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CHAPTER 1

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*Figure on previous page: Statue near the Mir mine of geologist Larissa Popugayeva on expedition in Yakutia. Under the guidance of Natalia Sarsadskikh, she discovered the first kimberlite pipe here, the diamondiferous Zarnitsa kimberlite, in 1954.*
1. INTRODUCTION

Diamonds have been known to people for at least five thousand years and the words ‘diamond’ (English), ‘diamant’ (Dutch) and ‘алмаз’ (Russian) all originate from the Greek word ‘αδαμάς’, which means invincible or untameable. Diamonds are recognised for their remarkable beauty and hardness and are probably the most wanted gemstone in a woman’s jewellery collection. In this work, however, I will shine a light on a different form of a diamond collection: science!

Diamond’s hardness allows it to withstand almost every physical and chemical form of destruction (e.g., transport in kimberlitic magma, erosion at the Earth’s surface, etc) and makes them an exceptional object to study and allows investigation of their origin and evolution. Not unimportantly, some diamonds are reported to be almost as old as the age of the Earth (Gurney et al. 2010) and consequently the evolution of the Early Earth can be studied through diamonds. Furthermore, the study of diamonds helps to unravel the processes hidden from the human eye at great depths in the Earth’s mantle where neither people nor advanced technology can reach.

1.1 Rationale and objectives of the research

Over the years many studies have been conducted on diamonds that were successful in determining the crystal properties, unravelling the physical conditions of diamond formation and discovering diamond deposits on the Earth’s surface. These studies subsequently led to large-scale production of synthetic diamonds. Additionally, through the study of diamonds, inclusions in diamonds and their host rock, insights have been gained into major processes on Earth that have contributed to revisions in geology books; for example theories on plate tectonics and craton accretion.

Important questions on the conditions of diamond formation in the subcontinental lithospheric mantle have successfully been resolved over the last few decades: • Where do diamonds form? • How are they brought to the Earth’s surface? • What are the pressure and temperature conditions of formation? • What is the mineralogy of the source region? • When did diamonds form? These topics will be succinctly summarised in the next paragraphs. To date, however, substantial controversy remains on several subjects that are essential to understand the processes and sources of diamond formation:

• What is the genetic origin of inclusions in diamonds - can inclusions be used to unravel the history of the diamond, i.e., did inclusions form at the same time as the diamond or can the inclusions be older than the diamond and consequently have a different history?
• What are the origins of carbon sources in the mantle - what is the nature of carbon isotope fractionation in the mantle under changing oxidation conditions? i.e., can carbon isotope ratios be used to determine if the heterogeneity of carbon isotope compositions of diamonds represent a mix of primitive mantle-derived carbon and subducted carbon?
• What is the timescale of diamond growth - the ages of diamond formation are well-known in some locations, but how long does it take for a diamond to grow, i.e., do diamonds form within a geologically short time span (e.g., hours or hundreds of years), or may it take hundreds of millions of years?
Recent advancements in analytical techniques, especially the techniques that allow in-situ analyses of small amounts of material, have greatly contributed to a better understanding of the conditions of diamond growth. Previously, analysing a few fg or pg ($10^{-15}$ g or $10^{-12}$ g, respectively) of material was impossible and analyses effectively lead to mixing of large sample volumes to obtain the required amount of material. Today, by contrast, it is possible to analyse a single inclusion in a diamond or a single spot on the diamond surface. Notably, ion microprobe techniques offer high spatial resolution for quantitative in-situ determination of the chemical and isotopic composition of diamonds.

Therefore, today with state-of-the-art techniques it is possible to go beyond questions associated with the larger diamond populations, and it is feasible to unravel in extreme detail the history of a single diamond.

In this thesis diamond crystals from the Siberian Archaean Craton containing mineral inclusions (Fig. 1.1) were subjected to multiple high precision, high spatial resolution, in-situ geochemical and isotope analyses to determine the processes responsible for diamond genesis. This goal was achieved through a detailed understanding of the growth history of individual diamond and the inclusions they contain, as diamonds may show complex internal growth structures. The objectives of the research carried out in this thesis are to use modern high resolution techniques to resolve the three highly debated topics discussed above, namely; What is the genetic origin of inclusions in diamonds? What are the origins of carbon sources in the mantle? What is the timescale of diamond growth?

