Chapter 3: Polycrystalline diamonds from kimberlites – snapshots of rapid and episodic diamond formation in the lithospheric mantle

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INTRODUCTION

Monocrystalline diamonds are the most valuable diamond type, economically. However, there are other varieties of diamond forged in Earth's lithospheric mantle, which, while not economically profitable, are of considerable value to the geosciences. Most prominent amongst these are fibrous diamonds (Weiss et al., 2022, this volume) and polycrystalline diamond aggregates (PDAs). Polycrystalline diamond aggregates are rocks in which the dominant mineral phase is diamond (Fig. 1), whereas fibrous diamonds are cuboid samples, sometimes with monocrystalline diamond cores and cloudy overgrowths ('coats'), or octahedral diamonds with fibrous cores (Weiss et al., 2022, this volume). The fibrous growth sectors are highly imperfect single crystals hosting millions of fluid and solid micro-inclusions (Navon et al., 1988). Polycrystalline diamond aggregates (PDAs) from kimberlites are the least well-studied of the diamond family. This chapter aims to showcase what we know of PDA-formation in the context of monocrystalline diamond formation, the origin of carbon enrichment in the cratonic lithosphere, and the identify the relationship(s) between polycrystalline diamond formation and plate tectonics.

NOMENCLATURE

Nothing better serves to illuminate the blurred line between academia and industry in diamond science than the diversity of, and etymology behind, the nomenclature applied to polycrystalline diamond. The most commonly used names are framesite, stewartite, diamondite, boart, and carbonado (Table 1). The names used to sub-divide the group originate from the lexica of both industry and academia and are based on appearance (e.g., grain size), application, value, and in some cases, physical properties. For instance, if a polycrystalline diamond aggregate contains unidentified or identified magnetic phases (presumably magnetite) then it can be termed stewartite, but if the sample is non-magnetic then the name framesite can be applied (Heaney et al., 2005). These names derive from two persons named Stewart and Frames, former mine managers at the Cullinan Mine (*Andy Moore, personal communication, 2021*). Both, stewartite and framesite can also be referred to as boart, which means the sample is not a single crystal and is not of gem quality, but that the sample is suitable for use as an abrasive. The etymology of the word diamondite follows a standard geological/petrographic classification scheme where rocks can be named according to their dominant mineral phase. For example, if a rock is dominantly comprised of clino- and/or ortho-

pyroxene then it can be called a pyroxenite, and so the argument was put forward that mantle xenoliths dominated by diamond should be referred to as diamondite (Kurat and Dobosi, 2000). Stewartite is the least commonly used name, either because most samples are non-magnetic or because most people do not check whether or not a framesite/diamondite is magnetic.

The carbonados are considered by most researchers to be a diamond sub-group of their own. Carbonados are dark-coloured, equidimensional, microporphyritic and often have a glassy diamond patina that can show slickensides (Haggerty, 2017). In short, carbonados do not look like the polycrystalline diamond aggregates found in kimberlites. Like PDAs associated with kimberlites, carbonados are porous, with about 10–15% pore space, but the pores are rounded rather than polygonal (Haggerty, 2017). The primary host rock for carbonados is unknown. They are found exclusively in an alluvial setting in Mid-Proterozoic (1–1.5 Ga) metaconglomerates overlying the São Francisco and Congo-Kasai cratons in Brazil and in Mesozoic sandstones in the Central African Republic (Fettke and Sturges, 1933; Leonardos, 1937; Trueb and De Wys, 1969; Haggerty, 1999). The two localities are paleo-geographically connected and once formed part of the supercontinent Rodinia (De Waele et al., 2008). The intergrowths and inclusions described from carbonados feature phases not usually associated with diamond from the Earth's mantle. They comprise phases associated with crustal and sedimentary rocks, such as florencite-goyazite-gorceixite, xenotime, kaolinite, quartz, orthoclase, zircon, and also a suite of very reducing phases, such as SiC, TiN, and Fe, Fe-Ni, W-Fe-Cr-V, Ni-Cr, Si, Sn metallic and alloyed phases (Haggerty, 2014; Heaney et al., 2005). The mixture of uncommon syngenetic and epigenetic inclusions, including crustal inclusions, have been posing a challenge to develop models explaining their genesis which encompass a wide range of scenarios, including extraterrestrial origins (Heaney et al., 2005; Haggerty, 2014). As carbonados are geologically much less constrained than polycrystalline diamond aggregates from kimberlites there is a risk that the new findings for the kimberlitic PDAs do not apply to carbonado. Consequently, a summary of the carbonado literature in this chapter would contribute little that has not been said before. For details on carbonado, we direct the reader to the extensive reviews existing in the literature for carbonados, such as Haggerty (2014, 2017) and Heaney et al. (2005).

Herein, we use the term "polycrystalline diamond aggregate" (PDA) to group all polycrystalline samples (Fig. 1). This review is concerned with the origin and geological significance of PDAs from kimberlites which host silicates and oxides. This is because their direct association with kimberlites and their intergrowths/inclusions provide *bona fide* geological context, without which all inferences are devoid of any meaningful relation with geological processes, or events.

POLYCRYSTALLINE DIAMOND AGGREGATES FROM KIMBERLITES

To our knowledge, polycrystalline diamond aggregates (Fig. 1) have, thus far, only been reported in the peer-reviewed literature from Group I kimberlites. PDAs amount to as much as 20% of the diamond production in Southern African and Yakutian kimberlites, including Orapa, Venetia, Cullinan (Premier), Jwaneng, Mirny, Aikhal, Yubileinaya and Sytykanskaya (Orlov, 1977; Kaminsky et al., 1981; Gurney and Boyd, 1982; McCandless et al., 1989; Smelova, 1994; Kirkley et al., 1995; Jacob et al., 2000; Sobolev et al., 2016). PDAs can be up to several centimetres in size (several hundred carats) and comprise randomly oriented diamonds of variable size from ca. 5 μm to 5,000 μm (Sobolev, 1977; Rubanova et al., 2012) intergrown with silicates, oxides and other phases (Jacob et al., 2011). An important and notable difference to inclusions in monocrystalline diamonds is that non-diamond phases in PDAs are *intergrown* with the diamond grains, confirming a petrogenetic relationship, rather than representing material trapped during diamond formation or random epigenetic phases. Individual diamonds in PDAs are also found included

