The formation mechanisms of Polycrystalline diamonds: diamondites and carbonados

Ariam. M Aguilera Pradenas

Dissertation in geology at Lund University,
Bachelor thesis, no 459
(15 ECTS credits)

Department of Geology
Lund University
2015

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Cover Picture: Diamond in kimberlite (©The University of Auckland 2005).

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Pradenas Aguilera, A., 2015: The formation mechanisms of Polycrystalline diamonds: diamondites and carbonados. *Dissertations in Geology at Lund University*, No. 459, 23 pp. 15 hp (15 ECTS credits).

Abstract: Diamond is a cubic carbon mineral that possess many unique characteristics like extreme hardness and thermal conductivity. There are many types of diamonds like monocrystalline, polycrystalline and coated/ fibrous and in this bachelor thesis the focus was on polycrystalline diamonds; carbonado and diamondites (are divided in three different types of diamonds: eclogitic, perioditic -and websteritic-type). I made a literature study on the formation mechanism of diamondites to see whether they have different crystallisation histories than monocrystalline diamonds as some researchers argue. Determing a relationship, or lack thereof, between monocrystalline diamonds and diamondites could be valuable to the mining industry. I also made a literature study on the origin of carbonado because carbonados are important as abrasives in the industries. Constraining an origin for carbonados would give us valuable knowledge about their formation mechanisms, could help us to make synthetic carbonado which could be cheaper than prospecting for natural carbonado. Several origins for carbonado are proposed which are for example meteorite impact, uranium-rich carbonaceous sediments and mantle. The most likely origin is the mantle which is supported among others by textural observations (for example fluid inclusions) but to determine this with certainty a carbon-source needs to be identified in the mantle and komatiite related carbonados. Two different crystallization histories are proposed for diamondites which are; fluids/melts derived from upper mantle or fluids/melts that had a contribution of crustal material. At the moment it is more likely that the formation fluids of E -and P-type diamondites are derived from the upper mantle because there are more evidence that is consistently supported by both eclogitic -and perioditic diamondites. Regarding the websteritic diamondites their formation fluids are more likely to have a crustal origin as all evidence suggest this origin.

Aims: One of the aims of this study was to investigate if diamondites have the same crystallisation histories as monocrystalline diamonds. To determine a relationship, or lack thereof, between monocrystalline diamonds and diamondites could be valuable to the mining industry because this would help to predict the potential grade of kimberlite. Another aim was to determine the origin of carbonado. This is important to determine because carbonados are important as abrasives in the industries and if we know their origin we would know more about the formation mechanisms. This is useful information in order to make synthetic carbonado which could be cheaper than prospecting for natural carbonado.

Keywords: diamondite, polycrystalline, carbonado

Supervisors: Carl Alwmark and Leif Johansson

Subject: Bedrock geology

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Bildningsmekanismerna för Polykristallina diamanter: diamonditer och carbonados

Ariam.M Aguilera Pradenas

Pradenas Aguilera, A., 2015: The formation mechanisms of Polycrystalline diamonds: diamondites and carbonados. *Dissertations in Geology at Lund University*, No. 459, 23 pp. 15 hp (15 ECTS credits).

Sammanfattning: Det finns många typer av diamanter som till exempel monokristallina, polykristallina och belagda/fibrösa, vilka har egna karaktäristiska drag. Polykristallina diamanter kan delas in i två huvudgrupper carbonado och diamonditer, som i sin tur delas in i 3 typer; eclogitic, perioditic -and websteritic. Litteratur studien består av två delar, i den första delen undersöks bildningsmekanismen av diamonditer för att se om de har annorlunda kristalliserings mekanism än monokristallina diamanter. Förståelse för denna process kan vara viktig inom gruvindustrin. Den andra delen granskade härkomsten av carbonado som är viktiga inom industrin för slipmedel. Olika härkomster för carbonado har föreslagits bland annat meteoritnedslag, uranium-rika kolhaltiga sediment och manteln. För närvarande teorin som är mest sannolikt är manteln som stödjs av texturella observationer såsom fluid inklusioner och kristallografisk riktning. För att kunna veta att denna teori stämmer med säkerhet behöver man hitta en kolkälla i manteln och komatiite relaterade carbonados. Två olika kristalliserings mekanismer föreslås för diamonditer vilka är; fluider/smältor som härstammade från övre mantel eller fluider/smältor som hade ett bidrag från jordskorpans material. För närvarande är det mest troligt att bildnings fluiderna för E -and P-typ diamonditer härstammar från övre manteln. Vad gäller websteritic diamonditer bildades de från övre mantel fluider.

Nyckelord: diamonditer, polykristallina, carbonado

Handledare: Carl Alwmark and Leif Johansson

Ämnesinriktning: Berggrundsgeologi

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1 Introduction

Diamond properties and crystallisation origin

Diamond is a rare, cubic carbon mineral, formed when atoms bond with four other atoms at a distance of 1.544 x 10^{-10} meter creating a tetrahedral arrangement (Fig.1; Rossi 2007; Harlow and Davies 2005). This structural arrangement combined with the C–C bond, a covalent bond, accounts for the majority of the diamond properties like thermal conductivity, extreme hardness and compactness (Harlow and Davies 2005; Lodish et al. 1999). Diamonds possess other properties such as electrical insulation, transparency and a high refractive index. They are electrical insulators and transparent over a great part of the electromagnetic spectrum, due to the covalent bonding that causes a large band gap of 5.5 electron volts (eV) (Harlow and Davies 2005). A band gap is a gap between the valence band (where the electrons are held in place) and the conduction band (where the electrons can move around freely) and when materials are electrical insulators this gap makes it hard for an electron to get invigorated enough to jump from one to the other, which means they block the flow of electricity (Chandler 2010). The high refractive index of 2.41 is rare for a material with a low atomic number (^{12}C); the index is the result of electrons creating a dense area (Harlow and Davies 2005).

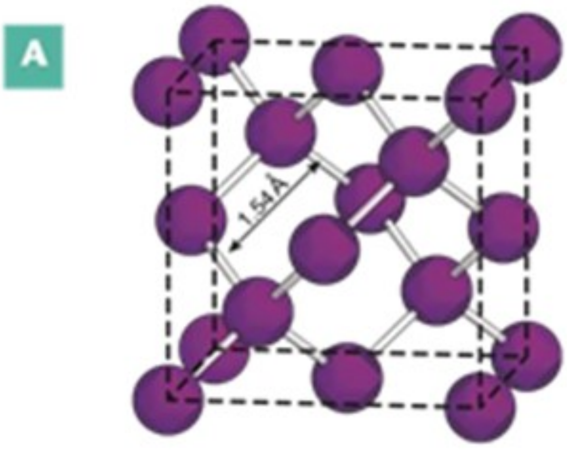
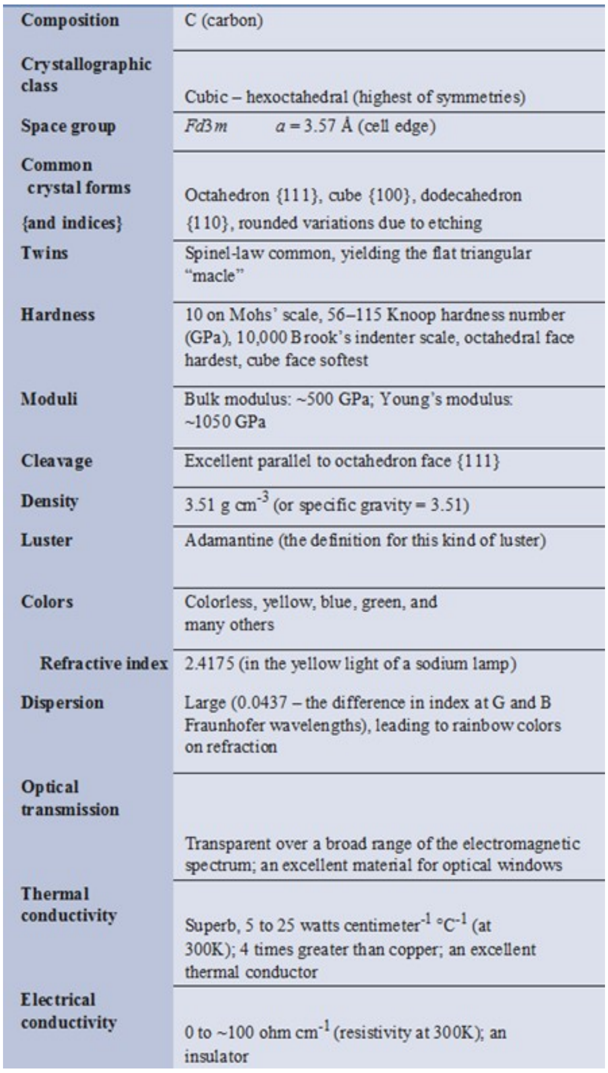


Fig. 1. A crystallographic model of the diamond structure displaying the tetrahedral arrangement with atoms distances of 1.544 x 10^{-10} meter (Harlow and Davies 2005).

