

REDOX CONDITIONS IN THE CRATONIC LITHOSPHERE AND IMPLICATIONS FOR METASOMATISM

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Declaration

The thesis contains the results of research done in the Research School of Earth Sciences, The Australian National University, between March 2010 and April 2014. I certify that this thesis contains no material which has been accepted or submitted for any other higher degree or graduate degree in any institution and to the best of the author's knowledge and belief, the thesis contains no material previously published or written by another person, except where stated or acknowledged otherwise.

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Canberra

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Abstract

The redox state of the cratonic lithosphere and its impact on metasomatism have been examined using garnet peridotite xenoliths from two kimberlite pipes (Wesselton and Kimberley) in the Kaapvaal Craton, South Africa. Conventional petrologic techniques, along with electron probe microanalysis (EPMA) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), were used to characterise the samples and identify metasomatic events. Evidence of at least one such event was found in the Wesselton samples. Iron K-edge X-ray absorption near-edge structure (XANES) spectroscopy was used to determine the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of garnet from both suites, and then calculate the oxygen fugacity ($f\text{O}_2$). The Wesselton samples were found to show a decrease in $f\text{O}_2$ (relative to the fayalite-magnetite-quartz buffer) with increasing pressure, which was overprinted by an oxidation event in zoned garnet crystals, which were observed in one sample. The $f\text{O}_2$ of the core of the zoned crystals was consistent with equilibrium with a carbonated silicate melt, and is possible that the oxidised nature of this melt is related to formation of the metasomatised rim observed, which is more oxidised than the garnet core. XANES spectroscopy was used to produce the first fully quantitative map of the distribution of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet for one of these crystals, which confirmed the variation in $f\text{O}_2$ between the core and rim, strengthening the relationship between oxidation and metasomatism. The interface between the two compositional zones showed a very short profile and this was examined using both electron probe microanalysis and NanoSIMS. The compositional profile at this interface was modelled as a diffusive process and it was found that the zonation formed in 2 - 10 years. The diffusion coefficients (relative to Ca) of Na, Cr, Ti and Y in mantle garnet were also determined for the first time.

Evidence of two metasomatic events was observed in the Kimberley samples, one related to the formation of secondary clinopyroxene, and the other related to the formation of phlogopite. These samples came from a small region of the mantle above the diamond-graphite transition, with relatively constant fO_2 , within the range expected for the cratonic mantle at that pressure. There was no evidence of a change in redox state due to the metasomatic events.

In addition to the study of garnet peridotite xenoliths, a series of high-pressure piston cylinder experiments were performed. These experiments examined the garnet-clinopyroxene partitioning behaviour of the rare earth elements (REE) in carbonated peridotite systems, with a particular focus on the effects of temperature and garnet Ca concentration. An empirical algorithm was produced to model the changes in the garnet-clinopyroxene partition coefficients ($D_{Ga/Cpx}$) with temperature and garnet Ca content. Earlier studies of natural garnet peridotite xenoliths (Lazarov et al. 2012) indicated that equilibration temperature and garnet Cr abundance (which correlates with Ca abundance in garnet lherzolites) are primary controls on garnet-clinopyroxene trace element partitioning. The current partitioning experiments indicate that $D_{Ga/Cpx}$ decreases with increasing Ca in garnet, whilst an increase in temperature leads to an increase for the heavy REE and a decrease for the light REE. This indicates that there will be a redistribution of the REE in peridotite systems as they cool from magmatic temperatures to the temperature recorded by the xenolith, however this process may be complicated if orthopyroxene or olivine also host REE at magmatic temperatures.

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Chapter 1: Introduction

1.1 Motivation

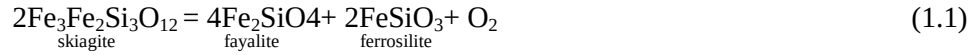
Knowledge of the evolution and processes that occur within the Earth's cratonic mantle is important in understanding a variety of geologic processes, including intraplate volcanism and formation of associated economic mineral deposits. One process of particular interest is kimberlite volcanism and its role in the crustal emplacement of economic diamond deposits. Kimberlite volcanism is also valuable as it provides a major source of mantle xenoliths, including garnet and spinel peridotites.

Kimberlite magmas entrain large volumes of mantle xenoliths and diamonds, whilst travelling through thick cratonic lithosphere at a rapid rate (Russell et al., 2012). Due to this fast rate of transport, we can make the assumption that mantle xenoliths retain a record of the conditions of the mantle immediately prior to eruption. Thus, the analysis of mantle xenoliths by various geochemical techniques can be used to calculate the temperature and pressure (and therefore depth) of origin of the samples, as well to identify the signatures of processes such as partial melting and metasomatism. Most geochemical analysis of peridotite xenoliths is undertaken using *in-situ* methods that allow for all the minerals present in a polished section or mounted rock chip to be analysed individually, as well as allowing for the identification of variation within individual grains. The two most common techniques used in these studies are electron probe microanalysis (EPMA), which allows for determination of major and minor element compositions with high spatial resolution of a few microns; and laser ablation-inductively couple plasma-mass spectrometry (LA-ICP-MS) for the determination of

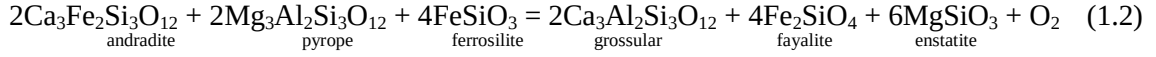
trace element abundances with spatial resolution of a few 10s of microns. A variety of experimentally derived relationships exist that can be used to calculate the equilibrium temperature and pressure of a xenolith using compositional data.

The most abundant rock in the cratonic mantle is peridotite, which consists of >60% olivine along with ortho- and/or clinopyroxene and possibly an aluminous mineral, generally spinel or garnet. The transition from spinel to garnet occurs at approximately 2 GPa. Diamond is another mineral that can be found in association with kimberlite-hosted garnet peridotite xenoliths, though it can only be found if the kimberlite has sampled a diamond source region. The presence of diamond in the cratonic mantle is strongly related to the composition, temperature and pressure, and redox state. In order for cratonic diamond to form, the source mantle region must contain carbon, at a reduced redox state (where C^0 is the preferred species rather than CO_2^{3-}), as well as being at high pressure (>4.5 GPa) and temperature (>1200 °C). Conventional techniques allow for the determination of composition, temperature and pressure with relative ease; however the determination of the redox state is more difficult.

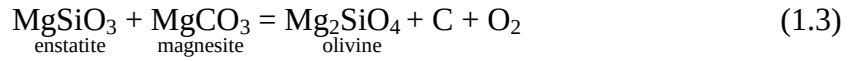
The redox state of the cratonic mantle is recorded in the speciation of multi-valent transition metals within minerals that can host the element in multiple oxidation states, such as Fe^{2+} and Fe^{3+} in garnet, spinel or pyroxenes. It is possible to determine the redox state of the mantle if $Fe^{3+}/\Sigma Fe$ (where $\Sigma Fe = Fe^{2+} + Fe^{3+}$) of garnet or spinel is known, along with compositions of other phases, using experimental calibrations of redox reactions involving Fe^{2+} and Fe^{3+} -bearing mineral components. Reactions relevant to garnet peridotite which have been calibrated are:



which is based on the skia gite component of garnet (Gudmundsson and Wood, 1995);
and:



which is based on the andradite component in garnet (Stagno et al., 2013). These experimental calibrations lead to the formulation of oxybarometers, which require precise measurement of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of garnet in peridotite. Diamond breaks down to graphite at ~ 4.5 GPa (Kennedy and Kennedy, 1976), whilst at more oxidising conditions both allotropes of C transform to carbonate (Figure 1.1). The stability of diamond or graphite relative to carbonate is limited by buffering reactions, such as the following:



which is known as the EMOD/G (enstatite-magnesite-olivine-diamond/graphite) reaction (Eggler and Baker, 1982, Luth, 1993, Stagno and Frost, 2010).

A number of studies have investigated the redox state of the mantle, as recorded by garnet peridotite xenoliths, using various different methods to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$. These include the EPMA-based flank method (Creighton et al., 2009, 2010), Mössbauer spectroscopy (McCammon et al., 2001, Woodland and Koch, 2003, Lazarov et al., 2009) and Fe K-edge X-ray Absorption Near-Edge Structure (XANES) spectroscopy (Yaxley et al., 2012). They showed a general trend for the mantle to become more reduced at depth (Figure 1.1), with some oxidation trends observed. It has also been suggested that carbonated silicate melts may have been in equilibrium with these

reduced mantle domains, and that these melts may be responsible for processes such as metasomatism (Stagno et al., 2013). Mössbauer spectroscopy is limited in spatial resolution and requires a long time period (days) for each analysis, whilst the flank method is also slow, whilst XANES spectroscopy has high spatial resolution (5-6 μm) and fast acquisition times (~ 30 minutes). Thus, it is becoming the preferred method for the in-situ determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet. Compositionally zoned garnets have previously been identified from the Wesselton kimberlite, South Africa, and were found to show an oxidation trend from core to rim, using Mössbauer spectroscopy (Griffin et al., 1999, McCammon et al., 2001). Fe K-edge XANES spectroscopy provides the opportunity to investigate any zonation in $\text{Fe}^{3+}/\Sigma\text{Fe}$ in more detail than previously possible, whilst other modern techniques such as LA-ICP-MS and NanoSIMS allows for the concurrent investigation of trace elements to very low concentrations and major elements at very high spatial resolutions, improving our understanding of metasomatic processes.

1.2 Aims

The broad aims of this PhD project were to investigate the Earth's cratonic mantle and how metasomatism and oxygen fugacity (redox state) are related to each other within it. This involved three major parts of the project, two of which were the study of different suites of kimberlite-bourne garnet peridotite xenoliths and the third of which was a high-pressure experimental study into trace element partitioning in peridotitic systems. The project was also structured around the application of five techniques to the study of garnet peridotite systems: EPMA, LA-ICP-MS, Fe K-edge XANES spectroscopy, NanoSIMS and experimental petrology.

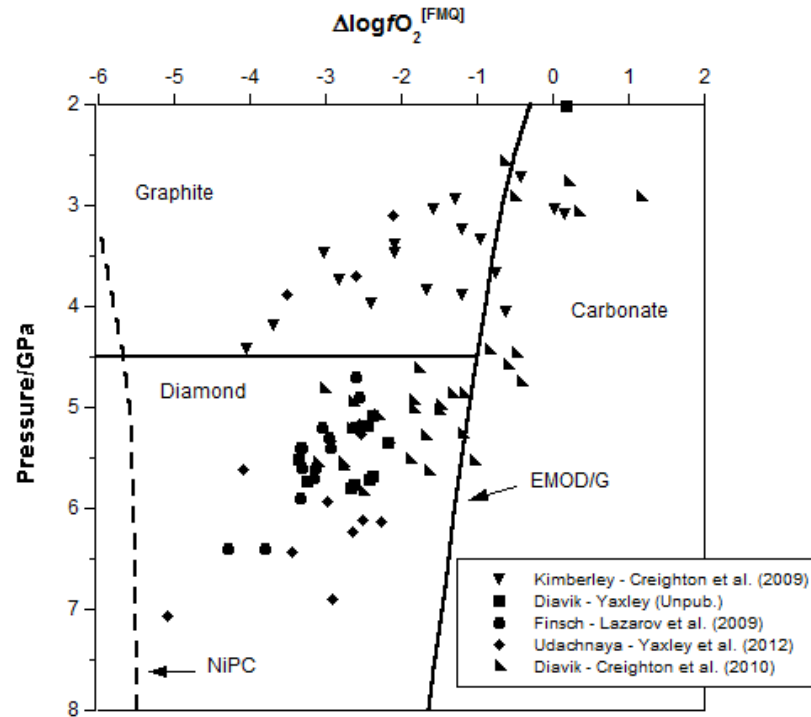


Figure 1.1: The stability fields of carbon-bearing phases (graphite, diamond and carbonate) in the Earth's upper mantle, where $\Delta \log fO_2^{[FMQ]}$ is the oxygen fugacity in log units, relative to the fayalite-magnesite-quartz buffer (Frost, 1991). A variety of xenolith suites from the literature are shown. NiPC is the Ni precipitation curve (O'Neill and Wall, 1987).

The first suite of xenoliths examined was sourced from the Wesselton mine in the Kaapvaal Craton (South Africa). These samples were studied using conventional EPMA and LA-ICP-MS techniques and XANES spectroscopy; with the aim of identifying any metasomatic events, as well as determine the oxygen fugacity of the sampled mantle and to examine any links between these. During this process a number of compositionally zoned garnet crystals were identified, similar to some that have previously studied from the same kimberlite (Griffin et al., 1999, McCammon et al., 2001). As these zoned garnets are very rare, detailed investigation of them was performed, with aim of discovering how they formed and their relationship to metasomatism and oxygen fugacity. XANES spectroscopy was used to examine the

distribution of $\text{Fe}^{3+}/\Sigma\text{Fe}$ and redox state, whilst NanoSIMS was used to investigate the compositional profile between zones in high resolution, as an attempt to understand the timescales involved in the zonation.

A second suite of xenoliths was sourced from the Kimberley pipe, also in the Kaapvaal Craton. A similar process was followed to examine these samples in order to identify any metasomatic events and investigate how they relate to the recorded oxygen fugacity. The final aim of the project was to perform a series of piston cylinder experiments to investigate the partitioning of the rare earth elements (REE), between garnet and clinopyroxene in a carbon-bearing peridotite system. This is important as there have been few experimental studies of mineral-mineral partitioning despite the fact that partitioning is commonly used to identify metasomatic processes within peridotites.

1.3 Thesis Structure

This thesis is structured as a collection of chapters which have been prepared as manuscripts for publication. Each chapter is presented as the complete version that has been or will be submitted for publication, except where noted otherwise. There are five of these chapters following this introduction, along with an overview of the thesis at the end, giving a total of seven chapters.

Chapter 2 describes the relationships between oxygen fugacity and metasomatism observed in the garnet peridotite xenoliths from the Wesselton pipe, including the results of the EPMA, LA-ICP-MS as well as Fe K-edge XANES spectroscopy, which is

used to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet, and the subsequent calculation of the oxygen fugacity. During this process a number of compositionally zoned garnet crystals were identified, similar to some that have previously studied from the same kimberlite (Griffin et al., 1999, McCammon et al., 2001). This chapter was submitted to *Lithos* in October 2013, and has been corrected following reviews received in December 2013. The submitted manuscript was co-authored by Gregory M. Yaxley, Andrew J. Berry and Vadim S. Kamenetsky.

Chapter 3 focusses on the quantitative mapping of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ in zoned garnet crystals from the Wesselton kimberlite and is based upon the article “*Quantitative mapping of the oxidative effects of mantle metasomatism*” which was published in *Geology* (Berry et al., 2013), of which I am a co-author. It has been rewritten and somewhat expanded by me for this thesis, including more information regarding the thermobarometric calculations and the equilibrium assumptions made between phases. The other authors of the published article were Andrew J. Berry, Gregory M. Yaxley, Alan B. Woodland, Martin D. de Jonge, Daryl L. Howard, David Paterson and Vadim S. Kamenetsky.

Chapter 4 describes the results obtained when NanoSIMS was used to investigate the diffusion of major and minor elements within the zoned garnet crystals identified in the Wesselton peridotite suite. This manuscript will shortly be submitted for publication and the co-authors are Michael C. Jollands, Jörg Hermann, Gregory M. Yaxley and Matt R. Kilburn.

Chapter 5 examines metasomatism and oxygen fugacity in a suite of phlogopite-bearing garnet peridotites from the Kimberley kimberlite. This manuscript will be submitted to *Contributions to Mineralogy and Petrology* in 2014 and is co-authored by Gregory M. Yaxley, Andrew J. Berry, Vadim S. Kamenetsky and David Paterson.

Chapter 6 presents the results of an experimental study into the partitioning of rare earth elements between garnet and clinopyroxene in carbonated peridotite assemblages. This chapter may be submitted for publication in the future and was co-authored by Gregory M. Yaxley.

Chapter 7 gives an overview of the thesis and its conclusions, along with possible directions to expand upon this study in the future. The Appendices that follow this chapter include the published article relating to Chapter 3 and supplementary material for the other chapters.

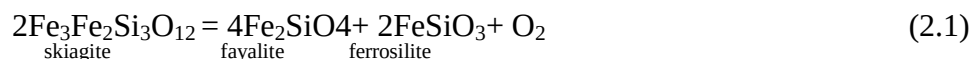
Chapter 2: Relationships between oxygen fugacity and metasomatism in the Kaapvaal subcratonic mantle, represented by garnet peridotite xenoliths in the Wesselton kimberlite, South Africa

A suite of 12 peridotite xenoliths from the Wesselton kimberlite were studied and found to sample the subcratonic lithospheric mantle from 3.6 to 4.7 GPa and 880 to 1120 °C. Major, minor and trace element compositions indicate that both metasomatised and un-metasomatised samples are present over this pressure range. $Fe^{3+}/\Sigma Fe$ in garnet from three xenoliths was determined using Fe K-edge XANES spectroscopy, enabling a redox profile as a function of depth through the subcratonic mantle to be determined. $\Delta \log fO_2^{[FMQ]}$ varied from 0 to -3.3 over the sampled pressure interval, with the un-metasomatised samples falling within the global trend of decreasing $\Delta \log fO_2^{[FMQ]}$ with increasing depth. Superimposed on this was an oxidation trend, at higher pressures (≥ 4.5 GPa), with $\Delta \log fO_2$ increasing by 1.5 to 2 units in the metasomatically enriched samples, indicating a clear link between metasomatism and oxidation at higher pressures. One potential source of this oxidation is a carbonated silicate melt, which will increase in carbonate content as $\Delta \log fO_2$ increases. Mantle minerals affected by this melt have the potential to shift from the diamond to carbonate stability fields, threatening the stability of diamond.

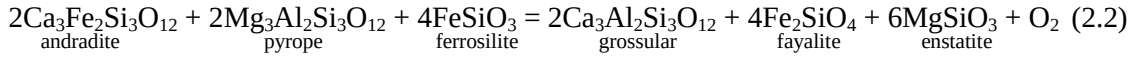
2.1 Introduction

The speciation of fluids within the Earth's mantle is controlled by oxygen fugacity (fO_2). This is a variable that is important but less frequently determined compared to pressure (P) and temperature (T), primarily due to difficulties in its quantification, because it controls speciation within the C-H-O-S system and it influences processes such as partial melting, metasomatism and diamond stability (Creighton et al., 2009, 2010, Luth et al., 1990, Taylor and Green, 1987, 1988, Yaxley et al., 2012). The entrainment and transport of garnet peridotite xenoliths from the upper mantle to the surface by deeply sourced and rapidly ascending kimberlite magmas allows the fO_2 of the deep cratonic lithosphere to be determined. The mineral chemistry of these xenoliths retains a record of the P, T and fO_2 of the subcratonic mantle from where they originated. Oxygen fugacity is recorded in the valence state of multivalent elements within mantle minerals. Iron, the most abundant multivalent element in these assemblages, exists as both Fe^{2+} and Fe^{3+} in garnet, spinel and pyroxenes. The fO_2 in these peridotitic assemblages is buffered by internal silicate-silicate and silicate-oxide equilibria between the phases that can accommodate both Fe^{2+} and Fe^{3+} .

Two different experimentally calibrated equilibrium reactions within the garnet peridotite facies can be used to calculate mantle fO_2 based upon the value of $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ (or $Fe^{3+}/\Sigma Fe$) in garnet. The first reaction uses the skiaegite ($Fe_3Fe_2Si_3O_{12}$) component in garnet (Gudmundsson and Wood, 1995).



The second, more recently calibrated reaction uses the Fe^{3+} -bearing andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) component, which has well characterised thermodynamic data (Stagno et al., 2013).



C-H-O fluids under reduced $f\text{O}_2$ conditions have been shown to exist predominantly as CH_4 and H_2O using experimental methods and thermodynamic models (Belonoshko and Saxena, 1992, Taylor and Green, 1987, Woodland and Koch, 2003), with the proportions of each species dependent upon fluid composition. Thermodynamic calculations by Woodland and Koch (2003) show that a C-H-O fluid at $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ [$f\text{O}_2$ in log units relative to the fayalite-magnetite-quartz (FMQ) redox buffer (Frost, 1991)] of about - 5.5 may contain 75% CH_4 and 25% H_2O at 6 GPa and 1400 °C. If this reduced fluid were to encounter a region in the mantle that was more oxidised it could evolve to the carbon-saturation surface (Taylor and Green, 1987), crystallising graphite or diamond depending upon the temperature and pressure, and leaving behind a residual fluid enriched in H_2O . The model of Woodland and Koch (2003) predicts that an increase in $f\text{O}_2$ of three orders of magnitude will result in the oxidation of methane to diamond and the subsequent removal of nearly all carbon from the fluid. The resulting increase in water activity in the residual fluid may provide the flux necessary to melt mantle peridotite, a putative process known as “redox melting” (Foley, 2011, Taylor and Green, 1987, 1988).

Oxygen fugacity is also an important control on diamond/graphite *versus* carbonate stability in the mantle, which is controlled by a number of compositionally dependent

buffering reactions within peridotites. In harzburgitic assemblages it is controlled by the reaction between enstatite, magnesite, olivine and diamond/graphite (EMOD/G):



In lherzolitic assemblages it is defined by the reaction between enstatite, magnesite, fayalite, diopside and diamond (EMFDD) (Eggler and Baker, 1982, Luth, 1993, Stagno and Frost, 2010):



A number of studies have reported a strong link between metasomatism and oxidation in the cratonic lithospheric mantle. Because of the molar volume changes (2.1) and (2.2), it is expected that $f\text{O}_2$ will decrease with increasing pressure (Frost and McCammon, 2008). However, increases in $\Delta\log f\text{O}_2^{\text{[FMQ]}}$ of 1-2 log units above the value expected due to this general decrease in $\Delta\log f\text{O}_2^{\text{[FMQ]}}$ with depth have been attributed to metasomatic enrichment in the deeper parts of the cratonic lithosphere (Creighton et al., 2009, McCammon et al., 2001, Yaxley et al., 2012).

Major and trace element compositions were determined for all phases in twelve xenoliths from the Wesselton kimberlite, South Africa. In addition, $\text{Fe}^{3+}/\Sigma\text{Fe}$ of garnet was determined for four garnet-bearing xenoliths. The $f\text{O}_2$ of three of these garnet-bearing samples was determined using the approach of Stagno et al. (2013) as they contained the phases required for the calculation: garnet, orthopyroxene, and olivine. We used a recently developed Fe K-edge X-ray Absorption Near-Edge Structure (XANES) spectroscopy technique (Berry et al., 2010) to measure $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnets from the suite. This technique has advantages over both Mössbauer spectroscopy (Woodland and Koch, 2003) and the flank method (Höfer and Brey, 2007), as it can

achieve both high spatial resolution and short data acquisition times (Berry et al., 2008, 2010), whilst maintaining similar precision in $\text{Fe}^{3+}/\Sigma\text{Fe}$ (± 0.01). Combining Fe K-edge XANES observations with conventional thermobarometry and trace element measurements (obtained using LA-ICP-MS) of garnet and clinopyroxene, we establish (1) redox conditions in a depth interval of ≈ 100 to ≈ 150 km in the Kaapvaal Craton, showing decreasing $\Delta\log f\text{O}_2^{\text{[FMQ]}}$ with increasing depth, and (2) evidence of a pre-eruption metasomatic event that oxidised the outer rim of some garnet crystals, and placed them very close to the carbon/carbonate stability limit.

2.2 Geological setting and nature of the samples

The Wesselton kimberlite is one of the five major diamond-bearing pipes near the township of Kimberley, South Africa that were mined extensively from the late 1800s onwards. It was emplaced into the Archean Kaapvaal Craton 86 – 90 Ma ago (Allsopp and Barrett, 1975, Kramers and Smith, 1983, Smith et al., 1985). The studied xenoliths were collected from material excavated during mining. Other garnet peridotite xenoliths from Wesselton were studied by Griffin et al. (1999) and McCammon et al. (2001), who found significant zonation in major and trace element concentration for some garnet crystals.

A general trend of decreasing $\Delta\log f\text{O}_2^{\text{[FMQ]}}$ with increasing depth has been observed for the Kaapvaal Craton using garnet $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined by Mössbauer spectroscopy (Lazarov et al., 2009, Woodland and Koch, 2003). The related milli-Mössbauer technique was used to measure an oxidation event from rim to core in zoned harzburgitic garnets (Griffin et al., 1999, McCammon et al., 2001). Creighton et al. (2009) used the flank method (Höfer and Brey, 2007) to determine $f\text{O}_2$ beneath the

Kaapvaal craton and found that the mantle became more reduced with depth with $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ of -2 at 110 km and $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ of -4 at 210 km.

2.3 Analytical Methods

The major and minor element compositions of phases in the xenoliths were determined by wavelength dispersive (WDS) electronprobe microanalysis (EPMA) using the Cameca SX100 at the Research School of Earth Sciences (RSES), Australian National University. A focused beam with a 1 μm diameter was used with an accelerating voltage of 15 kV and a beam current of 20 nA. A range of well characterised natural mineral standards were used for elemental calibration.

Trace element compositions of garnet and clinopyroxene were determined by LA-ICP-MS using the Agilent 7500 instrument at RSES. The analytical procedures were similar to those reported in Eggins et al. (1998). Analyses were performed with a spot size of 105 μm and an acquisition time of 90 s, 30 s which (laser off) was used to establish a baseline. Thirty-seven elements were analysed and NIST 612 glass was used as the calibration standard, with BCR-2G as a secondary standard. EPMA determined abundances of CaO in garnet and clinopyroxene were used as internal reference elements, with the data reduced using the method of Eggins et al. (1998).

Fe K-edge XANES spectroscopy was used to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet. $\text{Fe}^{3+}/\Sigma\text{Fe}$ was determined from an empirical calibration curve relating the intensity of a post-edge feature in the XANES spectra to $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined by Mössbauer spectroscopy for a series of peridotitic garnet standards (Berry et al., 2010). Previous studies used the ratio

of two post-edge features (7138.4 and 7161.7 eV) (Berry et al., 2010, Yaxley et al., 2012), however, Berry et al. (2013) suggested that the intensity of the feature at 7138.4 eV will give a more precise calibration curve over the limited range of $\text{Fe}^{3+}/\Sigma\text{Fe}$ values observed in garnet from peridotite xenoliths, as opposed to the entire range of possible $\text{Fe}^{3+}/\Sigma\text{Fe}$ values.

The standard garnets were from garnet peridotite xenoliths from several kimberlite localities in the Kaapvaal Craton (Kimberley, South Africa and Letseng-la-Terae, Lesotho) (Woodland and Koch, 2003) and the Slave Craton (Diavik, Canada) (Yaxley – Unpublished Data). $\text{Fe}^{3+}/\Sigma\text{Fe}$ values were determined by Mössbauer spectroscopy, using the method described by Woodland and Koch (2003), and range from 0.022 to 0.122.

The Fe K-edge XANES spectra were recorded over two sessions at the X-ray Fluorescence Microscopy (XFM) beamline of the Australian Synchrotron (Paterson et al., 2011). The excitation energy was selected using a Si(111) double crystal monochromator and calibrated by defining the first derivative peak of an Fe foil spectrum to be 7112.0 eV. The spectral resolution at the Fe K-edge was 1.9 eV. The beam was focused by Kirkpatrick-Baez mirrors, to give an analysis spot of $\sim 3 \times 3 \mu\text{m}$ for this study. Samples were mounted at 45° to both the incident beam and a single element silicon drift detector (Vortex EM, SII Nanotechnology, Northridge, CA) with digital signal processing (DXP Saturn, XIA LLC, Hayward, CA). All spectra were recorded in fluorescence mode and the incident flux and sample to detector distance were adjusted to ensure that the total incoming count rate was within the linear range of

the detector. All spectra were recorded with an approximately constant detector dead time of 12-14%. To decrease the relative contributions of elements lighter than Fe to the total detected fluorescence, a layer of Al foil was placed between the sample and the detector. Spectra were recorded from 7070 to 7295 eV, using step sizes of 0.5 eV for the baseline (7070 – 7108 eV), 0.3 eV for the edge and 2.5 eV above 7170 eV, and a count time of 3 s per point.

2.4 Mineral Chemistry

A suite of twelve polished sections (300 μm thickness) from 12 individual peridotite xenoliths, sourced from the Wesselton Pipe, Kimberley, South Africa, was studied using a variety of petrographic and analytical techniques. A summary of the sample labels, phases observed, textural type and rock name is shown in Table 2.1, which also indicates the samples analysed by XANES spectroscopy. Based on the xenolith textural type classification of Harte (1977), all samples are classed as porphyroclastic, except KBD9 which has a mosaic-porphyroclastic type. Heavy fracturing and alteration are present throughout the suite. Five of the xenoliths are classified as lherzolites based upon the mineral assemblage observed, whilst six are classified as harzburgites. KBD4 is classified as a wehrlite as no orthopyroxene was observed. Four samples contain garnet, with three of these (KBD7, 12, 18) being garnet lherzolites and the other (KBD15) is a garnet harzburgite. Spinel lamellae, formed as a result of exsolution within orthopyroxene, were found in KBD10, and were likely formed as a result of decompression (Kushiro and Yoder, 1966). Average major, minor and trace element mineral compositions for all samples are presented in Table 2.2. The spinel in KBD10 was too small for LA-ICP-MS analysis and their trace element concentrations are not shown.

Table 2.1: Summary of the samples studied, including the phases observed, rock type and textural type. The samples which were analysed by XANES to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet, and subsequent determination of $f\text{O}_2$ are also indicated. Ga = garnet, ol = olivine, opx = orthopyroxene, cpx = clinopyroxene, sp = spinel.

	Phases Observed	Rock Type	Textural Type	Ga $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined	$f\text{O}_2$ determined
KBD4	Ol, Cpx	Wehrlite	Porphyroclastic		
KBD5	Ol, Opx	Harzburgite	Porphyroclastic		
KBD6	Ol, Opx, Cpx	Lherzolite	Porphyroclastic		
KBD7	Ol, Opx, Ga	Garnet Lherzolite	Porphyroclastic	Y	Y
KBD8	Ol, Opx	Harzburgite	Porphyroclastic		
KBD9	Ol, Opx	Harzburgite	Mosaic Porphyroclastic		
KBD10	Ol, Opx, Sp ¹	Harzburgite	Porphyroclastic		
KBD12	Opx, Cpx, Ol, Ga	Garnet Lherzolite	Porphyroclastic	Y	Y
KBD15	Ol, Cpx, Ga	Garnet Harzburgite ²	Porphyroclastic	Y	
KBD17	Ol, Opx, Cpx	Lherzolite	Porphyroclastic		
KBD18	Ol, Opx, Ga	Garnet Lherzolite	Porphyroclastic	Y	Y
KBD19	Ol, Opx	Harzburgite	Porphyroclastic		

1 - Present only as lamellae within orthopyroxene

2 - Based upon on Cr/Ca systematics (see Figure 2.4)

Garnets throughout the suite are heavily altered and kelyphitic breakdown rims can be seen on nearly all crystals. Three garnet crystals from sample KBD12 showed significant compositional zoning in major and minor elements. These zoned crystals showed higher Ti, Cr, Fe, Ca and Na in the rim relative to the core; whilst Al and Mg were lower in the rim relative to the core. These crystals have been described in Berry et al. (2013) and representative elemental maps are shown in Figure 2.1. Similarly zoned garnet crystals from Wesselton xenoliths were reported by Griffin et al. (1999) and McCammon et al. (2001).

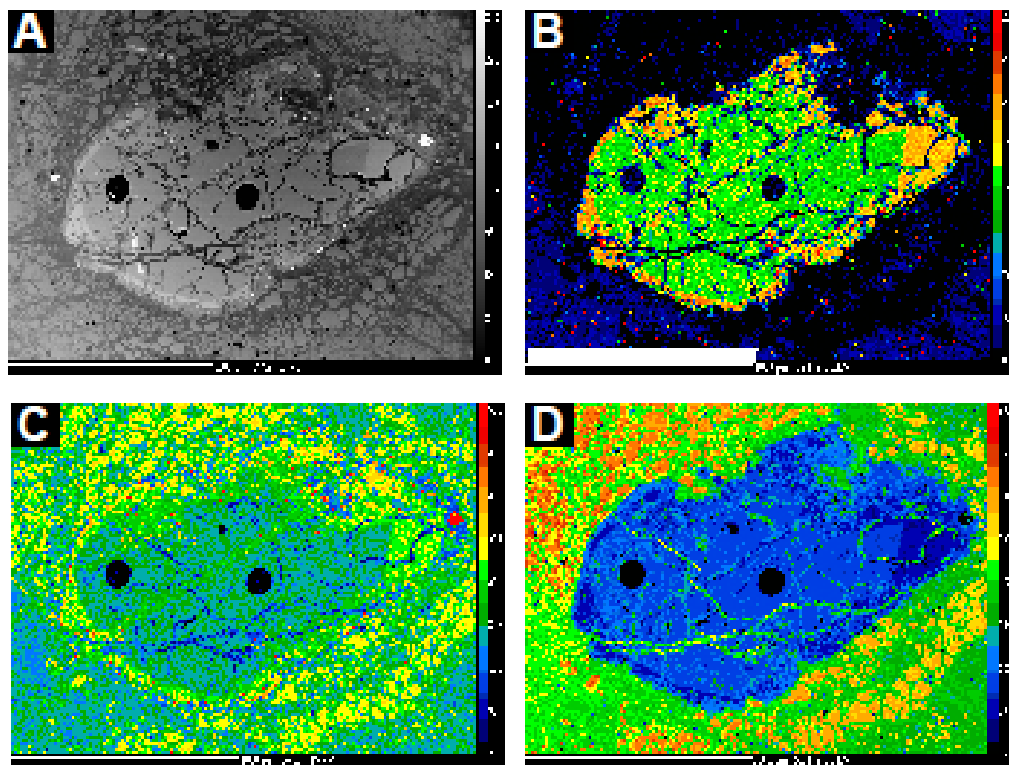


Figure 2.1: Elemental maps, obtained using an electron microprobe, showing (A) back-scattered electron image, (B) Ca distribution, (C) Fe, (D) Mg in sample KBD12 ga4 from the Wesselton kimberlite, South Africa. Images show a zoned garnet, surrounded in places by kelyphite (green in C, blue in D) in a matrix of olivine and orthopyroxene. Circular features in garnet are pits produced by LA-ICP-MS. The scale bar in B is 1.0 mm.

Using the garnet classification system of Grütter et al. (2004), which is predominantly based upon Ca-Cr systematics, all garnets can be classified as lherzolitic (G9) except for KBD 18 and the rims of the zoned garnet from KBD12, which are classified as harzburgitic (G10). The mineralogy of KBD7 and KBD 15, along with their relatively high Mg#, lead to their classification in the lherzolitic (G9) field rather than the overlapping low-Mg pyroxenitic (G5) field (Figure 2.2). All lherzolitic samples were found to contain modal clinopyroxene. In the unzoned garnet, Mg# ranges from 81.7 to 87.6, with CaO varying from 4.1 to 5.3 wt.% and Cr₂O₃ varying from 3.5 to 4.8 wt.%.

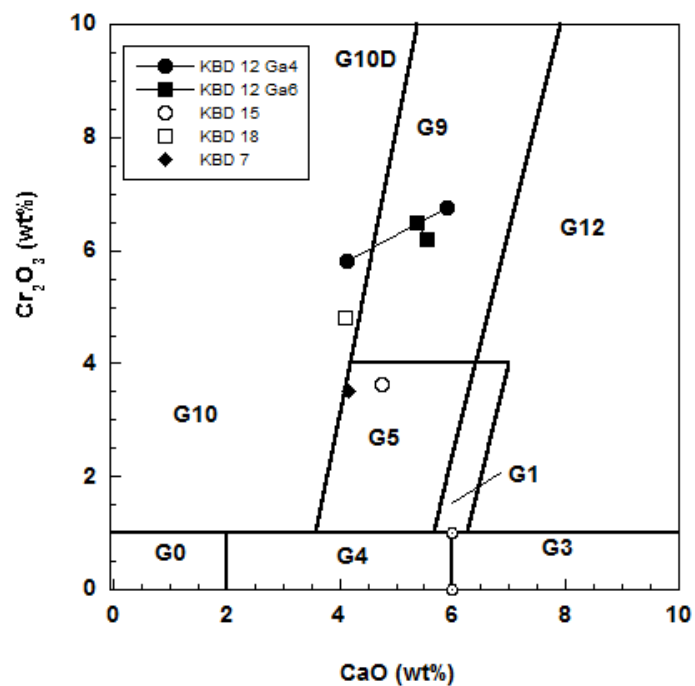


Figure 2.2: Classification of garnets from the suite, based upon Ca-Cr systematics (Grütter et al., 2004).

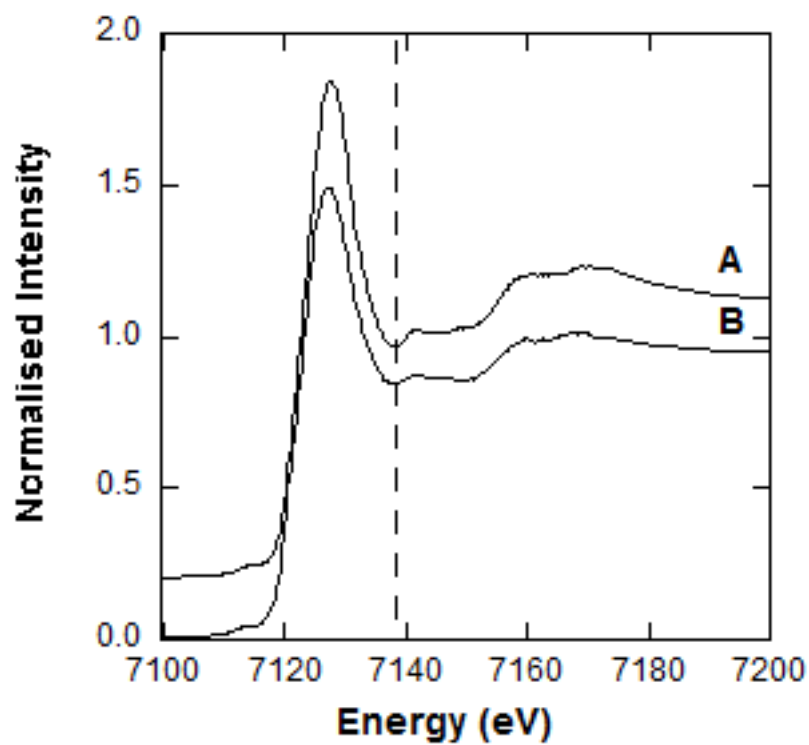


Figure 2.3: Fe K-edge XANES spectra of two garnets from Wesselton, with A (KBD18-Ga2) being less oxidised than B (KBD12-Ga1), as well as being shifted upwards by 0.2 intensity units for clarity.

