EXPRESS LETTER

Micron-scale δ^{13}C determination by NanoSIMS in a Juina diamond with a carbonate inclusion

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Juina diamonds present a wide spectrum of mineral inclusions, covering both peridotitic and eclogitic composition. Among the most rare inclusions, carbonates are interpreted as an evidence of deep recycling of sedimentary carbon into the transition zone or the lower mantle. Yet, the δ^{13}C values measured in three FIB-TEM foils by NanoSIMS 50 of an alluvial diamond with a carbonate inclusion range between $-8.85 \pm 1.32‰$ and $-2.31 \pm 1.88‰$ with a mean total value of $-5.0 \pm 2.3‰$. These values are in the range of typical mantle carbon, as measured in diamonds of peridotitic paragenesis. Similar δ^{13}C values from -8.5 to $-4.4‰$ are reported in literature for five other Juina diamonds with carbonate inclusions. We can postulate either that the diamond is peridotitic and carbonate precipitated from fluids and survived to the reduction to diamond or that formed from reduction of carbonatitic melts in the upper mantle, percolating through eclogite.

Keywords: sub-lithospheric diamonds, Juina, carbonate, lower mantle, peridotite, eclogite

INTRODUCTION

Diamonds form in the lithospheric mantle at depths between 150 and 200 km (Shirey *et al.*, 2013; Cartigny *et al.*, 2014). A small amount of diamonds is recognized to form in the transition zone and even in the lower mantle (e.g., Harte *et al.*, 1999; Stachel *et al.*, 2005). These "sub-lithospheric" (also called superdeep) diamonds are particularly abundant in the Juina area, Mato Grosso, Brazil (Fig. 1) and thereby have been the subject of numerous studies. In particular, the presence of syngenetic mineral inclusions such as calcium silicate perovskite (CaSiPvk) and ferropericlase (or magnesiowüstite, (Mg,Fe)O) point out to diamond formation at depths between 500 km up to 800 km (Stachel *et al.*, 2005). The δ^{13}C of Juina diamonds measured in earlier works have provided different results, leading to contradictory interpretations on the origin of these diamonds. The studies after Hutchinson *et*

al. (1999), Kaminsky *et al.* (2001), Palot *et al.* (2012) and Zedgenizov *et al.* (2014) showed that alluvial diamonds having lower mantle inclusions with metaperidotitic affinity have slightly variable δ^{13}C-values around $-5‰$, typical of mantle carbon (Javoy *et al.*, 1986) (Fig. 2). These C isotopic values are consistent with the ^{15}N-depleted character of the studied diamonds (Palot *et al.*, 2012). On the other hand, diamonds from the nearby kimberlite pipes (Juina-5; Collier-4), display a more dispersed range of δ^{13}C values from $-4.8‰$ to $-28.3‰$ (Bulanova *et al.*, 2010; Walter *et al.*, 2011; Thomson *et al.*, 2014), more characteristic of an eclogitic paragenesis (Cartigny, 2005). It was suggested that these diamonds originate from organic sedimentary carbon subducted at great depths (Bulanova *et al.*, 2010; Walter *et al.*, 2011; Thomson *et al.*, 2014).

At depths exceeding 250 km, oxygen fugacity is seen as too low for diamond or carbonate to be stable (e.g., Stagno *et al.*, 2013). Carbon would instead occur either as carbide or dissolved in the free metal phase (1 wt%; Frost *et al.*, 2004). To account for the occurrence of diamond from both the transition-zone and the lower mantle, diamond formation would occur through redox reactions between an oxidized fluid (e.g., a melt derived from

