Toward a Robust Elastic Geobarometry of Kyanite Inclusions in Eclogitic Diamonds

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Robust elastic geobarometry of kyanite inclusions in eclogitic diamonds

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Abstract

Here we report, the first results from elastic geobarometry applied to a kyanite inclusion entrapped within an eclogitic diamond from Voorspoed mine, South Africa. The investigation involved the application of micro-Raman spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, single-crystal and micro-powder X-ray diffraction, electron microprobe analysis, ab-initio calculations and finite element modeling. The investigated diamond contained at least five inclusions of kyanite, one inclusion of eclogitic garnet and one epigenetic multiphase inclusion, very close to the diamond surface, composed of hematite, quartz, iron-sulfide and plagioclase. For this study we selected one of the kyanite inclusions not showing any evidence of fluid rims and/or fractures at the diamond-inclusion interface. Application of elastic geobarometry to very elastically anisotropic kyanite inclusions is challenging, as current models do not allow for elastic anisotropy. In order to minimize the effects of anisotropy, we have explored the effects of deviatoric stress on Raman modes via ab-initio density functional theory. The results allowed us to select the Raman mode (at ca. 638 cm^{-1}) that is the least sensitive to deviatoric stress. The shift of this band in the inclusion still trapped within the diamond relative to the inclusion in air was used to determine a residual pressure on the inclusion of 0.184±0.090 GPa. By using this value and an isotropic thermoelastic model we calculate an entrapment pressure of 5.2±0.2 GPa (~ 160 km depth) for an FTIR N-aggregation residence temperature of 1119±50 °C. This is the first geobarometric determination for a diamond from the Voorspoed kimberlite. It overlaps with P-T estimates obtained by traditional chemical geobarometry for diamonds from other kimberlites from the same Kaapvaal craton, supporting the reliability of our estimates. Our protocol can be used for geobarometry of further kyanite-bearing diamonds and may provide a guide for robust geobarometry of other types of mineral inclusions in diamonds, both eclogitic and peridotitic.

Key words: diamond inclusion, kyanite, eclogite, Voorspoed, South Africa, geobarometry

1. Introduction

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Eclogitic rocks from the Earth's upper mantle are generally considered to have originated as a result of subduction processes, which represent one of the main mechanisms that drive plate tectonics. Mantle eclogite is also one of the principal host rocks for diamonds and probably constitutes a particularly favorable environment for diamond formation from circulating C-bearing fluids or melts (Stachel and Luth, 2015). Knowing the depth at which these rocks were formed provides us with fundamental constraints to our understanding of ancient subduction events and of processes responsible for diamond formation and carbon recycling in the Earth (Shirey et al., 2013). Available geobarometers for eclogitic rocks are based on the incorporation of the tschermakitic component ($CaAl_2SiO_6$) in omphacitic clinopyroxene coexisting with garnet (e.g., Beyer et al., 2015). According to Beyer et al. (2015), their geobarometer can be applied to natural eclogites equilibrated at pressures between 2 and 7 GPa and temperatures between 900 and 1500 °C. These ranges encompass those in which eclogitic diamonds are probably formed (Stachel and Harris, 2008), suggesting a potential application of this method to clinopyroxene–garnet inclusion pairs contained in these diamonds. However, as the activity of $CaAl_2SiO_6$ in clinopyroxenes from eclogitic diamonds is often very low, chemical analyses must be of superior quality in order to obtain reliable results. Moreover, if the Fe^{3+}/Fe^{2+} ratios in clinopyroxene and garnet significantly exceed the values in the calibration experiments, inaccurate pressures will be obtained in the absence of Fe^{3+}/ Fe^{2+} measurements (Beyer et al., 2015). Unfortunately, these measurements are not commonly available. These drawbacks may severely limit the usefulness of the eclogite geobarometer when applied to data from the literature. Geobarometry of inclusions in diamonds based on clinopyroxene–garnet equilibria is further complicated by the fact that, in many cases, the two minerals do not occur together in the same diamond or are not in contact with each other and thus may not have been incorporated under the same conditions.