Fe K-edge XANES spectroscopy was used to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ for multiple garnet crystals from four samples. Spectra were compared after subtraction of a constant baseline and normalization to the average energy above 7235 eV. Figure 2.3 shows representative spectra, whilst the calibration curve, which is the linear best fit to the data, obtained from the standards, as shown in Figure 2.4. The variation within samples KBD7 and KBD15 did not exceed the precision of the technique (± 0.01) and thus they are reported as single values whilst KBD18 showed significant variation across the four garnet crystals analysed (0.03 – 0.10), and as such they are reported individually, despite being located within 20 mm of each other on the slide. Three of these crystals were analysed multiple times and these measurements agreed with each other. Core and rim measurements were recorded on three zoned garnet crystals from KBD12 and these pairs are reported individually. Across all samples $\text{Fe}^{3+}/\Sigma\text{Fe}$ varies from 0.024 to 0.208, which falls within the range typical of Cr-pyrope garnets (Creighton et al., 2009, Creighton et al., 2010, Woodland and Koch, 2003, Yaxley et al., 2012). The distribution of $\text{Fe}^{3+}/\Sigma\text{Fe}$ for a segment of one crystal from KBD12 (Ga4) was quantitatively mapped using Fe K-edge XANES spectroscopy and showed a sharp increase from core to rim, similar to the variation in other major elements (Berry et al., 2013).

The standard deviation of the difference between the $\text{Fe}^{3+}/\Sigma\text{Fe}$ values of the standards as determined by Mössbauer spectroscopy and that inferred from the line of best fit is ± 0.009 . This suggests that the uncertainty in values obtained using the calibration curve is not larger than that of the Mössbauer spectroscopy data and thus we estimate the precision of our results to be ± 0.01 . $\text{Fe}^{3+}/\Sigma\text{Fe}$ values obtained for garnet bearing Wesselton samples using this calibration curve are given in Table 2.2.

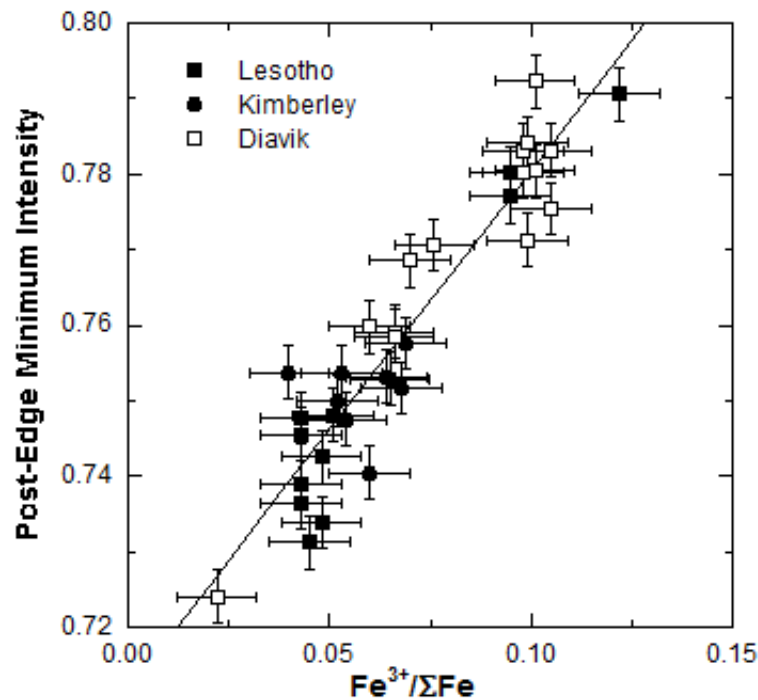


Figure 2.4: Correlation between the minimum Fe K-edge XANES intensity of the post-edge and $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined by Mössbauer spectroscopy of mantle garnets from various locations. Line is linear best fit to data.

For the examination of trace element behaviour, four values are reported for garnet from sample KBD12, an unzoned garnet (ga3), the core of one zoned garnet (ga6) the core and rim of a different zoned garnet (ga4). The other three garnet bearing samples (KBD7, 15 and 18) showed no substantial variation across individual crystals and are thus reported as average values, leading to a total of seven garnets being compared. Garnet Ti contents, as measured by LA-ICP-MS, exhibit a bimodal distribution, with three samples having greater than 1400 ppm Ti (KBD12-ga4rim, KBD2-ga3 and KBD15) whilst the remainder have less than 100 ppm. A similar pattern is seen for Y with the high Ti garnets having greater than 200 ppm Y, whilst the low Ti garnets have less than 3 ppm Y (Figure 2.5a). Zr showed a similar, though less well-defined trend, with the highest Ti garnets having the high Zr values (Figure 2.5b).

Table 2.2: Representative major, minor and trace element data for garnet (ga) and clinopyroxene (cpx) from 6 samples from the suite. Cations were calculated on the basis of 6 oxygen atoms for cpx and 12 for garnet. Garnet $\text{Fe}^{3+}/\Sigma\text{Fe}$ was measured by Fe K-edge XANES. For cpx, all Fe was assumed to be Fe^{2+} . $[\text{Mg}\# = 100*\text{Mg}/(\text{Mg} + \text{Fe}^{2+})]$. “nd” = not determined. “bdl” = below detection limit.

	KBD 4		KBD 5		KBD 6		KBD 7			KBD 8		KBD 9		
	ol	cpx	ol	opx	ol	opx	cpx	ol	ga	opx	ol	opx	ol	opx
SiO ₂	41.19	54.87	41.49	57.04	41.51	58.24	1.19	41.68	42.97	58.58	41.24	55.94	41.17	57.71
TiO ₂	0.03	0.41	0.00	0.00	0.01	0.01	54.73	0.00	0.01	0.00	0.00	0.00	0.01	0.04
Al ₂ O ₃	0.03	2.51	0.02	2.36	0.04	0.45	0.17	0.00	21.00	0.79	0.08	2.72	0.02	0.57
Cr ₂ O ₃	0.04	3.05	0.00	0.79	0.01	0.58	15.28	0.02	3.51	0.27	0.01	0.79	0.02	0.36
Fe ₂ O ₃		nd							0.38					
FeO	7.57	2.38	6.52	4.18	6.68	4.52	0.01	6.32	5.27	3.83	6.75	4.28	7.05	4.01
MnO	0.09	0.07	0.08	0.09	0.09	0.11	21.36	0.07	0.24	0.07	0.08	0.09	0.07	0.09
MgO	49.27	15.42	49.85	34.84	50.98	36.37	1.97	51.36	22.51	36.00	49.79	33.63	49.71	34.94
NiO	0.36	0.05	0.39	0.09	0.43	0.08	2.33	0.36	0.00	0.07	0.36	0.08	0.39	0.10
CaO	0.05	17.01	0.03	0.56	0.00	0.23	0.03	0.03	4.16	0.49	0.05	0.87	0.07	0.36
Na ₂ O	0.13	2.87	0.13	0.10	0.04	0.08	0.00	0.00	0.01	0.13	0.06	0.07	0.05	0.16
K ₂ O	0.04	0.04	0.05	0.03	0.00	0.37	0.06	0.00	0.00	0.00	0.04	0.02	0.03	0.04
P ₂ O ₅	0.01	0.00	0.00	0.00	0.00	0.00	0.11	0.00	0.02	0.00	0.00	0.00	0.04	0.00
Total	98.78	98.67	98.55	100.08	99.79	101.04	97.23	99.86	100.06	100.24	98.47	98.50	98.61	98.36
Mg#	92.06	92.03	93.16	93.69	93.15	93.49	92.13	93.54	88.38	94.37	92.93	93.33	92.62	93.94
Sc	3.36	26.3	5.43	12.7	5.14	3.01		1.11	79.9	1.81	1.64	11.1	4.03	6.08
V	10.9	315	4.60	62.1	4.46	33.2		6.40	171	41.1	1.46	45.8	6.84	30.0
Co	270	18.1	526	56.8	437	51.0		148	40.3	56.8	139	51.0	295	125
Ni	5301	318	11227	715	8972	661		3088	50.0	892	2854	653	6856	2488
⁶⁹ Ga	0.60	8.36	0.70	0.93	0.48	2.48		0.20	3.5	1.29	0.20	0.93	0.54	1.06
⁷¹ Ga	0.24	8.52	0.02	0.71	0.02	0.28		0.06	3.53	1.13	0.01	0.77	0.17	0.65
Ge	0.98	1.17	1.87	1.08	1.59	1.16		0.49	1.47	1.13	0.54	1.04	0.95	1.54
Rb	bdl	0.44	bdl	bdl	0.71	19.22		0.07	bdl	0.37	bdl	bdl	0.15	0.79
Ba	0.56	4.14	bdl	bdl	1.90	46.01		0.15	0.05	0.33	1.80	bdl	1.55	3.57
Th	0.01	0.10	bdl	bdl	0.03	0.39		bdl	0.04	bdl	bdl	bdl	0.04	0.10
U	bdl	0.03	bdl	bdl	0.03	0.29		bdl	0.05	bdl	bdl	bdl	bdl	0.02
Nb	0.20	0.85	0.01	0.04	1.63	9.52		0.13	0.40	0.13	0.06	0.03	2.44	1.45
Ta	0.01	0.04	bdl	bdl	0.02	0.22		0.01	0.04	0.02	bdl	bdl	0.11	0.08
La	0.07	2.18	bdl	bdl	0.02	0.56		bdl	0.17	0.03	bdl	bdl	0.26	0.49
Ce	0.12	7.69	bdl	bdl	0.05	1.28		bdl	1.18	0.09	bdl	bdl	0.57	1.13
Pb	0.07	0.24	0.07	0.03	0.12	0.32		0.02	0.05	0.04	0.02	0.02	0.05	0.08
Pr	0.04	1.37	bdl	bdl	bdl	0.14		bdl	0.38	0.01	bdl	bdl	0.06	0.14
Sr	0.27	101	0.02	0.09	0.66	9.05		0.07	1.15	2.19	0.46	0.10	2.07	6.63
P	nd	43.6	nd	17.90	nd	22.86		nd	114	21.87	nd	15.35	nd	93.7
Nd	0.13	7.12	bdl	bdl	0.06	0.47		bdl	3.11	0.07	bdl	bdl	0.25	0.52
Sm	bdl	1.95	bdl	bdl	bdl	0.08		bdl	1.02	bdl	bdl	bdl	0.07	0.11
Zr	0.61	62.9	0.09	0.03	0.09	1.92		0.03	5.20	0.16	bdl	0.03	1.50	2.44
Hf	0.02	3.50	bdl	bdl	bdl	0.03		bdl	0.10	bdl	bdl	bdl	0.04	0.07
Eu	bdl	0.61	bdl	bdl	bdl	0.02		bdl	0.22	bdl	bdl	bdl	0.02	0.03
Ti	371	2438	0.18	0.33	3.42	31.41		2.40	48.0	11.31	0.07	0.91	101.67	215
Gd	bdl	1.66	bdl	bdl	bdl	0.05		bdl	0.37	bdl	bdl	bdl	0.04	0.07
Tb	bdl	0.20	bdl	bdl	bdl	0.01		bdl	0.03	bdl	bdl	bdl	bdl	0.01
Dy	bdl	1.03	bdl	bdl	bdl	0.05		bdl	0.22	bdl	bdl	bdl	bdl	0.04
Li	nd	0.98	nd	2.07	nd	1.21		nd	bdl	0.59	nd	1.30	nd	1.31
Y	0.01	3.79	bdl	bdl	0.03	0.23		bdl	2.64	0.01	bdl	bdl	0.05	0.23
Ho	bdl	0.15	bdl	bdl	bdl	0.01		bdl	0.08	bdl	bdl	bdl	bdl	0.01
Er	bdl	0.31	bdl	bdl	bdl	0.03		bdl	0.38	bdl	bdl	bdl	bdl	0.02
Tm	bdl	0.03	bdl	bdl	bdl	bdl		bdl	0.09	bdl	bdl	bdl	bdl	bdl
Yb	bdl	0.14	bdl	bdl	bdl	0.03		bdl	0.78	bdl	bdl	0.01	bdl	0.02
Lu	bdl	0.02	bdl	bdl	bdl	bdl		bdl	0.15	bdl	bdl	bdl	bdl	bdl

Table 2.2 continued

	KBD10			KBD12			KBD15			KBD17			
	ol	opx	sp	ol	opx	cpx	ga	ol	cpx	ga	ol	opx	cpx
SiO ₂	40.72	56.94	0.07	40.85	57.15	54.66	41.49	40.40	54.42	42.05	40.66	58.24	54.77
TiO ₂	0.00	0.00	1.33	0.01	0.11	0.44	0.33	0.02	0.42	0.45	0.00	0.07	0.19
Al ₂ O ₃	0.01	2.20	24.25	0.01	0.88	2.89	19.48	0.01	2.59	21.07	0.01	0.49	1.41
Cr ₂ O ₃	0.02	1.06	14.15	0.03	0.43	2.96	4.37	0.02	1.58	3.64	0.05	0.45	2.95
Fe ₂ O ₃						nd			nd	1.65			nd
FeO	6.47	4.41	0.01	7.29	5.14	2.51	8.12	8.49	2.86	5.84	8.27	5.05	2.45
MnO	0.08	0.09	0.43	0.09	0.09	0.08	0.28	0.09	0.07	0.29	0.11	0.12	0.08
MgO	52.04	34.31	43.93	51.37	34.84	16.04	20.34	50.47	17.01	20.61	50.28	35.55	16.81
NiO	0.36	0.07	13.62	0.38	0.12	0.05	0.01	0.33	0.03	0.01	0.40	0.13	0.06
CaO	0.03	0.46	0.09	0.05	0.70	17.70	5.27	0.05	18.62	4.74	0.06	0.60	18.86
Na ₂ O	0.03	0.02	0.00	0.02	0.16	2.75	0.10	0.02	1.81	0.06	0.03	0.16	1.92
K ₂ O	0.00	0.01	0.14	0.00	0.01	0.02	0.02	0.00	0.02	0.00	0.00	0.01	0.05
P ₂ O ₅	0.00	0.00	bdl	0.00	0.00	0.02	0.03	0.00	0.02	0.02	0.00	0.00	0.02
Total	99.74	99.57	98.01	100.10	99.63	100.12	99.83	99.91	99.46	100.46	99.87	100.88	99.57
Mg#	93.48	93.27	88.95	92.63	92.33	91.92	81.70	91.38	91.38	86.31	91.55	92.61	92.43
Sc	0.63	14.43			3.64	31.7	131	3.11	29.4	102	4.86	4.06	34.3
V	3.74	62.97			46.1	340	307	10.85	325	184	5.70	16.8	117
Co	67.5	50.18			68.6	22.6	39.6	245	20.8	38.3	410	76.6	25.0
Ni	164	596.20			1018	365	49.7	4239	332	43.1	7926	1143	452
⁶⁹ Ga	2793	1.09			4.64	8.79	11.8	0.48	8.64	11.5	0.46	1.83	3.36
⁷³ Ga	1.24	0.88			4.19	8.95	12.3	0.24	8.90	12.1	0.14	1.67	3.18
Ge	0.74	1.29			2.93	nd	2.41	1.15	1.37	2.02	1.61	1.68	1.36
Rb	1.61	0.33			1.01	nd	0.07	bdl	0.50	0.07	bdl	0.16	0.23
Ba	0.10	1.02			1.89	4.71	bdl	bdl	4.00	0.28	bdl	0.73	8.85
Th	0.08	1.29			0.05	0.07	0.01	bdl	0.08	0.01	bdl	0.02	0.28
U	bdl	0.20			0.02	0.04	0.05	bdl	0.07	0.02	bdl	0.01	0.10
Nb	0.11	0.23			0.49	0.76	0.97	0.28	1.02	0.30	0.22	0.17	2.11
Ta	bdl	bdl			0.04	0.07	0.06	0.01	0.05	0.01	0.02	0.01	0.09
La	0.28	0.01			0.29	2.09	0.06	0.01	2.53	0.03	bdl	0.13	2.96
Ce	bdl	5.86			0.64	8.94	0.65	0.01	9.53	0.19	bdl	0.26	11.19
Pb	bdl	0.52			0.13	0.22	0.68	0.03	0.27	0.05	0.19	0.03	0.46
Pr	bdl	0.90			0.07	1.57	0.31	0.00	1.79	0.09	bdl	0.03	2.05
Sr	0.41	2.80			4.12	110	1.06	0.05	190	0.63	0.07	2.35	215
P	nd	14.15			29.96	46.3	146	nd	60.5	128	nd	26.0	64.0
Nd	bdl	0.32			0.28	8.08	3.12	bdl	9.73	1.06	bdl	0.12	10.39
Sm	bdl	bdl			0.06	2.18	1.39	bdl	2.67	1.07	bdl	0.04	2.52
Zr	0.01	0.28			1.34	69.8	22.0	0.56	54.5	75.3	0.74	0.69	40.0
Hf	bdl	0.05			0.05	3.61	0.35	0.02	2.71	1.35	bdl	0.03	2.50
Eu	bdl	0.33			0.02	0.70	0.50	0.01	0.82	0.55	bdl	0.01	0.74
Ti	16.9	3.21			550.42	2485	2266	330	2420	2908	227	593	1006
Gd	bdl	bdl			0.04	1.79	1.56	bdl	2.18	2.36	bdl	0.03	1.90
Tb	bdl	bdl			0.01	0.23	0.22	bdl	0.25	0.52	bdl	bdl	0.22
Dy	bdl	bdl			0.03	1.12	1.48	bdl	1.24	4.49	bdl	0.03	1.04
Li	nd	1.57			1.43	1.45	0.11	nd	0.67	bdl	nd	1.28	0.78
Y	0.54	0.18			0.13	3.97	8.14	0.02	4.60	29.4	0.01	0.11	3.88
Ho	bdl	bdl			0.01	0.16	0.29	bdl	0.18	1.08	bdl	0.01	0.15
Er	bdl	bdl			0.01	0.33	0.86	bdl	0.38	3.57	bdl	0.01	0.32
Tm	bdl	0.00			0.00	0.03	0.14	bdl	0.04	0.56	bdl	bdl	0.04
Yb	bdl	0.32			0.01	0.13	0.94	bdl	0.20	3.82	bdl	bdl	0.20
Lu	bdl	0.16			0.00	0.02	0.17	bdl	0.02	0.59	bdl	bdl	0.03

Table 2.2 continued

	KBD18			KBD19	
	ol	opx	ga	ol	opx
SiO ₂	41.56	58.56	42.78	41.69	57.49
TiO ₂	0.00	0.01	0.01	0.00	0.00
Al ₂ O ₃	0.04	0.79	20.77	0.01	2.60
Cr ₂ O ₃	0.03	0.38	4.80	0.01	0.78
Fe ₂ O ₃			0.75		
FeO	6.34	3.90	5.51	7.00	4.35
MnO	0.06	0.07	0.27	0.09	0.09
MgO	50.86	36.09	22.24	51.29	35.08
NiO	0.42	0.11	0.01	0.38	0.08
CaO	0.03	0.30	4.09	0.02	0.89
Na ₂ O	0.04	0.11	0.04	0.02	0.04
K ₂ O	0.01	0.01	0.00	0.01	0.00
P ₂ O ₅	0.04	0.00	0.02	0.00	0.00
Total	99.42	100.33	101.30	100.51	101.40
Mg#	93.46	94.28	87.79	92.89	93.50
Sc	1.24	2.31	111	1.58	12.4
V	5.57	55.1	206	1.96	71.1
Co	151	64.6	46.1	148	57.7
Ni	3316	927	41.9	2963	714
⁶⁹ Ga	0.23	1.20	1.77	0.23	1.07
⁷¹ Ga	0.02	0.81	1.88	0.04	0.82
Ge	0.36	1.09	1.50	0.50	1.09
Rb	bdl	0.16	0.55	0.02	0.01
Ba	0.47	2.10	0.07	0.38	0.95
Th	bdl	0.03	0.01	bdl	bdl
U	bdl	0.01	0.16	bdl	bdl
Nb	0.91	0.51	0.59	0.02	0.08
Ta	0.03	0.04	0.01	bdl	bdl
La	bdl	0.13	0.09	0.05	0.04
Ce	0.01	0.37	2.76	0.08	0.06
Pb	0.03	0.15	0.38	0.51	0.06
Pr	bdl	0.06	1.77	0.01	0.01
Sr	0.01	1.64	1.79	0.34	0.49
P	nd	24.1	191	nd	16.90
Nd	0.01	0.28	13.4	0.06	0.02
Sm	bdl	0.04	2.06	bdl	bdl
Zr	0.44	0.87	30.3	0.01	0.06
Hf	0.01	0.02	0.56	bdl	bdl
Eu	bdl	0.01	0.43	bdl	bdl
Ti	8.09	28.7	67.4	0.29	1.13
Gd	bdl	0.03	1.04	bdl	bdl
Tb	bdl	bdl	0.11	bdl	bdl
Dy	bdl	0.01	0.52	bdl	bdl
Li	nd	0.70	0.10	nd	1.42
Y	bdl	0.04	2.22	0.02	0.01
Ho	bdl	bdl	0.08	bdl	bdl
Er	bdl	bdl	0.18	bdl	bdl
Tm	bdl	bdl	0.03	bdl	bdl
Yb	bdl	bdl	0.22	bdl	0.01
Lu	bdl	bdl	0.05	bdl	bdl

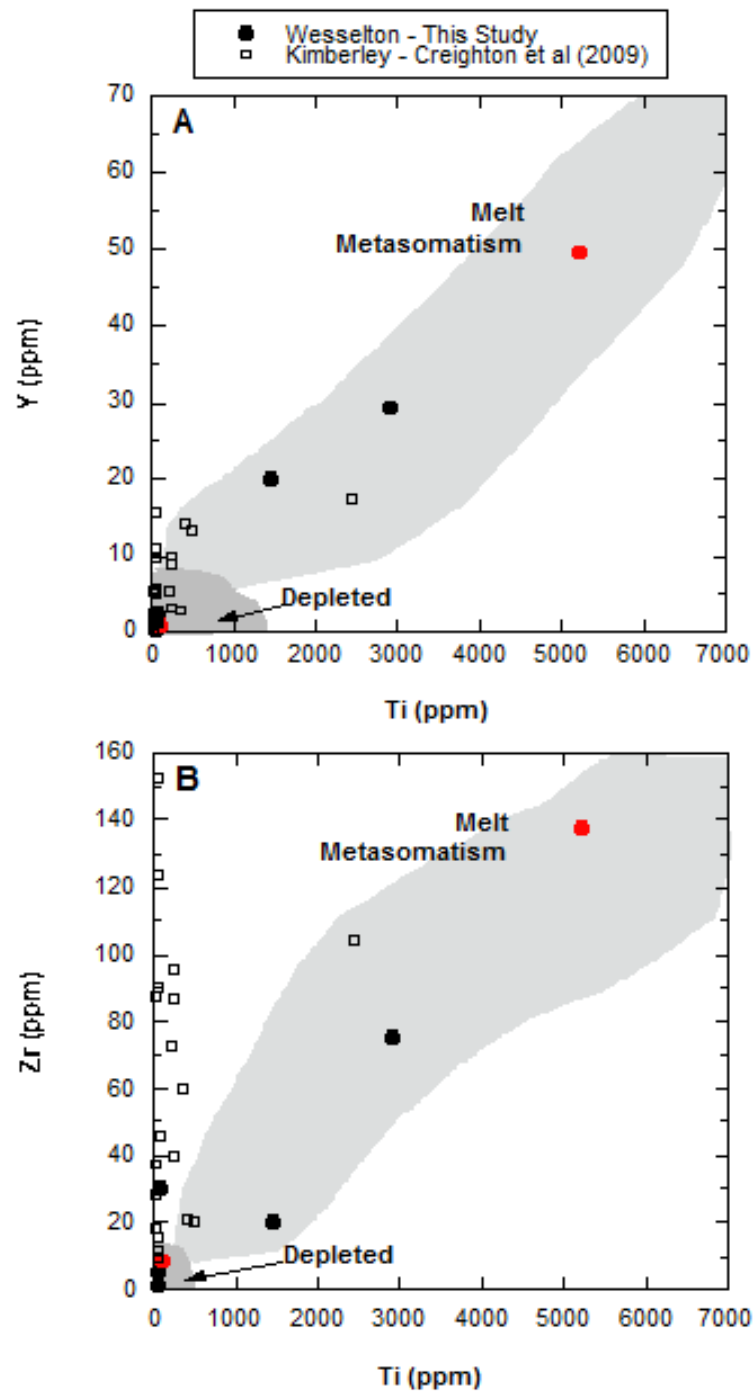


Figure 2.5: Plots of (A) Y and (B) Zr against Ti in garnets from the current study (black symbols) and the Kaapvaal samples of Creighton et al. (2009) (open squares). The zoned garnet from xenolith KBD12 is shown as red symbols with the core being depleted and the rim in the melt metasomatism field. “Depleted” and “Melt Metasomatism” fields are after Griffin and Ryan (1995).

Garnet rare earth element (REE) patterns show significant variation from “strongly sinusoidal” (KBD7) to “sinusoidal” (KBD18, KBD12 cores) to “normal” (KBD15, KBD12-ga4 rim, KBD12-ga3) (Figure 2.6). On primitive mantle normalized plots (denoted REE_N) (Palme and O'Neill, 2007) strongly sinusoidal patterns exhibit steeply positive sloping heavy REE_N (HREE_N) from Lu to a minimum between Gd and Ho. From this minimum the patterns slope negatively to a maximum at Pr, Nd or Sm and then slope down to depleted low REE (LREE_N) values (Figure 2.6a). These garnets are depleted in Ti, Y and Zr (Figure 2.5). Garnets with normal patterns have segments of HREE_N and medium REE_N (MREE_N), that are slightly positively sloped on the normalized REE_N diagram. From the MREE_N to the LREE_N the slope is more steeply positive, gradually becoming steeper towards La (Figure 2.6b). The garnets with normal REE_N patterns are also relatively enriched in Ti, Y and Zr. KBD12-ga4, which showed zonation in major elements, was also found to be zoned in trace elements, with its core having a sinusoidal REE_N pattern and the rim a normal pattern. It is thought that KBD12-ga6 would show a similar relationship, however it was not possible to analyse its rim using LA-ICP-MS as it was too thin for a reasonable sized laser ablation spot.

Olivine crystals range in Mg# from 91.3 to 93.5 [where $Mg\# = 100 \text{ Mg}/(\text{Mg} + \text{Fe}^{2+})$], in MnO content from 0.06 to 0.10 wt.% and NiO from 0.33 to 0.42 wt.%. Mg# and MnO are negatively correlated. These values are similar to those reported from other peridotite xenoliths from Wesselton by Griffin et al. (1999) and also to the typical range exhibited by on-craton peridotite xenoliths world-wide (91-94) (Pearson et al., 2003). Orthopyroxene crystals form two distinct populations based upon Al₂O₃ and Cr₂O₃ contents, with opx from four samples containing 2.2 to 2.8 wt.% Al₂O₃ and 0.20 to 0.57

wt.% Cr_2O_3 whilst opx from the other six samples contains 0.45 to 0.88 wt.% Al_2O_3 and 0.78 to 1.06 wt.% Cr_2O_3 . Across all orthopyroxenes CaO varies from 0.23 to 0.90 wt.%.

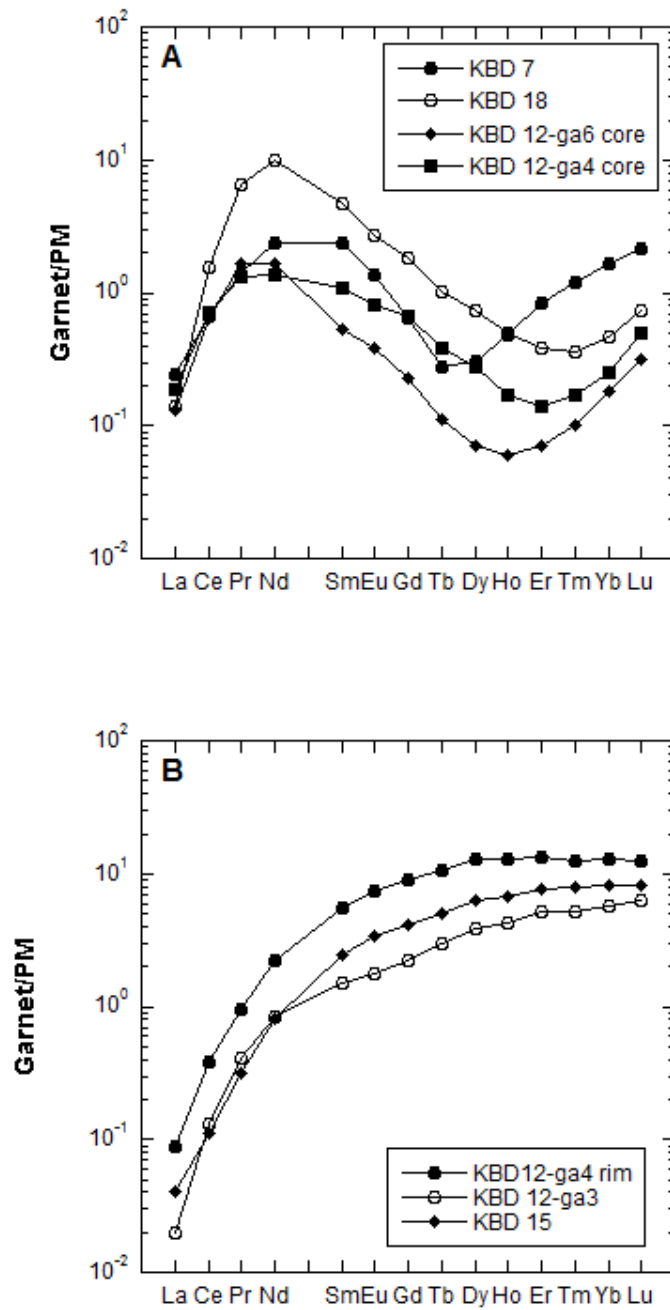


Figure 2.6: Primitive Mantle normalized (Palme and O'Neill, 2007) REE contents of garnets from the current suite. (A) Garnets with strongly sinusoidal patterns; (B) garnets with normal patterns.

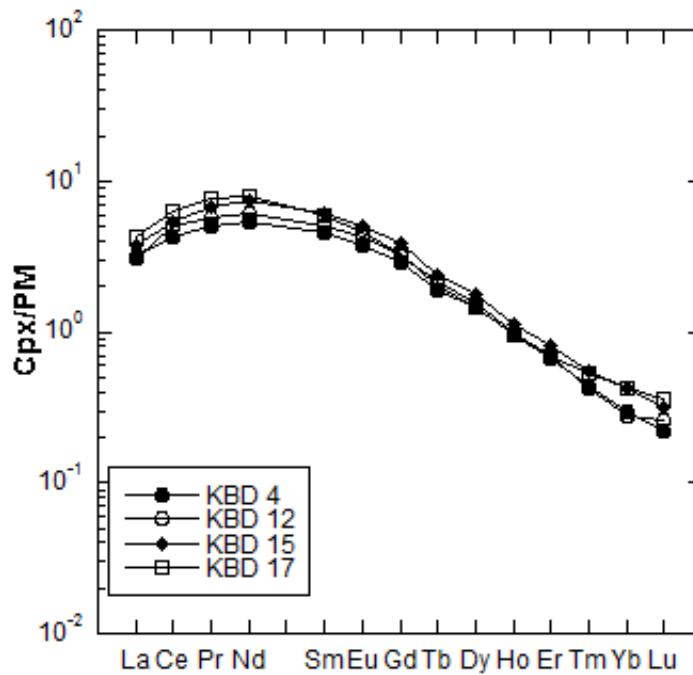


Figure 2.7: Primitive Mantle normalized (Palme and O'Neill, 2007) REE contents of clinopyroxene from the current suite.

Clinopyroxenes from all samples vary in CaO content from 17.0 to 23.4 wt.%, in Na₂O from 1.19 to 2.87 wt.% and in Cr₂O₃ from 1.58 to 3.05 wt.%. Mg# ranges from 91.4 to 92.4. Ti abundance showed a bi-modal distribution with two samples having ≤ 0.19 wt.% TiO₂ and the remainder ≥ 0.40 wt.%. Samples with Ti-enriched garnet also had Ti-enriched clinopyroxene. Clinopyroxene normalized REE patterns were all “normal” (Figure 2.7), with a peak at Nd and a steady decrease to Lu.

2.5 Discussion

2.5.1 Thermobarometry

A number of thermometers and barometers previously calibrated with data from high-pressure experiments and from natural samples were used to calculate equilibrium temperatures and pressures for the samples using the approach of Nimis and Grütter (2010). Table 2.3 shows thermobarometric results for two combinations of thermometer and barometer, including the two pyroxene thermometer, T [BKN90] and garnet-orthopyroxene barometer, P [BKN90] of Brey and Köhler (1990); and the Ca-in-opx thermometer, T [Ca-Opx] of Brey and Kohler (1990), which uses the Al-in-opx barometer, P [NG85] of Nickel and Green (1985) as its input pressure. The combination of T [Ca-Opx] and P [NG85] was selected for further use as not all samples had clinopyroxene analyses available and it produced similar values to the combination of T [BKN90] and P [BKN90]. T [Ca-Opx] varied from 887 to 1122 °C and P [NG85] from 3.58 to 4.74 GPa. Mean compositions over individual samples for olivine, orthopyroxene and clinopyroxene were used in these calculations, along with mean garnet compositions for individual crystals. Individual garnet compositions were used for samples that have had $Fe^{3+}/\Sigma Fe$ determined by Fe K-edge XANES spectroscopy, thus allowing the investigation of heterogeneities between garnet crystals in the same sample. These calculations are based on the assumption that garnet crystals are in equilibrium with the surrounding pyroxenes and olivine. Comparison of the REE_N patterns from KBD12 showed that the rim of the zoned garnets was in equilibrium with both pyroxenes, however for the purpose of the calculation it was assumed that the core was also in equilibrium, allowing for P , T and fO_2 to be determined and compared. Because orthopyroxene was not present in KBD15, the clinopyroxene thermometer and barometer of Nimis and Taylor (2000) was used and returned estimates of 4.15 GPa and 1104 °C.

Table 2.3: Results of thermobarometric and redox calculations. P [NG85] (± 0.4 GPa) and T [Ca-Opx] (± 50 °C) are the pressure and temperature of equilibrium following the method of Nimis and Grütter (2010). P [BKN90] (± 0.4 GPa) and T [BKN90] (± 50 °C) are the pressure and temperature of equilibrium based upon Brey and Köhler (1990) $\text{Fe}^{3+}/\Sigma\text{Fe}$ (± 0.01) values were determined using the Fe K-edge technique described by Berry et al. (2010) and $\Delta\log f\text{O}_2^{\text{FMQ}}$ (± 0.6) was calculated using the calibration of Stagno et al. (2013). The values shown are the mean of replicate measurements for all garnets in KBD7 and KBD15, the core or rim of garnet crystals in KBD12 and individual garnets in KBD18. * indicates that the Nimis and Taylor (2000) clinopyroxene thermometer (± 50 °C) and barometer (± 0.4 GPa) were used due to the absence of orthopyroxene.

		P [NG85] (GPa)	T [Ca-in- Opx] (°C)	P [BKN90] (GPa)	T [BKN90] (°C)	$\text{Fe}^{3+}/\Sigma\text{Fe}$	$\Delta\log f\text{O}_2^{\text{FMQ}}$
KBD7	depleted	4.09	1008			0.030	-3.33
KBD15	depleted	4.15*	1104*			0.099	
KBD12-ga1-c	depleted	4.54	1112	4.19	1150	0.095	-1.19
KBD12-ga1-r	enriched	4.51	1111	4.18	1149	0.179	-0.06
KBD12-ga4-c	depleted	4.74	1122	4.59	1158	0.057	-2.43
KBD12-ga4-r	enriched	4.61	1116	4.53	1156	0.098	-1.02
KBD12-ga6-c	depleted	4.78	1124	4.71	1160	0.069	-2.26
KBD12-ga6-r	enriched	4.65	1118	4.61	1158	0.123	-0.67
KBD18-ga1	depleted	3.58	887			0.103	-0.50
KBD18-ga2	depleted	3.58	887			0.062	-1.41
KBD18-ga3	depleted	3.59	887			0.051	-1.75
KBD18-ga6	depleted	3.52	884			0.033	-2.40

Figure 2.8 shows the distribution of the samples in P-T space. Three samples show a gradual increase in pressure and depth from KBD18 (3.6 GPa and 890 °C) through KBD7 (4.1 GPa and 1000 °C) to KBD12 (4.7 GPa and 1120 °C). These samples sit close to an estimated cratonic geotherm with heat flow of 43 mW m^{-2} (Pollack and Chapman, 1977), whilst KBD15 (4.2 GPa and 1104 °C) lies just off this geotherm. This P-T distribution is consistent with other recent garnet peridotite xenolith studies from Wesselton and other localities in the Kaapvaal craton (Creighton et al., 2009, Griffin et al., 1999, McCammon et al., 2001).

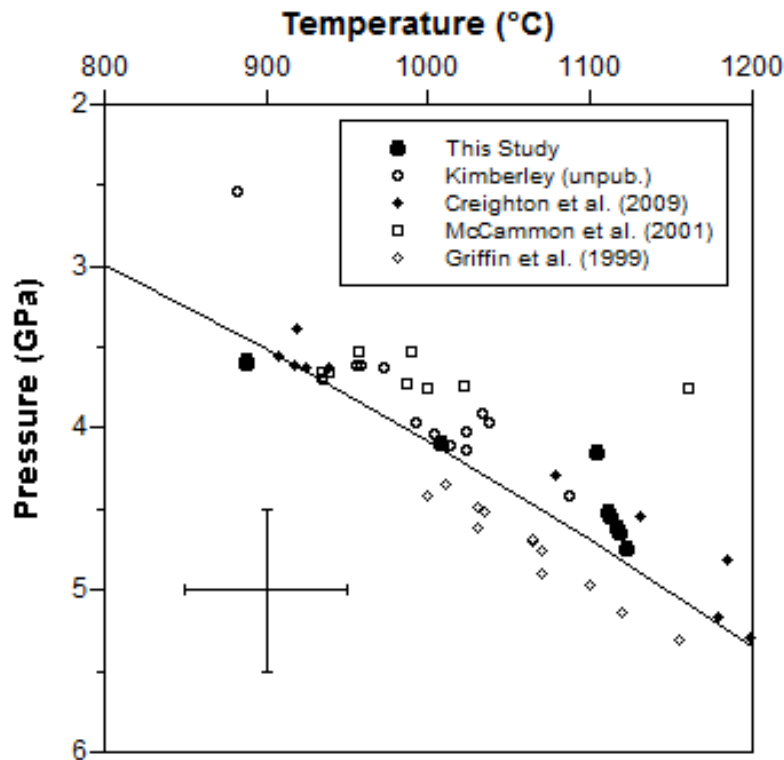


Figure 2.8: P [NG85] against T [Ca-in-Opx] (Nimis and Grütter, 2010) for the current suite as well as our own unpublished Kimberley data, the Kaapvaal data of Creighton et al. (2009) and other Wesselton data (Griffin et al., 1999, McCammon et al., 2001). The curved line is an estimated 43 mW m^{-2} geotherm (Pollack and Chapman, 1977). The standard error (1σ) in the calculated temperature and pressure is indicated on the figure.

2.5.2 Melt Metasomatism

Evidence for metasomatism in a number of the samples from this suite can be seen in the range of Ti, Y and Zr abundances in garnet and co-existing clinopyroxene and the REE_N patterns of garnet and clinopyroxene (Stachel et al., 1998, 2004). Some samples (KBD7, KBD18, KBD12-ga4 core) are clearly relatively depleted with garnet Ti < 1000 ppm, Zr < 10 ppm and Y < 5 ppm, but others (KBD12-ga1, KBD12-ga4 rim) are enriched, containing higher abundances of these three elements (Griffin and Ryan, 1995). Samples with low-Ti garnets have sinusoidal garnet REE_N whilst high-Ti garnets have normal garnet REE_N and clinopyroxene REE_N patterns.

