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P-T-X Constraints on Ilmenite Unit Cell and Relationship to Kimberlitic and Non-Kimberlitic Sources

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Abstract

This research investigates the mineral ilmenite, focusing on the relationship between crystal structure and mineral chemistry and/or pressure data. Ilmenites were obtained from diamond-rich and diamond-poor kimberlites and non-kimberlitic localities, to discriminate between these populations. Crystallographic results showed a delineation between kimberlitic and non-kimberlitic ilmenites at a c-axis value of 14.02 (±0.01) Å. Adding mineral chemistry and pressure data enhances the separation of kimberlitic and non-kimberlitic samples; however, this is not the case for diamond-rich versus diamond-poor kimberlites, even with three-dimensional and cluster analyses. A subset of kimberlitic ilmenites (manganese rich) were found with c-axis values and mineral chemical concentrations similar to non-kimberlitic ilmenites.

By reanalyzing ilmenite samples from previous theses at Western, reinterpretation of complexities in the past data could be done, and a measure of reliability could be determined. The 14.02 (±0.01) Å c-axis unit cell value seems consistent, enabling X-ray diffraction to potentially be used as an alternative to mineral chemical methods for diamond exploration.

Keywords: ilmenite, crystal structure, X-ray diffraction, kimberlite, diamond, exploration, mineral chemistry, barometry, rutile, cluster analysis.
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List of Symbols and Units

Symbols

n = integer
\( \lambda \) = wavelength of radiation
\( d \) = inter-planer spacing
\( \theta \) = angle between incident ray and the crystal’s lattice planes
\( \theta_1 \) = angle between the sample and source
\( \theta_2 \) = angle between the sample and the detector
Kα = emission lines result when an electron transition to the innermost “K” shell from a 2p orbital of the second or “L” shell
P = pressure
\( P_0 \) = first pressure using Ashcheakov’s method
\( P_1 \) = pressure after first correction using Ashcheakov’s method
\( P_2 \) = pressure after second correction (final pressure) using Ashcheakov’s method
\( T^\circ C \) = temperature in Celsius
\( T^\circ K \) = temperature in Kelvin
MW = Molecular weight
MF = Molar fraction
\( \alpha \) = activity

Units

\( ^\circ \) = degree
mm = millimetre
\( \mu m \) = micrometer
Å = Angstrom
nA = nanoampere
kV = kilovoltage
g/mol = grams per mole
wt\% = weight percent
ppm = parts per million
K = Kelvin
\( ^\circ C \) = Celsius
kbar = kilobar
GPa = Gigapascal
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Chapter 1: Thesis Overview

1.1 Introduction

Ilmenite can be found in various igneous and metamorphic rock types and it is a significant mineral for kimberlite exploration. Due to its resistance to both chemical and physical weathering agents it is preserved over significant erosional distances and long-time durations. High preservation potential allows for better documentation of ilmenite compared to other minerals in the same rock. Ilmenite, and the elements that make up its chemical structure, has several economic uses. The titanium element is used in white pigmentation and use in wide bandgap semiconductors (Wilson et al. 2005). The mineral ilmenite itself is used as a magnetic signature for paleomagnetism, along with its appearance in kimberlitic sources gives it use in diamond exploration (Mitchell 1973; Pasteris 1980; Wyatt et al. 2003). It is this connection with diamond exploration, that has fueled an array of research for ilmenite. Minerals that have associations with diamond bearing kimberlites, have been deemed “kimberlite indicator minerals” (KIMs) and have enabled exploration companies to employ them as vectors when searching for diamonds (Wyatt et al. 2003; Kaminsky and Belousova 2009; Carmody et al. 2014). Due to the good preservation of ilmenite, it is one of the first minerals to be acquired when searching for kimberlites, particularly in glaciated terrains. Work has also been done using ilmenite, either by itself or in conjunction with other minerals, to calculate the pressure of the host rock formation (Zhao et al. 1999; Ashchepkov et al. 2014).

Research into ilmenite’s crystal structure, mineral chemical composition, and pressure of formation, will enable an understanding of the mineral’s role in both kimberlitic and other igneous or metamorphic rock types (Pasteris 1980; Feenstra and Peters 1996; Linton et al. 1999; Wyatt et al. 2003). The research presented here builds upon past knowledge using the fundamental properties of ilmenite. Previous work on ilmenite’s unit cell parameters was done by Harwood (2009) and later by Maunder (2016), where each attempted to differentiate ilmenite from various rock types by using the mineral’s crystal structure and chemical composition as kimberlitic indicators.

To date, ilmenites that originated from the mantle and were brought up through kimberlitic processes can be separated from those that did not, using mineral chemical signatures. However, its crystal structure has not been fully developed as an indicator parameter.
This study adapts the research done by Harwood (2009) and Maunder (2016). The difference is that it performed the comparison on a larger sample base, obtaining more ilmenites from diamond-bearing and diamond-poor kimberlite localities, along with the acquisition of non-kimberlitic samples. It also utilized the formation pressure of the ilmenites as another parameter, in addition to the change in crystal structure. Pressure was acquired via geobarometry. Then, by using three-dimensional and cluster analysis software, this study looked to discern any differences that may have been missed by more conventional means.

1.2 Thesis Outline

This study is comprised of five major chapters, in addition to thesis overview from Chapter 1. Chapter 2 focuses on the background literature, specifically for kimberlites, the parameters of ilmenite, and the uses for ilmenite in kimberlitic exploration. Chapter 3 outlines the methods that were used for this research, which includes already-established tools and techniques, as well as developing newer approaches. This encompasses the parameters and methods used for Micro X-ray Diffraction (μXRD) and Electron Probe Micro-Analysis (EPMA), along with the equations and restrictions for the thermometer and barometer work, and the cluster variation analysis. Chapter 4, the results section, outlines the data collected from the instrumentation and imaging, along with the comparison to literature. Chapter 5 discusses trends in the results, where the various data are examined for comparisons. This portrays the crystallographic, mineral chemical, and pressure data with that of the various graphing methods and software to determine if crystal structure alone can be used as a possible technique to differentiation between kimberlitic and non-kimberlitic samples, along with diamond-rich and diamond-poor kimberlites. Chapter 6 gives concluding remarks about this research, along with ideas for future work.

1.3 Hypothesis

With the understanding that kimberlitic and non-kimberlitic ilmenites form under different pressure conditions, which influences their mineral chemistry, this should be reflected in their crystal structure. Due to the smaller size of kimberlitic ilmenites’ cations (magnesium), and their formation under compression at depth, their unit cell size should be smaller than that of non-kimberlitic samples. Due to the alternating arrangement of ilmenite’s layers perpendicular to
the c-axis, it will most likely show more prominent results than the a-axis in this hexagonal structure. By the above arguments, there should be a discrimination between the two rock types, allowing the unit cell parameters to be used as a tool for industry purposes, specifically diamond exploration. This may be less evident when ilmenites from diamond-rich and diamond-poor kimberlites are compared, as their mineral chemistry and formation pressures may be too similar.

1.4 Thesis Goals

There are six overall goals for this thesis in its attempt to utilize ilmenite for kimberlitic exploration. 1) To understand how the crystal structure of ilmenite changes as a function of mineral composition and pressure. 2) Discriminate between ilmenite samples from kimberlitic and non-kimberlitic localities using ilmenite’s crystal structure parameters, with or without the mineral composition and/or pressure. 3) Discriminate between ilmenite samples from diamond-rich and diamond-poor kimberlite localities using ilmenite’s crystal structure parameters, with or without the mineral composition and/or pressure. 4) Resolve the inconsistencies and complexities that arose in the Harwood (2009) and Maunder (2016) studies by reanalyzing the same ilmenite samples. 5) Comparing the reanalyzed data from this research with that of Harwood (2009) and Maunder (2016), to determine the reliability and repeatability of these methods. 6) The overarching goal for this thesis is to develop a crystallographic approach to diamond exploration, using ilmenite’s crystal structure as an alternative to its mineral composition.
Chapter 2: Background Literature

2.1 Introduction

This thesis focuses on the mineral ilmenite, specifically using it to separate kimberlitic and non-kimberlitic rock types. As such, this chapter focuses on the knowledge acquired and methods developed by previous researchers. The outlined information will include details on the formation of kimberlites, along with the formation of mantle ilmenites which are brought up by kimberlitic ascension. Information about the crystal structure and its susceptibility to change as a function of mineral composition and formation pressure will be provided. This chapter will also give details about the thermometers and barometers used to determine the formation pressure of the ilmenites for this study, along with information about the mineral rutile, which was used in some of the temperature and pressure equations.

2.2 Kimberlites

Kimberlites are one of the main rock types in which diamonds can be transported and found. However, even though diamonds are associated with these rock types, they themselves are not part of the kimberlitic mineral assemblage, as kimberlites act as the transport mechanism for diamond xenocrysts from source rocks within the mantle (Dawson 1971; Mitchell 1993). Other igneous rock types such as lamproites and lamprophyres also have the capability of hosting xenocrystic diamonds, however these cases are rarer.

Kimberlite is a term referred to an inequigranular rock, with a suite of megacrysts giving it a porphyritic characteristic (Dawson 1971). These partially-melted, mantle-derived igneous rocks are volatile-rich, potassic ultramafic (K > Na) transport mechanisms for lower mantel materials, including diamonds (Dawson 1971; Clement et al. 1984; Mitchell 1993). The volatile rich aspect stems from the concentration of approximately 5 wt% H₂O and 10 wt% CO₂ components (Dawson 1971; Clement et al. 1984). The potassic aspect of this definition refers to the high K₂O concentrations, which is mainly held within the mineral phlogopite (Clement et al. 1984). Lastly, the ultramafic aspect refers to the generally low SiO₂ abundance in kimberlites, which usually does not exceed 40 wt% (Dawson 1971; Clement et al. 1984).
The megacryst suite is composed primarily of olivine, enstatite, Cr-diopside, pyrope garnet, spinel, picro-ilmenite, and phlogopite, which is encompassed in a fine-grained matrix of carbonates, phlogopite, magnetite, perovskite, and secondary mineralization of serpentine (Dawson 1971; Skinner and Clement 1979; Moore 1987). Some of the dominant kimberlitic indicator minerals (KIMs) are shown in Figure 2-1. The term megacryst is used because there is an abundance of both phenocryst and xenocryst minerals; there are minerals that formed from the kimberlite source and minerals with an unknown formation history respectively. Most of the minerals that form within these and megacryst suites, with the exception of olivine, rarely form in more than accessory abundances (Clement et al. 1984). Most diamonds form from deep mantle origins (> 150 km) and are held within the matrix of kimberlites when they are present, except for eclogitic diamonds form within subduction zones (Dawson 1971; Mitchell 1993). Diamonds are relatively rare in kimberlites, forming concentrations of less than 2.0 ppm (Kjarsgaard 2007a). From the mineral assemblages in kimberlites, the rock type is found to be

![Figure 2-1: Photomicrographs of kimberlitic indicator minerals (KIMs). A) mauve peridotitic garnet with an alteration rim. B) red peridotitic garnet. C) and D) orange low-Cr garnets. E) and F) chromite. G) and H) ilmenite (highlighted in yellow due to focus with this thesis). I) and J) Cr-diopside. K) kimberlite concentrate. L) microdiamonds (modified from Nowicki et al. 2007).]
rich in concentrations of Mg, third row transition elements such as Co, Cr, and Ni, along with incompatible elements such as Ba, Nb, P, Sr, Ta, Th, U, and LREEs (Kjarsgaard 2007a).

The majority of kimberlites are confined to cratons, which are accumulations of ancient continental crust, however, most diamond-barren kimberlites can be found on the boundaries of these cratons, in the belts of younger Precambrian rocks (Dawson 1971; Mitchell 1993). The boundary between the lithosphere and asthenosphere can be postulated as potential shear zones, due to the underlying asthenosphere applying a drag force to overlying lithosphere (Kennedy et al. 2002). The lithospheric boundaries, along with the diamond stability field within the mantle can be seen in Figure 2-2. Kimberlitic magmatism is noted most evidently in Precambrian ages; however, other ages are recorded as Cretaceous (Dawson 1971; Sparks et al. 2006). Beneath these cratons, held within the upper mantle of the earth, ultramafic rocks of lherzolite and depleted harzburgite and dunite compositions are most common, with discrete pockets of eclogitic components dispersed throughout (Mitchell 1993). The tertiary diagram for ultramafic mantle rocks can be seen in Figure 2-3.

There are two main groupings of kimberlites which have been established by mineralogy, mineral chemical data, and isotopic signatures. The first and most common is termed as Group 1 Kimberlites, which carry similar characteristics to ocean island basalts, and are thought to have origins in the asthenosphere (Ringwood et al. 1992; Mitchell 1993). Group 2 Kimberlites, also called “Orangeites”, are micaceous in description with a greater enrichment of light rare earth elements (LREE) and may be the result of partial melting in the lithosphere (Ringwood et al. 1992). The Group 2 Kimberlites are compositionally more related to lamproites, another potentially diamond-bearing system, and the absence of these rock types in other cratonic provinces is usually related to later metasomatic events (Mitchell 1993). Kimberlites have long been established as the transport mechanism for the mantle material. Two primary upper mantle sources for the material can be observed. The most common of the two sources is ultramafic igneous material known as peridotites, with the most common of these being the rock type lherzolite (Dawson 1971; Ringwood et al. 1992). The second subducted most common diamond carrying rock type is metamorphically altered oceanic crusts called eclogites, which accumulate beneath the continental cratons (Dawson 1971; Smyth and Caporuscio 1984: Ringwood et al. 1992). Both of these source rocks can be noted in Figure 2-2.
One of the main discoveries in determining which minerals were associated with diamonds, and thus which minerals may be used as candidates for diamond exploration, was made by looking at the mineral inclusions in diamonds themselves (Sutton 1921; Stachel and Harris 2008). These inclusions reflected the xenocryst material in the kimberlites, forming the two groups of either peridotitic or eclogitic inclusions (Mitchell 1993). Peridotitic inclusions predominantly consist of forsteritic olivine, Cr-rich garnet, Cr-diopside, and enstatite, with similar compositions to lherzolites and harzburgites in the upper mantle, with just a slight enrichment of chromium (Mitchell 1993). The eclogitic inclusions on the other hand consist of pyrope-almandine garnets, omphacitic pyroxene, kyanite, and coesite, which relates more readily to the compositions of eclogitic xenoliths (Mitchell 1993). In neither case is the mineral ilmenite listed as an inclusion in diamond, however, this mineral shows up in numerous kimberlites from around the world. Ilmenite is listed as a kimberlite indicator mineral (KIM) and not a diamond indicator mineral (due to its rarity as diamond inclusions). These rare cases have shown ilmenite inclusions in numerous localities around the world (Brazil, Democratic Republic of Congo, United States, Russia, and Tanzania), which in some cases may be later infilling events, but it is

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**Figure 2-2:** Cross-section of Archean craton. Shows the stability field of diamond and graphite within the lithosphere and asthenosphere. Also portrays the locations of the kimberlite (K) and lamproite (L) sources of peridotitic (GL) and eclogitic (E) material (modified from Mitchell 1993).
unlikely that all of them are a result of this (Meyer and Svisero 1975; Ntanda et al. 1982; Meyer and McCallum 1986; Sobolev et al. 1997; Stachel et al. 1998). For most diamond inclusions, not only ilmenite ones, there is the risk that they are synchronous without being sygeneti (Nestola et al. 2017).

The minerals in diamonds have been shown to be within equilibrium at pressures of 50 to 60 kbar, which relates to around 150 to 250 km depths, and temperatures of 900 to 1400°C, which are characteristic conditions of the upper mantle (Ringwood et al. 1992; Mitchell 1993, Kjarsgaard 2007). As these conditions also relate to the stability of diamond formation, this would relate to diamond growth occurring within the upper mantle (Mitchell 1993).

As mentioned before, kimberlites are rich in volatiles, which are predominantly carbon dioxide and carbon monoxide, with some being water and methane components (Dawson 1971; Wyllie 1980; Sparks et al. 2006). Even though we term kimberlites as “volatile-rich”, the solubilities of these volatiles are not as high as required in the emplacement of kimberlitic melts, which was seen by Kamenetsky et al. (2014). For kimberlites to contain diamonds or graphite,
this would suggest that even at depth, the oxygen fugacity is not high enough to oxidize all the carbon in kimberlites (Wyllie 1980). The magma itself would also require pre-enriching events, such as metasomatism, in order to account for the abundance of incompatible elements in kimberlitic material (Ringwood et al. 1992). Therefore, this proto-kimberlite melt would be nearly anhydrous, aluminosilicate-poor, Na-Ca carbonate, enriched in lithophile trace elements, halogens, and sulphur (Kamenetsky et al. 2014). One model for the origin of kimberlitic melts invokes partial melting at the base of the lithosphere, beneath the thick cratons (Sparks et al. 2006). This model suggests the formation of a heterogenous source via metasomatic processes at 150 to 200 km depth, relating more to Group 2 Kimberlites. Another model relates to Group 1 Kimberlites, with the formation of melt at the transition zone of the mantle (400 to 650 km depth), in association with mantle plumes (Sparks et al. 2006). This was influenced and modeled by the discovery of majorite (a lower mantle garnet polymorph) as diamond inclusions (Ringwood et al. 1992; Sparks et al. 2006). Magmatic carbonate has also been theorized as a vital mechanism for the formation of Group 1 Kimberlites, as it would induce partial melting at lower temperatures (Francis and Patterson 2009).

The ascension of fluid could also result in metasomatic interactions, as the volatile components in the magma undergo metamorphic alteration, replacing the minerals in the upper mantle rocks (Wyllie 1980). The volatile content compressed in kimberlites is one of the main theories behind their rapid ascension through the mantle and crust. There are a few ideas on how the rapid emplacement of these kimberlitic materials occurred; whether they are from the top down or bottom up. Each of these models would require a conduit to breach the surface, allowing for magma at greater depths to rise quickly up from explosive interactions at shallower depths, as the uprising vapours change from CO₂-rich to H₂O-rich (Wyllie 1980; Sparks et al. 2006). These relatively low-temperature melts, would arrive rapidly to the surface, and due to their unique rheological properties, would be able to ensnare and bring up mantle and crustal material (Kamenetsky et al. 2014).

Sparks et al. (2006) devised a four-stage model for the formation of kimberlites from the top to the bottom, with the first three stages illustrated in Figure 2-4. The first stage (Figure 1-4A) is the initial creation of the crater zone, where either near surface groundwater leads to a phreatomagmatic event, over time widening and deepening the crater, or a dendric netting of
volatile-rich magma rising and intruding into the country rock; which relates to the work done by Wyllie in 1980. The second stage (Figure 1-4B) forms the pipe of the kimberlite, where the explosive activity widens and deepens the conduit, while country rock breaks apart and falls into the kimberlite. During the ascension of the magma, rapid cooling results in the crystallization of the kimberlitic matrix (predominantly olivine). This cooling process is a result of both the interaction of groundwater and transfer of heat to the country rock, along with the adiabatic expansion of the volatile-rich magma, endothermic reactions between the mantle-derived minerals, and the entrainment of xenocrysts. As pressure increases and begins to exceed that of the wall rock, this process would accelerate. This would then lead to the third stage (Figure 1-4C), where the pipe begins infilling, as breccia and volcanic material fall and settle inside the diatreme of the kimberlite. The roots of the kimberlite are then preserved as magma that can not penetrate and interact anymore, leading to a decline in activity. The fourth and final stage then takes place through the rest of the kimberlite’s life, as metamorphism after the eruption(s) lead to the alteration of the minerals in the kimberlite from hydrothermal activities. This process gives way to the dominant serpentinization seen in kimberlites (Sparks et al. 2006).
A newer model was established by Wilson and Head III (2007), with their kimberlitic emplacement working from the bottom to the top (Figure 1-5). Their first stage (Figure 2-5A and Figure 2-5B) relates to the propagation of the magma conduit from its deep source. They postulated that the magma itself would contain as much as 20 wt% CO$_2$, and due to the inability to diffuse this volatile phase, would create a foam layer beneath the tip of the conduit. This would enable an explosive event, and as the supply of CO$_2$ is renewed into the system, the dyke would grow upwards. The second stage (Figure 2-5C) relates to the ascension of the magma and the fracturing of the wall-rock it is intruding upon. The stress upon the country rock would change from tensile to compressive, where smaller dykelets can be seen as a way to decrease the pressure. The number of wall-rock xenoliths in the kimberlite can be related to the rock strength. In stage three (Figure 2-5D), the dyke breaches the surface, allowing for a release of the volatile gas, where adiabatic expansion produces a volcanic explosion, imploding the country rock around the kimberlite. Depressurization and rapid cooling are initiated in stage four (Figure 2-5E and Figure 2-5F), where the incorporation of solid particles via liquid fragments in the rising magma can be seen. In the fifth stage (Figure 2-5G), the gas expands in the dyke, allowing for an accelerated ventilation process, breaking apart the already-weakened country rock, and forming the diatreme zone of the kimberlite. Cooling processes in the deeper portion of the kimberlite halt the rise of magma, inhibiting further eruptions. The final stage (Figure 2-5H) follows the post-explosion processes, with the formation of the crater zone via tuff and pyroclastic material. This may also result in the formation of a crater lake, if groundwater is prevalent in the area. Similar to the model by Spark et al. (2006), metamorphic events via hydrothermal alteration would be prevalent after the kimberlitic emplacement.

Due to the post-magmatic alteration events replacing olivine and carbonate material, the bulk kimberlitic material does not fully represent the kimberlite melts that were emplaced (Kamenetsky et al. 2014). The rapid nature of these events leads to difficulty in obtaining ages for the various zones within the kimberlite, and thus postulation is still ongoing regarding which model is correct. With the increase in the number of chronological methods being developed, this debate may one day be solved. It may well be that both models are correct depending on the variables in each kimberlite’s specific locality. What can be noted is that kimberlitic pipes can not only be established from a single event, but also form numerous explosive processes or a long-term continuous event with interactions from the mantle (Wyllie 1980). Due to the volatile
nature of these events, they can be linked to already established, weakened structures, which the propagation of fluid and magma can utilize (Wyllie 1980).

Figure 2-5: Sequence of Events for Kimberlitic Emplacement. This figure shows events from generation, ascent, and eruption of the kimberlitic magma. A) Dyke propagation, B) Production of magmatic foam, C) Dyke ascent and wall fracturing, D) Surface being broke by dyke tip and implosion of walls, E) Propagation of magma and country rock, F) Diatreme begins to form, G) Increased pressure and fluidization to, H) Aftermath of event. The blue circles represent the movement of ilmenite (modified from Wilson & Head III 2007).
Even with the identification of a kimberlite, or other diamond bearing rock, this does not necessarily establish a source for diamonds, because as mentioned before diamonds are xenocrysts within these rocks. Resorption and removal of diamonds via magmatic processes can also result in the absence of diamonds (Mitchell 1993). Other than kimberlites, which are primary diamond deposits from mantle-derived igneous rocks, diamond deposits can also be established from the weathering and erosion of the source rocks; such is the case for many placer and alluvial mines, such as those in South America and Africa (Mitchell 1993; Shcheka et al. 2006). The porous nature of kimberlites allows them to be highly susceptible to these post-emplacement alteration events, which allow for high levels of weathering processes (Kjarsgaard 2007a).

One of the original kimberlite models, noted as the Dawson model (seen on the left side of Figure 2-6), was used to differentiate different facies in the kimberlite structure. This model was established by Dawson 1971, and has been modified and adapted throughout the years by other geologists. The observations for this model were established by exploration and mining in the Southern Africa region, with the lower part derived from the Kimberly area in South Africa, the upper portion from kimberlites in Tanzania, Botswana, Angola, and the Democratic Republic of Congo, while observations from Mali established the addition of the Tuff ring (Dawson 1971; Hawthorne 1975; Mitchell 1986; Kjarsgaard 2007b). As such, the original model was a

![Figure 2-6: South African kimberlite model. Left side is the older terminology, while right is the revised. The revision allowed for easier comprehension worldwide due to its use in rock-type instead of facies (modified from Kjarsgaard 2007b).](image-url)
composite structure, formed from the fitting together of observations from various localities. This South African Kimberlite pipe model showed a simple stratification with crater, diatreme, and hypabyssal facies. A revised set of a terminology was established by Kjarsgaard 2007b (and later enhanced by Scott-Smith et al. 2013), which subdivided the model into kimberlite types rather than facies, with the changes being noted on the right side of Figure 2-6. The pyroclastic kimberlite (PK) and resedimented volcaniclastic kimberlite (RVK) were held within the crater zone at the top of the pipe, volcaniclastic (VK) and kimberlitic breccia (KB) consisted of the infilled portion of the diatreme zone, and lastly the root zone of the pipe consisted of the hypabyssal kimberlite (HK). Due to the variability of rock types, this model was intended to remove assumptions from exploration studies when the entire kimberlite was not observed.

Due to the high porosity of kimberlites, they are susceptible to weathering processes post emplacement (McClenaghan and Kjarsgaard 2007). Fluvial processes most commonly affect kimberlites in arid environments, such as those found in Africa and Australia. Kimberlites that are found in temperate to tundra environments can also be affected by glacial alteration, such as those found in Canada or Russia (Seigal 2006; McClenaghan and Kjarsgaard 2007). Both cases result in a dispersion of kimberlitic material away from the source (Seigal 2006; McClenaghan and Kjarsgaard 2007). The susceptibility to weathering processes causes the less robust material to be destroyed farther away from the kimberlite. This causes either stream deposits or glacial trains of varying mineralogy away from the kimberlite. The major zones of kimberlite indicator minerals from closest to the kimberlite (most susceptible to erosion) to farthest out (most resistant to erosion) are: garnet, chromite, and then ilmenite (McClenaghan and Kjarsgaard 2007). Figure 2-7 shows a schematic for the dispersion train created from glacial erosion, along with a secondary stream for the dispersion from fluvial processes.

