| 1 | Diamond formation beneath the Coromandel area, southwestern São Francisco Craton – The role of |
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| 2 | re-fertilization and subduction |
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| 19 | Abstract |
| 20 | The lithospheric mantle underpinning the Alto Paranaíba Igneous Province, southwestern São Francisco |
| 21 | Craton, was investigated through a study of 82 diamonds and their mineral inclusions from the Coromandel |
| 22 | (Douradinho River), Verde River (northern Coromandel), Abaeté, Frutal, and Romaria deposits. Mineral |
| 23 | inclusion abundances show that lherzolite is the main diamond source-rock, followed by eclogite, |

harzburgite and minor websterite. The limited chemical depletion recorded in lherzolitic inclusions suggests

a post-Archean origin or modification of the lithospheric mantle beneath this part of the São Francisco

craton. Sinusoidal rare earth element patterns for lherzolitic garnet inclusions indicate variable but overall

low degrees of metasomatism by fluids or silico-carbonatitic (proto-kimberlitic) melts. These results

contrast with previous studies on mineral inclusions in diamonds (Canastra range, southern Coromandel;

Rio da Prata system, northeastern Coromandel; our new data on the Frutal area, southwestern Coromandel),

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30 where a dominance of harzburgitic inclusions documents a more depleted, likely Archean, cratonic root. 31 Bulk rock compositions reconstructed from eclogitic and websteritic inclusions establish a clear link 32 between subduction processes and diamond formation in the Coromandel region. Calculated bulk rare earth 33 element patterns match typical sections of upper oceanic crust, where plagioclase accumulation is 34 uncommon. Pyroxene inclusion-based geothermobarometry indicates that lherzolitic and websteritic 35 diamonds formed and last resided along a ~39 mW/m² model geotherm. Projection of eclogitic garnet-36 clinopyroxene pairs onto this 39 mW/m² geotherm places their origin near the base of the lithosphere (>37 180 km depth). Low nitrogen contents and high aggregation states (up to 100 %B) indicate that eclogitic, 38 websteritic, and part of the lherzolitic diamond populations experienced extended (2.0 Byr) mantle 39 residence at high temperatures (> 1200 °C). The similarity in mantle residence temperatures and the shared 40 presence of minor negative Eu anomalies for eclogitic and websteritic diamonds and their inclusions may 41 be indicative of a common origin, following emplacement of subducted oceanic crust beneath the São Francisco Craton margin likely during a Paleoproterozoic orogeny (2.2-1.9 Ga). Based on our results, future 42 43 exploration efforts in the Alto Paranaíba region should shift their focus from harzburgitic to lherzolitic and 44 eclogitic indicator minerals to find new diamond deposits and kimberlites in this area.

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Keywords: Inclusions in diamonds. São Francisco Craton. Alto Paranaíba Igneous Province.
Geothermobarometry. Nitrogen aggregation. Eclogite.

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49 **1. Introduction**

50 Diamond formation in the mantle is considered to be a metasomatic process. The agents of 51 metasomatism, melts or supercritical fluids, react with the mantle rocks and diamond crystallizes either 52 isochemically, as a consequence of cooling and oversaturation in carbon, or in the course of wall-rock 53 buffered redox reactions (Stachel and Luth 2015). Unlike other mantle minerals, diamond is chemically 54 inert, isolating its mineral inclusions from subsequent metasomatic modification. The study of inclusions 55 in diamond allows to characterize the rocks that form the substrates for diamond precipitation, revealing 56 that among lithospheric diamonds worldwide, 65% are derived from peridotitic sources, 33% are eclogitic 57 and 2% websteritic (Stachel and Harris 2008). Sublithospheric diamonds, from the asthenosphere, transition 58 zone and lower mantle, are rare and account for only about 1-2 % of the worldwide diamond production. 59 Mineral inclusions in diamonds, therefore, primarily provide pristine information on both the nature and 60 origin of the subcontinental lithospheric mantle and the origin of its diamond endowment.

61 The presence of alluvial diamonds and their close spatial association to mantle-derived igneous 62 rocks of the Alto Paranaíba Igneous Province (APIP) bring into focus the gaps in our understanding of the 63 origin and evolution of the lithospheric mantle beneath the southwestern margin of the São Francisco 64 Craton. Diamonds studied here are all derived from alluvial deposits and their primary volcanic sources are 65 still unknown. Pereira et al. (2017, and references therein) recognize evidence of young, proximal, and primary sources for diamonds from the same context. From our visual observation alone, diamond 66 67 populations from each of the alluvial deposits have a unique set of physical characteristics and these first 68 order distinctions are further confirmed by the analytical results presented in this study (e.g., through 69 distinct nitrogen characteristics and inclusion chemistries). We, therefore, regard the studied diamonds as 70 being relatively proximal (within a few tens of km at most) to their primary sources, rather than reflecting 71 craton-scale mixing of diamonds from multiple sources.

72 In the southwestern part of the São Francisco Craton, the occurrence of valuable alluvial diamonds 73 and kimberlites related to the APIP stimulated decades of exploration for the primary sources of diamonds, 74 from the late 1960's to the 2000's. Diamonds in the APIP are especially sought after due to the common 75 occurrence of sizable stones (>100 ct). Such large stones are particularly abundant in the context of three 76 rivers that run parallel in SE-NW orientation, immediately south of the town of Coromandel, named 77 Douradinho, Santo Inácio and Santo Antônio do Bonito (Pereira and Fuck 2005). In the Santo Antônio do 78 Bonito River, the largest gem diamond ever found in Brazil was recovered in 1938, weighting 726.6 ct. 79 Throughout the years, the Coromandel and Abaeté areas have also produced a considerable amount of high-80 value pink stones.

81 Diamond exploration in the Alto Paranaíba region, largely based on indicator minerals, culminated 82 in the discovery of the hundreds of intrusive bodies known to date. Despite these discoveries, the evaluation 83 techniques applied at the time classified most of the kimberlites as non-economic, and exploration 84 companies left the area at the beginning of the 2000's. In the APIP, only a few kimberlites are known to be 85 diamondiferous and no link to the valuable alluvial diamond deposits could be established so far. Although 86 a large number of intrusions are already known in the APIP, as the erosion of the Cretaceous Mata da Corda 87 Group progresses, new Cretaceous intrusions are being revealed, such as the recently discovered Osvaldo 88 França 1 kimberlite (Carvalho et al. 2022).

To map the nature of the lithospheric mantle beneath the APIP, we present the first study on diamonds and their mineral inclusions from this area. We analyzed the nitrogen systematics of the host diamond along with the major and trace element composition of their mineral inclusions, focusing on diamonds from the Douradinho River, Verde River, Abaeté, Romaria, and Frutal deposits. Geothermobarometry of the inclusions and nitrogen thermometry of the diamonds aids in understanding 94 the formation conditions of the diamonds and their lithospheric residence. The composition of the mineral 95 inclusions is used to determine the nature of the diamond substrate. The paragenetic abundances in the 96 studied diamonds provides new implications for diamond exploration.

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98 2. Overview of the São Francisco Craton basement and the Alto Paranaíba Igneous Province

99 The oldest components so far identified in the São Francisco Craton date back to 4.1 Ga, and events 100 recorded up to 2.5 Ga indicate stabilization of the cratonic nuclei predominantly in the Neoarchean (Teixeira 101 et al. 2017). Exposed in the southernmost and northeastern portions of the craton, Archean rocks are in 102 direct contact with Paleoproterozoic orogenic belts that register the collision between the São Francisco 103 and Congo paleocontinents at ~2.1-2.0 Ga, with indications of subduction-related events starting at 2.47 Ga 104 (Alkmim and Teixeira 2017; Barbosa and Barbosa 2017). Following the development of sedimentary basins 105 along its passive margins and in rift zones that infringed onto the cratonic nucleus, the Brasiliano Orogeny 106 in the Neoproterozoic shaped the current outline of the São Francisco Craton (Heilbron et al. 2017). 107 Delineating its southwestern limits, the east-verging thrust sheets of the Southern Brasília belt formed as a 108 result of the convergence of the Amazonian, São Francisco-Congo and Paranapanema blocks, where 109 subduction-related regional metamorphism is dated between 650 and 630 Ma (Pimentel 2016).

110 Cretaceous alkaline/ultramafic magmatism, structurally controlled by the Azimuth 125 lineament 111 (Bardet 1977), intruded the metasedimentary rocks of the Brasília belt in western Minas Gerais and eastern 112 Goiás states, giving rise to the APIP (Fig. 1). At that time, the Brasília belt acted as a topographic high, 113 separating the distribution of sediments between the Paraná basin to the west, and São Francisco basin to 114 the east. The volcanoclastic deposits of the APIP are mainly of kamafugitic affinity and comprise the Mata 115 da Corda Group, the upper Cretaceous section of the São Francisco basin, and time-equivalent occurrences 116 in the Paraná basin (Fig. 1). Although intruding metasedimentary rocks of the Neoproterozoic Brasília 117 mobile belt, several studies have shown that all APIP rock types were likely sourced from the subcontinental 118 lithospheric mantle (e.g., Carlson et al. 1996). The lithospheric mantle beneath the Alto Paranaíba area, at 119 a depth of 150 km, is characterized by low seismic velocities (Carvalho et al. 2022), contrasting high 120 velocities in the cratonic nucleus (Rocha et al. 2019). Tomographic (Rocha et al. 2019) and gravimetric 121 (Pereira and Fuck 2005) data indicate that the cratonic lithosphere of the São Francisco Craton extends 122 underneath the Brasília Belt.

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124 **3. Samples and Methods**

125 Our study is based on 82 diamonds recovered from artisanal mines in the southwestern part of the 126 São Francisco Craton. Most diamonds are from placer deposits of the Abaeté (n=6), Douradinho River 127 (n=25) and Verde River (n=27), and from a Cretaceous conglomerate at Romaria (n=11). In addition, this 128 study examined diamonds from placer deposits at Frutal (n=13), in westernmost part of study area. The 129 Frutal placer deposits may have received some contribution - via sediment transport - from the APIP areas, 130 but such a contribution is currently debated and unconstrained (Fig. 1). In all figures, a specific color is 131 used for each sample locality: orange = Abaeté; blue = Douradinho River; grey = Frutal; yellow = Romaria; 132 green = Verde River. The first two letters of all sample numbers indicate the sample location: AB = Abaeté, 133 DR = Douradinho River, FT = Frutal, RM = Romaria, VR = Verde River.

Sample preparation and analyses were performed using facilities at the University of Alberta,
Canada. Ranging in mass from 0.08 to 2.2 ct, the diamonds were broken using a steel-crusher for the
recovery of mineral inclusions and analysis of diamond fragments.

137 Diamond fragments were analyzed for their nitrogen concentrations and aggregation states using a 138 micro-Fourier transform infrared spectrometer (μ -FTIR), Thermo Fisher Nexus 470, attached to a 139 Continuum IR microscope. The detector was cooled with liquid nitrogen. Using a squared aperture size of 140 100 μ m, spectra were taken in transmission mode over the range of 4000 to 650 cm⁻¹ by averaging 200 141 scans with a resolution of 4 cm⁻¹. Spectral deconvolution and nitrogen quantification were accomplished 142 following the procedure described in Stachel et al. (2018a).

143 Mineral inclusions were recovered from 21 diamonds via cracking. The inclusions were mounted 144 individually in epoxy resin in 6 mm brass pips and polished for microprobe analysis. Major and minor 145 element concentrations were measured using a JEOL JXA-8900R EPMA with an accelerating voltage of 146 20 kV and a beam current of 30 nA. For a sulfide inclusion, an accelerating voltage of 15 kV was used. Peak count times were 15–20 s and background time was half the peak time, resulting in oxide detection 147 148 limits of typically ≤ 0.02 wt%. Al, Ca and Cr trace concentrations in olivine were measured using a 149 CAMECA SX100 Electron Probe Microanalyzer (EPMA) with an accelerating voltage of 20 kV and a 150 beam current of 300 nA. The detailed protocols of olivine trace element analysis using EPMA are given in 151 Bussweiler et al. (2019). Our analyses of reference material SC-GB agree within uncertainty with the values 152 stated in that study. For all microprobe analyses, three spots on average were measured per sample and, 153 after assessing compositional homogeneity, averaged.

