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Toward a Robust Elastic Geobarometry of Kyanite Inclusions in Eclogitic Diamonds

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(Article begins on next page)

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3 **Robust elastic geobarometry of kyanite inclusions in eclogitic diamonds**

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Formattato: Apice

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16
17 **Abstract**

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

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

41
42 **1. Introduction**

43 Eclogitic rocks from the Earth's upper mantle are generally considered to have originated as a result
44 of subduction processes, which represent one of the main mechanisms that drive plate tectonics.
45 Mantle eclogite is also one of the principal host rocks for diamonds and probably constitutes a
46 particularly favorable environment for diamond formation from circulating C-bearing fluids or
47 melts (Stachel and Luth, 2015). Knowing the depth at which these rocks were formed provides us
48 with fundamental constraints to our understanding of ancient subduction events and of processes
49 responsible for diamond formation and carbon recycling in the Earth (Shirey et al., 2013). Available
50 geobarometers for eclogitic rocks are based on the incorporation of the tschermakitic component
51 ($\text{CaAl}_2\text{SiO}_6$) in omphacitic clinopyroxene coexisting with garnet (e.g., Beyer et al., 2015).
52 According to Beyer et al. (2015), their geobarometer can be applied to natural eclogites equilibrated
53 at pressures between 2 and 7 GPa and temperatures between 900 and 1500 °C. These ranges
54 encompass those in which eclogitic diamonds are probably formed (Stachel and Harris, 2008),
55 suggesting a potential application of this method to clinopyroxene–garnet inclusion pairs contained
56 in these diamonds. However, as the activity of $\text{CaAl}_2\text{SiO}_6$ in clinopyroxenes from eclogitic
57 diamonds is often very low, chemical analyses must be of superior quality in order to obtain reliable
58 results. Moreover, if the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios in clinopyroxene and garnet significantly exceed the values
59 in the calibration experiments, inaccurate pressures will be obtained in the absence of $\text{Fe}^{3+}/\text{Fe}^{2+}$
60 measurements (Beyer et al., 2015). Unfortunately, these measurements are not commonly available.
61 These drawbacks may severely limit the usefulness of the eclogite geobarometer when applied to
62 data from the literature. Geobarometry of inclusions in diamonds based on clinopyroxene–garnet
63 equilibria is further complicated by the fact that, in many cases, the two minerals do not occur
64 together in the same diamond or are not in contact with each other and thus may not have been
65 incorporated under the same conditions.

66 A different approach to geobarometry that is independent of chemical equilibrium is that employed
67 in “elastic geobarometry” of inclusion–host systems (Rosenfeld and Chase, 1961; Adams et al.,
68 1975a,b; Barron, 2005). This technique is based on the determination of the remnant pressure (P_{inc})

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

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

91 Elastic geobarometry has been applied to various types of inclusions in diamonds with variable
92 apparent success (Harris et al., 1970; Izraeli et al., 1999; Sobolev et al., 2000; Howell and Nasdala,
93 2008; Howell et al., 2010; Nestola et al., 2011; Howell, 2012; Howell et al., 2012; Küter et al.,
94 2016; Anzolini et al., 2016; Anzolini et al., 2018). Only two of these studies involved eclogitic

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

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

117

118

119 **2. Geology and samples**

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

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

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

139

140 The sample investigated is diamond JW9453_Lot23_Stone1 (Figure 2). The diamond is a broken
141 distorted and partially resorbed dodecahedron with remnant octahedral faces, measuring 4.15×2.58
142 $\times 1.65$ mm. Its total weight was 0.258 carats. The diamond contained multiple mineral inclusions,
143 among which a garnet and several kyanites were identified by micro-Raman spectroscopy and X-
144 ray diffraction (see “Results and discussion” section). After the preliminary in-situ measurements,