2.3 The Mineral Ilmenite

The mineral ilmenite has the simplified formula FeTiO₃. However, more realistically it is represented generally by the formula A²⁺B⁴⁺O₃, where the A-site is most commonly Fe²⁺ but can substitute readily for Cr, Co, Fe³⁺, Mg, Mn, Ni, and Zn, while the B-site is predominately Ti with minute substitutions for Al, Nb, Si, V, and Zr (Horiuchi and Hirano 1982; Feenstra and Peters 1996; Anthony et al. 1997; Linton et al. 1999; Wilson et al. 2005; Yamanaka et al. 2005).
Elements such as Ca and Ba tend be very minimal in the ilmenite structure due to their large radii, which in higher concentrations instead forms perovskite structures (Yamanaka et al. 2005). Ilmenite is a naturally occurring mineral which is present in both crustal and mantle derived igneous rocks (Haggerty and Sautter 1990; Wilson et al. 2005). Ilmenite’s structure is a function of composition, pressure, and temperature, where the substitution of the elements varies systematically due to the formation pressure and temperature (Wilson et al. 2005; Yamanaka et al. 2005). These parameters in turn affect the mineral’s electronic, magnetic, and optical properties, however this can vary systematically with the cation radius for the substituting elements (Wilson et al. 2005; Yamanaka et al. 2005).

In ilmenite, the A- and B-sites are comprised of alternating layers which follow the pattern -A-B-□-B-A- (where the □ is a vacancy) (Wilson et al. 2005; Yamanaka et al. 2005). This stacking lies perpendicular to the c-axis. The ilmenite structure consists of the A- and B-cations in octahedral coordination in a face- and edge-sharing configuration, where each of the octahedra

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**Figure 2-7:** A schematic for the post-emplacement weathering agents and dispersal train from a glacial altered terrain, with a subsequent fluvial event. A) shows the plan view with possible outlines in purple of the major heavy mineral zones indicated. B) shows the cross-section view (modified from McClenaghan and Kjarsgaard 2007).
shares one of their faces with the other type of cation, while the other face is shared with this octahedral vacancy (Lima-de-Faria 1994; Wilson et al. 2005; Yamanaka et al. 2005). This creates a hexagonal crystal structure with point group R$\bar{3}$, where the c-axis becomes a threefold rotation axis, and the A- and B-sites are then octahedrally coordinated with the oxygen ions (Lima-de-Faria 1994; Anthony et al. 1997; Wilson et al. 2005; Yamanaka et al. 2005). This orientation can be seen in Figure 2-8, using the common FeTiO$_3$ composition. As the bond lengths differ between the A- and B-site cations, as a function of their radii, this causes the smaller, stronger B-site cations (smaller radii) to act more rigidly compared to the longer, weaker A-site cations (larger radii), where compression is more readily available (Yamanaka et al. 2005). These bond distances and thus the crystal structure itself is a representative function of the pressure (as well as temperature and mineral composition) during the mineral’s formation (Yamanaka et al. 2005). Thus, an increase pressure (i.e. formation at lower depths) will cause compression of the c-axis of ilmenite’s structure, causing a decrease in the volume.

Minerals that bear A$^{2+}$B$^{4+}$O$_3$ compositions are found to either crystalize with perovskite structures (high coordination) or as sesquioxide structures (low coordination) which consists primarily of ilmenite and lithium niobate (LiNbO$_3$) structures. (Linton et al. 1999; Wilson et al. 2005).
Within the mantle as pressures increase, enstatite will transition to garnet (majorite), followed by a transition to the ilmenite structure, and then the perovskite phase as mentioned before (Karki et al. 2000; Akaogi et al. 2015). If temperatures are high enough, then garnet, ilmenite, and perovskite will form together (Karki et al. 2000). A study by Akaogi et al. (2015) experimentally derived a tolerance factor for the high-pressure mineral transformations, in which compounds whose factors where found between 0.8 and 0.9 commonly crystallized into ilmenite, and with an increase in pressure into perovskite. They then showed that all ilmenites bearing the \( \text{A}^{2+}\text{TiO}_3 \) general formula would transform into perovskite at high pressure, followed by a conversion into the lithium niobate structure as pressure decreased.

As pressure and depth increases, the ilmenite structure incorporates an increasing amount of magnesium content within it, which is usually seen in kimberlites, hornfels, and dolomitic calc-silicate rocks (Feenstra and Peters 1996; Linton et al. 1999). Before reaching the deep mantle, ilmenite can have both Fe and Mg concentrations stable within its structure, yet as depth continually increases the Fe in the A-site substitutes out for Mg, and the Ti in the B-site substitutes out for Si, creating the ilmenite structure with the formula of MgSiO\(_3\) (Horiuchi and Hirano 1982; Linton et al. 1999). Magnesium and silicon are more stable at high pressures due to their more rigid octahedron coordination, and thus these elements are a proxy for depth (Horiuchi and Hirano 1982; Weidner and Ito 1985). MgSiO\(_3\) ilmenite is predicted to be important in subduction related zones in the transition and upper mantle (Karki et al. 2000).

Ilmenites that have high concentrations of zinc are usually found in metamorphosed Mn-Zn ore deposits, while higher concentrations of manganese are found in felsic igneous rocks, Mn-rich metasediments, and metamorphosed Mn-Fe deposits (Feenstra and Peters 1996). Ilmenites that have Fe\(^{3+}\) substitution indicate an increase in oxygen fugacity, which is coupled together with a decrease in the overall volume (Feenstra and Peters 1996).

When an excess of other elements are present during ilmenite crystallization, exsolution readily occurs on cooling. In crustal ilmenites the exsolved phase can consist of hematite (Fe\(_2\)O\(_3\)), pyrophanite (MnTiO\(_3\)), and geikielite (MgTiO\(_3\)), while in mantle ilmenites exsolution is rarer, consisting mainly as magnetite (Fe\(_3\)O\(_4\)) and ulvöspinel (Fe\(_2\)TiO\(_4\)) (Feenstra and Peters 1996; Tan et al. 2016). The most common solid solution in crustal ilmenites is that with hematite, which is due to it encompassing an extended range of temperature and oxygen fugacity (Tan et al. 2016). With reducing conditions being more relevant in the mantle, magnetite (which
bears Fe\(^{2+}\) and Fe\(^{3+}\), instead of only Fe\(^{3+}\)) is more commonly found to be exsolved from ilmenite (Tan et al. 2016). Ilmenite-chromite exsolution has also been noted in rare cases, which can be attributed to either primary exsolution of ulvöspinel in chromite, followed by oxidation to ilmenite (Bøe 1978).

### 2.4 Ilmenite as Kimberlitic/ Diamond Indicator Mineral

Magnesium ilmenite (or more commonly referred to as picroilmenite) is a characteristic accessory mineral in kimberlitic processes. Ilmenite however, is noted as predominantly useful in Group I kimberlites, as Group II kimberlites and lamproites show scarce amounts of ilmenite (Gurney et al. 1979). Kimberlitic picroilmenites, as the name would suggest, are attributed to higher concentrations of Mg, with lower enrichment in Fe when compared to the wide variety of ilmenites from non-kimberlitic igneous (gabbros, norite, granites, and anorthosites) rocks (Pasteris 1980; Wyatt et al. 2003). The increase in Mg could be attributed to the stability of Mg over Fe with greater depths in the mantle, along with the termination of mafic silicate mineral formation at depths (such as olivine) allowing for an excess Mg content to be taken in to the ilmenite structure (Pasteris 1980).

Ilmenite can be found in kimberlites as either small irregular grains in the kimberlite matrix, large crystalline megacryst, or intergrowths with silicate phases, magnetite, rutile, or perovskite (Mitchell 1973; Pasteris 1980; Wyatt et al. 2003). The term macrocryst is used when referring to grains larger than groundmass size, regardless or origin (either phenocryst or xenocryst); while megacryst refers to large grains with mantle xenolith origins (Pasteris 1980). Small (< 50 μm to even smaller than 10 μm) ilmenite grains are common in the groundmass of kimberlites (Moore 1987). When compared to the larger ilmenite grains, they exhibited enriched Cr-concentrations (Moore 1987). Ilmenite however could also be found of metasomatic origin, intergrown within megacrysts, or part of the mica-amphibole-rutile-ilmenite-diopside (MARID) rock type (Dawson and Smith 1977; Wyatt and Lawless 1984; Moore 1987; Schulze 1987; Wyatt et al. 2003). Rare cases are ilmenite included within diamonds. These inclusions have showed varying compositions from close to pure FeTiO\(_3\) and extremely low Cr\(_2\)O\(_3\), to enriched MgO and low Cr\(_2\)O\(_3\) (Meyer and Svisero 1975; Moore 1987).

Exsolution lamellae are rather rare in the kimberlitic picroilmenites, especially when compared to other igneous Mg-poor ilmenites. The most common exsolved phases are spinel
structure minerals along the (0001) planes in ilmenite, which include ulvöspinel (Fe$_2$TiO$_4$) and magnetite (Fe$_3$O$_4$) (Mitchell 1973). Occasionally ilmenite has been seen to exsolve chromite (FeCr$_2$O$_4$), implying enriched Cr-concentrations upon formation (Moore 1987). Intergrowths of rutile (TiO$_2$) have also been reported. However, it is noted that this could either be exsolution or lamellae or as replacement of ilmenite, requiring texture examination of the minerals to determine if they formed together or if rutile came later (Mitchell 1973; Moore 1987). Perovskite on the other hand is an extremely common mineral associated with ilmenite, however it usually occurs as reaction rims, formed by the reaction of ilmenite with kimberlitic fluids and not exsolution behaviour (Mitchell 1973). The distinct rarity of exsolution in Mg-ilmenites has been commonly attributed with the formation at high pressure and temperature within the mantle, followed by the rapid quenching during ascent via kimberlitic transport fluids (Mitchell 1973).

Whether large ilmenite grains formed as phenocrysts in kimberlitic melts, or whether they were derived from another source in the mantle, and thus xenocrysts, was highly contested. Groundmass ilmenite was petrographically suggested to crystallize directly from the kimberlite magma, as and such is determined to be phenocrystic (Pasteris 1980; Moore 1987). Non-groundmass ilmenite however is where controversy comes in. One theory suggests that crystallization with a relatively constant pressure and wide temperature range would imply kimberlitic affinity (Gurney et al. 1979). The other viewpoint would counteract with the temperature of ilmenite formation being well above that of kimberlitic solidus (Schulze 1984). The phenocryst model would imply formation in a chemically zoned magma, after which ilmenite is then incorporated into a later, unrelated kimberlite liquid (Boyd and Nixon 1973; Pasteris et al. 1979). However, the lack of deformation and zonation of Mg to Fe-rich liquids is not readily explained with the phenocryst model (Moore 1987). The xenocryst model suggests an injection of kimberlitic liquid into fracture networks at depth, which would account for the range of crystallization temperature along with no requirements for chemical modification of the various volumes of kimberlite (Harte and Gurney 1980; Moore 1987). The interpretation of the large macro- and megacryst suite of ilmenite as xenocrystic in kimberlites is now the most predominant case based on chemistry and textural evidence.

If the eruption conditions of the kimberlite, or later conditions in the kimberlite (such as metasomatism), were to increase the oxidation in the system, diamonds would be destroyed. This then allows for a good use of the Fe$^{3+}$/Fe$^{2+}$ ratio in ilmenites as a way to measure the oxidation
state of the system (Lindsley 1991; Gurney and Zweistra 1997; Schulze et al. 1995; Nowicki et al. 2007; Carmody et al. 2014). As the mantle increases its oxidation state, the preservation potential of diamond decreases. An increase in oxidation causes Fe$^{2+}$ to convert to Fe$^{3+}$ in the ilmenite structure, which can record the diamond preservation potential of the kimberlite (Gurney and Zweistra 1997). The plot for this preservation potential can be seen in Figure 2-9. This however would not correlate to the presence diamonds in the rock, but rather to the likelihood that they would have been destroyed from the increase in oxidation.

![Figure 2-9: Fe$_2$O$_3$ vs. MgO plot (the oxidation state of Fe was calculated using the Droop 1987 equations), separated into four sections based on preservation potential; 1) High Fe and Low Mg with no preservation, 2) Marginal preservation, 3) Intermediate, 4) High Mg and Low Fe with best preservation. This shows that at higher oxidation states within the mantle and during kimberlitic emplacement, the preservation of diamonds is reduced (modified from Gurney and Zweistra 1997).}
By comparing the MgO and TiO$_2$ wt% concentrations of ilmenites, Kimberlitic and non-Kimberlitic ilmenites could be separated (Wyatt et al. 2003). This graph, along with the division line colored red, can be seen in Figure 2-10. Kimberlitic ilmenites were found to lie on the higher MgO side of the plot, with various other igneous (non-Kimberlitic) ilmenites lying to on the other side of the division (seen in Figure 2-10A). This is one of the original aids in characterizing ilmenites for exploration geology, to ascertain whether or not an ilmenite belonged to a Kimberlitic paragenesis from mineral chemical analyses. However, this could not show if a Kimberlite bore any diamonds. It was noted however that certain Kimberlitic ilmenites exhibited chemical substitution which increased the MnO and lowered the MgO concentrations, thus causing those ilmenites to fall out of the Kimberlitic zone (Wyatt 1979; Wyatt et al. 2003). Therefore, another line was established to compensate for this, which can be noted in Figure 2-10B via the dashed purple line. Wyatt et al. (2003) also used the Cr$_2$O$_3$ content of ilmenites to fingerprint localities. Non-Kimberlitic samples contain very low to near zero Cr-concentrations, and each Kimberlite seemed to bare varying patterns of Cr$_2$O$_3$ contents, which could potentially be used to source minerals to specific Kimberlites.

The acquisition of mineral chemical data for ilmenite inclusions in diamonds revealed one with an increased manganese composition (Kaminsky and Belousova 2008). In various deposits around the world, some ilmenites are seen to have a rim of Mg-poor, Mn-rich composition which is similar in composition to this ilmenite inclusion (Feenstra and Peters 1996; Kaminsky and Belousova 2008). Research was able to determine a few chemical compositional comparisons between the Mn-ilmenite inclusion, picroilmenites, and Mn-rich ilments from various rock types (Kaminsky and Belousova 2008). Figure 2-11 shows this comparison with the ilmenite inclusions in diamonds, with those of both Mn-ilmenites and picroilmenites. These characteristics were noted as increased vanadium, yet decreases nickel concentrations for the Kimberlitic and diamond samples. The theory was that the picroilmenite samples would bear signatures of a magnanese-enrichment event as a last stage product in the formation of a low-Mg, high-Mn rim around the samples (Feenstra and Peters 1996; Kaminsky and Belousova 2008).

The problems with interpreting ilmenite inclusions within diamond is the question on whether the fluid that formed these inclusions was from the same parent fluid that formed the diamonds. This is still debated. One theory would suggest that the C-O-H fluid (a fluid which consists mainly of CO$_2$, CH$_4$, H$_2$O, CO, and O$_2$) would at high pressure not only extract out the
Figure 2-10: Graphs of TiO₂ vs. MgO for ilmenite. Ilmenite samples that lie on the right of the red line are represented by kimberlitic, while those that lie on the left are non-kimberlitic. Exploration companies use this graph to discern the viability of ilmenites for kimberlitic exploration. A) Samples from North America, showing predominantly kimberlitic populations, B) Samples from West Africa that have mixed populations. The dashed purple line represents a second division line when higher concentrations of Mn are observed in ilmenites (modified by Wyatt et al. 2003).
carbon to form diamonds, but also equilibrate with the ilmenite minerals at depth (Simakov 2014). The other theory for the paragenesis for these ilmenite inclusions is formed by crystallization from fluids or magma which are distinct entities from the ones that produced their diamond hosts. Experimental work showed that TiO$_2$ concentrations would have been problematic in carbonatitic fluids, causing issues for the solubility of ilmenite components, and thus a degree of uncertainty for diamond and ilmenite to both form from the same parent fluid (Litvin et al. 2014).

A study by Carmoday et al. (2014), compared a variety of diamond-poor and diamond-rich kimberlitic deposits from Russian localities (Figure 2-12). They specifically analyzed the mineral ilmenite from these deposits with an aim to determine if there was a mineral chemical discrimination between ilmenites from the two kimberlite populations. Their study suggested that the Zr/Nb ratio of ilmenite could be a potential indicator of whether a kimberlite was diamondiferous, with diamond-bearing kimberlites falling above Zr/Nb = 0.37. This division and graph can be seen in Figure 1-11. They hypothesized that this could be the result of metasomatic events via carbonatitic fluid with a volatile-rich concentration inducing a higher concentration of zirconium compared to niobium.
As pressure is an essential component that could influence the crystal structure of ilmenite, a barometer was needed to calculate the pressure of formation. An ilmenite monomineral barometer was established by Ashchepkov (2006), which was created based on the correlation of magnesium and titanium in picroilmenites from 30 kimberlitic pipes located in Africa, North and South America, and Russia. This equation used the weight percent of the oxides TiO$_2$, MgO, Cr$_2$O$_3$, and MnO in order to determine the formation pressure of the ilmenite samples. This was compared to common peridotite barometric methods, giving promising results. Research by Ashchepkov and others (2014), tweaked this barometer, adding corrections in order to refine the results. These corrections considered the FeO concentration in the ilmenite, as the amount of Iron remaining compared to the amount substituted for magnesium was a crucial variable. They then calibrated their equation based on clinopyroxene thermobarometry, giving much more refined results. Due to the necessity of magnesium in this equation, its use is restricted to ilmenites with enriched concentrations of Mg, such as those found in kimberlites. Fe-rich ilmenites found in other igneous rocks do not satisfy the conditions for calibrations, and thus pressure cannot be obtained from them.

Figure 2-12: Plot of Zr/Nb vs. Nb/Ta to differentiate diamond-poor and diamond-rich kimberlites via ilmenite composition. The line at Zr/Nb = 0.37 represents a threshold ratio. Samples that fall to the right of this threshold, with higher concentrations of Zr, are economic in grade (modified by Carmody et al. 2014).
The mono-ilmenite equation has substantial utility when dealing with kimberlitic ilmenites for two reasons. The first is that due to the erupting processes of kimberlites and the formation of new minerals in the pipes, the determination of in situ equilibrium between minerals, even if they are in contact, is difficult. The second is that the rare exsolution found in picroilmenites are incredibly fine.

Due to the high-Mg restriction on the mono-mineral equation, another barometer was needed to determine pressures for Fe-rich ilmenites, such as non-kimberlitic or Mn-rich ilmenites. An oxygen rutile-ilmenite barometer was established by Zhao and others (1999), which utilized the oxygen fugacity of ilmenite, along with the activity of FeTiO$_3$ and Fe$_2$O$_3$ in ilmenite, and TiO$_2$ in rutile. It was shown that oxygen fugacity could be calculated using these activities, along with the pressure and temperature of the system. This could then be rearranged so that the pressure could be determined via the temperature, oxygen fugacity, and the activities of the minerals. This equation was compared to other oxygen barometers, where it showed considerable correlation. This of course required the ilmenite and rutile minerals to be in equilibrium in order for an accurate result to be produced.

The rutile-ilmenite barometer was later subjected to testing by Tao and others (2017), where they were able to give slight corrections along with aid in using the barometer. This enabled for molar fractions of the oxides to be used instead of activity coefficients, along with pressures to be determined at lower temperatures. In both cases temperature needed to be determined, and unlike the mono-ilmenite method which lacked an ilmenite thermometer, a rutile thermometer was available. A mono-mineral rutile thermometer was established by Zack and others (2004), which utilized the strong temperature sensitivity of zirconium concentrations in the mineral. As long as the rutile and ilmenite were held in equilibrium, the combination of the rutile thermometer and rutile-ilmenite barometer could establish a formation pressure of the ilmenites.

2.6 Rutile

Rutile is a common accessory mineral that can be associated with high-grade metamorphic, igneous, and even hydrothermal ore deposits (Swoope et al. 1995; Zack et al. 2002). The simple chemical formula for rutile is TiO$_2$, where the Ti$^{4+}$ ion is held between six oxygen ions in a tetragonal structure, whereupon these oxygens then lie at the corners of an
octahedron and are surrounded by three Ti$^{4+}$ ions (Swoope et al. 1995; Luvizotto et al. 2009). Rutile is also known for its substitution with trace elements, as it can encompass Cr, Mo, Nb, Sb, Sn, Ta, W, and Zr (Zack et al. 2000; Zack et al. 2004; Luvizotto et al. 2009). The concentration of zirconium in rutile as mentioned above, is incredibly temperature dependent, allowing for the use of the rutile mono-mineral thermometer (Zack et al. 2004). Rutile’s correlation to temperature can also be seen from the thermal expansion of the tetragonal structure, predominantly in the c-axis direction (Sugiyama and Takéuchi, 1991).

Rutile can also be associated with the mineral ilmenite and it can be found in kimberlite rock types (Coenraads et al. 1991; Zack et al. 2002; Luvizotto et al. 2009; Alirfirova et al. 2015). Ilmenite can also break down and alter to form rutile and/or titanite (Angiboust and Harlov, 2017). Ilmenite can also crystallize with intergrowths of rutile within kimberlites or intergrown in MARID rock types (Mitchell 1973; Moore 1987). However, as mentioned before, it is difficult in most cases to determine if rutile formed before, after, or in equilibrium with ilmenites in kimberlites. Thus, mineral grain boundary textured information would be needed to determine if they are in equilibrium. This could also be assumed if both the mono-ilmenite and rutile-ilmenite barometers yielded similar pressures.
Chapter 3: Methodology

3.1 Introduction

This chapter focuses on the methods and instruments used during the analyses of the ilmenite grains for this research. Details are provided about which localities where chosen, along with their respective rock types. As the difference between Kimberlitic and non-Kimberlitic rock types, along with diamond-rich and diamond-poor kimberlites, was important, localities where chosen accordingly. This chapter outlines the methods and parameters for both Micro X-ray Diffraction and Electron Probe Micro-Analysis, to determine the crystal structure and mineral chemistry used in this research. Mineral chemistry was then used to determine the formation pressure, and as such the equations for temperature and pressure are detailed. In order to be repeatable, all the steps used from sample selection, mounting and polishing, instrument analyses, pressure calculations, and multi-dimensional software are outlined below.

3.2 Sample Localities

This research was able to utilize ilmenite samples from localities around the world. As the aim of this study was to distinguish differences between Kimberlitic and non-Kimberlitic ilmenites, using unit cell parameters, both types were sought after. Most of the Kimberlitic localities are confirmed to have diamonds obtained from them. Samples were also obtained from Kimberlites that are diamond-poor to sub-economic in grade. Samples were obtained from various sources, including researchers, companies, and mineral collections. Herb Helmstaedt, Professor at Queen’s University provided samples from the Aultman Kimberlite of Wyoming, U.S.A., the Bobbejaan Kimberlite of Northern Cape, South Africa, the Dutotispan Kimberlite of Northern Cape, South Africa, the Jaggersfontein Kimberlite of Free State, South Africa, the Monastery Kimberlite of Free State, South Africa, the Premier Kimberlite of Gauteng, South Africa, and the Lake Bullenmerri Kimberlite of Victoria, Australia. The Dutotispan samples were provided as loose grain ilmenite samples, the Monastery sample was a single macrocryst ilmenite, while the rest of the samples provided by Dr. Helmstaedt were heavy mineral separates. Harwood (2009) then mounted a portion of the Premier samples within epoxy on thin sections. Epoxy mounted samples from the Attawapiskat Kimberlite of Ontario, Canada, were provided by Bruce Wyatt of De Beers, with chemical data that could determine which minerals were ilmenite.
Ralf Tappart, Professor at Lakehead University, provided eight epoxy mounted pucks with ilmenite samples all from South Australia, Australia. One of these was from the NAC-H1A kimberlite of the Nackara area, another from the Eurelia-K7 kimberlite from the Eurelia area, and six from the from the UCO-H77A kimberlite of the Monk Hill area. Chemical data were provided for all the epoxy mounts, except for two from the Monk Hill mounts. As six epoxy mounts for the Monk Hill area were not needed, a single mount was chosen (UCO-H77a-2-T4). Loose grained ilmenites were obtained from the Hibou Dyke of the Renard Mine, located in Quebec, Canada, and provided by Robin Hopkins of Stornoway Diamonds. A large bucket of heavy mineral separates from the Star kimberlite of Saskatchewan, Canada, and was provided by George Read of Shore Gold Inc. These extracts were divided into magnetic and non-magnetic batches, which were then subdivided into grains that were < 3.35mm and grains that were > 3.35mm. Ilmenite were obtained from the Udachnaya kimberlite of the Sakha Republic, Russia, provided by Thomas Stachel, Professor at the University of Alberta, but originally from Roger Morton. Loose grain ilmenites from three localities were provided by Beth McClenaghan from the Geological Survey of Canada, which were from the B30, Diamond Lake, and TB kimberlites, all of which are diamond-poor kimberlites, and located in Ontario, Canada. Another sub-economic kimberlite locality which ilmenites were obtained from was the Sheiba kimberlite of the Northwest Territories. This epoxy mounted puck was provided by Tom Nowicki of Mineral Services Canada, which came with mineral chemical data to aid in the identification of the ilmenite grains. Lastly, there were six non-kimberlitic samples provided by the Dana Collection of the University of Western Ontario. These include locality Dana 333 from Colorado, U.S.A., Dana 481 from Manitoba, Canada, Dana 499 from Quebec, Canada, Dana 746 from South Australia, Australia, Dana 3610 from Ontario, Canada, and Dana K48 from Georgia, U.S.A. The names, location, and rock type for each of the samples within this report are listed in Table 3-1, while Figure 3-1 has the locations upon the map.

