

## Proto-kimberlitic ultra-deep diamonds from Collier 4 kimberlite pipe, Juina, Brazil.

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Collier 4 kimberlite pipe, located within the Cretaceous (91.6-94.6 Ma) Juina Kimberlite Field, is one of the possible primary kimberlite sources for the ultra-deep inclusion-bearing alluvial diamonds previously studied from the Rivers Sao Luiz and Sorriso (e.g. Harte et al., 1999, Kaminsky et al., 2001, Hayman et al., 2005).

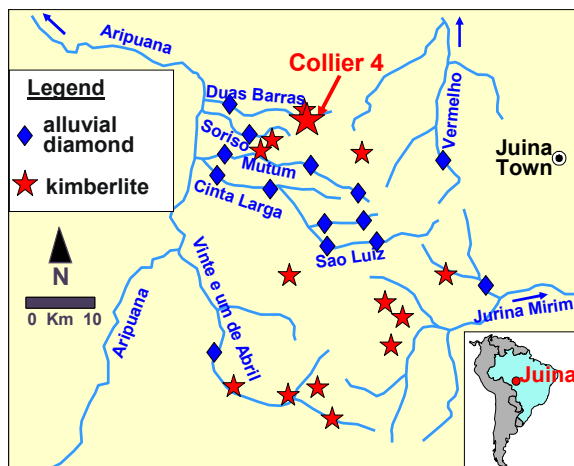


Fig. 1. Map of Juina Diamond field.

The Field is situated near the northern border of the Palaeozoic Parecis Basin and is underlain by the Mesoproterozoic sialic Rio Negro–Juruena Mobile Belt developed during tectonothermal reworking along the southern margin of the Amazon Craton.

The Juina Field is one of the many expressions of Cretaceous alkaline volcanicity developed along the AZ125° lineament ascribed to the passage of the Brazilian continent over the Trindade Plume. The disputed geological evolution of the Rio Negro – Juruena Mobile Belt (lateral versus vertical accretion?) results in controversy over Juina's kimberlite geotectonic setting ("on-craton" or "off craton"). Eclogites and garnet lherzolites are the most abundant mantle xenoliths in the kimberlites and have been dated at ca. 1.6 Ga (Costa et al., 2003), suggesting a link to Mesoproterozoic subduction of oceanic crust during formation of the Mobile Belt.

### Methods and samples

30 diamonds with mineral inclusions were selected for study under optical microscope from a Rio Tinto collection. The diamonds are 2 - 3.5 mm in size colourless or brown transition forms and more rare octahedrons and dodecahedrons; some macles and aggregates present. Most of the crystals are broken, heavily resorbed, plastically deformed and have internal cracks and deep etch channels (Fig. 2).

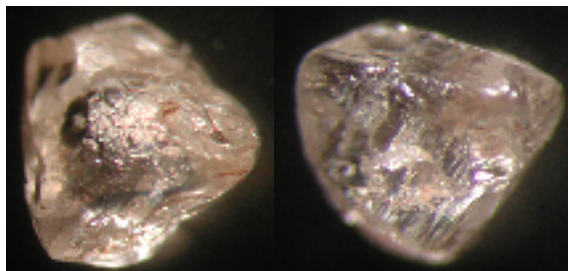


Fig. 2. Diamonds J1 and J2 (width 3.5 and 2.5mm)

The diamonds were polished for producing parallel central plates and exposing inclusions and studied by PL, CL, FTIR, SEM, EMP and SIMS methods.

