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Earth's Inner Workings Revealed through Mineral Inclusions in Diamond

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Abstract

Earth's Inner Workings Revealed through Mineral Inclusions in Diamond

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Mineral inclusions in diamond, brought to the surface through kimberlitic eruptions, provide a unique glimpse into the geochemical inner workings of Earth's deep interior. Diamonds source a wide range of depths in the mantle. While most diamonds originate from the upper 200 km of the Earth's mantle, aptly called super-deep diamonds originate from depths ranging between 300 and 1000 km serving as the only natural samples from such depths. By studying mineral inclusions in diamond an insight into the chemical cycling between the Earth's surface and interior is gained. In the first study, I co-developed a fast high-throughput method for the fast identification of minerals inclusions while they remain encased in diamond with the GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS). Prior to 2011, most mineral inclusions in diamond were limited to destructive methods for identification. By studying these inclusions in-situ high-pressure phases, oxidation states, and remnant inclusion pressures are preserved, providing valuable insight into the geochemical conditions (i.e. redox conditions) and the geochemical recycling of Earth's deep interior (i.e. recycling of biocritical elements such as H, B, C, P, S, Cl, and Ca). This method is now being used by other researchers at GSECARS, where the new setup is now accessible through the General User Program at the Advanced Photon Source. In the second study, I investigated inclusions in a suite of 121 diamonds from Juína, Brazil a locality known to produce super-deep diamonds from the transition zone (410-660 km) and lower mantle (>660 km).

These diamonds were investigated by Fourier Transform Infrared (FTIR) spectroscopy, ultraviolet (UV) imaging, and synchrotron X-ray microtomography to characterize their atomic-scale defects (N, H, and B) and mineral inclusions. A subset of 41 diamonds were selected for study by synchrotron X-ray diffraction to determine the diversity of mineral inclusions, the orientation distribution of the inclusions, and to search for potentially hydrous minerals. A total of 107 mineral inclusions were successfully identified via their lattice parameters while they remained encased in diamond, representing one of the largest catalogs of mineral inclusions in diamonds from a single locality. In the third study, I investigated the first known blue-colored olivine, found included within a Type IaAB triangular macle (twinned) diamond, using a variety of non-destructive techniques including: X-ray microtomography, FTIR Spectroscopy, single-crystal X-ray diffraction, X-ray fluorescence, photoluminescence spectroscopy, UV fluorescence imaging, Raman spectroscopy, Mössbauer spectroscopy, visible absorption spectroscopy, and X-ray absorption near-edge structure. UV-VIS absorption spectroscopy and the presence of metallic Fe-Ni alloy within the olivine inclusion suggest trace Cr^{2+} as the possible cause of the blue color. XANES spectroscopy revealed that the average Cr valence state of the blue olivine was 2.98(3) and did not show a peak at the diagnostic Cr^{2+} energy. However, if we consider how much Cr^{2+} could be present based on two times the standard deviation, the valence could be as low as 2.92 (8% Cr^{2+}). Therefore, we cannot rule out reduced Cr as the cause of the unique blue color, but future experimental work is required to determine how much reduced Cr is needed to cause a blue color in olivine.

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1. Chapter 1

Thesis Overview

1.1 Introduction

Our dynamic Earth is divided into four distinct layers: the atmosphere, crust, mantle, and core. The upper three – atmosphere, crust, and mantle – are connected to each other over geologic time through plate tectonics. The majority of our planet's surface is covered by water, which plays a critical role in our planet's habitability and serves as one of the catalysts of volcanism and plate tectonics, a unique feature of our planet within the solar system. With the rapidly expanding number of known extra-solar planets (exoplanets) in the habitable zones of their stars, it becomes increasingly important to understand the role that chemical recycling plays in Earth's habitability. Understanding the extent to which the surface and interior are communicating through geochemical recycling remains the goal of many geological fields such as mineral physics, geophysics, and geochemistry.

The mantle constitutes ~ 84% of the Earth's volume and extends from the base of the crust (at 10-60 km) all the way to 2900 km depth, where the isolated iron-rich core is found. As we have no direct access to these depths, we must rely on natural samples brought to the surface in various types of volcanic eruptions, laboratory experiments, seismological imaging, and geodynamic modeling to ascertain the composition of the mantle. Gems are coveted for their societal, economic, and industrial importance, but also hold information about the composition of the Earth's interior through the minerals included within them. The distribution of chemical elements in the mantle is potentially heterogeneous at different scales, and certain gemstones are associated specifically in regions where melting, fluids, and fractionation occurs. Diamonds in particular capture and preserve mantle minerals, providing sampling of the mantle at otherwise unattainable depths. Minerals included within diamonds are protected by the unique properties of

diamond, mainly its chemical inertness and stiffness. While most diamonds originate in the mantle roots of the continental lithosphere, some diamonds form much deeper within the convecting upper mantle, transition zone, and lower mantle (Nestola et al., 2018; Palot et al., 2016; Pearson et al., 2014; Shirey et al., 2013; Stachel and Harris, 2008). Super-deep diamonds refer to diamonds that originate from depths > 300 km. Currently, five localities are known to have diamond-bearing kimberlites, a carbonate-rich volcanic rock, with super-deep diamonds; these localities include: Jagersfontein, South Africa, Juína, Brazil, Kankan, Guinea, and Lac de Gras, Canada (Stachel et al., 2005). Within in the past decade, Juína, Brazil diamonds provided evidence that both the water and carbon cycles may extend deep within the mantle (Palot et al., 2016; Pearson et al., 2014; Walter et al., 2011). Thus, more studies focusing on identifying all mineral inclusions within large suites of Juína diamonds are required to better constrain the possible extent of the hydration of the mantle as well as obtain an understanding of the origin of Earth's water. My thesis focuses on determining the inclusion mineralogy of a new suite of 121 diamonds from Juína, Brazil, obtained through collaboration with researchers at the University of Alberta, Canada, and the Deep Carbon Observatory at Carnegie Institution for Science. To characterize the mineralogy of such a large number of diamonds, each potentially containing dozens of micro-inclusions, I developed synchrotron X-ray diffraction methods for high-throughput analysis. The results of this work are applied broadly to improving our understanding of the Earth's dynamic interior and chemical interactions between the crust and mantle.

Chapter 2 focuses on a fast, high-throughput methodology I co-developed with the GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS) at the Advanced Photon Source, USA for the identification of micromineral inclusions in rough diamonds. The techniques and routines developed in this work were crucial for the work performed in Chapter 3, and are also

now being used by other researchers at GSECARS, where the new setup is now accessible through the General User Program at the Advanced Photon Source. The methodology developed in Chapter 2 impacts the diamond inclusion research field by providing the capability to quickly identify by single-crystal X-ray diffraction methods mineral inclusions in large diamond suites, which will greatly increase our knowledge of the geochemical cycling and the composition of Earth's mantle. A manual detailing a standard operating procedure for the collection of X-ray diffraction data on mineral inclusions in diamond is given in Appendix A. Chapter 3 implements the developed methodology from Chapter 2 to study a large suite of diamonds from known super-deep locality Juína, Brazil. This chapter identified 107 inclusions in 41 different diamonds as well as focused on studying the defects within the diamonds themselves. By employing numerous non-destructive methods to study these diamonds and their inclusions, valuable growth history and geochemical information about the mantle is obtained. Chapter 4 details a complex study on a unique blue olivine inclusion trapped inside a diamond macle. This chapter compiles the numerous extensive non-destructive techniques employed over the years characterizing the olivines included within this triangular macle diamond. Extensive effort was made into determining the origin of the olivine's unique blue color. UV-VIS absorption spectroscopy and the presence of metallic Fe-Ni alloy within the olivine inclusion suggest trace Cr^{2+} as the possible cause of the blue color. All the work presented in this thesis further supports the need for more studies to utilize non-destructive and high-throughput identification methods to study large diamond suites of super-deep diamonds to gain a better understanding of the composition and geochemical cycling of Earth's dynamic mantle.

1.2 Chapter 2

In chapter 2, entitled *Fast identification of mineral inclusions in diamond at GSECARS using synchrotron X-ray microtomography, radiography, and diffraction*, I present the method I co-developed with the GeoSoilEnviro Center for Advanced Radiation Sources at the Advanced Photon Source (GSECARS), USA for the in-situ identification of micromineral inclusions in diamond. This work is published in the Journal of Synchrotron Radiation (Wenz et al., 2019). Diamond inclusions provide valuable insight into the geochemistry and dynamic of Earth's interior. However, a major challenge in achieving thorough yet high rates of analysis of mineral inclusions in diamond derives from the micrometer scale of most inclusions often requiring synchrotron radiation. This problem is further exacerbated by the high refractive index of diamond, ($n \sim 2.4$), which precludes standard optical centering methods used in most synchrotron X-ray techniques to center the inclusion within the X-ray beam. In this work, I describe and demonstrate the fast, high throughput methodology emplaced at GSECARS for the in-situ identification of mineral inclusion in rough diamonds by collecting 3D diffraction data on 53 inclusions in diamond within 72 hours of beamtime. By identifying all inclusions within large diamond suites, a more thorough sampling of inclusion mineralogy is obtained, which in turn sheds light onto the composition of Earth's mantle.

Diamonds contain pieces of the Earth's interior and sample the vast majority of Earth's mantle (Harte et al., 1999; Shirey et al., 2013; Stachel and Harris, 2009; Pearson et al., 2014). Within the past decade, diamonds provided evidence of the geochemical cycling of surface carbon into the lower mantle (Walter et al., 2011). Even more recently, diamonds provided evidence that the mantle is hydrous to an extent, with the discovery of ringwoodite, a high-pressure polymorph of olivine stable within the transition zone (Pearson et al., 2014) as well as

evidence of hydrous bearing fluids found as deep as 1000 km (Palot et al., 2016). Tschauner et al., (2018) also found inclusions of ice VII in numerous diamonds indicating the presence of hydrous fluids. Studying diamonds and their inclusions provides us with unprecedented information about the history and chemical conditions of the crust and the mantle.

Up until 2011, most studies identified mineral inclusions by extracting or exposing them through the breaking or polishing of the diamond. While this method provides exact chemical composition, via electron microprobe analysis, it results in the loss of certain geochemical information, such as the remnant pressure an inclusion is under (Angel et al., 2015) as well as oxidation states. In addition, extracting an inclusion runs the inherit risk of losing the inclusion as breaking the diamond is never entirely predictable. Thus, to preserve geochemical information such as remnant inclusion pressure and oxidation states an effort to study these inclusions while they remain encased in diamond was employed starting in 2011. Nestola et al., (2011) performed the first single crystal structure refinement on an inclusion in diamond. This inclusion was rather large at ~80 micrometers and the diamond had two parallel faces, thus allowing for optical centering of the inclusion in the X-ray beam. Later in 2016, Nestola et al., went on to carry out in situ structure refinements on clinopyroxenes trapped in diamonds using synchrotron radiation. Centering of inclusions in irregular shaped diamonds requires a combined microtomography and X-ray diffraction approach, which was initially employed by Nestola et al., (2012) using lab sources in Padova, Italy. Laboratory sources are ideal for the study of a few large inclusions but a methodology to study inclusions within large diamond suites was required to achieve a better sampling of inclusions in super-deep diamond. This is what the work in Chapter 2 of my thesis aimed to establish.

Microtomography locates all inclusions within a diamond that are absorbing 28.6 keV as small as 10-20 μm . The inclusions absorb X-rays more than the diamond itself and thus appear darker on the radiograph, while brighter on the reconstructed tomographic slice (Rivers et al., 1999). Microtomography also enables users to identify whether any microcracks are present within a diamond, thus providing information on how representative a given inclusion is of the mantle as a whole. In addition, microtomography also allows for the pre-screening of inclusions. The reconstructed tomographic slices, maps of absorption, provide the ability to distinguish between high and low X-ray absorbing inclusions. Some inclusions absorb more than others as a result of their compositional differences (difference in atomic weight). If longer scan times are employed and the inclusion is a high absorbing mineral in a low absorbing host or vice versa than inclusions smaller than a pixel ($\sim 4.5 \mu\text{m}$) should be able to be observed.

Single crystal X-ray diffraction on inclusions requires another method of centering the inclusion in the X-ray beam. Diamond's high refractive index combined with the irregular morphology of most super-deep diamonds precludes typical optical centering protocols. Thus, we developed an attachment to the beamline, which enabled a live radiograph image of the diamond. Live radiography ensured that inclusions $> 10 \mu\text{m}$ are centered in the X-ray beam, which is detailed further in this chapter. While we potentially can detect inclusions $< 10 \mu\text{m}$ with microtomography such inclusions would be challenging to center in the live 2D-radiography system due to the higher signal/noise in the live radiograph image. Over the course of my time here at Northwestern we continued to optimize and improve the technique. Back in 2016, when we started developing the methodology, we successfully collected and identified two inclusions. By 2018, we could collect on 53 inclusions in 72 hours of beamtime. As of 2019, a new Pilatus 1 M detector was installed on the beamline, which drastically improved collection times and data

processing. Using this detector in 2019, we were able to collect on a total on 135 inclusions within 72 hours. Thus, this newly available methodology impacts the diamond inclusion research field by providing the capability to quickly identify mineral inclusions in large diamond suites, which will greatly increase our knowledge of the geochemical cycling and the composition of Earth's mantle.

1.3 Chapter 3

In chapter 3, entitled *In situ identification of mineral inclusions in diamonds from Juína, Brazil*, I present a detailed study of a new suite of 121 diamonds from Juína, Brazil, a locality known to produce super-deep diamonds from the transition zone (410-660 km) and lower mantle (>660 km). These diamonds were investigated by Fourier Transform Infrared (FTIR) spectroscopy, ultraviolet (UV) imaging, and synchrotron X-ray microtomography to characterize their atomic-scale defects (N, H, and B) and mineral inclusions. A subset of 41 diamonds were selected for study by synchrotron X-ray diffraction to determine the diversity of mineral inclusions, the orientation distribution of the inclusions, and to search for potentially hydrous minerals. A total of 107 inclusions in 41 were identified by their lattice parameters, obtained via the methodology developed and detailed in Chapter 2, representing one of the largest catalogs of mineral inclusions in diamonds from a single locality.

Less than 1% of diamonds found worldwide contain sub-lithospheric inclusions (Hayman et al., 2005). Juína, Brazil diamonds source great depths within Earth's mantle and bring up such sub-lithospheric inclusions with some frequency (Araujo et al., 2013; Harte and Harris, 1994; Kaminsky et al., 2001; Palot et al., 2016; Pearson et al., 2014; Tappert and Tappert, 2011). As early as the 1990's, lower mantle inclusions were discovered in Juína diamonds, specifically from

the São Luiz placer (Harte and Harris, 1994; Harte et al., 1999; Kaminsky, 2012). Thus, diamonds from Juína, Brazil have gained scientific attention, especially during the last two decades as they have provided significant geochemical evidence pertaining to the geochemical cycling of carbon and water within the Earth's mantle (Walter et al., 2011; Palot et al., 2016; Pearson et al., 2014). Juína is located in the Mato Grosso State of Brazil, which sits inside of the Amazonian Craton. The Juína kimberlite field follows the NW-SE trending alkaline magmatism associated with the Trindade plume, which passed underneath South America (Thomson et al., 2014). The Juína kimberlites erupted at ~ 92-95 Ma (Heaman et al., 1998). Thus, Juína placer diamonds are thought to originate from kimberlites that are Cretaceous in age (Araujo et al., 2013; Harte et al., 1999).

Most diamonds from this region contain characteristically little to no nitrogen, with about 65% classified as Type IIa diamonds (Araujo et al., 2013; Kaminsky et al., 2001). FTIR spectroscopy allows for the detection and quantification of impurities within a given diamond, which ultimately determines the classification of the diamond type. Diamond type refers to the presence or absence of nitrogen within a diamond. Type I diamonds contain nitrogen and Type II diamonds contain zero nitrogen according to the gemology community (Breeding and Shigley, 2009). However, the mineralogical literature alters this classification system by calling Type II diamonds as diamonds containing less than 20 ppm nitrogen (Araujo et al., 2013). Regardless of this discrepancy in nomenclature, Type II diamonds are considered to not contain enough nitrogen to be detected by FTIR. Type I diamonds are further subdivided into Type Ia and Type Ib. Type Ia diamonds contain aggregated nitrogen impurities, whereas Type Ib contain single nitrogen atoms. Type Ia diamonds are even further subdivided based on how the nitrogen is aggregated, with Type IaA consisting of aggregated nitrogen pairs and Type IaB containing four nitrogens

surrounding a vacancy. The degree of nitrogen aggregation depends on temperature and residence times in the mantle (Taylor et al., 1990). Type II diamonds either contain no nitrogen (Type IIa) or contain boron impurities (Type IIb). Diamonds display important absorption features over the range of 400 to 4000 cm^{-1} , which is divided into three different zones based on how the chemical bonds between carbon atoms and any impurities vibrate when exposed to IR energy (Breeding and Shigley, 2009). Nitrogen impurities appear within the one-phonon region, while the two-phonon and three-phonon regions contain the intrinsic absorption features related to the C-C bonds of the diamond. The three-phonon region is the region in which absorption features relating to boron and hydrogen impurities appear (Breeding and Shigley, 2009).

Photoluminescence spectroscopy is used to detect part per billion level optical defects within the diamond (Eaton-Magaña and Breeding, 2016). Common defects in Juína diamonds consist of nitrogen related defects, which appear at 415, 503, and 741 nm (Yuryeva et al., 2015). The 415 nm defect is referred to as the N3 defect, which consists of three nitrogens surrounding a vacancy (Eaton-Magaña and Breeding, 2016). Another defect occurs at 503.2 nm and is referred to as the H3 or NVN^0 defect; this results from two nitrogens separated from a vacancy. The GR1 (V^0) peak at 741 nm represents an uncharged vacancy in diamond, a feature usually seen in irradiated natural diamonds (Breeding and Shigley, 2009). By employing numerous non-destructive techniques to characterize both the inclusions and the diamond, we gain an insight into the composition of the mantle.

1.4 Chapter 4

In chapter 4 entitled, *Blue-colored olivine inclusion in diamond: evidence for divalent chromium in the mantle?*, I present data on a blue olivine included within a triangular macle

diamond. This study is a culmination of years of work and summarizes results from a variety of non-destructive techniques employed on the blue olivine inclusion and the surrounding colorless olivine inclusions. Microtomography revealed no evidence of any cracks within the diamond, thus indicating these minerals did not alter via interaction with kimberlitic magma. X-ray diffraction mapping revealed the blue olivine inclusion as strained, which is consistent with our results of this inclusion being under a current pressure of 0.2 GPa. The exact cause of the unique blue color remains unknown, however UV-VIS absorption spectroscopy and the presence of metallic Fe-Ni alloy within the olivine inclusion suggest trace Cr^{2+} as the possible cause of the blue color. XANES spectroscopy revealed that the average Cr valence state of the blue olivine was 2.98(3) and did not show a peak at the diagnostic Cr^{2+} energy. However, if we consider how much Cr^{2+} could be present based on two times the standard deviation, the valence could be as low as 2.92 (8% Cr^{2+}). Therefore, we cannot rule out reduced Cr as the cause of the unique blue color, but future experimental work is required to determine how much reduced Cr is needed to cause a blue color in olivine.

Olivine group minerals stand out as one of the best studied minerals as these minerals are thought to make up greater than 50% of the Earth's upper mantle and up to 38% of the whole mantle (Ganapathy and Anders, 1974; Ringwood and Kesson, 1977). Olivine group minerals are orthosilicates that have the general chemical formula X_2SiO_4 , where X represents a divalent cation (Mg, Fe, Ca). This study focuses on ferromagnesian olivine, $(\text{Mg,Fe})_2\text{SiO}_4$, which constitutes the majority of the upper mantle (>60%) in a pyrolitic model (Ringwood, 1969; Ringwood and Kesson, 1977). The term olivine throughout the rest of this study refers to an olivine phase along the forsterite (Mg_2SiO_4) - fayalite (Fe_2SiO_4) solid solution series ($\text{Mg, Fe})_2\text{SiO}_4$. Mantle olivine falls within a narrow compositional range close to forsteritic

composition as evidenced by diamond inclusions which bring up olivines with compositions ranging from Fo92 to Fo95, where the subscript to Fo (forsterite) gives the percent component of forsterite (Meyer and Boyd, 1972). Olivine has an orthorhombic structure (Space group: Pbnm) and consists of a slightly distorted hexagonal close packed array of oxygen atoms (Smyth et al., 1997; Hazen, 1976). The olivine structure consists of three sites: two octahedral sites and one tetrahedral site. Iron and magnesium fractionate over the two non-equivalent octahedral sites M1 and M2. The M2 site is slightly more distorted than M1 and iron fractionates preferentially into the M1 site at high temperatures (Heinemann et al., 2007). Silicate tetrahedra share edges within the olivine structure.

Olivine's idiochromatic green coloration results from the presence of Fe^{2+} ions (Koivula, 1981; Nassau, 1978; White and Keester, 1966). Fe^{2+} contains 6d electrons often considered as a half-filled d^5 shell with one additional electron and is one of the most abundant transition metal ions in minerals. Fe^{2+} resides in octahedral coordination within olivine. The crystal field splitting of Fe^{2+} is $10,000 \text{ cm}^{-1}$ and absorption spectra of olivine feature an intense peak near $10,000 \text{ cm}^{-1}$ (1μ) which tails out to $\sim 14,200$ ($\sim 0.7 \mu$) due to Jahn Teller distortions. The green color does not result from an absorption band in the visible range but rather results from a strong absorption in the NIR range absorbing much of the red, thus the transmitted light is green (Farrell and Newnham, 1965; White and Keester, 1966). The presence of Ni^{2+} is also thought to play a role in the green coloration of olivine although the extent remains to be determined (Koivula, 1981). Higher abundance of iron leads to a darkening and sometimes brown appearance of olivine (Filiberto et al., 2020). However, most olivine inclusions in diamond appear colorless (Tappert and Tappert, 2011).

Olivine often contains low amounts of minor elements such as Al, Ca, Mn, and Ni. Additionally, olivine inclusions contain relatively high concentrations, ~ 0.10 wt. % (one order of magnitude above terrestrial olivine), of Cr_2O_3 (Burns et al., 1973). Studies hypothesize that the oxidation state of Cr in olivine inclusions in diamond could consist of Cr^{2+} replacing Mg^{2+} , as they probably formed in more reducing conditions similar to those of lunar and meteorite olivine (Burns et al., 1973; Burns, 2005). Incorporation of trace elements into the crystal structure provides geochemical information about the mantle's abundance of such elements and can give constraints on the oxygen fugacity. Thus, determining whether the olivine's unique blue color was in fact caused by reduced chromium was important in understanding the environment of formation of this diamond. In this chapter, we report the oxidation state of both Fe and Cr within the blue olivine as well as report the results of the lattice parameters, structure refinement, and X-ray fluorescence mapping of the blue olivine inclusion.

2. Chapter 2

Fast identification of mineral inclusions in diamond at GSECARS using synchrotron X-ray microtomography, radiography, and diffraction

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Fast identification of mineral inclusions in diamond at GSECARS using synchrotron X-ray microtomography, radiography, and diffraction

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2.1 Abstract

Mineral inclusions in natural diamond are widely studied for the insight that they provide into the geochemistry and dynamics of the Earth's interior. A major challenge in achieving thorough, yet high rates of analysis of mineral inclusions in diamond derives from the micrometer-scale of most inclusions, often requiring synchrotron radiation sources for diffraction. Centering microinclusions for diffraction with a highly-focused synchrotron beam cannot be achieved optically because of the very high index of refraction of diamond. We developed a fast, high-throughput method for identification of micromineral inclusions in diamond at GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS), Advanced Photon Source (APS), Argonne National Laboratory (ANL). Diamonds and their inclusions are imaged using synchrotron 3D

computed X-ray microtomography on beamline 13-BM-D of GSECARS. The location of every inclusion is then pinpointed onto the coordinate system of the 6-circle goniometer of the single-crystal diffractometer on beamline 13-BM-C. Because the bending magnet branch 13-BM is divided and delivered into 13-BM-C and 13-BM-D stations simultaneously, numerous diamonds can be examined during coordinated runs. The fast, high-throughput capability of the methodology is demonstrated by collecting 3D diffraction data on 53 diamond inclusions from Juína, Brazil, within about 72 total hours of beamtime.

2.2 Introduction

Most diamonds are thought to crystallize in the mantle roots of the continental lithosphere (Stachel & Harris 2008), whereas so-called super-deep diamonds and their inclusions are believed to crystallize in the convecting upper mantle, transition zone, and even lower mantle (Nestola et al., 2018; Palot et al., 2016; Pearson et al., 2014; Pearson et al., 2003; Shirey et al., 2013; Stachel et al., 2005). Provided that the host diamonds are not cracked, minerals included within them are essentially encapsulated in an inert preservation vessel during eruption to the surface in kimberlitic magmas. The study of these micromineral inclusions provides insight into the geochemistry and dynamics of the Earth's crust-mantle system from otherwise unattainable depths (Harte, 2011; Pearson et al., 2014; Smith et al., 2018). In the past, the study of diamond inclusions has been largely limited to destructive techniques, such as breaking the diamond to release inclusions or grinding away the host diamond to expose inclusions at the surface. In addition, the use of laboratory-source X-rays limits the minimum size of inclusion that can be identified by X-ray diffraction. Destructive extraction techniques have the inherent risk of losing or altering the inclusions, which are usually under remnant pressure inside the diamond host (Angel et al., 2015a).

Thus, by studying these encapsulated inclusions using non-destructive methods, properties like inclusion pressure, oxidation state, high-pressure phases, and volatile content remain preserved.

To date, in-situ identification of mineral inclusions in diamond via non-destructive methods remains challenging as the very-high refractive index of diamond ($n \sim 2.4$) hinders typical identification methods, such as optical microscopy or Raman spectroscopy, unless the inclusion is very close to a flat diamond surface. The high n of diamond also makes optical centering methods for single-crystal diffraction time consuming (Kunz et al., 2002; Nestola et al., 2012). In 2011, the first in-situ crystal structure refinement of an inclusion in diamond was performed on an olivine crystal measuring $\sim 80 \mu\text{m}$ in largest dimension using a sealed-tube Mo $K\alpha$ source (Nestola et al., 2011). In that study, two large and parallel faces of the diamond facilitated optical centering of the inclusion. Subsequently, synchrotron radiation has been employed to carry out in-situ structure refinements of clinopyroxenes entrapped in diamond (Nestola et al., 2016). Centering microinclusions inside highly irregular diamonds with an X-ray beam for diffraction can be accomplished by combining tomography with X-ray diffraction. Recently, this combined approach was employed by Nestola et al. (2012) using lab sources in Padova, Italy. The use of a lab source is ideal for the study of large ($>50 \mu\text{m}$) inclusions, but a method to quickly identify the multitude of smaller inclusions in large, available suites of super-deep diamonds is required to obtain a more thorough sampling of inclusion mineralogy.

In this paper we describe a fast, high-throughput and non-destructive methodology for identifying microinclusions in diamond as small as $10\text{-}20 \mu\text{m}$ in maximum dimension by combining synchrotron microtomography with a newly-developed radiography system now installed on the single-crystal diffraction beamline of GSECARS, Advanced Photon Source. Such

a fast yet thorough method allows for all inclusions within the full volume of each diamond to be identified, thus allowing for a better relative modal proportion of inclusions to be obtained as smaller inclusions, which would be missed if only utilizing optical methods are not overlooked. In addition, the use of microtomography prior to diffraction provides detailed information on the integrity of the diamond host, revealing microcracks that may indicate the potential for metasomatic alteration of the inclusions. By identifying all microinclusions within a suite of super-deep diamonds more information about the environment wherein superdeep diamonds form is obtained. The efficiency of the system is demonstrated by collecting 3D diffraction data from 53 inclusions in 23 total different diamonds from Juína, Brazil, all within a total of about 72 hours of beamtime. This result is unachievable by any other method.

2.3 Experimental

2.3.1 Synchrotron Microtomography

Synchrotron microtomography was used to physically locate mineral inclusions within the diamond was conducted at GSECARS, beamline 13-BM-D of the APS. The configuration of the 13-BM branch allows for simultaneous delivery of the X-ray beam to both 13-BM-D (microtomography) and 13-BM-C (single-crystal X-ray diffraction) beamlines. Thus, during coordinated runs the diamonds go directly from 13-BM-D to the newly developed 2D radiography and single-crystal diffraction system at 13-BM-C, which hosts the Partnership for eXtreme Xtallography (PX²) facility, a collaboration between University of Hawaii and GSECARS supported by the Consortium for Materials Properties Research in the Earth Science (COMPRES). This facility is funded by COMPRES to advance crystallographic studies of minerals and materials at condition of extreme pressures, temperatures and strain rates. A schematic diagram of the

microtomography beamline illustrates the configuration used for super-deep diamonds many of which have irregular shapes (Fig. 2.1). A monochromatic beam with an energy of 28.9 keV was chosen for this approach as this energy closely matches the operating energy of the 13-BM-C (28.6 keV) diffraction beamline. Due to the diffraction of the scintillator itself, Ce-doped LuAG, the exact operation energy of 13-BM-C could not be used as artifacts appeared in the tomographic reconstructions. Choosing a similar operating energy guarantees that all inclusions visible at 13-BM-D beamline will also appear in the 2D radiography system at 13-BM-C. Due to the variability in both size and shape of super-deep diamonds, an adjustable field of view is required to accurately map all inclusions. A typical field of view for large diamonds (~6 mm) is around 8.70 mm by 5.44 mm. Collection times are on the order of fifteen minutes per diamond, thus within a 24-hour time period full tomography on the entire volume of over 90 diamonds is achievable.

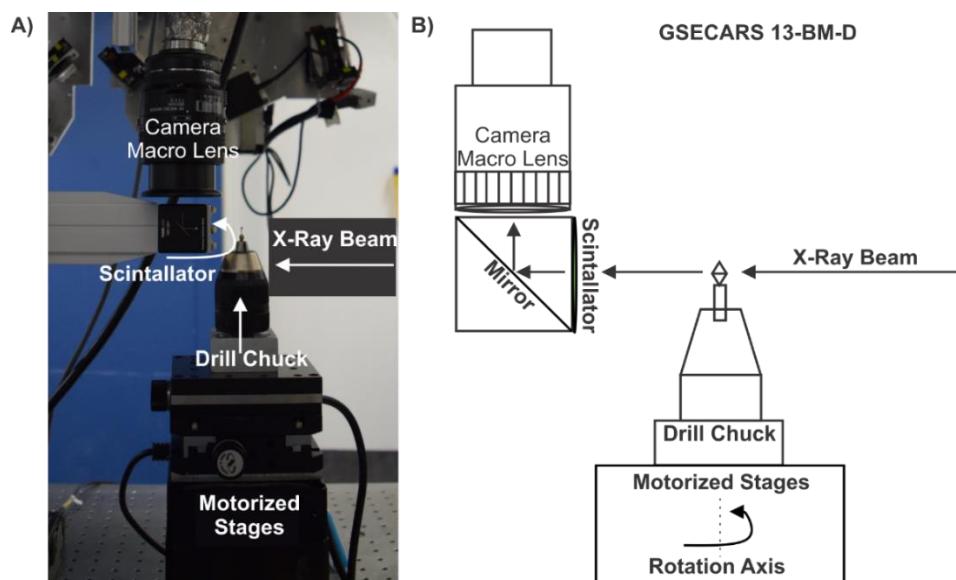


Fig. 2.1: A) Photograph and B) schematic of the microtomography setup at 13-BM-D, GSECARS, Advanced Photon Source.

2.3.2 Synchrotron X-ray Diffraction

Single-crystal X-ray diffraction measurements were carried out at GSECARS, beamline 13-BM-C of the APS. Combining microtomography and X-ray diffraction required development of a portable 2D radiography attachment at 13-BM-C for the centering procedure. The components of this live radiograph system consist of a scintillator, mirror, a 5x objective, and a GigE camera. All components are mounted to a motorized stage, which enables the radiography system to drive in and out of the X-ray beam (Fig. 2.2). Thus, the 2D radiography setup does not interfere with the 6-circle goniometer during the diffraction collection. EPICS areaDetector (Rivers, 2018; Rivers, 2010) and ImageJ (Schneider et al., 2012) is used to view the live radiograph while allowing for the constant normalization to a flat field image.

The first step to setup the diffraction experiment is to identify the rotation axis of the diffractometer and intersect the X-ray beam with it. The rotation axis of the diffractometer is setup in the horizontal direction that is perpendicular to the incident X-ray (Zhang et al., 2017). A focused X-ray beam with a full width at the half maximum of 12 μm (H) by 18 μm (V) is achieved by horizontal and vertical Kirkpatrick-Baez mirrors (Eng et al., 1998). The rotation axis of the diffractometer is visualized by rotating a 25 μm diameter tungsten wire. Once the tungsten wire ceases to precess during rotation, the tungsten wire coincides with the rotation axis. The X-ray beam vertical position is then adjusted until maximum absorption is detected. At this stage, the X-ray beam intersects the rotation axis of the diffractometer and the tungsten wire is then removed. The incident beam position is marked on the scintillator's image with a virtual crosshair, which corresponds to the intersection of the rotation axis and the X-ray.

Obtaining a live radiograph image of the inclusion on the 13-BM-C diffraction beamline requires defocusing the X-ray beam to increase the field of view (FOV). An FOV of ~ 100 μm (H)

by 250 μm (V) is achieved by defocusing the Kirkpatrick-Baez mirrors, giving a magnified image of the inclusion for centering. Each inclusion is located by observing its absorption shadow in the radiograph image. Locating inclusions in this magnified FOV requires the use of the high-resolution (4.5 mm/pixel) microtomography data obtained at beamline 13-BM-D prior to diffraction. Without microtomography data it can take an hour or more to locate an inclusion within such a magnified FOV, whereas with the microtomography map it takes only a few minutes. Once an inclusion is found within the FOV and placed into the virtual crosshair, a rotation-centering of the inclusion is performed at 5-degree steps thus centering the inclusion on the rotation axis. Once the inclusion is properly centered, the X-ray beam then is refocused back to the virtual crosshair, and the scintillator is driven out of the beam path. Single-crystal X-ray diffraction using the 6-circle goniometer proceeds following standard X-ray diffraction protocols (Zhang et al., 2017). It takes 5 minutes to collect a wide-scan diffraction image (rotation of 180°) and 30 minutes for step scan collections (steps in scan 180, exposure time per degree 1 sec, rotation of 180°) using the MAR 165 CCD detector. The new Pilatus 1M detector with a 1 mm silicon sensor implemented in 2019 will speed these collections times up to a few minutes. Thus, 13-BM-C allows for fast diffraction analysis on a multitude of inclusions.

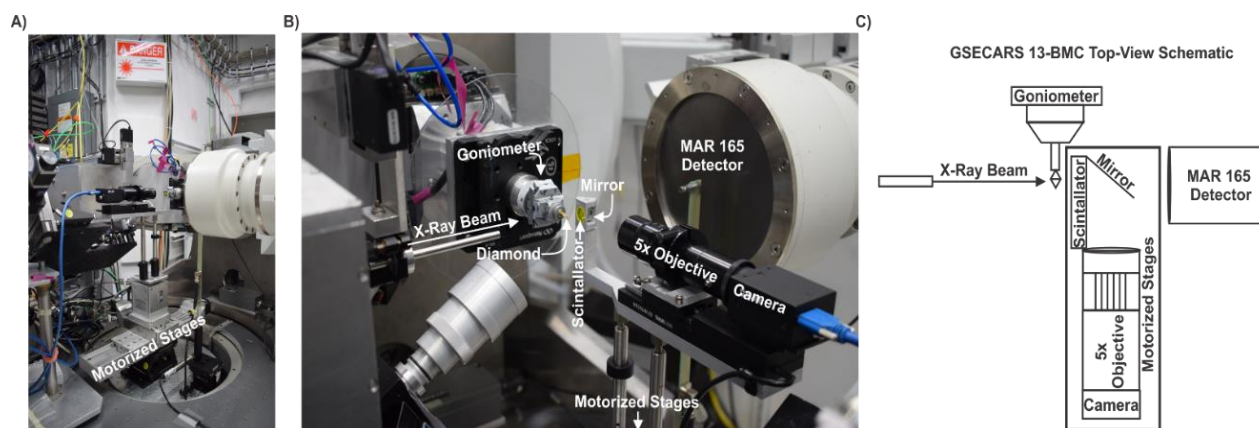


Fig. 2.2: A) Photograph of the entire portable radiograph attachment. B) Close up photograph of the portable radiograph system. C) A top-view schematic of the portable radiograph system at 13-BM-C. The rectangle represents the motorized stage, yet also highlights the main components that make up the newly developed portable 2D radiograph system available at 13-BM-C.

2.4 Results

To demonstrate the capabilities of this new fast, high-throughput combined synchrotron microtomography and X-ray diffraction technique, a suite of sixty-one diamonds from Juína, Brazil were studied. Microtomography data were collected on all sixty-one diamonds using a CMOS camera with 1920x1200 pixels, 4.5 micron pixel size on the sample, 1 second exposure time, and 900 projections. All microtomography data on the sixty-one diamonds were collected within a 24-hour period.

X-ray diffraction data, obtained using the newly developed live 2D radiograph centering technique at 13-BM-C, were collected on 53 inclusions found within 23 of these potentially super-deep diamonds within a 72-hour period. Sample to detector distances and tilt were calibrated using diffraction of LaB_6 . Single-crystal inclusion diffraction data were processed using the ATREX (previously GSE_ADA) (Dera et al., 2013) program, which handles peak searching and fitting

routines allowing for the generation of a peak list. To index the peaks, the peak list generated in ATREX was read into the Reciprocal Space Viewer (RSV) (Dera et al., 2013) program, where peak indexing, orientation matrix determination and refinement of lattice parameters were performed. For powder inclusions as well as mixed phase inclusions (inclusions with both powder and single-crystal phases) diffraction images were first integrated in DIOPTAS (Prescher & Prakapenka, 2015), a program designed specifically for handling the large amounts of data collected at XRD beamlines, to generate intensity versus 2θ plots. These 2θ plots were then imported into the General Structure and Analysis System II (GSAS-II) (Toby & Von Dreele, 2013) program, for further processing, indexing, and refinement of lattice parameters. Inclusions were ultimately identified via their lattice parameters.

Lattice parameters for the 53 inclusions are shown in Table 2.1. A summary of all minerals found from these diamonds is given in Table 2.2. The majority of inclusion phases form solid solutions. Thus, unit-cell volumes are dependent on both composition and remnant pressure. Phases along the hematite (Fe_2O_3) to ilmenite (FeTiO_3) solid solution are referred to as titanohematite (Brown et al., 1993). Phases along the magnetite (Fe_3O_4) to ulvöspinel (Fe_2TiO_4) solid solution are referred to as titanomagnetite (Bosi et al., 2009). Olivine phases refer to those along the forsterite (Mg_2SiO_4) to fayalite (Fe_2SiO_4) solid solution series. Following standard mineralogical nomenclature the (Mg,Fe)O oxides are classified such that samples containing <50 mol% FeO are referred to as ferropiclasite and those with >50 mol% are magnesiowüstite (Jacobsen et al. 2002; Prewitt and Downs, 1998). We note however that there is large uncertainty in the composition of such inclusions studied in situ with lattice parameters alone. For (Mg,Fe)O, assuming the variation of lattice parameter with $X_{\text{Fe}} = \Sigma\text{Fe}/(\Sigma\text{Fe}+\text{Mg})$ and an average bulk modulus

K_{T0} of 160 GPa from the study of Jacobsen et al. (2002), the value of X_{Fe} would be underestimated by about 0.088 (or 8.8 mol% FeO) per GPa of remnant pressure.

It is interesting to note that the majority of the inclusions identified in our study are ferropericlasite (Mg,Fe)O. Ferropericlasite is reported previously as a predominate mineral in Juína diamonds, and it often has been associated with signifying a lower mantle origin (Anzolini et al., 2019; Kaminsky, et al., 2009), especially when associated with low-Ni enstatite often interpreted as retrogressed bridgmanite (Harte et al., 1999; McCammon, 2001; Stachel et al., 2000). Without association with other lower mantle minerals it is hard to say that ferropericlasite is of lower mantle origin as it can form in the upper mantle by the decomposition of Mg-carbonates (Nestola, 2017). Studies have argued that given that the number of ferropericlasite inclusions found in super deep diamonds does not match the expected volume fraction (~12 %) typical of the lower mantle (Frost and McCammon, 2008; Kaminsky, 2012), and that the compositions often are more non-pyrolitic, Fe-rich (Mg,Fe)O indicate that the inclusions may not be representative of the lower mantle but rather associated with conditions of diamond growth (Nimis et al., 2018). Thomson et al. (2016) proposed that the presence of (Mg,Fe)O inclusions may be related to the reactions between the carbonatitic melt and reduced mantle peridotite. The range of intermediate and Fe-rich compositions reported in ferropericlasite inclusions in diamond may represent different stages of the reaction (Thomson et al., 2016). Because the numerous ferropericlasite inclusions in the current suite of Juína diamonds are not associated with any high-pressure mineral inclusions, they are possibly associated with the melt reactions proposed by Thomson et al. (2016) and Nimis et al. (2018). However, seven of our ferropericlasite inclusions (6b04b/b2; 6b07c/c2; 6b07d/d2; 6b07e/e2; 6b21c/c2, 6b37a/a2, 6b56b/b2) also exhibited titanomagnetite, which we originally interpreted as another inclusion in close proximity to the ferropericlasite. Upon further inspection

of the microtomography it is thought that these inclusions could in fact actually represent an exsolution. Given that there is a large uncertainty in the composition of such inclusions studied in situ using lattice parameters alone it is possible that for these seven inclusions identified initially as titanomagnetite might actually be magnesioferrite a common exsolution associated with ferropericlase, which would suggest a lower mantle origin (Akaogi et al., 2019; Kaminsky et al., 2015; Wirth et al., 2014).

Table 2.1: Symmetry-constrained lattice parameters of 53 inclusions identified in a suite of diamonds from Juína, Brazil. Single crystal inclusions denoted by * superscript the rest of the inclusions are powder.

