

From the lithosphere to the lower mantle: An aqueous-rich metal-bearing growth environment to form type IIb blue diamonds

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1	From the lithosphere to the lower mantle: an aqueous-rich metal-bearing growth
2	environment to form type IIb blue diamonds
3	
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19	Type IIb diamonds; blue diamonds; boron; nitrogen; mineral inclusions; aqueous fluids; Fe-Ni

20 alloys; lithosphere.

21 **Abstract**. A study of five diamonds containing mineral and fluid inclusions, selected among forty-22 nine specimens from the Cullinan Mine, South Africa, was carried out to better document the origin 23 and formation of type IIb diamonds. The combination of several in-situ non-destructive techniques 24 was used to identify the mineralogy and the chemical composition of primary and secondary 25 inclusions. These inclusions include breyite, larnite, graphite, Fe-Ni-Cu native metallic alloys, 26 sulfides of the pyrrhotite group, Ni-rich oxide and potential hydrous ferric sulfates. A common and 27 abundant hydrous fluid containing $H_2O + CH_4$ was also identified. From the various observations, 28 we suggest that these type IIb diamonds grew in an aqueous oxidized fluid reacting with a reduced 29 mantle characterized by low oxygen fugacity. Remnant pressures recorded in primary breyite by 30 Raman shifts and XRD measurements enabled the calculation of minimal entrapment pressures of 31 inclusions using elastic geothermobarometry. Applying pressure corrections caused by elastic 32 relaxation, minimum trapping pressures from 4.9 GPa to 5.6 GPa were calculated, suggesting 33 lithospheric depths consistent with the occurrence of numerous graphite inclusions. The association 34 of breyite and larnite, which is often considered as an indicator of sublithospheric origin, also 35 occurs at pressures of 6 GPa or lower in a carbonate/Ca-rich environment. The B-poor and N-36 absent features of type IIb diamonds do not support the classic subduction-related model of their 37 formation. Whereas high-pressure minerals would host boron in cold subducting slabs, slabs are 38 also important carriers of nitrogen into the deep mantle, with this latter element mostly absent in 39 these diamonds. In our alternative model, the mantle is equally proposed to be the source of boron, 40 while maintaining that metallic alloys or N speciation between fluid and melt would still prevent 41 the incorporation of nitrogen, leading to the expression of the blue, boron-related and N-poor 42 features of type IIb diamonds. The observed mineralogical assemblage neither proves 43 sublithospheric origin nor excludes lithospheric depths of formation for these diamonds. Hence, 44 we propose that type IIb diamonds form in a mantle continuum, from sublithospheric to45 lithospheric depths.

1. Introduction

47 The study of natural diamonds and their mineral/fluid inclusions provides unique constraints 48 on the mineralogy of the Earth's mantle from 120 km to approximately 800 km depth, i.e., from 49 the lithosphere down to the lower mantle (Harte, 2010; Shirey et al., 2019). Diamonds are also a 50 unique sample from which to infer the nature of parent metasomatic C-O-H-N-S fluids or melts 51 percolating through the mantle (e.g., Schrauder and Navon, 1994; Cartigny et al., 2014; Smit et al., 52 2016; Stachel et al., 2017).

53 In addition to the traditional classification based on their nitrogen and boron content, 54 diamonds are also classified based on the mineralogy and geochemistry of their solid and fluid 55 inclusions. Most diamonds are of lithospheric origin (above 300 km depth) and are believed to 56 grow in C-O-H-N-S fluids (see reference above). Lithospheric diamonds usually contain olivine, 57 pyroxene, garnet, spinel and sulfides (e.g., Meyer, 1987; Stachel and Harris 2009) as typical 58 mineral inclusions. Superdeep diamonds (formed at depths between 410 to 800 km) are rare and 59 contain typically majorite garnet, ferropericlase, Ca-perovskite and bridgmanite (e.g., Shirey et al., 60 2013). The nature and composition of the parent fluids of sublithospheric diamonds are more 61 difficult to assess because the oxygen fugacity should be much lower at these depths 62 (approximately FMQ-5; Frost and McCammon, 2008). It is suggested that C, H and O in metal-63 saturated regions of the deep mantle are buffered to reduced compositions, with C being either 64 dissolved into metallic liquids or existing as CH₄-rich fluids (e.g., Shirey et al., 2019).

65 Based on the traditional classification, blue diamonds are defined as type IIb, having almost 66 no nitrogen, while the blue color results from the presence of boron (≤ 8 ppm; Gaillou et al., 2012). 67 Boron, which substitutes for carbon in the crystal lattice of diamonds (Chrenko, 1973), is a highly mobile element in aqueous fluids and exhibits incompatible behavior during partial melting. It is
concentrated in oceanic sediments (1-100 ppm), hydrothermally-altered oceanic crust (9-70 ppm),
as well as serpentinite (10-90ppm) and is often considered to be an indicator of slab contribution
to island-arc melts (e.g., De Hoog and Savov, 2018).

72 Type IIb blue diamonds are very rare, constituting only $\leq 0.02\%$ of the diamonds extracted 73 worldwide (King et al., 1998; Gaillou et al., 2012). They are found in a few kimberlites from South 74 Africa (Cullinan Mine), Botswana (Orapa and Karowe) and – of uncertain origin – from alluvial 75 deposits in India (Kollur Mine). They are very expensive on the diamond market and therefore not 76 readily available for research, as demonstrated by the scarcity of published studies (King et al., 77 1998; Gaillou et al., 2012; Smith et al., 2018a and b). Recently, based on inclusions of majorite, 78 jeffbenite and bridgmanite trapped in a series of type IIb diamonds, Smith et al. (2018a) proposed 79 that blue diamonds are sublithospheric and originate within either the transition zone or the lower 80 mantle, in relation to subduction settings.

81 Here, a collection of forty-nine type IIb diamonds extracted from the Cullinan Mine 82 (formerly Premier Mine), South Africa, was studied. Five of these diamonds contain single or 83 multi-phased inclusions and thus they were the focus of this study. Among these, five inclusion-84 bearing diamonds were studied with a combination of non-destructive in-situ methods to preserve 85 the gems and avoid loss of the inclusions, with the aim of identifying their parent fluids and their 86 growth conditions. Further, this study addresses why these type IIb diamonds contain both no 87 nitrogen and very little boron, and discusses the appropriateness of linking boron-bearing 88 diamonds to boron-rich environments, such as subduction zones.

89 **2. Materials and Methods**

90 2.1 Geological background and samples

91 The Cullinan kimberlite is located in the Gauteng Province, 130 km north-east of 92 Johannesburg, in the center of the Kaapvaal craton, one of the oldest fragments of continental 93 lithosphere of Archean age (Fig. 1). The crystallization ages of the Kaapvaal crust range from 3.6 to 94 2.6 Ga, and its mantle root – made up of highly-depleted mantle peridotites of dunite/harzburgite 95 composition (Viljoen et al., 2004) – is as old as 3.5 Ga (Moser et al., 2001). The region became a 96 stable continental plate at 3.0 Ga (Moser et al., 2001) and successively underwent one of the oldest 97 recognized episodes of plate subduction 2.93-2.88 Ga ago (Schmitz et al., 2004). The Kaapvaal 98 craton was intruded by repeated injections of magma, which gave rise to the layered structure of 99 the Bushveld Complex at 2.05 Ga, refertilizing the lithosphere by melt-related metasomatic 100 processes. The Cullinan kimberlite emplaced through the ultramafic-to-mafic rocks of the 101 Bushveld Complex (Allsopp et al., 1989) at 1.18±0.30 Ga (Scoates and Friedman, 2008). This 102 deposit is well-known for its large, colorless diamonds, such as the largest gem-quality rough 103 diamond ever found, the Cullinan (3106 carats rough crystal), as well as its blue diamonds, such as 104 the Cullinan Dream (24.18 ct fancy blue cut from a 122.5-ct rough).



Figure 1. Simplified geological map of South Africa, with the Kaapvaal and the Zimbabwe cratons of Archean age.
Blue diamond symbols indicate type IIb diamond mines. Abbreviations: Le.=Lesotho; S.=Swaziland.

Previous investigations revealed that most of the diamonds from the Cullinan Mine are of lithospheric origin (Deines et al., 1989; Thomassot et al., 2007), while Moore and Helmstaedt (2019) identified a bimodal population: 1) a Mg-rich suite (basic to ultrabasic, corresponding to sublithospheric diamonds; and 2) a Ca-rich suite (including breyite) linked to the websteritic suite 112 and thus of lithospheric provenance. A few specimens are sublithospheric, as inferred from the 113 discovery of a perovskite-structured polymorph of $CaSiO_3$ (Nestola et al., 2018). In a detailed study 114 of inclusions trapped in exceptional gem diamonds from Letseng mine (Lesotho), Smith et al. 115 (2016) proposed a model involving crystallization from a redox-sensitive metallic liquid phase in 116 the deep mantle. These large gems, referred to as CLIPPIR (for Cullinan-Like, Inclusion-Poor, 117 relatively Pure, Irregularly shaped and Resorbed), contain inclusions of solidified Fe-Ni-C-S melt, 118 wrapped in a thin fluid layer of $CH_4 \pm H_2$ that would involve a subduction-related formation under 119 metal-saturated conditions.

