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Mantle-related carbonados? Geochemical insights from diamonds from the Dachine komatiite (French Guiana)

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ABSTRACT

Carbonado is a unique type of polycrystalline diamond characterised, among others, by ^{13}C-depleted isotope compositions (δ^{13}C ~ -25‰ vs. PDB), little advanced nitrogen aggregation (Ib-IaA) and sintered (ceramic-like) diamond grains. Its origin remains an enigma, with models proposing a formation either in the Earth's crust or even within an exploding super-nova. The possibility that carbonado formed in the Earth's mantle is often rejected because diamond with carbonado-like geochemical features has never been found in rocks, such as kimberlites, that carry diamonds from the mantle.

In this study, it is shown that the C- and N- stable isotope compositions, nitrogen contents and nitrogen speciation of diamonds from the Dachine komatiite (French Guyana) exhibit unambiguous similarities with carbonados. These include C-isotopes (from -32.6 to +0.15‰, mode at ~-27‰), N-aggregation (only Ib-IaA diamonds, from 2 to 76% of N-pairs) and N-isotopes (from -4.1 to +6.9‰, average ~ +2.1 ± 2.9‰), which all strikingly match the carbonado data. This evidence illustrates that the main geochemical arguments usually called to reject a mantle origin of carbonado are no longer valid. A model linking carbonado crystallisation from komatiite volatiles is developed. In this model, the sintering is produced by the high temperature of the komatiite magma thus accounting for their absence in colder kimberlites. The low δ^{13}C compositions of carbonados would be inherited from the transition zone (> 300 km depths), which is known to yield diamonds with distinct C-isotope distributions compared to most lithospheric diamonds (150–300 km depths). This model can account for most available observations of carbonados, including their large size, sintering, photoluminescense/cathodoluminescence features and geochemical characteristics.

1. Introduction

All carbonado diamonds are polycrystalline, but the reciprocal is not true, i.e. a polycrystalline diamond is not necessarily a carbonado. Most classifications for polycrystalline diamonds are established according to the size(s) of diamond crystallites; accordingly, the term carbonado *sensu lato* would apply to the most fine-grained polycrytsalline diamonds (e.g. Jeynes, 1978). In this scheme, the diamond origin and/or formation is neglected and the different geological types of polycrystalline diamonds, including impact-related diamonds, mantle-derived polycrystalline diamonds (i.e. from kimberlites and lamproites and their alluvials), metamorphic diamonds (formed in-situ in rocks subducted at ultra-high pressures), extraterrestrial diamonds (i.e. found in meteorites) and carbonado *sensu stricto* (i.e. using criteria defined below) would be lumped together. The lack of an appropriate geological classification for polycrystalline diamonds has led to confusion even in the most recent literature. Some impact-related diamonds from Yakutia (also often referred to as *Yakutite*), as well as diamonds from meteorites or from the mantle were termed *carbonado* (e.g. Moriyoshi et al., 1983; Galimov et al., 1985; McCall, 2009), even though their origin, formation and occurrence are likely distinct (see below). Some other classifications exist. These are based, for example, on either their internal structure, magnetic properties, or resistance to polish. All these classification systems will mix the different sorts of polycrysalline diamonds together (see Jeynes, 1978).

The more common definition used among geoscientists is based on the fused or sintered properties of the diamond grains in carbonado (i.e. a diamond ceramic) (Trueb and DeWys, 1971; Haggerty, 1999; Kletetschka et al., 2000; Yokochi et al., 2008). Orlov (1977, p. 17) early recognised the unique properties of carbonado emphasising “their independent source of carbon and their very specific crystallisation conditions” and accordingly separated carbonados from other types of diamond; he described them as variety X.

Carbonados were early recognised to be unique in many aspects, including strongly depleted C-isotope compositions (Vinogradov et al., 1966), most having δ^{13}C between -30 and -23‰ and a few higher values up to -5.6‰ (where $\delta^{13}C = (^{13}C/^{12}C_{sample}/^{13}C/^{12}C_{PDB} - 1) \times$

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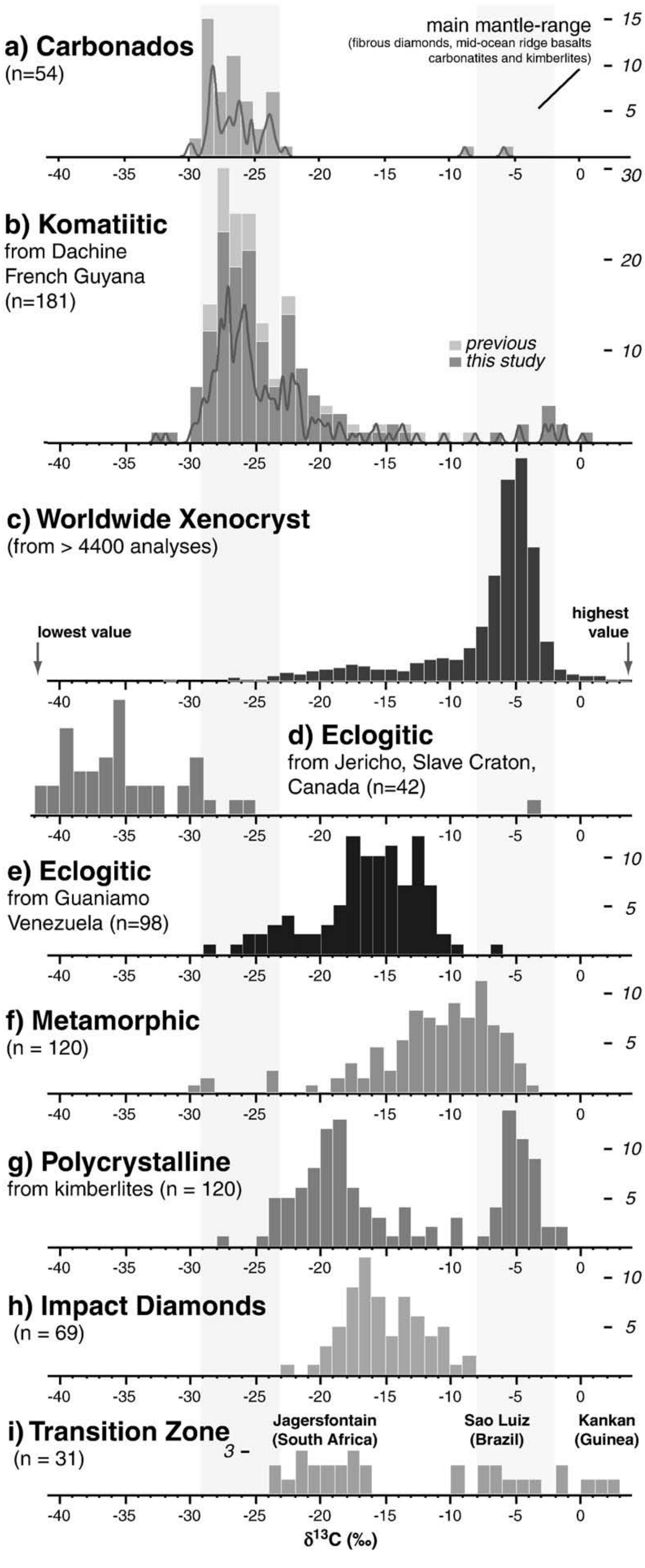
a) Carbonados
(n=54)
main mantle-range
(fibrous diamonds, mid-ocean ridge basalts carbonatites and kimberlites)
15
10
5
30
b) Komatiitic
from Dachine
French Guyana
(n=181)
20
10
previous
this study
c) Worldwide Xenocryst
(from > 4400 analyses)
lowest value
highest value
d) Eclogitic
from Jericho, Slave Craton,
Canada (n=42)
e) Eclogitic
from Guaniamo
Venezuela (n=98)
f) Metamorphic
(n = 120)
g) Polycrystalline
from kimberlites (n = 120)
h) Impact Diamonds
(n = 69)
i) Transition Zone
(n = 31)
3
Jagersfontain
(South Africa)
Sao Luiz
(Brazil)
Kankan
(Guinea)
-40
-35
-30
-25
-20
-15
-10
-5
0
δ13C (‰)

