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# GARNET, CLINO- AND ORTHOPYROXENE <br> INCLUSIONS IN DIAMONDS: IMPLICATIONS FOR THE SYNGENESIS/PROTOGENESIS 

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#### Abstract

Diamonds are the deepest Earth's materials which can reach unaltered the surface of our planet. Such feature makes diamonds the main, if not the only, object of study for the investigations of the deepest parts of the Earth and they are considered to provide records of deep geological processes over much of the planet's existence. Particularly, absolute ages for diamond formation are fundamental to place these records in a time framework, but their chemical and physical properties allow us to obtain only a few geochemical, geochronological and geothermobarometric information. Since the 60s, the common assumption of syngenesis, i.e., diamond and inclusions were formed simultaneously, has permitted the individuation of the ages of diamonds through the dating of their inclusions. Nevertheless, some recent works have suggested that some typical inclusions in diamond, especially olivine and sulphide, are protogenetic, i.e., they were formed before the diamond host. Other three minerals commonly included in diamonds are garnet, clino- and orthopyroxene. Such minerals are used for acquiring important knowledge on diamonds, in particular garnet and clinopyroxene permit the dating through the $\mathrm{Sm}-\mathrm{Nd}$ dating system, but the genetic relationships between these mineral inclusions and diamonds are insufficiently studied.

This thesis work provides the robust crystallographic evidence that garnet, clinoand orthopyroxene inclusions are protogenetic, based on the random orientations of a big number of inclusions in respect to their host diamonds for a great collec-


tion of diamonds from 11 localities worldwide. The implications of these results are incisive in the study of diamonds, especially for the dating methods applied to garnet and clinopyroxene. Under these circumstances, a diffusion model for the $\mathrm{Sm}-\mathrm{Nd}$ system has been calculated at the typical P-T range of the diamond formation. It demonstrates that isotopic resetting would generally occur over geologically short time-scales for garnet and over extremely long time-scales for clinopyroxene. Therefore, despite protogenicity, the majority of garnet-based ages effectively corresponds to the time of diamond formation, while clinopyroxene has been shown unsuitable for dating the diamonds.

## Riassunto

I diamanti costituiscono la materia terrestre più profonda che riesce a raggiungere la superficie del nostro pianeta senza subire alcuna alterazione. Tale peculiarità rende i diamanti il principale, se non il solo, oggetto di studio per le investigazioni delle parti più interne della Terra e si ritiene che contengano traccia dei processi geologici profondi su gran parte dell'esistenza del nostro pianeta. In particolare, l'età assoluta della formazione dei diamanti è fondamentale per definire questi processi in un arco temporale, ma le loro caratteristiche chimiche e fisiche ci consentono di studiare solo poche informazioni geochimiche, geocronologiche e geotermobarometriche. Dagli anni ' 60 , la comune assunzione di singenesi, secondo la quale il diamante e le sue inclusioni si formano simultaneamente, ha permesso lo studio dell'età dei diamanti tramite la datazione delle loro inclusioni. Tuttavia, recenti lavori suggeriscono che alcune tipiche inclusioni in diamanti, in particolare l'olivina e i solfuri, siano protogenetiche, ovvero si sono formate precedentemente rispetto al diamante. Altri tre minerali comunemente inclusi in diamanti sono il granato, il clinopirosseno e l'ortopirosseno. Questi minerali sono utilizzati per acquisire importanti conoscenze sui diamanti, in particolare il granato e il clinopirosseno permettono la datazione tramite il sistema $\mathrm{Sm}-\mathrm{Nd}$, ma il rapporto di geneticità tra questi minerali e il diamante non sono sufficientemente studiate.

Questo lavoro di tesi fornisce l'evidenza cristallografica che le inclusioni di granato, clinopirosseno e ortopirosseno sono protogenetiche, basandosi sull'orienta-
zione casuale delle inclusioni analizzate rispetto al loro diamante ospite su una collezione di diamanti provenienti da 11 località diverse da tutto il mondo. Le implicazioni che hanno tali risultati sono incisive sullo studio dei diamanti, in particolare sul metodo di datazione utilizzato su granato e clinopirosseno; sotto queste circostanze, è stato calcolato un modello di diffusione per il sistema Sm-Nd alle tipiche condizioni di formazione dei diamanti. Questo modello dimostra che il resetting del sistema isotopico del granato avviene in tempi geologicamente brevi e quello del pirosseno in tempi estremamente lunghi, quindi la maggior parte delle età ricavate dal granato corrispondono effettivamente al momento di formazione del diamante, mentre il clinopirosseno si è rivelato non idoneo per la datazione dei diamanti.

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## Chapter 1

## Introduction

### 1.1 What is a diamond?

Diamond is a native carbon mineral with singular properties. It forms in the Earth's mantle below the depth of about $130-150 \mathrm{~km}$, but it can reach the surface as xenolith by means of unusual deep eruptions of volcanic rocks, the kimberlites. Its formation in the mantle rocks is mainly caused by a metasomatic process acted by a free fluid phase, the so-called "C-O-H-bearing fluid or melt", which infiltrates in the rocks and reacts with them, forming diamonds through oxidation-reduction reactions involving carbonate or methane (Shirey et al., 2013). Other settings in which natural diamonds can form are the ultra-high-pressure metamorphic terranes, with processes similar to the reactions occurring in the mantle, and for the impacts of extraterrestrial body, in which diamonds recrystallize by means of the graphite to diamond phase transition reaction or precipitate from impact melts, but their formation represents an extremely unusual condition.

Generally, the deep subcratonic lithosphere is the principal source of the terrestrial diamonds. Such diamonds, called lithospheric, are generated in a depth of 120 to 250 km and represent the $99 \%$ of the global diamond population, while the other


Figure 1.1.1: three-dimensional diagram which describes the basic relationship between a continental craton, the mantle keel and the convecting mantle. It also shows the field of diamonds formation. Modified from Shirey et al. (2013). $\mathrm{G}=$ graphite, $\mathrm{D}=$ diamond, $\mathrm{LAB}=$ lithosphere/asthenosphere boundary.
$1 \%$ corresponds to the super-deep diamonds, from 300 to 1000 or more km of depth (Stachel and Harris, 2008). Cratons are old, cold and stable continental crusts, considered almost untouched in the last 2.0 Gyr from the tectonic point of view. The thickness of the Archean and Proterozoic cratonic lithospheres is commonly $>200$ km , with the maximum depth registered of 250 km (see Figure 1.1.1). Therefore, the geotherms related to the cratonic areas are lower than the Phanerozoic continental crusts: the surface heat flow of a cratonic area is about $40 \mathrm{~mW} / \mathrm{m}^{2}$, against the about $65 \mathrm{~mW} / \mathrm{m}^{2}$ of a younger continental crust and the about $100 \mathrm{~mW} / \mathrm{m}^{2}$ of an oceanic crust (Pollack et al., 1993; Hasterok and Chapman, 2011). The Figure 1.1.2 displays the conditions at which diamonds form, considering the conductive geotherms for the range of surface heat flow relative to a cratonic area (Pollack and Chapman,


Figure 1.1.2: the diagram shows the graphite to diamond phase transition, i.e., the field of stability of diamonds (Day, 2012). The blue dashed lines are conductive geotherms for a surface heat flow of 35,40 and $45 \mathrm{~mW} / \mathrm{m}^{2}$, while the blue line is the $1300{ }^{\circ} \mathrm{C}$ mantle adiabat (Hasterok and Chapman, 2011)
1977). Such singular conditions permit the formation of diamonds in a big section of the cratonic lithospheres.

Diamond is not only the hardest natural material, but at the same time is able to travel from the very deep regions of our planet remaining nearly uncorrupted over time, owing to its feature of almost perfect inert. Nevertheless, their chemical and physical properties allow us to obtain only little knowledge on the formation environment. Therefore, majority of the information on the genesis of diamonds is revealed from their fluid and mineral inclusions (see Figure 1.2.1 for a good example of inclusion-bearing diamond). In detail, the mineral inclusions allow us to investigate the P-T of formation, the geochemical environment and the age, but such analyses are possible only with the assumption that the data exhibited by the
inclusions are applicable to the diamond. This presumption can be undoubtedly valid if the inclusion is cogenetic with the host diamond, i.e., it is syngenetic, but in other situations this supposition can fall.

At present, the genetic relationship between diamond and its inclusion is still uncertain and even now it is the object of an active debate. The syngenesis is commonly assumed since the 60s (e.g., Harris, 1968), but several more recent works suggest that the minerals used for such analyses are protogenetic, i.e., they are formed before their host diamonds (e.g., Thomassot et al., 2009; Nestola et al., 2014; Milani et al., 2016; Jacob et al., 2016; Nestola et al., 2017). The answer to this question can have crucial implications on what we know about diamonds.

### 1.2 The aim of this thesis work

The aim of the present thesis work is the study of the protogenetic/syngenetic relationships between garnet, clino- and orthopyroxene inclusions with respect to their host diamond. In more detail, such investigation is done with a crystallographic approach based on the analysis of the reciprocal orientations between inclusions and hosts for a large amount of diamonds from 11 mines distributed over 3 continents. The implications that the results of this analysis can have are particularly in the dating of diamonds. Indeed, garnets and pyroxenes are commonly used for determining the age of diamonds, but if they were entrapped into a diamond after their formation, the dating method applied to them, i.e., the Sm-Nd method, cannot be useful. In such case, the validity of the radiometric dating depends on the closure temperature and the equilibration time of the $\mathrm{Sm}-\mathrm{Nd}$ system for garnets and pyroxenes.


Figure 1.2.1: one of the analysed diamonds, the diamond lot_22_stone_36, from the Voorspoed mine, South Africa. The great number of inclusions of clinopyroxene and orthopyroxene makes it an important and relevant sample in such analysis.

## Chapter 2

## Syngenesis/protogenesis

### 2.1 Genetic relationships between diamonds and their inclusions

A great suite of inclusions of different origins can be found into monocrystalline diamonds. From the fluid inclusions, which have carbonatitic to hydrous and silicic composition, to the mineral inclusions, with a range of possible composition from the typical eclogitic to the peridotitic paragenesis, such inclusions allow us to study important information about diamonds and their formation environment (Shirey et al., 2013). The mineral inclusions are especially used for the investigation of the P-T of formation, the geochemical environment and the age, but not only.

The genetic relationship between an inclusion in respect to its host can be of three different types (Meyer, 1987):

- if the inclusion was formed earlier than the host, it is classified as protogenetic;
- if inclusion and host grew simultaneously, the inclusion is called syngenetic;
- if the inclusion has crystallised later than the host, it is defined epigenetic.

The identification of the epigenetic minerals is simple because they can form only in fractures of the diamonds or for alteration processes which affect the preexistent inclusions and the diamond itself. On the other hand, the distinction between the syngenetic and the protogenetic relationship of an inclusion-host pair is more complex (Shirey et al., 2013).

### 2.2 Debate on syngenesis/protogenesis

The discrimination of the syngenetic-protogenetic feature of an inclusion is important in the study of diamonds. If an inclusion is syngenetic, all the information acquired by it is unequivocally correlated to the host-diamond. But in the other case, if the inclusion is protogenetic, the collected data can describe conditions of an environment preexistent with respect to the diamond formation. Thus, such determination permits to understand how much we can investigate a diamond through its inclusion.

Since the 60 s, the syngenesis represents a common assumption in the study of diamonds. The syngenesis implies the mutual growth of inclusion and host minerals, thus it can occur for the direct precipitation from an initial fluid or melt or for dissolution/re-crystallization processes of the inclusion during the percolation of the so-called "C-O-H-bearing fluid or melt". However, the syngenesis implies the equilibrium between both the mineral during their formation. The first proof used by supporters of the syngenesis is the imposition of the morphology of diamonds on their inclusions (e.g., Harris, 1968; Meyer, 1985; Pearson and Shirey, 1999; Sobolev et al., 2009, also the Figure 2.2.1). This criterion is based on the belief that diamonds, owning a "form-energy" greater than their typical inclusions, can impose their morphology during the mutual growth (Harris and Gurney, 1979). The
second used proof is the epitaxial relationship between an inclusion and its host diamond, expressed by the preferred crystallographic orientation of the inclusion with respect to its diamond host (e.g., Futergendler and Frank-Kamenetsky 1961; Harris and Gurney 1979; De Vries et al. 2011). These criteria are the object of a scientific debate, which at present is not still concluded.

At the beginning, the first proof was criticised by Taylor et al. (2003a) and Taylor et al. (2003b), which interpreted the imposed morphology on a garnet as the evidence of a multi-stage evolution, expressed by the sinusoidal chondrite-normalized Rare Earth Element (REE) patterns. This contestation, in turn, was contradicted by Stachel et al. (1998, 2004), which related the same REE patterns of garnet to a genesis strongly connected to the interaction between the mantle peridotite and the diamond forming fluids enriched in rare elements. Moreover, Nestola et al. (2014) proposed two possible mechanisms with which an olivine inclusion can assume the morphology of the diamond, i.e., the tardive diffusion creep on the inclusion after the entrapment and the selective partial dissolution during the formation and the growth of the host-diamond (see Figure 2.2.2). Then, Agrosì et al. (2016) related the presence of "stepped figures" on the surface of an olivine inclusion with diamond-imposed morphology to a mechanism of selective partial dissolution occurring during the entrapment of inclusions, which can explain the theory proposed by Nestola et al. (2014). On the other hand, such figures represent also an indicator of syngenesis if they are located in the interface between the olivine and the diamond (Agrosì et al., 2016).

Other works, which proposed the protogenesis for the sulphide inclusions with diamond-imposed morphology, are Thomassot et al. (2009), based on geochemical evidences, and, more recently, Jacob et al. (2016), which identified ductile deformation structures in sulphide inclusions that indicate their pre-existence in respect to the diamond.


Figure 2.2.1: at the left, an example of olivine inclusions with the morphology imposed by the diamond host, from Agrosì et al. (2016). At the right, an example of diamond-morphology imposed inclusion of clino- and orthopyroxene of the diamond lot_22_stone_36, from this study.

The second proof is based on several works since the 50s, in which apparent orientations between specific direction vectors of the inclusions with the host diamonds were described (e.g., Mitchell and Giardini, 1953; Hartman, 1954; Futergendler and Frank-Kamenetsky, 1961; Frank-Kamenetskii, 1964). These observations signify a more robust proof of syngenesis for many authors (e.g., Harris and Gurney, 1979; Pearson and Shirey, 1999), but they were founded on an incomplete and limited collection of samples and display some incoherences (Nestola et al., 2014). More recent and precise approaches are based on the crystallographic study of the reciprocal orientations with EBSD and single-crystal X-ray diffraction methodologies and other high-resolution techniques for comprehending the diamond growth (Shirey et al., 2013). De Vries et al. (2011) applied EBSD method combined with Cathodoluminescence and FIB-SEM to chromite inclusions, suggesting a syngenetic relationship from changes in the relative growth zones shared by oriented inclusions and diamonds. However, this interpretation is in contrast with the correlation between the Cathodoluminescence-sensitive zones located in the surroundings of the inclusion and the effect of strain given by the inclusion to the host diamond (Davies
and Crossfield, 1973).
Furthermore, the single-crystal X-ray diffraction technique permits to analyse a large amount of olivine inclusions with diamond-imposed morphology from different localities (Nestola et al., 2014; Milani et al., 2016), in which the absence of a specific orientation of the inclusions with respect to their hosts indicates the protogenesis. Such observation is confirmed by Bruno et al. (2016), which individuate an extremely low chemical affinity between olivine and diamond, which denies every possible reciprocal orientation. In addition, the individuation of inclusions of the corresponding mineral species located in the same diamond with an iso-orientation apparently random with the host represents a stronger evidence of protogenesis (Nestola et al., 2014; Milani et al., 2016; Nestola et al., 2017). The mechanism which describes the development of such circumstance is the same illustrated in the Figure 2.2.2.

Currently, this debate is still unconcluded, nevertheless the recent data exhibit that the protogenesis seems to be more valid than the syngenesis. Such data are mainly collected on olivine inclusions, but the syngenetic/protogenetic relationships of the other common mineral inclusions with the host diamonds is less studied. Thus, some minerals typically included in diamonds and used for important research, e.g., the dating and the formation environment, are lacking in a precise investigation about the genetic relations with respect to their host.

The objective of this thesis work represents not only the analysis on the genetic relationships of garnet, clino- and orthopyroxene, i.e., the most common silicates included in diamonds outside olivine, but also an extensive integration of the global systematic survey about syngenesis/protogenesis for silicate inclusions with a large amount of samples for both the mineral species.


Figure 2.2.2: the mechanism of formation of diamond suggested by Nestola et al. (2014). Since $t_{0}$ to $t_{4}$, the so-called C-O-H fluid percolates in the rock and partially dissolves the preexistent crystals. Some of the remains are into the diamond while it is crystallizing. Also if they are not completely dissolved minerals, they appear as different crystals, but their crystallographic orientations are the same because they derive from the same initial mineral. Modified from Nestola et al. (2014).

## Chapter 3

## Age of diamonds

### 3.1 Geochronology

The scientific discipline of determining the age of the minerals and the rocks is called Geochronology and has different applications in every branch of the Earth Science. Several approaches can be applied for dating the sample: relative and absolute methods allow us to understand the history of our sample.

In the field of study of diamonds, the radiogenic isotope geochemistry represents the only technique for dating the diamonds. The fundamental concepts of this method are founded on the radioactive decay processes: the atom nuclei are constituted by precise combinations of protons and neutrons, but some atoms are more stable than the others. The reason of this fact is related to the forces occurring between the nucleons and to the organization of the possible existing nuclei. Different models describe the energies of all the nuclei. Thus, the majority of the nuclides is unstable and tends to reach a lower energy and a more stable configuration through the decay processes. Decay of radioactive atoms can be defined by a simple equation:

$$
\begin{equation*}
A \rightarrow B+x+\Delta E \tag{3.1}
\end{equation*}
$$

where $A$ represents the radioactive parent nuclide, $B$ represents the radiogenic daughter nuclide, $x$ represents the emitted particles and $\Delta E$ is the energy set free by the decay.

The decay reactions depend on the nature of the involved nuclide and on its energy state. Temperature, pressure and the other external parameters do not influence the course of a decay reaction. From the Law of Radioactive Decay, we obtain the probability of decay of a nucleus, $\lambda$, also known as decay constant. The rate of decay of N nuclides in the time $d t$ is related to $\lambda$ by means of the equation:

$$
\begin{equation*}
\frac{d N}{d t}=-\lambda N \tag{3.2}
\end{equation*}
$$

The Equation 3.2 is known as Basic Equation of Radioactive Decay. Through a simple mathematical resolution, we can display this law as:

$$
\begin{equation*}
N=N_{0} e^{-\lambda t} \quad \frac{N}{N_{0}}=e^{-\lambda t} \tag{3.3}
\end{equation*}
$$

where $N_{0}$ is the number of nuclides at time $t=t_{0}$ and N at time $t=t_{1}$.
If we assume that half of the starter number of nuclides is decayed, or rather the ratio $N / N_{0}$ is equal to $1 / 2$, we can extract the half-life, $t_{1 / 2}$, of a radioactive decay reaction:

$$
\begin{equation*}
t_{1 / 2}=\frac{\ln 2}{\lambda} \tag{3.4}
\end{equation*}
$$

which is a used parameter to understanding how quickly the considered atom decays.

