazil is included in the present volume (Burnham et al., 2016), and one diamond, P16, has exceptionally interesting N zoning features. This diamond is peridotitic, with an olivine inclusion in the core, but no inclusions in the outer zones. Unfortunately no dates are available so it is not possible to perform a rigorous thermal modeling calculation. For the purposes of this study we will assume an arbitrary mantle residence time of 2 billion years.. The ultrafast map (Figure 5a), cathodoluminescence (figure 5b) and birefringence (figure 5c) all demonstrate a well defined zonal structure, with a sector zoned, high N core and a low N overgrowth. At the edge another thin N-bearing zone can be seen in the ultrafast map (figure 5a). As there are other diamonds from Machado River with a superdeep origin, it is tempting to suggest that the low N overgrowth (around 20 ppm N) with “tatami” patterned anomalous birefringence is a superdeep overgrowth on a diamond core of lithospheric origin. Figure 5 d-g show the results of fitting a high quality line scan. The model temperature for the core is constant at about 1240°C, but the spectra for the low N zone are not of sufficient quality to calculate a reliable model temperature. The thin outer rim gives a model temperature of 1120±20°C. Unless the second of the three stages of diamond growth was very close to the exhumation date (and our

choice of 2 billion years residence is a gross overestimate), it seems that the model temperature of the core is too low to be consistent with an overgrowth of sublithospheric diamond and a period of residence at sublithospheric pressures and temperatures.

4.3 Line scan of diamond from the Argyle lamproite, Australia

Diamonds from Argyle are unusual in that they appear to originate from deeper than most other lithospheric diamonds, and show extensive plastic deformation. Many of the diamonds from Argyle have extreme zoning in terms of N concentration (and hence N aggregation). One of the most spectacular examples is Arg26 (figure 6). It mostly has low N (around 30 ppm) but with some very N rich zones with up to 1000 ppm N. By comparison with other diamonds in the suite, Arg 26 is assumed to be eclogitic and hence have a mantle residence time of 400 million years (Richardson, 1986). The model temperature is essentially constant despite the large variations in N, but there is more noise in the model temperature calculation compared with Mur 70 and Mur 33 because (i) there are zones with very low N concentration and (ii) there are zones with very high aggregation, so quantification of A concentration (and hence %1aB) is more difficult. The most precise model temperatures can be obtained for points with high N concentration and approximately equal concentrations of A and B, so this diamond represents a far from optimal case. The relatively constant model temperature across the diamond therefore provides a good validation of the method. Panel (f) shows the area of the 3107 cm^{-1} peak, and in this case it closely follows the profile of N concentration.

It has been suggested previously that plastic deformation enhances the rate of nitrogen aggregation, but data from this diamond (and others from Argyle) provides no evidence to support this hypothesis.

4.4 Map of diamond from the Murowa kimberlite, Zimbabwe.

Figure 6 shows some two-dimensional distributions of features in another diamond from Murowa, Mur 265. The parageneses of Mur 265 is unknown as it does not contain any inclusions, but based on other diamonds from the suite it is likely to be peridotitic. The cathodoluminescence image (figure 6a) suggests that there is a small inner core of cuboid growth, with the majority of the stone having a fairly featureless bright luminescence. Overgrown on the core there is a rim with oscillatory zoning. The main features can be seen in the ultrafast map shown in figure 6b (the colour

scale represents the height of the absorption at the main B frequency), notably a low N inner core, a homogeneous main core and some narrow zones in the rim. Panels (c) to (f) are quantitatively fitted from a data set with higher spectral resolution than the ultrafast map in (b), but lower spatial resolution. (c) shows the %1aB, (d) shows the area of the 3107 cm^{-1} peak (note the H rich cuboid core and the narrow zone of H enrichment at the boundary between core and rim – see section 5.3), (e) shows the total nitrogen concentration and (f) shows the model temperature. The map of model temperature is particularly interesting as it shows fairly constant values of about 1140°C in the core and about 1110°C in the rim. This is unequivocal evidence for a overgrowth of a rim that is significantly younger than the core. The best way to extract information on the overall thermal history of the diamond will be the subject of the next part of this paper.