10^3) (Fig. 1a; $\delta^{13}C_{average} = -26.0 \pm 3.9‰$, $n = 61$; Vinogradov et al., 1966; Galimov et al., 1985; Ozima et al., 1991; Kamioka et al., 1996; Shelkov et al., 1997; Burgess et al., 1998; Kagi et al., 2007; Kagi and Fukura, 2008; Yokochi et al., 2008). Carbonado normally only occurs in placer deposits and has never been found in rocks, such as kimberlites, that carry mantle diamonds to the Earth's surface. In addition, carbonados are porous (up to 30%), black-grey, almost graphitic in appearance, non-gemmy, polycrystalline diamonds, up to 3167 carats in size (see Table 1 in Svisero, 1995), made of sintered diamond grains varying usually below 20 µm (i.e. cryptocrystalline diamond) and up to a few hundred micrometers in size (Trueb and DeWys, 1969; Trueb and Butterman, 1969; De et al., 1998; Rondeau et al., 2008). The relationship between the largest diamonds and the diamond cryptocrystalline matrix remains unclear, the latter being described either as *blasts* or *phenocrysts* (e.g. Trueb and Butterman, 1969; Shelkov et al., 1997; Yokochi et al., 2008), which may or may not be related to several protracted diamond growth events. With the exception of a few as yet unconfirmed reports from Venezuela and Guyana (Kerr et al., 1948), carbonado is mainly found in Meso-proterozoic alluvial deposits in Brazil and Central Africa (for reviews, see Haggerty, 1998, 1999; Heaney et al., 2005). On the basis of striking petrographic (Trueb and Butterman, 1969; Trueb and DeWys, 1971; De et al., 1998) and geochemical (Shelkov et al., 1997) similarities, as well as an occurrence within the same stratigraphic horizons (Trueb and DeWys, 1971), it is generally accepted that the carbonados were deposited contemporaneously ~1.7 Ga ago well before opening of the south Atlantic (~0.120 Ga ago). Carbonados were deposited at sites separated by over 2000 km and the main historical mining localities are/were located in the state of Bahia in Brazil (Svisero, 1995 for review) and in both the west and east Ubangi region of the Central African Republic.

The randomly oriented sintered crystals of carbonados make them harder than diamond. Owing to their unique mechanical properties (toughness and strength), they are of industrial use (mainly grinding and drilling). Growing synthetic carbonado is thus a goal to achieve in mineral science (e.g. Hall, 1970; Wentorf et al., 1980; Irifune et al., 2003; Kaner et al., 2005). In this respect, key data for mineral synthesis engineering could be obtained from the study of natural carbonados. Yet understanding carbonado genesis is actually one of the most enigmatic problems in diamond geology. Current hypotheses for carbonado origin are diverse but generally unsatisfactory, with models suggesting formation in the Earth's crust, either at low (Kaminsky, 1991) or high pressures (Smith and Dawson, 1985), in subduction zones (Robinson, 1978), in the Earth's mantle (e.g. Kagi et al., 1994) or even within an exploding super-nova (Haggerty, 1998, 1999; Garai et al., 2006).

Because of their porous nature, it is still unclear whether the minerals included within the pores of carbonados are secondary or not (Trueb and DeWys, 1969; Dismukes et al., 1988; Haggerty, 1998). Most inclusions in carbonados are typically crustal inclusions, such as florencite, orthoclase, magnetite and quartz (Trueb and DeWys, 1969). The high amounts of atmospheric gases (e.g. Ozima et al., 1991) or enrichement in light rare earth elements (Shibata et al., 1993; Kagi et al., 1994; Kamioka et al., 1996), might thus be either considered as primary crustal features (Kaminsky, 1991; Ozima et al., 1991; Shibata et al., 1993; Kamioka et al., 1996), primary mantle features (Kagi et al., 1994) or secondary (epigenetic) crustal features (e.g. Haggerty, 1998). Similarly, high amounts of polycyclic aromatic hydrocarbons (Kaminsky, 1991) might be either considered as primary (Kaminsky, 1991) or secondary (e.g. Haggerty, 1998) crustal features. The evidence for significant parentless fissiogenic xenon (Ozima et al., 1991) clearly illustrates a complex history for carbonado within a changing environment, at least, in terms of U- and Th-concentrations (Ozima et al., 1991). There is, however, an increasing consensus that some reduced inclusions of silicon carbide (De et al., 1998), titanium nitride (Jones et al., 2006), and Fe, Ti, Ni, and Si (Gorshov et al. 1996, 1997; De et al., 1998) would be primary. Rutile and ilmenite have been described as a mantle mineral assemblage (Gorshov et al., 1996). Yet rutile can be stable at temperatures of e.g. 400 °C (e.g. Zack et al., 2004) and its occurrence cannot be considered as a definitive proof for their deep mantle origin.

The possibility that carbonados form in the Earth's upper mantle has been rejected early (e.g. Frantsesson and Kaminski, 1974; Orlov, 1977; Haggerty, 1999) because of their unusual C-isotope data, which are closer to organic matter than typical upper-mantle values, their absence in kimberlites or lamproites, lack of mineral inclusions commonly found in mantle diamonds, such as olivine, garnet or pyroxenes. In this respect, carbonado must be distinguished from other mantle-related polycrystalline types of diamonds such as boart, framesite, balla or stewartite (see Jeynes, 1978; Heaney et al., 2005) that can be common among kimberlites (Harris, 1992) and up to 25% in the Orapa kimberlite in Botswana (Robinson et al., 1984)—as, for the latter, diamond grains are larger, unsintered, and are accordingly more fragile.

The present paper demonstrates that diamonds found in the Dachine komatiite have geochemical characteristics that are nearly identical to carbonados and that, accordingly, the geochemical arguments usually called to reject a mantle origin of carbonado are no longer valid.

2. Dachine komatiite and samples characteristics

In this study, diamonds from the Dachine area (4°48'N, 53°40'W, ~200 km SW of Cayenne) in French Guiana were investigated. These are the only diamonds recovered so far from a komatiite, so it is worth summarising the main geochemical characteristics of the Dachine komatiite body.

The Dachine komatiite outcrops extend over several hundreds of hectares (i.e. 1 ha = 2.47 ac) along a north–south trending dyke, 3.5 km long, 300 to 1000 m wide, and emplaced at 1.9 Ga ago within the 2.1 ± 0.1 Ga old Inini greenstone belt (Capdevila et al., 1999). Located within the primary equatorial forest, the body is both heavily weathered and difficult to access. As with most komatiites, the Dachine body was metamophosed, here to greenshist faciès and was originally described as a diamond-bearing ultramafic talc-shist. The suggestion that the Dachine body is a komatiite is accordingly not based upon textural/petrographic criteria but upon its chemical composition. The Dachine body is indeed characterised by high MgO contents (17–28 wt%) and rather low concentrations of incompatible and immobile elements. For example, La and Nb contents are 9.4 ± 4.1 and 3.9 ± 2.0 ppm, respectively ($n = 9$) (Capdevila et al., 1999), much lower than kimberlites (La = 171 ± 93 and Nb = 165 ± 93 $n = 23$ for Groups I and II South African kimberlites) (Becker and Le Roex, 2006), but within the range of komatiites (see also Fig. 3 in Capdevila et al., 1999 and Fig. 11.9 in Arndt et al., 2008). In this respect, there is some consensus that the original composition is clearly distinguishable from the kimberlite/lamproite rock clan and compares well with

Fig. 1. Carbon isotope distributions of carbonados, diamonds from the Dachine komatiite and other types of crustal or mantle diamonds. The figure illustrates the close similarities between Dachine and carbonados C-isotope distributions and their distinctions with other types of diamonds. Data sources: for carbonados: Vinogradov et al. (1966); Galimov et al. (1985); Ozima et al. (1991); Kamioka et al. (1996); Shelkov et al. (1997); Burgess et al. (1998); Kagi et al. (2007); Kagi and Fukura (2008); Yokochi et al. (2008); for Dachine diamonds: this study, McCandless et al. (1999), Cartigny et al. (2001b); for worldwide xenocryst diamonds : modified from Cartigny (2005); for eclogitic diamonds from Guianiamo (Venezuela): Galimov et al. (1999); Kaminsky et al. (2000); for eclogitic diamonds from Jericho (Slave Craton, Canada) : De Stefano et al. (2009); for polycrystalline diamonds from kimberlites, mostly from Orapa (Botswana) and Mir (Siberia): McCandless et al. (1989); Kirkley et al. (1991); Deines et al. (1993); Burgess et al. (1998); Shelkov et al. (1997); Reutsky et al. (1999); Jacob et al. (2000, 2004); Maruoka et al. (2004); Gautheron et al. (2005); for impact diamonds: Hough et al. (1995, 1998); Koeberl et al. (1997); Shelkov et al. (1998); for metamorphic diamonds : modified from Cartigny (2005); for transition zone diamonds: see review by Stachel et al. (2005); for the 'main mantle range' defined by fibrous (i.e. kimberlite-related) diamonds, carbonatites, carbonates from kimberlites, see e.g. Cartigny et al. (1998, 2003) and references therein.

komatiite chemical data (Capdevila et al., 1999; Bailey, 1999; Demouchy, 2000). Xenoliths, which are common and absent within kimberlite and komatiite respectively, have not yet been reported at Dachine. The occurrence of diamonds within Dachine komatiite is unclear; it might be exceptional (i.e. other komatiites never contained any diamonds) or alternatively the Dachine komatiite ascent rate, its magma oxidation, and/or its volcaniclastic nature were distinct and thus Dachine is unique in having preserved some of its original diamonds from resorption.