Garnet crystals show evidence for both melt metasomatism and depletion across the entire pressure range sampled. These samples are porphyroclastic and exhibit the same melt metasomatism trends as the porphyroclastic samples from the Bultfontein kimberlite (Kimberley, South Africa) described by Creighton et al. (2009). The sharp zonation seen in garnets from KBD12 suggest that there was minimal time for re-equilibration after the metasomatic before eruption and quenching, Griffin et al. (1999) suggested a timescale of tens to hundreds of years. The absence of these rims on other samples may indicate that there was sufficient time for re-equilibration prior to eruption.

2.5.3 An oxygen fugacity profile in the Kaapvaal Craton

Oxygen fugacities for three of the four garnet-bearing samples were calculated using the experimental calibration of Stagno et al. (2013) for the fO_2 buffering reaction (2) for garnet peridotite assemblages. This calculation was performed using P [NG85], T [Ca-Opx], XANES-determined $Fe^{3+}/\Sigma Fe$, and EPMA determined garnet compositions and Fe# (where $Fe\# = Fe/(Fe + Mg + Ca)$ of olivine and orthopyroxene. The fO_2 of sample KBD 7 could not be determined as orthopyroxene was not observed. Results are expressed relative to the fO_2 of the FMQ buffer ($\Delta \log fO_2^{[FMQ]}$) at the P-T conditions of each sample, in Table 2.3. $\Delta \log fO_2^{[FMQ]}$ varies from -3.2 to -0.5. The overall uncertainty in fO_2 resulting from the error in the XANES measurements (0.01 in $Fe^{3+}/\Sigma Fe$) and in the oxybarometer's calibration, is estimated to be ± 0.6 log units (Stagno et al., 2013), however, this uncertainty becomes larger at low values of $Fe^{3+}/\Sigma Fe$, approaching ± 1 log units at $Fe^{3+}/\Sigma Fe$ of 0.02. The experimental calibration of Stagno et al. (2013) was preferred over the earlier calibration of Gudmundsson and Wood (1995) for two reasons: (1) the former has been calibrated over a pressure range of 3–7 GPa rather than a single pressure of 3 GPa, which is more appropriate for the samples in question and

(2) it is based upon thermodynamic data that is better constrained than that used in the earlier calibration, which was based on skiaquite. This equilibrium is based upon the Fe^{3+} bearing andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) component, for which recently improved thermodynamic data is available (Holland and Powell, 2011), whilst it is also less sensitive to the skiaquite ($\text{Fe}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) component, which has less well known thermodynamic data (Gudmundsson and Wood, 1995, Stagno et al., 2013).

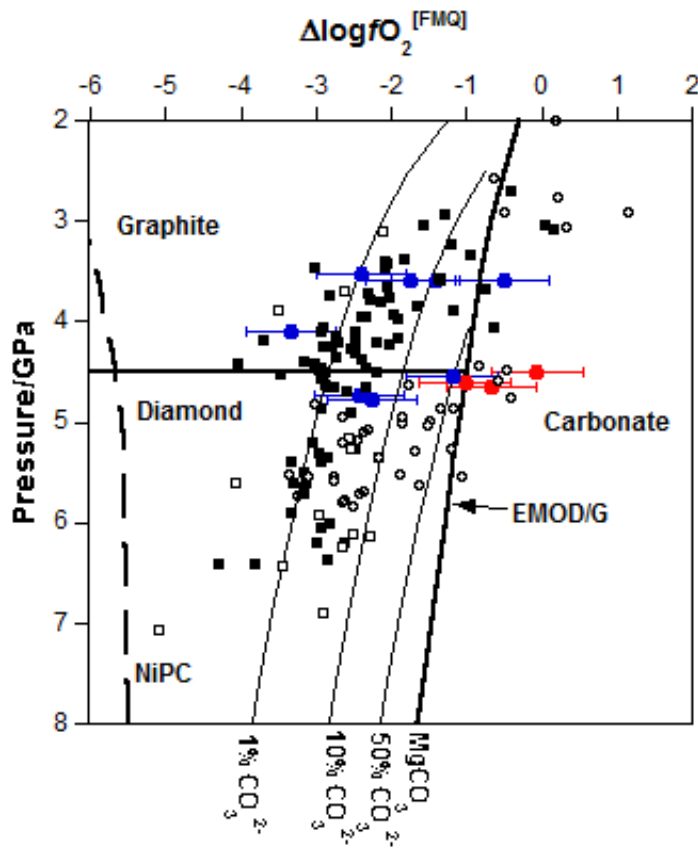


Figure 2.9: Plot of $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ versus equilibrium pressure for the current Wesselton samples shown in Table 2.3 (blue circles – depleted, red circles – enriched). Other studies are also shown: black circles – Kaapvaal Craton (our unpublished Kimberley data; Woodland & Koch, 2003; Creighton et al., 2009; Lazarov et al., 2009), open circles – Slave Craton (Creighton et al., 2009; Yaxley et al., unpublished), and open squares – Siberian Craton (Yaxley et al., 2012). The Wesselton samples have error bars for $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ of ± 0.6 log units. The curves to the left of EMOD/G indicate the $f\text{O}_2$ of melts in equilibrium with diamond or graphite, for different carbonate (CO_3^{2-}) contents (expressed as molar percentage of MCO_3 where M is a divalent cation) (Stagno and Frost, 2010). The pressure of the diamond graphite transition is based on a 43 mW m^{-2} geotherm. EMOD and EMOG refer to the diamond limiting reaction enstatite + magnesite = olivine + C + O_2 (Luth, 1993) in the graphite and diamond stability fields respectively. NiPC is the Ni precipitation curve from O'Neill and Wall (1987).

A general trend of decreasing $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ with pressure has been identified across the global dataset of garnet peridotite xenoliths (Woodland and Koch, 2003, Yaxley et al., 2012) and the more reduced samples from Wesselton ($\Delta\log f\text{O}_2^{[\text{FMQ}]} < -1$) fall within the field that defines this trend (Figure 2.9). Two samples also show an oxidation trend defined by multiple crystals within the sample (KBD12 at ≈ 4.6 GPa and KBD18 at ≈ 3.6 GPa).

A number of studies have reported Fe^{3+} in garnet from kimberlite derived garnet peridotite xenoliths from various cratons (Kaapvaal, Slave, Siberian) using Mössbauer spectroscopy (Lazarov et al., 2009, McCammon et al., 2001, McCammon and Kopylova, 2004, Woodland and Koch, 2003), the electron microprobe based flank method (Creighton et al., 2009, 2010, Höfer and Brey, 2007) and Fe K-edge XANES (Berry et al., 2013, Yaxley et al., 2012). These studies have described a link between enrichment of the cratonic lithosphere and oxidation. In the Kaapvaal craton, and other similar locations, there is a steady decrease in $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ with depth from values of 0 to -1 at 2 to 3 GPa to around -4.5 at ≈ 6.5 GPa, when recalculated using equilibrium (2) (Lazarov et al., 2009, Woodland and Koch, 2003, Yaxley et al., 2012). One study of depth- $f\text{O}_2$ relationships in the Kaapvaal craton reported a change to shallower slope in $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ below 140 km (Woodland and Koch, 2003), however, more recent studies including the current one, do not show this feature (Creighton et al., 2009, Lazarov et al., 2009). The trend of deeper garnet peridotites being more reduced than shallower samples means that low pressure samples are far more likely to sample the carbonate stability field than high pressure samples, as can be seen in Figure 2.9, where there are very few samples in the carbonate field above 4.7 GPa, with those in the field being within error ($\Delta\log f\text{O}_2^{[\text{FMQ}]} \pm 0.6$) of the EMOG/G reaction curve. In the lower pressure

regions there are many samples sourced from the carbonate stability field, including some from this study as well as from Creighton et al. (2010).

Some of the metasomatised garnet peridotites from the Kaapvaal craton showed a sufficient level of oxidation (up to $\Delta\log f\text{O}_2^{[\text{FMQ}]} = 0$) to induce magnesite rather than diamond stability (Creighton et al., 2009). This effect presumably overprints the depth- $f\text{O}_2$ relationship reported by Woodland and Koch (2003), and has also been observed in the garnet peridotites from the Diavik kimberlite in the Slave craton (Creighton et al., 2010). This trend is particularly evident in one xenolith from our study, KBD12, which exhibits a significant oxidation trend from two individual garnet cores to rims of -2.4 to -1 and -1.5 to -0.23 log units relative to FMQ (Table 2.3) at a constant pressure. In combination with the knowledge that the rim is in equilibrium with the surrounding assemblage, this provides evidence that the oxidation was caused by a metasomatic agent that affected the sampled mantle material. The enrichment of trace elements (such as Ti, Y, Zr) in garnet rims relative to cores, from sample KBD12, supports the hypothesis that the oxidation was caused by a metasomatic agent at high pressures (≥ 4.5 GPa). Our samples and others from Wesselton also have Ca-enriched rims compared to the core, with these rims also higher in Fe^{3+} , as determined by both milli-Mössbauer and XANES spectroscopy (Griffin et al., 1999, McCammon et al., 2001). $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ increased by up to 1.5 log units from core to rim, to an extent that the rims have crossed into the carbonate stability field relative to the EMO/G reaction (3) (Figure 2.9). Conversely garnet at lower pressures (< 4.5 GPa) is generally depleted in trace elements, regardless of $\Delta\log f\text{O}_2^{[\text{FMQ}]}$, as was seen in our sample KBD18 as well as samples from Kimberley (Creighton et al., 2009) and Diavik (Creighton et al., 2010). KBD 18 is an interesting case as it shows variation in $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ of 2 log units across

four garnet crystals, which are all located within 20 mm of each other in the section examined. These garnets are smaller than other garnets in the suite (such as the zoned crystals in KBD12), and as such the variation in $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ may be a result of the diffusive re-equilibration that occurs when an oxidised agent impacts upon reduced mantle material. In this situation the final $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ will be a weighted average of the initial value and the value of the metasomatic agent. Therefore smaller crystals are more likely to completely re-equilibrate, however the amount of metasomatic input will vary due to size, giving a variable final $\Delta\log f\text{O}_2^{[\text{FMQ}]}$. Major and trace element compositions across this xenolith are consistent, with the only variation being in $\text{Fe}^{3+}/\Sigma\text{Fe}$. Thus it can be said that the more oxidised values at low pressures ($\Delta\log f\text{O}_2^{[\text{FMQ}]}$ of -1 to 1) are part of the normal trend of decreasing $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ with increasing pressure whereas similar $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ at deeper pressures are generally associated with metasomatic processes (Creighton et al., 2009, Yaxley et al., 2012).

The relatively low oxygen fugacities recorded by some of the samples are below those required for equilibrium with a carbonatite melt, but indicate that they could coexist with a carbonated silicate melt in which the activity of carbonate components would be lower (Stagno et al., 2013). A carbonated silicate melt is one possible agent responsible for the metasomatism that led to the oxidation of some samples, particularly the rims of the zoned garnets of KBD12. The oxidation process observed in these samples is close to isobaric, thus $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ increases to the point that some samples are in the carbonate stability field, and would destabilise graphite or diamond. Figure 2.9 shows the P - $f\text{O}_2$ values for a number of garnet peridotite xenolith suites from the Kaapvaal (Creighton et al., 2009, Lazarov et al., 2009, Woodland and Koch, 2003), Slave (Creighton et al., 2010) and Siberian Cratons (Yaxley et al., 2012). This shows a strong

link between the Kaapvaal craton samples at the field containing between 1 and 10 % carbonate in a silicate melt below 4 GPa, whereas the Slave craton samples a wider range in fO_2 and thus carbonate concentration. The single suite from the Siberian Craton samples a large range in both depth and fO_2 . This suggests that substantial parts of the Kaapvaal cratonic mantle below 4 GPa have been metasomatised by carbonated silicate melts containing up to 10% carbonate. The enriched samples from Wesselton show an oxidation trend that overprints this earlier carbonated silicate melt trend.

2.6 Conclusions

- (1) The Wesselton kimberlite has sampled the Kaapvaal cratonic lithosphere from a pressure range of at least 3.6 to 4.7 GPa. All samples lie with close to or on a geotherm of 43 mW m^{-2} , which is typical of the Kaapvaal craton.
- (2) There is evidence of metasomatic enrichment in a number of samples, especially the rims of the zoned garnets from sample KBD12. This metasomatic event is likely to have occurred contemporaneously or close to contemporaneous with entrainment of the xenoliths in the kimberlite magma. There is also a set of samples that are depleted in the metasomatic indicator elements of Ti, Y and Zr.
- (3) The developing technique of Fe K-edge XANES spectroscopy (Berry et al., 2010, 2013) was applied to garnets from this suite to determine their $Fe^{3+}/\Sigma Fe$ values. This enabled the determination of a redox profile through the lithospheric section sampled by the xenoliths. The more reduced samples ($\Delta \log fO_2^{[FMQ]} < -1$) fell within the region of the global dataset that shows a decrease in fO_2 with increasing depth.
- (4) Overprinting this trend is an oxidation trend that increases $\Delta \log fO_2^{[FMQ]}$ by 1.5 to 2.0 units in garnets in KBD12, particularly in the rims of the zoned crystals, at

4.7 GPa. These more oxidised samples are enriched in elements such as Ca, Ti, Y and Zr, which provides strong evidence of metasomatism, thus inferring that the metasomatic agent was also responsible for this oxidation. This relationship between metasomatism and oxidation was only evident at higher pressures (> 4.5 GPa) and thus was not seen in sample KBD18, with the oxidation in this sample interpreted as part of the normal range of fO_2 at lower pressures.

- (5) The position of the samples in depth- fO_2 space indicate that they may have been in equilibrium with a carbonated silicate melt, with the isobaric oxidation process instigated by the metasomatism causing an increase in the carbonate activity in this melt until the system crossed the EMOD equilibrium, leading to the formation of carbonate phases that threaten the stability of diamond in the melt.

2.7 Acknowledgements

We gratefully acknowledge the assistance of Robert Rapp with the electron microprobe analyses and Charlotte Allen with the LA-ICP-MS analyses. This research was undertaken on the X-ray fluorescence microprobe beamline at the Australian Synchrotron, Victoria, Australia. We gratefully acknowledge the support of the beamline scientists, David Paterson, Martin de Jonge and Daryl Howard. This work was partly funded by an Australian National University PhD Scholarship to BJH and an Australian Research Council Future Fellowship to GMY and AJB. An earlier draft of this manuscript was greatly improved as a result of thorough reviews by Dante Canil and Michel Grégoire.

Chapter 3: Quantitative mapping of the oxidative effects of mantle metasomatism

X-ray absorption near-edge structure spectroscopy was used to quantitatively map the distribution of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet in a garnet peridotite xenolith from the Wesselton kimberlite, South Africa. This map was produced by recording the fluorescence intensity at four distinct energies for each pixel of the map, rather than recording the entire spectrum. Natural garnet standards from peridotites, which have previously had their $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined using Mössbauer spectroscopy, were used to develop a linear calibration curve. This was then used to convert the fluorescence intensity into $\text{Fe}^{3+}/\Sigma\text{Fe}$, and in turn produce a quantitative map with a resolution approaching that obtained using an electron microprobe. This map reveals zoning in $\text{Fe}^{3+}/\Sigma\text{Fe}$ between the core and the rim that correlates with the zoning observed in other elements. The $f\text{O}_2$ of the rims shows that the zonation preserves evidence of an oxidising metasomatic event that may threaten the stability of diamond in this system. The presence of such rare compositional zoning indicates that the metasomatic event happened shortly before entrainment and eruption in the host kimberlite. It would be expected that most metasomatic zoning would not be preserved due to diffusive re-equilibration within the samples, leading to the homogenisation of the crystals with an $f\text{O}_2$ that is a weighted average of the original cratonic mantle (core) and the metasomatic agent (rim).

3.1 Foreword

This chapter is based upon a peer-reviewed journal article of which I am a co-author. The article “*Quantitative mapping of the oxidative effects of mantle metasomatism*” was published in *Geology* (Vol. 41, No. 6, p. 683-686) in June 2013 and can be found in Appendix A. The chapter has been partially written by myself and is a more detailed version of the published paper, which was mainly written by Andrew Berry with significant contributions from myself and the other co-authors. The other authors were Andrew J. Berry, Gregory M. Yaxley, Alan B. Woodland, Martin D. de Jonge, Daryl L. Howard, David Paterson and Vadim S. Kamenetsky.

The samples analysed for this chapter were part of the suite from the Wesselton kimberlite that I have analysed for my project (see also Chapters 1 and 3). As such I performed all the petrography, major and trace element analysis, as well as the elemental mapping. I was also a part of the team that recorded the XANES spectra and maps and I produced the map of $\text{Fe}^{3+}/\Sigma\text{Fe}$ distribution in garnet (the main result from the paper) using Matlab. Andrew Berry and Greg Yaxley were responsible for the development of the calibration that allows Fe K-edge XANES spectroscopy to be applied to mantle garnets (Berry et al. 2010) and were also involved in the collection of spectra and maps. Andrew Berry wrote the manuscript with significant input from Greg Yaxley and myself. Alan Woodland provided some of the standards for the XANES spectroscopy, including performing the Mössbauer spectroscopy of these; he also calculated the $f\text{O}_2$ of the samples for the published article, though the calculations presented here are my own. Martin de Jonge, Daryl Howard and David Paterson are the beamline scientists for the X-ray Fluorescence Microscopy beamline of the Australian Synchrotron and were involved in the development and application of Fe K-edge

XANES spectroscopy and mapping to the samples. Vadim Kamenetsky provided the samples.

The material presented in the article is presented in this chapter in my own words and is expanded and updated from the published version. The two lead authors (Andrew Berry and Greg Yaxley) are aware that I am reproducing the article and both agree that it can and should be a part of my thesis as it involves work that I have been heavily involved with.

3.2 Introduction

Mapping the distribution of major and minor elements in geological samples allows for the identification of mineral phases as well as compositional zoning, intergrowths, exsolution, diffusion profiles and inclusions. These maps, which can be obtained routinely using an electron microprobe, can be used to interpret the history of the samples and identify processes that have occurred (Yang and Rivers, 2001). Most elements in the rock-forming minerals exist in only one oxidation state (Si^{4+} , Al^{3+} , Ca^{2+} , Mg^{2+} , Na^+ , K^+), whereas Fe occurs as both Fe^{2+} and Fe^{3+} . The two oxidation states of Fe behave as different elements geochemically (e.g. during partitioning) and as such the proportion of Fe^{2+} and Fe^{3+} (expressed as $\text{Fe}^{3+}/\Sigma\text{Fe}$), in minerals that can host both species, can record the oxygen fugacity ($f\text{O}_2$) at which a mineral crystallised. Minerals such as garnet, which have multiple sites and substitutions that incorporate the two Fe species, make it difficult to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ using stoichiometry. Thus a number of techniques have been investigated to quantify $\text{Fe}^{3+}/\Sigma\text{Fe}$, including redox titrations (Yokoyama and Nakamura, 2002), Mössbauer spectroscopy (Woodland and Koch, 2003) and the electron microprobe based flank method (Höfer and Brey, 2007). These techniques all give precise and accurate values. However, the redox titration method is completely destructive, whilst Mössbauer spectroscopy is both time-consuming and lacking in spatial resolution, and the flank method is complex and time consuming, making them unsuitable for fast, high-resolution, in-situ determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$, which is required for mapping.

X-ray absorption near edge structure spectroscopy is a technique that is becoming more commonly used to quantify $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Wilke et al., 2001, Berry et al., 2003, Borfecchia et al., 2012), as well as the oxidation states of other elements (Berry et al., 2006). The

method for obtaining XANES spectra has significant advantages over techniques, including the ability to acquire spectra in air with micron scale resolution on a variety of samples with a polished surfaces including thin sections and epoxy mounts (Delaney et al., 1998, Berry et al., 2008). In order to develop a map in a reasonable time period, it is necessary to record rapidly either spectra as a function of position, as is done in energy dispersive XANES (Muñoz et al., 2006) or images as a function of energy, either the fluorescence (Etschmann et al., 2010) or the attenuation (De Andrade et al., 2011). Whilst these capabilities exist, they are still being developed and are available only at a limited number of synchrotron facilities. A more common approach is to record images at a number of energies for spectral features that correspond with the oxidation state ratio of interest (Sutton et al., 1995). This approach has been used for elements such as S (Métrich et al., 2009) and Se (Pickering et al., 2000), which have relatively large changes in spectral range with oxidation state. Applying this technique to mantle minerals and melts is difficult as the differences in $\text{Fe}^{3+}/\Sigma\text{Fe}$ are very small and thus it is necessary to identify spectral features that are sufficiently sensitive to these values. In order to create a quantitative map it is necessary to use standards to convert the parameterization of the feature to values of $\text{Fe}^{3+}/\Sigma\text{Fe}$. No previous oxidation state mapping study has been able to approach the accuracy and precision (± 0.01) required to apply this in a meaningful way to garnet peridotites and many other geological samples.

A XANES spectroscopy method has recently been developed for the determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in mantle garnets (Berry et al., 2010). This calibration makes use of the intensities of two post-edge features, at 7138.4 and 7161.7 eV respectively, rather than the energy at the $1s \rightarrow 3d$ pre-edge peak, which is conventionally used for quantification (Wilke et al., 2001). This method is able to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ at the same level of

accuracy and precision obtained for the standards using Mössbauer spectroscopy (± 0.01).

Garnet peridotite xenoliths from the diamond bearing Wesselton kimberlite in South Africa have been found to contain some garnets which are compositionally zoned in major and trace elements (Griffin et al., 1999). A follow-up study determined $\text{Fe}^{3+}/\Sigma\text{Fe}$ by Mössbauer spectroscopy using a 400 μm analysis spot, with each analysis taking between 1 and 5 days. The core was found to have $\text{Fe}^{3+}/\Sigma\text{Fe}$ of 0.05 ± 0.02 and the rim 0.08 ± 0.04 , though these values overlap within error (McCammon et al., 2001). This zonation results from metasomatism in the lithospheric mantle and may be able to impose an $f\text{O}_2$ that is oxidising enough to cause diamond breakdown or resorption (Griffin et al., 1999, McCammon et al., 2001). The presence of such zonation and the $f\text{O}_2$ that it records are potentially important in the use of garnet as a diamond indicator mineral. XANES spectroscopy is able to produce quantitative maps of the distribution of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in mantle garnet, with a resolution comparable to elemental maps obtained using an electron microprobe.

3.3 Methods

3.3.1 Samples

A garnet lherzolite xenolith from the Wesselton kimberlite, South Africa was found to contain multiple zoned garnet crystals (Chapter 1), which were subsequently examined using Fe K-edge XANES spectroscopy (Figure 3.1 and 3.2). A suite of garnet peridotite xenolith thin sections from Kimberley (South Africa) and Lesotho were used as standards, along with garnet separates mounted in epoxy from the Diavik kimberlite

(Slave craton, Canada). The $\text{Fe}^{3+}/\Sigma\text{Fe}$ of these standards was determined by Mössbauer spectroscopy of powdered garnet from the same xenoliths as the thin sections or separates (Woodland and Koch, 2003, Yaxley et al. unpublished data). Major element compositions, backscattered electron images and elemental maps were obtained using the Cameca SX100 electron microprobe at the Research School of Earth Sciences, Australian National University. Operating conditions for elemental mapping an accelerating voltage of 15 kV, beam current of 100 nA and a step size of 2 μm .

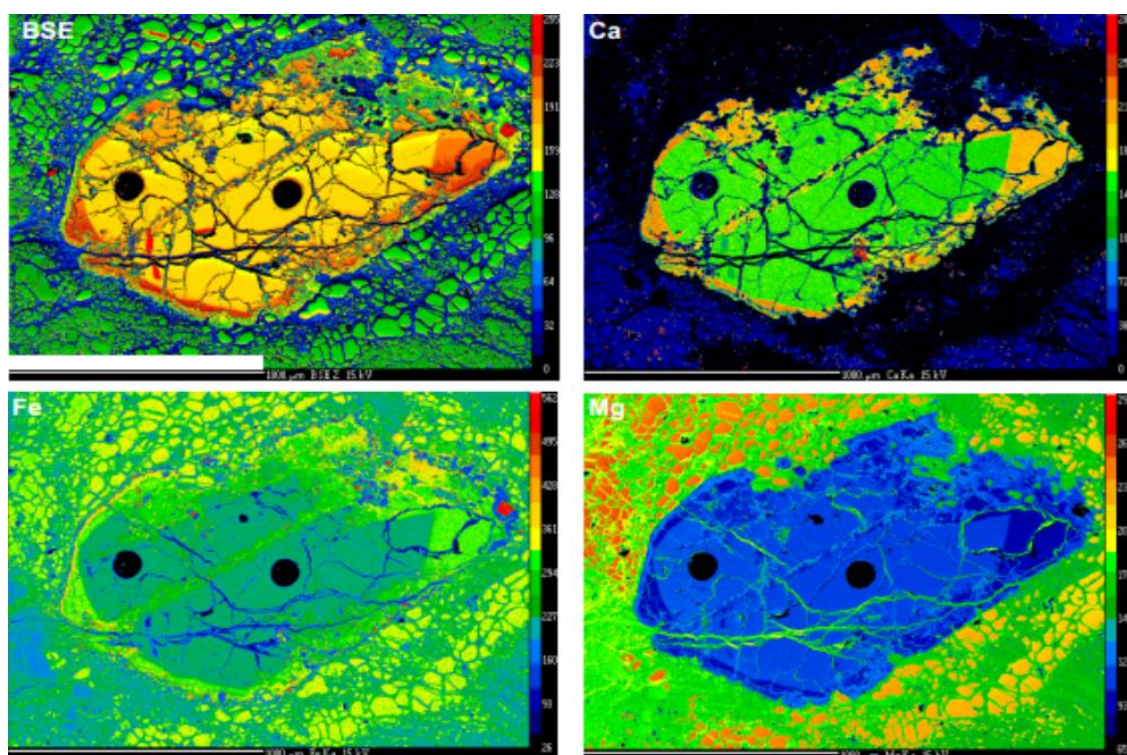


Figure 3.1: Chemical zonation in garnet, ga4, from sample KBD12, as shown in a false BSE image and elemental maps for Ca, Fe and Mg, obtained using EPMA. Scale on the BSE image is 1000 μm and the circular features are pits from LA-ICP-MS analysis.

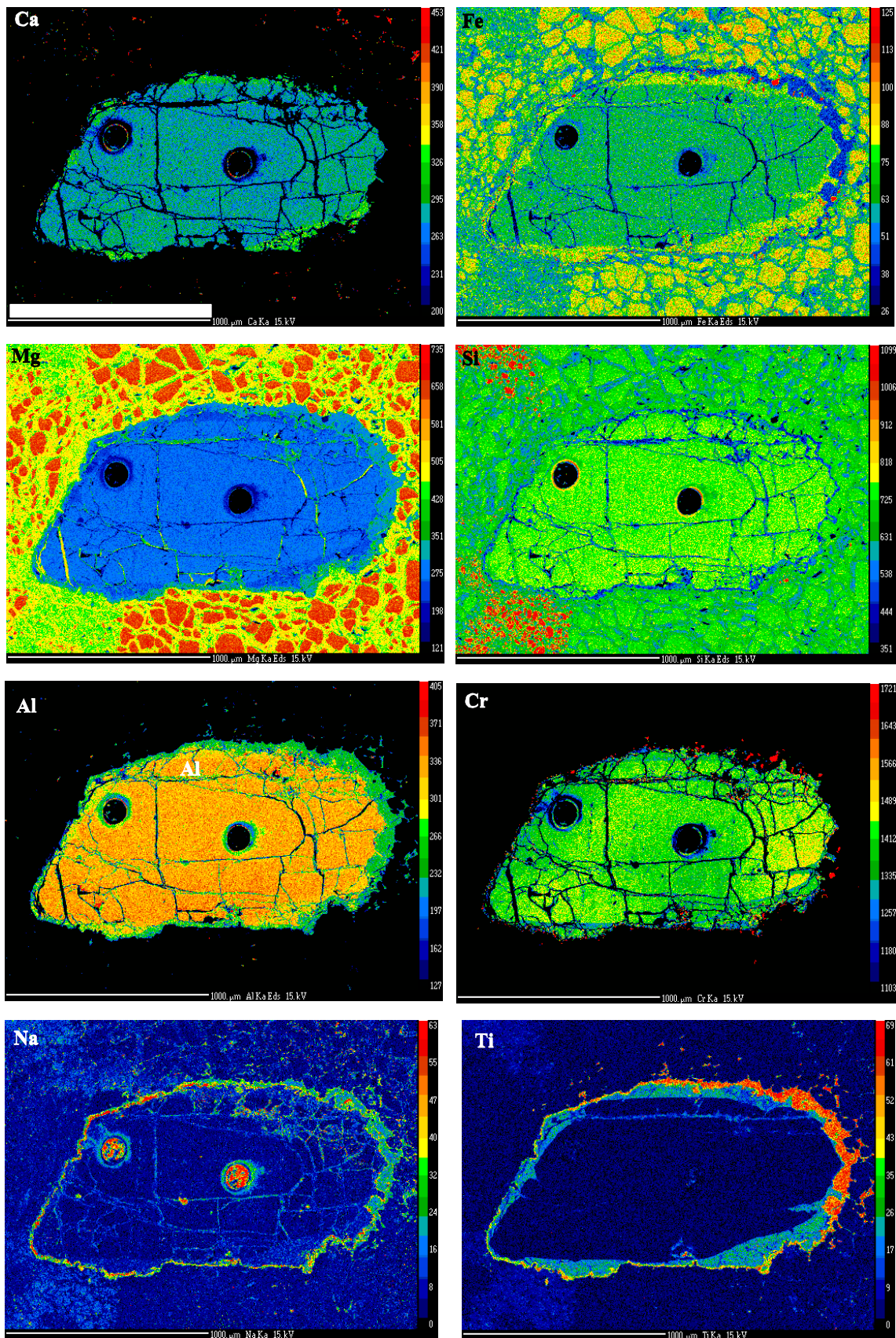


Figure 3.2: Elemental maps, acquired using an electron microprobe, showing distributions of Ca, Fe, Mg, Si, Al, Cr, Na and Ti in sample KBD12-ga6. Circular features in garnet are pits produced during LA-ICP-MS analysis. Scale on the Ca map is 1000 μm.

3.3.2 Iron K-Edge XANES Spectroscopy

Iron K-edge XANES spectra were recorded at the X-ray fluorescence microprobe (XFM) beamline of the Australian Synchrotron (Paterson et al., 2011). A Si(111) double crystal monochromator was used to select the excitation energy and it was calibrated by defining the first derivative peak of an Fe foil spectrum to be 7112.0 eV. The spectral resolution was 1.9 eV at the Fe K-edge. Kirkpatrick-Baez mirrors were used to focus the beam and produce an analysis spot of $\sim 3 \times 3 \mu\text{m}$ for this study. The samples were mounted at 45° to both the incident beam and a single element silicon drift energy dispersive detector (Vortex EM, SII Nanotechnology, Northridge, California) with digital signal processing (DXP Saturn, XIA LLC, Hayward, California). Fluorescence mode was used to collect all spectra, with the incident flux and the sample-to-detector distance adjusted to ensure the total incoming count rate was within the linear range of the signal processing electronics. The spectra were recorded from 7075 to 7300 eV with a step size of 0.5 eV in the baseline (up to 7103 eV), 0.3 eV for the edge and 2.5 eV for the post-edge (above 7175 eV), with a count time of 3 s for each point. Comparison of spectra was possible after subtracting a constant baseline and normalising to the average intensity above 7235 eV. The fluorescence intensity of the Wesselton garnets as a function of position was mapped by scanning the sample stage horizontally and vertically at excitation energies of 7075, 7138.4, 7161.7 and 7300 eV. Each map was normalised to the beam intensity and then had the baseline map (7075 eV) subtracted. The baseline-corrected maps at 7138.4 and 7161.7 eV were normalised by the 7300 eV map (total fluorescence) to account for variations in the total Fe content. Thus the ratio of the normalised maps at 7138.4 and 7161.7 eV is a map of $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Berry et al., 2010).

3.4 Results

3.4.1 Major and Trace Element Zonation

Examination of garnets in garnet peridotite from the Wesselton kimberlite using back scattered electron (BSE) imaging revealed significant compositional zoning in two crystals (Ga4 and Ga6) from sample KBD12. This zoning was initially investigated by performing EPMA transects across the boundary between zones (Chapter 4) and then elemental maps were produced using an electron microprobe (Figures 3.1 and 3.2). The rims were found to be enriched in Na, Ca, Fe, Ti, and Cr relative to the core, whilst Al and Mg were depleted (Table 3.1). Consequently the Mg# of the rim was lower than the core.

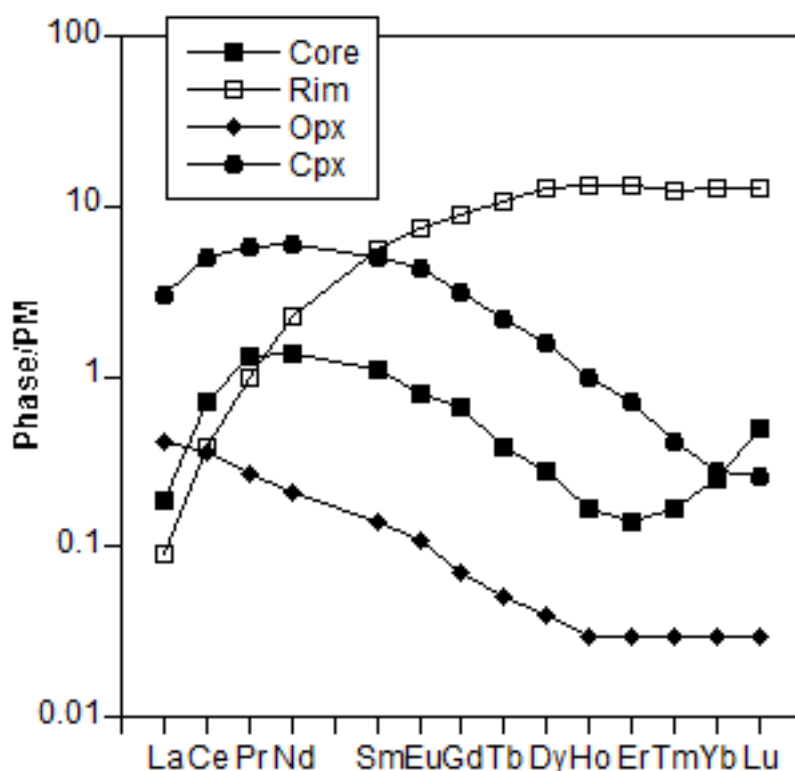


Figure 3.3: Primitive mantle normalised REE diagrams for the core and rim of Ga4, along with coexisting ortho- and clinopyroxene.

The garnets are Cr-rich pyrope, was a pyrope mole fraction of 0.8 in the core, which drops to 0.7 in the rim; Cr_2O_3 in the core ranges from 4.8 to 5.8 wt. %, whilst in the rim it ranges from 6.2 to 6.8 wt.%. Kelyphite, an intergrowth predominantly composed of spinel and pyroxene, surrounds the garnet rim and was likely formed during ascent of the kimberlite magma. The REE_N patterns for the core and rim of Ga4 are shown in Figure 3.3, with the core showing a sinusoidal pattern and the rim a normal pattern, with abundances increasing from the LREE_N to the HREE_N . This shows a slight decrease in the abundance of the LREE in the rim relative to the core, whilst the abundances of the HREE are substantially higher in the rim relative to the core. Comparison of the garnet REE_N patterns with those of clinopyroxene and orthopyroxene shows a similar relationship between the garnet rim and the pyroxenes as has been observed in peridotites that have reached equilibrium (e.g. Hermann et al., 2006). This indicates that the garnet rim is in equilibrium with the surrounding peridotite assemblage. The REE_N pattern for the core of Ga6 is similar to that of the core of Ga4, however its rim was too thin for analysis by LA-ICP-MS. Major and trace element concentrations for the pyroxenes along with olivine major element concentrations are shown in Table 3.1.

3.4.2 Determination and Mapping of $\text{Fe}^{3+}/\Sigma\text{Fe}$

Iron K-edge spectra of the core and the rim of Ga4 are shown in Figure 3.4, though the differences between the two spectra are slight. XANES spectra for the standards were recorded in order to produce a calibration curve, with the correlation between the ratio of the features at 7138.4 and 7161.7 eV (E2 and E3 in Figure 3.4) and $\text{Fe}^{3+}/\Sigma\text{Fe}$ shown in Figure 3.5. The standard deviation between this line of best fit and the Mössbauer spectroscopy determined values of $\text{Fe}^{3+}/\Sigma\text{Fe}$ is ± 0.01 ; this suggests that the

Table 3.1: Average major element compositions (wt.%), cation values and trace element abundances (ppm) for individual phases including the core and rim of both Ga4 and Ga6.