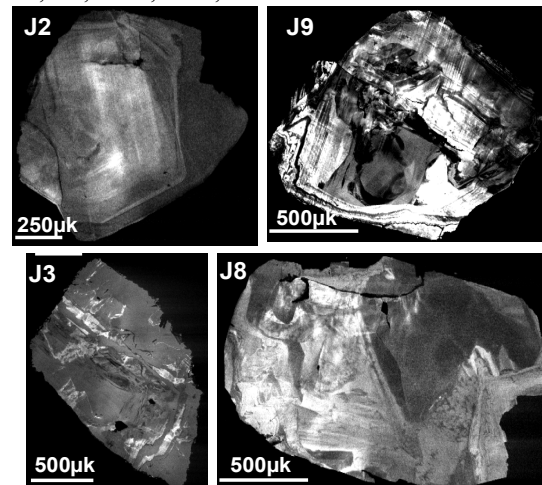


Fig. 3. CL images of some Collier4 diamonds.

CL imagery of the diamonds (Fig 3) displays their complex internal structure: deformations and stresses, breakages and resorption.

All but two diamonds studied are N-free type II. J7 stone has 66 ppm N which is completely aggregated type 1aB and J3 diamond contains moderate N concentration and is type 1aA- 1aB (Table 1).

### Chemistry of inclusions

The syngenetic diamond inclusions have eclogitic-style chemistry (Table 1).

Table 1 Collier 4 diamond inclusion paragenesis

Ds No	FTIR	Syngenetic inclusions	Paragenesis.
J-1	type II	CaTi-prv+CaSi-prv; Po; Majorite	UD
J-2	type II	"Ca-epidote"+Ky; Fe; MgFeAl-spinel; Gt	UD
J-3	1aA-1aB	Six Cpx; CaMgFeAl-phase	E
J-4	type II	Gt; Carbonate micro-inclusion	E
J-5	type II	Po+Mgt; SiO <sub>2</sub>	E (UD?)
J-6	type II	Fe-Cu-sulphide	E (UD?)
J-7	1aB+PI	Fe-Cu-sulphide	E (UD?)
J-8	type II	Cpx+"Mg-epidote"-phase; SiO <sub>2</sub> Po+FeO	UD
J-9	type II	Majorite	UD
J-10	type II	CaTi+CaSi-prv; Po.	UD
J-11	no data	Not identified black microinclusions	unknown
J-12	no data	Not identified black microinclusions	unknown
J-13	type II	K-Al-Mg-Fe-Ti-Si- micro-inclusion	unknown
J-14	no data	Two CaSi-prv inclusions	UD
J-15	no data	Po	E
J-16	no data	Po	E
J-17	no data	SiO <sub>2</sub>	E (UD?)
J-18	type II	Fe+FeO	unknown
J-19	no data	SiO <sub>2</sub> + Ky	E (UD?)
J-20	type II	"Ol"; Ca-Mg-Fe-Al-carbonate micro-incl.	UD

Among them the ultradeep paragenesis comprises: CaSi-perovskite ± CaTi-perovskite, Ca-majorite, SiO<sub>2</sub> and "olivine" (former wadsleyite). This silicate phases association is stable in the Transition Zone (TZ) according to experimental results.

The majoritic component in the Collier 4 garnets is low and gives equilibration pressure of 7-10 GPa (Fig. 4).

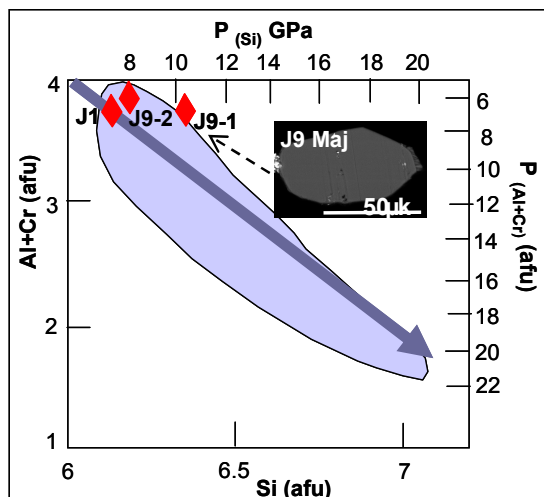
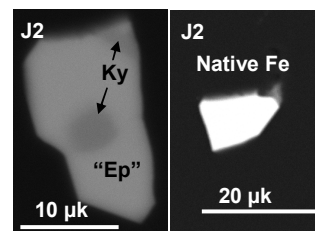


Fig. 4. (Al + Cr) vs Si per atomic formula unit (afu) in majorite inclusions from diamonds J1 and J9.