However, we cannot measure the starter number of nuclides, but we can calculate the quantity of the daughter nuclides, $D . N, N_{0}$ and $D$ are related by the relationship:

$$
\begin{equation*}
D=N_{0}-N \tag{3.5}
\end{equation*}
$$

thus:

$$
D=N e^{\lambda t}-N=N\left(e^{\lambda t}-1\right)
$$

but we shall consider the starter presence of the daughter nuclide in the system. $D_{0}$ expresses this value and it must be put into the equation:

$$
\begin{equation*}
D=D_{0}+N\left(e^{\lambda t}-1\right) \tag{3.6}
\end{equation*}
$$

But the Equation 3.6 needs the precise absolute analysis of the parent and daughter isotopes. Easier is the measurement of the ratios between two isotopes, so we rewrite the last equation using the ratios of the parent and daughter atoms to a nonradiogenic isotope $S$ :

$$
\begin{equation*}
\left(\frac{D}{S}\right)=\left(\frac{D_{0}}{S_{0}}\right)+\left(\frac{N}{S}\right)\left(e^{\lambda t}-1\right) \tag{3.7}
\end{equation*}
$$

We can rewrite the Equation 3.7 considering that $R$ is the ratio of the daughter nuclide $D$ to the chosen non-radiogenic isotope $S, R_{0}$ is the starter ratio of the daughter nuclide $D_{0}$ to the non-radiogenic isotope $S_{0}$ and the ratio of the parent nuclide $N$ to the non-radiogenic isotope $S$ is directly proportional to ratio of the parent to the daughter atoms, $R_{P / D}$. Thus:

$$
\begin{equation*}
R=R_{0}+R_{P / D}\left(e^{\lambda t}-1\right) \tag{3.8}
\end{equation*}
$$

The Equation 3.2 is the basis of the geochronological calculations through the radiogenic isotope geochemistry. The validity of this equation depends on two assumptions: at the time $t=t_{0}$ the system is at the isotopic equilibrium, or rather $R_{0}$ is constant, and the system is closed during the range of time $d t$. If these two rules are not respected, the chronological data are not correct. By means of this mathematical approach, we can draw a straight line called isochron in a diagram $R-R_{P / D}$, where
$R_{0}$ represents the intercept and $\left(e^{\lambda t}-1\right)$ is the slope.
The mathematical method and the formulas reported in this section are extracted from White (2013).

In nature, four main types of radioactive decay reactions can occur, which involve different particles and loss of energy. The radioactive decay can occur in distinct types of mechanisms:

- Alpha decay: it is characterized by the loss of two protons and two neutrons from the parent nuclide. So, it presents the emission of a ${ }_{2}^{4} \mathrm{He}$ and a $\gamma$ ray;
- Beta decay: it is defined by the change of a neutron to a proton, or vice versa. The first case is called $\beta^{-}$decay and presents the emission of a negatron, an antineutrino and a $\gamma$ ray; the other case is called $\beta^{+}$decay, or sometimes electron capture, and presents the emission of a positron, a neutrino and a $\gamma$ ray;
- Gamma decay: it is a particular type of decay in which the atoms does not change, but only presents a loss of energy. This loss modifies the state of the nucleus from excited to a more stable situation, expressed by the emission of a $\gamma$ ray;
- Spontaneous fission: it is defined as the split of a bigger nucleus to two or more non-identical nuclei. It presents also the emission of some neutrons and a great amount of energy.


### 3.2 Dating systems applied to diamonds

In the Earth Science, many decay systems are useful, e.g. Rb-Sr, Sm-Nd, Lu-Hf, U-Th- Pb systems and many others. The crystallographic and the chemical properties of diamonds prevent us from studying their age because they do not contain
elements useful for dating systems. For this reason, dating of diamonds is possible only through the study of the inclusions. Indeed, if we establish the assumption that the age exhibited by an inclusion is the same of the host diamond, we can date diamonds by means of their inclusions. Furthermore, the common premise of syngenesis accepted since the 60s for the most of the inclusions in diamonds (see the Chapter 2) has strengthened this assumption and has permitted the dating of diamonds. According to Stachel and Harris (2008), only four systems are useful to study the age of diamonds: Re-Os system on sulphide inclusions, $\mathrm{Sm}-\mathrm{Nd}$ system on garnet and pyroxene inclusions, Ar-Ar system on eclogitic clinopyroxene inclusions and U-Pb system on sulphide inclusions. The first two are undoubtedly the most used and the most important.

The Re-Os system in based on the $\beta^{-}$decay of ${ }^{187} \mathrm{Re}$ to ${ }^{187} \mathrm{Os}$, with a half-life of about 42 Gys (Lindner et al., 1989). The method used in this dating system consists in the calculation of the Re-Os isochron: it operates with the described mathematical approach, therefore we consider the ${ }^{188} \mathrm{Os}$ as the reference non-radiogenic isotope. The equation of the Re-Os isochron is:

$$
\begin{equation*}
\left(\frac{{ }^{187} \mathrm{Os}}{{ }^{188} \mathrm{Os}}\right)=\left(\frac{{ }^{187} \mathrm{Os}_{0}}{{ }^{188} \mathrm{Os}_{0}}\right)+\left(\frac{{ }^{187} \mathrm{Re}}{{ }^{188} \mathrm{Os}}\right)\left(e^{\lambda t}-1\right) \tag{3.9}
\end{equation*}
$$

Re and Os are highly siderophile elements (HSE), so they prefer metal or sulphide phases over silicate minerals. Therefore, this system is used in cosmochemistry and in high-temperature geochemistry and it finds important application in the sulphide and metal ores (see Shirey and Walker (1998) for an extensive review). In diamonds, this system is used in single sulphide inclusions. Some important studies used this system method (e.g., Shirey and Richardson, 2011; Richardson et al., 2004, 2001; Pearson et al., 1998, 1999, see Figure 3.2.1 for an example of such analyses).


Figure 3.2.1: example of a dating of diamonds through the Re-Os isochron dating method. Modified from Richardson et al. (2004).

The $\mathrm{Sm}-\mathrm{Nd}$ system is founded on the $\alpha$ decay of ${ }^{147} \mathrm{Sm}$ to ${ }^{143} \mathrm{Nd}$. The half-life of this system is about 106 Gys (DePaolo and Wasserburg, 1976). The isochron of this system considers the ${ }^{144} \mathrm{Nd}$ as the reference non-radiogenic isotope, thus:

$$
\begin{equation*}
\left(\frac{{ }^{143} \mathrm{Nd}}{{ }^{144} \mathrm{Nd}}\right)=\left(\frac{{ }^{143} \mathrm{Nd}_{0}}{{ }^{144} \mathrm{Nd}_{0}}\right)+\left(\frac{{ }^{147} \mathrm{Sm}}{{ }^{144} \mathrm{Nd}}\right)\left(e^{\lambda t}-1\right) \tag{3.10}
\end{equation*}
$$

Furthermore, the Nd Model Age was introduced in this system. Model ages are based on the assumption that the segregation of melt from the mantle forming the Bulk Silicate Earth has deviated the composition ${ }^{143} \mathrm{Nd} /{ }^{144} \mathrm{Nd}$ and ${ }^{147} \mathrm{Sm} /{ }^{144} \mathrm{Nd}$ from the initial isotopic evolution line. Considering constant ${ }^{147} \mathrm{Sm} /{ }^{144} \mathrm{Nd}$, the intersection point between these two progressions indicates the age of the formation of the sample. After DePaolo and Wasserburg (1976), the Nd isotopic composition of the CHUR (CHondritic Uniform Reservoir) is assumed equal to the Nd isotopic composition of the Bulk Silicatic Earth, so the CHUR Model Age was introduced
(McCulloch and Wasserburg, 1978):

$$
\begin{equation*}
t=\tau_{\text {CHUR }}=\frac{1}{\lambda} \ln \left(\frac{\left({ }^{143} \mathrm{Nd} /{ }^{144} \mathrm{Nd}\right)_{\text {sample }}-\left({ }^{143} \mathrm{Nd} /{ }^{144} \mathrm{Nd}\right)_{\text {CHUR }}}{\left({ }^{147} \mathrm{Sm} /{ }^{144} \mathrm{Nd}\right)_{\text {sample }}-\left({ }^{147} \mathrm{Sm} /{ }^{144} \mathrm{Nd}\right)_{\text {CHUR }}}\right) \tag{3.11}
\end{equation*}
$$

It is also called the time of fractionation. Another reference isotopic evolution used for this calculation instead of the CHUR is the Depleted Mantle (DM), the method is the same. Sm and Nd are present in silicates, thus we can employ this dating method on garnets, clinopyroxenes and feldspars. Important studies which used this system of dating are for example Richardson (1986), Richardson et al. (1990), Richardson et al. (2004) and Richardson and Harris (1997), see Figure 3.2.2 for an example of such analyses.


Figure 3.2.2: example of a dating of diamonds through the $\mathrm{Sm}-\mathrm{Nd}$ isochron dating method. Modified from Richardson et al. (2004).

The other two systems are of minor importance because they are available in rare minerals and the methods are complex. Ar-Ar system is possible only on eclogitic clinopyroxene inclusions, but a study highlights that the use of this method on cleaved single crystals shows ages similar to the eruption of the kimberlite (Burgess et al., 1992). On the other hand, the analyses with the laser drilling into diamonds

| Mineral | Percentage |
| :--- | ---: |
| Garnet | 29 |
| Sulphide | 24 |
| Mg-chromite | 14 |
| Olivine | 14 |
| Clinopyroxene | 12 |
| Orthopyroxene | 6 |
| Coesite | 0.5 |
| Rutile | 0.5 |

Table 3.3.1: relative abundance of silicate, oxide and sulphide inclusions in cratonic lithospheric diamond. The sub-lithospheric diamonds represent about the $99 \%$ of all the diamonds collected in the world, so this percentages can be considered as the probability to find such types of mineral included in diamonds. These values are acquired by the data presented in Stachel and Harris (2008).
appear to give truthful results. Differently from the last method, $\mathrm{U}-\mathrm{Pb}$ can be applied only on sulphide inclusions with an high level of Pb and on zircon inclusions. This method is rarely used and has shown no realistic ages in some cases (Stachel and Harris, 2008).

### 3.3 Sm-Nd system validity for diamonds

How we can observe in the Table 3.3.1, garnets and clinopyroxenes represent together about the $41 \%$ of all the inclusions included into diamonds, while sulphides represent about the $24 \%$. On the basis of these percentages, $\mathrm{Sm}-\mathrm{Nd}$ system appears to be the most important dating system for diamonds.

The contents of Nd and Sm in garnet and clinopyroxene inclusions in diamonds are shown in the Table 3.3.2. Such abundances are defined in the order of few ppm, so these two mineral inclusions can contain a relative great quantity of these two elements. These properties of clinopyroxene and garnet permit the study of the age of diamonds.

Differently, orthopyroxene contains a extremely small quantity of Sm and Nd , how is exhibited in the Table 3.3.3. Thus, the dating of diamonds through this
mineral cannot be possible.
To sum up, $\mathrm{Sm}-\mathrm{Nd}$ system is a precise and important tool in the study of diamonds, but its weak point is the assumption about the syngenetic relationship between inclusion and host. Are we sure that the measured age is of the diamond? The discussion presented in the Chapter 2 highlights that the protogenesis is no longer only a possibility for some mineral species typically included in diamonds, thus the assumption that the inclusion shows the same age of the diamond host can fall.

In the case of protogenesis, the age recorded by the inclusion depends on the moment at which the isotopic decay system was closed. We can assume that the isotopic decay system is closed when a mineral becomes included by the diamond host, which operates as a shield that prevents the diffusional interaction with the surroundings, and when a mineral cools down below the closure temperature. On the other hand, an open system is subject to the diffusive interaction with solids, fluids and melts as a function of temperature, elemental diffusivity and effective grain size.

According to Dodson (1973), the closure temperature of a dating system is defined as the temperature at which the system starts to register the radiometric chronological data, or rather the apparent age. Whenever the system oversteps the closure temperature, the radiogenic system resets. Thus, considering the closure temperature of a protogenetic mineral inclusion is important, because if the temperature of entrapment is higher than the closure temperature of such mineral, the system becomes closed and starts to register the radiogenic dating information. In the other case, if the mineral inclusion is entrapped when the isotopic system is already closed, i.e., under the temperature of closure, the related age is of the moment at which the mineral reached the closure temperature.

Dodson (1973) proposed a simplified analytical solution for the closure temperature $T_{C}$, which was also reviewed by Ganguly and Tirone (1999) and made

|  | Median | Average | Sigma | Min | Max | N |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: |
| Eclogitic Garnet |  |  |  |  |  |  |
| Nd | 1.00 | 2.92 | 4.73 | 0.08 | 29.60 | 65 |
| Sm | 0.87 | 3.25 | 6.97 | 0.20 | 40.80 | 65 |
| Peridotitic Garnet |  |  |  |  |  |  |
| Nd | 3.26 | 4.72 | 6.91 | 0.03 | 45.10 | 111 |
| Sm | 0.75 | 1.17 | 1.34 | 0.01 | 7.90 | 111 |
| Eclogitic Clinopyroxene |  |  |  |  |  |  |
| Nd | 2.94 | 3.76 | 2.99 | 0.93 | 13.00 | 25 |
| Sm | 0.83 | 1.02 | 0.68 | 0.05 | 3.00 | 25 |
| Peridotitic Clinopyroxene |  |  |  |  |  |  |
| Nd | 6.06 | 9.00 | 11.04 | 1.32 | 37.84 | 17 |
| Sm | 0.49 | 1.16 | 1.48 | 0.09 | 6.36 | 17 |

Table 3.3.2: Nd and Sm composition (median, average, standard deviation, minimum and maximum value, number of samples) of eclogitic and peridotitic garnet and of eclogitic and peridotitic clinopyroxene inclusions into diamonds. The data are expressed in ppm. These values are counted from the data collected in Stachel et al. (2004), Viljoen et al. (2010), Taylor et al. (1996), Harris et al. (2004), Aulbach et al. (2002), Stachel et al. (2000), Wang et al. (2000), Stachel and Harris (1997), Tappert et al. (2005), Wang and Gasparik (2001) and Davies et al. (2004).

|  | Median | Average | Sigma | Min | Max | N |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: |
| Orthopyroxene |  |  |  |  |  |  |
| Nd | 0.02 | 0.15 | 1.32 | $<0.01$ | 0.22 | 186 |
| Sm | 0.02 | 0.04 | 0.08 | $<0.01$ | 0.08 | 186 |

Table 3.3.3: Nd and Sm composition (median, average, standard deviation, minimum and maximum value, number of samples) of mantle peridotite orthopyroxenes. The data are expressed in ppm. Because of too few orthopyroxene trace compositions are published, the orthopyroxenes of peridotitic rocks represent a good substitute for understanding the possible Sm and Nd amount in orthopyroxene inclusions. These values are counted from the data collected in Scott et al. (2016), Witt-Eickschen and O'Neill (2005) and Hellebrand et al. (2005).
applicable to petrological and geochronological approaches: the closure temperature can be measured as a function of the cooling rate, the diffusivity of the element, the shape and the size of the crystal.

Therefore, the closure temperatures of garnet and clinopyroxene were calculated for the Sm-Nd system. All these values consider crystals with spherical shape and 1 mm of diameter:

- the closure temperature of a garnet with the pyrope composition is delineated in a range of about $750-900^{\circ} \mathrm{C}$ with a cooling rate included between 1 and $100^{\circ} \mathrm{C} / \mathrm{Mys}$ (Van Orman et al., 2002). Moreover, a garnet with the almandine composition has the closure temperature of about $660^{\circ} \mathrm{C}$ with a cooling rate of $2^{\circ} \mathrm{C} / \mathrm{Mys}$ (Tirone et al., 2005);
- a clinopyroxene with the diopside composition has the closure temperature of about $200^{\circ} \mathrm{C}$ higher than a garnet with the same physical, so it is included in a range of about 1000 and $1150^{\circ} \mathrm{C}$ with a cooling rate included between 1 and $100^{\circ} \mathrm{C} / \mathrm{Mys}$ (Van Orman et al., 2001, 2002).

If we consider that the typical conditions for diamond formation in the mantle are defined in a range of temperatures between 900 and $1400{ }^{\circ} \mathrm{C}$ (Stachel et al., 2005; Stachel and Harris, 2008; Pearson et al., 2014), the closure temperature of garnets for $\mathrm{Sm}-\mathrm{Nd}$ system is lower than such conditions. On the other hand, the closure temperature of clinopyroxenes is within the typical range for diamond formation, so we must measure the temperature of entrapment, i.e., the temperature of formation of the diamond, for using the Sm-Nd dating system on these minerals. To get to the point, garnet appears appropriate for dating the diamond, while clinopyroxene can be useful for the dating only when the temperature of formation of the diamond host is higher than their closure temperature.

However, the mathematical resolution provided by Dodson (1973) and Ganguly
and Tirone (1999) is referred to the diffusion in solids. So, we need also to consider that fluids and melts can interact with the isotopic system. Indeed, the presence of microinclusions of carbonatitic, hydrous and saline fluids represents an evidence that the fluid and/or melt phase play an important role in the formation of diamonds (Weiss et al., 2015; Izraeli et al., 2001; Navon et al., 1988). These melts/fluids are mobile sources of incompatible elements as LILE and REE which carries out metasomatic reactions with the mantle minerals and promotes the diffusional exchange. Some previous works highlighted the presence of signs of metasomatic agents in minerals entrapped into diamonds (e.g., Shimizu and Sobolev, 1995; Jacob et al., 2016).

At present, we know little about the diamond formation in the mantle. It is demonstrated that some polycrystalline diamonds constituted by micron-size crystallites can be formed in a short time, possibly also in hours (Jacob et al., 2014). On the other hand, a recent study makes in evidence that monocrystalline diamonds might present different stages of growth and resorption, in a time range which can extend also to several hundreds of million years (Gress et al., 2018). During this time, the inclusions are in contact with the metasomatic fluids.

Thus, the last step is understanding the time required by garnet and clinopyroxene to equilibrate the isotopic system with the surrounding fluid for Sm and Nd . Such time is called equilibration time. If it is short, the mineral inclusion can reach the equilibrium during the different phases of growth and resorption, so such mineral can be used for dating the diamond formation. But if it is long, we cannot know if the isotopic system has reached the equilibrium in every possible stage of growth and resorption.

## Chapter 4

## Samples

### 4.1 Provenances and features of the analysed samples

The investigation of this thesis work is on 35 diamonds containing in total 89 inclusions: 30 garnet inclusions (19 peridotitic and 11 eclogitic), 27 clinopyroxene inclusions ( 26 peridotitic and 1 eclogitic) and 32 orthopyroxene inclusions. These samples are from 11 diamond mines of 3 continents (Figure 4.1.1): 11 diamonds from the Udachnaya kimberlite (Russia), 4 diamonds from the Jericho kimberlite (Canada), 6 diamonds from the Voorspoed kimberlite (South Africa), 4 diamonds from the Jwaneng kimberlite (Botswana), 1 diamond from the Letlhakane kimberlite (Botswana), 1 diamond from alluvial deposits of the Meratus Mountains (Borneo), 1 diamond from alluvial deposits of an unknown locality (Madagascar), 3 diamonds from the Premier kimberlite (South Africa), 1 diamond from the Finsch kimberlite (South Africa), 2 diamonds from the Koffiefontein kimberlite (South Africa) and 1 diamond from the Bultfontein kimberlite (South Africa). The Table 4.1.1 and its continuation Table 4.1.2 show the distribution of the studied inclusions.

Some of the studied crystals are located in multiple inclusions, in which there
is the presence of two of more crystals of the same or different mineral species. However, many inclusions show the diamond-morphology imposition due to the crystallization of the hosts.