3.3 Preliminary Loose Grain Selection

The preliminary stage of this research was initiated to determine which loose grains in the separates could be confirmed as ilmenite, before they were mounted for further study. Figure 3-2a shows a sample batch of heavy mineral separates. The final confirmation was through Micro X-ray Diffraction (μXRD), as the mineralogy of the sample can be interpreted from the results.
However, as this takes time and resources, grains that best embodied the appearance and physical properties of ilmenite were chosen before the preliminary μXRD analyses.

This was done by initially using a Bausch & Lomb Microscope with 0.7 to 3 times magnification, coupled with a Fiber-Lite DC-95 Regulated Illuminator. This allowed for the retrieval of grains of black colour, opaque transparency, and metallic to submetallic lustre. As this step would easily separate the ilmenite grains from those of garnet, olivine, diopside, and other silicate minerals found in kimberlites, this step was crucial. The next step however was attempting to distinguish ilmenite grains from those of chromite, magnetite, or other black opaque minerals. The properties used were magnetism, streak, lustre, and form. As ilmenite displays no cleavage and its hexagonal crystal structure is not readily seen in loose grains, any samples that had the spinel octahedron form, or even triangular faces, could be removed. If the sample was strongly magnetitic, this would be presumably magnetite and could be also removed. Chromite’s streak is that of a dark brown, while ilmenite (as well as magnetite) streak black. The lustre of chromite can also range from metallic to dull, so if any grains were dull in appearance or had a dark brown streak, they could be removed. A common mineral that is associated with

**Figure 3-1:** World map with the locations of all the samples used in this report. Locations in blue circles indicate economic grade (diamond-bearing) kimberlites, in yellow squares are diamond-poor kimberlites, and locations in orange triangles are ilmenites from non-kimberlitic samples. Bobbejaan and Premier both have Mn-rich ilmenite samples denoted by their purple stripes.
ilmenite is rutile, which is normally a brownish-yellow mineral, however in some cases does display an almost black coloration. Rutile could be distinguished due to its adamantine lustre and more reddish-brown than black color. Perovskite on the other hand can be very similar to ilmenite based on lustre, color, and sometimes a lack of form, however this mineral displays a grayish white streak. Figure 3-2b shows potential ilmenite grains obtained from the heavy mineral separates.

Table 3-1: Sample Locality and Type Information

<table>
<thead>
<tr>
<th>Locality</th>
<th>Label</th>
<th>Sublabel</th>
<th>Location</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aultman</td>
<td>AT</td>
<td></td>
<td>Wyoming, U.S.A.</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>Attawapiskat</td>
<td>ATT</td>
<td></td>
<td>Ontario, Canada</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>Bobbejaan</td>
<td>BB</td>
<td></td>
<td>Northern Cape, South Africa</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>Dutoitspan</td>
<td>DS</td>
<td></td>
<td>Northern Cape, South Africa</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>Eurelia</td>
<td>ER</td>
<td></td>
<td>South Australia, Australia</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>Hibou (Renard)</td>
<td>HR</td>
<td></td>
<td>Quebec, Canada</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>Jagersfontein</td>
<td>JF</td>
<td></td>
<td>Free State, South Africa</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>Lake Bullenmerri</td>
<td>LB</td>
<td>LB BMa</td>
<td>Victoria, Australia</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LB BMb</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>LB BMc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monk Hill</td>
<td>MH2</td>
<td></td>
<td>South Australia, Australia</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>Monastery</td>
<td>MO</td>
<td></td>
<td>Free State, South Africa</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>Nackara</td>
<td>NA</td>
<td></td>
<td>South Australia, Australia</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>Premier</td>
<td>PR</td>
<td></td>
<td>Gauteng, South Africa</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td></td>
<td>ST</td>
<td>ST -3.35 Mag</td>
<td>Saskatchewan, Canada</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST -3.35 Non-Mag</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST +3.35 Mag</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST +3.35 Non-Mag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Udachnaya</td>
<td>UD</td>
<td></td>
<td>Sakha Republic, Russia</td>
<td>DB-Kimberlite</td>
</tr>
<tr>
<td>B30</td>
<td>B30</td>
<td></td>
<td>Ontario, Canada</td>
<td>DP-Kimberlite</td>
</tr>
<tr>
<td>Diamond Lake</td>
<td>DL</td>
<td></td>
<td>Ontario, Canada</td>
<td>DP-Kimberlite</td>
</tr>
<tr>
<td>Sheiba</td>
<td>SH</td>
<td></td>
<td>Northwest Territories, Canada</td>
<td>DP-Kimberlite</td>
</tr>
<tr>
<td>Triple B</td>
<td>TB</td>
<td></td>
<td>Ontario, Canada</td>
<td>DP-Kimberlite</td>
</tr>
<tr>
<td>Dana 333</td>
<td>333</td>
<td></td>
<td>Colorado, U.S.A.</td>
<td>Non-Kimberlite</td>
</tr>
<tr>
<td>Dana 481</td>
<td>481</td>
<td></td>
<td>Manitoba, Canada</td>
<td>Non-Kimberlite</td>
</tr>
<tr>
<td>Dana 499</td>
<td>499</td>
<td></td>
<td>Quebec, Canada</td>
<td>Non-Kimberlite</td>
</tr>
<tr>
<td>Dana 746</td>
<td>746</td>
<td></td>
<td>South Australia, Australia</td>
<td>Non-Kimberlite</td>
</tr>
<tr>
<td>Dana 3610</td>
<td>3610</td>
<td></td>
<td>Ontario, Canada</td>
<td>Non-Kimberlite</td>
</tr>
<tr>
<td>Dana K48</td>
<td>K48</td>
<td></td>
<td>Georgia, U.S.A.</td>
<td>Non-Kimberlite</td>
</tr>
</tbody>
</table>

*DB-Kimberlite stands for Diamond-Bearing Kimberlite  
**DP-Kimberlite stands for Diamond-Poor Kimberlite

The separated grains were then mounted on glass slides using acid-free double-sided tape (Figure 3-3), at proximal distances apart as to not have contamination during the μXRD analyses. Each glass slide then corresponded to a specific locality and was labeled as such. The details for
the preliminary loose grain tape-mounts, along with the number of grains upon each mount, is listed in Table 3-2.

![Figure 3-2: Star Kimberlite > 3.35 mm and magnetic batch; A) 9.35 kg bag of heavy mineral separates. B) Potential ilmenite grains obtained from the batch.]

<table>
<thead>
<tr>
<th>Locality</th>
<th>Label</th>
<th>Sub-label</th>
<th>Total Grains</th>
<th>Total Grains Analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aultman</td>
<td>AT</td>
<td></td>
<td>53</td>
<td>40</td>
</tr>
<tr>
<td>Bobbejaan</td>
<td>BB</td>
<td></td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>Dutoitspan</td>
<td>DS</td>
<td></td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>Hibou (Renard)</td>
<td>HR</td>
<td></td>
<td>29</td>
<td>24</td>
</tr>
<tr>
<td>Jaggersfontein</td>
<td>JF</td>
<td></td>
<td>44</td>
<td>41</td>
</tr>
<tr>
<td>Lake Bullenmerri*</td>
<td>LB</td>
<td>LB BMa</td>
<td>38</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LB BMb</td>
<td>36</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LB BMc</td>
<td>27</td>
<td>10</td>
</tr>
<tr>
<td>Premier</td>
<td>PR</td>
<td></td>
<td>23</td>
<td>16</td>
</tr>
<tr>
<td>Star**</td>
<td>ST</td>
<td>ST -3.35 Mag</td>
<td>35</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST -3.35 Non-Mag</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST +3.35 Mag</td>
<td>31</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST +3.35 Non-Mag</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>Udachnaya</td>
<td>UD</td>
<td></td>
<td>38</td>
<td>32</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>465</td>
<td>345</td>
</tr>
</tbody>
</table>

* The samples from the Lake Bullenmerri kimberlite were provided from three vials: LB BMa, LB BMb, and an unlabelled vial which was thusly named LB BMc.

** The samples from the star kimberlite were divided into batches of < 3.35 mm (-3.35) and > 3.35 mm (+3.35), and each of those had magnetic (Mag) and non-magnetic (Non-Mag) groupings.
3.4 Preliminary Micro X-Ray Diffraction

In order to determine if the tape mounted samples were ilmenite, this required the use of
the Micro X-Ray Diffraction (μXRD) instrumentation in the Powder and Micro X-Ray
Diffraction Facility in the Biological & Geological Sciences Building at Western University in
London, Ontario, Canada (Figure 3-4a). This particular model is a Brüker D8 Discover micro X-
ray diffractometer, which enables in situ, whole rock analyses (Flemming 2007). The instrument
runs at 35 kV and 45 mA, with an X-ray beam collimated to 300 μm. The X-rays were produced
from a Cobalt source (Kα λ = 1.78897 Å), which are focused down towards the stage.

Samples were placed at a distance of 12 cm from the aperture. If the beam interacts with
a mineral upon the stage, the X-rays will be diffracted at specific angles based on the mineral’s
internal lattice structure. These diffracted rays are then monitored by a general area detector
diffraction system (GADDS), where a two-dimensional image is produced. The 0-0 geometry of
the diffractometer, allows the sample-stage to remain horizontal, while the source and the
detector are able to move independently from one another. The stage can move along the x-y-z
directions, allowing for multiple samples or spots upon a sample to be analyzed during the same
run, while the laser and microscope can remain stationary. The X-ray source and GADDS lie
upon opposite sides of the stage/sample, so that the detector can record the X-rays that are
diffracted from the lattice planes of the sample. In order for an X-ray to be detected, it must
satisfy Bragg’s Law (Bragg and Bragg 1915).
\[ n\lambda = 2dsin\theta \]  

(3-1)

Where \( n \) is the integer, or rather the order of diffraction, \( \lambda \) is the wavelength of the radiation, \( d \) is the inter-planar spacing, and \( \theta \) is the angle between the incident ray and the crystal’s planes.

As this project involves single crystal analyses, as opposed to a random orientation powder analyses, there will be a bias for certain peak positions, and even the omission of certain peaks depending on orientation. To mitigate this effect, a function called Omega (\( \omega \)) scan was used which could continuously satisfy Bragg’s Law, allowing \( 2\theta \) to remain constant by varying \( \theta_1 \) (Fitzpatrick et al. 2005). This was done by having the source and detector both rotate clockwise simultaneously, while keeping the stage fixed. This then allowed for Bragg’s Law to be satisfied when the following equation is true.

\[ \theta_1 + \theta_2 = 2\theta \]  

(3-2)

Where \( \theta_1 \) is the angle between the sample and source and \( \theta_2 \) is the angle between the sample and the detector. The schematic for this instrumentation and this function can be seen in Figure 3-4b.

Two frames of data were then collected to encompass the necessary \( 2\theta \) range for the ilmenite samples. This allowed for an increased probability of finding peaks which could either be related to ilmenite (and thus passed onto the next step) or unrelated to ilmenite (which could then be noted and removed from testing). The parameters for the preliminary analyses remained consistent throughout (Table 3-3) and allowed for the grains to be studied through the range 19.5 to 108.6° in \( 2\theta \). The smallest \( 2\theta \) peaks for ilmenite were exhibited are exhibited around 22°, while the largest value was exhibited at around 107°. This large range not only allowed for a greater probability to encounter peaks based on ilmenite d-spacing, but also allowed for more peaks to be exhibited for minerals that were not ilmenite.

<table>
<thead>
<tr>
<th>Table 3-3: Instrument Parameters for Loose Grain Mounts</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Frame (number)</strong></td>
</tr>
<tr>
<td>---------------------</td>
</tr>
<tr>
<td>1st</td>
</tr>
<tr>
<td>2nd</td>
</tr>
</tbody>
</table>

The GADDS then produces two-dimensional images from these analyses, with the two frames stitched together into one continuous \( 2\theta \) array. On these images there can be bright rings, spots, or a series of spots which appear to form the shape of a ring (asterisms). The rings indicate
polycrystalline structures, while the spots are related to single crystallites. The asterisms form from crystallites that have undergone strain. The positions of these bright rings or spots as a function of $2\theta$, can be used to calculate the d-spacing (inter-planar spacing) of the mineral’s
crystal lattice. The brightness of these rings and spots are a function of intensity, and thus frequency of specific types of inter-planar spacings within the crystal.

These two-dimensional images could then be imported into the program Diffrac.Eva (EVA), where they are integrated into a one-dimensional pattern, where peaks are displayed on the position and intensity plot. Peak positions can then be used to determine the identity of the minerals in the sample, the Miller indices of the sample, and the unit cell parameters of the mineral’s crystal structure. The mineral identification can be done by determining the peak position with the “peak search” function, and then by search these positions in the International Center of Diffraction Data (ICDD) database within EVA to determine which files are more closely related to the sample. The file used for the phase identification of the preliminary ilmenite samples was Mg-ilmenite file PDF 27-0247, which was sourced from a paper by Liu and others (1974). The other main mineral patterns used for this procedure were that of chromite, magnetite, and rutile, and thus any samples matching these could be removed after the preliminary analyses, so that they could be avoided in the subsequent study of ilmenite. The results for the initial runs could then be cumulated to determine if more samples were required for a certain locality, or if enough data were obtained.

As the preliminary analyzes were underway it was decided that 20 ilmenite grains from each locality would be a representative number. However, it was also established that μXRD data collection would continue for a locality until either 20 ilmenite grains were found, or until 50 candidate grains had been run, which ever came first. Table 3-2 shows the total grains analyzed, and thus the result of the ilmenite identification.

### 3.5 Mounting and Polishing Samples

From the preliminary results, ilmenite grains were selected to be mounted so that a more refined set of data could be established using μXRD, and so that Electron Probe Micro Analysis (EPMA) could be done on the samples. Each puck was designed to hold 20 grains, and thus priority was given to the grains that were confirmed to be ilmenite based on the preliminary μXRD, rather then grains that only had the potential to be ilmenite.

The epoxy selected was EpoxyMount from Allied High Tech Products, Inc. This two-stage epoxy (resin and hardener) was selected above others due to Allied also having an Epoxy Dissolver, which would be utilized in case any of the grains needed to be liberated from their
mounts later on. Mounts were made to test out the reliability of the epoxy before being used on any important ilmenite samples, thus scrap grains from ST (Star) -3.35 Mag were chosen. A high vacuum grease was used to coat the inside of a 1-inch diameter acrylic mold. The grease was used to both prevent the epoxy from solidifying to the mold, along with keeping the grains in place at the bottom (Figure 3-5). Tweezers were used to carefully place the grains in a regular array. At this stage an additional grain was used as a marker, which would allow for a way up and starting position for running experiments. For these mounts the marker grain was placed on the top right, so once mounted the marker would be on the top left of the puck.

The epoxy was created by mixing in 10 grams of hardener with 3.5 grams of resin, attempting to be precise to 0.5 grams. This was then mixed in a way so that the hardener and resin were fully homogenous, yet not vigorous enough that would allow an excessive amount of air to be entrapped. The epoxy was then poured into the molds, where with time (usually over night) would solidify to form the epoxy mounts. In total, four tests were done, each of them differing the temperature factor of the epoxy. The details for this are provided in Table 3-4.
Table 3-4: Epoxy Mount Tests

<table>
<thead>
<tr>
<th>Test</th>
<th>Conditions for Test</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Direct application of heat from hot plate to the mold for five minutes, then sudden quench into water</td>
<td>The sudden drop in temperature resulted in massive crystallization of the epoxy for an unusable mount</td>
</tr>
<tr>
<td>2</td>
<td>No heat or water, simply pouring in epoxy to mold and allowing to harden</td>
<td>Successful mount, numerous air bubbles within</td>
</tr>
<tr>
<td>3</td>
<td>Put the mold into a vat of hot water, let harden in there</td>
<td>Successful mount, with only a minor amount of air bubbles</td>
</tr>
<tr>
<td>4</td>
<td>Put the mold into a vat of hot water for 10 minutes, then place it into a vat of cold water to harden</td>
<td>Successful mount, with only a minor amount of air bubbles</td>
</tr>
</tbody>
</table>

The best results were from boiling water upon a hot plate and placing the water into a petri dish. The mold would then be placed into the hot water just after the epoxy was poured in. The water level was crucial for this, as if water poured into the mold it could cause crystallization of the epoxy. Thus, filling it up slowly (even so much as using pipet) was necessary. The hot water would allow for the air bubbles in the epoxy to rise to the surface before dissipating. This would then sit within the hot water until it naturally cooled. Around four hours later (or over night to be safe), the epoxy would be hardened and easily popped out of the mold (Figure 3-6).

Figure 3-6: Unpolished 1 inch diameter epoxy mounts with Monastery on the left and Diamond Lake on the right.
From there, the mounted samples were polished to ensure that the grains were at the surface of the puck, and that this surface was ideally smooth. Three varying grits of diamond lapping film, along with an alumina powder, were purchased from Electron Microscopy Sciences. The lapping film grits were 30 μm, 15 μm, and 3 μm, while the alumina powder was 0.3 μm. To ensure quality polishing, one of the test epoxy pucks was selected to undergo the procedure. Initially the samples would be ground until the majority of the grains were visible on the surface by hand grinding the mounts in a circular motion on sandpaper with the aid of water to reduce stress. Using the same tactics thereafter, the samples were ground on each of the lapping films from largest grit to smallest, using around 70 cycles in one direction followed by 70 cycles in the other direction to ensure homogenous polishing. Then on a billiard cloth, water was combined with Alpha Alumina Powder for a final polish. Using a microscope after each separate paper/cloth polish, the mounts could be checked to determine if the samples needed to be polished again. Polishing was done on a polished quartzite slab to ensure a flat surface that also had the strength to support the process. A polished mount can be seen in Figure 3-7.

![Polished Diamond Lake puck. Note the marker grain on the top left of the puck which indicates way up and direction.](image-url)
Samples could then be mounted and polished with success, following the techniques from the test pucks. The results from the $\mu$XRD allowed for a number of adequate grains for further testing. However, as these grains were not limited to the first twenty or so, the grains selected for mounting in epoxy were renumbered for ease. The new epoxy mount numbers can be seen in Table 3-5 with the original loose grain numbers beside them. The locality abbreviation for all of the samples remained the same, except for the Star kimberlites, where ST -3.35 Mag and ST -3.35 Non-Mag were changed to STM and STN respectively.

### Table 3-5: Original Loose Grain identification, converted to the New Epoxy Mount Numbers

<table>
<thead>
<tr>
<th>New Epoxy Mount Numbers</th>
<th>Original Loose Grain Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AT * ** ***</td>
</tr>
<tr>
<td>Marker Grain</td>
<td>3</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>6(2)**</td>
</tr>
<tr>
<td>5</td>
<td>7(2)**</td>
</tr>
<tr>
<td>6</td>
<td>8(2)**</td>
</tr>
<tr>
<td>7</td>
<td>5(3)**</td>
</tr>
<tr>
<td>8</td>
<td>1(b)***</td>
</tr>
<tr>
<td>9</td>
<td>3(b)***</td>
</tr>
<tr>
<td>10</td>
<td>11(b)***</td>
</tr>
<tr>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>13</td>
<td>16</td>
</tr>
<tr>
<td>14</td>
<td>19</td>
</tr>
<tr>
<td>15</td>
<td>19</td>
</tr>
<tr>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>17</td>
<td>21</td>
</tr>
<tr>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td>19</td>
<td>24</td>
</tr>
<tr>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>21</td>
<td>27</td>
</tr>
</tbody>
</table>

* The PR and AT locality, due to low number of ilmenite grains, were mounted together.
** The AT locality has preliminary samples designated by X(2) or X(3), where the X is the specific sample number to either the 2nd or 3rd $\mu$XRD analysis, which where not a continuation, but rather selected individually based on other parameters.
*** The AT and JF localities had a second tape mount, and thus samples designated by X(b) have the X being the specific sample number to the tape mount b.

Additionally, samples were mounted that did not undergo the preliminary analyses. These samples were the diamond-poor kimberlite ilmenites from the B30, Diamond Lake (DL), and TB
kimberlites, the macrocryst ilmenite from the Monastery (MO) kimberlite, and the non-kimberlitic samples of Dana 333, Dana 481, Dana 499, Dana 746, Dana 3610, and Dana K48. As these samples had no additional work upon them, their layout upon the epoxy mount was purely arbitrary. The diamond-poor kimberlites, being loose mineral grains, were mounted in a similar fashion as the preliminary samples, having an indicator grain at the top, then mounted in rows. The rest of the samples were mounted as chunks of rock, broken from their sample. The MO, Dana 333, Dana 499, and Dana 3610 samples were all mounted as one big portion, while the Dana 746 sample was mounted as two portions, and the Dana 481 and Dana K48 samples were mounted as three separate portions.

3.6 Micro X-Ray Diffraction of Mounted Samples

With samples mounted and polished, μXRD was run on each of the pucks in order to obtain more reliable data for analyses. Due to the difference in height between individual grain sizes and flat surface of the puck, the parameters for the μXRD analyses were altered to prevent the samples from colliding into the beam source. The only parameter that was changed was the 1st frame’s $\theta_1$ value from $6^\circ$ to $10^\circ$ to compensate for this (Table 3-6). This still allowed for a pattern to be obtained from $23.4^\circ$ to $108.6^\circ$ in 2$\theta$ space.

<table>
<thead>
<tr>
<th>Frame (number)</th>
<th>$\theta_1$ ($^\circ$)</th>
<th>$\theta_2$ ($^\circ$)</th>
<th>Width ($^\circ$) = Omega Angle</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>10</td>
<td>39</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>2nd</td>
<td>40.5</td>
<td>43</td>
<td>13</td>
<td>45</td>
</tr>
</tbody>
</table>

μXRD analyses were also done on the previously mounted ilmenite samples. The previous worked epoxy samples of the Attawapiskat (ATT), Premier (PR1 and PR2), and Sheiba (SH) kimberlites were initially examined by Harwood (2009) and Maunder (2016), and thus were chosen to be reanalyzed as a comparison. This would allow a contrast between machine parameters, source material, software, time, and human error. The mounted grains of Eurelia (ER), Monk Hill (MH2), and Nackara (NA) from Australia were also analyzed using μXRD. In each case, the samples already had labeled numbers associated with them that matched with previous μXRD and/or mineral chemical data, and thus the ilmenites maintained their numeric labels for easier comparison later on.
3.7 Corundum Calibration

Unlike the preliminary μXRD analyses where phase identification and significant peaks were the main priority, at this stage of the research useable data were now more important. The peak positions need to be reliable for unit cell parameter determination, and thus calibrations were done to ensure that. This calibration consisted of preforming a μXRD analysis upon a corundum XRD Flat-Plate Intensity Standard from the U.S. Department of Commerce, National Institute of Standards and Technology. The parameters for this standard were run after focusing on a single point on the corundum plate, but the sample was oscillated 3 mm in the XY during analysis to increase the number of grains that satisfied the diffraction condition in order to approximate random distribution. In this analysis θ₁ = θ₂ = 20°, the width (distance between the frames) was 44°, and time was set at 30 minutes per frame. From the GADDS image, a pattern could be generated into EVA where the frames could be combined and the d-spacings established for the peaks. A pattern from the ICDD database, PDF 46-1212, was used as a standard for this calibration. The result’s peaks were matched with three of the standard’s peaks, calculating the difference between the d-spacing. Since a coupled analysis was used to obtain two frames, the peaks around the (0 2 4) peak was used to compare the frames against one another as they both exhibited this peak. The peak positions used for comparison, along with their d-spacing and acceptable d-spacing limits are listed in Table 3-7. If the difference between the values was negligible, then the internal parameters of the instrumentation at that time were satisfactory for μXRD analyses of the ilmenite mounts. This would mean that there was negligible shift between the peak positions during the analyses, and thus any measurements obtained for the peaks were reliable.

Table 3-7: Corundum Calibration Details

<table>
<thead>
<tr>
<th>Millar Indices of Peak</th>
<th>d-spacing Comparison Value</th>
<th>Acceptable Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 0 4)</td>
<td>2.55085</td>
<td>± 0.001</td>
</tr>
<tr>
<td>(1 1 6)</td>
<td>1.60233</td>
<td>± 0.0005</td>
</tr>
<tr>
<td>(3 0 0)</td>
<td>1.37372</td>
<td>± 0.0005</td>
</tr>
<tr>
<td>(0 2 4)</td>
<td>Frame 1 and Frame 2 peak comparison</td>
<td>± 0.00075</td>
</tr>
</tbody>
</table>

3.8 Unit Cell Refinement

Once the GADDS images were collected from the epoxy mounted samples, the two-data could then be imported into EVA. As before, the “peak search” function was important, however, unlike using the peak positions to determine the phases in the sample, they would be
used to determine the ideal starting parameters. By using this function, the software determines
the idealized peak points based on the width and shape. Thus, the peak positions are not
subjectively chosen, but rather a function of calculations. The default width for this feature is set
at 0.15° 2θ, with a default threshold set a 1. Due to the low intensity of some of the peaks
observed, the threshold value needed to be lowered to 0.5 on average. A minimum of three
peaks was need for the refinement, however some samples showed sixteen unique peaks. Once
the positioning of the peaks was established, a DIF file was created based on those peaks.
However, peaks that were not associated with the ilmenite structure (other mineral phases from
alteration or exsolution for example) were omitted from the DIF file.

The data file was then compared with numerous ilmenite patterns that were obtained
from the ICDD database, each one bearing unique a- and c-axis values. The quality of the
patterns was filtered, so that any Deleted, Low Precision, or Questionable files were not selected.
The ideal files where those labeled Star (*) as they are reliable analyses on real samples. A few
(usually two or four) patterns would then be selected for the initial starting parameters for a
specific sample. These patterns were chosen based on overall similarity in positioning with the
sample’s peak positions and numbers, along with the reliability of the pattern file. The ilmenite
files from the ICDD database that were used as comparisons, yet not necessarily the starting
parameters, are listed in Table 3-8.