Inclusion	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (Å ³)	Symmetry Constraints	Mineral
6b_04b*	8.509(2)	8.509(2)	8.509(2)	90	90	90	616.0(2)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
6b_04b2*	4.255(1)	4.255(1)	4.255(1)	90	90	90	77.1(6)	cubic	ferropericlase $(\text{Mg}_x, \text{Fe}_{1-x})\text{O}$
6b_05a*	4.246(4)	4.246(4)	4.246(4)	90	90	90	76.6(2)	cubic	ferropericlase $(\text{Mg}_x, \text{Fe}_{1-x})\text{O}$
6b_05b*	4.255(2)	4.255(2)	4.255(2)	90	90	90	77.0(2)	cubic	ferropericlase $(\text{Mg}_x, \text{Fe}_{1-x})\text{O}$
6b_05c*	4.259(1)	4.259(1)	4.259(1)	90	90	90	77.3(1)	cubic	magnesiowüstite $(\text{Mg}_{1-x}, \text{Fe}_x)\text{O}$
6b_05d*	4.262(2)	4.262(2)	4.262(2)	90	90	90	77.4(2)	cubic	magnesiowüstite $(\text{Mg}_{1-x}, \text{Fe}_x)\text{O}$
6b_05e*	4.251(2)	4.251(2)	4.251(2)	90	90	90	77.4(2)	cubic	ferropericlase $(\text{Mg}_x, \text{Fe}_{1-x})\text{O}$
6b_06a*	4.276(2)	4.276(2)	4.276(2)	90	90	90	78.2(1)	cubic	magnesiowüstite $(\text{Mg}_{1-x}, \text{Fe}_x)\text{O}$
6b_06b*	4.271(7)	4.271(7)	4.271(7)	90	90	90	77.9(1)	cubic	magnesiowüstite $(\text{Mg}_{1-x}, \text{Fe}_x)\text{O}$
6b_07a	2.868(9)	2.868(9)	2.868(9)	90	90	90	23.6(2)	cubic	Fe (bcc) with some alloy
6b_07b	2.868(5)	2.868(5)	2.868(5)	90	90	90	23.6(1)	cubic	Fe (bcc) with some alloy

6b_07c*	4.276(2)	4.276(2)	4.276(2)	90	90	90	78.2(1)	cubic	magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)
6b_07c2*	8.442(5)	8.442(5)	8.442(5)	90	90	90	601.7(3)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
6b_07d*	4.204(5)	4.204(5)	4.204(5)	90	90	90	75.3(3)	cubic	ferropericlasite ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
6b_07d2*	8.511(1)	8.511(1)	8.511(1)	90	90	90	601.7(3)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
6b_07e*	4.320(7)	4.320(7)	4.320(7)	90	90	90	81.0(4)	cubic	wüstite FeO
6b_07e2*	8.490(5)	8.490(5)	8.490(5)	90	90	90	612.0(2)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
6b_08c*	5.083(1)	5.083(1)	5.083(1)	90	90	120	314.6(3)	hexagonal	ilmenite FeTiO_3
6b_09	4.640(6)	10.005(9)	3.028(3)	90	90	90	140.6(2)	orthorhombic	goethite (FeOOH)
6b_10b	5.032(1)	5.032(1)	13.759(3)	90	90	120	301.7(1)	hexagonal	hematite Fe_2O_3
6b_10c	5.140(3)	5.140(3)	13.420(2)	90	90	120	307.5(2)	hexagonal	titanohematite ($x\text{FeTiO}_3[1-x]\text{Fe}_2\text{O}_3$)
6b_11b*	8.396(2)	8.396(2)	8.396(2)	90	90	90	591.8(2)	cubic	magnetite Fe_3O_4
6b_12a*	4.273(2)	4.273(2)	4.273(2)	90	90	90	78.0(3)	cubic	magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)
6b_12b*	4.270(1)	4.270(1)	4.270(1)	90	90	90	77.9(2)	cubic	magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)
6b_12c*	4.280(9)	4.280(9)	4.280(9)	90	90	90	78.4(5)	cubic	magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)
6b_12d*	4.274(3)	4.274(3)	4.274(3)	90	90	90	78.1(5)	cubic	magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)
6b_17b*	4.270(1)	4.270(1)	4.270(1)	90	90	90	77.8(2)	cubic	magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)

6b_17c*	4.285(1)	4.285(1)	4.285(1)	90	90	90	78.7(5)	cubic	magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)
6b_21c*	4.279(2)	4.279(2)	4.279(2)	90	90	90	78.3(2)	cubic	magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)
6b_21c2	8.405(2)	8.405(2)	8.405(2)	90	90	90	593.8(2)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
6b_23*	4.232(8)	4.232(8)	4.232(8)	90	90	90	75.8(3)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
6b_29a*	4.261(2)	4.261(2)	4.261(2)	90	90	90	77.8(2)	cubic	magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)
6b_29b*	4.253(1)	4.253(1)	4.253(1)	90	90	90	76.9(1)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
6b_34a*	4.243(2)	4.243(2)	4.243(2)	90	90	90	76.4(2)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
6b_34b*	4.245(1)	4.245(1)	4.245(1)	90	90	90	76.5(1)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
6b_34c*	4.252(2)	4.252(2)	4.252(2)	90	90	90	76.8(2)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
6b_37a	4.254(2)	4.254(2)	4.254(2)	90	90	90	77.0(2)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
6b_37a2	8.379(2)	8.379(2)	8.379(2)	90	90	90	588.0(4)	cubic	magnetite Fe_3O_4
6b_39a	5.037(5)	5.037(5)	13.769(1)	90	90	120	302.5(4)	hexagonal	titanohematite ($x\text{FeTiO}_3[1-x]\text{Fe}_2\text{O}_3$)
6b_39b	5.038(7)	5.038(7)	13.761(1)	90	90	120	302.5(5)	hexagonal	titanohematite ($x\text{FeTiO}_3[1-x]\text{Fe}_2\text{O}_3$)
6b_46*	11.584(3)	11.584(3)	11.584(3)	90	90	90	1554.4(6)	cubic	almandine $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$
6b_48b	4.744(4)	10.185(1)	5.978(7)	90	90	90	288.8(6)	orthorhombic	olivine ($\text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4$)

6b_53*	4.246(1)	4.246(1)	4.246(1)	90	90	90	76.5(1)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
6b_54b*	6.609(2)	6.609(2)	6.001(3)	90	90	90	262.1(2)	tetragonal	zircon ZrSiO_4
6b_56a	4.758(7)	10.209(6)	5.972(7)	90	90	90	290.1(4)	orthorhombic	olivine ($\text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4$)
6b_56b	4.759(8)	10.209(8)	5.976(1)	90	90	90	290.4(5)	orthorhombic	olivine ($\text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4$)
6b_56b2	8.394(6)	8.394(6)	8.394(6)	90	90	90	591.4(1)	cubic	magnetite Fe_3O_4
6b_56c	4.754(1)	10.205(7)	5.978(1)	90	90	90	290.0(6)	orthorhombic	olivine ($\text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4$)
6b_56d	4.756(1)	10.206(1)	5.981(1)	90	90	90	290.3(6)	orthorhombic	olivine ($\text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4$)
5a_09a	5.077(3)	5.077(3)	13.894(4)	90	90	120	310.1(2)	trigonal	hematite Fe_2O_3
5a_09b	5.069(2)	5.069(2)	13.931(5)	90	90	120	310.1(2)	trigonal	hematite Fe_2O_3
5a_10f*	4.281(8)	4.281(8)	4.281(8)	90	90	90	78.5(4)	cubic	ferropericlase (Mg,FeO)
5a_20c*	4.245(9)	4.245(9)	4.245(9)	90	90	90	76.47(7)	cubic	ferropericlase (Mg,FeO)

Table 2.2: Summary of all minerals found in the 23 total diamonds from the São Luiz locality in Juína, Brazil.

Mineral	Number of Inclusions
ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)	13
magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)	14
wüstite FeO	1
magnetite (Fe_3O_4)	3
titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$	5
hematite (Fe_2O_3)	1
titanohematite ($x\text{FeTiO}_3[1-x]\text{Fe}_2\text{O}_3$)	5
olivine ($\text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4$)	5
iron (Fe)	2
goethite (FeOOH)	1
ilmenite (FeTiO_3)	1
garnet $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$	1
zircon (ZrSiO_4)	1

The advantages of high-resolution microtomography extend beyond the X-ray centering procedure as this technique also reveals information on both the number and quality of the inclusions. Super-deep diamonds exhibit rough irregular shapes as well as different surface textures, which often preclude optical observation. Tomography reveals all inclusions even those not visible with optical microscopes as well as provides a way to check that the inclusion is pristine. Super-deep diamonds experience extreme stresses and therefore some exhibit microcracks only visible via tomography (Fig. 2.3A). These cracks often lead up to or surround an inclusion, which indicates that an inclusion may have interacted with kimberlitic magma or has cracked as a result of a difference in the elastic relaxation between the inclusion and the host diamond. Such information is lost when inclusions are extracted and yet this information is important when considering how representative an inclusion is of the mantle.

The capability to pre-screen inclusions also exists with microtomography. The reconstructed slices, maps of the absorption, provide the ability to distinguish between high X-ray absorbing inclusions and low X-ray absorbing inclusions. Differences in absorption indicate compositional differences due to the mean atomic weight differences. Inclusions with high iron contents like ferropericlase, (Mg,Fe)O, appear brighter in the tomographic slice than inclusions with lower absorbing material such as silicates or graphite (Fig. 2.3B; 2.3C).

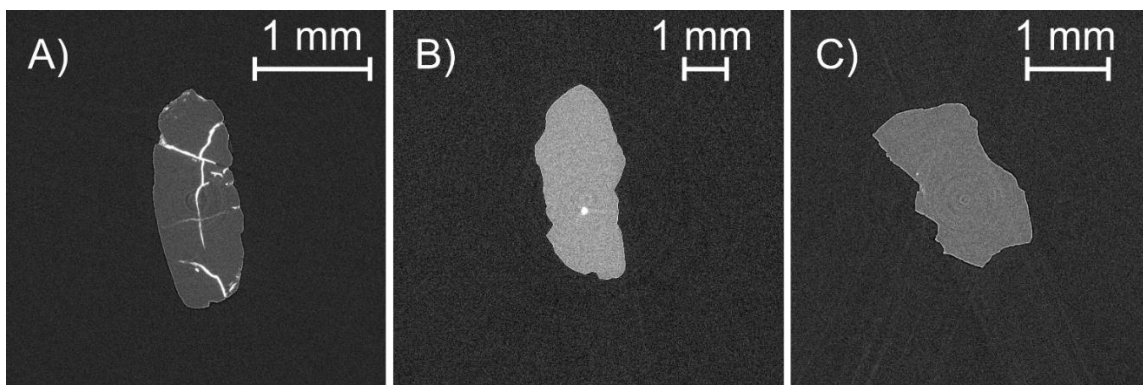


Fig. 2.3: A) Tomographic slice of diamond 6b_24 exhibiting multiple cracks. B) Tomographic slice of diamond 6b_09 with a high absorbing goethite inclusion, FeOOH . C) Tomographic slice of diamond 6b_56 with a less absorbing silicate inclusion olivine, $(\text{Mg,Fe})_2\text{SiO}_4$.

2.5. Conclusion

A fast, high-throughput method developed at GSECARS (Sector 13) of the APS provides the opportunity for dozens of inclusions within a diamond suite to be identified within days (Fig. 2.4). Identifying all inclusions within a diamond suite garners an insight into the composition and geochemical cycling of Earth's dynamic mantle that remains unattainable with small sample sets. Serving as the only samples from such depths, diamond inclusions hold the key to unlocking the secrets of Earth's mantle such as the composition of the mantle as well as its oxidation state.

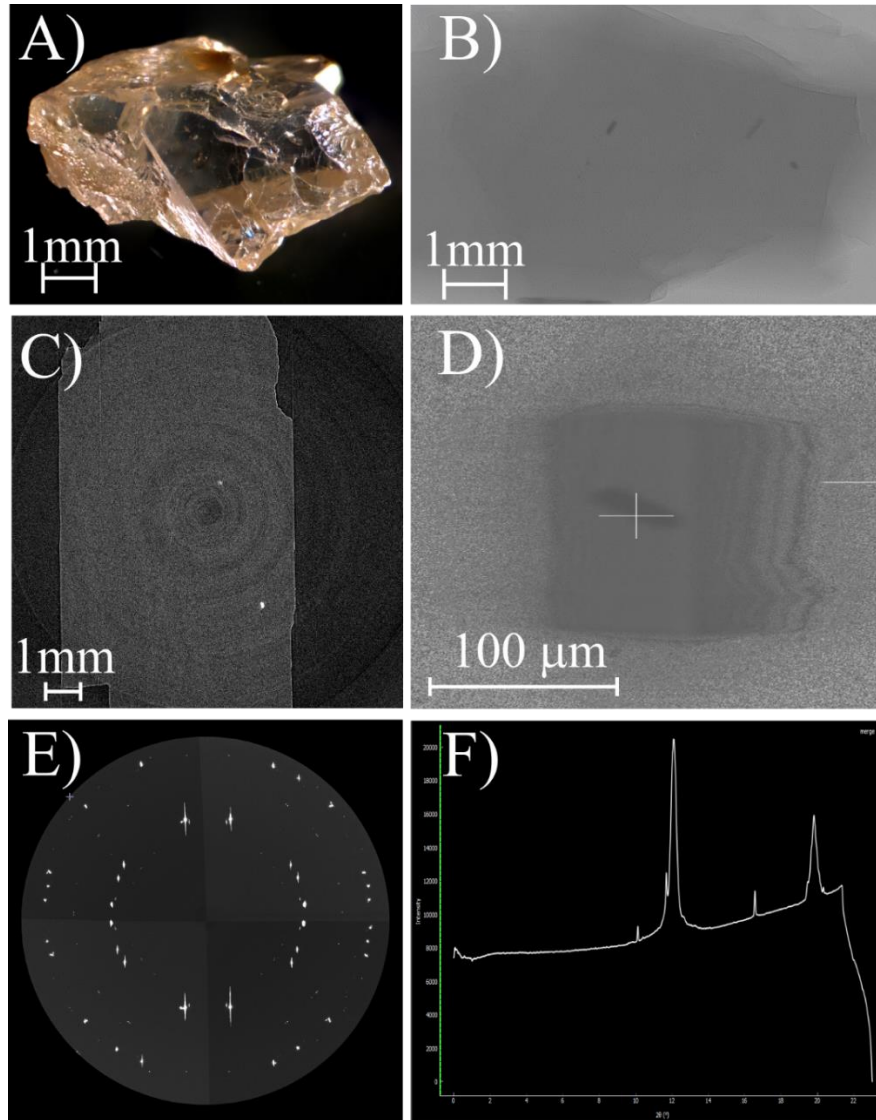


Fig. 2.4: A) A photomicrograph of Juína diamond 6B_06. B) Radiograph of diamond 6B_06 taken at 13-BM-D. C) Reconstructed slice of diamond 6B_06 from 13-BM-D data. Rings seen in image are artifacts. D) Radiograph of one of the ferropericlasite inclusions in B taken at 13-BM-C. E) Wide scan (180° rotation) XRD image of a ferropericlasite inclusion in diamond 6B_06 shown in D. F) Integrated Diffraction Pattern of ferropericlasite inclusion in diamond 6b_06 image produced using DIOPTAS (Prescher & Prakapenka, 2015).

2.6 Funding Information

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3. Chapter 3

In situ identification of mineral inclusions in diamonds from Juína, Brazil

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In situ identification of mineral inclusions in diamonds from Juína, Brazil

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3.1 Abstract

Diamonds and their mineral and fluid inclusions provide glimpses into the composition of Earth's deep interior where carbonate-rich magmas from subducting slabs interact with the mantle during diamond formation. A new suite of 121 diamonds from Juína, Brazil, a locality known to produce super-deep diamonds from the transition zone (410-660 km) and lower mantle (>660 km), were investigated by Fourier Transform Infrared (FTIR) spectroscopy, ultraviolet (UV) imaging, and synchrotron X-ray microtomography to characterize their atomic-scale defects (N, H, and B) and mineral inclusions. Among all 121 new Juína diamonds studied, 72 are very low in nitrogen

(type IIa), 43 exhibit small amounts of nitrogen with B-center clusters (type IaB), and six show A-centered nitrogen clusters. About 64% of the Juína suite studied here exhibit hydrogen defects by the presence of the 3107 cm^{-1} absorption band. A subset of 30 diamonds were selected for photoluminescence (PL), revealing optical defects typical of diamond with PL peaks at 415 nm (N3), 503 nm (H3), 536 nm, 612 nm, and 741 nm (GR1). A subset of 41 diamonds were selected for study by synchrotron X-ray diffraction to determine the diversity of mineral inclusions, the orientation distribution of the inclusions, and to search for potentially hydrous minerals. A total of 107 mineral inclusions were successfully identified via their lattice parameters while they remained encased in diamond, representing one of the largest catalogs of mineral inclusions in diamonds from a single locality. The most common inclusions (~50%) are ferropericlase $[(\text{Mg}_x\text{Fe}_{1-x})\text{O}, x > 0.5]$ or magnesiowüstite $[(\text{Mg}_x\text{Fe}_{1-x})\text{O}, x < 0.5]$. Based on the lattice parameters, 40% of the (Mg,Fe)O inclusions are inferred to be magnesiowüstite, a composition containing more Fe than would be expected for average lower mantle ($x \sim 0.2$). The abundance of magnesiowüstite, along with the absence of pyroxene inclusions suggests that the (Mg,Fe)O inclusions in this Juína suite represent a redox reaction product between the carbonatitic melt and reduced mantle peridotite.

3.2 Introduction

Diamonds capture and preserve mantle minerals as inclusions, providing samples of deep-mantle mineralogy. Diamonds typically form beneath continental cratons within the lithospheric mantle roots that extends to depths $> 250\text{ km}$ ($\sim 8\text{ GPa}$), which combined with their relatively low temperatures make an ideal environment for diamond formation. However, some diamonds originate from depths greater than 300 km and are referred to as super-deep diamonds (Harte et

al., 1999; Kaminsky et al., 2001; Nestola et al., 2018; Palot et al., 2016; Pearson et al., 2014; Scott-Smith et al., 1984; Shirey et al., 2013; Stachel and Harris, 2008). Juína, Brazil is known for bringing up super-deep diamonds with high frequency. In the past few years, diamonds from Juína revealed valuable geochemical information on Earth's dynamic mantle, with the discovery of hydrous ringwoodite and water-bearing fluids in a ferropericlasite from the lower mantle (Hutchison et al., 2001; Palot et al., 2016; Pearson et al., 2014). As such, there is a need to identify inclusions within large diamond suites from this region to obtain a better understanding of the geochemical cycling and composition of Earth's dynamic mantle (Harte, 2011; Pearson et al., 2014; Smith et al., 2018).

Numerous studies have investigated the nitrogen contents of Juína diamonds and found them characteristically low in nitrogen, with any nitrogen present consisting of highly aggregated nitrogen (Araujo et al., 2013; Kaminsky et al., 2001; Yuryeva et al., 2015). Thus, Juína diamonds typically classify as Type IIa (no nitrogen) or Type IaB (four nitrogen surrounding a vacancy). Only one previous study to date investigated the photoluminescence and ultraviolet fluorescence characteristic of Juína diamonds (Yuryeva et al., 2015). Such studies are valuable as these two techniques provide information into the growth characteristic and distribution of defects within a diamond. Most Juína diamonds originate at greater depths and thus, their growth histories are more complex as they were subject to higher pressures and temperatures (Araujo et al., 2013).

By studying diamond from this region using a variety of non-destructive techniques, a better understanding of the dynamic mantle beneath South America is obtained. In the past, the study of diamond inclusions was largely limited to destructive techniques, which included breaking the diamond to release inclusions or grinding away the diamond to expose inclusions at the surface. Such techniques resulted in loss of certain geochemical information such as the loss

of remnant inclusion pressure, which provides insight into inclusion entrapment conditions (Angel et al., 2015). Thus, there is a need to study these inclusions while they remain in diamond, in order to provide insight into the inner working of Earth's mantle. Only a few studies to date utilized lab source and synchrotron diffraction to identify inclusions while they remain encased in diamond (Nestola et al., 2016; Nestola et al., 2012; Nestola et al., 2011). In 2019, a method to quickly identify a multitude of smaller inclusions in diamonds was developed at the GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS), Advanced Photon Source (APS), USA (Wenz et al., 2019). This method was described in detail in Chapter 2 and highlighted some of the X-ray diffraction results from the study detailed in this current Chapter.

This study presents a thorough spectroscopic and X-ray diffraction study of diamonds from Juína, obtained in 2016. Nitrogen and hydrogen defects are characterized by FTIR spectroscopy and UV-VIS light stimulated PL. A high-throughput X-ray microtomography, radiography and single-crystal diffraction system at GSECARS (Wenz et al. 2019) was used identify the mineralogy of 107 inclusions by their lattice parameters. The in situ, or non-destructive nature of the method allows not only the identification of all mineral inclusions larger than a few micrometers in size, but also facilitates a study of the mineral inclusion orientations relative to the diamond host. The orientation information can be used to infer the syngenetic or epigenetic nature of mineral inclusions in diamond (Nestola reference here). In this new suite of superdeep diamonds from Juína, by far most of the inclusions can be identified as either ferropericalse or magneisowustite, which show a preferred orientation of the [100] axes parallel to the diamond host [100] axis, indicting the likely syngenetic nature of mineral inclusion growth during diamond growth and evidence that the abundant iron oxide is a redox product of diamond precipitation from carbonate melt at deep mantle conditions.

3.3 Experimental

3.3.1 Sample Description

The alluvial diamonds in this study originate from either the Sao Luiz deposits (61 diamonds) or the Chapado Plateau (60 diamonds), both about 30 km west of Juína, Brazil (Fig 3.1), and were obtained by D.G. Pearson and S. Shirey in 2016 and in 2018 respectively.

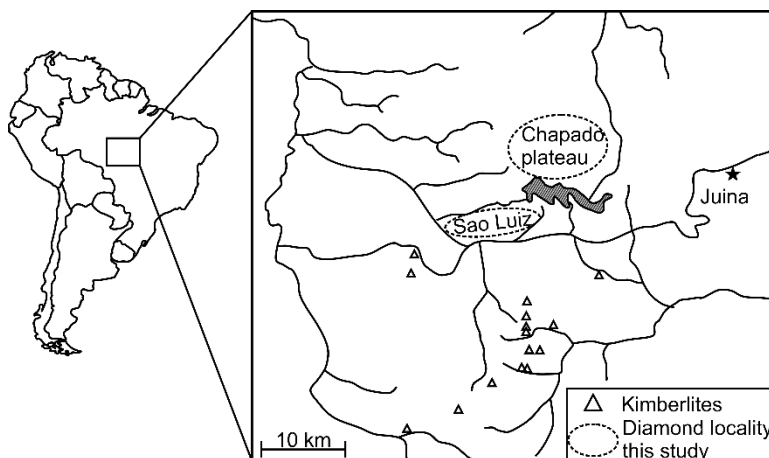


Fig. 3.1: Location of the alluvial diamonds in this study along with known kimberlites localities within Juína, Brazil (modified after Araujo et al., 2013).

All 121 diamonds in this study remained in their natural rough states, with an average length of 3.86 mm and average weight of 0.235 carats (0.047 g). The majority of the stones displayed a yellow-brown hue in plane polarized light (Fig. 3.2). Oxides coated the outside of some of these diamonds, which upon sonication in acetone significantly diminished. Stronger methods of cleaning like aqua regia were avoided so as not to alter any inclusions as some of these diamonds contain stress cracks. Most of the diamonds within the two suites exhibited an irregular morphology. All diamonds displayed numerous textural features, which included triangular plates, deformation lines, and trigons. Triangular plates, growth layers, varied in thickness and typically formed multiple imbricated plates, thus appearing much like steps (Tappert and Tappert, 2011). A

variety of resorption and textural features, such as surface frosting, was also present in numerous diamonds within this study (Fig. 3.2).

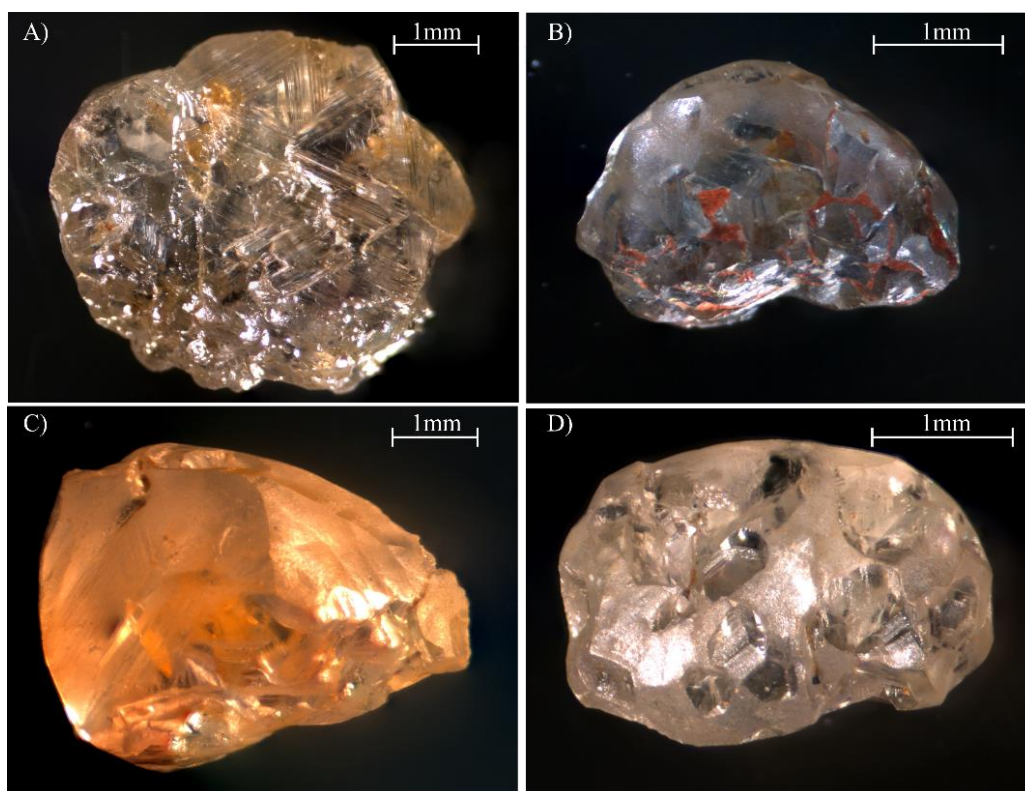


Fig. 3.2: A) Diamond 6b_10 exhibited imbricated triangular plates. B) Diamond 6b_24 was covered with oxides on the surface. C) Diamond 6b_21 displayed deformation lines. D) Diamond 6b_28 showed evidence of surface frosting.

Cross-polarized light microscopy highlighted areas of strain within the diamonds (Fig. 3.3). Strain induced birefringence was more apparent in some diamonds than others. However, the majority of diamonds displayed birefringence, which is expected given the extreme stresses associated with their likely superdeep (>300 km) that would have resulted in plastic deformation induced strain as well as birefringence from stress induced cracking (Howell, 2012).

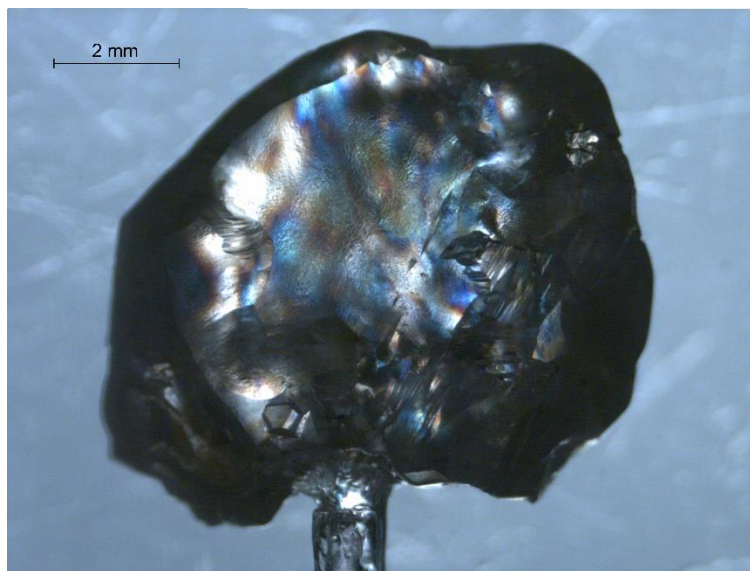


Fig. 3.3: A representative cross-polarized photomicrograph of diamond 5a08. This diamond displayed strain induced birefringence.

3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were collected on a nitrogen cooled Nicolet iN10 infrared microscope at the Gemological Institute of America. The detector was cooled with liquid nitrogen, while the sample stage was purged continuously with dry air. Spectra were collected over the range of 650-6000 cm^{-1} covering the one, two, and three phonon regions of diamond (Breeding and Shigley, 2009). Background spectra and sample measurements were collected with 100 scans at a resolution of 1 cm^{-1} . All background spectra were automatically subtracted from the diamond spectra. FTIR spectra were fitted using the computer code DiaMap (Howell et al., 2012).

3.3.3 Photoluminescence (PL) Spectroscopy

Photoluminescence spectroscopy was conducted on a Renishaw InViaTM Raman confocal microspectrometer at the Gemological Institute of America. Measurements were made with the following laser excitation wavelengths and corresponding gratings: 325 nm (2400 lines/mm), 488

nm (1800 lines/mm), 514 nm (1800 lines/mm), 633 nm (1800 lines/mm), and 830 nm (2400 lines/mm). Photoluminescence spectra were collected over the range of 327-1000 nm with a collection time of 12 seconds. Spectra were recorded with a Renishaw CCD detector. All spectra were collected on the diamonds while immersed at liquid nitrogen temperature (77 K) to improve the intensity and sharpness of any observed peaks.

3.3. 4 Ultraviolet (UV) Fluorescence Imaging

Ultraviolet fluorescence images were collected on a DiamondViewTM instrument at the Gemological Institute of America. Collection settings varied, however typical collections consisted of the following parameters: integration time = 0.44 seconds, aperture = 65%, field = 95%, and gain = 3.61 db.

3.3.5 Synchrotron Microtomography

Microtomography was conducted at the GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS), beamline 13-BM-D, of the Advanced Photon Source (APS), Argonne National Laboratory, USA. A monochromatic beam with an energy of 28.9 keV was used for the data collection as this energy closely matches to the operation energy of the X-ray diffraction beamline 13-BM-C (28.6 keV) (Wenz et al., 2019). Diffraction of the Ce-doped LuAG scintillator prohibited use of the exact energy utilized at 13-BM-C. Microtomography data was collected on all the diamonds using a CMOS camera with 1920 X 1200 pixels. Typical field of view consisted of 8.70 mm by 5.44 mm for large diamonds. Collection parameters consisted of 1 second exposure, 900 projections, and 4.5 μm pixel size on the sample.

3.3.6 Synchrotron X-ray Diffraction

Synchrotron X-ray diffraction data were collected at GSECARS beamline 13-BM-C of the APS using a six-circle goniometer combined with 2D-radiography to optically center each inclusion in the goniometer for single-crystal X-ray diffraction following the procedure of Wenz et al. (2019). Measurements were collected on 155 inclusions within 64 diamonds at this beamline. This study utilized either a MAR 165 CCD detector or Pilatus 1 M detector. Collection parameters for the MAR detector consisted of 1 second/degree exposure time, 180 steps, and a rotation of 180°. Sample to detector distances and tilt were calibrated using diffraction of LaB₆. Collections using the MAR 165 CCD detector took thirty minutes per detector position. Collection parameters on the Pilatus 1 M detector consisted of a 1 second/degree exposure time, 340 steps, and a rotation of 340°. Collection times took around 5 minutes for each detector position.

Single-crystal diffraction data collected on the MAR 165 CCD detector were processed on the ATREX program (previously GSE_ADA; Dera et al., 2013). This program handled peak searching and fitting routines and resulted in the generation of a peak list. Refinement of lattice parameters and orientation matrix determination were performed in the Reciprocal Space Viewer program (Dera et al., 2013). Data collected on the Pilatus 1 M detector were processed using APEX3 (Bruker AXS Inc, 2016), which handled peak searching, peak fitting, lattice parameter refinement, and orientation matrix determination. Diffraction images of all powder inclusions as well as mixed phase inclusions (inclusions with both powder and single-crystal phases) were first integrated in DIOPTAS (Prescher & Prakapenka, 2015) to generate intensity versus 2θ plots. These 2θ plots were then imported into the General Structure and Analysis System II (GSAS-II) (Toby

& Von Dreele, 2013) program, for further processing, indexing, and refinement of lattice parameters. Inclusions were ultimately identified via their lattice parameters.

3.3.7 μ X-ray Fluorescence

μ X-ray fluorescence mapping was carried out at beamline 13-ID-E of GSECARS using an X-ray operating energy of 18 keV with a focused beam of 1 μ m by 2 μ m. X-ray fluorescence was measured with a 4-element Vortex ME4 silicon drift diode detector and Xspress 3 digital X-ray multi-channel analyzer system. Map sizes were 201 μ m by 201 μ m with a step size of 2 μ m and 30 ms of dwell time. X-ray fluorescence maps and spectra were processed with the GSE Mapviewer software, which is part of the Larch software package (Newville, 2013).

3.4 Results

3.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to detect impurities within all 121 diamonds by collecting over the one, two, and three phonon regions of diamond (Breeding and Shigley, 2009). Covering these absorption regions of diamond ensured the detection of any nitrogen, boron, or hydrogen impurities. Hydrogen and nitrogen impurities appeared in the stones in the three and one phonon region respectively. Approximately 60% of these diamonds were determined to be Type IIa, while 36% classified as Type IaB (Fig. 3.4; Table 3.1). Both of these diamond types were expected for Juína diamonds, given their likely superdeep (>300 km) origin, and were consistent with a previous study (Araujo et al., 2013) finding that 65% of the diamonds were Type IIa. While the majority of the stones contained little to no nitrogen those that contained nitrogen were considered highly aggregated with B centers (Kaminsky et al., 2001; Yuryeva et al., 2015). Only a total of six samples showed evidence of A aggregated nitrogen, which indicated a shallower depth or shorter mantle

residence time (Fig. 3.5). Hydrogen impurities at 3107 cm^{-1} were observed in 64% of the diamonds within this study. The presence of the hydrogen impurity absorption feature (3107 cm^{-1}) was not surprising given that most natural type Ia diamonds display this feature, considered to represent a C-H stretching mode (Goss et al., 2014).

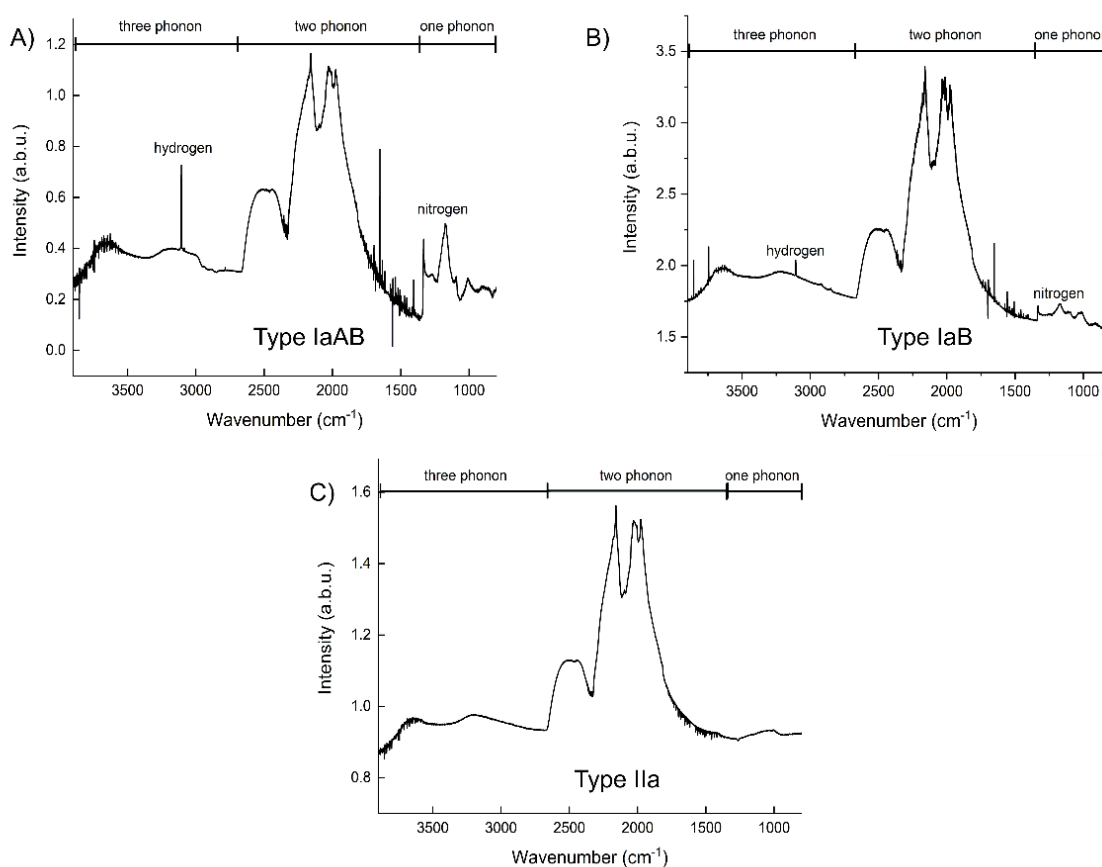


Fig. 3.4: A) A representative FTIR absorption spectrum of a Type IaAB diamond (diamond 6b26). B) A representative FTIR absorption spectrum of a Type IaB diamond (diamond 6b44). C) A representative FTIR absorption spectrum of a Type IIa diamond (diamond 6b55).

Table 3.1: Summary of the classified diamond type for all one hundred and twenty-one diamonds in this study.

Diamond Type	Number of Diamonds
Type IaAB	6
Type IaB	43
Type IIa	72
Total	121

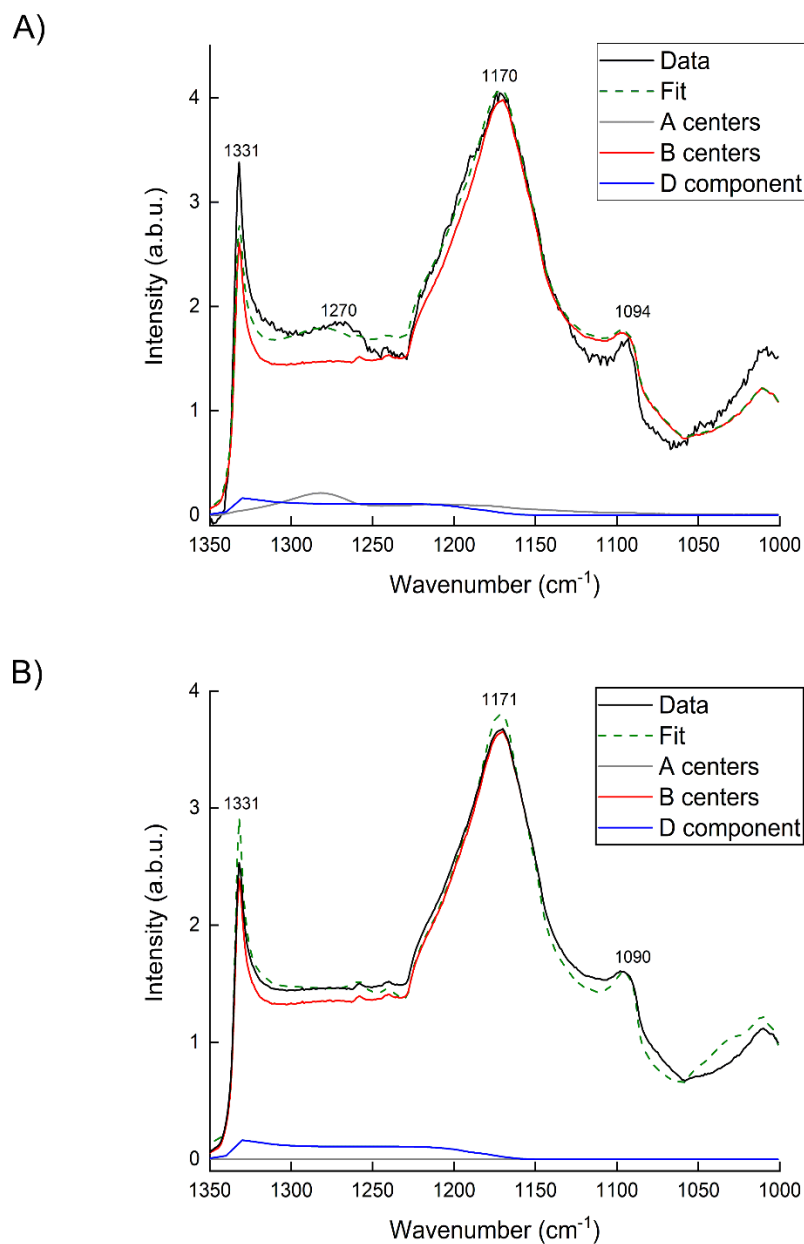


Fig. 3.5: A) A representative FTIR spectrum of a type IaAB diamond (diamond 6b26). B) A representative FTIR spectrum of a type IaB diamond (diamond 6b44). Nitrogen A, B, and D centers fitted via DiaMap represented with the grey, red, and blue lines (Howell et al., 2012). The green dashed line represents the overall fit to the data.