	Ga4		Ga6		Ol	Opx	Cpx
	core	rim	core	rim			
SiO ₂	42.40	41.17	43.40	41.63	40.85	57.15	54.66
TiO ₂	0.01	0.75	0.021	0.75	0.02	0.11	0.44
Al ₂ O ₃	19.52	17.29	20.78	18.03	0.02	0.88	2.89
Cr ₂ O ₃	5.81	6.76	4.87	6.20	0.03	0.43	2.96
FeO	5.86	8.47	4.20	6.93	7.29	5.14	2.51
MnO	0.24	0.26	0.29	0.26	0.09	0.09	0.08
MgO	22.79	19.52	22.32	20.37	51.37	34.84	16.04
NiO	0.00	0.03	0.01	0.02	0.38	0.12	0.05
CaO	4.12	5.89	4.13	5.54	0.05	0.70	17.70
Na ₂ O	0.01	0.08	0.02	0.15	0.02	0.01	2.75
K ₂ O	bdl	bdl	bdl	0.01	bdl	0.16	0.02
P ₂ O ₅	0.02	0.01	bdl	0.05	0.01	0.01	0.02
Total	100.8	100.22	100.04	99.92	100.11	99.64	100.12
Cations based on:	12 O	12 O	12 O	12 O	4 O	3 O	6 O
Si	2.999	2.996	0.0005	0.0407	0.991	0.986	1.971
Ti	0.001	0.041	2.9857	2.9865	0	0.001	0.012
Al	1.626	1.484	1.5568	1.5246	0	0.018	0.123
Cr	0.325	0.389	0.3712	0.3512	0.001	0.006	0.084
Fe	0.346	0.515	0.3490	0.4917	0.148	0.074	0.076
Mn	0.015	0.016	0.0147	0.0155	0.002	0.001	0.003
Mg	2.398	2.117	2.3467	2.1796	1.857	0.896	0.862
Ni	0	0.001	0.0005	0.0013	0.007	0.002	0.001
Ca	0.313	0.459	0.4143	0.4257	0.001	0.013	0.684
Na	0.002	0.012	0.0120	0.0206	0.001	0.006	0.192
K	0	0	0.0006	0.0010	0	0	0.001
P	0.001	0.001	0.0016	0.0029	0	0	0.001
Sum	8.024	8.032	8.0537	8.0414	3.009	2.003	4.009
Mg#	87.4	80.4	87.1	81.6	92.6	92.4	91.9
Fe#	0.113	0.167	0.112	0.159	0.074	0.075	0.047
Sc	107	123	5.05			3.64	31.1
V	185	205	4.98			46.1	343
Co	40.9	46.2	111			68.6	22.1
Ni	55.6	95.0	43.9			1018	364
⁶⁹ Ga	2.66	nd	302			4.64	9.02
⁷¹ Ga	2.64	9.4	38			4.19	9.23
Ge	1.44	nd	55.5			2.93	nd
Rb	0.20	0.01	2.46			1.01	4.04
Ba	0.31	0.08	2.63			1.89	nd
Th	0.02	0.01	1.49			0.05	0.07
U	0.03	0.02	0.04			0.02	0.04
Nb	0.78	0.34	1.27			0.49	0.64
Ta	0.02	0.03	0.25			0.04	0.06
La	0.13	0.06	1.54			0.29	2.01
Ce	1.26	0.70	0.88			0.64	8.87
Pb	0.11	0.07	bdl			0.13	0.22
Pr	0.36	0.26	0.09			0.07	1.56
Sr	1.36	1.00	1.16			4.12	110
P	75.1	133	0.45			30.0	45.5
Nd	1.79	3.00	2.20			0.28	8.04
Sm	0.48	2.41	0.23			0.06	2.17
Zr	8.76	138	0.06			1.34	69.9
Hf	0.16	nd	0.13			0.05	3.63
Eu	0.13	1.21	0.01			0.02	0.70
Ti	100	5222	0.05			550	2421
Gd	0.38	5.15	0.01			0.04	1.78
Tb	0.04	1.11	0.03			0.01	0.23
Dy	0.20	9.23	0.01			0.03	1.11
Li	0.19	nd	0.08			1.43	1.44
Y	0.85	50	0.02			0.13	3.91
Ho	0.03	2.07	0.03			0.01	0.16
Er	0.07	6.13	0.04			0.01	0.32
Tm	0.01	0.89	0.07			bdl	0.03
Yb	0.11	5.89	0.03			0.01	0.12
Lu	0.04	0.89	0.05			bdl	bdl

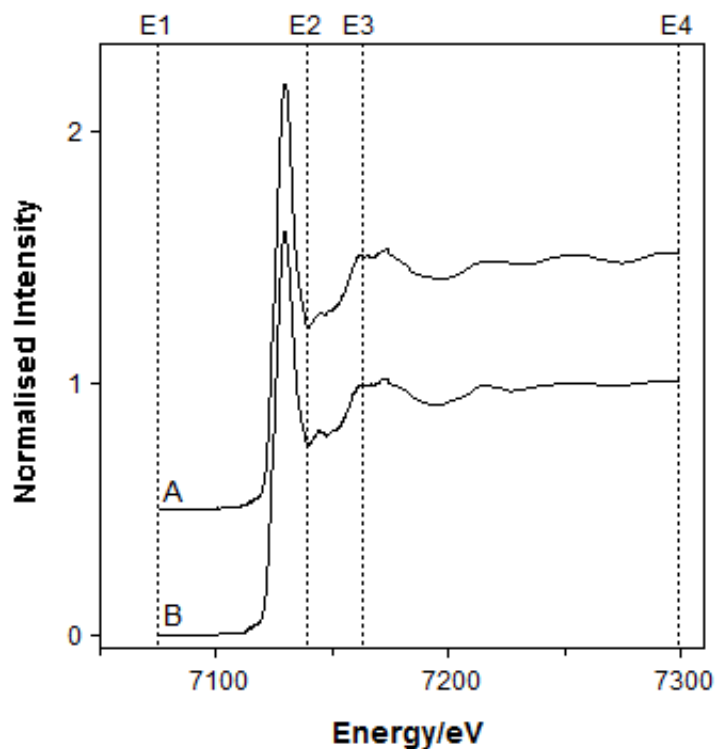


Figure 3.4: Fe K-edge XANES spectra of core (A) and rim (B) of the zoned garnet shown in Figure 3.1. Energies (E1-E4) at which images were recorded to produce $\text{Fe}^{3+}/\Sigma\text{Fe}$ maps are indicated.

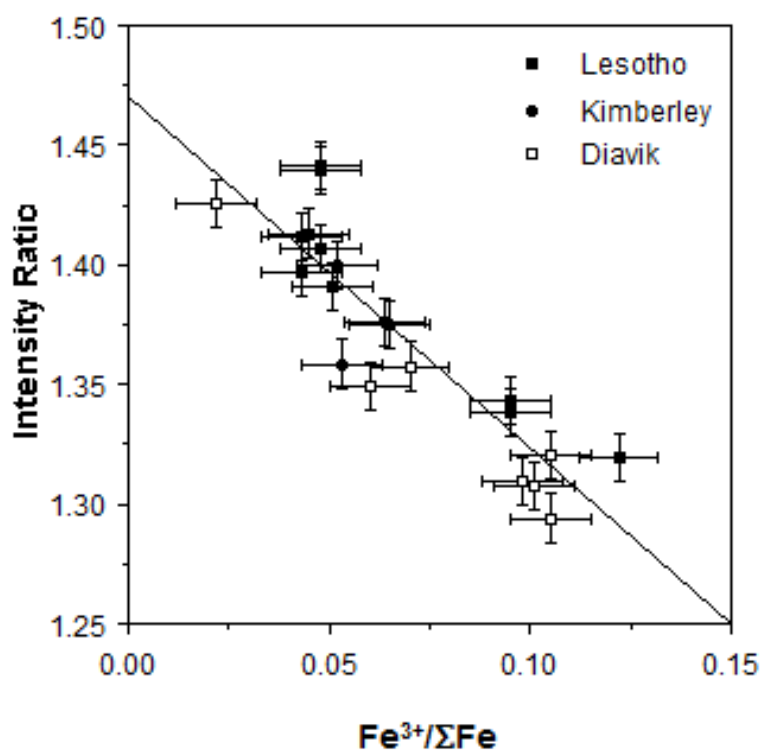


Figure 3.5: Correlation between the Fe K-edge XANES intensity ratio at 7134.8 and 7161.7 eV and $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined by Mössbauer spectroscopy of mantle garnets from various locations. The line is a linear best fit to the data and is the correlation used in the determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$.

accuracy and precision is comparable to that of Mössbauer spectroscopy (± 0.01). This calibration is then used to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the unknowns (Yaxley et al., 2012). Spot analyses of the core and rim for two crystals, ga4 and ga6, from sample KBD12 were performed however only ga4 was mapped.

The distribution of $\text{Fe}^{3+}/\Sigma\text{Fe}$ for a small segment of the zoned garnet, KBD12-ga4, is shown in Figure 3.6d, alongside a BSE image and Ca and Fe elemental maps, which also shows the zonation. This map corresponds to the ratio of the fluorescence intensities at 7138.4 and 7161.7 eV, which can be converted to $\text{Fe}^{3+}/\Sigma\text{Fe}$ using the calibration curve as shown in Figure 3.5. As this calibration is only applicable to garnet the colour scale, which indicates $\text{Fe}^{3+}/\Sigma\text{Fe}$, in Figure 6d is accurate for garnet, but not the other phases present, which are shown in black in the figure. A separate calibration and set of standards would be required to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ in other minerals that can host both Fe^{2+} and Fe^{3+} . $\text{Fe}^{3+}/\Sigma\text{Fe}$ values of 0.075 ± 0.15 and 0.125 ± 0.11 were obtained for the core and the rim respectively, by taking the average of multiple measurements performing during mapping. The map took approximately 14 h to acquire with an area of $500 \times 600 \mu\text{m}$, a step size of $5 \times 6 \mu\text{m}$ and dwell time of 1 s per point.

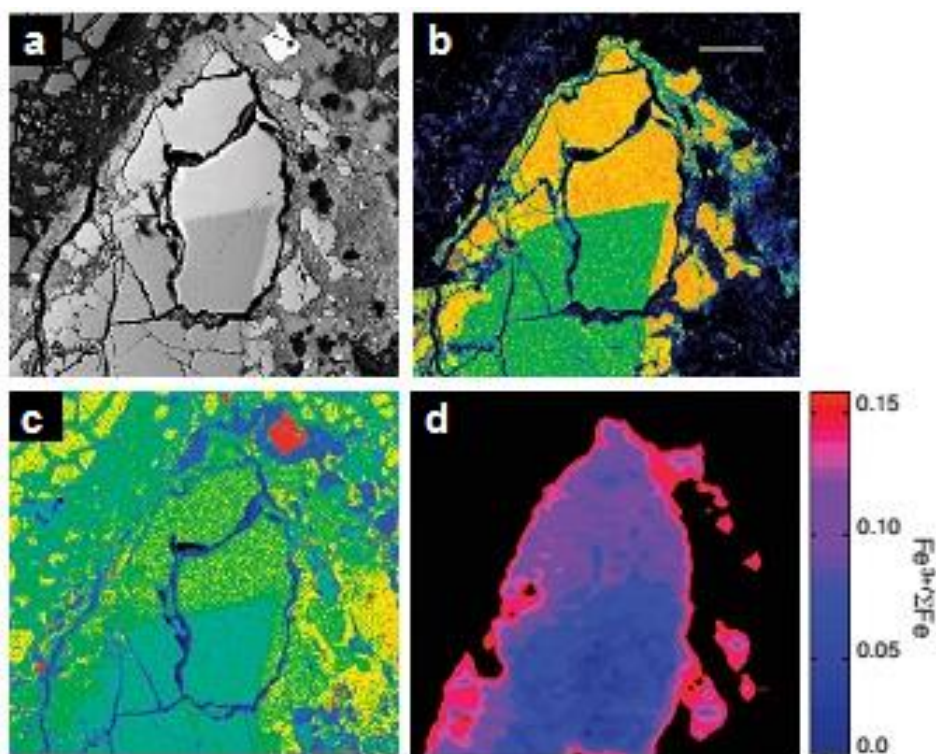


Figure 3.6: (a) BSE image of zoned garnet, KBD12-ga4, in a matrix of kelyphite, olivine and serpentine from the Wesselon kimberlite, South Africa. (b) Ca elemental map. (c) Fe elemental map. (d) XANES derived map of $\text{Fe}^{3+}/\Sigma\text{Fe}$. Colour scale indicates $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet. Scale bar in (b) is 100 μm .

3.5 Discussion

3.5.1 Mapping of $\text{Fe}^{3+}/\Sigma\text{Fe}$

There is a very strong correlation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ map (Figure 6d) with the BSE image (Figure 6a) and elemental maps of Ca and Fe (Figures 6b and 6c); grain boundaries and zonation are clearly defined, though the resolution of the map is below that obtained by EPMA. This reduction in resolution can be related to the spot size, which at 3 μm is larger than that of EPMA (typically 1 μm); and the far larger penetration depth of the X-rays, with one absorption length at the Fe K-edge being ~ 40 μm , compared to the excitation depth of a 15kV electron beam which is of the order of 5 μm . This results in the projection of a three dimensional analysis volume onto a two dimensional plane. This effect is further exaggerated by the experimental configuration, which places the sample at 45° to the X-ray beam, though this is the standard configuration for

fluorescence measurements. It is possible to improve the resolution by decreasing the spot size to sub-micron level; or by orienting the sample perpendicular to the incident beam; however the greater penetration depth will always be an issue.

The ability to map the relatively small but significant differences in $\text{Fe}^{3+}/\Sigma\text{Fe}$ that occur in mantle garnets both precisely and accurately (± 0.01 when referenced to point analyses and standards for which full XANES spectra were acquired) is very novel and an exciting development. Previous attempts to map $\text{Fe}^{3+}/\Sigma\text{Fe}$ in minerals had a typical accuracy of ± 0.05 - 0.15 , which is a significant proportion of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ range exhibited by mantle garnet, typically 0 to 0.25 (Berry et al., 2010). Earlier maps which show relative variations in $\text{Fe}^{3+}/\Sigma\text{Fe}$ are at best only semi-quantitative, as they lack appropriate standards (Muñoz et al., 2006, De Andrade et al., 2011). XANES spectra for isotropic minerals, such as garnet, are independent of crystallographic orientation, which is a significant advantage when using Fe K-edge XANES spectroscopy. For this study, the ratio of the intensities of the features at 7134.8 and 7161.7 eV was used to quantify $\text{Fe}^{3+}/\Sigma\text{Fe}$; however it has been found that over the range observed in mantle garnet the variation in the normalised intensity of the feature at 7134.8 eV is sensitive enough to produce similar results.

The technique that was used to produce the map is calibrated for garnet, and as such only the garnet region of the map can be considered to quantitatively show the distribution of $\text{Fe}^{3+}/\Sigma\text{Fe}$. For the other phases present in the map, such as olivine, pyroxene or kelyphite the map is black, as these phases have different XANES spectra, and as such it is not possible to use XANES spectroscopy to determine the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of

different phases simultaneously. This technique, which uses a Vortex dispersive drift detector, requires approximately 14 hours to map a region of $500 \times 600 \mu\text{m}$, however the Maia detector at the Australian Synchrotron would shorten this time substantially, allowing an oxidation state map of an entire thin section to be obtained in a matter of hours (Etschmann et al., 2010).

The intensity of spectral features on a XANES spectrum should be constant between experimental sessions and across beamlines, however more accurate results will be obtained if the method is calibrated by analysing standards before each session. There is potential to apply this mapping technique to garnets from a wide variety of geologic settings, including but not limited to eclogites, metapelites and skarns, however different calibrations would be required for garnets of different compositions (Berry et al., 2010). Theoretically it should also be possible to extend this method to other cubic minerals, such as spinel, though this would require appropriate standards and the identification of spectral features that vary with $\text{Fe}^{3+}/\Sigma\text{Fe}$. According to the map, the garnet core has lower $\text{Fe}^{3+}/\Sigma\text{Fe}$ than the rim (0.075 to 0.125), which is similar to values obtained using Mössbauer spectroscopy for the core (0.05) and the rim (0.08) of garnets from a different xenolith from same kimberlite (McCammon et al., 2001). Conversion of garnet $\text{Fe}^{3+}/\Sigma\text{Fe}$ from the map into $f\text{O}_2$ requires knowledge of the equilibrium pressure and temperature for the xenolith, along with the composition of coexisting olivine and orthopyroxene.

Table 3.2: Equilibrium pressure (GPa) and temperature (°C) for the core and rim of each garnet as determined using various combinations of thermometer and barometer, along with XANES determined $\text{Fe}^{3+}/\Sigma\text{Fe}$ and calculated $\Delta\log f\text{O}_2$. Details for the thermometers and barometers can be found in the text. For example, P[NG₈₅/Ca-opx_{BKN}] indicates that pressure was determined using P[NG₈₅] in conjunction with T[Ca-opx_{BKN}].

	Ga4		Ga6	
	Core	Rim	Core	Rim
Incorporating known Fe^{3+}				
P[NG ₈₅ /Ca-opx _{BKN}]	4.74	4.61	4.78	4.65
P[NTcpx]	4.06	4.06	4.06	4.06
P[NG ₈₅ /TA98]	4.33	4.28	4.35	4.29
P[BKN/BKN]	4.59	4.53	4.71	4.61
T[Ca-opxBKN/NG ₈₅]	1122	1116	1124	1118
T[NTcpx]	1023	1023	1023	1023
T[TA98/NG ₈₅]	1042	1040	1043	1041
T[BKN/BKN]	1158	1156	1160	1158
T[C94]	1075	1178		1034
T[G89]	1129	1360		1046
All Fe as Fe^{2+}				
P[NG ₈₅ /Ca-opxBKN]	4.75	4.64	4.81	4.68
P[NG ₈₅ /TA98]	4.34	4.30	4.37	4.31
P[BKN/BKN]	4.62	4.60	4.77	4.66
T[Ca-opxBKN/NG ₈₅]	1122	1117	1125	1119
T[TA98/NG ₈₅]	1042	1041	1043	1041
T[BKN/BKN]	1158	1158	1161	1159
$\text{Fe}^{3+}/\Sigma\text{Fe}$	0.057	0.098	0.069	0.123
$\Delta\log f\text{O}_2^{\text{[FMQ]}}$ [S13]	-2.43	-1.02	-2.26	-0.67
$\Delta\log f\text{O}_2^{\text{[FMQ]}}$ [GW95]	-3.82	-1.21	-3.71	-1.09

3.5.2 Thermobarometry and Oxybarometry

As shown in Figure 3.3, the rim of the garnet is in equilibrium with orthopyroxene and clinopyroxene, and thus olivine is also assumed to be in equilibrium with this assemblage. This assumption underlies our determination of the equilibrium pressure and temperature for the garnet using a variety of thermometers and barometers as shown in Table 3.2. For any combination of thermometer and barometer, an iterative process is used to determine the equilibrium temperature and process. For example, the Al in orthopyroxene barometer (P[NG₈₅] - Nickel and Green, 1985) gives a pressure of 4.6 GPa for the rim of ga4 when combined with the Ca in orthopyroxene thermometer (T[Ca-opx] - Brey et al., 1990), however it returns a lower pressure of 4.3 GPa when

combined with the two-pyroxene thermometer (T[TA98] - Taylor, 1998). The Cr in clinopyroxene barometer (P[NTcpx] - Nimis and Taylor, 2000), gave a pressure of 4.1 GPa when combined with the enstatite in clinopyroxene thermometer (T[NTcpx] - Nimis and Taylor, 2000). Another garnet-orthopyroxene barometer (P[BKN] - Brey and Köhler, 1990) gives a pressure of 4.5 GPa, when combined with a two-pyroxene thermometer (T[BKN] - Brey and Köhler, 1990). The difference between the values obtained using the garnet-orthopyroxene barometers (P[NG85] and P[BKN]) and the Cr in clinopyroxene barometer (P[NTcpx]) is primarily attributed to the use of garnet compositions, and the exchange mechanisms within the system. The difference between the two values calculated using P[NG85] is close to the error of the barometer (± 0.3 GPa) and can be related to the differing methods for determining temperature, either single or two-clinopyroxene. The values determined using the three garnet-orthopyroxene barometers are likely to be within error of each other.

There was also some variation the temperatures determined using different iterative thermometers, the rim of Ga4 was found to have equilibrated at 1110 °C using T[Ca-opx] in conjunction with P[NG85], whilst a value of 1040 °C was determined when using T[TA98] in conjunction with P[NG85]. Combining T[NTcpx] and P[NTcpx] gave a temperature of 1020 °C. A temperature of 1160 °C was obtained using T[BKN] in conjunction with P[BKN]. Two different Ni in garnet thermometers were also used to determine the equilibrium temperature, using the Ni content determined by LA-ICP-MS (T[G89] - Griffin et al., 1989, T[C94] - Canil, 1994). A temperature of 1180 °C was determined using T[C94], whilst T[G89] gave a value of 1360 °C. The value obtained using T[C94] is close to that obtained using T[BKN], however it is outside of the calibrated temperature range for that thermometer (900 – 1100 °C). The temperature

obtained using T[G89] is anomalously high, which may be related to the rim being enriched in Fe, Cr and Ni relative to most of the samples studied in the derivation of the thermometer, this value was not considered any further as it deviated so far from all other thermometers. Overall the determined temperatures vary by 130 °C, indicating that would all fall within ± 65 °C of the mean, which is a level of accuracy similar to the standard error of most thermometers (± 50 °C).

All the temperatures and pressures previously discussed were calculated using compositional data that accounted for the Fe^{3+} content in the garnet (as determined using XANES), however many studies of garnet peridotites fail to account for this during the determination of the equilibrium conditions. Table 3.2 also shows the values obtained when the temperature or pressure is calculated assuming all Fe is present as Fe^{2+} . There is no significant difference in the calculated temperatures, which is expected as the garnet composition will not affect the two-pyroxene thermometers, whilst the small amount of Fe^{3+} in orthopyroxene does not affect the garnet-orthopyroxene thermometers (Matjuschkin et al., 2014). Failing to account for the Fe^{3+} content of garnet when determining pressure also has a minor effect, leading to a slight overestimation of between 0.1 and 0.7 GPa. Thus the effect of Fe^{3+} on the garnet-orthopyroxene barometers is minimal, however when data is available it should still be used.

The temperature and pressure obtained using the combination of P[NG85] and T[Ca-opx] were used in the determination of the $f\text{O}_2$, though the small variations between the combinations are not likely to have a significant effect on the calculation. These

estimates of temperature and pressure were used in conjunction with oxybarometer of Stagno et al. (2013) to obtain $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ values of -2.4 for the core and -1.0 for the rim of Ga4. The older calibration of Gudmundsson and Wood (1995) gives values of -3.8 for the core and -1.2 for the rim (Table 2). The newer calibration by Stagno et al. (2013) is preferred for this sample as it was calibrated over a pressure range of 3 to 7 GPa, which is appropriate for our samples whereas the earlier calibration is based upon experiments at only 3 GPa. The $f\text{O}_2$ value obtained for the core is more reducing than that obtained by McCammon et al. (2001) for a different xenolith from the same kimberlite [$\Delta\log f\text{O}_2^{[\text{FMQ}]} = -2.1$ using Gudmundsson and Wood (1995)], this can be explained in part by the lower pressure of garnet equilibrium (3.7 GPa compared to 4.7 GPa), along with molar volume change in that oxybarometer reaction, $2\text{Fe}_3\text{Fe}_2\text{Si}_3\text{O}_{12} = 4\text{Fe}_2\text{SiO}_4 + \text{Fe}_2\text{Si}_2\text{O}_6 + \text{O}_2$, which shifts to the left at higher pressures.

3.5.3 Metasomatic Implications

The position of the core and rim of both ga4 and ga6 in P - $f\text{O}_2$ space is shown in Figure 3.7. The garnet cores fit within the general trend of decreasing $f\text{O}_2$ with increasing depth, as defined by previous studies, whilst the rims are several orders of magnitude more oxidised and cross the EMO/G buffer, entering the region in P - $f\text{O}_2$ space where diamond may become destabilised in favour of carbonates. Metasomatism of the lithospheric mantle is common (McGuire et al., 1991, Lazarov et al., 2009, Creighton et al., 2009, 2010, Yaxley et al., 2012), however the survival of metasomatic rims is a rarely observed phenomenon. Under mantle conditions it is expected that any such zonation will be rapidly lost as diffusive re-equilibration homogenises the crystal over a short time period. The preservation of these rims, along with the very narrow diffusion profiles at the interface between the core and rim, indicate that the metasomatism

occurred very shortly (2-10 years) before the xenoliths were quenched by entrainment and transport to the surface by the kimberlite (more details in Chapter 4). For garnets that had sufficient time to re-equilibrate, the fO_2 would be expected to be somewhere between that of the metasomatic event (rim) and the original cratonic value (core), giving a mass-balance average that masks the true fO_2 of metasomatism. The metasomatic oxidising trend observed in garnets from the Udachnaya East kimberlite, Russia (Yaxley et al., 2012), could easily be the result of such a process. This means that mantle metasomatism may actually be more oxidising than previously thought and more likely to threaten the stability of diamond.

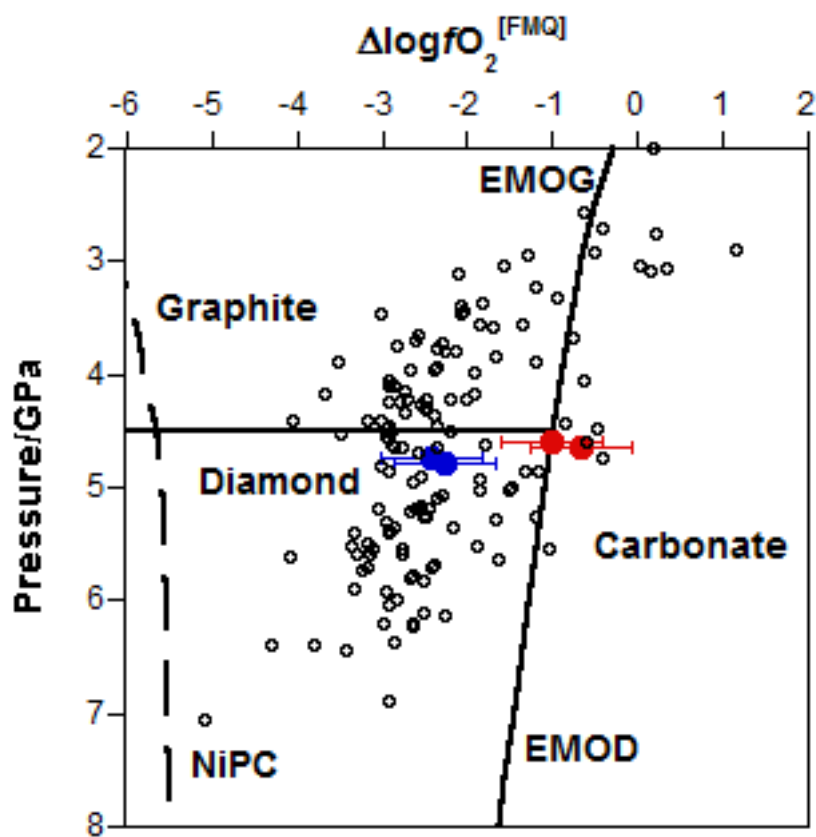


Figure 3.7: Pressure and $\Delta\log fO_2^{[FMQ]}$ of the core (blue circles) and rim (red circles) for ga4 and Ga6, along with data from other peridotite xenoliths (open circles – Creighton et al. 2009, 2010; Lazarov et al. 2009; Yaxley et al. 2012, unpublished data; Woodland and Koch 2003; and Chapter 4). The stability fields of graphite, diamond and carbonate are shown, along with Ni precipitation curve (NiPC) and the EMOG/G reaction.

3.6 Conclusion

Iron K-edge XANES spectroscopy was used to determine the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the core and rim of two zoned garnets found in a garnet peridotite xenoliths from the Wesselton kimberlite. This was then used to determine the $f\text{O}_2$ represented by the original cratonic mantle (core - $\Delta\log f\text{O}_2 = -2.3 - 2.4$) and the overprinting metasomatic event (rim - $\Delta\log f\text{O}_2 = -0.7 - 1.0$). This metasomatic event was oxidising enough to threaten the stability of diamond in this region of the cratonic mantle. A quantitative map of the distribution of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in a segment of garnet was produced and showed that zonation in Fe^{3+} followed the same trend as other elements. The presence of the compositional zoning is an indicator that metasomatism occurred close enough to the time of eruption to prevent homogenisation of the garnet through diffusive re-equilibration.

Chapter 4: Diffusion of major and minor elements within mantle garnet: A study of naturally zoned crystals using NanoSIMS

Linear compositional profiles in zoned garnet from a peridotite xenolith from the Wesselton kimberlite, South Africa have been examined using EPMA (Na, Al, Mg, Ca, Cr, Fe, Mn and Ti) and NanoSIMS (Na, Ca, Cr, Fe, Mn, Ti and Y). Profile lengths (<10 μm) determined by NanoSIMS were consistently shorter than those obtained by EPMA, indicating that the high spatial resolution (800 nm spot size) of the NanoSIMS was necessary to adequately measure the profiles. The profiles were modelled as a diffusive process by fitting to a solution of Fick's second law, with published diffusivity values then used to determine the time taken for Ca, Fe and Mn to reach the observed state of frozen disequilibrium. Estimates of the time taken to yield the diffusion profiles were 2 – 10 years based on Ca, whilst Mn and Fe were less than 100 days. This timeframe was then used to determine the diffusion coefficients, relative to Ca, of Na, Ti, Fe, Cr, Mn and Y. These elements fell into three groups based upon their relative diffusivities: Mn ($\log D = \text{Ca} + 0.53 \text{ m}^2\text{s}^{-1}$) and Fe ($\text{Ca} + 0.61 \text{ m}^2\text{s}^{-1}$) diffused faster than Ca; Na ($\text{Ca} + 0.11 \text{ m}^2\text{s}^{-1}$) and Cr ($\text{Ca} + 0.05 \text{ m}^2\text{s}^{-1}$) diffuse at a similar rate; whilst Ti ($\text{Ca} - 0.26 \text{ m}^2\text{s}^{-1}$) and Y ($\text{Ca} - 0.17 \text{ m}^2\text{s}^{-1}$) diffuse slower than Ca. This is the first determination of the diffusion coefficient for Na, Cr, Ti and Y in peridotitic garnet. The mixing behaviour between the core and rim of the garnet was also investigated by examining the changes in the REE_N patterns, and it was found that as little as 8% of rim material is necessary to remove the depleted HREE_N signal observed in the core.

4.1 Introduction

Minerals within the Earth's mantle have the ability to record changes in composition, temperature, and pressure and oxygen fugacity over time. Garnet is one of the best minerals for recording these changes, as it is stable over a large pressure range and is resistant to alteration when transported to the surface (Ganguly, 2010, Carlson, 2012). Changes in composition may relate to changes in fluids or melts in the localised area and are best recorded by zoning within crystals, which may be subsequently modified by diffusive relaxation. The length and shape of concentration-distance profiles at this interface, if they are interpreted as diffusion profiles, can be used to determine either the duration of a thermal event or the rate at which diffusion occurred (Carlson, 2006).

In order to access the information available from a diffusion profile and related zoning it is necessary to experimentally determine the rate at which individual elements diffuse under the relevant P, T and fO_2 conditions. Once these rates of intracrystalline diffusion are constrained it is possible to determine timescales that relate to the thermal events and metasomatic processes, which are responsible for changes in garnet composition (Griffin et al., 1996, Carlson, 2006). In addition to metasomatism, diffusion rates can also be used to quantify regional heating or cooling, geologic uplift and to properly interpret garnet-based geochronometers and thermometers (Carlson, 2006, Chakraborty, 2008).

Chemical zonation in garnet from the mantle is relatively rare, though it has been identified in a small number of garnet peridotites from southern Africa, including Lesotho (Smith and Boyd, 1987), the Frank Smith mine (Griffin et al., 1989) and the

Wesselton mine, South Africa (Griffin et al., 1999, McCammon et al., 2001); as well the Colorado Plateau, United States (Smith, 1988, Smith and Ehrenberg, 1984).

In this contribution, zoned garnet crystals in a garnet peridotite xenolith from the Wesselton kimberlite have been used to quantify the timescales related to the metasomatic event responsible for the zonation. We have used highly spatially resolved techniques, including electron probe microanalysis (EPMA) and NanoSIMS to measure the concentration profiles in these crystals. These profiles were then fitted to a solution of the diffusion equation and published diffusion coefficients were used to determine the time frame related to the formation of profile. The calculated times were then used to determine diffusion coefficients, relative to published values for Ca, for Na, Cr, Ti, Mg, Mn Fe and Y. This is the first time that these values have been obtained for Na, Cr, Ti and Y in peridotitic garnet.

4.2 Methods

4.2.1 Samples

Two garnet crystals (KBD12-ga4 and ga6) in a single garnet peridotite xenolith from the Wesselton kimberlite with strong compositional zoning were identified from our recent studies (Berry et al., 2013; Chapter 1). Backscattered electron (BSE) imaging and elemental mapping show that the rims are enriched in Na, Ca, Ti, Cr and Fe whilst Al and Mg are depleted relative to the core (Figure 4.1). These crystals equilibrated at 4.6 - 4.8 GPa (calculated using the Al-in-orthopyroxene barometer - Nickel and Green, 1985), at around 1120 °C (Ca-in-orthopyroxene thermometer - Brey and Köhler, 1990) (Table 4.1). Rare Earth Element (REE) patterns confirm that orthopyroxene is in

equilibrium with the rim of the garnet. There is a significant difference in $\Delta\log f_{O_2}^{[FMQ]}$ from core to rim, with KBD12-ga4 varying from -2.43 to -1.02 and KBD12-ga6 from -2.26 to -0.67 (determined using the method of Stagno et al., 2013).

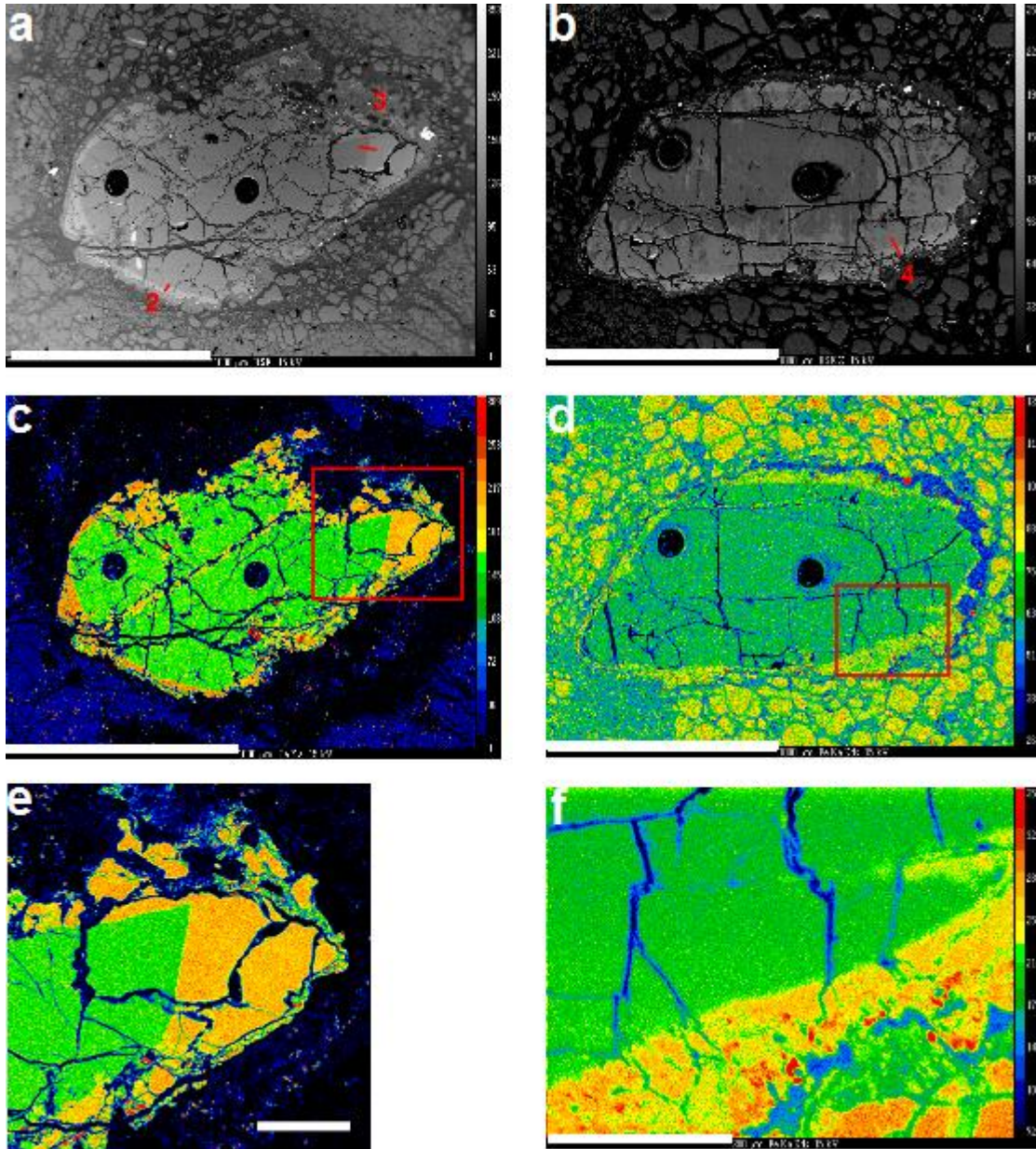


Figure 4.1: Back scattered electron images of: (a) KBD12gt4 and (b) KBD12gt6; elemental maps of (c) Ca in KBD12gt4 and (d) Fe in KBD12gt6; (e) and (f) higher resolution elemental maps as indicated in (c) and (d). Scale bars are 1000 μm in (a) to (d); and 200 μm in (e) and (f). The location of the NanoSIMS linescans are marked in (a) and (b). Black circles are pits from laser ablation analysis.

Table 4.1: Major element compositions (wt.% oxide), garnet end-member compositions, pressure (± 0.5 GPa) temperature (± 50 °C) and oxygen fugacity (± 0.6) of the samples (Chapter 1). End-members of garnet are almandine (alm), pyrope (prp), spessartine (sps), grossular (grs) and knorringite (kno)

	KBD12-ga4		KBD12-ga6	
	Core	Rim	Core	Rim
SiO ₂	42.41	41.17	43.40	41.63
TiO ₂	0.016	0.746	0.021	0.753
Al ₂ O ₃	19.51	17.29	20.78	18.03
Cr ₂ O ₃	5.815	6.763	4.871	6.195
FeO	5.847	8.466	4.200	6.934
MnO	0.243	0.257	0.291	0.255
MgO	22.76	19.52	22.32	20.37
NiO	0.002	0.025	0.005	0.022
CaO	4.125	5.886	4.134	5.538
Na ₂ O	0.014	0.084	0.017	0.148
K ₂ O	bdl	0.001	bdl	0.011
P ₂ O ₅	0.015	0.009	bdl	0.047
Total	100.8	100.2	100.0	99.9
X _{alm}	0.1069	0.1560	0.0809	0.1296
X _{prp}	0.7417	0.6413	0.7669	0.6783
X _{sps}	0.0045	0.0048	0.0057	0.0048
X _{grs}	0.0966	0.1390	0.1021	0.1326
X _{kno}	0.0503	0.0589	0.0444	0.0547
P (GPa)	4.74	4.61	4.78	4.65
T (°C)	1112	1116	1124	1118
$\Delta \log f_{O_2}^{[FMQ]}$	-2.43	-1.02	-2.26	-0.67

4.2.2 Electron Probe Microanalysis

Elemental mapping, back-scattered electron (BSE) imaging and analysis of the garnet compositions were performed using the Cameca SX100 microprobe at the Research School of Earth Sciences, Australian National University, as described in Chapter 1. Transects across the compositional interface were also obtained, using a step size of either 1 or 2 μm . A focused, 1 μm diameter beam was used with an accelerating voltage of 15 kV and a beam current of 20 nA; well characterised natural mineral samples were used as calibration standards. However, the electron beam excites a sample volume 3 – 5 μm in diameter, which leads to significant overlap between neighbouring analysis spots.

4.2.3 NanoSIMS Analysis

In order to better characterise the diffusion profiles, high resolution line-scans were performed with the CAMECA NanoSIMS 50 at the Centre for Microscopy, Characterisation & Analysis, University of Western Australia, using an O^- primary ion beam. The magnetic field of the mass spectrometer was tuned to deflect mass 89 (Y) into the fixed detector, allowing the electron multipliers on the four movable trolleys to be positioned to detect other lighter elements. The second detector was always used to detect the reference element, $^{29}Si^+$, with three different configurations being used during analysis, as the physical size of the detectors prevents simultaneous analysis of elements with similar masses, such as $^{23}Na^+$ and $^{24}Mg^+$ or $^{52}Cr^+$, $^{55}Mn^+$ and $^{56}Fe^+$. The first, third and fourth detectors were positioned so that the following three suites could be detected: [^{23}Na , ^{29}Si , ^{40}Ca , ^{52}Cr , ^{89}Y], [^{24}Mg , ^{29}Si , ^{40}Ca , ^{55}Mn , ^{89}Y] and [^{27}Al , ^{29}Si , ^{48}Ti , ^{56}Fe , ^{89}Y]. All secondary ions were detected simultaneously. The mass spectrometer was tuned to high resolution using an entrance slit of 30 μm , an aperture slit of 200 μm , and a 10% reduction in the signal at the energy slit. Two different spot configurations were used, one with a primary current of ~ 17 pA and the other ~ 1.6 pA, using a 200 μm source aperture (D0) and a 300 μm primary aperture (D1). Peak positions were calibrated using the NIST NBS610 reference glass for all elements, except Y and Cr, which were calibrated using xenotime and Cr-metal respectively.