98 in the non-diamond phases, indicating the syngenetic formation of diamond, silicate, oxides, carbide, and
99 fluid components (Kurat and Dobosi, 2000; Jacob et al., 2004; Mikhail et al., 2019b).
100
101 The high porosity of some PDAs (up to 30%; Heaney et al., 2005; Jacob et al., 2011), the release of
102 detectable ^{3}He when crushed under vacuum (Gautheron et al., 2005; Mikhail et al., 2019a), and the
103 presence of trace amounts of hydrogen (e.g. 38± 5 ppm; Fourel et al., 2017) indicate the presence of fluids
104 trapped during formation. In some cases, it appears that these intergrowths are not shielded from their
105 surroundings and can thus be subject to metasomatic alteration. For example, a micro-computed
106 tomography (µCT) study of a PDA sample from Orapa, Botswana (Jacob et al., 2011) presents spectacular
107 hematite alteration rims around magnetite (Fig. 2), illustrating epigenetic metasomatic changes facilitated
108 by the high porosity and permeability in some PDAs.
109
110 This chapter summarizes data on the diamond and non-diamond components in kimberlite-related
111 PDAs. This information is synergized into a narrative of what we know and what we will still need to
112 know as informed by these data. We show how the geochemical and petrological insights distinguish
113 PDAs from the monocrystalline diamond types (gem and fibrous types) and explain what they reveal about
114 our collective understanding of mantle metasomatism, tectonic volatile fluxing, and the deep carbon cycle.
115
116
117   **INSIGHTS FROM DIAMOND GEOCHEMISTRY**
118
119 Polycrystalline diamond growth is the result of heterogeneous nucleation and rapid crystal growth
120 driven mainly by carbon supersaturation (Sunagawa, 2005). Hence, while monocrystalline diamonds can
121 show extended histories of slow growth (Howell et al., 2012b; Timmerman et al., 2019a), PDA formation
122 appears to be rapid (Orlov, 1977). Therefore, because of their rapid formation, both fibrous diamonds and
123 polycrystalline diamond aggregates provide important and complementary perspectives on diamond
124 formation processes compared to the time-integrated story recorded by some monocrystalline diamonds.
125
126 **Source(s) of diamond-forming metasomatic fluids**
127
128 The origin of PDA-forming fluids has been evaluated using the δ^{13}C and δ^{15}N values for the diamond
129 component of PDAs (Shelkov et al., 1997; Jacob et al., 2000; Maruoka et al., 2004; Mikhail et al., 2013;
130 Mikhail et al., 2014c), and using helium isotope constraints from micro- to nano-inclusions in the rocks
131 (Burgess et al., 1998; Gautheron et al., 2005; Mikhail et al., 2019a).
132
133 The stable isotope ratios of carbon and nitrogen for crustal and mantle derived material show
134 distinctions between their average values (Hoefs, 2009 and references therein) (Fig. 3). Hence, for
135 diamonds, these stable isotope systems can be useful indicators for their sources and elucidate crust–
136 mantle interaction (Stachel et al., 2022, this volume). This picture is complicated due to significant stable
137 isotope fractionation effects, which can occur at high temperatures and pressures and in associated closed
138 and open system diamond formation processes (Stachel et al., 2022, this volume). Owing to the similarity
139 of the mass difference between the heavy and light isotopes for carbon and nitrogen, the equilibrium stable
140 isotope fractionation factors for carbon and for nitrogen are similar in magnitude at mantle temperatures,
141 and these are usually within 1–2‰ depending on the species involved (Richet et al., 1977; Deines, 1980;
142 Polyakov and Kharlashina, 1995; Reutsky et al., 2008; Reutsky et al., 2015; Petts et al., 2016). However,
143 the specific fractionation reactions in the Earth's mantle seem to play a bigger role for carbon (e.g.,
144 decarbonation) than for nitrogen (Cartigny et al., 2014; Petts et al., 2016). Progressive fractionation of an
145 evolving fluid in a closed system (i.e., Rayleigh fractionation) has been suggested to explain
146 monocrystalline diamonds that display continuous, coupled changes in carbon and nitrogen isotopic values

147 (Petts et al., 2015). On the other hand, open system mixing of fluids (e.g., Petts et al., 2015) or separate
148 fluid pulses with different isotopic compositions (e.g., Wiggers de Vries et al., 2013; Smit et al., 2016)
149 have been suggested to explain the observed variability in the carbon and nitrogen isotope values of some
150 other diamonds, including PDAs (Jacob et al., 2017 and Fig. 4). Thus, nitrogen concentrations of diamonds
151 and their corresponding nitrogen isotope values ($\delta^{15}N$) complement the $\delta^{13}C$ values to trace the source of
152 diamond-forming fluids in the deep Earth (Javoy et al., 1986; Boyd and Pillinger, 1994; Cartigny et al.,
153 1998a).

155 In general, PDA diamond geochemistry is characterized by ^{13}C-depletion and ^{15}N-enrichment, higher
156 than average nitrogen abundances, a lower than average occurrence of nitrogen-free samples, and a range
157 of nitrogen aggregation states (Mikhail et al., 2019b and references therein). The carbon isotope values
158 for PDAs show a large range from $\delta^{13}C = -1‰$ to $-30‰$ (Fig. 3) with modes at $-5‰$ and $-18‰$ (Deines,
159 1980; Maruoka et al., 2004; Mikhail et al., 2013; Jacob et al., 2014; Sobolev et al., 2016; Mikhail et al.,
160 2019b). However, when plotting only those data where combined C-N isotope systematics for garnet-
161 bearing PDA samples are considered (to enable meaningful comparisons between the different isotopic
162 and paragenetic systems), the mode at $-5‰$ is not present. It is noteworthy that, alongside peridotitic and
163 websteritic PDAs only a small subset of eclogitic and websteritic monocrystalline diamonds show ^{13}C-
164 depletion with mean values positioned lower than the $-20‰$ (e.g., eclogitic samples from Dachine (French
165 Guiana; Smith et al., 2016) and Jericho (Northern Canada; De Stefano et al., 2009). However, what
166 distinguishes the PDAs from monocrystalline diamonds is the fact that all parageneses (eclogitic,
167 websteritic, and peridotitic) are found to show ^{13}C-depletion (Maruoka et al., 2004; Mikhail et al., 2014a,
168 2019b), with a mode at $-18‰$, while peridotitic monocrystalline diamonds plot with the mode at $-5‰$
169 (Table 2).

171 The $\delta^{15}N$ values range from $-6.1‰$ to $+22.6‰$ (Gautheron et al., 2005; Mikhail et al., 2014c; Jacob et
172 al., 2017) with an average of $+8.4‰$ (Table 2) – an average value that is significantly more ^{15}N-enriched
173 than for all other diamond types (Table 2). The ^{15}N-enrichment in PDAs is important because the interior
174 and exterior of Earth show a pronounced and statistically significant isotopic disequilibrium for nitrogen,
175 where the upper mantle is ^{15}N-depleted and the crustal reservoirs are ^{15}N-enriched (Boyd and Pillinger,
176 1994). Thus, the ^{15}N-enriched nature of PDAs supports involvement of crustal material in their formation.
177 In addition, oxygen isotopic values for garnets in PDAs from Venetia (Jacob et al., 2000) and Orapa
178 (Mikhail et al., 2019b) show $\delta^{18}O$ values from $+5.96$ to $+8.09‰$, which are higher than $\delta^{18}O$ values for
179 the ambient mantle ($\delta^{18}O = 5.5‰$; Mattey and MacPherson, 1993). The origin of ^{18}O-enriched or depleted
180 oxygen in mantle samples is considered to be *bona fide* evidence for material altered in a thermal
181 environment of too low energy to be assignable to the deep Earth, this is based on evidence that
182 equilibrium stable isotope fractionation for $^{18}O/^{16}O$ at temperatures $> 800\ °C$ and at high pressures are
183 negligible and cannot explain a shift of $\delta^{18}O$ value $> \pm 1‰$ (Chacko et al., 2001).