3.4.2 Photoluminescence (PL) Spectroscopy

Photoluminescence spectroscopy on a subset of 30 diamonds (15 São Luiz, 15 Chapado) was used to detect parts per billion (ppb) level optical defects within the diamond (Eaton-Magaña and Breeding, 2016). Previous PL studies on Sao Luiz diamonds focused on polished plates, while this study kept all diamonds in their rough natural state. PL spectroscopy revealed multiple optical defects within the diamond (Fig. 3.6). The first defect appeared at 415 nm (known as the N3 defect) and is attributed to three nitrogen atoms surrounding a vacancy in the diamond (Eaton-Magaña and Breeding, 2016). Another defect occurred at 503.2 nm and is referred to as the H3 or NVN⁰ defect, which resulted from two nitrogen atoms separated from a vacancy. The H3 defect is naturally occurring optical feature in natural diamonds and is feature often associated with the N3 defect (Zaitsev 2001). The GR1 (V⁰) peak at 741 nm represented an uncharged vacancy in diamond, a feature attributed to irradiated or plastically deformed natural diamonds (Breeding and Shigley, 2009; Collins, 1982; Yuryeva et al., 2015). Two other optical defects commonly observed in the diamonds in this study occurred at 536.6 nm and 612.5 nm, however the exact cause of these defects remains unknown (Hainschwang et al., 2006; Mironov et al., 2015; Yuryeva., et al., 2015). The optical defects observed in this study at 415, 503, 536, 612, and 741 nm agreed with the PL results from other Juína diamond studies (Yuryeva et al., 2015).

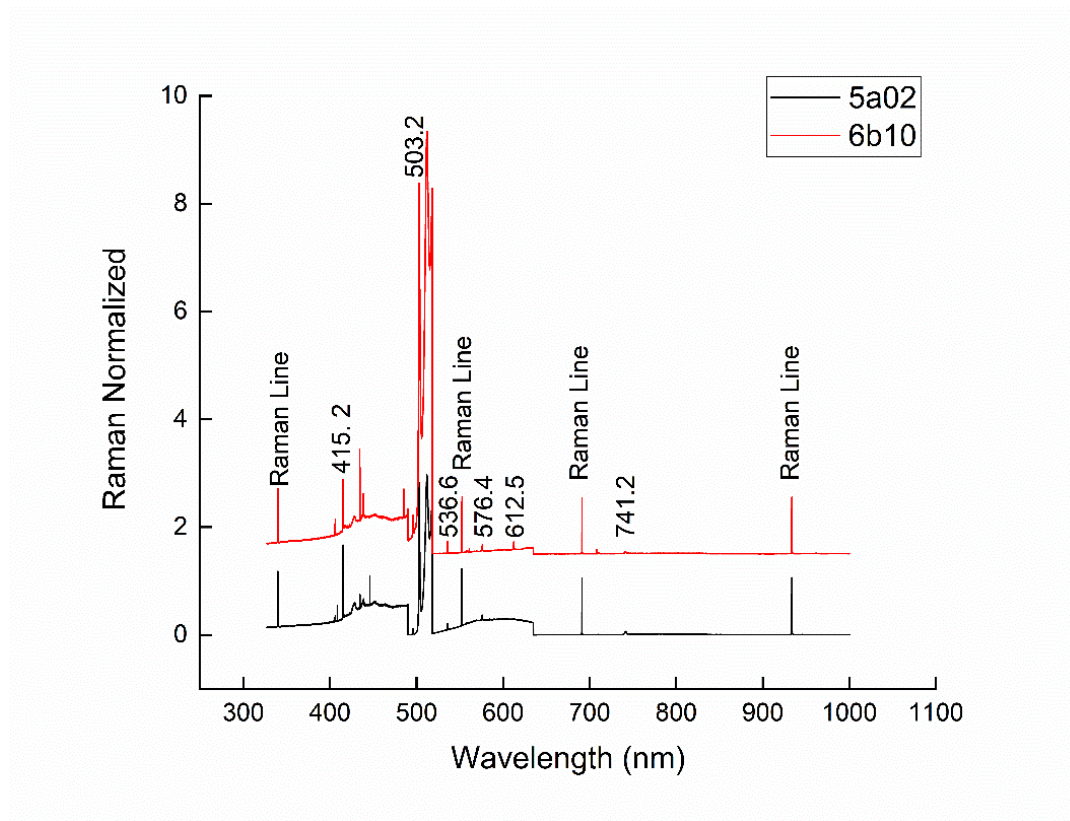


Fig. 3.6: A representative merged photoluminescence spectra of São Luiz diamond 6b10 and Chapado diamond 5a02 using a 325, 488, 514, 688 and 830 nm laser excitation source. As multiple excitation sources were utilized the Raman lines from the diamond appeared throughout the spectrum and are labeled accordingly. Common optical defects observed at 415, 503, 536, 612, and 741 nm.

3.4.3 Ultraviolet (UV) Fluorescence Imaging

About 60% of the Juína diamonds in this study exhibit blue fluorescence with localized areas of green fluorescence (Fig. 3.7). Both colors within a single diamond indicate multiple defect centers. Pure blue fluorescence was observed in 39% of all diamonds in this study (Fig. 3.8), while only two diamonds were predominated by green emission. Fluorescence observed in this study, agreed with the findings of Yuryeva et al., (2015), which studied diamond plates from São Luiz.

The defect responsible for the blue emission is the N3 defect (N_3V), which was observed in the PL spectrum at 415 nm. Green emission is related to the H3 defect (NVN^0), which appeared in the PL spectrum at 503 nm. Blue fluorescence observed in the majority of diamonds agrees with UV and PL results from other studies focused on low nitrogen Type IIa diamonds (Breeding and Shigley, 2009; Yuryeva et al., 2015). None of the diamonds in this study phosphoresced, which was expected as phosphorescence in natural diamonds remains uncommon and typically only occurs in type IIb and chameleon diamonds (Eaton- Magaña and Breeding, 2016).

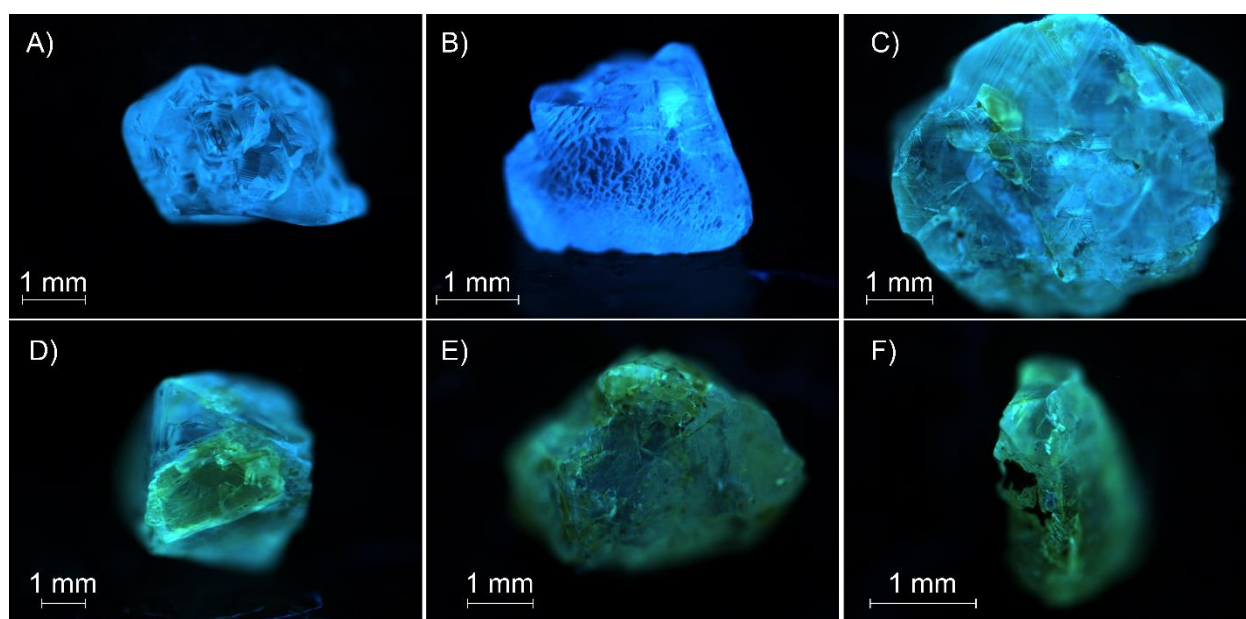


Fig. 3.7: A) A representative pure blue fluorescence image of diamond 6b41. B) Fluorescence image of diamond 5a41. This diamond exhibited blue fluorescence and highlighted unique textural features. C) A representative fluorescence image of a diamond with some mixed emission colors (diamond 6b10) D) A representative fluorescence image of a diamond with more mixed emission colors (diamond 6b39) E) A representative fluorescence image of a diamond with a predominate

green emission color mixed with blue (diamond 6b33). F) A representative fluorescence image of a diamond with a predominate green emission color (diamond 6b30).

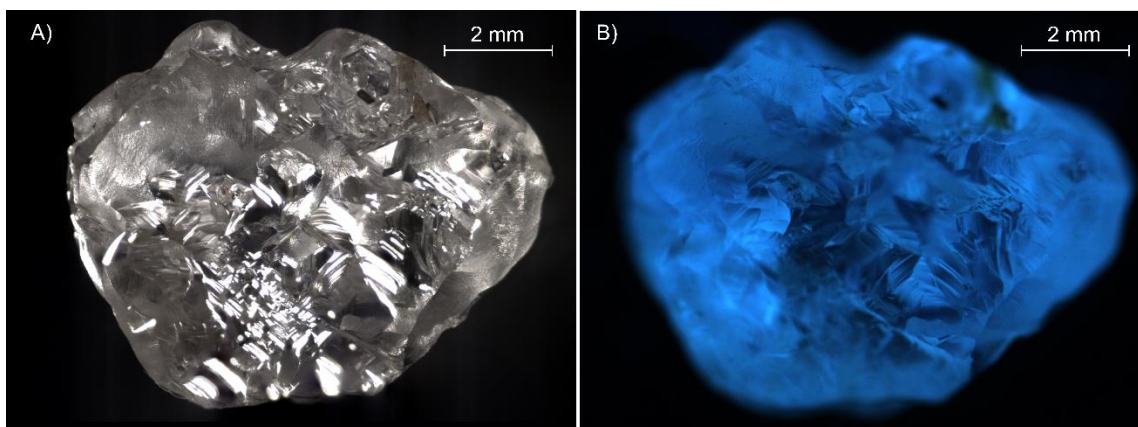


Fig. 3.8: A) Photomicrograph of diamond 6b09. B) Fluorescence image of diamond 6b09 taken with a Diamond View instrument. This diamond exhibited blue fluorescence.

3.4.4 Synchrotron Microtomography

All one hundred and twenty-one diamonds remained in their irregular, rough natural state. Due to the irregularity in shape and range of surface textures presented by these diamonds, most inclusions could not be located with optical microscopy (Fig. 3.9). Synchrotron tomography revealed all inclusions larger than $\sim 10 \mu\text{m}$ within all 121 diamonds (Fig. 3.9 and Fig. 3.10). Microtomography provides an additional advantage as it can reveal microcracks within the diamonds (Fig. 3.11). Cracks that lead up to inclusions indicate possible interaction of the inclusion with kimberlitic magma, thus no longer representing a pristine unaltered sample from the mantle. In a study by Bulanova et al., (1996), sulfide inclusions that showed cracks leading to the surface contained high levels of the trace elements Pb and Zn and were interpreted to reflect interaction of the inclusion with the kimberlitic magma. By locating all cracks within a diamond an idea of how representative a particular inclusion is of the mantle is obtained. Examples of inclusions that are

unaltered and those that exhibit cracks are shown in Fig. 3.11. Microtomography was also used as a guide to locate and center inclusions for single-crystal X-ray diffraction using the online radiography system at beamline 13-BM-C of GSECARS (Wenz et al., 2019).

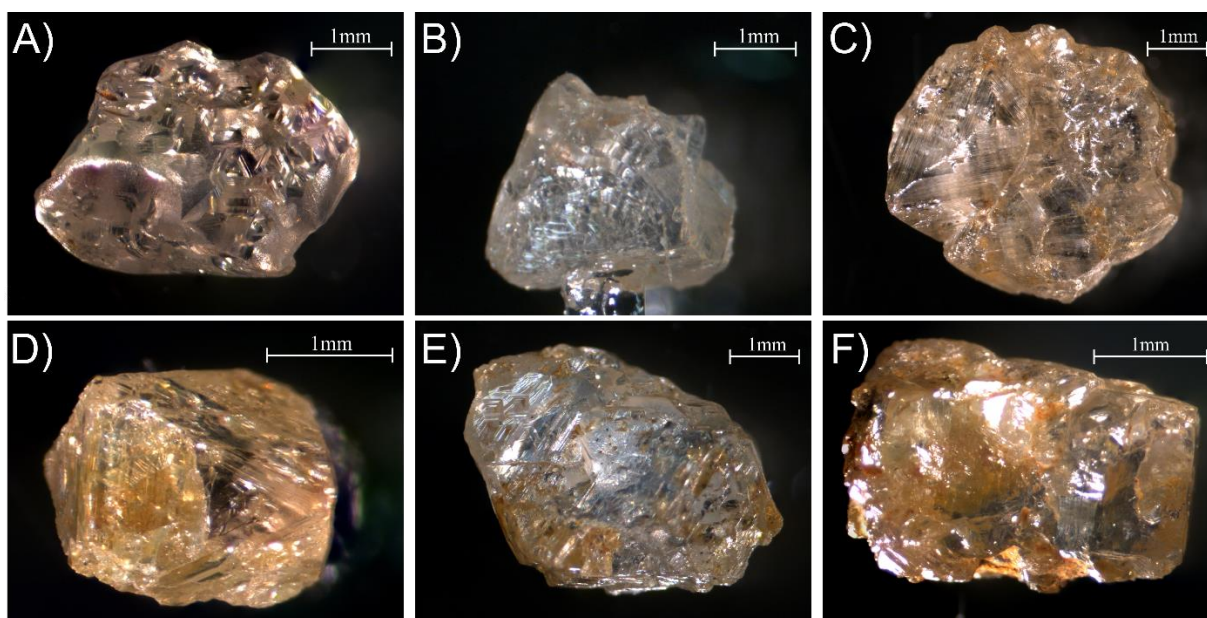


Fig. 3.9: A) Photomicrograph of diamond 6b41. B) Photomicrograph of diamond 5a41. C) Photomicrograph of diamond 6b10. D) Photomicrograph of diamond 6b39. E) Photomicrograph of diamond 6b33. F) Photomicrograph of diamond 6b30. The majority of these diamonds contained inclusions; however they are not visible with optical microscopy.

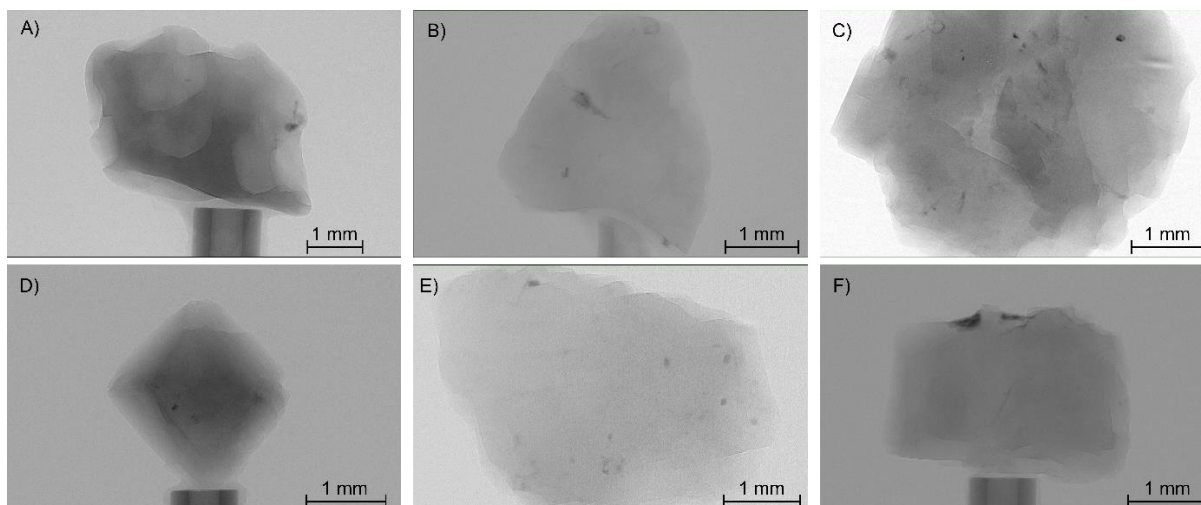


Fig. 3.10: A) Radiograph of diamond 6b41. B) Radiograph of diamond 5a41. C) Radiograph of diamond 6b10. D) Radiograph of diamond 6b39. E) Radiograph of diamond 6b33. F) Radiograph of diamond 6b30. Radiography revealed inclusions within all these diamonds.

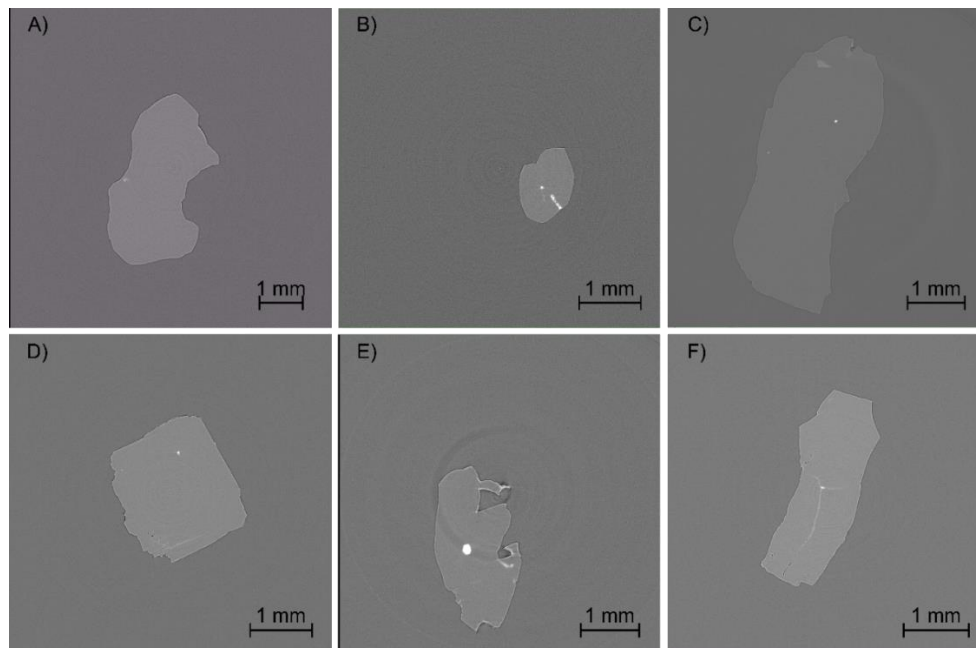


Fig. 3.11: A) A representative tomographic slice of a diamond with a faint inclusion (diamond 6b41) B) A representative tomographic slice of a diamond that showed evidence of cracking,

however this crack does not interact with the inclusion (diamond 5a41) C) A representative tomographic slice of a diamond with pristine inclusions (diamond 6b10). D) A representative tomographic slice of diamond with a pristine inclusion (diamond 6b39). E) A representative tomographic slice of diamond, which contained a high absorbing inclusion (diamond 6b33.) F) A representative tomographic slice of a diamond, which displayed cracks leading up to an inclusion (diamond 6b30).

In agreement with optical microscopy (birefringence), nearly all 121 diamonds exhibit stored strain by microtomography, wherein Bragg diffraction conditions sweep across the diamonds rotating in the X-ray beam. (Fig. 3.12). Such strain is a common feature observed in microtomography of natural diamonds (Rivers et al., 1999). Ultimately, this diffraction does not introduce artifacts in the tomographic reconstruction slices (Fig. 3.13).

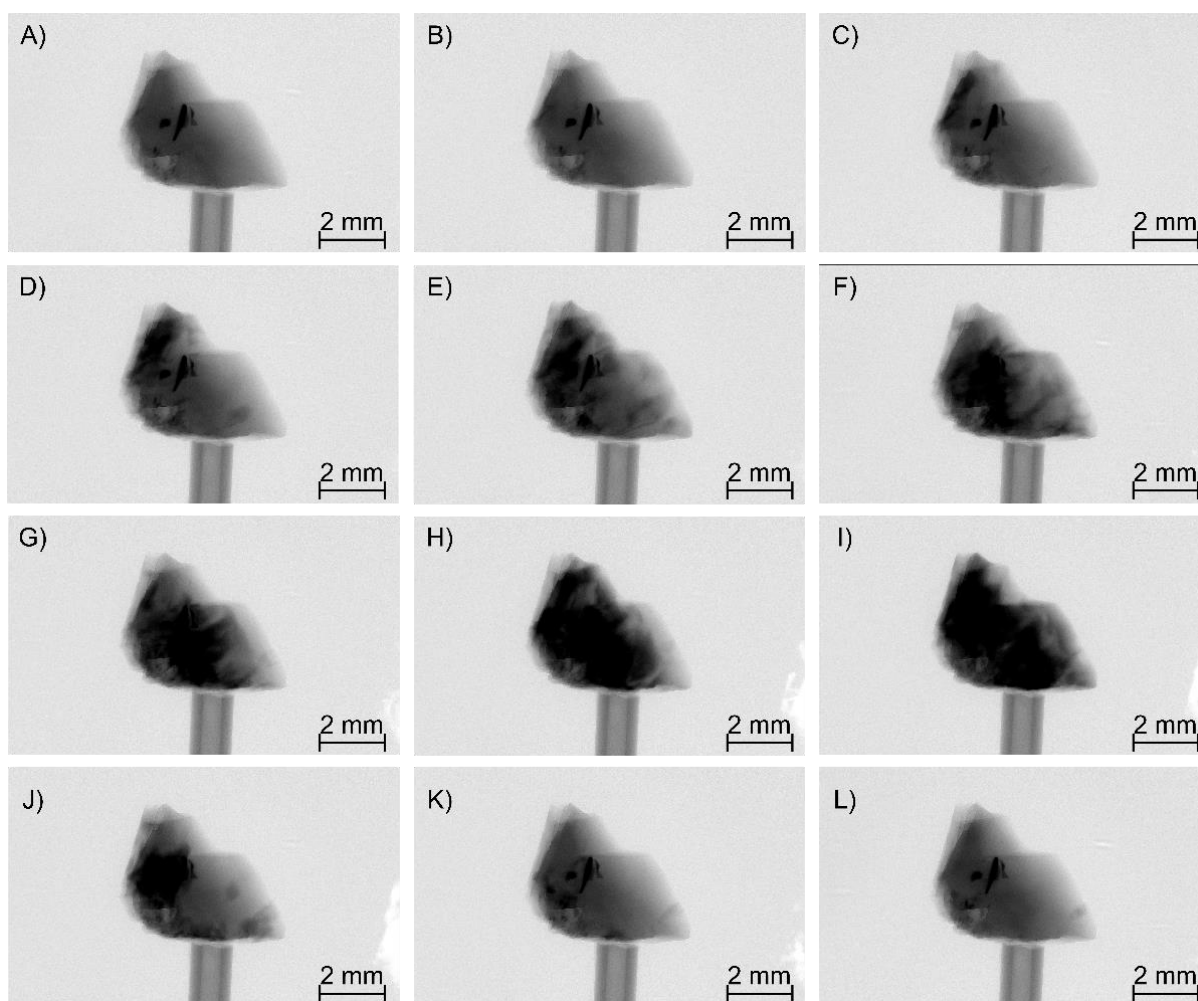


Fig. 3.12: A-L) Radiographs of diamond 6b013 covered a total of 2.4° . Each image was 0.2° from the previous image. Dark regions indicated the diffraction of the diamond. As the entire diamond does not diffract at the same time, this implied that the diamond is strained.

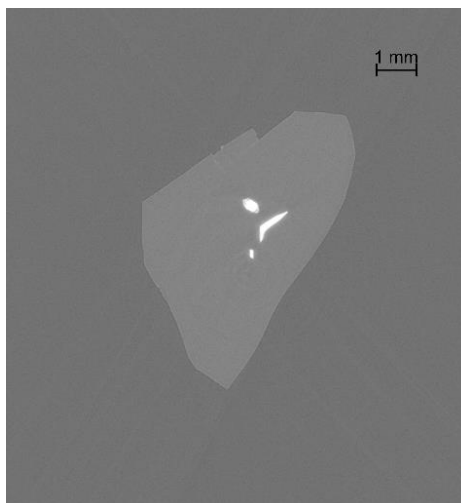


Fig. 3.13: Tomographic slice of diamond 6b13 showed no artifacts induced by the diffraction of the diamond.

3.4.5 Synchrotron X-ray Diffraction

Synchrotron X-ray diffraction was performed on a selected subset of 41 Juína diamonds. Diffraction images of the inclusions fell into one of the following three categories: single crystal, powder, or single crystal and powder (Fig. 3.14). While X-ray diffraction data was collected on for 155 inclusions in 64 diamonds in this study, some of these diamonds and their inclusions proved too challenging for characterization given the mixed phases (powder and single crystal or multigrain) combined with the state of the old MAR 165 CCD detector and the previous analysis software. As of 2019, the new Pilatus 1 M detector and APEX 3 analysis software (Bruker AXS Inc, 2016), provided an improved data collection and processing system, which can handle these more complex inclusions. Thus, if some of the more challenging inclusions were remeasured on the new system these complex phases could subsequently be identified. The new system also drastically increased the number of inclusions capable of analyzing within a 72-hour beamtime (53 inclusions with MAR 165 CCD to 135 inclusions with Pilatus 1 M). Thus, future studies

utilizing this beamtime could make significant progress on identifying the mineral inclusions in the remaining diamonds of the suite. Ultimately, a total of 107 inclusions within 41 diamonds were successfully characterized via their lattice parameters obtained with XRD in this study (Table 3.2.).

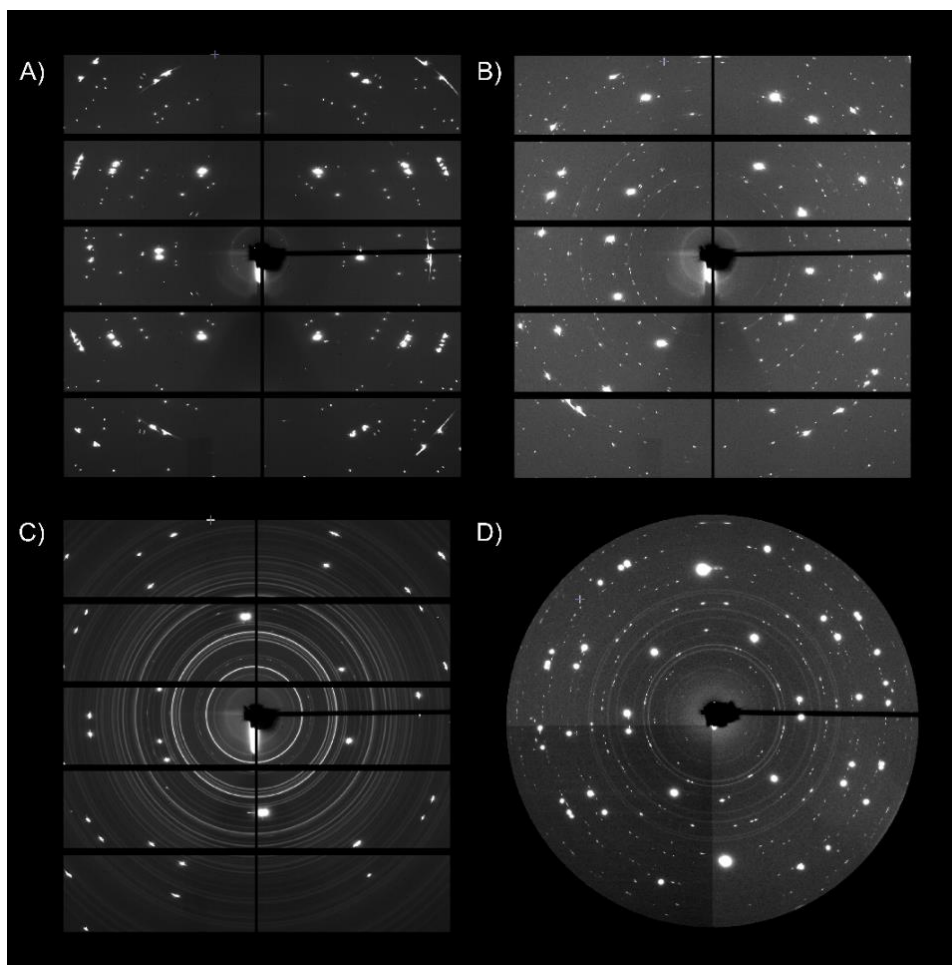


Fig. 3.14: A) A representative diffraction image of a single crystal inclusion (diamond 5a27). B) A representative diffraction image of a multi-grain inclusion (diamond 5a23). C) A representative diffraction image of a powder inclusion (diamond 5a57). D) A representative diffraction image of a mixed single crystal and powder phase inclusion (diamond 6b56). Images produced using DIOPTAS (Prescher and Prakapenka, 2015).

Table 3.2: Symmetry-constrained lattice parameters of 107 inclusions identified in a suite of diamonds from the São Luiz and Chapado locality in Juína, Brazil. Inclusions previously reported in Wenz et al., (2019) denoted by ¹ superscript in front of the inclusion name. Single Crystal inclusions denoted by * superscript the rest of the inclusions are powder.

Inclusion	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Symmetry Constraints	Mineral
6b04a*	8.3664(7)	8.3664(7)	8.3664(7)	585.62(5)	cubic	magnetite Fe ₃ O ₄
¹6b_04b*	8.509(2)	8.509(2)	8.509(2)	616.0(2)	cubic	titanomagnetite Fe _{1+x} (Fe _{2-2x} Ti _x)O ₄
¹6b_04b2*	4.255(1)	4.255(1)	4.255(1)	77.1(6)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
¹6b_05a*	4.246(4)	4.246(4)	4.246(4)	76.6(2)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
¹6b_05b*	4.255(2)	4.255(2)	4.255(2)	77.0(2)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
¹6b_05c*	4.259(1)	4.259(1)	4.259(1)	77.3(1)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
¹6b_05d*	4.262(2)	4.262(2)	4.262(2)	77.4(2)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
¹6b_05e*	4.251(2)	4.251(2)	4.251(2)	77.4(2)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
6b05f*	4.230(5)	4.230(5)	4.230(5)	75.71(3)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
6b05g*	4.248(4)	4.248(4)	4.248(4)	76.63(7)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
6b05h*	4.249(1)	4.249(1)	4.249(1)	76.69(2)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
6b05i	8.392(6)	8.392(6)	8.392(6)	591.0(6)	cubic	magnetite Fe ₃ O ₄
¹6b_06a*	4.276(2)	4.276(2)	4.276	78.2(1)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
¹6b_06b*	4.271(7)	4.271(7)	4.271(7)	77.9(1)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
¹6b_07a	2.868(9)	2.868(9)	2.868(9)	23.6(2)	cubic	Fe (bcc) with some alloy
¹6b_07b	2.868(5)	2.868(5)	2.868(5)	23.6(1)	cubic	Fe (bcc) with some alloy
¹6b_07c*	4.276(2)	4.276(2)	4.276(2)	78.2(1)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
¹6b_07c2*	8.442(5)	8.442(5)	8.442(5)	601.7(3)	cubic	titanomagnetite Fe _{1+x} (Fe _{2-2x} Ti _x)O ₄
¹6b_07d*	4.204(5)	4.204(5)	4.204(5)	75.3(3)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
¹6b_07d2*	8.511(1)	8.511(1)	8.5107	601.7(3)	cubic	titanomagnetite Fe _{1+x} (Fe _{2-2x} Ti _x)O ₄
¹6b_07e*	4.320(7)	4.320(7)	4.320(7)	81.0(4)	cubic	wüstite FeO
¹6b_07e2*	8.490(5)	8.490(5)	8.490(5)	612.0(2)	cubic	titanomagnetite Fe _{1+x} (Fe _{2-2x} Ti _x)O ₄
¹6b_08c*	5.083(1)	5.083(1)	5.083(1)	314.6(3)	hexagonal	ilmenite FeTiO ₃
¹6b_09	4.640(6)	10.005(9)	3.028(3)	140.6(2)	orthorhombic	goethite (FeOOH)
¹6b_10b	5.032(1)	5.032(1)	13.759(3)	301.7(1)	hexagonal	hematite Fe ₂ O ₃

¹⁶b_10c	5.140(3)	5.140(3)	13.420(2)	307.5(2)	hexagonal	titanohematite ($x\text{Fe} \text{ TiO}_3[1-x]\text{Fe}_2\text{O}_3$)
¹⁶b_11b*	8.396(2)	8.396(2)	8.396(2)	591.8(2)	cubic	magnetite Fe_3O_4
¹⁶b_12a*	4.273(2)	4.273(2)	4.273(2)	78.0(3)	cubic	magnesiowüstite ($\text{Mg}_{1-x},\text{Fe}_x$)O
¹⁶b_12b*	4.270(1)	4.270(1)	4.270(1)	77.9(2)	cubic	magnesiowüstite ($\text{Mg}_{1-x},\text{Fe}_x$)O
¹⁶b_12c*	4.280(9)	4.280(9)	4.2796	78.4(5)	cubic	magnesiowüstite ($\text{Mg}_{1-x},\text{Fe}_x$)O
¹⁶b_12d*	4.274(3)	4.274(3)	4.274(3)	78.1(5)	cubic	magnesiowüstite ($\text{Mg}_{1-x},\text{Fe}_x$)O
6b_12e*	4.262(2)	4.262(2)	4.262(2)	78.22(3)	cubic	magnesiowüstite ($\text{Mg}_{1-x},\text{Fe}_x$)O
6b_12f	8.398(2)	8.398(2)	8.398(2)	592.2(4)	cubic	magnetite Fe_3O_4
6b_12g	8.399(5)	8.399(5)	8.399(5)	78.4(5)	cubic	magnetite Fe_3O_4
6b17a*	8.439(3)	8.439(3)	8.439(3)	600.93(21)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
¹⁶b_17b*	4.270(1)	4.270(1)	4.270(1)	77.8(2)	cubic	magnesiowüstite ($\text{Mg}_{1-x},\text{Fe}_x$)O
¹⁶b_17c*	4.285(1)	4.285(1)	4.285(1)	78.7(5)	cubic	magnesiowüstite ($\text{Mg}_{1-x},\text{Fe}_x$)O
¹⁶b_21c*	4.279(2)	4.279(2)	4.279(2)	78.3(2)	cubic	magnesiowüstite ($\text{Mg}_{1-x},\text{Fe}_x$)O
¹⁶b_21c2	8.405(2)	8.405(2)	8.405(2)	593.8(2)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
¹⁶b_23*	4.232(8)	4.232(8)	4.232(8)	75.8(3)	cubic	ferropericlae ($\text{Mg}_x,\text{Fe}_{1-x}$)O
6b_23b*	4.233(3)	4.233(3)	4.233(3)	75.86(5)	cubic	ferropericlae ($\text{Mg}_x,\text{Fe}_{1-x}$)O
6b_26*	4.236(2)	4.236(2)	4.236(2)	76.00(12)	cubic	ferropericlae ($\text{Mg}_x,\text{Fe}_{1-x}$)O
¹⁶b_29a*	4.261(2)	4.261(2)	4.261(2)	77.8(2)	cubic	magnesiowüstite ($\text{Mg}_{1-x},\text{Fe}_x$)O
¹⁶b_29b*	4.253(1)	4.253(1)	4.253(1)	76.9(1)	cubic	ferropericlae ($\text{Mg}_x,\text{Fe}_{1-x}$)O
6b_29c	8.411(4)	8.411(4)	8.411(4)	595.1(9)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
¹⁶b_34a*	4.243(2)	4.243(2)	4.243(2)	76.4(2)	cubic	ferropericlae ($\text{Mg}_x,\text{Fe}_{1-x}$)O
¹⁶b_34b*	4.245(1)	4.245(1)	4.24489	76.5(1)	cubic	ferropericlae ($\text{Mg}_x,\text{Fe}_{1-x}$)O
¹⁶b_34c*	4.252(2)	4.252(2)	4.252(2)	76.8(2)	cubic	ferropericlae ($\text{Mg}_x,\text{Fe}_{1-x}$)O
¹⁶b_37a	4.254(2)	4.254(2)	4.254(2)	77.0(2)	cubic	ferropericlae ($\text{Mg}_x,\text{Fe}_{1-x}$)O
¹⁶b_37a2	8.379(2)	8.379(2)	8.379(2)	588.0(4)	cubic	magnetite Fe_3O_4
¹⁶b_39a	5.037(5)	5.037(5)	13.769(1)	302.5(4)	hexagonal	titanohematite ($x\text{FeTiO}_3[1-x]\text{Fe}_2\text{O}_3$)
¹⁶b_39b	5.038(7)	5.038(7)	13.761(1)	302.5(5)	hexagonal	titanohematite ($x\text{FeTiO}_3[1-x]\text{Fe}_2\text{O}_3$)
¹⁶b_46*	11.584(3)	11.584(3)	11.584(3)	1554.4(6)	cubic	almandine $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$
¹⁶b_48b	4.744(4)	10.185(1)	5.978(7)	288.8(6)	orthorhombic	olivine ($\text{Mg}_x,\text{Fe}_{2-x})_2\text{SiO}_4$

¹6b_53*	4.246(1)	4.246(1)	4.246(1)	76.5(1)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
¹6b_56a	4.758(7)	10.209(6)	5.972(7)	290.1(4)	orthorhombic	olivine (Mg _x ,Fe _{2-x}) ₂ SiO ₄
¹6b_56b	4.759(8)	10.209(8)	5.976(1)	290.4(5)	orthorhombic	olivine (Mg _x ,Fe _{2-x}) ₂ SiO ₄
¹6b_56b2	8.394(6)	8.394(6)	8.394(6)	591.4(1)	cubic	magnetite Fe ₃ O ₄
¹6b_56c	4.754(1)	10.205(7)	5.978(1)	290.0(6)	orthorhombic	olivine (Mg _x ,Fe _{2-x}) ₂ SiO ₄
¹6b_56d	4.756(1)	10.206(1)	5.981(1)	290.3(6)	orthorhombic	olivine (Mg _x ,Fe _{2-x}) ₂ SiO ₄
6b_60a	11.852(2)	11.852(2)	11.852(2)	1665.0(8)	cubic	grossular Ca ₃ Al ₂ Si ₃ O ₁₂
5a_04a*	4.262(2)	4.262(2)	4.262(2)	77.43(3)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
5a_04b*	4.260(5)	4.260(5)	4.260(5)	77.30(9)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
5a_05a*	4.268(7)	4.268(7)	4.268(7)	77.75(12)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
5a_05c*	4.284(6)	4.284(6)	4.284(6)	78.60(11)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
5a_06a*	4.250(3)	4.250(3)	4.250(3)	76.76(18)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
5a_06b*	4.256(2)	4.256(2)	4.256(2)	77.11(4)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
5a_06c*	8.428(2)	8.428(2)	8.428(2)	598.6(10)	cubic	titanomagnetite Fe _{1+x} (Fe _{2-2x} Ti _x)O ₄
5a_06d*	4.252(1)	4.252(1)	4.252(1)	76.88(2)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
5a_08a*	4.239(3)	4.239(3)	4.239(3)	76.18(17)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
¹5a_09a	5.077(3)	5.077(3)	13.894(4)	310.1(2)	hexagonal	titano hematite (xFeTiO ₃ [1-x]Fe ₂ O ₃)
¹5a_09b	5.069(2)	5.069(2)	13.931(5)	310.1(2)	hexagonal	titano hematite (xFeTiO ₃ [1-x]Fe ₂ O ₃)
5a_10a*	4.262(3)	4.262(3)	4.262(3)	77.44(3)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
5a_10b*	8.447(2)	8.447(2)	8.447(2)	602.66(15)	cubic	titanomagnetite Fe _{1+x} (Fe _{2-2x} Ti _x)O ₄
¹5a_10f*	4.281(8)	4.281(8)	4.281(8)	78.5(4)	cubic	magnesiowüstite (Mg _{1-x} ,Fe _x)O
5a_15a	5.035(1)	5.035(1)	13.764(2)	302.2(7)	hexagonal	titano hematite (xFeTiO ₃ [1-x]Fe ₂ O ₃)
5a_15b	5.029(9)	5.029(9)	13.735(2)	300.8(5)	hexagonal	hematite Fe ₂ O ₃
5a_15c	5.038(2)	5.038(2)	13.770(4)	302.6(1)	hexagonal	titano hematite (xFeTiO ₃ [1-x]Fe ₂ O ₃)
5a_15d	5.033(1)	5.033(1)	13.758(3)	301.8(9)	hexagonal	hematite Fe ₂ O ₃
5a_15e	5.030(4)	5.030(4)	13.750(6)	301.4(2)	hexagonal	hematite Fe ₂ O ₃
5a_17a*	6.613(2)	6.613(2)	6.613(2)	262.87(16)	tetragonal	zircon ZrSiO ₄
5a_20a*	4.245(3)	4.245(3)	4.245(3)	76.5(5)	cubic	ferropericlase (Mg _x ,Fe _{1-x})O
5a_20b*	8.488(2)	8.488(2)	8.488(2)	611.4(1)	cubic	titanomagnetite Fe _{1+x} (Fe _{2-2x} Ti _x)O ₄

15a_20c*	4.245(9)	4.245(9)	4.245(9)	76.47(7)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
5a_23a*	6.614(4)	6.614(4)	5.999(3)	262.5(4)	tetragonal	zircon ZrSiO_4
5a_23b*	8.422(2)	8.422(2)	8.422(2)	597.4(1)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
5a_23c*	8.432(2)	8.432(2)	8.432(2)	599.5(1)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
5a_23d	4.206(2)	4.206(2)	4.206(2)	74.4(1)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
5a_23e	8.404(1)	8.404(1)	8.404(1)	593.60(3)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
5a_23f	8.397(6)	8.397(6)	8.397(6)	592.1(1)	cubic	magnetite Fe_3O_4
5a_23g*	4.259(3)	4.259(3)	4.259(3)	77.3(2)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
5a_26a*	4.254(5)	4.254(5)	4.254(5)	76.9(1)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
5a_26b*	8.360(5)	8.360(5)	8.360(5)	584.2(4)	cubic	magnetite Fe_3O_4
5a_26c*	4.262(3)	4.262(3)	4.262(3)	77.4(5)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
5a_26d*	4.253(8)	4.253(8)	4.253(8)	76.9(1)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
5a_26e*	4.259(1)	4.259(1)	4.259(1)	77.3(2)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
5a_26f	5.038(6)	5.038(6)	13.764(1)	302.6(4)	hexagonal	titanohematite ($x\text{FeTiO}_3[1-x]\text{Fe}_2\text{O}_3$)
5a_27a*	4.270(3)	4.270(3)	4.270(3)	77.9(1)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
5a_27b*	4.241(1)	4.241(1)	4.241(1)	76.3(2)	cubic	ferropericlase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)
5a_32a*	8.426(2)	8.426(2)	8.426(2)	598.2(1)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
5a_36a*	4.768(1)	10.239(2)	6.001(1)	293.0(1)	orthorhombic	olivine ($\text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4$)
5a_36b*	6.610(6)	6.610(6)	5.004(1)	262.3(6)	tetragonal	zircon ZrSiO_4
5a_41a*	4.770(8)	10.243(2)	6.017(2)	294.0(9)	orthorhombic	olivine ($\text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4$)
5a_53a*	8.422(4)	8.422(4)	8.422(4)	597.4(3)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
5a_57a	4.746(25)	10.220(4)	5.969(30)	289.5	orthorhombic	olivine ($\text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4$)
5a59a*	8.489(3)	8.489(3)	8.489(3)	611.6(2)	cubic	titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$
5a59b*	4.272(1)	4.272(1)	4.272(1)	78.0(3)	cubic	magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)

A summary of all mineral inclusions found in this study is given in Table 3.3. The majority of inclusion phases formed solid solutions, thus their unit-cell parameters depended on both composition as well as remnant pressure. All solid solutions are further described in Chapter 2 of this dissertation (Wenz et al., 2019). The majority of the inclusions identified in this study, ~ 49%, were ferropericlasite or magnesio-wüstite, in agreement with previous studies on Juína diamonds (Anzolini et al., 2019; Kaminsky et al., 2010; Nimis et al., 2018). Following standard mineralogical nomenclature, the (Mg,Fe)O oxides are classified such that samples containing <50 mol% FeO are referred to as ferropericlasite and those with >50 mol% are magnesio-wüstite. Because unit-cell parameters depend on both composition and pressure, there is mutual uncertainty in both parameters. For (Mg,Fe)O, assuming the variation of lattice parameter with $X_{\text{Fe}} = \Sigma\text{Fe}/(\Sigma\text{Fe}+\text{Mg})$ and an average bulk modulus K_{T0} of 160 GPa from the study of Jacobsen et al. (2002), the value of X_{Fe} would be underestimated by about 0.088 (or 8.8 mol% FeO) per GPa of remnant pressure (Wenz et al., 2019). Typical remnant pressures on inclusions range from 0.1 – 2 GPa (Anzolini et al., 2018; Howell et al., 2012; Pearson et al., 2014; Nestola et al., 2011a). The majority of the ferropericlasite/magnesio-wüstite inclusions in this study were not associated with high-pressure mineral inclusions and therefore cannot be said to originate in the lower mantle. Given the chemical variability and lack of high-pressure mineral inclusions, these inclusions may represent different stages of reactions between the carbonatitic melt and reduced mantle peridotite proposed by Nimis et al., (2018) and Thomson et al., (2016). However, it is important to note that seven of the ferropericlasite inclusions (6b04b/b2; 6b07c/c2; 6b07d/d2; 6b07e/e2; 6b21c/c2, 6b37a/a2, 6b56b/b2) also exhibited titanomagnetite, which we originally interpreted as another inclusion in close proximity to the ferropericlasite. Upon further inspection of the microtomography it is thought

that these inclusions could in fact actually represent an exsolution. Given that there is a large uncertainty in the composition of such inclusions studied in situ using lattice parameters alone it is possible that for these seven inclusions identified initially as titanomagnetite might actually be magnesioferrite a common exsolution associated with ferropericlaase, which would suggest a lower mantle origin (Akaogi et al., 2019; Kaminsky et al., 2015; Wirth et al., 2014). While this study assumed inclusions fall along certain solid solutions, we recognize that these inclusions are complex and some could contain more Mg than we discussed. Especially in the case of titanomagnetite, which could contain some Mg as the study by Akaogi et al., (2019) pointed out. However, the goal of our study was to identify the inclusions while they remained encased in diamond via their lattice parameters. Further constraints on the composition of these inclusions would require further work including structure refinements and X-ray fluorescence.