A different approach to geobarometry that is independent of chemical equilibrium is that employed in "elastic geobarometry" of inclusion–host systems (Rosenfeld and Chase, 1961; Adams et al., 1975a,b; Barron, 2005). This technique is based on the determination of the remnant pressure (P_{inc})

that develops on the inclusion upon exhumation, as a consequence of the contrast of thermo-elastic properties (i.e. compressibility and thermal expansion) between the inclusion and the host. In principle, elastic geobarometry could be applied to any mineral inclusion in a diamond formed at any pressure (P) and temperature (T), provided the interactions are purely elastic, P_{inc} can be determined, and the elastic properties of the two minerals are known in order to back-calculate the entrapment pressure (P_{trap}).

The first condition requires that after entrapment no brittle or plastic deformation occurs that would modify the stress field inside and outside the inclusion. The P_{inc} can be determined by comparing measures of P-dependent parameters (e.g., positions of Raman peaks or X-ray diffraction measures of unit-cell volumes) with those collected on crystals loaded in diamond-anvil cells and immersed in typically hydrostatic pressure-transmitting media (e.g. Angel et al., 2007; Klotz et al., 2009). However, since minerals (including cubic ones) are generally elastically anisotropic, an inclusion in a diamond at room conditions generally is under a non-hydrostatic stress field. Under these conditions, the P_{inc} can only be considered as the average of the three normal stresses acting on the inclusion (see Anzolini et al., 2018 for further discussion on this topic). Also, to correctly determine P_{inc}, the effects of deviatoric stresses on the measured P-dependent parameters should be taken into account. At present this can only be done by using a combination of computational and experimental methods (Anzolini et al. 2018). The presence of a fluid film surrounding the inclusion, which has recently been documented in several lithospheric diamonds (Nimis et al., 2016), may further complicate the modelling of the inclusion–host system. The most important effect of a fluid rim could be to make the stress field close to hydrostatic. However, to back-calculate P_{trap} the equation of state of the fluid should also be known, which is not presently the case.

Elastic geobarometry has been applied to various types of inclusions in diamonds with variable apparent success (Harris et al., 1970; Izraeli et al., 1999; Sobolev et al., 2000; Howell and Nasdala, 2008; Howell et al., 2010; Nestola et al., 2011; Howell, 2012; Howell et al., 2012; Küter et al., 2016; Anzolini et al., 2016; Anzolini et al., 2018). Only two of these studies involved eclogitic

diamonds, and specifically two coesite inclusions (Sobolev et al., 2000; Howell et al., 2012), but they yielded contrasting results, leaving doubts as to the suitability of coesite as a reliable geobarometer and/or of Raman spectroscopy as the best technique to determine P_{inc}. Due to the complexity of the calculations, all of the above studies were based on a number of simplified assumptions, such as spherical inclusion geometry, isotropic elastic properties and, except the latest works, hydrostatic conditions and linear elasticity. In fact, practical methods that avoid the assumption of linear elasticity and explicitly take into account geometric effects have only recently been developed (Angel et al., 2014; Angel et al., 2015a,b; Mazzucchelli et al., 2018). In particular, Mazzucchelli et al. (2018) showed that neglecting the effect of the inclusion shape on P_{inc} (as done in all previous studies) may severely bias the geobarometric results. Finally, none of the studies published so far took into account the possible presence of a fluid rim around the inclusions.

In this study, elastic geobarometry is applied for the first time to kyanite inclusions in an eclogitic diamond from the Voorspoed kimberlite (South Africa). Kyanite is a challenging mineral because it is not amenable to classical geobarometry and its strong elastic anisotropy complicates the elastic interactions with the diamond. We have determined P_{inc} by micro-Raman spectroscopy, which is the most widely used method to study mineral inclusions still trapped within diamonds and have calculated P_{trap} using state-of-the-art equations of state for kyanite and diamond. Different from previous studies of this kind, to obtain the most robust pressure estimations, (i) we have checked for the absence of fluid rims around the inclusions, (ii) we have incorporated an analysis of the effects of deviations from hydrostaticity, and (iii) we have applied the new approach based on finite element modeling (FEM) by Mazzucchelli et al. (2018) to correct P_{inc} for the shape of the kyanite inclusions, which are far from being spherical.