Previously, a xenocryst origin for Dachine diamonds was suggested (but see below). Capdevila et al. (1999) proposed that Dachine diamonds might represent metamorphic diamonds picked up by the ascending magma whereas McCandless et al. (1999) suggested that they likely represent diamonds resulting from the disaggregation of mantle eclogites.

Two opposite models account for the genesis of komatiite: (1) melting a subduction-related hydrated source at moderate pressures (< 2.5 GPa) and temperature (e.g. Parman et al., 2001, 2004) or (2) by melting a nearly dry (i.e. a few hundred ppm of carbon and water see e.g. Shimizu et al., 2009) mantle source at greater depths (down to the transition zone) and thus much higher temperatures (e.g. Arndt et al., 1998). The occurrence of diamond which is not stable below pressure of ~4.5 GPa along a typical cratonic geotherm (the warmer the geothemal gradient, the deeper the graphite/diamond transition) together with low TiO_2/Al_2O_3-ratios ~0.1 (wt/wt) of Dachine (Capdevila et al., 1999) are both in support of a deep origin of the Dachine komatiite magma (Capdevila et al., 1999; Arndt et al., 2008). Although relatively rich in diamonds (from 0.06 up to 10.5 carat/100 tons), the small size of gem-quality crystals (< 2.4 mm) recovered so far has precluded any economical mining (Bradford, 2000).

The investigated samples ($n = 141$, Da-1 to -141) were single, not polycrystalline (i.e. so they cannot be carbonados) macrodiamonds (by definition >500 microns in every dimension) that were randomly selected from a larger set (~300) of samples. In agreement with a previous report (McCandless et al., 1999), most crystals (~90%) are irregular in shape (Fig. 2). The stones show features that are typical of mantle-derived diamonds, the majority being intensively resorbed, octahedra (Fig. 2) and cuboids showing the typical negatively oriented trigons on octahedral faces and tetragonal pits on cuboid faces. The samples do not show any sign of transport features (McCandless et al., 1999), suggesting that the diamonds are found in their host primary rock. According to Capdevila et al. (1999), syngenetic inclusions would mostly consist of sulfides, but no chemical data have been reported yet. In the present sample set, colors vary from white to light brown with a few (~10) yellow-green, this being again in agreement with a previous description (e.g. McCandless et al., 1999). Eight yellow-green samples (Da-142 to -149) were further selected from a distinct and larger set of samples for N-isotope analysis. These appear to be richer in both N and ^{13}C, and owing to sample bias, these are not included in any statistics.

Fig. 2. Photograph of Dachine diamonds. Each sample is about 1 mm in size. Although cuboids cubo-octahedra and octahedra were recognised from time to time, as illustrated by the photograph, most of the investigated samples were of irregular shape. Courtesy of the Muséum National d'Histoire Naturelle de Paris. For a colour version of the figure, the reader is referred to the web version of this article.

3. Analytical techniques

The nitrogen content and defect speciation of diamonds were determined using Fourier Transform InfraRed (FTIR) microspectroscopy. Nitrogen-bearing and N-free diamonds are classified as Type I and Type II, respectively (Kaiser and Bond, 1959). In diamond, nitrogen substitutes for carbon atoms (i.e. it is within the diamond crystal structure) as three main defects, which all give rise to specific absorptions in the 1400–900 cm^{-1} region. Diamonds with isolated N-atoms (C-defects) are classified as Ib (Smith et al., 1959), as IaA when containing doubled bonded N-pairs (A-defects, Davies, 1976), and as IaB (B-defects) when containing clusters of four N-atoms and a vacancy (Jones et al., 1992). For Type I diamonds, N-content and aggregation state were determined using absorption coefficients of 25.0 at ppm cm^{-1} for C (Kiflawi et al., 1994) and 16.5 at ppm cm^{-1} for A (Boyd et al., 1994a).

C- and N-stable-isotope measurements were undertaken following procedures described in Cartigny et al. (2004b). Type II (i.e. N-free) diamonds were combusted in a pure O_2 atmosphere, produced CO_2 being analysed for carbon isotopic compositions using a conventional dual-inlet mass spectrometer (Finnigan Delta XP) data being expressed in delta notation relative to the PDB standard, $\delta^{13}C = (^{13}C/^{12}C_{sample}/^{13}C/^{12}C_{PDB} - 1) \times 10^3$, with an accuracy better than 0.1‰ (2σ). Type I (i.e. N-bearing) diamonds were combusted using another vacuum-line to allow for characterision of C- and N-stable isotopes and N-contents (hereafter referred to as N_{comb}). After diamond combustion in a pure O_2 atmosphere, the CO_2 produced was trapped using CaO (to give calcium carbonate). Traces amount of carbon monoxide, hydrogen, methane or water in the nitrogen gas that would cause isobaric interferences were removed cryogenically through a double purification on Cu held at 600 °C and 450 °C, respectively. After quantification of the nitrogen amount using a capacitance manometer with precision of > 5% (2σ), the nitrogen was analysed using a home-made triple collector static mass spectrometer with accuracies better than ±0.5‰ (2σ) and expressed in delta notation relative to Air, $\delta^{15}N = (^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{Air} - 1) \times 10^3$. For $\delta^{13}C$ measurements, CO_2 was recovered after heating the CaO to 850 °C and analysed as described above. Although the accuracies on $\delta^{15}N$ are better than ±0.5‰ (2σ) – as attested by the analyses of international IAEA-N1 and -N2 standards – errors reported in Supplementary Table 1 can be larger and take into account a maximum blank contribution of 3.5 ng with $\delta^{15}N$ taken between -20 to 0‰ (estimates are about -10 ± 5‰).

4. Results

N-contents are low, with most (~97%) samples having nitrogen contents below detection limit (~20 ppm, Type II diamonds). Such a high proportion of Type II is unique: in comparison, it usually ranges from 2 to 55% in worldwide kimberlites (summary in Cartigny et al., 2009, p. 859). Nitrogen-bearing (Type Ia) diamonds ($n = 5$, up to 164 ppm) are restricted to yellow/greenish samples. For these, nitrogen substituting for carbon is present exclusively as a mixture of single and pairs of N-atoms (Type Ib-IaA diamonds) ranging from 2 to 76% of N-pairs (Supplementary Table 1), the occurrence of single N-atoms accounting for their yellow color (Smith et al., 1959).

Diamonds were subsequently analysed for $\delta^{13}C$, which range from -32.6 to +0.15‰ with most (90%) below -20‰ (average ~ -24.1‰, $n = 141$; Supplementary Table 1; Fig 1b). These results are consistent with previously available data on Dachine microdiamonds ($n = 32$; McCandless et al., 1999; Cartigny et al., 2001b). The comparison between macro- and microdiamonds in kimberlites is useful as diamond geochemical (e.g. C-isotopes) or physical (e.g. shape color) characteristics can vary according to diamond size, thus outlining the potential existence of several diamond populations (Harris, 1992; Pattison and Levinson, 1995). From the limited data available, no obvious distinct characteristics seem to exist.

δ^{15}N-values range from –4.1 to +6.9‰ (average ~ +2.1 ± 2.9‰, $n = 12$). There is no relationship with the other parameters, but it is emphasised that 6 of 12 samples analysed for δ^{15}N have high δ^{13}C (> -6‰), illustrating that the samples with the highest N-contents tend to occur among diamonds with high δ^{13}C values.

