Evidence for two growth events with a billion year hiatus from a single eclogitic diamond (Mir kimberlite, Yakutia)
CHAPTER 6

Abstract

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Acknowledgements

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Figure on previous page: Monument at the entrance to the town of Mirny, which grew around the Mir diamond mine.
ABSTRACT

An eclogitic octahedral macrodiamond from the Mir Kimberlite (Yakutia) has a complex internal structure with distinctive core, intermediate and rim growth areas. Carbon isotope ratios change abruptly from depleted δ13C values of ~16.6‰ in the core to a mean mantle-like signature of ~6.8‰ in the intermediate and ~7.5‰ in the rim areas, establishing that at least two main stages of diamond formation took place from fluids/melts with different carbon isotope reservoirs. These two stages of growth are separated by an oscillatory zone that records an episode of intensive diamond dissolution and regrowth. The Mir Kimberlite pipe is known to contain eclogitic diamonds with both light and heavy carbon isotopes but this is the first case where both populations have been found in a single Mir diamond.

Multiple sulphides and two silicate inclusions occur at the boundary of the oscillatory zone with the intermediate area of the diamond. Silicate inclusions are composite and there is textural and compositional disequilibrium between the mineral phases. A primary omphacite phase has Mg# 66, a high jadeite content, 0.3 wt% K2O and contains no Cr. Texturally later omphacites in the same composite inclusions have Mg#70, lower jadeite, no potassium and 0.3 wt% Cr2O3 and occur together with interstitial albite and single grains of phlogopite. Late omphacites are 1.6-3 times higher in Ti, Ba and Yb. This later mineral assemblage was formed as the result of decompression of primary omphacite in a partly open system in the presence of a fluid/melt enriched in K, Cr, Ti, Ba, Yb and possibly water. Estimated formation pressure for primary omphacite based on experimental data is 6 GPa and significantly less than 6 GPa for later omphacites.

A mantle residence time of 1.7 Ga is implied for the core, following recently published results that couple a 2.1 Ga Re-Os sulphide inclusion age to diamonds with δ13C values of < -10‰ at Mir, relative to 0.36 Ga emplacement age of the kimberlite. This yields an integrated mantle residence temperature of ~1100-1170°C calculated from N content and aggregation. Based on N aggregation relationships and a 0.6 Ga mantle residence time, implied by the 0.9 Ga Re-Os isochron age for the sulphide inclusions in the current study, a temperatures of ~1100°C is inferred for the intermediate and rim diamond areas.

The two diamond growth episodes may correspond with ~2.1 Ga subduction and ~1 Ga rifting events recorded in the local Siberian lithosphere and suggests diamond growth linked to tectono-thermal events in the cratonic lithosphere. Furthermore, the diamond is shown to survive these major tectono-magmatic events during which decompression can locally produce volatile and trace element enriched small degree melts from the lithosphere that cause metasomatism and late diamond re-growth after partial resorption. Such metasomatic activity is also recorded by textural and compositional evidence from diamondiferous eclogite xenoliths from kimberlites.

We suggest that at ~2.1 Ga an early eclogitic diamond population characterised by low-nitrogen and depleted δ13C values formed at a mantle depth of ~185 km during the final assembly of the Siberian craton associated with active subduction. These diamonds were then partially resorbed during their uplift to a shallower mantle depth of ~120 km by plume-type magmatism at the end of the Proterozoic. At this depth, the second population of eclogitic diamonds characterised by moderate nitrogen content and typical mean-mantle δ13C values (~5‰), grew at ~1 Ga.
1. INTRODUCTION

Natural diamond is a high pressure-temperature mineral that can remain unchanged within the mantle for billions of years recording the presence and nature of deep mantle carbon (e.g., Pearson and Shirey, 1999). Hence, diamonds brought to the surface by kimberlite magmas preserve pristine geochemical and petrological information on Earth’s ancient history related to the formation and evolution of the early mantle and crust (Richardson et al., 1984; Pearson et al., 2003, Shirey et al., 2004). Syngenetic mineral inclusions in diamonds derived from the upper mantle have two main geochemical affinities: peridotitic (P) and eclogitic (E) (Meyer and Boyd, 1972; Sobolev, 1974), although a minor websteritic suite intermediate between P and E compositions is also recognised (Stachel and Harris, 2008). Kimberlitic diamonds of all parageneses are xenocrysts derived from diamondiferous eclogites and peridotites. They are liberated from their silicate host rocks during emplacement in the crust via kimberlite magmatism (Bonney, 1899; Sobolev, 1974; Robinson 1978).

Peridotitic diamonds (P-Type) have distinctive geochemical characteristics that are within a relatively narrow range when compared to eclogitic diamonds. They contain inclusions of olivine (Fo 93-97), Mg-chromite, Cr-pyrope with high Mg#, enstatite, Cr-diopside, and Ni-sulphides (see Stachel and Harris, 2008 for a review). The compositional range reported for the specific parageneses of peridotitic inclusions varies from harzburgite-dunitic through lherzolitic to wehrlitic. Yet, within any single diamond, the chemistry of silicate inclusions of any particular species is almost identical, e.g. olivines in the same diamond will show little variation in Fo content. Chromites from single diamonds are the only exception and sometimes show a systematic variation in chemistry from inclusions located in the core towards those situated in the diamond rim (Bulanova, 1995; Sobolev and Yefimova, 1998). Peridotitic diamonds exhibit C isotope compositions consistent with the mean mantle value, where δ¹³C values range from -5 to -8‰ (see Cartigny, 2005 for a review) and individual crystals are limited to δ¹³C variations typically within 4‰ (Navon, 1999; Bulanova et al., 2003; Cartigny, 2005). Additionally oxygen isotope compositions of garnets from peridotitic diamondiferous xenoliths also exhibit compositions akin with the ambient upper mantle (δ¹⁸O of 5.3 ± 0.6‰; Spetsius et al., 2008). Harzburgitic diamonds typically yield Archean ages of 2.8-3.5Ga inferred by study of different radiogenic isotope systematics of silicate and sulphide inclusions (Richardson et al., 1984; 1993; Pearson, 1999; Gurney et al., 2010), whilst the lherzolitic group has younger Proterozoic ages (Richardson et al., 1993; Pearson et al., 1998; Gurney et al, 2010).

Conversely, eclogitic diamonds (E-Type) show a broader range of geochemical characteristics that imply formation within a wider variety of environments. Multiple inclusions of garnet and clinopyroxene from single eclogitic diamonds may record substantial compositional variation. For example, Sobolev et al. (1998a) reported large chemical variations for 35 garnet and 5 clinopyroxene inclusions within a single eclogitic diamond from the Mir pipe. Also, Bulanova (1995) and Taylor et al. (1998) recorded marked decreases of 25.5 to 14.4% in the Ca/Ca+Mg ratio of eclogitic garnets from core to rim located inclusions in an individual diamond from the Mir pipe. In comparison to peridotitic diamonds, eclogitic samples also record a larger range of δ¹³C from +5 to -41‰.
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(Cartigny, 2005 and references therein). Carbon isotope variation within single eclogitic diamonds can exceed 10‰ (Hauri et al., 2002; Bulanova et al., 2003; Schulze et al., 2004; Wiggers de Vries et al., 2007). Furthermore, garnets from eclogitic diamondiferous xenoliths record wide values of δ18O from +4.7 to +9.7‰ (Spetsius et al., 2008). Additionally, dating of eclogitic diamonds has provided evidence of their formation in distinct episodes over a wide range of geological time from 2.9 to 1.9 Ga (Richardson et al., 1990; Smith et al., 1991; Pearson et al., 1998; Richardson et al., 2001; Aulbach et al., 2009; Shirey and Richardson, 2011). Therefore eclogitic diamonds appear to form under variable conditions and from variable sources, in contrast to their peridotitic counterparts.