A pure diamond is colourless but diamonds can have different colours as a result of the presence of other elements (Table 1; Harlow and Davies 2005).Diamond normally crystallized in an environment with high pressures (more than 40 kbars) and temperatures above 950°C, conditions found in the lithospheric mantle at depths between 150 and 250 km (Harlow and Davies 2005; Shirey and Shigley 2013). However some diamonds (5 % of all diamonds analysed worldwide) have been found to have formed at a much greater depth than 250 km (up to 800 km depth) (Stachel 2001; Stachel et al. 2005; Harte 2010). Due to the high pressure in which diamonds crystallized the density of diamonds is high; 3.51g cm^3 (Cartigny 2005).

Table. 1. A summary of diamond properties (Harlow and Davies 2005).



Composition	C (carbon)
Crystallographic class	Cubic – hexoctahedral (highest of symmetries)
Space group	$Fd3m$ $a = 3.57$ Å (cell edge)
Common crystal forms {and indices}	Octahedron {111}, cube {100}, dodecahedron {110}, rounded variations due to etching
Twins	Spinel-law common, yielding the flat triangular “macle”
Hardness	10 on Mohs’ scale, 56–115 Knoop hardness number (GPa), 10,000 Brook’s indenter scale, octahedral face hardest, cube face softest
Moduli	Bulk modulus: ~500 GPa; Young’s modulus: ~1050 GPa
Cleavage	Excellent parallel to octahedron face {111}
Density	3.51 g cm^{-3} (or specific gravity = 3.51)
Luster	Adamantine (the definition for this kind of luster)
Colors	Colorless, yellow, blue, green, and many others
Refractive index	2.4175 (in the yellow light of a sodium lamp)
Dispersion	Large (0.0437 – the difference in index at G and B Fraunhofer wavelengths), leading to rainbow colors on refraction
Optical transmission	Transparent over a broad range of the electromagnetic spectrum; an excellent material for optical windows
Thermal conductivity	Superb, 5 to 25 watts $centimeter^{-1}$ $°C^{-1}$ (at 300K); 4 times greater than copper; an excellent thermal conductor
Electrical conductivity	0 to ~100 ohm cm^{-1} (resistivity at 300K); an insulator

As previously mentioned, diamonds possess extreme hardness, this property enabled it to withstand weathering which makes it a tool for investigating the mantle (Harlow and Davies 2005). Furthermore they are also used as gems and as super abrasives. In the industrial market of super abrasives, it is estimated that 800 million carats are used annually yielding a profit of US $ 10^9 (Harlow and Davies 2005).

Kimberlitic -and lamproitic magmas

The majority of diamonds were brought to the surface through pipes during intrusion of kimberlitic -or lamproitic magmas (Fig 2; Nixon 1995). Kimberlitic -and lamproitic magmas formed at a depth that allowed for the transport of diamonds but they also prevented them from transforming into graphite and dissolving in the magmas due to fast ascent (Cartigny 2005). The greater part of kimberlites and lamproites are barren of diamonds. The diamondiferous magma normally intruded stable continental crust (older than 2500 Myr) (Robb 2005). Nevertheless some diamondiferous magma have also intruded adjacent regions particularly associated mobile belts (Ferrini and Sassano 1999). As a result of kimberlites and lamproites normally being younger than diamonds, they do not have to be linked to the origin of diamonds, indicating that they are just the pathways through which diamonds reached Earth's surface (Ferrini and Sassano 1999).

Kimberlites and lamproites contain the following main minerals; olivine, clinopyroxene, phlogopite and apatite but they differ in accessory minerals (Ferrini and Sassano 1999). These rocks can have the same origin in the mantle which is the enriched mantle type 1 (EM1) but kimberlites have also been derived from another part of the mantle, the depleted mantle (has

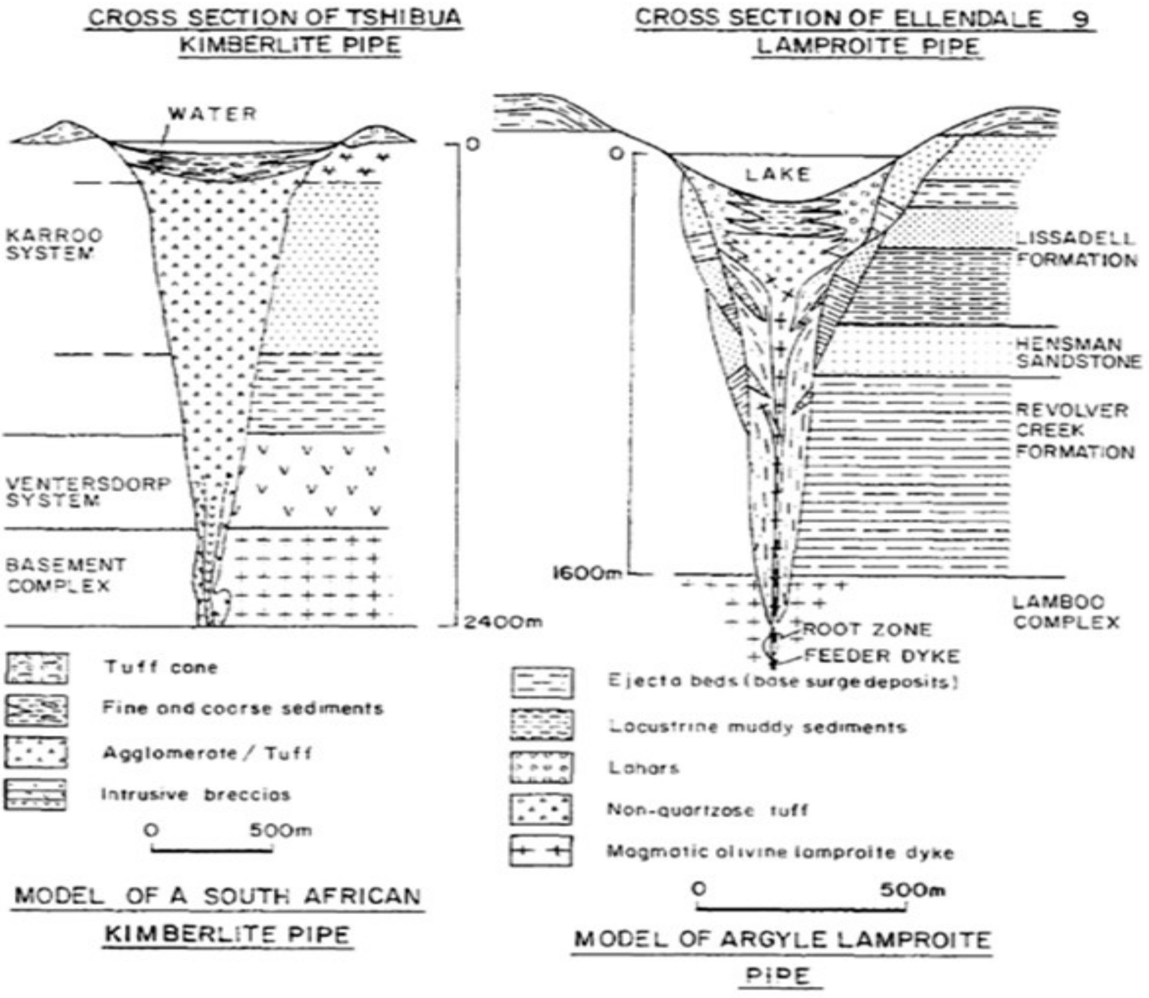


Fig. 2. A model suggestion for kimberlite -and lamproite pipe (Nixon 1995).

low $^{206}Pb/^{204}Pb$, $^{87}Sr/^{86}Sr$ and high $^{143}Nd/^{144}Nd$) which has experienced one or more periods of fractionation involving extraction of basaltic magma (Jackson 2008; Kononova et al. 2010; Condie 2001). Lamproites are usually greenish-grey in colour and ultrapotassic whereas kimberlites are more or less potassic with a bluish or greyish-brown colour. Furthermore lamproites differ from kimberlites by having a higher amount of Silicon, Iron and trace elements Zirconium, Niobium, Strontium, Barium and Rubidium. Another difference between kimberlites and lamproites is that lamproites have a lower amount of Magnesium, Iron and Calcium. Both of these rocks display similar forms when found, horn -or core-like masses and they can sometimes be found in the same diamondiferous pipes in spite of belonging to intrusive phases of different ages (Ferrini and Sassano 1999).