185 The nitrogen concentrations in PDAs cover a large and unevenly distributed range from 4 to 3635 at.
186 ppm N with an average nitrogen abundance of 496 ± 715 ppm (Table 2). These nitrogen concentration
187 data are not resolvable from monocrystalline diamonds or fibrous diamond samples, but the latter show
188 higher average nitrogen abundances of around 922 ± 360 ppm. The different average nitrogen
189 concentrations unfortunately do not carry much significance due to the overlap of the datasets and
190 considering the spread of data. In general, the spread of nitrogen concentrations in PDAs are not dissimilar
191 from every other diamond type, where monocrystalline samples show lower average nitrogen abundances
192 with 396 ± 350 and 649 ± 483 ppm for peridotitic and eclogitic monocrystalline samples, respectively
193 (Cartigny, 2005). These poorly defined averages for the nitrogen concentrations in mantle diamonds are
194 sometimes used to argue for kinetic uptake of nitrogen in diamond during growth, where the slow diffusion
195 of nitrogen in diamond (Koga et al., 2003) prohibits re-equilibration after formation (see Mikhail and

196 Howell, 2016, for a discussion). Compared to the concentrations of nitrogen, the stable isotope data are
197 significantly distinct in their distribution and significance. Collectively, the role for a subducted crustal
198 organic component for the significant ^{13}C-depletion is supported by the high nitrogen concentrations and
199 very positive nitrogen isotope values for PDAs (Shelkov et al., 1997; Gautheron et al., 2005; Jacob et al.,
200 2014, 2017; Mikhail et al., 2014c, 2019a) because the combined $\delta^{13}C$ vs $\delta^{15}N$ vs N ppm data are typical
201 for material from Earth's surface (Boyd and Pillinger, 1994).
202
203   When crushed under vacuum, PDAs release gas (Gautheron et al., 2005; Mikhail et al., 2019a), and
204 this requires the presence of fluid micro-inclusions to explain the release of detectable ^3He after crushing
205 (Gautheron et al., 2005; Mikhail et al., 2019a). Therefore, to shed more light on the origin of diamond-
206 forming fluids one can apply noble gas isotope data to complement and test hypotheses developed using
207 C-N stable isotope data (e.g., $^3He/^4He$). This is useful because, while C and N isotope systems are powerful
208 tracers of subducted material, ^3He is an equally powerful tracer for an otherwise hidden mantle signature
209 within crustal-source dominated ^{13}C-depleted and ^{15}N-enriched systems. This is because ^3He is a
210 primordial isotope and one of the most incompatible elements in silicate systems (Brooker et al., 2003;
211 Jackson et al., 2013). Therefore, ^3He is not transferred into the solid Earth after degassing (instead, it is so
212 light that it is lost to space). However, an unavoidable issue is ^4He ingrowth due to radioactive alpha
213 decay. The degree of nitrogen aggregation in PDAs, fibrous and monocrystalline diamonds is consistent
214 with millions to billions of years of mantle residence (Mikhail et al., 2019a and references therein)
215 permitting ^4He growth due to alpha decay of U and Th in the sample, which decreases the $^3He/^4He$ ratios
216 over time (Timmerman et al., 2019a, b). This results in a relationship between $^3He/^4He$ and ^3He
217 concentration shown in Fig. 4, reflecting radiogenic ^4He production since the fluids were trapped in
218 diamond (see caption to Fig. 4).
219
220   After considering ingrowth of ^4He due to the decay of U and Th in the sample it is clear that the PDAs
221 and some monocrystalline diamonds characterized by low $\delta^{13}C$ (commonly interpreted to indicate a crustal
222 origin for the diamond-forming carbon), show high $^3He/^4He$ ratios typical for mantle fluids (Gautheron et
223 al., 2005; Mikhail et al., 2019a). The spread of data can be explained by mixing between a He-rich, high
224 $^3He/^4He$ mantle source with $\delta^{13}C = -5‰$ and a He-poor, low $^3He/^4He$ crustal component with $\delta^{13}C$
225 between −15 and −30‰ (akin to the crustal organic carbon field in Fig. 3). The involvement of a crustal
226 component is strongly supported by the ^{15}N-enrichment in the ^{13}C-depleted PDA samples and best matches
227 either altered oceanic crust (Cartigny et al., 2014) or organic material hosted in sedimentary rocks
228 (Thomazo et al., 2009). Hence, the He-C-N isotope systematics in PDAs could be described by mixing
229 between fluids released from subducted altered oceanic crust and mantle material, and mass balance skews
230 the measured values towards the dominant component (Mikhail et al., 2019a). Therefore, although the
231 ^{13}C-depleted carbon and ^{15}N-enriched nitrogen provide evidence for crustal sources for some of the PDA-
232 forming fluids, the high $^3He/^4He$ ratios in PDAs from Orapa reveal an unambiguous mantle component
233 for these strongly ^{13}C-depleted samples (Mikhail et al., 2019a).
234
235   In terms of PDA petrogenesis, these data characterize the PDA-forming metasomatic fluids as hybrids
236 with subducted origins that have remobilized volatile elements in the subcratonic lithospheric mantle,
237 initiated by subducted fluid percolating and interacting with potentially ancient material in the lithospheric
238 mantle (first shown by Jacob et al., 2000).
239
240 **Nitrogen aggregation and mantle residence times**
241
242   Nitrogen is the most abundant lattice-bound impurity in diamond. Over time, nitrogen defects as a
243 function of temperature from single nitrogen atoms (C centers, Type Ib), to pairs of atoms (A centres,
244 Type IaA), to 4 nitrogen atoms tetrahedrally arranged about a vacancy (B centres, Type IaB; Evans and

245 Qi, 1982). This sequence is quantified and expressed as the degree of nitrogen aggregation in %. The first
246 step in this process (C to A centre aggregation) occurs quite rapidly while the second step (A to B centre)
247 occurs much more slowly, where the exact rate of conversion depends on the temperature and nitrogen
248 concentration (Chrenko et al., 1977). The A to B centre aggregation follows a second-order kinetics law
249 (Evans and Qi, 1982), meaning nitrogen aggregation can be used to estimate either the average temperature
250 of residence or the duration of diamond residence in the mantle (assuming the other is known).
251 Furthermore, platelets – planar interstitial carbon aggregates found on the {100} crystal planes – are the
252 by-products of B centre formation and are prone to degradation during residence in the mantle (Woods,
253 1986). The nitrogen aggregation data are fitted to a second-order kinetic model (e.g., Howell et al., 2012a,
254 2012b) to ascertain information about the number, or depth, of the diamond-forming events.

256 As revealed by infrared spectroscopy, nitrogen aggregation states for PDAs span the whole spectrum
257 from pure IaA to pure IaB (Mikhail et al., 2014c). Platelet characteristics are found to be regular, meaning
258 they preserve their time-dependent history and have not been degraded by deformation and/or heating.
259 There is no correlation between paragenesis (as defined by garnet geochemistry) and any of the IR
260 characteristics for PDAs from Orapa (Mikhail et al., 2019b).