Cathodoluminescence (CL) imaging typically reveals simple octahedral internal growth zonation for both peridotitic and eclogitic diamonds; complicated zonation is more rare. Seventy percent of a collection of several thousands Yakutian diamonds display simple octahedral growth zonation with only 30% recording complex histories where the crystal habit changing during growth (Bulanova, 1995). Within the cores of diamonds several crystal habits can exist (cubo-octahedrons, cubes, aggregates or broken crystals) that were overgrown by later octahedral layers (Seal, 1966; Tolansky, 1966; Varshavsky, 1968; Frank, 1969; Genshaft et al., 1977; Lang, 1979; Beskrovanov, 1992; Bulanova et al., 1995). Diamonds from kimberlites also exhibit internal and external features of resorption and etching. The final stage of external diamond resorption is generally regarded as taking place during upward transportation in kimberlite magma (Orlov, 1977; Robinson, 1978; Robinson et al., 1989), but individual crystals have complicated histories of early stages of resorption, etching, fracturing, breakage and new stages of re-growth. These complex diamonds provide unambiguous evidence of changing fluid-melt activity and stress in the mantle and represent a valuable record of evolving geological conditions during diamond formation, mantle residence, metasomatism in the sub-continental mantle and finally, their transportation history toward crustal emplacement.

Several fundamental unresolved questions remain about diamond genesis. Are distinct diamond carbon isotope compositions the result of isotopic fractionation during diamond growth, or an indication of sourcing from different carbon reservoirs, or the end product of a combination of these models? Is there any age difference between the eclogitic diamonds with enriched and/or depleted 13C values relative to the mean mantle?

Here we investigate a monocrystalline diamond from Mir, Yakutia, which exhibits distinct growth zones with variable δ13C values across concentric growth zones. These zones show both 13C-depleted and mean-mantle δ13C values. In addition, the sample contains mineral inclusions indicating a sharp change in composition and, possibly, a change in pressure-temperature (P-T) parameters during formation. The aim of our study is to reconstruct the conditions of diamond growth, to explain what processes caused the sharp changes in the internal structure, isotope composition and chemistry of inclusions, and to show how these relate to the origin of eclogitic diamonds in general. The results of our study are compared with published data on eclogitic diamonds from the Mir pipe and on a global scale.
2. METHODS

The diamond was sawn into three parts along two parallel dodecahedral planes so that a central plate, an intermediate plate and one off-cut could be manufactured. The central plate with the core area exposed on both sides was polished until inclusions were exposed at the surface. Two thick plates, i.e., intermediate and peripheral, were also produced from the diamond off-cuts by polishing with the core area only exposed on one side of the intermediate plate. The central plate was used for in situ geochemical analysis of inclusions by EMP, and the coupled N content and \(^{13}C/^{12}C\) composition of the diamond using secondary ionization mass spectrometry (SIMS). The intermediate plate was broken to extract non-exposed sulphide inclusions (Wiggers de Vries et al., in press) and the diamond fragments were subjected to a C and N isotope investigation by a conventional combustion mass spectrometric method.

The internal structure of the diamond was investigated using CL imaging at University College London with a nuclide luminoscope microscope attachment. The uncoated specimen was mounted on a copper plate with soluble carbon dag to ensure electrical conductivity and prevent excessive heating. An accelerating voltage of 12 KV was used and the beam current was maintained close to 0.8 mA.

Infrared spectral analyses on the central diamond plate were performed in core-rim profiles using a Nicolet Nexus FTIR Spectrometer equipped with a Continuum Microscope at The Research Department of HRD Antwerp in Lier, Belgium. Transmission spectra were recorded with a resolution of 4 cm\(^{-1}\) over a 7000–400 cm\(^{-1}\) range. The aperture size was set to 19 μm and 200 scans were collected per spectrum. Nitrogen concentrations and aggregation states were calculated by deconvolution of the FTIR spectra using the method of Mendelssohn and Milledge (1995). The spectral analyses were taken at points that were also analysed by SIMS for C-isotope composition and N concentration.

Mineral inclusions were analyzed in situ in the central diamond section at Birkbeck College, University of London, using a Jeol 773 Superprobe with an Oxford Instrument ISIS energy dispersive system (EDS). Data were collected at 15kV for 100 seconds count-time with a 2 μm beam diameter.

Trace element concentrations of clinopyroxene inclusions were determined using a Cameca IMS-4f ion-microprobe at the Edinburgh Ion Microprobe Facility (EIMF). The primary beam was ~11 keV 16O- ions (~15keV net impact energy), with a sample current of 2 nA that corresponds to a spatial resolution of ~15 μm at the sample surface. The secondary ion accelerating voltage of 4500 V was offset by 75 eV (energy window of 40 eV) to reduce molecular ion transmission. Calibration was performed on synthetic international glass standards under identical operating conditions. Repeated standard analysis indicates an accuracy better than 10% relative for the rare-earth elements (REE), Ba, Sr, Nb, Zr and Y. Hf, Rb, Th and U are accurate to within 30% relative (Harte and Kirkley, 1997).

Re/Os isotope data of sulphide inclusions were determined by Thermo Finnigan Triton thermal ionisation mass spectrometer and Thermo Finnigan Element2 high-resolution mass spectrometer using preparation technique of Pearson et al. (1998). The whole procedure and primary data on sulphide inclusions from Yakutian diamonds are given in a separate paper (Wiggers de Vries et al., in press).
The carbon isotope data were acquired across the diamond plate at EIMF with a Cameca SIMS 1270, using a ~3 nA primary 133Cs+ beam. Secondary ions were extracted at 10 kV, and 12C- (~2.0 x107cps) and 13C- (~1.0 x109cps) were monitored simultaneously on dual Faraday cups (L'2 and H'2). Each analysis involved a pre-sputtering time of 60 seconds, followed by data collection in two blocks of five cycles, amounting to a total count time of 40 seconds. The internal precision of each analysis is < 0.2‰. To correct for instrumental mass fractionation all data were normalised to internal standards derived from synthetic diamond standard SNYAL with δ13C PDB of -23.924‰ (B. Harte, personal communication). The standards were mounted in the same sample holder as the unknown and measured throughout the analytical sessions.

Bulk combustion stable isotope data and N concentrations of the broken fragments from different diamond areas were determined at Open University (UK) using three different fully automated static mode mass spectrometers fed from a common extraction system (Wright et al., 1988; Shelkov, 1997; Boyd et al., 1998; Verchovsky et al., 1998; Mikhail, 2011). The δ13C, δ15N and N/C ratio data were obtained simultaneously on samples treated by a single temperature programme. The blank levels for N were better than 0.5 ng above 700 °C, and N ppm was measured in μg/g. δ13C and δ15N stable isotopic compositions are expressed relative to the PDB (for C) and Air (for N) with analytical precision better than 0.5‰.

3. SAMPLE DESCRIPTION AND GEOLOGICAL SETTING

Diamond 1703 is from the Mir kimberlite. It is a 5 mm sized colourless octahedron elongated along one L2 axis, having several colourless inclusions of silicates and dark sulphides surrounded by rosettes of black local cracks. All inclusions have cubic diamond-imposed morphology and no cracks connected to the crystal surface and therefore are considered primary.