High-resolution linescans were acquired using the linescan – beam control mode on the NanoSIMS acquisition software. The software is used to acquire an image with a field of view of 25 μm and a resolution of 256×256 pixels, giving a pixel size of 98×98 nm, with a dwell time of 3 ms/pixel. These images, in conjunction with a coarse-scale line-scan were used to determine the position of the interface between the core and rim

of the crystal. Once the interface was identified, line-scans were defined that were perpendicular to it, and at each pixel on the line a small 3×3 pixel scan is performed around the central pixel. A ~ 17 pA beam with a diameter of ~ 600 nm gave an effective scan width of 800 nm. The dwell time was 500 ms/pixel, giving a total count of 4.5 s per point. Each point was pre-sputtered for two cycles (9 s) before the measurement was recorded on a third pass (final 4.5 s), this process allowed for the implantation of ions on the sample surface and the removal of any surface contamination. For the smaller spot, with a beam current of ~ 1.6 pA and a diameter of 300 nm, the effective scan width was 500 nm. A dwell time of 800 ms/pixel was used, giving a total count time of 7.2 s per measurement, with two passes performed at each point, one as pre-sputter and one for measurement. Data were corrected for 44 ns deadtime, and each element was expressed as the total amount of counts measured. To remove potential tuning artefacts, such as variations in the primary beam current or secondary ion transmission, each measurement was normalised to the $^{29}\text{Si}^+$ signal.

Linescans were obtained using a ~ 17 pA beam current first, with each elemental suite being collected in individual scans parallel to each other, approximately $3 \mu\text{m}$ apart; all scans of one suite were collected before moving on the next set of elements. Scans with a lower beam current of ~ 1.6 pA, and therefore a smaller scan width, were superimposed over the same line as used previously.

4.3 Results

4.3.1 Electron Probe Microanalyser Linescans

EPMA linescans were performed on both crystals, including a 34 μm transect with 1 μm spacing on KBD12-ga4, near NanoSIMS position 3 (Figure 4.1a) and transects of ~ 80 μm length at the top and bottom of KBD12-ga6 (Figure 4.1b). The concentration profiles obtained for most elements show a sigmoidal shape with the width varying between elements (Figure 4.2), when the profile width is defined as the width between the plateaus at either end of the profile. Mean profile lengths vary from 5 to 12 μm , Mg and Fe have the longest profiles whilst Ti and Al are the shortest (Figure 4.3). Profile lengths for Fe, Mg, Ca, Na and Cr clusters between 8 and 12 μm , whilst Al and Ti have shorter profile lengths, though there is still overlap with the lower ranges of the other elements. The variation between the rim and core values for Mn was similar to the scatter in the data and thus the profile width could not be determined.

4.3.2 NanoSIMS Linescans

Linescans using NanoSIMS were performed at two locations on KBD12-ga4 (Figure 4.1a) and one on KBD12-ga6 (Figure 4.1b), with both small and large diameter spots used to measure each of the three suites of elements at each site. The measured concentration profiles from KBD12-ga4 exhibit a sigmoidal shape for all elements except Al and Mg. The scatter in the data for these elements is similar to the difference between the core and rim and as such the profile could not be determined. Figure 4.4 shows four different Ca profiles from two locations on KBD12ga4, which all have very similar shapes and profile lengths, showing that the results are reproducible. Profiles from KBD12-ga6 generally exhibit a sigmoidal shape, though some elements have a more defined shape than others. Y, Ti and Na showed the most well defined sigmoidal

shapes whilst the change between the core and rim values had a more curved profile for Ca, Cr and Mg (Figure 4.5). The scatter of the data for Al obscured any recognisable profile between the core and rim.

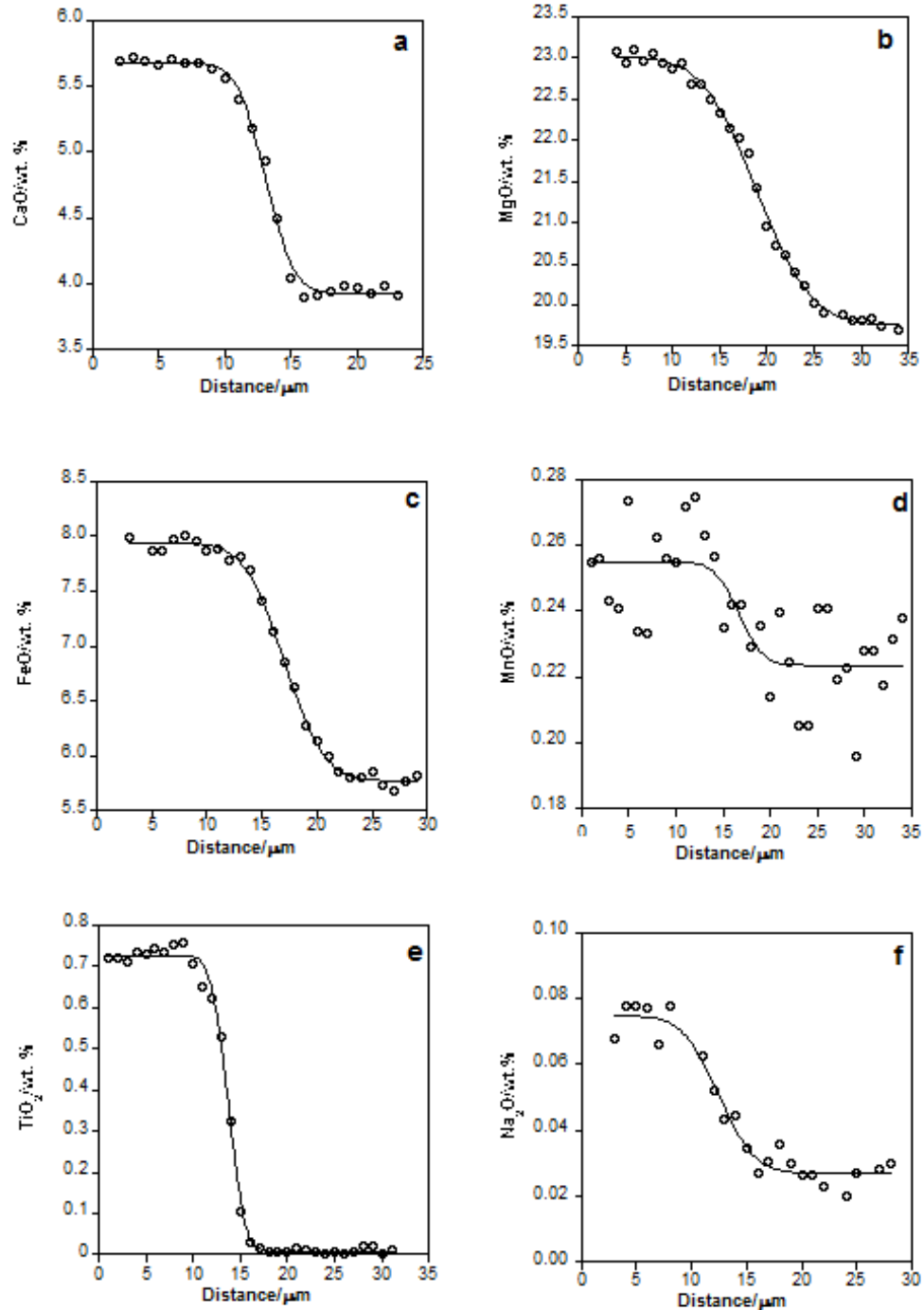


Figure 4.2: Diffusion profiles measured by EPMA for KBD12-ga4 for different oxides: (a) CaO, (b) MgO, (c) FeO, (d) MnO, (e) TiO₂ and (f) Na₂O. The open circles are the measured concentrations whilst the black line is the fitted solution to the diffusion equation.

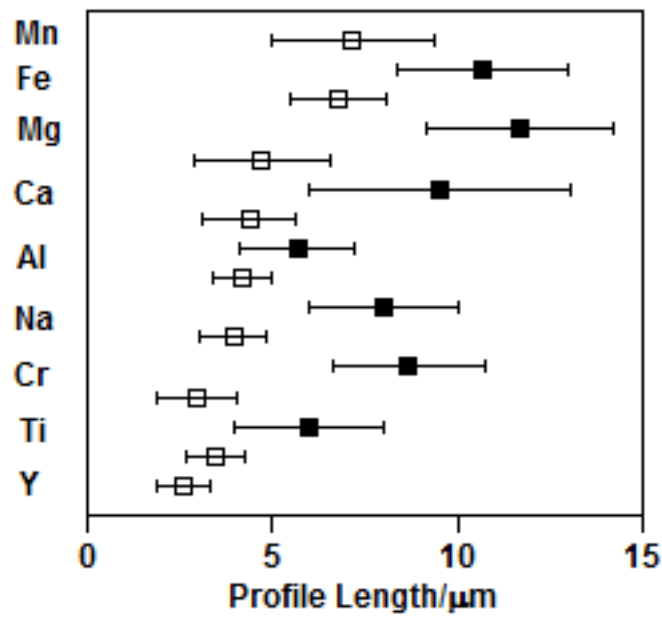


Figure 4.3: Mean length of the compositional profiles observed by EPMA and NanoSIMS for different elements. Black squares are EPMA results, open squares are NanoSIMS results. Only NanoSIMS data is available for Mn and Y.

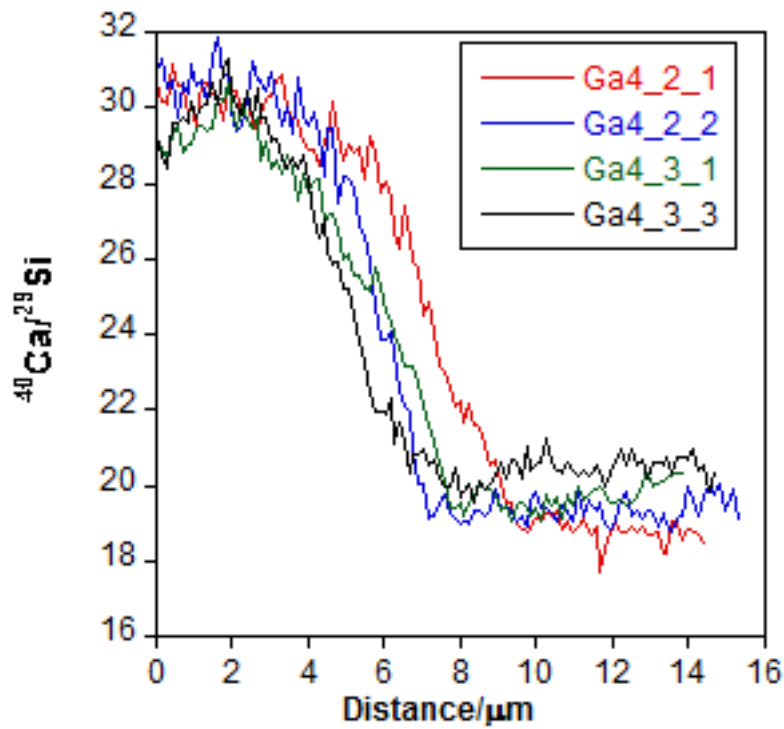


Figure 4.4: Comparison of compositional profiles for Ca from four profiles at two locations on sample KBD12ga4, obtained using NanoSIMS.

Profile lengths were determined by visually examining the data to identify where the profile had levelled off at either side of the change in composition and measuring the length between these points. The mean profile length varied from 2.6 to 7.2 μm (Figure 4.3). Y, Ti and Cr had the shortest profiles of between 2.6 and 3.5 μm , followed by Na, Al, Ca and Mg, with lengths from 3.9 to 4.7 μm . The longest profiles of 6.8 to 7.2 μm were exhibited by Fe and Mn. The range of observed profile lengths, shown by the standard deviation in Figure 4.3, increases with the length of the profile.

4.4 Discussion

4.4.1 Comparison of Core and Rim Signals

The NanoSIMS method used to record the compositional profiles is not a quantitative technique and the signal can't easily be converted into concentration, however the ratio of the core and rim signals can be used to compare the result with EPMA and laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS) results (Figure 4.6). Major elements, including Fe and Ca, show a very good agreement between the NanoSIMS and EPMA ratios; however the NanoSIMS signal suggests a larger difference between the core and rim than EPMA. The ratios for Cr and Mn fall close to but below the 1:1 line, again indicating a larger difference in the NanoSIMS signal.

Sodium sits slightly above the 1:1 line, indicating a larger difference based on the EPMA results. The comparison for Ti shows a ratio approximately three times larger for EPMA, indicating a substantial difference; which may be related to the low Ti concentration in the core, which is less well constrained. The ratios obtained from LA-

ICP-MS for Ti and Y both fall above the 1:1 line, with the variation in Ti being similar to EPMA, whilst the ratio for Y is approximately 1.5 times that observed by NanoSIMS.

4.4.2 Profile Lengths: EPMA vs. NanoSIMS

The compositional profiles were initially measured using EPMA, with a step size of 1 or 2 μm and an effective analysis volume with a diameter of 3-5 μm , and they were found to be 5-10 μm in length. However as the analysis volume was similar in size to the diffusion profile, we could not be certain if this causes any distortion in the observed diffusion profile. Therefore the higher resolution of NanoSIMS was employed to record the diffusion profile with a step size of 100 nm and an approximate analysis spot of 800 nm. Both of these techniques have a significant overlap in the area analysed by adjacent spots, which will affect the shape of profile. The effect of this overlap on the NanoSIMS measurements is minimised by rastering a 3×3 pixel grid at each location.

The length of the profiles obtained using NanoSIMS is consistently shorter than those obtained using EPMA (Figure 4.3), with the observed range also smaller. This indicates that the higher step-size and analysis volume used in EPMA leads to an overestimation of the length of the compositional profile compared to NanoSIMS. The larger number of analysis spots in each profile obtained using NanoSIMS also helped to improve the understanding of the shape of the profile and increased the resolution of the profiles.

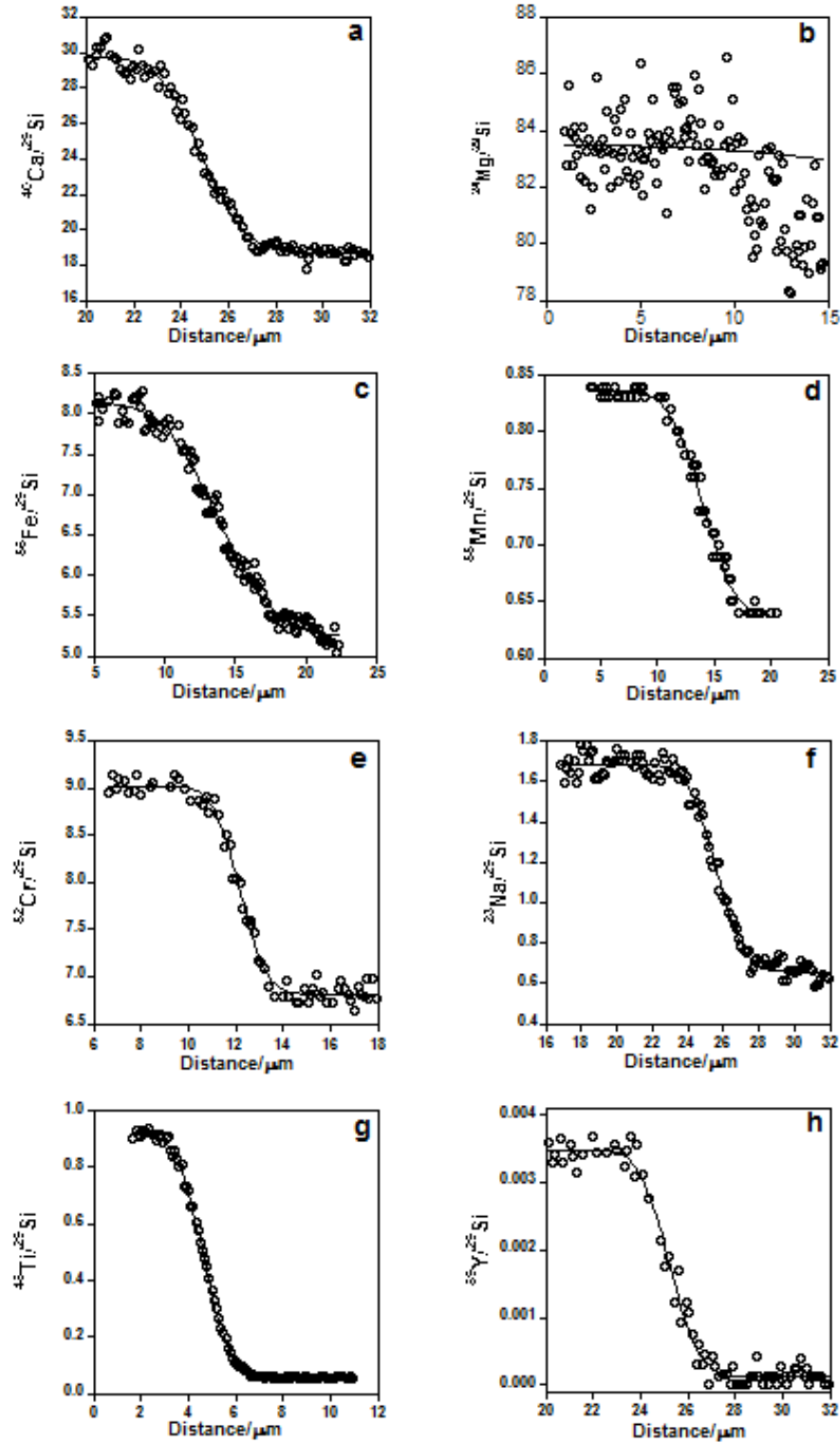


Figure 4.5: Compositional profiles as measured by NanoSIMS, as well as modelled solution to the diffusion equation. Profiles from sample KBD12-ga4 are (a) Ca, (b) Mg, (c) Fe, (d) Mn, (e) Cr, (f) Na, (g) Ti and (h) Y. Profiles from sample KBD12-ga6 are (i) Ca, (j) Fe, (k) Ti and (l) Y. All profiles except (g) were obtained using a beam current of ~ 17 pA, (g) was obtained using a beam current of ~ 1.6 pA. Measured results are shown as open circles whilst the black line is the modelled diffusion profile. Some profiles have been cropped to only show the interface the plateau at either side.

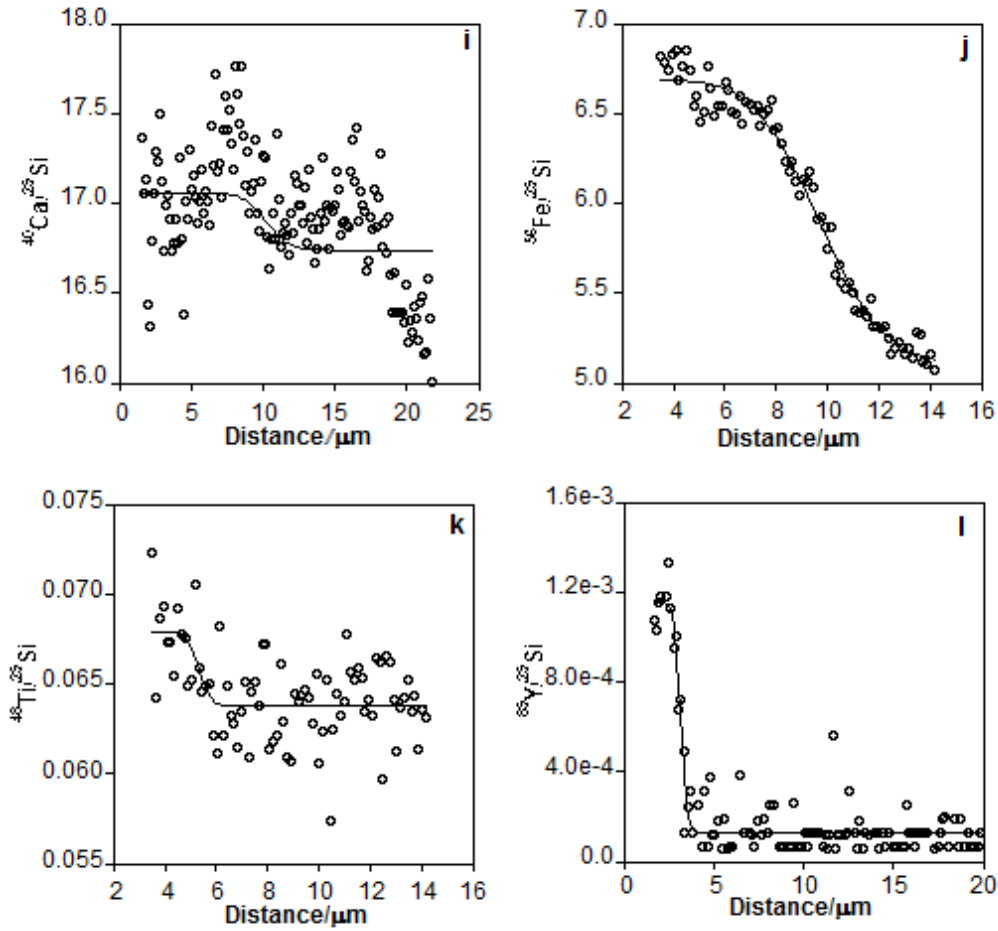


Figure 4.5: Continued.

4.4.3 Diffusion Modelling

The compositional profiles observed across the zoned interface are similar in shape to those observed for experimental interdiffusion profiles in coupled garnet systems (e.g. Loomis et al., 1985); thus it was decided to model the profile as a diffusive process. The compositional profiles recorded by either EPMA or NanoSIMS were fitted to a solution of Fick's second law for one-dimensional diffusion in an extended source of infinite extent, as solved by Crank (1975).

$$C(x, t) = \frac{1}{2} C_0 \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \quad (4.1)$$

Where $C(x,t)$ is the concentration at point x at time t , C_0 is the initial concentration, erfc is the complimentary error function, x is a position along a one dimensional line, and D is the diffusion coefficient with units such as m^2s^{-1} . The temperature dependence of diffusion coefficients for major elements (Ca, Mg, Fe and Mn) in garnets has been determined by the diffusion couple method at high temperatures ($>1000^\circ\text{C}$), often using synthetic end member compositions (e.g. Cygan and Lasaga, 1985, Loomis et al., 1985, Chakraborty and Ganguly, 1992, Chakraborty and Rubie, 1996, Ganguly et al., 1998). These calibrations can have large errors when extrapolated down to lower temperatures, however attempts have been made to record diffusion rates on natural samples to minimise this (Carlson, 2006). As diffusivity varies due to garnet composition, temperature, pressure and oxygen fugacity, it is necessary to adjust published values to suit the conditions relating to the system being modelled. An empirical relationship that links a number of studies for Fe, Mg, Mn and Ca using a least-squared regression has been established by Carlson (2006).

Diffusion coefficients are assumed to be constant throughout the thermal event (i.e. constant T , P and $f\text{O}_2$ conditions) and equal in both the core and rim of the garnet. The latter assumption is not strictly correct given the difference in major element composition across the zones, but the symmetry of diffusion profiles at the measured resolution allows this assumption to be made without affecting the results. The initial situation is modelled with the interface being a step function from the region of high concentration to a region of low concentration. As the width of the diffusion profile is very small compared to the extent of the surrounding zone, modelling assumes that both the core and rim extend infinitely away from the region of diffusion.

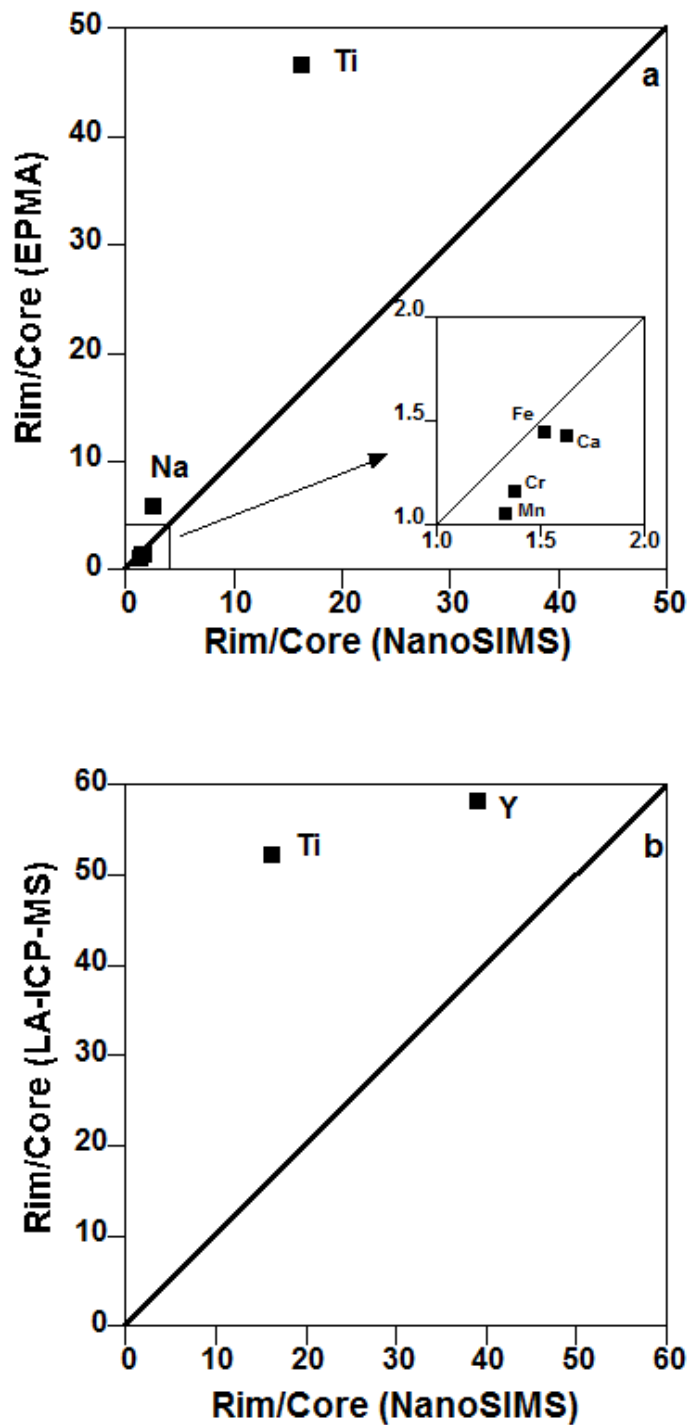


Figure 4.6: Comparison of the ratio of signals obtained for compositional profiles using different techniques. (a) EPMA vs. NanoSIMS, inset image zooms in on elements with ratios below 2 and (b) LA-ICP-MS vs. NanoSIMS. The black line has a slope of 1 and indicates that the two techniques returned the same ratio.

For the sampled garnets, equation (4.1) must be modified slightly to account for the fact that the measurements are not centred on a zero point and also that the initial low concentration is not zero. Thus we use the following equation, which is simply a translation of equation 4.1 and does not change the validity of the solution:

$$C(x, t) = \left(\frac{1}{2} C_{\text{diff}} \operatorname{erfc} \frac{x - F_c}{2\sqrt{(Dt)}} \right) + C_{\text{low}} \quad (4.2)$$

Where C_{diff} is the difference in concentration between the high and low values of the diffusion profile, C_{low} is the low concentration, which shifts the profile and allows for the low side of the interface to be treated as $C = C_0$. A correction factor, F_c , is used to shift the profile to the centre of the sigmoid on the interface. This equation is based upon a profile that has high concentration on the left and low concentration on the right when concentration is plotted relative to position; if the profile occurred in the opposite direction, it was reversed before any fitting occurred to give the profiles observed in Figure 4.5. The solution to the diffusion equation is produced by minimising the least-squares fit to the observed data. If either D or t is known, the other can be obtained by forcing the theoretical curve to the data.

The solution to the diffusion equation was first used to determine the time required to produce the observed diffusion profiles, with diffusion coefficients for Fe, Ca, Mg and Mn calculated for a known garnet composition, pressure, temperature and oxygen fugacity (Carlson, 2006).

$$\ln D^* = \ln D_{0,alm}^* + k(a_0 - a_{0,alm}) + \frac{-(Q+P\Delta V^+)}{RT} + \frac{1}{6} \ln \left(\frac{fO_2}{fO_2^{gr}} \right) \quad (4.3)$$

Where D^* is the garnet self-diffusion coefficient, D^*_0 is a frequency factor, k is a sensitivity factor to the unit cell dimension a_0 , Q is an Arrhenius activation energy, ΔV^+ is an activation volume, R is the gas constant and fO_2^{gr} is the oxygen fugacity of the graphite-oxygen buffer of Chakraborty and Ganguly (1992). Values for $\ln D^*_{0,alm}$, k , Q , and ΔV^+ , based upon least-squares error minimization of a large number of data sets, were obtained from Carlson (2006) and are shown in Table 4.2. The unit cell dimension can be calculated as a weighted average of the mole fractions of the following end-members: almandine (Fe^{2+} component), pyrope (Mg), spessartine (Mn) and grossular (Ca); for which published values are available (Ganguly et al., 1993, Geiger and Feenstra, 1997). This unit cell calculation ignores the significant Cr_2O_3 component (4-6 wt. %) in the garnet. The average unit cell dimension for these crystals is 1.1515 nm; incorporating the Cr content in this calculation will not have a significant effect, with difference in dimension being $\sim 0.1\%$ (Woodland et al., 2009).

Once D had been calculated for the major divalent cations, Mn, Fe, Mg and Ca, the measured diffusion profiles obtained using NanoSIMS were used to extract the time. Least squares regression is used to fit the recorded diffusion profile to the equation (4.2), with the difference between the data and the model minimised. Following the determination of the time from the major cations, the same process was then used to determine the diffusivities of other elements (Ti, Na, Cr, and Y) based on the calculated time. Times for the element with the best-constrained profile, Ca, were also used to determine diffusivities for the other major divalent cations, which were compared with published values.

Attempts were made to fit all profiles obtained using both EPMA and NanoSIMS to equation (4.2), however the difference between the data and model was too large for some profiles. An acceptable fit was based on the R^2 value obtained, which was maximised in all cases. The fits obtained for Al, Cr and Mn from EPMA were not close enough to the observed data for any further modelling to occur. An acceptable difference between the data obtained using NanoSIMS and the model for Al and Mg could not be obtained, so no further investigation into these elements was undertaken. The shape of the profiles obtained for Ca in sample KBD12-ga6 did not fit the model and thus it was not possible to confidently use any of the profiles from this sample in the determination of time or relative diffusivities.

4.4.4 Diffusion Timeframes

In modelling timescales using diffusion experiments, the assumption must be made, given our present level of understanding, that diffusion of an element in a given matrix can be described simply using a single diffusion coefficient. It has been suggested that Ca diffusion in garnet is more complex than other the other major divalent cations (Fe, Mg, Mn) in that the activation energy for atomic jumps is a function of activation energies on both the octahedral and dodecahedral sites (Chakraborty and Borinski, 2010), such that two coefficients are needed to describe the diffusive motion of the single cation. Given, however, that this effect is presently poorly understood and not quantified, it is assumed that the empirical equation of Carlson (2006) adequately describes diffusion rates for the purposes of determining timescales.

The timeframe associated with the diffusion event was determined based on the profiles obtained for the major divalent cations, Ca, Fe, Mg (EPMA only) and Mn (NanoSIMS

only) using published diffusivity values (Table 4.2). EPMA profiles gave a time of 13 years based on Ca, 7 years for Mg and 95 days for Fe (Table 4.3). The shorter profiles obtained using NanoSIMS correlated with shorter timeframes. A timeframe of 2 – 10 years was determined using Ca, whilst the Fe and Mn gave times between 20 and 100 days (Table 4.3). The difference between these values is strongly related to the difference in diffusion coefficients, with values for Fe and Mn two orders of magnitude higher than that of Ca; whilst profiles for Fe and Mn are about 2 μm longer than that of Ca ($\sim 4 \mu\text{m}$).

Table 4.2: Parameters taken from Carlson (2006) as used in the calculation of diffusion coefficients for Ca, Mg, Fe and Mn. Also shown are the calculated diffusivities, including values relative to Ca ($\log D_{\text{Ca}}$).

	Fe	Mg	Mn	Ca
$\ln D^*_{0,\text{alm}}$	-17.64	-19.95	-17.62	-22.57
K (1/nm)	465.7	419.9	496.9	511.1
Q (kJ/mol)	264.55	244.21	264.44	230.56
ΔV (cm³/mol)	13.568	8.565	9.631	9.795
a_0 (nm)	1.1525	1.1456	1.1614	1.1852
$\log D$ (m²s⁻¹)	-18.29	-19.27	-18.30	-20.45
$\log D_{\text{Ca}}$ (m²s⁻¹)	2.16	1.18	2.16	

These timeframes are extremely short in geological terms and are substantially quicker than the several 10^4 years estimated by Griffin et al. (1999) for Ca, Zr and Y, however the diffusion profiles for those samples were much longer ($>100 \mu\text{m}$) than observed in the current study. Sheared garnet peridotite xenoliths, from Frank Smith mine, South Africa, with similar zoning patterns as seen in the current study were analysed using a proton probe (Griffin et al., 1989). Diffusion in these samples was modelled to have occurred in less than 240 years; however the uncertainty is up to three orders of magnitude, which overlaps with results from this study.

4.4.5 Relative Diffusivities

Diffusion coefficients for Na, Fe, Mg, Mn, Ti, Cr and Y, relative to published values for Ca, were determined using the time obtained for Ca (Table 4.3). The elements fall into three groups based upon their relative diffusivities, as determined using NanoSIMS: with Fe ($\log D = \text{Ca} + 0.61 \text{ m}^2\text{s}^{-1}$) and Mn ($\text{Ca} + 0.53 \text{ m}^2\text{s}^{-1}$) diffusing faster than Ca; Na ($\text{Ca} + 0.11 \text{ m}^2\text{s}^{-1}$) and Cr ($\text{Ca} + 0.05 \text{ m}^2\text{s}^{-1}$) diffusing at a similar rate to Ca; with Ti ($\text{Ca} - 0.26 \text{ m}^2\text{s}^{-1}$) and Y ($\text{Ca} - 0.17 \text{ m}^2\text{s}^{-1}$) diffusing slower than Ca. The relative diffusivities determined for Fe and Mn are significantly slower than those calculated for published values ($\text{Ca} + 2.16 \text{ m}^2\text{s}^{-1}$ for both Fe and Mn). This indicates that published diffusion coefficients for Fe and Mn are not necessarily suitable for modelling diffusion in garnet formed at similar conditions to those in this study.

Table 4.3: Diffusion times as determined from diffusion profiles obtained by EPMA and NanoSIMS in days. Diffusivity values determined for a variety of elements, relative to published values for Ca, using the modelled diffusion profiles and either the time obtained for Ca. Only a single profile was modelled using EPMA data, thus no standard deviation is presented.

	EPMA	NanoSIMS	
Time (days)		Average	Std Dev
Ca	4861	2070	993
Fe	95	62	13
Mg	2437		
Mn		72	37
Log D/m²s⁻¹ (relative to Ca)			
Na	0.28	0.11	0.39
Ti	-0.18	-0.26	0.01
Fe	0.59	0.61	0.16
Mg	1.34		
Cr		0.05	0.48
Mn		0.53	0.50
Y		-0.17	0.25

Diffusion rates for Fe, Mn and Mg have been observed to be faster than Ca in a variety of natural (Kohn, 2004) and experimental studies (Cygan and Lasaga, 1985,

Chakraborty and Ganguly, 1992, Ganguly et al., 1998). However these experiments have not been performed at similar conditions to the current study, with a maximum pressure of 4.0 GPa (Ganguly et al., 1998), though some early studies were performed as low as 1 bar (Cygan and Lasaga, 1985), compared to pressures of 4.6 to 4.8 GPa. Experimental studies were also performed under more oxidised conditions close to the magnetite-hematite buffer, compared with our samples that are 1-2 orders of magnitude below the fayalite-quartz-magnetite buffer. Other detailed studies of diffusion in garnet have focussed on metamorphic settings, which are at lower temperatures and pressures, such as Kohn (2004), which estimated diffusion to have occurred over 500,000 years at 550 °C and 8 kbar. In addition, this discrepancy may relate to the aforementioned (but currently poorly constrained) potential dependence of Ca diffusion on diffusive jumps on two sites, which leads to a discrepancy in relative Ca-Fe, Mg diffusion rates between natural and experimental garnets.

Previous studies into the diffusion of Cr and Y in garnet have focussed on metamorphic garnets at lower temperature and pressure to this study. Studies of the diffusion profiles observed in natural almandine from the Makhavinekh Lake Pluton, Labrador found the diffusion coefficients for Y, Cr and REEs to be 0.5-1.5 log units below that of the major divalent cations at ~700-900 °C and 0.53 GPa (Carlson, 2012). The profiles observed in these garnet are substantially longer than those observed by this study (10-20 mm compared to <12 µm), whilst the composition of the garnet was significantly different; being close to end-member almandine, with small amounts (<2 wt.%) of CaO (Berg, 1977, McFarlane et al., 2003) and trace amounts (<500 ppm) of Cr (Carlson, 2012); compared to the Cr-rich pyrope garnet of this study. Our results, which show the diffusion coefficient of Y to be 0.17 ± 0.25 log units below that of Ca, are slightly faster

to those of Carlson (2012) , however, Carlson showed that the difference between Ca and Y decreases with increasing temperature and as such the results may be similar at equivalent conditions. Direct comparison of the results for Cr are difficult as Cr_2O_3 is a major component of the garnet in this study, being present at 4-7 wt.%, which is higher than Ca; whilst in Carlson's study it was a trace component.

Whilst there have been some studies on Cr and Y, there have not been previous determinations of the diffusion coefficients for Na and Ti in garnet. Investigation of all these elements in peridotitic garnets has been rare and this study was a unique opportunity to expand our understanding of diffusion in garnet over more minor and trace elements (Table 4.3). It is notable that the rates of diffusion of the measured cations cluster around two values; the faster diffusing Fe, Mn and Mg, and the slower diffusing Na, Cr, Y, Ti and Ca. This is a commonly observed phenomenon in other silicates; the diffusion of most cations in olivine appear to cluster around the rates of either Fe-Mg interdiffusion (e.g. various cations - Morioka, 1980, Spandler and O'Neill, 2010) or Si self-diffusion (e.g. Ti in olivine - Cherniak et al., 2012), depending on their site location. The diffusion rates of trace elements in silicates are generally fixed to the rate of the inverse flux of the major element occupying the same site in the crystal structure; if the major element is unable to vacate the site, no position will be available for the trace element to move into. The attainment of charge balance is also necessary during the diffusion process; this can be accomplished in a simple system by vacancy production or removal, or in a more complex natural system by coupled substitution and diffusion. Some elements, such as Na^+ and Y^{3+} , are not able to substitute directly onto their preferred dodecahedral site without charge balance from other elements, such that their diffusion rate is effectively coupled to that of another element. Therefore, the

relative diffusion coefficients calculated in this study may not be relevant in other settings where different major and trace element compositions exist; but provide the first set of data for peridotitic garnets of this type.