Trace element concentrations of garnet and clinopyroxene inclusions were analyzed using a Resonetics M-50-LR 193 nm ArF excimer laser ablation system with a Laurin-Technic S-155 two-volume ablation cell coupled to a Thermo Scientific Element IIXR inductively coupled plasma mass spectrometer 157 (ICP-MS). Depending on the inclusion size, samples and standards were ablated with a spot size of 15 to 158 90 μ m at a frequency of 10 Hz and a laser fluence of ~3.5 J/cm². Trace elements were measured on the following masses: ⁴⁵Sc, ⁴⁹Ti, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, 159 ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸⁰Hf and ¹⁸¹Ta. Each spot analysis consisted of 40 s of 160 161 background acquisition and 60 s of sample ablation, followed by a wash time of 40 s. For spot sizes from 23 to 90 µm, NIST SRM 612 glass was used as the primary standard and NIST614 was used as a quality 162 163 control. For spot sizes of 15 µm, NIST SRM 610 was used as the primary standard and NIST612 to assess the accuracy of the concentrations. ⁴³Ca contents, previously measured by EPMA, were used as internal 164 standard. The agreement of values measured for secondary standards was better than 10% for all spot sizes 165 166 employed.

For some mineral phases, their chemical structure was confirmed via Raman spectroscopy. Raman spectra were collected using a Horiba Scientific's LabRAM HR Evolution mounted with an Olympus optical fiber microscope. Using a monochromatic laser with a 532 nm frequency, Raman spectra were collected using 3 accumulations, acquisition time of 30 seconds, and 50% laser intensity.

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172 **4. Results**

173 4.1. Diamonds characteristics

All diamonds were examined for their color, morphology, surface features, and nitrogen characteristics. Colors range from colorless to brown, with additional yellowish/yellow and rare pink and greenish samples. Most diamonds are intensely resorbed and dodecahedral shapes predominate. Widespread surface features are hillocks, plastic deformation lines and minor frosting. In addition, edge abrasion related to alluvial transport is widespread. The occurrence of irradiation-induced green and brown spots on diamond surfaces is restricted to the Verde River and Frutal populations.

Figures 2a and b show the distribution of color and morphology among the five diamond populations studied. Brown diamonds principally occur in the Douradinho River, Verde River and Abaeté populations, while Frutal and Romaria diamonds are typically colorless. Considering diamond morphology, Douradinho River has a unique population of flat dodecahedrons, and two hemimorphic diamonds occur. Less resorbed octahedral and transitional dodecahedral-octahedral morphologies are most prominent in Romaria diamonds.

186 Nitrogen contents range from below detection (<5 at.ppm) to ~2300 at.ppm, with nitrogen 187 abundances >1000 at.ppm being restricted to diamonds from Frutal and Romaria (**Fig. 2c**). For ~10% of 188 the diamonds, significant intra-crystal variations in nitrogen content (>300 at.ppm) were detected; in these 189 cases, rims are generally lower in nitrogen content and aggregation state. The full range in aggregation (0-190 100 %B with %B=100N_B/(N_A+N_B)) from pairs of nitrogen (A-centres) to four nitrogen around a vacancy 191 (B-centres) was observed. Douradinho River diamonds are distinct by an unusual dominance (56%) of high 192 aggregation states (>89 % B; Fig. 2d) and a high proportion (\sim 30%) of diamonds with [N] <12 ppm (mainly 193 as Type IaAB). At Frutal and Romaria, low to intermediate (0-67 %B) aggregation states dominate. Despite 194 high nitrogen aggregation states of Douradinho River diamonds, the planar defects (platelets) invariably 195 associated with the formation of B centers (Woods 1986) are not common. Plastic deformation, which is 196 widespread among samples from Douradinho River, or thermal pulses are regarded as causes for platelet 197 degradation (Woods 1986; Evans et al. 1995). Approximately 80% of the diamonds show hydrogen-related 198 impurities (absorbance at 3107 cm⁻¹). Overall, Frutal diamonds have the strongest hydrogen-related 199 absorbance, with no relationship to total nitrogen contents. A positive correlation between N and H contents 200 is, however, recognized for diamonds with eclogitic inclusions. The single websteritic diamond from 201 Douradinho River is also notably hydrogen-rich.

202 4.2. Mineral inclusions

203 Mineral inclusions from 21 diamonds were analyzed for major and trace element compositions. 204 Four locations are represented among these diamonds, as indicated in **Table 1**. No inclusions were 205 recovered from Romaria diamonds. Inclusions range in size from ~30 to 500 μ m (**Fig. 3**), and mainly 206 display cubo-octahedral morphologies imposed by their host diamonds. Chemically identified minerals, in 207 order of decreasing abundance, are olivine, omphacite, enstatite, Cr-diopside, pyrope-almandine, Cr-208 pyrope, Mg-chromite, coesite and sulfide. Based on inclusion chemistry (**Supplementary Data 1**), 209 diamonds are assigned to the peridotitic (n=14), eclogitic (n=6) and websteritic (n=1) suites (**Table 1**).

210 4.2.1. Major element chemistry of peridotitic/websteritic inclusions

Olivine was recognized in 10 diamonds, mainly as multiple colorless inclusions of a single phase 211 212 or together with enstatite, Cr-diopside and garnet. In one case, olivine forms a touching, graphite-coated 213 pair with a Cr-diopside (Fig. 3a and b; Supplementary Fig. 1a). Graphite-coating of olivine is widespread 214 among Douradinho River diamonds (Fig. 3a and c). Olivine Mg# (molar 100Mg/(Mg+Fe)) varies from 215 91.2 to 94.4. For three diamonds of lherzolitic paragenesis (based on co-occuring Cr-diopside inclusions), 216 olivine Mg# ranges from 91.5 to 92.0. Calcium contents reveal two distinct groups; a high-Ca group (CaO 217 > 340 ppm), in which samples display positive correlations of Ca with Cr and Al, and a low-Ca group (CaO 218 < 215 ppm), in which such correlations are absent (Fig. 4a). Olivines from the low-Ca group all have Mg# 219 >93 and are likely of harzburgitic paragenesis (Stachel and Harris 2008). Olivines in the high-Ca group have Mg# <92.5 and are likely lherzolitic, especially as this group includes all samples of known lherzolitic paragenesis. Douradinho River olivines display the highest Cr_2O_3 contents in both the low- and high-Ca groups.

223 Colourless to faint green enstatite occurs in five diamonds, both as single crystals and touching 224 with clinopyroxene (Fig. 3d and 5a). Mg# ranges from 92.8 to 94.0, with the exception of one enstatite 225 (Mg# 89.4) touching with a clinopyroxene in a Douradinho River diamond (Fig. 5b). The low Mg-number 226 of the latter is comparable to enstatite of the transitional websteritic-lherzolitic association in diamonds 227 from Voorspoed, South Africa (Viljoen et al. 2018). Compared to Voorspoed websteritic and transitional 228 websteritic-lherzolitic enstatites, the Douradinho River enstatite, however, has higher CaO (Fig. 4b), TiO₂, 229 and Na₂O contents (1.25, 0.12 and 0.23 wt%, respectively). Based on its low Mg# and Cr and high Na-Ti-230 Mn contents, this enstatite is likely of websteritic (pyroxenitic) paragenesis (c.f., Stachel and Harris 2008). 231 All other enstatites coexisting with clinopyroxene fall into the lherzolitic field (Fig. 4b). A magnesium-rich 232 enstatite (Mg# 93.9) from a Frutal diamond, which cannot be assigned to a specific paragenesis based on 233 co-existing inclusions, has CaO-Mg# characteristics that suggest a likely harzburgitic paragenesis (Fig. 4b).

234 **Cr-diopside** occurs in four diamonds, both as touching or non-touching associations with olivine, 235 enstatite and Cr-pyrope (Fig. 3a and b, 5a and b). The typical emerald-green color of Cr-diopside is not 236 very saturated in the studied samples, with Cr_2O_3 contents varying from 0.47 to 1.18 wt%. Mg# varies from 237 93.8 to 94.5, except for the one augite grain (Mg# 88.9; sample DRP01) that forms a touching pair with the 238 websteritic enstatite described above. Intergrowth/exsolution of orthopyroxene and clinopyroxene is a 239 common feature in websteritic and transitional websteritic-lherzolitic diamonds from Voorspoed (Viljoen 240 et al. 2018) and Namibia (Leost et al. 2003). Like the touching enstatite, the low Mg# of this clinopyroxene 241 is comparable to transitional websteritic-lherzolitic clinopyroxenes from Voorspoed, but at lower CaO and 242 higher TiO₂ contents. High Ca in enstatite and low Ca in clinopyroxene document a high formation 243 temperature for this websteritic inclusion pair (Brey and Köhler 1990; see below). Relative to the lherzolitic 244 Cr-diopsides from this study, the websteritic crystal has an elevated jadeite content and is Cr poor.

245 Purple Cr-pyrope was found in two diamonds from Douradinho River and one diamond from 246 Abaeté (Fig. 3a and d). Based on chemical composition (Fig. 4c) and consistent with their coexistence 247 with Cr-diopside, two garnets are assigned to the lherzolitic paragenesis. The third garnet, from Douradinho 248 River, does not coexist with other minerals and despite a formal harzburgitic designation (classification of 249 Grütter et al. 2004), falls right onto the compositional boundary between harzburgitic and lherzolitic garnets 250 (Fig. 4c). In addition, this garnet has the lowest Mg# (85.1) of the set, which is closer to the average value 251 for worldwide lherzolitic inclusions (84.7) than to harzburgitic inclusions (88.2; Stachel and Harris 2008), 252 consistent with a lherzolitic origin. In general, Mg# from the studied garnets, varying from 85.1 to 86.5, are

relatively high compared to lherzolitic garnet inclusions worldwide (Stachel and Harris, 2008). Cr_2O_3 varies widely between the analyzed crystals (5.44 to 12.8 wt%) and MnO content ranges from 0.23 to 0.28 wt% and is positively correlated to Cr_2O_3 .

256 Black Mg-chromite occurred in two diamonds, one from Verde River and one from Douradinho 257 River, and based on composition (Mg# 57.2-57.9 and Cr# of 82.8-89.7, respectively) was assigned to the 258 peridotitic suite. The Mg-chromite from Verde River has an unusually high and variable ZnO content (0.44 259 to 1.44 wt%) with an average value of 12 points (0.88 wt%) presented in **Supplementary Data 1**. High Zn 260 chromites were previously reported as inclusions in diamonds from the Canastra area, in Brazil (Tappert et 261 al. 2006). The high Zn inclusion has a cubo-octahedral morphology and no fractures connecting to the 262 diamond surface were observed, excluding an epigenetic origin (Fig. 3e). One additional Mg-chromite, 263 with Cr# of 68.2, was identified as a minute (5 µm) inclusion in an olivine from an Abaeté diamond. The 264 composition of this chromite is poorly constrained due to analytical overlap with the host olivine. The low 265 Mg# (91.9) of the host olivine suggests a lherzolitic paragenesis.

266 4.2.2. Major element chemistry of eclogitic inclusions

267 Omphacite was recognized in five diamonds, showing both green and blue colors. The observed 268 colors cannot be linked to variations in chemical composition. Omphacite is included without and with 269 eclogitic garnet, both as touching and non-touching pairs, and always outnumbers garnet inclusions in the 270 same diamond (Fig. 3f). In one diamond, omphacite coexists with garnet and coesite (DRR04). Omphacite 271 contains up to 6.45 wt% NaO and up to 11.7 wt% Al_2O_3 , with a near 1:1 correlation between Na and Al (r² 272 = 0.98). Aluminum slightly predominates over Na + K in apfu, indicating the additional presence of a small 273 Tschermaks component. The Mg-number range is 58.4 to 69.8 and K_2O varies from 0.05 to 0.50 wt%. In 274 two Douradinho River diamonds, omphacite exsolved a TiO_2 phase, identified as rutile via Raman 275 spectroscopy (Supplementary Fig. 1b). In two diamonds, one from Douradinho River and one from Verde 276 River, small patches and veins of a SiO₂ and Al₂O₃ rich material were observed in two otherwise notably 277 K₂O poor omphacites (Fig. 5c).