Table 3.3: Summary of all minerals found in the 41 total diamonds from the São Luiz locality in Juína, Brazil.

Mineral	Number of Inclusions
ferropericlaase ($\text{Mg}_x\text{Fe}_{1-x}\text{O}$)	31
magnesiowüstite ($\text{Mg}_{1-x}\text{Fe}_x\text{O}$)	21
wüstite FeO	1
magnetite (Fe_3O_4)	9
titanomagnetite $\text{Fe}_{1+x}(\text{Fe}_{2-2x}\text{Ti}_x)\text{O}_4$	16

hematite (Fe_2O_3)	4
titanohematite ($x\text{FeTiO}_3[1-x]\text{Fe}_2\text{O}_3$)	7
olivine ($\text{Mg}_x\text{Fe}_{2-x}\text{SiO}_4$)	8
iron (Fe)	2
goethite (FeOOH)	1
ilmenite (FeTiO_3)	1
garnet ($\text{Fe}_3, \text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$)	2
zircon (ZrSiO_4)	4

3.4.6 Orientation of Ferropericlasite and Magnesio-wüstite Inclusions Relative to the Diamond Host

The orientation matrix of all ferropericlasite and magnesio-wüstite inclusions were obtained from synchrotron single-crystal X-ray diffraction. Nimis et al. (2018) reported the majority of 9 ferropericlasite and magnesio-wüstite inclusions as having cubic crystallographic axes within $3\text{--}8^\circ$ of those of the host diamond. They interpreted the specific crystallographic orientation relationship to imply that these inclusions nucleated during the growth history of the diamond, or syngenetic. Thus, it was of interest for our study to further investigate if any special crystallographic orientation relationships existed between the mineral inclusions and diamond hosts. Two thirds of the 52 the ferropericlasite and magnesio-wüstite inclusions had reliable orientation matrices, used in the following analysis with OrientXplot (Angel et al. 2015a) to calculate and plot the relative

orientations between inclusions and their host (Fig. 3.15). In contrast to the study of Nimis et al. (2018), none of our ferropericlase or magnesiowüstite inclusions fell within 3-8 degrees of those of the host diamond. However, rather than being apparently randomly oriented, all ferropericlase or magnesiowüstite inclusions exhibit $[100]$ axes pointing within the direction contained by $[100]$, $[110]$, and $[111]$ of the diamond host (Fig. 3.16).

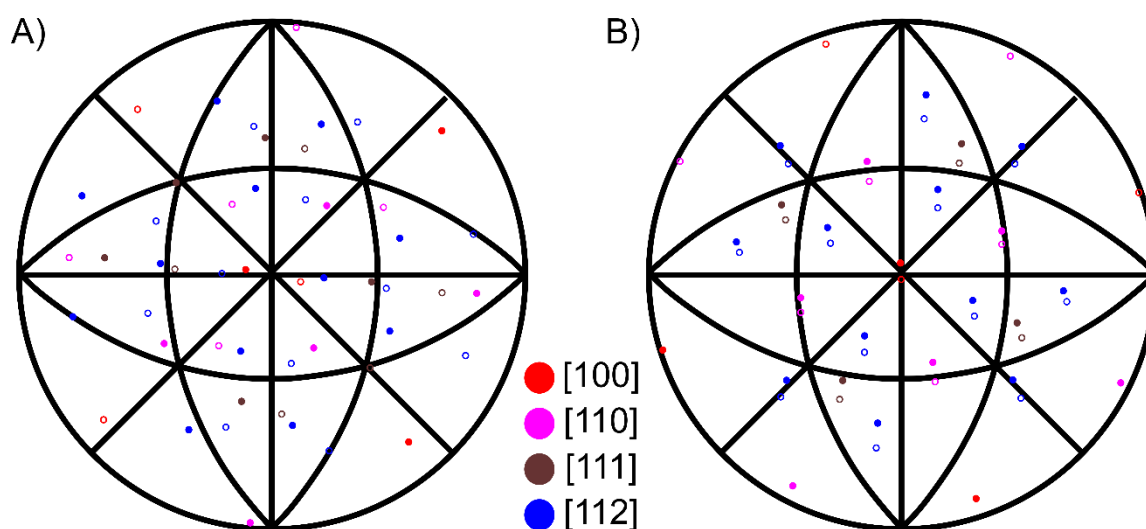


Fig. 3.15: A) A stereographic plot showing the relative orientation of the ferropericlase inclusions with respect to their host diamond with all symmetry operators of each inclusion applied. B) A stereographic plot showing the relative orientation of the magnesiowüstite inclusions with respect to their host diamond with all symmetry operators of each inclusion applied. Open circles represent downward projection. The software OrientXplot calculated the relative orientations between the inclusion and their host (Angel et al., 2015a).

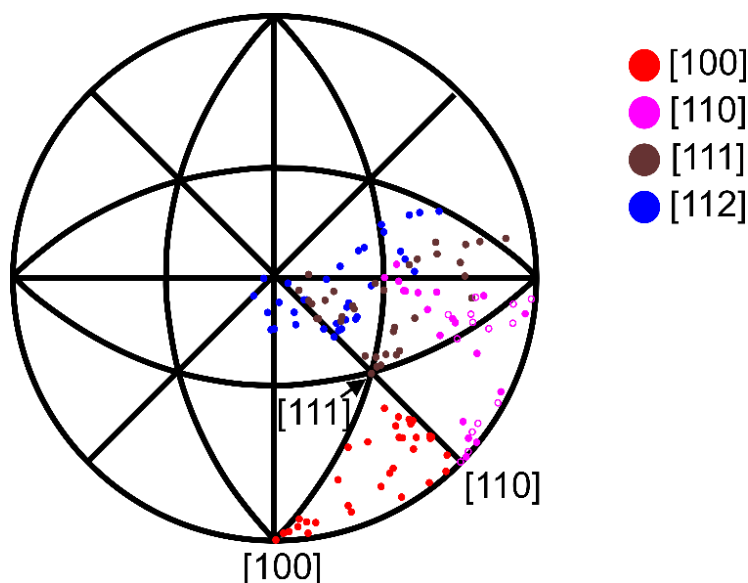


Fig. 3.16: A stereographic plot showing the relative orientation chosen of the ferropericlase and magnesiowüstite inclusions (colored circles) with the a axis of the inclusion in the asymmetric unit of the host, c axis in the upper hemisphere (stereo net with $[100]$, $[110]$, and $[111]$ directions labeled). Open circles represent downward projection. The software OrientXplot calculated the relative orientations between the inclusion and their host (Angel et al., 2015a).

3.4.7 X-ray Fluorescence

X-ray fluorescence spectra were collected on two magnesiowüstite inclusions in diamond 6b06 to determine the elemental composition of the inclusion while it remains encased in diamond. XRF spectra of the olivine inclusions revealed the presence of the following elements: Ti, Cr, Fe, Ni, and Zn (Fig. 3.17). The spectra of each magnesiowüstite inclusion appear nearly identical (Fig. 3.17). Elements present in these spectra agree with typical elements found in inclusions in diamonds from Juína, Brazil (Kagi et al., 2016).

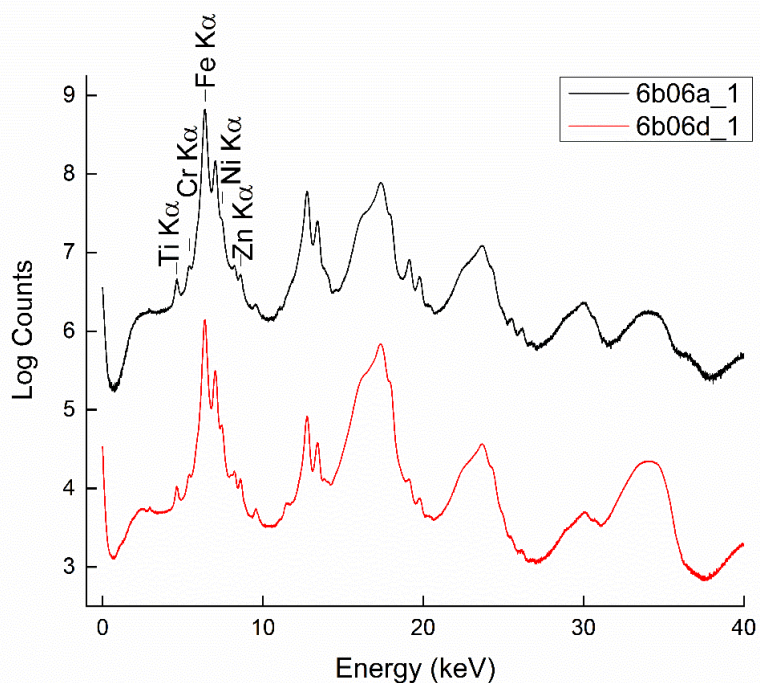


Fig. 3.17: X-ray fluorescence spectrum of the magnesiowüstite inclusions in diamond 6b06.

XRF mapping allowed for a visual representation of the distribution of these elements within the inclusions. Iron was distributed rather homogeneously in inclusion 6b06a, while iron distribution varied in inclusion 6b06b (Fig. 3.18). This varied distribution would contribute to slight changes in lattice parameters depending on the spot that the XRD was collected on the inclusion. XRF mapping on inclusions would be advantageous to future studies focusing on the homogeneity of inclusions as well as more detailed elemental composition of inclusions.

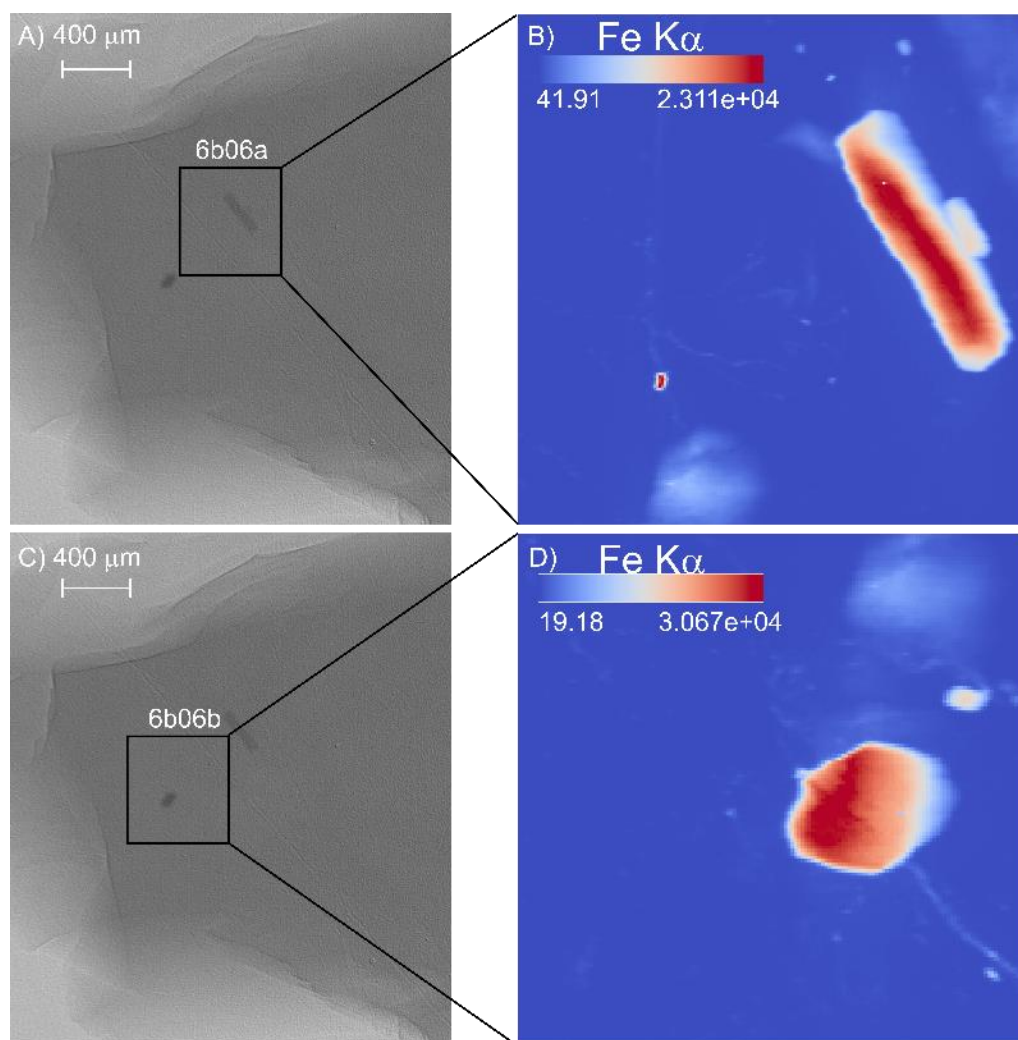


Fig. 3.18: A) Radiograph of diamond 6b06 with inclusion 6b06a highlighted in the black box. B) X-ray fluorescence map of inclusion 6b06a. C) Radiograph of diamond 6b06 with inclusion 6b06b highlighted in the black box. D) X-ray fluorescence map of inclusion 6b06b.

3.5 Conclusions

This study investigated a suite of one hundred and twenty-one diamonds from Juína, Brazil. To our knowledge, this study contained the largest in-situ identification of diamond inclusions. Diamonds in this study contained low amounts of nitrogen, with 60% of the

diamonds considered as Type IIa. Of the diamonds found to contain nitrogen the nitrogen was highly aggregated with B centers (Type IaB), which suggest high temperatures or long mantle residence times. This constituted 36% of all diamonds in this study of which the average total nitrogen content was 36.6 ppm. The majority of the diamonds, ~60%, in this study emitted blue fluorescence with areas of localized green emittance, which indicated multiple optical defects present with the diamonds. These optical defects were observed in the PL spectra, which showed optical defects at 415 nm, 503 nm, 536 nm, 612 nm and 741 nm. All optical defects were consistent with previous studies on Juína diamonds (Yuryeva et. al., 2015). A total of one hundred and seven inclusions in a total of forty-one diamonds were successfully characterized via their lattice parameters, while they remained encased in diamond. The majority of these inclusions, ~ 49%, were ferropericlase and magnesiowüstite. These inclusions displayed some crystallographic preferences and that combined with their intermediate and Fe-rich compositions are thus interpreted to have formed at the same time as the growth of the diamond. Given the range of composition these inclusions likely represent different stages of reactions between the carbonatitic melt and reduced mantle peridotite proposed by Nimis et al., (2018) and Thomson et al., (2016). Future investigations of these diamond suites would include X-ray diffraction on the remaining diamonds, solving some of the more complicated inclusions phases, as well as performing structure refinements and X-ray fluorescence studies to further constrain the exact compositions using in-situ methodology.

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4. Chapter 4

Blue-colored olivine inclusion in diamond: evidence for divalent chromium in the mantle?

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Blue-colored olivine inclusion in diamond: evidence for divalent chromium in the mantle?

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4.1 Abstract

We report the first known blue-colored olivine, found included within a Type IaAB triangular macle (twinned) diamond. The inclusion and diamond host were characterized using X-ray microtomography, FTIR Spectroscopy, single-crystal X-ray diffraction, X-ray fluorescence, photoluminescence spectroscopy, UV fluorescence imaging, Raman spectroscopy, Mössbauer spectroscopy, visible absorption spectroscopy, and X-ray absorption near-edge structure. Based on the tomography results there is no evidence of cracking or infiltration of the kimberlitic magma into the diamond. The composition based on single-crystal X-ray diffraction intensity data is Fo₉₂, and the confining pressure on the inclusion is about 0.2 GPa, which was obtained from the

estimation of inclusions initial unit-cell volume and an appropriate equation of state. Valence states of iron and chromium in the blue inclusion were found to be dominantly Fe^{2+} and Cr^{3+} respectively. UV-VIS absorption spectroscopy and the presence of metallic Fe-Ni alloy within the olivine inclusion suggest trace Cr^{2+} as the possible cause of the blue color.

4.2 Introduction

Diamonds sample the Earth's interior, entrapping mantle minerals as inclusions and transporting them to the surface. Diamond hosts provide a perfect protective environment for these mineral inclusions, due to the chemical inertness and extreme strength of diamond. Mineral inclusions in diamond, whether syngenetic or cogenetic, provide unique samples of the mantle from otherwise unattainable depths, thus containing valuable geochemical information about the conditions of the Earth's dynamic mantle. Within the past decade, significant geochemical discoveries including the first terrestrial occurrence of ringwoodite (Pearson et al., 2014), ice-VIII (Tschauer et al., 2018), and the discovery of CaSiO_3 -perovskite (Nestola et al., 2018).

Olivine group minerals stand out as one of the best studied minerals as these minerals are thought to make up greater than 50% of the Earth's upper mantle and up to 38% of the whole mantle (Ganapathy and Anders, 1974; Ringwood and Kesson, 1977). Olivine group minerals are orthosilicates that have the general chemical formula X_2SiO_4 , where X represents a divalent cation (Mg, Fe, Ca). This study focuses on ferromagnesian olivine, $(\text{Mg,Fe})_2\text{SiO}_4$, which constitutes the majority of the upper mantle (>60%) in a pyrolitic model (Ringwood, 1969; Ringwood and Kesson, 1977). The term olivine throughout the rest of this study refers to an olivine phase along the forsterite (Mg_2SiO_4) - fayalite (Fe_2SiO_4) solid solution series $(\text{Mg,Fe})_2\text{SiO}_4$. Mantle olivine falls within a narrow compositional range close to forsteritic

composition as evidenced by diamond inclusions which bring up olivines with compositions ranging from Fo92 to Fo95 ($X_{Fa} 0.05 - X_{Fa} 0.08$), where the subscript to Fo (forsterite) gives the percent component of forsterite $X_{Fa} 0.05 - X_{Fa} 0.08$ (Meyer and Boyd, 1972).

Olivine is orthorhombic (Space group: Pbnm) and consists of a slightly distorted hexagonal close packed array of oxygen atoms (Smyth et al., 1997; Hazen, 1976). The olivine structure consists of three cation sites: two octahedral sites and one tetrahedral site. Iron and magnesium fractionate over the two non-equivalent octahedral sites M1 and M2. The M2 site is slightly more distorted than M1 and iron fractionates preferentially into the M1 site at high temperatures (Heinemann et al., 2007). The isolated silicate tetrahedra share two edges with M1 octahedra and one edge with M2 octahedra.

The idiochromatic green color of olivine results from the presence of Fe^{2+} ions (Koivula, 1981; Nassau, 1978; White and Keester, 1966). Fe^{2+} contains 6d electrons often considered as a half-filled d^5 shell with one additional electron and is one of the most abundant transition metal ions in minerals. The crystal field splitting of Fe^{2+} in octahedral coordination in olivine is $10,000\text{ cm}^{-1}$ and absorption spectra of olivine feature an intense peak near $10,000\text{ cm}^{-1}$ ($1\text{ }\mu$) which tails out to $\sim 14,200$ ($\sim 0.7\text{ }\mu$) due to Jahn Teller distortions. The green color results from a strong absorption in the NIR range absorbing much of the red, thus transmitting green (Farrell and Newnham, 1965; White and Keester, 1966). The presence of Ni^{2+} is also thought to play a role in the green coloration of olivine, although the extent remains to be determined (Koivula, 1981). Higher abundance of iron leads to a darkening, and oxidation can produce a brown color from the formation of hematite (Filiberto et al., 2020). However, because of their small ($<1\text{ mm}$) size, most olivine inclusions in diamond appear colorless (Tappert and Tappert, 2011).

In this paper we investigate a triangular macle diamond, which contains to our knowledge the first known occurrence of a blue-colored olivine, with the purpose of trying to ascertain why the olivine is blue. The color may be attributed to the presence of reduced Cr (Cr^{2+}), which may lead to new understandings of the conditions under which diamonds form in the mantle. The blue olivine inclusion remained encased in the diamond host for all the measurements conducted in this study to preserve the most geochemical information, requiring non-destructive methods throughout.

4.3 Methodology

4.3.1 Diamond Sample Description

Diamond macles are a type of contact twin, which are an intergrowth of two flattened octahedral crystals connected along an octahedral plane. One crystal is rotated in the contact plane by 180° with respect to the other crystal, resulting in their characteristic triangular shape (Tappert and Tappert, 2011). If two diamond macles are oriented in opposite directions the result is a star-shaped diamond twin. The macle in this study is triangular and edges of the diamond macle measure 4.50 mm X 4.15 mm X 4.07 mm (Fig 4.1.). The diamond contains six visible inclusions: a blue olivine, four colorless olivines, and a purple garnet (Fig. 4.1). The diamond is classified as peridotitic based on its mineral assemblage, along with the characteristic color of the garnet, typical of Cr-rich pyrope (Tapper and Tappert, 2011).

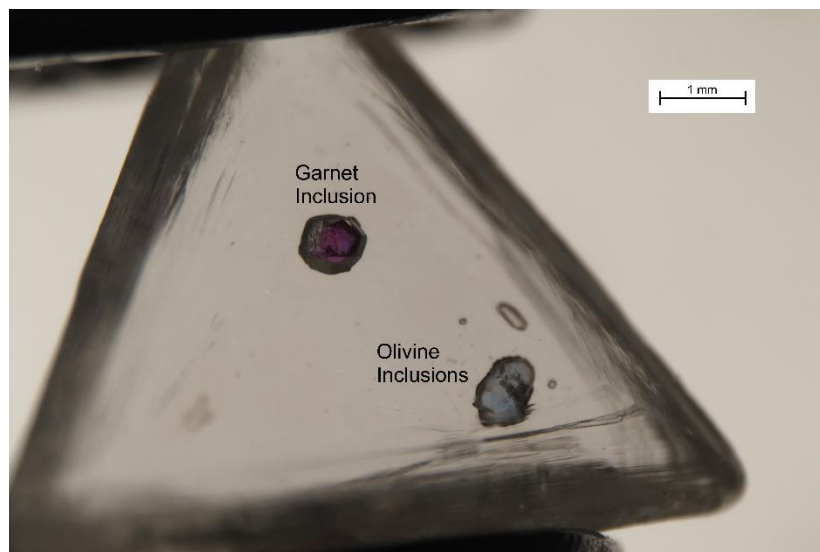


Fig. 4.1: Unpolarized light photomicrograph of the triangular macle diamond. Photo taken at the Gemological Institute of America.

The blue olivine inclusion measures $\sim 456 \mu\text{m}$ X $\sim 296 \mu\text{m}$ and is $\sim 101 \mu\text{m}$ thick by microtomography. Graphite surrounds the edges of the inclusion as well as part of the surface (Fig. 4.2). Four smaller colorless olivine inclusions surround the blue olivine and hereafter are referred to throughout this study as Inc 1 - Inc 4 (Fig. 4.2). Dimensions of all inclusions were obtained from microtomography and are listed in Table 4.1.

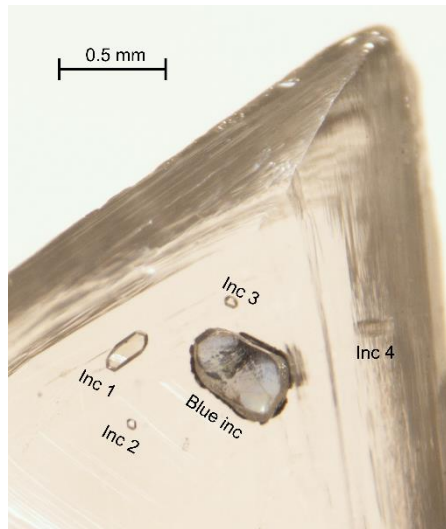


Fig. 4.2: Unpolarized light photomicrograph of all olivine inclusions within the triangular macle diamond. Photo taken at the Gemological Institute of America.

Table 4.1: Dimensions of all inclusions within the triangular macle diamond measured by microtomography. Errors are $\pm .3\mu\text{m}$.

Inclusion	Length (μm)	Height (μm)	Thickness (μm)
Blue inc	456	296	101
Inc1	246	93	100
Inc 2	53	37	36
Inc 3	132	37	83
Inc4	113	74	69
Garnet	436	407	232

Cross-polarized light microscopy reveals strain induced birefringence of the diamond itself (Fig. 4.3), a common feature of most natural diamonds (Seal, 1966; Tolansky, 1966). All olivine inclusions display a range of interference colors, with the most extensive display featured within the blue olivine inclusion (Fig. 4.3).

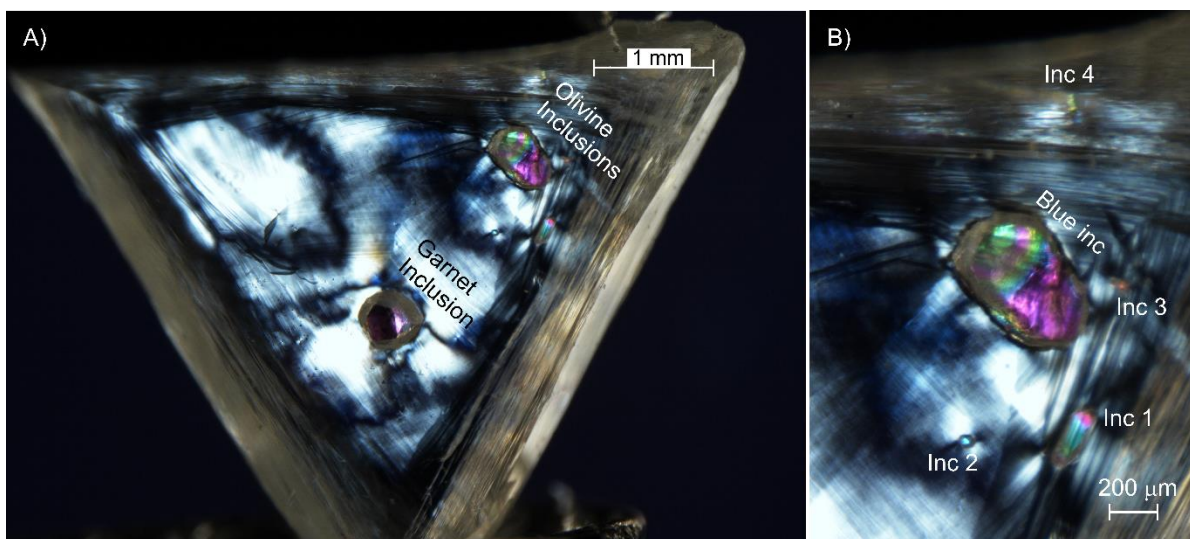


Fig. 4.3: A) Cross-polarized light photomicrograph of the triangular macle diamond showing all mineral inclusions. B) Magnified cross-polarized light photomicrograph showing all olivine inclusions within the triangular macle diamond. The blue olivine inclusion displays a range of interference colors. Photos taken at the Gemological Institute of America.

4.3.2 Olivine Sample Description

Characterization of the olivine inclusions using various non-destructive techniques requires comparison to natural and synthetic olivine samples spanning a range of compositions. Olivine samples were measured for the following non-destructive techniques: X-ray diffraction, X-ray Absorption Near Edge Structure (XANES), and visible absorption spectroscopy. All olivine samples utilized for comparison are described within this section.

Five olivine samples varying in iron composition ($X_{\text{Fa}0}$ - $X_{\text{Fa}0.180}$) were used to calibrate the Xcalibur diffractometer at the Bayerisches Geoinstitut, Germany (Fig. 4.4). Details on this calibration are given in later sections entitled 4.3.6 Conventional X-ray Diffraction and 4.4.4 Conventional X-ray Diffraction of Olivine Samples. These olivine samples are referred to throughout this study as OL 0 - OL 4. All samples are synthetic single crystals except for OL 1, which is a natural single crystal of Lanzarote olivine. The Lanzarote olivine is volcanic in origin.

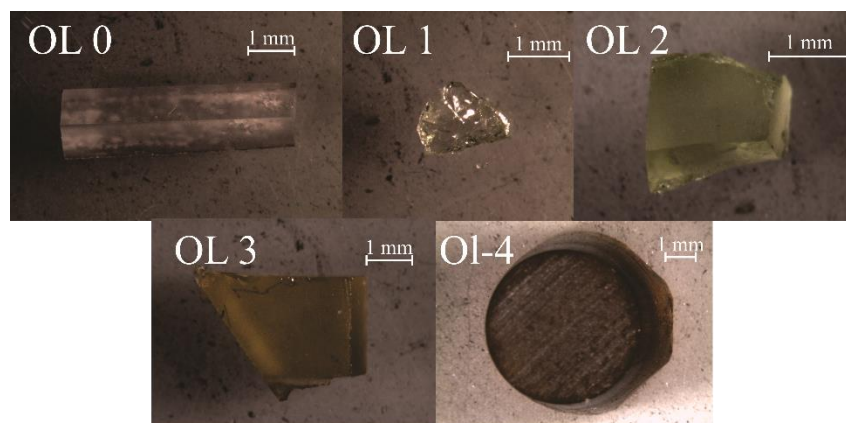


Fig. 4.4: Unpolarized light photomicrograph of all five olivine samples utilized for the calibration of the Xcalibur diffractometer at the Bayerisches Geoinstitut.

Visible absorption spectroscopy measurements included a comparison of the blue olivine inclusion spectra to a synthetic Cr-doped forsterite, synthesized by the Czochralski method (Takei, 1976) at the Cornell Department of Material Sciences. This sample was polished on the 010 plane, duplicating the blue inclusion orientation (Fig. 4.5).

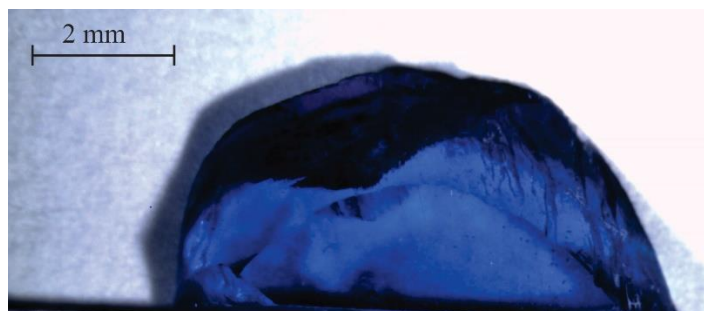


Fig. 4.5: Synthetic Cr-doped forsterite, polished along the 010 plane. Sample thickness is 1.66 mm.

Synthetic olivine and glass rich in Cr^{2+} were utilized for XANES measurements (Bell et al., 2017). Olivines were grown from $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS) liquids under redox conditions (-1.7 iron wüstite oxygen buffer conditions). CMAS glass rich in Cr^{2+} surrounds the Cr^{2+} rich olivine crystals (Fig. 4.6). Cr^{2+} and Cr^{3+} rich glasses, often used as standards for XANES, from Hanson and Jones (1998) were also measured.



Fig. 4.6: Photomicrograph of the synthetic Cr^{2+} rich olivine crystals and surrounding CMAS glass. Sample was obtained from Aaron Bell (Bell et al., 2017).

4.3.3 Synchrotron Microtomography

Synchrotron microtomography was conducted at GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS), beamline 13-BM-D, of the Advanced Photon Source (APS), Argonne National Laboratory, USA. A monochromatic beam with an energy of 19.0 keV was used for data collection. Microtomography data was collected on the triangular macule diamond using a Coolsnap camera. A total of four tomographic data sets were collected each contained 719, 900, 1200, and 1200 projections respectively. These different data sets were collected varying both the magnification as well as the sample to scintillator distance. Pixel size on the sample for the four tomographic data sets consisted of 7.0, 3.5, 1.6, and 1.6 μm respectively.

4.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were collected on a nitrogen cooled Nicolet iN10 infrared microscope at the Gemological Institute of America. The detector was cooled with liquid nitrogen, while the sample stage was purged continuously with dry air. Spectra were collected over the range of 300-6000 cm^{-1} covering the one, two, and three phonon regions of diamond (Breeding and Shigley, 2009). Background spectra and sample measurements were collected over 90 seconds and had a spectral resolution of 1 cm^{-1} . All background spectra automatically were subtracted from the diamond spectra. FTIR spectra were fitted using the computer code DiaMap (Howell et al., 2012).

4.3.5 Electron Microprobe Analysis

The chemical composition of the four Fe-containing olivine samples used for calibration of the Xcalibur diffractometer were measured with a JEOL JXA-8200 electron microprobe operated in WDS mode, using an accelerating voltage of 15 kV and a beam current of 15 nA at the Bayerisches Geoinstitut. The olivine samples were analyzed using a focused beam of 1 μm and a

counting time of 20 seconds for all elements. The concentrations of Si, Mg, Al, Na, Ca, Mn, Ti, Ni, Zn, Fe, and Cr were determined using the following standards: andradite, enstatite, spinel, albite, andradite, manganese titanate, nickel metal, zinc sulfide, iron metal, and chromium metal, respectively. Line segments were measured across all olivine samples.

4.3.6 Conventional X-ray Diffraction

Conventional lab source single-crystal X-ray diffraction measurements were carried out on the triangular macle diamond as well as the five olivine samples. These measurements were performed on an Xcalibur diffractometer equipped with a graphite monochromator, MoK α radiation, and a point source detector at the Bayerisches Geoinstitut. Full reciprocal sphere coverage was obtained with the following data collection settings: operation energy = 50kV/40 mA, $2\theta_{\text{max}}$ = 70 degrees, exposure time = 10 seconds/degree, step size = 0.2 degrees, and a detector distance = 45 mm. Centering of all samples followed standard optical centering protocols. The OL 0 sample was used to calibrate the Xcalibur diffractometer instrument settings by analyzing this same crystal using a Huber four circle diffractometer at the Bayerisches Geoinstitut equipped with MoK α radiation, operated at 50kV and 40 mA with a point source detector. Eight-position centering was employed on the Huber diffractometer for better resolution of the lattice parameters as this method eliminates diffractometer deviations that cause the setting angles of a single reflection to diverge from the “true” angles (Angel et al., 2000). The SINGLE software (Angel et al., 2014a) was used for the eight-position centering procedure as well as the vector-least squares refinement, which resulted in the following lattice parameters for OL 0: $a=4.75472$ (10) Å, $b=10.19512$ (10) Å, and $c= 5.98058$ (12) Å and a unit-cell volume of 289.908 (9) Å³. The

technique of employing two types of diffractometers to measure inclusions in diamond was previously utilized by Nestola et al., (2011a).

Data reduction for all XCalibur diffractometer collections was performed using the CrysAlis package (Oxford Diffraction, 2006). Detector parameters were allowed to refine to match the Huber lattice parameters of OL 0. These detector parameters were then used in data reduction for all the other olivine samples as well as the olivine inclusions (Table 4.2). In CrysAlis, the space group was changed from the crystallographic (*Pnma*) to the mineralogical representation (*Pbnm*). The intensity data set and errors were finalized and used for refinement.

Table. 4.2: Detector parameters used in the CrysAlis package for data reduction (Oxford Diffraction, 2011).

Parameter	Value
d1	0.422
d2	0.268
dd	45.054
x	517.746
y	483.111
om	0.037
th	0.303

ka	0.027
al	49.981
be	-0.029
b2	-0.190

Crystal structure refinements were based on the square of the structure factors (F^2) using the SHELX97 program package (Sheldrick, 2008) in the WingX System (Farrugia, 1999). Two refinement models were generated: one using ionic scattering factors (sfac) and the other using neutral sfac for Mg, Fe, Si, and O. The ionic and neutral sfacs were obtained from The International Tables for Crystallography Volume C (Maslen et al., 2004; Table 6.1.1.4), with the exception of O^{2-} from Tokonami (1965). All atoms were refined anisotropically. The iron versus magnesium content were refined at the M1 and M2 sites with the constraint $X_{Mg} + X_{Fe} = 1$ for each site, whereas Si was considered to fully occupy the tetrahedral site. Reflections with an error/esd value greater than 4 were examined in the CrysAlis package (Oxford Diffraction, 2006) using the hkl feature and were discarded if found to be outliers.

4.3.7 Synchrotron X-ray Diffraction

Synchrotron X-ray diffraction data collections on the triangular macle diamond were performed at GSECARS beamlines 13-ID-D and 13-BM-C of the APS. Single-crystal X-ray diffraction mapping was employed at beamline 13-ID-D using a 37 keV operation energy and a focused beam of 3 μm by 5 μm . An X-ray diffraction map of the blue olivine inclusion, 270 μm X

150 μm , was collected with a 15 second exposure time and step size of 10 μm using the Pilatus 1 M detector. Single-crystal X-ray diffraction was also performed at GSECARS beamline 13-BM-C utilizing the six-circle goniometer and the newly developed 2D-radiography now available for diamond inclusion work (Wenz et al., 2019). This 2D-radiography setup ensured that the inclusions were properly centered in the X-ray diffraction beam, as diamond's high refractive index ($n = 2.4$) complicates typical optical centering methods. Measurements were collected on all inclusions at this beamline with the exception of Inc 2, which proved challenging to center in the radiograph due to the strong diffraction of diamond as a result of the inclusion's position within the triangular macle diamond. Collection parameters consisted of a 1 second/degree exposure time, 340 steps, and a rotation of 340° using the Pilatus 1 M detector. It is not thought that the beam would damage the sample, as the monochromator reduces the synchrotron beam by three orders of magnitude and that combined with the Compton scattering of air and the diamond surrounding the inclusion means the power on the sample would be ~ 1 mW.

4.3.8 μX -ray Fluorescence

μX -ray fluorescence mapping was carried out at beamline 13-ID-E of GSECARS using an X-ray operating energy of 18 keV with a focused beam of 1 μm X 2 μm . X-ray fluorescence was measured with a 4-element Vortex ME4 silicon drift diode detector and Xspress 3 digital X-ray multi-channel analyzer system. Map sizes were 400 μm X 400 μm with a step size of 2 μm and 20 ms of dwell time. X-ray fluorescence maps and spectra were processed with the GSEMapviewer software, which is part of the Larch software package (Newville, 2013).