The 350 Ma aged Mir pipe kimberlites (Kinny et al., 1997) intrude Cambro-Ordovician terrigenous sediments, carbonates, evaporites and late Devonian diabases. The crystalline basement rocks are biotite-amphibole tonalite-trondjemite gneisses, granite-gneisses and granites with Nd model ages ~3.3 to 2.6 Ga (Smelov et al, 1998; Kovach et al., 2000) that form part of the Archean granite-greenstone complexes of the Tunguska Terrain (Fig. 1). The neighbouring basement of the North-Asian Craton, including the Siberian platform (Fig. 1), is formed of Archean and Paleoproterozoic terrains (Rosen and Turkina, 2007; Smelov and Timofeev, 2007). Collision of these terrains at 1.99 – 1.86 Ga resulted in formation of the Siberian platform basement (Rosen and Turkina, 2007). Basalt-andesite-rhyolitic paragneiss and intrusive complexes of granulite and amphibolite facies occurring to the Eastern terrains from the Tunguska Terrain were formed on the active continental margins between 2.4 and 1.98 Ga (Velikoslavinskii, 2006; Smelov et al., 2012). At approximately the same time the Bellyhsko-Fedorovskaya subduction zone was active beneath the Tunguska Terrain (Fig. 1) providing a potential source of eclogite xenoliths and eclogitic diamonds with 13C-depletion from the Mir pipe. The existence of the Mesoproterozoic Nurbinsky rift to the South of Mir pipe was identified by deep drilling, where basic rocks (gabbro-diabases and diabases) were found at a depth of 2.7-3.3 km. These Proterozoic basic rocks (~1.2 Ga TNdDM model-age) and have compositions comparable to ocean island basalts (Kovach et al., 2000).
4. RESULTS

4.1 Diamond internal structure

The detailed internal diamond morphology of the central plate is revealed in the CL image, Fig. 2a. The diamond has distinctive core-, intermediate- and rim-areas.

The core area has a distorted octahedral shape and is composed of two zones. An inner core zone with a relatively isometric shape made up of cubic-rounded-aggregate-mixed growth forms is located on the left side of the core area. It is characterised by a pink-white CL colour that is usually attributed to the presence of carbonate (Chinn, et al., 1995). The mechanism of diamond growth during this first nucleating stage appears to have been unfaceted (hummocky) (Moore and Lang, 1972; Sunagawa, 1984). An outer core zone with a generally octahedral shape and dark blue CL colour is elongated along the L2 axes with an approximate 4:1 aspect ratio and was formed by a layer-by-layer growth mechanism (Sunagawa, 1984). The shape of the outer core is more complex than a simple octahedron. The right-hand parts are faceted and have an almost planar octahedral form, but the top and left-hand parts have the shape of a selectively resorbed octahedron (Fig. 2a).
The oscillatory zone is the first onset of growth of the intermediate, and is characterised by fine multiple zoning that can be interpreted as oscillating resorption along with re-growth. The intermediate and rim areas have simple octahedral zonation with elongation along the L2 axes inherited from the core (Fig. 2 a). These two areas show paler blue CL response, compared to the core area, while the rim area has slightly darker CL compared to the intermediate area. The mechanism of crystal growth of both areas was tangential.

The growth history of diamond is therefore as follows: (1) growth of the core, (2) resorption of the core area as documented by the oscillatory zone, (3) growth of intermediate and rim areas. Thus the diamond records an interruption in its growth, with a clear interval of resorption at the onset of the second major stage of formation.

4.2 Location and composition of the inclusions

The contact between the oscillatory zone and the intermediate diamond area is decorated with mineral inclusions. Two silicate and two sulphide inclusions exposed on the surface of the central diamond plate are associated with the actual contact (Fig. 2a, b). In this illustrative plane of section, the silicate inclusions contact the oscillatory zone, and one sulphide is positioned within the oscillatory zone (Fig.2a, po). Three other sulphide inclusions of the same location were close to the surface, but still inside of the intermediate diamond plate. These three sulphides were all extracted after breakage of the intermediate plate and were used for Re/Os datings.

4.2.1 Major element chemistry of silicates and oxides

The two silicate inclusions are composite (Fig. 2 b, c and d).

The small inclusion mainly consists of omphacite characterised by Cr# (100xCr/Cr+Al) <10. This composition falls within the world-wide range of eclogitic clinopyroxene diamond inclusions (Stachel and Harris, 2008; Fig. 3a). The other mineral phases are interstitial albite and a single 4 µm sized grain of phlogopite (Fig. 2c). The omphacite is inhomogeneous and consists of three areas with different composition (Fig. 2c). The area located in the left lower corner of the inclusion (Omph-1), has high K₂O and Na₂O contents (Table 1, Fig. 3b). Two areas in the upper right side of the inclusion (Omph-2 and -3), are less rich in Na₂O, do not contain K₂O and are correspondingly poorer in jadeite (Jd) and richer in diopside compared to Omph-1 (Table 1, Fig. 3b, c). On a Na₂O - MgO diagram that classifies clinopyroxenes from mantle eclogites and diamonds (Fig. 3b; Taylor and Neal, 1989) Omph-1 is located on the boundary between group C (low Mg#, high Jd) and group B (higher Mg#, moderate Jd) clinopyroxenes. The composition of Omph-2 is comparable to those of group B clinopyroxenes and the composition of Omph-3 approximates chemistry of group A clinopyroxenes (high Mg#, low Jd) (Fig 3b). Compared with usual homogeneous composition of inclusions in diamonds, a minor inhomogeneity is observed in all major elements in Omph-2 and -3 (Fig. 3 c and Table 1).

The textural relationships of mineral phases in the inclusion suggest that Omph-1 is a primary phase and that interstitial Omph-2 and -3, albite and phlogopite are later phases. The apparent penetration of Omph-3 and albite as a vein into Omph-1 (bottom side of Fig. 2c) demonstrates their later origin, presumably as the result of breakdown of Omph-1 or its
partial secondary alteration. Calculated bulk chemistry for the areas of Omph-2 + Omph-3 + Alb is very close to the composition of Omph-1 (Table 1), which suggests that Omph-2, -3 and albite were most likely formed by re-equilibration of Omph-1 during decompression. Albite and phlogopite have compositions typical of such minerals in eclogites (Spetsius and Serenko, 1990).

The big inclusion is more homogenous, and mainly composed of clinopyroxene similar in chemistry to the Omph-1 in the small inclusion (Table 1, Fig. 2, 3). Only one corner of the big inclusion is polyphase (Fig. 2d). Comparable to the small inclusion, it contains clinopyroxene with chemistry equivalent to Omph-3 and interstitial albite that appears to have formed later than Omph-1. In addition, a rutile grain is surrounded by a 5 μm narrow ilmenite rim, which occurs along the contact with Omph-3 plus albite area (Fig. 2d). The textural relationships, again, indicate that the ilmenite rim has a later origin associated with formation of Omph-3 and albite. The rutile analysis has a low total due to the small size of the mineral grain (Table 1). The ilmenite contains small amounts of SiO₂, Al₂O₃ and Na₂O, which are most likely recorded in the analysis due to overlap of the EMP beam with the
surrounding albite plus Omph-3 area. The ilmenite rim has TiO₂, FeO and MgO contents indistinguishable from ilmenite from Mir eclogitic xenoliths (Spetsius and Serenko, 1990), although it’s MgO content (6.53 wt. %) may partly be influenced by the surrounding Omph-3.

It is remarkable that Omph-1 in both inclusions contains no chromium but later Omph-2 and -3 have 0.15 and 0.27 wt% of Cr₂O₃, respectively (Table 1). This indicates a partly open system during the formation of Omph -2, -3 and the phlogopite, with an influx of chromium, potassium and water.