![Fig. 1.1. Three Yakutian diamonds with mineral (sulphide) inclusions. (a) Plane-faced, colourless, octahedral diamond #P-4193 (23 mg) from 23rd Party Congress. (b) Dodecahedron #P-4118-13 (127 mg) from 23rd Party Congress with stepped-development of faces. (c) Damaged octahedroid #E-1603 (372 mg) from Mir with micro-lamination due to dissolution by kimberlitic magma.](image)

(1) Genetic origin of inclusions in diamonds

The genetic origin of inclusions in diamonds is a crucial question in the context of this thesis; i.e., were inclusions formed simultaneously with the diamond host (syngenetic inclusion) or are they trapped older inclusions (protogenetic inclusion)? Inclusions in diamonds are considered vital for understanding diamond petrogenesis because they retain a record of P-T conditions, the mineralogical and geochemical environment of diamond formation and timing of diamond growth. Inclusions in diamonds are generally regarded as syngenetic, however, to date major uncertainties regarding this assumption exist (Taylor et al. 2003).
Chapter 3 describes the set up of a new micron-scale technique to provide quantitative criteria to help resolve the ongoing discussion about the formation of mineral inclusions in diamonds. The technique employed combines cathodoluminescence (CL) and electron backscatter diffraction (EBSD) using a focused ion beam-scanning electron microscope (FIB-SEM) instrument. EBSD quantitatively identifies the crystallographic orientations of the diamond and included minerals at individual points. The other part of technique involves sequential milling of micron-scale slices with a FIB followed by CL imaging on each newly created surface. These consecutive CL images allow a 3D reconstruction (3D-CL) of the shape of the inclusion and the geometry of the diamond zonation around it because the diamond-inclusion interface and diamond zonation patterns are well preserved during slicing. The combined technique contributes to a better understanding of the complex growth histories of diamond and the micron-scale inter-relations between host diamond and inclusions.

(2) Sources of carbon in the mantle
Over the last few decades the origins of carbon within diamond has remained the subject of debate and therefore in this work the carbon isotope (and nitrogen content and aggregation state) variability is studied at the micron-scale in individual diamonds (chapter 4). Worldwide there is strong evidence that the precursors of diamond-forming C-H-O-S fluids are a mix between primary mantle-derived melts and Archaean SCLM/subducted Archaean crust (e.g., Aulbach et al. 2009b; Richardson et al. 2009) and, secondly, there is a strong correlation between the formation of eclogitic diamonds and subduction, as subducted biogenic carbon on average has carbon isotope compositions of < -10‰ (Kirkley et al. 1991). However, major uncertainties still exist about the significance of these observations as models based on mantle heterogeneity or Rayleigh fractionation appear able to partially explain the heterogeneity in carbon isotope composition within diamonds (Stachel et al. 2009).

By means of studying the carbon isotope, nitrogen content and aggregation state variability at individual points along core-rim traverses in individual diamonds, the scale and magnitude of variation can be assessed. Better knowledge of the chemical variation on the micron-scale will potentially resolve the origin of the chemical and carbon isotope variability in diamonds and thereby constrain the processes that control diamond formation, including the influence of different fluid/melt sources on isotope fractionation during diamond formation. Additionally, the study of nitrogen content and aggregation state will provide constraints on temperatures of diamond growth and the magnitude of relative age differences between diamond cores and rims (Taylor et al. 1990; Mendelssohn and Milledge 1995). Consequently, by examining co-variation in δ13C values and nitrogen content and aggregation state, it can also be established if individual diamonds are formed in single or multiple growth events. This latter topic will be the key theme in chapter 4.

(3) Timescale of diamond growth
The ability to obtain Re-Os isotope data from single sulphides included in diamonds (i.e., analysing a few fg of material; Pearson et al. 1998) has provided important constraints on the timing of diamond formation worldwide. However, it is still unknown how long it takes for a diamond to grow (Navon 1999) and dating of single inclusions in single diamonds can potentially help to resolve this ongoing question (chapter 5). The fact that diamond
formation worldwide was episodic (e.g., review papers of Gurney et al. 2010; Helmstaedt et al. 2010) raises the question whether single diamonds formed during different growth stages, i.e., if they have a multistage growth history.