4.3.9 Photoluminescence Spectroscopy

Photoluminescence spectroscopy measurements were conducted on a Renishaw InVia™ Raman confocal microspectrometer at the Gemological Institute of America. Measurements were made with the following laser excitation energies and corresponding gratings: 325 nm (2400 lines/mm), 488 nm (1800 lines/mm), 514 nm (1800 lines/mm), 633 nm (1800 lines/mm), and 830 nm (2400 lines/mm). Photoluminescence spectra were collected over the range of 327-1000 nm with a collection time of 12 seconds. Spectra were recorded with a Renishaw CCD detector. All spectra were collected on the diamond while immersed at liquid nitrogen temperature (77 K) to improve the intensity and sharpness of any observed peaks.

4.3.10 UV Fluorescence Imaging

Fluorescence images were collected on a DiamondView™ instrument at the Gemological Institute of America. This instrument utilizes ultra-violet radiation to induce fluorescence in diamond. The following collection settings were used: integration time = 5.2 seconds, aperture = 80%, field = 100%, and gain = 21.21 db.

4.3.11 Raman Spectroscopy

Confocal Raman spectroscopy was performed at Northwestern University using a custom-built Raman spectroscopy system. This system is equipped with an Olympus BX microscope, a Mitutoyo 100× objective, and a 458.5 nm Melles-Griot (Model 85-BLS-601) solid-state, diode-pumped laser. Unpolarized Raman spectra were collected in back-scatter geometry through a confocal aperture into a 0.5 m focal-length Andor Shamrock 303i spectrograph with 1200 lines per mm diffraction grating. Spectra were collected on an Andor Newton DU970 CCD camera cooled to -90 °C with a thermoelectric cooler.

4.3.12 Mössbauer Spectroscopy

Mössbauer spectroscopy measurements were carried out at beamline 3-ID of APS using a point source detector (400 μm in diameter). Calibration was done using a Fe foil. Collection time consisted of a total of twelve days for the blue olivine inclusion.

4.3.13 Visible Absorption Spectroscopy

All visible absorption spectroscopy measurements were carried out with a Fourier Transform Bruker IFS 120 HR high resolution spectrometer using a Bruker IR microscope at the Bayerisches Geoinstitut. Tungsten and xenon arc lamp sources were used for all measurements and the spectra were subsequently merged. An aperture of 1.95 mm ensured the collection on a clean part of the blue olivine inclusion. The light source was modulated via a Michelson interferometer with a quartz beam splitter (covered in a dielectric coating). Absorption spectra were obtained after Fourier transformation of the interferogram and subtraction of the background spectrum. Background spectra were obtained by analyzing the light source in air. For the diamond inclusion samples, background measurements were collected on the diamond itself, as the light source must pass through the diamond to analyze the blue olivine inclusion, thus, producing a spectrum associated only with the blue olivine inclusion. The absorption spectrum for all samples ranged from 8,000- 25,000 cm^{-1} . The number of scans varied from 200-2000.

4.3.14 X-ray Absorption Near Edge Structure (XANES) Spectroscopy

Cr *K*-edge XANES data was collected at GSECARS beamline 13-ID-E of the APS. All spectra were acquired in fluorescence mode using a cryogenically cooled Si (111) monochromator coupled with a silicon-drift X-ray detector offset at a 45° angle from the sample. The monochromatic energy was calibrated using metallic Cr foil. XANES spectra were collected over

the range of 5909 eV to 6205 eV. The monochromator energy step was 2.5 eV over the range of 5909 eV to 5979 eV and was decreased to 0.15 eV steps in the range of 5979 eV to 6029 eV. Over the range of 6029 eV to 6205 eV energy steps of 2.0 eV were utilized. A Cr^{2+} and Cr^{3+} glass standards (Hanson and Jones, 1998) and a Cr^{2+} olivine and CMAS glass sample (Bell et al., 2017) were measured for comparison to the olivine inclusions. Spectra were processed with the ATHENA program (Ravel and Newville, 2005) following the methodology laid out in Goodrich et al., (2013), which relies on the intensity of the absorption associated with the 1s-4s electron transition.

4.4 Results

4.4.1 Synchrotron Microtomography

Synchrotron microtomography was used to locate all mineral inclusions within the triangular macle diamond as well as evaluate if any microcracks exist within the diamond itself. Microtomography revealed no evidence of cracking, indicating that all the inclusions within this diamond have not undergone alteration via interaction with kimberlitic magma (Fig. 4.7; Fig. 4.8). Thus, the unique blue color of this olivine is not thought to represent an alteration feature from interaction with kimberlitic magma.

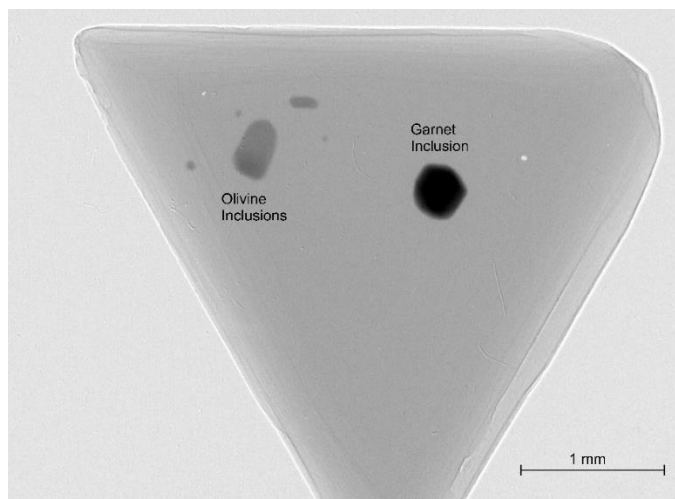


Fig. 4.7: Radiograph of the triangular macle diamond.

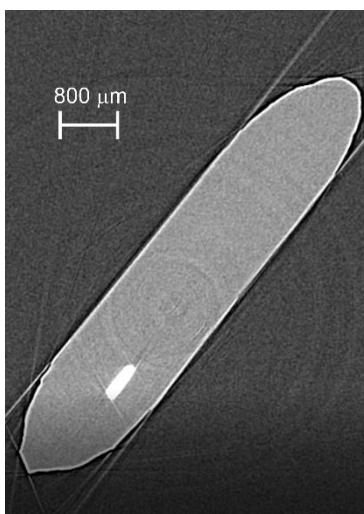


Fig. 4.8: Tomographic slice of the triangular macle diamond showing the blue olivine inclusion. No cracks are evident.

As stated in section 4.3.1 Diamond Sample Description, optical microscopy showed evidence of strain within the diamond. Microtomography further confirms the presence of strain.

If unstrained, the whole triangular macle diamond would satisfy the Bragg diffraction condition and thus, appear entirely dark when it diffracted in the incident beam. However, upon rotation only certain parts of the diamond satisfy the Bragg diffraction condition as a result of strain on the diamond lattice. Thus, dark areas appear to move across the diamond upon rotation (Fig. 4.9). Ultimately, this diffraction does not introduce artifacts in the tomographic reconstruction slices but it is a commonly seen feature in the tomography of diamonds (Rivers et al., 1999).

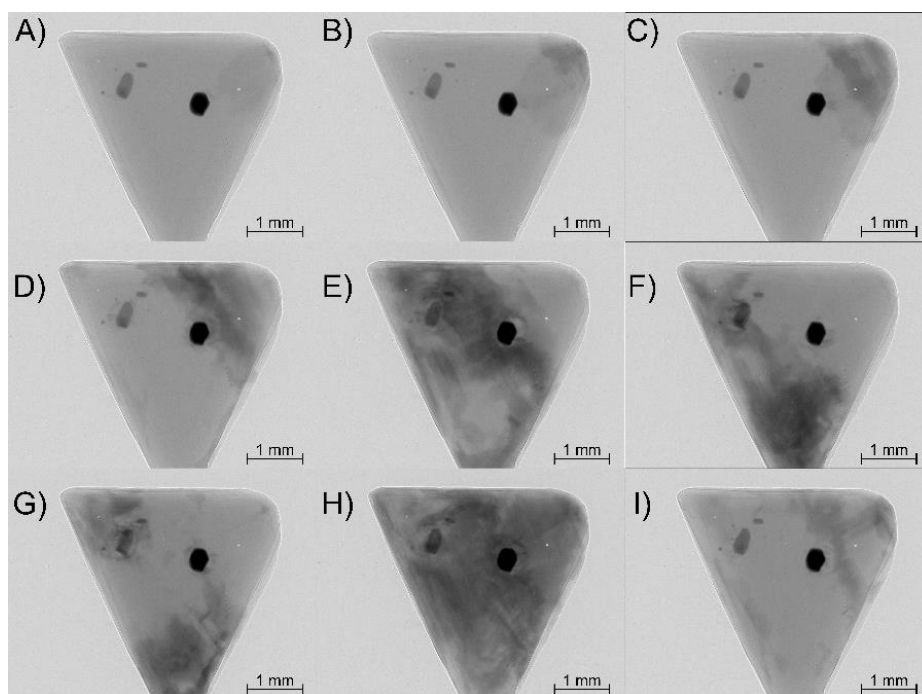


Fig. 4.9: A-I) Radiographs of the triangular macle diamond covering a total of 4.5° . Each image is 0.5° from the previous image. Dark regions are the diffraction of the diamond. As the entire diamond does not diffract at the same time, this indicates that the diamond is strained.

4.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy allows for the detection of impurities within a given diamond, which ultimately determines the classification of the diamond type. Diamond type refers to whether a diamond contains any nitrogen. Type I diamonds contain nitrogen and Type II diamonds contain zero nitrogen according to the gemology world (Breeding and Shigley, 2009). However, the mineralogy world alters this classification system by calling Type II diamonds as diamonds containing less than 20 ppm nitrogen (Araujo et al., 2013). Regardless of this discrepancy in nomenclature, Type II diamonds are considered to not contain enough nitrogen to be detected by FTIR. Type I diamonds are further subdivided into Type Ia and Type Ib. Type Ia diamonds contain aggregated nitrogen impurities, whereas Type Ib contain single nitrogen atoms. Type Ia diamonds are even further subdivided based on how the nitrogen is aggregated, with Type IaA consisting of aggregated nitrogen pairs and Type IaB containing four nitrogens surrounding a vacancy. The degree of nitrogen aggregation depends on temperature and residence times in the mantle (Taylor et al., 1990). Type II diamonds either contain no nitrogen (Type IIa) or contain boron impurities (Type IIb).

FTIR spectroscopy was used to detect impurities within the triangular macle diamond by collecting over the one, two, and three phonon regions of diamond (Breeding and Shigley, 2009). Covering these absorption regions of diamond ensured the detection of any nitrogen, boron, or hydrogen impurities. Nitrogen impurities would appear within the one phonon region, while the two phonon and three phonon regions contain the intrinsic absorption features related to the C-C bonds of the diamond. The three phonon region is the region in which absorption features relating

to boron and hydrogen impurities would appear (Breeding and Shigley, 2009). FTIR spectra of the triangular macle diamond reveal both the presence of nitrogen and hydrogen impurities (Fig. 4.10).

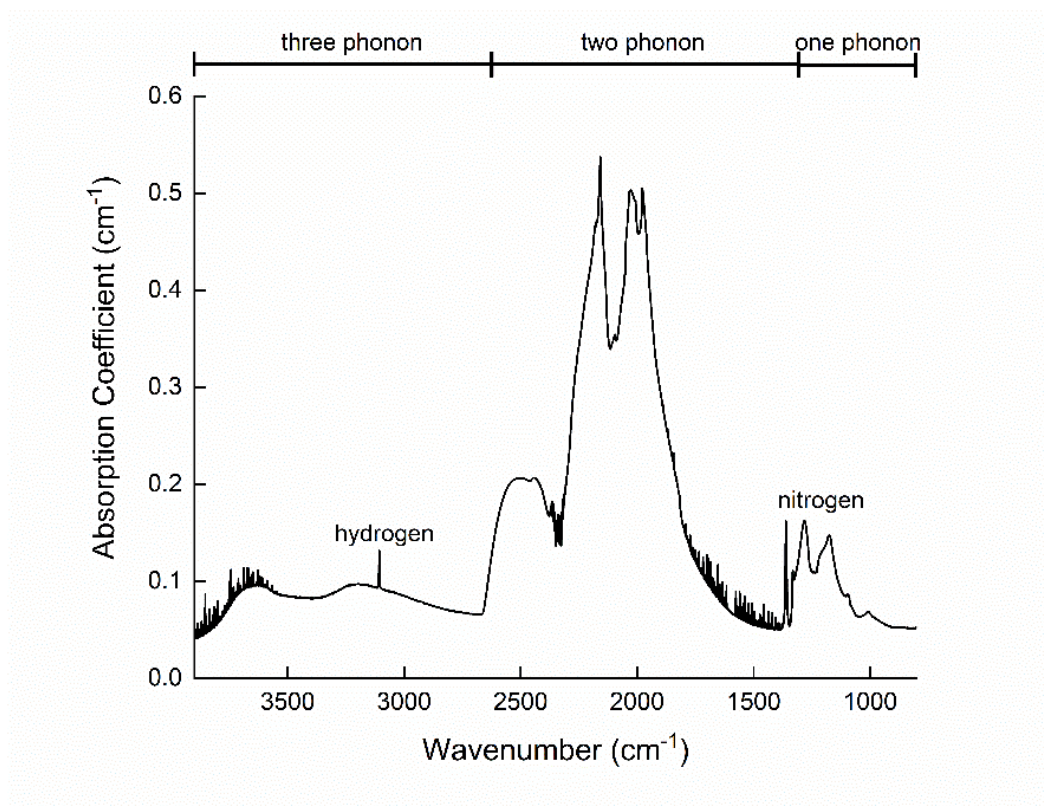


Fig. 4.10: An FTIR absorption spectrum of the triangular macle diamond showing the one, two, and three phonon regions of diamond. Evidence of nitrogen and hydrogen impurities are present.

The one phonon region shows evidence of both A (1087, 1213, and 1278 cm⁻¹) and B (1092, 1173, and 1330 cm⁻¹) aggregated nitrogen defects present within the triangular macle diamond, which is indicative of a type IaAB diamond (Fig. 4.11). The triangular macle diamond contains a total of 91 ppm of nitrogen with 57.6% being type IaB. A small presence of platelets (1371 cm⁻¹) is observed with an area of 4.6 cm⁻², which is common in diamonds that contain aggregated nitrogen (Speich et al., 2018). The presence of the hydrogen impurity absorption

feature (3107 cm^{-1}) is not surprising given that most natural type Ia diamonds display this feature, which is considered a C-H stretching mode (Goss et al., 2014). The presence of A aggregated nitrogen indicates that this diamond likely formed in the upper mantle (Shirey et al., 2013).

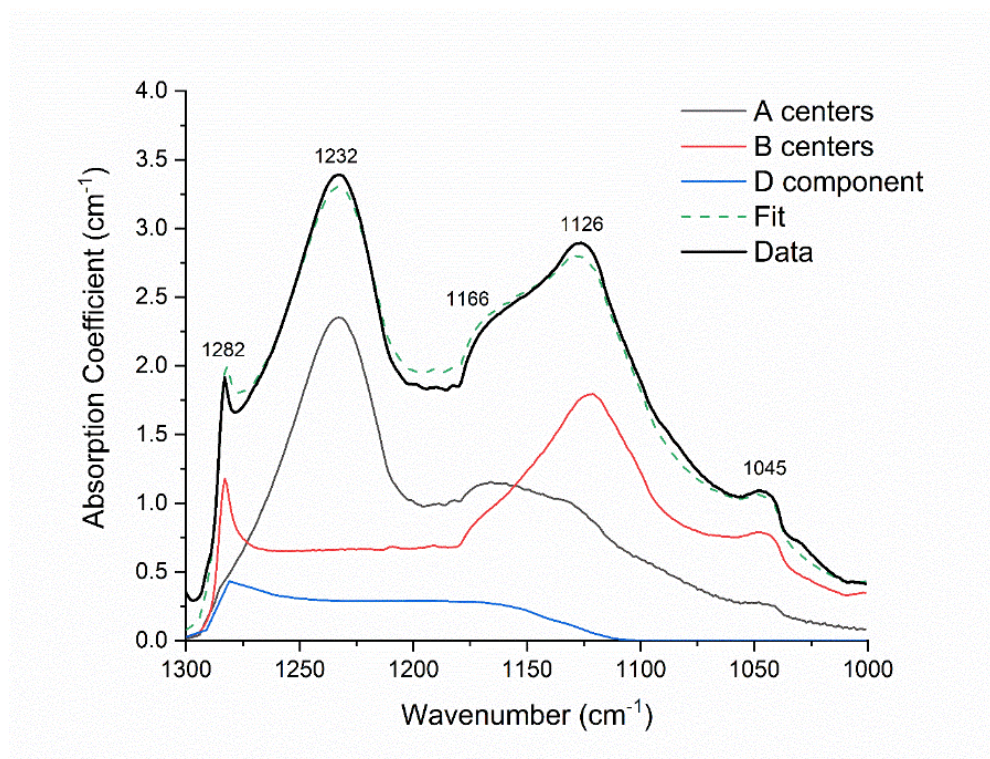


Fig. 4.11: An FTIR spectrum of the one phonon (nitrogen impurity) region of diamond. Grey, red and blue lines show the fit of the nitrogen A and B centers as well as the D component fitted via DiaMap (Howell et al., 2012). The black line represents the overall fit to the data.

4.4.3 Electron Microprobe Analysis (EMPA)

EMPA was performed on all four iron containing olivine samples so as to measure their chemical compositions. EMPA collections along the line segments revealed the samples as homogeneous. Iron contents of the four samples varied between 0.168 (2) and 0.360 (22) atoms per formula unit (a.p.f.u.). All EMPA results are provided in Table 4.3.

Table 4.3: EMPA data of the four iron containing olivine samples given in average oxide wt. %, a.p.f.u, and mole fraction of fayalite (X_{fa}).

Sample	OL 1	OL 2	OL 3	OL 4
SiO ₂	40.07 (0.23)	39.86 (0.18)	39.91 (0.18)	38.48 (0.27)
FeO	8.25 (0.15)	8.80 (0.09)	8.70 (1.04)	16.98 (1.56)
MgO	51.51 (0.16)	50.87 (0.15)	51.48 (0.87)	44.76 (1.23)
Total	100.49 (0.38)	100.20 (0.34)	100.17 (0.22)	100.25 (0.28)
a.p.f.u				
Si	0.975 (8)	0.975 (6)	0.974 (7)	0.975 (11)
Fe	0.168 (2)	0.180 (1)	0.178 (14)	0.360 (22)
Mg	1.868 (4)	1.855 (3)	1.873 (21)	1.689 (26)
X_{fa}	0.084 (2)	0.090 (2)	0.089 (7)	0.180 (10)

4.4.4 Conventional X-ray Diffraction of Olivine Samples

Single crystal X-ray diffraction measurements were carried out on five olivine samples of known composition (composition determined via EMPA). The purpose of collecting on these samples was to calibrate the Xcalibur diffractometer at the Bayerisches GeoInstitut in a way such that given any olivine measured on that diffractometer, following the same structure refinement protocols, a reliable composition of that sample could be obtained. The unit-cell parameters from the single crystal X-ray diffraction of the five olivine samples are shown in Table 4.4.

Table 4.4: Unit-cell parameters of the five olivine samples with 1 σ errors.

Sample	a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)	V ($\text{\AA}^3$)
OL O	4.75597 (13)	10.19100 (3)	5.98020 (2)	289.850 (15)
OL 1	4.76153 (13)	10.22910 (3)	5.91205 (15)	291.811 (14)
OL 2	4.76229 (12)	10.22240 (3)	5.90180 (14)	291.615 (12)
OL 3	4.77114 (17)	10.24770 (3)	5.99980 (2)	293.348 (17)
OL 4	4.76764 (16)	10.24750 (3)	5.99958 (18)	293.119 (16)

Structural refinements were subsequently performed on all olivine samples using both ionic and neutral sfacs as described in the previous section entitled 4.3.6 Conventional X-ray Diffraction. Refinements using the two sets of sfacs resulted in similar values (Table 4.5).

Table. 4.5: X_{Fa} of all olivine samples using both ionic and neutral sfacs with 1 σ errors.

Sample	Ionic (X_{Fa})	Neutral (X_{Fa})
OL0	1.0	1.0
OL1	0.90728 (14)	0.91971 (15)
OL2	0.89909 (14)	0.899745 (15)
OL3	0.87105 (15)	0.89064 (15)
OL4	0.80363 (16)	0.82538 (16)

According to Nestola et al., (2011a), Fe and Mg occupancies in olivine are better constrained by ionic sfacs. Therefore, all data in this study refer to refinements with ionic sfacs. The R_{int} values of the refinements ranged from 0.024- 0.036. Figure 4.12 shows how well the mole fraction of fayalite (X_{Fa}) obtained from the structure refinement model compares to that obtained from the electron microprobe data.

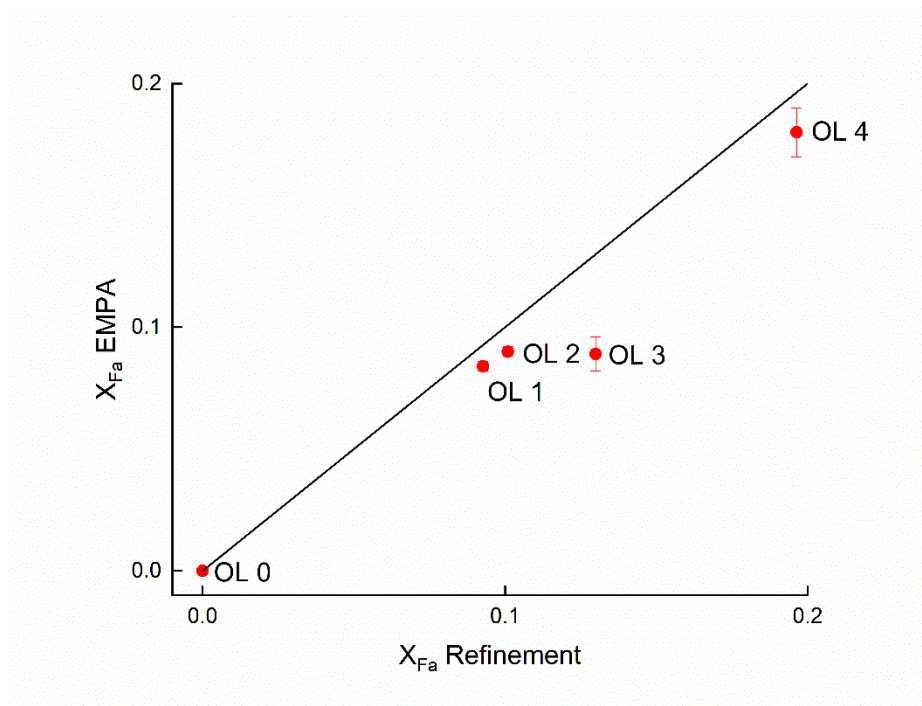


Figure 4.12: Comparison of the X_{Fa} results of the five olivines from microprobe to that from structure refinement. The black line is a 1:1 reference line.

Structure refinement compositions resulted in higher iron contents for most olivine samples compared to the composition obtained from the microprobe. OL 1, OL 2, and OL 4 form a linear relationship and are thought to result from minor and trace elements refining as iron in Shelx. Only

Mg and Fe are refined in the crystal structure model, so other elements like Cr, Mn, and Ni refined as the heavier Fe atom, resulting in slightly higher abundance of Fe than the chemical analysis.

An example of an olivine structure obtained from refinement is shown in Figure 4.13. The Mg and Fe were allowed to fractionate between the M1 (orange) and M2 sites (green) in the structure refinement for each Fe-bearing olivine.

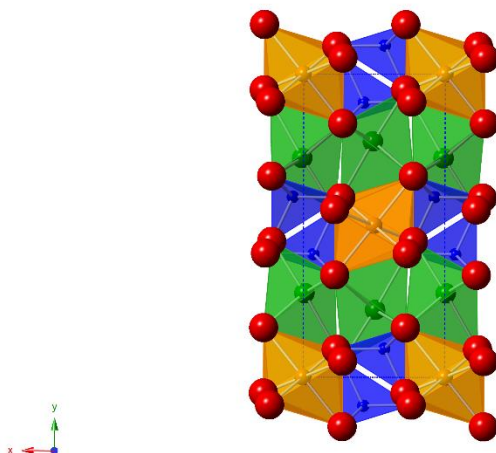


Figure 4.13: OL 0 crystal structure from refinement. Orange, green, and blue polyhedral represent the M1, M2, and Si sites, respectively. Red spheres represent O atoms. The M2 site is the most distorted octahedral site. The dashed rectangle is the unit-cell. Images were generated using CrystalMaker® Software Ltd. Oxford England.

To investigate the ordering of the five olivine samples the long range order parameter (Q) was calculated using equation 4.1 (Table 4.6).

$$Q = (X_{\text{Fe}}^{\text{M1}} - X_{\text{Fe}}^{\text{M2}}) / \sum Fe \quad \text{Eq. [4.1]}$$

Table 4.6: Long range order parameters, Q, for the olivine samples.

Sample	Q
OL0	0
OL1	0.079163
OL2	0.041673
OL3	0.067016
OL4	0.054642

The values of Q ranged from 0 to 0.08 and thus, the olivine samples in this study indicate that Fe is fractionating slightly more into the M1 site. This preference of Fe for the M1 site over the M2 site is characteristic for olivines formed at high temperatures (Heinemann et al., 2007). The OL 1 sample is the most anti-ordered with a Q value of 0.08. Ol 1 originates from a volcanic setting (high temperature, fast cooling), which is consistent with the preference of Fe for the M1 site at high temperatures (Heinemann et al., 2006).

4.4.5 Conventional X-ray Diffraction of Olivine Inclusions

The single crystal diffraction of the olivine inclusions was collected and refined in the same way as the prior five olivine samples. It is important to note that the blue inclusion was found to be twinned with the following twinning law, $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$. The resulting lattice parameters are given in Table 4.7.

Table 4.7: Blue olivine inclusion unit-cell dimensions with 1σ errors.

Sample	a (Å)	b (Å)	c (Å)	V (Å ³)
Inc. 1	4.7698 (8)	10.2140 (2)	5.9841 (15)	291.54 (1)
Inc. 2	4.7573 (8)	10.1920 (3)	5.9844 (11)	290.17 (12)
Inc. 3	4.7667 (8)	10.2260 (3)	5.9817 (11)	291.96 (11)
Blue Inc	4.7607 (3)	10.2161 (5)	5.9901 (5)	291.34 (3)

Inclusion 2 has the smallest volume observed, which could be explained by two scenarios. Scenario one, perhaps this inclusion formed at a greater depth. Another more likely scenario suggests that the volume might not be well constrained due to the interference of the diamond in the diffraction collection, which results from the crystal position with respect to the diamond. Some planes such as plane *bc* were more affected than other planes such as *ac* (Fig. 4.14). This latter reason is the most likely scenario as further study at APS revealed that diamond diffraction strongly interferes with this inclusion as it only is visible in radiographs at 0° and 180° . In between 0° and 180° diamond diffraction blocks the visibility of the inclusion in the radiography and thus, precludes reliable centering in the X-ray diffraction beam.

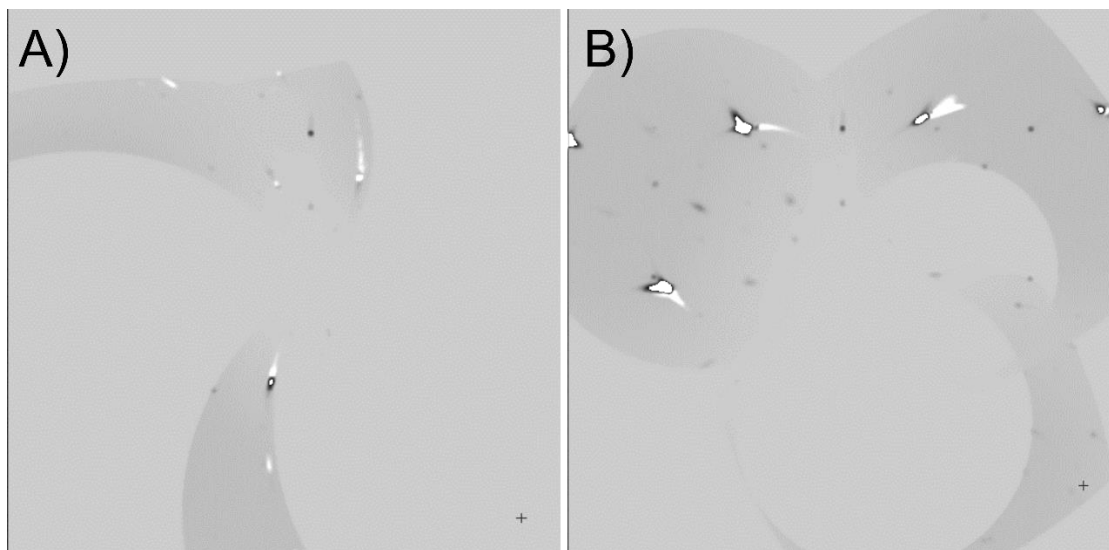


Figure 4.14: Reconstructed precession photographs made using the CrysAlis package (Oxford Diffraction, 2006). A) *bc* plane for Inc 2 B) The *ac* plane for Inc 2. There is a difference in XRD 2θ coverage in these two planes due to diamond interference.

Details on the structure refinements performed on all inclusions reported in Tables 4.8 - 4.15. The R_{int} of the inclusions ranged from (0.017-0.085).

Table 4.8: Atomic coordinates of the blue olivine inclusion.

Atom	Wyckoff	X	Y	Z
Si	8d	0.42958(12)	0.09422(6)	0.25(0)
Mg(M1)	4a	0	0	0
Fe(M1)	4a	0	0	0
Mg(M2)	8d	0.99021(14)	0.27767(7)	0.25(0)
Fe(M2)	8d	0.99021(14)	0.27767(7)	0.25(0)
O1	8d	0.76623(34)	0.09148(15)	0.25(0)
O2	8d	0.22034(32)	0.44765(15)	0.25(0)
O3	8d	0.27787(23)	0.16316(11)	0.03338(2)

Table 4.9: Displacement parameters of the blue olivine inclusion.

Atom	U11	U22	U33	U23	U13	U12	Ueq
Si	0.00333(28)	0.00777(27)	0.00860(31)	0	0	0.00030	0.00657(19)
Mg(M1)	0.00516(33)	0.01100(34)	0.00974(39)	-0.00091(29)	-0.00070(21)	-0.00008(2)	0.00863(23)
Fe(M1)	0.00516(33)	0.01100(34)	0.00974(39)	-0.00091(29)	-0.00070(21)	-0.00008(2)	0.00863(23)
Mg(M2)	0.006448(35)	0.00827(34)	0.01043(39)	0.	0	-0.00003(2)	0.00839(24)
Fe(M2)	0.006448(35)	0.00827(34)	0.01043(39)	0.	0	-0.00003(2)	0.00839(24)
O1	0.00388(55)	0.00979(62)	0.01019(67)	0	0	0.00031(45)	0.00795(3)
O2	0.00575(56)	0.00849(57)	0.01003(65)	0	0	0.00050(47)	0.00809(29)
O3	0.00528(42)	0.01006(43)	0.01038(48)	0.00132(38)	-0.00018(36)	0.00032(32)	0.0087(24)

Table 4.10: Atomic coordinates of Inc 1.

Atom	Wyckoff	X	Y	Z
Si	8d	0.42650(14)	0.09425(8)	0.25(0)
Mg(M1)	4a	0	0	0
Fe(M1)	4a	0	0	0
Mg(M2)	8d	0.99043(17)	0.27756(9)	0.25(0)
Fe(M2)	8d	0.99043(17)	0.27756(9)	0.25(0)
O1	8d	0.76667(42)	0.09180(19)	0.25(0)
O2	8d	0.22070(34)	0.44757(19)	0.25(0)
O3	8d	0.27842(24)	0.16325(15)	0.03359(23)

Table 4.11: Displacement parameters of Inc 1.

Atom	U11	U22	U33	U23	U13	U12	Ueq
Si	0.00669(41)	0.00395(91)	0.00687(5)	0	0	0.00002(2)	0.00584(3)
Mg(M1)	0.00934(5)	0.00787(55)	0.01002(55)	-0.00104(33)	-0.00081(25)	0.00003(24)	0.00908(34)
Fe(M1)	0.00934(5)	0.00787(55)	0.01002(55)	-0.00104(33)	-0.00081(25)	0.00003(24)	0.00908(34)
Mg(M2)	0.01029(51)	0.00447(59)	0.00931(54)	0.	0	0.00013(25)	0.00802(34)
Fe(M2)	0.01029(51)	0.00447(59)	0.00931(54)	0.	0	0.00013(25)	0.00802(34)
O1	0.00787(79)	0.00793(109)	0.00790(98)	0	0	-0.00089(54)	0.00790(46)
O2	0.00868(71)	0.00611(105)	0.00726(93)	0	0	-0.00048(61)	0.00735(43)
O3	0.00816(63)	0.00716(71)	0.00790(69)	0.00104(45)	0.00019(44)	0.00076(41)	0.00774(36)

Table 4.12: Atomic coordinates of Inc 2.

Atom	Wyckoff	X	Y	Z
Si	8d	0.42643(2)	0.09429(15)	0.25(0)
Mg(M1)	4a	0	0	0
Fe(M1)	4a	0	0	0
Mg(M2)	8d	0.99021(23)	0.27774(16)	0.45951(132)
Fe(M2)	8d	0.99021(23)	0.27774(16)	0.45951(132)
O1	8d	0.76580(57)	0.09163(39)	0.5(0)
O2	8d	0.22037(48)	0.44788(4)	0.5(0)
O3	8d	0.27809(34)	0.16351(28)	1.0(0)

Table 4.13: Displacement parameters of Inc 2.

Atom	U11	U22	U33	U23	U13	U12	Ueq
Si	0.00529(5)	0.01275(91)	0.00910(53)	0	0	0.0016(38)	0.00905(4)
Mg(M1)	0.00721(64)	0.01326(104)	0.01064(58)	-0.00025(57)	-0.00081(28)	0.00044(49)	0.01037(45)
Fe(M1)	0.00721(64)	0.01326(104)	0.01064(58)	-0.00025(57)	-0.00081(28)	0.00044(49)	0.01037(45)
Mg(M2)	0.00865(64)	0.01040(113)	0.01042(58)	0.	0	0.00015(41)	0.00982(47)
Fe(M2)	0.00865(64)	0.01040(113)	0.01042(58)	0.	0	0.00015(41)	0.00982(47)
O1	0.00576(103)	0.01390 (237)	0.01072(113)	0.	0	0.00091(95)	0.01013(76)
O2	0.00639(107)	0.01346(235)	0.01127(111)	0.	0	0.00299(101)	0.01038(76)
O3	0.00672(85)	0.01355(171)	0.01178(83)	0.00057 (96)	-0.00131(51)	0.00029(8)	0.01069(59)

Table 4.14: Atomic coordinates of Inc 3.

Atom	Wyckoff	X	Y	Z
Si	8d	0.42649(15)	0.09421(7)	0.25(0)
Mg(M1)	4a	0	0	0
Fe(M1)	4a	0	0	0
Mg(M2)	8d	0.99030(17)	0.27756(11)	0.25(0)
Fe(M2)	8d	0.99030(17)	0.27756(11)	0.25(0)
O1	8d	0.76519(43)	0.0915(2)	0.25(0)
O2	8d	0.22147(37)	0.44753(4)	0.25(0)
O3	8d	0.27845(26)	0.16373(15)	0.03320(21)

Table 4.15: Displacement parameters of Inc 3.

Atom	U11	U22	U33	U23	U13	U12	Ueq
Si	0.00203(51)	0.00956(63)	0.01228(51)	0	0	0.00005(22)	0.00796(39)
Mg(M1)	0.00407(59)	0.012878(68)	0.01461 (55)	-0.00156(31)	-0.00056(24)	0.00022(23)	0.01049 (41)
Fe(M1)	0.00407(59)	0.012878(68)	0.01461 (55)	-0.00156(31)	-0.00056(24)	0.00022(23)	0.01049 (41)
Mg(M2)	0.00544(57)	0.01056(7)	0.01482 (56)	0.	0	0.00038(27)	0.01027(41)
Fe(M2)	0.00544(57)	0.01056(7)	0.01482 (56)	0.	0	0.00038(27)	0.01027(41)
O1	0.00231(8)	0.01249 (128)	0.01337(79)	0.	0	-0.0002(54)	0.00939(52)
O2	0.00490(78)	0.00929(123)	0.01467(78)	0.	0	-0.00124(67)	0.00962(5)
O3	0.00310(72)	0.01111(88)	0.01360(67)	0.00131 (42)	-0.00045(38)	0.00092(42)	0.00927(44)

Composition of the olivine inclusions fall within a narrow range, X_{Fa} 0.08 – X_{Fa} 0.98 (Table 4.16 and Fig. 4.15). These compositions agree with olivine inclusions in other studies, which range from X_{Fa} 0.5 – X_{Fa} 0.8 (Meyer and Svisero, 1975; Meyer and Boyd, 1972).

Table 4.16: Inclusion compositions represented as mole fraction of fayalite, X_{Fa} .

Inclusion	X_{Fa}
Blue inc	0.080735 (22)
Inc 1	0.09226 (18)
Inc 2	0.083665 (19)
Inc 3	0.097870 (18)

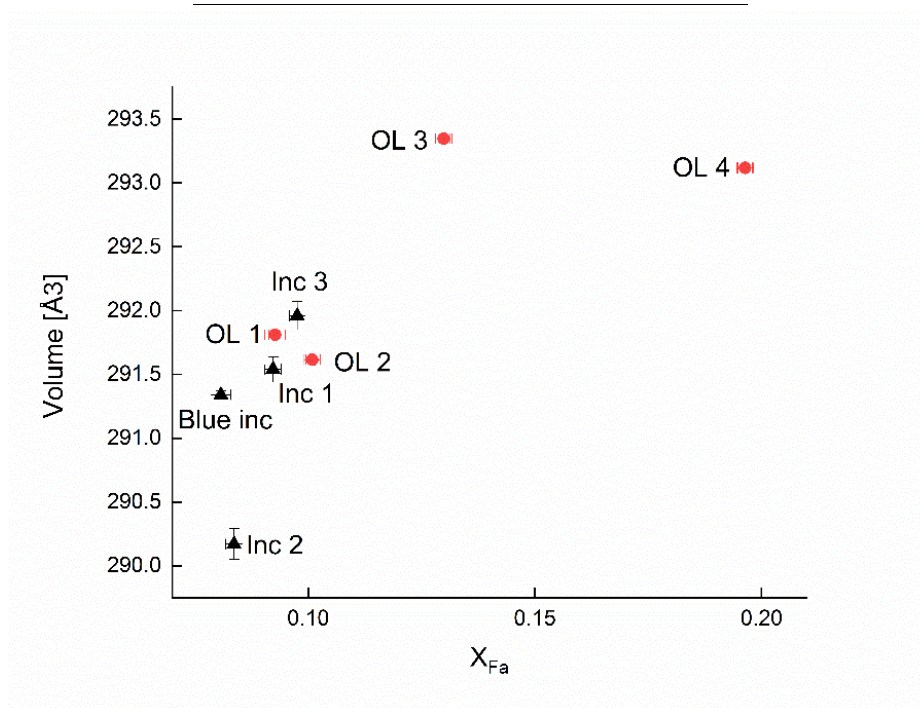


Fig. 4.15: Inclusion compositions represented as mole fraction of fayalite, X_{Fa} . Red circles represent olivine samples and black triangles represent olivine inclusions.

Long range order parameters for the inclusions, calculated in the same manner as discussed in the section entitled 4.4.4 Conventional X-ray Diffraction of Olivine Samples, are reported in Table 4.17. Once again, a slight preference of the Fe for the M1 site is observed (Fig. 4.16) suggesting high temperature formation, which agrees with the formation of these olivine inclusion in the upper mantle (Heinemann et al., 2006).

Table 4.17: Long range order parameters for the inclusions.

Inclusion	Q
Blue Inc	0.01207655
Inc 1	0.03940003
Inc 2	0.03149465
Inc 3	-0.01169979

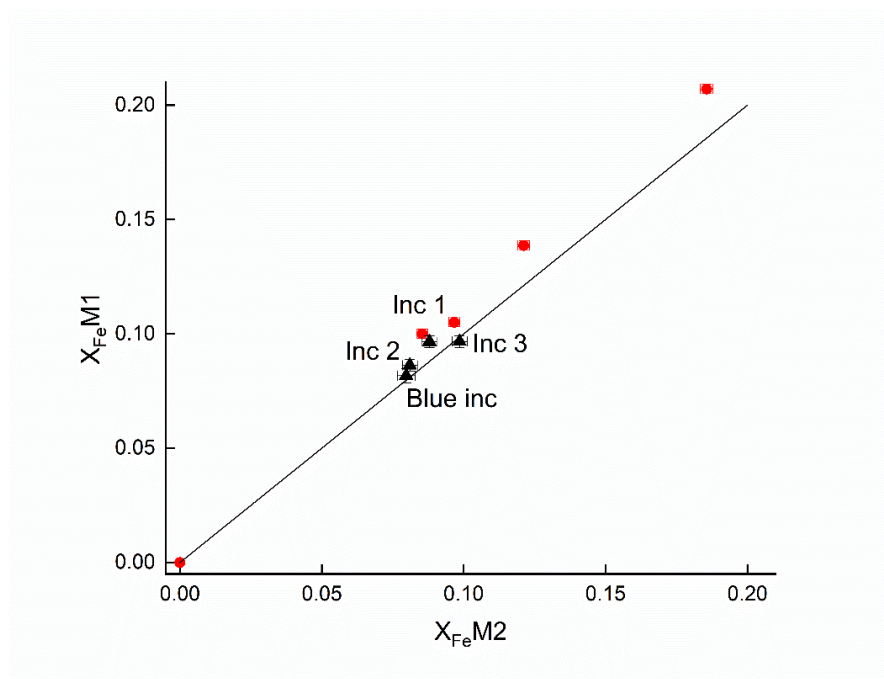


Figure 4.16: Amount of Fe in M1 site versus the amount of Fe in the M2 site. The black line is a 1:1 line. There is a slight preference of Fe in the M1 site suggesting these olivines formed at high temperatures.