Orange colored **pyrope-almandine** was recovered from four diamonds, two from Douradinho River and two from Verde River, all coexisting with clinopyroxene (**Fig. 3f**). The garnets have a low Cr_2O_3 content (max. 0.04 wt%), low Mg# (34.1 to 41.2), and variably high CaO concentrations (from 7.15 to 13.4 wt%; **Fig. 4c**). Although falling into the normal compositional ranges for eclogitic garnet inclusions worldwide (Stachel and Harris 2008), the studied garnets are notably Ti-rich (TiO₂ up to 1.48 wt%). The only garnet with TiO₂ <1 wt% is in direct contact with the above mentioned omphacite crystal with rutile exsolutions (**Fig. 5d**); a second, non-touching garnet in the same diamond has a TiO₂ content of 1.46 wt%. High TiO₂ (>1 wt%) garnet inclusions are common in eclogitic diamonds from Argyle (Jaques et al. 1989;
Stachel et al. 2018a) and Voorspoed (Viljoen et al. 2018) and widespread among low-Cr majoritic garnet
inclusions in diamonds from the Juína area, Brazil (Wilding 1990, Burnham et al. 2015), and the Monastery
(Moore et al. 1991) and Premier kimberlites (Korolev et al. 2018), South Africa. In the garnets studied here,
TiO₂ is negatively correlated with Al₂O₃ and positively correlated with CaO and Na₂O (0.23 to 0.40 wt%).

290 Coesite coexists with pyrope-almandine and omphacite in a diamond from Douradinho River. One
291 of the coexisting clinopyroxenes in this diamond contains the silica-rich patches and veins described above.
292 The coesite composition is essentially pure silica and the crystal structure was confirmed via Raman
293 spectroscopy (Supplementary Fig. 1c).

A golden colored, cubo-octahedral **sulfide** was recovered from one diamond from Verde River. Based on a low Ni content (1.69 wt%), it was assigned to the eclogitic paragenesis. The sulfide grain has a homogeneous composition and no exsolutions were observed. Fe and S contents are 56.7 and 38.5 wt%, respectively, matching the composition of pyrrhotite. Concentrations of Cu range from 0.73 to 2.64 wt%, with the average value of nine points (1.55 wt%) presented in Sup. Table 1.

299 *4.2.3. Trace elements*

300 Clinopyroxene and garnet trace element compositions (**Supplementary Data 2**) were analyzed via 301 LA-ICP-MS and the resulting rare earth element patterns (REE_N, N = CI-chondrite normalized; 302 McDonough and Sun 1995) patterns are presented in **Figure 6**. Coexisting assemblages document that 303 LREE are preferentially partitioned into clinopyroxene while garnet is the main host for MREE and HREE.

Peridotitic clinopyroxenes have REE_N patterns with negative slopes for the LREE_N-MREE_N or, in one instance, flat MREE_N-HREE_N. MREE and HREE are generally strongly depleted relative to CIchondrite (**Fig. 6a**). A clinopyroxene that occurs touching with enstatite in a lherzolitic diamond from Abaeté (ABT03 in **Fig. 5a**) has an incomplete REE_N pattern due to the small laser spot size used but nevertheless documents superchondritic concentrations of Eu, Ho, Er and Lu, with a positive MREE_N-HREE_N slope. The single websteritic clinopyroxene (DRP01) has a humped pattern, peaking at Nd (~ 10x chondritic abundance), followed by a gradual drop-off to Lu (**Fig. 6a**).

311 Lherzolitic garnets either have sinusoidal REE_N patterns peaking at Ce-Nd and showing a minimum 312 at Dy (at Douradinho River) or are strongly LREE depleted with a positive slope from Tb_N to Lu_N (at 313 Abaeté; **Fig. 6b**). All three garnets have approximately chondritic Lu concentrations and enrichment in 314 LREE decreases with increasing Mg#. Omphacite has humped REE_N patterns, peaking at Nd for most samples, followed by negative slopes for MREE_N-HREE_N (**Fig. 6c**). An omphacite from Douradinho River (DRR04), coexisting with garnet and coesite, has lower LREE_N abundances and a steeper positive slope within LREE, peaking at Sm-Eu (**Fig. 6c**). Omphacite VRM17 from Verde River is unusual with a steep drop-off from Nd to Sm, followed by a negative slope within MREE_N and relatively flat HREE_N.

Eclogitic garnets have steep positive slopes within LREE_N, up to Sm_N, followed by fairly flat MREE_N-HREE_N at ~30x chondritic abundance (**Fig. 6d**). The highest LREE, with a chondritic La abundance, occur in a garnet from Verde River (VRM17).

323 *4.3. Geothermobarometry*

Application of various geothermobarometers to the studied touching and non-touching inclusion assemblages results in estimates of the pressure and temperature conditions of last equilibration or of diamond formation, respectively. Data for multiple inclusions of the same type (either touching or nontouching) within the same diamond were averaged.

328 Diamond ABT04 from Abaeté contains a non-touching lherzolitic assemblage of garnet, 329 clinopyroxene, orthopyroxene and olivine allowing an evaluation of multi-phase equilibrium and 330 consequent assessment of the reliability of the applicable mineral exchange thermobarometers used for the 331 remaining diamonds: coexisting garnet and clinopyroxene, coexisting orthopyroxene and clinopyroxene, 332 and olivine only (cf., Nimis and Grütter 2010). Equilibrium between clinopyroxene and orthopyroxene is 333 documented by very good agreement of the Ca-in-opx (1036 °C, Brey and Köhler 1990), enstatite-in-cpx (1048 °C, Nimis and Taylor 2000) and two pyroxene (1069 °C, Taylor 1998) thermometers, calculated for 334 335 a fixed pressure of 50 kbar. Equilibrium between garnet and the two pyroxenes is indicated by very similar 336 temperature estimates to the pyroxene-based results using the Mg-Fe exchange between garnet and 337 clinopyroxene (1109 °C; Krogh 1988). On the other hand, the temperatures given by the Al-in-olivine (1216 338 °C, Bussweiler et al. 2017; 1231 °C, De Hoog et al. 2010) and Cr-in-olivine (1215 °C, De Hoog et al. 2010) 339 thermometers, although in mutual agreement, are noticeably higher, differing by 146 to 195 °C from the 340 enstatite-in-clinopyroxene based estimates.

For lherzolitic diamond ABT03, containing a touching enstatite-Cr-diopside pair plus non-touching olivine and enstatite, the same difference was noticed between the olivine-based and pyroxene-based thermometry results. For the non-touching enstatite, the Ca-in-opx thermometer (Brey and Köhler 1990) gives a temperature of 1037 °C, while the olivine thermometers (Bussweiler et al. 2017; De Hoog et al. 2010) give temperatures between 1206 and 1222 °C. Diamond DRR08 contains a touching assemblage of olivine-clinopyroxene-orthopyroxene and non-touching garnet, olivine and clinopyroxene inclusions. Disagreement between pyroxene, pyroxenegarnet and garnet-olivine based thermometers indicates disequilibrium for both the minerals in the touching assemblage and among the non-touching inclusions. Observation of disequilibrium for a touching inclusion assemblage is unusual and likely relates to incomplete re-equilibration to changing thermal conditions (e.g., Stachel and Luth (2015).

After application of the compositional filters of Grütter (2009), the single clinopyroxene thermometer of Nimis and Taylor (2000) in combination with the updated calibration of the Cr-in-cpx geobarometer of Sudholz et al. (2021) was applied to the inclusions in the two well-equilibrated lherzolitic diamonds from Abaeté (ABT04 and ABT03). For the non-touching assemblage of ABT04 we obtain a temperature of 1038 °C and a pressure of 45 kbar, while cpx touching with opx in ABT03 yields 1089 °C and 50 kbar. Clinopyroxene touching with opx from the single websteritic diamond (DRP01 from Douradinho River) records a much higher temperature and pressure of ~1350 °C and 63 kbar.

359 For the samples containing only olivine, temperatures were calculated with the Cr-in-olivine (De 360 Hoog et al. 2010) and Al-in-olivine (Bussweiler et al. 2017; De Hoog et al. 2010) thermometers, assuming 361 a fixed pressure of 50 kbar. This results in temperatures between 1209 and 1260 °C for olivine-bearing 362 Douradinho River diamonds and between 1040 and 1171 °C for Abaeté and Frutal samples. Based on the 363 above comparison with pyroxene thermometry, these olivine-based temperature estimates may, however, 364 be 100-200 °C too high. The Cr correction for the Al-in-olivine thermometer assigns all Cr present to the 365 trivalent state (De Hoog et al. 2010). High Cr contents in some olivine inclusions in diamond have, however, 366 been interpreted to result from the presence of divalent Cr and, consequently, De Hoog et al. (2010) 367 provided a second formulation of their thermometer without Cr correction. Temperatures calculated with 368 that version of Al-in-olivine thermometer differ by -34 to +15 °C and, on average, are 16 °C lower, 369 compared to the Cr-corrected version, which is within the average expected difference of 20 °C for the two 370 calibrations (De Hoog et al., 2010).

- The chromite inclusion in diamond DRS06 yields a temperature of 1194 °C (Zn-in-spinel; Ryan et al. 1996). Given the extremely high Zn content in chromite from diamond VRM11, the thermometer was not applied to this inclusion as it would result in an unrealistic low temperature estimate.
- For the eclogitic garnet and clinopyroxene pairs (n=3), temperatures range from 1238 to 1280 °C (Krogh 1988), calculated at a fixed pressure of 50 kbar. A touching pair of garnet and clinopyroxene in diamond DRP05 results in a ~100 °C lower temperature.
- 377

378 **5. Discussion**

379 5.1. Diamond substrate - a heterogeneous mantle

Here we discuss the compositionally heterogeneous lithospheric mantle beneath the southwestern margin of the São Francisco Craton and compare the diamond inclusion data from this study with diamond and xenocryst data from adjacent areas. In our dataset, peridotite appears to be the dominant diamond substrate, followed by eclogite. The additional presence of exotic websteritic diamond sources is indicated by a single sample. This compositional heterogeneity is well represented in diamonds from Douradinho River only, where all paragenesis were recorded (n=10; where 6 are peridotitic, 3 are eclogitic and 1 is websteritic).

387 5.1.1. Re-fertilized peridotitic mantle

388 Olivines trapped within diamonds are reliable indicators of the depletion level in cratonic 389 lithosphere (Pearson and Wittig 2014). The high abundance of inclusions with lherzolitic affinity observed 390 in the Abaeté and Douradinho River populations (Table 1; 70% of peridotitic diamonds) indicates that the 391 mantle beneath the Coromandel/Abaeté areas is less depleted, or more re-fertilized, compared to 392 neighboring areas within the confines of the Sao Francisco Craton, as revealed by other diamond studies 393 (Kaminsky et al. 2001; Tappert et al. 2006) (Fig. 1). Kaminsky et al. (2001) analyzed diamonds from the 394 Rio da Prata system, located more than 100 km to the northeast of Coromandel (between Presidente Olegário and João Pinheiro), recording an average olivine Mg# of 93.4 (n=28), consistent with strongly 395 396 depleted (harzburgitic) sources. Tappert et al. (2006) studied diamond inclusions from the Canastra area, 397 ~200 km south of Coromandel, again documenting the predominance of highly magnesian (depleted) 398 olivines (n=4; Mg# of 93.8) over possible lherzolitic olivine (n=1; Mg# of 91.5). The limited data obtained 399 for Frutal diamonds in this study (n=2; **Table 1**), ~250 km to the southwest of Coromandel (**Fig. 1**), also 400 indicate strongly depleted (harzburgitic) mantle sources, consistent with the olivine inclusion data from the 401 nearby Canastra area (Tappert et al. 2006).