Furthermore, dating Yakutian diamonds, and especially dating of E-type crystals, will provide better constraints on the evolution of the Siberian Craton, as to date little age information exists for Yakutian diamonds (see review papers of Gurney et al. 2010). Additionally, dating of E-type diamonds from Yakutia may contribute to the discussion about the precursor of the melts generated prior to diamond formation and may indicate if Paleoproterozoic diamond formation was widespread (Gurney et al. 2010). Nitrogen aggregation states will also be examined here to validate the Re-Os isotope ages.

1.2 Outline of the thesis

A general introduction to lithospheric diamonds and the research in this thesis, including the geological setting of Yakutian diamonds, is given below (i.e., paragraphs 1.3 and 1.4). A morphological and chemical introduction into the Yakutian diamonds and their inclusions (Fig. 1.2) is given in chapter 2 and this chapter also classifies the studied diamond samples based on geographical origin and chemical characteristics. Chapters 3-6 present the data, and each of these chapters systematically assesses one of the goals of this PhD project. Chapters 3-6, all of which have been published (or submitted) as peer-reviewed articles, each include an outline of the approach, results and conclusions to each topic. This approach leads to some repetition but I feel it would discredit these carefully prepared articles if they were taken apart again to avoid the repetition. In order to keep the repetition to a minimum, an overview and description of the various analytical techniques applied here, is provided in the appendix. In the final chapter (chapter 7), the obtained results are combined and assessed to form the synthesis of the thesis.

Fig. 1.2. Diamond inclusions. (a) Large sulphide inclusion (~1 mm in diameter) in diamond #E-4142 from 23rd Party Congress. The sulphide appears transparent and is surrounded by disk-like (‘rosette’) fractures that are coloured black due to sulphide extrusion. (b) Two peridotitic purple garnet inclusions and two colourless, elongated olivine inclusions (all <40 µm in diameter) with a cubo-octahedral external morphology indicative of an imposed morphology during syngenetic growth, in diamond #P-616 from Mir.
Chapter 1 (i.e., the present chapter) summarises the objectives of the research in this thesis, addresses the origin and history of diamond formation in the lithospheric mantle and provides an insight into the geological setting of Yakutian diamonds.

Chapter 2 provides a brief description and classification of the different diamond samples and their mineral inclusions that are used in this thesis for micron-scale study.

Chapter 3 addresses the genetic origin of mineral inclusions in diamonds (i.e., the first objective of the research), and presents a new, combined, micron-scale technique ‘3D-CL imaging and Electron Backscatter Diffraction’ including the results obtained with this technique on a Yakutian diamond.

Chapter 4 addresses the sources of carbon in the mantle (i.e., the second objective of the research) by revealing micron-scale variations along coupled δ¹³C-N abundance traverses in Yakutian diamonds.

Chapter 5 addresses the timescale of diamond growth (i.e., the third objective of the research) by Re-Os isotope dating of multiple single sulphide inclusions (Fig. 1.3) in single Yakutian diamonds.

Chapter 6 effectively illustrates the history of a single Yakutian diamond. The complex growth history of this diamond typically demonstrates the implications of the different topics in this thesis, i.e., growth of a single diamond from different C-bearing reservoirs at different times.

Chapter 7 is the synthesis, and summarises the implications and conclusions of the research carried out in this thesis (i.e., in chapters 3-6). Furthermore, some recommendations for future research are given.

Fig. 1.3. Typical Yakutian sulphide inclusion (unfortunately broken through the middle into two pieces) with a cubo-octahedral external morphology extracted from diamond #E-1237 from Mir. The background scalebar is 100 µm (i.e., 0.1 mm).
1.3 Lithospheric/cratonic diamonds

1.3.1 Origin and occurrence worldwide

The majority of the world’s natural diamonds (~99%) recovered to date formed in the lithospheric mantle beneath Archaean cratons that present ancient crust, i.e., 4-2.5 Ga old (Bowring et al. 1990; Pearson and Wittig 2008). These diamonds are also referred to as cratonic diamonds and are generally of gem-quality. Cratonic diamonds are also recovered from secondary deposits, both recent and ancient placers deposits that formed due to erosion of a primary diamond deposit in an Archaean craton (Helmstaedt et al. 2010).