4.4.6 Calculating the Current Pressure on the Inclusions

All olivine inclusions in this study remain encased in the diamond, thus these inclusions are ultimately constrained by the diamond host. Such constraints mean that the pressure, volume, and temperature relationship expected of a free crystal do not apply. Diamond is extremely stiff with a bulk modulus of 444 GPa (Angel et al., 2015), which means that an inclusion enclosed in diamond will be unable to relax to its atmospheric volume. Therefore, while the host diamond sits at atmospheric conditions its inclusions actually remain under some pressure (P_{inc}), unless this pressure is released via a crack in the diamond (Angel et al., 2015). As stated in the section entitled

4.4.1 Synchrotron Microtomography, the triangular macle diamond exhibits no evidence of cracking, which means that all of the inclusions remain under some pressure.

Calculating the P_{inc} of an inclusion requires an initial volume of the inclusion; the volume if the inclusion were at atmospheric pressure. From the single crystal X-ray diffraction, a volume for each inclusion was obtained, however these volumes represent the volume of the inclusion under some pressure. Back calculations of what the volume would be if the inclusion was under atmospheric pressure require a reliable relationship between the unit-cell volume as a function of iron content. Previous studies examined the variation of the unit-cell volume as a function of fayalite composition (Schwab and Küstner, 1977). This data ranged in composition from $X_{Fa} 0 - X_{Fa} 1$, with a second order polynomial fit to the data (Fig. 4.17) (Schwab and Küstner, 1977). Unfortunately, a region of scatter appears in the Schwab and Küstner (1977) data, which corresponds to where the composition of the inclusions in this study lie. The scatter is not appropriately fit by the polynomial, therefore use of this polynomial in pressure calculations would result in a P_{inc} of 0 for all inclusions. Thus, indicating a cracked diamond that released pressure.

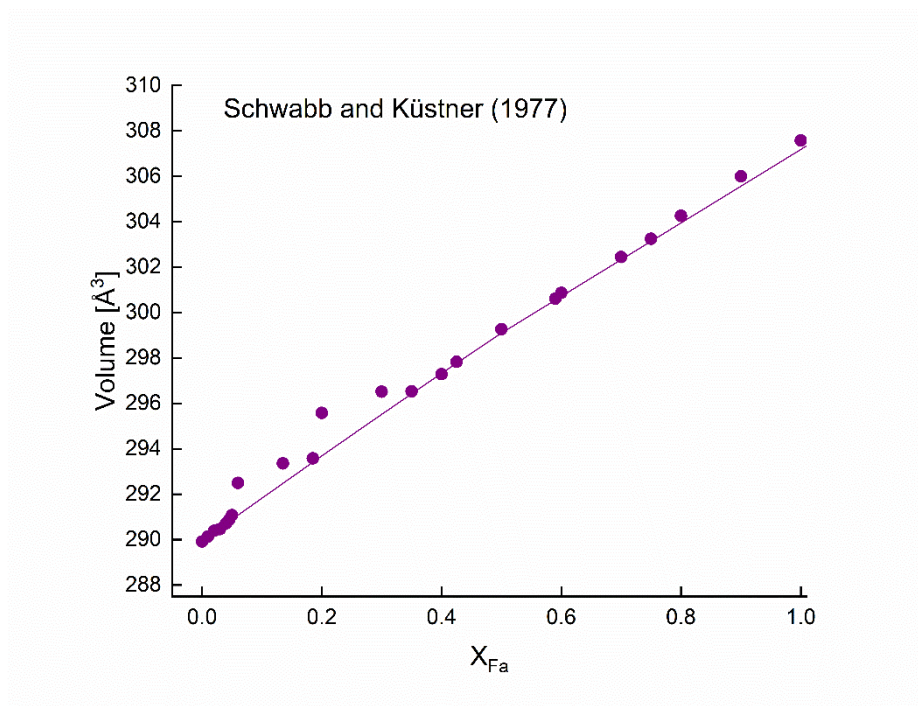


Figure 4.17: Volume as a function of X_{Fa} . Purple circles are the full data set from Schwab and Küstner (1977). The purple line is the second order polynomial fit of Schwab and Küstner (1977) data.

As mentioned in section 4.4.1 Synchrotron Microtomography 4.3.1, no evidence of cracking appears in the diamond so to address this issue, the unit-cell volume of the five olivine samples of this study were plotted together with the Schwab and Küstner (1977) data (Fig. 4.18). The olivine samples show a similar scatter as the data reported by Schwab and Küstner (1977). This scatter may result from the distribution of Fe between the M1 and M2 sites of the olivine structure, however there is no direct correlation between the degree of order and the deviation from the trend reported by Schwab and Küstner (1977) and thus the scatter cannot be caused only by Mg and Fe ordering.

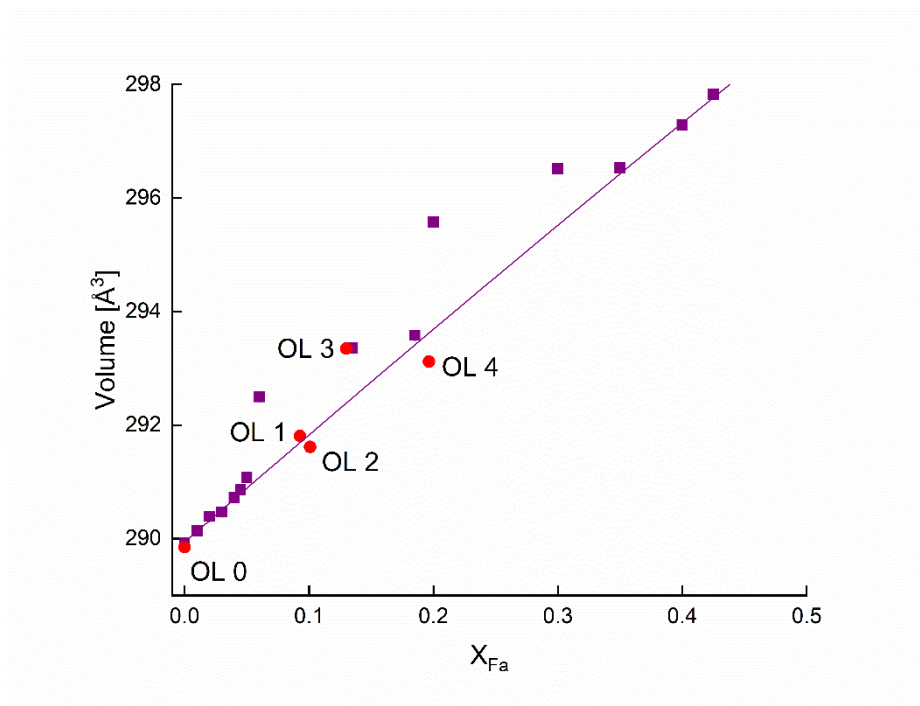


Figure 4.18: Volume as a function of X_{Fa} . Purple circles are data from Schwab and Küstner (1977). The purple line is the second order polynomial that Schwab and Küstner (1977) fit to their data. Red circles are the five olivine samples from this study.

To constrain the area of interest, data from Schwab and Küstner (1977), along with those of the five olivine samples of this study, were fitted with a second order polynomial over the range of X_{Fa} 0 - X_{Fa} 0.5 (Fig. 4.19). A second order polynomial resulted in a slightly better fit to the scattered data and a better R^2 value (eq. 4.2). An F-test would need to be performed to determine whether the fit is statistically significant. All olivine inclusions fall below the new fit, meaning they remain under some pressure.

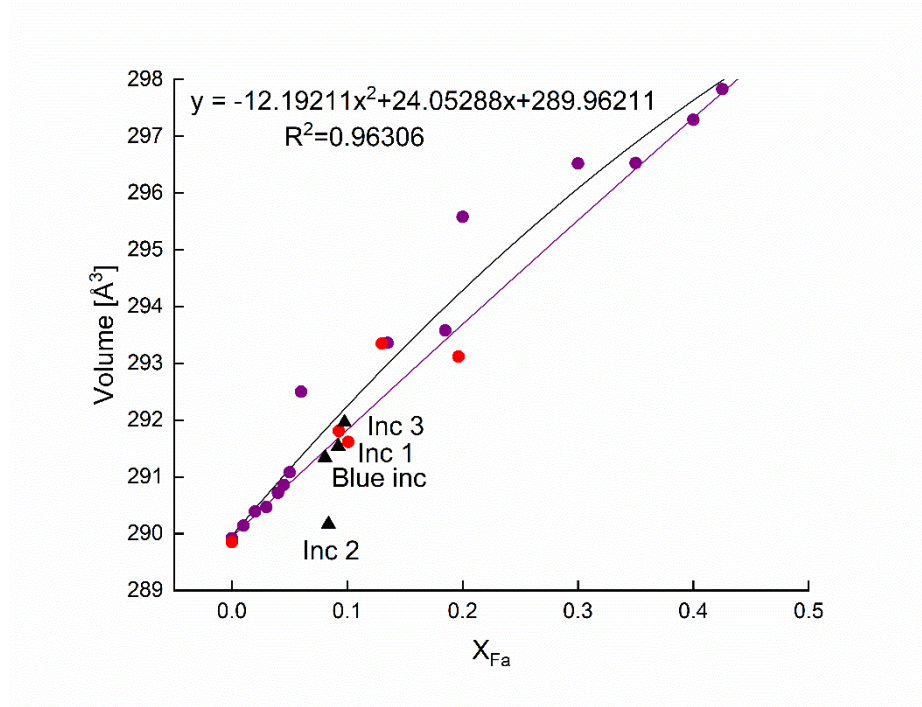


Figure 4.19: Volume as a function of X_{Fa} . Purple circles are data from Schwab and Küstner (1977) and the red circles are the five olivine samples from this study. The purple line is the Second order polynomial of Schwab and Küstner (1977) and the black line is the second order polynomial fit in this study. Black triangles are the inclusions, which plot below the fit indicating they are currently under pressure.

$$V = -12.19211X_{fay}^2 + 24.05288X_{fay} + 289.96211 \quad [4.2]$$

Using the fit described by equation 4.2, the initial unit-cell volumes of the inclusions were calculated (Table 4.18). Knowing the initial volume, as well as the composition of the inclusions allows for a calculation of the P_{inc} of the inclusions utilizing an appropriate equation of state (EOS). Even though olivine is one of the most studied mineral groups, significant scatter exists in the range of bulk moduli (K) found in the literature. For pure forsterite and fayalite the

bulk moduli range between 123 GPa – 132 GPa and 113 GPa – 136 GPa respectively (Nestola et al., 2011b). Few studies investigate the bulk modulus of intermediate composition, but of the ones that have the bulk moduli range from 123 GPa – 131 GPa. Much of the literature assumes a first pressure derivative (K') of 4, which is unreliable because K and K' are strongly related to the fit of the pressure and volume data (Angel, 2000). Nestola et al., (2011a) and Nestola et al., (2011b) investigated the EOS without fixing K' to 4, while looking at intermediate compositions. Their findings indicated that K and K' is constant within error for compositions ranging from $X_{\text{Fa}} 0.38 - X_{\text{Fa}} 0.08$ with K ranging from 123 GPa – 126 GPa and $K' 5.1 - 5.6$. The inclusions compositions agree with those reported by Nestola et al., (2011a). Thus, this EOS is utilized in this study, with $K=123,4$ GPa and $K' = 5$. Using the EOSfit7c P-V calculator (Angel et al., 2014a) the resulting inclusion pressures (P_{inc}) range from 0.10-0.74 GPa (Table 4.18).

Table 4.18: The calculated pressures the inclusions are currently (P_{inc}) under along with the composition of the inclusions, their original volume (V_0) obtained from equation 4.2, and the volume from X-ray diffraction.

Inclusion	X_{Fa}	$V_0 (\text{\AA}^3)$	$V_{\text{XRD}}(\text{\AA}^3)$	$P_{\text{inc}} (\text{GPa})$
Blue inc	0.080735(22)	291.82 (8)	291.34 (3)	0.20 (5)
Inc 1	0.09226(18)	292.07(8)	291.54 (10)	0.23 (5)
Inc 2	0.083665(19)	291.88(8)	290.17 (12)	0.74 (5)
Inc 3	0.0097870(18)	292.19 (8)	291.96 (11)	0.10 (5)

The pressure on the blue olivine inclusion is 0.2 GPa, which agrees with other olivine inclusions, usually ranging from 0.2-0.4 GPa (Nestola et al., 2011a). The high pressure of Inc 2 once again likely results from unreliable volumes due to diamond interfering with the diffraction collection.

4.4.7 Possible Depths of Formation

To get an idea of the possible entrapment pressure and temperatures for these inclusions, isomekes can be used (Angel et al., 2015a). It is important to remember that an isomeke is a line in P-T space that represents possible entrapment pressures and temperatures that would result in the pressure that the inclusions are under now (P_{inc}). These are not lines along which the diamond traveled. The isomeke calculations were performed using EOSfit7c (Angel et al., 2014a). An EOS for both the host (diamond) and the inclusion (olivine) were used. The host EOS was taken from Angel et al., (2015a) with a $K = 444$ GPa and a $K' = 4$. The same EOS used (from Nestola et al., (2011a)) for the calculation of P_{inc} were used for the inclusions. Another reason that this particular EOS was chosen for the olivine, besides the similar composition, is that this was used in a study by Angel et al., (2015a) which investigated the effect of the uncertainties in the diamond EOS parameters in the entrapment pressures of olivines. They concluded that the uncertainties in entrapment pressure was no more than 0.0001 GPa at low temp and 0.008 GPa at high temperatures (Angel et al., 2015a). The uncertainties in the P_{inc} are higher than those for the isomeke from the diamond EOS parameters.

All of the inclusion isomekes cross the graphite diamond stability field. The graphite diamond stability field was calculated using the thermodynamic data set of Holland and Powell (1990). All inclusions except inclusion 2 cross at ~ 4.3 GPa; inclusion 2 crosses at ~ 2.5 GPa (Fig.

4.20). Where they cross the stability field corresponds to the lowest possible entrapment pressure. Where exactly along the line these inclusions were entrapped cannot be said. Inclusion 2 which might have formed at greater depths as indicated by its smaller volume would be expected to have been entrapped well above its minimum entrapment pressure of ~ 2.5 GPa. The transformation of olivine to the polymorph wadsleyite depends upon the Fe content and temperatures. It is expected that an olivine of composition Fo90 at a temperature of 1400°C would transform between 12.8-13.5 GPa. The inclusions in the macle-twin diamond are olivine and not wadsleyite and therefore, must have been entrapped below ~ 13 GPa (Frost, 2003). This information allows for further constraint of the possible entrapment pressures and temperatures.

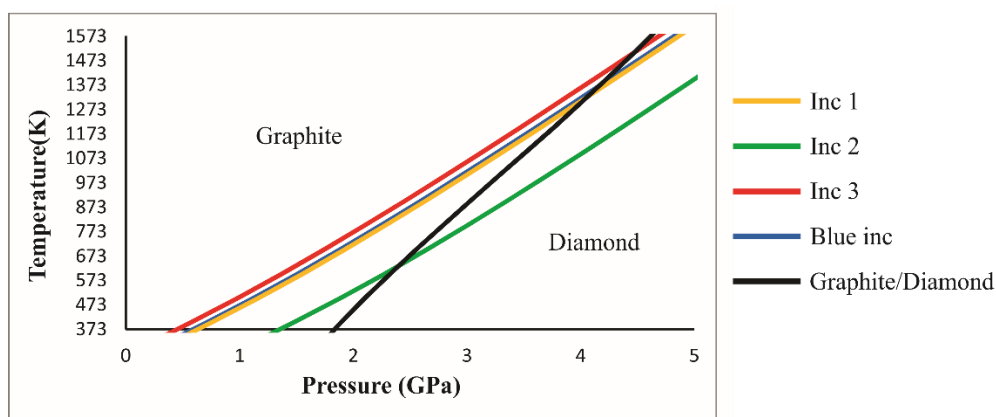


Fig. 4.20: Possible entrapment pressure and temperatures for the olivine inclusions. Inclusion 2 (yellow) has an entrapment pressure beginning at ~ 2.5 GPa, whereas all the other inclusions (orange, blue and red) are at ~ 4.3 GPa. The graphite diamond stability field was calculated using thermodynamic data set of Holland and Powell (1990).

The possible entrapment temperatures are in agreement with some Siberian diamond olivine inclusions at 1100-1500 K (Nestola et al., (2011a)). This would be consistent with a

geotherm with a surface heat flow between 40 and 45 mWm^{-2} (Pollack and Chapman, 1977). A study by Nimis (2002) found numerous inclusions, from various localities around the world, of a lherzolitic paragenesis to be consistent with a $\sim 42 \text{ mWm}^{-2}$ conductive geotherm. In that same study it was found that the formation occurred near the graphite diamond boundary. The pressure and temperature estimates for all of their numerous diamond inclusions were broadly consistent with a relatively cool thermal region expected of cratonic lithospheres (Nimis, 2002). The temperatures estimated by the isomekes seem to be consistent with other studies with geotherms corresponding to a surface heat flow 40 and 45 mWm^{-2} and consistent with a cratonic lithosphere. The entrapment conditions of the inclusions seem reasonable for the upper mantle and gives an idea of the possible formation depths of the olivine inclusions in this macle-twin diamond.

4.4.8 Orientation of the Olivine Inclusions Relative to the Diamond Host

The orientation matrix of the olivine inclusions in this triangular macle diamond were obtained from the single crystal X-ray diffraction collected at the Bayerisches Geoinstitut. The orientations of the olivine inclusions relative to the host diamond were plotted as a stereographic projection using the software OrientXplot (Angel et al., 2015a). As mentioned in section 4.3.1 Diamond Sample Description, the triangular macle diamond shape results from a flattening of two octahedral crystals connected along an octahedral plane (Tappert and Tappert, 2011). Thus, two solutions exist for the orientation plot (Fig. 4.21). Regardless of the diamond matrix utilized, the stereographic projections all show the b axis of the olivine inclusions oriented parallel or almost parallel to the [111] direction of the diamond (Fig. 4.21). The orientation of the blue olivine inclusion remains identical with respect to both diamond matrices, which suggests that the blue olivine actually lies within both diamond crystals. Whereas, the other olivine inclusions shift their

a and c axis depending on which diamond matrix is used and therefore likely lie in only one of the diamond crystals.

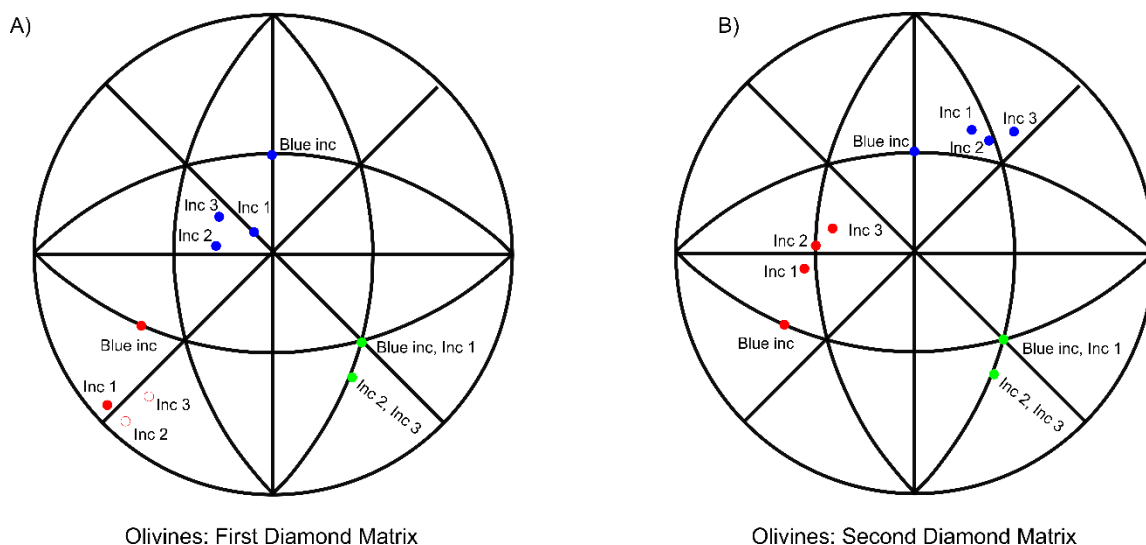


Fig. 4.21: A stereographic plot showing the relative orientation of the olivine inclusions with respect to their host diamond. A) A stereographic plot created using the first diamond matrix. B) A stereographic plot created using second diamond matrix. Red circles represent the a axis of the inclusion. Green circles and blue circles represent the b and c axis of the inclusion respectively. Open circles represent downward projection. The software OrientXplot calculated the relative orientations between the inclusion and their host (Angel et al., 2015a).

From these stereographic projections it appears that there is a preference for the olivines in the triangular macle diamond to have their b axis parallel to the $[111]$ direction of the diamond. This agrees with the results of Mitchell and Giardini (1953) as well as with three olivines from the Nestola et al., (2014) study. However, in the study by Nestola et al., (2014) only three of their forty-three olivines displayed this preferred orientation. The orientation of the olivine inclusions in the triangular macle diamond possibly reflect remnant parts of one original mono-crystal. This

interpretation implies that the olivine inclusions are protogenetic, which means the olivine inclusions existed prior to the diamond. However, syngensis versus protogenesis remains heavily debated in the field of the diamond research and without hard evidence such as the diamond included in a rock fragment that also contains an olivine inclusion on the outside for comparison, we cannot say with certainty whether the olivine inclusions in this study were protogenetic (Nestola et al., 2017). From these plots alone, it remains difficult to tell whether or not the smaller olivine inclusions were in fact originally part of the bigger blue olivine inclusion. Regardless of the interpretation, the fact remains that the b axis of all inclusions falls nearly parallel with the [111] direction of diamond implying some constraint on growth or one large monocrystal.

4.4.9 Synchrotron X-ray Diffraction on Inclusions

Numerous synchrotron X-ray diffraction measurements were performed on the blue olivine inclusions as well as its neighboring inclusions investigating whether any nanoprecipitates might be present; a potential cause of the unique blue color of the olivine. X-ray diffraction mapping was performed over the entire blue olivine inclusion. However, no evidence of any nanoprecipitates were found. Only diffraction peaks related to diamond and olivine are present in the diffraction data (Fig. 4.22). Mapping revealed slight variations in the lattice parameters across the blue olivine inclusion, likely a result of strain in the crystal and slight compositional variations (P_{inc} of blue inc = 0.2 GPa). The average lattice parameters, from 201 diffraction patterns, for the blue olivine is $a=4.7607(3)$, $b=10.2235(5)$, $c=5.9925(5)$, and $V=291.664(1)$.

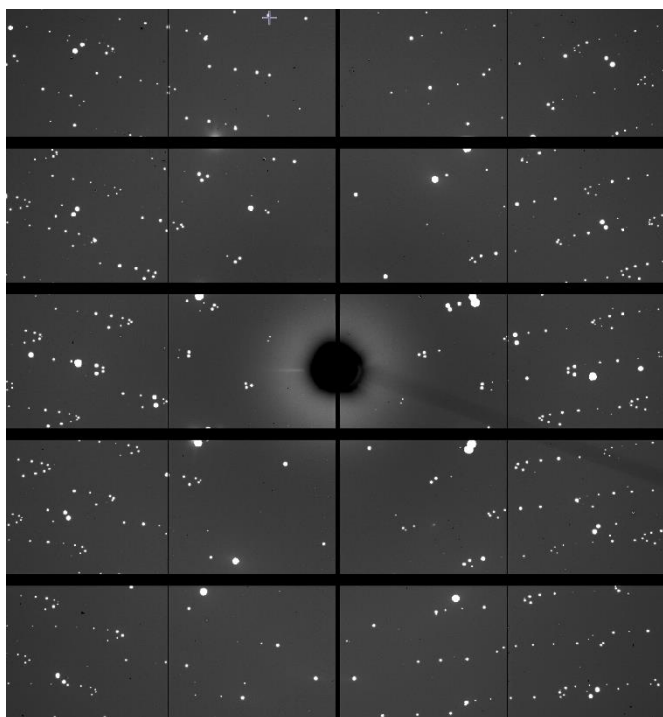


Fig. 4.22: A representative diffraction image of the blue olivine inclusion from the X-ray diffraction map.

Synchrotron single crystal diffraction measurements performed at 13-BM-C utilized the live radiography setup for centering inclusions in diamonds (Wenz et al., 2019). As such, all inclusions from this data set are properly centered in the X-ray beam. As the beam size is smaller at a synchrotron source, the lattice parameters differ from the measurements done at the Bayerisches Geoinstitut. These lattice parameters represent the lattice parameters in very specific regions of the inclusions and as we know from the XRD mapping at 13-ID-D slight variations in lattice parameters exist across the inclusion. The conventional X-ray diffraction measurements provide a better average of the whole inclusion. Synchrotron collections performed in a variety of areas across the inclusions further ensures that no nanophases were present in the inclusions.

Therefore, nanophases are not believed to be the cause of the unique blue color of the olivine inclusion. Radiography of Inc 2 confirms that diamond diffraction interferes heavily with this inclusion due to its position within the diamond. This agrees with earlier theories from the diffraction data obtained at the Bayerisches Geonstitut, suggesting that Inc 2's smallest volume results from interference of the diamond with the inclusion. The intense diffraction shadows moving across the radiograph image precluded centering this inclusion in the X-ray beam. As a result, reliable diffraction data was not obtained on this inclusion. Inclusion 4 previously was not collected on in Bayreuth as this inclusion proved challenging to center using optical methods due to its location within the diamond. Radiography of Inc 4 enabled proper centering and the lattice parameters of this inclusion fall in the same range as the other olivine inclusions (Table 4.19).

Table 4.19. Unit-cell parameters of all inclusions within the triangular macle diamond. The diffraction of the diamond precluded the live radiography centering technique for Inc 2 and thus, unit-cell parameters are not listed for this inclusion.

Inclusion	a (Å)	b (Å)	c (Å)	V (Å ³)
Blue olivine	4.7585(17)	10.2213(34)	5.9904(18)	291.361(28)
Inc1	4.7655(4)	10.2245(11)	5.9910(6)	291.91(5)
Inc2	NA	NA	NA	NA
Inc3	4.7605(8)	10.2132(16)	5.9921(9)	291.33(14)
Inc4	4.7613(5)	10.2130(11)	5.9931(6)	291.43(9)

Garnet	11.5555(9)	11.5555(9)	11.5555(9)	1543.02(37)
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4.4.10 X-ray Fluorescence

X-ray fluorescence spectra were collected on the blue olivine inclusion to determine the elemental composition of the inclusion while it remains encased in diamond. XRF spectra of the olivine inclusions reveal the presence of the following elements: Ti, Cr, Fe, Ni, and Zn (Fig. 4.23). The spectra of each olivine inclusion appear nearly identical (Fig. 4.23). Elements present in these spectra agree with typical elements found in most olivine inclusions in diamond (Griffin et al., 1992). Diamond inclusions are well known for being more Cr rich than most olivines, and the spectra of all inclusions show some evidence of the presence of chromium (Meyer and Boyd, 1972). No unusual elements stand out in the XRF spectrum, besides gold, which resulted from contamination from the beam stop.

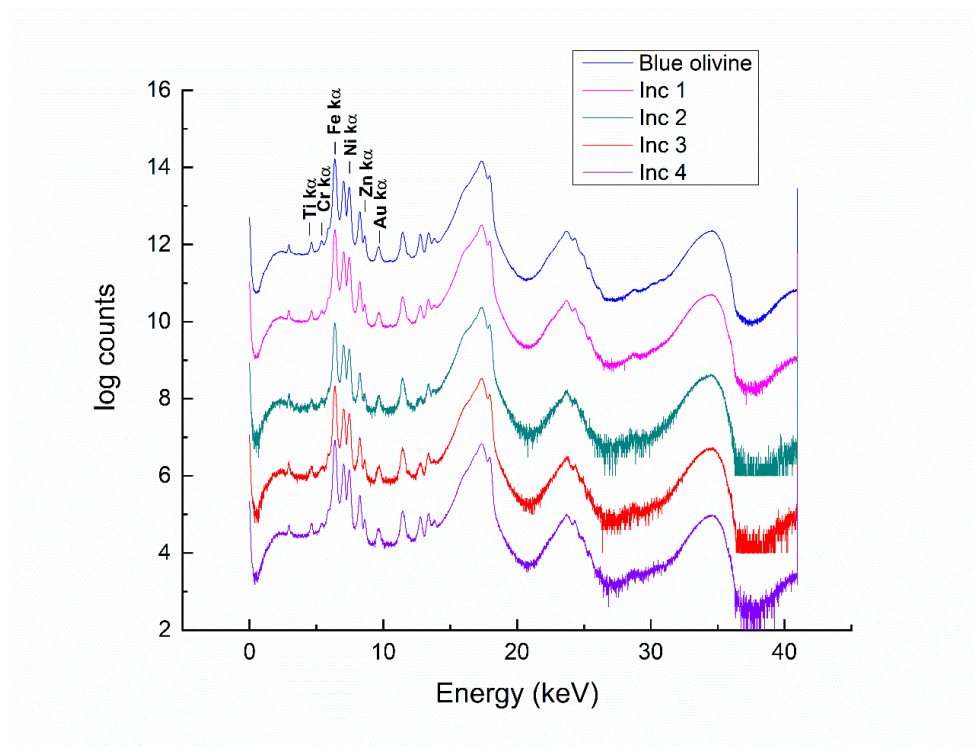


Fig. 4.23: X-ray fluorescence spectrum of the olivine inclusions in the triangular macle diamond.

XRF mapping allowed for a visual representation of the distribution of these elements within the inclusions (Fig. 4.24). Titanium is homogeneously distributed across the inclusions. Whereas, certain parts of the blue olivine inclusion appear to have more chromium than others. Nickel and iron are distributed in the same manner throughout the inclusions and are also concentrated in the Cr rich region, which is consistent with the thought that there is presence of a Fe-Ni alloy in that region. Further studies need to be done to confirm this. The varied distribution of elements such as chromium in the blue olivine inclusion agrees with the synchrotron X-ray diffraction mapping data that showed slight variation in lattice parameters across the inclusion.

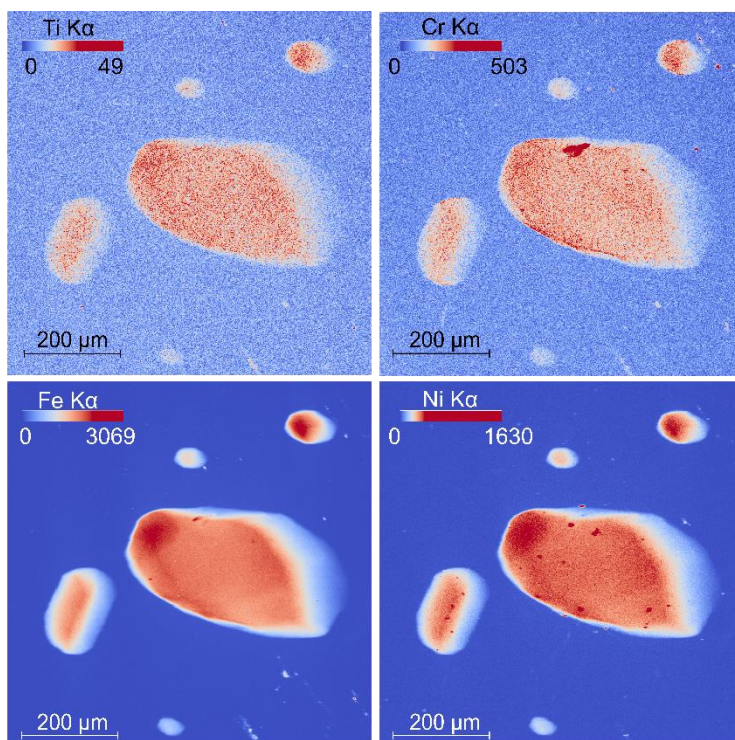


Fig. 4.24: X-ray fluorescence mapping of all olivine inclusions showing the various distributions of elements throughout the inclusions.

An XRF map was also taken over the entire triangular macle diamond ensuring that there were no anomalies in the diamond itself that might explain the unique blue color of the olivine. XRF maps are shown for Ti, Cr, Fe, and Zn (Fig. 4.25). Overall, the triangular macle diamond appears homogenous.

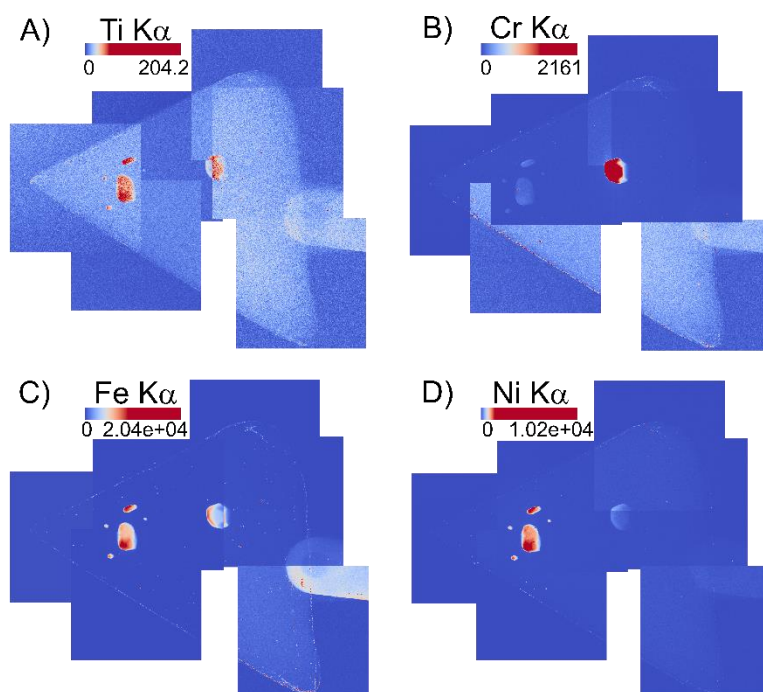


Fig. 4.25: X-ray fluorescence map of the entire triangular macle diamond showing the various distributions of elements.

4.4.11 Photoluminescence Spectroscopy

Photoluminescence spectroscopy on the triangular macle diamond was used to detect ppb level optical defects within the diamond (Eaton-Magaña and Breeding, 2016). Photoluminescence spectroscopy of the triangular macle diamond revealed a multiple defect within the diamond (Fig. 4.26). The first defect appears at 415 nm and is referred to as the N3 defect, which consists of three nitrogens surrounding a vacancy (Eaton-Magaña and Breeding, 2016). Another defect occurs at 503.2 nm and is referred to as the H3 or NVN^0 defect, this results from two nitrogens separated from a vacancy. The GR1 (V^0) peak at 741 nm represents an uncharged vacancy in diamond, a feature usually seen in irradiated natural diamonds (Breeding and Shigley, 2009). The defect seen at 612.5 nm does not have a known cause yet but is present in most diamonds (Hainschwang et

al., 2006). Overall, the photoluminescence spectrum reveals nothing unusual for a natural type IaAB diamond.

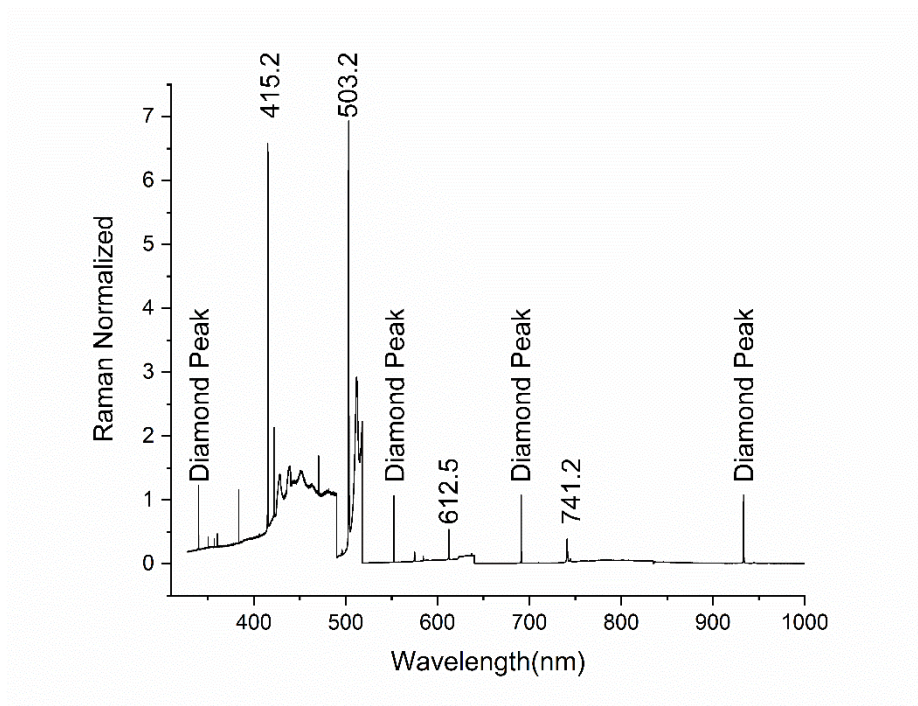


Fig. 4.26: Merged photoluminescence spectra for the triangular macle diamond using a 325, 488, 514, 688 and 830 nm laser excitation source. As multiple excitation sources were utilized the Raman lines from the diamond are seen throughout the spectrum and are labeled accordingly.

Photoluminescence spectra collected on the blue olivine inclusion show similar results to that of the triangular macle diamond (Fig. 4.27). However, there is an addition of a peak at 512 and 519 nm, which would require further studies as photoluminescence spectra of olivine varying in composition are needed for comparison.

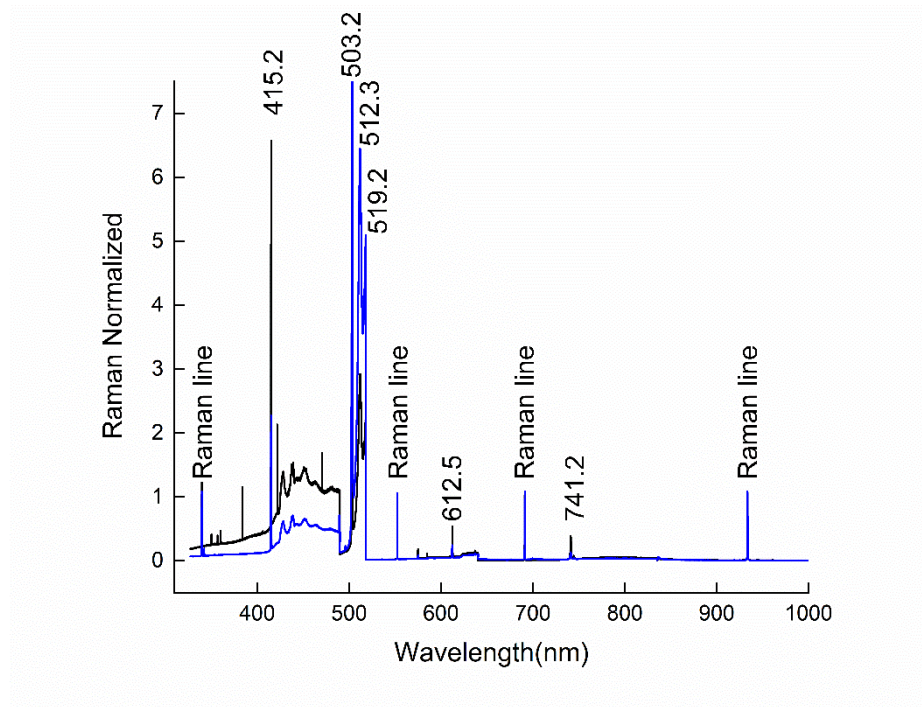


Fig. 4.27: Merged photoluminescence spectra for the triangular macle diamond as well as the blue olivine inclusion using a 325, 488, 514, 688 and 830 nm laser excitation source. As multiple excitation sources were utilized the Raman lines from the diamond are seen throughout the spectrum and are labeled accordingly.

4.4.12 Diamond Fluorescence Imaging

Diamond fluorescence imaging illuminates surface fluorescence of diamonds with short UV light. This fluorescence image illuminates color causing optical defects as well as provides information on growth histories of diamonds (Shigley and Breeding, 2013). Diamond fluorescence imaging revealed a greenish-blue UV fluorescence color (Fig. 4.28). This color originates from the 415 nm (N_3/N_3V) and 503 nm (H_3/NVN^0) optical defects, which were observed in the Photoluminescence spectrum (Breeding and Shigley, 2009). A cross hatching pattern exists in parts of the triangular macle diamond, which represents dislocations within the diamond (Breeding

and Shigley, 2009). The triangular macle diamond displayed blue phosphorescence after excitation time of five seconds (Fig. 4.29). Phosphorescence in diamonds typically only occurs in a few natural diamonds such as chameleons and type IIb diamonds (Eaton- Magaña and Breeding, 2016).

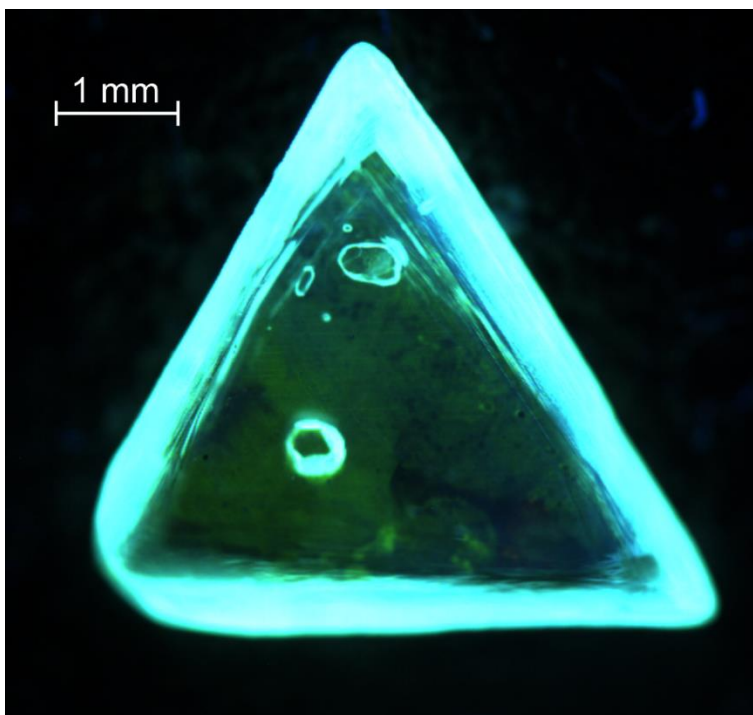


Fig. 4.28: Fluorescence image of the macle taken with a Diamond View instrument.