The pattern for the selected peaks would then be uploaded into a program called
CELREF, where the unit cell parameters of the database ilmenite pattern that best matched the
sample was used as a starting a- and c-axis value for the initial refinement (Laugier and Bochu
2000). With the appropriate peaks matching up, a refined unit cell parameter could be
established. In order for the data to be reliable, the refinement on both the a- and c-axis values
were required to have errors below 0.005 Å. If the error values were too high, then the data were
initially rechecked to determine if wrong peaks or Miller indices were chosen. From there other
starting parameters would be checked that were similar in position with the sample. If the data
could not be refined after trying 2 to 4 starting parameters set by the ICDD files, then the
samples was deemed “unrefinable” and was not used for further work.

It was after the values were refined that the samples Attawapiskat, Premier, and Sheiba
could be compared with the old localities. For reliability, only refined values with idealized
errors could be compared to one another. From the refined values one can calculate the volume
of the unit cell to see how the axes affect one another. This would then allow for a comparison of not only the unit cell axes (a- and c-axis), but also the volume of the unit cell between the present and past studies. The Premier (PR) and Sheiba (SH) samples were compared with the Harwood (2009) data, and the Attawapiskat (ATT), Premier (PR), and Sheiba (SH) samples were compared with the Maunder (2015) data.

Table 3-8: Ilmenite ICDD Cards Used for Comparison and Starting Parameters

<table>
<thead>
<tr>
<th>File Name</th>
<th>Origin</th>
<th>a-axis (Å)</th>
<th>c-axis (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDF 03-0778 (B)</td>
<td>Dow Chemical Co., Midland, MI, USA.</td>
<td>5.083</td>
<td>14.04</td>
</tr>
<tr>
<td>PDF 03-0781 (B)</td>
<td>United Steel Co., Sheffield, England, UK.</td>
<td>5.0791</td>
<td>14.135</td>
</tr>
<tr>
<td>PDF 03-0789 (B)</td>
<td>British Museum (Natural History)</td>
<td>5.08</td>
<td>14.04</td>
</tr>
<tr>
<td>PDF 29-0733 (*)</td>
<td>National Bureau of Standards. 1978. 15: 34</td>
<td>5.0884</td>
<td>14.093</td>
</tr>
<tr>
<td>PDF 71-1140 (C)</td>
<td>Morosin et al. 1978. Journal of Applied Crystallography. 11: 121.</td>
<td>5.087</td>
<td>14.042</td>
</tr>
<tr>
<td>PDF 73-1255 (C)</td>
<td>Raymond and Wenk. 1971. Contributions to Mineralogy and Petrology. 30: 135.</td>
<td>5.085</td>
<td>14.088</td>
</tr>
<tr>
<td>PDF 73-1256 (C)</td>
<td>Raymond and Wenk. 1971. Contributions to Mineralogy and Petrology. 30: 135.</td>
<td>5.091</td>
<td>14.056</td>
</tr>
<tr>
<td>PDF 75-1203 (C)</td>
<td>Wechsler 1984. American Mineralogist. 69: 176.</td>
<td>5.0884</td>
<td>14.0855</td>
</tr>
<tr>
<td>PDF 75-1208 (C)</td>
<td>Wechsler and Prewitt 1984. American Mineralogist. 69: 176.</td>
<td>5.0889</td>
<td>14.0933</td>
</tr>
<tr>
<td>PDF 01-075-9540 (*)</td>
<td>Yamanaka et al. 2007. Physics and Chemistry of Minerals. 34: 307.</td>
<td>5.0881</td>
<td>14.091</td>
</tr>
<tr>
<td>PDF 04-017-8867 (I)</td>
<td>Harrison et al. 2000. American Mineralogist. 85: 194.</td>
<td>5.0828</td>
<td>14.033</td>
</tr>
</tbody>
</table>

Quality in brackets is either Star (*), Blank (B), Calculated (C), or Indexed (I)
Due to time and resource constraints, only four out of the six non-kimberlitic samples could be moved to the chemical acquisition stage of the research. The localities that were dismissed were Dana 481 and Dana 746. The Dana 481 patterns rarely matched any ilmenite peaks, and if they did they were obscure and rare ilmenite synthetic parameters, which in most of the cases did not result in data below the error standard. Sample Dana 746 on the other hand showed only a single spot of ilmenite with the rest pertaining to the mineral rutile.

**3.9 Reflected Light Microscopy of Mounted Samples**

Before the samples were taken to the Earth and Planetary Materials Analysis Laboratory at Western University, they were taken to the Optical Microscopy Laboratory next door to be examined using an Olympus BX51 microscope. This microscope was attached to an Olympus TH4-100 reflected light apparatus, along with an Olympus UC30 camera. This allowed for some of the samples to be viewed in Reflected Light to determine if zonation, exsolution, or separate mineral phases could be distinguished initially.

**3.10 Electron Probe Micro Analysis of Mounted Samples**

The Earth and Planetary Materials Analysis Laboratory houses a JXA-850F Field Emission Electron Microprobe (Figure 3-8), which performs Electron Probe Micro Analysis (EPMA) on the samples. Two things needed to be done before the ilmenite grains could be placed within the chamber: carbon coating and instrumental calibration (described later). A carbon coat was applied to the surface of the ilmenite grains (roughly 20 nm thickness) using an Evaporation Carbon Coater, as to prevent charging on the surface of the grains.

In EPMA, a beam of electrons interacts with the sample to liberate electrons from the inner shell of the atom, causing an outer shell electron to drop lower to take its place. This drop in energy produces an X-ray. These X-rays are characteristic to each element, and thus can be used to fingerprint which elements are present in the sample. This requires an electron source, and in this case a Schottky type field emitter, which condenses the electrons into an electron beam. This beam is then emitted towards the sample, which is housed within a vacuum chamber to prevent any contamination with gas, vapor, or outside interferences. The electron beam then liberates the inner shell electrons and produces a characteristic X-ray for each specific element.
These X-rays are then diffracted using analyzing crystals so that Bragg’s Law can be applied to discriminate between the X-rays and focus them towards an X-ray detector.

The EPMA instrumentation used has 5 Wavelength Dispersive Spectrometers (WDS), each capable of using one of two of their analyzing crystals during analyses (Table 3-9). These discriminate X-rays from the sample by their wavelengths, as only certain wavelengths satisfy Bragg’s Law for each crystal, and thus can be tuned. Also, with the instrumentation is a Silicon Drift Energy Dispersive Spectrometer (EDS), which instead of measuring a specific element individually with quantitative precision, is able to rapidly determine a broader array of all the elements in the sample, discriminated by their X-ray energies. There is also a Backscattered Electron detector, a Secondary Electron detector, and a Panchromatic Cathodoluminescence detector.
Table 3-9: JXA-850F Electron Microprobe Spectrometers and Analyzing Crystals

<table>
<thead>
<tr>
<th>Spectrometer</th>
<th>Analyzing Crystals</th>
<th>Abbreviation</th>
<th>Elements (Ka)</th>
<th>Elements (La)</th>
<th>Elements (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Thallium Acid Phthalate J-type</td>
<td>TAP-J</td>
<td>O to P</td>
<td>Cr to Nb</td>
<td>Pd to Au</td>
</tr>
<tr>
<td></td>
<td>Layered Diffracting Elements 2</td>
<td>LDE2</td>
<td>B to O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pentaerythritol J-type</td>
<td>PETJ</td>
<td>Al to Mn</td>
<td>Kr to Tb</td>
<td>Yb to U</td>
</tr>
<tr>
<td></td>
<td>Lithium Fluoride</td>
<td>LiF</td>
<td>K to Rb</td>
<td>Cd to U</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Pentaerythritol H-type</td>
<td>PETH</td>
<td>Si to Ti</td>
<td>Rb to Ba</td>
<td>Hf to U</td>
</tr>
<tr>
<td></td>
<td>Lithium Fluoride H-type</td>
<td>LiFH</td>
<td>Ca to Ga</td>
<td>Sn to Au</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Thallium Acid Phthalate</td>
<td>TAP</td>
<td>F to P</td>
<td>Mn to Nb</td>
<td>La to Hg</td>
</tr>
<tr>
<td></td>
<td>Layered Diffracting Elements 1</td>
<td>LDE1</td>
<td>C to Ne</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Pentaerythritol L-type</td>
<td>PETL</td>
<td>Si to Cr</td>
<td>Kr to Eu</td>
<td>Lu to Bi,</td>
</tr>
<tr>
<td></td>
<td>Lithium Fluoride L-type</td>
<td>LiFL</td>
<td>Ca to Rb</td>
<td>Sb to U</td>
<td>Th to U</td>
</tr>
</tbody>
</table>

Calibrations and corrections needed to be taken before quantitative analyses could be performed. This involved both the in-lab standards used in the EPMA lab, along with world wide standards see in Table 3-10.

Table 3-10: World Standards used for EPMA

<table>
<thead>
<tr>
<th>Element</th>
<th>Standard Material</th>
<th>Standard Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Corundum</td>
<td>Harvard 126097</td>
</tr>
<tr>
<td>Ca</td>
<td>Diopside</td>
<td>Smithsonian USNM 117733 - Natural Bridge, NY</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
<td>Astimex, 99.997% chip, Alfa Aesar, USA</td>
</tr>
<tr>
<td>Fe</td>
<td>Ilmenite</td>
<td>Smithsonian USNM 96189 - Ilmen Mnts., USSR</td>
</tr>
<tr>
<td>Mg</td>
<td>Periclase</td>
<td>Astimex, synthetic</td>
</tr>
<tr>
<td>Mn</td>
<td>Rhodonite</td>
<td>Astimex, locality unknown</td>
</tr>
<tr>
<td>Na</td>
<td>Albite</td>
<td>CM Taylor, Amelia, County, VA, USA</td>
</tr>
<tr>
<td>Nb</td>
<td>Niobium</td>
<td>Astimex, 99.96% wire, Alfa Aesar, USA</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
<td>Astimex, 99.97% wire, Alfa Aesar, USA</td>
</tr>
<tr>
<td>Si</td>
<td>Quartz</td>
<td>Unknown provenance</td>
</tr>
<tr>
<td>Ta</td>
<td>Tantalum</td>
<td>Astimex, 99.996% wire, Alfa Aesar USA</td>
</tr>
<tr>
<td>Ti</td>
<td>Ilmenite</td>
<td>Smithsonian USNM 96189 - Ilmen Mnts., USSR</td>
</tr>
<tr>
<td>V</td>
<td>Vanadium</td>
<td>Astimex, 99.8% wire, Alfa Aesar, USA</td>
</tr>
<tr>
<td>Zr</td>
<td>Zirconium</td>
<td>Astimex, 99.7% wire, Alfa Aesar, USA</td>
</tr>
</tbody>
</table>

Initially on some of the Attawapiskat (ATT), Premier (PR), and Sheiba (SH) samples, elemental maps were created. These maps were created from 4 μm pixel sizes, with each pixel dwelling for 10 ms. The Attawapiskat maps were done at an accelerating voltage of 20 kV, probe current of 10 nA, and a spot beam (~100 nm). The Premier and Sheiba maps were done at an accelerating voltage of 15 kV, probe current of 100 nA, and a spot beam (~100 nm). Individual maps were created with the wavelength dispersive spectrometers (WDS) for the elements Mg (TAP), Fe (LiF), Mn (LiFH), and Cr (LiFL), while Ti was created with the energy dispersive spectrometer (EDS). The ATT samples had maps using Zr (TAP), while the PR and SH samples
Instead had Cathodoluminescence (CL) maps created. A small section of sample ATT 37 was done with 2 μm pixel size map with the probe current instead at 100 nanoamps, however this revealed nothing vastly different then with the 4 μm map. Backscattered Electron (BSE) images were also created for all the samples.

All the samples then underwent chemical analysis using the WDS which analyzed for the presence of Al, Cr, Fe, Mg, Mn, Nb, Ti, V, and Zr. Localities ATT, PR, and SH also were analyzed for Ta, while the rest of the localities were instead analyzed for Ca, Na, Ni, and Si. This was done at 15 kV, with a probe current of 50 nA, and a spot size of 1 μm. Tantalum was originally selected because a study by Carmody and others (2014) compared the ratio of Zirconium and Niobium against Zirconium and Tantalum. Their analyses showed that the Zr/Nb ratio was potentially influenced by the presence of diamonds, and that Tantalum was not affected majorly. However, due to time and run restrictions, along with the element not showing any support for diamond potential, Ta was removed from further analyses. Ni was added because it can be a trace element in ilmenite, especially picroilmenites, and because Kaminsky and Belousova (2008) noticed a decrease in nickel concentrations when diamonds were present. Si on the other hand was selected due to the increased substitution of Si for Ti lower in the mantle (Horiuchi and Hirano 1982). The Si could then be used as a placement for depth in the mantle when comparing the kimberlitic samples. Ca and Na were chosen as there was room for more light elements during the analyses which would not hinder the run time.

The data obtained was in weight percent oxide (wt%), which refers not to the percent of the element (e.g. Ti) in the mineral, but rather the percent of the element as an oxide (e.g. TiO₂) in the mineral. A Backscattered Electron Image was also obtained for each sample that underwent the mineral chemical analyses.

Fe was collected as Fe_{total}, and once the chemical data were obtained, there needed to be a correction done to the data to account for the oxidation state of iron in ilmenite. In most cases ilmenite will have Fe^{2+} in it’s A-site, however there can be substitution for Fe^{3+} as well (Linton et al. 1999). As the EPMA instrumentation can not distinguish oxidation states of an element, the equation established by Droop (1987) was required to differentiate the Fe^{2+} and Fe^{3+} within the ilmenites. A spreadsheet was used where the elemental data could be inserted and a normalization on both the oxygen and cation sites of the mineral could be established. This would normalize the oxygen with two cations and the cations with three oxygen to satisfy ilmenites base formula.
A²⁺B⁴⁺O₃. Once this was done the Fe³⁺ could be differentiated and a new total weight percent oxide could be calculated due to the slight increase in weight of F³⁺₂O₃ vs. Fe²⁺O.

### 3.11 Barometry of Mounted Samples

Two barometers were used for calculating the approximate pressure of ilmenite formation. The first was developed by Ashchepkov (2006) as a mono-mineral barometer using just ilmenite. The second was developed by Zhao and others (1999) as a rutile-ilmenite oxygen barometer. In either case, temperature was required for the equations. This resulted in one of three approaches that could be established. The first approach was using a thermometer to determine the formation temperature. The second was by determining the range of formation temperatures for the ilmenites, which was based on literature for specific localities. Lastly if all else failed, the third approach was to use a large range of temperatures that are plausible for ilmenite formation in the mantle.

The initial equation in Ashchepkov’s barometer is as follows:

\[
P_0 = (TiO_2 - 23) \times 2.15 - (T^°C - 700)/20 \times MgO \times Cr_2O_3 - 1.5 \times MnO \times T^°C/1273 \quad (3-3A)
\]

\[
P_1 = 10 \times (60 - P_0)/60 + P_0 \quad (3-3B)
\]

Where \(P_0\) is the first pressure found in kbar, \(P_1\) is pressure after the first correction, \(T^°C\) is the temperature in Celsius, and \(TiO_2, MgO, Cr_2O_3,\) and \(MnO\) are their corresponding weight percent oxides.

This equation was then recalibrated and developed further by Ashchepkov and others (2014) where they tweaked both \(P_0\) and \(P_1\) equations, but also added another correction equation.

\[
P_0 = (TiO_2 - 23.5) \times 2.15 - (T^°K - 750)/20 \times MgO \times Cr_2O_3 - 1.45 \times MnO \times T^°K/1273 \quad (3-3C)
\]

\[
P_1 = P_0 + (60 - P_0)/6.2 \quad (3-3D)
\]

\[
P_2 = P_1 + \frac{35.4 - FeO}{0.9} + \left(0.20 - \frac{Fe}{Fe + Mg}\right) \times 0.1 \times P_1 \quad (3-3E)
\]

Where \(P_0, P_1,\) and \(P_2\) are all in kbar, \(T\) is the temperature in Kelvin, \(TiO_2, MgO, Cr_2O_3, MnO,\) and \(FeO\) are their corresponding weight percent oxide, and \(Fe/(Fe+Mg)\) is the ratio of Fe to Mg in the sample. This equation was chosen because only the composition of ilmenite was required to determine the pressure which was useful, as most of the ilmenite samples were obtained as mineral separates with no spatial connection to minerals that may have coexisted with it. As picroilmenites rarely form in equilibrium with other mantle minerals, this equation also removed the necessity to assume equilibrium with those minerals (Ashchepkov et al. 2014).
As enough MgO wt% was required for the above equations to be feasible (> 3-5 wt% MgO), this barometer was sufficient for most kimberlitic ilmenites (~98% of the samples). This barometer could be used for the non-kimberlitic samples, if temperature was known or calculated and if the magnesium values were above the threshold. This meant that if temperature could be calculated from Dana 333 (~9.5 wt% MgO) this barometer would be applicable. For Dana 499 and K48 (~3.5 wt% MgO) this barometer could potentially be used.

Unlike the kimberlitic ilmenites, the non-kimberlitic samples had little formation details supplied with them. This meant that neither literature or temperature estimation hypotheses could be established. Thus, temperature needed to be calculated first. The equation of choice was developed as a rutile thermometer by Zack and others (2004). It uses the concentration of Zirconium in the rutile, which was seen in Mn-rich ilmenites from Bobbejaan, a single grain from Sheiba, and the samples Dana 499, Dana 3610, and Dana K48.

\[ T(°C) = 134.7 \times \ln(\text{Zr in ppm}) - 25 \]

As the EPMA results were in weight percent oxide, the ZrO\(_2\) concentration needed to be converted to elemental concentration. This can be done by using a conversion factor which is the result of the molecular weight of Zr over the molecular weight of ZrO\(_2\).

\[ Zr(\text{wt%}) = \frac{Zr O_2(\text{wt%}) \times MW_{Zr}}{MW_{ZrO_2}} \]

\[ Zr(\text{wt%}) = \frac{Zr O_2(\text{wt%})}{123.2118g/mol} \times 91.224g/mol \]

\[ Zr(\text{wt%}) = ZrO_2(\text{wt%}) \times 0.74031 \]

However, the results are that of Zr in weight percent element, when the equation requires Zr in ppm. As 1 wt% would be equivalent to 1 gram of that element in 100 grams, and as 1 ppm means 1 gram in 1,000,000 grams, this could then result in 1 gram of a substance equating to 10,000 ppm.

\[ Zr(\text{ppm}) = ZrO_2(\text{wt%}) \times 0.74031 \times 10,000 \]

The next step it is to use the rutile-ilmenite oxygen barometer by Zhao and others (1999). This equation solves for oxygen fugacity, and thus needs to be rearranged so that it solves for pressure.

\[ \log fO_2 = 22.59 - 25925/T - 3.09\log T + 0.0016535P + 48.836 P/T - 4\log a_{\text{FeTiO}_3}^{\text{il}} + 2\log a_{\text{Fe}_2\text{O}_3}^{\text{il}} + 4\log a_{\text{TiO}_2}^{\text{rut}} \]

\[ P = \frac{(-604.778(4\log a_{\text{FeTiO}_3}^{\text{il}} - 25925/T - 3.09\log T + 2\log a_{\text{Fe}_2\text{O}_3}^{\text{il}} - 4\log a_{\text{FeTiO}_3}^{\text{il}} - \log fO_2 + 22.59)T)}{T + 29534.9} \]

Even with temperature found, for this equation there still requires the oxygen fugacity and the concentration of TiO\(_2\) in rutile and FeTiO\(_3\) and Fe\(_2\)O\(_3\) in ilmenite. The oxygen fugacity
can be extrapolated by using the log($f_O^2$) vs. $T$ graphs of the rutile-ilmenite oxygen barometer, which were developed for high temperatures by Zhao and others (1999), seen in Figure 3-9a, along with lower formation temperatures by Tao and others (2017), see in Figure 3-9b. In order to do so however, the temperatures simply need to be converted from Kelvin to Celsius, and then by using the diagram, where the temperature intersects the Rutile-Ilmenite (RI) barometer line, the log of oxygen fugacity can be extrapolated. This of course does leave a small amount of potential error due to approximate oxygen fugacity compared to direct calculation.

It can be also noted that the concentrations of TiO$_2$, FeTiO$_3$, and Fe$_2$O$_3$ needed to be substituted for their molecular fractions in this equation (Tao et al. 2017). The chemical constituents can be converted from weight percent oxide to molar fraction by dividing each of the weight percent oxides obtained from the EPMA by their representative molar weight to obtain the moles of that oxide. Then taking the moles of the oxide in question, one divides that by the sum of the moles for all of the oxide constituents. The value obtained will be the molar fraction of the oxide in question. The equation below shows an example of calculating the molar fraction of TiO$_2$ in Rutile, where TiO$_2$ has a molar weight of 79.8988 g/mol.

\[
MF_{TiO_2} = \frac{(TiO_2(\text{wt\%})/79.8988g/mol)}{\text{Total Moles of Oxides in Ilmenite}}
\]  

With all the factors in place, the pressure of the ilmenite-rutile system can be calculated. This of course hinges on the assumption that the rutile and the ilmenite are in fact in equilibrium.

![Figure 3-9](image_url)

**Figure 3-9:** Rutile-ilmenite (RI) log$f_O^2$ vs. $T$(°C) plots used to extrapolate the oxygen fugacity from temperature. A) High temperature plot developed by Zhao et al. 1999 (modified). B) Lower temperature plot developed by Tao et al. 2017 (modified), with the red line being a calculated buffer curve. In both cases the rutile-ilmenite barometer is outlined in purple.
One way to try and determine this is by looking at the Back-Scatter Images of the samples. If the textures show reabsorption, alteration, or any other texture that may reveal that these minerals did not form together, then this equation will not be a valid estimation of the pressure for ilmenite formation. As rutile is a common accessory mineral with ilmenite due to chemical similarities (TiO$_2$ components), these minerals can be commonly found together in igneous and metamorphic rocks, and thus the rutile-ilmenite oxygen barometer is a suitable equation to use for the non-kimberlitic ilmenites.

### 3.12 Three-Dimensional Plotting

Using the limited two-dimensional plotting space of Excel, unit cell parameters can only be compared to either chemical composition or pressure. However, as both composition and pressure may inherently affect the crystal structure, the ideal situation is the comparison of all three functions. The multi-dimensional plotting tool Plotly was utilized in order to compare multiple variables at once. This program was developed by the Plotly technical company based in Montreal, Canada. It allows for the easy import of data, with a wide choice of graphing styles. The graphing type chosen for comparison was 3D-Scatter, which allowed for three variables to be plotted against one another, grouping shapes based on locality, as well as the potential use of colour as a fourth variable. The ideal plots of choice could then use selected mineral chemical element and pressure along the x-, y-, and z-axes, while the unit cell parameter could be associated by the color of symbol. In other instances, pressure was used as the coloration. This could also work for looking at up to three mineral chemical signatures when comparing it to unit cell parameters and/or pressure, instead of only two parameters in Excel.

### 3.13 Cluster Analysis

Cluster analysis was deemed a useful procedure to compare all the data in turn and hopefully allow for the discrimination between certain localities that may have been missed by the naked eye. As the localities of this research are confirmed already to be non-kimberlitic, diamond-bearing kimberlites, and diamond-poor kimberlites, this could allow for an easier comparison to see if unit cell parameters, chemical composition, and/or pressure could be used to separate the localities into distinct groupings. Cluster analysis is the term used for the separation of objects into distinct groups, where the objects that lie within the groups are more similar to
each other then they would be with objects outside of their group (Kaufman and Rosseeuw 2009). Using appearance is an excellent way to group data into clusters, yet the human eye can only take in so much processing information at a time. By utilizing computer programs, data can be analyzed and sorted into various clusters that might have been missed upon first inspection (Romesburg 2004). The software used in this research is called PolySNAP 3 and was developed by the University of Glasgow in Glasgow, Scotland (Barr et al. 2009).

This program was selected as it can compare multiple data sets, which can include numerical data sets such as the refined unit cell parameters from CELREF, the weight percent oxide data from the EPMA, and the pressure values established from the barometers. Unfortunately, when comparing the data there became an issue when blank cells were involved in the data sets. These blanks arose either from certain values not being obtained (e.g. from elements not being detected by the EPMA). In some instances, a certain locality did not have a specific element obtained, which was analyzed by the other localities (e.g. Ni from Nackara). While in other cases, a specific element was obtained from only some of the localities (e.g. Ta from Attawapiskat, Premier, and Sheiba). If the mineral chemical data were missing from only a few localities, then that element was removed from comparison. If, however, a certain locality was missing an element that was deemed necessary for comparison that most of the others had, then that locality was dropped from the comparison. In the instance where the detection limit was too high for a certain element and the result was “not-detected”, then a numeric value of 0.00 was given for that element in its place. As the cluster analysis is merely qualitative spatial awareness of quantitative data, the insertion of zero values as an assumption was deemed acceptable.

The clustering was done twice. The first time it was done using all the datasets to compare kimberlitic and non-kimberlitic samples to see if any prevailing groups were discriminated. The second time it was done using only the kimberlitic samples, thus attempting to see if the diamond-bearing kimberlites were separated out from the diamond-poor kimberlite samples. In each case the starting parameters of c-axis unit cell values, mineral chemical data, and pressure calculations were compared interchangeably to determine which groupings would emerge. By using the program’s “cut-line” function, groups could be seen based on similarity. By observing the similarities of the groups, and the level at which they separate, trends could potentially be seen between the ilmenite populations.
Chapter 4: Results

4.1 Introduction

This chapter outlines the data collected throughout by various analytical instrumentation throughout this thesis. The data may aid in the endeavour to determine the difference between ilmenites from kimberlitic and non-kimberlitic sources, along with ilmenites found in diamond-rich and diamond-poor kimberlites, using crystallographic approaches. These comparisons were also made with mineral chemistry, to see which elements influence the crystal structure more. Finally, a comparison was made with the Harwood (2009) and Maunder (2016) data to see where problems may have occurred in their research, and if these methods can be reproduced.