Natural diamonds of different origin also occur, such as sublithospheric diamonds (i.e., ‘ultradeep diamonds’ that form as deep as 650 km; Scott-Smith et al. 1984; Harris 1992; McCammon 2001), ultrahigh-pressure diamonds (i.e., occurring in collisional orogenic belts; Ogasawara 2005) and diamonds that formed at the Earth’s surface in impact craters (Masaitis 1995). Nevertheless, these latter deposits are scarce and mainly contain micro-diamonds of <1 mm.

1.3.1.1 Archaean cratons

The presence of Archaean cratonic crust is an import condition for lithospheric diamond formation, because Archaean crust is relatively thick compared to younger crustal regions (e.g., review paper of Stachel and Harris, 2008). As a result a combination of temperature and pressure conditions that is ideal for diamond formation is typically found beneath these cratons (i.e., 130-200 km depth and 900-1400 ºC). Archaean cratons are found in Australia, Africa, Brazil, Canada, India and Russia (Fig. 1.4; Pearson and Wittig 2008). Roughly 50% of the world’s cratonic diamond deposits is found in central and southern Africa in countries such as The Democratic Republic of Congo and Botswana (Dan Hausel 2006).

1.3.1.2 Transport in kimberlites

Lithospheric diamonds are mined from kimberlite and lamproite volcanic pipes in Archaean cratons (Boyd and Gurney 1986), which bring them to the surface within a few hours (e.g., O’Hara et al. 1971; Edwards and Russell, 1998). Kimberlites are potassic ultra-basic igneous rocks (Mitchell 1995) that are derived as magma from the mantle and brought to the surface through deep faults. Importantly, the kimberlites contain various rock types that were sampled during ascent, i.e. xenoliths derived from the mantle, crust and sedimentary cover.

1.3.1.3 Xenocrystic origin

Xenoliths or xenocrysts (pre-existing rocks or crystals in an igneous host) are very abundant in kimberlitic rocks. Cratonic diamonds are considered to be xenocrysts from the sub continental lithospheric mantle (SCLM) and the kimberlites thus only act as transporting media (e.g., Richardson et al. 1984). Consequently, xenoliths and xenocrysts can be significantly older than their transporting medium.

1.3.2 Pressure-Temperature regime

Worldwide, mineral inclusion geothermobarometry on lithospheric diamonds indicate formation at pressure and temperature conditions in the SCLM ranging approximately between 130-200 km depth (equalling to pressures of 4.5-6 GPa) and 900-1400 ºC (Boyd and Gurney,
Fig. 1.4. Global distribution of the cratons (regions of crust >2.5 Ga old), after Pearson and Wittig (2008).
1986; Stachel and Harris, 2008). The cratonic roots beneath the Archaean cratons are significantly cooler than the convecting mantle at similar depths and consequently the graphite-diamond transition is raised to a shallower depth within the subcratonic lithosphere, creating a diamond ‘stability field’ within these cratonic roots (Fig. 1.5; Stachel and Harris, 2008).

Fig. 1.5. Schematic vertical section through the Earth’s crust and part of the upper mantle showing that beneath Archaean cratons the lithosphere may extend to over 200 km in depth, after Stachel and Harris (2008).