Diamonds can be found either as single crystals in the kimberlitic matrix or as minerals within xenoliths of peridotite, eclogite or websterite which are named P-E-W-type diamonds respectively (Robb 2005; Mikhail 2013). Regarding diamonds found within xenoliths they can either be transported by kimberlitic -or lamproitic magma. P-E-W-type are not only host rocks for diamonds that are found as minerals within them but also for other diamonds that have mineral inclusions reflecting similarities with either periodite, eclogite or websterite (Mikhail et al. 2013; Carlson 2005). If the mineral inclusion in the diamond is Cr-pyrope garnet, diopside, enstatite, chromite or olivine the nature of the host rock (paragenesis) will be perioditic. In order to establish eclogitic paragenesis pyrope almandine garnet, omphacite, coesite or kyanite has to be present as mineral inclusion in the diamond (Carlson 2005). The websteritic paragenesis is rare and is not clearly defined because this suite include both "perioditic" and "eclogitic" inclusions (Stachel and Harris 2008; Aulbach et al. 2012). The "perioditic" inclusions in the websteritic paragenesis have unusually low Mg# (Gurney et al. 1994) while the "eclogitic" garnet inclusion have low Ca content and " eclogitic" clinopyroxene inclusions have elevated Mg# and Cr# (Stachel and Harris 2008).

Mantle diamonds

The majority of diamonds found on Earth were carried to the surface by either kimberlitic or lamproitic magmas and are called mantle diamonds but there are other types of diamonds that were not carried this way to the surface which are for are for example polycrystalline diamonds; carbonado and meteoritic nanodiamonds (Huss 2005; Ogasawara 2005; Mikhail et al. 2013).

Diamonds that are derived from the mantle can be divided into three main morphological groups: polycrystalline, monocrystalline and coated or fibrous diamond (Mikhail et al. 2013).

Polycrystalline diamonds

Polycrystalline diamonds can be divided into two groups: diamondites that are mantle diamonds associated with kimberlites and carbonados, alluvial diamonds not found in association with kimberlites (Heaney 2005; Mikhail et al. 2013).

Polycrystalline diamonds; diamondites

Diamondites are fine-grained (<100 µm) to coarse grained and consist of primarily of diamond of different sizes that are randomly oriented with inclusions and intergrowths of pyrrhotite, garnet, clinopyroxene, magnetite, Fe-carbides, iron, ilmenite and rutile (Fig 3; Mikhail et al. 2014).

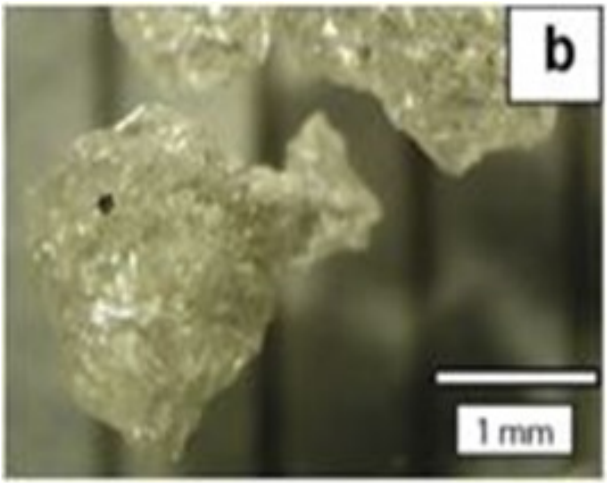


Fig. 3. A diamondite sample (Mikhail et al. 2013).

The most dominant paragenesis in this type of diamond is websteritic where garnet is the dominant mineral inclusion therefore referred as websteritic garnet type diamonds (Fig 4; Mikhail et al. 2013). In addition, diamondites can also consist of perioditic paragenesis but this type is more dominant in monocrystalline diamonds (Fig 4; Mikhail et al. 2013). Diamondites does not always consist of one paragenesis several analyses have shown a mixed eclogitic and perioditic paragenesis where orange garnet with low Cr and moderate Ca content represent the eclogitic paragenesis and pink garnets with high Cr and low Ca content characterize the perioditic paragenesis (Gurney and Boyd 1982; McCandless et al. 1989; Kirkley et al. 1991).

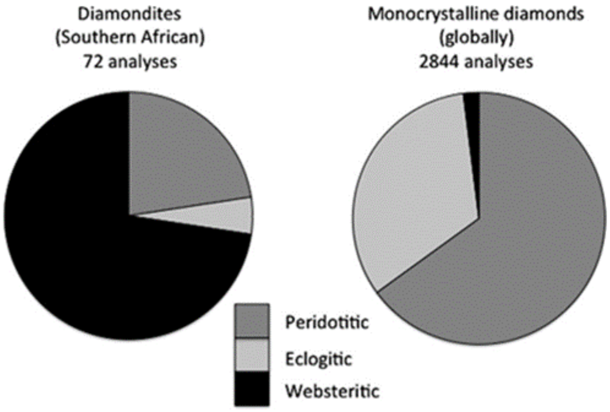


Fig. 4. Distribution of paragenesis in diamondites and monocrystalline diamonds (Mikhail et al. 2013).

The carbon isotope distribution in diamondites have two major modes at ca -5‰ and -20‰ (Fig 5b; Mikhail et al. 2013) whereas the other types of diamonds monocrystalline and coated show similar carbon isotope distribution with one major mode at ca -5‰ (Fig 5a and c; Mikhail et al. 2013). A significant observation in the carbon isotope distribution of diamondites is the low -20‰ values which represent the P -type diamondites, these values are rare for perioditic mantle material (Mikhail et al. 2013). The diamondites have also low ^{3}He/^{4}He ratios implying little contribution from primordial mantle-derived ^{3}He and ^{21}Ne/^{22}Ne ratios that is consistent with the crustal nucleogenic production ratio (Burgess et al.1998; Honda et al. 2004).

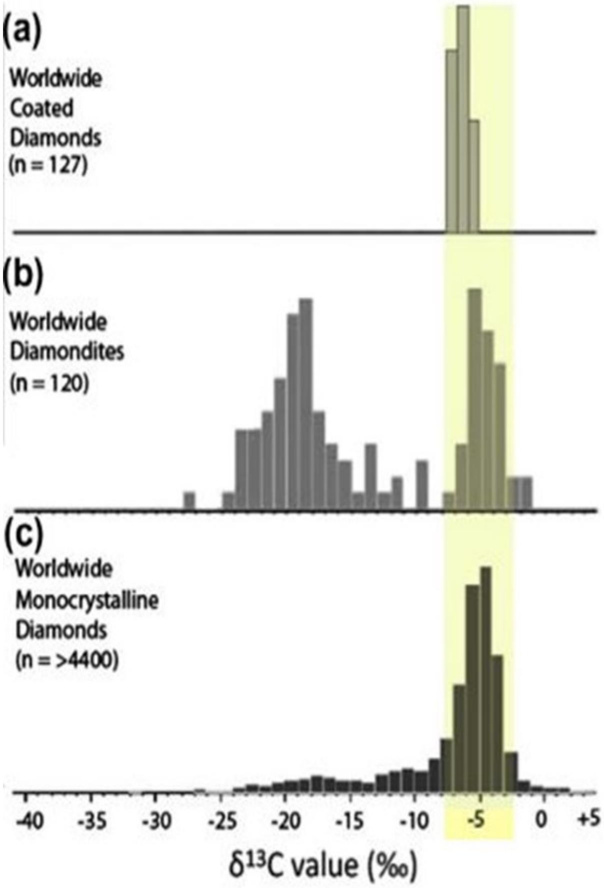


Fig. 5. Carbon isotope distributions for different types of diamonds. The yellow bar represent the mean mantle (Mikhail et al. 2013).