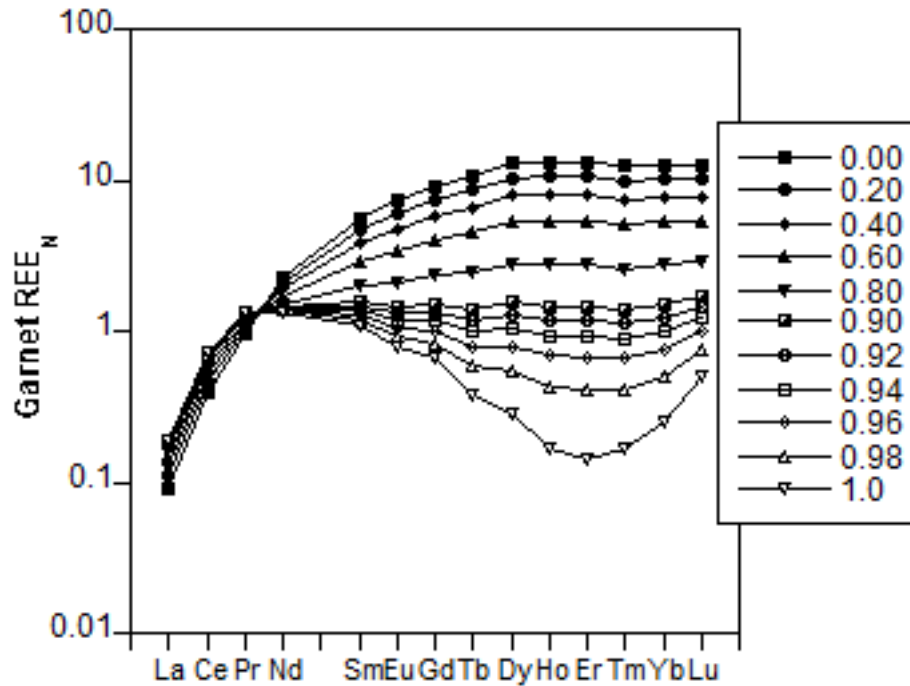


Figure 4.7: Primitive Mantle normalised garnet REE patterns, show the mixing between the core and rim of KBD12ga4. Individual patterns are shown as a fraction of core material, thus 1.0 is the core and 0 is the rim.

4.4.6 Geological Implications

The existence of the compositional zones, combined with the short timescales calculated by diffusion modelling indicates that there was insufficient time between the onset of the metasomatic event responsible for the zoning, and the entrainment of the peridotites in the erupting kimberlite magma, to allow for complete re-equilibration in the crystals. Other studies of similar zoning in peridotitic garnet have suggested that the zones were formed close to the time of entrainment and eruption (Griffin et al., 1989, 1999, Chakraborty and Ganguly, 1992). If it can be assumed that the eventual fate of a zoned

crystal is re-equilibration until it is homogenous, with a composition that is a weighted average of the pre-existing core and the metasomatic rim, then the presence of zones indicates that the process was interrupted, and potentially quenched by its entrainment in the kimberlite magma and subsequent emplacement in the crust. Primitive Mantle normalised garnet rare earth element (REE_N) patterns for the core show a ‘sinusoidal’ pattern with depleted heavy REE_N ($HREE_N$) whilst the rim has a ‘normal’ pattern with enriched $HREE_N$. Figure 4.7 shows the REE_N patterns that mixing varying proportions of the core and rim should produce. This shows that only a small input of rim material, as little as 8 %, is required to change the sinusoidal REE_N pattern into a normal pattern. This indicates that the proportion of incoming metasomatic material does not need to be very large to lead to full re-equilibration of garnet, eliminating any compositional zoning over time.

4.5 Conclusion

Detailed examination of the compositional profiles observed in zoned garnet from kimberlite-borne peridotite xenoliths was performed using NanoSIMS and EPMA. It was found that EPMA consistently overestimates the profile length, with profile lengths determined by NanoSIMS consistently shorter and having a smaller range in length. The compositional profiles were modelled as the product of a diffusive process. A timeframe of 2 – 10 years was determined using the Ca NanoSIMS profiles whilst Fe and Mn returned times of less than 100 days. The diffusivities of Na, Cr, Mn, Fe, Ti and Y relative to Ca ($\log D = -20.45 \text{ m}^2\text{s}^{-1}$) were determined; with this being the first time diffusion coefficients have been determined for Na, Cr, Ti and Y in peridotitic garnet. It was found that Mn ($\log D = \text{Ca} + 0.53 \text{ m}^2\text{s}^{-1}$) and Fe ($\text{Ca} + 0.61 \text{ m}^2\text{s}^{-1}$) diffuse faster than Ca; whilst Na ($\text{Ca} + 0.11 \text{ m}^2\text{s}^{-1}$) and Cr ($\text{Ca} + 0.05 \text{ m}^2\text{s}^{-1}$) diffuse at a similar rate; and Ti

(Ca $-0.26 \text{ m}^2\text{s}^{-1}$) and Y (Ca $-0.17 \text{ m}^2\text{s}^{-1}$) diffuse slower. The mixing behaviour between the core and rim material was modelled by examining changes in REE_N profiles and it was found that as little as 8% of rim material is required to remove the depleted HREE_N signal observed in the core.

4.6 Acknowledgements

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Chapter 5: Metasomatism and oxygen fugacity of phlogopite bearing garnet peridotites from the Kimberley kimberlite, South Africa

A suite of garnet peridotite xenoliths from the Kimberley kimberlite, South Africa, some of which were phlogopite bearing, were examined to investigate their redox state and metasomatic history. Petrographic examination identified two generations of clinopyroxene, which was confirmed by differences in their major and trace element compositions. Primary clinopyroxene, cpx-1, was characterised by large crystals along with low Cr_2O_3 and TiO_2 contents and depleted HREE_N abundances whereas secondary clinopyroxene, cpx-2, contained greater amounts of Cr_2O_3 and TiO_2 and enriched HREE_N abundances, occurred as small crystals, and was generally found in association with phlogopite or altered garnet. The samples derive from a limited depth interval, recording equilibration pressures of 3.8 to 4.3 GPa and temperatures of 910 to 1020 °C. Iron K-edge XANES spectroscopy was used to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ of garnets, allowing determination of the redox state, with $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ varying from -1.8 to -2.6. The oxidation state observed in the suite indicates that this mineral assemblage could have been in equilibrium with a silicate melt containing between 1 and 10 % CO_3^{2-} . Trace element relationships support the possibility of two metasomatic events; one related to the formation of phlogopite and sinusoidal garnet REE_N patterns and another responsible for the formation of the secondary clinopyroxene, cpx-2.

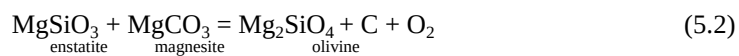
5.1 Introduction

Determining the oxygen fugacity (fO_2) of the cratonic lithosphere is important for building our understanding of many processes, including metasomatism, partial melting and diamond stability (Taylor and Green, 1987, 1988). Garnet peridotite xenoliths record the fO_2 of the upper mantle; these were accidentally entrained in kimberlite magmas and rapidly transported to the surface, providing a record of lithospheric fO_2 at the time of kimberlite eruption. The compositions of minerals in peridotite record the pressure (P), temperature (T) and fO_2 of the location in the lithosphere from which they were sampled. The fO_2 is recorded in minerals by multivalent elements such as Fe, which exists as Fe^{2+} and Fe^{3+} . Within peridotites the fO_2 is buffered by silicate-oxide exchange equilibria involving phases such as spinel, garnet and pyroxene, which can all host both Fe^{2+} and Fe^{3+} . One of these reactions is based upon the Fe^{3+} -bearing andradite ($Ca_3Fe_2Si_3O_{12}$) garnet component:



The andradite component acts as a redox sensor, recording mantle fO_2 , which is a function of $Fe^{3+}/\sum Fe$ [where $\sum Fe = (Fe^{2+} + Fe^{3+})$] in the garnet (Stagno et al., 2013).

The stability of diamond/graphite relative to carbonate in the mantle is strongly dependent on fO_2 with oxidising conditions increasing the stability of carbonate phases. In peridotite assemblages, the stability of diamond/graphite relative to carbonate is limited by buffering reactions such as EMOD/G:



in harzburgitic assemblages or by EMFDD:



in lherzolitic assemblages (Eggler and Baker, 1982, Luth, 1993, Stagno and Frost, 2010).

Thermodynamic modelling and experimental studies have shown that the speciation of CHO-fluids is heavily dependent upon the redox state of the surrounding mantle, with reduced conditions favouring the formation of CH₄ and H₂O, in proportions determined by the $f\text{O}_2$ (Belonoshko and Saxena, 1992, Taylor and Green, 1987, Woodland and Koch, 2003). According to thermodynamic calculations by Woodland and Koch (2003) a CHO-fluid at $\Delta\log f\text{O}_2^{\text{FMQ}} = -5.5$ [$f\text{O}_2$ in log units relative to the fayalite-magnetite-quartz (FMQ) redox buffer (Frost, 1991)] contains ~75% CH₄ and 25% H₂O at 1400 °C and 6 GPa. If this fluid were to become more oxidised it may become saturated in carbon, and could then precipitate diamond or graphite depending upon the P and T conditions, with the remaining fluid being H₂O rich (Taylor and Green, 1987). This increase in water activity combined with changes in $f\text{O}_2$ may provide a trigger for flux melting of the mantle in a process known as redox melting (Foley, 2011, Taylor and Green, 1987, 1988). Experiments investigating the coexistence of diamond (or graphite) and carbonate melt in peridotitic systems have found that the activity of dissolved carbonate in a silicate melt will increase as conditions become more oxidising, until a carbonate melt forms when the EMOD/G buffer (see later) is crossed (Stagno and Frost, 2010, Stagno et al., 2013). These carbonate bearing silicate melts may play an important role in the metasomatism of the cratonic lithosphere (Chapter 2).

Determinations of the fO_2 of garnet peridotite xenoliths from around the globe, including the Kaapvaal Craton, show that most xenoliths were sourced from the region in P - fO_2 space where carbonated silicate melts are stable, rather than the carbonate stability field (Stagno et al., 2013, Yaxley et al., 2012). The exceptions to this are some metasomatised garnet peridotites from the Kaapvaal and Slave cratons (Creighton et al., 2009, 2010, Chapter 2), including zoned garnets from Wesselton (Berry et al., 2013), which appear to be sourced from the carbonate stability field. Thus, the determination of the fO_2 recorded by mantle samples may allow constraints to be placed on mantle processes, including metasomatism, partial melting and diamond crystallization or resorption.

Phlogopite occurs in a variety of ultramafic mantle rocks, including garnet lherzolites, garnet harzburgites and phlogopite-rich peridotites, which are further classified by their mineral assemblage as follows. Two of the phlogopite-bearing peridotite assemblages are MARID (mica-amphibole-rutile-ilmenite-diopside; Dawson and Smith, 1977) and the PIC (phlogopite-ilmenite-clinopyroxene) suites (Grégoire et al., 2002, Jones, 1987). It has been proposed that MARID and PIC rocks are related to alkaline magmas linked to Group I and II kimberlites respectively (Grégoire et al., 2003). The trace element and isotopic compositions of these suites have been compared to those of clinopyroxenes from garnet peridotites in an attempt to link alkaline magmas to metasomatism (Grégoire et al., 2003). LREE-enriched clinopyroxenes and sinusoidal garnet REE patterns (Nixon et al., 1981, Stachel et al., 1999) from most garnet peridotite xenoliths from the Kaapvaal craton indicate enrichment by a LREE-rich fluid (e.g. Woodland and Koch, 2003). A number of different sources have been suggested for this putative metasomatic fluid including water-rich fluids (Winterburn et al., 1990), carbonatites

(Griffin et al., 1992) and methane-rich fluids (Stachel et al., 1999), and it is possible that a number of these processes have similar geochemical signatures. More recently it has been suggested that carbonated silicate melts may be stable at the fO_2 where most xenoliths are sourced and as such may be the source of metasomatism (Stagno and Frost, 2010, Stagno et al., 2013).

Peridotite xenoliths from the Kaapvaal craton have been extensively studied over the last two decades to identify and understand metasomatic processes and redox profiles in the cratonic lithosphere (Creighton et al., 2009, Grégoire et al., 2002, 2003, Griffin et al., 1999, Lazarov et al., 2012a, b, Chapter 2, McCammon et al., 2001, Woodland and Koch, 2003). The fO_2 of the Kaapvaal cratonic mantle has been investigated using a variety of techniques including Mössbauer spectroscopy (Woodland and Koch, 2003), the electron microprobe-based flank method (Creighton et al., 2009) and Fe K-edge X-ray Absorption Near-edge Structure (XANES) spectroscopy (Chapter 2). In some suites, there is a general decrease in fO_2 with increasing depth. Xenoliths investigated in these studies equilibrated at pressures from 2.7 to 6.4 GPa, while $\Delta\log fO_2^{[FMQ]}$ varied from -4.3 to 0.15 when calculated using the approach of Stagno et al. (2013) [all $\Delta\log fO_2^{[FMQ]}$ values in this manuscript have been calculated using this approach]. Some samples, however, show a metasomatic oxidation trend (Creighton et al., 2009, Chapter 2). Metasomatism has been identified in both harzburgites and lherzolites from across the craton, in particular from the Kimberley, Wesselton and Finsch pipes (Griffin et al., 1999, Lazarov et al., 2012a, McCammon et al., 2001, Woodland and Koch, 2003). Lherzolites from the Bultfontein pipe have been oxidised by fluids that are rich in LREE, with the redox state approaching the FMQ buffer, and contain higher modal proportions of clinopyroxene and phlogopite than harzburgites (Creighton et al., 2009).

Harzburgites from the same suite are mildly metasomatised with enrichment in Y but not Zr, which can be related to the MARID suite of peridotites (Creighton et al., 2009). A suite of predominantly harzburgitic xenoliths from the Finsch mine were found to have $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ of -2.5 to -4.7 (Lazarov et al., 2009). They were interpreted as having been initially strongly depleted based upon the high Mg# of olivine and high Cr# of garnet, before experiencing metasomatic enrichment, possibly by COH fluids containing roughly equal proportions of CH_4 and H_2O .

Here we use Fe K-edge XANES spectroscopy (Berry et al., 2010, 2013) to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnets from the suite and hence determine $\Delta\log f\text{O}_2^{[\text{FMQ}]}$. This technique can determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ with similar precision (± 0.01) to Mössbauer spectroscopy but has superior spatial resolution and significantly shorter data acquisition times (Berry et al., 2008, 2010, 2013). We have used this data in conjunction with conventional thermobarometry, based on major and trace element analysis of all phases by electronprobe microanalysis (EPMA) and laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS) respectively, to (1) determine the $f\text{O}_2$, pressure (P) and temperature (T) of the suite of studied xenoliths (2) examine the metasomatic history, and (3) compare the results to the global dataset.

5.2 Petrography

A set of nine polished sections (80 μm thickness) from nine different garnet peridotite xenoliths from the Kimberley mine, South Africa, were studied (K1-K9). All samples contain abundant olivine and orthopyroxene, both of which are heavily fractured, and all samples can be classified as porphyroclastic. There are two distinct textural populations of clinopyroxene, cpx-1 and cpx-2. Cpx-1, which is found in samples K1, K2 and K3, is characterised by large crystals (>1 mm) that are heavily fractured (Figure 5.1a). Cpx-2, present in samples K4, K5, K6 and K7, occurs as small crystals (<0.3 mm) near phlogopite, garnet alteration rims or at the edge of large orthopyroxene crystals (Figure 5.1c-d). These cpx-2 crystals appear to have formed interstitially to crystals of olivine and orthopyroxene. Clinopyroxene in sample K9 is completely enclosed in phlogopite, and could not be classified as either cpx-1 or cpx-2 (Figure 5.1e) on compositional grounds (see later). No clinopyroxene is present in sample K8. Garnet is present in all sections and has a bimodal size distribution. Large (>1 mm diameter) crystals are present in all samples (Figure 5.1b) whilst clusters of smaller (<0.5 mm) crystals are found in two samples, K3 and K9 (Figure 5.1f). All garnet crystals exhibit significant fracturing and substantial alteration rims are present on large crystals from three samples (K4, K7, K8). All samples show evidence of infiltration by a phase that cross-cuts the fractures in olivine and orthopyroxene, which is interpreted to have formed at a late stage, possibly in relation to the kimberlite magma, however, it was too fine-grained for analysis. As cpx-2 and the related phlogopite are fine-grained, relative to cpx-1, and form in interstitial spaces, they are expected to have formed a later stage, after olivine, orthopyroxene and the coarse-grained cpx-1.

5.3 Analytical methods

Major and minor element compositions of individual phases were determined by EPMA using the Cameca SX100 at the Central Science Laboratory, University of Tasmania using five wavelength X-ray dispersive spectrometers, an accelerating voltage of 15 kV, beam current of 10 nA, beam diameter of 5 μm , and the PAP matrix correction algorithm. Well characterised natural mineral samples were used as primary standards, whilst San Carlos olivine, Kakanui hornblende (Jarosewich et al., 1980) and Delegate clinopyroxene were used as secondary standards. The analysis conditions and standards for each element are given in Appendix B1, whilst the values obtained for the secondary standards are shown in Appendix B2. Back-scattered electron images were obtained using the Hitachi 4300 SE/N Schottky field emission scanning electron microscope (FESEM) at the Centre for Advanced Microscopy, Australian National University (ANU), with an operating voltage of 15 kV and an emission current of 0.6 nA.

Trace element contents were determined using the Agilent 7700 ICP-MS instrument with a coupled Excimer 193 nm laser ablation system at the Research School of Earth Sciences, ANU. Analyses were performed with a spot size of 105 μm and an acquisition time of 90 s, 30 s of which (laser off) was used to establish a baseline. NIST 612 glass was used as the calibration standard, and BCR-2G as a secondary standard (Appendix B3). EPMA determined abundances of Ca were used as the internal reference element for garnet and pyroxene, whilst Si was used for olivine and phlogopite. The data was reduced with the Iolite program (Paton et al., 2011) using standard values from Jochum et al. (2011).

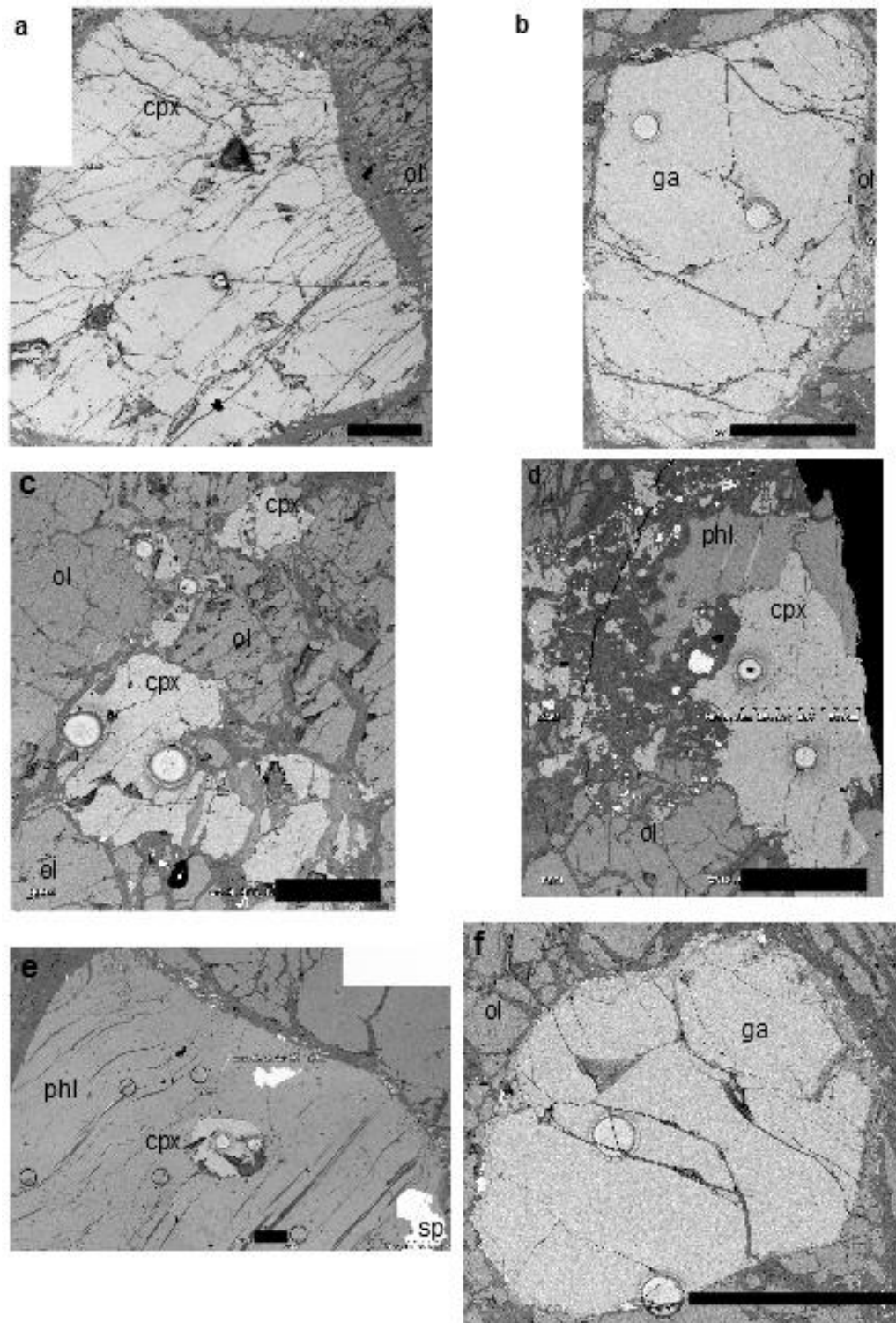


Figure 5.1: Composite backscattered electron images of: (a) cpx-1, sample K1; (b) coarse garnet, K3; (c) cpx-2, K5; (d) cpx-2 and phlogopite, K6; (e) clinopyroxene enclosed in phlogopite, K9; and (f) small garnet, K3. The black scale bar in each image is 500 μm . Circular features in (b-f) are pits from LA-ICP-MS analysis.

$\text{Fe}^{3+}/\Sigma\text{Fe}$ of garnet was determined using Fe K-edge XANES spectroscopy at the X-ray Fluorescence Microscopy (XFM) beamline of the Australian Synchrotron (Paterson et al., 2011). The excitation energy was selected using a Si(111) double crystal monochromator and calibrated by defining the first peak in the derivative spectrum of Fe foil to be 7112.0 eV. The beam was focused using Kirkpatrick-Baez mirrors to a diameter of 3-4 μm , although the X-rays penetrate garnet and thus analyse to a depth of $\sim 40 \mu\text{m}$. Samples were mounted at 45° to the incident beam and a single-element silicon drift fluorescence detector (Vortex EM, SII Nanotechnology, Northridge, California) with digital signal processing (DXP Saturn, XIA LLC, Hayward, California). The incident flux was adjusted for each sample to maintain an approximately constant detector count rate, within the linear range of the signal processing electronics, at the "white line". Fluorescence from Ca and Cr were preferentially removed relative to that from Fe by Al foil placed between the sample and detector. Spectra were recorded from 7070-7295 eV with a step size of 0.5 eV from 7070-7108 eV, 0.3 eV from 7108-7170 eV, and 2.5 eV above 7170 eV, with a count time of 3 s per point for a total scan time of almost 30 min. Spectra were compared after subtraction of a constant baseline, normalisation to the average intensity above 7230 eV, and a five point smoothing of the resulting values.

The quantification of $\text{Fe}^{3+}/\Sigma\text{Fe}$ is dependent on an empirical correlation between the minimum intensity of a post-edge feature in a XANES spectrum (at 7138.4 eV) to the $\text{Fe}^{3+}/\Sigma\text{Fe}$ value determined by Mössbauer spectroscopy for a suite of standards from the Diavik (Yaxley, unpublished data) and Kaapvaal (Woodland and Koch, 2003) Cratons. This approach is slightly different to that used in previous studies (the ratio of features at 7138.4 and 7161.7 eV; Berry et al. 2010, 2013, Yaxley et al. 2012) but is simpler and

equally precise for peridotitic garnets. The standards were presented as crystals in polished epoxy resin (Diavik) and as thin sections on glass (Kaalpvaal). Representative XANES spectra are shown in Figure 5.2, and the calibration curve, which is a linear best fit to the data obtained from the standards, is shown in Figure 5.3, with the values available in Appendix B4. The uncertainty in the $\text{Fe}^{3+}/\Sigma\text{Fe}$ values determined by Mössbauer spectroscopy is estimated as ± 0.01 (Woodland and Koch, 2003). The standard deviation of the difference between the $\text{Fe}^{3+}/\Sigma\text{Fe}$ values of the standards and the line of best fit is ± 0.009 . This suggests that the uncertainty in values determined by XANES is not larger than that associated with the Mössbauer values and thus we estimate the accuracy of our results to be ± 0.01 .

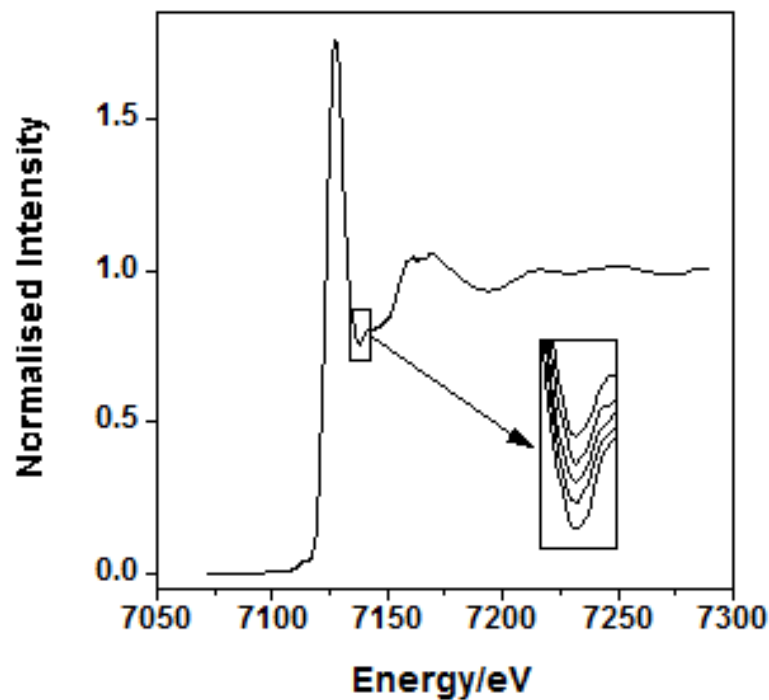


Figure 5.2: Fe K-edge XANES spectrum of a garnet standard with $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.067$. The inset shows the region of the spectrum near 7138.4 eV for garnets with (from bottom to top) $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.024, 0.048, 0.067, 0.084$ and 0.109 .

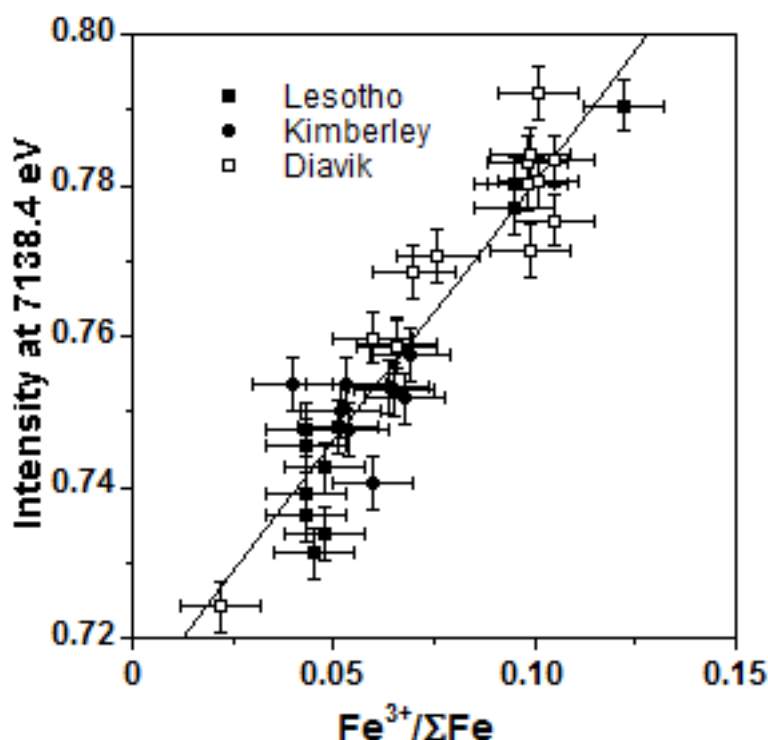


Figure 5.3: Calibration curve, showing the correlation between the Fe K-edge XANES intensity at 7138.4 eV and $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the standard garnets determined by Mössbauer spectroscopy. The line is the linear best fit to the data.

5.4 Results

5.4.1 Mineral Chemistry

The garnets range in Mg# number [$\text{Mg\#} = 100 \times \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$] from 82.6 to 85.8 and have pyrope-rich compositions; Fe^{2+} was calculated from the total FeO value determined using EPMA and $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined by XANES spectroscopy. The Cr_2O_3 content varied from 4.1 to 7.8 wt.% and the CaO content from 4.4 to 5.3 wt.% (Table 5.1). Garnets from seven of the nine samples are lherzolitic (G9), while the remaining two are classified as harzburgitic (G10D), using the Cr/Ca classification system of Grütter et al. (2004) (Figure 5.4).

Table 5.1: Major (wt.% oxide), and trace element (ppm) contents of garnet. Cations were calculated on the basis of 12 oxygen atoms. Fe³⁺ was determined by Fe K-edge XANES spectroscopy. [Mg# = 100 × Mg/(Mg + Fe²⁺)]. “bdl” = below detection limit; “nd” = not determined; “n” number of analyses obtained. Errors are given as one standard deviation (σ), where no error is given only a single measurement was obtained.

Sample	K1	σ	K2	σ	K3	σ	K4	σ	K5	σ	K6	σ	K7	σ	K8	σ	K9	σ
n	10		11		12		10		4		6		17		4		24	
Na ₂ O	0.03	0.05	0.03	0.03	0.03	0.03	0.04	0.03	0.05	0.02	0.05	0.03	0.07	0.04	0.02	0.02	0.04	0.04
SiO ₂	41.09	0.42	41.35	0.26	41.66	0.26	41.04	0.21	41.46	0.18	41.23	0.44	41.11	0.28	41.12	0.23	41.45	0.26
Al ₂ O ₃	20.05	0.27	19.78	0.25	20.94	0.27	19.43	0.21	20.22	0.31	18.80	0.39	18.58	0.28	18.05	0.14	20.07	0.21
MgO	19.91	0.32	20.20	0.33	20.77	0.25	19.89	0.20	20.09	0.26	20.69	0.40	19.83	0.27	20.39	0.29	20.43	0.23
K ₂ O	bdl		0.01	0.03	0.01	0.03	0.01	0.02	bdl		0.01	0.02	bdl		0.01	0.03	0.01	0.03
CaO	5.21	0.08	5.21	0.10	5.20	0.12	5.15	0.12	4.75	0.05	4.45	0.31	5.32	0.09	4.47	0.42	5.12	0.09
Cr ₂ O ₃	4.61	0.10	5.13	0.18	4.11	0.12	5.89	0.17	4.81	0.07	6.85	0.27	6.97	0.17	7.83	0.07	4.99	0.19
Fe ₂ O ₃	1.13		0.99		0.70		0.84		1.26		nd		nd		0.72		0.81	
FeO	6.19	0.14	6.18	0.14	5.74	0.11	6.44	0.11	6.85	0.09	7.03	0.14	7.17	0.15	6.19	0.15	6.35	0.11
P ₂ O ₅	0.07	0.01	0.05	0.01	0.07	0.01	0.03	0.01	0.06	0.01	0.02	0.03	0.04	0.01	0.04	0.02	0.05	0.01
MnO	0.38	0.10	0.36	0.09	0.31	0.07	0.40	0.11	0.46	0.04	0.45	0.07	0.46	0.09	0.40	0.06	0.33	0.07
TiO ₂	0.08	0.04	0.15	0.03	0.02	0.03	0.16	0.03	0.24	0.04	0.19	0.11	0.26	0.04	0.07	0.06	0.14	0.04
Total	98.71		99.41		99.50		99.29		100.21		99.71		99.77		99.27		99.77	
Na	0.005		0.005		0.004		0.005		0.007		0.007		0.010		0.003		0.006	
Si	2.987		2.987		2.983		2.978		2.977		2.979		2.980		2.991		2.981	
Al	1.718		1.685		1.768		1.662		1.712		1.601		1.588		1.548		1.701	
Mg	2.157		2.175		2.217		2.151		2.150		2.228		2.142		2.211		2.190	
K	0.000		0.001		0.001		0.001		0.000		0.001		0.000		0.001		0.001	
Ca	0.406		0.403		0.399		0.400		0.366		0.345		0.414		0.349		0.395	
Cr	0.265		0.293		0.233		0.338		0.273		0.391		0.399		0.450		0.284	
Fe ³⁺	0.031		0.027		0.019		0.023		0.034		nd		nd		0.020		0.022	
Fe ²⁺	0.414		0.406		0.367		0.419		0.453		0.425		0.435		0.401		0.409	
P	0.004		0.003		0.004		0.002		0.004		0.001		0.002		0.002		0.003	
Mn	0.024		0.022		0.019		0.025		0.028		0.028		0.028		0.025		0.020	
Ti	0.004		0.008		0.001		0.008		0.013		0.010		0.014		0.004		0.008	
Total	8.014		8.015		8.012		8.013		8.016		8.017		8.014		8.005		8.018	
Mg#	83.9	0.20	84.3	0.35	85.8	0.18	83.7	0.25	82.6	0.34	84.0	0.42	83.1	0.22	84.7	0.16	84.3	0.18

Sample	K1	σ	K2	σ	K3	σ	K4	σ	K5	σ	K6	σ	K7	σ	K8	σ	K9	σ
n	17		16		12		6		1		2		6		4		26	
Sc	114	2	122	6	88	7	173	15	126		275	51	158.1	0.7	51	6	35.1	0.6
Ti	522	5	1096	437	57	5	1060	53	nd		1755	107	1705	31	99	18	261	4
V	188	3	179	14	174	20	228	21	278		205	48	253	7	99	18	50.7	0.8
Co	41.3	0.9	43	4	40	5	43	6	41		48	10	39.4	0.8	13	2	11.7	0.2
Ni	46.7	1.3	63	40	59	15	44	4	68		24	5	37.0	0.6	14	1	14.7	0.2
Ga	3.4	0.1	4.14	0.53	2.60	0.22	2.56	0.15	6.45		3.8	1.0	2.6	0.1	0.89	0.21	1.11	0.04
Rb	0.7	0.3	5	19	0.30	0.53	15	27	0.01		29	24	0.45	0.9	0.05	0.06	0.02	0.00
Sr	4.6	0.3	5	12	3	8	29	37	0.03		30	18	2	2	1.1	1.1	0.22	0.01
Y	9.0	0.3	13	3	1.76	0.14	11	3	40		58	12	19.2	0.2	0.54	0.22	3.5	0.5
Zr	127	3.	101	6	64	6	44	7	99		107	4	82.6	0.7	9	5	26.9	0.2
Nb	0.41	0.06	0.9	2.2	0.44	0.11	0.77	0.45	0.20		4.60	0.33	0.29	0.02	0.20	0.09	0.07	0.00
Ba	0.48	0.15	22	83	2	7	40	77	nd		30	18	0.6	1.1	0.45	0.74	0.07	0.00
La	0.11	0.03	0.4	1.0	0.11	0.24	0.06	0.05	0.01		2.2	0.9	0.09	0.01	0.12	0.12	0.02	0.00
Ce	0.53	0.07	1.0	1.6	0.47	0.36	0.50	0.14	0.32		4.2	1.9	0.71	0.11	0.69	0.36	0.12	0.01
Pr	0.20	0.01	0.23	0.15	0.19	0.03	0.20	0.04	0.15		0.55	0.25	0.21	0.03	0.19	0.05	0.00	0.01
Nd	2.62	0.10	2.40	0.56	2.53	0.19	2.23	0.43	1.70		3.6	1.1	2.04	0.19	1.79	0.20	0.66	0.05
Sm	2.36	0.08	2.00	0.13	2.21	0.12	1.98	0.30	1.98		2.38	0.03	1.81	0.06	0.67	0.22	0.53	0.01
Eu	1.00	0.03	0.85	0.03	0.77	0.06	0.67	0.10	0.91		1.17	0.06	0.87	0.03	0.19	0.10	0.23	0.00
Gd	3.10	0.14	2.92	0.16	1.87	0.19	2.23	0.60	4.06		5.05	0.75	3.45	0.08	0.43	0.30	0.81	0.02
Tb	0.42	0.01	0.49	0.04	0.19	0.02	0.35	0.09	0.82		1.18	0.20	0.64	0.01	0.04	0.03	0.13	0.01
Dy	2.23	0.10	2.93	0.44	0.66	0.06	2.24	0.60	6.68		9.7	2.3	4.22	0.07	0.18	0.11	0.78	0.09
Ho	0.34	0.02	0.50	0.10	0.07	0.01	0.41	0.10	1.52		2.25	0.60	0.73	0.02	0.02	0.01	0.13	0.02
Er	0.76	0.03	1.22	0.26	0.13	0.02	1.00	0.24	4.45		7	2	1.76	0.04	0.04	0.01	0.32	0.06
Tm	0.10	0.01	0.16	0.04	0.02	0.002	0.13	0.03	0.61		1.07	0.34	0.22	0.01	bdl		0.04	0.01
Yb	0.65	0.06	1.11	0.23	0.21	0.02	0.84	0.18	4.14		8	2	1.31	0.03	0.050	0.00	0.29	0.06
Lu	0.11	0.01	0.18	0.04	0.05	0.01	0.13	0.03	0.59		1.16	0.43	0.19	0.01	0.010	0.00	0.05	0.01
Ta	0.03	0.01	0.05	0.11	0.029	0.004	0.04	0.01	nd		nd		nd		nd		nd	
Pb	0.04	0.06	0.04	0.07	0.02	0.02	0.08	0.08	bdl		0.49	0.01	0.01	0.01	0.010	0.01	bdl	
Th	0.014	0.003	0.04	0.07	0.02	0.02	0.01	0.01	bdl		0.16	0.21	0.03	0.00	0.030	0.02	bdl	
U	0.018	0.002	0.02	0.03	0.014	0.005	0.05	0.01	0.01		0.17	0.00	0.06	0.01	0.030	0.01	0.01	0.00
Sm/Tm _N	4.13		2.01		19.20		2.56		0.54		0.37		1.37				2.10	

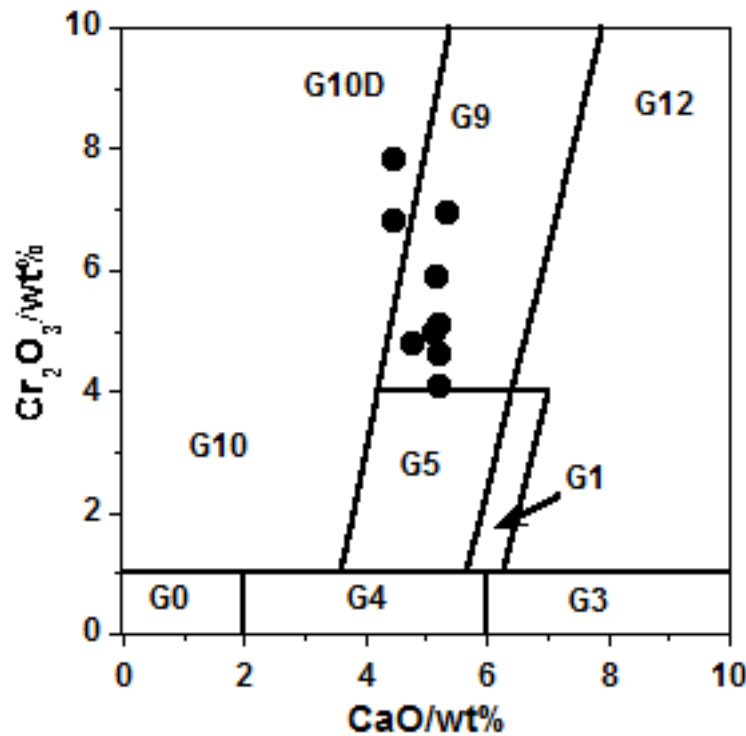


Figure 5.4: Classification of garnets in the present study using the Cr-Ca scheme (Grütter et al. 2004). The field G9 is lherzolite whilst G10D is harzburgitic.