### Table 1. EMP analysis of mineral phases in two polymineral inclusions from diamond 1703 (wt. %)

<table>
<thead>
<tr>
<th>Incl.</th>
<th>Small inclusion</th>
<th>Big inclusion</th>
<th>Bulk*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Omph-1 core</td>
<td>Omph-2 core</td>
<td>Omph-3 core</td>
</tr>
<tr>
<td></td>
<td></td>
<td>rim</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>55.14</td>
<td>53.7</td>
<td>55.34</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.02</td>
<td>0.42</td>
<td>0.72</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.6</td>
<td>5.37</td>
<td>6.64</td>
</tr>
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<td>Cr₂O₃</td>
<td>0.00</td>
<td>0.00</td>
<td>0.11</td>
</tr>
<tr>
<td>FeO</td>
<td>7.78</td>
<td>8.69</td>
<td>9.72</td>
</tr>
<tr>
<td>MnO</td>
<td>0</td>
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<tr>
<td>MgO</td>
<td>8.72</td>
<td>10.9</td>
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<td>CaO</td>
<td>9.94</td>
<td>15.1</td>
<td>11.3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>7.36</td>
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<td>4.06</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.32</td>
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</tr>
<tr>
<td>Total</td>
<td>99.88</td>
<td>99.2</td>
<td>98.81</td>
</tr>
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</table>

Note: Omph – omphacite; Phlog – phlogopite; Ab – albite; Ru – rutile; all analysis are average of 3 measurements
It is apparent therefore that there were two different geochemical environments for formation of Omph-1 and Omph-2, -3 and therefore the nature of these inclusions, especially, with regard to the time of diamond formation is complex. Omph-1 is more likely syngenetic to the core and protogenetic to the intermediate and rim areas; Omph-2 and -3 are possibly syngenetic to the intermediate and rim areas of the diamond.

4.2.2 Trace element chemistry of the omphacite phase
The trace element concentrations of clinopyroxene in the big inclusion are given in Table 2. Four measurements were taken: one in the inclusion centre, two in the intermediate part (all Omph-1) and one at the inclusion rim (Omph-3). All four analyses have similar Sr, Y, and REE concentrations, but the rim analysis (Omph-3) is enriched in Ti (factor of 1.7) and Ba (factor of 3). These relatively high Ti compositions may be partially explained by the involvement of rutile and ilmenite associated with Omph-3 formation. However, the elevated Ba and Ti are more likely to be the result of later metasomatic processes that also produced phlogopite.

Chondrite-normalised REE abundances of the omphacites (Fig. 3d) are close to the median REE patterns of eclogitic pyroxenes worldwide (Stachel et al., 2004). The most significant difference between Omph-1, -2 and -3 is expressed by their Eu anomaly. The Eu anomaly is absent or slightly positive in primary omphacite-1 and negative in omphacite-3, which is in equilibrium with the albite phase.

4.2.3 Composition of sulphides and their Re/Os isotope dating
The Ni content in the two pyrrhotites (Po) exposed to the surface ranges from 1.26 to 3.3 and there are small variations in Cu and Co: 0.5 – 1.7 and 0 – 0.26 (wt%), respectively. Their compositions

<table>
<thead>
<tr>
<th>Incl. zone</th>
<th>core 1 Omph-1</th>
<th>inter. 1 Omph-1</th>
<th>inter. 2 Omph-3?</th>
<th>rim Omph-3</th>
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<tr>
<td>Ti</td>
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<td>2350</td>
<td>2340</td>
<td>3730</td>
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<td>0.22</td>
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<td>4.9</td>
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<td>0.86</td>
<td>0.85</td>
</tr>
<tr>
<td>Nd</td>
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<td>4.97</td>
<td>4.64</td>
<td>4.55</td>
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<tr>
<td>Sm</td>
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<td>0.81</td>
<td>0.99</td>
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<td>Eu</td>
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</tr>
<tr>
<td>Gd</td>
<td>0.76</td>
<td>0.81</td>
<td>0.55</td>
<td>1.01</td>
</tr>
<tr>
<td>Er</td>
<td>0.61</td>
<td>0.72</td>
<td>0.58</td>
<td>0.22</td>
</tr>
<tr>
<td>Yb</td>
<td>0.22</td>
<td>0.42</td>
<td>0.69</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Note: Omph –omphacite; Incl. – Inclusion; inter. - intermediate
were determined from the sulphide matrix washoff after unsuccessful Re-Os isotope analyses (unpublished data D.G. Pearson). The low Ni contents of these sulphides are consistent with an eclogitic origin (Yefimova et al., 1983; Bulanova et al., 1996; Aulbach et al., 2009).

The other three unexposed pyrrhotite inclusions were extracted for Re/Os dating from the contact between the oscillatory zone and the intermediate zone. Their compositions were determined from the sulphide matrix washoff after the Re-Os isotope analyses (Wiggers de Vries et al., in press). Their Ni and Cu concentrations are 1-1.1 wt% and 0.6-0.8 wt%, respectively, and the (Ni+Cu)/Fe and Cu/(Fe+Ni+Co+Cu) ratios range between 0.019 to 0.021 and 0.009 to 0.012, correspondingly. These major element composition of sulphides is characteristic for inclusions from eclogitic diamond population with low δ13C values at Mir pipe (i.e., <-10‰; Wiggers de Vries et al., in press).

The three 1703 pyrrhotites have also Re and Os concentrations typical for eclogitic inclusions (148-711.5 ppb and 6.8-95.2 ppb, respectively; Pearson et al., 1998), and are
characterized by radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios (1.083-2.660). The $^{187}\text{Re}/^{188}\text{Os}$ ratios range between 42.8 - 139.7. Together with pyrrhotites from other Mir eclogitic diamonds, the three 1703 pyrrhotites define a 12-point isochron with an age of 0.91 ± 0.14 Ga (2σ) with a lower $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.65 ± 0.18 (Wiggers de Vries et al., in press). This isochron age is characteristic for a diamond population at Mir specifically with mantle-like δ$^{13}\text{C}$ values (i.e., ~-4.5 to -7‰; Wiggers de Vries et al., in press).

4.3 Nitrogen abundance and aggregation (FTIR)

The N concentration is moderate in the inner diamond core, varying from 134 to 178 ppm, low in the outer core (typically circa 40 ppm) and highest in the intermediate and rim areas with a range of ~450 and ~300 ppm, respectively (Fig. 4a). The degree of N aggregation in the diamond generally is low, i.e., changing from 4 – 8 % in the inner core to 10% in the outer core. It increases up to 20 % near the oscillatory zone, dropping to 2 – 4% in the intermediate and rim areas (Fig. 4a). The outer core near the contact with oscillatory zone has the lowest N content but is the most aggregated compared to all other regions of the diamond (Fig. 4a). These results are at odds with the nitrogen aggregation theory stating that the degree of N aggregation in diamonds correlates positively with N abundance, temperature and residence time (Evans and Harris, 1989). However, the low N contents mean that the error in the degree of N aggregation in the outer core is large (> 10%) such that the N aggregation of the entire core is possibly constant.

4.4 Nitrogen content and carbon isotope composition (SIMS data)

Four measurements of N abundance were made by SIMS at different points across the central diamond plate (Fig. 4a). The nitrogen concentrations identified by SIMS agree well with the FTIR results at the same positions and indicate that N contents are relatively homogenous throughout the thickness of the plate (Table 3, Fig. 4a).