5. Discussion

5.1 Thermal modeling

Most of the diamonds we have studied are heterogeneous in terms of nitrogen concentration (N_{tot}); the examples described in this paper are not unusual. In some cases there is a gradual variation of N_{tot} , in others there are sharp discontinuities and frequently there is oscillatory zoning. Many diamonds show all of these types of zoning. In many diamonds, the variation in A and B defect concentrations that accompanies variation in N_{tot} is such that each pixel gives the same model temperature. In other diamonds there is a very clear discontinuity between a core with a higher model temperature and a rim with a lower model temperature. Let us consider how such features can and cannot be explained. Firstly, it should be remembered that model temperatures are calculated with an assumption of diamond residence time in the mantle, that is usually based on some radiometric dating of inclusions either within that particular sample, or more commonly of other diamonds from the same suite. Fortunately, for typical residence times of diamonds of greater than 1 Ga, uncertainty in time does not have a huge influence on the model temperature. So the case of a diamond with, for example, a 1140°C model temperature core and 1100°C model temperature rim, one of the few explanations that is not possible is that the core resided in the mantle at 1140°C and then that the rim grew and then the diamond resided at 1100°C ! The reason is that the model temperatures are based on the same assumed mantle residence time, which cannot be correct if the rim is younger than the core. As we can be absolutely certain that the core of the diamond predates the rim, the best way to understand the nitrogen aggregation in the two parts is to split the history of

the diamond into two stages. Firstly the core grows over a period of time that can be assumed to be effectively instantaneous on the timescale of N aggregation, secondly the core resides in the mantle for a period t_1 at temperature T_1 . Next there is second period of diamond growth which again can be assumed to be instantaneous followed by a second residence period in the mantle, t_2 at temperature T_2 . Finally the diamond is exhumed from the mantle by a kimberlite or other magma, brought to the surface and nitrogen aggregation ceases. If the age of inclusions in the core of the diamond and the date of exhumation are known, we know t_1+t_2 . If we assume that the temperature during each of the two stages is constant, with values of T_1 and T_2 respectively we can constrain the temperature-time history of the diamond. Firstly, for the core, the concentration of A at time t_1 can be described by

$$[A]_{t_1} = \frac{[N]}{1 + x \cdot t_1 \cdot [N]} \quad \text{equation 4}$$

this is a variation of equation 2 where the initial concentration of A is replaced by total nitrogen concentration, since the C to A aggregation will be effectively complete before significant A to B aggregation occurs. x is the second order rate constant for temperature T_1 , given by

$$x = A \cdot e^{-\frac{E_a}{RT_1}} \quad \text{equation 5}$$

where A and E_a are taken from Taylor et al (1996).

For the second stage of aggregation in the core, the concentration of A at time t_2 is given by

$$[A]_{t_2} = \frac{[A]_{t_1}}{1 + y \cdot t_2 \cdot [A]_{t_1}} \quad \text{equation 6}$$

since the starting concentration of A during the second stage of aggregation is $[A]_{t_1}$. y is the second order rate constant for temperature T_2 , given by

$$y = A \cdot e^{-\frac{E_a}{RT_2}} \quad \text{equation 7}$$

For the rim there is only one phase of aggregation, with a duration of t_2 and temperature T_2 , so the correct rate equation is

$$[A]_{t_2} = \frac{[N]}{1 + y \cdot t_2 \cdot [N]} \quad \text{equation 8}$$

The result of these equations is that there is a range of solutions that can explain the data. If the rim is considered first, for a given value of N concentration and aggregation a short t_2 implies a high value for T_2 , and a longer t_2 implies a lower T_2 . But if $t_1 + t_2$ is fixed, a short t_2 implies a long t_1 and hence a low T_1 . The logic can become complicated, so the easiest way to constrain the options is to make a plot of t_1 and t_2 vs T .

As an example of this idea, Figure 8 is based closely on the data for Mur 70. The initial diamond growth is assumed to be at 3.2 Ga with exhumation at 0.5 Ga, giving a total time in the mantle ($t_1 + t_2$) of 2.7 billion years (Smith et al., 2009). Following the explanation above, the concept that is explored here is that the following events took place.

- (i) Growth of the core of the diamond at 3.2 Ga.
- (ii) A period of constant temperature (T_1) residence in the mantle. This is known as the first stage of annealing.
- (iii) Growth of the rim at an unknown time between 3.2 and 0.5 Ga.
- (iv) A second period of constant temperature (T_2) residence in the mantle. This is known as the second stage of annealing.