Olivine ranges in Mg# from 91.2 to 92.8, consistent with values reported previously for the Kimberley region (Creighton et al., 2009, Grégoire et al., 2003, Chapter 2) and the world-wide data set for on-craton peridotite xenoliths (91-94) (Pearson et al., 2003) (Table 5.2). The Mg# of orthopyroxene varied from 92.3 to 93.8, Al₂O₃ from 0.64 to 0.79 wt.% and CaO from 0.32 to 0.51 wt.% (Table 5.3). The orthopyroxene compositions are similar to those of other peridotites from the Kimberley (e.g. Creighton et al., 2009), with high Cr₂O₃ (0.28 to 0.44 wt.%) and low Al₂O₃ (< 0.80 wt.%).

Table 5.2: Major (wt.% oxide), and trace element (ppm) contents of olivine. Cations were calculated on the basis of 4 oxygen atoms. [Mg# = $100 \times \text{Mg}/(\text{Mg} + \text{Fe})$]. “bdl” = below detection limit; “n” number of analyses obtained. Errors are given as one standard deviation (σ). LA-ICP-MS analysis was not performed on samples K1, K2 and K6.

Sample	K1	σ	K2	σ	K3	σ	K4	σ	K5	σ	K6	σ	K7	σ	K8	σ	K9	σ
n	3		9		5		6		6		8		11		4		8	
Na ₂ O	0.02	0.03	0.01	0.02	0.00	0.03	bdl		0.01	0.01	0.02	0.04	0.03	0.04	0.01	0.01	0.05	0.05
SiO ₂	40.59	0.33	40.74	0.17	40.87	0.16	40.88	0.25	40.84	0.27	40.97	0.24	40.96	0.23	40.99	0.19	40.97	0.23
Al ₂ O ₃	0.04	0.04	0.02	0.02	0.02	0.04	0.02	0.02	0.00	0.01	0.01	0.01	0.01	0.02	0.00	0.01	0.01	0.03
MgO	49.71	0.39	49.84	0.35	51.15	0.40	50.23	0.36	49.92	0.24	50.63	0.45	50.42	0.28	50.42	0.27	50.26	0.15
K ₂ O	0.01	0.01	0.01	0.02	0.00	0.02	0.00	0.05	0.00	0.02	0.00	0.04	0.01	0.03	0.01	0.03	0.02	0.03
CaO	0.04	0.01	0.03	0.01	0.03	0.02	0.02	0.03	0.01	0.03	0.02	0.03	0.02	0.02	0.02	0.02	0.03	0.03
Cr ₂ O ₃	0.02	0.01	0.03	0.02	0.03	0.02	0.03	0.02	0.02	0.02	0.04	0.02	0.05	0.02	0.04	0.01	0.03	0.02
FeO	7.90	0.21	7.83	0.14	7.02	0.08	7.66	0.08	8.62	0.08	7.42	0.12	7.58	0.13	7.35	0.13	8.02	0.14
P ₂ O ₅	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.02	0.01	0.01
MnO	0.04	0.05	0.08	0.05	0.08	0.04	0.11	0.07	0.11	0.07	0.10	0.04	0.10	0.06	0.13	0.05	0.09	0.06
TiO ₂	bdl		0.01	0.05	bdl		0.03	0.02	0.03	0.05	0.02	0.03	0.03	0.03	bdl		0.03	0.03
Total	98.34	0.23	98.59	0.56	99.16	0.28	98.96	0.52	99.56	0.41	99.21	0.54	99.21	0.42	98.94	0.43	99.50	0.32
Na	0.001		0.000		0.000		0.000		0.000		0.001		0.001		0.000		0.002	
Si	1.002		1.003		0.997		1.002		0.999		1.000		1.001		1.003		1.000	
Al	0.001		0.000		0.001		0.000		0.000		0.000		0.000		0.000		0.000	
Mg	1.828		1.828		1.859		1.834		1.820		1.842		1.836		1.839		1.829	
K	0.000		0.000		0.000		0.000		0.000		0.000		0.000		0.000		0.001	
Ca	0.001		0.001		0.001		0.001		0.000		0.000		0.001		0.000		0.001	
Cr	0.000		0.001		0.000		0.001		0.000		0.001		0.001		0.001		0.001	
Fe	0.163		0.161		0.143		0.157		0.176		0.152		0.155		0.150		0.164	
P	0.000		0.000		0.000		0.000		0.000		0.000		0.000		0.000		0.000	
Mn	0.001		0.002		0.002		0.002		0.002		0.002		0.002		0.003		0.002	
Ti	0.000		0.000		0.000		0.001		0.001		0.000		0.000		0.000		0.001	
Total	2.998		2.997		3.002		2.997		3.000		2.999		2.999		2.997		3.000	
Mg#	91.8	0.19	91.9	0.12	92.8	0.09	92.1	0.09	91.2	0.09	92.4	0.07	92.2	0.10	92.4	0.13	91.8	0.13

Sample	K1	σ	K2	σ	K3	σ	K4	σ	K5	σ	K6	σ	K7	σ	K8	σ	K9	σ
n					6		6		2				8		2		6	
Li					1.07	0.10	1.37	0.11	1.79	0.18			1.35	0.06	1.16	0.03	1.64	0.04
Be					bdl		0.002	0.002	bdl				0.001	0.002	bdl		bdl	
B					19.88	0.58	17.30	0.28	14.23	0.03			15.49	0.55	12.20	0.11	12.5	0.5
Na					53	3	90	21	83	18			92	32	95	2	79	4
Al					62	27	38	16	30.1	0.6			30.0	1.9	33.56	0.01	70	60
P					74.8	1.1	57	13	76.1	0.8			61	14	56	5	48	12
Ca					142	22	11	50	109	4			115	55	90	6	155	25
Sc					2.06	0.05	2.49	0.09	1.97	0.06			2.38	0.05	1.81	0.01	1.95	0.06
Ti					3.97	0.12	87	7	150.0	0.1			143	6	20.99	0.23	53	1
V					4.70	0.10	3.86	0.33	4.23	0.01			4.80	0.06	6.25	0.01	4.58	0.13
Co					131	1	133.3	1.1	134.2	0.8			132	1	130.4	0.5	136.6	0.3
Ni					3222	36	3089	24	2111	250			3012	54	3041	11	3186	19
Cu					1.79	0.06	2.42	0.07	2.40	0.04			2.48	0.05	1.57	0.00	2.58	0.08
Ga					0.02	0.01	0.02	0.004	0.03	0.01			0.03	0.01	0.02	0.00	0.04	0.01
Rb					bdl		0.03	0.05	0.01	0.02			0.02	0.03	bdl		bdl	
Sr					bdl		0.7	0.9	bdl				0.52	0.96	bdl		0.02	0.05
Y					bdl		0.01	0.02	bdl				0.01	0.02	bdl		bdl	
Zr					0.21	0.02	0.52	0.16	0.323	0.05			0.51	0.20	0.28	0.00	0.26	0.04
Nb					0.45	0.03	0.85	0.14	0.973	0.03			0.75	0.16	0.57	0.01	0.23	0.05
Ba					bdl		1.0	1.4	bdl				0.7	1.3	bdl		bdl	
La					bdl		0.087	0.11	bdl				0.06	0.11	bdl		bdl	
Ce					0.001	0.001	0.173	0.22	bdl				0.14	0.26	bdl		bdl	
Pr					bdl		0.017	0.02	bdl				0.01	0.02	bdl		bdl	
Nd					bdl		0.060	0.08	bdl				0.04	0.08	bdl		bdl	
Sm					bdl		0.007	0.01	bdl				0.01	0.01	bdl		bdl	
Eu					bdl		0.002	0.003	bdl				bdl		bdl		bdl	
Gd					bdl		0.01	0.01	bdl				0.003	0.01	bdl		bdl	
Tb					bdl		0.001	0.001	bdl				bdl		bdl		bdl	
Dy					bdl		0.002	0.003	bdl				bdl		bdl		bdl	
Ho					bdl		0.001	0.001	bdl				0.001	0.001	bdl		bdl	
Er					bdl		0.001	0.002	bdl				0.001	0.002	bdl		bdl	
Tm					bdl		bdl		bdl				bdl		bdl		bdl	
Yb					bdl		bdl		bdl				bdl		bdl		bdl	
Lu					bdl		bdl		bdl				bdl		bdl		bdl	
Pb					0.003	0.001	0.013	0.01	0.005				0.011	0.01	bdl		bdl	
Th					bdl		0.013	0.02	bdl				0.009	0.02	bdl		bdl	
U					bdl		0.002	0.003	bdl				0.002	0.004	bdl		bdl	

Table 5.3: Major (wt.% oxide), and trace element (ppm) contents of orthopyroxene. Cations were calculated on the basis of 6 oxygen atoms. [Mg# = $100 \times \text{Mg}/(\text{Mg} + \text{Fe})$]. “bdl” = below detection limit; “nd” = not determined; “n” number of analyses obtained. Errors are given as one standard deviation (σ), where no error is given only a single measurement was obtained.

Sample	K1	σ	K2	σ	K3		K4	σ	K5	σ	K6	σ	K7	σ	K8	σ	K9	σ
n	16		12		15		15		11		10		12		16		14	
Na ₂ O	0.12	0.04	0.12	0.04	0.09	0.05	0.12	0.03	0.14	0.05	0.18	0.07	0.15	0.06	0.14	0.04	0.13	0.04
SiO ₂	57.15	0.40	57.44	0.28	57.60	0.27	57.41	0.35	57.45	0.24	57.38	0.89	57.59	0.30	57.64	0.28	57.39	0.28
Al ₂ O ₃	0.76	0.04	0.78	0.04	0.75	0.04	0.72	0.06	0.71	0.05	0.73	0.05	0.75	0.04	0.64	0.09	0.79	0.04
MgO	35.25	0.28	35.24	0.31	35.92	0.28	35.51	0.27	35.33	0.16	35.56	0.22	35.53	0.23	35.64	0.28	35.45	0.21
K ₂ O	0.01	0.02	0.01	0.02	bdl		bdl		0.01		bdl		bdl		0.01	0.02	0.01	0.03
CaO	0.47	0.04	0.48	0.03	0.47	0.04	0.35	0.03	0.39	0.04	0.36	0.02	0.33	0.04	0.32	0.03	0.51	0.03
Cr ₂ O ₃	0.29	0.03	0.34	0.04	0.28	0.02	0.40	0.03	0.33	0.04	0.43	0.08	0.44	0.03	0.38	0.03	0.34	0.03
FeO	4.87	0.10	4.75	0.06	4.25	0.09	4.67	0.12	5.26	0.16	4.53	0.10	4.66	0.12	4.38	0.07	4.80	0.16
P ₂ O ₅	bdl		bdl		bdl		bdl		bdl		bdl		bdl		bdl		bdl	
MnO	0.12	0.06	0.10	0.03	0.04	0.04	0.12	0.07	0.10	0.04	0.11	0.06	0.14	0.06	0.13	0.05	0.10	0.04
TiO ₂	0.03	0.04	0.05	0.04	0.00	0.04	0.05	0.05	0.10	0.04	0.04	0.04	0.08	0.04	0.02	0.04	0.02	0.03
Total	99.04		99.28		99.35		99.32		99.77		99.31		99.62		99.27		99.52	

Na	0.004		0.004		0.003		0.004		0.005		0.006		0.005		0.005		0.004	
Si	0.989		0.991		0.990		0.989		0.988		0.989		0.989		0.992		0.988	
Al	0.015		0.016		0.015		0.015		0.014		0.015		0.015		0.013		0.016	
Mg	0.909		0.906		0.920		0.912		0.906		0.914		0.910		0.914		0.910	
K	0.000		0.000		0.000		0.000		0.000		0.000		0.000		0.000		0.000	
Ca	0.009		0.009		0.009		0.007		0.007		0.007		0.006		0.006		0.009	
Cr	0.004		0.005		0.004		0.005		0.004		0.006		0.006		0.005		0.005	
Fe ²⁺	0.070		0.068		0.061		0.067		0.076		0.065		0.067		0.063		0.069	
P	0.000		0.000		0.000		0.000		0.000		0.000		0.000		0.000		0.000	
Mn	0.002		0.001		0.001		0.002		0.001		0.002		0.002		0.002		0.001	
Ti	0.000		0.001		0.000		0.001		0.001		0.000		0.001		0.000		0.000	
Total	2.003		2.001		2.002		2.002		2.003		2.003		2.001		2.001		2.004	

Mg#	92.8	0.15	93.0	0.10	93.8	0.13	93.1	0.15	92.3	0.22	93.3	0.15	93.2	0.16	93.5	0.12	92.9	0.23
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Sample	K1	σ	K2	σ	K3	K4	σ	K5	σ	K6	σ	K7	σ	K8	σ	K9	σ
n	4		4		1	3		4		10		9		7		8	
P	26	5	30	16	41	33.21	5	104	119	264	502	23	8	100	12	70	5
Sc	7.5	0.7	6.7	0.7	5.1	7.2	0.3	8	7	17	26	4.62	0.24	16	1	10.98	0.18
Ti	163	18	265	14	24	368	4	20	11	834	1381	529	28	189	62	748	19
V	47	7	39	4	45	52	2	16	12	37	26	51	5	213	8	114	2
Co	69	8	62	6	63	64	3	146	164	502	822	58	5	279	25	176	3
Ni	1037	129	969	128	1051	756	71	3576	4196	3380	3318	869	68	4352	411	2804	52
Ga	1.32	0.13	1.4	0.2	1.05	1.18	0.07	0.6	0.2	0.76	0.22	1.13	0.09	3.8	0.3	4.03	0.12
Rb	0.21	0.20	1.3	2.0	0.42	0.36	0.07	bdl		0.02	0.04	0.25	0.45	0.06	0.35	0.35	0.69
Sr	7	13	5	8	6	5	2	2	2	1	2	2	3	4.5	4.4	2.01	1.73
Y	0.03	0.01	0.08	0.06	0.06	0.09	0.02	1	1	0.6	1.1	0.09	0.05	0.04	0.07	0.13	0.02
Zr	0.76	0.14	1.1	1.0	0.8	0.96	0.33	5	4	4	4	0.87	0.48	1.16	0.80	1.51	0.13
Nb	0.18	0.09	0.42	0.57	0.66	0.70	0.30	0.9	1.1	3	6	0.32	0.36	1.01	0.65	0.29	0.10
Ba	0.77	0.75	2.3	2.3	1.5	6	7	0.12	0.19	0.11	0.14	2	3	0.2	5.2	0.56	1.22
La	0.05	0.07	0.27	0.49	1.6	0.30	0.24	0.11	0.12	0.05	0.08	0.13	0.27	0.05	0.49	0.06	0.11
Ce	0.13	0.17	0.6	1.1	3.0	0.66	0.48	0.32	0.34	0.17	0.24	0.32	0.55	0.32	0.93	0.19	0.25
Pr	0.02	0.02	0.07	0.11	0.25	0.06	0.04	0.06	0.06	0.03	0.04	0.04	0.05	0.05	0.10	0.03	0.02
Nd	0.09	0.06	0.26	0.40	0.78	0.26	0.18	0.30	0.19	0.17	0.17	0.15	0.18	0.30	0.33	0.17	0.09
Sm	0.03	0.01	0.04	0.06	0.07	0.02	0.01	0.12	0.02	0.06	0.06	0.03	0.03	0.07	0.05	0.05	0.02
Eu	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.05	0.02	0.02	0.03	0.01	0.01	0.02	0.02	0.01	0.00
Gd	0.02	0.01	0.03	0.04	0.03	0.01	0.02	0.17	0.10	0.08	0.10	0.03	0.01	0.04	0.06	0.04	0.01
Tb	bdl		bdl		bdl	bdl		0.03	0.02	0.01	0.02	bdl		bdl		0.01	0.00
Dy	0.01	0.00	0.02	0.02	0.01	0.01	0.01	0.23	0.22	0.11	0.17	0.02	0.01	0.01	0.03	0.03	0.01
Ho	bdl		bdl		bdl	bdl		0.05	0.05	0.02	0.04	bdl		bdl		bdl	
Er	bdl		bdl		bdl	bdl		0.15	0.16	0.07	0.12	0.01	0.00	bdl		0.01	0.00
Tm	bdl		bdl		bdl	bdl		0.02	0.02	0.01	0.02	bdl		bdl		bdl	
Yb	bdl		bdl		bdl	bdl		0.14	0.15	0.06	0.11	bdl		bdl		bdl	
Lu	bdl		bdl		bdl	bdl		0.02	0.02	0.01	0.02	bdl	0	bdl		bdl	
Ta	0.02	0.01	0.03	0.03	0.04	0.06	0.00	nd		nd		nd		nd		nd	
Pb	0.02	0.01	0.04	0.04	0.05	0.06	0.03	0.02	0.01	0.03	0.04	0.02	0.03	bdl		0.02	0.01
Th	bdl		0.03	0.05	0.14	0.04	0.04	bdl		bdl		0.02	0.04	bdl		0.01	0.02
U	bdl		0.01	0.01	0.05	0.02	0.01	bdl		bdl		0.01	0.01	bdl		bdl	

One population of clinopyroxene, cpx-1, has Mg# that ranged from 92.6 to 94.1, CaO concentrations ranging from 19.35 to 21.16 wt. %, Cr₂O₃ from 1.55 to 2.10 wt. %, Al₂O₃ from 1.83 to 2.30 wt.% and TiO₂ concentrations below 0.07 wt.% (Table 5.4). The clinopyroxene crystal from sample K9, which is enclosed in phlogopite, has a similar major element composition to those classified as cpx-1. Crystals classified texturally as cpx-2 have lower Mg# (91.3 to 92.6) and CaO (17.12 to 18.12 wt.%) but higher concentrations of Cr₂O₃ (2.96 to 4.40 wt. %), Al₂O₃ (3.05 to 3.18 wt. %) and TiO₂ (0.24 to 0.28 wt. %).

Phlogopite is aluminous (11.71 to 13.10 wt.% Al₂O₃) with K₂O ranging from 9.62 to 10.60 wt.%, TiO₂ from 0.22 to 0.96 wt.%, and Mg# from 93.7 to 94.4 (Table 5.5). Most of these values are similar to those observed in both phlogopite-garnet and phlogopite peridotites from the Kimberley area, but Mg#s are higher than those of both the MARID (80-91) and PIC (91-93) suites (Grégoire et al., 2002, 2003).

5.4.2 Trace Elements

Garnets from the suite exhibit a bimodal distribution in Ti content with four samples (K1, K3, K8, K9) having less than 600 ppm Ti and the remaining samples more than 1000 ppm Ti (Table 5.1). Y varied from 0.5 to 60 ppm across the suite of samples. Primitive mantle normalised garnet rare earth element (REE_N) patterns show a variety of shapes ranging from normal to sinusoidal (Figure 5.5). The most strongly sinusoidal patterns occur for samples K3 and K8, which show a steep increase in REE_N from La to Sm followed by a decrease to Tm and a further increase to Lu. Five samples (K1, K2, K4, K7 and K9) show a weakly sinusoidal trend where there is only a slight decrease in concentration in the heavy REEs (HREE); the remaining two samples (K5 and K6) have

Table 5.4: Major (wt.% oxide), and trace element (ppm) contents of clinopyroxene. Classification as either cpx-1 or cpx-2 is also indicated. Cations were calculated on the basis of 6 oxygen atoms. [Mg# = $100 \times \text{Mg}/(\text{Mg} + \text{Fe})$]. “bdl” = below detection limit; “nd” = not determined; “n” number of analyses obtained. Errors are given as one standard deviation (σ), where no error is given only a single measurement was obtained. Sample K7 did not have large enough crystals for LA-ICP-MS analysis.

Sample	K1	σ	K2	σ	K3	σ	K4	σ	K5	σ	K6	σ	K7	σ	K9	σ
Classification	Cpx-1		Cpx-1		Cpx-1		Cpx-2		Cpx-2		Cpx-2		Cpx-2		-	
n	7		8		8		1		11		12		6		4	
Na ₂ O	1.84	0.19	2.00	0.11	1.47	0.16	3.39		2.86	0.15	3.19	0.38	3.18	0.15	1.87	0.10
SiO ₂	54.06	0.24	53.89	0.40	54.29	0.28	54.85		54.19	0.33	53.82	0.62	54.16	0.24	54.40	0.15
Al ₂ O ₃	2.04	0.07	2.30	0.08	1.83	0.04	3.58		3.05	0.08	3.10	0.31	3.14	0.09	2.35	0.05
MgO	16.57	0.21	16.40	0.22	17.07	0.17	14.32		15.20	0.18	14.84	0.59	14.69	0.15	16.52	0.10
K ₂ O	0.02	0.04	0.02	0.03	0.00	0.02	0.00		0.01	0.02	0.03	0.04	0.02	0.02	0.00	0.04
CaO	20.22	0.16	19.35	0.17	21.16	0.18	17.38		18.21	0.27	17.12	0.74	17.72	0.16	19.46	0.15
Cr ₂ O ₃	1.74	0.07	2.10	0.05	1.55	0.05	3.70		2.96	0.08	4.40	0.32	3.82	0.09	2.04	0.03
FeO	2.30	0.10	2.33	0.10	1.89	0.04	2.40		2.59	0.09	2.11	0.09	2.27	0.08	2.36	0.07
P ₂ O ₅	0.02	0.01	0.02	0.02	0.02	0.01	0.03		0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.01
MnO	0.05	0.07	0.09	0.05	0.07	0.05	0.11		0.08	0.04	0.09	0.06	0.09	0.06	0.09	0.05
TiO ₂	0.04	0.03	0.07	0.04	0.02	0.04	0.28		0.25	0.04	0.27	0.03	0.24	0.02	0.07	0.02
Total	98.86		98.54		99.34		99.99		99.40		98.97		99.34		99.14	
Na	0.130		0.142		0.104		0.237		0.202		0.226		0.22		0.132	
Si	1.978		1.976		1.975		1.979		1.972		1.967		1.973		1.980	
Al	0.088		0.099		0.079		0.152		0.131		0.133		0.135		0.101	
Mg	0.904		0.896		0.926		0.770		0.825		0.808		0.797		0.896	
K	0.001		0.001		0.000		0.000		0.001		0.001		0.001		0.000	
Ca	0.793		0.760		0.825		0.672		0.710		0.670		0.691		0.759	
Cr	0.050		0.061		0.045		0.106		0.085		0.127		0.110		0.059	
Fe	0.070		0.072		0.058		0.072		0.079		0.065		0.069		0.072	
P	0.001		0.001		0.001		0.001		0.001		0.001		0.000		0.001	
Mn	0.001		0.003		0.002		0.003		0.003		0.003		0.003		0.003	
Ti	0.001		0.002		0.000		0.008		0.007		0.007		0.006		0.002	
Total	4.017		4.012		4.014		4.001		4.014		4.008		4.010		4.004	
Mg#	92.8	0.32	92.6	0.23	94.1	0.15	91.4		91.3	0.26	92.6	0.41	92.0	0.16	92.6	0.20

Sample	K1	σ	K2	σ	K3	σ	K4	σ	K5	σ	K6	σ	K7	σ	K9	σ
n	6		7		6		2		20		19				4	
P	69	28	162	185	55	30	244	23	78	24	79	25			25	44
Sc	23.8	2.5	28	3	13	3	63	6	53	15	51	14			1.8	0.2
Ti	538	657	599	92	113	147	1309	30	708	709	797	601			38	2
V	280	27	281	25	585	280	380	30	263	145	238	94			19.3	0.3
Co	23	5	46	48	69	269	20	1	21	5	21	5			1.9	0.8
Ni	445	141	858	823	127	164	359	15	224	254	175	136			33	8
Ga	2.7	0.7	3.02	0.30	1.42	0.52	3.21	0.16	5.0	2.8	5.0	2.9			0.21	0.03
Rb	11	26	1.4	1.9	0.04	1.13	3.55	0.80	1.6	3.7	1.7	3.8			0.04	0.09
Sr	366	16	308	95	447	54	293	1	228	39	222	27			25	4
Y	1.18	0.39	2.3	0.8	0.42	0.53	8.90	0.22	6.5	1.6	6.6	1.4			0.14	0.07
Zr	44	8.0	45	9	21	13	129	3	76	6	76	7			2.80	0.88
Nb	2.9	3.8	2.5	2.2	1.3	2.4	3.08	0.02	2.0	1.3	2.1	1.3			0.11	0.18
Ba	47	96	354	889	18	38	19.9	0.9	16	22	16	22			0.4	0.81
La	4.9	1.4	6.3	4.9	5.0	0.6	9.3	0.6	6.5	2.6	6.5	2.6			1.0	1.5
Ce	19	3.0	19	10	21	2	29	2	22	6	22	6			2.7	3.2
Pr	3.48	0.36	3.1	1.2	3.8	0.4	4.67	0.17	4.0	1.2	4.1	1.3			0.37	0.32
Nd	19.4	1.5	16	5	21	2	24	1	19.6	4.2	20	4			1.7	1.1
Sm	4.21	0.35	3.49	0.73	3.73	0.39	5.52	0.11	4.9	1.0	4.9	1.0			0.29	0.13
Eu	1.03	0.10	0.94	0.21	0.73	0.14	1.61	0.01	1.4	0.30	1.44	0.30			0.07	0.03
Gd	2.03	0.27	2.20	0.49	1.19	0.32	4.20	0.07	3.55	0.57	3.58	0.55			0.15	0.07
Tb	0.15	0.03	0.21	0.05	0.07	0.04	0.51	0.00	0.41	0.07	0.42	0.07			0.01	0.01
Dy	0.47	0.12	0.84	0.25	0.18	0.17	2.50	0.10	1.93	0.33	2.00	0.28			0.05	0.02
Ho	0.05	0.02	0.10	0.03	0.02	0.02	0.39	0.02	0.28	0.07	0.29	0.06			bdl	
Er	0.07	0.03	0.16	0.06	0.03	0.04	0.80	0.05	0.58	0.19	0.60	0.17			0.01	0.01
Tm	0.01	0.00	0.01	0.01	bdl		0.09	0.01	0.06	0.03	0.06	0.02			bdl	
Yb	0.02	0.02	0.06	0.02	0.01	0.02	0.43	0.04	0.31	0.18	0.33	0.16			bdl	
Lu	bdl		bdl		bdl		0.05	0.01	0.04	0.03	0.04	0.02			bdl	
Ta	0.17	0.22	0.12	0.10	0.1	0.1	0.24	0.01	nd		Nd				nd	
Pb	0.50	0.07	0.58	0.34	0.5	0.1	0.56	0.11	0.45	0.18	0.45	0.19			0.04	0.01
Th	0.37	0.62	0.38	0.45	0.12	0.15	0.69	0.03	0.23	0.16	0.23	0.16			0.1	0.1
U	0.04	0.02	0.10	0.12	0.03	0.05	0.13	0.01	0.05	0.02	0.05	0.02			bdl	

Table 5.5: Major (wt.% oxide), and trace element (ppm) contents of phlogopite. [Mg# = $100 \times \text{Mg}/(\text{Mg} + \text{Fe})$]. “bdl” = below detection limit; “n” number of analyses obtained. Errors are given as one standard deviation (σ).

Sample	K1	σ	K2	σ	K6	σ	K7	σ	K9	σ
	4		9		10		12		9	
Na ₂ O	0.24	0.04	0.17	0.09	0.26	0.07	0.51	0.21	0.16	0.04
SiO ₂	40.95	0.10	40.80	0.51	40.78	0.72	40.65	0.73	41.07	0.26
Al ₂ O ₃	11.71	2.33	12.93	0.26	12.91	0.88	13.10	1.04	12.42	1.67
MgO	26.26	2.69	25.15	0.48	24.90	0.60	25.34	1.41	25.74	2.29
K ₂ O	9.62	2.01	10.54	0.42	10.60	0.33	9.64	0.86	10.11	1.42
CaO	0.00	0.03	0.00	0.01	0.00	0.02	0.05	0.11	0.00	0.02
Cr ₂ O ₃	0.65	0.15	0.93	0.33	1.15	0.45	1.30	0.63	0.76	0.12
FeO	2.98	0.15	2.99	0.18	2.65	0.08	2.75	0.19	2.82	0.34
P ₂ O ₅	0.02	0.01	0.00	0.01	0.01	0.01	0.01	0.02	0.00	0.01
MnO	0.02	0.03	0.02	0.03	0.03	0.06	0.03	0.04	0.02	0.02
TiO ₂	0.22	0.03	0.52	0.40	0.96	0.37	0.83	0.43	0.39	0.06
Total	93.00	1.59	94.46	0.45	94.71	0.54	94.74	0.79	93.88	1.45
Mg#	94.0	0.27	93.7	0.46	94.4	0.16	94.3	0.60	94.2	0.96
n	9		9		4		7		11	
Sc	3	1	3.6	0.2	13	5	4.3	0.9	3.6	0.5
Ti	2095	706	4467	111	16055	1287	6745	611	4391	281
V	133	46	139	3	271	9	131	6	135	7
Cr	5965	2100	7311	56	21353	1413	8693	299	6999	462
Mn	203	73	206	10	253	40	298	89	223	44
Co	74	26	82.1	0.8	75	8	74	2	79	5
Ni	2235	786	2575	22	1702	567	2289	100	2496	170
Cu	1.9	0.6	2.3	0.4	1.5	0.1	2.3	1.0	2.34	0.39
Zn	34	12	40.9	0.7	28	2	34.1	1.6	39	1
Ga	9.8	3.4	12.8	0.2	8.2	0.5	10.1	0.2	12.4	0.9
Rb	314	110	529	4.9	604	80	616	46	511	34
Sr	25	12	19.6	3.3	39	11	73	31	24	23
Y	0.03	0.02	0.04	0.08	0.1	0.2	0.19	0.17	0.1	0.1
Zr	6.7	2.0	6.5	2.2	22	6	8.5	5.5	6.9	3.4
Nb	22	8	17.1	0.7	54	9	19.8	3.2	16.7	1.6
Cs	4.6	1.6	6.3	0.1	5.2	0.4	5.65	0.52	6.16	0.34
Ba	1319	442	1377	153	1466	337	2607	245	1275	134
La	0.04	0.05	0.04	0.08	0.15	0.16	0.35	0.43	0.8	1.9
Ce	0.07	0.09	0.06	0.14	0.29	0.33	0.49	0.57	1.1	2.9
Pr	0.01	0.01	0.01	0.01	0.03	0.04	0.05	0.06	0.10	0.25
Nd	0.03	0.04	0.02	0.05	0.15	0.22	0.17	0.19	0.32	0.81
Sm	bdl		bdl		0.03	0.05	0.03	0.04	0.04	0.11
Eu	0.02	0.01	0.03	0.00	0.05	0.02	0.05	0.01	0.03	0.02
Gd	bdl		bdl		0.03	0.05	0.03	0.03	0.03	0.07
Tb	bdl		bdl		bdl		bdl		bdl	
Dy	bdl		bdl		0.02	0.03	0.02	0.03	0.01	0.03
Ho	bdl		bdl		bdl		0.01	0.01	bdl	
Er	bdl		bdl		0.01	0.02	0.01	0.01	bdl	
Tm	bdl		bdl		bdl		bdl		bdl	
Yb	bdl		bdl		0.01	0.01	0.01	0.01	bdl	
Lu	bdl		bdl		bdl		bdl		bdl	
Hf	0.20	0.06	0.21	0.05	1.00	0.29	0.24	0.12	0.23	0.12
Ta	1.92	0.67	1.79	0.05	5.88	0.98	1.53	0.23	1.68	0.09
Pb	0.14	0.05	0.11	0.00	0.25	0.10	0.33	0.02	0.09	0.01
Th	0.02	0.01	0.01	0.02	0.01	0.02	0.17	0.04	bdl	
U	0.01	0.00	0.01	0.01	0.01	0.01	0.04	0.02	bdl	

normal patterns with a gradual increase towards the HREE_N. Two samples (K2 and K6) show a slight enrichment in La relative to Ce; in sample K2 it is only observed in 2 of the 16 analyses whilst it is observed in the only two analyses of K6. This enrichment occurs in samples that show either sinusoidal or normal REE_N patterns and was also observed in some garnets from the nearby Bultfontein kimberlite (Creighton et al., 2009). The ratio Sm/Tm_N provides a measure of how sinusoidal a garnet REE_N pattern is, with values greater than 1 indicating a sinusoidal pattern, whilst values less than 1 correspond to a normal pattern. Low Sm/Tm_N, and the related normal patterns are also associated with increased concentrations of Y and Ti, whilst sinusoidal patterns are found in samples with lower concentrations of these two elements (Table 5.1)

Orthopyroxene contains significant amounts of Ni (750 – 4400 ppm), Co (50 – 500 ppm), V (15 – 215 ppm) and Ti (20 – 840 ppm), which generally exceed the ranges reported by Grégoire et al. (2003). Other trace elements, including the REEs were either below the LA-ICP-MS detection limits or present in very minor amounts (Table 5.3).

The two different groups of clinopyroxene, cpx-1 and cpx-2, have distinctly different trace element compositions (Table 5.4), which are most clearly illustrated by their average REE_N patterns (Figure 5.6). Both populations have similar light REE_N (LREE_N) abundances (below Sm), but different middle and heavy REE_N concentrations. Cpx-1 is characterised by HREE_N values that are below 1, whilst cpx-2 has HREE_N values approximately one order of magnitude larger. The enclosed clinopyroxene of sample K9 shows a similar REE_N pattern to cpx-1; however, all elements have concentrations that

are nearly one order of magnitude lower. Clinopyroxene grains in sample K7 were too small for analysis by LA-ICP-MS.

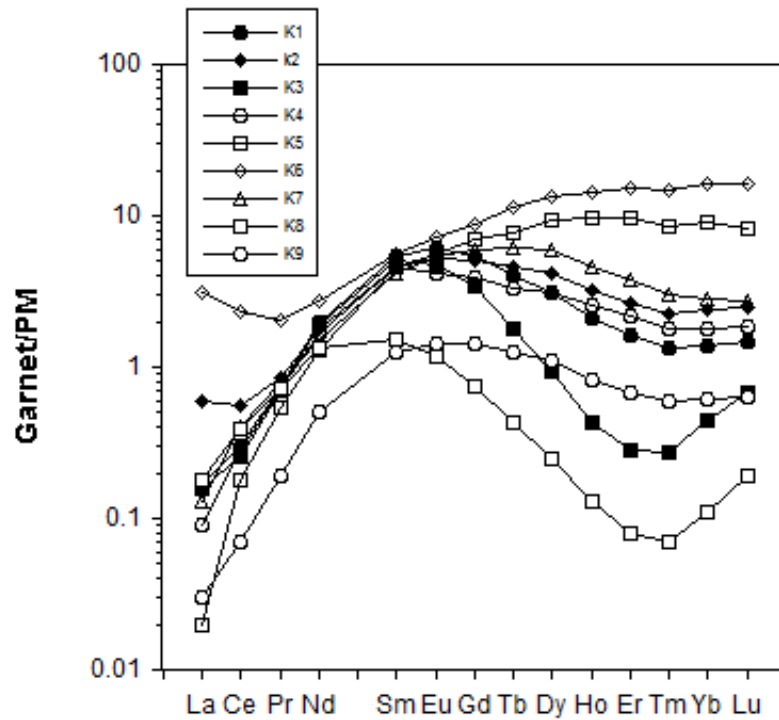


Figure 5.5: Rare earth element patterns for garnet, normalised to primitive mantle (Palme and O'Neill, 2007). Black symbols indicate samples where cpx-1 is present, open symbols indicate the presence of cpx-2, white symbols represent no clinopyroxene (K8) or fully enclosed clinopyroxene (K9).

The most abundant trace elements in olivine are Ni (2100 – 3200 ppm) and Co (130 – 135 ppm), whilst V (3 – 6 ppm), Sc (1.8 – 2.5 ppm) and Ti (4 – 150 ppm) are low compared to olivine from similar settings (Grégoire et al., 2003) (Table 5.2).

Phlogopite shows a wide range of trace element compositions, with one sample, K6, generally having higher trace element values than all other samples (Table 5.5). Transition metals are generally enriched compared to phlogopite from other garnet

peridotites (Grégoire et al., 2003), with Ni (1700 – 2600 ppm), Co (73 – 83 ppm), V (130 – 270 ppm), and Rb (300 – 620 ppm). Values for Ba (1300 – 2600 ppm), Zr (6 – 9 ppm), Nb (17 – 22 ppm), Ta (1.6 – 2.5 ppm) and Sr (20 – 75 ppm) are similar to those observed by Grégoire et al. (2003), however, K6 is enriched in Zr (22 ppm), Nb (55 ppm) and Ta (5.9 ppm). Ga is lower than previously reported with values of 8 – 13 ppm, while most other trace elements are close to or below the detection limit.

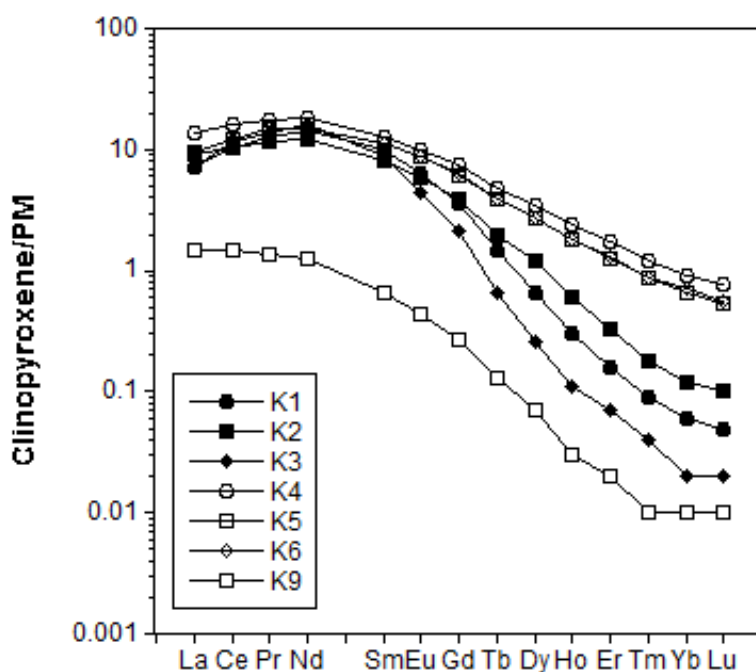


Figure 5.6: Rare earth element patterns for clinopyroxene, normalised to primitive mantle (Palme and O'Neill, 2007). Black symbols indicate samples where cpx-1 is present, open symbols indicate the presence of cpx-2, white symbols represent fully enclosed clinopyroxene (K9).