4.2 Preliminary Micro X-Ray Diffraction Analyses

The large 2θ area of detection from the μXRD analyses, allowed for an abundant amount of ilmenite matching peaks to be witnessed. When ilmenite was identified, the most common pattern exhibited by the mineral on the GADDS image was streaking, however spots and asterism were also common. These patterns can be seen in Figure 4-1.

As certain peaks can relate to both ilmenite and certain spinel structure minerals, this large width was essential for the distinction between them. The ratio of confirmed ilmenites to total grains analyzed was dependent on the locality in question. The highest percentage of ilmenites found was that in the Hibou (HR) locality with 87.5% of the grains analyzed being ilmenite. The lowest was that of the Lake Bullenmerri (LB) locality with approximately 10% of them being potential ilmenites. The results of the preliminary μXRD can be seen in Table 4-1.

In most cases the mineralogical identification for the sample, if it was not ilmenite, was as either chromite, magnetite, or other spinel group mineral, perovskite, or rutile. In some cases, however, the mineral was identified by μXRD as an amphibole (such as hornblende), garnet, goethite, hematite, periclase, or titanite. X-ray diffraction patterns of many of the ilmenite grains exhibited weaker peaks that were explained by the ilmenite database patterns. Two situations then arose in these cases, which can be noted in Figure 4-1. The first situation was lines of varying thickness (narrow to broad) seen on the GADDS images, relating to fine grained material such as clay minerals or the reaction rim (Figure 4-2A and 4-2B). The second was spots, streaks, or asterism that had similar patterns to ilmenite (Figure 4-2C). In the first case, these
could be explained as coatings or fine-grained alteration of the ilmenite, and the minerals that were usually found in these situations were anatase, aragonite, calcite, perovskite, saponite, and various sulfides (such as sphalerite). In the second case, this could either be attributed to alteration minerals, exsolution, or minerals that crystallized within the xenocryst aggregates alongside ilmenite. The minerals found in these cases were chromite, magnetite, and various spinels, diamond, fayalite, rutile, and perovskite.

![Figure 4-1](image1.png)

**Figure 4-1:** Preliminary loose ilmenite grains with photograph on the left and GADDS image on the right; A) Spots in SH -3.35 Non-Mag Sample 7, B) Streaks in BB Sample 3, C) Asterism in BB Sample 1.

In some cases, the predominant mineralogical peaks were shown to match that of the ilmenite structure, with the addition of being associated with weaker mineralogical peaks. The
question then is whether these weaker peaks were coatings, alteration, exsolution, or *in situ* crystallization. If the GADDS image for the particular sample exhibited distinctly different textures, where the ilmenite structure correlated to single spots, streaks, or asterism, while the weaker peaks correlated to fully developed rings, this would indicate two different types of structures, one being the crystalized ilmenite and the other being a fine-grained coating upon it. If the GADDS image displayed subtle differences between single spots, streaks, or asterism, this could indicate separate crystallizations or alteration, where as if the images exhibited no visual differences this may correlate to exsolution. As *in situ* crystallization and exsolution are the ideal cases, these needed to be separated out from alteration mineralogy and would need to be confirmed using other methods such as Reflected Light Microscopy and/or Back Scatter Electron imaging.

**Table 4-1:** Results of the Preliminary μXRD to find Ilmenite grains

<table>
<thead>
<tr>
<th>Locality</th>
<th>Label</th>
<th>Sub-Label</th>
<th>Total Grains</th>
<th>Total Grains Analyzed</th>
<th>Ilmenites Found</th>
<th>Possible Ilmenites Found</th>
<th>Ilmenites with Possible Exsolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aultman</td>
<td>AT</td>
<td>-</td>
<td>53</td>
<td>40</td>
<td>7</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>Bobbejaan</td>
<td>BB</td>
<td>-</td>
<td>32</td>
<td>32</td>
<td>22</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>Dutoitspan</td>
<td>DS</td>
<td>-</td>
<td>27</td>
<td>27</td>
<td>21</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>Hibou (Renard)</td>
<td>HR</td>
<td>-</td>
<td>29</td>
<td>24</td>
<td>21</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>Jagersfontein</td>
<td>JF</td>
<td>-</td>
<td>44</td>
<td>41</td>
<td>16</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Lake Bullenmerri</td>
<td>LB</td>
<td>LB BMa</td>
<td>38</td>
<td>16</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LB BMb</td>
<td>36</td>
<td>24</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LB BMc</td>
<td>27</td>
<td>10</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Premier</td>
<td>PR</td>
<td></td>
<td>23</td>
<td>16</td>
<td>12</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>Star</td>
<td>ST</td>
<td>ST -3.35 Mag</td>
<td>35</td>
<td>31</td>
<td>19</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST -3.35 Non-Mag</td>
<td>36</td>
<td>36</td>
<td>21</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST +3.35 Mag</td>
<td>31</td>
<td>8</td>
<td>6</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ST +3.35 Non-Mag</td>
<td>16</td>
<td>8</td>
<td>5</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Udachnaya</td>
<td>UD</td>
<td>-</td>
<td>38</td>
<td>32</td>
<td>21</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>465</td>
<td>345</td>
<td>176</td>
<td>19</td>
<td>117</td>
</tr>
</tbody>
</table>

After the preliminary work, addressed in the methods, the localities were assessed for their overall amount of ilmenite grains (as seen in Table 4-1, along with if they would used for further work. All of the localities except for Lake Bullenmerri (LB) were initially deemed worthy and were thus mounted. The Lake Bullenmerri locality was removed from further testing due to the lack in usable data obtained from the preliminary work. This was also done as already mounted ilmenite grains were obtained from Australia, specifically the Eurelia (ER), Monk Hill (MH2), and Nackara (NA) kimberlites. The newer Australian samples were also provided with compositional data, and thus were considered superior to the Lake Bullenmerri locality for the
next stage. Due to time constrictions, the +3.35 mm sub-grouping of the Star kimberlite (ST) was removed as well. The magnetic vs. non-magnetic portion of this locality were still considered for the next stage, to see if this would reveal any unique differences, and were thus named STM and STN respectively.

After the mounting stage of the preliminary work, three other localities were deemed unnecessary for specific reasons. During polishing, some of the ilmenites were removed from the Jaggersfontein (JF) puck, and thus only fourteen ilmenites had the capability of being analyzed. As the Monastery (MO) kimberlite was also from the Free State province of South Africa, the

Figure 4-2: Preliminary loose ilmenite grains with photograph on the left and GADDS image on the right; A) Rings of rutile in AT(2) Sample 7, B) Rings of saponite in SH -3.35 Non-Mag Sample 9, C) Streaks of chromite in DS Sample 1.
removal of the Jaggersfontein puck at this point was justified. For the Aultman (AT) and Premier (PR) localities, both had only a small number of grains at fourteen, and due time constraints, they were both not deemed necessary for further testing. The Premier kimberlite was previously analyzed from the glass slide epoxy mounts of Harwood (2009) and Maunder (2016), and the locality would still be considered with those mounts instead of the one created for this study.

4.3 Micro X-Ray Diffraction of Epoxy Mounts

Unlike the preliminary μXRD analyses, these tests were not aimed towards finding ilmenite grains, but rather determining the unit cell parameters (See Appendix 1) with high accuracy and finding the best possible starting parameters for these grains. This was done by comparing the data to a suite of database patterns from the ICDD database, using the graphical interface provided by the EVA program. These could then be used to refine the unit cell parameters. Even with the large number of patterns, there was a smaller subset of them that were the dominant matches. A select few noticeably matched the kimberlitic ilmenites, while another grouping favored the non-kimberlitic and manganese ilmenites.

In most cases the confirmed kimberlitic locality samples would match up with four ilmenite patterns. These patterns were consistent throughout the matching processes and were also characteristically lower in their c-axis values than most of the other patterns. Figure 4-3 and Figure 4-4 shows two samples with these ICDD pattern files, while Table 4-2 lists all four of them.

<table>
<thead>
<tr>
<th>File Name</th>
<th>Origin</th>
<th>a-axis (Å)</th>
<th>c-axis (Å)</th>
</tr>
</thead>
</table>

Quality in brackets is either Calculated (C) or Star (*)
Two of these patterns however, even though they did have different PDF file names with slightly varying compositions ($\text{Mg}_{0.208}\text{Fe}_{0.955}\text{Ti}_{0.833}\text{O}_3$ vs. $\text{Mg}_{0.21}\text{Fe}_{0.96}\text{Ti}_{0.83}\text{O}_3$), were from the same paper and had the same $a$- and $c$-axis values, thus they can be treated as a single set of starting parameters. This means that there were three main kimberlitic matching unit cell parameters (Belokoneva et al. 1978; Wechsler and Prewitt 1984; Liferovich and Mitchell 2005).

Figure 4-3: Ilmenite from the Bobbejaan kimberlite, Sample 17; A) Photograph of polished sample, B) GADDS image of sample with streaking, C) $\mu$XRD data portrayed on EVA with ICDD ilmenite patterns to match the peak positions.
These patterns could then be utilized in the CELREF program in order to refine the ilmenite unit cell parameters for each sample. Each pattern could be matched up to a grain, resulting in almost repeatable unit cell parameters, ranging from zero to only hundredths of an angstrom (Å) difference in most cases. CELREF required at least 3 peak positions as input in order to work. Some of the samples were unusable due to a lack of diffraction peaks. In other cases, it was the poorly defined peaks, where the low quality of the data made it difficult to determine where the center of the peak was positioned, and thus would be unreliable when refining. The most often situation for unusable data was the simple case of CELREF being
unable to refine the a-axis, c-axis, or both parameters below 0.005 Å; with more cases of inability to refine the a-axis value. The results of the refinement can be seen in Table 4-3.

While undergoing the refinement process, it was revealed that the starting unit cell parameters of the kimberlitic samples could be picked arbitrarily in most cases (from the four main ICDD patterns), even if this was not the case during the data compilation. The refined a-axis parameters ranged from 5.013 to 5.129 Å (keeping in mind the maximum 0.005 Å error), while the c-axis values varied from 13.730 to 14.095 Å. Apart from a select few grains from the Bobbejaan (BB), Monk Hill (MH2), Premier (PR), and Sheiba (SH), all of the kimberlitic ilmenites exhibited c-axis unit cell parameter values of less than 14.03 Å. Upon closer examination of the two MH2 and single SH grains, it was either found that the exported data were misinterpreted, or that the miller indexing of that particular grain was incorrect. This left five out of fifteen grains of the BB locality, and four of six grains with the PR locality which were all within error and with no peak selection mishaps. This means that out of the 247 refined ilmenite samples, ten of them were below 14.03 Å, or rather ~4% of them were below this value. With the exception of these nine grains of higher c-axis value, the range in kimberlitic ilmenite unit cell parameters has the a-axis as 5.013 to 5.120 Å and the c-axis as 13.730 to 14.023 Å.

### Table 4-3: Total Samples refined, along with reasons for unsuccessful refinement

<table>
<thead>
<tr>
<th>Locality</th>
<th>Label</th>
<th>Ilmenites Successfully Refined</th>
<th>Could not refine due to lack of peaks</th>
<th>Unsuccessful refinement due to a-axis</th>
<th>Unsuccessful refinement due to c-axis</th>
<th>Unsuccessful refinement due to both a- and c-axis</th>
<th>Percent Success Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attawapiskat</td>
<td>ATT</td>
<td>11</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>91.67</td>
</tr>
<tr>
<td>Bobbejaan</td>
<td>BB</td>
<td>16</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>80.00</td>
</tr>
<tr>
<td>Dutoitspan</td>
<td>DS</td>
<td>18</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>90.00</td>
</tr>
<tr>
<td>Eurelia</td>
<td>ER</td>
<td>13</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>86.67</td>
</tr>
<tr>
<td>Hibou (Renard)</td>
<td>HR</td>
<td>16</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>80.00</td>
</tr>
<tr>
<td>Monk Hill</td>
<td>MH2</td>
<td>33</td>
<td>4</td>
<td>6</td>
<td>0</td>
<td>1</td>
<td>75.00</td>
</tr>
<tr>
<td>Monastery</td>
<td>MO</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100.00</td>
</tr>
<tr>
<td>Nackara</td>
<td>NA</td>
<td>22</td>
<td>2</td>
<td>7</td>
<td>2</td>
<td>0</td>
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Unlike the preliminary μXRD results, weaker mineralogical peaks in the EVA patterns were far less common. Rarely did any of the samples show GADDS image patterns revealing possible fine-grained coating, most likely due to the removal of such a coating during the polishing process. The rarity of non-coating mineralogy could be most likely attested to the removal of alteration rims from the ilmenite surface; it is common for kimberlitic ilmenites to exhibit rutile, perovskite, titanite, magnetite, and enstatite as reaction rims. Some samples did show possible rutile and spinel peaks, however far weaker and less common throughout. Reflected Light Microscopy and Back Scatter Electron images could potentially reveal the answer to these. Figure 4-5 shows Eurelia Sample 23 with a weak rutile peak, Figure 4-6 shows Hibou Sample 11 with a weak spinel group (chromite) peak, Figure 4-7 shows Hibou Sample 1 with a calcite peak and Figure 4-8 shows Bobbejaan Sample 16 with rutile and titanite peaks.

Unlike the kimberlitic samples, the initial pattern selected for the non-kimberlitic samples had a greater impact on the end result of the unit cell refinement. Therefore, it was more imperative that the most similar pattern was chosen in each of the cases. Four dominant patterns emerged, that allowed for data that could be refined (Raymond and Wenk 1971; Morris et al. 1978; Ohgaki et al. 1989; Harrison et al. 2000). Table 4-4 shows these patterns, while Figure 4-9 shows a Dana 333 target with chromite peaks, while Figure 4-10 shows an ilmenite exsolution seen as a doublet in the GADDS image. It was found that in the Dana 746 sample, that almost all of the analyses turned out to be rutile instead of ilmenite by μXRD. The search for rutile in association with ilmenite would have been useful for later barometry work, however with a clear lack of ilmenite this sample was removed from further testing. For sample Dana 481, two different ilmenite patterns were the closest match, though not extremely close at that (Table 3-5). Both patterns were indexed with higher Mg concentrations, with one having higher Ni and the other Ge associated with it. Unlike the other non-kimberlite samples, the few that analyses down on sample Dana 481 could not be refined below error using these patterns, and thus this locality was also removed from further testing. Samples Dana 333, Dana 499, Dana 3610, and Dana K48 on the other hand, all gave refined a-axis unit cell parameter values that ranged from 5.024 to 5.144 Å, and c-axis values from 14.015 to 14.127 Å.
In most cases the a-axis values for kimberlitic ilmenites tended to be slightly lower on average, while the c-axis values separated almost completely into two groups. A line could be made on the graph at a c-axis value of 14.02 Å +/- 0.01 Å, which would completely separate the kimberlitic and non-kimberlitic ilmenite samples except for 5 Bobbejaan, and 3 Premier samples (Figure 4-11). Even though the ilmenites from the diamond-poor kimberlite localities had a tighter range of 5.061 to 5.096 for the a-axis and 13.876 to 14.018 for the c-axis, there was no discernable difference between them and the diamond-rich samples with µXRD alone.

Figure 4-5: Ilmenite from the Eurelia kimberlite, Sample 23: A) Photograph of polished sample, B) GADDS image of sample with spots, C) µXRD data portrayed on EVA with weak rutile peaks.
**Table 4-4:** Dominant ICDD ilmenite patterns used for the non-kimberlitic samples

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Quality in brackets is either Star (*), Calculated (C), or Indexed (I)

**Table 4-5:** The two ICDD ilmenite patterns used in an attempt to refine sample Dana 746

<table>
<thead>
<tr>
<th>File Name</th>
<th>Origin</th>
<th>a-axis (Å)</th>
<th>c-axis (Å)</th>
</tr>
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</table>

Quality in brackets is Star (*)

**Figure 4-6:** Ilmenite from the Hibou dyke, Sample 11; A) Photograph of polished sample, B) GADDS image of sample with spots and asterism, C) μXRD data portrayed on EVA with weak chromite peaks.
Figure 4-7: Ilmenite from the Hibou dyke, Sample 1: A) Photograph of polished sample, B) GADDS image of sample with spots and streaks, C) μXRD data portrayed on EVA with calcite peaks.
Figure 4-8: Ilmenite from the Bobbejaan locality, Sample 16; A) Photograph of polished sample, B) GADDS image of sample with spots, C) μXRD data portrayed on EVA using higher c-axis ICDD patterns, along with rutile and titanite peaks.
Figure 4-9: Ilmenite from sample Dana 333, target 8; A) Photograph of target location on sample, B) GADDS image of sample with streaking, C) μXRD data portrayed on EVA with chromite (or other spinel) peaks.
Figure 4-10: Ilmenite from sample Dana K48, target 13; A) Photograph of target location on sample, B) GADDS image of sample with doublet spots, C) μXRD data portrayed on EVA showing two ilmenite pattern matches for the grain and the exsolved ilmenite.
Electron Probe Micro Analysis of Epoxy Mounts

The initial stage before the Electron Probe Micro Analysis (EPMA) was the Reflected Light imaging. This method did show some mineralogical differences on the rims of some of the samples, along with some samples showing a few spots in the center of the ilmenite grains. It did not reveal any exsolution in any of the samples. Reflected Light imaging was done on only a few localities (Attawapiskat, Eurelia, and Monk Hill) initially, and as there was no discernable results that would aid in the observation of exsolution within the ilmenite grains, this method was not used for any of the other localities. The Reflected Light images can be seen in the example from Attawapiskat in Figure 4-12.

Elemental maps were created initially with the Attawapiskat, Premier, and Sheiba localities, with Premier and Sheiba having Cathodoluminescence images created as well. Both of these were done in hopes of showing zonation, varying mineralogy, and exsolution. These images can be seen in the Premier sample in Figure 4-13 and the Sheiba sample in Figure 4-14.

Figure 4-11: Plot of c-axis vs. a-axis unit cell parameters. The diamond-rich kimberlitic ilmenite samples are represented by the circles, the diamond-poor kimberlitic ilmenite samples by the squares, and the non-kimberlitic ilmenite samples by the triangles. The red line illustrates the 14.02 Å division between most of the kimberlitic and non-kimberlitic ilmenites, with the yellow zone as the 0.01 Å error.
In most of the ilmenite grains there was a homogenous concentration of elements through the ilmenite. Some of the Premier samples did show a rim, along with areas around cracks, of higher manganese compared to the Mg-rich cores. Some of the Sheiba samples showed signs of exsolution, specifically with higher concentrations of chromium being seen. However, as these rims and exsolution were also observed in the Backscattered Electron (BSE) images, due to time restrictions, they were not done on any of the other samples.

Wavelength dispersive spectroscopy was done on all the refined ilmenite samples to obtain quantitative mineral chemical data (See Appendix 1). This was also done on any exsolution or points of interest seen via BSE images, which was noted by variations in color. In most cases there was various minerals as reaction rims around the ilmenites, which could consist of ilmenite, rutile, titanite, perovskite, spinel, magnetite, olivine, diopside, or calcite. Due to the disequilibrium associated with the reaction rims, data were collected only on a few selected grains with caution. In other cases, various minerals were found inside the ilmenite grains as either inclusions or exsolution (Seen in Figure 4-15). The inclusion’s mineralogy tended to be most commonly chemically variable ilmenite, magnetite, spinel, perovskite, and titanite. The exsolution was found to be most commonly ilmenite as well, along with magnetite, and spinel. In most of the cases, the exsolution was too fine to be recorded accurately by the EPMA, and thus contamination from the ilmenite host inevitably occurred.

For the Bobbejaan locality, a select number of grains were seen as distinctly different from the rest of the samples. These grains were much brighter in the BSE images, and they displayed textures and minerals not found within the other Bobbejaan samples, such as rutile, enstatite, and titanite. When the EPMA data were collected it was noted that these grains exhibited very low concentrations of MgO wt% compared to FeO wt%, with higher concentrations of MnO wt% compared to the other grains (approximately 3 to 5 wt% higher). The mineral chemical data matched that of Mn-rich ilmenite rims seen around the Premier ilmenites previously mentioned in this research, along with being noted by Harwood (2009). It was noted that the Bobbejaan and Premier samples that had c-axis unit cell parameter values above the c-axis value of 14.02 (±0.01) Å were associated with higher concentrations of MnO (3.2 to 5.1 wt%). As Mn-rich ilmenites have been debated in literature as to the extent of their relationship with in kimberlites, the origin of these samples was decided to be impartial (no distinction was made between kimberlitic or non-kimberlitic) and thus these samples were
Figure 4-12: Attawapiskat Sample 1; A) Reflected Light image, B) Backscattered Electron image (Maunder 2016), C) Fe Element Map, D) Mg Element Map, E) Mn Element Map, F) Cr Element Map. Note the reaction rim evidently seen in the Reflected Light, Fe-Element Map, and Mg-Element Map along the top right of the grain.
Figure 4-13: Premier 1 Sample 1; A) Cathodoluminescence image B) Backscattered Electron image. C) Fe Element Map, D) Mg Element Map, E) Mn Element Map, F) Cr Element Map. Note the rim and crack in filling sections of Mn-rich ilmenite within the sample.
Figure 4-14: Sheiba Sample 86; A) Cathodoluminescence image B) Backscattered Electron image, C) Fe Element Map, D) Mg Element Map, E) Mn Element Map, F) Cr Element Map. Note the exsolution seen in the BSE and Cr-Element Map.
simply deemed Mn-IIm for labelling purposes. With the reclassification of these Mn-rich grains as distinct from kimberlitic and non-kimberlitic populations, this then established a complete separation between the kimberlitic and non-kimberlitic samples at 14.02 (±0.01) Å on the c-axis unit cell parameter, seen in Figure 4-16. Kimberlitic ilmenites can be seen having values less than 14.02 (±0.01) Å, while non-kimberlitic ilmenites have value greater than 14.02 (±0.01) Å.

Figure 4-15: Backscattered Electron Images; A) Bobbejaan Sample 3 which consists of Mn-rich ilmenite around a core of Mg-rich ilmenite along with Rutile, Titanite, and Enstatite intergroths, B) Magnetite exsolution in Monastery Target 1, C) Chemically different ilmenite exsolution in Sheiba Sample 86.
As expected, most of the non-kimberlitic samples had MgO wt% concentrations below that of picroilmenites, with the exception of Sample Dana 333, with concentrations averaging 9.55 wt%. These samples also on average had higher FeO and TiO$_2$ wt% concentrations, while having lower, to almost non-detectable Cr$_2$O$_3$, Nb$_2$O$_5$, NiO, V$_2$O$_3$, and ZrO$_2$ concentrations. Sample Dana 333 and 3610 also had higher MnO concentrations, at on average 3.3 wt%.

Most of the non-kimberlitic ilmenites showed pervasive magnetite exsolution, lack of reaction rims, and large rutile mineral associations. These can be seen in Figure 4-17. Sample Dana 3610 had exsolution that was too fine to be detected by EPMA, however, it was still abundant throughout the sample. Sample Dana K48 had rutile minerals within it, however, the ZrO wt% was not within detectable limits, and thus it was not usable with the Zr-rutile thermometer. The only non-kimberlitic sample that did not have rutile associated with it, was Sample Dana 333, which also made it unusable for the thermometer. Sample Dana 333 was the only sample that instead had ilmenite and then also magnetite with exsolution of ilmenite.

**Figure 4-16**: Plot of c-axis vs. a-axis unit cell parameters, with the Mn-rich ilmenites differentiated. The diamond-rich kimberlitic ilmenite samples are represented by the circles, the diamond-poor kimberlitic ilmenite samples by the squares, the non-kimberlitic ilmenite samples by the triangles, and the Mn-rich ilmenites by the “x”s. The red line illustrates the 14.02 Å division between all of the kimberlitic and non-kimberlitic ilmenites, with the yellow zone as the 0.01 Å error.
Figure 4-17: Backscattered Electron images of non-kimberlitic ilmenites; A) Sample Dana 333 Target 18 with dark grey as ilmenite, and light grey as magnetite with exsolution of ilmenite, B) Sample Dana 333 Target 15 with closer view of ilmenite exsolution in magnetite, C) Sample Dana 499 Target 3 with rutile inclusion in ilmenite, D) Sample Dana 499 Target 9 with magnetite exsolution within ilmenite, E) Sample Dana 3610 Target 3 with rutile minerals around ilmenite, F) Sample Dana K48 Target 2 with ilmenite and nodules of ilmenite and spinel.
4.5 Discrimination diagrams

Three prominent methods in the literature were used to compare the mineral chemical data. The first being that from Wyatt et al. (2003), in a comparison of the TiO wt% against the MgO wt% for the ilmenites to determine if they are mineral chemically kimberlitic or not (Figure 4-18). From this figure one can see a separation between the kimberlitic and non-kimberlitic ilmenites based on the trend developed by Wyatt and others. Two things can be noted in this plot however. The first being that the enriched manganese ilmenites from the Bobbejaan and Premier locality fall in the non-kimberlitic side of the plot. The second is that the non-kimberlitic Sample Dana 333 falls in between the two trend lines on the graph. In most cases the TiO$_2$ vs. MgO wt% graph is established with the red line, where kimberlitic samples fall to the right, and non-kimberlitic samples to the left. However, in cases of elevated MnO wt% concentrations, another trend line is used (seen by the dashed purple line). The majority of Sample Dana 333 plots between the two trend lines. This sample does show elevated MnO wt% with an average of 3.33 wt%, which is below the Bobbejaan and Premier MnO wt% concentrations, but well above the usual < 0.3 wt% MnO seen in the other samples.