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

147

148 **3. Experimental**

149 **3.1. *Micro-Raman spectroscopy***

150 Raman measurements were carried out using a Thermo Scientific™ DXR™ Raman Microscope
151 using a 532-nm laser as excitation source at the Department of Geosciences, University of Padova.
152 Reflected and transmitted light optics were used to select analysis locations. The analyses were
153 performed using a 50× Long Working Distance objective with ~2.5 cm⁻¹ spectral resolution and 1.1
154 μm spatial resolution at 10 mW of power. Spectra were recorded in the range extending from 100 to
155 3500 cm⁻¹. To maximize the signal-to-noise ratio, each spectrum was collected four times using an
156 exposure time of 30 s, and then merged together at the end of the acquisition. Spectral fitting was
157 carried out using the Thermo Scientific™ OMNIC™ Spectral Software.

158

159 **3.2. *Fourier Transform Infrared Spectroscopy***

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

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

172

173 ***3.3. Single-crystal X-ray diffraction***

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

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

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

194

195 ***3.4. Electron microprobe analysis***

196 The chemical compositions of Kyanite_1 and garnet were determined using a Cameca-Camebax
197 SX50 electron microprobe operated in WDS mode at an accelerating voltage of 20 kV, current of
198 20 nA, with a $\sim 1 \mu\text{m}$ beam diameter, and with 10 and 5 s counting times on the peak and
199 background, respectively. The acquired data were converted to oxide wt% using the PAP correction
200 program supplied by Cameca (Pouchou and Pichoir, 1991). The following standards, spectral lines
201 and analytical crystals were used: Al_2O_3 (Al-K α , TAP), wollastonite (Si-K α , Ca-K α , TAP), Fe_2O_3
202 (Fe-K α , LiF), MnTiO_3 (Mn-K α , LiF; Ti-K α , PET), albite (Na-K α , TAP), olivine (Mg-K α , TAP),
203 Cr_2O_3 (Cr-K α , LiF). For the Kyanite_1 inclusion, Na, Ca and Mn contents were below the
204 experimental detection limits. The oxide wt% reported in Table 1 were obtained by averaging 12
205 point analyses for Kyanite_1 and 11 point analyses for the garnet.

206

207 **4. Results and discussion**

208 *4.1. X-ray diffraction*

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

212 $a = 11.5123 \pm 0.0005 \text{ \AA}$ and $V = 1525.76 \pm 0.22 \text{ \AA}^3$ (crystal enclosed)

213 $a = 11.5115 \pm 0.0009 \text{ \AA}$ and $V = 1525.44 \pm 0.36 \text{ \AA}^3$ (crystal released)

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

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

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

235

236 *4.2. Chemistry*

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

241 $[Fe_{1.188}Ca_{0.897}Mg_{0.870}Na_{0.068}Mn_{0.019}][Al_{1.910}Ti_{0.061}Cr_{0.001}]Si_{3.002}O_{12}$, which can be expressed in terms
242 of almandine (Alm), grossular (Gro) and pyrope (Pyr) end-members (normalized to 100) as:

243 $Alm_{40\pm 1}Gro_{30\pm 1}Pyr_{30\pm 1}$.

244

245 *4.3. Micro-Raman spectroscopy*

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

248 not get any reliable Raman signal from the black inclusion located very close to the diamond
249 surface (Figure 2). Specifically, we could confidently identify five separate inclusions of kyanite. A
250 sixth inclusion, marked as Kyanite_6? in Figure 2, showed similar optical properties as the other
251 kyanites, but its Raman signal was totally masked by a superimposed Raman spectrum similar to
252 those reported by Nimis et al. (2016) and ascribed to the presence of a hydrous silicic fluid rim with
253 Si(OH)_4 and $\text{Si}_2\text{O(OH)}_6$ components (see Figure 3). The same Raman features were observed
254 around Kyanite_2, Kyanite_3, Kyanite_4, Kyanite_5 and the garnet inclusion. Only Kyanite_1
255 showed no fluid signal at the interface with the host diamond.