120 In the present study, a set of forty-nine type IIb diamonds from the Cullinan Mine production 121 were selected and donated when the mine was still owned by De Beers (Fig. 2). The forty-nine 122 diamonds are broken fragments from larger original crystals, faint-to-fancy blue in color, ranging 123 from 1.5 to 5 mm in diameter with a similar rounded, irregular appearance. Despite being 124 fragments, the presence of cleaved surfaces, conchoidal-to-irregular fractures and growth marks on 125 thirty-two of the forty-nine specimens allowed in-situ measurements such as micro-FTIR, which 126 revealed measurable amounts of uncompensated boron, confirming their type IIb nature. The 127 irregular and rough surfaces of the remaining seventeen specimens made measurement of their 128 boron content impossible. The detailed description of the totality of specimens is reported in Table 129 1.



Figure 2. Photographs of the forty-nine type IIb diamonds donated by De Beers group from the Cullinan Mine.

Table 1. Summary of the FTIR, micro-Raman and SXRD measurements as well as inclusion descriptions of the studied type IIb

133 diamonds.

Name	Weigh (ct)	^t Size (mm)	Description	Inclusion type	FTIR (B ppm)	Raman ¹	SXRD	XRF	SEM-EDX
B1-1	0.27		Fancy light blue crystal with an irregular shape and a fracture	None	NM	nm	nm	nm	nm
B2-1		2.5 × 2.5	Faint blue crystal with an irregular shape and conchoidal fractures	None	NM	nm	nm	nm	nm
B2-2	0.52	2.5×2	Faint blue crystal with an irregular shape	None	NM	nm	nm	nm	nm
B2-3	_	3.6 × 2.4	Faint blue crystal with an irregular shape and growth marks on the surface	None	NM	nm	nm	nm	nm
B3-1		4.2×2.4	Light blue crystal with an irregular shape and growth marks on the surface	Primary: black, flat dendritic inclusions	NM	NM ²	nm	nm	nm
B3-2	0.40	4.8 × 3.12	Light blue crystal with an irregular shape and several cleaved surfaces	None	0.08	nm	nm	nm	nm
B3-3		4.5 × 3	Fancy light blue crystal with an irregular shape, a cleaved surface and iridescent colors in a fracture	None	0.61	nm	nm	nm	nm
B4-1	0.23	4×2	Faint blue macle, growth marks on the surface and iridescent colors in a fracture	Primary: small black inclusion	0.29	nm	nm	nm	nm
B5-1	0.60	2.4 × 3.48	Fancy light blue crystal with an irregular shape	Primary and Secondary: small black inclusions close to the surface	NM	NM	nm	nm	nm
B5-2		3.2 × 2.4	Fancy light blue crystal with an irregular shape and a cleaved surface.	Primary: small black inclusions	NM	nm	nm	nm	nm

B5-3		3.24×2.4	Fancy light blue macle, growth marks on the surface and broken surfaces	None	0.29	nm	nm	nm	nm
B6-1	0.28	3.2 × 1.6	Faint blue crystal with an irregular shape, conchoidal fractures and iridescent colors in a fracture	Primary: black and colorless inclusions	NM	Graphite, breyite, larnite	nm	Fe-Ni- Cu alloy	nm
B7-1	0.26	2.96 × 2	Faint blue crystal with an irregular shape, growth marks on the surface and conchoidal fractures	None	0.39	nm	nm	nm	nm
B8-1			Light blue crystal with an irregular shape, a cleaved surface and growth marks on the surface	Primary and Secondary: cubo- octabedral shaped mineral inside a	0.22	Graphite, H ₂ O, methane	Graphite,	Fe-Ni allov	nm
		1.5×2.4	eleureu surrace and growin marks on the surrace	circular inclusion in healed		monuno	fcc-(Ni,Fe),	unoy	
				fractures, and black inclusions			<i>bcc</i> -(Fe,N1),		
B8-2	0.93	2.04×3.6	Light blue crystal with an irregular shape, and a cleaved surface	Primary: black inclusions	0.23	Graphite	nm	nm	nm
B8-3		4.2×3	Light blue-gray crystal with an irregular shape	Primary: small black inclusions	0.35	NM	nm	nm	nm
B8-4		4.5 × 3	Faint blue crystal with an irregular shape and a cleaved surface	None	0.23	nm	nm	nm	nm
B9-1		3 × 3	Light blue-gray crystal with an irregular shape and growth marks on the surface	Primary: small black inclusions	0.23	NM	nm	nm	nm
B9-2	0.72	3×2	Fancy light blue macle, several cleaved surfaces and growth marks on the surface	Primary: small black inclusions	NM	nm	nm	nm	nm
B9-3	0.75	3.6 × 2.4	Faint blue crystal with an irregular shape and growth marks on the surface	Primary: small black inclusions	0.12	nm	nm	nm	nm
B9-4		2.4 × 3.6	Faint blue crystal with an irregular shape and growth marks on the surface	Primary: small black inclusions	0.34	nm	nm	nm	nm
B10-1	0.20	4×2	Faint blue crystal with an irregular shape and growth marks on the surface	None	NM	nm	nm	nm	nm
B11-1	0.22	4.2×2.4	Faint blue-gray crystal with an irregular shape and growth marks on the surface	Primary: small black inclusions	0.17	NM	nm	nm	nm

B12-1 0.37	2.3×2.2	Faint blue crystal with an irregular shape and growth marks on the surface	Primary: small black inclusions	0.29	nm	nm	nm	nm
B12-2	2.7 × 4	Faint blue crystal with an irregular shape, growth marks on the surface and iridescent colors in a fracture	None	0.13	nm	nm	nm	nm
B12-3	4.2×2.4	Fancy light blue crystal with an irregular shape	Primary: small black inclusions	0.24	nm	nm	nm	nm
B13-1 0.12	3.5×1.5	Fancy light blue crystal with an irregular shape	Primary: small black inclusions	NM	nm	nm	nm	nm
B14-1 0.20	3.2×2.16	Fancy light blue crystal with an irregular shape	None	0.28	nm	nm	nm	nm
B14-2	3.6×1.6	Fancy blue crystal with an irregular shape	None	0.43	nm	nm	nm	nm
B15-1	3 × 3.2	Fancy light blue crystal with an irregular shape	None	NM	nm	nm	nm	nm
B15-2 0.36	1.2×3.6	Faint blue crystal with an irregular shape and growth marks on the surface	None	NM	nm	nm	nm	nm
B15-3	3.6×2.4	Fancy light blue crystal with an irregular shape	None	0.32	nm	nm	nm	nm
B16-1	4 × 3	Fancy blue crystal with an irregular shape, a cleaved surface, growth marks on the surface and iridescent colors in a fracture	Primary: black inclusions and Secondary: black cubo-octahedral shaped mineral inside a circular inclusion in healed fractures	0.38	Graphite, H ₂ O, methane	Graphite, (Fe,Ni)O	Fe-Ni- Cu alloy	NiO, (Ni,Fe) alloys, pyrrhotite
B16-2	4.44×2.4	Faint blue crystal with an irregular shape and a cleaved surface	Primary: small black inclusions	NM	NM	nm		nm
B16-3 ^{1.10}	3×2.4	Fancy blue crystal with an irregular shape	None	NM	NM			
B16-4	3.2×2.8	Faint blue crystal with an irregular shape	None	0.19	nm	nm	nm	nm
B16-5	5 × 2.5	Fancy blue crystal with an irregular shape and a cleaved surface	Primary: small black inclusions	0.54	nm	nm	nm	nm
B16-6	3.6×2.4	Light fancy blue crystal with an irregular shape	None	NM				

B16-7	3.52 × 4.2	Light fancy blue crystal with an irregular shape and iridescent colors in a fracture	None	0.08	nm	nm	nm	nm
B16-8	4×1.6	Fancy blue-gray crystal with an irregular shape and a cleaved surface	None	NM				
B16-9	3 × 3	Light fancy blue crystal with an irregular shape and iridescent colors in a fracture	None	0.30	nm	nm	nm	nm
B17-1 0.07	2.88×2.4	Faint blue crystal with an irregular shape and growth marks on the surface	None	0.04	nm	nm	nm	nm
B18-1 0.13	2.7×4	Faint blue-gray crystal with an irregular shape and growth marks on the surface	Primary: black inclusions	NM	Graphite, H ₂ O, methane	nm		nm
B19-1 0.17	5.64 × 2.4	Faint blue-gray crystal with an irregular shape and a cleaved surface	None	0.32	nm	nm	nm	nm
B20-1		Fancy blue crystal with an irregular shape and conchoidal fractures	Primary: small and large black inclusions	0.31	Graphite, O-H,	Graphite,	Fe-Ni-	nm
	2.4×3.36				breyite, larnite,	breyite,	Cu alloy	
0.31	2.17(0.00				ferricopiapite	<i>bcc</i> - (Fe,Ni),		
						fcc-(Ni,Fe)		
B20-2	2×3.5	Light fancy blue-gray crystal with an irregular shape and a cleaved surface	Primary: small black inclusions	NM	NM	nm	nm	nm
B21-1		Light fancy blue crystal with a flat shape, a	Primary: small black inclusions	0.19	NM	nm	nm	nm
	4.56 × 2.96	cleaved surface and muescent colors in a macture						
B21-2 0.22	2.5 × 3.6	Light fancy blue-gray crystal with an irregular shape and growth marks	Primary and Secondary: small black inclusions	0.09	NM	nm	nm	nm
B21-3	3.2 × 3.1	Light fancy blue crystal with an irregular shape and a cleaved surface	None	0.25	nm	nm	nm	nm

134 1: measured if contains inclusions; NM: not measurable in situ; nm: not measured

Twenty-four of the forty-nine diamonds display either single phase or multiple phase inclusions, including both solids and fluids. Among them, five diamonds (samples B6-1, B8-1, B16-1, B18-1 and B20-1) exhibit measurable inclusions with non-destructive techniques such as FTIR and micro-Raman spectroscopy (Fig. 3). These five samples were studied in situ, to prevent any irreversible damage on the inclusions, except for specimen B16-1 which had been selected to expose a part of its inclusions.