262 The nitrogen aggregation state for several diamond grains from individual PDA samples are
263 homogeneous, in contrast with monocrystalline diamonds which can show highly variable nitrogen
264 aggregation states between different growth zones reflecting multiple growth events (Boyd et al., 1987;
265 Palot et al., 2013; Bulanova et al., 2014; Timmerman et al., 2017). Orapa PDAs show varying degrees of
266 aggregation (10–76%B) and plot along calculated isotherms as a function of nitrogen abundance which
267 can be fit to residence temperatures between 1100 and 1175 °C. However, the calculations of average
268 mantle residence temperatures for PDAs in Mikhail et al. (2019b) assume residence time of 1000 m.y.
269 (Fig. 6). The aggregation process is controlled less by time than it is by temperature, and if we revere the
270 calculation and vary temperature the reliability of these models is shown to be justifiably questionable.
271 For example, if the model is computed with an elevated temperature of 1200 °C (increase of 25 °C from
272 the maximum) or at 1400 °C (increase of 200 °C from the maximum), then the predicted mantle residence
273 times for a sample with 76%B (and 600 ppm N) are 500 million years and 660,000 years, respectively.

275 Despite this, there is no evidence for higher-than-average residence temperatures (>1200 °C) for the
276 Orapa PDAs, so the observation of regular and internally continuous nitrogen aggregation data (Mikhail
277 et al., 2019b) means that the nitrogen aggregation data for each sample can be used to interpret their time–
278 temperature history (with large uncertainties). Nevertheless, there are PDAs that show evidence for higher
279 formation temperatures than 1200 °C, both at Orapa (Jacob et al., 2016) and also at Venetia, but nitrogen
280 aggregation data unfortunately do not exist for these specific samples. One sample from the Venetia
281 kimberlite, for example, was found to contain droplets of metallic iron and iron carbide and this
282 assemblage requires temperatures above the liquidus of this system of 1370 °C at relevant pressures (Jacob
283 et al., 2004).

285 All Orapa PDAs show B-centres of varying degrees, and this requires several hundred million years
286 of residence in the mantle prior to emplacement in the crust at 91 Ma (Fig. 6). This is not the case for all
287 PDAs, where data for PDAs of unknown provenance show nitrogen with very low and very high degrees
288 of nitrogen aggregation (0–100%B; Mikhail et al., 2014c). These samples also show high temperature
289 deformation and annealing structures in electron backscattered diffraction which perhaps could be argued
290 to require significant mantle residence times (Rubanova et al., 2012). What can be stated, using these data,
291 is that nitrogen aggregation data from PDA samples strongly oppose any notion that the carbon
292 supersaturation event responsible for PDA-formation is temporally-associated with diamond-transporting
293 kimberlite metasomatism (as has been proposed for fibrous samples; Boyd et al., 1994b).

INSIGHTS FROM THE GEOCHEMISTRY OF NON-DIAMOND COMPONENTS IN POLYCRYSTALLINE DIAMOND AGGREGATES

Geochemical and petrological studies of the non-diamond constituents are beset with technical challenges, many of them caused by the hardness anisotropy of diamond combined with the random orientation of the grains in PDAs and the high refractive index of diamond. For example, preparing PDAs for *in situ* microanalysis is exceedingly difficult due to the almost impossible task of producing adequately well-polished surfaces (Rubanova et al., 2012; Jacob et al., 2017). Similarly, the *ex situ* optical identification of the non-diamond phases or textural relationships is commonly obscured by the opaque nature of most PDAs (see Fig. 1) – the result of the many opaque impurities combined with the high optical refractivity of diamond. These challenges are intensified by the fact that the non-diamond phases, such as silicates, which hold a wealth of geochemical information, are present only in minor or trace amounts and can be heterogeneously distributed within a single sample (Mikhail et al., 2019b). To date, effective examination of the non-diamond phases in PDAs, such as garnet, requires mechanical disaggregation using a crusher which destroys all in situ petrographic data. For example, on some occasions, only after the mechanical extraction of the garnet did it transpire that a single PDA was host to multiple distinct populations of websteritic garnets, and even revealing garnets of different paragenesis within a single PDA, such as sample ORF53 from Orapa which was host to one purple (peridotitic) and one orange (websteritic) garnet (Mikhail et al., 2019b). This 'lucky' find of two very different garnets in one sample, in fact highlights a notable characteristic of the non-diamond components in PDAs, which is that they contain disequilibrium assemblages at grain-scale. Importantly, touching pairs of chemically homogeneous silicates of a single paragenesis (e.g., peridotitic-websteritic-eclogitic) as they are encountered in inclusions in monocrystalline diamond, are yet to be identified in PDAs.

Modern high-resolution computed tomography (µCT) offers an alternative and non-destructive method to optical microscopy and has occasionally been applied in PDAs (Fig. 2; Jacob et al., 2011; Logvinova et al., 2015). Multi-scale petrographic study of PDAs by µCT is still expensive but will most likely gain popularity with increasing access (i.e., supply vs. demand).

Macro-inclusions and intergrowths

The most common non-diamond phases found in PDAs are garnets, followed by clinopyroxenes, but other phases can be present in significant abundances, including Mg-chromite, rutile, magnetite, sulphides and cohenite (iron carbide) (Gurney and Boyd, 1982; Kirkley et al., 1991; Jacob et al., 2000; Dobosi and Kurat, 2002, 2010; Jacob et al., 2011, 2014, 2016; Mikhail et al., 2019b). Olivine and orthopyroxene are notably absent. Touching parageneses of silicate minerals are almost absent and often, PDAs host either only one mineral (most often garnet) or minerals of different parageneses which cannot have formed in equilibrium with each other. In addition, PDAs are known to display magnetism which requires the presence of magnetite and other magnetic phases (Jacob et al., 2011, 2016). It is worth pointing out that magnetite is a rare inclusion in PDAs, but its occurrence is more abundant in PDAs than in monocrystalline diamonds (Harris, 1968; Sobolev et al., 1989) and may explain the magnetic properties of stewartite.

For diamond inclusions in general, garnet and clinopyroxene data are sub-divided into three groups, termed peridotitic, websteritic, and eclogitic, according to their silicate paragenesis. The assignment of inclusion paragenesis is empirical. For example, if assigned simply by colour then websteritic garnets are sometimes wrongly classified as eclogitic, as both are orange, and indeed some workers have classified websteritic garnets as low-Ca eclogitic (e.g., Jacob et al., 2000; Kurat and Dobosi, 2000). It is more

accurate to use the major element geochemistry of garnet inclusions, such as the weight percent abundances of Cr_2O_3 and CaO (Fig. 7a), where peridotitic are categorized by high-Cr and eclogitic garnets by low Cr- and high-Ca (Sobolev et al., 1973), and websteritic garnets are intermediate in composition (Gurney and Boyd, 1982). The paragenetic distinction(s) for pyroxenes is less clear (Fig. 7b), where a peridotitic paragenesis is assigned for clinopyroxenes with Mg-number [(Mg/Mg+Fe) × 100] >85, Cr-number [(Cr/Cr+Al) × 100] >10, and <2 wt.% Na_2O (Aulbach et al., 2002). Alternatively, all garnet and clinopyroxene inclusions can be classified according to their endmember compositions (Fig. 7c, d).