![Figure 4-18: TiO$_2$ vs. MgO wt% graph established by Wyatt and others (2003), with the data from this research. The diamond-rich kimberlite ilmenites can be seen as circles and the diamond-poor kimberlites as squares. Both of these populations fall to the right of the red line (with the exception of one MO target). The non-kimberlite samples are shown as triangles and the Mn-rich ilmenites as “x”s. With the exception of 333’s targets, both of these fall to the left of the red line. 333 then exhibits targets falling mostly between the dotted purple line and the solid red line.](image-url)
The other two graphs were based on the diamond potential for the kimberlitic ilmenites, and thus the non-kimberlitic localities were omitted from the plots. The first plot compares the MnO and V$_2$O$_3$ wt%’s, along with the plot of two ilmenite inclusions in diamonds (Figure 4-19). This method and the literature ilmenite inclusion data were developed and obtained by Kaminsky and Belousova (2008). Their plots showed that one of the ilmenite inclusion values was more comparable to the picroilmenites found in kimberlites, whereas the other inclusion was comparable to the Mn-ilmenites from them. When comparing the mineral chemical data in the MnO and V$_2$O$_3$ wt% plot, the picroilmenites fall on a similar plane for MnO concentration as one of the ilmenite inclusions of Kaminsky and Belousova (2008), however, the V$_2$O$_3$ concentrations varied quite extensively instead of a tight grouping. The Mn-ilmenite values on the other hand did not show any grouping or trends toward the more Mn-rich ilmenite inclusion, instead have both much higher concentrations of MnO. The Premier samples did show relatively similar V$_2$O$_3$ concentrations to the inclusion reported in Kaminsky and Belousova (2008).

**Figure 4-19:** MnO vs. V$_2$O$_3$ wt% concentration plot established by Kaminsky and Belousova (2008) using the ilmenite inclusions data from their report as a comparison with the data from this research. The diamond-rich kimberlite ilmenite (circles) and diamond-poor kimberlite ilmenites (squares), can be seen at very minimal values of MnO, encompassing a large range of V$_2$O$_3$. The Mn-rich ilmenite samples (“x”’s) are seen with minimal spatial relationship to these inclusions.
The last graphing method was developed by Carmody and others (2014), where they compared the Nb/Ta against the Zr/Nb values in ppm (Figure 4-20). The graph showed that the more diamond-rich kimberlites could be separated from the more diamond-poor localities at a Zr/Nb value of 0.37, with the more diamond-rich localities having values greater than this. The Nb/Ta did not show any discernable difference, and as Ta was only collected from a very small number of localities in this study, the Zr/Nb was instead plotted against the c-axis unit cell parameter value, as the y-axis plot was arbitrary for this graph. When plotting both the diamond-rich and diamond-poor localities on this graph, there seemed to be no separation as both kimberlites types fell on either side of the 0.37 line. In most cases the SH and TB localities did follow this trend, having Zr/Nb values in most cases below the 0.37 line. The B30 and DL localities on the other hand plotted mainly above this line. For the diamond-rich kimberlites, there was complete scatter. The ATT, BB, HR, MO, PR, STN, and UD localities had most of their samples plotted below the 0.37 line, which would indicate diamond-poor. The DS, ER, MH2, and STM localities on the other hand seemed to be evenly scattered across the boundary. In most cases the BB and PR Mn-ilmenite samples fell below the 0.37 line.

**Figure 4-20:** c-axis unit cell parameter vs. Zr/Nb graph, modified from the Nb/Ta vs. Zr/Nb graph by Carmody and others (2014). There graph showed that diamond-rich kimberlites from their localities fell to the right of the 0.37 Zr/Nb line (red dashed line), while diamond-poor kimberlites fell to the left. Here we can see that it is a cluster of diamond-rich kimberlites (seen as circles) and diamond-poor kimberlites (seen as squares) on both sides of the line. Mn-rich ilmenites (seen as “x”s) predominantly stay on the left side.
4.6 μXRD and EPMA Comparison

With the c-axis unit cell parameter being able to differentiate between kimberlitic and non-kimberlitic ilmenite samples, this could now be compared with mineral chemical data to determine if there are any discrete chemical differences between localities and rock type which related to c-axis unit cell parameters. The c-axis unit cell parameter value was compared with elemental concentrations (analyzed as weight percent oxides). The elements were chosen based off the substitution into ilmenite’s basic structure of $A^{2+}B^{4+}O_3$. For the A-site, the oxides that were selected were FeO, MgO, MnO, Fe$_2$O$_3$, Cr$_2$O$_3$, and NiO, while the B-site was TiO$_2$, ZrO$_2$, SiO$_2$, Nb$_2$O$_5$, V$_2$O$_3$, Al$_2$O$_3$. For ease in comparison, the samples were separated into five categories by either location, diamond-potential, or rock type. These categories were: Canadian (Figure 4-21), African (Figure 4-22), Australian and Russian (Figure 4-23), Diamond-Poor (Figure 4-24), and Non-Kimberlitic (Figure 4-25). As the Bobbejaan and Premier localities revealed ilmenite samples of Mn-enrichment, separate titles were established for these samples, being BB Mn-IIm and PR Mn-IIm respectively.

The goal was to determine if there were any trends formed between the c-axis parameter and the mineral chemical data, and to determine which elements, if any, correlated to unit cell size. In most cases there was no discernable trend formed, instead the data either was grouped within one massive cluster, or a horizontal array with the c-axis parameter being almost constant. There are a small number of mineral chemical constituents that do show varying degrees of pattern development. The Canadian localities show a small increase in the c-axis parameter as the MnO concentrations increase (seen in Figure 4-21E). Manganese has an ionic radius of 0.83 Å when octahedrally coordinated (Klein and Dutrow 2007). This is larger than both magnesium and iron, and thus if manganese is substituting into the mineral then an increase in the c-axis would be the result. The Bobbejaan locality shows an increasing c-axis value with elevated concentrations of Fe$_2$O$_3$ (Figure 4-22B), however, as the Fe$^{3+}$ atom would be slightly smaller than the Fe$^{2+}$ atom due to the loss of an electron, this increase in c-axis value may have resulted from the substitution of Fe$^{3+}$ in place of Mg in the sample. What was noted was the high concentrations of Cr$_2$O$_3$ in some of the Kimberlitic samples, specifically with some of the Attawapiskat, Hibou, Monk Hill and Sheiba samples. These concentrations are much higher then what is seen in normal picroilmenites, however, for the Attawapiskat and Sheiba are similar to the data found by Harwood (2006) and Maunder (2016). The Mn-rich Bobbejaan samples also
show this slight increase in c-axis due to Fe$_2$O$_3$, just not as clearly, however they also show a decrease in the c-axis value with increasing concentration of TiO$_2$. There does also appear to be a subtle increase in c-axis values with decreasing SiO$_2$ as well (Figure 4-22K). Both of these could be the result of higher ionic radii elements being substituted, such as niobium or zirconium. C-axis increases with V$_2$O$_3$ increase (Figure 4-22J), however, V$^{3+}$ has a smaller radius than Ti$^{4+}$, which could relate to the preferential substitution of V$^{3+}$ over Si$^{4+}$ in the B-Site. Eurelia and Monk Hill show a vague increase in c-axis with increasing FeO (Figure 4-23A), which fits with the larger size of iron over magnesium. The inverse situation can be seen in the Eurelia locality with the decrease in c-axis value corresponding with increasing MgO (Figure 4-23C). There is a very subtle and scattered decrease in c-axis values as the NiO concentrations increase in Eurelia and Monk Hill (Figure 4-23F).

For the non-kimberlitic samples, rather then individual samples revealing patterns between c-axis values and mineral chemical data, instead trends are formed from the entirety of the Dana collection samples. We notice again that the c-axis shows increasing values with increasing FeO, and decreasing values with increasing MgO (Figures 4-25A and Figure 4-25C). There is an increase in the c-axis as the larger Nb substitutes in for the smaller Ti (Figure 4-25H), yet then a decrease in the c-axis unit cell value as the even smaller Si substitutes in (Figure 4-25K). There is also a subtle increase in c-axis values with increasing Mn concentrations for localities Dana 333 and Dana 3610 (Figure 4-25E).
Figure 4-21: Ilmenite samples from Diamond-rich Canadian kimberlites Attawapiskat (ATT), Hibou (HR), and Star with either magnetic (STM) or non-magnetic (STN). A) c-axis vs. FeO, B) c-axis vs. Fe$_2$O$_3$, C) c-axis vs. MgO, D) c-axis vs. Cr$_2$O$_3$, E) c-axis vs. MnO (with a zoomed in portion of the graph), F) c-axis vs. NiO.
Figure 4.21 continued: Ilmenite samples from Diamond-rich Canadian kimberlites Attawapiskat (ATT), Hibou (HR), and Star with either magnetic (STM) or non-magnetic (STN). G) c-axis vs. TiO$_2$, H) c-axis vs. Nb$_2$O$_5$, I) c-axis vs. ZrO$_2$, J) c-axis vs. V$_2$O$_3$, K) c-axis vs. SiO$_2$, L) c-axis vs. Al$_2$O$_3$. 
Figure 4-22: Ilmenite samples from Diamond-rich African kimberlites Bobbejaan (BB), Dutoitspan (DS), Monastery (MO), and Premier (PR). Bobbejaan and Premier both have Mn-rich ilmenite samples as well (BB Mn-Ilm and PR Mn-Ilm respectively). A) c-axis vs. FeO, B) c-axis vs. Fe₂O₃, C) c-axis vs. MgO, D) c-axis vs. Cr₂O₃, E) c-axis vs. MnO (with a zoomed in portion of the graph), F) c-axis vs. NiO (with zoomed in portion of the graph).
Figure 4-22 continued: Ilmenite samples from Diamond-rich African kimberlites Bobbejaan (BB), Dutoitspan (DS), Monastery (MO), and Premier (PR). Bobbejaan and Premier both have Mn-rich ilmenite samples as well (BB Mn-Ilm and PR Mn-Ilm respectively). G) c-axis vs. TiO$_2$, H) c-axis vs. Nb$_2$O$_5$, I) c-axis vs. ZrO$_2$, J) c-axis vs. V$_2$O$_3$, K) c-axis vs. SiO$_2$, L) c-axis vs. Al$_2$O$_3$. 
Figure 4-23: Ilmenite samples from Diamond-rich Australian and Russian localities. Eurelia (ER), Monk Hill (MH2), Nackara (NA), and Udachnaya (UD). A) c-axis vs. FeO, B) c-axis vs. Fe$_2$O$_3$, C) c-axis vs. MgO, D) c-axis vs. Cr$_2$O$_3$, E) c-axis vs. MnO (with a zoomed in portion of the graph), F) c-axis vs. NiO.
Figure 4-23 continued: Ilmenite samples from Diamond-rich Australian and Russian localities. Eurelia (ER), Monk Hill (MH2), Nackara (NA), and Udachnaya (UD). G) c-axis vs. TiO$_2$, H) c-axis vs. Nb$_2$O$_5$, I) c-axis vs. ZrO$_2$, J) c-axis vs. V$_2$O$_3$, K) c-axis vs. SiO$_2$, L) c-axis vs. Al$_2$O$_3$. 
Figure 4.24: Ilmenite samples from Sub-economic to Diamond-poor kimberlite localities B30, Diamond Lake (DL), Sheiba (SH), Triple B (TB). A) c-axis vs. FeO, B) c-axis vs. Fe₂O₃, C) c-axis vs. MgO, D) c-axis vs. Cr₂O₃, E) c-axis vs. MnO (with a zoomed in portion of the graph), F) c-axis vs. NiO.
Figure 4-24 continued: Ilmenite samples from Sub-economic to Diamond-poor kimberlite localities B30, Diamond Lake (DL), Sheiba (SH), Triple B (TB). G) c-axis vs. TiO$_2$, H) c-axis vs. Nb$_2$O$_5$, I) c-axis vs. ZrO$_2$, J) c-axis vs. V$_2$O$_3$, K) c-axis vs. SiO$_2$, L) c-axis vs. Al$_2$O$_3$. 
Figure 4-25: Ilmenite samples from Non-Kimberlitic localities Dana 333, Dana 499, Dana 3610, and Dana K48. A) c-axis vs. FeO, B) c-axis vs. Fe$_2$O$_3$, C) c-axis vs. MgO, D) c-axis vs. Cr$_2$O$_3$ (with a zoomed in portion of the graph), E) c-axis vs. MnO, F) c-axis vs. NiO.
Figure 4-25 continued: Ilmenite samples from Non-Kimberlitic localities Dana 333, Dana 499, Dana 3610, and Dana K48. G) c-axis vs. TiO$_2$, H) c-axis vs. Nb$_2$O$_5$, I) c-axis vs. ZrO$_2$, J) c-axis vs. V$_2$O$_3$, K) c-axis vs. SiO$_2$, L) c-axis vs. Al$_2$O$_3$ (with zoomed in portion of the graph).
4.7 Thermometry and Barometry

Due to the xenocrystic nature of ilmenites from the kimberlitic localities, an estimation range based on literature could not always be found. Temperature ranges for the various other minerals, along with estimations of kimberlite eruption temperatures could be extrapolated, however, as ilmenites are xenocrystic minerals in the kimberlites, these temperatures could not be used for their formation in the mantle. Thus, for kimberlitic ilmenite samples that did not have literature values explicitly, a 350 Kelvin range between 1123.15 to 1473.15 K was approximated for an average formation temperature for ilmenites within the mantle (Ringwood et al. 1992; Mitchell 1973; Mitchell 1993; Wilson et al. 2005). This range then allowed for an estimation of the formation pressure of the ilmenite, by obtaining what may be its maximum, minimum, and average pressure, keeping in mind an error in this method due to estimation. The majority of the kimberlitic ilmenite pressure calculations were done by using the Ashchepkov et al. (2014) mono-ilmenite barometer. As the temperature in most cases was given as a range of values, the pressure was also obtained as Pressure Minimum, Pressure Maximum, and Pressure Average (Appendix 2). The overall range calculated from the kimberlitic ilmenite samples was from 0.42 to 8.09 GPa. Only five samples from the kimberlitic ilmenites fall below 3.0 GPa, as the overall average is around 6.18 GPa. Due to the range of pressures, there is degree of error when looking at the Pressure Average. The average error is around 0.36 GPa, however it varies from 0.02 to 2.85 GPa depending on the sample. The Sheiba and Attawapiskat kimberlites had the tightest pressure values, while the Nackara kimberlite had the largest range of error. The range of pressure for each locality can be seen in Table 4-5.

For the non-kimberlitic samples, the presence of rutile with textures that could be identified as indicative of equilibrium state between the ilmenite and rutile assemblage, allowed for the temperature to be obtained by the zirconium concentration of the rutile. This was accomplished by using the Zack et al. (2008) rutile thermometer. Then by using the Zhao et al. (1999) rutile-ilmenite barometer, the pressure could be extrapolated. The pressure was calculated for the Samples Dana 499 and Dana 3610, along with the Mn-ilmenite samples from the Bobbejaan locality using this method. Bobbejaan’s Mn-ilmenite samples showed pressures similar or higher than the pressures obtained from the Mg-rich ilmenites in that locality. Pressure was not able to be obtained from Premier’s Mn-ilmenite samples due to lack of rutile for the rutile-ilmenite method, along with concentrations of MgO wt% not being high enough for the
mono-ilmenite method. The non-kimberlitic Samples Dana 333 and Dana K48 either lacked rutile or lacked rutile with detectable Zr concentrations to be used for the rutile-ilmenite method. Unlike the kimberlitic samples, where an estimation range could be established for their formation temperature, the non-kimberlitic samples did not literature temperature values. The pressures obtained can be found in Appendix 2, along with the equations used to calculate the errors. The ranges of pressure for the samples can be found in Table 4-6.

Table 4-6: Temperature and Pressure values of Epoxy Mounted Ilmenites

<table>
<thead>
<tr>
<th>Locality</th>
<th>Label</th>
<th>Samples/Targets (#)</th>
<th>Locality Temp. Min (K)</th>
<th>Locality Temp. Max (K)</th>
<th>Locality Pressure Min (GPa)</th>
<th>Locality Pressure Max (GPa)</th>
<th>Locality Pressure Average (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Attawapiskat</td>
<td>ATT</td>
<td>11</td>
<td>1073</td>
<td>1323</td>
<td>6.17</td>
<td>6.58</td>
<td>6.40</td>
</tr>
<tr>
<td>Bobbejaan</td>
<td>BB</td>
<td>11</td>
<td>1623.15</td>
<td>1823.15</td>
<td>5.28</td>
<td>7.09</td>
<td>6.27</td>
</tr>
<tr>
<td></td>
<td>BB Mn-Ilm</td>
<td>5</td>
<td>975.89</td>
<td>1258.27</td>
<td>6.48</td>
<td>9.58</td>
<td>8.04</td>
</tr>
<tr>
<td>Dutoitspan</td>
<td>DS</td>
<td>18</td>
<td>1123.15</td>
<td>1473.15</td>
<td>4.32</td>
<td>7.25</td>
<td>6.25</td>
</tr>
<tr>
<td>Eurelia</td>
<td>ER</td>
<td>13</td>
<td>1123.15</td>
<td>1473.15</td>
<td>7.05</td>
<td>8.09</td>
<td>7.66</td>
</tr>
<tr>
<td>Hibou (Renard)</td>
<td>HR</td>
<td>16</td>
<td>1123.15</td>
<td>1473.15</td>
<td>6.53</td>
<td>7.57</td>
<td>6.97</td>
</tr>
<tr>
<td>Monk Hill</td>
<td>MH2</td>
<td>31</td>
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<td>1473.15</td>
<td>3.96</td>
<td>6.98</td>
<td>5.69</td>
</tr>
<tr>
<td>Monastery</td>
<td>MO</td>
<td>7</td>
<td>1123.15</td>
<td>1473.15</td>
<td>1.51</td>
<td>6.14</td>
<td>4.77</td>
</tr>
<tr>
<td>Nackara</td>
<td>NA</td>
<td>19</td>
<td>1123.15</td>
<td>1473.15</td>
<td>2.87</td>
<td>7.80</td>
<td>5.74</td>
</tr>
<tr>
<td>Premier</td>
<td>PR</td>
<td>3</td>
<td>1023.15</td>
<td>1773.15</td>
<td>6.46</td>
<td>7.40</td>
<td>7.01</td>
</tr>
<tr>
<td>Star</td>
<td>STM</td>
<td>14</td>
<td>1123.15</td>
<td>1473.15</td>
<td>5.74</td>
<td>7.04</td>
<td>6.60</td>
</tr>
<tr>
<td></td>
<td>STN</td>
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<td>1473.15</td>
<td>5.71</td>
<td>7.09</td>
<td>6.25</td>
</tr>
<tr>
<td>Udachnaya</td>
<td>UD</td>
<td>14</td>
<td>1123.15</td>
<td>1473.15</td>
<td>4.56</td>
<td>5.67</td>
<td>5.35</td>
</tr>
<tr>
<td>B30</td>
<td>B30</td>
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<td>1473.15</td>
<td>0.42</td>
<td>6.09</td>
<td>5.08</td>
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<tr>
<td>Diamond Lake</td>
<td>DL</td>
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<td>1473.15</td>
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<td>6.01</td>
<td>5.01</td>
</tr>
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<td>Sheiba</td>
<td>SH</td>
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<td>1123.15</td>
<td>1473.15</td>
<td>6.89</td>
<td>7.38</td>
<td>7.13</td>
</tr>
<tr>
<td>Triple B</td>
<td>TB</td>
<td>22</td>
<td>1123.15</td>
<td>1473.15</td>
<td>5.31</td>
<td>7.22</td>
<td>6.68</td>
</tr>
<tr>
<td>Dana 499</td>
<td>499</td>
<td>7</td>
<td>813.02</td>
<td>914.09</td>
<td>0.79</td>
<td>5.40</td>
<td>4.20</td>
</tr>
<tr>
<td>Dana 3610</td>
<td>3610</td>
<td>11</td>
<td>665.79</td>
<td>665.79</td>
<td>0.98</td>
<td>2.97</td>
<td>2.54</td>
</tr>
</tbody>
</table>

There were two cases in which both the Ashchepkov et al. (2014) mono-ilmenite barometer and the Zhao et al. (1999) rutile-ilmenite barometer could be tested against one another. The first is with the Sheiba locality, in which rutile was found in Sample 85. This grain gave a calculated temperature of 1122.45K with the Zack et al. (2008) rutile thermometer.
However, as this grain was not attached to any ilmenite, equilibrium was questionable. Thus, both barometers were used to calculate pressure and see if they are similar. The second is with the Sample Dana 499, in which the MgO wt% concentration was high enough to be potentially used by the Ashchepkov et al. (2014) mono-ilmenite barometer. Therefore, the temperatures were calculated with the Zack et al. (2008) rutile thermometer, and then the pressures obtained from both barometers could be compared. These comparisons can be seen in Table 4-7.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rutile-Ilmenite Pressure Average (GPa)</th>
<th>Mono-ilmenite Pressure Average (GPa)</th>
<th>Pressure Difference (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheiba 1</td>
<td>4.71 (±0.05)</td>
<td>7.00 (±0.23)</td>
<td>2.30</td>
</tr>
<tr>
<td>Sheiba 10</td>
<td>4.84 (±0.05)</td>
<td>7.27 (±0.23)</td>
<td>2.43</td>
</tr>
<tr>
<td>Sheiba 11</td>
<td>4.94 (±0.05)</td>
<td>7.17 (±0.26)</td>
<td>2.22</td>
</tr>
<tr>
<td>Sheiba 17</td>
<td>4.40 (±0.05)</td>
<td>7.38 (±0.23)</td>
<td>2.99</td>
</tr>
<tr>
<td>Sheiba 20</td>
<td>4.52 (±0.05)</td>
<td>7.18 (±0.22)</td>
<td>2.66</td>
</tr>
<tr>
<td>Sheiba 21</td>
<td>4.52 (±0.05)</td>
<td>7.18 (±0.23)</td>
<td>2.66</td>
</tr>
<tr>
<td>Sheiba 22</td>
<td>4.70 (±0.05)</td>
<td>6.99 (±0.23)</td>
<td>2.29</td>
</tr>
<tr>
<td>Sheiba 32</td>
<td>4.72 (±0.05)</td>
<td>7.13 (±0.23)</td>
<td>2.40</td>
</tr>
<tr>
<td>Sheiba 36</td>
<td>4.66 (±0.05)</td>
<td>7.11 (±0.23)</td>
<td>2.45</td>
</tr>
<tr>
<td>Sheiba 51</td>
<td>5.12 (±0.05)</td>
<td>7.29 (±0.24)</td>
<td>2.16</td>
</tr>
<tr>
<td>Sheiba 55</td>
<td>4.89 (±0.05)</td>
<td>7.12 (±0.23)</td>
<td>2.23</td>
</tr>
<tr>
<td>Sheiba 68</td>
<td>5.05 (±0.05)</td>
<td>7.29 (±0.24)</td>
<td>2.24</td>
</tr>
<tr>
<td>Sheiba 73</td>
<td>4.58 (±0.05)</td>
<td>7.09 (±0.23)</td>
<td>2.52</td>
</tr>
<tr>
<td>Sheiba 81</td>
<td>4.53 (±0.05)</td>
<td>6.92 (±0.23)</td>
<td>2.38</td>
</tr>
<tr>
<td>Sheiba 86</td>
<td>5.47 (±0.05)</td>
<td>7.20 (±0.24)</td>
<td>1.72</td>
</tr>
<tr>
<td>Dana 499 1</td>
<td>4.73 (±0.05)</td>
<td>4.69 (±0.44)</td>
<td>0.04</td>
</tr>
<tr>
<td>Dana 499 2</td>
<td>1.41 (±0.05)</td>
<td>3.53 (±0.37)</td>
<td>2.1</td>
</tr>
<tr>
<td>Dana 499 5</td>
<td>4.64 (±0.05)</td>
<td>4.68 (±0.45)</td>
<td>0.04</td>
</tr>
<tr>
<td>Dana 499 7</td>
<td>4.84 (±0.05)</td>
<td>4.71 (±0.46)</td>
<td>0.13</td>
</tr>
<tr>
<td>Dana 499 9</td>
<td>4.93 (±0.05)</td>
<td>4.72 (±0.45)</td>
<td>0.21</td>
</tr>
<tr>
<td>Dana 499 14</td>
<td>4.39 (±0.05)</td>
<td>4.65 (±0.44)</td>
<td>0.26</td>
</tr>
<tr>
<td>Dana 499 16</td>
<td>4.47 (±0.05)</td>
<td>4.45 (±0.42)</td>
<td>0.02</td>
</tr>
</tbody>
</table>

What can be noted from Table 4-6 is that the pressure values of the Sheiba sample are quite different. Thus, as the pressures from Table 4-6 for the Sheiba locality are more reliable, as it does not incorporate the rutile grain. As for the Dana 499 data, they appear to be relatively similar (with the exceptions of Dana 499 Target 2), which gives reliability for using both barometers. Due to the presence of rutile in the sample, and the relatively small wt% MgO in Dana 499, the rutile-ilmenite barometer is still preferable due to the smaller error values, however, the mono-ilmenite barometer simply confirms a basis for its pressure.
4.8 Comparison with Previous Studies

A select number of ilmenite samples were previously analyzed by Ben Harwood (2009) and/or Duncan Maunder (2016). Harwood looked at the localities PR and SH, while Maunder looked at ATT, PR, and SH. These samples were then re-run to try and determine if the data could be replicated with Maunder’s work being a close approximation of current techniques and apparatus calibrations, and Harwood’s work having different instrumentational parameters. All three data sets were achieved by μXRD analyses at the Powder and Micro X-Ray Diffraction Facility in the Biological & Geological Sciences Building at Western University. The same instrument, the Bruker D8 Discover micro X-ray diffractometer was used by all three. The micro X-ray diffractometer’s instrumental parameters for the Maunder (2016) research, other then the change in detector type, was consistent with this research. The Harwood (2009) instrumental parameters were all different. The hypothesis is that the change in instrumental parameters should not affect the data acquired. All three studies then used the Omega Scan program to obtain a coupled two-dimensional signature, with the parameters for the analyses varying between the studies. Maunder’s work would then aid in determining if the data could be replicated under approximately similar conditions, while Harwood’s would enable a comparison of vastly different conditions to determine the extent of parameter change to obtain replicated data. The instrumentational parameters can be seen in Table 4-8, and the μXRD acquisition parameters can be seen in Table 4-9.