402 An overall lower degree of depletion in the mantle beneath the Coromandel area is also evident 403 from our garnet inclusions and previously published xenocrysts data from five kimberlites in the 404 Coromandel area (Fig. 4c; n=532; Andrade 2012; Andrade and Chaves 2011; Carvalho et al. 2022; 405 Coldebella et al. 2020), which show an almost complete absence of harzburgitic garnets, indicating that the 406 sub-cratonic lithospheric mantle beneath Coromandel experienced only comparatively low degrees of 407 partial melting, or was strongly re-fertilized. The shaded area in **Figure 4c** includes 7363 analyses of garnet 408 xenocrysts from five additional kimberlites in Coromandel area by DeBeers (Pereira and Fuck 2005; 409 Skinner 1996). These data are consistent with the moderately depleted character observed here for

410 inclusions in diamond. In keeping with the olivine compositions, garnet from the neighboring Rio da Prata 411 and Canastra areas reveals a more depleted mantle compared to Coromandel and Abaeté. Garnet inclusions 412 studied by Kaminsky et al. (2001; n=4) indicate a highly depleted mantle source for Rio da Prata system 413 diamonds, with CaO contents varying from 0.91 to 4.61 wt%. Xenocryst data for kimberlites from the 414 Canastra area (n=1482) (Andrade 2012; Costa 2008; Hill et al. 2015) are also consistent with a higher 415 degree of depletion in the sub-cratonic lithospheric mantle for that area.

In this study no inclusions were recovered from diamonds from Romaria. Literature data for inclusions in Romaria diamonds (Meyer and Svisero 1975; Svisero 1978) indicate the presence of heterogeneous diamond source rocks, similar to the Coromandel lithospheric mantle. For four diamonds, the previous work documented a harzburgitic garnet-enstatite pair, an eclogitic sulfide, a lherzolitic clinopyroxene (Cr-diopside), and an olivine with Mg# 92. Xenocryst data for Romaria (n=72) (Coelho 2010) register an overall mildly depleted signature, similar to Coromandel.

422 Steep positive HREE_N slopes observed for the lherzolitic garnet inclusions of Abaeté and 423 Douradinho River indicate highly depleted precursors for both areas (Fig. 6b; Stachel et al. 2004). 424 Sinusoidal/LREE-enriched trace element patterns indicate that the lithospheric mantle under these areas 425 was affected by metasomatism, re-fertilizing the original depleted substrates. The LREE_N-HREE_N patterns 426 observed for lherzolitic garnet inclusions in this study strictly differs from the low degree of sinuosity 427 common to worldwide lherzolitic inclusions (Stachel et al. 2004; Fig. 6b). Unlike worldwide occurrences, 428 garnets from the dominant lherzolitic diamond population from the Victor kimberlite, Canada, show a 429 strong degree of sinuosity (Stachel et al. 2018b; Fig. 6b). Regarding the type of metasomatism (melt versus 430 fluid), the widely used Zr/Y indicator (Griffin and Ryan 1995; Fig. 7a) shows that worldwide lherzolitic 431 garnet inclusions invariably follow a melt metasomatic trend, while Victor lherzolitic garnets fall along a 432 fluid metasomatic trend. In our case, the metasomatic agent cannot be determined from the Zr/Y ratios in 433 garnet, as concentrations are too low, reflecting a depleted signature (Fig. 7a). Nevertheless, the dominant 434 sinusoidal character of the garnet REE_N patterns is indicative of fluid-dominated or mild melt-driven 435 metasomatic overprint (e.g., Stachel and Harris 2008).

The intensity of metasomatic overprint for the Abaeté and Douradinho River areas, however, is markedly different. The one lherzolitic garnet from the Abaeté area, which has subchondritic LREE, fairly unfractionated La_N/Eu_N and low LREE_N/HREE_N (**Fig. 6b**), is the least metasomatized of all the garnets. Following modelling by Shu and Brey (2015), the REE_N pattern of garnet ABT04 could be explained through equilibration of pre-metasomatic garnet with only ~0.15% carbonatitic melt (relative to garnet). The high Ti/Eu of the Abaeté garnet (**Fig. 7b**), however, implies modification through a medium carrying significant Ti, such as protokimberlite or megacryst magma (Kargin et al. 2016). The Douradinho River garnets, showing sinusoidal REE_N patterns with LREE from 1 (DRR08) to 10x (DRS04) chondrite abundances, would be consistent with equilibration with \sim 1 to 3% of metasomatic carbonatitic melt. Based on their elevated Zr/Hf and moderately low Ti/Eu (**Fig. 7b**), the Douradinho River garnets suggest metasomatic equilibration with a medium that is transitional between carbonatite and kimberlite melts.

447 Similar to the garnets, clinopyroxenes from lherzolitic diamonds from Douradinho River show highly fractionated REE_N patterns, with La at ~10x chondritic abundances and subchondritic HREE_N (Fig. 448 449 **6a**). The two clinopyroxenes from Abaeté have much lower LREE–HREE ratios than the Douradinho River 450 clinopyroxene, with La at chondritic (ABT03) to subchondritic (ABT04) abundance, consistent with the 451 mild metasomatic overprint inferred for garnet ABT04. Clinopyroxenes ABT03 and ABT04 both have 452 positive HREE_N slopes. ABT03 carries super-chondritic MREE_N-HREE_N and has the highest level of Ti 453 enrichment observed in this study. As discussed above, the high Ti for cpx in ABT03 is inconsistent with 454 carbonatite-driven metasomatism and points to interaction with a proto-kimberlite or megacryst magma-455 like melt.

456 5.1.2. Evidence for a recycled oceanic crust component

Eclogitic xenocrysts recovered in the Coromandel area are rare compared to the relatively high abundance of eclogitic inclusions in diamonds (~30%) in this study and their documented occurrence in the larger region (Rio da Prata system, Kaminsky et al. 2001; Abaeté area, Meyer and Svisero 1975; Romaria, Svisero 1978; Canastra, Tappert et al. 2006). A similar situation exists for the Argyle lamproite, where, although more than 90% of diamonds are derived from eclogitic sources, not a single eclogitic xenocryst has ever been documented (Luguet et al. 2009; Stachel et al. 2018a).

463 Eclogitic garnet and clinopyroxene inclusions studied here have a restricted compositional range 464 in Mg# (34-41 for garnet and 58-70 for clinopyroxene). Based on the Ca# (26-37, with molar Ca=100Ca/(Ca+Mn+Fe+Mg)) and Mg# of non-touching garnet inclusions, the protoliths can be classified 465 466 as high-Ca (Ca# > 20) and low-Mg (Mg# < 60) (Aulbach and Jacob, 2016). Using the proposed mineral 467 modes of Aulbach and Jacob (2016; 55% garnet and 45% cpx), whole-rock compositions were 468 reconstructed for eclogitic diamonds with analyzed garnet and clinopyroxene inclusions (DRR04, DRP05, 469 VRM17; Supplementary Data 1). High FeO (12.9-15.5 wt%) and low MgO (6.3-8.5 wt%) contents result 470 in low Mg# (45 to 52), reflecting an evolved character of the eclogitic protoliths. The calculated bulk rock 471 major-element compositions, with Al₂O₃ varying from 15.2 to 16.5 wt% and CaO from 10.9 to 13.6 wt%, 472 are broadly similar to that of MORB (Gale et al. 2013). Such evolved compositions, combined with elevated 473 Na and Ti contents and the presence of coesite inclusions, point to derivation as oceanic crust through 474 recycling (Jacob 2004). This interpretation of recycled oceanic crust as the source of eclogitic inclusions in diamonds is consistent with the widespread occurrence of eclogitic diamonds along craton margins, as
observed at Orapa, Jwaneng, Argyle and Voorspoed (Aulbach et al. 2017; Richardson et al. 2004; Stachel
et al. 2018a; Viljoen et al. 2018), where younger material was accreted to the cratonic nuclei via subduction
(Shirey et al. 2001).

479 The flat $MREE_N$ -HREE_N patterns observed in garnets (Fig. 6d) provide further evidence for a lowpressure origin like MORB (Jacob 2004). Due to strong partitioning of Eu²⁺ into plagioclase (McKenzie 480 and O'Nions, 1991), the presence of positive Eu anomalies ($Eu_N/Eu^* > 1.05$; $Eu^* = (0.5^*Gd_N + 0.5^*Sm_N)$) 481 482 is commonly used to identify plagioclase accumulation and consequently gabbroic protoliths (Aulbach and 483 Jacob 2016; Jacob 2004). Among the analyzed eclogitic garnets (n=4), only one from Verde River shows a 484 minor positive Eu anomaly (VRT04; $Eu_N/Eu^* = 1.10$), while the other three garnets have small negative 485 anomalies ($Eu_N/Eu^* = 0.87$ to 0.93). Therefore, gabbros located in the deeper portions of oceanic crust are 486 not the principle protolith for the eclogitic diamond substrates but instead basaltic pillow lavas and sheeted 487 dikes from the shallow oceanic crust that experienced minor plagioclase fractionation dominate. Due to 488 strong Sr partitioning into plagioclase (McKenzie and O'Nions, 1991), plagioclase fractionation should 489 also be documented by negative Sr anomalies in photoliths. Calculated bulk trace element patterns 490 (Supplementary Data 2) display negative Sr anomalies ($Sr_N/Sr^* < 1.05$; $Sr^* = (0.5*Pr_N + 0.5*Nd_N)$, with Sr_N/Sr* varying from 0.8 to 1.02, consistent with the observation of minor negative Eu anomalies. 491

492 Bulk rock trace element patterns show a positive slope within the LREE_N and almost flat MREE_N-493 HREE_N at ~20x chondritic abundance (Fig. 7c). MREE-HREE for calculated Douradinho River bulk rocks 494 perfectly matche NMORB (Gale et al. 2013) while the Verde River bulk rock falls slightly below NMORB. 495 LREE are depleted relative to NMORB for all calculated bulk rocks (Fig. 7c). Such LREE depletion 496 combined with NMORB-like MREE-HREE patterns indicates extraction of 10-20% melt in the garnet 497 facies during protolith subduction (e.g., Stachel et al. 2004). A peak at Nd for one calculated bulk rock 498 (VRM17) and a slightly concave slope in the LREE_N for DRP05 suggest that melt depletion was followed 499 by minor metasomatic re-enrichment in highly incompatible trace elements such as the LREE.

Low Mg# of the analyzed garnets, omphacites and calculated bulk rocks indicate that the eclogitic diamond substrates did not have a cumulate origin, even for the one sample with the slight positive Eu anomaly. Instead, major and trace element data suggest that the eclogitic diamond substrates originated from shallow subducted oceanic crust (pillow lavas and sheeted dikes), as already inferred from the presence of mild negative Eu anomalies in three samples.

505 5.1.3. Presence of a websteritic substrate

506 Websteritic suite diamonds are relatively rare, accounting for only ~2% worldwide (Stachel and 507 Harris 2008). Their occurrence was first noted at Orapa (western edge of the Zimbabwe craton; Gurney et 508 al. 1984), and other important localities with websteritic diamonds include Venetia (Limpopo Belt; Aulbach 509 et al 2002), Voorspoed (eastern Witwatersrand Block of the Kaapvaal Craton; Viljoen et al. 2018), and the 510 coastal deposits of Namibia (Leost et al 2003). Here, we report the first occurrence of a websteritic diamond 511 in Brazil. The formation of websteritic diamond substrates has previously been related to reactions between 512 slab-derived dacitic melts and peridotitic lithospheric mantle (Yaxley and Green 1998; Aulbach et al. 2002). 513 Alternatively, an inclusion suite ranging from lherzolitic over lherzolitic-websteritic to websteritic in 514 diamonds from the Voorspoed mine was interpreted to reflect plume impingement and melt infiltration of 515 the lithospheric mantle during the 2.72 Ga Ventersdorp large igneous province (Viljoen et al. 2018).

The MREE_N-HREE_N concentrations and pattern of the websteritic clinopyroxene from Douradinho River (DRP01) are similar to those of eclogitic clinopyroxenes (**Fig. 6c**). The positive slope within LREE_N, peaking at Nd-Sm, however, is steeper than observed for eclogitic omphacites. A minor negative Eu anomaly ($Eu_N/Eu^*=0.96$) observed for the websteritic clinopyroxene further suggests a link to subducted oceanic crust. Thus, for the case discussed here, the origin of the websteritic diamond substrate likely relates to hybridization of lithospheric lherzolite through reaction with eclogite-derived melt, as proposed in other studies (Aulbach et al., 2002; Smit et al. 2014; and references therein).