Figure 3. Photographs of the five type IIb diamonds containing multi-phased mineral inclusions selected for this
study: (A) sample B6-1, (B) sample B18-1, (C) sample B20-1, (D) sample B8-1 and (E) sample B16-1.

144 **2.2 Methods**

145 2.2.1 Cryo ion-beam milling

146 To obtain one mirror-polished section and to preserve the inclusions from tearing, sample

147 B16-1 was exposed using ionic argon cryo-polishing, performed under high vacuum and at -100°C.

A Leica EM TIC 3X Ion Beam Milling System device was used, which allows perfect polishing using three broad argon ion beams. The three ion beams intersect at the edge of a tungsten carbide mask, which partially hides the sample. The area of the sample that is exposed to the beams (100 μ m from the edge) was sputtered at 10kV, 3.5mA. The diamond milling rate is almost 10 times lower than the Si milling rate at 10 kV (300 μ m/h with Ar⁺).

153 2.2.2 Micro-FTIR spectroscopy

154 To determine the uncompensated boron concentration, Fourier Transform InfraRed (FTIR) 155 spectroscopy measurements were performed on the forty-nine specimens (Table 1; Fig. 4). A 156 Bruker IFS 66v/s FTIR spectrometer, equipped with a continuum infrared microscope with a $32 \times$ 157 transmission/reflection objective and an aperture of $250 \times 250 \mu m$, was used at the Institut de 158 Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), Sorbonne Université. 159 Absorbance was measured at the maximum light transmission for 72 s over a spectral range of 600 160 to 6000 cm⁻¹ and a spectral resolution of 4 cm⁻¹, with 128 scans accumulated for each spectrum. 161 Background spectra were collected for 72 s before analyses and are subtracted from each measured 162 absorbance spectrum. Diamond spectra were normalized to 12.2 Au (absorbance units) at 1994 cm⁻¹ wavenumbers to convert from absorbance to absorption coefficient values (Collins, 1982). 163 164 Boron concentration was determined in thirty-two of the forty-nine samples (Table 1) at 2800 cm⁻ ¹ using an absorption coefficient of 0.035 ppm cm⁻¹ to obtain the uncompensated boron content in 165 166 atomic ppm (Fisher et al., 2009).



168 *Figure 4. FTIR* spectra of sample B16-1. Typical boron-related bands are labeled on the spectrum with their 169 wavelength values. The boron concentration of 0.38 ppm is calculated using *FTIR* spectra normalization at 1994 cm⁻¹, with y = 12.2 Au (absorbance/cm).

171 2.2.3 Micro-Raman spectroscopy

Confocal micro-Raman spectroscopy measurements were performed in situ on all accessible 172 173 inclusions trapped in the diamonds to identify their nature. The samples were analyzed using a 174 micro-Raman Invia Renishaw spectrometer at the Centre de Recherche sur la Conservation of the 175 Muséum National d'Histoire Naturelle, Paris. A 532 nm wavelength excitation laser beam of a 2 176 µm size was used for inclusion characterization, with scales ranging between 900 cm⁻¹ and 3600 177 cm⁻¹ at a power of less than 10% (corresponding to 8.5 mW on the sample at a magnification of 20 178 ×) to avoid any damage to the inclusions. Additionally, spectra were baseline corrected. Micro-179 Raman spectral imaging was performed on one inclusion with a high power of 50% (8.5 mW) on 180 large areas of $20 \times 20 \,\mu\text{m}$.

181 2.2.4 Scanning electron microscopy

Scanning electron microscopy was performed at the IMPMC using a SEM-FEG Zeiss electron microscope. Imagery was performed on two bulk specimens (B16-1 and B8-1) using a voltage of 2 kV. Quantitative chemical analyses at the surface of the polished section of diamond B16-1 were obtained by energy dispersive X-ray (EDX) analysis, with a voltage of 15 kV using international standards (Astimex Standards Ltd.) as calibrants.

187 2.2.5 X-ray diffraction

188 X-ray diffraction (XRD) patterns were collected in situ on inclusions trapped in diamonds 189 using the micro X-ray diffractometer installed at the Pression Structure Imagerie par Contraste à 190 Haute Énergie (PSICHÉ) beamline of the SOLEIL synchrotron facility in Saclay, France. A 191 monochromatic (33 keV) micro-focused beam (15 \times 20 μ m VxH) was used. Inclusion-bearing 192 diamonds were fixed on copper pinholes to facilitate pre-alignment in the X-ray beam. The 193 inclusions were then optically-aligned on the vertical rotation axis of the goniometer using the 194 high-resolution objectives available on the beamline. Diamond refraction was further minimized 195 by selecting only those inclusions very close to the surface (46 inclusions). This protocol allowed 196 for the collection of data on large angle ranges $(\pm 20^{\circ})$, both increasing statistics while minimizing 197 the effect of phase-preferential orientation inside the inclusions. Complementary in-situ XRD was 198 performed at IMPMC, using a RIGAKU MM007HF Mo rotating anode X-ray diffractometer 199 (17.48 KeV; wavelength of 0.7093 Å) equipped with Elliptical CMF/VariMax optics and a double image plate Raxis IV++ detector (300×300 mm, 1×10^6 :1 photons/pixel, 100×100 µm). This 200 201 configuration allowed for a beam size of 200 µm at the surface of the sample. Data analysis was 202 performed using DIOPTAS software (Prescher and Prakapenka, 2015) to obtain 2D projections 203 and GSAS software (Toby, 2001) to identify the phases.

204 2.2.6 X-ray fluorescence

205 X-ray fluorescence (XRF) analyses were carried out in situ on several dozen inclusions 206 trapped close to the surface of the diamonds at the Laboratoire Archéomatériaux et Prévision de 207 *l'Altération* of CEA-Saclay, France. A high-flux X-ray generator, equipped with a XENOCS[®] FOX2D MO 25-25P multilayer mirror with a Mo source at 17.48 keV (Mo-Ka), was used to 208 209 generate a monochromatic X-ray beam of $30 \times 50 \mu m$, with a flux of ca. 1 Mph/s. XRF spectra 210 were collected through a Ketek AXAS Vitus Si-drift detector (SDD $- 10 \text{ mm}^2$ of active area) in 211 reflection geometry. In-situ measurements of inclusions in the diamonds were monitored by a 212 camera equipped with a focusing zoom. The strong absorption of fluorescence due to the thickness 213 of the diamonds between the inclusions and the detector compromised the measurements of low-214 energy elements such as S, Si, K, Na and Ca, therefore allowing detection only above 6 KeV (i.e., 215 Fe, Ni, Cu...). Semi-quantitative chemical analyses were carried out in situ on a few dozen 216 inclusions trapped close to the surface of the diamonds.

217 **3. Results**

218 3.1 Boron contents

Boron concentration determined by FTIR spectroscopy ranged from 0.04 at.ppm to 0.61 at.ppm with a median value of 0.27 at.ppm (Table 1). It is worth remembering that only the uncompensated boron concentration (i.e., boron not compensated by another atom, usually nitrogen) can be measured using this method, which represents a lower limit for the real boron content in diamonds (Gaillou et al., 2012). As expected for type IIb diamonds, no nitrogen was detected by FTIR.

225 *3.2.Mineralogical description of the inclusions*

226 3.2.1.Primary inclusions

227 Primary inclusions are defined as trapped during the growth of the host crystal (Roedder, 228 1979). These inclusions are therefore isolated inside the crystal, totally surrounded by the diamond 229 without any connection to either the exterior or to another inclusion. They are therefore 230 contemporaneous to or predate the formation of the diamond (i.e., syngenetic or protogenetic, 231 respectively). Primary inclusions were found in B6-1, B16-1, B18-1 and B20-1 (Table 1). They 232 occur as a single phase or as an association of multiple phases, forming isolated bodies, which are 233 anhedral and more-or-less flat, possibly with a thin envelope of fluid-to-solid mixture (Fig. 5A, B 234 and C). Their size varies from 20 to 500 µm in diameter within the stones. These inclusions provide 235 information about the growth environment, the parent fluids of the diamond and/or the 236 synchronous solid/fluid phases present during its growth.