The carbon isotope values of the different diamond areas are shown in Table 3 and Figs 4a and 5. Low δ$^{13}\text{C}$ values of -15.3 to -16.6‰ characterize the core area, whereas the intermediate area including the oscillatory zone has a narrow range in δ$^{13}\text{C}$ values from -6.2 to -6.8‰ and the rim is the most homogeneous in composition with -7.3 to -7.7‰. Both intermediate and rim values are compatible with the range shown by the mean mantle (Deines, 2002). An additional high spatial resolution SIMS traverse (15 points) made at an angle of 40 degrees across the contact between the diamond outer core zone and intermediate area revealed that the 10‰ change in carbon isotope composition at the outer core-oscillatory zone contact is very abrupt (Fig. 5; Wiggers de Vries et al., 2007). The SIMS spot analyses are 20 μm in diameter and less than 1 micron deep, allowing analyses of individual growth layers of the diamond. This resolution ensures that there was no averaging of the separate growth zones on a 5 μm scale.

The co-variation of N abundance and carbon isotopes in the diamond is shown in Fig. 4b. The inner core has a low nitrogen concentration and the most $^{13}\text{C}$-depleted carbon isotope compositions. The outer core also exhibits $^{13}\text{C}$-depletion coupled with the lowest N concentration. The changes in N content and carbon isotope composition across the outer core-intermediate contact are abrupt as both values increase to 599 ppm and -6.2‰, respectively (Figure 4b).
Core-rim spatially determined $\delta^{13}C$ values from other octahedral eclogitic diamonds from the Mir pipe are compared with the isotope composition of diamond 1703 in Fig. 4c. Octahedral diamonds with mantle-like carbon isotope ratios record a slight increase in $\delta^{13}C$ during growth, comparable to the intermediate-rim of 1703. The core area of diamond 1703 is identical in composition with a population of homogeneous $^{13}C$-depleted diamonds from Mir (1591, 1594 on Fig. 4c and other samples from this locality; (Wiggers de Vries et al., in press). Diamond 1703, therefore, appears to combine in one crystal the two populations of eclogitic diamonds recognized in the Mir kimberlites, i.e., it exhibits both $^{13}C$-depletion and mantle-like $\delta^{13}C$ values.

4.5 Nitrogen isotope composition (combustion data).

Nitrogen isotope analyses were undertaken on fragments of the broken diamond plate made from off-cuts, where the central area was still present on one side only. The exact location of the diamond pieces was difficult to document, because the plate broke into many fragments after cracking and because the nature of the combustion technique produces averaged results for the combusted material (i.e., one value for zoned diamond fragments - ergo, hybrids of what was loaded into the furnace). Therefore we were not able to assess the N isotope data.
spatially, in the same precise manner as the $^{13}$C-contents using the SIMS. In Table 3 the results are presented for the three diamond fragments that best match the SIMS nitrogen abundance and $\delta^{13}$C values for individual growth zones. All three diamond fragments exhibit negative $\delta^{15}$N values that slightly increase from -7.8‰ in the inner core to -3.9‰ in the outer core and -4.3‰ in the intermediate/rim diamond areas. The limited N isotope data records no direct correlation with N concentration or $\delta^{13}$C values (Table 3). From our comparison of isotope analysis between SIMS and combustion techniques it follows that the latter technique is difficult to apply to isotopically heterogeneous diamonds where the aim is to determine the isotopic compositions of individual growth zones as opposed to bulk isotopic compositions.

5. DISCUSSION

5.1 The history of formation of the diamond

5.1.1 Two discrete diamond growth stages: evidence from internal structure, N content and aggregation

The internal structure together with N content and aggregation clearly documents two main episodes of diamond formation, interrupted by dissolution at the onset of the second stage of growth. The earlier core area contains 2.5-3 times less nitrogen compared to the intermediate and rim areas, while the N aggregation data of these different areas are comparable.

The abrupt boundary between the core and the intermediate area is marked by an oscillatory zone that originated as the result of intense dissolution possibly alternating with
very short periods of re-growth (Fig. 2a, b). This dissolution could be caused by introduction of a more oxidizing fluid. When conditions for diamond growth became stable again the intermediate and finally rim areas formed during a second episode of diamond growth. The nitrogen concentration in this period of growth is relatively high, while the nominal aggregation state is lower than in the central core (Fig. 4a). A simple interpretation of the nitrogen aggregation systematics is that they suggest shorter mantle residence times for the intermediate and rim areas. Nonetheless, the uncertainties in the estimated N aggregation are such that we cannot resolve clear differences in integrated residence temperature but there are clear differences in the combined N concentrations and aggregation patterns. The internal structure of the diamond together with results of N content and aggregation therefore document two main discreet episodes of formation interrupted by a phase of intensive dissolution, albeit in a complex and perplexing manner.

5.1.2 Pressure evolution during two-stage formation inferred from clinopyroxene compositions

In agreement with the abrupt main changes in internal structure, the silicate inclusions formed during initial growth in the intermediate zone of the diamond consist of minerals that display disequilibrium textures and variable compositions. The primary Omph-1 has potassium and jadeite contents higher than Omph-2 and –3, as the latter phases are associated with albite formed in decompression reactions. The K and Na contents in Omph-1 (0.016 and 0.563 per formula unit, respectively) imply formation at ~6 GPa (Harlow, 1997; Harlow and Davies, 2004; Safonov et al., 2005). The presence of small amounts of Cr and Ba in Omph-2 and –3 and the phlogopite grain identified on the edge of Omph-3 (Fig. 2c), suggests that a metasomatic melt/fluid was introduced during formation of this later, at lower pressure, re-equilibrated mineral assemblage.

We envisage that the polyphase inclusions originally represented by Omph-1 and located in the core zone, were exposed to rapidly changing chemical environments after a period of diamond resorption. Consequently, formation of omphacite-2,-3, albite,
phlogopite and ilmenite in the inclusions most likely took place during new growth events after the inclusions were liberated from the diamond core paleo-crystal. Both inclusions were again encapsulated into the diamond during formation of the first growth layers of the intermediate area, i.e. they are protogenetic with respect to the intermediate area. The pressure estimate supports the likelihood for 1703 diamond being formed in association with underplating of a subducted slab beneath the lithospheric mantle base, which lies at ~190 km depth in the region of the Mir pipe (Griffin et al., 1999).

5.1.3 Re/Os isotope ages evidence for two stage growth
Consistent with the clinopyroxene inclusions data, the composition and age of the sulphides from oscillatory zone/intermediate area contact also support a two-stage growth history of the diamond. In a detailed study of sulphide-bearing Yakutian diamonds (Wiggers de Vries et al., in press) two ages for eclogitic diamonds with sulphide inclusions are identified in the Mir pipe:

1. Diamonds grown from fluids/melts with low δ¹³C values (< -10‰) contain pyrrhotite inclusions with a high initial Os isotope composition (¹⁸⁷Os/¹⁸⁸Osᵢ = 2.22 ± 0.03), giving a Re-Os isochron age of 2.12 ± 0.21 Ga. Such high initial ratio of eclogitic sulphides is characteristic of formation in subducted oceanic crust (e.g., Pearson et al., 1998).

2. Diamonds grown from fluids/melts with mantle-like δ¹³C values of ~ -4.5 to -7‰ contain pyrrhotite inclusions with lower initial Os isotope composition (¹⁸⁷Os/¹⁸⁸Osᵢ = 0.65 ± 0.18). These sulfides yield a Re-Os isochron age of 0.91 ± 0.14 Ga.