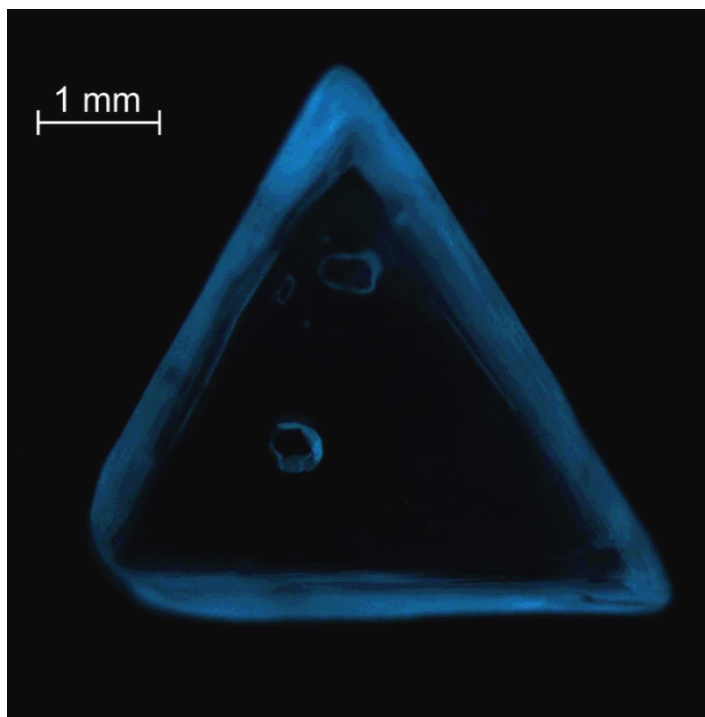


Fig. 4.29: Phosphorescence image of the macle taken with a Diamond View instrument with an excitation time of 5 seconds

4.4.13 Raman Spectroscopy

Raman spectroscopy serves as an identification tool providing detailed information about the chemical bonds within a mineral, thus each mineral has a characteristic Raman spectrum. The characteristic Raman spectrum of olivine contains 8 modes in total assigned to the stretching of the SiO_4 tetrahedra (Iishi, 1978). Five of these modes are often intense and present in the majority of olivine Raman spectra. Within the blue olivine inclusion these five bands are seen at ~ 824 , ~ 855 , ~ 883 , ~ 920 , $\sim 961 \text{ cm}^{-1}$ (Fig. 4.30). Thus, the Raman spectrum agrees well with that of typical olivine. The characteristic intense doublet at ~ 824 and $\sim 855 \text{ cm}^{-1}$ corresponds to the symmetric and antisymmetric stretching mode of the isolated SiO_4 tetrahedra (Guyot et al., 1986).

Stretching vibrations involve a change in bond length and as such with increasing iron content, the frequency shifts slightly to lower frequencies. No frequency shift is observed between the blue olivine inclusion and the San Carlos olivine, which agrees with the compositional data of the blue inclusion obtained from structural refinement ($X_{\text{Fa}} 0.08$) as it closely matches that of San Carlos olivine at $\sim X_{\text{Fa}} 0.08$ (Kuebler, et al., 2006). Overall, the Raman spectrum of the blue olivine inclusion matches closely to that of normal San Carlos olivine, with one exception that the band at 920 cm^{-1} is not as intense in the blue olivine as it is for the San Carlos olivine.

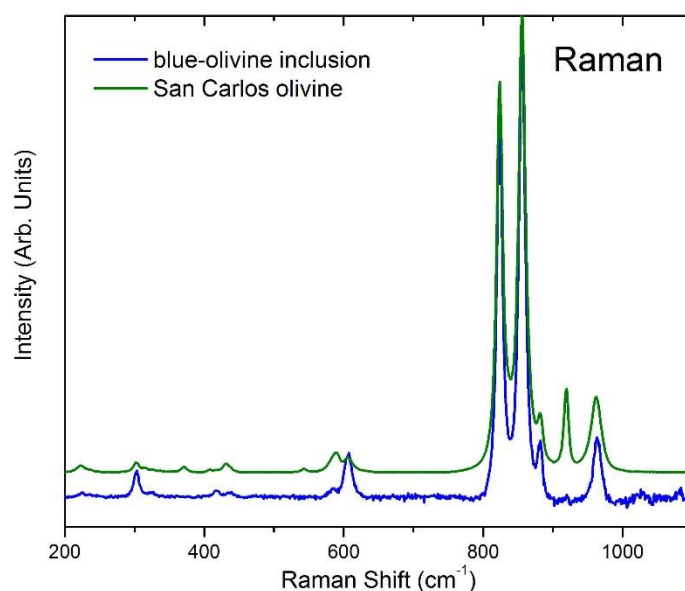


Fig. 4.30: Raman spectrum of both the blue olivine inclusion and San Carlos olivine.

4.4.14 Mössbauer Spectroscopy

Mössbauer spectra were collected to investigate the valence state of Fe within the blue olivine inclusion. Spectra revealed the valence of the iron in the blue olivine inclusion as Fe^{2+} (Fig. 4.31). Both the quadrupolar splitting and the isomer shift of the blue olivine inclusion (Table 4.20)

fall within the values for divalent iron and there is no presence of Fe^{3+} , which is consistent with other Mössbauer studies of iron in olivines (Frost and McCammon, 2009; Shinno, 1981). The garnet inclusion contains both Fe^{2+} and Fe^{3+} (Fig. 4.31; Table 4.21), which is consistent with other garnet inclusions in diamond (McCammon et al., 1998).

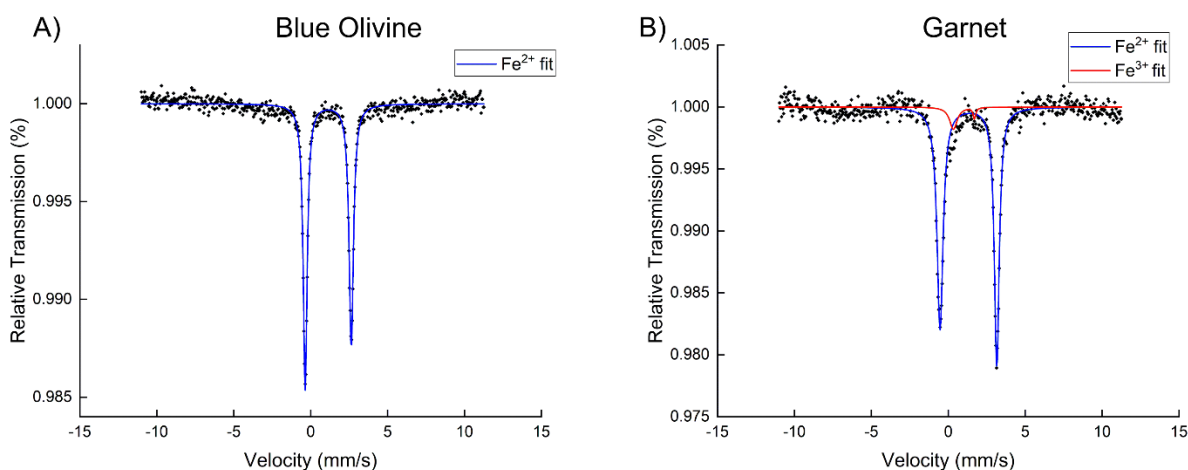


Fig. 4.31: A) Mossbauer spectrum of the blue olivine inclusion B) Mossbauer spectrum of the garnet inclusion.

Table 4.20. Isomer shift and quadrupolar splitting values for the blue olivine inclusion.

Iron Valence State	Isomer Shift (mm/s)	Quadrupolar Splitting (mm/s)
Fe^{2+}	1.143(1)	2.993(2)
Fe^{3+}	NA	NA

Table 4.21. Isomer shift and quadrupolar splitting values for the garnet inclusion.

Iron Valence State	Isomer Shift (mm/s)	Quadrupolar Splitting (mm/s)
Fe^{2+}	1.143(1)	2.993(2)
Fe^{3+}	0.0(1)	0.0(1)

Fe^{2+}	1.311(2)	3.687(4)
Fe^{3+}	1.020(3)	1.370(6)

4.4.15 Visible Absorption Spectroscopy

Optical absorption spectroscopy was performed to determine the valence state of transition metals within the blue olivine inclusion. The presence of transition metals in minerals often results in colors (Nassau, 1978). Due to the unique blue color of the olivine inclusion a plausible suspect for the origin of this color is the presence of reduced chromium (Cr^{2+}). Olivine inclusions typically contain relatively high concentrations, ~ 0.10 wt. % (one order of magnitude above terrestrial olivine), of Cr_2O_3 (Burns et al., 1973). As inclusions potentially form in more reducing conditions, similar to those of lunar and meteorite olivines, it is largely speculated that olivine inclusions could contain Cr^{2+} , which fit into either the M1 or M2 site of the olivine (Burns et al., 1973; Burns, 2005). Chromium's role in the origin of the blue color in both natural and synthetic diopsides remains largely debated in the literature. Ikeda and Yagi (1977) suggest the blue color results from Cr^{3+} in tetrahedral sites, although due to the high octahedral (CSFE) of Cr^{3+} this is unlikely to occur in tetrahedral coordination but would favor octahedral coordination. Schreiber (1977) proposed Cr^{4+} replacing Si in the diopside structure, while Burns (2005) suggests that the blue is a result of Cr^{2+} ions. While this topic remains largely debated visible absorption measurements were performed to investigate valence states of chromium within the blue olivine inclusion.

Visible absorption measurements of the blue olivine inclusion reveal a broad band around ~ 600 nm. A similar band around ~ 600 nm is evident for a San Carlos olivine, spectrum obtained from George Rossman's mineral spectroscopy server, however, this band is not as broad as the

band seen in the blue olivine inclusion (Fig. 4.32). The synthetic Cr doped forsterite spectra differed from the blue olivine inclusion. Initially, this synthetic sample was thought to contain reduced chromium (Cr^{2+}). However, the synthetic Cr doped forsterite spectrum is extremely polarized, a characteristic not expected for Cr^{2+} . This agrees with a long-standing debate over whether these Cr doped forsterites actually contain Cr^{3+} or Cr^{4+} or some mixture of the two cations (Park et al., 1993). As the synthetic Cr doped forsterite spectrum closely matched to Henderson et al., (2000), this sample likely contains Cr^{4+} . However, Fe^{2+} ions often obscure the weaker bands of Cr^{2+} , Cr^{3+} , and Ti^{3+} and as the blue olivine inclusion contains only Fe^{2+} this is a potential issue with the visible absorption measurements (Burns, 1975).

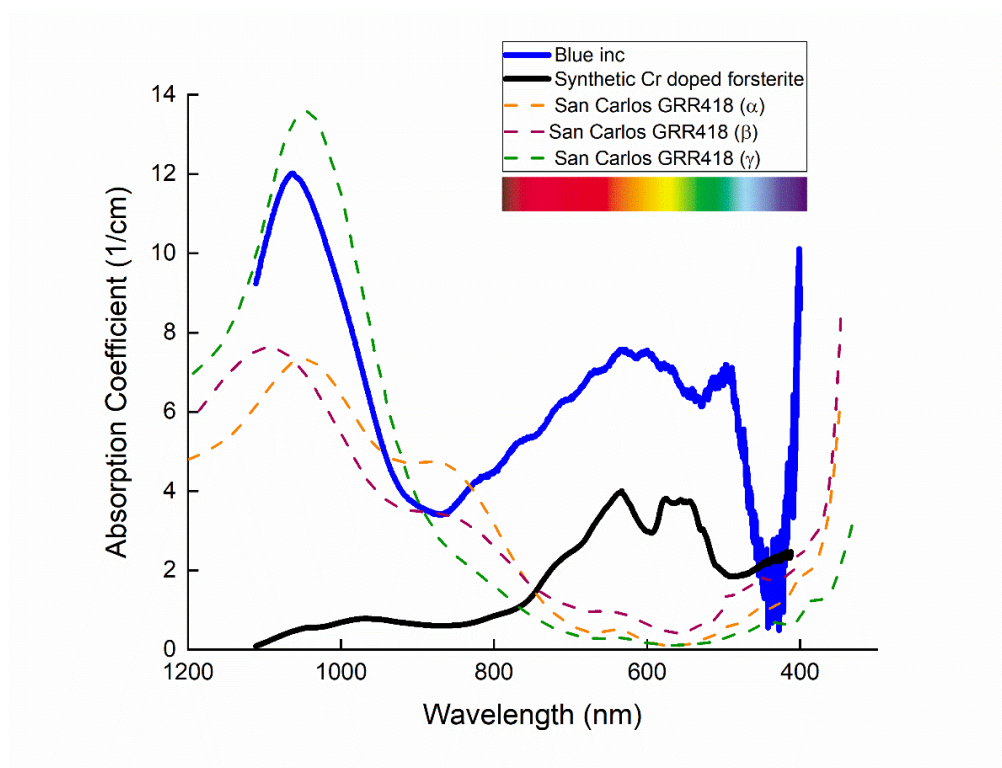


Figure 4.32: Visible absorption spectra of the blue olivine inclusion (Hans Keppler) compared to the spectra from a synthetic Cr doped forsterite, and a San Carlos olivine (GRR418) from George Rossman's mineral spectroscopy server (Rossman, 2010).

4.4.16 XANES Spectroscopy

XANES spectra were collected to investigate the valence state of Cr within the blue olivine inclusion, as visible absorption measurements remained inconclusive. XANES spectra of the blue olivine inclusion contained numerous diffraction peaks from the diamond abundant throughout the spectra. However, the diffraction peaks did not interfere with the analysis. Valence results obtained from both the Cr^{2+} and Cr^{3+} glasses agree well with Hanson and Jones (1998) at 2.0 and 2.90 respectively. The Cr^{2+} rich glass and olivines from Bell et al., (2017) revealed valences of 2.36 and 2.37 respectively, thus these samples contained ~64% Cr^{2+} . Determination of valence states of both the glass and olivine samples agreed well with the previous valence determinations in the Hanson and Jones (1998) and Bell et al., (2017) studies. Twenty-two XANES spectra across the blue olivine inclusion were averaged and resulted in a Cr valence of 2.98(3). A representative spectrum of the blue olivine inclusion and a comparison of the inclusion to a Cr^{2+} rich glass is shown in Fig. 4.33 and Fig. 4.34 respectively. The valences of the surrounding inclusions, Inc 1 and Inc 2, are close to the blue olivine inclusion with valences of 3.0 and 2.95 respectively. Thus, it appears that the blue olivine inclusion contains chromium with a predominate valence state of Cr^{3+} . If we consider how much Cr^{2+} could be present based on two times the standard deviation, the valence could be as low as 2.92 (8% Cr^{2+}). However, there is no obvious peak at the diagnostic Cr^{2+} energy (Fig. 4.34). Future studies need to be performed to investigate how much Cr^{2+} is

required to cause olivine to become blue. Perhaps 8% Cr^{2+} is enough reduced Cr to cause this color change.

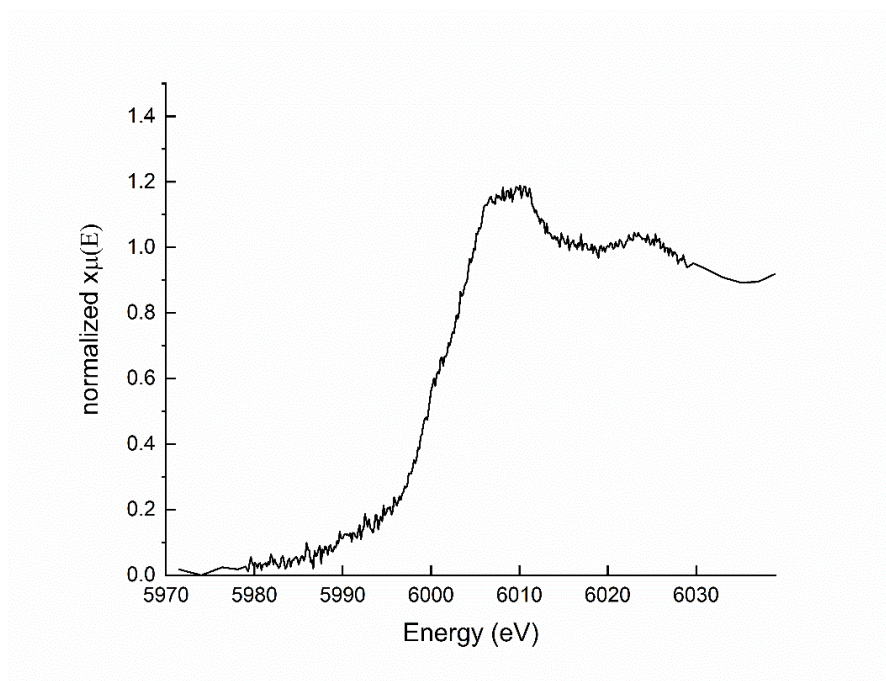


Figure 4.33: XANES spectra of the blue olivine inclusion.

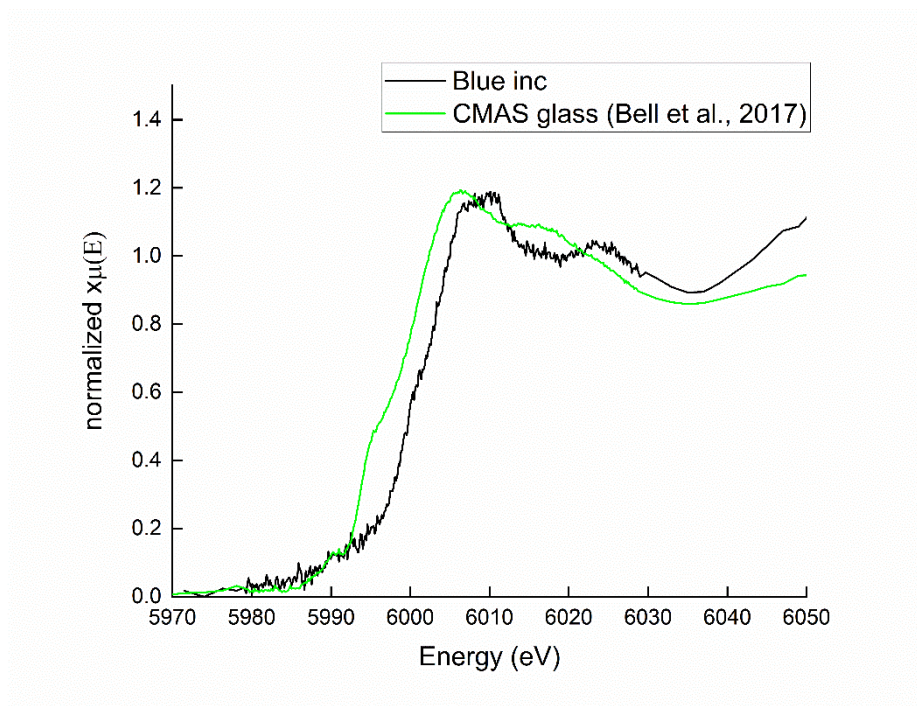


Figure 4.34: XANES spectra of the blue olivine inclusion compared to the CMAS Cr^{2+} rich glass (Bell et al., 2017). The Cr^{2+} peak associated with the $1s - 4s$ absorption peak is present in the CMAS glass spectrum at ~ 5994 eV.

4.5 Conclusion

This study reports the first known blue-colored olivine, found included within a Type IaAB triangular macle (twinned) diamond. Microtomography revealed no evidence of cracks in the diamond, thus the blue olivine and its surrounding inclusions are considered pristine. The blue olivine inclusion has a composition of Fo_{92} , and sits at a remnant pressure of 0.2 GPa as determined via single crystal X-ray diffraction experiments and the use of an appropriate equation of state. This result agrees with other olivine inclusions in diamonds (Nestola et al., 2011a). XRF mapping revealed evidence of elements commonly found in mantle olivines such as Ti, Cr, Fe, Ni, and Zn

(Griffin et al., 1992). UV-VIS absorption spectroscopy and the presence of metallic Fe-Ni alloy within the olivine inclusion suggest trace Cr^{2+} as the possible cause of the blue color. Valence states of both iron and chromium were investigated as transition metal ions often produce color changes in minerals. Mössbauer spectroscopy revealed all iron in the blue olivine inclusion as Fe^{2+} , which is typical for olivines and thought to produce the characteristic green color of olivines (Koivula, 1981; Nassau, 1978; White and Keester, 1966). XANES spectroscopy determined the valence state of Cr in the blue olivine inclusion as predominantly Cr^{3+} , with an average Cr valence of 2.98(3). If we consider how much Cr^{2+} could be present based on two times the standard deviation, the valence could be as low as 2.92 (8% Cr^{2+}). However, there is no obvious peak at the diagnostic Cr^{2+} energy. Thus, the question remains what is the source of the unique blue color? Our study cannot rule out the possibility of reduced Cr for the cause of the color, thus future experimental studies need to be performed to investigate how much Cr^{2+} is required to cause olivine to become blue. Future XANES work to investigate the valence state of the other transition metals present in the olivine as mixed valences may help in understanding the unique blue color. However, as the sample is in diamond performing XANES on these other transition metals may prove challenging as the absorption and the diffraction of diamond provide challenges for data collections. Ultimately, this study utilized a variety of non-destructive techniques to characterize the blue olivine and surrounding inclusions including X-ray microtomography, FTIR Spectroscopy, single-crystal X-ray diffraction, X-ray fluorescence, photoluminescence spectroscopy, UV fluorescence imaging, Raman spectroscopy, Mössbauer spectroscopy, visible absorption spectroscopy, and X-ray absorption near-edge structure. This study has nearly exhausted the amount of geochemical information that can be obtained while the sample remains

encased in the diamond. Extraction of the inclusion might provide further insight into the cause of the blue color, however such studies risk losing or altering the inclusion.

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119, e54660.

6. Appendices

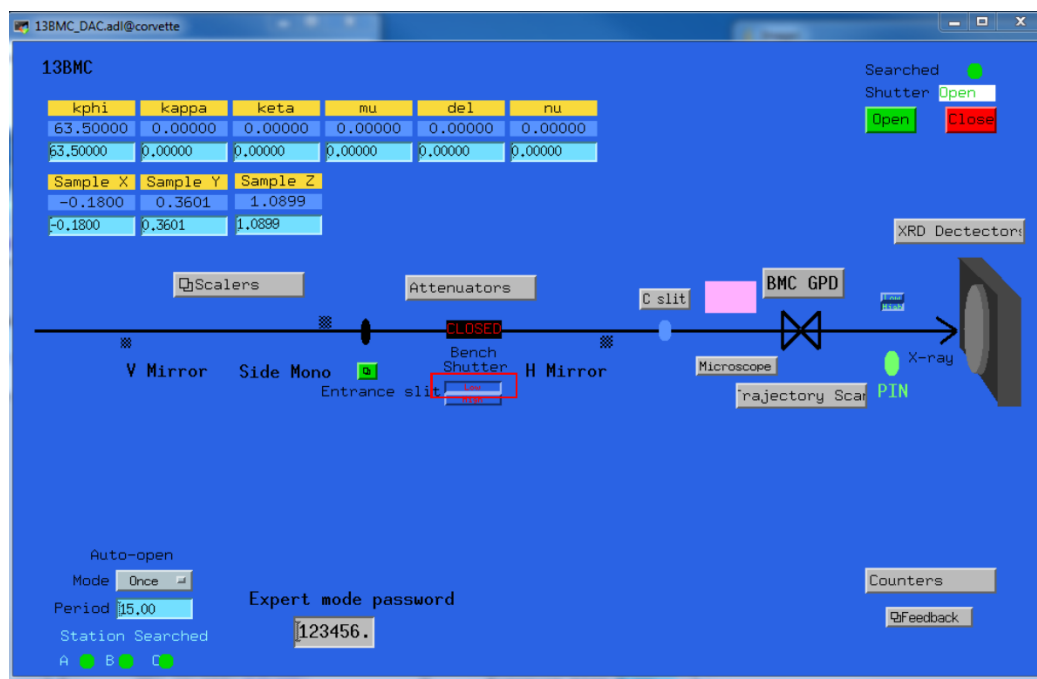
Appendix A

Operating Procedure for the Live 2D-Radiography System Available at 13-BM-C

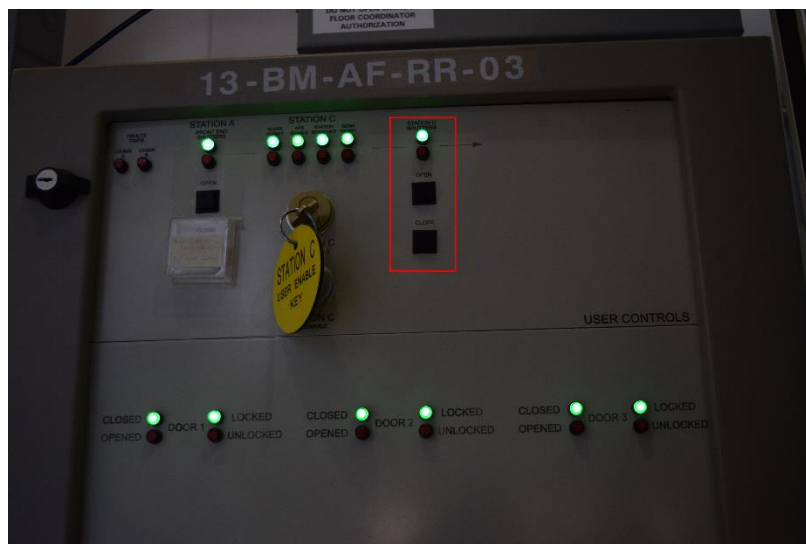
Below is a step by step operating procedure designed for utilizing the new 2D-radiography system now available at the GeoSoilEnviro Center for Advanced Radiation Sources (GSECARS) 13-BM-C beamline at the Advanced Photon Source (APS), USA. This portable 2D-radiography system is part of the non-destructive fast high-throughput methodology for studying mineral inclusions in diamond, which is described in Chapter 2 of this thesis and is published in the Journal of Synchrotron Radiation (Wenz et al., 2019).

Entering the Beamline Station at 13-BM-C

- Close the X-ray shutter by hitting the low button on the 13BMC_DAC.adl window.

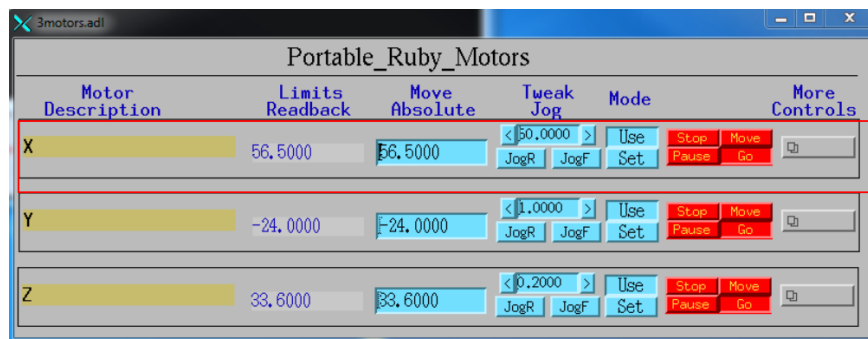


- Confirm that the shutter is truly closed by looking at the panel on the wall and hitting the close button. Wait for the green light to turn red. The red light means it is safe to enter.

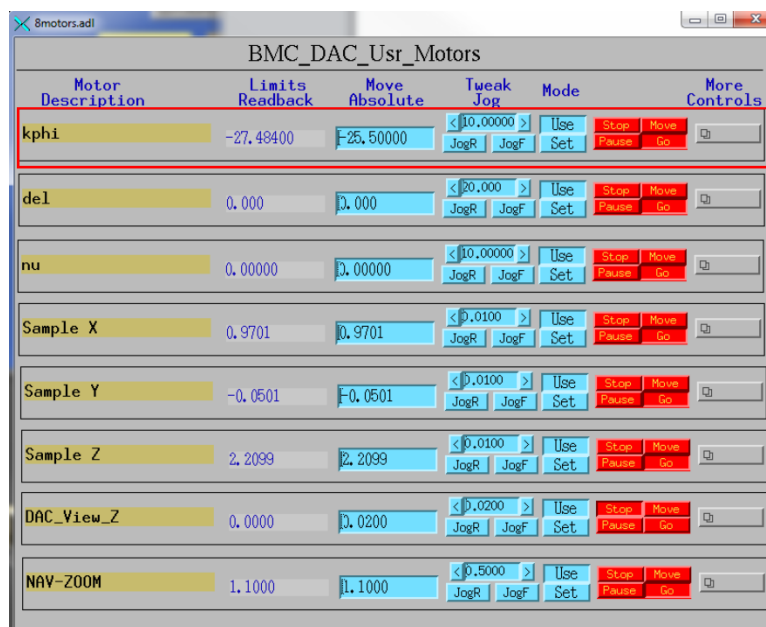


Mounting the Sample

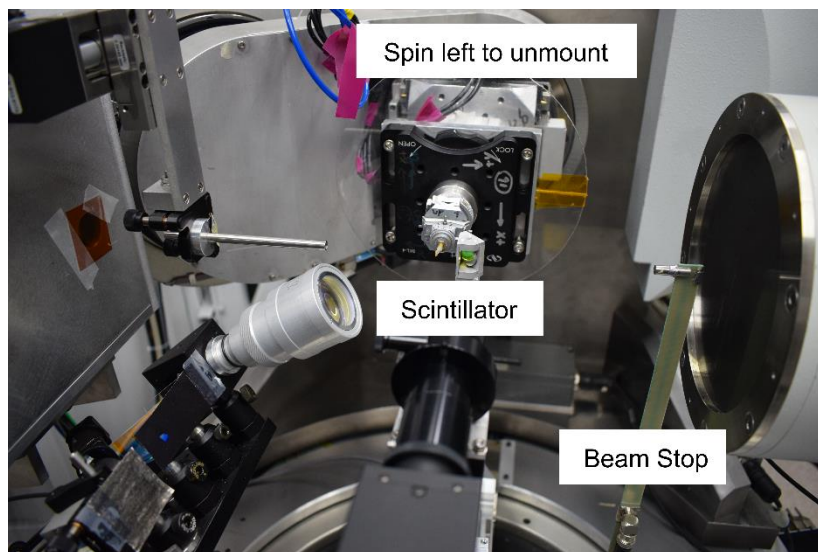
- First ensure that the newly developed 2D-radiography setup is out of the way of all motors. To do this find the window called portable motors (3moters.adl). Within this window move portable motor X to a position defined by the beamline scientist. In this case the position was 56.0. **Note: This exact position may change from beamtime to beamtime so talk to the beamline scientist to confirm what number should be used to drive the 2D-radiograph system out of the beam.**



- Now using the window entitled BMC_DAC_Usr_Motors (8motors.adl) make sure the kphi motor is at 0°.



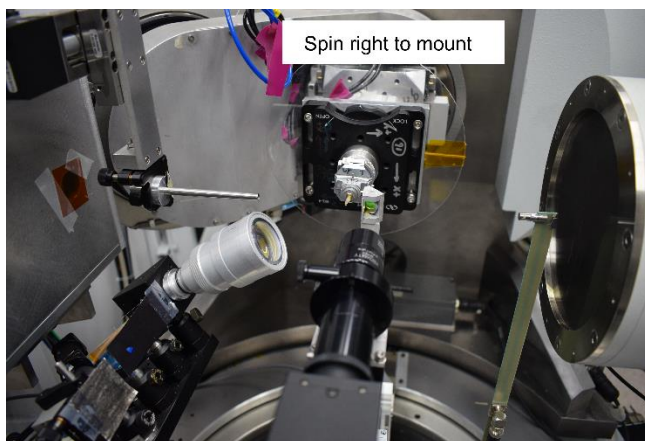
- Retrieve the sample mounting plate, which holds the goniometer by spinning the dial on the plate mount left (towards the word open) **while holding onto the plate**. Remove the plate carefully. Take care not to hit the beamstop or scintillator.



- Use the smallest wrench located on the station table to loosen the top most pin hole of the goniometer. Place the sample in the goniometer making sure the orientation of the brass pin is correct based on the tomographic image taken prior at 13-BM-D. Tighten the pin in the goniometer with the wrench once the sample is positioned correctly. Make sure that the sample is secure as the sample will be rotating.



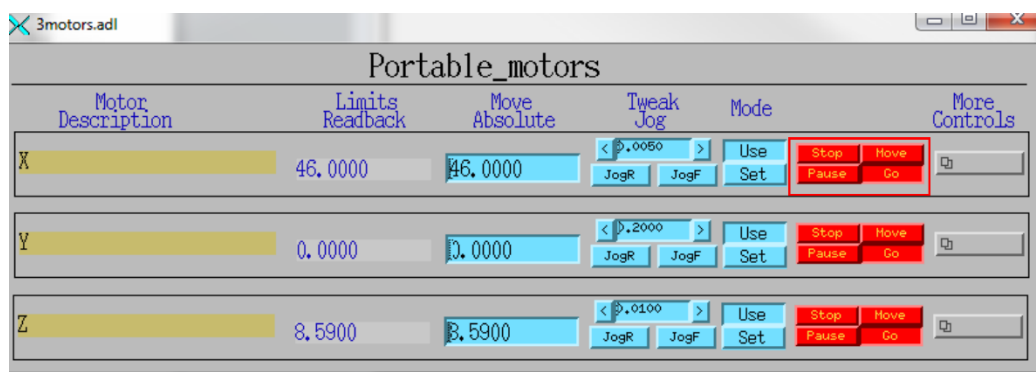
- Place the sample plate back on the X-ray diffraction system. Spin to the right to lock the plate (make sure it engages properly before letting go).



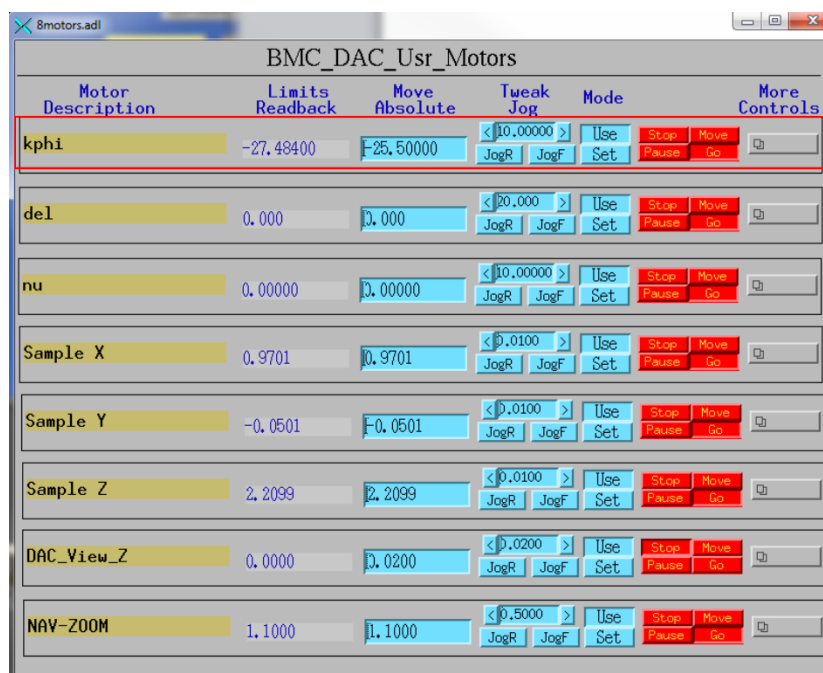
Engaging the 2d-radiography system

- Get up on the X-ray diffraction platform and make sure it looks like the 2D-radiography system will clear the sample and the goniometer when it moves in.
- Have one person remain up on the platform to watch as the system is driven in. Another person should use the portable motors (3motors.adl) window to move portable motor X to -8.5. This moves in the scintillator (**remember this position may change from beamtime to beamtime so talk to the beamline scientist to figure out the position**).

Note: If it looks like the 2D-radiography system will hit anything then hit red stop button next to portable motor X.



- Next rotate the kphi motor in small 10° increments. Make sure that upon rotation the sample will not hit the scintillator. Check to see that if you rotate the sample to $+90^\circ$ and -90° that it will clear the scintillator.
- After checking that the sample will clear over that 180° range now rotate kphi back to 0° .

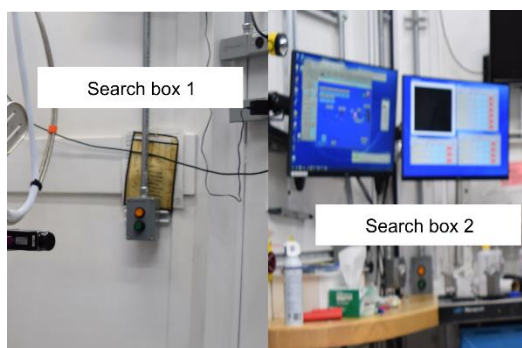


Emergency Stop of Detector Motors in Station

- If you are in the station and see that the X-ray detector is going to collide with anything, which only would happen if you are changing the detector positions while in the station then one should hit the red emergency motor stop button, located behind the X-ray detector near search box 1. This button immediately stops the detector motors. If one accidentally hits this button then make sure to **pull and twist** out. The red button will pop back out when done properly. If this motor stop button is engaged you will not be able to collect data.

Exiting the Beamline Station 13-BM-C

- To exit the 13-BM-C station, one must make sure that the station is clear of all people. Only one person should search the station.
- To search the station first hit the green button on search box 1 and ensure that no one is inside. Then go over and hit the green button on search box 2 making sure no one is in the room.

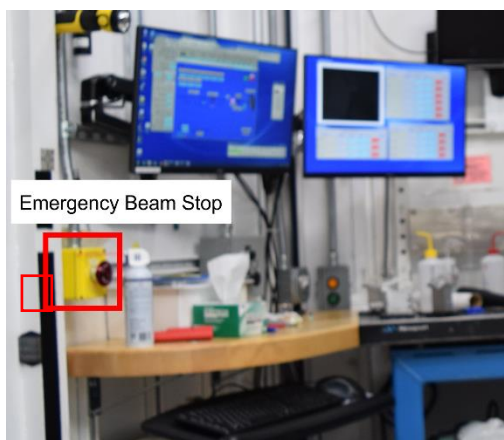


- Once the beamline station is clear, press and hold the door close button on the panel located outside the station. This panel is used to tell the interlock system that the room is empty. **You must only press this door close button when you are certain that there is nobody in the room, because as soon as the door is closed the shutter will open.**



Emergency Stop to use if one is Stuck in Station

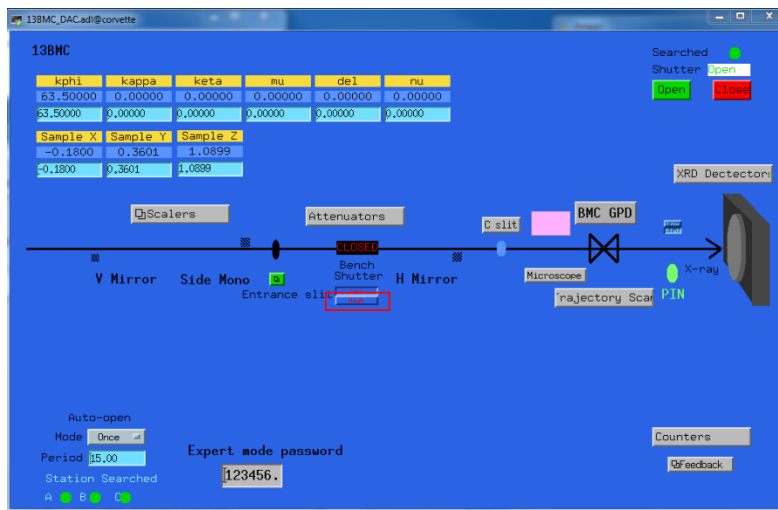
- If you are inside the station and the station door starts to close hit the red emergency beam stop button. This button dumps the beam for that whole beamline. Only hit this if you are still in the room. If one accidentally hits this button make sure to pull it straight out (will pop out) before searching and closing the hutch.



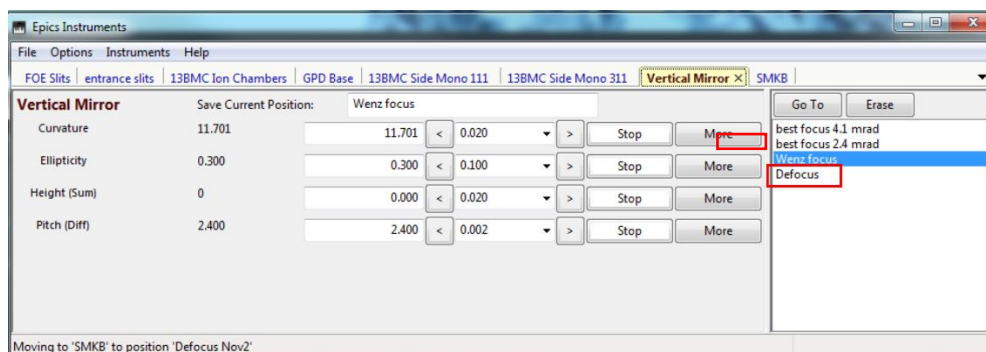
Preparing for the Live Radiograph Image

- To improve the image from the 2D-radiography system the station lights should be turned off. In addition to the station lights there is an extra light source located over search box 1 inside the station. Ask the beamline scientist to turn off this light because for the highest quality image there should be as little light as possible inside the station.
- Look at the wall panel and check that the red light turns green as this means the beam is inside the station.