Generally, the mineral species found as inclusions into diamonds reflect the mineralogical composition of the cratonic mantle rocks, i.e., mainly peridotite and eclogite. Obviously, the garnets, clino- and orthoyroxenes included in diamonds are solid solutions, of which the composition is strongly related to the source.

The Table 4.1.3 displays the crystallographic parameters of the end-members of the mineral series investigated in this work study, while the properties of such mineral inclusions in diamonds are below.

### 4.1.1 Garnet

Garnet can be present in diamonds with different perceived colours. The colour variability of garnets reflects the chemical composition, thus a colour range from pale pinkish to purple is typical for peridotitic garnets and a colour range from pale orange to orange indicates an eclogitic garnet. Green garnets are rare and have a peridotitic composition (Stachel and Harris, 2008).

The difference between these two main types can be defined also from the chemical point of view: peridotitic garnets have generally the composition of the Cr pyrope with high Mg -contents, while eclogitic garnets are Fe - and Ca -richer and a very low Cr-concentration. The average compositions of the two types is exposed in the Table 4.1.4.

In more detail, the Ca and Cr amounts on garnets are strongly related to the source. Grütter et al. (2004) proposed different groups of garnet inclusions on the basis of the contents of these two major elements. Thanks to this classification, plotting the composition of a garnet inclusion in a $\mathrm{CaO}-\mathrm{Cr}_{2} \mathrm{O}_{3}$ diagram represents an useful method to understand the provenance of the diamond host (Figure 4.1.2).


Figure 4.1.1: geographic distribution of the studied diamonds in relation to Archean cratons. The green filled circles are referred to the kimberlite-hosted diamonds, the yellow filled circles to the alluvial diamonds. The localities are: Udachnaya Mine (UD), Jericho Mine (JE), Voorspoed Mine (VO), Jwaneng Mine (JW), Letlhakane Mine (LK), Alluvial deposits of the Meratus Mountains (Borneo) (SK), Alluvial deposits of an unknown locality in Madagascar (MA), Premier Mine (PR), Finsch Mine (FI), Koffiefontein Mine (KF) and Bultfontein Mine (PM). The crustal age/craton basemap is modified from Pearson and Wittig (2008).

| Mine | Country | Diamond | Inclusion | Mineral |
| :---: | :---: | :---: | :---: | :---: |
| Udachnaya kimberlite | Russia | Dio_1 | Dio_1 | P-Cpx, Opx |
|  |  | Dio_2 | Dio_2 | P-Cpx, Opx |
|  |  | Eclo_2 | Eclo-2 | E-Cpx |
|  |  | Grt_E_1 | Grt_E_1 | E-Grt |
|  |  | Grt_E_2 | Grt_E_2_1 | E-Grt |
|  |  |  | Grt_E_2_2 | E-Grt |
|  |  |  | Grt_E_2_3 | E-Grt |
|  |  | Grt_E_3 | Grt_E_3_1 | E-Grt |
|  |  |  | Grt_E_3-2a | E-Grt |
|  |  |  | Grt_E_3_2b | E-Grt |
|  |  |  | Grt-E_3-3 | E-Grt |
|  |  |  | Grt_E_3-4 | E-Grt |
|  |  |  | Grt-E_3-5 | E-Grt |
|  |  |  | Grt_E_3-6 | E-Grt |
|  |  | Grt_E_4 | GrtEE-4 | E-Grt |
|  |  | Grt_P_1 | Grt_P_1 | P-Grt |
|  |  | GrtP_P2 | GrtP_P2 | P-Grt |
|  |  | GrtP_3 | GrtP_3 | P-Grt |
|  |  | GrtP_4 | GrtP_4 | P-Grt |
| Jericho kimberlite | Canada | Jer_1 | Jer_1_A, | E-Grt |
|  |  | Jer_4 | Jer_4_A | E-Grt |
|  |  | Jer_6 | Jer_6_A | E-Grt |
|  |  | Jer_9 | Jer_9-A | E-Grt |
| Voorspoed kimberlite | South Africa | Lot_23_Stone_1 | JW9453_Lot_23_Stone_1 | E-Grt |
|  |  | Lot_7_Stone_24 | JW9453_Lot_7_Stone_24 | E-Grt |
|  |  | Lot_7-Stone_29 | JW9453_Lot-7_Stone_29 | E-Grt |
|  |  | Lot_22_Stone_36 | Lot_22_Stone_36_inc_1 | P-Cpx, Opx |
|  |  |  | Lot_22_Stone_36_inc_1 | P-Cpx, Opx |
|  |  |  | Lot_22_Stone_36_inc_2 | P-Cpx, Opx |
|  |  |  | Lot_22_Stone_36_inc_3 | P-Cpx, Opx |
|  |  |  | Lot_22_Stone_36_inc_4 | P-Cpx, Opx |
|  |  |  | Lot_22_Stone_36_inc_5 | P-Cpx, Opx |
|  |  |  | Lot_22_Stone_36_inc_6 | P-Cpx, Opx |
|  |  |  | Lot_22_Stone_36_inc_7 | P-Cpx, Opx |
|  |  |  | Lot_22_Stone_36_inc_8 | P-Cpx, Opx |
|  |  |  | Lot_22_Stone_36_inc_9 | $\mathrm{P}-\mathrm{Cpx}$, Opx |
|  |  |  | Lot_22_Stone_36_inc_10 | P-Cpx |
|  |  |  | Lot_22_Stone_36_inc_11 | P-Cpx, Opx |
|  |  | Lot_26_Stone_1 | Lot_26_Stone_1_inc_1 | Opx |

Table 4.1.1: distribution of the diamonds and their inclusions analysed in this thesis work. The abbrevations of the mineral names are based on Whitney and Evans (2010). The two prefixes "P" and "E" indicate rispectively the peridotitic and the eclogitic origin and composition of the mineral.

\begin{tabular}{|c|c|c|c|c|}
\hline \& \& Lot_34_Stone_2
Lot_8_Stone_4 \& Lot_34_Stone_2_inc_1 Lot_34_Stone_2_inc_2 Lot_34_Stone_2_inc_3 Lot_8_Stone_4_inc_1 Lot_8_stone_4_inc_2 Lot_8_Stone_4_inc_3 Lot_8_Stone_4_inc-4 Lot_8_Stone_4_inc_5 \& \begin{tabular}{l}
P-Cpx, Opx \\
P-Cpx, Opx \\
P-Cpx, Opx \\
P-Cpx, Opx \\
P-Cpx, Opx \\
P-Cpx, Opx \\
Opx \\
P-Cpx, Opx
\end{tabular} \\
\hline Jwaneng kimberlite \& Botswana \& \[
\begin{aligned}
\& \text { JW083 } \\
\& \text { JW102 } \\
\& \text { JW243 }
\end{aligned}
\] \& \[
\begin{aligned}
\& \text { JW083_1 } \\
\& \text { JW083_2 } \\
\& \text { JW102_2 } \\
\& \text { JW243_1 }
\end{aligned}
\] \& \[
\begin{aligned}
\& \text { P-Grt } \\
\& \text { P-Grt } \\
\& \text { P-Grt } \\
\& \text { P-Grt }
\end{aligned}
\] \\
\hline Lethakane kimberlite \& Botswana \& LK58 \& \[
\begin{aligned}
\& \text { LK58_1 } \\
\& \text { LK58_2 }
\end{aligned}
\] \& \[
\begin{aligned}
\& \text { P-Grt } \\
\& \text { P-Grt }
\end{aligned}
\] \\
\hline Alluvial deposits, Meratus Mountains \& Borneo \& CEM_161 \& CEM_161 \& P-Grt \\
\hline Alluvial deposits, unknown locality \& Madagascar \& Madagascar \& Madagascar \& Opx \\
\hline Premier kimberlite \& South Africa \& PR2

PR4

PR5 \& \begin{tabular}{l}
PR2_1 <br>
PR2_3 <br>
PR2_4 <br>
PR2_5 <br>
PR2_6 <br>
PR4_2 <br>
PR4_3 <br>
PR4_4 <br>
PR5_1 <br>
PR5-2

 \& 

Opx <br>
P-Cpx <br>
Opx <br>
P-Cpx, Opx <br>
Opx <br>
P-Cpx <br>
P-Cpx <br>
P-Cpx <br>
Opx <br>
Opx
\end{tabular} <br>

\hline Finsch kimberlite \& South Africa \& Nat Comm Finsch \& Protogenesi Nat Comm \& P-Cpx <br>

\hline Koffiefontein kimberlite \& South Africa \& $$
\begin{aligned}
& \text { KF2 } \\
& \text { KF3 }
\end{aligned}
$$ \& \[

$$
\begin{aligned}
& \text { KF2 } \\
& \text { KF3 }
\end{aligned}
$$

\] \& \[

$$
\begin{aligned}
& \mathrm{Opx} \\
& \mathrm{Opx}
\end{aligned}
$$
\] <br>

\hline Bulffontein kimberlite \& South Africa \& PM1 \& | PM1_1 |
| :--- |
| PM1_2 | \& \[

$$
\begin{aligned}
& \text { Opx } \\
& \text { Opx }
\end{aligned}
$$
\] <br>

\hline Total \& 6 \& 35 \& 69 \& 89 <br>
\hline
\end{tabular}

Table 4.1.2: continuation of the Table 4.1.1.

|  | V | a | b | c | $\alpha$ | $\beta$ | $\gamma$ |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| Grt |  |  |  |  |  |  |  |
| Prp | 1503.78 | 11.46 | 11.46 | 11.46 | 90.0 | 90.0 | 90.0 |
| Alm | 1527.13 | 11.52 | 11.52 | 11.52 | 90.0 | 90.0 | 90.0 |
| Grs | 1663.16 | 11.85 | 11.85 | 11.85 | 90.0 | 90.0 | 90.0 |
| Uv | 1728.32 | 12.00 | 12.00 | 12.00 | 90.0 | 90.0 | 90.0 |
| Cpx |  |  |  |  |  |  |  |
| Di | 440.18 | 9.75 | 8.92 | 5.25 | 90.0 | 105.4 | 90.0 |
| Hd | 450.29 | 9.84 | 9.02 | 5.25 | 90.0 | 105.0 | 90.0 |
| Jd | 410.09 | 9.44 | 8.71 | 5.23 | 90.0 | 107.5 | 90.0 |
| Opx |  |  |  |  |  |  |  |
| En | 832.65 | 18.24 | 8.82 | 5.18 | 90.0 | 90.0 | 90.0 |
| Fs | 872.45 | 18.43 | 9.08 | 5.22 | 90.0 | 90.0 | 90.0 |

Table 4.1.3: crystallographic data of the end-members of the garnet, clinopyroxene and orthopyroxene series present as diamond-inclusions. These values are average data extracted from a collection of crystallographic parameters of synthetised crystals, in detail the garnet values refer to Bass (1986); Leger et al. (1990); Chopelas (2005); Hofmeister and Chopelas (1991); Zhang et al. (1999); Bass (1989); Conrad et al. (1999); Armbruste et al. (1992), the clinopyroxene values refer to Nolan and Edgar (1963); Zhang et al. (1997); Raudsepp et al. (1990); Prencipe et al. (2000); Tunnock et al. (1973); Zhao et al. (1994); Redhammer et al. (2000); Huber et al. (2004); Nolan (1969) and the orthopyroxene values refer to Hugh-Jones (1997); Ghose et al. (1986); Tarantino et al. (2002); Akimoto et al. (1964); Stephenson et al. (1966); Sueno et al. (1976); Matsui et al. (1968). The cell parameters are expressed in $\AA$ armstrong and ${ }^{\circ}$ degree. The abbrevations of the parameters are: $\mathrm{V}=$ unit cell volume; $\mathrm{a}, \mathrm{b}, \mathrm{c}, \alpha, \beta, \gamma=$ cell parameters. The abbrevations of the mineral names are based on Whitney and Evans (2010).

|  | Peridotitic Garnet | Eclogitic Garnet |
| :--- | ---: | ---: |
| $\mathrm{P}_{2} \mathrm{O}_{5}$ | 0.03 | 0.09 |
| $\mathrm{SiO}_{2}$ | 41.92 | 39.98 |
| $\mathrm{TiO}_{2}$ | 0.09 | 0.64 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 17.67 | 21.92 |
| $\mathrm{Cr}_{2} \mathrm{O}_{3}$ | 8.19 | 0.10 |
| $\mathrm{~V}_{2} \mathrm{O}_{3}$ | 0.04 | 0.04 |
| FeO | 5.68 | 16.04 |
| MnO | 0.24 | 0.36 |
| MgO | 23.28 | 10.82 |
| CaO | 2.69 | 9.84 |
| $\mathrm{Na}_{2} \mathrm{O}$ | 0.02 | 0.26 |
| $\mathrm{~K}_{2} \mathrm{O}$ | 0.01 | 0.02 |

Table 4.1.4: average major element compositions of peridotitic and eclogitic garnets. The data are expressed in terms of wt.\% (Stachel and Harris, 2008).


Figure 4.1.2: the diagram describes the composition variability of the garnet inclusions in diamonds. The blue ellipse indicates the field of the peridotitic garnet composition, while the red ellipse is related to the eclogitic garnets composition. Modified from Stachel and Harris (2008).

Websteritic garnet is another type of such mineral derived from a websteritic source, but it represents a small percentage of all the studied inclusions (Stachel and Harris, 2008).

### 4.1.2 Clinopyroxene

Also clinopyroxenes are useful for identifying the provenance of diamonds. Differently from the garnet, all the clinopyroxenes are of one colour, green. The intensity of the colour can say us few information on the provenance: a pale green is related to an eclogitic omphacite, while an emerald green indicates a peridotitic Cr -diopside (Stachel and Harris, 2008), but the optical analyses based on the perceived colour of pyroxenes are not precise.

Peridotitic clinopyroxenes have a great amount of Mg and Cr , while the eclogitic have less contents of these two elements but they are richer in Al and Na . The average contents of peridotitic and eclogitic clynopyroxenes are expressed by the Table 4.1.5.

Generally, the low contents of Cr of omphacites are in contrast to a high per-

|  | Peridotitic Clinopyroxene | Eclogitic Clinopyroxene |
| :--- | ---: | ---: |
| $\mathrm{P}_{2} \mathrm{O}_{5}$ | 0.01 | 0.05 |
| $\mathrm{SiO}_{2}$ | 54.77 | 54.90 |
| $\mathrm{TiO}_{2}$ | 0.17 | 0.44 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 1.58 | 8.63 |
| $\mathrm{Cr}_{2} \mathrm{O}_{3}$ | 1.63 | 0.10 |
| $\mathrm{~V}_{2} \mathrm{O}_{3}$ | 0.03 | 0.05 |
| FeO | 2.52 | 5.84 |
| MnO | 0.10 | 0.10 |
| NiO | 0.06 | 0.04 |
| MgO | 17.39 | 10.97 |
| CaO | 19.59 | 13.79 |
| $\mathrm{Na}_{2} \mathrm{O}$ | 1.41 | 4.59 |
| $\mathrm{~K}_{2} \mathrm{O}$ | 0.21 | 0.34 |

Table 4.1.5: average major element compositions of peridotitic and eclogitic clinopyroxenes. The data are expressed in terms of wt. \% (Stachel and Harris, 2008).


Figure 4.1.3: the diagram describes the composition variability of the clinopyroxene inclusions in diamonds. The blue ellipse indicates the field of the peridotitic clinopyroxene composition, while the red ellipse is related to the eclogitic clinopyroxene composition. Modified from Stachel and Harris (2008).
centage of Al. Thus, the cut-off between peridotitic and eclogitic garnet is defined by the relative quantity of Cr and Al . The $\mathrm{Cr} \#$ is a good tool to define this limit:

$$
\mathrm{Cr} \#=\frac{100 \mathrm{Cr}}{\mathrm{Cr}+\mathrm{Al}}
$$

In this notation it is located between 7 and $10 \%$ (Stachel and Harris, 2008), as is indicated in the Figure 4.1.3. We can find also websteritic clinopyroxenes, but they represent a small percentage.

### 4.1.3 Orthopyroxene

Orthopyroxene inclusions are difficult to recognise with optical observations because in diamonds they are perfectly colourless. The presence of orthopyroxenes indicates a peridotitic source of the host diamond, indeed eclogitic diamonds cannot contain orthopyroxene.

|  | Peridotitic Orthopyroxene |
| :--- | ---: |
| $\mathrm{P}_{2} \mathrm{O}_{5}$ | 0.02 |
| $\mathrm{SiO}_{2}$ | 57.82 |
| $\mathrm{TiO}_{2}$ | 0.03 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 0.69 |
| $\mathrm{Cr}_{2} \mathrm{O}_{3}$ | 0.41 |
| $\mathrm{~V}_{2} \mathrm{O}_{3}$ | 0.02 |
| FeO | 3.94 |
| MnO | 0.09 |
| NiO | 0.13 |
| MgO | 36.22 |
| CaO | 0.34 |
| Na 2 O | 0.05 |
| $\mathrm{~K}_{2} \mathrm{O}$ | 0.02 |

Table 4.1.6: average major element compositions of peridotitic orthopyroxenes. The data are expressed in terms of wt.\% (Stachel and Harris, 2008).

The composition of such mineral is generally high in Mg , from 28 to $40 \mathrm{wt} . \%$, which is in opposition to the Fe-content that can be between 2.08 and $11.86 \mathrm{wt} . \%$
(Stachel and Harris, 2008). The average composition of orthopyroxenes is defined in the Table 4.1.6.

### 4.2 Geological Settings

The analysed samples are from 9 kimberlites which are located in 4 cratons and from 2 different alluvial deposits. In this study, the variability of the kimberlite eruption and craton ages, of the trace and major composition of the volcanic pipes and the wall rocks, of the depths and the ages of formation of diamonds/inclusions and of the types of the contained inclusions is extremely high. The big number of studied inclusions on diamonds found in so many localities is necessary for having a good statistics. Thus, such analysis is not representative only for a local situation, but it can be extended to a global survey of diamonds.

### 4.2.1 Kaapvaal Craton

The Kaapvaal craton is the southern part of the Kalahari group. Kalahari is a big Archean craton localised in the Republic of South Africa, the Republic of Botswana, the Republic of Zimbabwe, the Kingdom of Lesotho and the Kingdom of eSwatini. It is composed by two different parts, called Kaapvaal and Zimbabwe cratons, separated by the Limpopo Belt (Griffin et al., 2003).

This section is constituted by Archean terranes distinct in ages structural trends: the Southeastern, the Central, the Pietersburg and the Western Terrane. The associated rocks are mainly composed by granitic and tonalitic gneisses and greenstone belts with the presence of granitoid intrusions. However, they are largely covered by clastic and volcano-sedimentary covers. The wide range of ages of the terranes is defined between 3.7 and 2.6 Gyr , while the youngest group composed by sediments was formed at about 2.4 Gyr. At the end, the mafic-ultramafic Bushveld Complex
intruded in the area at about 2.1-2.0 Gyr (Griffin et al., 2003).
This craton is particularly rich in diamondiferous kimberlites. Indeed, 18 of the studied diamonds are from this area, in detail from six kimberlites: Premier, Finsch, Koffiefontein, Bultfontein, Jwaneng and Voorspoed kimberlites (see Figure 4.2.1).