523 5.2. Pressure and Temperature Constraints

524 For the Abaeté area, a non-touching clinopyroxene (diamond ABT04) and a touching opx-cpx pair 525 (ABT03), the former indicating the conditions of diamond formation and the latter the conditions of last equilibration, both follow a \sim 39 mW/m² model geotherm (Hasterok and Chapman 2011; Fig. 8). From 526 Douradinho River, a touching pair of websteritic opx-cpx (DRP01) falls onto the high P-T end of the same 527 528 conductive model geotherm. The calculated temperatures for the eclogitic diamonds from Douradinho and 529 Verde rivers (average $1257 \pm 23^{\circ}$ C) indicate that they formed at unusually hot conditions, compared to 530 worldwide eclogitic inclusions (mean: 1174 °C; Stachel and Harris 2008). Similar high temperatures are 531 documented for eclogitic diamonds from Argyle (mean: 1250 °C; Stachel et al. 2018a). Further support for eclogitic diamond formation at high temperatures comes from the high Ti contents in the studied eclogitic 532 garnet inclusions. The strong negative correlation between Ti and Al ($r^2 = 0.97$) observed for the eclogitic 533 534 garnets indicates that Ti in garnet was mainly accommodated via substitution in the octahedral site. Aulbach 535 (2020) argued that a temperature-dependent coupled substitution with Na is the dominant incorporation 536 mechanism for Ti in garnet from mantle eclogite. Consequently, elevated Ti in the studied garnets indicates 537 higher-than-average temperatures of diamond formation. The occurrence of rutile exsolutions then is a 538 consequence of cooling after diamond formation, causing the solubility of Ti in garnet/clinopyroxene to

decrease. Further evidence for cooling after eclogitic diamond formation is provided by a ~100 °C lower
temperature derived from touching (1184 °C) compared to non-touching (1280 °C) garnet-clinopyroxene
in eclogitic diamond DRP05.

542 A paleo-geotherm for the study area was previously constructed by Read et al. (2004), using 543 clinopyroxene xenocrysts from 95–89 Ma kimberlites in the Alto Paranaíba Igneous Province. Their data approximately correspond to a 37 mW/m² model geotherm (Hasterok and Chapman 2011). This geotherm 544 falls below the \sim 39 mW/m² model geotherm derived here from touching and non-touching inclusions in 545 diamond. Projecting the garnet-cpx thermometry for eclogitic inclusions onto a 39 mW/m² geotherm (Fig. 546 8) indicates a deep lithospheric origin. Projection onto a 37 mW/m² model geotherm results in even higher 547 548 pressures, with some inclusions reaching temperatures in excess of the mantle adiabat. This observation, 549 however, is not conclusive evidence against a conductive geotherm as low as the one derived by Read et al. (2004) and the observed difference of 2 mW/m² to our results is still considered within the uncertainty 550 range of geothermobarometry-derived geotherms. 551

552 5.3. Time-averaged mantle residence temperatures based on nitrogen aggregation

553 The aggregation of nitrogen via diffusion in the diamond lattice is a time and temperature dependent 554 process and mantle residence temperatures can be estimated using an approximation of mantle residence 555 time and the interrelationship between nitrogen content and nitrogen aggregation state (Fig. 9; Taylor et al. 556 1990, 1996). In the absence of radiometric ages for diamonds from the Alto Paranaíba Province, we use 557 indirect geological constraints to derive possible mantle residence times. The occurrence of eclogitic 558 diamonds and the almost complete absence of peridotitic inclusions with a highly depleted, harzburgitic-559 dunitic character, point to diamond formation younger than 3.0 Ga (Shirey and Richardson 2011). In the 560 context of the southwestern São Francisco Craton, subduction events with the potential to re-fertilize the 561 lithospheric mantle and initiate growth of eclogitic and lherzolitic diamonds occurred during a 562 Paleoproterozoic orogeny (2.2-1.9 Ga) and during the Brasiliano Orogeny (650-610 Ma) (Alkmim and 563 Teixeira 2017; Barbosa and Barbosa 2017; Heilbron et al. 2017). The latter involved consumption of 564 voluminous oceanic lithosphere of the Goiás-Pharusian Ocean, culminating in the formation of the Brasília Belt (Pimentel 2016). Kimberlites related to the Alto Paranaíba Igneous Province intruded in the Cretaceous 565 566 (~90 Ma; Read et al. 2004).

Hence, we calculate "minimum" temperatures for diamond storage in the mantle considering a maximum residence time of 2.0 byr; shortening the residence time to 500 myr would increase mantle residence temperatures by only about 37 °C, on average. Two groupings in time-averaged equilibration temperatures can be identified (**Fig. 9**): 1) Residence temperatures >1200 °C, which include >90% of 571 Douradinho River samples, at least 50% of Abaeté samples, ~ 40% of Verde River samples and few samples 572 from the Frutal and Romaria areas; 2) Residence temperatures <1150 °C, which includes most samples 573 from the Frutal, Romaria and Verde River areas.

Average mantle residence temperatures (2.0 byr residence) are ~100 °C higher for Douradinho River samples (1270 °C) compared to the other studied diamond populations (Verde River: 1170 °C; Romaria: 1140 °C; Frutal: 1130 °C). No average residence temperature is given for Abaeté diamonds as only six samples were studied, of which two were Type IIa diamonds (no nitrogen detected). The high average residence temperature of Douradinho River samples matches that calculated for the eclogitic diamonds (1260 °C) and of the residence temperature of the single websteritic sample (1310 °C).

580 Compared to diamond populations worldwide, the residence temperatures for Douradinho River diamonds and, more specifically, for the eclogitic population from Douradinho and Verde rivers, are very 581 582 high. Calculated for a shorter storage time of 0.5 byr, eclogitic diamonds from worldwide localities have 583 an average mantle residence temperature of 1167 °C (Stachel et al. 2018a). Unusually high residence 584 temperatures are, however, recognized for eclogitic diamonds from Argyle (average and median: 1300 °C; 585 Stachel et al. 2018a). Recalculating the temperatures for eclogitic diamonds from the present study to 0.5 586 byr mantle residence (i.e., formation related to the Brasiliano Orogeny), then the average values increase 587 from 1299 to 1342 °C. Temperatures for the eclogitic diamonds calculated at 2.0 byr mantle residence are, however, more consistent with the mineral inclusion geothermometry (Table 1), suggesting that a 588 589 Paleoproterozoic orogeny is a more likely cause of diamond formation. The generally high temperatures 590 for the eclogitic diamond population in the Coromandel area further show that the subducted oceanic crust 591 likely accreted to the base of the lithosphere, similar to the case of the Argyle area (e.g., Jaques et al. 1989; 592 Stachel et al. 2018a; Timmerman et al. 2019).

593 Peridotitic diamonds occur in both the low and high temperature groups. The very small number 594 of diamonds with mineral inclusions in the low temperature group prevent a meaningful assessment of the 595 involved diamond substrates. At Douradinho River diamonds, peridotitic (average: 1215 °C) and eclogitic 596 (1295 °C) diamonds were both exposed to high time-averaged residence temperatures.

597 5.4. A diamond and mantle formation model for the Coromandel area

The nature of the cratonic lithosphere in the Coromandel area is poorly constrained due to Neoproterozoic (and younger) cover rocks occurring in the southwestern margin of the São Francisco Craton (Pimentel 2016) that obscure the basement and due to limited mantle xenolith studies. Based on diamond inclusion chemistry, we propose that the lithosphere underlying the Alto Paranaíba Igneous Province either is post-Archean, as previously suggested by Read et al. (2004), or represents originally Archean lithosphere that was highly re-worked and re-enriched during Proterozoic times. **Figure 10** illustrates our model for the formation of the different types of diamonds recognized in this study, as discussed below.

606 The São Francisco Craton clearly comprises an Archean core (Teixeira et al. 2017). Dominantly 607 harzburgitic diamond populations typical of Archean depleted mantle were previously recognized at 608 Canastra and Rio da Prata areas (Kaminsky et al. 2001; Tappert et al. 2006). Our diamond inclusion study, 609 however, documents a less depleted, lherzolitic lithospheric mantle beneath the Alto Paranaíba region, 610 containing additional eclogitic and rare websteritic diamond sources. The eclogitic inclusion-bearing 611 diamonds from this study record low Mg# and reconstructed bulk rock trace element patterns consistent 612 with recycled oceanic crust. Two main orogenies could account for the subduction of oceanic crust in the 613 area: a Paleoproterozoic event (2.2-1.9 Ga) and the Brasiliano Orogeny (650-610 Ma) (Alkmim and 614 Teixeira 2017; Barbosa and Barbosa 2017; Heilbron et al. 2017). As mantle residence temperatures 615 calculated for 2.0 byr mantle residence are comparable to the formation temperatures of non-touching 616 eclogitic inclusions, an origin during a Paeloproterozoic orogeny is considered more likely. This 617 interpretation is supported by the presence of subduction-related segments of Paleoproterozoic orogens 618 occurring in the southernmost (Alkmim and Teixeira 2017) and northeastern portions (Barbosa and Barbosa 619 2017) of the São Francisco craton margin. The absence of strongly subcalcic garnets and an overall very 620 low proportion of harzburgitic garnets as xenocrysts in kimberlites characterizes lithosphere of late Archean 621 to Paleoproterozoic origin (c.f., Grütter et al. 1999; Fig. 4c). Lherzolitic diamonds are particularly abundant 622 in pericratonic/thermally-modified areas, as observed for the Victor mine (Superior Craton affected by 1.1 623 Ga Midcontinent rift; Stachel et al. 2018b), the Buffalo Hills kimberlites (Paleoproterozoic Buffalo Head 624 Terrane; Banas et al. 2007), and Ellendale olivine lamproites (Neoproterozoic King Leopold Orogen; Smit 625 et al. 2010). The dominantly lherzolitic and eclogitic diamond population recorded in the Alto Paranaíba 626 region is therefore consistent with post-Archean lithosphere. Re-depletion model ages of ~2.4 Ga derived 627 for peridotite xenoliths from mafic-alkaline rocks of the Alto Paranaíba Igneous Province (Carlson et al. 628 2007) provide further support for post-Archean lithosphere underlying the southwestern São Francisco 629 Craton.

Radiogenic isotope studies of magmatism in the region support the influence in the mantle of a Paleoproterozoic orogeny. Kamafugitic, kimberlitic, and lamproitic rocks from the APIP have been studied for Os-Sr-Nd-Pb isotope systematics, showing a lithospheric source for these magmas (Carlson et al. 1996). In particular, the radiogenic Os of kamafugitic samples indicates pyroxenite/websterite/eclogite source rocks in the lithospheric mantle, consistent with the eclogitic and websteritic diamond discovery in our study for the same region. Pb isotope compositions of alkaline rocks in the southwestern part of the São Francisco Craton indicate the influence of an old (>2 Ga) component in the lithosphere (Carlson et al. 1996).
Similarly, a HIMU component (hybridization of an ancient subducted oceanic crust-derived melt with the
ambient mantle; Hanyu et al. 2011) has been hypothesized to be present in the base of the lithosphere or
brought up by a mantle plume (Bizzi 1996). The HIMU signature could also be created by a metasomatic
overprint.

Projecting the hot temperatures of eclogitic diamonds onto a 39 mW/m² geotherm indicates formation between ~180 and 200 km depth. This is consistent, within error, with a seismically defined lithosphere/asthenosphere boundary at 181 km in the region (Priestley et al. 2018). The absence of a majorite component in the studied garnet inclusions, or of any other sublithospheric inclusions, suggests that sublithospheric diamond sources were not tapped during the Alto Paranaíba igneous event, unlike in the Juína region to the NW (Burnham et al. 2015; Wilding 1990).

647 5.4.1. Implications for diamond exploration

648 The results from this study motivate a reevaluation of best approaches to diamond exploration in 649 the Alto Paranaíba region. The observed low abundance of diamonds with harzburgitic inclusions indicates 650 that traditional exploration techniques, focusing on the presence of sub-calcic garnets in mineral 651 concentrates (Gurney 1984), do not apply here. The prevalence of lherzolitic inclusions in diamonds from 652 Alto Paranaíba (42%; comprising at least 67% of the peridotitic diamond population) highlights that 653 exploration techniques must consider lherzolitic (G9) garnets as well. Although an effective way to explore 654 for lherzolitic diamonds has not been developed to date, Grütter et al. (2004) showed that besides Cr₂O₃ in 655 garnet as a barometric proxy, low MnO contents and Ca intercept values may indicate likely derivation of 656 lherzolitic garnets from the diamond stability field. Another approach should consider the presence of 657 lherzolitic xenocryst garnets displaying the same sinusoidal REE_N patterns frequently observed for 658 lherzolitic inclusions. Sinusoidal REE_N patterns are not a common feature of lherzolitic garnet xenocrysts 659 (Stachel et al. 2004), so if observed, the style of metasomatic overprint documented by such patterns may 660 be employed to indicate the presence of lherzolitic substrates likely associated with diamonds.