5. Discussion

5.1. Geochemical similarities between Dachine diamonds and carbonados

The worldwide distribution of carbon isotope compositions for mantle diamonds is characterised by a mode at δ^{13}C ~ -5‰ (Fig 1c, Cartigny, 2005 for review), in sharp contrast with the mode at ~-24‰ of Dachine diamonds (Fig. 1b). Diamonds from a single kimberlite usually exhibit a δ^{13}C distribution very similar to that illustrated within Fig. 1c, i.e. with a majority of diamonds falling within a restricted δ^{13}C range from -8 to -2‰. There are a few exceptions, however; notably, the eclogitic diamonds from Guianamo kimberlites in Venezuela (Galimov et al., 1999; Kaminsky et al., 2000) in which the δ^{13}C distribution (Fig. 1e) shows a mode between -15 and -20‰ and eclogitic diamonds from Jericho, Slave Craton, Canada (De Stefano et al., 2009), which show a δ^{13}C mode ~ -38‰ (Fig. 1d). The δ^{13}C mode of Guianamo diamonds is still about 5 to 10‰ higher than the Dachine diamonds. If Jericho diamonds illustrate that some diamond populations can have a δ^{13}C mode that is even lower than for carbonados, their aggregation is too advanced (i.e. IaAB diamonds, De Stefano et al., 2009, see below) to compare with carbonados. Comparison with other mantle diamond subpopulations such as polycrystalline xenocrysts from kimberlites (Fig. 1g), impact-related (Fig. 1h) or metamorphic diamonds (found in crustal rocks subducted at ultra-high-pressures, Fig. 1f) further emphasises the unique characteristics of Dachine diamonds. The observed ^{13}C-depletion among diamonds from Dachine, including octahedra and cuboids (and their respective resorbed forms), macro (this study) and microdiamonds (McCandless et al., 1999; Cartigny et al., 2001b), Types I and II diamonds demonstrate that the diamond population(s) sampled by the Dachine kimberlite is(are) characterised by a strong ^{13}C-depletion. It is possible that yellow-green Type I samples reflect a second population characterised by higher ^{13}C/^{12}C ratios, but this is not a prerequisite. Actually, the slightly bimodal distribution of Fig. 1b results from plotting the additional Type I diamonds (Da-142 to 149) that were further selected to increase δ^{15}N measurements (see Section 2). More likely (see below), the low abundance of diamond with high δ^{13}C values (only 10% are > -20‰) represents the tail of a strongly positive asymmetric distribution.

Nitrogen in diamonds is originally incorporated as single atoms (Ib diamond). At mantle temperatures, a second-order kinetic process causes nitrogen to diffuse to form first pairs of N-atoms (IaA diamonds). Nitrogen aggregation can be described through the relation (Chrenko et al., 1977; Kiflawi et al., 1997), $1/C - 1/C_o = A \exp [-Ea/RT] \times t$. For Ib to IaA aggregation, C denotes for the number of remaining C-defects (in at.ppmN), C_o the total nitrogen content (in at ppm N), A the pre-exponential factor (1.48×10^8 at ppm^{-1} s^{-1}, Taylor et al., 1996), Ea the activation energy (from 5.0 to 6.0 eV, Taylor et al., 1996; Kiflawi et al., 1997), T for temperature (in K) and t for time (in seconds). Thus, higher temperature, residence time and/or N-content lead to higher levels of aggregation. In the present study, we did not consider the lower 4.5 eV activation energy for Ib to IaA aggregation,

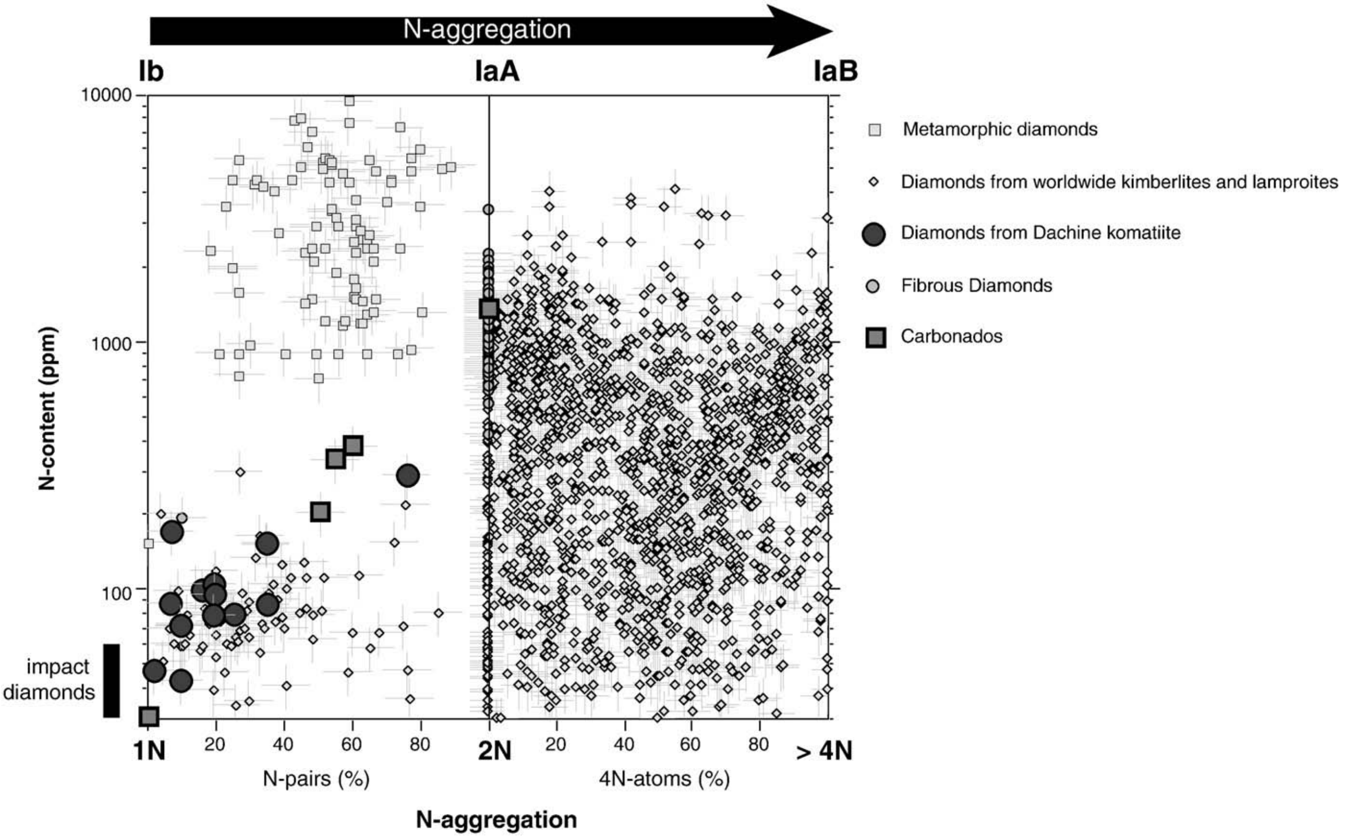

Fig. 3. N-content and N-aggregation state of Dachine diamonds (large open circles), carbonado (large open squares) and other types of diamonds including worldwide xenocryst diamonds from kimberlites and lamproites (open diamonds), fibrous/coated (phenocryst) diamonds (open circles), metamorphic microdiamonds from ultra-high pressure rocks (filled squares). Data source listed in Cartigny et al. (2004a) and additionnal data are from Dobrzhinetskaya et al. (2006) for metamorphic diamonds and Shelkov et al. (1997) and Garai et al. (2006) for carbonados.

as the most recent results have shown that it only applies to synthetic diamonds owing to greater levels of either vacancies and/or nickel impurities (Kiflawi et al., 1998; Vins, 2004). This is supported by previous observations (D. Fisher, pers. comm.) and our own on-going work (Cartigny and DeCorte, unpublished).

Subsequently, over Ga time scales, N-pairs further migrate to form clusters of 4-N atoms (IaB diamond). Because most diamonds (> 95%) in kimberlites and lamproites are xenocrysts, having resided up to 3 Ga in mantle rocks at temperatures of ~1000 to 1300 °C (Stachel and Harris, 2008 for review), they display advanced aggregation states, >99.9% being of the IaA-IaB type (Fig. 3). In kimberlites or lamproïtes, diamonds of Type Ib-IaA are extremely rare (~0.1%; Dyer et al., 1965; Taylor et al., 1996; Mc Kenna et al., 2004; Cartigny et al., 2004a; King et al., 2005; Fig. 3) and always occur together with IaA-IaB diamonds. For example, the Swartruggens kimberlite dyke (South Africa), which is known to yield the greatest abundance of Ib-IaA diamonds, they represent ~5% of the production, i.e. 95% being IaAB diamonds (Mc Kenna et al., 2004). Dachine diamonds are thus unique in containing exclusively Ib-IaA diamonds. Owing to their low N-contents (< 5 ppm; e.g. Shelkov et al., 1997), no nitrogen aggregation data are available yet on impact-related diamonds. According to their short residence time of a few Ma at high temperatures (e.g. De Corte et al., 2000), metamorphic diamonds (i.e. formed in subducting crustal rocks and found in ultra-high pressures metamorphic terranes) are the only samples known to lie exclusively within the Ib-IaA aggregation sequence (Finnie et al., 1994; De Corte et al., 1998, 1999; Cartigny et al., 2004a; Dobrzhinetskaya et al., 2006). Thus, although similar in terms of aggregation state, mantle diamonds (including Dachine) are still different from metamorphic diamonds (Fig. 3) in terms of nitrogen concentrations, the latter being higher by ~two orders of magnitude, showing no Type II diamond (Fig. 3) and by sample size (exclusively microdiamonds). In terms of N-aggregation, the only samples that Dachine diamonds resemble are carbonados (Fig. 3, Shelkov et al., 1997; Garai et al., 2006; Kagi and Fukura, 2008). Earlier, Kagi et al. (1994) attributed the sharp IR absorption peak within a carbonado at 1384 cm^{-1} to nitrogen platelets, which means that this sample would lie within the IaA-IaB aggregation sequence (Woods, 1986), implying long residence time at high temperature, demonstrating *de facto* carbonado formation in the Earth's mantle. However, if the 1384 cm^{-1} absorption peak would be related to the occurrence of platelets, additionnal related peaks at 1332, 1175 and 1096 cm^{-1} should be present (see Clark and Davey, 1984; Woods, 1986). This was, however, not the case. Thus, so far, all available data show that carbonados lie within the Ib-IaA aggregation sequence.