This dataset shows that garnets in PDAs are most commonly websteritic, with peridotitic and eclogitic compositions less common for PDAs than as inclusions in monocrystalline diamond (Fig. 8a). Considering the available data (from Orapa, Venetia, Mirny, and unknown) we find that 57% of the garnets from PDAs are websteritic (Fig. 8a), compared with only 3% of worldwide monocrystalline diamond garnet inclusions (Stachel and Harris, 2008; Fig. 8b). In contrast to the websteritic character of garnets in PDAs, the clinopyroxenes found in PDAs are most often peridotitic (79%; Fig. 8c), which contrasts with clinopyroxenes in monocrystalline diamond inclusions (18%; Fig. 8d). Whether the relative abundances or formation mechanisms for websteritic diamond inclusions represent pre-metasomatic mineralogical heterogeneity in the upper mantle (Stachel and Harris, 2008), eclogitic melt metasomatism (Aulbach et al., 2002; Kiseeva et al., 2016), or fluid metasomatism coeval with diamond formation (Mikhail et al., 2019b, 2021) is as yet unresolved. Characteristically, the most abundant mineral in the lithospheric mantle, olivine, is a notable absentee in PDAs. In addition, wehrlitic garnets and clinopyroxenes are absent, indicating that the striking absence of olivine is not a simple sampling bias, but is also reflected by the range of major element compositions for the silicates hosted in PDAs dominated by olivine-free websteritic/eclogitic parageneses (Figs. 7–8). The relatively high abundance of websteritic garnets in PDAs (Figs. 7–8) and the absence of olivine are a distinctive characteristic of PDAs that is not seen in the inclusion chemistry of monocrystalline diamonds from the same localities, such as Orapa (Mikhail et al., 2019b), or globally (Figs. 7–8), where peridotitic and eclogitic compositions represent the majority of the monocrystalline diamond yield (Figs. 7–8).

Trace elements and radiogenic isotopes of silicates in PDAs

Garnets intergrown with diamond in PDAs show typical chondrite-normalized rare earth element (REE) patterns with depleted LREE and relatively flat to convex-upward MREE to HREE (Fig. 9a-c). Peridotitic garnets have mildly sinusoidal patterns (Fig. 9a), similar to those included in monocrystalline diamonds (Stachel et al., 2004). Most of the websteritic garnets show no LREE enrichment and only some have mildly enriched LREE patterns (Fig. 9b), while this group has the highest HREE abundances of up to 55 × chondrite. Europium anomalies are not pronounced and, if present, are mostly within 15%, with one exception of a markedly positive Eu-anomaly (50%) in an eclogitic garnet from Orapa (ORF78, Mikhail et al., 2019b). Out of the four published trace element datasets for clinopyroxenes (Fig. 9d), two peridotitic samples (solid lines in Fig. 9d) have the highest REE abundances followed by a websteritic clinopyroxene (dotted line) and an omphacite (dashed line). Neither clinopyroxenes nor garnets show a correlation for REE abundances with their chromium content.

The notion for the involvement of ancient lithospheric material is provided by the unradiogenic $^{87}Sr/^{86}Sr$ isotopic ratios (0.703189 to 0.703589) and unradiogenic Nd isotopic ratios of −15.9 to −21.7 (ε_{Ndi}) observed in four ^{18}O-enriched websteritic garnet samples from ^{13}C-depleted PDAs from Venetia (Jacob et al., 2000). These data fall towards the unradiogenic end of a large range of ε_{Ndi} values for individually analysed peridotitic diamond inclusions from Venetia of −62 to +157 (Koornneef et al., 2017), and are typical for ancient lithospheric material.

Micro-inclusions

While the release of detectable He, Ne, Ar and Xe after crushing of the PDAs under vacuum (Gautheron et al., 2005; Mikhail et al., 2019a) is circumstantial evidence for the presence of micro- to nano-fluid inclusions in PDAs, direct observation of small inclusions requires Focussed Ion Beam assisted Transmission Electron Microscopy (FIB-TEM) (Klein-BenDavid et al., 2006; Wirth, 2009). For PDAs, these studies can relate minerals included in the diamond grains to those intergrown with them and thus can identify the type of metasomatic overprint in these rocks. A PDA from Orapa contained magnetite, pyrrhotite, rutile and omphacite as micro-inclusions in the diamond grains. However, magnetite grains that were not fully encapsulated by diamond showed hematite and silicate alteration rims (Fig. 2; Jacob et al., 2011), whereas pyrrhotite grains were present only as micro-inclusions in diamonds and not as intergrown phases. This indicated a primary or even protogenetic nature of pyrrhotite and an unambiguous metasomatic overprint for the magnetites, thus highlighting the importance of recognising epigenetic changes in PDAs before petrological models are developed.

Fluid inclusions in diamonds in this sample contained solid phases in the form of nanometre-sized grains of rutile, pyrrhotite and omphacites (but not magnetite), and silicic quench phases (i.e., non-stoichiometric Si-bearing phases detected in cavities that formerly contained fluid. (Jacob et al., 2011). Diamond-related fluids worldwide range compositionally between four end-members, namely a saline fluid rich in Cl, K, Na, H_2O and carbonate, a silicic end-member rich in Si, Al, K and H_2O, high Mg- and low Mg-carbonatitic endmembers rich in Mg, Ca, Fe, K and carbonate, where both show continuous compositional arrays with the silicic endmember on a ternary diagram (Weiss et al., 2009, 2011). The PDA sample from Orapa contained a 10 nm-sized carbonate inclusion in addition to the silicic phases; hence, the diamond-related fluid composition in this sample is silicic and water-bearing with rare carbonates, while halides are absent. In the context of the general composition of diamond fluids worldwide (Weiss et al., 2022, this volume), these observations place this specific sample close to the silicic fluid endmember (Weiss et al., 2022, this volume). Based on these data, it could be hypothesized that fluid inclusions in PDAs have a compositional range similar to that found in other varieties of diamond, consistent with REE modelling of garnets (Mikhail et al., 2019b), but testing this hypothesis will have to await further direct observations in the future.

Depth of origin

The scarcity of silicate inclusions (as opposed to silicate intergrowths) and the virtual absence of touching mineral phases in polycrystalline diamond aggregates has so far prevented attempts to derive a depth of formation for PDAs. Only one example is documented where a pressure estimate could be derived for the PDA from Orapa, described in *Micro-inclusions* above (Jacob et al., 2016). One of the pyrrhotite inclusions in diamond displayed a partially developed nanocrystalline reaction corona consisting of magnetite (Fig. 10). Transmission Kikuchi Diffraction (TKD) established epitaxy between pyrrhotite, magnetite corona and diamond host, indicating that the diamond nucleated on the magnetite corona which, in turn, formed at the expense of pyrrhotite via a redox reaction with the carbon–bearing fluid. Further TKD analysis of the nanocrystalline magnetite corona revealed textural evidence, namely twinning, which is typical for phase transitions and similar to twinning observed in back reactions of a high-pressure assemblage of $Fe_4O_5 + Fe_2O_3$ that replaces magnetite at pressures above 10–11 GPa at 1000–1600 °C (Schollenbruch et al., 2011; Woodland et al., 2012; Uenver-Thiele et al., 2017). The magnetite-($Fe_4O_5 + Fe_2O_3$) phase boundary at ca. 10 GPa is thus a minimum pressure estimate for this sample, which must originate from ca. 320–330 km, close to the base of the Kaapvaal subcratonic lithosphere beneath the Orapa kimberlite cluster (Fouch et al., 2004).