1.3.3 Paragenesis
The dominant rock type forming the lithosphere beneath cratonic crust is peridotite, with eclogite and pyroxenitic assemblages making up less than 2% of the volume (Schulze 1989). Diamond formation in the lithospheric mantle is generally associated with two different rock-types in the cratonic mantle roots, implying diamond formation in different growth environments: 1) peridotites, which generally consist of olivine, chromite, orthopyroxene, garnet (Cr-pyrope) and (diopsidic) clinopyroxene (e.g., Fig. 1.2b), and 2) eclogites, which predominantly consist of garnet (pyrope-almandine) and (omphacitic) clinopyroxene (Meyer and Boyd 1972). Importantly, the mineral inclusions found in diamonds are also related to both types of mineralogy. Therefore, on the basis of the mineralogy and chemistry of mineral inclusions, diamonds are classified into two predominant parageneses, i.e., a peridotitic (P-type diamonds) or an eclogitic (E-type diamonds) suite, although a rare (2%) websteritic paragenesis (W-type) that is intermediate between P- and E-type suites has also been documented (Gurney et al. 1984). The P-type suite can be subdivided into a harzburgitic, a lherzolitic rock type (depending on Mg# of the inclusion) and a very rare (1%) wehrlitic suite (Sobolev et al. 1973). Worldwide, the abundance of inclusion types is ~65% (P-type), ~33% (E-type) and ~2% (W-type; Stachel and Harris 2008). Surprisingly, despite the lower abundance of E-type diamonds, diamond-bearing eclogitic xenoliths are far more abundant than P-type diamond-bearing xenoliths (Navon 1999). This apparent difference is believed to be the result of the easier breakdown of P-type xenoliths due to the impact of decarbonation reactions during their transport in highly volatile kimberlites.
1.3.4 Genetic origin of inclusions
Unlike the minerals in peridotitic and eclogitic xenoliths that may have been modified during mantle storage and uplift, the inclusions in the diamonds generally document the mineralogy at the time of diamond formation as the diamond effectively acts as an inert barrier (Taylor and Anand 2004). Consequently, the inclusions in diamonds are generally regarded as syngenetic (i.e., co-crystallisation of inclusion and diamond) and a record of the diamond’s formation history. However, major uncertainties regarding this assumption exist (Taylor et al. 2003), which are very important considering that inclusion studies significantly contribute to the interpretation of the diamond’s growth history. For example, protogenetic (i.e., crystallisation of a mineral prior to being trapped by diamond) and epigenetic (i.e., formation or modification of inclusion after diamond formation) diamond inclusions have also been reported (chapter 3). Cracks that developed after growth can connect an inclusion to the diamond surface, and any alteration process could modify the inclusion and transform it into an epigenetic inclusion. Fortunately, the absence of cracks or healed cracks can readily be verified with CL imaging of the diamonds and used to establish if diamond inclusions are epigenetic.

1.3.5 Ages: Constraints on craton evolution
Lithospheric diamond formation occurred episodically in the SCLM, whereby most cratonic diamonds formed between 3.5 and 1 Ga ago based on isotopic dating of mineral inclusions (Gurney et al. 2010). The oldest diamonds recovered from the lithosphere, nonetheless, are micro-diamonds that were included in detrital zircons, which range in age between 4.3-3.1 Ga, from Archaean rocks in Jack Hills, Australia (Menneken et al. 2007). The geochemistry of the zircons suggests formation associated with granite formation that indicates hydrous melting at depth, either within thickened basaltic crust or related to subduction style tectonics. Additionally, the micro-diamonds have light δ 13C values down to -24‰ and are associated with graphite that has δ 13C value as low as -58‰ (Nemchin et al. 2008). These data may indicate recycling of biogenic carbon to depth but currently such an interpretation cannot be fully validated but the implication is that major vertical tectonics were active in the early Archaean (Hadean).

For cratonic diamonds there is a systematic relationship between the ages obtained and the inclusion paragenesis of the diamonds with P-type diamonds (harzburgitic) generally being older (Gurney et al. 2010). Furthermore, the ages of P- and E-type diamond inclusions demonstrate that the episodes of lithospheric diamond formation correlate with craton-forming events (e.g., Shirey et al. 2004; Gurney et al. 2005, 2010; Helmstaedt et al. 2010; Shirey and Richardson 2011). The oldest cratonic diamonds range in age between 3.5-3.1 Ga and are harzburgitic (i.e., P-type diamonds) occurring in the Kaapvaal- (Southern Africa), Slave- (Canada) and Siberian Cratons (Gurney et al. 2010). Lherzolitic diamonds (i.e., also P-type diamonds) are younger than the diamonds associated with harzburgitic host rock, and 2030-1900 Ma old. These lherzolitic diamonds can occur in the same pipes as the harzburgitic diamonds, and are believed to have formed due to addition of a basaltic component to the SCLM (Richardson and Shirey 2008; Richardson et al. 2009). Additionally, the majority of E-type diamonds is reported to have formed during the Proterozoic (Gurney
et al. 2010). The ages of E-type diamond formation range between 2900-582 Ma, and this relatively widespread range in ages is associated with multiple generations of diamonds in the different cratons worldwide. The worldwide absence of E-type inclusions in Palaeoarchaean diamond populations, which can be linked to deep subduction via continental collision, suggests the late initiation of subduction (Shirey and Richardson 2011).