Diamondites are different from coated -and monocrystalline diamonds in many aspects; mineral paragenesis, morphology, carbon isotope compositions, nitrogen isotope compositions, and inclusion compositions (including micron-nano inclusions) (Jacob et al. 2000; Mikhail et al. 2013). Although there are many petrological differences between diamondites and coated/ monocrystalline diamonds there are few studies on diamondites. Diamondites compared with other morphological groups are not rare, they make up to 50% of the total production of Orapa diamond which is one of the world's most productive diamond mines (Mikhail et al. 2013). Some researches (Burgess et al. 1998; Honda et al. 2004; Mikhail et al. 2013; Kurat and Dobosi 2000; Maruoka et al. 2004; Gautheron et al. 2005) argue that the diamondites crystallization processes are distinctly different from monocrystalline diamonds and propose different theories.

Monocrystalline diamonds

Monocrystalline diamonds (Fig 6; Tappert and Tappert 2011) formed through precipitation from a metasomatic fluid within solid eclogite or periodite and sometimes in websteritic compositions (Mikhail et al. 2013). W-type monocrystalline diamonds constituted only 2% of 2844 analyses (Fig.4; Mikhail et al. 2013) obtained until 2013 which means that the majority of monocrystalline diamonds are either P -or E-type diamonds.

Fig. 6. Two monocrystalline diamonds (Tappert and Tappert 2011).

The low $\delta^{13}C$ values <-10 ‰ in E -and W-type diamonds are commonly explained by the recycling of crustal organic carbon by subduction into the mantle (Stachel et al. 2009). Another explanation for the low values could be a high-temperature stable isotope fractionation in the mantle which also has been suggested for diamondites (Heaney et al. 2005).

Coated diamonds

Coated diamonds (Fig 7; Wang et al. 2003) are cubic and consist of a mixture of polycrystalline-monocrystalline diamond where the mono crystals have been overgrown by a thick turbid polycrystalline coat laden with micro-inclusions of fluid (Shirey and Shigley 2013; Burgess et al. 1998). If the coat is composed of elongated forms of diamond then it will exhibit a fibrous structure and can be termed fibrous diamond (Shirey and Shigley 2013). The coated diamonds exhibit a light- to dark grey colour depending on the nature and abundance of the micro-inclusions (Wang et al. 2003). Some observations have indicated that coated diamonds crystallized from fluids that are rich in C, O, H, N and low Si (Mikhail et al. 2013).

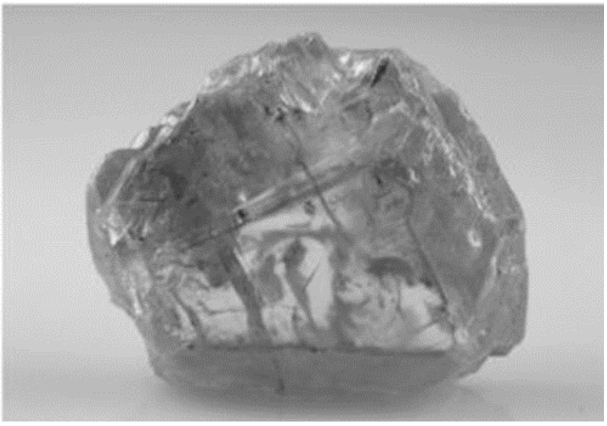


Fig. 7. A coated diamond (Wang et al. 2003).

Placer diamond

Polycrystalline diamonds; carbonados

Carbonados (Fig 8; Ketcham and Koeberl 2013) are hard black-grey polycrystalline masses (of 8-12 mm in size) consisting of sintered diamond grains usually below 20μm and up to a few hundred micrometers in size (Cartigny 2010; Kogel et al. 2002). Carbonados normally occur in alluvial placer deposits in Brazil and central Africa (Cartigny 2010). An alluvial placer deposit forms by selective concentration of heavy minerals that have eroded from a bedrock deposit within a river system (Mudaliar et al. 2007; Stanaway 2012).

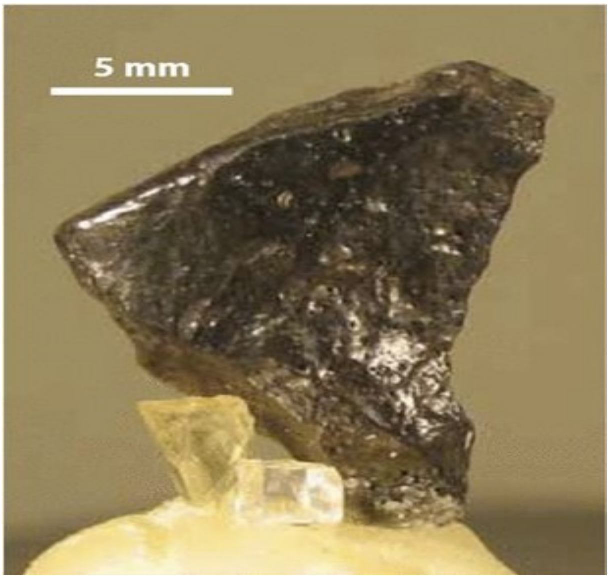


Fig. 8. Dark carbonado diamond with samples of calcite, apatite and almandine garnet (Ketcham and Koeberl 2013).

Carbonados are used for industrial purposes primarily grinding and drilling (Cartigny 2010). They are different from other mantle diamonds by their low $^{13}C/^{12}C$ isotope ratios ($\delta^{13}C$ values ranging from -21‰ to -32‰, with major modes at -24‰ and -26‰), high porosity, absence of mantle derived mineral inclusions and textural variation (Ishibashi et al. 2012; Ketcham and Koeberl 2013). The most common texture is porphyritic which consist of small (10–250 µm) euhedral diamonds cemented together by smaller (<1 µm) microdiamonds (De et al. 1998; Petrovsky et al. 2010; Ketcham and Koeberl 2013). Subplanar dislocations can sometimes be observed in the smaller crystals and have been interpreted as defect lamellae. The larger crystals have normally no defect lamellae (Ketcham and Koeberl 2013).

The most abundant inclusion in carbonado is the hydrated phosphate florencite, however more than 30 minerals have been identified for example orthoclase, quartz and kaolinite which are of crustal origin. The inclusions typically found in diamonds associated with kimberlite that are of mantle origin have never been found in carbonados (Heaney et al. 2005). Lastly low $^{3}He/^{4}He$ ratios and high ^{4}He content have been observed interpreted being caused by a subduction of crustal component (Basu et al. 2013; Robinson 1978).

2 Methods

This literature study was focused on finding scientific information about diamondites and the characterisation of formation fluid. Research was also directed on finding information about carbonado origin. Before focusing on diamondites and carbonados a general investigation of diamonds was performed.

The sources used for the literature study was geology books and the database engineering village.com for finding the scientific articles.

3 Results

As previously mentioned, diamondites were brought to the surface by kimberlites and some workers for example Honda et al. (2004) and Maruoka et al. (2004) consider them to have different crystallization histories than monocrystalline diamonds. Several theories are proposed to explain their crystallization histories. Some researchers like Burgess et al. (1998) and Honda et al. (2004) suggest that there is a contribution of crustal material involved in the fluid when they crystallized while others suggest that it crystallized from upper mantle melts/ fluids that contained a carbonatitic component (Kurat and Dobosi 2000).

Polycrystalline diamondite formation mechanism

Kurat and Dobosi (2000) investigated the character of the formation fluid for diamondites on the basis of trace element abundances. In the study two diamondites were selected with different mineral assemblages, one had a lilac garnet and green clinopyroxene assemblage while the other had an orange garnet assemblage. Those assemblages are similar to garnet inclusions in diamonds and garnets from known upper mantle eclogites and peridotites. The source of the diamondites samples is unknown but it was assumed to be from Botswana (a country in Africa)since similar samples have been described from this place before.