To reiterate, the key point is that nitrogen in the core aggregates during both stages one and two, but nitrogen in the rim can only aggregate after the formation of the rim, i.e. during the second stage. To produce the observed aggregation in both core and rim there is an interplay between the timing of rim growth and the temperatures during the two stages of annealing. The blue circles and green squares in figure 8 represent the pairs of temperatures that would have prevailed during the first and second stages of annealing for the time of rim growth (relative to initial growth) shown on the x-axis. So, for example if the rim grew at 2.7 Ga, or 500 million years after the core, the temperature during the first stage of annealing is implied to be 1176 °C and the temperature during the second stage of annealing is implied to be 1109 °C. Thus the temperature experienced by the diamond in the lithosphere during the second stage of annealing is 67 °C lower than during the first stage. This is perhaps reasonable, bearing in mind the secular cooling of the mantle and diffusive cooling of the cratonic lithospheric roots over the span of geological time. If instead we assume that the

temperature experienced by the diamond was constant over its whole history in the mantle prior to exhumation, we can date the timing of the rim growth by the crossing of the two lines. This occurs at 2115 million years after the growth of the core and implies a temperature of 1139 °C. It could be argued that the rim is a late stage feature, perhaps growing shortly before exhumation from a fluid related to the kimberlite melt that transported the diamond to the surface. The calculations imply that for growth of the rim 1 million years before exhumation the temperature of the first stage would be 1134°C but the short second stage would be at 1317°C. If the second stage were only 1000 years long the temperature would rise to 1565°C. For very short times the temperature would be sufficiently high (at the pressures of the lithosphere) for diamond to become unstable with respect to graphite, and also hotter than any likely temperature conditions in the melt. There is therefore a constraint to the possible timing of the overgrowth.

It should be emphasized that the assumption of constant temperature during the two phases of annealing is clearly a simplification, but this approach nonetheless provides a substantial improvement on the conventional analysis and interpretation of FTIR data for diamonds. One aim of future work is to identify diamonds with multiple inclusions, distributed between growth zones of different ages. If two dates for separate growth events could be identified in the same diamond (i.e. t_1 and t_2 were both known), a diagram such as the one in figure 8 would give valuable information on the thermal evolution of the mantle lithosphere.

5.2 Problem with overlapping zones

In section 4.1 it was noted that a physically unrealistic “kick up” in model temperature can be seen in the line scans for Mur70 and Mur33. This experimental artifact is seen in many of the line scans and maps recorded in this laboratory (many more than the examples presented here) but it can be explained and indeed quantitatively predicted as follows. In an idealized scenario, the volume of diamond sampled by the infrared beam is homogeneous with respect to nitrogen concentration and hence (for a given thermal history) aggregation state. This would always be the case if the sampled volume were infinitely small, but as explained in section 3.2 there is a practical limit to the volume sampled, and this causes predictable deviations from the correct model temperature. This can be best explained using the following hypothetical example. Consider a diamond with three zones, core, intermediate and rim that all formed so closely in time that they can be considered to have the same mantle residence time of 2.7 Ga. The core contains 1600 ppm N

which is 82% aggregated to 1aB, the intermediate zone has 100 ppm N at 22% aggregation and the rim zone is the same as the core with 1600 ppm N and 82% aggregation (figure 9a). If the volume sampled by the infrared beam were infinitely small, every measured point on the diamond would give a model temperature of 1140°C, however for realistic analyzed volumes, there will be points at the boundaries between zones that sample a mixture of the two zones (figure 9b). If, for example the analyzed volume consists of 10% of the high N zone and 90% of the low N zone, the apparent N concentration would be $((0.1 \times 1600) + (0.9 \times 100))$ ppm or 250 ppm, but the apparent N aggregation would be $((0.1 \times 1600 \times 82) + (0.9 \times 100 \times 22))/250$ or 60.4% 1aB. Thus the apparent N concentration is reduced from 1600 to 250 ppm, but the apparent N aggregation is only reduced from 82% to 60.4%. The effect of this mixing is to produce an anomalously high apparent temperature for the points where two zones overlap. The model temperature for this example is shown in figure 9c. The effect will be most pronounced where there is a large difference between N concentrations in the two zones, but is predictable if the N concentrations and aggregation states of the two zones are known.