The Premier kimberlite is situated in the Central Terrane and has an emplacement age of about 1180 Myr (Richardson, 1986; Richardson et al., 1993) the geochemical data indicate the affinity with the I group of kimberlites (see Smith, 1983; Becker and Roex, 2005 for an extensive review). The diamond formation was calculated in a thermally perturbed lithosphere with a range of temperatures of 1100 to $1400{ }^{\circ} \mathrm{C}$ and a range of pressures of 4.5 to 6.5 GPa , through the geothermobarometry on the chrome diopside inclusions (Nimis, 2002), and is dated at 1930 Myr with the Sm-Nd isochron (Richardson et al., 1993). Furthermore, the formation of the diamond in the mantle can be related to metasomatism and heating event of the Bushvelt Complex (Richardson et al., 1993).

The Finsch kimberlite is situated in the Western Terrane and its eruption is calculated at about 118 Myr (Smith, 1983), it also classified in the II group of kimberlites. Together with the Premier kimberlite, these two mines are important in the study of diamonds because they provided a great number of samples rich in inclusions for the science (Stachel and Harris, 2008). The diamond formation is strongly related to the diamonds of the Kimberly kimberlite. Furthermore, Boyd et al. (1985) and Richardson et al. (1984) calculated an age of about 3.3 Gyr in 150 to 200 km of depth in the lithosphere.

The Koffiefontein kimberlite is localised in the Western Terrane and is linked to the I group (Smith, 1983; Becker and Roex, 2005), its age is calculated at about 90 Myr (Rickard et al., 1989). The peculiarity of such kimberlite is the great presence of sulphide in inclusion-bearing diamonds, about 42\%. The Re-Os isochron measurements on these sulphides show younger ages of the peridotitic sulphides,
which crystallized close to the time of the kimberlitic eruption, and older ages of the eclogitic (Pearson et al., 1998). The diamonds of this mine are formed at the condition of about 1100 to $1250^{\circ} \mathrm{C}$ and about 5 GPa (Rickard et al., 1989).

The Bultfontein kimberlite was formed in the Western Terrane, the eruption age is at about 84 Myr (Allsopp et al., 1989) and it has a geochemical affinity with the I group of kimberlites (Smith, 1983; Becker and Roex, 2005). The condition of diamond formation is defined in a range of 1080 to $1320{ }^{\circ} \mathrm{C}$ of temperature and 4.5 to 7.5 GPa of pressure, through the clinopyroxene-garnet geothermobarometer (Phillips et al., 2004), while the ages are of about 3.1 Gyr for the peridotitic and of about 2.9 Gyr for the eclogitic diamonds (Richardson et al., 1984, 2001). These data are measured in inclusions with the assumption that they are syngenetic with the diamond hosts.

The Jwaneng kimberlite is located in the northern part of the Western Terrane, its age is about 235 Myr (Kinny et al., 1989) and it belongs to the I group (Smith, 1983). Studies of the diamond formation show two main ages, one Proterozoic at about 1.5 Gyr and another Archean at about 2.9 Ga (Richardson et al., 2004), in a shallow depth of about 160 to 180 Km (Shirey et al., 2004). This diamondiferous kimberlite presents a unusual predominance of the eclogitic diamond-inclusion suite (Gurney et al., 1984, 1995; Deines et al., 1993).

The Voorspoed kimberlite is localised in the Southeastern Terrane. The eruption age is about 131 Myr (Phillips et al., 1998) and the geochemical data show an affinity with the II group (Howarth and Skinner, 2012). There is only a few information about the diamond formation, only Nestola et al. (2018) suggests a pressure of formation of a diamond of 5.2 GPa, calculated through the elastic method on a kyanite inclusion, and an aggregation residence temperature of about $1120^{\circ} \mathrm{C}$, measured with the FTIR method.


Figure 4.2.1: localization of the southern african kimberlites in which were extracted some analysed diamonds, the red filled circles are the geographic positions of the interested mines. This geological map contains also information about Kaapvaal and Zimbabwe cratons. Modified from Griffin et al. (2003).

### 4.2.2 Zimbabwe Craton

The other section of the Kalahari craton is the northern Zimbabwe craton. It is divided into different parts: the central Tokwe Terrane, an accretionary terrane in tectonic contact with the northern Magondi terrane (Nguuri et al., 2001) and other magmatic belts, the youngest of which is the famous Great Dike (Griffin et al., 2003). The rock compositions is tonalitic to granodioritic, overlaid with volcanic and clastic sediments, and the greenstone belts in the central terrane, while the other terrane is formed by a complex accretion with the presence of remains of an ancient subducted oceanic crust and turbidites (Kusky, 1998). On the other hand, the magmatic belts which separate these two portions have a suite of rocks composed by mafic and ultramafic komatiites, their intrusive equals in the southern parts (Bickle and Nisbet, 1996) and a basaltic to rhyolitic volcanic series intruded by plutons of the northern zones (Wilson, 1979). The associated ages are about 3.5 to 2.9 Gyr for the older portions and about 2.8 to 2.6 Gyr for the accretion and the magmatic events (Kusky, 1998; Griffin et al., 2003).

Only 1 diamond is from this craton, it was extracted from the Letlhakane kimberlite in Botswana (see Figure 4.2.1). This kimberlite has affinity with the I group and was probably emplaced at 93 Myr , as the near Orapa kimberlite (Stiefenhofer et al., 1997). The diamond formation occured in a range of 3.3 to 2.9 Gyr (Shirey et al., 2004).

### 4.2.3 Siberian Craton

The central Siberian craton is situated in the Asian Russia and represents a portion of the Proterozoic Pangea-I strongly connected with the North American Craton. The complex geodynamics is characterised by a first fragmentation of the Archean Pangea-0 in different terranes. Successively, the collision of such blocks of Archean
crust occured through fault zone deformation, high T metamorphism and an intense erosion at the end (Rosen, 2002). Complessively, this craton is composed by Archean shields, as the Anabar Shield, and Proterozoic foldbelts. The rock composition is defined by granites and greenstones in the terranes and granulites and gneiss in the exhumed deeper parts of the tectonic units (Glebovitsky et al., 2008). The break-up of the Pangea-0 started at 3.5 Gyr and evolved in 4 main events, while the collision is dated at 1.9 to 1.8 Gyr (Rosen, 2002).

11 of the diamonds analysed in this thesis work are found in the Siberian craton, they are precisely from the Udachnaya kimberlite, localised in the Anabar province (see Figure 4.2.2). This kimberlite is of the I-group kimberlite type and erupted at 365 Myr (Kinny et al., 1997). Sm-Nd dating method on garnet inclusions shows an age of formation of diamonds of about 2.0 Gyr, while Re-Os on sulphide inclusions indicates 3.5 to 3.1 Gyr (Richardson and Harris, 1997; Pearson et al., 1999).


Figure 4.2.2: geographic position of the Udachnaya kimberlite in the Siberian craton. Modified from Nimis et al. (2009).

### 4.2.4 Slave Craton

The Slave craton is localised in Canada, it is a small Archean nucleus of the North American Craton. The Siberian craton and the North American craton are strongly correlated: these two cratons composed a unique megacraton at the end of the Proterozoic collision event at 1.9 to 1.8 Gyr. The existence of such huge paleocontinent is justified by the connection of ages and positions between the Archean terranes and the foldbelts of the two cratons (Condie and Rosen, 1994). Thus, the North American craton sequence is very similar to the just described Siberian craton, from the chronological and tectonic points of view (Rosen, 2002). In detail, the Slave Craton is composed by granites and gneisses of age 4.0 to 3.6 Gyr and a younger sedimentary series dated at 2.7 Gyr. At the end, a felsic intrusive event occurred at 2.6 Gyr (Griffin et al., 1999).


Figure 4.2.3: the red filled circle indicates the geographic location of the Udachnaya kimberlite in the Slave craton. Modified from Price et al. (2000).

This study involves 4 diamonds from the Jericho kimberlite, situated in the central zones of such craton (see Figure 4.2.3). The eruption of this kimberlite is dated at about 173 Myr (Heaman et al., 1997) and it is classified in the I group of kimbelites (Kopylova et al., 1998). The formation of the diamonds is dated at 1.8 to 1.0 Gyr, with temperatures defined between $11001200{ }^{\circ} \mathrm{C}$ (Heaman et al., 2006; De Stefano et al., 2009).

### 4.2.5 Alluvial Deposits

Not all the diamonds investigated in this study are extracted from a primary deposit of kimberlites, 2 of them are alluvial. The first is from the Republic of Madagascar, but we have a few information about this deposit. Recent studies highlight the link between the Proterozoic continental terrane of Madagascar, precisely the Antananarivo Domain, with the diamondiferous Dharwar craton in India (Moine et al., 2014; Tucker et al., 2014). This relationship makes the Madagascar a potential area for the diamond mining. Indeed, The De Beers Group of Companies started an exploration campaign in Madagascar in 2003-2004, in which two significant sized diamonds of 23 and 8 carats were found (Spar, 2006; unpublished data). Such diamond derives probably from the locality of Midonge, in the south-east, or from the Horombe locality, in the central highlands.

The second diamond, instead, is from an alluvial deposit of the southern Borneo. In this big island localised in the central Indonesia, several important alluvial deposits of high quality diamonds are situated on Phanerozoic tectonic ophiolites, plutonic intrusions and sedimentary sequences (Van Leeuwen, 2014). The provenance of such diamonds is actually unknown and their formation can be described by different proposals of settings: they can be formed in some undiscovered kimberlite sources, in the adjacent Meratus ophiolite complex, by ultra high pressure metamorphism of the close terranes and/or in an obducted subcontinental lithospheric
mantle. The formation conditions calculated for the peridotitic suite of diamonds are in a range 930 to $1250{ }^{\circ} \mathrm{C}$ and 4.8 to 6.0 GPa (Kueter et al., 2016).

## Chapter 5

## Methodologies

### 5.1 Single-crystal X Ray Diffraction

The orientations of the samples were determined by the single-crystal X-ray diffraction. The measurements were performed at the Department of Geosciences, University of Padova, with a Rigaku Oxford Diffraction Supernova Diffractometer equipped with a Dectris Pilatus 200K area detector and a Mova X-ray micro-source (Mo $\mathrm{K} \alpha$ radiation, $0.7107 \AA$ of wavelength). The source operates at 50 kV and 0.8 mA and the sample-detector distance is 68 mm . However, the spot-size of the analyses at the sample is $120 \mu \mathrm{~m}$, this allows us to study also small inclusions included in diamonds.

The analysis procedure is characterized by a first optical centering of the inclusion at the diffractometer, this step is not simple because the high refractive index of diamond can modify the position of the inclusions into diamonds. Then, the second step is the acquisition of the diffraction data, thus this stage is important not only for the acquisition of the orientation of the inclusions, but also for the precise individuation of the mineral species. At the end, the data reduction was performed automatically using the CrysAlis software (Rigaku Oxford Diffraction). The same
method was used by Milani et al. (2016).
The analysis instrument is equipped with a high precision kappa 4-circle kappa goniometer (Figure 5.1.1). The four circles which defines this geometry are:

- $\omega$, of which the axis is perpendicular the horizontal plane. This circle is located at the base of the goniometer;
- $\kappa$, of which the axis is inclined of about $45^{\circ}$ with respect to the plane of rotation of the $\omega$ circle. It is arranged on the $\omega$ circle and contains the goniometer head;
- $\phi$, of which the axis corresponds to the goniometer head axis. Its axis of rotation is inclined of the same angle which is between $\omega$ and $\kappa$ in respect to the plane of rotation of the $\kappa$ circle;
- $\theta$, which is coaxial with the $\omega$ circle. Such circle permits the rotation of the detector.

This type of goniometer is advanced with respect to the typical Eulerian system with the four circles $\phi, \chi, \omega$ and $\theta$. The relationships between the Kappa system and the Eulerian system are dependent on the angle between $\kappa$ and $\omega$, called $\alpha$, so:
$\sin \alpha \sin \frac{1}{2} \kappa_{k}=\sin \frac{1}{2} \chi_{e} \quad \cos \alpha \sin \frac{1}{2} \kappa_{k}=\sin \delta \cos \frac{1}{2} \chi_{e} \quad \cos \frac{1}{2} \kappa_{k}=\cos \delta \cos \frac{1}{2} \chi_{e}$
with $\delta=90^{\circ}+\omega_{e}-\omega_{k}=-90^{\circ}+\phi_{e}-\phi_{k}, \quad \theta_{e}=\theta_{k}$ and the subscripts $e$ and $k$ indicate the system.

Thanks to this method, we can analyse the orientation of an inclusion and its diamond host in respect to the coordinates axis system of the diffractometer at the same time. The extracted data are expressed as UB matrices, so for every inclusion we have a couple of UB matrices. Then, we can study the orientation of the analysed


Figure 5.1.1: the representation of the 4 circles of the kappa geometry and of the Cartesian axis system on the diffractometer used for the analyses of this thesis work.
inclusion with respect to the diamond with a mathematical operation of rotation of such matrices.

### 5.2 UB-matrix

The UB matrix, or orientation matrix, is a mathematical approach to express the orientation and the lattice parameters of a crystal. It represents the product of two different matrices: $U$ represents the angular orientation of the crystal in respect to the Cartesian coordinate system of the diffractometer and $B$ represents the reciprocal lattice of the crystal. The concept of UB matrix was introduced by Busing and Levy (1967) and was reviewed by Angel et al. (2000), Yokoyama et al. (2008) and others.

We assume $v_{r}$ as the column vector which contains the physical properties of the crystal in terms of the reciprocal lattice vectors and $v_{c}$ as the column vector of
the Cartesian description of the crystal. So, $B$ is defined as:

$$
\begin{equation*}
v_{c}=B v_{r} \tag{5.1}
\end{equation*}
$$

We can also describe $B$ as a matrix. Considering $a, b, c, \alpha, \beta, \gamma$ as the lattice constants of the crystal and $a^{*}, b^{*}, c^{*}, \alpha^{*}, \beta^{*}, \gamma^{*}$ as the reciprocal lattice constants of the crystal:

$$
B=\left[\begin{array}{ccc}
a^{*} & b^{*} \cos \gamma^{*} & c * \cos \beta \\
0 & b^{*} \sin \gamma^{*} & -c^{*} \sin \beta^{*} \cos \alpha \\
0 & 0 & 1 / c
\end{array}\right]
$$

Furthermore, we assume the $\phi$-axis system, a set of Cartesian axes rigidly connected to the $\phi$-axis of the Eulerian 4-circle goniometer, for describing the U matrix. If we consider all the instrumental angles set to zero, the $\phi$-axis system is defined by the $x$-axis aligned with the scattering vector, the $y$-axis in the direction of the primary beam and the $z$-axis fixed in the vertical instrument axis (Figure 5.2.1).

Considering $v_{\phi}$ as the column vector which describes the Cartesian $\phi$-axis system:

$$
\begin{equation*}
v_{\phi}=U v_{c} \tag{5.2}
\end{equation*}
$$

The $U$ matrix is a $3 \times 3$ matrix which connect the three components of the $v_{\phi}$ with the $v_{c}$, so it can be expressed as:

$$
U=\left[\begin{array}{lll}
u_{x x} & u_{x y} & u_{x z} \\
u_{y x} & u_{y y} & u_{y z} \\
u_{z x} & u_{z y} & u_{z z}
\end{array}\right]
$$

At the same way, we can describe this system using the other three axes $\chi, \omega$ and $\theta$ of a conventional instrumental goniometer in Eulerian system and the related three Cartesian axis systems. When all the instrumental angles are set to zero, such


Figure 5.2.1: the Cartesian axis system described by Busing and Levy (1967), with some modifications. a., it indicates generally the Eulerian geometry of the instrument in respect to the Cartesian axis system; b., it shows the orientation of the $\phi$-axis system with the instrumental angles set to zero: $x$-axis is aligned with the scattering vector, the $y$-axis is in the direction of the primary beam and the $z$-axis is fixed in the vertical instrument axis.
axis systems coincide. The relationships between these systems are:

$$
\begin{equation*}
v_{\chi}=\Phi v_{\chi}, v_{\omega}=X v_{\chi}, v_{\theta}=\Omega v_{\omega} \tag{5.3}
\end{equation*}
$$

with:
$\Phi=\left[\begin{array}{ccc}\cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1\end{array}\right], X=\left[\begin{array}{ccc}\cos \phi & 0 & \sin \chi \\ 0 & 1 & 0 \\ -\sin \chi & 0 & \cos \chi\end{array}\right], \Omega=\left[\begin{array}{ccc}\cos \omega & \sin \omega & 0 \\ -\sin \omega & \cos \omega & 0 \\ 0 & 0 & 1\end{array}\right]$
The product of the $U$ and $B$ matrices contains all the information about the lattice parameters and the orientation of the crystal with respect to the diffractometer axis system.

The calculation of the UB matrix is possible with the calculation of the unit cell parameters through the random research of a big number of reflections generated by the planes which satisfy the Bragg's Law. Another method to calculate the UB matrix without knowing the unit cell parameters is using the setting angles of three reflections with certain Miller indices. If we consider a plane in diffraction, $h, k$ and $l$ are the Miller indices of such reflecting plane, thus the corresponding column
vector in the reciprocal lattice system is given by:

$$
h_{r}=\left[\begin{array}{l}
h \\
k \\
l
\end{array}\right]
$$

The product of $h_{r}$ and UB matrix allows us to calculate the respective set of diffractometer coordinates, expressed by the $h_{\phi}$ vector, or rather the vector in the $\phi$-axis system:

$$
\begin{equation*}
h_{\phi}=U B h_{r} \tag{5.4}
\end{equation*}
$$

such vector is defined by three component $h_{\phi 1}, h_{\phi 2}$ and $h_{\phi 3}$, calculated in respect to the positions of the diffractometer axes, while its length is given directly from the reciprocal of the interplanar spacing $d_{h k l}$ in $\AA$ of the plane in diffraction. Moreover, the $h_{\phi}$ vector can be described in terms of the diffractometer setting angles $\chi, \omega$ and $\phi$, at which the reflection h is in diffraction. The last angle, $\theta$, is given by the length of the $h_{\phi}$ vector through the Bragg's Law:

$$
h_{\phi}=\frac{1}{d_{h k l}}\left[\begin{array}{l}
h_{\phi 1} \\
h_{\phi 2} \\
h_{\phi 3}
\end{array}\right]=\frac{2 \sin \theta}{\lambda}\left[\begin{array}{c}
\cos \omega \cos \chi \cos \phi-\sin \omega \sin \phi \\
\cos \omega \cos \chi \sin \phi+\sin \omega \cos \phi \\
\cos \omega \sin \chi
\end{array}\right]
$$

Thus, to resolve the UB matrix we need three reflections. If we consider that the $h_{r}$ vectors of the reciprocal lattice system of such three planes in diffraction are included in the $H_{r}$ matrix and the relative $h_{\phi}$ scattering vectors are included in the $H_{\phi}$ matrix, we can compute the relationship:

$$
\begin{equation*}
H_{\phi}=U B H_{r} \tag{5.5}
\end{equation*}
$$

Thanks to the Equation 5.5, diffractometers can easily calculate the UB matrix for all the analysed crystals.

### 5.3 OrientXplot

The measured orientation matrices collected with the single-crystal X-ray diffraction describe the orientation of the inclusions and their respective hosts with respect to the axis system of the diffractometer. Through a mathematical approach of the matrices, we can obtain the absolute orientation of an inclusion in respect to the diamond. This method permits also to acquire the angles between the inclusion axes and the diamond host axes for every single inclusion.