Compared to African and Canadian diamonds, there is less age information for Siberian diamonds (see review paper of Gurney et al. 2010). Peridotitic diamonds from Udachnaya are well studied and yield Re-Os model ages of 3.5-3.1 Ga (Pearson et al. 1999b) and a Sm-Nd model age of 2 Ga (Richardson and Harris 1997). Argon age constraints from E-type clinopyroxenes from the same locality, however, have large uncertainties due to potential Ar loss. The significance of the diversity of ages ranging between 425-1149 Ma is therefore unclear (Burgess et al. 1992). Additionally, the origin of the relatively young ages reported for in total eight E- and P-type diamonds from Mir is unclear with ages ranging between 213-582 Ma, as revealed by Re-Os isotope dating of sulphide inclusions and inferred from zonation in garnet inclusions (Shimizu and Sobolev 1995; Shimizu et al. 1997; Pearson et al. 1999a, 2000). To date, there is no age information for 23rd Party Congress diamonds.

1.3.6 Carbon isotopes: Constraints on sources of carbon
The carbon isotope composition of lithospheric diamonds worldwide ranges between -41‰ and +5.0‰ (Cartigny et al. 2004; De Stefano et al. 2009). However, 72% of samples are in a 3‰ range around a value of -5‰ (Kirkley et al. 1991; Navon 1999; Pearson et al. 2003; Cartigny 2005; Stachel et al. 2009). This narrow range in δ13C values is typical of mantle derived magmas (Javoy et al. 1986; Mattey 1987; Galimov 1991; Javoy and Pineau 1991). Nevertheless, the origin of heterogeneity amongst carbon isotope composition between diamonds has been explained by three models: (1) Heterogeneity in primordial mantle carbon (Deines 1980; Deines et al. 1987; Boyd et al. 1994b); (2) Distinct mantle carbon sources formed by the recycling of subducted biogenic crustal carbon (Sobolev and Sobolev 1980; Kirkley et al. 1991); (3) Intra-mantle fractionation of carbon (Deines 1980; Javoy et al. 1984, 1986; Galimov 1991; Cartigny et al. 2001; Thomassot et al. 2007; Stachel et al. 2009).

To date the ultimate source of the diamond-forming fluids/melts remains highly debated as models based on mantle heterogeneity or Rayleigh fractionation appear unable to fully explain the variations in carbon isotope composition within diamonds (Stachel et al. 2009).

There is a general correlation between diamond paragenesis and δ13C value (Sobolev et al. 1979). E-type diamonds span almost the entire range in carbon isotope ratios, while P-type diamonds exhibit a narrower range from -26.4‰ to +0.2‰ and within this narrower range P-type values predominantly range between -10‰ and 0‰ (Cartigny 2005).

Yakutian diamonds have δ13C values that are typical for worldwide populations (Fig. 1.6). Previously studied diamonds with octahedral growth (i.e., micro-, gem-quality- and coated diamonds) from Mir and Udachnaya record δ13C values that range between -17‰ to -13‰ for a small number of E-type crystals and between -9‰ to -1‰ for the majority of E- and P-type crystals (Galimov 1984, 1991; Boyd et al. 1992; Snyder et al. 1995; Hauri et al. 1999; Bulanova et al. 2002; Hauri et al. 2002; Reutsky and Zedgenizov 2007; Stepanov et al. 2007; Wiggers de Vries et al. 2007; Shatsky et al. 2008; Liu et al. 2009; Spetsius et al. 2009).
1.3.7 Nitrogen content and aggregation
The chief impurity in the natural diamond crystal lattice are nitrogen atoms, however, Si, Al, Ca, Mg and Mn are also very common (1-100 ppm; Raal 1957; Fesq et al. 1975; Orlov 1977). Nitrogen substitutes for carbon in the crystal lattice. Nitrogen plays a key role in the properties of diamonds, such as conductivity and (CL) colour. Nitrogen atoms are present in diamonds in concentrations that vary from zero up to 5000 ppm, whereby worldwide P-type and E-type diamonds have average nitrogen concentrations of ~200 and ~300 ppm, respectively (Bibby 1982; Cartigny 2005; Stachel and Harris 2009b). Nitrogen is recognised as a compatible element during diamond growth under oxidising and reducing conditions (Thomassot et al. 2007; Stachel et al. 2009; Smart et al. 2011) and is widely used to classify diamonds (Evans 1992; Mainwood 1994). Diamonds with low to undetectable nitrogen concentrations (<10 ppm) are classified as type II and diamonds with higher nitrogen concentrations as type I. Further classification is based on the manner of nitrogen distribution within the diamond crystal lattice, i.e., as single substitutional atoms or nitrogen aggregates.