Exploration for eclogitic diamond populations in the region (~30% of inclusion-bearing diamonds) is hampered by the low abundance of eclogitic garnets in the xenocryst record (**Fig. 4c**). This bias may imply limited preservation of eclogitic xenocrysts caused by the character of the magma(s) that brought the diamonds up to the Earth's surface (e.g., absence of eclogitic garnet xenocrysts in the Argyle lamproite; Stachel et al. 2018a). A recent study of an "exotic" kimberlite from the Coromandel area (Carvalho et al. 2022) reveals a rock with an enriched component in the magma source (including Ti-, Ca- and Zr-rich phases, atypical of kimberlites), sharing similarities with lamproites. Consequently, even a low abundance of eclogitic garnets recovered during exploration may be a good indication for the likely presence of eclogitic diamonds.

670

671 6. Conclusions

Silicate inclusions in diamonds produced at Abaeté, Verde River and Douradinho River in the Alto 672 673 Paranaíba Igneous Province, reveal a prevalence of the lherzolitic and eclogitic suites (>70%) and the first 674 occurrence of a websteritic diamond in Brazil. This contrasts with findings for diamond populations from 675 neighboring regions in the southwestern São Francisco Craton that formed dominantly in harzburgitic 676 substrates. Consistently low levels of chemical depletion of peridotitic lithospheric mantle underlying the 677 Alto Paranaíba Igneous Province, recorded in mineral inclusions from this study and in garnet xenocryst 678 data compiled from literature, suggest either a post-Archean origin or significant re-enrichment and 679 reprocessing of older mantle in the Proterozoic. Sinusoidal REE_N patterns of lherzolitic garnet inclusions 680 are related to variably low levels of metasomatism by carbonatite-kimberlite or proto-kimberlite melts for 681 the Coromandel and Abaeté areas in the Alto Paranaíba Igneous Province. Trace element patterns of 682 eclogitic inclusions suggest derivation from upper sections of subducting slabs, while a single websteritic 683 inclusion pair may relate to precipitation from eclogite-derived melts that were hybridized through 684 interaction with ambient lherzolitic mantle. High temperatures calculated for the eclogitic and websteritic 685 inclusion suites indicate crystallization near the base of the lithosphere. Very high aggregation states of 686 nitrogen, observed especially in Douradinho River diamonds, indicate prolonged mantle residence at 687 unusually high temperatures. Prolonged residence near the base of the lithosphere is consistent with the 688 high abundance of deformed/brown diamonds and an origin related to Paleoproterozoic orogenic accretion 689 and growth of the craton (2.2-1.9 Ga), rather than subduction and collision related to the relatively young 690 Brasiliano Orogeny (0.65-0.61 Ga). The predominance of lherzolitic and eclogitic diamonds in the Alto 691 Paranaíba region documented here, combined with the poor representation of eclogitic garnets among 692 xenocryst populations, require new approaches to evaluate the diamond potential of kimberlite or 693 kimberlite-like rocks carrying diamonds derived from these substrates.

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- 941
- 942 Figure captions:

Figure 1: Simplified geological map showing the sampling locations of the diamond populations for
this and previous studies in relation to the Neoproterozoic Brasília belt and the cover rocks of the
Paraná (PRB) and São Francisco (SFB) basins. The indicated limit of the São Francisco
paleocontinent is after Rocha et al. (2019). The boundaries of Minas Gerais (MG) with São Paulo
(SP) and Goiás (GO) states are indicated.

- Figure 2: Characteristics of the studied diamonds regarding a) color, b) morphology, c) nitrogen content and d) nitrogen aggregation state. In (b) the following abbreviations for morphologies are used: Oct/D-oct = Octahedral/dodecahedral-octahedral; Dod = Dodecahedral; Hemi = Pseudohemimorphic; Cleav = Cleavage fragment. In (d) diamonds are grouped according to the relative percentage of nitrogen in A and B centers (expressed as %A and %B), or the abundance of nitrogen (<5 ppm for Type IIa).
- Figure 3: a) Garnet, clinopyroxene and olivine inclusions in diamond DRR08; on the right side, note a touching cpx-ol pair that is covered by a thick graphite layer. b) Released cpx-ol pair observed in (a) with thick graphite coating. c) Graphite coating of olivine inclusions and associated small fractures in a Douradinho river diamond. d) Olivine, greenish enstatite, and purple garnet in a lherzolitic diamond from Abaeté. e) Opaque chromite inclusion in a Verde River diamond. f) Eclogitic garnet and clinopyroxene in a diamond from Douradinho River; note a touching pair of grt-cpx and the bluish color of the non-touching cpx.
- Figure 4: a) Cr₂O₃ vs. CaO contents (ppm) in olivines; the data points may be grouped according to
- 962 their Mg#. The open circles correspond to samples assigned to the lherzolitic paragenesis based on
- 963 coexistence with clinopyroxene. b) CaO vs. Mg# in enstatites from this study (see (a) for legend of
- 964 symbols) and from websteritic and transitional websteritic-lherzolitic diamonds from Voorspoed

965 (Viljoen et al. 2018); the fields for the various parageneses are from Stachel and Harris (2008). c) 966 Cr_2O_3 vs. CaO diagram for garnets with fields for parageneses after Grütter et al. (2004). Garnet 967 inclusions from this study (large colored circles), garnet inclusions from previous studies (small 968 colored diamonds; Kaminsky et al. 2001; Meyer and Svisero 1978; Tappert et al. 2006), and garnet 969 xenocrysts from the Canastra (small triangles; Andrade 2012; Costa 2008; Hill et al. 2015), Romaria 970 deposit (small squares; Coelho 2008), and Coromandel areas (small circles; Andrade 2012; Andrade 971 and Chaves 2011; Carvalho et al. 2022; Coldebella et al. 2020; and shaded area representing the 972 density of garnet xenocryst compositions from Skinner (1996) reported in Pereira and Fuck (2005)).

Figure 5: Backscattered electron images of a) touching pair of opx-cpx in a lherzolitic diamond from
Abaeté; b) touching pair of opx-cpx in the single websteritic diamond from Douradinho River; c) cpx
(light grey) containing a silica- and aluminum-rich phase (darker grey) in an eclogitic diamond from
Douradinho River, and d) rutile exsolution in a grt-cpx touching pair from a Douradinho River
diamond (photo of inclusion still inside diamond is shown as Fig. 3f).

- 978 Figure 6: CI-chondrite-normalized (McDonough and Sun 1995) REE element patterns of peridotitic 979 (a) clinopyroxene and (b) garnet, and eclogitic (c) clinopyroxene and (d) garnet inclusions in 980 diamonds. For comparison, the websteritic clinopyroxene DRP01 is presented in both (a) and (c) 981 plots. Garnets and clinopyroxenes are represented by solid and dashed lines, respectively (see legend 982 as inset in (d)). In (b), dotted lines represent calculated patterns for varying degrees of equilibration 983 of garnet with 0.15 to 3% of a hypothetical carbonatitic melt (after Shu and Brey 2015). In grey, the 984 field for lherzolitic inclusion garnets from Victor kimberlite is indicated (after Stachel et al. 2018b). 985 Yellow shaded field indicates average composition of lherzolitic garnet inclusions from worldwide 986 sources (after Stachel et al. 2004). For ABT03 and ABT04 clinopyroxenes, due to a very small laser 987 beam (<33 µm), only a limited number of REE are above the limit of detection (as seen in (a)).
- 988 Figure 7: a) Y versus Zr plot (after Griffin and Ryan 1995) for lherzolitic garnet inclusions. Colored
- 989 fields indicate the composition of lherzolitic garnet inclusions from worldwide localities (green) and
- 990 the Victor kimberlite (blue) (after Stachel et al. 2018b); b) Zr/Hf versus Ti/Eu for lherzolitic garnet
- 991 inclusions in diamonds. Indicated fields are after Shu and Brey (2015); c) CI-chondrite-normalized
- 992 (McDonough and Sun 1995) REE for reconstructed eclogite bulk rock compositions from this study.
- 993 The NMORB composition of Gale et al. (2013) is shown for reference.
- Figure 8: Pressure and temperature conditions derived from clinopyroxene inclusions (Nimis and
 Taylor 2000; Sudholz et al. 2021) in two lherzolitic diamonds from Abaeté (filled and open orange
 circles) and the single websteritic diamond from Douradinho River (blue circle). Clinopyroxene

997 touching with orthopyroxene (diamond mantle residence conditions) is indicated as open symbols, 998 isolated clinopyroxene (diamond formation conditions) as filled symbol. Temperatures for eclogitic 999 garnet and clinopyroxene (open and filled symbols again for touching and non-touching inclusions, 1000 respectively; thermometer of Krogh 1988) in diamonds from Douradinho and Verde rivers, 1001 calculated for a fixed pressure of 50 kbar and (associated grey field with arrow) projected onto a 1002 39mW/m² model geotherm. The diamond/graphite curve is from Day (2012). Geotherms and mantle 1003 adiabat are from Hasterok and Chapman (2011).

Figure 9: Nitrogen concentration vs. aggregation state ($\%B=N_B/(N_A+N_B)$) for the different diamond sample populations studied (Abaeté = orange; Douradinho River = blue; Frutal = grey; Romaria = yellow; Verde River = green). The paragenesis of diamonds with analyzed mineral inclusions is indicated by the different symbol shapes. Isotherms are calculated after Taylor et al. (1990, 1996) for mantle residence times of 0.5 and 2 byr, as indicated.

1009 Figure 10: Schematic model illustrating subcretion of a slab fragment beneath the southwestern 1010 margin of the São Francisco Craton during an accretionary event and the associated formation of 1011 the eclogitic, websteritic and lherzolitic diamonds observed in the present study. A minor 1012 harzburgitic diamond population present may predate this event. Eclogitic diamonds formed within 1013 the slab, either during subduction and associated prograde metamorphism or during subsequent fluid-driven diamond-forming events. The subduction and devolatilization of oceanic lithosphere 1014 1015 caused refertilization of the overlying subcratonic lithospheric mantle, with consequent 1016 crystallization of lherzolitic diamonds. Slab-derived melts reacted with peridotite leading to 1017 precipitation of websteritic diamonds.

1018

1019 **Table captions:**

Table 1: Characteristic of the diamonds analyzed for their mineral inclusions. T_{Nitrogen} for a mantle residence time of 2 byr calculated after Taylor et al. (1990, 1996). For diamonds with 0%B and with 1022 100%B, the assumed detection limits for nitrogen B and A centers (1 and 99 %B) were used instead to obtain maximum and minimum residence temperature estimates, respectively.

1024

1025 Supplementary items

1026 **Figure captions:**

Supplementary Figure 1: Representative Raman spectra of (a) graphite coat on olivine (diamond
DRR08, shown as Fig. 3a), (b) rutile exsolutions (spectrum of non-touching omphacite from diamond
DRP05), and (c) coesite inclusion in diamond DRR04. All spectra were recorded after inclusion
extraction from the host diamond at room temperature.

- 1031
- 1032 **Table caption:**
- 1033 Supplementary Table 1: Major element data (wt%) for mineral inclusions in diamond recovered in
- 1034 this study. For olivine, EPMA trace element analyses (ppm) for CaO, Al₂O₃ and Cr₂O₃ are provided
- 1035 as well. Bulk rock eclogite compositions were calculated based on 55% garnet and 45%
- 1036 clinopyroxene.
- 1037 Supplementary Table 2: Trace element data for mineral inclusions, including calculated bulk rock
- 1038 trace element eclogite.