245 Ni inclusions of various shapes and a gray hue. F) View of the same healed fracture, but closer to the fracture

entrance; inclusions are ~20 μm in size with the same hexagonal graphite crystal in the center, surrounded by a fluid

247 envelope. The healing of the fracture formed small cubo-octahedral-shaped diamonds, the grain boundaries of which

248 connect the inclusions to each other. G) View of the same healed fracture at the fracture entrance. Inclusions exhibit

the same graphite crystals (in gray) in the center, but their envelopes follow the morphology of the central graphite.

250 They get larger, up to ~50 μm, and seem to be thicker. The cubo-octahedral diamond crystals healing the fracture are

visible in the bottom part of the image, and display iridescent colors likely caused by optical density changes.

252 *3.2.2.Secondary inclusions*

253 The term "secondary inclusion" is defined as an inclusion trapped by the healing of fractures 254 in the host crystal at some unspecified time after its growth (Roedder, 1979). Secondary inclusions 255 are not isolated, occurring always in association with other inclusions, and postdate the trapping of the primary inclusions. Usually forming within a host crystal's fractures, caused by fluid 256 257 infiltration, secondary inclusions are possibly associated with protogenetic crystals and also 258 manifest as inclusions aligned along lines or planes after the healing of fractures during a second 259 stage of diamond growth (Fig. 5D). In our samples, they formed suites of inclusions, aligned along 260 planes corresponding to the healing of the fractures by a second generation of diamond material 261 and are associated with large dark inclusions (Figs. 5D-G and 6). This alignment is consistent with 262 a melt trapped along a crystalline plane.

Diamonds B8-1 and B16-1 exhibit similar secondary healed fractures. In both cases, the outer part of the fracture displays iridescence, though this does not extend to the innermost part of the fracture, indicating that the fracture is completely sealed from the exterior. These fractures are filled with multi-phased inclusions of various compositions and sizes: a mesh of small isolated inclusions (5 to 15 μ m), whose sizes increase up to 50 μ m close to the edge of the fracture, together with a few isolated small anhedral inclusions (Figs. 5E, F and G and 6); and large (> 300 μ m)

- 269 clusters with a metallic aspect (Fig. 5D). In sample B8-1, three parallel healed fractures were
- 270 observed, forming three layers of inclusions along cleavage planes (Fig. 6).



272 Figure 6. Images of secondary inclusions trapped in healed fractures of sample B8-1. A) Mosaic view of the entire

273 healed fracture. From bottom to top, highlighted: a group of smaller multi-phased inclusions (5-10 μm size); a group

of medium (15-20 μm) to large inclusions (30-50 μm) together in the middle of the healed fracture; a group of larger

275 inclusions (\geq 50 µm) at the end of the fracture. In the upper rectangle of this picture, central graphite crystals appear.

B) Isolated inclusions observed mainly in the middle part of the fracture, formed within an envelope embedded with

277 central graphite crystals. This morphology may be inherited from protogenetic graphite crystals trapped in the

278 inclusions, the latter of which are connected by the grain boundaries between the diamond crystals that have healed

the fracture. Some spherical, isolated graphite-free inclusions are also observed. C) View of the inner part of the

280 fracture, composed of isolated inclusions from two populations: multi-phased with central graphite and metallic

281 daughter crystals; and flat metallic inclusions of various shapes. No grain boundaries and no secondary diamond

282 crystals were observed between the inclusions, suggesting the complete healing of the fracture.

283 The healed fractures run from the edge of the crystal to ~1 mm inside the crystal (1400 \times 284 800 μ m for sample B8-1 and 4500 \times 1800 μ m for sample B16-1). Healed fractures exhibit distinct 285 zonations from the core to the rim, with a cluster of small, isolated round and flat inclusions 286 observed in the innermost part of the fracture, located in the core of the diamond, associated with 287 shapeless metallic inclusions (Fig. 5E). The size of the inclusions progressively increases (from 5 288 to $> 50 \mu$ m) toward the surface (Figs. 5F, G and 6A), associated with a healing process which 289 creates a mosaic of small diamond crystals mimicking the hexagonal shape of graphite. These 290 crystals seem to be connected to each other, forming a network of grain boundaries (Figs. 5F, G 291 and 6B).

292 Most of the isolated inclusions inside healed fractures show spherical to cubo-octahedral 293 shapes, with the inclusions trapping hexagonal graphite crystals within the fracture (e.g., Fig. 6B). 294 Their sizes range from 5 to 15 µm in diameter in the inner part of the healed fracture, where they 295 are isolated from each other (Figs. 5E and 6C), to $< 50 \mu m$ in diameter at the limit of the fracture, 296 where they are all connected with the grain boundaries of a small cubo-octahedral shaped diamond 297 network (Fig. 5G). The geometry of the healed fractures and their various inclusions are illustrated 298 in Figs. 5D, G and 6. Inclusions of Fe-Ni alloys and carbon (Fig. 5C-D) have previously been 299 observed in fractures of diamonds with similar appearance (Smith et al., 2017; Shatsky et al.,

300 2020). However, it is worth noting that, here, no carbides were identified in our samples, with301 graphite being the main C-bearing phase found in the inclusions instead (Fig. 5C-D).

302 SEM imaging of the surface of diamonds B8-1 and B16-1 revealed that both diamonds have 303 been fractured and healed (Figs. 7A, B). The composite inclusions (central crystal + envelope) 304 exhibit cubo-octahedral shapes (Figs. 7A, C) and are connected with each other through new 305 diamond crystal grain boundaries. Diamond B8-1 ($3 \times 2 \times 1$ mm size) displays growth marks on 306 its surface made of several triangular and six-sided pits, indicating minor resorption of the crystal. 307 Diamond B16-1 ($3 \times 2 \times 1$ mm size), by contrast, displays a resorbed surface with no visible 308 growth marks. In this case, the euhedral cubo-octahedral shape of the graphite crystals trapped in 309 the so-called secondary inclusions (Fig. 7A) would be more fittingly described as syngenetic 310 (Glinnemann et al., 2003), i.e., trapped together with the fluid rather than formed after the closure 311 of the inclusion, with their shape therefore imposed by the diamond. It is worth noting that diamond 312 B16-1 contains both primary and secondary inclusions crystallized in a subsequent generation of 313 diamond, from which at least two growth episodes can be inferred.



314

Figure 7. SEM images of secondary inclusions in diamonds B8-1 and B16-1. A to B: at the diamonds' surfaces (left to right: B8-1 & B16-1), where healed fractures are visible; C to F: diamond B16-1 after experiencing cryo-ionic polishing perpendicular to the fracture. A) The surface of sample B8-1 exhibits triangular and six-sided pits, which correspond to the prints of the now-empty fluid inclusions. B) As with B8-1, sample B16-1's surface displays a resorbed texture. C) Close-up of one inclusion, just below the surface, that is still closed in sample B16-1. A few smaller crystals in the fluid have been observed. D) Close-up of one inclusion that exhibits a large area (in gray) corresponding to the deposition of the residue from the fluid in sample B16-1. The hole from which the fluid escaped

322 is visible at the center of the image, with the deposition forming a small channel and a large elongated area. E) Close-

323 up of one open inclusion from which the fluid is lost in sample B16-1. Small remaining minerals, consisting of almost

324 pure Ni and NiO, as shown by the EDX analyses in Table 2 (red crosses, inclusion 1), are still attached to the walls

- 325 of the cavity. F) Close-up of one inclusion located in the same healed fracture in sample B16-1, which exhibits three
- 326 different metallic alloys, as shown by the EDX analyses in Table 2 (red crosses, inclusion 2). The small holes represent
- 327 the escape of a fluid phase, as indicated by the deposition at the surface on the left of the inclusion.

328 3.3 Micro-Raman analyses

329 3.3.1.Primary inclusions

330 In-situ micro-Raman analyses of inclusions allowed for the identification of primary 331 inclusions in samples B-6, B-16, B18-1 and B-20 (see Supplementary Materials, Table 1). The G 332 and 2D (D overtone) modes of graphite (Ferrari, 2007) were identified in five selected diamonds 333 (Figs. 8, 9 and displayed in Fig. 10). They are observed at variable wavenumbers of ~1583-1590 cm^{-1} and ~2726-2740 cm^{-1} , with the observed variability being possibly caused by a residual 334 335 pressure effect. The high intensities of the Raman bands for diamond and graphite (Figs. 8B, D 336 and F) made it difficult to observe other phases, if any were present. Modes in the hydroxyl 337 stretching region (3200-3800 cm⁻¹) are also present in all primary inclusions of samples B6-1, 338 B18-1 and B20-1 (Figs. 8B, D, 10A and C), attesting to the presence of aqueous fluid-bearing 339 inclusions.

Three Raman peaks observed at 663, 990 and 1050 cm⁻¹ in an isolated inclusion of sample B6-1 (Fig. 8A and 10A) are attributed here to breyite (formerly referred to as CaSiO₃-walstromite; Brenker et al., 2020). In another inclusion from sample B6-1, breyite is associated with a different phase that has been identified as larnite, β -Ca₂SiO₄ (Fig. 8C and 10B; Joswig et al., 1999). In sample B20-1, micro-Raman analysis revealed the presence of two inclusions of breyite and larnite

345 (Fig. 8E), and seven isolated primary inclusions of an unknown hydrous ferric sulfate phase. The 346 Raman spectrum shows strong analogies with ferricopiapite, $Fe^{3+}_{2/3}Fe^{3+}_4(SO_4)_6(OH)_2$ 20(H₂O) 347 (Figs. 8G, H and 10D), a mineral usually observed as a weathering or Fe³⁺ precipitation product. 348 Further investigations would be required to characterize these hydrous ferric sulfate minerals.