However, the effects of the symmetries of the two crystals produce ambiguities in their orientations. These ambiguities are born during the indexing of the diffraction patterns: two reflections equivalent for the symmetry effect cannot be distinguished from the diffractometer, or rather, these two reflections say us the same information. Practically, if we consider for example an orthorhombic crystal, e.g., the olivine, the physical properties in the [100] direction are the same of the [ 100 ]. Therefore, the differences between the [100] and [ 100 ] directions cannot be defined by a diffractometer, so the reflections given by two planes (100) and (100) in diffraction cannot be distinguished. The analogous occurs respectively for the (010) and ( $0 \overline{1} 0$ ) and for the (001) and ( $00 \overline{1}$ ) planes (Angel et al., 2015). The ambiguities produced by the symmetry properties of the minerals can create problems on the analyses of the orientation between two crystals, with them the orientation distribution seems more random than it really is (Nestola et al., 2014).

The method for reducing these ambiguities is transforming the UB matrices of the inclusions through an operation which is congruent with the symmetry of the mineral. These transformations follow a criterion to eliminate all the ambiguities
and simplify the study of the reciprocal orientations of the inclusions with their hosts.

Every inclusion presents many equivalent possible descriptions of the orientation in respect to its host, the precise number depends on the symmetry of the mineral inclusion and the host. In more detail, the symmetries of the minerals analysed in this thesis work, garnet, clinopyroxene and orthopyroxene, are respectively defined by the point groups $m 3 m, 2 / m$ and $m m m$, while the diamond is $m 3 m$. The ambiguities can be described by the multiplicity of the point groups of inclusion and host without the inversion symmetry element. Therefore:

- the subgroup of garnet without the inversion symmetry element is the point group 432, so it has 24 different relative orientation;
- the subgroup of clinopyroxene with the researched properties is the point group 2, thus it has 2 different relative orientation;
- the subgroup of orthopyroxene without the inversion symmetry is the point group 222, so it has 4 different relative orientation;
- the subgroup of diamond with the wanted properties is the same of garnet, the point group 432 , therefore it has 24 different relative orientation.

Combining all the relative orientations of inclusion and its host, we obtain the numbers of the possible equivalent descriptions of the orientation relationship for the three studied inclusion-host systems (Angel et al., 2015).

On the basis of this method, garnet and diamond have $24 \times 24=576$, clinopyroxene and diamond have $2 \times 24=48$ and orthopyroxene and diamond $4 \times 24=96$ possible equivalent descriptions of the orientation relationship.

The treatment of the collected data were performed with the OrientXplot software (Angel et al., 2015). This program permits the representation of the reciprocal


Figure 5.3.1: interface of the OrientXplot software during its use (Angel et al., 2015).
orientations of the inclusions and their hosts in a stereogram and supplies the numerical angle data between the inclusion and host axes (see Figure 5.3.1). Generally, such stereogram contains the stereographic projection of the mineral host. However, the software can transform the UB matrices for all the studied inclusion-host systems. It provides two different criteria for eliminating the ambiguities and choosing one of the symmetrically equivalent descriptions of the orientation relationship. The first method consists of setting a primary axis of the inclusion, selected by us, within an asymmetric unit of the host located and a secondary axis, once again selected by us, closed to one of the z axis of the stereogram. The second method, instead, is essentially the selection of a primary axis of the inclusion which will be closed to a chosen axis of the host.

## Chapter 6

## Results and discussion

### 6.1 Geometrical approach

The collected data were treated and plotted in stereograms through the use of the OrientXplot software (Angel et al., 2015). The UB matrices of the inclusions and the hosts were elaborated on the basis of the first criterium provided by the program to eliminate the symmetry ambiguities (see Chapter 5). For all the mineral inclusions, the a-axis is chosen as primary axis located within the asymmetric unit of the host, while the b -axis is arranged close the z -axis of the stereogram. The Figure 6.1.1 reports an example of the rearrangement used in such phase of the data treatment.

### 6.2 Global stereograms

Two types of global stereograms were plotted in such analysis: [1] an untreated diagram for both the mineral species and [2] an unambiguous diagram for both the mineral species.

The first representation of the reciprocal orientations between the inclusions and


Figure 6.1.1: the first stereogram shows the plotting of an inclusion-host pair without the symmetry elaboration, the second displays the same pair with the symmetry rearrangement of the UB matrix based on the described method. The red circles represent the poles of the a-axes of the inclusions, the green circles represent the poles of the b-axes of the inclusions, the blue circles represent the poles of the c-axes of the inclusions and the black circles represent the poles of the axes of the diamonds. The filled circles indicate the projection of the poles in the positive hemisphere, while the open circles specify the negative hemisphere. The area coloured by grey is the asymmetric unit of diamond considered by OrientXplot in the first method of geometrical treatment of the UB matrices. The inclusion considered in this example is the lot_22_stone_36_inc_1 orthopyroxene inclusion.
its diamond hosts is executed by the simple plotting of the collected UB matrices without removing the ambiguities [1]. Such operation has been done to observe how much the orientation distribution seems to be random. The Figure 6.2.1 displays respectively the untreated orientations for garnet, clino- and orthopyroxene inclusions.

The second representation is performed by the elaboration of the UB matrices of inclusions and diamonds for removing the symmetry ambiguities [2]. The Figure 6.2.2 shows the reciprocal orientations of garnet, clino- and orthopyroxe. In such diagrams we can easily observe the interested orientation without any incertitudes.

The software permits also to calculate the angles between the axes of the inclusions in respect to the axes of the host diamonds. The Table 6.2.1, Table 6.2.2 and

Table 6.2.3 show respectively the angles for garnet, clino- and orthopyroxene inclu-


Figure 6.2.1: orientation distribution of the studied garnet, clino- and orthopyroxene inclusions with respect to their host diamonds without the symmetry rearrangement of the UB matrices [1]. The symmetry effects make the representation more random and ambiguous than it effectively is. The legend is the same indicated in the Figure 6.2.1.


Figure 6.2.2: stereographic projection of the studied garnet, clino- and orthopyroxene inclusions in respect to their host diamonds without the symmetry ambiguities [2]. The legend is the same indicated in the Figure 6.2.1.
sions without the symmetry ambiguities. The error associated to such calculation is about $2^{\circ}$ (Nestola et al., 2014), so the reported data are approximate to the units.

### 6.3 Stereograms of single diamonds

Both garnets, clino- and orthopyroxenes show no special orientations relative to the diamonds plotted in the unambiguous stereograms and they do not display a systematics of special angles between their axes with the axes of the host diamonds, except few orthopyroxene inclusions (see Table 6.2.1, Table 6.2.2 and Table 6.2.3). Nonetheless, some diamonds present isoorientated inclusions in respect to among them, but not with the host diamond. Thus, the third representation [3] of the unambiguous distribution of the orientations between inclusions and hosts for every diamond with such important systematics represents a more precise analysis on these isooriented inclusions.

The Figure 6.3.1 displays the unambiguous reciprocal orientations of the garnet inclusions of the diamonds Grt_E_3 and JW083. The Figure 6.3.2 displays the unambiguous reciprocal orientations of the clinopyroxene inclusions of the diamonds PR4, lot_22_stone_36 and lot_34_stone_2. The Figure 6.3.3 displays the unambiguous reciprocal orientations of the orthopyroxene inclusions of the diamonds lot_22_stone_36 and lot_34_stone_2.

### 6.4 Discussion about the treated data

The observation of the plotted global stereograms highlights undoubtedly the random orientation of the inclusions with respect to their host diamonds, except some rare orthopyroxene inclusions of different diamonds which show and apparent special orientation with some axes of the diamond. Despite such few inclusions, these

|  | Grt |  | a1 |  |  | a2 |  |  | a3 |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Code | Dia | a1 | a2 | a3 | a1 | a2 | a3 | a1 | a2 | a3 |
| 1 | Grt_E_1 | 25 | 65 | 86 | 96 | 85 | 8 | 66 | 154 | 83 |
| 2 | Grt_E_2_1 | 42 | 56 | 69 | 110 | 98 | 22 | 55 | 145 | 85 |
| 3 | Grt_E_2_2 | 43 | 55 | 68 | 97 | 115 | 26 | 48 | 135 | 104 |
| 4 | Grt_E_2_3 | 45 | 48 | 77 | 115 | 82 | 26 | 55 | 137 | 68 |
| 5 | Grt_E_3_1 | 43 | 48 | 82 | 112 | 78 | 25 | 55 | 136 | 67 |
| 6 | Grt_E_3_2A | 47 | 50 | 70 | 74 | 132 | 47 | 48 | 112 | 130 |
| 7 | Grt_E_3_2B | 45 | 51 | 71 | 78 | 129 | 41 | 48 | 118 | 125 |
| 8 | Grt_E_3_3 | 13 | 78 | 86 | 96 | 79 | 13 | 79 | 164 | 78 |
| 9 | Grt_E_3_4 | 46 | 50 | 72 | 95 | 111 | 22 | 45 | 133 | 101 |
| 10 | Grt_E_3_5 | 47 | 50 | 69 | 75 | 131 | 45 | 47 | 113 | 128 |
| 11 | Grt_E_3_6 | 48 | 48 | 70 | 73 | 131 | 46 | 47 | 111 | 129 |
| 12 | Grt_E_4 | 40 | 50 | 87 | 99 | 84 | 11 | 52 | 140 | 79 |
| 13 | Grt_P_1 | 40 | 50 | 88 | 69 | 118 | 36 | 57 | 127 | 126 |
| 14 | Grt_P_2 | 36 | 61 | 71 | 109 | 95 | 20 | 61 | 151 | 85 |
| 15 | Grt_P_3 | 36 | 61 | 70 | 108 | 98 | 20 | 60 | 150 | 88 |
| 16 | Grt_P_4 | 40 | 50 | 89 | 68 | 118 | 37 | 58 | 127 | 127 |
| 17 | CEM_161 | 27 | 64 | 85 | 87 | 107 | 17 | 63 | 148 | 107 |
| 18 | JW9453_lot_7_stone_24 | 15 | 75 | 87 | 95 | 80 | 11 | 76 | 162 | 79 |
| 19 | JW9453lot_7_stone_29 | 30 | 66 | 73 | 109 | 91 | 19 | 67 | 156 | 83 |
| 20 | JW9453_lot_23_stone_1 | 41 | 53 | 74 | 116 | 82 | 28 | 61 | 142 | 68 |
| 21 | Jer_1_A | 38 | 52 | 89 | 73 | 113 | 30 | 58 | 133 | 120 |
| 22 | Jer_4_A | 34 | 60 | 75 | 116 | 74 | 31 | 69 | 145 | 64 |
| 23 | Jer_6_A | 42 | 52 | 73 | 107 | 95 | 18 | 53 | 142 | 83 |
| 24 | Jer-9_A | 41 | 55 | 70 | 91 | 119 | 29 | 49 | 131 | 111 |
| 25 | JW102_2 | 36 | 59 | 75 | 106 | 93 | 16 | 59 | 149 | 84 |
| 26 | LK58_1 | 46 | 53 | 67 | 81 | 132 | 43 | 46 | 117 | 124 |
| 27 | LK58_2 | 49 | 48 | 69 | 118 | 90 | 28 | 54 | 138 | 72 |
| 28 | JW243_1 | 39 | 55 | 76 | 118 | 74 | 33 | 66 | 140 | 61 |
| 29 | JW083_1 | 29 | 64 | 80 | 102 | 88 | 13 | 65 | 154 | 83 |
| 30 | JW083_2 | 29 | 64 | 79 | 104 | 86 | 14 | 65 | 153 | 80 |
|  |  |  |  |  |  |  |  |  |  |  |

Table 6.2.1: the table shows the angles between the axes of the garnet inclusions and the diamond after the software elaboration of the UB matrices for removing the ambiguities. The highlighted parameters indicate the same orientations of some inclusions into the same diamond. The yellow coloured parameters are referred to the isooriented garnet inclusions of the Grt_E_3 diamond, the green coloured parameters are referred to the isooriented garnet inclusions of the JW083 diamond. The reported data are in degree.

|  | Cpx |  |  | a |  |  | b |  |  | c |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Code | Dia | a1 | a2 | a3 | a1 | a2 | a3 | a1 | a2 | a3 |
| 31 | PR2_3 | 14 | 78 | 85 | 99 | 69 | 23 | 97 | 159 | 70 |
| 32 | PR2_5 | 20 | 76 | 77 | 97 | 26 | 116 | 125 | 74 | 40 |
| 33 | PR4_2 | 47 | 51 | 68 | 63 | 89 | 152 | 138 | 56 | 112 |
| 34 | PR4_3 | 38 | 54 | 81 | 52 | 139 | 104 | 105 | 84 | 164 |
| 35 | PR4_4 | 40 | 51 | 80 | 50 | 137 | 103 | 104 | 85 | 165 |
| 36 | Lot_8_stone_4_inc_1 | 17 | 73 | 84 | 76 | 126 | 141 | 114 | 50 | 130 |
| 37 | Lot_8_Stone_4_inc_2 | 32 | 62 | 80 | 82 | 84 | 169 | 135 | 43 | 91 |
| 38 | Lot_8_Stone_4_inc_3 | 35 | 62 | 71 | 122 | 33 | 82 | 114 | 113 | 36 |
| 39 | Lot_8_Stone_4_inc_5 | 25 | 66 | 83 | 95 | 95 | 8 | 81 | 170 | 94 |
| 40 | Dio_1 | 17 | 74 | 84 | 83 | 132 | 43 | 90 | 138 | 133 |
| 41 | Dio_2 | 30 | 63 | 76 | 80 | 136 | 49 | 77 | 129 | 139 |
| 42 | Eclo_2 | 29 | 65 | 74 | 97 | 110 | 22 | 77 | 157 | 109 |
| 43 | Protogenesi Nat Comm | 22 | 77 | 78 | 89 | 132 | 45 | 86 | 140 | 133 |
| 44 | lot_22_stone_36_inc_1 | 11 | 79 | 89 | 82 | 141 | 53 | 99 | 129 | 140 |
| 45 | lot_22_stone_36inc_2 | 20 | 75 | 78 | 93 | 40 | 130 | 126 | 60 | 49 |
| 46 | lot_22_stone_36inc_3 | 49 | 50 | 67 | 102 | 49 | 137 | 151 | 77 | 65 |
| 47 | lot_22_stone_36inc_4 | 41 | 60 | 64 | 54 | 143 | 95 | 85 | 80 | 168 |
| 48 | lot_22_stone_36inc_5 | 14 | 78 | 81 | 79 | 168 | 87 | 97 | 94 | 173 |
| 49 | lot_22_stone_36_inc_6 | 44 | 46 | 87 | 105 | 79 | 19 | 65 | 149 | 73 |
| 50 | lot_22_stone_36_inc_7 | 47 | 48 | 73 | 67 | 132 | 52 | 66 | 119 | 142 |
| 51 | lot_22_stone_36inc_8 | 25 | 65 | 83 | 65 | 134 | 127 | 111 | 63 | 143 |
| 52 | lot_22_stone_36inc_9 | 50 | 50 | 66 | 100 | 48 | 137 | 152 | 78 | 65 |
| 53 | lot_22_stone_36inc_10 | 43 | 50 | 78 | 64 | 134 | 55 | 74 | 119 | 146 |
| 54 | lot_22_stone_36inc_11 | 49 | 56 | 122 | 89 | 48 | 44 | 56 | 129 | 56 |
| 55 | lot_34_stone_2_inc_1 | 43 | 57 | 68 | 113 | 35 | 114 | 139 | 89 | 46 |
| 56 | lot_34_stone_2_inc_2 | 25 | 67 | 78 | 112 | 23 | 94 | 115 | 95 | 28 |
| 57 | lot_34_stone_2inc_3 | 42 | 56 | 68 | 114 | 36 | 113 | 136 | 88 | 45 |

Table 6.2.2: the table shows the angles between the axes of the clinopyroxene inclusions and the diamond after the symmetry removal of the ambiguities. As in the Table 6.2.1, the highlighted parameters indicate the same orientations of some inclusions into the same diamond. The yellow coloured parameters are referred to the isooriented clinopyroxene inclusions of the PR4 diamond, the orange coloured parameters are referred to the isooriented clinopyroxene inclusions of the lot_22_stone_36 diamond, the fuchsia coloured parameters are referred to the isooriented clinopyroxene inclusions of the lot_34_stone_2 diamond. The reported data are in degree.

Chapter 6: Results and discussion

| Code | Opx |  | a |  |  | b |  |  | c |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Dia | a1 | a2 | a3 | a1 | a2 | a3 | a1 | a2 | a3 |
| 58 | Madagascar | 46 | 49 | 72 | 105 | 100 | 18 | 47 | 137 | 90 |
| 59 | KF2 | 28 | 65 | 78 | 77 | 140 | 53 | 66 | 119 | 141 |
| 60 | KF3 | 47 | 52 | 66 | 114 | 96 | 26 | 54 | 141 | 80 |
| 61 | PM1_1 | 30 | 61 | 80 | 87 | 114 | 24 | 60 | 141 | 112 |
| 62 | PM1_2 | 38 | 55 | 77 | 84 | 119 | 29 | 53 | 131 | 115 |
| 63 | PR2_1 | 45 | 53 | 68 | 57 | 143 | 75 | 63 | 89 | 154 |
| 64 | PR2_4 | 28 | 65 | 77 | 93 | 111 | 22 | 62 | 147 | 107 |
| 65 | PR2.5 | 37 | 62 | 68 | 99 | 117 | 29 | 54 | 140 | 107 |
| 66 | PR2_6 | 44 | 46 | 84 | 95 | 95 | 6 | 46 | 136 | 90 |
| 67 | PR5_1 | 54 | 55 | 56 | 137 | 86 | 47 | 70 | 144 | 62 |
| 68 | PR5_2 | 51 | 58 | 58 | 140 | 71 | 53 | 81 | 142 | 53 |
| 69 | Lot_26_Stone_1 inc_1 | 47 | 49 | 72 | 99 | 106 | 18 | 45 | 135 | 96 |
| 70 | Lot_8_stone_4_inc_1 | 28 | 62 | 85 | 102 | 75 | 20 | 65 | 147 | 71 |
| 71 | Lot_8_Stone_4_inc_2 | 45 | 45 | 90 | 91 | 90 | 0 | 45 | 135 | 90 |
| 72 | Lot_8_Stone_4_inc_3 | 42 | 55 | 69 | 121 | 80 | 33 | 64 | 144 | 66 |
| 73 | Lot_8_Stone_4_inc_4 | 39 | 54 | 77 | 102 | 95 | 13 | 54 | 143 | 86 |
| 74 | Lot_8_Stone_4_inc_5 | 11 | 81 | 84 | 95 | 95 | 8 | 81 | 170 | 94 |
| 75 | Dio_1 | 43 | 60 | 62 | 133 | 58 | 59 | 89 | 134 | 44 |
| 76 | Dio 2 | 42 | 59 | 64 | 80 | 141 | 53 | 49 | 111 | 131 |
| 77 | lot_22_stone_36_inc_1 | 12 | 78 | 89 | 98 | 52 | 39 | 82 | 139 | 51 |
| 78 | lot_22_stone_36_inc_2 | 29 | 67 | 73 | 82 | 142 | 54 | 62 | 118 | 139 |
| 79 | lot_22_stone_36_inc_3 | 44 | 59 | 64 | 131 | 43 | 79 | 103 | 116 | 29 |
| 80 | lot_22_stone_36_inc_4 | 13 | 77 | 89 | 98 | 52 | 39 | 81 | 139 | 51 |
| 81 | lot_22_stone_36_inc_5 | 39 | 54 | 76 | 128 | 39 | 84 | 97 | 103 | 16 |
| 82 | lot_22_stone_36_inc_6 | 29 | 62 | 82 | 106 | 79 | 20 | 65 | 149 | 73 |
| 83 | lot_22_stone_36_inc_7 | 43 | 59 | 64 | 130 | 42 | 79 | 104 | 115 | 29 |
| 84 | lot_22_stone_36_inc_8 | 44 | 57 | 64 | 131 | 44 | 78 | 103 | 115 | 29 |
| 85 | lot_22_stone_36_inc_9 | 44 | 58 | 65 | 81 | 139 | 49 | 47 | 114 | 128 |
| 86 | lot_22_stone_36_inc_11 | 44 | 46 | 89 | 127 | 54 | 58 | 69 | 113 | 32 |
| 87 | lot_34_stone_2_inc_1 | 57 | 53 | 56 | 116 | 113 | 35 | 44 | 134 | 91 |
| 88 | lot_34_stone_2_inc_2 | 35 | 62 | 69 | 124 | 42 | 69 | 94 | 118 | 31 |
| 89 | lot 34 _stone 2 inc 3 | 56 | 52 | 56 | 114 | 110 | 33 | 44 | 135 | 90 |

Table 6.2.3: the table shows the angles between the axes of the orthopyroxene inclusions and the diamond with the symmetry operation of making unambiguous the orientations. As in the Table 6.2.1, the highlighted parameters indicate the same orientations of some inclusions into the same diamond. The blue and the cyan coloured parameters are referred to two different families of isooriented orthopyroxene inclusions of the lot_22_stone_36 diamond, the purple coloured parameters are referred to the isooriented orthopyroxene inclusions of the lot_34_stone_2 diamond. The reported data are in degree.