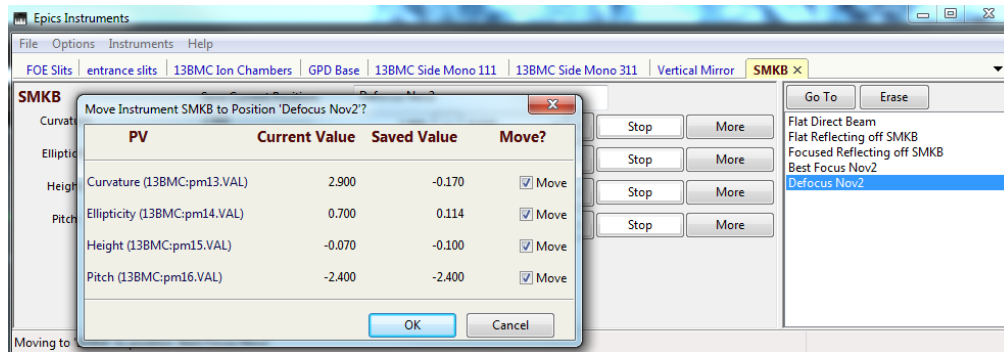
- Turn on X-ray beam in 13BMC_DAC.adl (blue) window by hitting the high button.



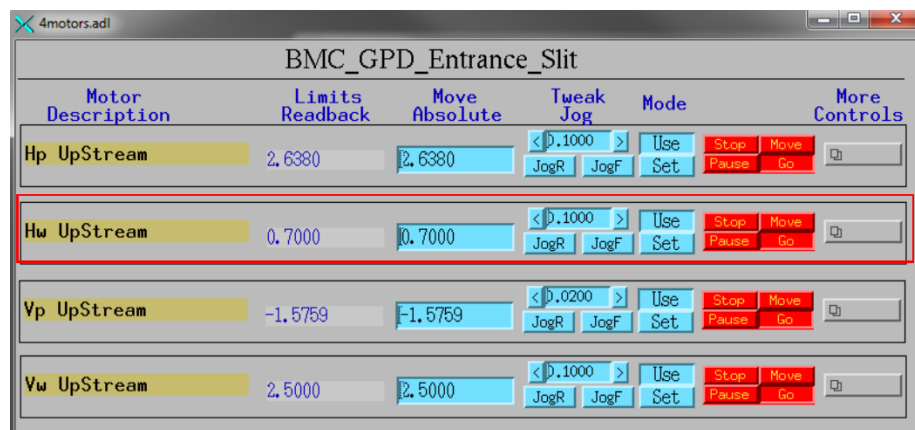
- Now expand the field of view the X-ray beam by defocusing the X-ray beam. To do this go to the epics piano window and to the vertical mirror tab. To defocus the beam hit defocus with current date, Hit go to and then ok. Note: These preset settings are done during the first run with the beamline scientist so once they are set up and saved, they will be used throughout the rest of the beamtime.



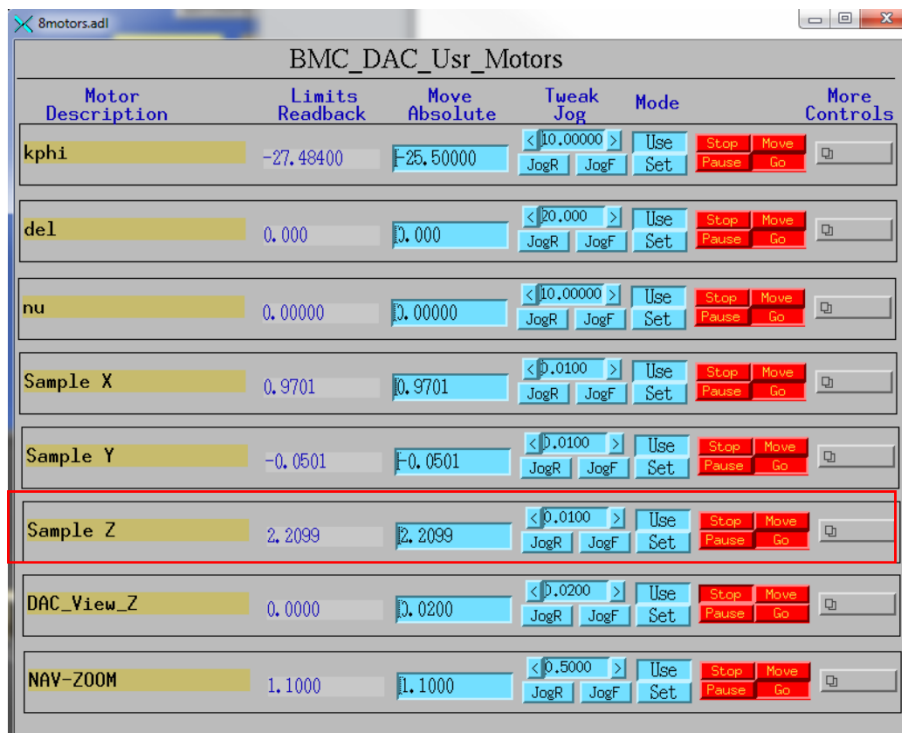
- In the same window go to the tab labeled SMKB and hit defocus, go to, and then ok.



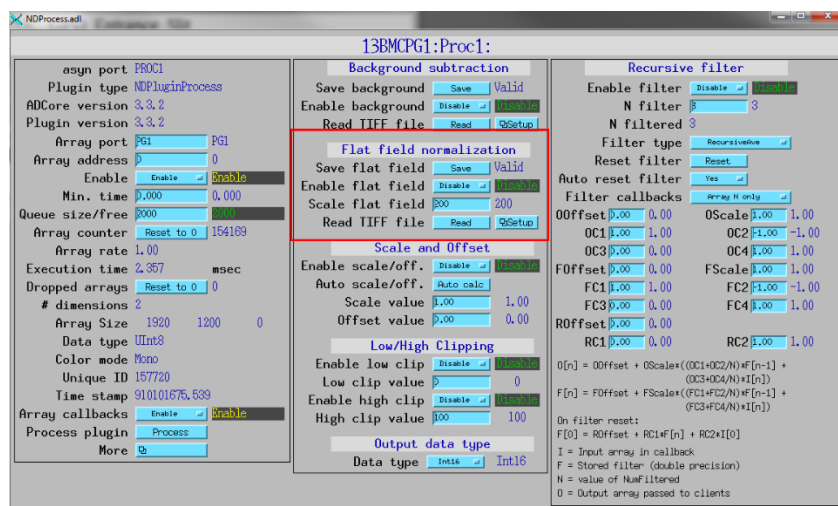
- In the BMC_GPD_Entrance_Slit window (4motors.adl) change the Hw Upstream motor to 2.0 (this widens the slit resulting in a wider image). **This number may change each beamtime ask the beamline scientist for the exact number.**



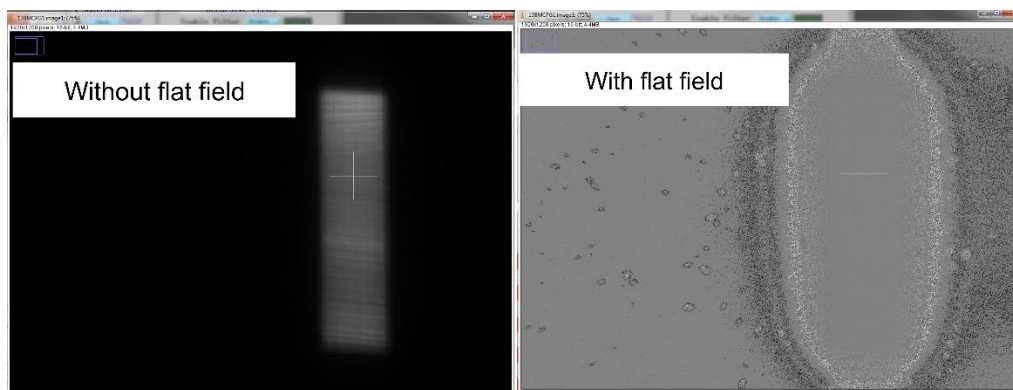
- In the window called BMC_DAC_Usr_Motors (8motors.adl) make sure that kphi is at 0° . Once confirming that kphi is at 0° one can now move the sample Z motor to -6.0. The sample Z motor moves the sample completely out of the field of view of the radiograph.



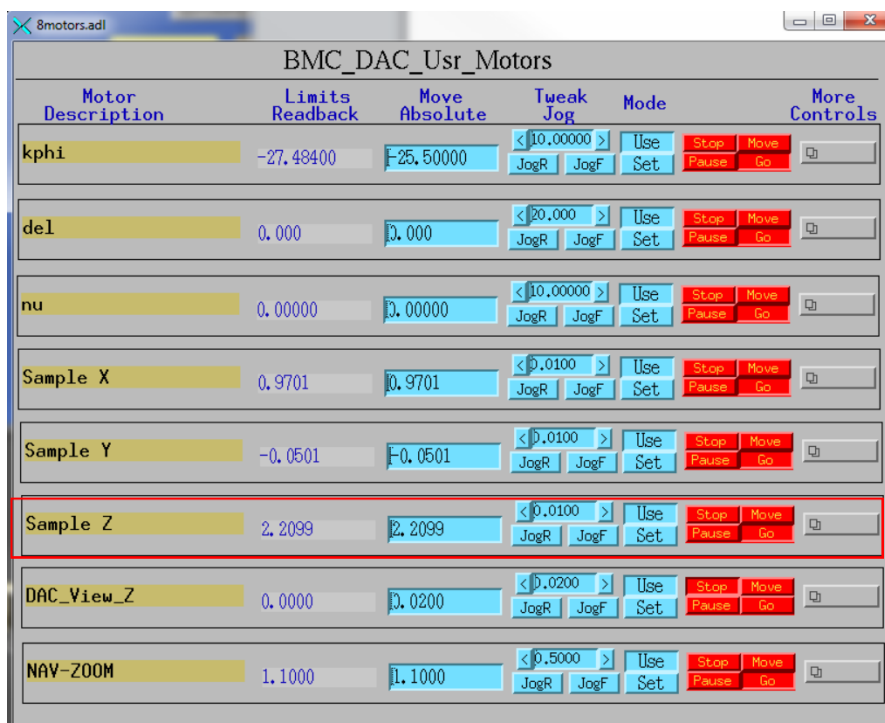
- Now that the sample is removed from the field of view go to the window called 13BMCPG1:Proc1 (NDProcess.adl). Under the flatfield normalization heading check that the enable flat field is set to disable. Then hit save next to save flat field. After hitting save now go to the enable flat field and select enable in the pull-down menu.



- The radiograph without the flat field enabled will look like the image below on the left. Once enabled, the radiograph image will look like the image on the right and contain fewer artifacts.

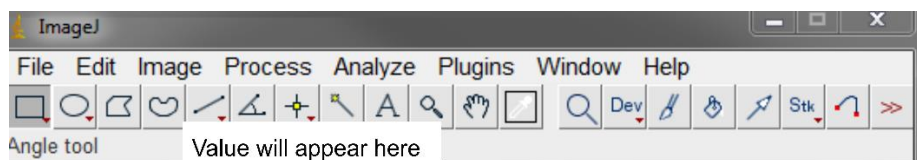


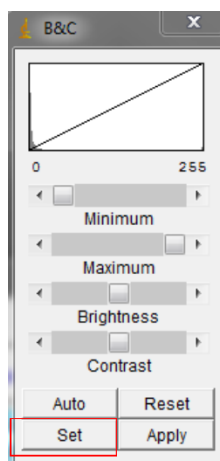
- Next in the window called BMC_DAC_Usr_Motors (8motors.adl) move the sample Z motor to 2.19. Note: this exact position changes each beamtime as well changes with each sample but this is a rough number to put the sample back into the field of view.



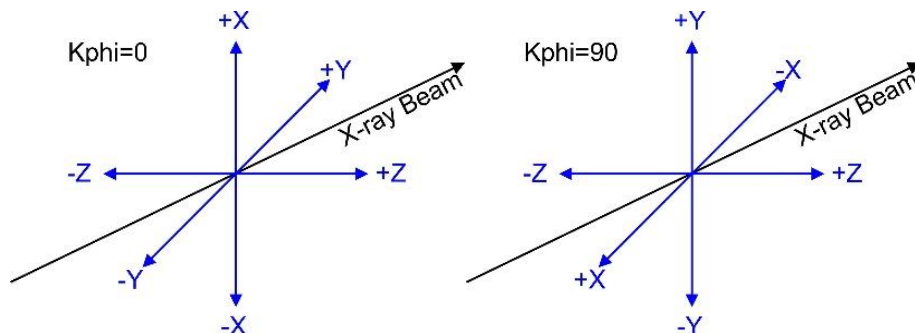
Finding an Inclusion in the Diamond

- First adjust the contrast in the ImageJ window with the live radiograph. Place the cursor in the radiograph and read the value displayed on the ImageJ bar. Then in the contrast window in ImageJ click set. Now enter the range of values that was seen in the radiograph. Values typically range between 150 and 200 so in this case one would enter the values 150 to 200 to get a better image. **Note: This is critical to find silicate inclusions.** If one only uses auto contrast then only oxides will be found so you must set values manually to find all inclusions.

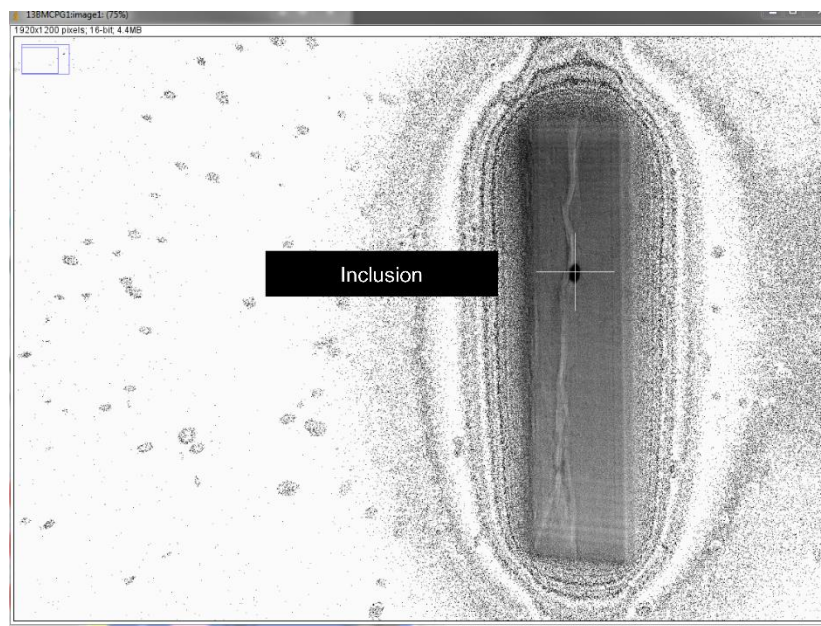




- Now one is ready to find inclusions. To move around in the diamond, use the window called BMC_DAC_Usr_Motors (8motors.adl). When $kphi=0^\circ$ use the motors sample X to move up and down and Sample Z to move left and right. Note: When $kphi=0^\circ$ don't move sample Y as it is the focus and one could ram the scintillator into the sample. If the focus needs adjusting one must go in the station and watch to make sure the scintillator will not hit. When $kphi=+90^\circ$ use the motors sample Y to move up and down and Sample Z to move left and right. Note: When $kphi=+90^\circ$ don't move sample X as it's the focus and one could hit the scintillator. Below are figures showing the geometry setup at $kphi=0^\circ$ and $kphi=+90^\circ$.

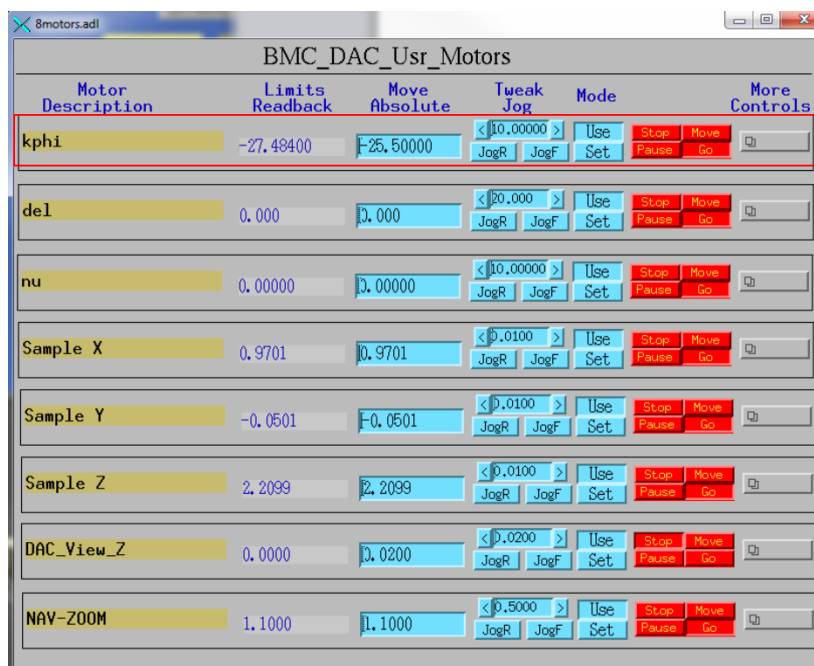


- Using the 13-BM-D tomography previously collected one can figure out how far to move to get close to the inclusion. Below is an example of what an inclusion looks like in the field of view.

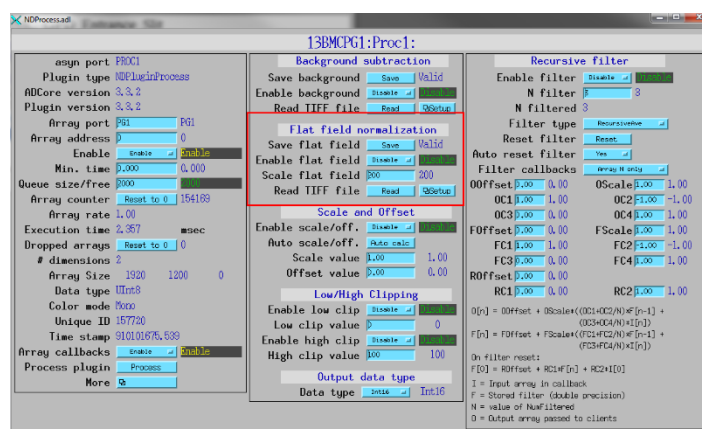


Centering the Inclusion in the X-ray Beam

- Once you have found an inclusion, using kphi start rotating the sample in small 10° steps up to $kphi=+90^\circ$. Upon rotation the inclusion will move away so use sample Y to adjust the inclusion back to the crosshair. Note: When at $kphi=0^\circ$ need to use sample X to adjust the sample. After reaching $kphi=+90$, now repeat the same process heading to $kphi=-90^\circ$. Once all the adjustments are done, rotate kphi back to zero making sure the inclusion stays in the center of the crosshair.

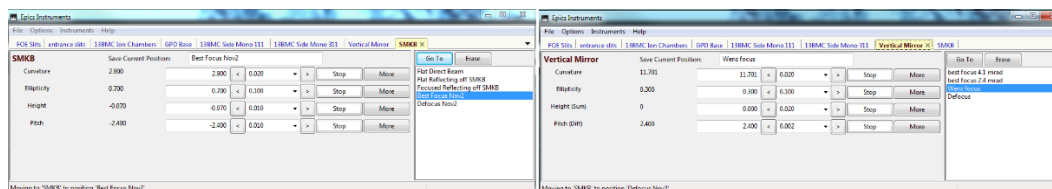


- Now that the inclusion is centered, in the window called 13BMCPG1:Proc1 (NDProcess.adl) under the flatfield normalization heading select disable.

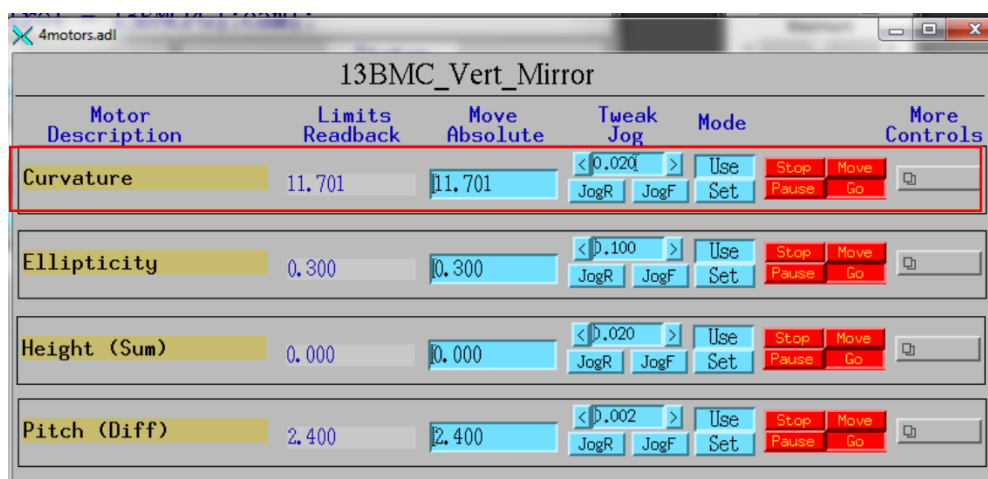


Refocusing the X-ray Beam

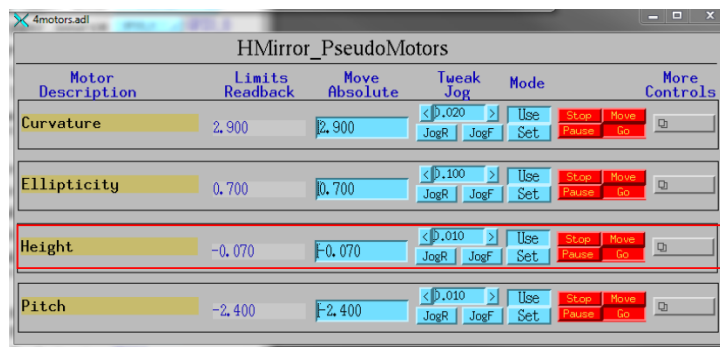
- Go to the Epics piano window and hit best focus on the SMKB tab and then vertical mirror tab hit focus. Again, these conditions are setup with the beamline scientist at the start of the beamtime. Thus, the exact names likely will be different during your beamtime.



- To shape the beam use the window 13BMC_vertical mirror (4motors.adl) and adjust the curvature motor so that the beam shape becomes rounder.

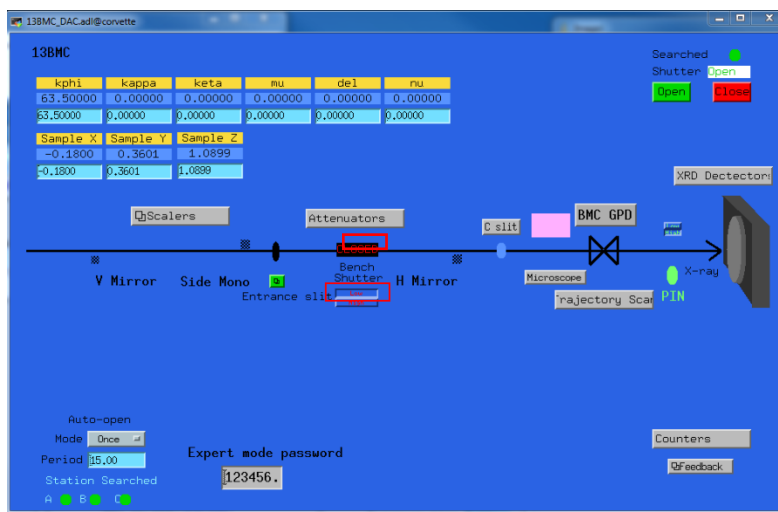


- To place the X-ray beam on the cross hair where the inclusion is centered use the window called Hmirror_pseudoMotors (4motors.adl). Within this window use the height motor only to position the beam left and right and place onto the crosshair.

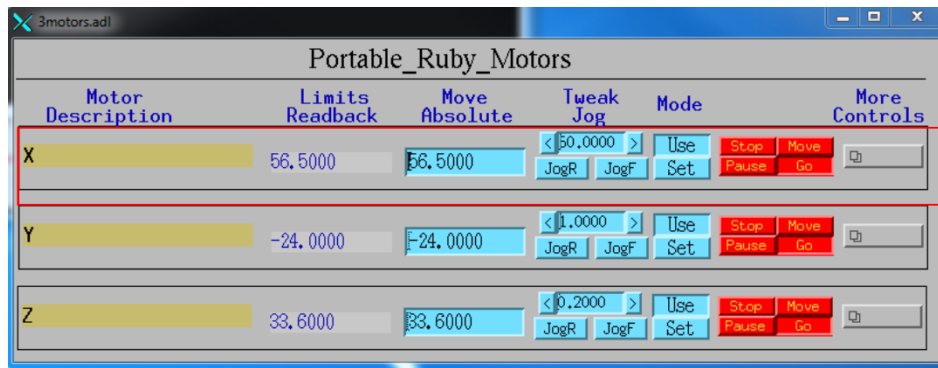


X-ray Diffraction Setup

- Turn off the X-ray beam in 13_BMC_DAC.adl by hitting the low button.



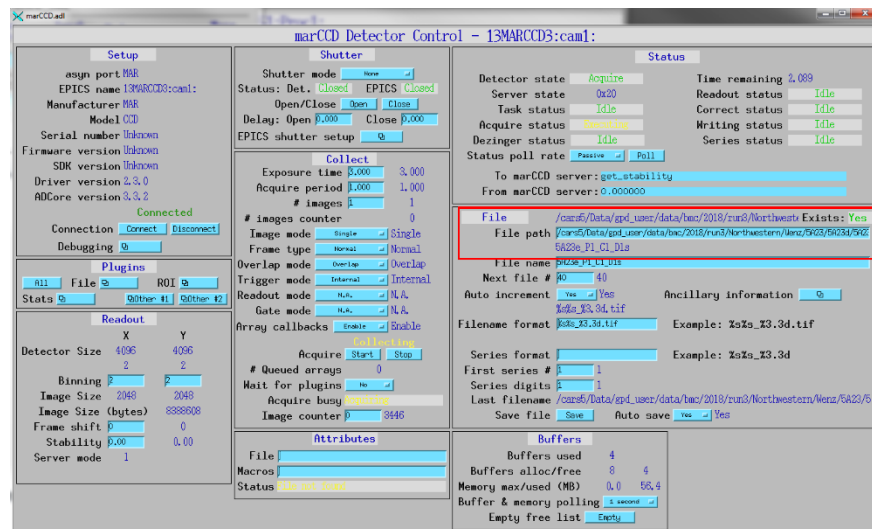
- To move the radiograph out of the beam use the window called portable motor X (3motors.adl) to 56.0. **Note: This number may change each beamtime ask the beamline scientist for the exact number.**



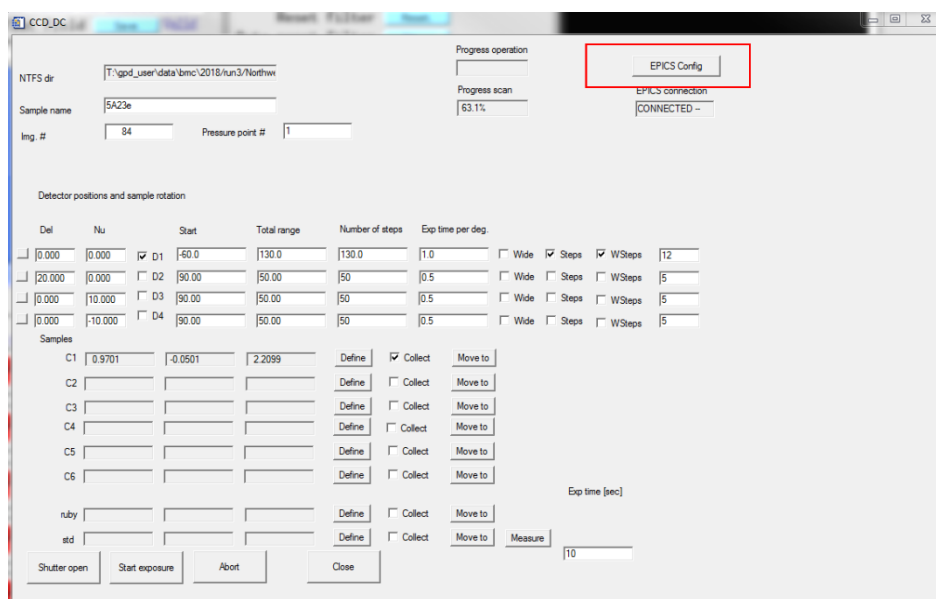
Using the MAR CCD Detector

- In windows explorer make a new directory on the second computer from the right.
- In the window marCCD.adl input the new directory under the file heading and hit enter.

Next to the heading exists it should say yes.



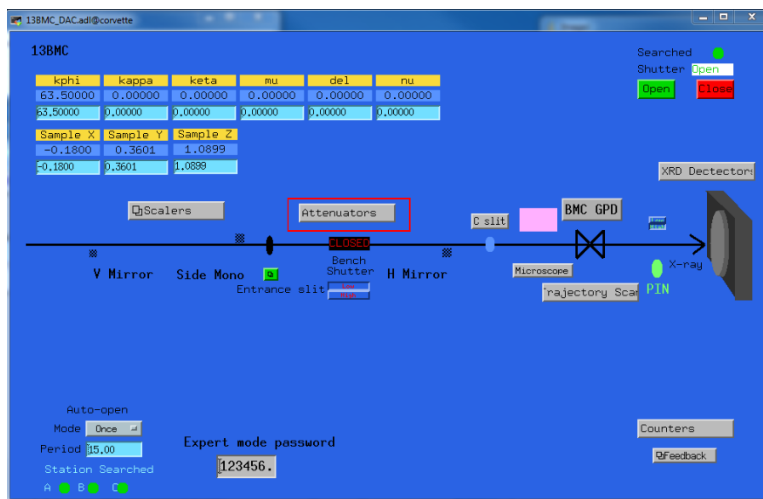
- Next open the window called CCD_DC and hit EPICS config and then hit connect in the pop-up window. Once the directory is updated then in the CCD_DC window change the sample name and change the image number to 1. To define the position of the inclusion hit the define button next to C1. This reads in the current sample X, Y, Z positions.
- Check the box that says collect next to the C1 position.



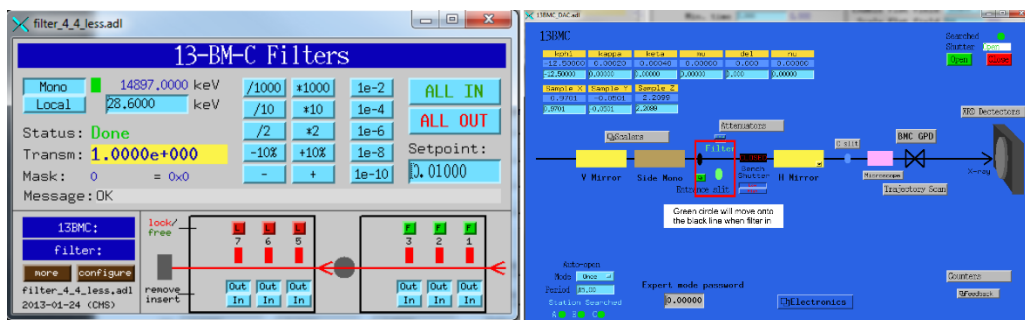
- Write down the sample X, Y, Z position in the logbook.
- Typical collection conditions: Under the detector positions and sample rotations header make sure the settings read Del=0, Nu=0, D1=check mark, Start=-90, Total range = 180, number of steps = 180, exposure time per degree = 1. These are the typical collection parameters. Sometimes other inclusions will pass in front of the inclusion of interest. If this happens, then one should make a note about what kphi angle this occurs at so you can collect in a range to avoid this interference.
- To collect a test image, check the box that says wide and hit start exposure.
- Check the test image to make sure the peaks of interest are not saturated.
- If the peaks are saturated then a filter will need to be added.

Adding Filters

- Click attenuators on the 13BMC_DAC.adl window and select filters.



- After clicking attenuators, a window will pop-up called 13BMC-Filters (filter_4_4_less.adl).
- Start by putting in filter 1 by clicking in and the light will turn green. A large green circle will move into the beam path on the 13BMC_DAC.adl window. Filter 1 means one order of magnitude. Filter 2 is two orders and so on. Note: only ever add in filter 1, 2, or 3 (not 5, 6, or 7).



- Always remove the filter after the collection is done. To remove the filter, click out and the light will turn red. Note: If the filter were left in the radiograph would not work.

Collecting a Complete Dataset

- Once the image looks good, after adding any appropriate filters, then collection of a full data set can begin.
- Check the boxes for steps and wide steps for the D1 detector position. Both steps and wide steps must be checked for the D1 position because of the way the motors move for the detector. Without the steps and wide steps, a proper refinement cannot be done.
- Then check the boxed for only wsteps for D2, D3, and D4 detector positions.
- Next check the collect box and hit start exposure.
- Make sure everything is working by watching the kphi motor as it should begin to rotate to -90° (the chosen start angle).
- Once the collection is finished a message will pop-up in the CCD_DC windows saying collection finished.

Pilatus Detector

- The beamline scientist will set up a file directory for you.
- Filters are not typically needed with the Pilatus detector
- Save the position of your inclusion in the new CCD_DC window
- Check the box for sum image
- Write down the sample X, Y, Z position in the logbook.

- Typical collection conditions: Under the detector positions and sample rotations header make sure the settings read Del=0, Nu=0, D1=check mark, Start=-90, Total range = 180, number of steps = 180, exposure time per degree = 1. These are the typical collection parameters. Sometimes other inclusions will pass in front of the inclusion of interest. If this happens, then one should make a note about what kphi angle this occurs at so you can collect in a range to avoid this interference.
- If you want to collect an additional detector positions manually enter the position by changing del= to 20 and nu to 0.

Procedure for finding a second inclusion in the same diamond

- Make sure to write down the sample X, sample Y, and sample Z positions of the previous inclusion from the BMC_DAC_Usr_Motors (8motors.adl) window.
- In that same window rotate kphi back to 0° (after a collection kphi will be at 90°).
- In the portable motors (3motors.adl) window move motor X to -8.5 bringing the radiograph in.
- Turn on the X-ray beam by hitting high on the 13BMC_DAC.adl window.
- Go to the epics piano window to the vertical mirror tab hit defocus, hit go to and then hit ok.
- In the epics piano window now go to the SMKB tab hit defocus, hit go to and then hit ok.
- In the BMC_DAC_Usr_Motors (8motors.adl) window change the sample Z to -6 **only when kphi is at 0°**.

- In the window 13BMCPG1: cam1 under the point grey area detector control heading find the collect label and change the exposure time to 1 second.
- In the 13BMCPG1:Proc1 window, under the flatfield normalization heading make sure it is disabled then click save, and select enable (should see brighter image - adjust contrast on ImageJ).
- In the window BMC_DAC_Usr_Motors, enter in sample Z position of the last inclusion measured.
- Remember to adjust the contrast of the radiograph by placing the curser in the radiograph and reading value on the horizontal ImageJ bar next to the contrast window. Values typically range between 150 and 200. Go to set in the contrast window and enter values (ex. 150 to 200) to get a better image.
- Now that the diamond is back in the field of view it's time to find more inclusions.
- Remember when searching around for more inclusions when kphi is at 0° move sample X to move up and down and move samples Z to move left and right. Remember don't move sample Y as this is the focus and might ram the sample into the scintillator. When K-phi is at $+90^\circ$ then sample Y is up and down and sample Z is left and right. Remember don't move sample X as this is the focus and might ram the sample into the scintillator.
- Once a new inclusion is found start the centering procedure so rotate kphi up to $+90^\circ$ in 10° steps, using sample Y to adjust the inclusion back to the crosshair (except at Kphi= 0° then use sample X to adjust).
- Once all the adjustments are done rotate kphi back to zero making sure the inclusions stays in the center of the crosshair.

- In the 13BMCPG1:Proc1 (or NDProcess.adl) window under the flatfield normalization heading select disable.
- Go to the epics piano window and hit best focus on SMKB tab, and then for the vertical mirror tab hit focus.
- To shape the beam use the window 13BMC_vertical mirror (4motors.adl) and adjust the curvature.
- To place the beam on the cross hair where the inclusion is centered use the window Hmirror_pseudoMotors (4motors.adl) use the height motor only to position the beam left and right and place onto the crosshair.
- Turn off beam in the 13BMC_DAC.adl window by hitting low.
- In the portable motors (3motors.adl) window move portable motor X (3motors.adl) to 46.0. This moves the radiograph setup out.
- Make a new directory in windows explorer on the second computer from the right.
- In the marCCD.adl window input the new directory under the file heading and hit enter. Next to the label exists it should say yes.
- In the window CCD_DC hit EPICS config and then hit connect in the pop-up window and make sure the directory is updated.
- Add the sample name to the CCD_DC window, change image number to 1, and hit define to C1 to read in the current sample X, Y, Z positions.
- Write the current positions in the log book and make sure that collect is checked.
- Typical collection conditions: Under the detector positions and sample rotations header make sure the settings read Del=0, Nu=0, D1=check mark, Start=-90, Total range = 180,

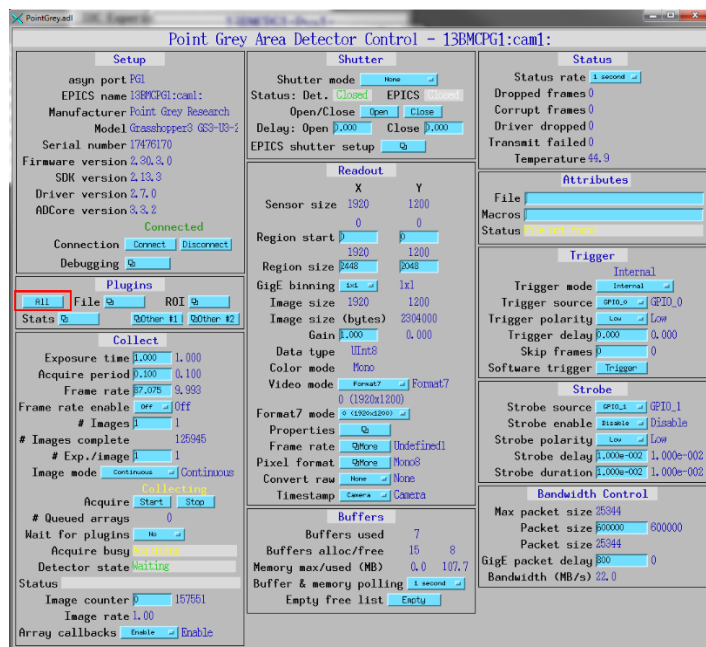
number of steps = 180, exposure time per degree = 1. These are the typical collection parameters. Sometimes other inclusions will pass in front of the inclusion of interest. If this happens, then one should make a note about what kphi angle this occurs at so you can collect in a range to avoid this interference.

- To collect a test image, check the box that says wide and hit start exposure.
- Check the test image to make sure the peaks of interest (non-diamond peaks) are not saturated.
- If the peaks are saturated then add a filter (see the prior adding a filters section).

Troubleshooting

If one cannot find the Proc1 window

- go to the Point Grey area detector window under the plugins hit all and this should pop-up a new window.
- Look for the missing window (Proc1) once found look along that horizontal line for the more button.
- Click on the more button should bring the window back.

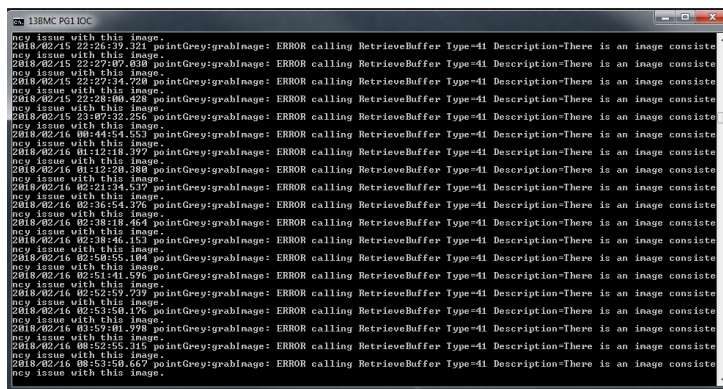


If the radiograph image window is closed

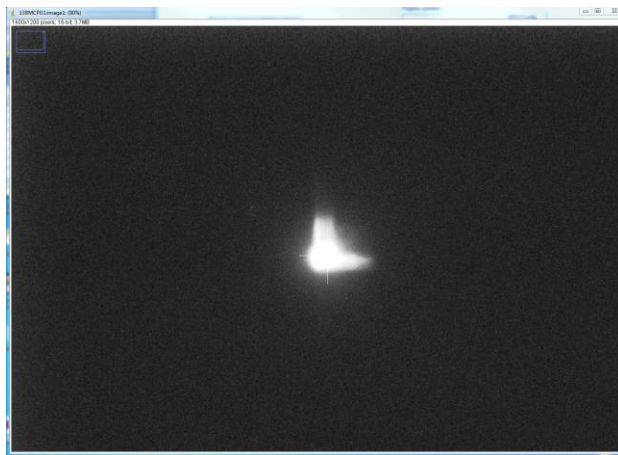
- Go to Exceed and find the Point Grey area detector control window and hit start collecting under the acquire heading.

If the camera stops refreshing

- Close the 13BMC-PG1-IOC cmd window.



- **Do not** close the 13BMC-PG1-image 1 window.



- Go into the station and find the black camera box with 2 ethernet cables and disconnect the black cable. Wait a few seconds and then plug it back in.
- Click on the desktop icon 13BMC_PG1_IOC.
- Check the ImageJ EPICS-AD_viewer-plugin window there should be a green bar where the name of the camera is. If not hit stop and then start again, which should refresh it.

If the CCD DC window freezes

- In IDL hit the up arrow on the keyboard and the CCD_DC program should appear.
- Hit run and then compile all.
- Hit the play button and run the project.