Coromandel

B

GO

Romaria

100 km

50

0

Frutal

SP RG

Verde River





Figure 3







Figure 5

















| Colorat.ppmcentresassemblageParagenesisestimatesColorless 42 001Lherzolitic50-1089*Brownish $ -$ 01Lherzolitic50-1089*Brownish 51 98 01+ Dio + EnLherzolitic50-1089*Brownish 51 98 01+ Dio + EnLherzolitic50-1089*Brownish 51 98 01+ Dio + EnLherzolitic45-1038*Colorless 46 70 01Lherzolitic45-1038*Vellowish10 27 01Lherzolitic45-1038*Vellowish10 27 01Lherzolitic60-1294**Vellowish10 27 01Lherzolitic60-1294**Vellow29890mp + Grt + CoeEclogitic60-1294**Colorless382100GrtLherzolitic60-1294**Vellow29890mp + Grt + CoeEclogitic60-1294**Colorless382100GrtLherzolitic60-1294**Colorless382100GrtLherzolitic60-1294**Colorless382100GrtLherzolitic60-1294**Colorless382100GrtHarzburgitic60-1294**Colorless26100Dio + EnMebsterfitic60-1294**Colorless27100GroBrownish949101Rownish3104ChCh | IdLocationctShapeColorat.ppmassemblageParagenesissetimatesAbaeté0.28ShapolessColoriess42001.herzoliticI.herzolitic50-1089*Abaeté0.33DodecahedronBrownish519801-blo + En + GrtLherzolitic50-1089*Abaeté0.37DodecahedronBrownish519801-blo + En + GrtLherzolitic50-1089*Abaeté0.37DodecahedronBrownish519801-blo + En + GrtLherzolitic50-1089*Abaeté0.37DodecahedronColorless467001Lherzolitic50-1089*Abaeté0.37OctahedronColorless467001Lherzolitic45-1038*Douradinko River1.12Shapolecs607001Lherzolitic50-1089*Douradinko River0.37DodecahedronColorless1001Lherzolitic45-1038*Douradinko River0.37BodecahedronColorless1001Lherzolitic45-1038*Douradinko River0.37BodecahedronColorless10001Lherzolitic45-1038*Douradinko River0.37MacleColorless10001Lherzolitic45-1038*Douradinko River0.37MacleColorless10001Lherzolitic45-1038*Douradinko River0.31MacleColorless2701Lherzoli | | | | | | z | %В | Mineral | | P-T | |
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| Douradinho River 2.21 Flat dodecahedron Colorless 8 71 Ol Harzburgitic Douradinho River 0.27 Hemimorphic Colorless 12 45 Ol Lherzolitic Douradinho River 0.43 Dodecahedron Yellow 29 89 Omp + Grt + Coe Eclogitic 60-1294** Douradinho River 1.73 Macle Colorless 37 79 Ol + Dio + En + Grt Lherzolitic 60-1294** Douradinho River 0.21 Macle Colorless 382 100 Grt Lherzolitic 60-1294** Douradinho River 0.21 Macle Colorless 382 100 Grt Lherzolitic 60-1294** Douradinho River 0.23 Shapeless Colorless 382 100 Grt Lherzolitic 63-1350** Douradinho River 0.08 Shapeless Colorless 226 100 Din + En + Grt Lherzolitic 63-1332** Douradinho River 0.03 Shapeless <td>Douradinho River 2.21 Flat dodecahedron Colorless 8 71 OI Harzburgitic Douradinho River 0.27 Hemimorphic Colorless 12 45 OI Lherzolitic 60-1294*** Douradinho River 0.37 Macle Colorless 12 45 OI Lherzolitic 60-1294*** Douradinho River 1.73 Macle Colorless 382 100 Grt Lherzolitic 60-1294*** Douradinho River 0.30 Shapeless Colorless 382 100 Grt Lherzolitic 60-1294*** Douradinho River 0.31 Macle Colorless 382 100 Grt Lherzolitic 60-1294*** Douradinho River 0.30 Shapeless Colorless 382 100 Grt Lherzolitic 63-1350** Douradinho River 0.30 Shapeless Colorless 226 100 Dio+En Websteritic 63-1350** Douradinho River 0.4 Macle Colorless 264 67 En Harzburgitc Eclogitic <td< td=""><td>DRM08</td><td>Douradinho River</td><td>1.12</td><td></td><td>Colorless</td><td>9</td><td>70</td><td>Omp</td><td>Eclogitic</td><td></td><td>1279</td></td<></td> | Douradinho River 2.21 Flat dodecahedron Colorless 8 71 OI Harzburgitic Douradinho River 0.27 Hemimorphic Colorless 12 45 OI Lherzolitic 60-1294*** Douradinho River 0.37 Macle Colorless 12 45 OI Lherzolitic 60-1294*** Douradinho River 1.73 Macle Colorless 382 100 Grt Lherzolitic 60-1294*** Douradinho River 0.30 Shapeless Colorless 382 100 Grt Lherzolitic 60-1294*** Douradinho River 0.31 Macle Colorless 382 100 Grt Lherzolitic 60-1294*** Douradinho River 0.30 Shapeless Colorless 382 100 Grt Lherzolitic 63-1350** Douradinho River 0.30 Shapeless Colorless 226 100 Dio+En Websteritic 63-1350** Douradinho River 0.4 Macle Colorless 264 67 En Harzburgitc Eclogitic <td< td=""><td>DRM08</td><td>Douradinho River</td><td>1.12</td><td></td><td>Colorless</td><td>9</td><td>70</td><td>Omp</td><td>Eclogitic</td><td></td><td>1279</td></td<> | DRM08 | Douradinho River | 1.12 | | Colorless | 9 | 70 | Omp | Eclogitic | | 1279 |
| Douradinho River0.27HemimorphicColorless1245OlLherzoliticDouradinho River0.43DodecahedronYellow2989Omp + Grt + CoeEclogitic60-1294**Douradinho River1.73MacleColorless9779Ol + Dio + En + GrtLherzoliticDouradinho River0.21MacleColorless382100GrtLherzolitic60-1294**Douradinho River0.21MacleColorless382100GrtLherzolitic60-1394**Douradinho River0.21MacleColorless2592ChrPeridotitic63-1350**Douradinho River0.08ShapelessColorless256100Dio + EnWebsteritic63-1350**Douradinho River0.03ShapelessColorless6467EnHarzburgitic63-1332**Frutal0.04MacleBrownish9491OlHarzburgitic63-1332**Verde River0.28DodecahedronBrownish3104ChrPeridotiticVerde River0.36DodecahedronColorless495100SulfEclogitic59-1272**Verde River0.26DodecahedronColorless1999Omp + GrtEclogitic59-1272** | Douradinho River 0.27 Hemimorphic Colorless 12 45 Ol Lherzolitic Douradinho River 0.43 Dodecahedron Yellow 29 89 Omp + Grt + Coe Eclogitic 60-1294*** Douradinho River 1.73 Macle Colorless 97 79 OI + Dio + En + Grt Lherzolitic 60-1294*** Douradinho River 0.21 Macle Colorless 382 100 Grt Lherzolitic 60-1294** Douradinho River 0.21 Macle Colorless 382 100 Grt Lherzolitic 60-1294** Douradinho River 0.30 Shapeless Colorless 382 100 Grt Lherzolitic 63-1350** Douradinho River 0.08 Shapeless Colorless 226 100 Dio + En Websteritic 63-1332** Douradinho River 0.42 Shapeless Colorless 226 100 Dio + En Websteritic 63-1332** Frutal 0.21 <td< td=""><td>DRM10</td><td>Douradinho River</td><td>2.21</td><td>Flat dodecahedron</td><td>Colorless</td><td>8</td><td>71</td><td>Ō</td><td>Harzburgitic</td><td></td><td>1273</td></td<> | DRM10 | Douradinho River | 2.21 | Flat dodecahedron | Colorless | 8 | 71 | Ō | Harzburgitic | | 1273 |
| Douradinho River0.43DodecahedronYellow2989Omp + Grt + CoeEclogitic60-1294**Douradinho River1.73MacleColorless9779OI + Dio + En + GrtLherzolitic60-1294**Douradinho River0.21MacleColorless382100GrtLherzolitic60-1294**Douradinho River0.30ShapelessColorless382100GrtLherzolitic60-1294**Douradinho River0.30ShapelessColorless2592ChrPeridotitic63-1350**Douradinho River0.08ShapelessColorless226100Dio + EnWebsteritic63-1350**Douradinho River0.03ShapelessColorless24667EnHarzburgitic63-1332**Frutal0.04MacleBrownish9491OIHarzburgitic63-1332**Verde River0.20DodecahedronBrownish3104ChrPeridotiticVerde River0.36DodecahedronYellowish5492Omp + GrtEclogitic59-1272**Verde River0.26DodecahedronColorless1999Omp + GrtEclogitic59-1272** | Douradinho River 0.43 Dodecahedron Yellow 29 89 Omp + Grt + Coe Eclogitic 60-1294** Douradinho River 1.73 Macle Colorless 97 79 Ol + Dio + En + Grt Lherzolitic 60-1294** Douradinho River 0.21 Macle Colorless 382 100 Grt Lherzolitic 60-1294** Douradinho River 0.21 Macle Colorless 382 100 Grt Lherzolitic 63-1332** Douradinho River 0.08 Shapeless Colorless 256 100 Omp + Grt Eclogitic 63-1332** Douradinho River 0.03 Shapeless Colorless 264 67 En Websterritic 63-1332** Frutal 0.27 Dodecahedron Colorless 64 67 En Mebsterritic 63-1332** Frutal 0.20 Dodecahedron Colorless 64 67 En Mebsterritic 63-1332** Frutal 0.04 <t< td=""><td>DRR01</td><td>Douradinho River</td><td>0.27</td><td>Hemimorphic</td><td>Colorless</td><td>12</td><td>45</td><td>O</td><td>Lherzolitic</td><td></td><td>1232</td></t<> | DRR01 | Douradinho River | 0.27 | Hemimorphic | Colorless | 12 | 45 | O | Lherzolitic | | 1232 |
| Douradinho River1.73MacleColorless977901+ Dio + En + GrtLherzoliticDouradinho River0.21MacleColorless382100GrtLherzoliticDouradinho River0.30ShapelessColorless382100GrtLherzoliticDouradinho River0.30ShapelessColorless2592ChrPeridotiticDouradinho River0.08ShapelessColorless226100Dio + EnWebsteriticDouradinho River0.42ShapelessColorless226100Dio + EnWebsteriticFrutal0.27DodecahedronColorless6467EnHarzburgiticFrutal0.04MacleBrownish9491OIHarzburgiticVerde River0.20DodecahedronBrownish3104ChrPeridotiticVerde River0.36DodecahedronColorless495100SulfEclogiticVerde River0.38DodecahedronYellowish5492Omp + GrtEclogiticVerde River0.26DodecahedronColorless1999Omp + GrtEclogitic | Douradinho River1.73MacleColorless977901+ Dio + En + GrtLherzoliticDouradinho River0.21MacleColorless382100GrtLherzoliticDouradinho River0.30ShapelessColorless2592ChrPeridotiticDouradinho River0.08ShapelessColorless2592ChrPeridotiticDouradinho River0.08ShapelessColorless26100Dio + EnWebsteriticDouradinho River0.27DodecahedronColorless6467EnHarzburgitcFrutal0.27DodecahedronColorless6467EnHarzburgitcFrutal0.04MacleBrownish9491OIHarzburgitcVerde River0.20DodecahedronColorless495100SulfEclogiticVerde River0.38DodecahedronYellowish5492Omp + GrtEclogiticVerde River0.36DodecahedronYellowish5492Omp + GrtEclogiticVerde River0.26DodecahedronYellowish5492Omp + GrtEclogiticVerde River0.26DodecahedronYellowish5492Omp + GrtEclogiticVerde River0.26DodecahedronYellowish5492Omp + GrtEclogiticVerde River0.26DodecahedronColorless1999Omp + Grt <t< td=""><td>DRR04</td><td>Douradinho River</td><td>0.43</td><td>Dodecahedron</td><td>Yellow</td><td>29</td><td>89</td><td>Omp + Grt + Coe</td><td>Eclogitic</td><td>60-1294**</td><td>1273</td></t<> | DRR04 | Douradinho River | 0.43 | Dodecahedron | Yellow | 29 | 89 | Omp + Grt + Coe | Eclogitic | 60-1294** | 1273 |