441   Assuming no metasomatic overprinting for any of the PDA garnets, single garnet geobarometry
442   performed using the machine learning-derived calibration of Thomson et al. (2021) yield average
443   pressures of 6.0 (StDev ± 0.8) and 7.4 (StDev ± 0.5) GPa for peridotitic and websteritic garnets,
444   respectively. The pressures for peridotitic and websteritic garnets were calculated using high and low Cr-
445   calibration for P-type and E/W-type garnets from (Wijbrans et al., 2016). However, corresponding
446   pressures calculated for samples containing multiple garnets yield pressure differences up to ±2 GPa,
447   which could be explained by metasomatic overprinting for one of the garnets at an undefined time after
448   diamond formation. These differences in pressure, however, also call into question the reliability of using
449   single garnet geobarometry for PDAs without knowing if the garnets have been isolated or exposed to the
450   mantle since PDA formation. In addition, the total fraction majorite content (i.e., Si-excess and considering
451   Mj + NaMj) for garnets in PDAs shows a maximum of 0.06 with an average of only 0.01 ($n = 104$).
452   Therefore, we find no evidence to support the notion that PDAs, as a group, are sourced from depths of
453   below the subcratonic lithosphere.

Constraints on the formation age(s) of PDAs

457   There are no *bona fide* formation ages for PDAs, as yet. However, the preservation of significant trace
458   element zonation in PDA-hosted garnets from Venetia (South Africa; Fig. 11) requires that these samples
459   precipitated shortly before kimberlite eruption, based on modelling the trace element heterogeneity using
460   known diffusion coefficients (Jacob et al., 2000). In addition, these same garnets show strongly
461   unradiogenic ε_{Nd} with values from −15.9 to −21.7 ε_{Nd} *(see above)*, typical for ancient lithospheric material,
462   which was used to argue for recent remobilization of this material upon the formation of PDAs at Venetia
463   (Jacob et al., 2000). Therefore, this means that the garnets contain older lithospheric material remobilized
464   with the diamond-forming fluid at Venetia. In contrast, garnets from Orapa PDAs show very little, if any
465   trace element variability within single garnets (Mikhail et al., 2019b). The geochemistry of garnets from
466   Orapa PDAs therefore provides no evidence of a young formation age and no reliable evidence for a
467   metasomatic event around the time of emplacement at 91 Ma (Mikhail et al., 2019b), in agreement with
468   the nitrogen aggregation results for the diamonds hosting these garnets (discussed earlier).

Oxidation State

472   Polycrystalline diamond aggregates are broadly similar to subcratonic lithospheric monocrystalline
473   diamonds with respect to the chemistry of the minerals included in and intergrown with the diamond
474   grains. Like monocrystalline diamonds, PDAs span a large range of ca. 7 log units in oxygen fugacity
475   (fO_2) as evidenced by their associated minerals: carbonates and magnetite in PDAs from Orapa indicate
476   oxidising conditions of around log$fO_2 = −6$ (Jacob et al., 2011), while cohenite (iron-carbide) as well as
477   native iron in PDAs from Venetia record distinctly reducing conditions of about log$fO_2 = −13$ (Jacob et
478   al., 2004, 2016); this characteristic reducing signature is shared with the monocystalline diamond suite at
479   this locality (Deines et al., 2001).

481   Redox reactions, involving redox couples of carbon-bearing fluids and Fe-Ni-bearing phases, are
482   proposed to be major diamond formation processes in the deep Earth's mantle (Rohrbach and Schmidt,
483   2011). PDAs have delivered the first direct evidence for redox freezing of diamond by reduction of
484   carbonatitic fluids with pyrrhotite to form magnetite and diamond (Jacob et al., 2016), while native iron
485   and iron carbide (cohenite) included in a websteritic garnet (Jacob et al., 2004) are products of oxidation
486   of a methane-bearing fluid. It should however be noted, that as of yet, the relationship between
487   monocrystalline diamonds and polycrystalline diamond aggregates is unknown. Since the database for
488   PDAs is much smaller than for monocrystalline diamonds, it is difficult to evaluate the abundance and
489   potential prevalence of certain oxidation states, but the large range of fO_2 is significant and suggests a

490 prominent role of redox gradients and transient, small-scale equilibria in their formation. Grain-scale
491 equilibrium, instead, is scarce and most often absent in PDAs.
492
493
494   **OVERVIEW OF CURRENT UNDERSTANDING FOR**
495   **POLYCRYSTALLINE DIAMOND FORMATION**
496
497   There can be no single model for polycrystalline diamond-formation, just like there is no single model
498 for monocrystalline diamond-formation. For example, no single model can explain why some samples
499 show high- and low- nitrogen aggregation (Mikhail et al., 2014c, 2019b) and no single model can reconcile
500 the range of oxygen fugacities required to stabilize carbonates + magnetite at Orapa (Jacob et al., 2011,
501 2016) and cohenite + native iron at Venetia (Jacob et al., 2004).
502
503   The mineral inclusions and intergrowths show no indication for derivation from depths well below the
504 subcratonic lithosphere, unlike some monocrystalline diamonds. Only one sample has yet allowed a
505 reliable determination of a depth of formation, placing it close to the base of the subcratonic lithosphere
506 of the Kaapvaal craton at the Orapa locality (Jacob et al., 2016), determined to be at 320–330 km by Fouch
507 et al. (2004). This depth of origin, combined with the absence of significant Si-excess in the garnets, may
508 mean that these diamond species primarily consist of remobilized material derived from the carbonate-
509 enriched keels of the subcratonic lithosphere (Foley, 2009; Jacob et al., 2000) and/or that carbon-rich
510 fluids from depth reacted and formed diamond upon entering the ductile to brittle deformation transition
511 zone at the base of the subcratonic lithospheric mantle as suggested by (Jacob et al., 2004). The fact that
512 PDAs have only been reported from plume-related Group I kimberlites and not from Group II kimberlites
513 that originate from subcratonic lithospheric sources (Le Roux et al., 2003; Becker and Le Roux, 2006)
514 agrees well with the depth of derivation for the PDAs from the base of the lithosphere. What is most
515 apparent is that some form of chemical interaction is involved between surface and mantle material, where
516 mixing between subducted crustal material, namely altered oceanic crust, with ambient mantle carbon and
517 the subcratonic lithospheric mantle is strongly supported by major, minor, and trace element systematics,
518 as well as several isotopic systems (He-C-N-O-Sr-Nd) acquired carbon, oxides, and silicates in the PDAs.
519
520   Most garnets in PDAs are websteritic, but the clinopyroxenes are mostly peridotitic (Figs. 7–8). The
521 predominance of websteritic garnets in PDAs (Figs. 7–8) and the absence of olivine (and of
522 orthopyroxene) are a distinctive characteristic of PDAs that are not seen in the inclusion chemistry of
523 monocrystalline diamonds (Figs. 7–8). Subcratonic garnet websterites are typically products of melt
524 interaction with mantle rocks (e.g., Rehfeldt et al., 2008; Mallik and Dasgupta, 2012). Hence, the
525 websteritic silicates in the PDAs are most likely hybrid phases and are, like the magnetites, reaction
526 products of the interactions of the carbon-bearing fluid with surrounding mantle material upon diamond
527 formation. For example, a recent study used a predictive thermodynamic modelling approach and was
528 able to fit the major element compositions websteritic garnet and clinopyroxenes for a large number of
529 PDAs, and also those from monocrystalline diamonds (Mikhail et al., 2021). This predictive
530 thermodynamic model was run using the extended Deep Earth Water model (Huang and Sverjensky,
531 2019), which enables the assessment of a huge range of variables (P-T-X). The model produces a reaction
532 pathway resulting from the reaction of an eclogitic fluid with a range of model peridotites (lherzolite,
533 harzburgite, and dunite) at 5 GPa, 1000 °C, and across a range of redox conditions ($\log fO_2 = -1$ to -6).
534 The outputs include the co-evolution for fluid composition (including fO_2 and pH) alongside carbon
535 speciation under isothermal and isobaric conditions, and the major element composition and modal
536 abundances for the precipitates (silicates and oxides in the case of Mikhail et al., 2021). The model does
537 not encompass all conditions and compositions observed in nature – it is S and Cr-free, limited to at 5 GPa
538 and 1000 °C and adopts a smaller range of fO_2 than observed for PDAs – but it does satisfy a range of

11

features common to all PDAs: Mikhail et al. (2021) show that fluid-rock interaction can result in the formation of (high-Mg) eclogitic, websteritic, and peridotitic garnets and clinopyroxenes from a single fluid during a diamond-forming metasomatic reaction (Fig. 12).