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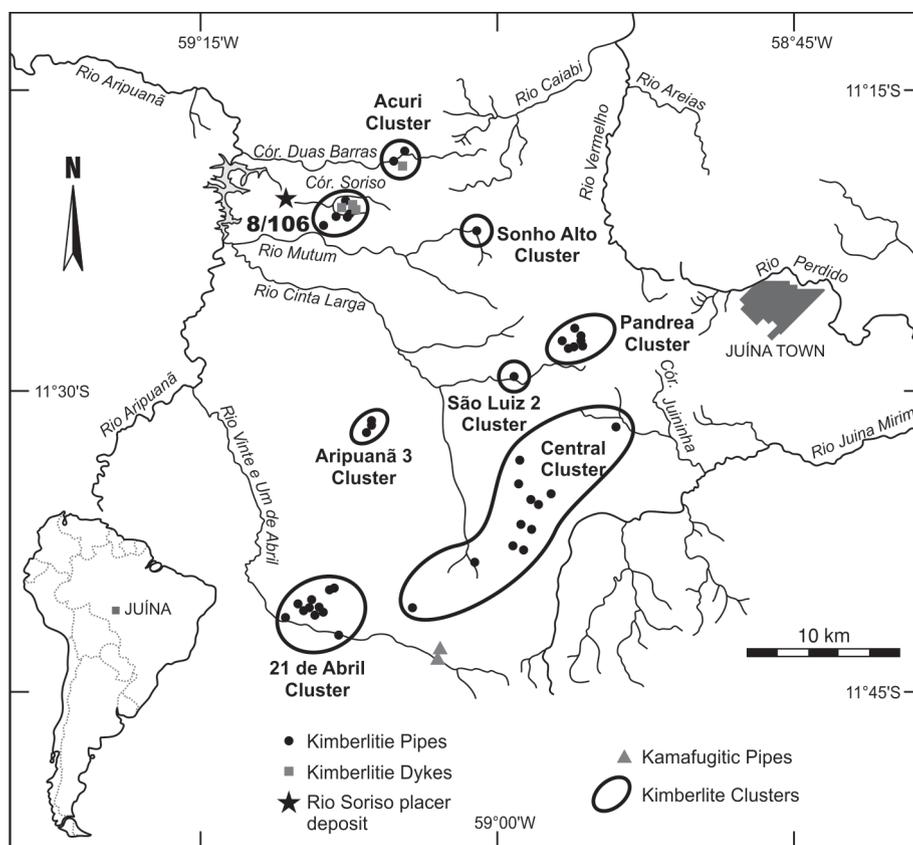**Present address: Dept. of Geoscience, University of Wisconsin-Madison, Madison, WI 53706, U.S.A.

Fig. 1. Juina locality, Mato Grosso, Brazil. The star indicates the position of the alluvial placer deposit of the Rio Soriso from where the studied sample 8/106 was collected. Redrawn and modified from Kaminsky et al. (2001).

the subduction slab) and the reduced mantle. In this model, diamond with carbonate inclusions are of particular interest and would record the carbonatitic nature of the growth medium leading, via its reduction, to diamond formation. Diamonds with carbonate inclusion were taken as additional evidence of sedimentary subducted carbon (Brenker *et al*., 2007). Here we report the carbon isotopic composition of a Juina diamond with a carbonate inclusion to better address the origin of this diamond and the associated carbonate. Because of the small size of the samples, $\delta^{13}C$ values were determined by using a NanoSIMS 50. This work is also the occasion to show the full capabilities of NanoSIMS to measure carbon isotopes in diamonds at nano- to micron-scale for which very few data exist in literature (Dobrzhinetskaya *et al*., 2007; Wang *et al*., 2015).

SAMPLES AND EXPERIMENTS

Sample 8/106 is an alluvial diamond collected at the Rio Soriso placer deposit (Hayman *et al*., 2005; Fig. 1). The sample was cut in Focused Ion Beam (FIB) individual foils for mineral inclusion studies (Wirth *et al*., 2009).