The major element composition of the three pyrrhotite inclusions from diamond 1703 are similar to sulphides in 1591 and 1594 Mir diamonds with low δ¹³C values (Fig. 4 c), i.e., belong to the “Group 1” of Wiggers de Vries et al. (in press). In contrast, the Re-Os isotope data of these pyrrhotites plot on the isochron for “Group 2”, which is consistent with formation event that precipitated eclogitic diamonds with mantle-like ¹³C-compositions (Wiggers de Vries et al., in press). These sulphides therefore appear to have a two-stage / hybrid origin. The sulphide major element compositions indicate their primary association with the ~ 2.12 Ga aged diamond core having low δ¹³C values. But spatially these sulphides are located in the first growth zones of the intermediate diamond area having typical mantle like δ¹³C values. Therefore we conclude that Os isotope systematics of these sulphides were affected by the fluid responsible for the second major episode of 1703 diamond growth from a mean mantle ¹³C-reservoir at ~0.9 Ga. Similar to the silicate inclusions, the sulphides can be classified as syngenetic to the core and protogenetic to the intermediate area.

5.1.4 Temperature constraints from FTIR
As outlined in the previous section, the core area of diamond 1703 is 2.1 ± 0.1 Ga old and we therefore assume a mantle residence time of circa 1.7 Ga, accounting for the 0.36 Ga age of the Mir kimberlite (Kinny et al., 1997; Pearson et al., 1997). At this assumption and using kinetic parameters from Mendelsohn and Milledge (1995) and Taylor et al. (1990), N abundances and aggregation states yield average mantle residence temperatures of 1075-1100°C for the inner core and 1150-1175°C for the outer core (Fig. 6). However, due to the larger uncertainties in degree of B-centre aggregation at lower N concentrations, the obtained temperatures are within error. On that basis, namely due to their relatively identical integrated
mantle residence temperature estimates, we propose that the two core zones of 1703 grew fast enough to be indistinguishable on geological timescales using N aggregation geothermometry.

The three pyrrhotite inclusions with a Re/Os regression age of 0.91 ± 0.14 Ga (Wiggers de Vries et al., in press), together with the emplacement age for the Mir Pipe, implies a maximum mantle residence time of 0.6 Ga for the intermediate and rim areas of the diamond. Consequently, N abundances and aggregation states in this region of the diamond yield integrated mantle residence temperatures of 1100°C (Fig. 6). Hence, the integrated mantle residence temperatures for the two main diamond growth periods are alike. Noteworthy, with the available data regarding the kinetics for N aggregation in diamond we cannot rule out the possibility that N aggregation is slower in diamonds with relatively low N contents (Taylor et al., 1990).

5.1.5 Carbon isotope composition and nitrogen concentrations – trends and correlations

The most remarkable characteristic of diamond 1703 is the abrupt change in carbon isotope composition between the core and intermediate/rim areas; ~ -16‰ in the core to ~ -6.5‰ and ~ -7.5‰ in the intermediate and rim, respectively. The very sharp 10‰ δ13C change at the outer core-oscillatory zone contact, intermittent by stages of resorption, is most likely not a result of continuous carbon isotope fractionation in the reservoir during diamond growth but suggests formation from melts/fluids with highly different isotopic composition possibly at different times and/or from different immiscible fluids. The final stage of diamond growth from intermediate to rim shows a trend with decreasing δ13C-content and N abundance (Fig. 4b), in agreement with predictions of the open system isotopic fractionation model of Cartigny et al. (2001), therefore the intermediate and rim areas would have formed in an open system.

Although rare, similar but more gradual δ13C zonation in eclogitic diamonds has been reported from the International kimberlite in Yakutia (Zedgenizov et al., 2006), Venezuela.

Fig. 6. %N in IaB form plotted against N ppm for diamond 1703. Isotherms shown are for a mantle residence time of 1.7 and 0.6 Ga.
(Schulze et al., 2004), Collier-4 kimberlite in Brazil (Bulanova et al., 2010, Fig. 7), Jericho kimberlite in Canada (Smart et al., 2011) and Juina (Brazil) and Kankan (Guinea) (Palot et al., 2012; Fig. 7b). The major change in carbon isotopes in these diamonds was explained by initial formation from fluid source related to subducted crustal material that was later overgrown by fluids related to the mean astenospheric/mantle carbon source as diamonds from the lower mantle were re-growing in the upper mantle; which is generally consistent with the isotope zonation of sample 1703.

5.1.6 Interpretation of nitrogen isotope data

Table 3 shows that there is no distinctive correlation between $\delta^{15}$N, N-content and $\delta^{13}$C in the different diamond zones, which may be partly explained by the limited spatial resolution of the bulk combustion technique applied for the N isotope measurements. When compared to worldwide data, the 1703 core plots in the range of 13C-depleted eclogitic stones and the intermediate and the rim areas are located in the range of eclogitic diamonds with $\delta^{13}$C.
values akin to the mean-mantle (Fig. 8). This worldwide dataset includes three eclogitic Yakutian diamonds with δ13C-depletion that are derived from the suite that form the 2.1 Ga Re-Os isochron age (analogous to 1703 core) at Mir, and also several eclogitic Yakutian diamonds with mean-mantle carbon isotope compositions (equivalent to 1703 intermediate and rim areas) from Mir (Fig. 8). The similarity between the different datasets suggests different sources for diamond formation through time.

The negative nitrogen isotope value of -7.9‰ for the diamond core, seems in contradiction to derivation from subducted oceanic lithosphere that includes sedimentary material, as very positive δ15N values are expected for such a protolith (Boyd and Pillinger, 1994). However, during subduction of crustal material and subsequent melting and/or metasomatism, the system could lose significant nitrogen if the stable species were N2 over NH3/NH4, due to the highly incompatible behaviour of N2 in all known mineral phases and melts (see Roskosz et al., 2006 and Watenphul et al., 2010 for discussions). Conversely, the degree of carbon removal from slabs subducted into the mantle and causing and/or melting (generating arc volcanism) is thought to be around 50% (Wallace, 2005), whereas for nitrogen it is potentially >90% (Fischer et al., 2002). Therefore, nitrogen in crustal organic material would be fractionated to a higher degree relative to carbon during subduction (i.e., removing 15N-enriched crustal nitrogen whilst simultaneously retaining 13C-depleted crustal organic carbon). This implies that nitrogen in diamond appears to have a mantle origin, i.e., 15N-depleted. The fact that diamond 1703 has 40-180 ppm nitrogen in

\[ \text{Fibrous diamonds} \]
\[ \text{Peridotitic} \]
\[ \text{Eclogitic ultra-heavy} \]
\[ \text{Eclogitic heavy} \]
\[ \text{Eclogitic light} \]
\[ \text{1137} \]
\[ \text{1703 inner core} \]
\[ \text{1703 outer core} \]

**Fig. 8.** δ13C - δ15N plot for diamond 1703 compared with world-wide diamond isotope compositions (Boyd and Pillinger, 1994; Cartigny et al., 1998; Bulanova et al., 2002). Data for several eclogitic Yakutian diamonds (Bulanova et al., 1998) are shown: M –Mir, U - Udachnaya, 23d - 23rd Party Congress pipes. Filled symbols – cores; unfilled - rims of individual diamonds with connecting lines. Isotopic trend for Mir diamond 1137 (Bulanova et al., 2002) of unknown paragenesis is also presented.
the core zone is consistent with this model because the mean nitrogen concentration for eclogitic diamonds is relatively low (378 ppm; Stachel and Harris, 2009). Therefore, this sample exhibits a nitrogen isotopic composition and abundance that is typical for mantle-derived nitrogen due to the escape of $^{15}$N-enriched crustal nitrogen following subduction, explaining the C-N isotopic compositions of sample 1703.