Figure 6.3.1: the unambiguous stereograms of the garnet inclusions in the diamonds GrtE_3 and JW083 [3]. The legend is the same indicated in the Figure 6.2.1.


Figure 6.3.2: the unambiguous stereograms of the clinopyroxene inclusions in the diamonds PR4, lot_22_stone_36 and lot_34_stone_2 [3]. The legend is the same indicated in the Figure 6.2.1.


Figure 6.3.3: the unambiguous stereograms of the orthopyroxene inclusions in the diamonds lot_22_stone_36 and lot_34_stone_2 [3]. The legend is the same indicated in the Figure 6.2.1.
data represent the evidence that the collected garnet, clino- and orthopyroxene inclusions have a protogenetic relationship with the diamonds in which they are included.

The few orthopyroxene inclusions which present an apparent orientation with the host diamonds are always contained in multiple inclusion in association with the clinopyroxene, thus we can assume that the genesis of both the crystals is correlated. Such inclusions are PR2_6, lot_8_Stone_4_inc_2, lot_34_Stone_2 inc_1 and lot_34_Stone_2_inc_3. However, the orientation of the clinopyroxenes included with such orthopyroxenes is random respect to the diamond, so two different situations can explain this fact:

- the first is that the orthopyroxenes are casually oriented with the diamond;
- the second is that the orthopyroxenes are syngenetic with the diamond and they are formed in the surroundings of the preexistent clinopyroxene;

Previous unpublished analyses on the inclusions of the diamonds lot_8_Stone_4 and lot_34_Stone_2, executed by the team of Chinn I., De Beers Exploration, London, United Kingdom, show the presence of exsoluted orthopyroxene lamellae in
clinopyroxene. Similar structures were studied in peridotites (Bozhilov et al., 1999), in which diopside commonly contains exsolution lamellae of clino- and orthoenstatite above $1000^{\circ} \mathrm{C}$ of temperature. On the basis of such observation, the orthopyroxene appears to be genetically related to the clinopyroxene, therefore the inclusions are protogenetic even if they are isooriented with the host diamond.

Furthermore, multiple sets of orientations of the inclusions are present inside the same diamonds. According to the suggestion of Nestola et al. (2014), such inclusions can represent the remnant parts of original monocrystals partially dissolved by the diamond-forming fluid or melt. The Figure 6.4.1 and Figure 6.4.2 display the spatial distribution of the inclusions in two diamonds with multiple sets of orientations, particularly the Grt E_3 which contains isooriented garnets and the lot_22_stone_36 which has isooriented clino- and orthopyroxenes. This represents another clear evidence of protogenesis.


Figure 6.4.1: in this diamond, Grt_E_3, a set of oriented garnet inclusion composed by Grt_E_3_2a - Grt_E_3_2b - Grt_E_3_5-Grt_E_3_6 is present. The vicinity of the oriented inclusions is clearly visible.


Figure 6.4.2: in this diamond, lot_22_stone_36, a set of oriented clinopyroxene inclusion and two sets of oriented orthopyroxene inclusions composed respectively by lot_22_stone_36_inc_3 lot_22_stone_36_inc_9, lot_22_stone_36_inc_1 - lot_22_stone_36_inc_4 and lot_22_stone_36_inc_3 lot_22_stone_36_inc_7 - lot_22_stone_36_inc_8 are present. Even in this case, the vicinity of the oriented inclusions is evident.

## Chapter 7

## Conclusions and implications

### 7.1 Conclusions about the syngenesis/protogenesis

The results of the present thesis work indicate that many, if not all, garnet, clinoand orthopyroxene inclusions in diamonds are protogenetic. The great variability of provenances and properties of the studied diamonds permits to extend this conclusion to a global systematics and deny every correlation with unusual conditions. These results are completely in line with some important works of the last decade (Jacob et al., 2016; Thomassot et al., 2009; Nestola et al., 2014; Milani et al., 2016; Nestola et al., 2017), which assume the protogenesis as the main genetic relationship between a great suite of typical inclusions and diamonds.

The consequences of the potential incomplete re-equilibration of these inclusions during their entrapment should be considered when the geochemical, geochronological and thermobarometric information about diamonds is collected on the inclusions. Particularly, the dating of diamonds is commonly investigated through the mineral inclusions object of such analysis, but with the disclosure of protogenesis, the validity of the dating method depends on the geochemical properties of the involved mineral species.

### 7.2 Implications for the $\mathbf{S m}$-Nd dating system

Thanks to the collaboration with Jacob D.E., Department of Earth and Planetary Sciences, Macquarie University, Australia, the equilibration times of garnet and clinopyroxene for the $\mathrm{Sm}-\mathrm{Nd}$ system have been calculated. The method to measure the diffusive equilibration times between the free-defect interested minerals, garnet and clinopyroxene, with the diamond-forming fluid is a numerical model of the diffusion considering the typical gradients of cratons and the diffusion coefficients corrected for the effect of pressure on the activation volume (Van Orman et al., 2001, 2002).

|  | $\mathrm{T}\left[{ }^{\circ} \mathrm{C}\right]$ | Time [Years] |
| ---: | ---: | ---: |
| Grt | 800 | $3 \times 10^{10}$ |
|  | 900 | $2 \times 10^{9}$ |
|  | 1000 | $1.5 \times 10^{8}$ |
|  | 1100 | $2 \times 10^{7}$ |
|  | 1200 | $3 \times 10^{6}$ |
|  | 1300 | $5.5 \times 10^{6}$ |
|  | 1400 | $1 \times 10^{5}$ |
| Cpc | 800 | $1.5 \times 10^{15}$ |
|  | 900 | $6.5 \times 10^{12}$ |
|  | 1000 | $1 \times 10^{11}$ |
|  | 1100 | $2 \times 10^{9}$ |
|  | 1200 | $8 \times 10^{7}$ |
|  | 1300 | $6.5 \times 10^{6}$ |
|  | 1400 | $5 \times 10^{5}$ |

Table 7.2.1: these data are extracted by the present diffusion model and show the equilibration time as a function of the temperature considering the pressure equal to 5 GPa . From such data we can understand the big difference in terms of equilibration time between clinopyroxene and garnet.

The Figure 7.2.1 shows the diffusion model of the $\mathrm{Sm}-\mathrm{Nd}$ system in garnet and clinopyroxene, it is modelled considering the spherical shape of the crystals with diameter of 0.5 mm . The times needed by clinopyroxene or the chemical equilibration are extremely long, especially at the low temperature, while the equilibration times of garnet are of many order of magnitude shorter than the clinopyroxene Table 7.2.1.

But in the real world the crystals have crystal lattice defects, which increase diffusion rates, and the inclusions in diamonds are most often small, between 0.1 and 0.5 mm in size (Stachel et al., 2005). In addition, we should consider also the effect of the partial dissolution/precipitation of the grains occurs upon interaction with the fluid/melt (Agrosì et al., 2016).

By means of such considerations, the equilibration times are likely to be considerably shorter than in the ideal case used for the model. Nonetheless, the equilibration times of clinopyroxene remain too long for using the Sm-Nd system for dating the diamond. Differently, garnet has relatively short times of equilibration, which makes its appropriate for the dating analyses.


Figure 7.2.1: modelling of equilibration time spans for $\mathrm{Sm}-\mathrm{Nd}$ system between a diamond-bearing fluid and defect-free garnet and clinopyroxene grains with spherical shape of 0.5 mm of diameter. The difference between the equilibration time of garnet and clinopyroxene is extremely evident: the values of the clinopyroxenes are very high, so this mineral for the $\mathrm{Sm}-\mathrm{Nd}$ system appears to be unsuitable to date the diamonds. On the other hand, the garnet needs a shorter time for the equilibration and it can be used for study the age of the diamond with the $\mathrm{Sm}-\mathrm{Nd}$ dating method.

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## Appendix A

## Procedure for modelling the

## equilibration time

The procedure used by Jacob D.E. and her scientific team for calculating the diffusion model of garnet and clinopyroxene considers that the equilibration of Nd and Sm depends on the diffusive mass-flux through the mineral/melt interface. The assumptions taken for the model are two: the grain-boundary is always in equilibrium with the surrounding fluid and the diffusion in the solid grains can be calculated with the Fick's Second Law:

$$
\begin{equation*}
\frac{\partial C(x, t)}{\partial t}=D \frac{\partial^{2} C(x, t)}{\partial x^{2}}, 0 \leq x \leq R \tag{A.1}
\end{equation*}
$$

where $C$ is the concentration of the element which are diffusing, $D$ is the diffusion coefficient and $R$ is the size of the crystal in the $x$-direction.

So, we consider $K$ as the equilibrium partition coefficient between the mineral and the melt (Johnson, 1998), then

$$
\begin{equation*}
C_{s}(R, t)=K C_{m}(t) \tag{A.2}
\end{equation*}
$$

Appendix A: Procedure for modelling the equilibration time

The diffusion coefficients $D$ for garnet and clinopyroxene are corrected using the activation volume reported in Van Orman et al. (2001) and Van Orman et al. (2002).

The model was run with the PDEPE built-in function in MATLAB. The concentration profile at the equilibration level is given by the equation:

$$
\begin{equation*}
\text { tol }=\left|\frac{i n t_{t=\infty}-\text { int }_{t}}{i n t_{\infty}-\text { int }_{t=0}}\right|, \quad \text { int }_{t}=\int_{0}^{R} C(x, t) d x \tag{A.3}
\end{equation*}
$$

## Appendix B

## Collected UB matrices

The UB matrixes of all the host-inclusion pairs collected and treated for obtaining the orientations are below.

Every host-inclusion pair is composed by two UB matrices: the UB matrix of the host is at the left and the UB matrix of the inclusion is at the right. However, every pair is appointed by a numerical code, such numbers are connected with the codes reported in Table 6.2.1, Table 6.2.2 and Table 6.2.3.

HOST 1 Diamond host Grt E_1 and INC 1 Garnet Grt_E_1
$\left[\begin{array}{ccc}0.058179 & 0.187759 & -0.020340 \\ -0.134125 & 0.057125 & 0.131776 \\ 0.133147 & -0.022159 & 0.144751\end{array}\right] \quad\left[\begin{array}{ccc}-0.021363 & 0.016862 & 0.055655 \\ 0.052040 & -0.018604 & 0.026319 \\ 0.024098 & 0.055704 & -0.008569\end{array}\right]$

HOST 2 Diamond host Grt_E_2_1 and INC 2 Garnet Grt_E_2_1

$$
\left[\begin{array}{ccc}
-0.138509 & 0.108492 & -0.086664 \\
0.132094 & 0.145543 & -0.023618 \\
0.052767 & -0.074492 & -0.176783
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.031781 & 0.008634 & -0.051472 \\
-0.028029 & -0.053917 & 0.008160 \\
-0.044855 & 0.027997 & 0.031431
\end{array}\right]
$$

HOST 3 Diamond host Grt_E_2_2 and INC 3 Garnet Grt_E_2_2

$$
\left[\begin{array}{ccc}
-0.087539 & -0.139529 & 0.108850 \\
-0.023216 & 0.133461 & 0.148612 \\
-0.177534 & 0.053569 & -0.075876
\end{array}\right] \quad\left[\begin{array}{ccc}
0.001848 & 0.059777 & -0.013621 \\
0.018028 & 0.012580 & 0.057354 \\
0.058676 & -0.005657 & -0.017210
\end{array}\right]
$$

HOST 4 Diamond host Grt_E_2_3 and INC 4 Garnet Grt E_2_3

$$
\left[\begin{array}{ccc}
-0.111902 & 0.136753 & 0.089436 \\
-0.147426 & -0.133679 & 0.028143 \\
0.078757 & -0.049826 & 0.176157
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.059766 & -0.013601 & -0.001657 \\
-0.012527 & 0.057390 & -0.017901 \\
0.005704 & -0.017079 & -0.058676
\end{array}\right]
$$

HOST 5 Diamond host Grt_E_3_1 and INC 5 Garnet Grt_E_3_1

$$
\left[\begin{array}{ccc}
-0.109943 & -0.131977 & 0.094311 \\
0.019053 & -0.124940 & -0.152227 \\
0.161484 & -0.076139 & 0.082425
\end{array}\right] \quad\left[\begin{array}{ccc}
0.021702 & -0.030756 & -0.048161 \\
0.012513 & 0.052706 & -0.028372 \\
0.055931 & -0.000004 & 0.024733
\end{array}\right]
$$

HOST 6 Diamond host Grt_E_3_2a and INC 6 Garnet Grt_E_3_2a

$$
\left[\begin{array}{ccc}
-0.110494 & -0.134466 & 0.095103 \\
0.020066 & -0.125417 & -0.151999 \\
0.161729 & -0.074574 & 0.083555
\end{array}\right] \quad\left[\begin{array}{ccc}
0.043064 & 0.034539 & 0.026365 \\
0.034804 & -0.005056 & -0.050055 \\
-0.026036 & 0.050306 & -0.023167
\end{array}\right]
$$

HOST 7 Diamond host Grt_E_3_2b and INC 7 Garnet Grt_E_3_2b

$$
\left[\begin{array}{ccc}
-0.110494 & -0.134466 & 0.095103 \\
0.020066 & -0.125417 & -0.151999 \\
0.161729 & -0.074574 & 0.083555
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.028640 & 0.041458 & 0.034572 \\
-0.001721 & 0.038519 & -0.047380 \\
-0.054150 & -0.023041 & -0.016551
\end{array}\right]
$$

HOST 8 Diamond host Grt_E_3_3 and INC 8 Garnet Grt_E_3_3

$$
\left[\begin{array}{ccc}
-0.110739 & -0.133324 & 0.096433 \\
0.017359 & -0.126561 & -0.153581 \\
0.164010 & -0.077337 & 0.081723
\end{array}\right] \quad\left[\begin{array}{ccc}
0.029604 & 0.030111 & 0.042357 \\
0.007262 & 0.046831 & -0.037983 \\
-0.052203 & 0.023941 & 0.019563
\end{array}\right]
$$

HOST 9 Diamond host Grt_E_3_4 and INC 9 Garnet GrtEE_3_4

$$
\left[\begin{array}{ccc}
-0.109497 & -0.132732 & 0.095956 \\
0.017737 & -0.126562 & -0.152186 \\
0.164394 & -0.075918 & 0.082275
\end{array}\right] \quad\left[\begin{array}{ccc}
0.009532 & 0.023353 & 0.055200 \\
0.037143 & 0.041840 & -0.024097 \\
-0.047410 & 0.037429 & -0.007658
\end{array}\right]
$$

HOST 10 Diamond host Grt_E_3_5 and INC 10 Garnet Grt_E_3_5

$$
\left[\begin{array}{ccc}
-0.110819 & -0.131191 & 0.097722 \\
0.015386 & -0.128080 & -0.153445 \\
0.165342 & -0.076164 & 0.079982
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.042483 & 0.035191 & -0.026453 \\
-0.034908 & -0.004652 & 0.050001 \\
0.026575 & 0.050007 & 0.023169
\end{array}\right]
$$

HOST 11 Diamond host Grt_E_3_6 and INC 11 Garnet Grt_E_3_6

$$
\left[\begin{array}{ccc}
-0.110494 & -0.134466 & 0.095103 \\
0.020066 & -0.125417 & -0.151999 \\
0.161729 & -0.074574 & 0.083555
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.042112 & 0.035264 & -0.027073 \\
-0.034890 & -0.003360 & 0.050184 \\
0.027301 & 0.049876 & 0.022636
\end{array}\right]
$$

Appendix B: Collected UB matrices

HOST 12 Diamond host Grt_E_4 and INC 12 Garnet Grt_E_4
$\left[\begin{array}{ccc}0.018778 & 0.195989 & -0.027625 \\ -0.110103 & 0.035552 & 0.162963 \\ 0.165990 & 0.000592 & 0.110484\end{array}\right] \quad\left[\begin{array}{ccc}0.043283 & 0.016416 & -0.040305 \\ -0.025161 & -0.036927 & -0.042067 \\ -0.035480 & 0.046200 & -0.019326\end{array}\right]$

HOST 13 Diamond host Grt_P_1 and INC 13 Garnet Grt_P_1

$$
\left[\begin{array}{ccc}
0.126753 & -0.098076 & -0.116602 \\
-0.092240 & -0.170245 & 0.043113 \\
-0.121716 & 0.026747 & -0.154087
\end{array}\right] \quad\left[\begin{array}{ccc}
0.045801 & -0.032793 & 0.024440 \\
0.025007 & -0.006618 & -0.055690 \\
0.032355 & 0.051487 & 0.008397
\end{array}\right]
$$

HOST 14 Diamond host Grt_P_2 and INC 14 Garnet Grt_P_2

$$
\left[\begin{array}{ccc}
-0.131872 & -0.092643 & 0.116678 \\
0.068331 & -0.175708 & -0.063393 \\
0.132105 & -0.001739 & 0.148732
\end{array}\right] \quad\left[\begin{array}{ccc}
0.020816 & -0.050860 & -0.026858 \\
-0.044535 & 0.003799 & -0.041739 \\
0.036384 & 0.033785 & -0.035751
\end{array}\right]
$$

HOST 15 Diamond host Grt_P_3 and INC 15 Garnet Grt_P_3

$$
\left[\begin{array}{ccc}
0.148166 & -0.089230 & -0.096562 \\
-0.092327 & -0.174081 & 0.019374 \\
-0.093456 & 0.030618 & -0.171771
\end{array}\right] \quad\left[\begin{array}{ccc}
0.037680 & 0.047826 & -0.007589 \\
0.022904 & -0.009179 & 0.056185 \\
0.042654 & -0.037317 & -0.023494
\end{array}\right]
$$

HOST 16 Diamond host Grt_P_4 and INC 16 Garnet Grt_P_4

$$
\left[\begin{array}{ccc}
-0.109640 & 0.123545 & 0.108610 \\
-0.140687 & -0.138314 & 0.015959 \\
0.086017 & -0.068802 & 0.165298
\end{array}\right] \quad\left[\begin{array}{ccc}
0.033991 & 0.046811 & 0.020598 \\
-0.015224 & 0.032899 & -0.049576 \\
-0.048814 & 0.022322 & 0.029815
\end{array}\right]
$$