27

- 350 Figure 8. Raman spectroscopy analysis of primary inclusions. A) Primary isolated inclusion of breyite in sample B6-
- 351 1. Reference spectra for brevite (dashed line) are from Anzolini et al. (2018). B) Graphite inclusion and water OH in
- 352 sample B18-1, with graphite and diamond references from the RRUFF database. C) Primary inclusions of breyite and
- 353 Ca₂SiO₄-larnite together in sample B6-1. **D**) Graphite inclusion, diamond and hydrous species (hydroxyl groups O-
- 354 *H*) in sample B20-1. *E*) Potential presence of primary inclusions of breyite and Ca₂SiO₄-larnite in sample B20-1. The
- 355 poor quality of the Raman spectra is attributed to the depth of the inclusions in the bulk diamond. F) Graphite
- 356 inclusion and diamond in sample B6-1. G and H) Unknown primary inclusion of a phase very close to a ferricopiapite,
- 357 with reference taken from the RRUFF database.



358

Figure 9. Raman spectroscopy analysis of secondary inclusions. **A)** Graphite and H₂O (O-H stretching and HOH

- bending modes) measured in the central part of the secondary inclusion in sample B8-1 and **B**) in sample B16-1. The
- 361 H₂O signal indicates that the rim (i.e., the envelope surrounding the graphite crystals) is a fluid phase. C) Water O-
- 362 H Raman mapping of a secondary inclusion in sample B8-1. D) Methane (CH₄) Raman mapping of a secondary
- 363 inclusion in sample B8-1. The high intensity of the graphite signal masks the fluid (OH, CH₄) signal at the center of
- 364 the maps.



Figure 10. Images of some of the inclusions analyzed by Raman spectroscopy. The center of the cross indicates the
location of analysis. A) Sample B6-1 inclusion of breyite. B) Sample B6-1 inclusion of breyite and Ca₂SiO₄-larnite.
C) Sample B18-1 cluster of graphite containing a fluid phase. D) One inclusion of ferricopiapite located roughly
fifteen micrometers below the surface of diamond B20-1. E, F & G) Secondary inclusions containing water and
methane in sample B8-1 and H) in sample B16-1.

371 3.3.2. Secondary inclusions

372 Micro-Raman analyses were performed on the inclusions within the diamond with the main 373 results displayed in Figs. 9 and 10. The multi-phased inclusions consist of central cubo-octahedral 374 crystals identified as graphite (Ferrari, 2007), surrounded by an envelope consisting of small bands related to OH stretching mode from 3255 to 3622 cm⁻¹ (Figs. 9A and B), together with water at 375 1642 cm⁻¹ and methane (CH₄) at ~2900 cm⁻¹ (Figs. 9C and D). Although graphite + methane micro-376 377 inclusions were observed previously by Smit et al. (2016) in Marange (Zimbabwe) diamonds, to 378 our knowledge, such multi-phased (Cgraphite, H2O, CH4) and cubo-octahedral-shaped inclusions 379 have never before been reported in any type of natural diamond. This assemblage recalls a high380 pressure hydrous fluid, possibly parented to the diamonds, trapped as primary and secondary 381 inclusions in the crystals.

382 *3.4. SEM and EDX analyses*

383 *3.4.1.Secondary inclusions*

Successive cryo-milling perpendicularly crossing the healed fracture in sample B16-1 allowed for the exposure of secondary inclusions composed of different phases (Fig. 7C-F). These phases consist of crystals embedded in a fluid that was subsequently lost upon decrepitation, together with associated minerals (Figs. 7E and F). Fluid loss is inferred from the presence of a layer of residues deposited on the diamond surface (Figs. 7D and E) too thin to be quantitatively analyzed.

390 A few remaining solid phases are present within the rims of these fluid-bearing inclusions 391 (Fig. 7E; inclusion 1), and depending on the position of the cryo-polishing, large minerals were 392 exposed (Fig. 7F; inclusion 2). SEM-EDX analyses demonstrate that the inclusions contain several 393 metallic alloys (Table 2; inclusions 1 and 2): a Ni-rich oxide containing Fe, Mg, Na, Si and Al (#1) 394 and an almost pure Ni phase associated with Fe, Cr and Si (#2). Isolated inclusions of composite 395 metallic alloys and sulfides also exhibit the same cubo-octahedral shape as graphite crystals 396 characterized by Raman analyses (Figs. 7 E-F). A strong association between graphite layers and 397 these metallic phases in other exposed secondary inclusions was observed. Additionally, a 398 composite inclusion (Table 2: inclusion 2; Fig. 7F) exhibits a layer of a FeNi-rich phase associated 399 with Cu alloy (#3) and a sulfide Fe-S phase with minor Cu (1.49 at%) (#4; pyrrhotite group). The 400 surface of inclusion 2 exposes small cavities most likely initially filled with a fluid (Fig. 7F).

401 **Table 2.** EDX analyses of two inclusions trapped in the healed fracture of sample B16-1 after the 402 inclusions were exposed by ionic polishing. Analyses are summed to 100. Images of inclusions 1 403 and 2 are displayed in Figs. 7E and 7F, respectively. Inclusion 1 leaked during diamond opening 404 and contains residual phases. Inclusion 2 contains a sulfide from the pyrrhotite group with Cu and 405 is included in a layer of an alloy composed of Fe, Ni, Cu and a Ni-bearing ferricopiapite.

Element C (at%)	Fe	Ni	S	Cu	Cr	Si	0	Na	Mg	Al	Ca	Κ	Total
Inclusion 1 #1	2.1	44.4				2.0	30.4	6.0	4.0	1.6	0.3	0.2	100
#1	2.1	44.4		I	I	2.0	39.4	0.0	4.0	1.0	0.5	0.2	100
#2	4.1	92.2			1.6	2.1							100
Inclusion 2													
#3	55.6	42.0		2.4									100
#4	50.5		48.0	1.5									100
#5	42.1	15.0	16.0				26.9						100

406

407 3.5. X-ray fluorescence of primary and secondary inclusions

408 XRF in-situ micro-analyses of near-surface primary and secondary inclusions confirmed 409 the presence of a metallic phase strongly associated with graphite (Fig. 11). Results further 410 confirmed the presence of Fe-Ni-Cu alloys associated with graphite and the hydrous phase detected 411 by micro-Raman spectroscopy and EDX. Metallic alloys are present in both secondary and primary 412 inclusions in four diamonds (B6-1, B8-1, B16-1 and B20-1). Their nature – i.e., metallic alloys or 413 oxides – cannot be determined by using these techniques alone.



414

415 **Figure 11.** In-situ X-ray fluorescence measurements performed on inclusions of sample B8-1. Elements are identified 416 thanks to the energy of their K- α and K- β rays in KeV. Results indicate the presence of Fe-Ni-rich alloys in the cluster 417 and in the isolated inclusions. It is not possible with this analysis to determine if they are native metals or oxides. For 418 each spectrum, the area investigated is shown in the associated four images corresponding to different positions in 419 the healed fracture. Crosses indicate locations in the large cluster and in the isolated inclusions where analyses were 420 undertaken for the presence of metallic inclusions.

421 3.6. X-ray diffraction of primary and secondary inclusions

422 XRD analyses of both primary and secondary inclusions from three diamonds (B8-1, B16423 1 and B20-1) revealed the presence of graphite in all inclusions and the coexistence of several
424 phases, either trapped together or isolated (Table 3 and Supplementary Materials, figures A-F).

425 **Table 3.** Diffraction patterns of selected inclusions in type IIb diamonds from SXRD micro-426 analysis. Synchrotron XRD patterns (wavelength 0.3738 Å) were processed with Rietveld 427 refinement. *bcc*-(Fe,Ni) alloy indicates a mixture mainly composed of Fe, while *fcc*-(Ni,Fe) alloy 428 is mainly composed of Ni.

#	Mineral phase	Unit cell parameters Å
B20-1-3	Graphite	a = 2.458, c = 6.443
	<i>bcc-(</i> Fe,Ni)	a = 2.861
	fcc-(Fe,Ni)	a = 3.572
B20-1-6	Graphite	a = 2.458, c = 6.419
	Breyite	a = 6.619, b = 9.213, c = 6.552, α = 83.4, β = 75.99, γ =
		69.88
	fcc-(Ni,Fe)	a = 3.570
B16-1-11	NiO	a = 4.187
B8-1-69	Graphite	a = 2.464, c = 6.716
	bcc-(Fe,Ni)	a = 2.868
	fcc-(Ni,Fe)	a = 3.588

430 No H₂O ice (VI or VII) could be identified, which is consistent with the amorphous character
431 of the hydrous phase either surrounding the graphite crystals in secondary inclusions (Figs. 5E and
432 5F) or forming the halo in primary inclusions (Fig. 5C).