An alternative explanation for a source with $\delta^{13}$C of -16‰ and negative $\delta^{15}$N could be the open system isotopic fractionation model of Cartigny et al. (2001) allowing nucleation of diamond 1703 from a typical mantle-derived source. The absence of olivine in eclogites allows escape of CO$_2$ from the system and could cause a runaway Rayleigh fractionation effect (Luth, 1993). If, for example, such a source fluid had an initial $\delta^{13}$C value of -6.2‰,

$\delta^{15}$N of -15 to -20‰ and Nppm = 493 (i.e., the start of the intermediate zone corresponds to the point 4 Table 3), removal of CO$_2$ and N will lead to $\delta^{13}$C value of -16‰, N ppm ~100 and $\delta^{15}$N still within the negative range. The modelling parameters are: $\Delta^{13}$C between diamond and CO$_2$ is $\sim$ -3.5‰ (Chacko et al., 1991), KN = 2.5 and increments of $f$ are 5%, applying the fractional crystallisation model of Cartigny et al. (2001). However, this model is unrealistic as it requires $\sim$ 45% carbon removal before the reservoir reaches a $\delta^{13}$C composition that is 10‰ different from the starting composition. Several stages of fractionation (Rayleigh type) would have a much larger effect on the $\delta^{13}$C composition of the reservoir and significantly accelerate the fractionation process towards a composition of -16‰. This would require the loss of even more carbon. Additionally, Smart et al. (2011) have shown that although the CO$_2$ escape model produces a carbon reservoir with lower $\delta^{13}$C values, only a small amount of the initial fluid/melt reaches a $\delta^{13}$C value less than -14‰ by this process and such a process cannot account for the formation of significant quantities of diamonds with $\delta^{13}$C values below this value. It is therefore concluded that despite the potential of Rayleigh fractionation of mantle fluids/melts towards low $\delta^{13}$C values, mixing of oceanic crust with mantle fluids/melts is a preferable model considering the significant volume of eclogitic diamonds with

<table>
<thead>
<tr>
<th>Diamond area</th>
<th>Point</th>
<th>N FTIR, (at. ppm)</th>
<th>N 1aB% (at. ppm)</th>
<th>N SIMS (at. ppm)</th>
<th>N Mass spec (at. ppm)</th>
<th>$\delta^{13}$C SIMS</th>
<th>$\delta^{13}$C Mass spec</th>
<th>$\delta^{15}$N Mass spec</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1a</td>
<td>134</td>
<td>4</td>
<td>117</td>
<td>-15.8</td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>1c</td>
<td>178</td>
<td>0</td>
<td>196</td>
<td>-16.6</td>
<td>-15.0</td>
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<tr>
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<td>8</td>
<td>-</td>
<td>-15.3</td>
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</tr>
<tr>
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<td>40</td>
<td>0</td>
<td>-</td>
<td>-15.8</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Outer core 3a</td>
<td>3a</td>
<td>39</td>
<td>10</td>
<td>42</td>
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<td>-15.9</td>
<td>-3.9</td>
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</tr>
<tr>
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<td>-</td>
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<td>3</td>
<td>-</td>
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</tr>
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<tr>
<td>Rim 7</td>
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<td>-</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Rim 8</td>
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<td>2</td>
<td>367</td>
<td>-7.6</td>
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</tbody>
</table>
13C-depletion and the compositional similarity of 1703 primary clinopyroxenes and eclogitic clinopyroxenes formed from subducted oceanic crust (Fig. 3b).

5.1.7 Conceptual model for formation of diamond 1703
The relationships between the internal structure, N content and aggregation, composition of inclusions, age of sulphide inclusions and carbon and nitrogen isotope values of the diamond can be explained by the following order of geological events in chronological order.

Formation of the core area
Progressive nucleation and growth of the diamond core at 2.1 Ga took place from a fluid source related to a mafic protolith characterized by moderate N content (circa 120 ppm), 13C-depleted carbon (circa -16‰) and a moderately negative nitrogen isotope value of -7.9‰. A suitable candidate for such a source is subducted mid ocean ridge basalt (MORB), which was firstly altered by seawater and enriched in organic carbon, and then metamorphosed into eclogite during subduction. Supporting the existence of subducted oceanic crust in the area, the carbon isotope composition of Archean and Paleoproterozoic graphite bearing metasedimentary gneisses of the Aldan and Anabar Shields, as well as eclogite xenoliths from kimberlites of Alakit field, range from δ13C values of -4 to -28‰ (average -15‰) (Galimov et al., 1990; Avchenko et al., 1993; Oleinikov et al., 2003). Additionally, the existence of the Billyakh-Fedorovskaya subduction zone is confirmed by formation of Paleoproterozoic basalt-andesite-rhyolitic sequences on the Aldan Shield and granitoid plutons on the Anabar Shield (Smelov et al., 2012). We suggest that syngenetic inclusions of Omph-1, rich in K and Na, were formed simultaneously with the outer core diamond zone at a pressure of ~6 GPa, which approximately corresponds to the basal part of the lithospheric mantle (~185 km).

Resorption of the core area
A period of diamond resorption occurred under sharply decreased P-T parameters. The most obvious reason for such a P-T change would be ascent to a shallower mantle level (< 185 km) as a consequence of a tectono-magmatic event. It is possible that formation of the Nurbinsky Mesoproterozoic rift is related to plume-type magmatism at the end of the Proterozoic. This tectono-magmatic process resulted in partial melting, magma production and uplifting of deep mantle material including diamondiferous eclogites that caused partial diamond resorption. After a period of dissolution the silicate and sulphide inclusions were partially exposed from the paleo-surface of the diamond crystal (present core) to the surrounding fluids.

Overgrowth and formation of the intermediate and rim areas
The oscillatory zone between the diamond core and intermediate areas records a period of several stages of a minor dissolution/re-growth. The silicate and sulphide inclusions were encapsulated again during new diamond growth. Omph-2 and -3 record exposure to a metasomatic melt/fluid enriched in Cr, Ti, Ba, K, Yb and water. Magmatic activity and formation of the Nurbinsky rift were completed at ~ 1.0 Ga and the localised mantle conditions (i.e., carbon concentration, temperature, pressure and redox state) were suitable again for diamond formation. This subsequent progressive diamond growth and formation
of the intermediate and rim diamond zones took place at a shallower lithospheric mantle level (<185 km) from a mantle fluid source characterized by higher N concentrations (300-600 ppm) and a $^{13}$C value akin to the mean-mantle (i.e.: -6.2 to -7.6‰).

5.2 Genetic relationships between eclogitic diamonds from kimberlites and eclogite xenoliths

5.2.1 Constraints from clinopyroxene in diamonds and diamondiferous eclogites

Mir eclogitic clinopyroxenes included in the diamonds contain less jadeite compared to their counterparts in the eclogite xenoliths (Fig 9), indicating a complex relationship between eclogitic diamonds in kimberlites and mantle eclogites (e.g., Ireland et al., 1994). The similarity in chemical composition between both Mir eclogitic diamonds and eclogitic xenoliths is indicative of a key role for metasomatic processes in their origin (Fig. 9).