HOST 17 Diamond host CEM_161 and INC 17 Garnet CEM_161

$$
\left[\begin{array}{ccc}
0.081540 & -0.168277 & -0.063691 \\
-0.180064 & -0.078478 & -0.021690 \\
-0.006392 & 0.066786 & -0.185522
\end{array}\right] \quad\left[\begin{array}{ccc}
0.027500 & -0.033801 & 0.043328 \\
-0.043493 & 0.016204 & 0.040265 \\
-0.033560 & -0.048701 & -0.016677
\end{array}\right]
$$

HOST 18 Diamond host JW9453_Lot_7_Stone_24 and INC 18 Garnet JW9453_Lot_7_Stone_24

$$
\left[\begin{array}{ccc}
-0.135915 & -0.095897 & 0.110471 \\
0.018400 & -0.161518 & -0.117407 \\
0.144970 & -0.069145 & 0.120799
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.042482 & 0.041923 & 0.011410 \\
-0.006316 & -0.021782 & 0.056472 \\
0.042996 & 0.038230 & 0.019557
\end{array}\right]
$$

HOST 19 Diamond host JW9453_Lot_7_Stone_29 and INC 19 Garnet JW9453_Lot_7_Stone_29

$$
\left[\begin{array}{ccc}
-0.104872 & -0.136683 & 0.086343 \\
-0.083606 & 0.141630 & 0.111302 \\
-0.145033 & 0.021207 & -0.134128
\end{array}\right] \quad\left[\begin{array}{ccc}
0.047308 & 0.017094 & 0.034492 \\
0.017817 & 0.038749 & -0.043600 \\
-0.034182 & 0.043870 & 0.025048
\end{array}\right]
$$

HOST 20 Diamond host JW9453_Lot_23_Stone_1 and INC 20 Garnet JW9453_Lot_23_Stone_1

$$
\left[\begin{array}{ccc}
-0.140243 & 0.102297 & 0.098379 \\
-0.081142 & -0.171130 & 0.050618 \\
0.111478 & -0.005322 & 0.163998
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.019797 & -0.057683 & 0.008536 \\
-0.042299 & 0.020426 & 0.039863 \\
-0.040127 & 0.006968 & -0.046223
\end{array}\right]
$$

HOST 21 Diamond host Jer_1 A and INC 21 Garnet Jer_1_A

$$
\left[\begin{array}{ccc}
-0.187177 & -0.007475 & 0.030128 \\
0.017906 & 0.164334 & 0.109447 \\
-0.035766 & 0.110987 & -0.162679
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.035706 & 0.013387 & -0.048270 \\
-0.037088 & -0.046998 & 0.014355 \\
-0.033758 & 0.037380 & 0.035451
\end{array}\right]
$$

HOST 22 Diamond host Jer_4_A and INC 22 Garnet Jer_4_A

$$
\left[\begin{array}{ccc}
0.095494 & -0.130638 & -0.113606 \\
-0.171399 & -0.092934 & -0.036734 \\
-0.029173 & 0.114335 & -0.160157
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.028621 & 0.005167 & -0.053684 \\
0.000095 & 0.060986 & 0.005712 \\
0.054130 & 0.002627 & -0.028727
\end{array}\right]
$$

HOST 23 Diamond host Jer_6_A and INC 23 Garnet Jer_6_A

$$
\left[\begin{array}{ccc}
-0.160806 & -0.044993 & 0.107349 \\
0.008491 & 0.174697 & 0.092319 \\
-0.115366 & 0.078954 & -0.140166
\end{array}\right] \quad\left[\begin{array}{ccc}
0.022586 & -0.054920 & -0.014972 \\
0.044799 & 0.027121 & -0.031797 \\
0.035121 & 0.000756 & 0.050138
\end{array}\right]
$$

HOST 24 Diamond host Jer_9_A and INC 24 Garnet Jer_9_A

$$
\left[\begin{array}{ccc}
-0.033396 & -0.092809 & 0.171895 \\
-0.004735 & 0.176590 & 0.096746 \\
-0.198105 & 0.012563 & -0.031404
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.057558 & 0.012350 & 0.016377 \\
0.016255 & 0.056988 & 0.014370 \\
-0.012591 & 0.017674 & -0.057356
\end{array}\right]
$$

HOST 25 Diamond host JW102_2 and INC 25 Garnet JW102_2

$$
\left[\begin{array}{ccc}
0.117806 & -0.109042 & -0.110581 \\
0.134969 & 0.144821 & -0.006591 \\
0.088605 & -0.075064 & 0.162450
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.027073 & -0.051830 & -0.018421 \\
-0.052252 & 0.017702 & 0.026776 \\
-0.017258 & 0.027511 & -0.051988
\end{array}\right]
$$

HOST 26 Diamond host LK58_1 and INC 26 Garnet LK58_1

$$
\left[\begin{array}{ccc}
0.112025 & -0.115972 & -0.117698 \\
0.151900 & 0.127725 & 0.015930 \\
0.066852 & -0.098735 & 0.158472
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.033081 & 0.043107 & 0.028645 \\
0.045744 & 0.008398 & 0.040122 \\
0.024268 & 0.042929 & -0.036649
\end{array}\right]
$$

HOST 27 Diamond host LK58_2 and INC 27 Garnet LK58_2

$$
\left[\begin{array}{ccc}
0.112114 & -0.112683 & -0.124937 \\
0.151908 & 0.125474 & 0.013825 \\
0.070714 & -0.106253 & 0.152169
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.050023 & -0.016794 & -0.031472 \\
-0.015978 & 0.059085 & -0.006301 \\
0.032051 & 0.003056 & -0.052445
\end{array}\right]
$$

HOST 28 Diamond host JW243_1 and INC 28 Garnet JW243_1

$$
\left[\begin{array}{ccc}
0.124544 & 0.085532 & -0.132529 \\
0.003359 & 0.162200 & 0.111970 \\
0.158208 & -0.067867 & 0.098651
\end{array}\right] \quad\left[\begin{array}{ccc}
0.016136 & 0.058784 & 0.007600 \\
-0.014583 & 0.011582 & -0.058510 \\
-0.057472 & 0.013526 & 0.017046
\end{array}\right]
$$

HOST 29 Diamond host JW083_1 and INC 29 Garnet JW083_1

$$
\left[\begin{array}{ccc}
-0.106089 & -0.108752 & 0.117165 \\
-0.030959 & 0.162065 & 0.109901 \\
-0.161778 & 0.039848 & -0.104931
\end{array}\right] \quad\left[\begin{array}{ccc}
0.024923 & 0.055181 & -0.009226 \\
0.000629 & 0.009756 & 0.060402 \\
0.055940 & -0.024641 & 0.003390
\end{array}\right]
$$

HOST 30 Diamond host JW083_2 and INC 30 Garnet JW083_2

$$
\left[\begin{array}{ccc}
-0.119546 & 0.108030 & 0.106085 \\
-0.112119 & -0.159648 & 0.032334 \\
0.104433 & -0.040217 & 0.162503
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.054572 & 0.025997 & -0.009495 \\
-0.011273 & -0.001782 & 0.060258 \\
0.025315 & 0.055430 & 0.006321
\end{array}\right]
$$

HOST 31 Diamond host PR2_3 and INC 31 Clinopyroxene PR2_3

$$
\left[\begin{array}{ccc}
0.113250 & -0.116181 & -0.118027 \\
-0.088757 & -0.164768 & 0.074605 \\
-0.138897 & 0.008816 & -0.144969
\end{array}\right] \quad\left[\begin{array}{ccc}
0.036726 & 0.066571 & 0.056728 \\
-0.047355 & 0.043142 & -0.102851 \\
-0.047625 & 0.008504 & 0.078803
\end{array}\right]
$$

HOST 32 Diamond host PR2_5 and INC 32 Diamond host X PR2_5

$$
\left[\begin{array}{ccc}
0.122988 & 0.051074 & -0.145062 \\
-0.031984 & 0.192541 & 0.045036 \\
0.153748 & -0.002305 & 0.128674
\end{array}\right] \quad\left[\begin{array}{ccc}
0.026742 & -0.020009 & 0.136625 \\
-0.071396 & -0.005959 & 0.009201 \\
-0.001616 & -0.077102 & -0.036536
\end{array}\right]
$$

HOST 33 Diamond host PR4_2 and INC 33 Clinopyroxene PR4_2

$$
\left[\begin{array}{ccc}
0.093427 & -0.120456 & -0.131610 \\
0.173652 & 0.099307 & 0.028321 \\
0.047808 & -0.124213 & 0.149805
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.065876 & 0.022796 & 0.023001 \\
-0.032830 & 0.006761 & -0.139279 \\
-0.022661 & -0.076941 & -0.005532
\end{array}\right]
$$

HOST 34 Diamond host PR4_3 and INC 34 Clinopyroxene PR4_3

$$
\left[\begin{array}{ccc}
-0.130651 & -0.119252 & 0.101920 \\
0.051488 & -0.157363 & -0.114169 \\
0.143481 & -0.048302 & 0.130598
\end{array}\right] \quad\left[\begin{array}{ccc}
0.061209 & 0.021113 & -0.041325 \\
0.037715 & -0.064921 & 0.064417 \\
-0.027487 & -0.042738 & -0.118593
\end{array}\right]
$$

HOST 35 Diamond host PR4_4 and INC 35 Clinopyroxene PR4_4

$$
\left[\begin{array}{ccc}
-0.100529 & 0.122629 & 0.125899 \\
0.117008 & 0.155926 & -0.052391 \\
-0.129604 & 0.050426 & -0.144734
\end{array}\right] \quad\left[\begin{array}{ccc}
0.062033 & 0.015497 & -0.042407 \\
0.034121 & -0.066120 & 0.066158 \\
-0.030567 & -0.043136 & -0.116984
\end{array}\right]
$$

HOST 36 Diamond host Lot_8_stone_4_inc_1 and INC 36 Clinopyroxene Lot_8_stone_4_foto_1 inc_1

$$
\left[\begin{array}{ccc}
-0.123674 & -0.058528 & 0.145409 \\
0.008549 & 0.178838 & 0.081615 \\
-0.155875 & 0.057763 & -0.108008
\end{array}\right] \quad\left[\begin{array}{ccc}
0.056712 & -0.040978 & 0.085250 \\
-0.033157 & -0.066159 & -0.056293 \\
0.038412 & 0.004056 & -0.098382
\end{array}\right]
$$

HOST 37 Diamond host Lot_8_Stone_4_inc_2 and INC 37 Clinopyroxene Lot_8_Stone_4_inc_2

$$
\left[\begin{array}{ccc}
0.083883 & 0.170994 & -0.054041 \\
-0.070936 & 0.083283 & 0.157414 \\
0.161353 & -0.043445 & 0.096481
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.048320 & 0.059838 & -0.038870 \\
0.000000 & 0.056621 & 0.046693 \\
-0.011520 & -0.021444 & -0.133074
\end{array}\right]
$$

HOST 38 Diamond host Lot_8_Stone_4_inc_3 and INC 38 Clinopyroxene Lot_8_Stone_4_inc_3

$$
\left[\begin{array}{ccc}
0.054555 & -0.168488 & -0.079874 \\
-0.163300 & -0.087334 & 0.072953 \\
-0.095744 & 0.046456 & -0.164090
\end{array}\right] \quad\left[\begin{array}{ccc}
0.010946 & -0.071231 & 0.058627 \\
-0.067033 & -0.023586 & -0.081350 \\
0.032903 & -0.024202 & -0.096891
\end{array}\right]
$$

HOST 39 Diamond host Lot_8_Stone_4_inc_5 and INC 39 Clinopyroxene Lot_8_Stone_4_inc_5

$$
\left[\begin{array}{ccc}
0.081485 & 0.168295 & -0.056180 \\
-0.072214 & 0.086440 & 0.159099 \\
0.164291 & -0.046156 & 0.096237
\end{array}\right] \quad\left[\begin{array}{ccc}
0.023097 & 0.024770 & 0.131400 \\
-0.039025 & -0.058081 & 0.039771 \\
0.060506 & -0.047241 & 0.020953
\end{array}\right]
$$

HOST 40 Diamond host Dio_1 and INC 40 Clinopyroxene Dio_1

$$
\left[\begin{array}{ccc}
-0.113640 & -0.121052 & 0.110263 \\
-0.033820 & 0.149452 & 0.124916 \\
-0.157034 & 0.054251 & -0.105916
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.038088 & 0.067964 & -0.025057 \\
0.061302 & 0.038824 & 0.071669 \\
0.021947 & 0.009270 & -0.116708
\end{array}\right]
$$

HOST 41 Diamond host Dio_2 and INC 41 Clinopyroxene Dio_2

$$
\left[\begin{array}{ccc}
-0.110050 & 0.131894 & 0.098364 \\
-0.103274 & -0.146974 & 0.078600 \\
0.127820 & -0.009534 & 0.151216
\end{array}\right] \quad\left[\begin{array}{ccc}
0.000000 & -0.038088 & 0.067964 \\
0.061302 & 0.038824 & 0.071669 \\
0.021947 & 0.009270 & -0.116708
\end{array}\right]
$$

HOST 42 Diamond host Eclo_2 and INC 42 Clinopyroxene Eclo_2

$$
\left[\begin{array}{ccc}
0.110043 & -0.126209 & -0.110436 \\
-0.127618 & -0.147309 & 0.045665 \\
-0.108694 & 0.048923 & -0.164474
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.040948 & -0.063046 & 0.014990 \\
-0.003902 & 0.027104 & 0.124144 \\
-0.063379 & 0.039487 & -0.061180
\end{array}\right]
$$

HOST 43 Diamond host Protogenesi Nat Comm and INC 43 Clinopyroxene Protogenesi Nat Comm

$$
\left[\begin{array}{ccc}
0.024273 & -0.172265 & -0.087583 \\
0.055381 & 0.102606 & -0.169398 \\
0.189422 & 0.005826 & 0.068218
\end{array}\right] \quad\left[\begin{array}{ccc}
0.009061 & -0.024695 & -0.121028 \\
0.020916 & 0.073306 & -0.027504 \\
0.070894 & -0.019238 & 0.068852
\end{array}\right]
$$

HOST 44 Diamond host lot_22_stone_36_inc_1 and INC 44 Clinopyroxene lot_22_stone_36_inc_1

$$
\left[\begin{array}{ccc}
0.144642 & 0.082349 & -0.104514 \\
-0.044224 & 0.173162 & 0.076854 \\
0.123087 & -0.035670 & 0.148398
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.033229 & 0.019608 & 0.100077 \\
0.043943 & -0.051569 & 0.088687 \\
0.052116 & 0.056315 & 0.047060
\end{array}\right]
$$

HOST 45 Diamond host lot_22_stone_36_inc_2 and INC 45 Clinopyroxene lot_22_stone_36_inc_2

$$
\left[\begin{array}{ccc}
0.097879 & 0.088747 & -0.143719 \\
0.046501 & -0.174319 & -0.074962 \\
-0.164762 & 0.005014 & -0.110318
\end{array}\right] \quad\left[\begin{array}{ccc}
0.047841 & 0.050011 & -0.041805 \\
0.060029 & -0.033516 & 0.095027 \\
0.006984 & -0.053671 & -0.097681
\end{array}\right]
$$

HOST 46 Diamond host lot_22_stone_36_inc_3 and INC 46 Clinopyroxene lot_22_stone_36_inc_3

$$
\left[\begin{array}{ccc}
0.146484 & -0.087445 & -0.100235 \\
0.075956 & 0.176256 & -0.045918 \\
0.111046 & -0.001782 & 0.161890
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.020421 & -0.004812 & -0.139970 \\
0.052079 & 0.054095 & -0.006806 \\
0.051021 & -0.057773 & 0.005745
\end{array}\right]
$$

HOST 47 Diamond host lot_22_stone_36_inc_4 and INC 47 Clinopyroxene lot_22_stone_36_inc_4

$$
\left[\begin{array}{ccc}
0.122897 & 0.133830 & -0.079225 \\
-0.085298 & 0.138757 & 0.111035 \\
0.131489 & -0.036477 & 0.143074
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.011119 & 0.058868 & -0.094653 \\
0.010910 & -0.051408 & -0.096494 \\
-0.074726 & -0.015518 & -0.038619
\end{array}\right]
$$

HOST 48 Diamond host lot_22_stone_36_inc_5 and INC 48 Clinopyroxene lot_22_stone_36_inc_5

$$
\left[\begin{array}{ccc}
0.078007 & -0.134965 & -0.126728 \\
-0.111786 & -0.142012 & 0.085653 \\
-0.144110 & 0.038839 & -0.131266
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.025992 & -0.051903 & -0.104141 \\
0.029443 & 0.043392 & -0.085430 \\
0.065232 & -0.040683 & 0.041643
\end{array}\right]
$$

HOST 49 Diamond host lot_22_stone_36_inc_6 and INC 49 Clinopyroxene lot_22_stone_36_inc_6

$$
\left[\begin{array}{ccc}
0.100771 & 0.087488 & -0.146490 \\
0.048845 & -0.175367 & -0.075270 \\
-0.164954 & 0.002518 & -0.112589
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.039935 & 0.056867 & 0.041737 \\
0.054312 & 0.005723 & 0.122416 \\
0.035640 & 0.055458 & -0.056465
\end{array}\right]
$$

HOST 50 Diamond host lot_22_stone_36_inc_7 and INC 50 Clinopyroxene lot_22_stone_36_inc_7

$$
\left[\begin{array}{ccc}
0.144962 & -0.087672 & -0.098685 \\
0.074789 & 0.173981 & -0.046379 \\
0.112454 & -0.004289 & 0.166237
\end{array}\right] \quad\left[\begin{array}{ccc}
0.024028 & 0.022335 & 0.134394 \\
0.060412 & -0.047843 & 0.018690 \\
0.039455 & 0.059872 & -0.034220
\end{array}\right]
$$

HOST 51 Diamond host lot_22_stone_36_inc_8 and INC 51 Clinopyroxene lot_22_stone_36_inc_8

$$
\left[\begin{array}{ccc}
0.147624 & -0.087135 & -0.099794 \\
0.074650 & 0.176001 & -0.046323 \\
0.115604 & -0.006817 & 0.166076
\end{array}\right] \quad\left[\begin{array}{ccc}
0.024464 & -0.022652 & -0.111706 \\
0.060754 & 0.047757 & 0.042542 \\
0.039849 & -0.060204 & 0.074884
\end{array}\right]
$$

HOST 52 Diamond host lot_22_stone_36_inc_9 and INC 52 Clinopyroxene lot_22_stone_36_inc_9

$$
\left[\begin{array}{ccc}
0.101267 & 0.087240 & -0.146775 \\
0.046160 & -0.178781 & -0.078037 \\
-0.166902 & 0.004192 & -0.113436
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.020528 & -0.004920 & -0.140456 \\
0.052583 & 0.054619 & -0.007013 \\
0.051351 & -0.058163 & 0.005561
\end{array}\right]
$$

HOST 53 Diamond host lot_22_stone_36_inc_10 and INC 53 Clinopyroxene lot_22_stone_36_inc_10

$$
\left[\begin{array}{ccc}
0.102468 & 0.086285 & -0.145524 \\
0.046052 & -0.175775 & -0.076984 \\
-0.165310 & 0.003868 & -0.111253
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.029429 & -0.073621 & -0.016699 \\
-0.059825 & 0.025590 & 0.041446 \\
-0.037487 & 0.015137 & -0.135013
\end{array}\right]
$$