256 257 *4.4. Determination of the internal pressure for Kyanite_1 inclusion*

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

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

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

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

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

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

297

298 *4.5. FTIR results and temperature of entrapment T_{trap}*

299 Based on the FTIR measurements, the host diamond studied in this work is a Type IaAB diamond
300 that contains 403 ppm nitrogen, of which 27% is aggregated into B defects. Other inclusion-bearing
301 diamonds from the same eclogitic sub-population identified in the Voorspoed sample set range in
302 nitrogen content up to 1442 ppm, and nitrogen aggregation up to 70% N as B defects. Using
303 constants from Leahy and Taylor (1997), the temperature of entrapment, T_{trap} , for the diamond
304 JW9453_Lot23_Stone1 can be calculated at 1110 °C, assuming a mantle residence time of 3 Ga,
305 with the full range of temperatures for this eclogitic sub-population extending from 1096 to 1141
306 °C. If a mantle residence time of 1.5 Ga is assumed, the T_{trap} for the diamond increases to 1127 °C
307 and the temperature range for the entire eclogitic sub-population is 1112 to 1159 °C. Therefore,
308 considering the uncertainties in the temperature determination and a residence time variation
309 between 1.5 to 3 Ga, we estimate a T_{trap} between 1060 and 1160 °C.

310

311 *4.6. Determination of the depth of formation*

312 The procedure to calculate the depth of formation using elastic geobarometry is described in detail
313 in a number of publications; the first approaches were detailed in Rosenfeld and Chase (1961) and
314 Adams et al. (1975a,b), followed by more recent publications by, e.g., Zhang (1998), Angel et al.
315 (2014a), Angel et al. (2015a,b) and the introduction of software EosFit7c and EosFit-Pinc by Angel
316 et al. (2014b) and Angel et al (2017b). All these works are based on the concept of the isomeke. As
317 comprehensively described in Angel et al. (2015a), an isomeke is a line in P - T space that represents
318 conditions under which the diamond and the inclusion would have the same volumes. The isomeke
319 that passes through P_{inc} at room temperature, once it has been corrected for elastic relaxation in the
320 host, is therefore the line of possible entrapment conditions for an inclusion in its host. The software
321 EosFit- P_{inc} allows the construction of this isomeke for our diamond-kyanite pair, provided we know
322 the internal pressure P_{inc} and the Equations of State (EoS) for the host and the inclusion, which for
323 our case are reported in Tables 4 and 5. The EoS for diamond were taken from Angel et al. (2015a).
324 For kyanite, the high-pressure data published by Liu et al. (2009) were considered, which are in

325 good agreement with the experimental results by Irfune et al., (1995); Yang et al., (1997); Friedrich
326 et al., (2004) and the ab initio calculation by Matsui et al., (1996) and have only relatively small
327 discrepancies with few other ab-initio calculations (Oganov and Brodholt, 2000; Winkler et al.,
328 2001). For thermal expansion data, we have compared different published datasets (including
329 Skinner et al., 1969; Winter and Ghose, 1979; Gatta et al., 2006; Liu et al., 2010). The high-
330 temperature data were then combined with the high-pressure data by Liu et al. (2009) up to 10 GPa
331 (i.e. within the hydrostatic limit for the methanol-ethanol pressure transmitting medium) and fit to a
332 thermal pressure equation of state (see Milani et al., 2017) using EosFit-GUI software (Gonzalez-
333 Platas et al., 2016). The dataset giving the best χ^2 (i.e. $\chi^2 = 1.45$) was a combination of the data by
334 Gatta et al. (2006) and Winter and Ghose (1979) together with the HP data from Liu et al. (2009),
335 with an Einstein temperature for kyanite of 903 °C (Holland and Powell, 2011). The shear modulus
336 for kyanite was taken from Ahrens (1995). All the resulting parameters are summarized in Table 4.
337 As we mentioned above, note that the concentrations of Fe³⁺, Ti and Mg in Kyanite_1 are so low
338 that any effect of these impurities on the thermoelastic properties can be considered to be absolutely
339 negligible.