2. Geology and samples

The Voorspoed kimberlite (and associated Voorspoed diamond mine) is located in the Free State Province of South Africa, where it forms part of a NE–SW-trending cluster of eleven Group 2 kimberlite occurrences, which were emplaced through the Witwatersrand Block of the Kaapvaal Craton and into the surrounding Phanerozoic Karoo Supergroup rocks approximately 145 Ma ago (De Wit et al., 2016) (Figure 1). Prior to mining, the oval-shaped kimberlite pipe was originally 12 ha in size at surface, some 6 ha of which consisted of a massive raft of upper Karoo Supergroup Stormberg basalt and associated breccias, which syn-eruptively collapsed into the pipe (De Wit et al., 2016).

The kimberlite consists of a combination of volcanoclastic and probable pyroclastic facies, with at least two different magma sources, each with distinct diamond populations (De Wit et al., 2016 and references therein). Current diamond production is dominated by relatively high-value colourless to near colourless stones, with some yellow diamonds and a small proportion of pink diamonds also reported. Large stones (+10.8 ct) and Type II diamonds are relatively common at Voorspoed, while brown diamonds are not often recovered (De Wit et al., 2016).

A suite of inclusion-bearing diamonds was collected from the run-of-mine production from Voorspoed for investigation into the age and paragenesis of the diamonds. From these, a sub-population of diamonds with an eclogitic paragenesis was identified, based on the presence of orange (almandine) eclogitic garnet and kyanite inclusions. One of these eclogitic diamonds was selected for investigation using elastic barometry techniques by micro-Raman spectroscopy.

The sample investigated is diamond JW9453_Lot23_Stone1 (Figure 2). The diamond is a broken distorted and partially resorbed dodecahedron with remnant octahedral faces, measuring 4.15 × 2.58 × 1.65 mm. Its total weight was 0.258 carats. The diamond contained multiple mineral inclusions, among which a garnet and several kyanites were identified by micro-Raman spectroscopy and X-ray diffraction (see “Results and discussion” section). After the preliminary in-situ measurements,

the diamond was combusted at 900°C for about 5 hours in order to release some of the inclusions, on which further X-ray diffraction and chemical analyses were performed.

3. Experimental

3.1. Micro-Raman spectroscopy

Raman measurements were carried out using a Thermo Scientific™ DXR™ Raman Microscope using a 532-nm laser as excitation source at the Department of Geosciences, University of Padova. Reflected and transmitted light optics were used to select analysis locations. The analyses were performed using a 50× Long Working Distance objective with ~2.5 cm^{-1} spectral resolution and 1.1 μm spatial resolution at 10 mW of power. Spectra were recorded in the range extending from 100 to 3500 cm^{-1}. To maximize the signal-to-noise ratio, each spectrum was collected four times using an exposure time of 30 s, and then merged together at the end of the acquisition. Spectral fitting was carried out using the Thermo Scientific™ OMNIC™ Spectral Software.

3.2. Fourier Transform Infrared Spectroscopy

A Bruker Hyperion 3000 infrared microscope attached to a Bruker Vertex 70 optical bench was used to analyse the nitrogen content and nitrogen aggregation state of inclusion-bearing eclogitic diamonds from Voorspoed, including diamond JW9453_Lot23_Stone1. The diamonds were mounted on the edge of a glass slide to permit unhindered passage of the infrared beam and were analysed in transmission mode by signal-averaging 32 scans with a resolution of 4 cm^{-1} over the spectral range from 4000 to 550 cm^{-1}. The resulting absorbance spectra were used to determine nitrogen content and the extent of nitrogen aggregation by deconvolution of the infrared spectral envelope in the 1400 to 1000 cm^{-1} region, utilising an in-house Excel macro written by Dr. David Fisher of De Beers Technologies UK. Nitrogen contents were calculated from the infrared absorption coefficients specified by Boyd et al. (1994, 1995) for IaA and IaB nitrogen. Errors in

nitrogen content and aggregation state are dependent on spectral quality (which is influenced by diamond morphology and clarity) and are of the order of 10%.

3.3. Single-crystal X-ray diffraction

After the micro-Raman spectroscopy measurements, the diamond host was combusted in order to release the kyanite inclusion for which the Raman spectrum had shown the largest shift with respect to room pressure data (see the "Result and discussions") (indicated as Kyanite_1 in Figure 2), the garnet inclusion and a further black inclusion that had not been identified by Raman (indicated as Black_1 in Figure 2).