In all investigated inclusions, Fe-Ni metallic phases are present, which is coherent with both
the XRF investigation of samples B6-1, B8-1, B16-1 and B20-1 (Supplementary Materials A-F)

435 and the EDX analyses of diamond B16-1 (Table 2). Furthermore, two different Fe-Ni alloys have 436 been identified using XRD: one Fe-rich alloy (Ni < 0.3), which crystallized in the *bcc* group 437 (hereafter referred to as "bcc-(Fe,Ni)") and a Ni-rich alloy, which crystallized in the fcc group 438 (referred to as "fcc-(Ni,Fe)") (Table 3). If an ambient pressure is assumed, the fcc-(Ni,Fe) unit cell 439 parameter would correspond to a composition of 0.5 < Ni < 0.6 (Cacciamani et al., 2010). 440 However, it should be noted that since the unit-cell parameters are both pressure- and composition-441 dependent, it is not possible to determine the composition and remnant pressure from the XRD 442 measurements alone. One inclusion exhibiting a rock-salt structure was identified in sample B16-443 1, with an XRD intensity peak consistent with NiO but likely with some substitutions with Fe or 444 Mg, as indicated by both the unit-cell parameters and the SEM-EDX analyses. The XRD analyses 445 of primary inclusions trapped in diamond B20-1 show that graphite and fcc-(Ni,Fe) are trapped 446 together with a breyite inclusion. The cell parameters of the breyite indicate low residual pressures 447 at ambient temperature.

448 3.7 Entrapment pressure calculation

The Raman spectrum of an isolated primary inclusion of breyite in diamond B6-1 exhibits three shifted peaks at 663, 990 and 1050 cm⁻¹ compared to the expected values of 656, 977 and 1037 cm⁻¹ at ambient conditions (Fig. 8A). Based on calibration curves obtained at different pressures by Anzolini et al. (2018), our observed Raman shifts on the B6-1 isolated breyite would correspond to a remnant pressure of 2.5 GPa (Anzolini et al., 2018). In diamond B20-1, graphite and hydrous phases coexist with primary inclusions which were identified by XRD as breyite, *fcc*-(Ni,Fe) and *bcc*-(Fe,Ni), while no oxides were detected. Assuming the experimental equation of state of Anzolini et al. (2016) and a unit cell volume of 363.78 Å, the residual pressure determined
from the XRD patterns for B20-1 breyite is 2.8 GPa.

458 It has been shown that the potential presence of undetected micro-cracks in the host diamond 459 surrounding breyite inclusions (even the smallest, with a diameter of $< 12 \ \mu m$) may induce a 460 pressure drop and an underestimation of the real diamond formation depth (Anzolini et al., 2016). 461 To the best of our knowledge, breyite inclusions in B6-1 and B20-1 diamonds do not display 462 decompression fractures of any sort. The similar residual pressures of 2.5 and 2.8 GPa calculated 463 from isolated brevites contained in two different diamonds, and using two different techniques 464 (micro-Raman spectroscopy and XRD), are evidence of the absence of decompression fractures, 465 as their presence would otherwise result in random residual pressures.

466 Based on the obtained remnant pressures from the Raman shifts and XRD measurements in 467 the two isolated primary inclusions of brevite from samples B6-1 and B20-1, it is possible to 468 calculate the minimal entrapment pressure of inclusions using elastic geothermobarometry (Angel 469 et al., 2014). Trapping pressures were calculated using the EosFit-Pinc software (Angel et al., 470 2017). It is worth noting that both B6-1 and B20-1 diamonds contain other breyites, but, here, are 471 associated with larnites (e.g., Fig. 10B). In presence of multi-phased inclusions, trapping pressures 472 cannot be correctly calculated due to the risk of each of the mineral pairs reacting elastically in a 473 different way, resulting in an underestimation of the remnant pressures (e.g., Cisneros and Befus, 474 2020). By applying a pressure correction induced by elastic relaxation, as proposed by Angel et 475 al., (2017), a trapping pressure of 2.5 GPa at 900-1400 °C would result in a recalculated pressure 476 of the isolated brevites in samples B6-1 and B20-1 ranging from 4.9 to 5.6 GPa, indicative of a 477 formation depth between 160 to 180 km. Although these remain minimum estimated pressures,

478 their consistency is striking, and collectively point to a lithospheric origin for the studied479 diamonds.

480 **4. Discussion**

481 *4.1 Where do type IIb diamonds form in the mantle?*

Consistent trapping pressure estimates from primary breyite inclusions in two different samples – as well as the mineralogy of their principal inclusions, such as larnite and graphite – suggest lithospheric formation depths between 160 to 180 km for our studied diamonds. Given that our proposed origin could be distinct with some of the available literature, hereafter, we provide a review of breyite and larnite stability and genesis.

487 Brevite and its high-pressure equivalent CaSiO₃-perovskite can be formed throughout the 488 entire mantle and their presence alone in a diamond does not provide univocal evidence for a lower 489 mantle origin (Moore and Helmstaedt 2019; Fedoraeva et al., 2019; Brenker et al. 2020). Indeed, 490 brevite in diamonds may have multiple origins. Some brevite can occur in lower mantle diamonds 491 as a direct back-transformation product at 10 GPa of CaSiO₃-perovskite. However, Fedoraeva et 492 al. (2019) have shown that brevite can also result from reaction between carbonate and SiO_2 or a 493 Si-rich fluid. The direct crystallization of both brevite and larnite (as observed in diamonds B6-1 494 and B20-1; Figs. 5A) can occur at pressures of ≤ 6 GPa and temperatures of 1300-1750 °C in a 495 carbonate/Ca-rich environment (Fedoraeva et al., 2019). Temperatures required to reach the 496 formation of breyite in Fedoraeva's experiments are slightly higher than those expected at the 497 calculated lithospheric depths of our samples, but it is worth noting that our diamonds contain 498 abundant aqueous fluids. Abundant available water would enable a sufficient decrease in temperatures during the reaction, allowing for the formation of breyite and larnite in thelithosphere, which would otherwise be impossible under normal temperature conditions.

501 Phase diagram interpretation indicates that the coexistence of breyite and larnite necessitates 502 a trapping pressure within the range 6-9 GPa at 900-1400 °C at the lithosphere/asthenosphere 503 boundary (Gasparik et al., 1994; Brenker et al., 2005 and 2007; Fedoraeva et al., 2019). 504 Additionally, Fedoraeva et al. (2019) suggested that infiltration of a CaCO₃- CaSiCO₃ melt into a 505 more reduced peridotitic mantle (see section 4.2) would result in a partial reduction of $CaCO_3$ and 506 precipitation of both diamond, brevite and larnite at depths ranging from 160 to 180 km. These are 507 both viable scenarios for the formation of brevite and larnite inclusions at lithospheric depths in 508 our studied diamonds. The strong association of Si-bearing inclusions and a water-rich fluid 509 composition (large quantity of graphite-water inclusions) is coherent with the scenario of direct 510 crystallization of both breyite and larnite at moderate pressures.

511 A sublithospheric origin of brevite or a CaSiO₃ precursor would require its association with 512 other inclusions such as ferropericlase, low-Ni enstatite (bridgmanite) or high pressure olivine 513 polymorphs (e.g., Smith et al., 2018; Brenker et al., 2020). One such example is the association of 514 ringwoodite with presumably secondary brevite observed in a sublithospheric type IIa diamond 515 from Juina (sample JUc29; Pearson et al., 2014). None of these typical sublithospheric mineral 516 phases were found in any of our diamonds, lending further evidence to a possible origin in the 517 lower mantle. Furthermore, if the type IIb diamonds studied here were formed under 518 sublithospheric trapping conditions, ice should be observed in inclusions at room temperature (e.g. 519 ice VII inclusions; Tschauner et al., 2018), whereas the XRD investigation did not reveal any 520 presence of any ice in the inclusions analyzed.

521 The lithospheric depths of diamond formation obtained from our recalculated residual 522 pressures are also consistent with the presence of primary graphite inclusions (those not related to 523 the healed fractures; Fig. 10A-D), which points to the crystallization of diamonds close to the 524 graphite-diamond inversion curve, corresponding to conditions of 4-4.5 GPa and 1200-1400 °C 525 (e.g., Bulanova, 1995; Day, 2012). Based on the observed mineralogy in our samples and previous 526 studies of Smith et al. (2018), we conclude that type IIb diamonds are capable, under certain 527 conditions, of growing within a mantle continuum, ranging from lithospheric to sublithospheric 528 depths.

529 4.2 Type IIb diamond parental fluids

This study documents that natural type IIb diamonds grow in the presence of fluids. This is a well-accepted concept but the fluids can be diverse both chemically and from their redox state (oxidized or reduced). In this section, different models for diamond formation are reviewed in order to propose a credible scenario for lithospheric-grown type IIb diamonds.