340 Calculations of P_{trap} have been performed using a $P_{\text{inc}} = 0.184(0.090)$ GPa at T_{trap} between 1060 and
341 1160 °C, a range that takes into account uncertainties in temperature estimates by IR spectroscopy.
342 The results are reported in Table 5. The P_{trap} estimates varies between 4.97 and 5.35 GPa at 1060
343 and 1160 °C, respectively. These estimates would correspond to a depth of about 160 km.

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

351 For Cpx inclusions, P and T were calculated using the Nimis and Taylor (2000) thermobarometer.
352 Cpx analyses were filtered according to Zibera et al. (2016) to select high-quality, Opx–Grt-
353 buffered compositions; Cpx inclusions in touch with Opx but without Grt were not used to avoid
354 any P-bias due to post-entrapment reequilibration (cf. Nimis, 2002). The great majority of P–T
355 estimates for Kaapvaal diamonds indicate conditions hotter than a 35-mW/m² geotherm. The two
356 obvious outliers refer to (i) a non-touching pair in which Opx and Grt were likely not in equilibrium
357 (cf. Phillips et al., 2004), and (ii) an Opx composition with 99.02% oxide and 4.018 cation totals,
358 very close to the adopted thresholds for analytical quality. Note that, although the Opx–Grt
359 thermometer is prone to large uncertainties (Nimis et al., 2015), due the P-dependency of the
360 thermometer errors in T estimates for Opx–Grt pairs would shift the points roughly along the same
361 conductive geotherm. In Fig. 5, our P–T estimates for kyanite in Voorspoed diamond overlap with
362 those for other diamonds from the same craton, suggesting that the estimates are reliable.

363

364 5. Conclusions

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

370 To our knowledge, our results represent the first geobarometric data for an inclusion in an eclogitic
371 diamond from the Voorspoed kimberlite, placing the diamond provenance at about 160 km depth
372 (i.e. $P_{\text{trap}} \sim 5.2$ GPa) for a temperature of formation of ca. 1120 °C. These estimates well match the
373 majority of P–T data retrieved from diamonds from Kaapvaal craton and fall on a conductive
374 geotherm calculated for a heat flow of slightly less than 40 mW/m².

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

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

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

391

392

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398

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659 **Figure and Table captions**

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

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

667 **Figure 3.** Typical Raman spectrum collected from kyanite and garnet inclusions in diamond
668 JW9453_lot_23_Stone_1 showing the same broad peaks at 667 and 798 cm^{-1} found in Nimis et al.
669 (2016) and indicating the presence of a hydrous silicic fluid containing $\text{Si}(\text{OH})_4$ and $\text{Si}_2\text{O}(\text{OH})_6$.

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

673 **Figure 5.** P-T estimates for Kyanite_1 inclusion (filled yellow box) including all experimental
674 uncertainties. P-T estimates for inclusions in peridotitic diamonds and diamondiferous xenoliths
675 from Kaapvaal kimberlites and conductive geotherms for 35 and 40 mW/m^2 heat flows (Hasterock
676 and Chapman, 2001) are shown for comparison. Source of compositional data for pyroxenes and
677 garnets used for P-T calculations: Boyd and Nixon (1970), Daniels and Gurney (1989), Dawson
678 and Smith (1975), Harris et al. (2004), McDade and Harris (1999), Moore and Gurney (1990),
679 Phillips et al. (2004), Prinz et al. (1975), Richardson (personal communication), Rickard et al
680 (1989), Shee et al. (1982), Stachel et al. (2004), Tappert et al. (2005), Tsai et al. (1979), Viljoen et
681 al. (1999), Wilding et al. (1994). The diamond-graphite boundary (black solid line) is from Day
682 (2012).

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

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

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

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

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

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

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