Once nitrogen-bearing diamonds are formed in the mantle, nitrogen aggregation occurs (Evans 1992; Mainwood 1994). Diffusion of nitrogen atoms in diamond leads to progressive aggregation of two (type IaA) towards four nitrogen atoms (type IaB). The rate of conversion of A-defect centres (i.e., pairs of nitrogen atoms) into B-defect centres (i.e., four nitrogen atoms surrounding a vacancy) is a function of nitrogen content, temperature and time. Therefore, the nitrogen IaB aggregation state can be used to calculate the temperatures and/or times of diamond residence in the mantle (Taylor et al. 1990; Mendelssohn and Milledge 1995).
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Theoretical calculations of the residence time of the diamonds in the SCLM have proven to be a good indicator of the age of the diamonds if the time of eruption of the kimberlite is known (Navon 1999). Worldwide, there is a good correlation between diamond age and nitrogen aggregation state (Richardson and Harris 1997; Pearson et al. 1998, 1999b). Additionally, there is also good agreement between inclusion thermometry and nitrogen aggregation thermometry (Evans and Harris 1989; Harris 1992; Navon 1999; Stachel and Harris 2008).

1.4 Geological setting of diamonds from the Siberian Craton

The diamonds in this study are derived from several kimberlite pipes in the governmental province of Yakutsk, i.e., ‘the Yakutian diamond province’, within the Siberian Craton (Fig. 1.7). Most geologic literature of this area is published in Russian, nevertheless, a comprehensive overview of the evolution of the Siberian Craton was published in English by Rosen et al. (1994). Most of the craton is covered by sediments and therefore geophysical imaging is a main tool in mapping the basement and, if available, drilling holes and xenoliths also provide insight into the local geology.

1.4.1 Siberian Craton

The Siberian Craton stretches from North to South all the way from Lake Baikal to the Arctic Ocean (Laptev sea), and approximately the same distance from east till west (Fig. 1.7). In total it occupies an area of 4x10^9 km². The craton itself consists of several Archaean micro-continents of different age (i.e., 3.5, 3.3, 3.1 and 2.5 Ga) that were assembled some 2.5 Ga ago (Rosen et al. 2002). The Siberian Craton is divided into five provinces, i.e., Tunguska, Anabar, Olenek, Aldan and Stanavoy Range, which each consist of one or more Archaean micro-continents.

The basement of the Siberian Craton mainly consists of two characteristic rock suites; Archaean tonalite-trondhjemite-granodiorite-greenstones (i.e., TTG-greenstones that are greenschist- and/or amphibolite-facies rocks) that separated from the mantle 3.5 and 2.5 Ga ago and 3.3 and 3.0 Ga Archaean granite-gneisses (i.e., granulite-facies rocks). The majority of these rocks is exposed on the Archaean Anabar and Aldan shields.

This Siberian ‘Paleoproterozoic supercontinent’, i.e., the Siberian Craton, experienced several supercontinental cycles that consist of accretion and subsequent break-up of landmasses caused by plate tectonics, i.e., Wilson cycles (Wilson 1968). After collision at ~1.9-2.0 Ga with other cratons, the cratons existed as one megacraton (Condie and Rosen 1994). This event was followed by heating of the crust thickened by collision that caused the anatectic melting of silicic magma. The ages of granite formation and metamorphism in the fault zones that bound the micro-continents, as well as metamorphism in the terranes, are alike. Zircons in the migmatites and granitoids yield ages of 1.8-2.0 Ga indicating that this amalgation event had a significant effect on the geological history of the Siberian Craton. After accretion ~1.1 Ga ago the Siberian Craton became part of the major supercontinent of Rodinia that existed until ~750 Ma. Late Paleozoic convergence between the Siberian and Baltica Cratons lead to the formation of the supercontinent Pangaea that existed during the Paleozoic and Mesozoic (Rosen 2002).