534 Synthetic diamond growth typically occurs through carbon supersaturation of metallic alloys 535 (e.g. Bataleva et al., 2016) and type IIb diamonds can be synthesized at lithospheric conditions, 536 under reduced conditions. Chepurov et al. (2007) grew type IIb diamonds from a mixture of 537 graphite as the carbon source, FeNi and FeCo alloys as solvents and B₂O₃ as the boron source. 538 Even if this mechanism contrasts with natural diamond formation complex redox reactions (e.g. 539 Pal'Yanov et al., 2005, 2013), these synthetic diamonds show some similarities with our natural 540 samples, in particular with respect to the occurrence of metallic inclusions. The coexistence of reduced and oxidized species in diamonds suggests redox reactions: for
example, Fe-C melt in equilibrium with FeO could dissolve up to 0.5 wt.% O (Sokol et al., 2017).
As it subsequently cools and crystallizes, oxygen would be released, yielding oxidized species.

544 Here, inclusions of primary Fe-Ni-Cu alloys, FeNi and FeNiO (Table 3), attest to the 545 presence of metallic phases at lithospheric depths. This suggests that fO_2 should be sufficiently 546 low to stabilize Fe-alloys even at lithospheric pressures, where fO_2 is generally considered to be 547 above the iron-wüstite (IW) buffer. This assemblage is rare but not unusual. Stachel et al. (1998) 548 reported the presence of Fe, FeS, FeNiS and FeO inclusions and a solid solution of Fe-FeO-Fe₃O₄ 549 as inclusion in lithospheric diamonds from the Mwadui Mine, Tanzania. They also reported an 550 inclusion consisting of a core of native iron rimmed by wüstite. Such an association might be 551 interpreted as evidence of redox processes, possibly associated with oxidized fluids. Indeed, the 552 presence of native iron, wüstite and magnetite in the same diamond indicated a variation in oxygen 553 fugacities from below iron-wüstite (IW) to above the wüstite-magnetite (WM) buffer. Stachel et 554 al. (1998) proposed diamond formation over a large range of fO_2 conditions, possibly along redox 555 fronts. These conditions recall those of high-pressure (6 GPa) diamond synthesis from Mg-Ca-556 carbonates and metallic Fe at dry conditions (Pal'yanov et al., 2013). Diamonds would form both 557 ahead of and behind the redox front because of the presence of a fO₂ gradient. However, the above-558 cited studies do not consider the presence of water, as observed in the primary and secondary 559 inclusions of the natural type IIb diamond studied here.

The presence of breyite and larnite in our diamonds could result from the reduction of Carich silico-carbonatitic fluids enriched in solutes (Fedoraeva et al., 2019), consistent with the inclusions mineral assemblage from diamond B16-1 (Table 2; Fig. 7E). Some experimental studies have demonstrated the significant role played by carbonate-bearing hydrous fluids in the growth
of diamonds (e.g., Pal'yanov et al., 1999; Sokol and Pal'yanov, 2008; Bureau et al., 2016; 2018)
and as a vector for determining the diamond's carbon source (e.g. Weiss et al., 2014; Jablon and
Navon, 2016 for natural samples).

567 In the type IIb diamonds analyzed in this study, diamond and graphite are in equilibrium 568 together with abundant water. Both graphite and CH₄-syngenetic inclusions were reported in 569 mixed-habit Type Ia (i.e., N-bearing) diamonds from Marange in Zimbabwe (Smit et al., 2016). In 570 the latter case, the intimate association of CH4 and graphite suggests that both phases co-571 crystallized from the diamond parent fluid. In the diamond stability field, it has also been proposed 572 that as hydrocarbon concentration in the aqueous fluid increases, initial diamond crystallization 573 gives way to co-crystallization of both diamond and graphite, followed ultimately by 574 crystallization of only graphite (Sokol et al., 2009).

In type IIb diamonds – and in Marange diamonds (Smit et al., 2016) – graphite would crystallize before diamond and would subsequently be trapped or serve as the seed for further diamond formation (Bulanova, 1995) during the fast diamond growth phase facilitated by the presence of water (Bureau et al., 2016). In this model, it is expected that diamonds should contain an abundance of nitrogen, as in the case of the Marange Mine diamonds. Here, the absence of nitrogen could be explained by the presence of metal and sulfur that would prevent the nitrogen from being incorporated into the diamonds (see next section).

582 Stachel et al. (2017) suggested that diamond formation in peridotite would not occur with 583 rock-buffered reactions, but rather would be buffered by the fluid itself, following the oxygen 584 conservative reaction in the lithosphere (Deines, 1980):

585
$$CO_2 + CH_4 = 2C + 2H_2O$$
 (1)

586 and assuming that all available CO₂ (or carbonate solutes dissolved in a hydrous/silicic fluid or 587 methane) is consumed during diamond and/or graphite crystallization. However, in this model, 588 diamond growth is supposed to occur at the water maximum (i.e., for a fluid consisting almost 589 exclusively of H₂O with minor CH₄ and CO₂; Foley, 2011; Stachel et al., 2017) at near constant 590 and buffered fO₂ close to FMQ-1, -2 (Fayalite-Magnetite-Quartz), corresponding to the conditions 591 of the redox EMOD reaction (Stachel et al., 2017). This model contrasts with the presence of 592 metallic liquids mingled with the aqueous fluid. Type IIb diamond formation may be closer to the 593 model for crystallization of Fe alloys, in association with diamonds that reacted with a surrounding 594 silicate proposed by Jacob et al. (2004). Citing a polycrystalline diamond of inferred lithospheric 595 provenance exhibiting cohenite, native iron and troilite enclosed within a garnet inclusion, they 596 suggest that the inclusions in the garnets reflect local and probably transient conditions within the 597 lithosphere, linked to diamond formation within a C-O-H fluid that reacted with the surrounding 598 silicate.

599 One could argue that the source of carbon for diamond growth may be a metallic liquid 600 (e.g., Smith et al., 2016), as experimentally achieved from mixture of FeNiS metals and iron 601 carbides at mantle conditions (Bataleva et al., 2016). In the absence of iron carbides, carbon may 602 be dissolved in these metallic melts, as demonstrated, for example, by experimental pressures of 603 1-15 GPa and temperatures of 1600-2300 °C inducing the solubility of carbon in FeNi metallic 604 liquids in equilibrium with silicates reaching a few wt.% (e.g., Malavergne et al., 2019). It is worth 605 noting that formation of our studied type IIb diamonds in a metal melt, a possible formation 606 mechanism proposed by Smith et al. (2014; 2016), it is however highly unlikely here. Our data

illustrate that the mantle environment where these type IIb diamonds grew is particularly rich in
water. With even the slightest presence of water in the melt (>0.5 % of water), diamond growth
will be completely inhibited, with graphite forming instead of diamond (Pal'yanov et al., 2012).

610

Type IIb diamond formation may be described by the following simplified equation:

$$611 \quad [3CaCO_3 + 2SiO_2]melt + 2H_2O + 9FeNi = FeNi + 8FeNiO + CH_4 + CaSiO_3 + Ca_2SiO_4 + 2C \quad (2)$$

612

 $(1 + 2\pi/2) + (1 + 2\pi/2) + (1$

613 In this scenario, the carbon source may be multiple: CO_3^{2-} or CO_2 dissolved in a melt and possibly 614 trace amount of C initially dissolved and released during crystallization of FeNi and FeNiO.

615 Based on the presence of Ca-bearing silicate minerals and C-O-H fluids in the studied diamonds, 616 the above scenario, involving carbonate reduction causing the formation of larnite and breyite, but 617 also possibly hydrous ferrous sulfate exhibiting a pre-existing ferricopiatite-like structure in the 618 host-rock. Combination reactions for carbonate reduction would release methane, metal alloys and 619 metal oxides, and silicate minerals, such as breyite and larnite, trapped in type IIb diamonds during 620 their syngenetic growth. In this model, N would be sequestrated/scavenged by the metallic phase 621 (Sokol et al., 2019) and/or by sulfur. Type IIb diamonds growing in fluids introduced in highly 622 reduced conditions would thus not incorporate any nitrogen. In this model the graphite-CH4 623 assemblage would represent the residual rather than the primitive fluid.

624

625 4.3. B- and N- poor type IIb diamonds: the key to identifying their growth environment

626 Nitrogen content in diamonds, including their core-to-rim variations, is commonly 627 interpreted as relating to their host fluid through their melt/fluid-diamond partitioning coefficient (Deines et al., 1989; Cartigny et al., 2001; Stachel et al., 2009), with this interpretation having been
used in previous studies (e.g. Thomassot et al., 2007; Smit et al., 2016).

630 The occurrence of boron in type IIb diamonds has led to the widespread adoption of the term "boron-rich diamond". Linking type IIb diamond genesis with fluids derived from "B-rich 631 632 environments", in particular subducted serpentinites (e.g., Smith et al., 2018a), however, suffers 633 from several shortcomings. Notably, B-recycling in the mantle, at depths beyond those of the back-634 arc (100 km), is the object of ongoing debate (De Hoog and Savov, 2018), with some researchers 635 suggesting recently that boron is actually not subducted in the deep mantle at all (McCaig et al., 636 2018). Furthermore, with a maximum B value of 10 atomic ppm, the B/C-ratios of type IIb diamonds are low, $< 10 \times 10^{-6}$, with this value remaining approximately three orders of magnitude 637 638 lower than that of the depleted or primitive mantle (B/C-ratio of approximately 6800×10^{-6} , 639 computed from ~0.3 ppm B and ~49 ppm C; McDonough and Sun, 1995; Chaussidon and Jambon, 640 1994; Cartigny et al., 2008; Le Voyer et al., 2017). Thus, the need to relate type IIb diamonds are 641 related to B-rich subducted serpentinites appears unjustified given that Earth's mantle is 642 sufficiently rich in boron at ~ 8 ppm to account for the B-content of type IIb diamonds (Gaillou et 643 al., 2012).