The composite inclusions of CaTiO<sub>3</sub>+CaSiO<sub>3</sub> in two diamonds are interpreted as retrograde exsolution phases from a complete perovskite solid solution which, according to experimental data, exists at

pressure >12 GPa in the TZ or Low Mantle (LM) (Kubo et al., 1997).

Fig. 5. SEM images of two-phases inclusion "Ca-epidote" + kyanite and native iron inclusion from diamond J 2.



The mineral assemblage: eclogitic garnet, "Ca-epidote-phase"+ kyanite, MgFeAl-spinel and native iron found in one diamond (Fig. 5) is probably also ultradeep but re-equilibrated into lower PT phases during transportation to the surface. The "epidote-phase" is similar in composition to natural epidote and to the experimental aluminium rich phase of high PT conditions of the TZ and LM, such as NAL (Miyajima et al., 2001). NAL formula is: [(K, Na, Ca)<sub>1</sub>(Mg, Fe)<sub>2</sub>]<sub>3</sub>(Al, Si)<sub>5.5-6.00</sub>O<sub>12</sub>. The "Ca-epidote" diamond inclusion has a MORB-type geochemical signature indicating an input of subducted material into the deep mantle.

"Olivine" identified in one diamond is Fo 90 and contains 0.19 NiO, 0.05 Al<sub>2</sub>O<sub>3</sub>, 0.03 Cr<sub>2</sub>O<sub>3</sub>, 0.14 CaO and 0.03 Na<sub>2</sub>O wt %, indicative of origin in the TZ or Low mantle (Brey et al, 2004). Compared with Upper mantle olivines there is also a high MnO concentration in this inclusion (0.17 wt %).

Upper Mantle eclogitic inclusions comprise Ti-Ca-almandine-pyropes G4, omphacite, kyanite, SiO<sub>2</sub> and low-Ni sulphides. Low Ni-sulphides are common; some micro-inclusions of Ca-Fe-Mg carbonates and iron of undistinguished paragenesis were also found.

The trace element chemistry of J9 majorites is similar to those summarised by Stachel (2001). Majorite J1 is exceptional because the highest concentration of REE ever reported (Fig. 6). Diamond J1 contains a two-perovskite inclusion where both CaSi- and CaTi-phases also have the highest content of REE compared with

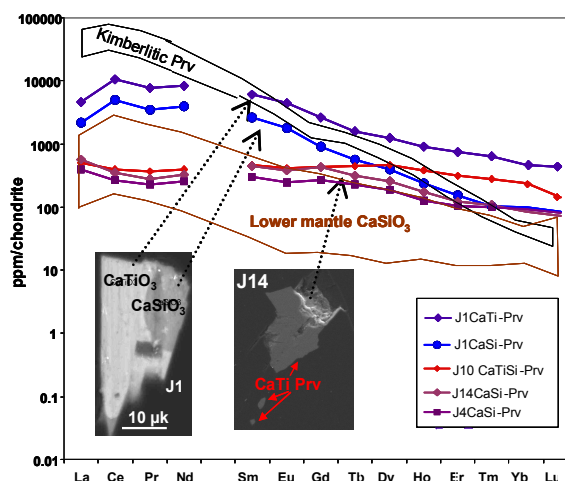


Fig 6. Chondrite normalised REE in the Collier 4 perovskite diamond inclusions.

known previously (Walter et al., in press). Such enrichment of eclogitic environments by incompatible elements during diamond formation could be explained by metasomatic input of carbonatitic melt.