Clinopyroxenes comparable in composition to those in the composite inclusions in diamond 1703 are common as inclusions in eclogitic diamonds from Yakutian kimberlites (Spetsius and Taylor, 2002; Anand et al., 2004, Shatsky et al., 2008). However, they have not been previously

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**Fig. 9.** Composition of 1703 omphacites compared with those of clinopyroxenes from diamondiferous xenoliths and diamond inclusions (Mir) (Sobolev et al., 1998b). The dotted arrow indicates the evolution from omph-1 to omph-3 and indicates the close relationship between clinopyroxene inclusions and eclogites (Ireland et al., 1994). A, B and C: eclogite clinopyroxene fields for mantle cumulates and subducted oceanic crust (Taylor and Neal, 1989; see also legend in Fig. 3). Ovals with “M” and “U” shows chemistry range of multiple pyroxene inclusions in the individual macro diamonds from Mir and Udachnaya (Sobolev et al., 1998). Compositional variation of clinopyroxenes from a single microdiamond (Mir) is from Sobolev et al. (2004). Range of chemistry of secondary (spongy) clinopyroxenes from diamondiferous xenoliths (Udachnaya) and composition of a clinopyroxene inclusion in a diamond from the Udachnaya pipe xenolith (Anand et al., 2004) are also shown.
reported as multiple phases in a single diamond inclusion. Primary and secondary generations of clinopyroxenes similar to 1703 omphacites have been described in diamondiferous eclogite xenoliths from Mir and Udachnaya kimberlites (Spetsius and Taylor, 2002; Anand et al., 2004, Shatsky et al., 2008; Fig. 9). The primary Cpx (similar to 1703 Omph-1) are surrounded by “spongy”-textured secondary Cpx (similar to 1703 Omph-2, -3) that originated during partial melting and metasomatism of eclogite xenoliths. Worldwide, the transition between the omphatic core and the diopside-augite rim in eclogitic clinopyroxenes is manifested by a consistent increase in FeO, MgO and CaO and a decrease in Al₂O₃ and Na₂O (Spetsius et al., 2009; Gonzaga et al., 2010). This transition is also marked by the appearance of the Ca Al₂Si₄O₁₂ component in pyroxene due to rapid breakdown of omphacite (Smyth, 1980).

Thus our comparison of textural and compositional features of clinopyroxenes in diamond 1703 and in Yakutian diamondiferous eclogites establishes their similarity (Fig. 9). Because Omph-1 from 1703 diamond is associated with growth of the ~2.1 Ga population of diamonds, it is more likely that the “primary” eclogite xenolith clinopyroxenes and the diamonds from these xenoliths would have a similar age (i.e., as summarised in Fig. 10). We suggest that Omph-2 and -3 from the 1703 crystal and the “secondary” Cpx from the xenoliths therefore would have been related to the formation of the ~1 Ga diamond population during a later metasomatic alteration of these eclogites. The chemical similarity identified

![Fig. 10. Re/Os dating of eclogitic diamonds (Yakutia) (Pearson et al., 1998; Wiggers de Vries et al., in press). 1703 sulphides are "hybrids": they are Po (alike Mir Gp.1) but with low initial Os isotope composition and ~1 Ga Re-Os age (alike Mir Gp. 2; Wiggers de Vries et al., in press). Belonging initially to the C-“light” diamond core of 2 Ga age, they were exposed to a new fluid and their Os isotope systematics were affected; 1 Ga age corresponds to this second stage of diamond formation from a "heavy" mantle-like carbon isotope reservoir. Note: Gp – group.](6)
between diamond-hosted clinopyroxenes and eclogite-hosted clinopyroxenes indicate their common origin and their long and complex history of formation in relation to metasomatic modification (Ireland et al., 1994; Fig 9), and future dating of Mir diamondiferous eclogites would provide direct evidence for such relationships.

5.2.2 Potential carbon isotope stratigraphy in the cratonic lithospheric mantle
In agreement with the scarce, but worldwide observation in section 5.1.5. that diamonds from the lower mantle were re-grown in the upper mantle, it has also been suggested that in the mantle beneath the Roberts Victor and Orapa kimberlites (South Africa) the isotope composition of carbon is a function of depth (Deines et al., 1987; 1993). These authors showed that the $\delta^{13}C$ value of relatively shallow mantle is restricted (-5‰ to -8‰), whereas with greater depth the range in $\delta^{13}C$ values widens and becomes $^{13}C$-depleted (down to -22‰). Our results agree with such a carbon isotope mantle stratigraphy under the Mir pipe with lower $\delta^{13}C$ at depth. Additionally, these published data sets define a relationship between eclogitic clinopyroxene inclusion chemistry and isotope composition of the diamond-hosts (Deines et al., 1987; 1993; 2010). Figure 11 demonstrates that eclogitic diamonds with low $\delta^{13}C$ composition contain omphacites with slightly higher jadeite content. A similar relationship is shown by the primary and secondary clinopyroxenes and related core – rim $\delta^{13}C$ isotope zonation in the diamonds from diamondiferous eclogites at Udachnaya described by Shatsky et al. (2008; Fig. 11). Therefore, it appears that eclogitic diamonds with mean-mantle and low $\delta^{13}C$ composition were formed in two different mantle environments at different geological times.

In the case of diamond 1703, the eclogitic diamonds with $^{13}C$-depletion most likely originated within deeper mantle horizons, and this early population was overgrown after transfer, including partially resorption, to another shallower mantle environment. Further

![Fig. 11. $\delta^{13}C$ of diamonds and Na,O in associated omphacites. Data used are: Udachnaya from Shatsky et al. (2008); Orapa from Deines et al. (1993); Premier from Deines et al. (1984); Roberts Victor from Deines et al. (1987).](image-url)
detailed work is required to establish if such relationships exist on a localised scale beneath the Siberian Craton, as is seen in Kaapvaal (Deines et al., 1987; 1993; 2010).

6. CONCLUSIONS

Reconstructed conditions for 1703 eclogitic diamond formation show that the changes in the internal structure, chemical and isotopic composition were caused by growth from two different fluid/melt sources interrupted by a period of resorption. The genesis of the ~2.1 Ga 1703 diamond core and other Mir E-type diamonds with $^{13}$C-depletion took place at a mantle depth of ~185 km and is more likely associated with a fluid source related to subducted oceanic lithosphere. Subduction at 2.5-2.0 Ga beneath the Tunguska Terrain is considered responsible for providing organic carbon for this population of E diamonds. The nature of the protoliths and the processes that formed the earliest diamond population with $^{13}$C-depletion are debatable. Based on the carbon isotope composition and chemistry of the diamond inclusions, the most likely candidate would be subducted MORB that was first altered by seawater, enriched in biogenic (organic) carbon, and then metamorphosed into eclogite.

We propose that growth of the intermediate and rim areas of diamond 1703 took place 0.9 Ga ago coincident with formation of the main Mir E-Type diamond population with carbon isotope signatures typical of the mean mantle (Wiggers de Vries et al., in press), and forming at shallower lithospheric depth of ~120 km during metasomatic events involving fluids enriched in K, Cr, Ti, Ba, Yb and possibly water. Textural and compositional evidence for metasomatic activity similar to that found in the intermediate and rim zones of the diamond studied here, is evident within diamondiferous eclogite xenoliths from Yakutian kimberlites. Such processes may have been responsible for the main stage of E-type diamond growth at Mir and elsewhere in the Siberian Craton.

The main conclusion from this research is that there were at least two pulses of eclogitic diamond growth at Mir, characterised by an early episode with isotopically light carbon and a later episode with heavy typical mantle-like carbon isotopic composition. These growth periods appear to have been separated by a billion year time period (Wiggers de Vries et al., in press). The distinct carbon isotope compositions in diamonds could be the result of formation from different carbon reservoirs, as recorded by sample 1703, where the role of isotopic fractionation during growth was non-substantial. It is suggested that carbon isotope composition of the mantle beneath the Mir kimberlite pipe is a function of depth.

Another important conclusion is that high spatial resolution, in-situ, microanalysis enables geochemical variations across small samples to be resolved. It is crucial to study the internal morphology in-situ in polished sections to fully understand the potentially complex formation histories of zoned diamonds in order to constrain a complete history of diamond formation.

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