The weakly advanced N-aggregation state of Dachine diamonds places tight constraints on the relationships between Dachine diamonds and the host komatiite. From the range of temperatures for komatiite magma generation here taken to vary between 1200 and 1600 °C (see Arndt et al., 1998; Parman et al., 2001), and taking into account their N-concentrations and aggregation states, a range of activation energies varying from 5.0 to 6.0 eV (Taylor et al., 1996; Kiflawi et al., 1997), one deduces that the overall residence time of Dachine diamonds within the mantle and/or komatiite host magma is less than 10^3 years (Fig. 4). Such a short residence time indicates that Dachine diamond formation was closely linked to komatiite eruption.

5.2. On the non-mantle origin of carbonados: a brief discussion of alternative models

The present paper primarily focuses on the geochemical similarities between carbonado and Dachine diamonds and will end with the proposition that carbonados could be komatiite derived. Yet, several alternative hypotheses have been proposed. The following section aims to outline their respective strengths and weaknesses (see also Haggerty, 1998; Heaney et al., 2005; Yokochi et al., 2008 for recent reviews).

As outlined earlier in this paper, because of the differences in geochemical characteristics between carbonados and mantle-derived diamonds, a mantle-derived origin for carbonado is often seen as unlikely (e.g. Frantsesson and Kaminski, 1974, but see Kagi and Fukura, 2008; Shelkov et al., 1997). It has been alternatively suggested that carbonados (1) represent impact-related diamonds (Smith and Dawson, 1985); (2) formed within uranium-rich carbonaceous sediments by implementation of alpha-particles (Kaminsky, 1991; Ozima et al., 1991); (3) are the result of subduction of organic carbon in the Earth's mantle (Robinson, 1978); or even (4) are extra-solar, being related to a supernova (Haggerty, 1998, 1999; Garai et al., 2006).

The impact-related model cannot account for the C-isotope distribution of carbonados (compare Fig. 1a and g). Furthermore, impact-related diamonds are smaller and by far less coesive than

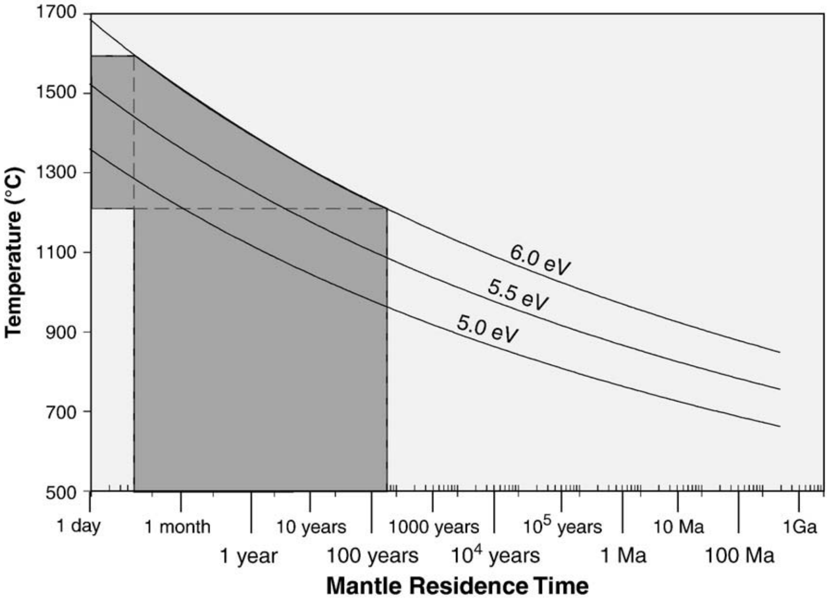

Fig. 4. Temperature–residence time relationships for Dachine diamonds as a function of activation energies (Taylor et al., 1996; Kiflawi et al., 1997). The parameters used here are $N_0 = 100$ at ppm and aggregation state = 50%, pre-exponential factor = 1.476×10^8. The diagram illustrates that the residence time of Dachine diamonds in the mantle and the komatiite magma was short, firmly linking Dachine diamond genesis to the komatiite volatiles.

carbonado (i.e. the grains are not sintered), and lonsdaleite, the impact-symptomatic hexagonal-form of impact diamonds (it occurs within *Yakutite*) has never been recognised in carbonado (Heaney et al., 2005 for review; Haggerty, 1998). The typical absorption at 1.8 eV observed in impact-related diamonds is also not observed within carbonados (see Yokochi et al., 2008). Many other arguments, such as N_2/Ar ratios (Shelkov et al., 1998; Yokochi et al., 2008), have been raised in the last 25 years and all of them have emphasised the distinction between carbonados and impact-related diamonds.

The formation of carbonados within a subducting slab, again, does not match the known $\delta^{13}C$ distribution of truly *subducted* diamonds (Fig. 1f). Similarities in terms of N-aggregation states (Fig. 3) exist but carbonados differ from metamorphic diamonds, the latter being characterised by their exclusively small size (e.g. De Corte et al., 1998, 1999) and much higher N-contents (Cartigny et al., 2004a and ref. therein).

The formation of carbonado within uranium-rich carbonaceous sediments by implementation of alpha particles (Kaminsky, 1991) is based on the undisputable evidence that U-rich carbonaceous sediments contain diamonds. Further support for such a model was brought by evidence for parentless fissiogenic xenon requiring residence within a U-Th rich environment (Ozima et al., 1991). High levels of polycyclic aromatic hydrocarbons (PAH) were also taken in support for a crustal carbon source (Kaminsky, 1991) although it cannot be proven that the PAH are primary and not secondary. Given that the protolith remains unknown, it can only be said that the carbon and nitrogen isotope data of carbonado broadly overlap Archean sedimentary data (see Thomazo et al., 2009 for review) and are accordingly not in contradiction with such a model. However, as no significant N-aggregation would occur over the Earth's history at temperatures <600 °C, it remains unclear how single nitrogen atoms (i.e. C-defects) could aggregate into A-defects. The most important argument against such a scenario is that diamonds in U-rich carbonaceaous sediments are only of a few nanometer in size, contrasting with the largest carbonado of 3167 carats, and the possiblity that these could aggregrate and sinter has been disproved (Daulton and Ozima, 1996).