Attempts to analyse in-situ Kyanite_1 did not provide any reliable results. The garnet was measured by SCXRD before and after its release using a Rigaku Oxford Diffraction SuperNova diffractometer, equipped with a Dectris Pilatus 200K area detector and with a Mova X-ray microsource (beam spot ~ 0.12 mm) (Nestola et al., 2016). For the measurements, a Mo*K*α-radiation, operated at 50 kV and 0.8 mA was used. The sample to detector distance was 68 mm. Data reduction was performed using the CrysAlis software (Rigaku Oxford Diffraction). The instrument is able to perform in "powder diffraction mode" to acquire X-ray diffractograms on polycrystalline grains with size down to 20-10 μm. This mode was used to identify one of the Black_1 inclusion.

After the determination of the necessary orientation matrixes (obtained using the Supernova above instrumentation), the garnet was analysed with a STOE STADI IV instrument equipped with a point detector and motorized by SINGLE software (Angel and Finger, 2011), which adopts the 8-positions centering procedure, to obtain accurate and precise unit-cell edge measurements. The unit-cell edges were obtained for the inclusion both in-situ and after its extraction from the host diamond by measuring 20 diffraction reflections.

3.4. Electron microprobe analysis

The chemical compositions of Kyanite_1 and garnet were determined using a Cameca-Camebax SX50 electron microprobe operated in WDS mode at an accelerating voltage of 20 kV, current of 20 nA, with a ~ 1 μm beam diameter, and with 10 and 5 s counting times on the peak and background, respectively. The acquired data were converted to oxide wt% using the PAP correction program supplied by Cameca (Pouchou and Pichoir, 1991). The following standards, spectral lines and analytical crystals were used: Al_2O_3 (Al-Kα, TAP), wollastonite (Si-Kα, Ca-Kα, TAP), Fe_2O_3 (Fe-Kα, LiF), $MnTiO_3$ (Mn-Kα, LiF; Ti-Kα, PET), albite (Na-Kα, TAP), olivine (Mg-Kα, TAP), Cr_2O_3 (Cr-Kα, LiF). For the Kyanite_1 inclusion, Na, Ca and Mn contents were below the experimental detection limits. The oxide wt% reported in Table 1 were obtained by averaging 12 point analyses for Kyanite_1 and 11 point analyses for the garnet.

4. Results and discussion

4.1. X-ray diffraction

The only inclusion that provided reliable results by single-crystal X-ray diffraction before combusting the diamond was the eclogitic garnet. The unit-cell edges and volumes before and after extraction of the inclusion from the host diamond were:

a =11.5123±0.0005 Å and V = 1525.76±0.22 Å^3 (crystal enclosed)

a =11.5115±0.0009 Å and V = 1525.44±0.36 Å^3 (crystal released)

The unit-cell volumes before and after extraction are identical within one uncertainty, indicating that, unfortunately, no residual pressure was preserved on the inclusion. The physical reason for this observation is not obvious. The absence of fractures at the inclusion-diamond interface excludes pressure release by brittle deformation. The effect of the non-spherical shape of the inclusion, which is close to cubo-octahedral, is predictably small (see Mazzucchelli et al., 2018). The presence of a relatively compressible fluid film around the inclusion (cf. Nimis et al., 2016) or plastic deformation in the diamond might account for some pressure release, but their possible effects on the final P_{inc} are still unknown (Angel et al., 2017). The proximity of this garnet to the external

surface of the diamond, which would affect the P_{inc}, cannot be invoked as the garnet was located deeply into the diamond host. An alternative explanation is that the garnet was entrapped at relatively high temperatures, i.e., along an isomeke passing close to P = 0 at room conditions (see Figure 3b in Angel et al., 2015b). Some of these possible explanations might also account for some previously reported garnet inclusions in diamonds, for which P_{inc} ranges from zero (Liu et al., 1990) to values of about 0.3-0.7 GPa (see for example Harris et al., 1970; Cohen and Rosenfeld, 1979; Küter et al., 2016). Whatever the reason for the null P_{inc}, it is clear that our garnet inclusion cannot be used to retrieve the pressure of entrapment through elastic geobarometry.

Inclusion Black_1 (Figure 2) was also studied after its release from the diamond and was found to be a multiphase inclusion comprised of hematite, quartz, an iron-sulfide and plagioclase. Given the low-pressure mineral assemblage and the fact that the inclusion was very close to the surface of the diamond, its origin is probably epigenetic. For this reason, this inclusion was not studied any further.