These studies showed the presence of micro- and nano-inclusions of ilmenite, phlogopite and spinel together with a single crystal of dolomite (500×70 nm) associated to ilmenite and graphite, the latter being possibly of secondary origin (Wirth *et al*., 2009). In this sample, inclusions typical of lower mantle conditions, such as perovskite or magnesiowüstite were not observed. Wirth *et al*. (2009) concluded that all the identified mineral inclusions are of the eclogitic association; yet the argument to conclude for an eclogitic paragenesis for this diamond was not based on the mineralogical association but was, instead, inferred from the measured low $\delta^{13}C$-values (i.e., 92% of diamonds with a $\delta^{13}C < -10$‰ are eclogitic, see data in Cartigny *et al*. (2014)).

The chemical composition of dolomite as determined by analytical electron microscopy (AEM) (at.%) is: Mg = 46.85–47.6, Ca = 48.75–49.1, Fe = 3.0–3.95, Mn = 0–0.24, and Sr = tr.–0.3 (Wirth *et al*., 2009).

Three FIB foils (15×10 μm and 200 nm of thickness) mounted on TEM grids were used for this study: foil 1160, 1163 and 1286. The grids, gently pressed on the surface of three holders filled with indium, were charged into a NanoSIMS 50 at AORI, the University of Tokyo. Inter-
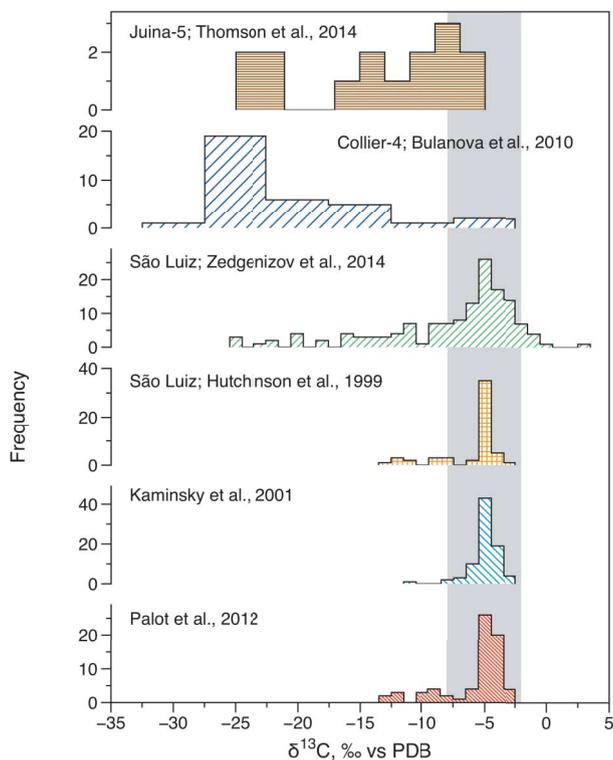
Fig. 2. Comparative histograms of $\delta^{13}C$ values measured in Juina diamonds from different studies. Diamonds from Kaminsky et al. (2001) and Palot et al. (2012) come from several localities within the Juina field. Carbon isotopic values by SIMS from Zedgenizov et al. (2014) are minimum and maximum values measured for each sample. Shaded area represents the range of $\delta^{13}C$ values for mantle carbon as defined by Javoy et al. (1986).

nal standard carbonado GM02 ($\delta^{13}C$ = –29.2‰; N = 85 ppm; Yokochi *et al.*, 2008) was used. To check the consistency of using a carbonado (i.e., a polycrystalline type of diamond) as a standard we analyzed one natural Ia (NIa) and one synthetic IIa (SIIa) diamond used in diamond anvil cell experiments. $\delta^{13}C$ values, measured by conventional mass spectrometry at *Institut de Physique du Globe de Paris* are –3.6 ± 0.1‰ and –20.9 ± 0.1‰, respectively. $^{13}C/^{12}C$ ratios and N amounts were measured by single detector collection mode and by multi-collection on 14 raster areas of 1×1 μm. Results were corrected for several instrumental effects. Details of analytical conditions, data corrections and results for sample and standards analyses are reported in Supplementary Materials.