Interestingly, most models generate ca. 2% by volume magnetite, which could speak to the formation of stewartite, and because the model also generated websteritic garnets (predominantly), this might speak to the formation of framesite (Fig. 12). The model in Mikhail et al. (2021) would remobilize ancient material via dissolution in the fluid and re-precipitate diamond + silicates + oxides (Jacob et al., 2000). This model of diamond growth progressively trapping material during a reaction pathway could also satisfy the occurrence of chemical zonation in PDAs (Fig. 4) and the fact that some PDAs host disequilibrium assemblages (i.e., mixed paragenesis) because the diamond-, silicate-, and oxide-forming fluid follows an evolving pathway. For garnets this would be from low pyrope-eclogitic to high pyrope-peridotitic (Fig. 12). This would provide the mechanism to preserve snapshots of the metasomatic reaction by occasionally trapping garnets and clinopyroxenes at different stages of the reaction thus forming a diamond with inclusions of mixed paragenesis in the same place (no mechanically challenging spatial mobility is required to explain the occurrence) and during the same metasomatic event.

Noteworthy, PDAs also contain protogenetic and epigenetic phases in addition to syngenetic phases which highlights the need for petrographically contextualized data (e.g., μCT datasets). However, the timing of PDA formation is currently the least constrained aspect of their story, and one of the most integral to any realistic geological model. Several lines of evidence discussed in the sections above support the notion that some PDAs are geologically 'old' while others are 'young' in relation to kimberlite emplacement, hence pointing to episodic formation of PDAs likely linked to large-scale geodynamic events. Ergo, we are confident to say that PDA-formation is dynamic and usually involves the tectonically-induced chemical disequilibrium and fluid metasomatism at the base of the SCLM following the interaction of indigenous and subducted carbonaceous material. But we find no evidence for a single model for polycrystalline diamond-formation (note, the model of Mikhail et al., 2021 does not fit the low-Mg eclogitic PDAs). Excitingly, these data also suggest that there is no single polycrystalline diamond-forming event, globally.

PERSPECTIVES ON FUTURE RESEARCH

Placing diamond formation into the context of large-scale tectonothermal processes, such as subduction and plume-lithosphere interaction, is a fundamental requirement for understanding the deep carbon cycle. Therefore, placing PDA formation into the context of diamond formation is essential. This review has outlined what we know and exposed some glaring gaps in the knowledge base. Some of the most pressing questions focus on the what, when, and how of PDA formation.

When did PDAs form?

The temporal relationship between the PDAs and other diamond types, and their host kimberlites, requires immediate attention. While recent instrumental developments have brought radiogenic isotope analysis of very small samples within reach (Koornneef et al., 2014), we do not currently have any direct age information for PDAs. Circumstantial evidence from preserved trace element zonation (Fig. 11) and nitrogen aggregation point to young ages for some samples, whereas mantle residence times for other PDAs are required to be long to explain their nitrogen aggregation characteristics (Fig. 6). PDA formation could be as dynamic as monocrystalline diamond formation with episodic formation spanning billions of years (Gurney et al., 2010; Timmerman et al., 2017), or they could result from distinct metasomatic

event(s) which may or may not be related to the formation of monocrystalline diamonds at specific localities (Mikhail et al., 2019b).

What formed PDAs?

The geochemistry of fluids for Orapa PDAs has been calculated using REE data from garnets and these data fit a model for a fluid geochemistry intermediate between the saline and carbonate endmembers (Mikhail et al., 2019b). Direct observations of the fluids by TEM in PDAs from Venetia instead showed carbonatitic-silicic chemistry (Jacob et al., 2014). More *in situ* analyses of the sub-micron fluid inclusions are required to quantify their major and minor element geochemistry to accurately chart their geochemistry within the established framework of the saline-silicic-carbonatitic ternary system (see Weiss et al., 2022, this volume).

How do PDAs form?

The source of PDA-forming fluids is variable and complex, of this there is no doubt. What is clear is that the source materials show mantle and crustal geochemical and isotopic signatures (Figs. 3, 4, 5), and the websteritic silicates are products of wallrock-fluid reactions (Mikhail et al., 2021). This requires some degree of mechanical exchange by subduction zone plate tectonics. However, the isotopic range of C-N data reveal that some PDAs form in distinct episodes with distinct isotopic sources. These data are recorded by spatially unconstrained stepped combustion (Mikhail et al., 2014a), but spatially resolved to be in the order of <20 μm using SIMS data for some samples (Fig. 4). It is unclear, however, on which time scales these diamond-forming events were recorded in this particular sample suite. It is also unclear how widespread element and isotope zonation is within PDAs, both in the diamond grains (Fig. 4) as well as in the silicates (Fig. 11) because of the difficulty in polishing flat surfaces required to map out zonation using CL imaging or SIMS or LA-ICPMS profiling. Further elucidation of the processes and timescales that lead to the formation of this species of diamond carries the potential to provide an important different perspective into the deep carbon cycle and link global geotectonic processes with the redox-freezing of carbon in the deep lithosphere.

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TABLES

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892   **Table 1.** Polycrystalline diamond aggregate terminology and characteristics.
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Name	Defining characteristics
Framesite	Polycrystalline and non-magnetic
Stewartite	Polycrystalline and magnetic
Boart	Morphology is not economically viable and comprises >1 diamond crystal
Diamondite	Any polycrystalline aggregate where diamond is the most abundant mineral phase
Carbonado	Black, polycrystalline, and only found in the Mid-Proterozoic (1–1.5 Ga) metaconglomerate overlying the São Francisco and Congo-Kasai cratons

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898   **Table 2.** Averages for samples where combined N and C data are available (no data considered when only one of
899   the isotope systems is reported). Note the large standard deviations for the mean nitrogen concentrations for PDAs
900   reflecting the large ranges of concentrations and the absence of a significant mean nitrogen abundance for PDAs.
901   Data sources: monocrystalline diamond (Cartigny et al., 1997; 1998a, 1998b, 1999, 2004, 2009; Palot et al., 2009;
902   Thomassot et al., 2009; Cartigny, 2010; Palot et al., 2012; Mikhail et al., 2014b; Smith et al., 2016), fibrous
903   diamond (Javoy et al., 1986; Boyd et al., 1987, 1992; Klein-BenDavid et al., 2010), and PDAs (Javoy et al., 1986;
904   Boyd et al., 1987, 1992; Shelkov, 1997; Klein-BenDavid et al., 2010).
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Diamond Type	n	$\delta^{13}C$ (‰)	StDev	$\delta^{15}N$ (‰)	StDev	N at.ppm	StDev
Monocrystalline (Peridotitic)	189	–4.6	1.9	–4.9	7.0	396	350
Monocrystalline (Eclogitic)	204	–9.5	8.2	–2.9	5.7	649	483
Fibrous	109	–6.5	3.1	–1.6	4.4	922	360
PDA	62	–18.1	5.4	+8.4	6.7	469	715

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FIGURE CAPTIONS

Figure 1. Images of silicate-bearing polycrystalline diamond aggregates from Orapa (a-d, from Mikhail et al., 2019b).