HOST 54 Diamond host lot_22_stone_36_inc_11 and INC 54 Clinopyroxene lot_22_stone_36_inc_11

$$
\left[\begin{array}{ccc}
0.144829 & -0.088815 & -0.102653 \\
0.075356 & 0.174656 & -0.044756 \\
0.110933 & -0.002982 & 0.165729
\end{array}\right] \quad\left[\begin{array}{ccc}
0.048445 & -0.052854 & 0.078172 \\
0.058002 & 0.035211 & -0.034969 \\
0.009917 & 0.048175 & 0.111749
\end{array}\right]
$$

HOST 55 Diamond host lot_34_stone_2_inc_1 and INC 55 Clinopyroxene lot_34_stone_2_inc_1

$$
\left[\begin{array}{ccc}
0.035581 & -0.139407 & -0.128492 \\
0.064615 & 0.132802 & -0.129938 \\
0.180275 & -0.017273 & 0.083276
\end{array}\right] \quad\left[\begin{array}{ccc}
0.010275 & 0.062185 & 0.088234 \\
-0.043131 & -0.035694 & 0.072709 \\
0.061898 & -0.035592 & 0.085749
\end{array}\right]
$$

HOST 56 Diamond host lot_34_stone_2_inc_2 and INC 56 Clinopyroxene lot_34_stone_2_inc_2

$$
\left[\begin{array}{ccc}
0.138703 & 0.134451 & -0.038910 \\
-0.124602 & 0.142524 & 0.050344 \\
0.056144 & -0.018078 & 0.183982
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.019953 & 0.070531 & 0.043275 \\
0.050363 & 0.034626 & -0.058353 \\
-0.054567 & 0.006800 & -0.123894
\end{array}\right]
$$

HOST 57 Diamond host lot_34_stone_2_inc_3 and INC 57 Clinopyroxene lot_34_stone_2_inc_3

$$
\left[\begin{array}{ccc}
-0.050983 & -0.157847 & -0.099641 \\
-0.152612 & -0.028282 & 0.119432 \\
-0.105278 & 0.109659 & -0.134131
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.001223 & -0.026671 & 0.127462 \\
0.000748 & -0.075270 & -0.044786 \\
0.076426 & 0.000272 & 0.041691
\end{array}\right]
$$

HOST 58 Diamond host Madagascar and INC 58 Orthopyroxene Madagascar

$$
\left[\begin{array}{ccc}
0.100442 & 0.133919 & -0.108243 \\
-0.078526 & 0.149702 & 0.097502 \\
0.153247 & -0.010517 & 0.130201
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.036538 & 0.021798 & -0.017424 \\
-0.001799 & -0.047653 & -0.111658 \\
-0.011660 & -0.062044 & 0.078744
\end{array}\right]
$$

HOST 59 Diamond host KF2 and INC 59 Orthopyroxene KF2

$$
\left[\begin{array}{ccc}
0.086360 & 0.149151 & -0.098400 \\
0.062052 & -0.127654 & -0.139640 \\
-0.168276 & 0.030099 & -0.101711
\end{array}\right] \quad\left[\begin{array}{ccc}
0.012517 & 0.074792 & 0.022398 \\
-0.005910 & 0.017814 & -0.131546 \\
-0.036295 & 0.022952 & 0.029088
\end{array}\right]
$$

HOST 60 Diamond host KF3 and INC 60 Orthopyroxene FK3

$$
\left[\begin{array}{ccc}
0.199858 & -0.006676 & 0.006241 \\
0.006863 & 0.200228 & -0.010593 \\
-0.009049 & 0.005921 & 0.200624
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.022833 & -0.005662 & 0.110070 \\
0.014348 & -0.073246 & 0.026207 \\
0.027967 & 0.032758 & 0.076764
\end{array}\right]
$$

HOST 61 Diamond host PM1_1 and INC 61 Orthopyroxene PM1_1

$$
\left[\begin{array}{ccc}
-0.133721 & -0.108321 & 0.099038 \\
0.071418 & -0.164832 & -0.084795 \\
0.128074 & -0.021460 & 0.150031
\end{array}\right] \quad\left[\begin{array}{ccc}
0.031262 & -0.033449 & -0.058239 \\
-0.001179 & 0.055356 & -0.099413 \\
0.023040 & 0.047948 & 0.074138
\end{array}\right]
$$

HOST 62 Diamond host PM1 2 and INC 62 Orthopyroxene PM1_2

$$
\left[\begin{array}{ccc}
-0.111318 & 0.109660 & 0.122707 \\
-0.087177 & -0.163202 & 0.067961 \\
0.138040 & -0.013197 & 0.138642
\end{array}\right] \quad\left[\begin{array}{ccc}
0.036058 & 0.022721 & -0.033709 \\
-0.003649 & 0.065458 & 0.078898 \\
0.013966 & -0.041089 & 0.107008
\end{array}\right]
$$

HOST 63 Diamond host PR2_1 and INC 63 Orthopyroxene PR2_1

$$
\left[\begin{array}{ccc}
0.050431 & -0.186327 & -0.039383 \\
0.177515 & 0.061889 & -0.066367 \\
0.075441 & -0.019132 & 0.184173
\end{array}\right] \quad\left[\begin{array}{ccc}
0.011094 & 0.004843 & 0.130278 \\
-0.021315 & 0.066139 & 0.014831 \\
-0.030385 & -0.044351 & 0.036744
\end{array}\right]
$$

HOST 64 Diamond host PR2_4 and INC 64 Orthopyroxene PR2_4

$$
\left[\begin{array}{ccc}
0.122052 & -0.107606 & -0.113950 \\
-0.082966 & -0.165957 & 0.071700 \\
-0.131274 & 0.003133 & -0.147016
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.024228 & 0.061342 & 0.011519 \\
0.025518 & 0.048135 & -0.058746 \\
-0.014987 & -0.017404 & -0.121858
\end{array}\right]
$$

HOST 65 Diamond host PR2_5 and INC 65 Orthopyroxene PR2_5

$$
\left[\begin{array}{ccc}
-0.144309 & -0.054624 & 0.122040 \\
0.040556 & -0.188880 & -0.034917 \\
0.126888 & -0.001373 & 0.152098
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.013406 & -0.019957 & -0.122751 \\
0.035779 & -0.006097 & -0.046239 \\
0.000807 & -0.077100 & 0.035693
\end{array}\right]
$$

HOST 66 Diamond host PR2_6 and INC 66 Orthopyroxene PR2_6

$$
\left[\begin{array}{ccc}
-0.145803 & -0.053433 & 0.121448 \\
0.043541 & -0.185853 & -0.037680 \\
0.127284 & -0.000935 & 0.151996
\end{array}\right] \quad\left[\begin{array}{ccc}
0.011721 & 0.056626 & 0.086426 \\
-0.032130 & -0.010066 & 0.073388 \\
0.017909 & -0.055519 & 0.075237
\end{array}\right]
$$

HOST 67 Diamond host PR5_1 and INC 67 Orthopyroxene PR5_1

$$
\left[\begin{array}{ccc}
-0.116865 & 0.088616 & 0.132224 \\
-0.125926 & -0.149577 & -0.019071 \\
0.090353 & -0.096125 & 0.147758
\end{array}\right] \quad\left[\begin{array}{ccc}
0.038093 & -0.014273 & -0.002023 \\
-0.004321 & -0.044148 & -0.113668 \\
-0.005426 & -0.065740 & 0.076535
\end{array}\right]
$$

HOST 68 Diamond host PR5_2 and INC 68 Orthopyroxene PR5_2

$$
\left[\begin{array}{ccc}
-0.108240 & 0.096561 & 0.124962 \\
-0.133354 & -0.147221 & -0.013956 \\
0.082513 & -0.093289 & 0.152837
\end{array}\right] \quad\left[\begin{array}{ccc}
0.038030 & -0.015114 & 0.002568 \\
-0.005039 & -0.057440 & -0.094361 \\
-0.005630 & -0.054154 & 0.099348
\end{array}\right]
$$

HOST 69 Diamond host Lot_26_Stone_1_inc_1 and INC 69 Orthopyroxene Lot_26_Stone_1_inc_1

$$
\left[\begin{array}{ccc}
0.164777 & 0.111483 & -0.018848 \\
-0.095242 & 0.150506 & 0.082158 \\
0.061969 & -0.057864 & 0.181814
\end{array}\right] \quad\left[\begin{array}{ccc}
0.009279 & 0.010247 & 0.131910 \\
-0.037310 & -0.008884 & 0.034518 \\
0.005436 & -0.079194 & 0.013836
\end{array}\right]
$$

HOST 70 Diamond host Lot_8_stone_4_foto_1_inc_1 and INC 70 Orthopyroxene Lot_8_stone_4_foto_1 inc_1

$$
\left[\begin{array}{ccc}
-0.123674 & -0.058528 & 0.145409 \\
0.008549 & 0.178838 & 0.081615 \\
-0.155875 & 0.057763 & -0.108008
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.028929 & 0.049638 & -0.033966 \\
0.017096 & 0.013482 & -0.120620 \\
-0.019489 & -0.061745 & -0.053929
\end{array}\right]
$$

HOST 71 Diamond host Lot_8_stone_4_foto_1_inc_2 and INC 71 Orthopyroxene Lot_8_stone_4_foto_1_inc_2

$$
\left[\begin{array}{ccc}
0.052592 & -0.175070 & -0.081129 \\
-0.163805 & -0.086730 & 0.072498 \\
-0.099458 & 0.048757 & -0.166955
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.018550 & 0.069779 & -0.012936 \\
0.032781 & 0.034358 & -0.044534 \\
-0.009203 & -0.019118 & -0.128285
\end{array}\right]
$$

HOST 72 Diamond host Lot_8_stone_4_foto_1_inc_3 and INC 72 Orthopyroxene Lot_8_stone_4_foto_1_inc_3

$$
\left[\begin{array}{ccc}
0.054555 & -0.168488 & -0.079874 \\
-0.163300 & -0.087334 & 0.072953 \\
-0.095744 & 0.046456 & -0.164090
\end{array}\right] \quad\left[\begin{array}{ccc}
0.005659 & 0.072370 & -0.053947 \\
-0.034317 & 0.023743 & 0.047805 \\
0.016882 & 0.024763 & 0.115226
\end{array}\right]
$$

HOST 73 Diamond host Lot_8_stone_4_foto_1_inc_4 and INC 73 Orthopyroxene Lot_8_stone_4_foto_1_inc_4

$$
\left[\begin{array}{ccc}
0.084793 & 0.168622 & -0.057550 \\
-0.069522 & 0.091116 & 0.164565 \\
0.164927 & -0.048263 & 0.096643
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.011605 & 0.073907 & -0.031054 \\
0.036428 & 0.019647 & -0.031855 \\
-0.006246 & -0.022978 & -0.128195
\end{array}\right]
$$

HOST 74 Diamond host Lot_8_stone_4_foto_1_inc_5 and INC 74 Orthopyroxene Lot_8_stone_4_foto_1_inc_5

$$
\left[\begin{array}{ccc}
0.081485 & 0.168295 & -0.056180 \\
-0.072214 & 0.086440 & 0.159099 \\
0.164291 & -0.046156 & 0.096237
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.011699 & -0.025229 & 0.121203 \\
0.019788 & 0.058714 & 0.059597 \\
-0.030565 & 0.047753 & -0.009726
\end{array}\right]
$$

HOST 75 Diamond host Dio_1 and INC 75 Orthopyroxene Dio_1

$$
\left[\begin{array}{ccc}
-0.113640 & -0.121052 & 0.110263 \\
-0.033820 & 0.149452 & 0.124916 \\
-0.157034 & 0.054251 & -0.105916
\end{array}\right] \quad\left[\begin{array}{ccc}
0.003877 & -0.078842 & 0.002596 \\
0.036343 & 0.007181 & -0.043016 \\
0.012077 & 0.004187 & 0.128074
\end{array}\right]
$$

HOST 76 Diamond host Dio_2 and INC 76 Orthopyroxene Dio_2

$$
\left[\begin{array}{ccc}
-0.110050 & 0.131894 & 0.098364 \\
-0.103274 & -0.146974 & 0.078600 \\
0.127820 & -0.009534 & 0.151216
\end{array}\right] \quad\left[\begin{array}{ccc}
0.014303 & -0.055112 & -0.083826 \\
0.035431 & 0.019077 & 0.037602 \\
-0.002137 & -0.054857 & 0.097561
\end{array}\right]
$$

HOST 77 Diamond host lot_22_stone_36_inc_1 and INC 77 Orthopyroxene lot_22_stone_36_inc_1

$$
\left[\begin{array}{ccc}
0.144642 & 0.082349 & -0.104514 \\
-0.044224 & 0.173162 & 0.076854 \\
0.123087 & -0.035670 & 0.148398
\end{array}\right] \quad\left[\begin{array}{ccc}
0.016882 & 0.019611 & -0.117058 \\
-0.022293 & -0.052724 & -0.065724 \\
-0.026474 & 0.057101 & -0.020461
\end{array}\right]
$$

HOST 78 Diamond host lot_22_stone_36_inc_2 and INC 78 Orthopyroxene lot_22_stone_36_inc_2

$$
\left[\begin{array}{ccc}
0.097879 & 0.088747 & -0.143719 \\
0.046501 & -0.174319 & -0.074962 \\
-0.164762 & 0.005014 & -0.110318
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.027386 & 0.044753 & 0.061968 \\
-0.027147 & -0.031694 & -0.082645 \\
-0.005921 & -0.059526 & 0.090820
\end{array}\right]
$$

HOST 79 Diamond host lot_22_stone_36_inc_3 and INC 79 Orthopyroxene lot_22_stone_36_inc_3

$$
\left[\begin{array}{ccc}
0.146484 & -0.087445 & -0.100235 \\
0.075956 & 0.176256 & -0.045918 \\
0.111046 & -0.001782 & 0.161890
\end{array}\right] \quad\left[\begin{array}{ccc}
0.010423 & -0.004739 & 0.130939 \\
-0.026737 & 0.054902 & 0.031938 \\
-0.025963 & -0.058299 & 0.019541
\end{array}\right]
$$

HOST 80 Diamond host lot_22_stone_36_inc_4 and INC 80 Orthopyroxene lot_22_stone_36_inc_4

$$
\left[\begin{array}{ccc}
0.122897 & 0.133830 & -0.079225 \\
-0.085298 & 0.138757 & 0.111035 \\
0.131489 & -0.036477 & 0.143074
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.009553 & 0.000417 & 0.131070 \\
0.027379 & -0.054345 & 0.026756 \\
0.025271 & 0.058677 & 0.022946
\end{array}\right]
$$

HOST 81 Diamond host lot_22_stone_36_inc_5 and INC 81 Orthopyroxene lot_22_stone_36_inc_5

$$
\left[\begin{array}{ccc}
0.078007 & -0.134965 & -0.126728 \\
-0.111786 & -0.142012 & 0.085653 \\
-0.144110 & 0.038839 & -0.131266
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.003373 & -0.061168 & 0.085989 \\
0.006351 & 0.049213 & 0.105222 \\
-0.037807 & 0.013662 & 0.008621
\end{array}\right]
$$

HOST 82 Diamond host lot_22_stone_36_inc_6 and INC 82 Orthopyroxene lot_22_stone_36_inc_6

$$
\left[\begin{array}{ccc}
0.100771 & 0.087488 & -0.146490 \\
0.048845 & -0.175367 & -0.075270 \\
-0.164954 & 0.002518 & -0.112589
\end{array}\right] \quad\left[\begin{array}{ccc}
0.020053 & -0.056937 & 0.061912 \\
-0.027296 & -0.005666 & 0.095162 \\
-0.017867 & -0.055444 & -0.074376
\end{array}\right]
$$

HOST 83 Diamond host lot_22_stone_36_inc_7 and INC 83 Orthopyroxene lot_22_stone_36_inc_7

$$
\left[\begin{array}{ccc}
0.144962 & -0.087672 & -0.098685 \\
0.074789 & 0.173981 & -0.046379 \\
0.112454 & -0.004289 & 0.166237
\end{array}\right] \quad\left[\begin{array}{ccc}
0.010332 & 0.004440 & -0.130839 \\
-0.026812 & -0.054917 & -0.032269 \\
-0.025473 & 0.059171 & -0.018941
\end{array}\right]
$$

HOST 84 Diamond host lot_22_stone_36_inc_8 and INC 84 Orthopyroxene lot_22_stone_36_inc_8

$$
\left[\begin{array}{ccc}
0.147624 & -0.087135 & -0.099794 \\
0.074650 & 0.176001 & -0.046323 \\
0.115604 & -0.006817 & 0.166076
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.010534 & 0.004959 & 0.129982 \\
0.026358 & -0.054351 & 0.031940 \\
0.025931 & 0.057955 & 0.019256
\end{array}\right]
$$

HOST 85 Diamond host lot_22_stone_36_inc_9 and INC 85 Orthopyroxene lot_22_stone_36_inc_9

$$
\left[\begin{array}{ccc}
0.101267 & 0.087240 & -0.146775 \\
0.046160 & -0.178781 & -0.078037 \\
-0.166902 & 0.004192 & -0.113436
\end{array}\right] \quad\left[\begin{array}{ccc}
0.010398 & -0.062819 & -0.072764 \\
-0.026589 & -0.043698 & 0.066127 \\
-0.025819 & 0.019265 & -0.097150
\end{array}\right]
$$

HOST 86 Diamond host lot_22_stone_36_inc_11 and INC 86 Orthopyroxene lot_22_stone_36_inc_11

$$
\left[\begin{array}{ccc}
0.144829 & -0.088815 & -0.102653 \\
0.075356 & 0.174656 & -0.044756 \\
0.110933 & -0.002982 & 0.165729
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.007747 & 0.078281 & 0.001993 \\
-0.034381 & -0.014306 & -0.052815 \\
-0.015049 & -0.007186 & 0.124622
\end{array}\right]
$$

HOST 87 Diamond host lot_34_stone_2_inc_1 and INC 87 Orthopyroxene lot_34_stone_2_inc_1

$$
\left[\begin{array}{ccc}
0.035581 & -0.139407 & -0.128492 \\
0.064615 & 0.132802 & -0.129938 \\
0.180275 & -0.017273 & 0.083276
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.005176 & -0.062486 & 0.082847 \\
0.021994 & 0.035590 & 0.093952 \\
-0.031302 & 0.035096 & 0.053038
\end{array}\right]
$$

HOST 88 Diamond host lot_34_stone_2_inc_2 and INC 88 Orthopyroxene lot_34_stone_2_inc_2

$$
\left[\begin{array}{ccc}
0.138703 & 0.134451 & -0.038910 \\
-0.124602 & 0.142524 & 0.050344 \\
0.056144 & -0.018078 & 0.183982
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.009945 & -0.061748 & 0.079258 \\
0.025030 & 0.024316 & 0.093598 \\
-0.027133 & 0.044859 & 0.058725
\end{array}\right]
$$

HOST 89 Diamond host lot_34_stone_2_inc_3 and INC 89 Orthopyroxene lot_34_stone_2_inc_3

$$
\left[\begin{array}{ccc}
-0.050983 & -0.157847 & -0.099641 \\
-0.152612 & -0.028282 & 0.119432 \\
-0.105278 & 0.109659 & -0.134131
\end{array}\right] \quad\left[\begin{array}{ccc}
-0.000628 & -0.026675 & 0.128510 \\
0.000416 & -0.075459 & -0.045364 \\
0.038621 & 0.000307 & 0.002650
\end{array}\right]
$$