4.2. Chemistry

The chemical compositions of Kyanite_1 and garnet are reported in Table 1. The cation proportions for Kyanite_1 indicate that the inclusion is made of practically pure Al_2SiO_5. The chemical analysis of the garnet clearly indicates an eclogitic composition, as expected. The cation proportions for the garnet provide the following formula:

$[Fe_{1.188}Ca_{0.897}Mg_{0.870}Na_{0.068}Mn_{0.019}][Al_{1.910}Ti_{0.061}Cr_{0.001}]Si_{3.002}O_{12}$, which can be expressed in terms of almandine (Alm), grossular (Gro) and pyrope (Pyr) end-members (normalized to 100) as: $Alm_{40\pm1}Gro_{30\pm1}Pyr_{30\pm1}$.

4.3. Micro-Raman spectroscopy

The host diamond (Figure 2) was fully analysed by micro-Raman spectroscopy. The most abundant inclusion mineral type was kyanite. In addition, we identified an inclusion of garnet whereas we did

not get any reliable Raman signal from the black inclusion located very close to the diamond surface (Figure 2). Specifically, we could confidently identify five separate inclusions of kyanite. A sixth inclusion, marked as Kyanite_6? in Figure 2, showed similar optical properties as the other kyanites, but its Raman signal was totally masked by a superimposed Raman spectrum similar to those reported by Nimis et al. (2016) and ascribed to the presence of a hydrous silicic fluid rim with $Si(OH)_4$ and $Si_2O(OH)_6$ components (see Figure 3). The same Raman features were observed around Kyanite_2, Kyanite_3, Kyanite_4, Kyanite_5 and the garnet inclusion. Only Kyanite_1 showed no fluid signal at the interface with the host diamond.

4.4. Determination of the internal pressure for Kyanite_1 inclusion

The Raman spectra measured on Kyanite_1 inclusion before and after its extraction from diamond are shown in Figure 4. The peak assignments were carried out using Thermo Scientific™ OMNIC™ Spectral Software and the band positions (only for the measurable peaks) before and after the release from the diamond host are reported in Table 2. A comparison between the two spectra shows a shift of the Raman peaks toward higher wavenumbers for the inclusion still enclosed within the diamond, which is typical of high-pressure conditions (see for example Hushur et al., 2009). This result indicates the presence of a non-null P_{inc} for the inclusion still enclosed within the diamond (Figure 4).

The absence of a fluid rim and of visible fractures around the inclusion, as well as the presence of a non-null P_{inc}, makes Kyanite_1 a good candidate for elastic geobarometry using currently available models. However, the lack of a fluid rim, combined with the strong elastic anisotropy of kyanite, also implies that the inclusion is under a non-hydrostatic stress. For this reason, we have adopted a special protocol to obtain a robust estimate of P_{inc}, which follows the same approach used by Anzolini et al. (2018) for a triclinic $CaSiO_3$-walstromite inclusion in diamond.

To calculate P_{inc}, we need to know how the Raman spectrum changes as a function of pressure. However, the only available Raman data for kyanite at variable pressure were collected under

hydrostatic conditions (Mernagh and Liu, 1991). Since the shifts of the different Raman peaks with increasing pressure may be significantly different in the presence of deviatoric stresses, any P_{inc} estimation based on Raman data from hydrostatic experiments would be unreliable. To estimate the effects of non-hydrostatic stresses on kyanite Raman measurements, we have determined by ab-initio calculations the positions of Raman bands from room pressure to 4 GPa under hydrostatic stress and under different uniaxial stresses oriented along the three crystallographic axes. The results are reported in Table 3. In order to ~~minimise~~minimize the effects of non-hydrostaticity on our P_{inc} estimations, we have selected from Table 3 only those Raman bands that showed an average difference with respect to the hydrostatic conditions of not more than 0.1 cm^{-1}. Only two bands satisfied such condition. Of these two bands we then selected the peak that showed the minimum deviation with respect to the shift that would show under hydrostatic conditions, which is the peak at about 637 cm^{-1}.

The observed shift of the selected Raman peak for our Kyanite_1 is of 0.41 cm^{-1} (see Table 2). Based on the pressure dependency of this peak (Table 3, column 5), which is 2.375 cm^{-1}/GPa, the P_{inc} is calculated to 0.173 GPa. Note that the concentrations of Fe^{3+}, Ti and Mg in the kyanite are so low that any effect of these impurities on the Raman spectrum can safely be neglected.