### Carbon isotope composition of diamonds

The diamonds display a very wide range of carbon isotopes: from heavy mantle to lightest organic values (Fig. 7). J20 with “olivine” inclusion and two eclogitic stones with sulphides are in the heavy mantle group of  $\delta^{13}\text{C}$  -6 to -7.5 ‰. Similar values are found in three rim zones of diamonds with CaSi-perovskites and majorite inclusions, which cores started from much lighter  $\delta^{13}\text{C}$  of -9 to -13.5 ‰. Diamonds with CaTi-perovskites and some eclogitic stones show similar or no change in core-rim signatures and lie in the interval of subducted carbon of -12 to -15 ‰  $\delta^{13}\text{C}$  (Fig. 7).

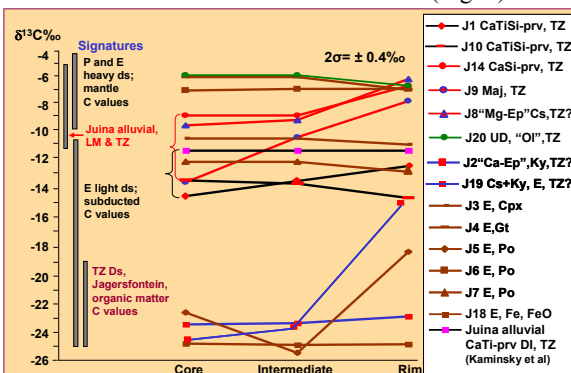


Fig. 7. Carbon isotope composition of Collier 4 diamonds in core – rim traverses.

The isotopically lightest diamonds contain kyanite, coesite and “Ca-epidote”. Similar to the diamonds with CaSi-perovskite inclusions they show  $\delta^{13}\text{C}$  increasing during growth, which probably indicates their precipitation from a  $\text{CO}_2$ -rich fluid. For crystals J2 and J18 such isotopic zonation is very abrupt, from core values of -23 to -25 ‰ to rim of -15 to -17 ‰  $\delta^{13}\text{C}$ .

The diamond core-signatures of extremely low  $\delta^{13}\text{C}$  are attributed to subducted organic matter and manifest nucleation of the diamonds in TZ horizons, where organic matter was not well mixed with isotopically heavy subducted carbonates. The rim zones were grown on other TZ levels where the two sources of subducted carbon were already mixed, resulting in the medium-light  $\delta^{13}\text{C}$  values. Such strong isotopic fractionation of a single carbon source during growth of one diamond is not a realistic process. The reason for this abrupt isotopic zonation in single crystals can be explained by diamond formation from different sources of carbon at different stratigraphic layers of the TZ to which the diamonds were uplifted or subducted.

### Formation of the diamonds and mineral inclusions

The phase relationships of the mineral inclusions and trace element chemistry show that they crystallised during different stages of differentiation of a diamond-forming Ca-rich melt/fluids. Thus some  $\text{Ca}(\text{Ti},\text{Si})\text{O}_3$ -

perovskite and Ca-majorites coexisted with a primary partial melt of a carbonated eclogite that formed in the TZ. Other inclusions may have crystallized within the deep Upper Mantle from rising differentiated carbonatite melt. Efforts to date a  $\text{Ca}(\text{Ti},\text{Si})\text{O}_3$ -perovskite inclusion by U-Pb by ion probe are suggesting a Cretaceous age, which is close to the kimberlite emplacement time. If the dating is correct the Collier 4 ultradeep diamonds are relatively young. Carbon isotope composition variation in core-rim traverses in single diamonds and phases of exsolution in the inclusions give evidence about the extensive scale of vertical movements of the diamond-forming system within the Earth. It is deep carbon recycling caused by processes of subduction and uplifting.

We consider the Collier 4 diamond protolith was partially-melted carbonated eclogite with diamonds formed from  $\text{CO}_2$ -dominated fluids. Sulphide presence may have lowered the oxygen fugacity of the carbonate-silicate melt/fluid from which diamonds crystallised. The presence of native iron gives evidence of extremely reduced conditions suitable for diamond formation. The Collier-4 kimberlite magmatism and the ultradeep diamonds could both be considered genetic, temporal and geographic results of the Trindade Plume event.

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