The most recent suggestion is that carbonado is a unique example of *exomineralisation* as it would form within an exploding super-nova. This model is based on two main observations: (1) some infrared absorption features (mostly C-O and C-H bonds) resemble synthetic diamonds grown under chemical vapor deposition (CVD) and (2) photoluminescence spectra resemble CVD diamond (Garai et al., 2006). It is emphasised that the occurrence of reduced inclusions in carbonado is not symptomatic of extraterrestrial environments (including meteorites), being also reported among impact-related rocks (SiC, e.g. Hough et al., 1995), metamorphic rocks (SiC and TiN, Dobrzhinetskaya et al., 2007) and mantle diamonds (SiC, Fe_3C, FeC, Fe; Leung et al., 1990; Jacob et al., 2004; Jones et al., 2008). There are many articles devoted to CVD diamond formation and characterisation. In broad terms, the typical conditions to grow CVD in the laboratory require a gas flux (primarily methane and hydrogen) introduced in a chamber under vacuum ($<10^{-4}$ mbar). The gas is ionised, e.g. using a microwave source, leading to the production of a plasma and to diamond deposition on a substrate (typically SiC or diamond). In their model linking carbonados to super-novas, Garai et al. do not account for either the large size of carbonados (carbonados are ~7 orders of magnitude larger than the largest extraterrestrial diamonds; e.g. Russell et al., 1996), their sintering, the occurrence of some blasts/phenocrysts or why, on Earth, they are geographically restricted. The model predicts a series of nuclear anomalies (among them enrichment in ^{12}C ^{16}O, ^{28}Si, ^{24}Mg and ^{14}N). Only C and N isotope data are available so far (e.g. Shelkov et al., 1997; Yokochi et al., 2008) and these values are terrestrial, e.g. not ^{15}N depleted (Shelkov et al., 1997; Yokochi et al., 2008) and do not compare with extraterrestrial diamond $\delta^{15}N$ values (most ~-300‰; e.g. Russell et al., 1996; Ott, 2003 for review). Furthermore, extraterrestrial materials are known to carry significant sample-scale isotope variability that reflects either the heterogeneity of the solar nebular, secondary process (e.g. spallation) or the uptake of pre-solar grains. This is at odd with the very restricted C- and N-isotope variability of carbonados (De et al., 2001; Yokochi et al., 2008). As discussed by Yokochi et al. (2008), the extra-terrestrial CVD formation of carbonados (Garai et al., 2006) is not supported by the low amounts of Ar in carbonados (i.e. high N_2/Ar ratios, Yokochi et al., 2008). Furthermore, the FTIR identification of C–O or C–H bonds within carbonados has not been confirmed yet (Kagi and Fukura, 2008) and may instead reflect contamination introduced during sample preparation (Kagi and Fukura, 2008). It is worth noting that the FTIR data of Kagi and Fukura (2008) show infrared characteristics (i.e. occurrence of carbonate and water) that resemble both mantle (e.g. Navon et al., 1988; Burgess et al., 2009 and ref. therein) and metamorphic diamonds (De Corte et al., 1998, 1999; Dobrzhinetskaya et al., 2006 and references therein). Importantly, these are typical of high-pressure fluids (i.e. >35 kbar) as opposed to conditions for CVD diamond formation and further supported by high residual pressures of >7 kbar within carbonados (Fukura et al., 2005).

In summary, the above models can account for some of the carbonado geochemical features (but again see Figs. 1 and 3), but none of these can account for either their large size or the sintering of diamond aggregates.

5.3. A model linking carbonado to komatiite magmas

Significantly, the only known environment where large diamonds, up to 3106 carats, occur is in the Earth's mantle. Yet this hypothesis fails to account for three early observations: (1) unusually depleted $\delta^{13}C$ compositions that do not resemble any mantle diamond populations known so far; (2) their absence within volcanic rocks, such as kimberlites or lamproites that usually carry diamonds from the mantle to the surface; and (3) lack of mantle silicate inclusions. More recent disparities include (4) the low aggregation states, (5) the occurrence of reduced inclusions (e.g. SiC), and (6) their photoluminescence features which again do not resemble mantle diamonds. Finally, (7) the process in the mantle that would allow for sintering of diamond crystallites remains an unaddressed question.

Although carbonados do indeed differ from mantle-related diamond populations known so far, they show striking geochemical similarities to diamonds from the Dachine komatiite. The observations include not only C-isotope compositions but also N-aggregation state (Figs. 1 and 3). Furthermore, although N-isotope data on carbonados might be affected by some secondary pore-related contamination (see Shelkov et al., 1997), available data ($\delta^{15}N = +2.3 \pm 4.5$‰ $n = 23$ Shelkov et al., 1997; Yokochi et al., 2008) are again, within error, identical to Dachine diamonds (2.1 ± 2.9‰). Thus, the long standing geochemical arguments that carbonados could not have formed in the mantle are contradicted by the present evidence.

I propose carbonados to be mantle-related and their formation to be closely related to the komatiite magma (Fig. 5). As the buoyant komatiite magma intrudes into the more *rigid* (i.e. colder and thus more viscous) continental lithosphere, the magma mostly rises by propagation of magma-filled cracks (Huppert and Sparks, 1985). Because propagation is favored by volatile elements concentrated within the cracks, certain zones are locally enriched with both volatile and the most mobile elements, including carbonate/CO_2 (Kagi and Fukura, 2008), N, H_2O, and U (Fig. 5B). Diamond precipitation occurs when komatiite-related oxidised carbon and water percolate into the reduced, diamond-free continental lithosphere (Fig. 5A). Precipitation of diamond leads to a residual medium depleted in carbon and thus to residual fluids further (locally) enriched in e.g. U and Th, which will ultimately be trapped within diamonds as small voids and/or inclusions.

In nature, the different diamond shapes are likely related to various degrees of carbon sursaturation, polycrystalline and monocrystalline diamonds being formed under higher and lower carbon sursaturation, respectively (Sunagawa, 1990). Thus, in a model in which polycrystalline (still unsintered) is formed under higher carbon sursaturation, their

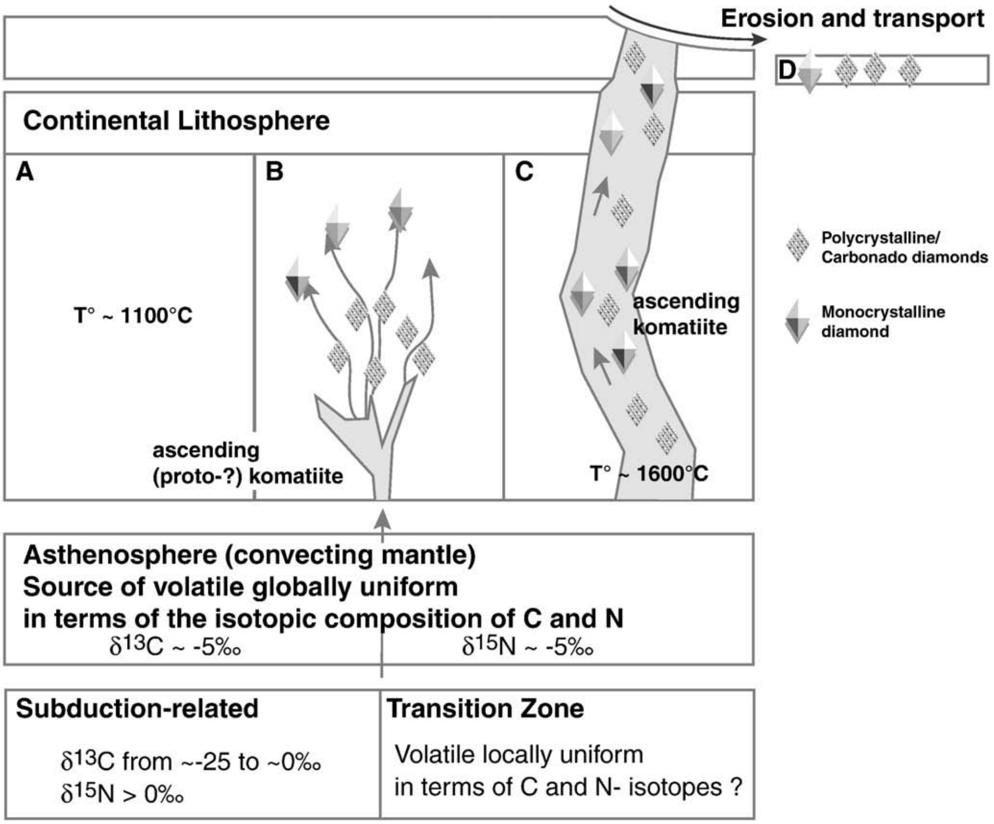

Fig. 5. Illustration of the carbonado formation in the Earth's continental mantle from komatiite-related volatiles. Inspired from Boyd et al. (1994b).

precipitation must also be associated with the formation/occurence of octahedrally shaped monocrystalline (i.e. not polycrystalline) diamonds (Fig. 5B) under a lower degree of C-saturation.

This model is so far similar to diamond growth conditions in the continental lithosphere proposed by Boyd et al. (1994b) to account for the formation of young, kimberlite-related, fibrous/coated diamonds. Although this is not a prerequisite (i.e. polycrystalline diamonds being ubiquitous in kimberlites, e.g. Harris, 1992), higher supersaturation conditions, and thus both higher diamond nucleation rate and diamond growth rate and accordingly larger sample size, could be enhanced by unusually low oxygen fugacities within the lithospheric mantle as might be suggested by the identification of silicon carbide and titanium nitride within carbonado (Gorshov et al. 1996, 1997; De et al., 1998; Jones et al., 2006) and iron carbide in a mantle-related polycrystalline diamond (Jacob et al., 2004). Newly formed diamonds are picked up and entrained to the surface by the ascending oxidised hot komatiite magma, the close relationship of the diamonds to their host magma accounting for their little advanced aggregation states (Fig. 5C). As implied by the little advanced N-aggregation levels, both microcrystallite blasts of carbonados must be time-related. The nitrogen aggregation state in diamond follows a second-order kinetic law depending thus upon N-contents, temperature and time (see §3); for a given N-content, N-aggregation is about the same within Dachine/carbonado (komatiite-related) and so-called fibrous (i.e. kimberlite-related) diamonds (Fig. 3). This implies either that Dachine and kimberlite had similar temperature/ascent rate or, more likely, that ascent rates for komatiites were higher if associated with higher magma temperatures. However, owing to a lack of sufficiently precise activation energy for Ib to IaA aggregation, no precise T-t path estimate can be provided yet (Fig. 4).