RESULTS

Supplementary Materials Table S1 reports the results of the $\delta^{13}C$ values obtained by single collector mode on the three FIB-TEM foils. Foil 1160 shows a $\delta^{13}C$ value
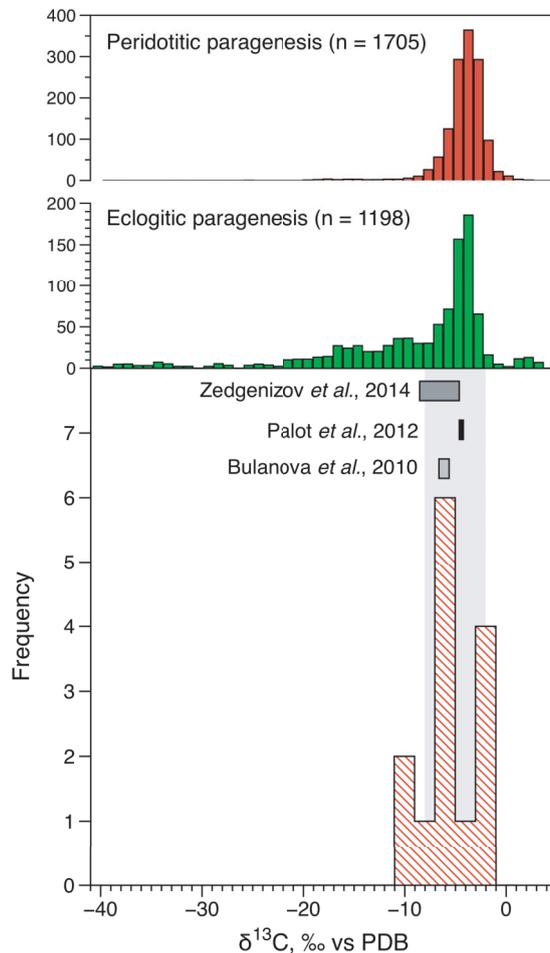

Fig. 3. Histogram of $\delta^{13}C$ values measured in Juina diamond 8/106 by EM4 single collector mode. Small boxes are the $\delta^{13}C$ values reported in literature for Juina diamonds with carbonate/dolomitic inclusions (Bulanova et al., 2010; Palot et al., 2012; Zedgenizov et al., 2014). Shaded area represents the range of $\delta^{13}C$ values for mantle carbon as defined by Javoy et al. (1986). Data are compared to $\delta^{13}C$ values of diamonds from eclogitic and peridotitic paragenesis (data from Cartigny et al. (2014)).

of –6.34 ± 2.02‰ (M ± 1 SD); foil 1163 shows $\delta^{13}C$ value of –5.64 ± 2.29‰; foil 1286 shows $\delta^{13}C$ value of –5.14 ± 0.84‰. The total average $\delta^{13}C$ value for sample 8/106 is –5.0 ± 2.3‰ (Fig. 3). We analyzed the amount of nitrogen in the diamond to be 62 ± 26 ppm but it could be the related to background contamination because SIIa standard sample shows similar N amounts of 59 ± 23 ppm while it should not contain detectable amounts of N, by definition. The NIa standard sample contains N amounts of 305 ± 85 ppm, as expected for Ia type diamond. It is worth noting that the FIB foil is too thin to provide accurate N-content data by transmission infrared spectroscopy, as commonly done in most diamond studies.

The present carbon isotopic results are quite different from those obtained on another FIB-TEM foil of the same sample by NanoSIMS 50 (Wirth *et al.*, 2007). The δ^{13}C were heterogeneous and ranging between -13.9 ± 1.9‰ and -25.8 ± 1.7‰. An inverse relation between the δ^{13}C and the atomic C/N ratio was observed, suggesting the mixing between two components: one heavier (δ^{13}C = -10‰) and one lighter (δ^{13}C = -28‰). Measurement of the organic foil supporting the FIB-TEM foil gave δ^{13}C of -20.7 ± 2.2 and -28.1 ± 1.7‰ suggesting that the lighter component could be local contamination.