Table 4-8: μXRD instrumentational parameters from all three studies

<table>
<thead>
<tr>
<th>Study</th>
<th>X-ray Source (λ in Å)</th>
<th>Voltage (kV)</th>
<th>Ampere (mA)</th>
<th>Beam size (μm)</th>
<th>Detector Type</th>
<th>Detector Distance (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harwood, 2009</td>
<td>Copper (1.5418)</td>
<td>40</td>
<td>40</td>
<td>500</td>
<td>Hi-Star</td>
<td>15</td>
</tr>
<tr>
<td>Maunder, 2016</td>
<td>Cobalt (1.78897)</td>
<td>35</td>
<td>45</td>
<td>300</td>
<td>Hi-Star</td>
<td>12</td>
</tr>
<tr>
<td>Galanneau, 2018</td>
<td>Cobalt (1.78897)</td>
<td>35</td>
<td>45</td>
<td>300</td>
<td>VÁNTEC-500</td>
<td>12</td>
</tr>
</tbody>
</table>

The refinements by all three studies were undergone with the CELREF program, as mentioned previously in this thesis. Therefore, only samples that were successfully refined by both theses were eligible for comparison. This then limited the number of samples that could be
compared, with 16 between Harwood and this research, and 7 between Maunder and this research.

Table 4-9: µXRD Data Analyses Parameters

<table>
<thead>
<tr>
<th>Study</th>
<th>Frame 1</th>
<th>Frame 2</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>θ₁</td>
<td>θ₂</td>
<td>Width</td>
</tr>
<tr>
<td>Harwood, 2009*</td>
<td>6 or 5°</td>
<td>38.5 or</td>
<td>34 or 29.5°</td>
</tr>
<tr>
<td>Maunder, 2016</td>
<td>18°</td>
<td>35°</td>
<td>25°</td>
</tr>
<tr>
<td>Galarneau, 2018</td>
<td>10°</td>
<td>39°</td>
<td>30°</td>
</tr>
</tbody>
</table>

* For the Harwood (2009) study, two different Omega Scan operations were done depending on the ilmenite. 18 of the ilmenite samples were collected with the first set of variables, and 26 were collected with the second set.

The refinements by all three studies where undergone with the CELREF program, as mentioned previously in this thesis. Therefore, only samples that were successfully refined by both theses were eligible for comparison. This then limited the number of samples that could be compared, with 16 between Harwood and this research, and 7 between Maunder and this research. The samples used to compare against the Harwood (2009) and Maunder (2016) studies are seen in Table 4-10 and 4-11 respectively.

From this data, each parameter measured in this report was compared to the same parameter from the past study (Figure 4-26 to Figure 4-27). The ideal situation was to obtain a pattern with the y-intercept being zero, and the slope being one. The comparison would also take into account the error of each unit cell parameter, along with the number of peaks used in the refinement, both of which aid in the determination of which methods result in more reliable data. From the a- and c-axis values the volume of the unit cell itself could be calculated from this equation:

\[ V = \frac{(a^2 \times c \times \sqrt{3})}{2} \]  

(4-1)

Where \( a \) and \( c \) correspond to the a-axis and c-axis unit cell parameters respectively in Å, and \( V \) is in Å³. The error for the volume values was also calculated using the propagations of error method (Skoog and West 1980).
Table 4-10: Ilmenite samples compared with the Harwood (2009) data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Locality</th>
<th># of peaks</th>
<th>c-axis error</th>
<th>a-axis error</th>
<th>c-axis error</th>
<th>a-axis error</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR1</td>
<td>PR1</td>
<td>3</td>
<td>0.0002</td>
<td>13.9884</td>
<td>0.0037</td>
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</tr>
<tr>
<td>PR2</td>
<td>PR2</td>
<td>6</td>
<td>0.0006</td>
<td>13.9103</td>
<td>0.0021</td>
<td>5.0669</td>
</tr>
<tr>
<td>SH</td>
<td>SH</td>
<td>5</td>
<td>0.0004</td>
<td>13.9464</td>
<td>0.0044</td>
<td>5.0693</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.0048</td>
<td>5.0512</td>
</tr>
<tr>
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<td>14.0021</td>
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<td>14.0323</td>
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<td></td>
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While the a-axis values from the Harwood (2006) data showed promising comparison (Figure 4-26A), forming a well-defined trend with most of the samples, the c-axis comparison (Figure 4-26B) was relatively scattered. The a-axis slope is near ideal, while the c-axis is relatively scattered, with only a small grouping of Sheiba with ideal comparisons. The volume comparison (Figure 4-26C) however does show a slightly better comparison, not as good as the a-axis alone, but does at least portray a relatively comparable trend. As volume does have the a-axis unit cell parameter having more influence upon the outcome, this could be why. The errors for the a-axis values are relatively similar between the studies, with in most cases the larger of the errors coming from the Harwood data set. The largest Harwood error is that of 0.012 Å, while the largest in the new data is only 0.0044 Å. The average for Harwood’s data is 0.00398 Å, and the new data has an average error of 0.00264 Å. While the errors for the a-axis are relatively noticeable between the samples, those for the c-axis values are incredibly small. The largest for Harwood’s data set is only 0.0013 Å, while the average of the entire set is 0.00053 Å. For the c-axis, new data does have a larger error over all, at about 0.004 Å, and the average being 0.0009 Å does make the new data a bit higher than the old.
The a-axis comparison (Figure 4-26A) with Harwood’s 2009 data showed that most of the Sheiba samples were relatively close to the data acquired in this thesis. The largest difference is seen with the comparison of PR1-1 and SH-24, Harwood’s largest and smallest a-axis values respectively. There is a large error value for PR1-1 in Harwood’s data, the largest of his a-axis
error values, however, SH-24 has one of the lowest error values. In the new data both samples have a similar error, yet not enough to warrant such a shift.

Figure 4-26: μXRD comparison plots against the data of the same samples from Harwood (2009). A) a-axis unit cell parameter comparison. B) c-axis a-axis unit cell parameter comparison.
For the c-axis (Figure 4-26B), there is a distinct separation between the Sheiba and Premier samples in the new data set, with the Premier favouring higher unit cell values. In most cases the Sheiba samples are situated around the 13.95 Å values, with samples Sheiba 24 and Sheiba 63 being the outliers. In the case of Sheiba 24, five peaks were used for the refinement, however, only three peaks were used for Sheiba 63, making it less reliable of the results. For the Premier samples, it is clear that there is distinct variation in the ilmenites. This variation could be attributed to target location, a major concern that was noted with the Premier samples in this thesis, as the Premier ilmenites were associated with rims and cracks of Mn-rich ilmenite, which were also associated with higher c-axis values. As it appears that the c-axis change is much more readily noticed than the a-axis values; an increase in Mn-rich ilmenite being detected by the μXRD could alter the c-axis values, without disturbing the a-axis values as much. This distinct difference between Harwood’s and the new data collected for the Premier samples could be
Figure 4-27: μXRD comparison plots against the data of the same samples from Maunder (2016). A) a-axis unit cell parameter comparison. B) c-axis a-axis unit cell parameter comparison.
associated with slight differences in beam position, where one experiment collected more data from Mn-rich spots on the samples in one case over the other.

Overall the Maunder (2016) data were much more comparable with the data collected for this thesis. Each axis comparison shows relativity similar values, which gives the plots a suitable slope. For the a-axis (Figure 4-27A) the largest error is in the new data at 0.005 Å, compared to Maunder’s 0.0047 Å, with the average error for the new set being 0.0018 Å, while Maunder’s is 0.0023 Å. This then extends to the c-axis values (Figure 4-27B) where the error maximum is for Maunder’s data is 0.0027 Å and the average is 0.00097 Å, while the new data has a maximum value of 0.004 Å and an average of 0.0011 Å. While the c-axis’ errors are quite small, the a-axis errors from both data sets are much larger. In most cases the number of peaks for refinement are similar if not the same, with the largest difference being for Attawapiskat 38 where Maunder had refined on seven peaks, and the new data only had four peaks (only five peaks were detected from the μXRD analysis).

Figure 4-27 continued: μXRD comparison plots against the data of the same samples from Maunder (2016). C) Volume of unit cell comparison.
From each of the cases there is a more reliable comparison between Maunder’s data and the new data collected, than compared to Harwood’s. This could mainly be attributed to the beam size when comparing the Premier locality for the Mn-rich issue. As the beam size was 500 μm larger for the Harwood data, there is a larger chance to either collect Mn-rich data, along with other contaminants. Increasing the 2θ range with the new data, would also all for more peaks to be observed. The detector type is different in the current research, as we are using a VÂNTEC-500 detector, compared to the Hi-Star detector, enabling better resolution (0.024 vs. 0.040 degree/pixel respectively). Other than human error during the refining process, there are other potential errors that could arise, causing differences in the values. The quality of the data is critical to the refinement, as a large noise could result in slight variations in the peak positions. The number of peaks being used in the refinement could affect the end result, as even though CELREF can refine on 3 peaks, that is less then ideal. What can also be observed is possible linear trends that vary from the y=x slope, which may be the result of systematic errors.

The other thing to note is the 14.02 ± 0.01 Å line on the c-axis values which may separate out the Kimberlitic form the non-kimberlitic samples. In these cases, the ATT and SH samples should fall below this line, while the PR samples could either fall below or above depending on if the data were collected in the Mg-rich or the later stage Mn-rich portions. For the Harwood data (see Figure 4-26B), there are three samples that fall above this line: Premier 1 sample 1 (PR1-1), Premier 2 sample 23 (PR2-23), and Sheiba sample 24 (SH-24). While PR2-23 is consistent in position above the trend with the new data, PR1-1 was below the line. However, as seen in the elemental maps for PR1-1, there is two large zones of Mg-rich/Mn-poor ilmenite, which are surrounded and separated by Mg-poor/Mn-rich ilmenite, and thus the discrepancy could be established from that. As for the SH-24 it is unclear as to what the discrepancy may be. As this sample in particular had the smallest a-axis value and the largest c-axis value among the samples compared, the problem could lie within the starting parameters for the refinement, or possibly the samples quality. For the Maunder comparison (see Figure 4-27B) only Premier 2 sample 19 is above the line in both data sets, which attributes to its elevated manganese concentrations. Thus, whether or not the SH-24 sample from Harwood’s data could be attributed to error, the 14.02 ± 0.01 Å separation is a still a useful tool, even with the small differences in the data sets.
Chapter 5: Discussion

5.1 Introduction

This chapter focuses on discussing the data collected from the analytical instrumentation from the previous chapter, the reasons for the results, and how they might apply to real world situations. This chapter also introduces the comparison with pressure, to determine how the crystal structure and mineral composition change as a function of increasing depth. It concludes with diagrams from multivariate and cluster analysis programs, which include all three parameters; these can give a better distinction between Kimberlitic and non-Kimberlitic sources.

5.2 μXRD Differentiation between Kimberlitic and Non-Kimberlitic Ilmenites

Comparison of the a- and c-axis unit cell parameters for various ilmenite localities, reveals a possible discrimination between the Kimberlitic and non-Kimberlitic samples. Figure 5-1 shows the c-axis versus the a-axis unit cell parameter plot, where a line at 14.02 (±0.01) Å could be seen, with the Kimberlitic ilmenites lying below this value, and non-Kimberlitic above.

There are two main reasons for this delineation between ilmenite paragenesis. The first is that Kimberlitic ilmenites have higher concentrations of magnesium compared to iron. The ionic radius (in octahedral coordination) of Mg$^{2+}$ is 0.72 Å, while the radius of Fe$^{2+}$ is 0.78 Å (Klein and Dutrow 2007). They are thus close enough that substitution is readily possible, but distinct enough to shrink the unit cell size when enough Mg has been substituted into the structure. The second reason is that the Kimberlitic ilmenites form at much deeper depths in the mantle, which due to the increased pressure would result in a smaller c-axis unit cell parameter than non-Kimberlitic ilmenites that form from lower pressures at shallower depths. What can be noted in Figure 4-2 however, is that even though there is an increased magnesium concentration in the Non-Kimberlitic Dana 333 sample it still plots above the 14.02 (±0.01) Å line, yet does have lower c-axis values than the other non-Kimberlitic ilmenites.

With more data there could be an argument for a changing a-axis parameter, as it does seem on average that values are higher for non-Kimberlitic samples. This may change that 14.02 (±0.01) Å line to a slope instead, taking into account how the a-axis might also change as a function of elemental substation and pressure. Yamanaka and others (2005) established the
compressive nature of the c-axis in ilmenite, which allows it to span the observed 0.4 Å, while the more rigid a-axis parameter fluctuates by only 0.13 Å. The range of c-axis values allows it to be a more readily noticeable parameter. As the a-axis does not discriminate between formation environments as clearly as the c-axis, for the time being it is the less reliable of the parameters.

One thing to note is the position of the Mn-ilmenites found in the Bobbejaan and Premier kimberlites which lie in the non-kimberlitic field, making them appear non-kimberlitic. These ilmenites were derived from a kimberlite locality, however, upon initial μXRD analyses they were situated above the 14.02 Å c-axis line. It was later revealed through EPMA that these samples (or rims on the majority of the samples in the Premier localities), were low-Mg, high-Mn ilmenites. These compositions were similar to those seen by Kaminsky and Belousova (2008), where they compared Mn-ilmenites with rare ilmenite inclusions in diamonds. As the Bobbejaan locality’s Mn-ilmenite samples were distinctly separated grains from the heavy mineral separates, it is unclear if they are related to the picroilmenite grains. In the case of the Premier samples however, the Mn components are sourced as rims, or even following cracks within the sample, relating more to later events. However, whether these events were late stage
Mn-rich formation in the mantle just prior to the Mg-rich stage, or whether the Mn component was acquired during or after the kimberlitic event is unclear. As they could not be accurately classified as kimberlitic or non-kimberlitic, they have simply been deemed Mn-ilmenites for non-biased classification.

For the kimberlitic samples, there were also four diamond-poor localities that could be compared with the diamond-rich localities. When compared as a whole there is no distinct separation between the two types of diamond populations. Both types fall below the 14.02 (±0.01) Å c-axis line (kimberlitic), however, below this line they are scattered and mixed within one another. It can be noted that the diamond-rich samples span a-axis unit cell parameter values of 5.013 to 5.12 Å, with the c-axis ranging from 13.73 to 14.023 Å, while the diamond-poor samples span an a-axis range of 5.061 to 5.096 Å and c-axis of 13.86 to 14.018 Å. It is more applicable to say that for the time being, no distinction between ilmenites from diamond-rich kimberlites and diamond-poor kimberlites, can be obtained from unit cell parameters alone.

5.3 μXRD and EPMA Comparison

Some localities then could be separated out based on composition, such is that of the Attawapiskat, Premier, and Sheiba when comparing V$_2$O$_3$ (Figure 4-21, Figure 4-22, and Figure 4-24). The Eurelia locality could be separated from the rest with FeO, MgO, NiO, and TiO$_2$ (Figure 4-23). Within the diamond-poor kimberlite samples there seemed to be clear groupings of the Sheiba and Triple B samples for the FeO, MgO, and Cr$_2$O$_3$ plots (Figure 4-24). What could also be separated readily was the Mn-ilmenites seen in the Bobbejaan and Premier locality, both in the African grouping (Figure 4-22). Disregarding their increased levels of c-axis values to separate them based on c-axis unit cell parameters, they could also be separated out mineral chemically by their FeO, MgO, and MnO values. The Premier samples than showed elevated concentrations in NiO and SiO$_2$ when compared with the rest. If the Premier samples are related to later stage Mn-rich ilmenite formation, compared to the Mn-rich ilmenite samples seen in the Bobbejaan locality, the NiO and SiO$_2$ concentrations could potentially distinguish the two, however more data would be needed to confirm this.
The c-axis unit cell parameter discrimination between kimberlitic and non-kimberlitic ilmenites can also be combined with the use of mineral chemical data that can separate the two populations as well. The higher levels of magnesium in kimberlitic ilmenites, allows for a plot of c-axis unit cell vs. MgO (wt%), which can separate the graph into different zones (Figure 5-2). This enables two parameters to discriminate ilmenites from kimberlitic and non-kimberlitic rock types, increasing the reliability of the results.

![C-axis parameter vs. MgO Concentration](image)

**Figure 5-2**: c-axis unit cell parameter vs. MgO (wt%) graph. The red line represents the 14.02 (±0.01) Å c-axis line that separates kimberlitic and non-kimberlitic ilmenite samples, while the blue line represents an arbitrary placement for the same separation from the magnesium concentration based on Wyatt et al. 2003. The top left quadrant represents Mg-poor Non-Kimberlitic rock types such as Gabbros, Norites, Granites, Anorthosites, etc. The top right represents the Mg-rich Non-Kimberlitic rock types such as Hornfels and Dolomitic Calc-Silicates. The bottom right represents ilmenites found in Kimberlitic rock types.

When comparing the plots from the diamond-rich kimberlite localities with that of the diamond poor ones based on the c-axis unit cell parameters against various mineral chemical concentrations (Figure 4-21 to Figure 4-24), there is little difference between the two populations. The c-axis parameter was already established to be of little use in differentiating the two populations, however the mineral chemical data did not reveal anything of note. The oxide ranges varied little between the populations, essentially overlapping. This then implies at the
moment that mineral chemistry cannot discern a difference in the crystal structure when diamonds are present.

5.4 μXRD and Pressure Comparison

When comparing the c-axis unit cell parameter with the calculated pressure for each ilmenite grain, it is noticeable that in most cases the c-axis values vary quite readily with near constant pressure. In a few of the kimberlite localities there is a subtle decrease in the c-axis values with lower pressure values. This can be seen in the Attawapiskat, Eurelia, Hibou, Sheiba and Star localities in Figure 5-3. This is the ideal case due to the compressional effect of the c-axis in ilmenite, causing it to decrease with increased pressure. Both the Monk Hill and Nackara localities from Australia show two semi-isolated pressure groupings (Figure 5-3C). The Monk Hill groupings are quite linear with a large c-axis variation and small pressure range, while the less defined Nackara groupings have a smaller c-axis variation and larger pressure range, comparatively. In some instances, such as the Bobbejaan and Dutoitspan from Africa (Figure 5-3B), and the diamond-poor kimberlite Diamond Lake (Figure 5-3D), there is instead more of a clustered or scattered pattern.

When comparing the diamond-rich kimberlites (Figure 5-3A to 5-3C) with those of the diamond poor localities (Figure 5-3D), there is no clear differentiation between the two populations. As the c-axis did not reveal any differences, as discussed previously, and the pressure would relate to formation within the mantle, which is common to both kimberlite types, it makes sense that the plots are similar.

For the non-kimberlitic samples (Figure 5-3E) there is a trend towards increased c-axis values at higher pressures. As this should relate to smaller c-axis values, this would not attest to compression, but instead may be a result of the chemical substitution of larger cations.

The Mn-ilmenite population of the Bobbejaan locality can also be compared (Figure 5-3B); pressure of the Premier Mn-ilmenite grains could not be determined as there was no rutile found in equilibrium with them. Compared to regular picroilmenite samples, the Mn-ilmenites show a greater dispersion of pressure values, creating a scattered pattern. The pressure calculated for the Mn-ilmenite also is on average greater than that of the picroilmenites, causing them to be somewhat isolated from the rest of the samples. The Mn-ilmenites of the Bobbejaan locality share similar c-axis parameters to the non-kimberlitic samples, however the pressure for their
formation is far greater. This could be attributed to their formation within the mantle with Mn-rich/Mg-poor fluids, as apposed to being incorporated into the kimberlitic during its later explosive transportation phase as would be the case for non-kimberlitic crustal samples.

Due to the non-isometric structure of ilmenite, the pressure exerted on the crystal is non-homogenous. As there may be some elastic effect upon the ilmenite grains as they are uplifted from the mantle, the unit cell parameter may not fully record the formation pressure. However, due to the compressibility noted by the c-axis of the ilmenite structure (Yamanaka et al. 2005), the c-axis may record the initial pressure more readily. As the formation pressure is not isotopic, due the heterogeneity of the mantle and potential shear zones, it is unclear which pressures in the mantle affect the ilmenite structure (Kennedy et al. 2002).

5.5 EPMA and Pressure Comparison

The comparison of the mineral chemical data with that of the ilmenite formation pressure (Figures 5-4 to 5-8) yields more notable patterns in the plots than seen for c-axis unit cell parameter. Most of the kimberlitic ilmenites showed a decrease in the concentration of FeO and an increase in MgO with increasing pressure. This fits the model for the increased substitution of magnesium at greater depths in the mantle. The Fe$_2$O$_3$ concentrations derived from the corrections, of Droop 1987, showed a greater scatter or horizontal trends than that of FeO in the kimberlitic samples. The Canadian localities do show a vague decrease in Fe$_2$O$_3$ with increased pressures, whereas the Diamond-Poor and Non-Kimberlitic localities show a much clearer trend of similar nature. This supports the interpretation that oxidized conditions, at more shallow depths, thus not allowing for the preservation of diamonds. For most of the kimberlitic samples the NiO and Cr$_2$O$_3$ concentrations appear to increase with greater depths, while there is a subtle decrease in the MnO values with higher pressure for the Canadian localities (Figure 5-4C). The NiO and Cr$_2$O$_3$ trends seem relatively consistent with increasing pressure for the Diamond-Poor (Figure 5-7D) and Non-Kimberlitic (Figure 5-8D) samples. As pressure increases the MnO seems to subtly increase for the Dana 3610 sample and remain constant for Dana 499 (Figure 5-8C). The increasing MnO for Dana 3610 does explain why the c-axis value was increasing with depth, however the constant MnO for locality 499 makes this anomaly still unclear.
Figure 5-3: Pressure vs. c-axis unit cell parameter plots. A) Canadian Diamond-rich Kimberlites, B) African Diamond-rich Kimberlites (with the Bobbejaan Mn-Ilm), C) Australian and Russian Diamond-rich Kimberlites, D) Diamond-poor Kimberlites, E) Non-Kimberlitic.
For the B-site substitution, in most cases there is an increase in TiO$_2$ concentrations with increasing pressure, however, this slope varies between localities. The Australian and Russian samples (Figure 5-6E) are relatively scattered in this plot, the Canadian samples (Figure 5-4E) have a very shallow slope, and the African (Figure 5-5E), Diamond-poor (Figure 4-6E), and Non-Kimberlitic (Figure 5-8E) samples show a more pronounced slope. In most cases there is a decrease in ZrO$_2$ concentrations with increasing pressures. The SiO$_2$, Nb$_2$O$_5$, and V$_2$O$_3$ concentrations are relatively undefined, giving rise to either scattered or linear horizontal trends, showing a constant pressure. For the Dana 3610 sample there does appear to be a possible increase of Nb$_2$O$_5$ with increasing pressure (Figure 5-8F). The Al$_2$O$_3$ does have in some of the localities increasing concentrations with greater depths, which diminish into plateaus at certain pressures.

The Mn-rich ilmenite from the Bobbejaan locality can also be compared with the kimberlitic samples (Figure 5-5). Due to the more scattered array of the samples, there are less definable trends noticed. The FeO and MgO values do not appear to vary with pressure (Figure 5-5A and Figure 5-5B). The Fe$_2$O$_3$ trend of decreasing concentration is quite clear, along with a trend towards increasing MnO values, with increasing pressure. The remaining mineral chemical constituents are then relatively scattered with few discernable patterns.

The most notable differences between the diamond-rich and diamond-poor Kimberlite samples is that of the individual groupings. For the diamond-rich samples the data is much more clustered, all following similar trends and overlapping. For the diamond-poor samples it seems more like isolated groups that together form a trend, but separate would reveal little to no trends (Figure 5-7). It could be possible that distinct diamond-poor groups could then be established, which could then be used as proxy for diamond quality, however, as the data ranges for both Kimberlite types are quite similar, there may not be any discernable differences. The steepness and decline of the Fe$_2$O$_3$ concentrations may also be a more notable difference between the two groups.
Figure 5-4: Ilmenite samples from Diamond-rich Canadian kimberlites Attawapiskat (ATT), Hibou (HR), and Star with either magnetic (STM) or non-magnetic (STN). A) pressure vs. FeO, B) pressure vs. MgO, C) pressure vs. MnO (with a zoomed in portion of the graph), D) pressure vs. NiO, E) pressure vs. TiO$_2$, F) pressure vs. Nb$_2$O$_5$, G) pressure vs. ZrO$_2$, H) pressure vs. V$_2$O$_3$. 
Figure 5-5: Ilmenite samples from Diamond-rich African kimberlites Bobbejaan (BB), Dutoitspan (DS), Monastery (MO), and Premier (PR). Bobbejaan has Mn-rich ilmenite samples as well (BB Mn-Ilm). A) pressure vs. FeO, B) pressure vs. MgO, C) pressure vs. MnO (with a zoomed in portion of the graph), D) pressure vs. NiO, E) pressure vs. TiO\(_2\), F) pressure vs. Nb_2O_5, G) pressure vs. ZrO_2, H) pressure vs. V_2O_3.
Figure 5-6: Ilmenite samples from Diamond-rich Australian and Russian localities. Eurelia (ER), Monk Hill (MH2), Nackara (NA), and Udachnaya (UD). A) pressure vs. FeO, B) pressure vs. MgO, C) pressure vs. MnO (with a zoomed in portion of the graph), D) pressure vs. NiO, E) pressure vs. TiO$_2$, F) pressure vs. Nb$_2$O$_5$, G) pressure vs. ZrO$_2$, H) pressure vs. V$_2$O$_3$. 
Figure 5-7: Ilmenite samples from Sub-economic to Diamond-poor kimberlite localities B30, Diamond Lake (DL), Sheiba (SH), Triple B (TB). A) pressure vs. FeO, B) pressure vs. MgO, C) pressure vs. MnO (with a zoomed in portion of the graph), D) pressure vs. NiO, E) pressure vs. TiO$_2$, F) pressure vs. Nb$_2$O$_5$, G) pressure vs. ZrO$_2$, H) pressure vs. V$_2$O$_3$. 
Figure 5-8: Ilmenite samples from Non-Kimberlitic localities Dana 333, Dana 499, Dana 3610, and Dana K48. A) pressure vs. FeO, B) pressure vs. MgO (with a zoomed in portion of the graph), C) pressure vs. MnO, D) pressure vs. NiO, E) pressure vs. TiO$_2$, F) pressure vs. Nb$_2$O$_5$, G) pressure vs. ZrO$_2$, H) pressure vs. V$_2$O$_3$. 