The sintering of diamond aggregates that make carbonados happened during ascent within the hot komatiite magma *en route* to the surface (Fig. 5C). Sintering was related to komatiite-related high temperatures – maybe up to 1600 °C (see Arndt et al., 2008) – for short amounts of time. This process is actually similar to that used for decades in the industry (e.g. Wentorf et al., 1980). The high temperatures of komatiites account for the presence of carbonado in these rocks and their absence in cooler kimberlites. The hot komatiite would lead to some partial resorption of diamond. Subsequent erosion of the komatiite body and transport (Fig. 5D) over large distances (>2000 km) lead to the surface patina displayed by some carbonados (Haggerty, 1998) and, owing to their toughness, to their preferential preservation over monocrystalline diamonds.

Given its porous nature, old age, transport and metamorphism, most of the original inclusions were altered and replaced by crustal material thus accounting for their enriched REE patterns (Shibata et al., 1993; Kamioka et al., 1996), the occurrence of typical crustal inclusions such as florencite, and their high contents of polycyclic aromatic hydrocarbons (Kaminsky, 1991). Finally, if one considers the old age (from 2.0 to 3.8 Ga; Ozima and Tatsumoto, 1997; Sano et al., 2002) and high U-contents concentrated within the inclusions/voids within either carbonados, polycrystalline or fibrous diamonds (up to 2000 ppb, see Burgess et al., 1998, 2009), there is room to account for parentless fissiogenic Xe of carbonados (Ozima et al., 1991). The model can account for further observations such as photoluminenscence data. The occurrence of N-V centers (a single nitrogen plus a vacancy) which gives rise to a red color in cathodoluminescence and typical photoluminescence at ~1.8 eV (Kagi et al., 1994, 2007; Yokochi et al., 2008) can result from annealing of Ib-polycrystalline diamonds (i.e. it is not only symptomatic of CVD diamonds, see Yokochi et al., 2008 for discussion) and can thus be further related to the high temperature of the komatiite magma.

The inference that carbon in komatiites is oxidised (rather than reduced) was made by Canil (1997), Kent et al. (2009) and Shimizu et al. (2009). While precipitating diamond, diamond being deprived in ^{13}C-isotope compared to oxidised carbon (Bottinga, 1969), diamond crystallisation leads to residual carbon enriched in ^{13}C. Thus, the positive skewness of the δ^{13}C distributions of both carbonados and Dachine diamonds (see also Thomassot et al., 2007 for discussion) is compatible with the earlier suggestion of e.g. Canil (1997). This is further supported by two previous observations on carbonado having illustrated that the phenocrysts/blasts have lower $^{13}C/^{12}C$ ratio than the matrix (De et al., 2001; Yokochi et al., 2008) and single trend within a carbonado (sample GM-01 of Yokochi et al., 2008). When diamond precipitates from oxidised carbon, nitrogen behaves as an incompatible element with respect to diamond (N-remains in the fluid), N-uptake being likely kinetic and controlled by the diamond rate of growth, higher rate of growth corresponding to higher N-contents (Boyd et al., 1994b; Cartigny et al., 2001b). This accounts for the differences in N-contents between Dachine diamonds and carbonados, predicting polycrystalline (i.e. later carbonado) to be N-richer than monocrystalline diamonds (Fig. 3). The model further predicts the residual carbon to be N-enriched with increasing diamond precipitation, accounting for the greater abundance of Type I Dachine diamonds with higher δ^{13}C values (Supplementary Table 1) without having to call for several diamond populations.

5.4. Where is and what made the low δ^{13}C reservoir?

As can be inferred from its diamonds, the Dachine komatiite magma had a C-isotope composition of $\delta^{13}C \sim -27‰$, significantly different from the canonical convective upper-mantle ($\delta^{13}C \sim -5‰$). Its inferred original $(C/N)_o$ ratio >~20000 and $\delta^{15}N \sim +2‰$ are unusual as well compared with most xenocryst diamonds from kimberlites ($(C/N)_o$ ratio ~200–500, $\delta^{15}N \sim -5 \pm 3‰$; e.g. Cartigny et al., 2001b, 2009). Although the existence of diamonds with distinctly low average δ^{13}C values is undisputable and not restricted to Dachine, their origin(s) remain(s) unclear (Stachel et al., 2005; De Stefano et al., 2009). The following paragraph explores where in the mantle could a reservoir with such low δ^{13}C values be located and what could have led to its existence.

The komatiite might have rather inherited its C-isotope composition by incorporating subducted organic carbon (average $\delta^{13}C \sim -25‰$, see Thomazo et al., 2009 for review). The C- and N-isotope values are broadly consistent with such a possibility although much higher N-contents are expected (see discussions in Cartigny et al., 1998, 2009). In support of such a possibility, several experimental studies proposed komatiites to be subduction-related (Parman et al., 2001, 2004); yet the corresponding depth of <90 kilometers is too shallow to account for the occurrence of diamonds (i.e. under standard continental geotherm of 38–40 mW m^{-2}, diamond is not stable before depths of ~150 km, see Stachel and Harris, 2008). In addition, such a hypothesis would require no significant contribution, via mixing, of either (i) upper mantle-related carbon ($\delta^{13}C \sim -5‰$) or (ii) subduction-related carbonate ($\delta^{13}C \sim 0‰$), the latter representing 80% on average of subducted carbon; these would otherwise drive the average δ^{13}C toward ^{13}C-richer compositions. An alternative model, in which the rising komatiite magma would be contamimated in large extent by subducted organic matter is even less plausible as the high magma temperatures would tend to move abroad from the diamond stability field (i.e. stabilising graphite rather than diamond). Because the probability of preserving any magma from a contribution of either upper mantle carbon or carbonate is very unlikely, it is difficult to envisage that this process could occur twice and in fact, the Dachine distribution is unique. Thus, such a scenario would certainly link carbonados to the Dachine komatiite. So far, no carbonado has, however, been reported within the Dachine diamond deposit and Dachine eruption age (~1.9 Ga) is within the lowest range of ages inferred for carbonados, from 2.0 to 3.8 Ga [(Ozima et al., 1991; Sano et al., 2002), the range reflecting large errors associated with the difficulty in analysing these samples]. Because large areas of the Dachine deposit remain uninvestigated, and that diamond grade appeared heterogeneous, such a possibility cannot be excluded, but is seen as unlikely however.

More likely, the low δ^{13}C values are inherited from the transition zone. The transition zone(s) (here defined as 300–660 km deep) yield eclogitic diamonds which, at a given locality, span a rather limited range of δ^{13}C values (of about 6‰; Stachel et al., 2005 for review; Fig. 1h). For three studied occurrences, Juina (Brazil), Kankan and Jagersfontain (from western and southern african cratons respectively), the C-isotope compositions of transition zone diamonds show δ^{13}C modes at ~-8, ~ +1 and ~-21‰, respectively (Fig. 1h, Stachel et al. 2005 for review), i.e. distinct from one locality to the other and different from the shallowest upper mantle value ($\delta^{13}C \sim -5‰$). A subduction-related signature has been suggested (e.g. Stachel et al., 2005; Tappert et al., 2005) but it remains unclear, however, how subduction could lead to such low variability in δ^{13}C values at a given locality over such large range of depths, but still distinct from the shallower diamonds (150–300 km). My interpretation differs from that of Stachel and coworkers in that I assume that these values are representative of the whole transition zone below a given craton and not only of eclogitic lithologies. In other words, I speculate that deep mantle domains might have distinct C-isotope compositions. If correct, this has fundamental implications, which can bear upon our understanding of C-isotope excursions in the geological record and their potential link with deep magmatism (e.g. Corsetti et al., 2005; Payne and Kump, 2007). In a model in which komatiite is generated at great depths (Arndt et al., 1998), one might thus expect carbon isotope signatures that are distinct from the shallower upper mantle, and predict $\delta^{13}C \sim -27‰$ for the transition zone below the Guianan craton. According to such a model, carbonados could be brought up to the surface by any komatiite emplaced within the Guiana shield. There is presently no C- or N-isotope data on undegassed and/or fresh komatiites that could support (but see Fig. 11 in Javoy et al., 1986 illustrating overall positive δ^{15}N-values) or disprove the present suggestion.