| Douradinho River0.21MacleColorless382100GrtLherzoliticDouradinho River0.30ShapelessColorless2592ChrPeridotiticDouradinho River0.03ShapelessColorless2592ChrPeridotiticDouradinho River0.03ShapelessColorless256100Dio + EnWebsteritic63-1350**Douradinho River0.04MacleBrownish949101Harzburgitic63-1332**Frutal0.04MacleBrownish949101Harzburgitic63-1332**Verde River0.20DodecahedronBrownish3104ChrPeridotiticVerde River0.36DodecahedronBrownish3104ChrPeridotiticVerde River0.36DodecahedronYellowish5492Omp + GrtEclogiticVerde River0.26DodecahedronColorless1999Omp + GrtEclogitic | Douradinho River0.21MacleColorless382100GrtLherzoliticDouradinho River0.30ShapelessColorless2592ChrPeridotiticDouradinho River0.08ShapelessColorless256100Dio + EnWebsteritic63-1330**Douradinho River0.08ShapelessColorless26100Dio + EnWebsteritic63-1332**Douradinho River0.27DodecahedronColorless6467EnHarzburgitc63-1332**Frutal0.27DodecahedronColorless6467EnHarzburgitc63-1332**Verde River0.20DodecahedronBrownish3104ChrPeridotitic63-1332**Verde River0.20DodecahedronColorless6467EnHarzburgitc63-1332**Verde River0.20DodecahedronColorless6467EnHarzburgitc63-1332**Verde River0.20DodecahedronColorless495100SulfEclogitic59-1272**Verde River0.26DodecahedronYellowish5492Omp + GrtEclogitic59-1272**Verde River0.26DodecahedronColorless1999Omp + GrtEclogitic59-1272**Verde River0.26DodecahedronColorless1999Omp + GrtEclogitic59-1272**Verde River0.26Dodecahedron | DRR08 | Douradinho River | 1.73 | | Colorless | 97 | 79 | OI + Dio + En + Grt | Lherzolitic | | 1216 |
| Douradinho River0.30ShapelessColorless2592ChrPeridotiticDouradinho River0.08ShapelessColorless226100Dio + EnWebsteritic63-1350**3Douradinho River0.08ShapelessColorless100100Dio + EnWebsteritic63-1332**3Frutal0.27DodecahedronColorless6467EnHarzburgitic63-1332**3Frutal0.27DodecahedronColorless6467EnHarzburgitic63-1332**3Verde River0.04MacleBrownish9491OlHarzburgitic63-1332**3Verde River0.20DodecahedronBrownish3104ChrPeridotitic7Verde River0.36DodecahedronColorless495100SulfEclogitic59-1272**7Verde River0.26DodecahedronColorless1999Omp + GrtEclogitic59-1272**7 | Douradinho River 0.30 Shapeless Colorless 259 2 Chr Peridotitic Douradinho River 0.08 Shapeless Colorless 26 100 Dio + En Websteritic 63-1350** 3 Douradinho River 0.08 Shapeless Colorless 26 100 Dio + En Websteritic 63-1332** 3 Frutal 0.27 Dodecahedron Colorless 64 67 En Harzburgitic 63-1332** 3 Frutal 0.27 Dodecahedron Colorless 64 67 En Harzburgitic 63-1332** 3 Verde River 0.20 Dodecahedron Colorless 64 67 En Harzburgitic 63-1332** 3 Verde River 0.20 Dodecahedron Colorless 495 100 Sulf Eclogitic 59-1272** 3 Verde River 0.26 Dodecahedron Yellowish 54 92 Omp + Grt Eclogitic 59-1272** 3 Verde River 0.26 Dodecahedron Yellowish | DRS04 | Douradinho River | 0.21 | Mac | Colorless | 382 | 100 | Grt | Lherzolitic | | 1290 |
| Douradinho River0.08ShapelessColorless226100Dio + EnWebsteritic63-1350**Douradinho River0.42ShapelessColorless100100Omp + GrtEclogitic63-1332**5Frutal0.27DodecahedronColorless6467EnHarzburgitic63-1332**5Frutal0.27DodecahedronColorless6467EnHarzburgitic63-1332**5Verde River0.20DodecahedronBrownish9491OIHarzburgitic5Verde River0.20DodecahedronBrownish3104ChrPeridotitic5Verde River0.36DodecahedronColorless495100SulfEclogitic59-1272**5Verde River0.26DodecahedronColorless1999Omp + GrtEclogitic59-1272**5 | Douradinho River 0.08 Shapeless Colorless 226 100 Dio + En Websteritic 63-1350** Douradinho River 0.42 Shapeless Colorless 64 67 En Harzburgitic 63-1332** 53 Frutal 0.27 Dodecahedron Colorless 64 67 En Harzburgitic 63-1332** 53 Frutal 0.27 Dodecahedron Colorless 64 67 En Harzburgitic 63-1332** 54 91 01 Harzburgitic 63-1332** 54 50 59 10 54 50 59 59 10 54 50 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 1272** 59 59 | DRS06 | Douradinho River | 0.30 | Shapeless | Colorless | 259 | 2 | Chr | Peridotitic | | 1067 |
| Douradinho River0.42ShapelessColorless1001000mp + GrtEclogitic63-1332**Frutal0.27DodecahedronColorless6467EnHarzburgitic63-1332**Frutal0.24MacleBrownish9491OIHarzburgitic7Verde River0.20DodecahedronBrownish3491OIHarzburgitic7Verde River0.36DodecahedronBrownish3104ChrPeridotitic7Verde River0.38DodecahedronColorless495100SulfEclogitic59-1272**7Verde River0.26DodecahedronColorless1999Omp + GrtEclogitic59-1272**7 | Douradinho River 0.42 Shapeless Colorless 100 100 0mp + Grt Eclogitic 63-1332** Frutal 0.27 Dodecahedron Colorless 64 67 En Harzburgitic Frutal 0.27 Dodecahedron Colorless 64 67 En Harzburgitic Frutal 0.04 Macle Brownish 94 91 OI Harzburgitic Verde River 0.20 Dodecahedron Brownish 310 4 Chr Peridotitic Verde River 0.36 Dodecahedron Colorless 495 100 Suff Eclogitic 59-1272** Verde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** Vierde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** Vierde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** Vierde River 0.26 Dodecahedron Colorl | DRP01 | Douradinho River | 0.08 | Shapeless | Colorless | 226 | 100 | Dio + En | Websteritic | 63-1350** | 1306 |
| Frutal0.27DodecahedronColorless6467EnHarzburgiticFrutal0.04MacleBrownish9491OIHarzburgiticVerde River0.20DodecahedronBrownish3104ChrPeridotiticVerde River0.36DodecahedronColorless495100SulfEclogiticVerde River0.48DodecahedronColorless495100SulfEclogiticVerde River0.26DodecahedronColorless1999Omp + GrtEclogitic | Frutal 0.27 Dodecahedron Colorless 64 67 En Harzburgitic Frutal 0.04 Macle Brownish 94 91 OI Harzburgitic Verde River 0.20 Dodecahedron Brownish 310 4 Chr Peridotitic Verde River 0.36 Dodecahedron Colorless 495 100 Sulf Eclogitic 59-1272** Verde River 0.26 Dodecahedron Yellowish 54 92 Omp + Grt Eclogitic 59-1272** Verde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** Vierde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** ine; Dio = diopside; En = enstatite; Grt = garnet; Omp = omphacite; Coe = coesite; Chr = chromite; Sulf = sulfide. 50-1272** 50 | DRP05 | Douradinho River | 0.42 | Shapeless | Colorless | 100 | 100 | Omp + Grt | Eclogitic | 63-1332** | 1331 |
| Frutal 0.04 Macle Brownish 94 91 OI Harzburgitic Verde River 0.20 Dodecahedron Brownish 310 4 Chr Peridotitic Verde River 0.36 Dodecahedron Colorless 495 100 Sulf Eclogitic 59-1272** Verde River 0.26 Dodecahedron Yellowish 54 92 Omp + Grt Eclogitic 59-1272** Verde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic | Frutal 0.04 Macle Brownish 94 91 OI Harzburgitic Verde River 0.20 Dodecahedron Brownish 310 4 Chr Peridotitic Verde River 0.36 Dodecahedron Colorless 495 100 Sulf Eclogitic 59-1272** Verde River 0.48 Dodecahedron Yellowish 54 92 Omp + Grt Eclogitic 59-1272** 7 Verde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** 7 Vincle River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** 7 Vincle River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** 7 Vincle River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** Vincle River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic | FTB05 | Frutal | 0.27 | Dodecahedron | Colorless | 64 | 67 | En | Harzburgitic | | 1210 |
| Verde River 0.20 Dodecahedron Brownish 310 4 Chr Peridotitic 7 Verde River 0.36 Dodecahedron Colorless 495 100 Sulf Eclogitic 59-1272** 7 Verde River 0.48 Dodecahedron Yellowish 54 92 Omp + Grt Eclogitic 59-1272** 7 Verde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic | Verde River 0.20 Dodecahedron Brownish 310 4 Chr Peridotitic Verde River 0.36 Dodecahedron Colorless 495 100 Sulf Eclogitic 59-1272** Verde River 0.48 Dodecahedron Yellowish 54 92 Omp + Grt Eclogitic 59-1272** Verde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** Vinite; Dio = diopside; En = enstatite; Grt = garnet; Omp = omphacite; Coe = coesite; Chr = chromite; Sulf = sulfide. 59-1272** 50-1272** | FTM01 | Frutal | 0.04 | Macle | Brownish | 94 | 91 | Ō | Harzburgitic | | 1243 |
| Verde River 0.36 Dodecahedron Colorless 495 100 Sulf Eclogitic Verde River 0.48 Dodecahedron Yellowish 54 92 Omp + Grt Eclogitic 59-1272** Verde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic | lecahedron Colorless 495 100 Sulf Eclogitic 59-1272** tecahedron Yellowish 54 92 Omp + Grt Eclogitic 59-1272** tecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** Grt = garnet; Omp = omphacite; Coe = coesite; Chr = chromite; Sulf = sulfide. | VRM11 | Verde River | 0.20 | Dodecahedron | Brownish | 310 | 4 | Chr | Peridotitic | | 1077 |
| Verde River 0.48 Dodecahedron Yellowish 54 92 Omp + Grt Eclogitic 59-1272** Verde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** 59 | lecahedron Yellowish 54 92 Omp + Grt Eclogitic 59-1272** r lecahedron Colorless 19 99 Omp + Grt Eclogitic 59-1272** Grt = garnet; Omp = omphacite; Coe = coesite; Chr = chromite; Sulf = sulfide. | VRM15 | Verde River | 0.36 | | Colorless | 495 | 100 | Sulf | Eclogitic | | 1282 |
| Verde River 0.26 Dodecahedron Colorless 19 99 Omp + Grt Eclogitic | lecahedron Colorless 19 99 Omp + Grt Eclogitic 1 Grt = garnet; Omp = omphacite; Coe = coesite; Chr = chromite; Sulf = sulfide. | VRM17 | Verde River | 0.48 | | Yellowish | 54 | 92 | Omp + Grt | Eclogitic | 59-1272** | 1264 |
| | | VRT04 | Verde River | 0.26 | | Colorless | 19 | 66 | Omp + Grt | Eclogitic | | 1361 |

| t = garnet; calculated | enstatite; Grt = garnet;) iteratively calculated | Dio = diopside; En = enstatite; Grt = garnet; P) and temperature (T) iteratively calculated | Brt = garnet; Omp = omphacite; Coe = coesite; Chr = chromite; Sulf = sulfide. | using Nimis and Taylor (2000) thermometer and Sudholz et al. (2021) barometer. |
|---------------------------|--|--|---|--|
| | enstatite; Gr) iteratively | <pre>)io = diopside; En = enstatite; () and temperature (T) iterativel</pre> | t = garnet | calculated |

** P and T estimated by projecting the calculated temperatures of Krogh (1988) onto the 39 mW/m² geotherm of Hasterok and Chapman (2011). *** Nitrogen-based temperature calculated for a mantle residence time of ~2.0 byr (after Taylor et al. 1990, 1996)

Table 1

Supplementary Figure 1



Supplementary Table 1

https://www.editorialmanager.com/lithos/download.aspx?id=1068965&guid=d59e8470-0669-4c73b159-4e0626c89aa0&scheme=1

Supplementary Table 2

https://www.editorialmanager.com/lithos/download.aspx?id=1068966&guid=20ffd830-43d0-418fa2dd-8f1195aaa41c&scheme=1