This P_{inc} value does not yet take into account the effects of crystal shape on the inclusion-diamond elastic interactions (Mazzucchelli et al., 2018). As evident from Figure 2, inclusion Kyanite_1 has an elongated, slightly irregular shape. This shape can reasonably be approximated by a prism with an aspect ratio of 3.5:1:1. The model developed by Mazzucchelli et al. (2018) provides for Kyanite_1 a shape factor of -0.066, assuming the elastic parameters for kyanite reported in Table 4. This shape factor allows to correct P_{inc} to the final value of 0.184(±0.090) GPa (Table 5). Such P_{inc} will be used to determine the P_{trap} for the diamond-kyanite pair as in the next section.

4.5. FTIR results and temperature of entrapment T_{trap}

Based on the FTIR measurements, the host diamond studied in this work is a Type IaAB diamond that contains 403 ppm nitrogen, of which 27% is aggregated into B defects. Other inclusion-bearing diamonds from the same eclogitic sub-population identified in the Voorspoed sample set range in nitrogen content up to 1442 ppm, and nitrogen aggregation up to 70% N as B defects. Using constants from Leahy and Taylor (1997), the temperature of entrapment, T_{trap}, for the diamond JW9453_Lot23_Stone1 can be calculated at 1110 °C, assuming a mantle residence time of 3 Ga, with the full range of temperatures for this eclogitic sub-population extending from 1096 to 1141 °C. If a mantle residence time of 1.5 Ga is assumed, the T_{trap} for the diamond increases to 1127 °C and the temperature range for the entire eclogitic sub-population is 1112 to 1159 °C. Therefore, considering the uncertainties in the temperature determination and a residence time variation between 1.5 to 3 Ga, we estimate a T_{trap} between 1060 and 1160 °C.

4.6. Determination of the depth of formation

The procedure to calculate the depth of formation using elastic geobarometry is described in detail in a number of publications; the first approaches were detailed in Rosenfeld and Chase (1961) and Adams et al. (1975a,b), followed by more recent publications by, e.g., Zhang (1998), Angel et al. (2014a), Angel et al. (2015a,b) and the introduction of software EosFit7c and EosFit-Pinc by Angel et al. (2014b) and Angel et al (2017b). All these works are based on the concept of the isomeke. As comprehensively described in Angel et al. (2015a), an isomeke is a line in *P–T* space that represents conditions under which the diamond and the inclusion would have the same volumes. The isomeke that passes through P_{inc} at room temperature, once it has been corrected for elastic relaxation in the host, is therefore the line of possible entrapment conditions for an inclusion in its host. The software EosFit-P_{inc} allows the construction of this isomeke for our diamond-kyanite pair, provided we know the internal pressure P_{inc} and the Equations of State (EoS) for the host and the inclusion, which for our case are reported in Tables 4 and 5. The EoS for diamond were taken from Angel et al. (2015a). For kyanite, the high-pressure data published by Liu et al. (2009) were considered, which are in

good agreement with the experimental results by Irfune et al., (1995); Yang et al., (1997); Friedrich et al., (2004) and the ab initio calculation by Matsui et al., (1996) and have only relatively small discrepancies with few other ab-initio calculations (Oganov and Brodholt, 2000; Winkler et al., 2001). For thermal expansion data, we have compared different published datasets (including Skinner et al., 1969; Winter and Ghose, 1979; Gatta et al., 2006; Liu et al., 2010). The high-temperature data were then combined with the high-pressure data by Liu et al. (2009) up to 10 GPa (i.e. within the hydrostatic limit for the methanol-ethanol pressure transmitting medium) and fit to a thermal pressure equation of state (see Milani et al., 2017) using EosFit-GUI software (Gonzalez-Platas et al., 2016). The dataset giving the best χ^2 (i.e. $\chi^2 = 1.45$) was a combination of the data by Gatta et al. (2006) and Winter and Ghose (1979) together with the HP data from Liu et al. (2009), with an Einstein temperature for kyanite of 903 °C (Holland and Powell, 2011). The shear modulus for kyanite was taken from Ahrens (1995). All the resulting parameters are summarized in Table 4. As we mentioned above, note that the concentrations of Fe^{3+}, Ti and Mg in Kyanite_1 are so low that any effect of these impurities on the thermoelastic properties can be considered to be absolutely negligible.