Figure 2. (a) μCT region of interest enlarging a 200 by 200 μm area showing pore space (red) and magnetite grains (purple) covered by a replacement envelope (green) of a mixture of hematite and a sheet silicate. Diamonds are rendered transparent in this view. (b) TEM HAADF image of a FIB foil cut from a diamond grain showing a replacement rim around magnetite consisting of a mixture of hematite and a sheet silicate.

Figure 3. Plot of $\delta^{13}C$ vs $\delta^{15}N$ values for select diamond types. Shown here is the mean mantle C-N stable isotope field, within which most fibrous diamonds plot (compiled by Cartigny et al., 2014). Also shown are the fields for eclogitic monocrystalline diamonds from Jwaneng and Orapa (Cartigny et al., 1998b; 1999). The PDA data are from Gautheron et al. (2005), Maruoka et al. (2004), and Mikhail et al., (2013; 2014a; 2019b). The data for the $\delta^{13}C$ and $\delta^{15}N$ values for subducted organics are from Halama et al. (2010; 2014) Busigny et al. (2019), and the compilation in Cartigny et al. (2014)

Figure 4. Cathodoluminescence image of a diamond fragment from a websteritic PDA from Venetia showing different growth zones with variable $\delta^{13}C$ values, indicating different growth pulses.

Figure 5. Helium isotope systematics of fluids released by *in vacuo* crushing and heating of PDAs, and monocrystalline and fibrous diamonds. The $^3He/^4He$ and $\delta^{13}C$ value of the modern convecting upper mantle (CUM) and the sub-continental lithospheric mantle (SCLM) are shown for reference (adapted from Mikhail et al., 2019a). The mixing lines shown in [a] are drawn between oceanic crustal-derived fluids with $\delta^{13}C$ = –20 and –30‰, and $^3He/^4He$ = 0.01 Ra, and mantle-derived fluids with $\delta^{13}C$ = –5‰ and $^3He/^4He$ = 9 Ra. The mixing lines plotted in [b] are hyperbolic as $[^4He]_{mantle}/[^4He]_{crust}$ is assumed to be 10. Note, the mantle $^3He/^4He$ endmember is slightly higher than the present-day upper asthenosphere and lithosphere mantle value, reflecting the U-Th decay-driven temporal evolution of $^3He/^4He$ in the silicate Earth (Porcelli and Elliot, 2008). Therefore, all $^3He/^4He$ ratios are minimum values, although it appears that diamonds with $>1 \times 10^{-12}$ ccSTP $^3He/g$ are largely immune to the effect of ingrowth because the ^4He production is too low to offset the R/Ra in this system (note the logarithmic scale of the *x*-axis). Comparative data are from Burgess et al. (1998), Gautheron et al. (2005), Broadley et al. (2018), Timmermann et al. (2018, 2019a, b), and Mikhail et al. (2019a).

Figure 6. Variation diagrams for the average degree of nitrogen aggregation (%) vs. nitrogen abundance (at.ppm) for the diamonds from PDAs (circle symbols) alongside the fibrous (square symbols) and monocrystalline diamonds (diamond symbols) from Orapa (adapted from Mikhail et al., 2019). Isotherms chart the residence times of 1000 m.y. using the DiaMap software (Howell et al. 2012a, b)

Figure 7. Inclusion parageneses and end-member compositions for garnets and clinopyroxenes from monocrystalline diamond and PDAs. The diamond inclusion database contains geochemical and metadata for > 9000 diamond inclusions. These plots utilize the clinopyroxene (*n* = 926), and garnet (*n* = 2628) data from lithospheric mantle diamonds. The data used here are sourced from Stachel and Harris (2008 and references therein) supplemented with more recent datasets (Cartigny et al., 2009; Smith et al., 2009; De Stefano et al., 2009; Sobolev et al., 2016; Tappert et al., 2009; van Rythoven and Schulze., 2009; Bulanova et al., 2010; Viljoen et al., 2009; Hunt et al., 2012; Miller et al., 2012; Smith et al., 2016; Mikhail et al., 2019a; Jacob et al., unpublished).

Figure 8. Pie charts reflecting the paragenesis for garnets (left) and clinopyroxenes (right) sourced from PDAs (left) and monocrystalline diamonds (right). The data for PDAs are sourced from Gurney and Boyd (1982); Gurney et al. (1984); Kirkley et al. (1995); Kurat and Dobosi (2010); Jacob et al., (2000; unpublished); Mikhail et al. (2019a); and Sobolev et al. (2016). The data for monocrystalline diamond inclusions are from Stachel and Harris (2008 and references therein).

Figure 9. Chondrite-normalised rare earth element (REE) patterns for garnets (a-c) and clinopyroxenes (d) from PDAs. Different signatures in (d) denote peridotitic (solid lines), websteritic (dotted line) and eclogitic (dashed line) clinopyroxenes. Data from Kurat and Dobosi (2010); Jacob et al., (2000); Mikhail et al. (2019), Sobolev et al., (2016). Chondrite data from Sun and McDonough (1989).

Figure 10. (a) TEM high angle annular dark field (HAADF) image of a diamond FIB foil showing a pyrrhotite inclusion with a magnetite rim. (b) Forescatter electron image of the magnetite corona. (c) Crystal preferred orientation of magnetite in the area indicated by a white rectangle in (b) colour-coded according to the legend and the reference frame (bottom right). Grain boundaries are in black, red lines are twin boundaries. Modified after Jacob et al. (2016).

Figure 11. Trace element zonation in three different grains of websteritic garnet in PDA from Venetia (sample V948, Jacob et al., 2000). (a) Spidergrams (normalized to primitive mantle: Sun & McDonough, 1989) show significant differences in most elements apart from titanium and the mid and heavy REE in the grains. (b) Variations in Nb/Ta and Zr/Hf ratios variation (blue – grain averages for three grains, black and orange are zones in two different grains), (c) compatible element Ni and Cr variations in the zoned grains.

Figure 12. Selected model results for predicted garnet compositions during progressive metasomatism and diamond formation at 5 GPa and 1000 °C. The lines for the runs plotted are thick enough to represent the average trajectories for an eclogitic fluid reacting with model peridotites (lherzolite, harzburgite, and dunite) and model peridotites (lherzolite, harzburgite, and dunite) + aragonite (dashed line). Data are from Mikhail et al. (2021) and the input and output files are available at https://doi.org/10.17630/32ebd3c0-bba6-4aa1-9b6d-c53a0a3b61e0. All comparative data shown are taken from the same sources as listed in the caption of Figure 7c.