DISCUSSION

The δ^{13}C measured in this Juina diamond are typical of both peridotitic and eclogitic paragenesis (most δ^{13}C from -8 to -2‰, centered on a value of -5 ± 1‰; Cartigny *et al.*, 2014) and in the range of "mantle" carbon as measured in MORBs, OIBs, carbonatites and kimberlites (δ^{13}C of -8 to -5‰; Javoy *et al.*, 1986; Fig. 3). This is in contrast with the much lighter δ^{13}C values measured in the diamonds from the Juina-5 kimberlite having inclusions of eclogitic composition equilibrated in the lower mantle (Walter *et al.*, 2011). The δ^{13}C values of these Juina-5 diamonds range from about -1 to -24‰, with four of the six diamonds having values less than -15‰, suggesting a sedimentary/recycled origin for the carbon (Walter *et al.*, 2011). Although, the lithospheric vs. sub-lithospheric nature of most diamonds from Collier-4 and Juin-5 kimberlites could not be accurately determined, a large number display low δ^{13}C values, considered to reflect the occurrence of subducted organic carbon in their mantle source.

Carbonates in sub-lithospheric diamonds have been also interpreted as an evidence of sedimentary/organic carbon (e.g., Wirth *et al.*, 2009; Harte, 2010; Brenker *et al.*, 2007). If this was the case, one predicts very variable δ^{13}C values. Yet, the result of this study suggests that the carbon involved in the diamond formation is mantle carbon and not sedimentary/organic carbon. Our results are in agreement with previous studies. On 397 Juina samples for which the δ^{13}C values are known (Hutchinson *et al.*, 1999; Kaminsky *et al.*, 2001; Bulanova *et al.*, 2010; Palot *et al.*, 2012; Thomson *et al.*, 2014; Zedgenizov *et al.*, 2014), only five additional samples contain carbonate: two diamonds analyzed by Bulanova *et al.* (2010) with δ^{13}C values from -6.6 to -5.6‰; one diamond from Palot *et al.* (2012) with δ^{13}C value of -4.4 ± 0.1‰; and two diamonds from Zedgenizov *et al.* (2014) with δ^{13}C values from -5.1 to -4.6‰ (with a $CaCO_3$ inclusion) and -8.5 to -6.4‰ (with a $MgCO_3$ inclusion), respectively. The measured δ^{13}C values are in the range to those measured here in sample 8/106 (Fig. 3).

There are several hypotheses that could explain these little variable δ^{13}C-compositions.

The first hypothesis is that diamond 8/106 was formed from reduction of carbonatitic melts (Pal'yanov *et al.*, 1999), the latter produced by partial melting of CO_2-bearing peridotite in the upper mantle (Jones *et al.*, 2013). This process can explain the typical "mantle" carbon isotopic composition of diamond 8/106. In this case, the carbonate inclusion would be inherited from the melt and survived its reduction into diamonds.

Wirth *et al.* (2009) calculated diamond formation pressure from 3 to 10 GPa, which indicate that they formed in the upper mantle. They further noticed nanometer-scale cavities and bubbles in the dolomite and between spinel and phlogopite nano-inclusions in sample 8/106. These findings suggest the presence of a volatile-rich fluid/melt which was likely released during the FIB cut procedure. Nanometer-sized inclusions of carbonates are widespread in so-called fibrous/coated diamonds (e.g., Navon *et al.*, 1988; Schrauder and Navon, 1994; Izraeli *et al.*, 2001; Zedgenizov *et al.*, 2004; Tomlinson *et al.*, 2006) and occur among the three end-members (i.e., carbonatitic, saline and hydrous-silicic) identified so far. An upper-mantle origin for carbonatitic/hydrous-silicic and possibly saline melts/fluids leading to the precipitation of fibrous/coated diamonds has been frequently proposed (e.g., Navon *et al.*, 1988; Boyd *et al.*, 1994; Weiss *et al.*, 2015) and is consistent with experimental studies (e.g., Bureau *et al.*, 2012). In such model, the trapped inclusions are co-genetic with their host-diamonds and they represent their parent fluid.