The considerations described here also apply to FTIR measurements on whole diamonds. If a whole diamond (whether in its natural morphology or cut as a gemstone) is studied by FTIR the resulting spectrum will be an integration of the whole path length through the diamond. As we have seen for Arg26 the nitrogen concentration can be zoned in very complex ways. If we imagine a diamond with 20% of the analyzed volume with 900 ppm N, 20% of the analyzed volume with 500 ppm N and 60% of the analyzed volume with 20 ppm N and a “true” model temperature of 1150°C the apparent model temperature would be 1170°C, the 20°C discrepancy being due purely to the predictable effect of heterogeneity within the diamond.

5.3 The relationship between N and H concentration in natural diamonds.

One of the most prominent features of FTIR spectra of diamonds is the narrow peak at 3107 cm^{-1} . This peak was observed as early as the 1950s, and has long been associated with some sort of H-related vibration (see Fritsch et al. 2007 for a historical review). Recently a convincing attribution of the peak to VN_3H has been made by Goss et al (2014). It is often stated that there is a correlation between N concentration and the height or area of the 3107 cm^{-1} peak (e.g. Goss et al., 2014). However, our detailed studies of line scans and maps have shown that this is not always correct. Whereas for Arg26 the profiles for total nitrogen concentration and 3107 cm^{-1} area do

match closely, for Mur70, Mur33 and Mur 265 there is no such correlation. A common feature we have observed is that there is a maximum in the intensity of the hydrogen-related 3107 cm^{-1} peak at the interface between the core and rim region of the diamonds. This is seen clearly in the line scan for Mur 70 and most impressively in the map for Mur 265. As diamond with high 3107 cm^{-1} often has cuboid growth (Fritsch et al., 2007) (for example in the core of Mur265) and the initial growth habit of diamond core zones is often cubic or cubo-octahedral (Bulanova, 1995) it is tentatively suggested that the second stage of diamond growth shows a similar effect. It is possible that diamond growth is initiated by the ingress of a hydrogen-rich fluid, and that as growth progresses the chemical composition of the fluid evolves to become less H-rich. Alternatively the first diamond growth is rapid and the elevated H concentration is associated with some non-equilibrium effect. It has also been suggested that the incorporation of H changes the kinetics of N aggregation, but there is no evidence for that effect in our data.

6. Future work

The approach taken here shows that there is a wealth of information that can be extracted from spatially resolved FTIR studies of diamonds that most previous studies have not used. The detailed variation in nitrogen and hydrogen (at least the hydrogen responsible for the 3107 cm^{-1} vibration) concentrations and the core-to-rim variation in model temperature provide valuable constraints on the history of diamond growth and storage in the mantle. However the limitation in terms of a unique thermal history for individual diamonds is that there is an interplay between annealing time and age. One approach towards obtaining a unique thermal history is to use diamonds with dated inclusions in different growth zones. This would be an ideal scenario but it is difficult to implement. An alternative approach that we are pursuing is to investigate alternative defect reactions that may have different activation energies from that for A to B aggregation. If successful this would allow unique temperature-time paths for diamonds (and hence the mantle lithosphere) to be defined, even for diamonds without inclusions. Possible candidate reactions are the growth of platelets, the degradation of platelets or the evolution of hydrogen containing defects.

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Figures.

Figure 1. Data from a core-rim line scan on Mur 70 plotted on a conventional plot of %1aB vs log N. The step size is 10 microns, the infrared beam was apertured to 20 x 20 microns at the sample. Many data points fall close together on the 1140°C isotherm and there are some points on a higher isotherm and some below. As this plot does not include any information on how each point relates to position within the diamond it is of limited value.

Figure 2. (a) an ultrafast map of Mur70 with the hotter colours representing higher infrared absorption at the frequency of the B defect vibration. (b) and (c) cathodoluminescence images of both sides of the diamond plate. (d) to (g) the same data as figure 1 from a core-rim line scan on Mur 70, but with the results of fits presented as a function of point number. (d) is the fitted A (green), B (red) and total N (blue) concentrations, (e) is % 1aB, (f) is the area of the 3107 cm⁻¹ vibration and (g) is the model temperature for each point based on a mantle residence time of 2.7 billion years.