The Siberian Craton is surrounded by sedimentary and volcanic belts that formed during and immediately after accretion (Rosen 2003). The craton is bound to the North and East by respectively the Taimyr Belt and the Verkhosyansk Belt. Both belts are Phanerozoic sedimentary
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foldbelts. In the southeast and west both the Mongolo-Okhotsk Belt and the Central Asian Belt bound the craton. These belts are respectively Mesozoic and Paleozoic volcanic foldbelts. The borders of the craton are deep, major Late Paleozoic faults that reach well into the mantle.

Due to major rifting of the accreted areas at ~1.8 Ga and 0.8 Ga, Riphean-Phanerozoic clastic sediments formed by erosion of the Early Proterozoic mountain belts and overlie the
craton with thicknesses varying from 1-12 km. In the Northwest flood basalts of the Siberian traps formed at the Permo-Triassic boundary cover the area. Consequently, nowadays only 25% of the Archaean basement is exposed.


1.4.2 Anabar Province

The Anabar Province is located in the center of the craton and hosts most of the diamondiferous kimberlites discovered on the Siberian Craton, including the pipes studied in this thesis (Fig. 1.7). The Magan and Daldyn granulite-gneiss Terranes (3.1 Ga), and the Markha TTG-greenstone Terrane (2.5 Ga) make up this province (Rosen et al. 1994). Granulite-facies metamorphism in the province is dated between 1.9-1.8 Ga, (Rosen 2002). The Daldyn and Markha Terranes are divided by the Kotuikan shear zone, which was active between 1.9 and 1.8 Ga as now defined by migmatites and granitoids (Rosen 2002). Granulite-facies metamorphism in the belt is dated at 1.88 Ga and intrusive granites between 1.87-1.82 Ga. The Billyakh thrustfault (1.8 Ga) separates the Anabar Province from the Olenek Province (Rosen 2002).

1.4.3 Diamondiferous kimberlite pipes

The governmental province Yakutia in Siberia is one of the largest diamondiferous provinces in the world (Fig. 1.7). In 1954 in this harsh and remote area where permafrost persists, geologist Larissa Popugayeva (Fig. at the beginning of chapter 1) discovered the first kimberlite pipe, the diamondiferous Zarnitsa kimberlite (Zarnitsa means ‘dawn’ translated from Russian), after tracing ‘G10’ garnets that are harzburgitic subcalcic pyropes known as marker minerals for diamond deposits (Gurney 1984). Subsequently, over one thousand kimberlites were discovered in Yakutia including Mir (‘peace’, in 1955), Udachnaya (‘lucky’, in 1955), 23rd Party congress (in 1959) and Aikhal (‘glory’, in 1960).

More than twenty different kimberlite fields and over thousand kimberlite bodies (Ionov et al. 2010) occur across the Siberian Craton. The majority of kimberlite pipes is found within the Daldyn and Alakit kimberlite fields within the Anabar Province (Rosen et al. 2002).

The diamonds in the current study originate from two fields from the Archaean terranes within the Anabar Province. The Mir and 23rd Party Congress kimberlites are located in the Malo-Botuobiya kimberlite field, Magan Terrane. The Udachnaya kimberlite is located approximately 400 km further North in the Daldyn kimberlite field, Markha Terrane (Fig. 1.7).

The Udachnaya and Mir kimberlites are the most well-known pipes from the Yakutian diamond province, as they are the most characteristic and economic. The Udachnaya kimberlite consists of two pipes of nearly similar age that merge on the surface in the form of a figure of 8, i.e., the Udachnaya-West kimberlite (largest and oldest) and the Udachnaya-East kimberlite (smallest and youngest). SHRIMP U-Pb ages for included perovskites are within error suggesting that both pipes intruded within a very short time interval ~365 Ma ago (Kinny et al. 1997).
Remarkably, the Mir kimberlite is the largest open-pit diamond mine in the world. The mine is 515 meters deep and has a diameter of 1200 meters (Fig. at the beginning of chapter 3). After 44 years of operation the Mir mine closed in 2001, having produced approximately 2 million carats of diamonds on an annual basis. Since 2009 underground mining started-up (http://www.eng.alrosa.ru) as it was proven that the remaining diamond reserves were sufficient to make underground exploitation economically viable.