The second hypothesis is that diamonds with carbonate inclusions are eclogitic. About 52% and 67% of eclogitic and peridotitc diamonds worldwide have δ^{13}C values of -5 ± 3‰ (Cartigny *et al.*, 2014), i.e., in the same range of those measured in the diamonds with carbonate inclusions (Fig. 3). The Juina diamond here studied could derive from reduction of carbonatitic melts percolating through eclogite (Galimov, 1991; Cartigny *et al.*, 1998) or be derived from eclogite-lithologies (e.g., Bulanova *et al.*, 2010). However, this last hypothesis is in contrast with findings of Walter *et al.* (2011) suggesting that "eclogitic suites" of diamonds originating from the lower mantle at Juina have overall very negative δ^{13}C down to -24‰, whereas "eclogitic suites" of diamonds originating from the upper mantle also have, overall, very negative δ^{13}C (Bulanova *et al.*, 2010; Thomson *et al.*, 2014). Therefore, the very homogeneous δ^{13}C values represent some sort of coincidence, and low δ^{13}C values can be predicted.

Harte (2015) has recently proposed an alternative hypothesis to explain the origin of these diamonds with carbonate inclusions. The mantle carbon would derive from the ultrabasic rocks of "peridotitic" composition composing the subducting oceanic mantle lithosphere. These

rocks are too far below the ocean floor to acquire organic carbon, thus they retain their primitive mantle carbon signatures. Accompanying carbonates might derive from ophicarbonate protoliths (Kerrick and Connolly, 1998). Such a view however is inconsistent with new data on the altered oceanic crust showing that abiotic reduction of carbon led to significant amount of reduced carbon with an overall negative $\delta^{13}C$ value (Shilobreeva *et al.*, 2011). Again, some C-isotope heterogeneity should be observed.

CONCLUSIONS

Formation of diamonds is a complex metasomatic process that occurs in the asthenosphere over a large range of depths and extends through time which is recorded through the chemistry of their micro- and nano inclusions (e.g., Stachel *et al.*, 2005). Unravelling the complexity of formation of the diamonds and related inclusions require reliable isotopic data at micron- or even nano-scale. The scope of the present study was twofold: to demonstrate the capability of NanoSIMS 50 to produced reliable carbon isotopic data at nanoscale and obtain precious information on the formation of rare carbonate inclusions in a Juina diamond. The analytical results of this work have shown that the precision (± 1–2‰; Table S1) on $\delta^{13}C$ on a 1×1 μm scale is 10 times higher than that from SIMS measurements (± 0.1‰) but the latter is obtained usually on much larger spots of 10–50 μm. Yet results are reliable as shown by comparing $\delta^{13}C$ measured by NanoSIMS 50 and by classical mass spectrometric techniques (Supplementary Materials Fig. S5). The $\delta^{13}C$ measured in the Juina diamond with a carbonate inclusion is consistent with previous analyses by SIMS (Bulanova *et al.*, 2010; Zedgenizov *et al.*, 2014) and mass spectrometry (Palot *et al.*, 2012) on similar diamonds containing carbonates from the Juina field. The lack of nitrogen isotopic data and of the carbon isotopic signature of the carbonate does not allow settling definitively the process of formation of this diamond and the included carbonate, but their little C-isotope variability is in favor of a formation from carbon from the convective mantle.

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SUPPLEMENTARY MATERIALS