Calculations of P_{trap} have been performed using a P_{inc} = 0.184(0.090) GPa at T_{trap} between 1060 and 1160 °C, a range that takes into account uncertainties in temperature estimates by IR spectroscopy. The results are reported in Table 5. The P_{trap} estimates varies between 4.97 and 5.35 GPa at 1060 and 1160 °C, respectively. These estimates would correspond to a depth of about 160 km.

In Figure 5, the P–T estimates for the kyanite inclusion are compared with P–T data for diamond inclusions and diamondiferous xenoliths from Kaapvaal kimberlites. For Grt–Opx–(Cpx) assemblages, P and T were calculated using a combination of the Nickel and Green (1985) Opx–Grt barometer with the Harley (1984) Opx–Grt thermometer or, if Cpx was present, with the more robust Taylor (1998) two-pyroxene thermometer. For four Na-rich Opx's, Carswell's (1991) modification to the barometer was used. To reduce the effect of propagation of analytical errors, only Opx analyses with 99–101% oxide totals and 3.98–4.02 cations per unit formula were used.

For Cpx inclusions, P and T were calculated using the Nimis and Taylor (2000) thermobarometer. Cpx analyses were filtered according to Ziberna et al. (2016) to select high-quality, Opx–Grt-buffered compositions; Cpx inclusions in touch with Opx but without Grt were not used to avoid any P-bias due to post-entrapment reequilibration (cf. Nimis, 2002). The great majority of P–T estimates for Kaapvaal diamonds indicate conditions hotter than a 35-mW/m^2 geotherm. The two obvious outliers refer to (i) a non-touching pair in which Opx and Grt were likely not in equilibrium (cf. Phillips et al., 2004), and (ii) an Opx composition with 99.02% oxide and 4.018 cation totals, very close to the adopted thresholds for analytical quality. Note that, although the Opx–Grt thermometer is prone to large uncertainties (Nimis et al., 2015), due the P-dependency of the thermometer errors in T estimates for Opx–Grt pairs would shift the points roughly along the same conductive geotherm. In Fig. 5, our P–T estimates for kyanite in Voorspoed diamond overlap with those for other diamonds from the same craton, suggesting that the estimates are reliable.

5. Conclusions

The strong difference in thermoelastic properties between kyanite and diamond and the presence of a sufficiently intense Raman band that is little sensitive to deviatoric stresses make kyanite a good candidate for the elastic geobarometry of eclogitic diamonds. Robust application of the elastic method requires that the kyanite inclusion is not surrounded by fluid or fractures and that a specific selection of Raman peaks is made to determine the residual pressure on the inclusion.

To our knowledge, our results represent the first geobarometric data for an inclusion in an eclogitic diamond from the Voorspoed kimberlite, placing the diamond provenance at about 160 km depth (i.e. P_{trap} ~ 5.2 GPa) for a temperature of formation of ca. 1120 °C. These estimates well match the majority of P-T data retrieved from diamonds from Kaapvaal craton and fall on a conductive geotherm calculated for a heat flow of slightly less than 40 mW/m^2.

The application of elastic geobarometry is not trivial for minerals characterized by strong elastic anisotropy. In our case, a multi-methodological study has been necessary (including experimental

and computational methods) in order to check for specific prerequisites (e.g. absence of interposed material between the inclusion and host) and to minimize the effect of deviations from assumptions (e.g. sphericity, hydrostaticity) that are required to perform calculations. Neglecting their effects may seriously bias the P_{trap} estimates. Just to provide some examples, neglecting the effect of the non-hydrostaticity issue by Raman spectroscopy would bring to an extremely high P_{inc} = 1.72 GPa (i.e. using the peak shift of the band positioned at ca. 290 cm^{-1}). Using such P_{inc} value to calculate the P_{trap} of our kyanite we would obtain a value equal to 8.8 GPa calculated at T = 1120°C, which is enormously higher than the value we provided (i.e. a P_{trap} about 3.5 GPa higher or a depth of formation about 100 km deeper).

We are confident that our protocol can be used for geobarometry of further kyanite-bearing diamonds and may provide a guide for robust geobarometry of other types of mineral inclusions in diamonds, both eclogitic and peridotitic. This approach may significantly increase the proportion of diamonds that are amenable to geobarometry and may thus contribute to provide more statistically relevant information on diamond formation depths.