In this study severe contamination of fluid inclusions were found during analysis by high trace elements signals (Fig 9). They detected that the fluid was rich in LREE, Sr, Ba, U, Th, Rb, Nb and Ta (Fig 10) in both garnets. Since these garnets are similar to garnets known from upper mantle eclogites and peridotites and have same content of LREE, Sr, Ba, U, Th, Rb, Nb and Ta, Kurat and Dobosi (2000) suggested they formed from upper mantle fluids of similar origin. The only difference in chemical compositions between "eclogitic" and "peridotitic'" garnets are the Cr and Ti content. The perioditic paragenesis has Cr_2O_3=5.2wt% and TiO_2=0.27wt% while the eclogitic paragenesis has lower Cr_2O_3=0.7wt% and higher TiO_2=0.61wt%. The Fe/Mg ratio on the other hand is about the same for both diamondites 0.82 and 0.84wt% respectively. The result of the low Fe/Mg ratios in both diamondites, suggest for a peridotitic source of the fluids.The high content of elements U, Th and Ta (High Field Strenght Elements) has been explained. to be caused by trace element partitioning between carbonates and silicates which implicates an involvement of carbonatitic com-

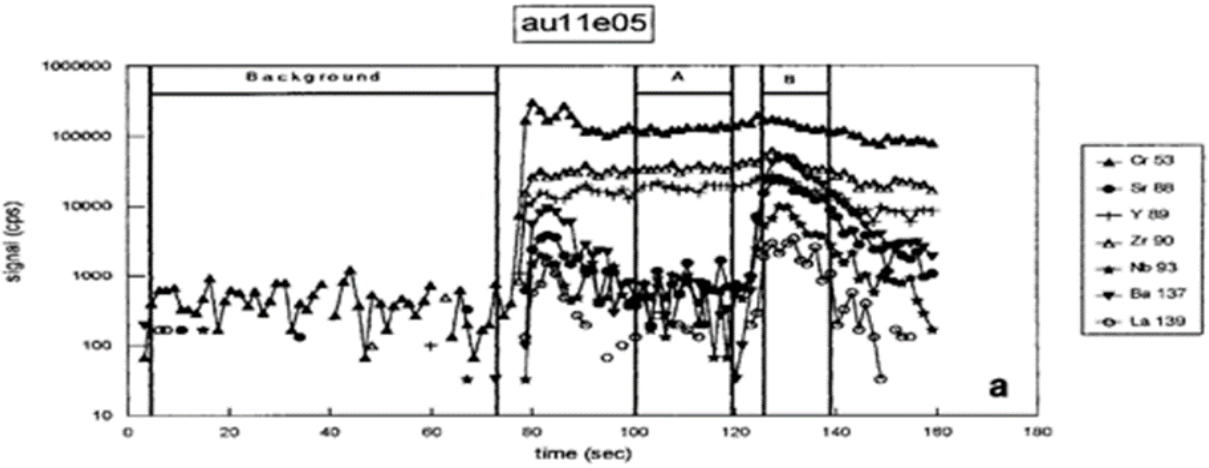


Fig. 9. Selected time resolved trace element signals obtained by the LA-ICP-MS for Dia 016 garnet. Observe the abrupt increase in count rate at ~125 seconds. The calculations that were used for analyses of garnet and fluid-rich garnet are marked A and B, respectively (Kurat and Dobosi 2000).

ponent in the formation fluids/melts of the diamondites. Due to the results in this study they concluded that the diamondites crystallized from upper mantle fluid/melts that had a carbonatitic component. (Kurat and Dobosi 2000).

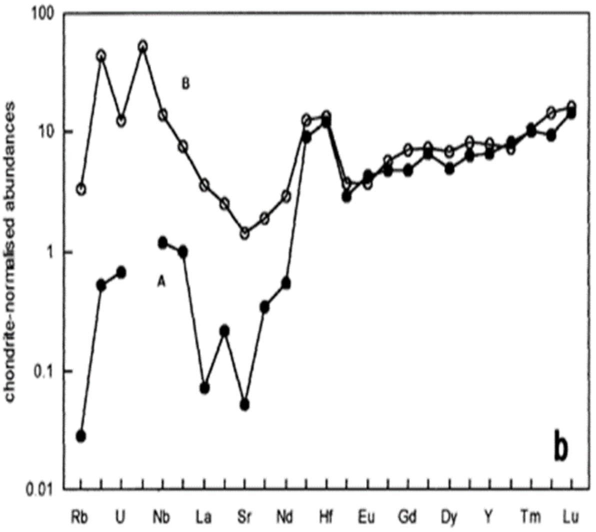


Fig. 10. Chondrite-normalized (Palme 1988) trace element abundances calculated for fluid-poor and fluid-rich garnet in Dia 016 from analysis periods (A and B) chosen in Fig.9. In this diagram the fluid is very rich in highly incompatible elements (Nd to Rb) (Kurat and Dobosi 2000).

Honda et al. (2004) investigated the noblegas geochemistry in ancient mantle by combining vacuum crushing and step-heating experiments and examining full suite of noble gas isotope and elemental abundances. Investigating the noble gas geochemistry helps to understand the structure of the Earth’s mantle and create a coherent model for its evolution. To investigate the noble gas geochemistry of ancient mantle four polycrystalline diamondites of eclogitic paragenesis from the Jwaneng kimberlite pipe (Botswana, a country in Africa) were used because diamonds have several characteristics that makes them useful as containers of mantle noble gases, for example they are extreme hard. In this study the neon isotope diagram (of ^{21}Ne/^{22}Ne–^{20}Ne/^{22}Ne) reveals that three polycrystalline diamondites samples are close to crustal nucleogenic neon values (Fig 11) which could mean that the nucleogenic neon observed in the Jwaneng diamondites possible produced in the crust and subsequently incorporated into the samples by subduction-related processes.Another result from this study that could support subduction- related processes is excess ^{129}Xe. The excess ^{129}Xe observed in the samples can be explained by addition of crustal nucleogenic xenon (which was produced from neutron capture of tellurium in the crust and then incorporated into the samples by subduction- related processes) but further confirmation is required to establish this process.

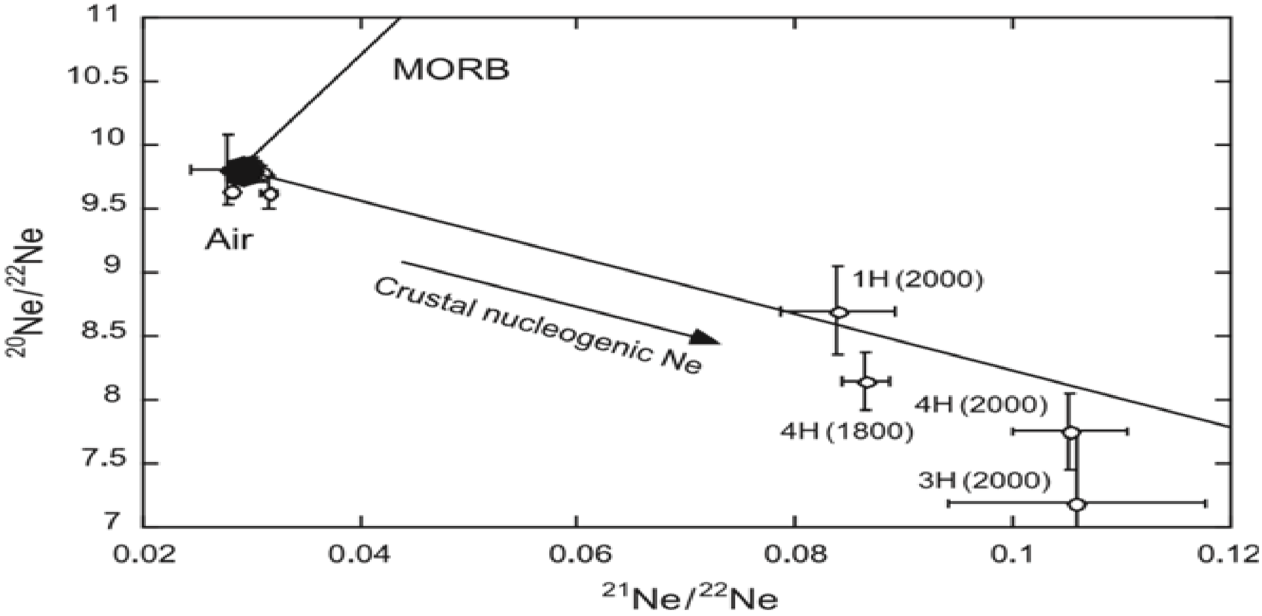


Fig. 11. Neon isotope diagram showing results from four diamondites samples, where three diamondites samples are close to crustal nucleogenic Ne (Honda et al. 2004).