In our view, the fundamental observation informing the origin of type IIb diamonds is not related to the occurrence of "high" boron content in these diamonds, but rather their low B-content coupled with even lower levels of nitrogen. Given that both the convective mantle and subducted material contain substantial amounts of nitrogen (e.g. Cartigny and Marty, 2013 for a review of mantle nitrogen; Philippot et al., 2007; Cannaò et al., 2020 for a review of subducted serpentinites), ensuring the presence of nitrogen in both the mantle and subducted serpentinite derived fluids/melts, boron, if present, would be prevented from expressing the typical spectroscopicfeatures found in type IIb diamonds.

652 Nitrogen partitioning (Kd-values) between fluid and diamond has been deduced or suggested in a number of previous studies, though the extent to which the phenomenon is said to 653 654 occur varies substantially and no consensus has yet been reached (e.g., Cartigny et al., 2014 for a 655 review on the subject). In the case of CH₄-rich fluids, two phenomena would be expected to occur: 656 given the compatible behavior of N (Thomassot et al., 2007; Stachel et al., 2017), the fluid would 657 become increasingly N-depleted with the progression of diamond crystallization while 658 simultaneously becoming ¹³C-depleted owing to the partitioning of C-isotopes between diamond 659 and CH₄ (Cartigny et al., 2014). These diamonds would therefore have low δ^{13} C-values, as can be 660 inferred from the few available data for large type II diamonds (from -20.8 to -1.8‰ vs. V-PDB; 661 Milledge et al., 1983; Smith et al., 2018a) in addition to having low N-contents, making the 662 presence of boron in these diamonds possible only when the partitioning value of boron in the fluid 663 is less than that of nitrogen. To the best of our knowledge, no Kd-values between fluid and diamond have been determined for boron, leaving open the possibility that type IIb diamonds 664 665 indeed grow from fluids with high B/C-ratios, albeit with very low Kd-values (i.e., boron would 666 be incompatible with respect to diamond). Given that significant amounts of boron (>1000 at.ppm) 667 can be incorporated into synthetic diamonds (Polyakov et al., 2001), the low B-content of type IIb 668 diamonds might reflect low B/C-ratios of the parental fluid at elevated Kd-values (ie., > 1). Still, 669 a preferable explanation is that the low N-character reflects low oxygen fugacities. Under metal-670 saturation conditions, nitrogen would be sequestrated in the metal phase (Sokol et al., 2019), whether the fluid derives from a reduced environment or, as documented here, from crystallization 671

of the diamond in oxidized fluids introduced in a reduced environment. Bolstering this argument,
experimental studies have suggested that in the metal-fluid system, nitrogen has a higher affinity
for iron and selectively accumulates in the metal phase, while some mobile carbon resides in the
fluid phase (Sokol et al., 2018).

The sequestration of N in metals can explain the absence of nitrogen in large 676 677 sublithospheric type II diamonds carrying metallic inclusions (Smith and Kopylova, 2014; Smith 678 et al, 2016). Given that boron is a lithophile element, the fluids/melts would, in a reduced 679 environment, develop rather high B/N-ratios. In this case, B-poor, nitrogen-free type IIb diamonds 680 would characterize the most reduced environment for diamond formation. An alternative 681 hypothesis for explaining the absence of N could be related to its speciation in the mantle as N₂ or 682 NH4⁺, both of which are incompatible in the diamond lattice into which nitrogen substitutes for 683 carbon as single atoms (Mikhail and Howell, 2016).

684

5. Conclusions

685 A detailed study of type IIb diamonds from the Cullinan Mine, South Africa, allowed 686 identification of hydrous fluids in primary and secondary inclusions, associated with methane, 687 graphite, metallic alloys, sulfides and oxides. The most important conclusions of this study are:

1) The mineralogical assemblage of primary inclusions shows the presence of breyite ± larnite and graphite. Breyite inclusions were used to estimate residual pressures of 2.5-2.8 GPa corresponding to minimal entrapment pressures of 4.9 to 5.6 GPa at the typical temperature range of 900-1400°C, otherwise known as the "diamond window". These physical conditions – together with the presence of brevite ± larnite and graphite inclusions and the 693absence of typical sublitospheric mineral association of $CaSiO_3$ + ferropericlase, low-Ni694enstatite or olivine polymorphs – are more consistent with lithospheric depths of formation695for type IIb diamonds, which were, until now, considered only of sublitospheric origin696(Smith et al., 2018a and b).

697 2) The type IIb diamonds studied here revealed numerous mineral and fluid inclusions: a 698 hydrous phase (H₂O, OH) with CH₄ and solute, Fe-Ni oxides, hydrous ferrous sulfates and 699 Fe-Ni \pm Cu alloys. The coexistence of reduced and oxidized species suggests complex redox 700 reactions, where the fO_2 should be sufficiently low for Fe-alloys to be stable under 701 lithospheric pressures; it may reflect local and probably transient conditions within the 702 lithosphere (Jacob et al., 2004), linked to the equilibrium of diamond with C-O-H fluids 703 such as those identified in the studied type IIb diamonds.

Finally, the lack of nitrogen and the presence of only negligible boron in type IIb diamonds
does not ultimately require a link with subduction setting, given Earth's mantle is
sufficiently B-rich to account for the formation of type IIb diamonds, while simultaneously
nitrogen is likely sufficiently sequestered by metallic alloys accompanying growth fluids
to explain its absence.

It is not the intent of the authors here to refute the sublithospheric origin of type IIb blue diamonds proposed by Smith et al. (2018a, b) and based on mineral assemblages typical of the lower mantle. Rather, we seek to suggest, based on our results suggesting lithospheric depths of formation, that type IIb diamonds form in a mantle continuum, from sublithospheric to lithospheric depths. In proposing this new framework for type IIb diamond formation and discussing the conditions under which it is viable, this work highlights the limited knowledge available concerning these peculiar diamonds, stemming principally from the absence of sufficient samples
to study. The mineral and fluid inclusion assemblages observed here, together with previous results
from Smith et al. (2018a,b), will be crucial in developing a well-constrained model of the formation
of type IIb diamonds.

719

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Supplementary Materials

967 **Table 1.** List of bands and species measured by micro-Raman spectroscopy (532 nm-wavelength

968 excitation laser). 1: Reich, 2004, 2: Auer et al., 2008, 3: Anzolini et al., 2018, 4: Men et al., 2014,

969 5: Sun et al., 2009, 6: Brenker et al., 2005, 7: Anthony et al., 2000.

Species	Raman shift cm ⁻¹
Primary inclusions	
Graphite ¹	~ 1580 ~2730
O-H stretching vibration ²	From 3200 to 4000
Breyite ³	~ 665 , ~985, ~1056 (weak)
CaSiO4-larnite ⁶	~168 ~540 ~ 848 ~ 864 ~908 ~984
Ferricopiapite ⁷	~210 ~460 ~481 ~608 ~ 991 ~1099 ~1147
Secondary inclusions	
Graphite ¹	~ 1580 ~2730
Methane ⁴	From 2900 to 2930
O-H stretching vibration ⁵	From 3200 to 4000
H ₂ O bending mode ⁵	~1640

971 SXRD diffraction patterns of selected inclusions in studied diamonds, with the method used in 972 parentheses. A) Primary inclusion of fcc-(Ni,Fe) alloy, bcc-(Fe,Ni) alloy and graphite in sample 973 B20-1 (Lebail method). B) Primary inclusion of bcc-(Fe,Ni) alloy, fcc-(Ni,Fe) alloy, brevite and 974 graphite in sample B20-1 (Rietveld method, except for graphite: Lebail method). C) Primary 975 inclusion of NiO in sample B16-1 (Rietveld method). D) Secondary inclusion of fcc-(Ni,Fe) alloy, 976 bcc-(Fe,Ni) alloy, graphite and bcc-(Ni,Fe) alloy in sample B8-1 (Rietveld method. E) Secondary 977 inclusion of bcc-(Fe,Ni) alloy, bcc-(Fe,Ni) alloy and fcc-(Ni,Fe) alloy in sample B8-1 (Rietveld 978 method). D and E diffraction patterns display a common, unidentified phase with peaks at 8.085, 979 9.115, 9.860 and 13.51 20. F) Secondary inclusion of fcc-(Ni,Fe) alloy, bcc-(Fe,Ni) and graphite 980 in sample B8-1 (Rietveld method). Synchrotron XRD patterns (wavelength 0.3738 Å) are 981 processed with Rietveld refinement with GSAS (Toby, 2001; Larson and Von Dreel, 2004). 982 Abbreviation: D=diamond. Phase identification of crystalline samples was performed using 983 references from the American Mineralogist Crystal Structure Database (Downs et al., 2003; 984 Cacciamani et al., 2010).



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