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Figure and Table captions

Figure 1. Map of the main tectonic terranes of southern Africa, with the location of the Voorspoed kimberlite (V) in the eastern Witwatersrand Block of the Kaapvaal Craton illustrated (CML = Colesberg Magnetic Lineament, TML = Thabazimbi-Murchison Lineament) (modified from Youssof et al., 2015).

Figure 2. Diamond JW9453_lot_23_Stone_1 investigated in this research project. Several inclusions are indicated by arrows (see the text for more details about their identification) (photo: Stefano Castelli, Department of Geosciences, University of Padova).

Figure 3. Typical Raman spectrum collected from kyanite and garnet inclusions in diamond JW9453_lot_23_Stone_1 showing the same broad peaks at 667 and 798 cm^{-1} found in Nimis et al. (2016) and indicating the presence of a hydrous silicic fluid containing $Si(OH)_4$ and $Si_2O(OH)_6$.

Figure 4. Raman spectra of Kyanite_1 measured while the inclusion was still trapped within the diamond (blue) and after its release from the diamond (red). The peak positions of the most significant Raman bands are reported.

Figure 5. P-T estimates for Kyanite_1 inclusion (filled yellow box) including all experimental uncertainties. P-T estimates for inclusions in peridotitic diamonds and diamondiferous xenoliths from Kaapvaal kimberlites and conductive geotherms for 35 and 40 mW/m^2 heat flows (Hasterock and Chapmann, 2001) are shown for comparison. Source of compositional data for pyroxenes and garnets used for P–T calculations: Boyd and Nixon (1970), Daniels and Gurney (1989), Dawson and Smith (1975), Harris et al. (2004), McDade and Harris (1999), Moore and Gurney (1990), Phillips et al. (2004), Prinz et al. (1975), Richardson (personal communication), Rickard et al (1989), Shee et al. (1982), Stachel et al. (2004), Tappert et al. (2005), Tsai et al. (1979), Viljoen et al. (1999), Wilding et al. (1994). The diamond-graphite boundary (black solid line) is from Day (2012).

Table 1. WDS microprobe analyses of (a) Kyanite_1 and (b) garnet inclusions.

Table 2. Raman peak positions for the measurable peaks of Kyanite_1 inclusion before and after its release from the diamond host.

Table 3. Raman spectra of kyanite calculated by ab-initio calculation methods (see Appendix). The columns named "Static room pressure" and "Static at 4 GPa" are relative to the band positions (in cm^{-1}) of the spectra calculated at room pressure and at 4 GPa hydrostatic conditions, respectively. Adjacent columns report the pressure dependencies (cm^{-1}/GPa) of each peak and the band positions of different non-hydrostatic spectra with different stress values applied to X, Y and Z crystallographic axes. For the static room pressure measurements, we have reported the relative intensity (with the most intense band assumed 1000). For the non-hydrostatic spectra along X, Y and Z, we have reported the band shifts with respect to the hydrostatic data at 4 GPa. The peak highlighted in bold and underlined is the selected one used to calculate the internal pressure, P_{inc}, as reported in Table 4.

Table 4. Equation of state parameters and equation of state types used in this work to calculate the depth of entrapment of Kyanite_1 inclusion. K_0 is the bulk modulus at room conditions, $K`$ and $K``$ are the first and second pressure derivatives of the bulk modulus, α_0 is the thermal expansion coefficient at 298 K and room pressure calculated with the Thermal pressure model, Th_E is the Einstein temperature and G_0 is the shear modulus at room conditions. The data for diamond are from Angel et al. (2015a); the high-pressure data for kyanite are from Liu et al. (2009), whereas the

high-temperature data for kyanite are from Winter and Ghose (1979) and Gatta et al. (2006). The shear modulus of kyanite is from Ahrens (1995).

Table 5. Pressures of entrapment (P_{trap}) calculated using a P_{inc} = 0.184 GPa (corrected for crystal shape) at 1110 and 1127 °C (corresponding to a residence time of 3.0 and 1.5 Ga, respectively) and at 1060 and 1160 °C, which bracket the entire possible range (including any uncertainty in the temperature determination) at which the diamond could be crystallized.