One last study that can be mentioned that support the theory of contribution of crustal material (by subduction of oceanic of oceanic lithosphere beneath a stable craton) in the formation fluid of diamondites was done by Mikhail et al. (2013), where they studied C-N isotope compositions and N-concentrations for 20 diamondites (12 websteritic and eight periodititic). The $\delta^{13}C$ values range from -28.5‰ to -4.6‰ for P-type garnet diamondites and -22.9‰ to -5.5‰ for W-type garnet diamondites. The $\delta^{15}N$ values obtained show a range from -6.1‰ to +22.6‰ where the highest $\delta^{15}N$ (negative $\delta^{15}N$ values is characteristic of mantle nitrogen) values belong to P-type diamondites. Most of this data, the C-N isotope compositions overlap with the C-N isotopic field for crustal organic carbon (Fig 12). There is also mantle contribution this was estimated from two samples of each type (periodititic and websteritic) $\delta^{13}C$ values of -4.6‰ and -5.5‰ respectively and $\delta^{15}N$ values of +5.2‰ and +2.7‰ respectively. The presence of mantle-carbon was explained to have been caused from the growth of polycrystalline diamond that acted as a nuclei for further diamond formation, absorbing any surrounding mantle derived carbon with $\delta^{13}C$ value of-5±3.

Most samples show N-concentrations below the field for pelagic organic materials, only three W-type diamondites were above 1000 ppm plotting in the field for pelagic organic materials indicating a pelagic (crustal) origin for the nitrogen found in these diamondites. Why most samples show N-concentrations below the field for pelagic organic materials can be explained in two ways. One way of explaining this is that nitrogen in the crustal organic material will be fractionated relative to carbon during subduction this will increase the C/N ratio of the subducted component greatly to lower N-concentrations. Another explanation is that not all of the diamondites forming carbon and nitrogen is of crustal origin, giving values that do not plot on the field for crustal material.

One of the studies that support the theory that diamondites crystallized from upper mantle melts/fluids is Gautheron et al. (2005). In this study they analyzed noble gas composition and the isotopes of C and N on six polycrystalline diamonds (four belonged to either periodititic-or eclogitic paragenesis). This analysis obtained radiogenic isotope ratio of helium R/Ra=0.14 ─ 1.29 (R=$^{3}He/^{4}He$ ratio, Ra=present-day atmospheric $^{3}He/^{4}He$ ratio; Anderson et al. 2006), $^{21}Ne/^{22}Ne$ ratios up to 0.0534 ccSTP/g, $^{40}Ar/^{36}Ar$ ratios 477 ─ 6056 ccSTP/g and $^{129}Xe/^{130}Xe$ ratios 6.54 ─ 6.91 ccSTP/g. The Ne ratios and the Ar ratios found in this study are similar to the ratios found in the mantle. The lowest

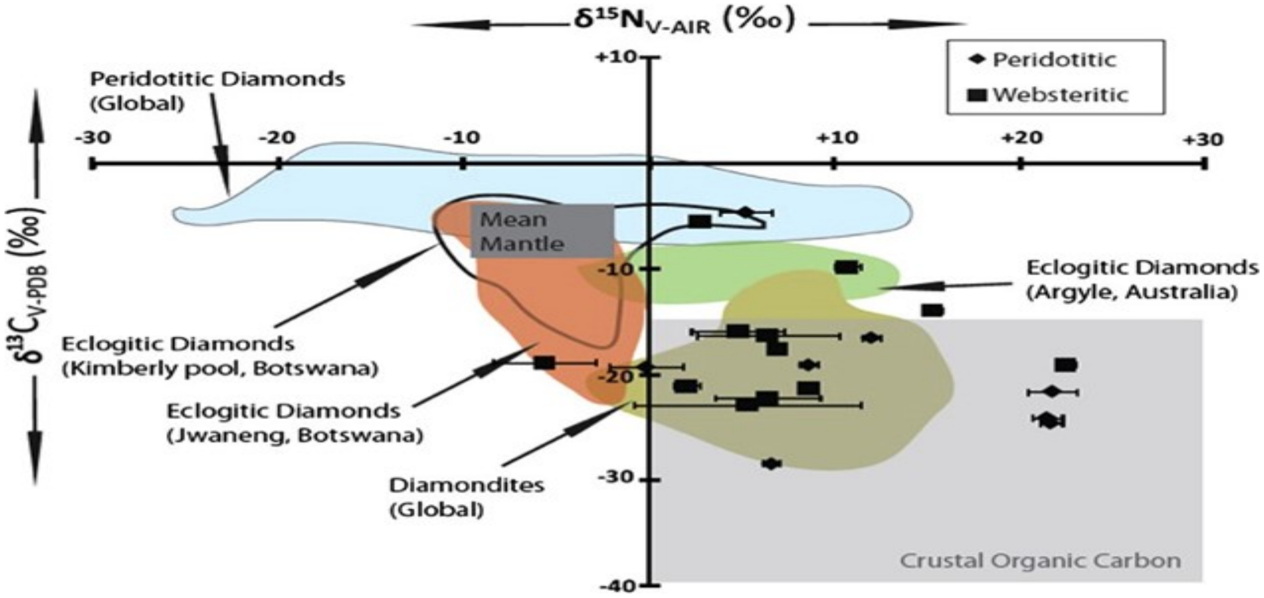


Fig. 12. A diagram for various mantle and crustal reservoirs with the samples (perioditic and websteritic) from the Mikhail et al. (2013) study. The fields are derived from the following: eclogite diamonds (Argyle, Australia Boyd and Pillinger 1994; Jwaneng, Botswana Cartigny et al. 1998; Kimberly pool, South Africa Cartigny et al. 1999), mean mantle (Cartigny 2005) other diamondites (Gautheron et al. 2005; Shelkov 1997), perioditic diamonds (Fuxian, China Cartigny et al. 1997; Orapa, Botswana Cartigny et al. 1999; Alluvial diamonds from Namibia Cartigny et al. 2004) and pelagic organic material (Thomazo et al. 2009).

value obtained in ^{129}Xe/^{130}Xe ratio is analogous to atmospheric source which could be caused by atmospheric contamination. Maruoka et al. (2003) also support that diamondite crystallized from upper mantle melts/fluids. They investigated the carbon isotope abundances from diamondites with periioditic -and eclogitic garnet. 35 diamondites of unknown origin were analyzed. 13 of the 35 diamondites were P-type diamondites and 19 were E-type diamondites; 3 did not have any inclusions. The δ^{13}C values obtained show a range from -3.2 to -27.9 ‰ and a peak around -18‰ for both periioditic and eclogitic diamondites. This peak could be explained by high temperature stable isotope fractionation (Rayleigh type) in an open system before diamondite formation. Partial oxidation of mantle CH_4 generated CO_2. This resulted in a mixture of ^{13}C-rich CO_2 and ^{13}C depleted CH_4 followed by ^{13}C-rich CO_2 reaction with olivine to form magnesite and clinopyroxene. Magnesite was subsequently removed from the system resulting in diamondites precipitation from ^{13}C depleted CH_4. Marouka et al. (2004) also support that the upper melts/fluids were carbonate rich because the CO_2 generated by partial oxidation in the mantle can incorporate carbonatitic fluids/melts.

An investigation that interpret their values to either be caused by upper mantle melts/fluids or crustal material is Burgess et al. (1998) study. For this research ten diamondites and eight carbonados were investigated. Six diamondites were of eclogitic paragenesis while the four others had unknown paragenesis. In this study He -and C-isotopes and U content was investigated. The values obtained from the diamondites were ^{3}He/^{4}He 0.1 ─ 3 Ra, bimodal δ^{13}C values -6 and -20‰ (Fig.13) and U content 26-160 ppb. The low values of ^{3}He/^{4}He and δ^{13}C and high U content could have been influenced by subduction of crustal material. However the low δ^{13}C value could also be explained by mantle C-isotope fractionation during growth of the micron-sized diamond crystallites and if this was the case then the low ^{3}He/^{4}He ratio cannot longer be explained by subduction of crustal material and another process is required to explain this. The low isotope ^{3}He/^{4}He ratio could then be explained by α-implementation of ^{4}He by U, Th rich minerals. The latter process and the mantle C-isotope fractionation suggest that the character of the formation fluid of diamondites came from the upper mantle.