6. Conclusions and future directions

The overall similarities of carbonados with komatiite-related diamonds from Dachine form the basis of a model linking carbonados to komatiite volatiles. Compared with previous models, the present one can account for most, if not all, observations made so far on carbonados.

This model remains admitedly speculative , i.e. carbonado still remains to be found in its primary host rock, but can be tested, on the field, through a series of three predictions: (1) some mantle-related silicate inclusions will be found within micrometer-sized carbonado crystallites; (2) some monocrystalline diamonds with low δ^{13}C values and little advanced N-aggregation are associated with carbonados in Meso-proterozoic alluvial deposits, and (3) several of these monocrystalline diamonds will contain reduced types of inclusions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2010.05.015.

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Supplementary Table 1 : C-, N-isotope compositions, N-contents and N-aggregation states of Dachine diamonds.

Sample name	Weight (mg)	Bulk Combustion					Infrared Spectroscopy	
		δ^{13}C (‰ vs PDB)	N-content (µg/g)	δ^{15}N (‰ vs AIR)	-	+	N-content (µg/g)	IaA (%)
Da-001	1,4100	-14,05						
Da-002	2,1533	-27,31						
Da-003	2,6926	-25,66						
Da-004	2,1035	-26,12						
Da-005	2,2833	-21,90						
Da-006	2,0129	-21,51						
Da-007	1,9830	-28,12						
Da-008	1,7452	-28,28						
Da-009	2,1346	-22,78						
Da-010	2,0556	-22,88						
Da-011	2,1978	-26,60						
Da-012	2,4383	-25,21						
Da-013	2,2845	-31,89						
Da-014	2,0226	-18,62						
Da-015	1,8874	-24,70						
Da-016	2,4210	-22,19						
Da-017	2,1931	-25,80						
Da-018	1,6055	0,15						
Da-019	1,8935	-28,81						
Da-020	1,4066	-27,10						
Da-021	1,8112	-26,43						
Da-022	1,9474	-27,53						
Da-023	2,0381	-25,31						
Da-024	1,8591	-17,54						
Da-025	1,5203	-25,97						
Da-026	2,0174	-25,73						
Da-027	1,6254	-27,72						
Da-028	1,7846	-27,64						
Da-029	1,8578	-21,62						
Da-030	1,9423	-25,81						
Da-031	2,0788	-26,48						
Da-032	1,9019	-27,64						
Da-033	2,1472	-26,56						
Da-034	1,9103	-25,32						
Da-035	1,9920	-27,08						
Da-036	2,0539	-21,87						
Da-037	2,0879	-20,18						
Da-038	1,6840	-26,96						
Da-039	1,8669	-27,72						
Da-040	1,3466	-21,79						
Da-041	1,8601	-26,51						
Da-042	1,3034	-28,53						
Da-043	2,0926	-29,15						
Da-044	1,5881	-26,07						
Da-045	2,4491	-23,47						
Da-046	1,7708	-25,33						
Da-047	2,0020	-19,73						
Da-048	1,9303	-20,78						
Da-049	1,3426	-26,19						
Da-050	2,3746	-22,18						
Da-051	1,9444	-25,02						
Da-052	2,6114	-27,07						

Supp. Table 1 (continued): C-, N-isotope compositions, N-contents and N-aggregation states of Dachine diamonds.

Sample name	Weight (mg)	Bulk Combustion					Infrared Spectroscopy	
		δ^{13}C (‰ vs PDB)	N-content (µg/g)	δ^{15}N (‰ vs AIR)	-	+	N-content (µg/g)	IaA (%)
Da-053	2,1600	-18,55						
Da-054	2,1486	-24,01						
Da-055	2,1756	-27,63						
Da-056	2,1185	-27,24						
Da-057	2,1985	-28,37						
Da-058	1,5885	-29,92						
Da-059	2,0783	-27,03						
Da-060	1,7211	-22,89						
Da-061	1,0676	-26,20						
Da-062	0,4157	-1,29					299	76
Da-063	0,6985	-29,04						
Da-064	2,3253	-25,35						
Da-065	2,2589	-29,22						
Da-066	2,3322	-21,65						
Da-067	2,0169	-24,26						
Da-068	2,1017	-23,51						
Da-069	1,8833	-22,34						
Da-070	1,6385	-22,77						
Da-071	2,0517	-22,81						
Da-072	2,2548	-24,07						
Da-073	2,2407	-27,60						
Da-074	1,6021	-25,71						
Da-075	2,1566	-25,88						
Da-076	2,6644	-22,41						
Da-077	1,5113	-26,13						
Da-078	2,5415	-13,61						
Da-079	2,0419	-26,48						
Da-080	2,1008	-27,16						
Da-081	2,0063	-27,02						
Da-082	3,3279	-19,94						
Da-083	1,9283	-22,98						
Da-084	1,8707	-24,68						
Da-085	2,1175	-27,04						
Da-086	2,4635	-27,62						
Da-087	2,5046	-19,34						
Da-088	2,6380	-24,33						
Da-089	1,7878	-16,12						
Da-090	0,6928	-25,80						
Da-091	2,3894	-22,98						
Da-092	1,5244	-22,12						
Da-093	2,6728	-15,68						
Da-094	1,9172	-25,80						
Da-095	2,2681	-24,97						
Da-096	1,8695	-23,78						
Da-097	2,1932	-20,62						
Da-098	2,2980	-28,98						
Da-099	1,9688	-23,47						
Da-100	2,5337	-27,67						
Da-101	2,7404	-24,28						
Da-102	3,1043	-20,20						
Da-103	1,0081	-4,64	161	+3,0	-0,8	+0,6	180	7
Da-104	2,1266	-26,03						

Supp. Table 1 (continued): C-, N-isotope compositions, N-contents and N-aggregation states of Dachine diamonds.

Sample name	Weight (mg)	Bulk Combustion					Infrared Spectroscopy	
		δ^{13}C (‰ vs PDB)	N-content (µg/g)	δ^{15}N (‰ vs AIR)	**-**	**+**	N-content (µg/g)	IaA (%)
Da-105	2,5296	-25,41						
Da-106	3,1056	-27,10						
Da-107	2,3093	-25,34						
Da-108	2,1965	-27,16						
Da-109	2,2869	-25,81						
Da-110	2,2868	-28,03						
Da-111	2,2353	-28,69						
Da-112	1,7924	-25,94						
Da-113	1,8762	-21,56						
Da-114	2,4820	-25,61						
Da-115	0,9008	-29,52	97	+1,3	-1,1	+0,5	111	19
Da-116	2,5146	-27,61						
Da-117	1,6234	-18,27						
Da-118	1,4730	-24,42						
Da-119	1,3454	-28,17						
Da-120	1,3183	-21,76						
Da-121	1,9572	-27,83						
Da-122	2,4354	-20,59						
Da-123	1,9581	-26,75						
Da-124	2,0238	-28,25						
Da-125	0,9554	-32,64	92	+2,3	-1,1	+0,6	92	35
Da-126	0,8052	-2,74	54	+4,6	-1,8	+0,9	45	10
Da-127	2,2584	-2,20					105	16
Da-128	0,8318	-26,97	25					
Da-129	1,8922	-26,56						
Da-130	2,1610	-22,23						
Da-131	1,5974	-29,69						
Da-132	1,8201	-28,02						
Da-133	1,8891	-23,71						
Da-134	1,6435	-25,55						
Da-135	1,8595	-24,90						
Da-136	1,7117	-26,04						
Da-137	1,8906	-22,99						
Da-138	2,0235	-28,44						
Da-139	1,1923	-26,41	31	-0,4	-2,0	+0,5		
Da-140	0,8622	-2,72	90	+3,6	-1,3	+0,7	76	10
Da-141	1,6131	-2,17	66	+4,2	-0,9	+0,6	92	7
Da-142	0,1847	-27,72					83	25
Da-143	4,3260	-24,05						
Da-144	1,9220	-1,24	54	+6,9	-1,0	+0,7	50	2
Da-145	1,4962	-4,78	16	+0,2	-3,5	+0,5	99	20
Da-146	1,9093	-14,73	39	+1,5	-1,4	+0,6	84	20
Da-147	1,9542	-26,95	27	-4,1	-7,0	-0,6	25	2
Da-148	5,6684	-23,77						
Da-149	2,5133	-6,16	171	+2,2	-0,7	+0,5	162	35