499 ▲ 3610
5.6 Three Dimensional Plots

Unlike the previous comparisons which separated graphs based on locality type, these graphs utilized all the localities at once, separating them into four groups: Diamond-Rich Kimberlites (DR Kim), Diamond-Poor Kimberlites (DP Kim), Non-Kimberlitic (Non-Kim), and Mn-Ilmenites (Mn-Ilm). In all the cases, either the c-axis unit cell parameter value or the pressure value was denoted by color.

In Figure 5-9A the comparison is made of the ilmenite samples TiO$_2$, MgO, and FeO weight percent, with the c-axis unit cell parameter being denoted by color. As expected, the Non-Kimberlitic ilmenites, and the Mn-rich ilmenites, have much higher FeO concentrations than the kimberlitic samples. With all populations, an increase in MgO comes with a decrease in FeO, relating to the A-site substitution. Smaller c-axis unit cell parameters are seen at higher MgO and lower FeO concentrations for the kimberlitic ilmenites, which is because the c-axis decreases in size with increasing levels of smaller radii cations. For the kimberlitic populations, there is also a decrease in c-axis values with higher concentrations of TiO$_2$. As for the non-kimberlitic samples, there is a trend for decreasing TiO$_2$ and FeO concentrations, with increasing MgO. There is no clear distinction from this graph between the diamond rich and diamond poor kimberlite populations from one another, nor the non-kimberlitic and Mn-ilmenites from another.

The non-kimberlitic Dana 333 sample is situated on the cusp of the kimberlitic samples, at higher MgO and TiO$_2$, but lower FeO than the other non-kimberlitic samples (outlined in Figure 4-9A). It was noted before that this sample was situated between the two separating trends on the TiO$_2$ vs. MgO plot developed by Wyatt and others (2003). If one were using the TiO$_2$ and MgO values to determine if this sample was kimberlitic or not, there is certainly a discrepancy using composition alone. However, as the rock type for Dana 333 is unknown, research is needed in order to confirm that this came from a non-kimberlitic rock. The composition of this ilmenite suggests that of a picroilmenite, which even though is commonly found in kimberlitic rocks, is not solely found there. As mentioned previously, picroilmenite can be associated with contact metamorphic or metasomatic rocks such as hornfels and dolomitic calc-silicates, respectively.

The Dana 333 sample is a very large granular specimen, which if compared to kimberlitic samples, would be associated with a rather large sized megacryst, which is not uncommon, but rare to see. The sample is associated with pervasive and large grained magnetite exsolution, whereas in kimberlitic rocks exsolution is normally incredibly fine grained and very rare to find.
When looking at the mineral chemical data, the manganese concentrations are higher than average for kimberlitic samples, and the nickel, niobium, and vanadium concentrations are lower, however this could be associated with regional differences instead of rock type. Looking at the location, it originated from Northern Colorado, near Lake City. Literature on Colorado does show that there are two main kimberlite groups in the state, however, both are on the far north (almost state boundary) while the Dana 333 sample was obtained from the far south side (Coopersmith et al. 2003). Contact metamorphic and metasomatic rocks were also noted as prevalent rock types in the Lake City (Irving and Bancroft, 1911). With this information it can be postulated that Dana Sample 333 most likely came from a crustal metamorphic rock type, which would be non-kimberlitic in nature. This means that even though the composition could portray a kimberlitic rock, the unit-cell parameter still reveals it to be of non-kimberlitic origin.

Figure 5-9B then shows the c-axis values denoted by color, comparing FeO and MgO concentrations with that of pressure. For the kimberlitic populations as the c-axis unit cell parameter increases, so does pressure and MgO concentration while the FeO concentration decreases. This trend matches the hypothesis that pressure will cause compression to the ilmenite structure, thus decreasing the c-axis value. Interestingly enough, the Mn-rich ilmenites from Bobbejaan have pressures matching or higher than the Mg-rich kimberlitic samples. As mentioned previously, the Mn ionic radii is larger than the Mg and Fe radii, which could mean that the Mn-ilmenite structure is influence more by mineral chemistry than by pressure.

From three-dimensional compositional graphs showing the pressure variation denoted by color, one can clearly see how the composition changes with depth. For Figure 5-10A there is a clear increase in MgO and TiO$_2$ and decrease in FeO with increasing pressure for the kimberlitic samples. The kimberlitic samples appear to form a gradational trend; however, the Mn-ilmenites have higher pressures, yet fall at similar compositions to the non-kimberlitic ilmenites. This is not the case with Figure 5-10B, where instead the graph consists of TiO$_2$ vs. NiO vs. Cr$_2$O$_3$, which shows a continuous trend being displayed between the non-kimberlitic and kimberlitic ilmenites. In this graph the non-kimberlitic samples show almost no Cr$_2$O$_3$ nor NiO concentrations and display relatively low TiO$_2$ values. As pressure increases then, this goes into elevated concentrations of all three weight percent oxides. This curve then reaches an apex, where some of the higher-pressure values are still seen with increasing NiO and Cr$_2$O$_3$, however the TiO$_2$ concentrations are lowered. Here it is noted that the Mn-ilmenites do not lie amongst...
the non-kimberlitic samples, a feature unique to this graph compared to the others. This may suggest that in order to discriminate between the Mn-ilmenites and non-kimberlitic ilmenites, the use of minor oxide concentrations is preferred. However, in both graphs of Figure 5-10, there is still no discrimination between the ilmenites from diamond-rich and diamond-poor kimberlites.

**Figure 5-9:** Three-dimensional plots with the c-axis unit cell parameter being denoted by color for the Diamond-Rich kimberlites (DR Kim), Diamond-Poor Kimberlites (DP Kim), Non-Kimberlitic (Non-Kim), and Mn-rich Ilmenites (Mn-Ilm). A) Plotting TiO$_2$, MgO, and FeO concentrations. Displays c-axis values at lower FeO and higher MgO. Note the non-kimberlitic Dana Sample 333 labeled. B) Plotting pressure, MgO, and FeO. Clear trend of decreasing c-axis unit cell values with increasing pressure and MgO and decreasing FeO for the kimberlitic samples.
**Figure 5-10:** Three-dimensional plots with the pressure being denoted by color for the Diamond-Rich kimberlites (DR Kim), Diamond-Poor Kimberlites (DP Kim), Non-Kimberlitic (Non-Kim), and Mn-rich Ilmenites (Mn-Ilm). A) Plotting TiO$_2$, MgO, and FeO concentrations. Clear gradational trend for the kimberlitic samples, with increasing pressure as MgO and TiO$_2$ increase and FeO decreases. B) Plotting TiO$_2$, NiO, and Cr$_2$O$_3$. Note the Mn-Ilmenite sample being separated from the non-kimberlitic samples.
5.7 Cluster Analysis

The differentiation between kimberlitic and non-kimberlitic ilmenites could be established through the use of c-axis unit cell-parameters, enhanced with the mineral chemical data and potential pressure of formation. However, in all the cases it was unclear if there were distinctions between kimberlites with diamond enrichment versus those that were sub-economic to diamond-poor. PolySNAP 3 was utilized as a cluster analysis tool in order to determine if there were any differences between the two kimberlite populations, as well as with the non-kimberlitic ilmenites that may have been previously missed. As c-axis unit cell parameter, mineral chemistry, and pressure could all be input into the program, a variety of different combinations could be examined. The results could then either be compared as dendrogram (branching) displays, or as three-dimensional plots. For the three-dimensional aspect of the diagrams, the metric multidimensional scaling (MMDS) plot was preferred due to its greater display for interpretation. It allowed for the groupings to be more clearly spaced in a spatial representation.

The first comparison included the c-axis unit cell parameter, mineral chemical data, and pressure calculations of both kimberlitic and non-kimberlitic samples. From this the data could be analysed by any combination of the three parameters (seen in Table 5-1). Once the program analysed the data, a series of “cut-lines” were used to compare the similarities of various clusters that formed. These cut-lines roughly equated to a percent similarity, and thus at a specific cut-line anything that is clustered together has that much similarity to the rest of the samples in the cluster. The cut-line would then be increase in value until the clustered populations began having no systematic grouping (i.e. when an ilmenite locality was spread across many clustered groups).

After the comparison of all the possible combinations of starting vectors was completed, two things were made apparent. The first was that in almost all the cases, the non-kimberlitic ilmenites (and Mn-rich ilmenites) could be separated out early on. The second was that with increasing cut-lines, the kimberlitic populations would separate into distinct groupings. The cut-lines and groupings from these analyses can be seen in Table 5-1. Using all three vectors (c-axis unit cell parameter, mineral chemical data, and pressure) gave the best results for the separations and comparisons of the ilmenite populations (Figure 5-11). In most cases there seems to be three clusters that separate out. The first grouping is that of the majority of the Monk Hill (MH2), Monastery (MO), Udachnaya (UD), B30, and Diamond Lake (DL) kimberlites. This grouping
also shares some similarities with the Dana 499 non-kimberlitic sample, and thus in some of the analyses were grouped together. The second group is that of the Bobbejaan (BB), Dutoitspan (DS), Star (STM and STN), and Triple B (TB) kimberlite. The third group is only that of the Eurelia (ER) locality. In some cases, there is a separation of the higher-pressure Monk Hill samples, which either form their own group or are joined within the Eurelia cluster.

Removal of the non-kimberlitic and Mn-rich ilmenite samples for the next cluster analyses, allowed for only the kimberlitic samples to be compared. This would then ideally find differences between the ilmenites from the diamond-rich kimberlites to those from the diamond-poor. The above procedure showed certain localities grouped together, and the idea was that with the removal of non-kimberlitic samples from the clustering, that new groups should hopefully form. However, like the previous analyses, the kimberlitic populations separated out into similar groups, with the diamond-poor kimberlite samples falling in each. Figure 5-12 shows the groupings of the kimberlite populations using all three starting vectors. There is clearly a divide amongst the kimberlitic ilmenites, in which certain kimberlites are more closely related to others. Another interesting note is the separation of certain ilmenite grains from the Monk Hill population, either forming their own group of with the Eurelia samples. These particular grains are from those associated with high-pressure values (seen in Figure 5-6). Therefore, there is enough data that may support that these Monk Hill ilmenites are from a different source in the mantle, or possibly from another kimberlitic event. With the diamond-poor kimberlite samples being separated into different clusters with the diamond-rich samples, a discrimination between the two populations was not found even with cluster analysis.
<table>
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<tr>
<th>Parameters used in the Cluster Analysis</th>
<th>Non-Kim Separation Cut-line</th>
<th>Mn-IIm Separation Cut-Line</th>
<th>Kimberlite Grouping Max Cut-Line</th>
<th>1st Group</th>
<th>2nd Group</th>
<th>3rd Group (Eurelia Only)</th>
<th>4th Group (High pressure MH2)</th>
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<td>C-axis Unit Cell Parameter</td>
<td>0.73</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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<td>Mineral chemistry</td>
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<td>0.83</td>
<td>0.83</td>
<td>MH2, MO, UD, B30, DL</td>
<td>BB, DS, STM, STN, TB</td>
<td>ER</td>
<td>MH2</td>
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<tr>
<td>Pressure</td>
<td>0.58*</td>
<td>N/A</td>
<td>0.82</td>
<td>UD, B30, DL 499</td>
<td>ER, TB, STM, STN</td>
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<td>N/A</td>
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<td>C-axis and Mineral chemistry</td>
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<tr>
<td>C-axis and Pressure</td>
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<td>Mineral chemistry and Pressure</td>
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<td>0.79</td>
<td>0.73</td>
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<td>All three</td>
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<td>0.64</td>
<td>0.87</td>
<td>MH2, UD, B30, DL</td>
<td>BB, DS, STM, STN, TB</td>
<td>ER</td>
<td>MH2, MO, UD, and DL</td>
</tr>
</tbody>
</table>

*Only the Dana Sample 3610 is separated
Figure 5-11: PolySNAP cluster analysis of ilmenite grains with kimberlitic and non-kimberlitic samples, along with Mn-rich ilmenites. A) Dendrogram and Cell display showing the branching comparison of the samples, along with the cut-line labeled in red. B) 3D MMD plot of the analysis. Highlighted are Kimberlitic, Non-Kimberlitic, and Mn-rich ilmenite populations.
Figure 5-12: PolySNAP cluster analysis of ilmenite grains with diamond-rich and diamond-poor kimberlites. A) Dendrogram and Cell display showing the branching comparison of the samples, along with the cut-line labeled in red. B) 3D MMDS plot of the analysis.
Chapter 6: Conclusions and Future Work

6.1 Conclusions

Ilmenite is an important mineral in exploration geology, due to its relationship with kimberlites which have the potential to host diamonds. Due to the resistance of ilmenite from physical and chemical weathering and erosional processes, they make good primary targets for exploration companions, especially those in glaciated terrains, where other minerals may be destroyed. The date, mineral chemistry has been the primary tool for determining which ilmenites are associated with kimberlites, mainly due to their increased magnesium concentration. If the formation temperature and pressure of mantle derived picroilmenites can be distinguished from those of other igneous and metamorphic samples, then this should affect not only the chemistry but also the crystal structure. From this research the unit cell parameters of the samples alone can differentiate between the kimberlitic and non-kimberlitic populations. This is primarily seen with the $14.02 \pm 0.01$ Å line for the c-axis values, with kimberlitic ilmenites have values below this. The cause of this size difference is most likely from the incorporation of smaller magnesium ion compared to iron, along with the greater depths causing compression of the structure. The marker line, the distinction between the two populations of ilmenite grains, has the potential to distinguish $\mu$XRD as a premier technique for KIMs research and exploration geology.

Regarding the Mg-rich kimberlitic sample Dana 333, this is a starting point for demonstrating the potential advantage of $\mu$XRD over mineral chemistry alone, because although its composition was similar to kimberlitic ilmenite, the c-axis still correctly recorded the sample as “non-kimberlitic” in origin. This is only a single case, and analysis of more non-kimberlitic picroilmenites is necessary to further test this conclusion. This would require obtaining several ilmenites from hornfels, dolomitic calc-silicates, and similar rock types, and having them undergo crystallographic and mineral chemical analyses to obtain a better understanding of these types of ilmenites, along with a greater reliability for this method.

The separation between kimberlitic and non-kimberlitic samples is then enhanced when incorporating mineral chemical and pressure data. Due to the enrichment of elements such as Mg and Ni, along with higher pressure values, the two populations separate quite clearly. This allows for gradients and trends to form either in individual localities, or as an entire grouping of the
samples. However, even though some of the major elements do reveal increasing or decreasing trends with changes in unit cell parameters, in most cases there is a general clustering or lack of pattern. Some trends can be enhanced by using the three-dimensional plots, with nit cell parameters or pressures denoted by the coloration. In majority though, it portrays that the major elements have the most impact upon the crystal structure, even more so than the pressure. By utilizing the cluster analysis program, the non-kimberlitic samples are in most cases grouped away from the rest of the samples early on.

Even though unit cell parameters are effective at discriminating kimberlitic and non-kimberlitic ilmenite, discriminating between ilmenite from diamond-rich and diamond-poor kimberlites is not possible using unit cell alone. The values for their a- and c-axis unit cell parameters are similar and clustered together. The difference between the two populations, if there is a difference, may be the result of subtle changes in minor elements, which do not affect the crystal structure compared to some of the major elements such as Fe or Mg. Even when with mineral chemistry and pressure are incorporated into the comparisons, there is no major separation. Instead, what can be noted with the cluster analysis results, utilizing c-axis unit cell, mineral chemical, and pressure values, is that a division into discrete clusters amongst the ilmenites from diamond-rich kimberlites can be seen. As the ilmenites from diamond-poor kimberlites are divided themselves amongst the groups, cluster analysis does not reveal any change in the ilmenite’s structure when diamonds are present in the mantle sample brought up by kimberlite ascension. It also appears that regarding the samples used in this research, the V$_2$O$_3$ and MnO concentrations, along with the Zr/Nb ratio, do not seem to give clear trends in relation to diamond potential, which is in disagreement with previous studies.

When comparing the results of this research with the previous two studies by Harwood (2009) and Maunder (2016), it is more evident that these results are more like those with the same instrumentational parameters (e.g. X-ray source, beam size, voltage, amperes, etc.). There is a slight concern regarding the Mn-rich rims and alteration associated with the Premier ilmenites, which could give rise to the problem of reproducibility with that locality between this and the previous research done.

For this research, ilmenite’s c-axis unit cell parameter has the potential to be a powerful discriminator for kimberlite exploration geology. Although it is unable to discriminate the
diamond potential, its c-axis unit cell parameter has been demonstrated to be an effective kimberlitic indicator with strong potential for application in diamond exploration.

6.2 Future Work

This research focused on using X-ray diffraction to obtain reliable unit cell parameter values in order to establish a base line for an exploration technique. This involved the samples being polished to ensure optimal X-ray coverage along with the removal of any alteration rims which may affect the results. For this procedure considerable time was required to mount and polish the grains. One way to improve upon this time factor would be to test the refinement of loose or in-situ ilmenite grains. Preliminary μXRD was performed on loose grains for phase identification purposes. These data did show promising X-ray peak numbers and intensities, but they were not calibrated for unit cell determination. In future, unpolished grains should work in a similar fashion as polished grains for unit cell determination, however testing would be needed. The optimal test for this would be to run a certain number of ilmenite grains unpolished, refine their data, and then run the sample samples after mounting and polishing.

The μXRD technique would be more useful for mineral exploration if it were faster. Another factor to be tested would be to reduce the run time of the μXRD sampling parameters, specifically the number of frames and collection time. Two frames were used to obtain a maximum number of peaks and an attempt to obtain higher resolution peaks. A single frame should allow for reduced run time. Reducing the experiment to run between 36 to 87° (51° maximum range at a detector distance of 12 cm) would still allow for the majority of peaks to be detected. It was found that approximately 80% of the detected peaks were found within that range (Figure 6-1 illustrates this range). The run time for this project was 75 minutes per sample for two frames, which with testing, could be reduced. For unit-cell refinement the peak position is important, which means that the resolution for the data must still be maintained. To test this, a series of samples should undergo μXRD a different 2 theta ranges, omega scan parameters, and run times starting at the maximum 75 minutes per sample and working its way down in 15-minute intervals. If the refinement can still be achieved on shorter run times or a single frame, this would be a more optional situation for application to industry.
Even though the c-axis’ 14.02 ± 0.1 Å division between the kimberlitic and non-kimberlitic ilmenite samples was promising, there was still a less obvious increase in the a-axis unit cell parameters for the non-kimberlitic samples. With more sampling from non-kimberlitic ilmenites, this could establish better statistics for the c-axis above 14.02 Å as well as determining if the a-axis should be considered when delineating the boundary between kimberlitic and non-kimberlitic ilmenites. The horizontal line at 14.02 Å using just the c-axis would become a gentle slope if one considered the a-axis; this may incorporate the outliers form both rock types. By collecting more data to delineate the boundary and/or by reanalysing the outliers for any errors, the incorporation of the a-axis may be validated (seen in Figure 6-2). Most of the kimberlitic samples lie between 5.057 to 5.096 Å, while the non-kimberlitic samples lie between 5.075 to 5.103 Å. Because of considerable overlap between these values, unlike the c-axis, the a-axis could not be fully utilized alone; however, if more analyses are undertaken, then a better understanding of the difference between the two ilmenite populations can be established.

Due to the xenocrystic nature of ilmenite grains within the kimberlite rocks, finding samples that are in equilibrium with other useful thermometer or barometer minerals is challenging. This is one of the main reasons why the formation conditions of the ilmenite samples are either unknown or encompasses a large range of values. If a closer approximation of the pressure conditions of formation was established from its crystal structure and mineral chemistry, this may enhance its representation as an indicator mineral. This may require a subset of lithified samples such as mantle xenoliths, with mantle minerals still together that could be
used as a thermometer or barometer. Another option is using the exsolution of magnetite or ulvöspinel in the ilmenites, however, for that to work, the exsolution would need to have occurred during the early formation processes. Due to the rarity and microscopic size of the exsolution, the instrumentation would need a smaller beam diameter to be able to collect the data without any contamination from the ilmenite host.

As for the ilmenite samples with enriched manganese concentrations, predominantly those associated with kimberlites or the mines they were collected from, their origin is still in question. Many localities from around the world have noted Mn-rich ilmenite rims around the picroilmenites, however, it is unclear how to attribute this associated. As the unit cell parameters of Mn-ilmenites are more closely associated with that of the non-kimberlitic samples, further testing would be needed to differentiate the two populations. If Mn-ilmenites are associated with mantle processes, which appears to be the case for the Bobbejaan kimberlite, then it will be problematic to separate them from non-kimberlitic ilmenites using crystallography alone. Some researchers argue that the manganese concentrations may be related to the diamond potential, and thus if this is the case then a greater suite of Mn-ilmenite localities should be analysed.
References


Mitchell Galarneau

Qualifications

- Dedicated graduate student with an academic background in kimberlitic, mineral chemical, petrographic, economical, and tectonic studies. Experience with numerous analytical devices during my thesis projects.

Education

University of Western Ontario (2016 to present)
- Currently working on a Masters in Earth Sciences under Dr. Roberta Flemming, with competition in September 2018
- Working on refining ilmenite as an indicator mineral for diamond exploration
- Trained in X-ray Diffraction analyses
- Grade average of 87%

International Diamond School (January-February 2018)
- Attend this course in Bressonne, Italy
- Modern research and ideas from top diamond and kimberlite collaborators

Diamond Exploration Short Course (April 2017)
- Course run by Dr. Herb Helmstaedt at the Queen’s University in Kingston, Ontario
- Hands-on course on kimberlites, diamonds, and indicator minerals

University of Alberta (2011 to 2015)
- Bachelors in Honors Geology
- Hands-on experience in Field School sessions in 2013, and 2014
- Knowledge in the use of FTIR analysis
- Current GPA: 3.24

Modern Volcanic Rocks Conference (February 2013)
- Attended the Hot Topics in Kimberlite Petrography conference
- Modern interpretation and nomenclature of kimberlites
- Hands-on application of the new kimberlite classification

Awards

- Mineralogical Association of Canada Travel Grant (2018)
- WGRS, University of Western Ontario (2016 to present)
- NSERC Undergraduate Research Award, University of Alberta (2014)
- Jason Lang Scholarship Competition, University of Alberta (2013 and 2014)
- University of Alberta Excellence Scholarship (2011)
- Alexander Rutherford Scholarship (2008 to 2011)

Academic Accomplishments and Contributions

- Teaching Assistant, Earth Sciences 2206, University of Western Ontario, September 2016 to December 2016, and September 2017 to current date
• Teaching Assistant, Earth Sciences 1089, University of Western Ontario, January 2017 to April 2017

**Employment**

**Lab Research** (May 2016 to August 2017, May 2017 to August 2018)
• Analytical and thesis-based research under Dr. Flemming

**Teaching Assistant** (September 2016 to April 2018)
• Running and maintaining the lab portion of Earth Sciences 2206, along with mentoring and marking students in Earth Sciences 1089 and 1086

**Ancaster Gem and Mineral Show** (September 2017)
• Aiding Grenville Minerals in organizing and selling various minerals at their booth in Ancaster, Ontario

**Microscope Tutoring** (August 2017)
• Mentoring a new master’s student under Dr. Banerjee at the University of Western Ontario, in optical microscopy

**NSERC USRA** (May 2014 to August 2014)
• Undergraduate Student Research Award
• Working with Dr. Thomas Stachel in research on diamond samples via FTIR analysis, SEM imaging, and SIMs analysis
• Useful as a geological work experience as well as a basis for my undergraduate thesis topic

**Affiliations**

• APGO Student Membership (2018 to present)
• CSPG Membership (2018 to present)
• MAC Member (2017 to present)
• APEGA Member-in-Training (2015 to 2016)
• APEGA ASAP (2013 to 2015)
• AME BC Student Member (2015)

**Volunteer Experience**

*Earth Sciences 2206 Minerals* (August 2017)
• Selecting over one hundred new samples to be placed in the Earth Sciences 2206 course at the University of Western Ontario

*London Gem and Mineral Show* (November 2016)
• Aiding the University of Western Ontario Earth Science booth
• Giving knowledge of the importance and fun of minerals

*Science Fundamentals* (2013-2014)
• Demonstrating the fun of science to elementary students, through interactive demonstrations
• Improved on the Rocks and Minerals demonstration first hand

*University of Alberta Orientation* (August to September of 2012)
• High School Orientation Leader
• Creating a positive, educational and personal experience for new University of Alberta undergraduates