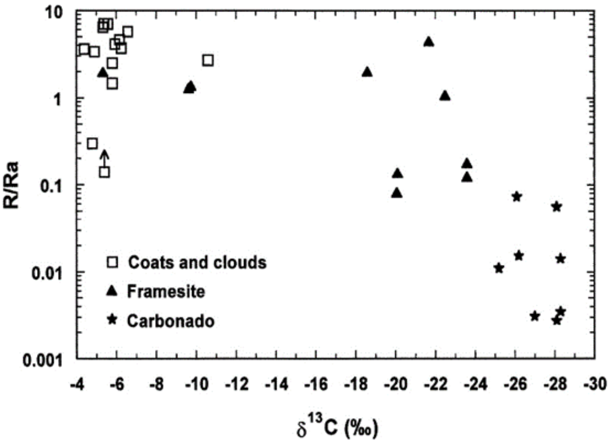


*Fig. 13.*Distribution of the ^{3}He/^{4}He vs δ^{13}C compositions in carbonados (Burgess et al. 1998).

Carbonado origin

It is unclear where carbonado formed and several hypothesis explaining their origin are proposed. Smith and Dawson (1985) propose that carbonado has a meteorite impact origin. They argue that a meteorite impact caused an impact metamorphism which explained carbonado characteristics like carbon isotope ratio (δ^{13}C -27.8‰) and inclusions of crustal materials. This could also explain londsalite an impact generated mineral which was present in one carbonado sample (Smith and Dawson 1985). However no known evidence for meteorite impact around the Brazilian carbonado deposits have been observed (Ozima and Tatsumoto 1996).

Another hypothesis is that they formed within uranium-rich carbonaceous sediments byimplementation of α-particles (Kaminsky 1991; Ozima et al. 1991). One argument for this hypothesis is the existence of U-rich carbonaceous sediments that contain diamonds. Another argument that support this hypothesis is high levels of polycyclic aromatic hydrocarbon, PAH (0.0020-0.0039%) which supports for a crustal carbon source but is has not been confirmed yet that these levels are primary and not secondary. If these values are primary it could support a crustal carbon source. Finally great amount of parentless fission ^{135}Xe has been identified, which is only achievable if the carbonaceous precursor of diamonds (and the diamonds itself) were formerly part of a material that was rich in U and finely dispersed over time (Daulton and Ozima 1996).

A mantle origin for carbonados has been rejected early due to several factors; their C- isotope data is closer to organic matter than typical upper mantle values, they are absent in kimberlites and lamproites and mineral inclusions that are commonly found in mantle diamonds for example garnet are absent in carbonados. Even though a mantle origin has been rejected, Cartigny (2010) obtained results that could be explained by mantle origin. He examined diamonds from the Dachine komatiite that have C-N isotope compositions, -32.6 to +0.15‰ (mode at ~-27‰) and -4.1 to +6.9‰ (average ~+2.1±2.9‰) respectively identical to those found in carbonado therefore Cartigny (2010) developed a model linking carbonado to komatiite magmas. In this model the sintering of diamond aggregates that form carbonado was developed within the hot komatiite magma on its way to the surface. The sintering of diamond aggregates formed to komatiite-related high temperatures perhaps up to 1600°C for short periods of time. The high temperatures of komatiite is the cause why carbonados are present in these rocks and not in the kimberlites. The transport of the komatiite together with the porous nature, old age - and metamorphism of carbonado caused alteration in the original inclusions and were replaced by crustal inclusions.

The low δ^{13}C (~-27‰) value in the Cartigny (2010) study is different from the convective upper-mantle δ^{13}C (~-5‰) value and is most likely to been inherited in the transition zone as the other suggestion, incorporation of subducted organic carbon in komatiite failed to explain this value because their obtained depth <90 km for the subducted organic carbon is to shallow to account for occurrence of diamond (is stable ~150 km depth). The transition zone is proposed because it yield eclogitic diamonds (transition diamonds). The transitions diamonds peculiar characteristic, the low δ^{13}C values that are different for different places, Juina (Brazil), Jagersfontain and Kankan (from southern and western african cratons respectively) for example show C isotopic modes of ~-8‰, ~+1‰, ~-21‰ respectively has not successfully been explained. Furthermore these values are also distinct from the shallower upper mantle value of ~-5‰.

Another study that propose a mantle origin is Ishibashi et al. (2012) where they studied the growth conditions of carbonado. Their observations revealed among others presence of: a certain crystal size distribution, fluid inclusions and {111} (a plane in the crystallographic structure) growth steps along grain boundaries. The crystal size distribution (Fig 14) pattern is similar in shape to those rapidly formed crystal in liquid media. The presence of fluid inclusions is supported by a negative crystal (an octahedral void) and isolated voids in single diamond crystals. They are interpreted to be fluid inclusions because they are found isolated thus is consistent with one of the mechanism that form fluid inclusion. Another argument explaining why they are interpreted to be fluid inclusions is the fact that they are primary texture since they are surrounded by the {111} growth steps (primary texture because they are found at diamond–diamond boundaries) where they formed to compensate the crystallographic orientation disproportion among neighboring crystals and were filled by the coexisting fluid. Furthermore their smooth surfaces indicate that near-equilibrium was obtained between the fluid and the host diamond and the type of fluid was suggested by infrared absorption spectra bands to be water.

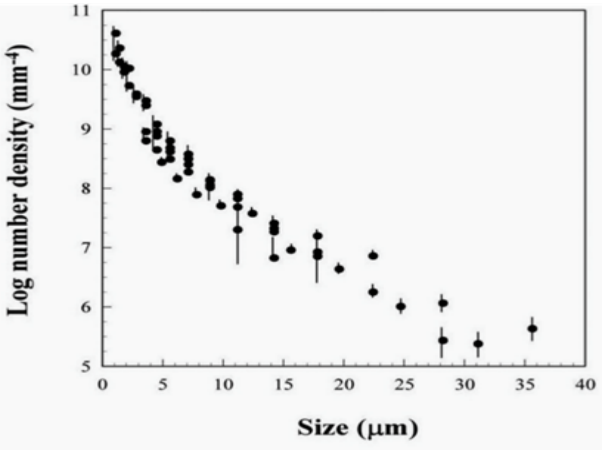


*Fig. 14.*Crystal size distribution of carbonado (Ishibashi et al. 2012).

4 Discussion

Diamondites

Crustal material can explain the following values; high δ^{15}N values (in websteritic -and perioditic diamondites), ^{13}C-depletion (in perioditic, eclogitic -and websteritic diamondites), high N-concentrations (in websteritic diamondites) low ^{3}He/^{4}He ratio and excess of ^{120}Xe isotopic compositions (in eclogitic diamondites) (Mikhail et al. 2013; Honda et al. 2004). However the ^{13}C depletion has also been suggested to reflect fluids/melts from the upper mantle (in eclogitic -and perioditic-type diamondites) and exactly which process that could have caused the ^{13}C-depletion is mantle C-isotope fractionation during growth of the micron-sized diamond crystallites. If the ^{13}C-depletion was caused by mantle C-isotope fractionation then the low ^{3}He/^{4}He ratio cannot longer be explained by subduction crustal material and another process is required to explain this, α-implementation of ^{4}He by U, Th rich minerals could cause low ^{3}He/^{4}He ratio (Maruoka et al. 2003; Burgess et al. 1998). This means that both mantle -and crustal components could have caused ^{13}C-depletion and low ^{3}He/^{4}He ratio.

There are two main arguments against the theory of contribution of crustal material. The first one is that eclogite diamonds with low δ^{13}C are ^{15}N-depleted which cannot reflect crustal material because crustal material are ^{15}N-enriched suggesting that they might not have a contribution of crustal material in their formation mechanism. However the majority of diamondites (of websteritic -and perioditic paragenesis) show crustal like ^{15}N-enrichment.

Another argument is that most monocrystalline diamonds with low δ^{13}C values have low N-concentrations. Those arguments are valid against the theory of contribution of crustal material for monocrystalline diamonds but diamondites are not monocrystalline diamonds and show ^{15}N-enrichment and high N-concentrations. Even though the diamondites could have a crustal contribution in the formation fluids they could also be closely related to monocrystalline diamond formation events as Mikhail et al. (2013) suggest. In the Mikhail et al. (2013) study the P -and

W-type garnets have REE-patterns that are analogous to eclogitic garnets. The REE-patterns were caused by incomplete mixing between volatile saturated eclogitic and perioditic melts, a process that is consistent with the model for websteritic garnet petrogenesis. This could mean that the diamondite formation (of eclogitic -and perioditic garnets) is closely related to websteritic monocrystalline diamond formation events. If a crustal contribution origin were to be determined they could at the same time be closely related to websteritic monocrystalline diamond formation events.