Figure 3. Data from a core-rim line scan on Mur 33 plotted on a conventional plot of %1aB vs log N. The data were extracted from a high-resolution map. Many data points fall close to the 1140°C isotherm but there are a significant number of points that plot at higher temperatures. The lack of spatial information in the plots make it impossible to explore the explanation for the higher temperature points.

Figure 4. (a) an ultrafast map of Mur 33 with the hotter colours representing higher infrared absorption at the frequency of the B defect vibration. (b) and (c) cathodoluminescence images of both sides of the diamond plate. (d) to (g) the same data as figure 2 from a core-rim line scan on Mur 33, but with the results of fits presented as a function of point number. (d) is the fitted A (green), B (red) and total N (blue) concentrations, (e) is % 1aB, (f) is the area of the 3107 cm⁻¹

vibration and (g) is the model temperature for each point based on a mantle residence time of 2.7 billion years.

Figure 5. (a) an ultrafast map of P16 with the hotter colours representing higher infrared absorption at the frequency of the B defect vibration. (b) cathodoluminescence image of one side of the diamond plate. (c) optical birefringence (d) is the fitted A (green), B (red) and total N (blue) concentrations from a high quality linescan, taken with a step size of 10 microns, the infrared beam was apertured to 20 x 20 microns at the sample. (e) is % 1aB, (f) is the area of the 3107 cm⁻¹ vibration and (g) is the model temperature for each point based on a mantle residence time of 2.0 billion years.

Figure 6. (a) an ultrafast map of Arg26 with the hotter colours representing higher infrared absorption at the frequency of the B defect vibration. (b) and (c) cathodoluminescence images of both sides of the diamond plate. (d) is the fitted A (green), B (red) and total N (blue) concentrations from a high quality linescan, with step size of 25 microns, the infrared beam was apertured to 25 x 25 microns at the sample. (e) is % 1aB, (f) is the area of the 3107 cm⁻¹ vibration and (g) is the model temperature for each point based on a mantle residence time of 0.4 billion years.

Figure 7. Two dimensional maps of the distribution of defects in Mur 265. (a) is cathodoluminescence, (b) is an ultrafast map with the hotter colours representing higher infrared absorption at the frequency of the B defect vibration, (c) to (e) are the results of fitting the high-quality dataset using a step size of 50 microns, with the infrared beam apertured to 50 x 50 microns at the sample. (c) is %1aB, (d) is the area of the 3107 cm⁻¹ peak, (e) is the total nitrogen concentration and (f) is the model temperature, based on a mantle residence time of 2.7 billion years.

Figure 8. An illustration of thermal modelling for Mur 70. The x-axis represents the time since the initial growth of the diamond at 3.2 Ga. Exhumation of the diamond occurred 2700 million years after growth, and the solid line at 3200 million years represents the present day. The grey shaded area is the time interval since exhumation where no significant aggregation can have occurred. Each pair of coloured symbols at a given time represents the temperature required during each stage of annealing to reproduce a core with 1600 ppm N and 82% 1aB and a rim with 400 ppm N and 20%

1aB. The two vertical dotted lines represent two possible scenarios. The grey dotted line is for a rim growth 500 million years after core growth (i.e. at 2.7 Ga) which, reading across to the temperature axis implies temperatures of 1176 °C and 1109 °C during the first and second stages of annealing. The pink dotted line is for the unique time of 2115 million years after the growth of the core where the temperature can be constant (at 1139 °C) during the whole history of the diamonds in the mantle.

Figure 9. Cartoon illustrating the effect of overlapping zones on the model temperatures calculated using FTIR. (a) Schematic plan view of a 110 plate of a diamond with three zones having different nitrogen concentrations and nitrogen aggregation. The three zones are all of the same age with a 2.7 Ga residence time in the mantle and the whole diamond experienced a constant temperature of 1140°C through the residence time in the mantle and each of the three zones would give a model temperature of 1140°C. (b) Zoomed area of (a) with a schematic line scan from core to rim across the sample. Eight of the points lie entirely within one or other of the homogeneous zones, but two (those marked with arrows) lie at boundaries with either 10% high-N zone and 90% low-N zone or 50% of the analysed volume in each zone. (c) Plot of the calculated model temperature as a function of the % high-N zone in the analysed volume. The model temperature can be as much as 19°C higher than the true residence temperature, and for these parameters the largest overestimate of the temperature occurs at 10% high-N zone mixed with 90% low-N zone.