As there are many evidence for crustal contribution there are also several evidence thatsupport upper mantle melts/fluids for eclogitic -and perioditic diamondites which are; Ar (ratios 477 ─ 6056 ccSTP/g) and neon ratios ($^{21}Ne/^{22}Ne$ up to 0.0534 ccSTP/g) have similar values to mantle values, inclusions (the orange -and lilac garnet inclusions are similar to garnet known form the upper mantle eclogites and periodites), high abundances of incompatible trace elements and strong positive abundance anomalies of HFSEs (Kurat and Dobosi 2000; Burgess et al. 1998). The only values that upper mantle melts/fluids cannot explain are the high $\delta^{15}N$ values obtained in websteritic -and periodititic diamondites and the high N-concentrations obtained in websteritic diamondites.

At the moment it is more likely that the formation fluids of E -and P-type diamondites were derived from the upper mantle because there are more evidence that is consistently supported by both eclogitic -and perioditic diamondites while the other hypothesis evidence are not consistently supported by both eclogitic -and periodititic diamondites. To determine this origin with certainty a process or processes that implicate mantle-origin are needed to explain high $\delta^{15}N$ values obtained in periodititic diamondites.

Finally the websteritic diamondites formation fluids are more likely to have a crustal origin as all evidence mentioned suggest this origin.

Carbonado

Some researchers propose a meteorite impact origin for carbonado (Smith and Dawson 1985). Impact metamorphism caused by a meteorite impact could explain the light $\delta^{13}C$ values, magnetic inclusions, crustal inclusions, and the high polycyclic aromatic hydrocarbon levels observed in carbonados. Pervasive defect lamellae which implies plastic deformation has been observed in some TEM studies of carbonados. However this can also be observed in another type of polycrystalline diamond; framesites (mantle diamond), originally and experimentally. Defect lamellae is therefore not restricted to shock metamorphism and can not be used as an argument to support the impact scenario (Heaney et al. 2005). A clear argument against the meteorite impact scenario is the absence of londsalite, a mineral found in yakutite, an impact generated variety of polycrystalline diamonds (has only been found in one sample of carbonado (Smith and Dawson 1985). Another argument against this process is shock wave calculations which have indicated that the maximum size for a diamond formed by impact is ~1 cm (impact-generated diamonds are normally submillimeter in dimension and less cohesive than carbonado), thus is not consistent with the 8-12 mm size of carbonado (Kogel et al. 2003). Finally the typical absorption of 1.8 eV observed in impact generated diamond is not observed within carbonados (Sano et al. 2002).

Other researchers (Kaminsky 1991: Ozima et al. 1991) propose that carbonados formed within uranium -rich carbonaceous sediments by implementation of α-particles. The arguments for this hypothesis are; the existence of U-rich carbonaceous sediments that contain diamonds, high levels of polycyclic aromatic hydrocarbon, PAH (0.0020-0.0039%) and parentless fission ^{135}Xe. The existence of U-rich carbonaceous sediments that contain diamonds is ruled out because these diamonds do not exceed 500 nm while carbonados are larger than this (8-12 mm in size) (Heaney et al. 2005). PAH values supports for a crustal carbon source but nothing has been mentioned that this source has to be uranium-rich as well. Since the PAH values has not been mentioned to be caused by uranium, these values only support for the carbonaceous part of the hypothesis and not uranium-part. The strongest argument of this hypothesis is the great amount of parentless fission ^{135}Xe, that is only possible if the carbonaceous precursor of diamonds (and the diamonds itself) were formerly part of a material that was rich in U and finely dispersed over time (Daulton and Ozima 1996). At the moment one strong argument is not enough to determine this as the origin of carbonados but if carbonados of smaller sizes were to be found this origin would be more possible.

The probability that carbonado formed in the mantle is often rejected because there are many parameters this origin can not explain, for example δ^{13}C -23‰ to -30‰ ratio (is closer to organic matter than upper mantle values) and their absence in kimberlites and lamproites (Cartigny 2010). However, Cartigny (2010) obtained results that could be caused by mantle origin. He examined diamonds from the Dachine komatiite that have C-N isotope compositions, -32.6 to +0.15‰ (mode at ~-27‰) and -4.1 to +6.9‰ (average ~+2.1±2.9‰) respectively identical to those found in carbonado therefore Cartigny (2010) developed a model linking carbonado to komatiite magmas. This model support the C-isotope compositions to originate from the transition zone, this is problematic because there are other C-isotope compositions (from other studies) that suggest to derive from this source as well. How can it be possible that the transition zone can have different C-isotope compositions? Another parameter that is also problematic to explain is the low variability at a given place from upper mantle δ^{13}C -5‰ values to transition zones δ^{13}C -21‰ values. Cartigny (2010) solve the mentioned problems by proposing that there are deep mantle domains that might have distinct C-isotope compositions, which could be true but at the moment no supporting data has been found for this nor samples of carbonados related to komatiite magmas.

Another study that propose a mantle origin is Ishibashi et al. (2012). They propose that carbonado crystallized from a carbon-oversaturated H_2O-bearing fluid due to the following observations; crystal size distribution, {111} (a plane in the crystallographic structure) growth steps along grain boundaries, and fluid inclusions. The crystal size distribution (Fig 14) pattern is similar in shape to those rapidly formed crystals in liquid media, which means that some type of liquid media was implicated in the formation of carbonados. The {111} growth steps along grain boundaries support that carbonado crystallized from a carbon-oversaturated H_2O-bearing fluid because other studies (for example Akaishi and Yamaoka 2000; Sokol et al. 2009) have reported the growth of {111} faces during the formation of polycrystalline diamond in carbon-oversaturated-H_2O-fluid and melt. Lastly the voids and the negative crystal with their smooth surface reveals that a coexisting fluid (had H_2O as revealed by infrared absorption spectra bands) was present (a near-equilibrium was obtained between the fluid and the host diamond).

It is clear by the above observations that a coexisting fluid was present during growth of the carbonado. The existence of a coexisting fluid during growth reveals that the host mineral phase (in this case it would be the carbonado-forming diamond) is under stable thermodynamic conditions and even supersaturated in the coexisting liquid phase, thus Ishibashi et al. (2012) conclude that carbonado crystallized from a carbon-oversaturated H_2O-bearing fluid where diamond is thermodynamically stable (for example in Earth's mantle). This suggestion is consistent with other observations (Fukura et al. 2005; Kagi and Fukura 2008) where the residual pressure in carbonado (central Africa) correlates with the stability field of diamond at high temperatures.

Finally even though the Ishibashi et al. (2012) study could neither identify the carbon source of carbonado a mantle origin is the most likely origin for carbonado at the moment as it is supported by many textural observations and could explain the absence of common mineral inclusions and why they are not found in association with kimberlites but to determine this with certainty the carbon source needs to be identified in the mantle as well as komatiite related carbonados.

5 Conclusions

Diamondites

- Eclogitic and perioditic diamondites are most likely to have been formed from upper mantle melts/fluids. To determine this with certainty a process or processes are needed to explain the high $\delta^{15}N$ values obtained in perioditic diamondites.

- The websteritic diamondites formation fluids are more likely to have a crustal origin as all evidence mentioned suggest this origin.

- Eclogitic, perioditic -and websteritic diamondites have distinct crystallization histories than monocrystalline diamonds.

Carbonados

- Carbonados are not formed by a meteorite impact because this hypothesis have no concrete evidence that links the characteristics to just a meteorite impact scenario and there are several clear arguments against this hypothesis.

- Parentless fission ^{135}Xe is the only argument that can evidence an origin from uranium-rich carbonaceous sediment but is not enough to determine this origin for carbonados. If smaller sizes of carbonados were to be found this could be a possible origin.

- Carbonado could be formed in the mantle since there are many textural observations that support this however to completely determine this we have to identify the carbon source of carbonado and komatiite related carbonados.

6 Acknowledgements

I would like to thank my family for their shown support during this process and above all my sister which was the person that was there for me the most. I would also like to thank my supervisors Carl Alwmark and Leif Johansson for their comments and guidance.

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