5.4.3 Garnet $\text{Fe}^{3+}/\Sigma\text{Fe}$

$\text{Fe}^{3+}/\Sigma\text{Fe}$ was determined for garnets in all samples except K6 and K7. Multiple crystals were analysed for four samples (K1 – 2 crystals, K2 - 2, K3 - 4 and K9 - 2) and a single crystal for K4, K5 and K8, only a single spot was analysed on each sample. The results

of multiple measurements were within ± 0.01 of the mean for that sample and are reported as the mean (Table 5.6). Crystals in sample K6 were too small to be analysed whilst spectra obtained for sample K7 were not consistent with garnet; these garnets are surrounded by thick alteration rims and it is likely that these rims were accidentally analysed in conjunction with the garnet. Mean $\text{Fe}^{3+}/\Sigma\text{Fe}$ varied from 0.047(10) to 0.070(10), which is within the range normally found for garnet peridotite xenoliths from the Kaapvaal Craton and other locations (Creighton et al., 2009, Woodland and Koch, 2003, Yaxley et al., 2012, Chapter 2).

Table 5.6: Calculated equilibrium temperatures ($^{\circ}\text{C}$) and pressures (GPa); $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined by XANES and the calculated $f\text{O}_2$. See text for details of calculations. Standard errors are ± 50 $^{\circ}\text{C}$ for T[TA98], ± 20 $^{\circ}\text{C}$ for T[Ca-opx], ± 0.4 GPa for p[NG85], ± 0.01 for $\text{Fe}^{3+}/\Sigma\text{Fe}$ and ± 0.6 log units for both $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ [S13] and $\Delta\log f\text{O}_2^{[\text{FMQ}]}$ [GW95].

Sample	K1	K2	K3	K4	K5	K6	K7	K8	K9
T[TA98]	917	992	903	925	932	970	910		1028
P[NG85] ¹	3.68	4.14	3.65	4.03	4.02	4.02	3.93		4.20
T[Ca-opx]	999	1014	1003	943	964	933	925	914	1020
P[NG85] ²	4.09	4.26	4.16	4.12	4.19	3.84	4.00	3.95	4.16
$\text{Fe}^{3+}/\Sigma\text{Fe}$	0.070	0.062	0.049	0.052	0.070			0.047	0.051
$\Delta\log f\text{O}_2^{[\text{FMQ}]}$ [GW95]	-2.27	-2.65	-2.96	-2.70	-2.31			-2.68	-2.93
$\Delta\log f\text{O}_2^{[\text{FMQ}]}$ [S13]	-1.86	-2.22	-2.54	-2.32	-1.85			-2.33	-2.53

¹P[NG85] calculated iteratively using T[TA98]

²P[NG85] calculated iteratively using T[Ca-opx]

5.5 Discussion

5.5.1 Petrogenesis

The two different populations of clinopyroxene in the suite, cpx-1 and cpx-2, have different textural relationships, and major and trace element compositions. Cpx-1 is characterised by large crystals that appear to have formed in equilibrium with the surrounding coarse-grained olivine, orthopyroxene and garnet. Grains classified as cpx-2 are far smaller and generally associated with garnet alteration rims, phlogopite or interstitial spaces in the olivine matrix. Thus, these clinopyroxenes are thought to have formed in a secondary event after formation of the coarser grains. None of the sections examined contained both cpx-1 and cpx-2. The phlogopite-enclosed clinopyroxene in

K9 has a different origin as its major element composition is similar to that of cpx-1 but all the REE have substantially lower abundances. One possible explanation for its appearance is the open-system replacement of clinopyroxene by phlogopite during a metasomatic event, leaving only a small core of clinopyroxene; the large crystal size of the phlogopite suggests that it may have been a primary clinopyroxene initially. This interpretation may also be consistent with the low REE abundances in phlogopite because the clinopyroxene inclusion is significantly lower in REE than other cpx-1 or cpx-2 grains.

5.5.2 Thermobarometry and Oxybarometry

Given that there are two generations of clinopyroxene in this suite (cpx-1 and cpx-2) and because both garnet and orthopyroxene are interpreted to form part of the primary assemblage, it was decided to also use the Ca in orthopyroxene thermometer of Brey and Kohler (1990), $T[\text{Ca-opx}]$, in combination with $P[\text{NG85}]$, which gave temperatures of 914 to 1020 °C and pressures of 3.84 to 4.26 GPa (Table 5.6). The Fe^{3+} content of garnet was included in the pressure determination to improve the accuracy of the calculation (Brey and Köhler, 1990). These two approaches returned pressures that agreed within ± 0.50 GPa and temperatures within ± 100 °C, with the largest variations in temperature correlating with the largest deviations in pressure. Although most samples contain both ortho- and clinopyroxene, use of the two pyroxene thermometer of Taylor (1998), $T[\text{TA98}]$ in combination with the garnet-orthopyroxene barometer of Nickel and Green (1985), $P[\text{NG85}]$ may be problematic because of the existence of two generations of clinopyroxene. This thermometer assumes that all clinopyroxene is in equilibrium with orthopyroxene and garnet, which, may not be valid for cpx-2. However, despite this, the $T[\text{TA98}]/P[\text{NG85}]$ combination yielded temperatures from

903 to 1028 °C and pressures from 3.65 to 4.20 GPa, essentially identical to T[Ca-in-OPX]/P[NG85], suggesting that cpx-1 and cpx-2 are both equilibrated with garnet and orthopyroxene in these samples. The calculated pressures and temperatures fall just below a cratonic geotherm of 43 mW m⁻², which is typical of the Kaapvaal and other cratons (Creighton et al., 2009), as shown in Figure 5.7.

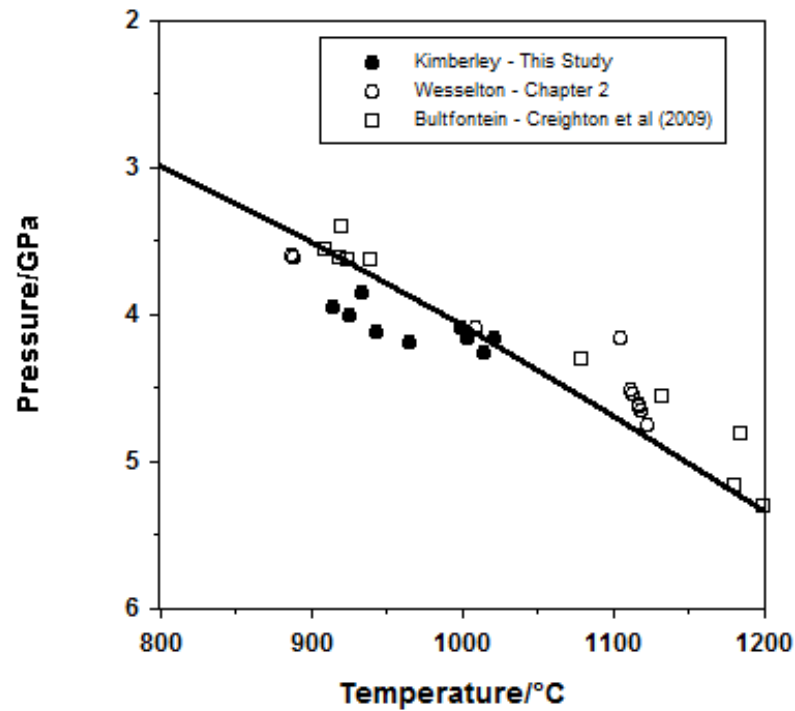


Figure 5.7: P[NG85] against T[Ca-opx] (Nimis and Grütter, 2010) for the current suite and other data from the Kimberley area (Creighton et al., 2009, Chapter 2). The curve is an estimated 43 mW m⁻² geotherm (Pollack and Chapman, 1977).

T[Ca-opx] in combination with P[NG85] was chosen for use in the calculation of fO_2 . The fO_2 recorded by the samples was determined using the methods of Stagno et al. (2013): fO_2 [S13]; and Gudmundsson and Wood (1995): fO_2 [GW95]; which require $Fe^{3+}/\Sigma Fe$ of garnets the compositions of coexisting garnet, orthopyroxene and olivine and the equilibrium temperature and pressure (Table 5.6). $\Delta \log fO_2^{[FMQ]}$ as calculated

using [S13] ranged from -1.85 to -2.54, with an average of -2.24. The standard error of the oxybarometer is ± 0.6 log units and thus all samples are within error of the average value. Values calculated using [GW95] were approximately 0.4 log units more reducing, ranging from -2.27 to -2.96, with an average of -2.64(60). The results obtained using the approach of Stagno et al. (2013) are preferred as this method was experimentally calibrated over a pressure range relevant to our samples.

5.5.3 Metasomatism

The textural and compositional differences between the two clinopyroxene populations suggest that cpx-2 was formed by a relatively late metasomatic event. In particular, high concentrations of Cr_2O_3 and Na_2O in clinopyroxene from both kimberlite- and basalt-sourced peridotites have been attributed to a metasomatic origin (Grégoire et al., 2002, 2003, van Achtebergh et al., 2001, Yaxley et al., 1998).

The textural relationships between phlogopite and other minerals suggest that it also has a metasomatic origin, with it appearing interstitially along crystal boundaries or in association with clinopyroxene, especially cpx-2. Phlogopite was found in samples that contain either cpx-1 or cpx-2. There is no substantial difference in phlogopite composition between samples and as such it is difficult to determine if the phlogopite observed in samples containing cpx-1 was formed at the same time as that in samples containing cpx-2.

Two trends relating to metasomatism have been identified in Y-Zr space for garnet from peridotite xenoliths by Griffin and Ryan (1995), both of which originate from a depleted

field with low Y and Zr (Figure 5.8). The first trend is characterised by a positive correlation between Y and Zr and is attributed to melt metasomatism. The data for garnets of the cpx-2 containing samples plot near this trend. A second trend is defined by a stronger increase in Zr relative to Y and was attributed to low temperature (900 – 1100 °C) metasomatism and the formation of phlogopite. This signature can be seen in all three of the cpx-1 containing samples, although phlogopite was only observed in two of these. It is entirely possible that phlogopite is present in the other xenoliths, but was not sampled in the sections examined. The remaining two samples plot in the depleted field, with one of these being a clinopyroxene free harzburgite (K8); and the other containing only a single clinopyroxene crystal enclosed in phlogopite (K9).

The textural relationships of cpx-2 and phlogopite are consistent with late metasomatic addition as they are fine grained and occur interstitially to olivine and orthopyroxene. Garnet in samples containing this metasomatic assemblage has Y-Ti-Zr concentrations that correspond to the ‘melt metasomatism’ style of Griffin and Ryan (1995), as shown in Figure 5.8. The two samples with the strongest melt metasomatism signature (K5, K6) have normal garnet REE_N patterns, whilst the remaining two samples containing cpx-2 (K4, K7) have weakly sinusoidal garnet REE_N normalised patterns (Figure 5.5). As the formation of this assemblage is related to a melt metasomatism event, which could well be associated with the host kimberlite; the lack of recrystallisation of this fine grained material to a coarse-grained assemblage supports this being a relatively recent event.

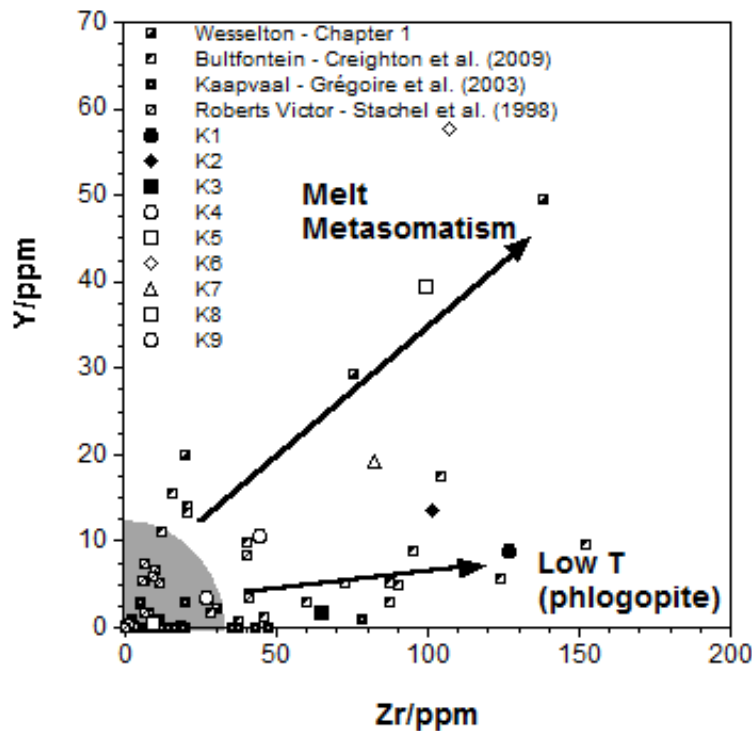


Figure 5.8: Y against Zr in garnets from the current study and other studies of the Kaapvaal craton. The grey shaded depleted field, melt metasomatism and low temperature (phlogopite) metasomatism trends are from Griffin and Ryan (1995).

Garnet from the samples containing cpx-1 (K1, K2, K3) have Y-Ti-Zr concentrations consistent with the ‘fluid metasomatism’ style of Griffin and Ryan (1995), as shown in Figure 5.8, whilst the REE_N patterns are strongly (K3) or weakly (K1, K2) sinusoidal (Figure 5.5). These also show a depleted HREE_N signature in clinopyroxene, which has been previously attributed to metasomatism within the Kaapvaal Craton (Grégoire et al., 2002, 2003). This indicates that the formation of cpx-1 and associated phlogopite may be related to a fluid metasomatism event. This event may have occurred earlier as it is characterised by coarser grained clinopyroxene and is cross-cut by later stage features.

5.5.4 Depth – fO_2 Systematics

A broad trend of decreasing fO_2 with increasing depth has been observed for the Kaapvaal cratonic lithosphere (Creighton et al., 2009, Lazarov et al., 2009, Woodland and Koch, 2003, Chapter 2) and also in other cratons such as the Slave and Siberian (Creighton et al., 2010, Yaxley et al., 2012). Earlier studies on the Kaapvaal craton observed a decrease in the slope of the depth - $\Delta \log fO_2^{[FMQ]}$ trend at depths below 140 km, which was attributed to metasomatic enrichment of sheared peridotites (Woodland and Koch, 2003), however, other studies suggest that this may have been a function of the sampling, rather than a broad trend (Creighton et al., 2009, Griffin et al., 2003). A difference in fO_2 associated with the texture of the garnet peridotites has also been proposed by a number of studies, with porphyroclastic or sheared peridotites generally being more oxidised than coarse or granuloblastic peridotites (Luth et al., 1990, Woodland and Koch, 2003). These peridotites typically have more fertile compositions, characterised by increased fayalite in olivine, which would normally lead to a reduction in the calculated fO_2 , however, they tend to also have higher $Fe^{3+}/\Sigma Fe$ in garnet, which counter-balances this effect, allowing for the oxidised state observed (Creighton et al., 2009, Luth et al., 1990). More recent studies have found that this divide between porphyroclastic and coarse peridotites is probably an artefact of sampling, rather than a true trend with samples of both types being both oxidised and reduced (Creighton et al., 2009).

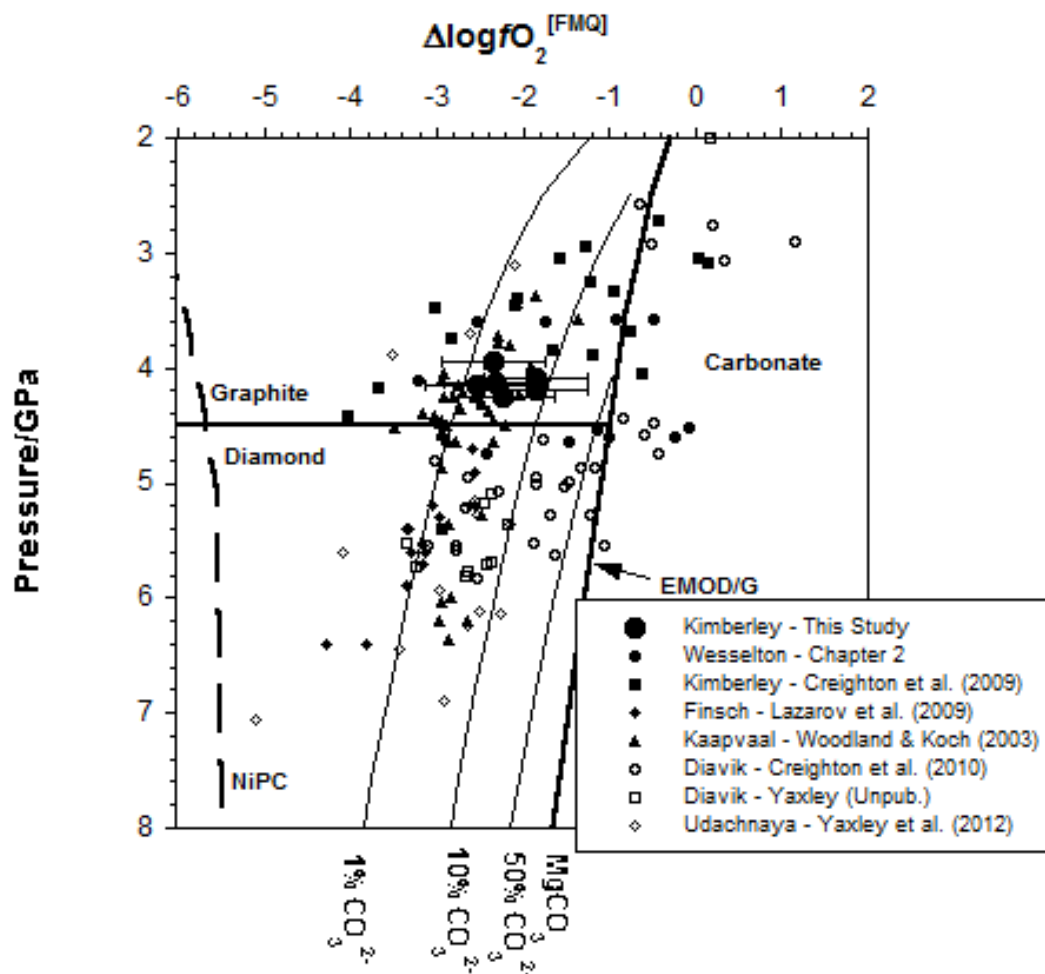


Figure 5.9: $\Delta \log fO_2^{[FMQ]}$ versus equilibrium pressure for the current study and from the literature. EMOD/G refers to the diamond limiting reaction enstatite + magnesite = olivine + C + O_2 (Luth, 1993) in the diamond and graphite stability fields respectively. The curves to the left of EMOD/G indicate the fO_2 of melts in equilibrium with diamond or graphite, for different carbonate (CO_3^{2-}) contents (expressed as molar percentage of MCO_3 where M is a divalent cation) (Stagno and Frost, 2010). The pressure of the diamond-graphite transition is based on a 43 mW m⁻² geotherm. NiPC is the Ni precipitation curve from O'Neill and Wall (1987).

The samples from the current study fall in a very small range of fO_2 -pressure space, within the graphite stability field (Figure 5.9). The samples have P- fO_2 values that are consistent with those observed for a number of cratons (Berry et al., 2013, Creighton et al., 2009, 2010, Lazarov et al., 2009, Yaxley et al., 2012). The fO_2 of these samples can provide constraints on the nature of the metasomatic agent that affected the samples, which sample the graphite stability field (Figure 5.9). It has been suggested that silicate melts, at pressures close to the diamond-graphite transition, can contain approximately

10% CO_3^{2-} at $\Delta\log f\text{O}_2^{\text{[FMQ]}}$ of -2 and 1% CO_3^{2-} at values of -3 (Stagno and Frost, 2010, Stagno et al., 2013). Our samples fall in this region, and thus may have been in equilibrium with a carbonated silicate melt with between 1 and 10% CO_3^{2-} , at some point during their history. However, the lack of variation in $f\text{O}_2$ for our samples indicates that the two metasomatic events occurred independently of the recorded redox state.

5.6 Conclusions

A suite of garnet peridotite xenoliths, some of which contained phlogopite, from the Kimberley pipe, South Africa were studied. There is strong evidence for two generations of metasomatic activity, one responsible for the formation of secondary clinopyroxene (cpx-2) and another related to the formation of phlogopite. Thermobarometry was used to determine that the xenoliths sample a small section of the cratonic mantle with $\Delta\log f\text{O}_2^{\text{[FMQ]}}$ ranging from -1.8 to -2.5. Thermobarometry indicates equilibrium pressures of 3.8 – 4.3 GPa and temperatures from 910 – 1020 °C. Based upon these conditions, the metasomatic fluid may have been a carbonated silicate melt with 1 – 10% CO_3^{2-} . As the $f\text{O}_2$ is relatively constant across all samples, it is probable that this metasomatism occurred prior to formation of secondary clinopyroxene and phlogopite.

5.7 Acknowledgements

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Chapter 6: Partitioning of Rare Earth elements between garnet and clinopyroxene in carbonated peridotitic assemblages

The trace elements abundances of minerals in garnet peridotite can be an important diagnostic tool in the identification of metasomatic signatures. However, because trace elements are redistributed to varying extents between all phases during post-metasomatic cooling (Witt-Eickschen and O'Neill, 2005), measured trace element abundances cannot in general be used to determine compositions of melts or fluids that are inferred to have been in equilibrium with the lithosphere represented by any xenoliths. Correction back to the temperature at which metasomatism occurred is necessary and this requires knowledge of the temperature, pressure and compositional dependencies of partition coefficients of trace elements between constituent mineral phases.

Witt-Eickschen and O'Neill (2005) determined the abundance of 30 trace elements in 16 well-equilibrated spinel lherzolites using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), and then quantified the trace element partitioning relationships in all phases as a function of temperature. This data was then used to develop a thermodynamically consistent model that allowed for effects of temperature to be investigated. By extrapolating the model to temperatures appropriate to basaltic melts, it was found that trace elements redistribute from clinopyroxene (the dominant host of incompatible trace elements) into orthopyroxene and even olivine. However,

there has been little work performed into the same phenomenon in garnet peridotite facies (Lazarov et al., 2012).

We have performed a series of piston-cylinder experiments to investigate how the partitioning of rare earth elements between garnet and clinopyroxene (the major hosts of trace elements in garnet peridotite) varies due to temperature, pressure and garnet composition in a carbonated peridotite system. It was found that the partition coefficients ($D_{Ga/Cpx}$) are highest for elements with smaller ionic radii, and they show a decrease with increasing CaO content or temperature, but an increase with increasing pressure.

6.1 Introduction

As peridotite is the major component in the Earth's upper mantle, it is regularly studied to determine how elements are distributed within the mantle; and how this distribution can be used to understand processes within the mantle. At pressures greater than 2 GPa, garnet replaces spinel as the main aluminous mineral in peridotite. Recent studies have suggested that silicate melts in equilibrium with garnet peridotites may also contain a small amount (<10 wt. %) of carbonate melt, which may be responsible for some of the commonly observed metasomatic signatures (Stagno and Frost, 2010, Stagno et al., 2013).

The distribution of minor and trace elements between minerals in peridotite is often used to identify and characterise the impact of various metasomatic agents. Normalised rare earth element patterns (REE_N) in garnet and clinopyroxene are commonly used to identify if metasomatism has occurred; whilst the relationship between Ti, Y and Zr has been used to identify different styles of metasomatism including melt metasomatism and fluid metasomatism (Griffin and Ryan, 1995).

Rare earth element patterns in mantle garnet generally fit within a continuum from 'strongly sinusoidal' to 'weakly sinusoidal' to 'normal' patterns (Stachel et al., 2004). When normalised to primitive mantle, sinusoidal patterns are characterised by an increasing enrichment trend from La to Nd, decreasing down to approximately Ho, before increasing again through to Lu, whilst normal patterns increase from La through Eu before levelling off across the heavy REEs (HREE) (Figure 6.1). Sinusoidal REE_N patterns are generally associated with harzburgitic garnets and correspond with the depleted field on a Zr-Y diagram, particularly in the Kaapvaal craton (Creighton et al.,

2009, Griffin and Ryan, 1995, Stachel et al., 2004). The sinusoidal nature of a REE pattern can be represented in the normalised ratio $[Sm/Tm]_N$, which will be >1 for sinusoidal patterns, but <1 for normal patterns. Figure 6.2 shows that garnets with high $[Sm/Tm]_N$ generally have low Y, indicating that sinusoidal garnet REE patterns almost always correlate with depleted Y signatures, this is particularly evident in samples from Kaapvaal craton (black symbols in Figure 6.2). Normal patterns are generally related to melt metasomatism, such as that observed in the phlogopite-ilmenite-clinopyroxene (PIC) suite and more common in garnet lherzolites, which also show enrichment in both Zr and Y (Creighton et al., 2009, Grégoire et al., 2003, Stachel et al., 2004).

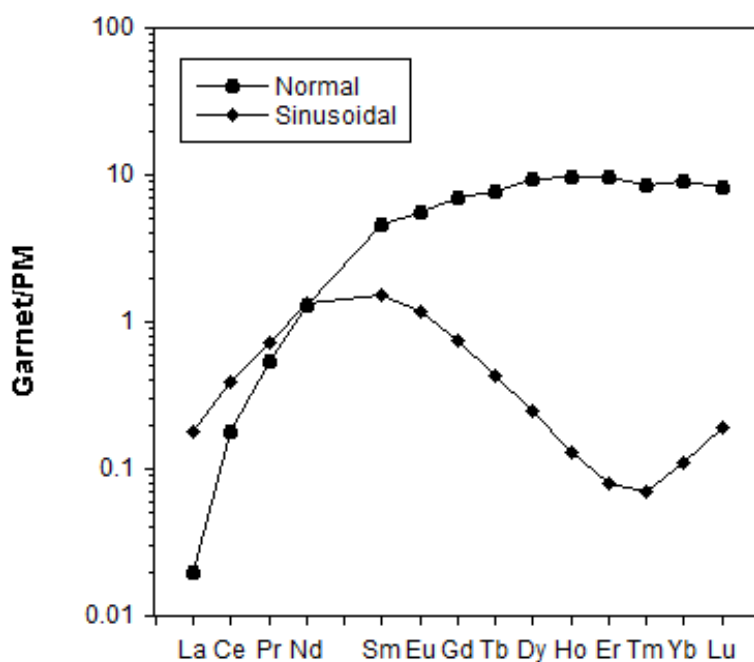


Figure 6.1: Garnet REE plots from Kimberley (South Africa), normalised to the primitive mantle values of Palme and O'Neill (2007).

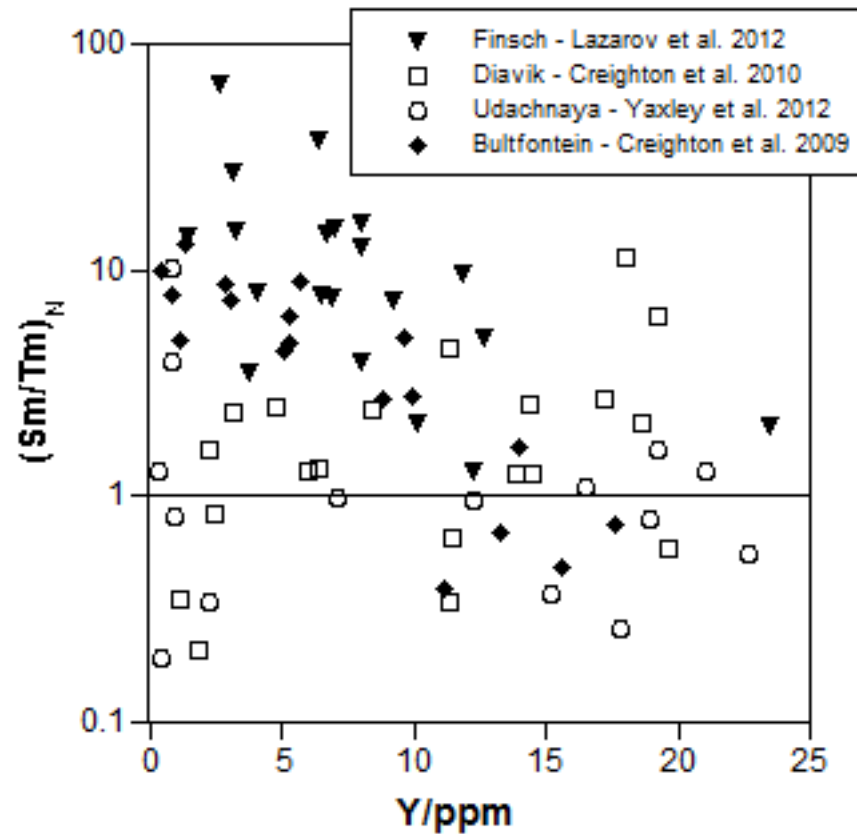


Figure 6.2: Y against $(\text{Sm}/\text{Tm})_N$ for a number of garnet peridotite suites. Suites with dark symbols are from the Kaapvaal craton (South Africa)

Understanding the partitioning of trace elements between minerals in a system is necessary to fully explore how metasomatic trends are recorded and also when applying isotopic systematics. The majority of the experimental studies of trace element partitioning have investigated the partitioning between minerals and melt (Johnson, 1998, Salters et al., 2002, Tuff and Gibson, 2007, Van Westrenen et al., 1999, 2000), though some studies have investigated mineral-mineral partitioning (Ganguly et al., 1998, Green et al., 2000, Van Orman et al., 2001, 2002, Witt-Eickschen and O'Neill, 2005).

Lazarov et al. (2012) performed a detailed study into the trace element partitioning between garnet, clinopyroxene and orthopyroxene from a suite of high temperature

(1200 °C, 6 GPa) garnet peridotite xenoliths from the Finsch mine in the Kaapvaal Craton, South Africa. They determined that major controls on partitioning between garnet and clinopyroxene are: temperature (and/or pressure) and garnet composition. The HREE, Y, Sc, Zr and Hf are preferentially incorporated into garnet whilst the light REE (LREE) and large ion lithophile elements (LILE) have a stronger affinity to clinopyroxene (Lazarov et al., 2012). The most important compositional variable is Ca, with higher Ca in garnet causing a higher compatibility of large cations, such as the LILE and LREE on the dodecahedral site (Lazarov et al., 2012). Experimental studies have concluded that the REE substitute for Ca on the dodecahedral site whilst elements with smaller ionic radii, including the high field strength elements (HFSE) and Sc, are likely to reside on the octahedral site (Van Orman et al., 2002, Van Westrenen et al., 1999, 2000). Chromium concentrations in garnet have been found to vary linearly with Ca in some samples, though a much wider range of Cr₂O₃ concentration relative to CaO is observed (Lazarov et al., 2009). A better correlation between partitioning and Cr₂O₃ has been observed, than is observed between the partition coefficient and CaO, particularly at higher Cr contents, despite the fact the most trace elements substitute for Ca not Cr (Gibson et al., 2008, Lazarov et al., 2009). This relationship may be explained by the substitution of the larger Cr³⁺ in place of the smaller Al³⁺ on the octahedral site, which distorts the crystal lattice, allowing greater substitution of large cations, such as Sr and LREE, for Ca on the dodecahedral site (Ringwood, 1977, Gibson et al., 2008, van Westrenen et al., 2000).

Recent studies into the composition of melts in equilibrium with peridotite in the mantle have suggested that carbonate bearing silicate melts are most likely to exist at the P, T and *f*O₂ conditions associated with garnet peridotite (Dasgupta et al., 2013, Stagno and

Frost, 2010, Stagno et al., 2013). Thus it is possible that the metasomatism observed in garnet peridotites, such as those from Wesselton, may be related to these carbonated silicate melts (Chapter 1).

The partitioning behaviour recorded in mantle xenoliths is unlikely to completely reflect the distribution of trace elements at magmatic temperatures because some degree of sub-solidus re-equilibration occurs as the mantle cools down to the temperature at which the xenoliths were entrained in the kimberlite. One previous study of trace element partitioning in spinel peridotites found that orthopyroxene and olivine can host a significant portion of the trace element balance at magmatic temperatures, however after sub-solidus re-equilibration clinopyroxene becomes the host of most trace elements (Witt-Eickschen and O'Neill, 2005). They strongly suggested that partition coefficients obtained from re-equilibrated peridotites should not be used to investigate partitioning behaviour at magmatic conditions. Thus, in order to fully understand the partitioning behaviour in peridotite systems it is necessary to experimentally determine the appropriate partition coefficients, by quenching directly from magmatic conditions, avoiding any sub-solidus re-equilibration.

A series of experiments have been performed to examine the partitioning of trace elements between garnet and clinopyroxene in peridotite systems. These experiments have examined the effects of temperature, pressure, garnet composition and the presence of carbonate in the system. Variations in garnet composition have been focussed on Ca.

6.2 Experimental Methods

6.2.1 Starting Composition and Preparation

Two base starting compositions were produced by using the composition of naturally occurring peridotites from Diavik, Canada (60505115 - Yaxley et al. in preparation) and Udachnaya, Siberia (UV45-03 - Yaxley et al., 2012). Mixes for each mineral (garnet, clinopyroxene, orthopyroxene and olivine) in each xenolith were prepared separately and then combined as necessary to create mixtures that would crystallise the required mineral assemblage. Starting mixes were produced by blending high purity synthetic oxides of Si, Ti, Al, Mg, Cr and Ni, and carbonates of Mn, Ca and Na. Fe was added as synthetically prepared fayalite (Fe_2SiO_4), which was produced by mixing haematite and silica, and firing in a one atmosphere furnace under oxidising conditions. The oxide and carbonate mix was fired overnight at 1000 °C to drive off the carbon, followed by the addition of the fayalite and a trace element mixture containing 30 trace elements to give approximate abundances of 20 - 55 ppm of each element. All four phases were combined with a dolomitic mix of synthetic CaCO_3 , MgCO_3 and K_2CO_3 to make a bulk peridotite composition, however the proportions were varied to produce higher modal proportions of garnet and clinopyroxene (Table 6.1). The garnet mix based upon the Diavik xenolith contained 5.3 wt.% CaO (referred to as ‘Diavik’) and the one based on the Udachnaya mix contained 6.3 wt.% CaO (‘UV45-03’). A third garnet mix was produced, based on the Diavik composition, but with a lower CaO content of 3.2 wt.% (‘Diavik 3% Ca’).

Table 6.1: Composition of the experimental starting material, including individual phases and peridotites.

	Diavik Ga	Diavik Cpx	Diavik Opx	Diavik Ol	Diavik 3% Ca Ga	UV45-03 Ga	UV45-03 Opx	UV45-03 Ol
Na ₂ O	0.07	1.34	0.19	0.00	0.07	0.00	0.05	0.00
SiO ₂	42.26	54.97	58.88	40.80	43.21	38.77	54.14	38.65
Al ₂ O ₃	20.06	1.70	0.69	0.00	20.51	18.78	0.75	0.00
MgO	20.51	17.97	32.86	49.95	20.97	17.50	34.21	48.11
CaO	5.31	19.41	1.12	0.12	3.19	6.25	0.54	0.00
Cr ₂ O ₃	3.07	0.77	0.22	0.03	3.14	5.54	0.24	0.00
FeO	7.66	3.44	5.66	8.58	7.83	7.68	4.86	7.75
NiO	0.02	0.07	0.14	0.41	0.02	0.00	0.09	0.39
MnO	0.27	0.10	0.11	0.11	0.28	0.49	0.13	0.10
TiO ₂	0.78	0.22	0.13	0.00	0.80	0.00	0.00	0.00
H ₂ O	0.00	0.00	0.00	0.00	0.00	5.00	5.00	5.00
Tr-3	0.19	0.19			0.20	0.14	0.14	0.14
Mg#	82.68	90.30	91.18	91.21	82.68	80.23	92.61	91.71
Cr#	9.31				9.31	16.51		

Peridotite Composition (wt. %)				Dolomite Composition	
	Dvk Pdt 02	UV45-03-2	UV45-03-3		
Ga	33.29	18.69	17.61	K ₂ CO ₃	5.01
Cpx	33.30	18.69	17.61	CaCO ₃	44.99
Opx	14.29	37.38	35.22	MgCO ₃	50.00
Ol	14.3	25.24	23.78	Tr-3	0.17
Dolomite	4.81	0	5.78		
Source					
Ga	Diavik	UV45-03	UV45-03		
Cpx	Diavik	Diavik	Diavik		
Opx	Diavik	UV45-03	UV45-03		
Ol	Diavik	UV45-03	UV45-03		

6.2.2 Experimental Design and Conditions

All experiments were conducted in 1.27 cm (0.5 inch) diameter end-loaded Boyd-England type piston cylinder apparatus at the Research School of Earth Sciences (RSES), Australian National University (ANU), using a 200 tonne press for runs at 3.5 GPa and a 500 tonne press for 5.5 GPa runs. A layered experimental design was employed, with layers of peridotite, clinopyroxene, garnet and peridotite placed inside graphite capsules with an internal diameter of 1.5-1.6 mm, which were inserted into Pt capsules of 3.5 mm external diameter (Figure 6.3). Approximately equal masses of each layer were loaded into each capsule. This graphite in Pt capsule design was employed to

avoid Fe loss by preventing contact between the mix and the outer capsule, whilst the layered design was employed as it ensured that there were large enough regions of garnet and clinopyroxene for LA-ICP-MS analysis. An assembly comprised of NaCl, Pyrex, graphite and MgO surrounded the Pt capsule.

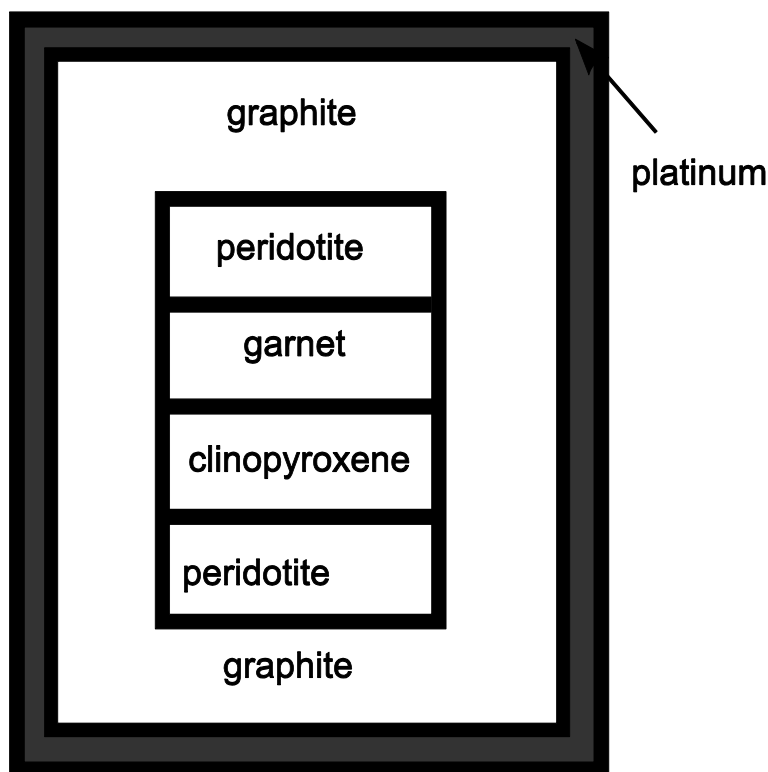


Figure 6.3: Schematic of the experimental capsule design (not to scale).

Five different temperature-series (series A-E – Table 6.2) were performed over the range of 1050 to 1350 °C. For experiments at 1250 °C and below, they were originally heated to 1350 °C for 2 h, to promote less nucleation of crystals and therefore a coarser grain size to assist with LA-ICP-MS analysis, before being cooled to the run temperature for 120 h and then quenched automatically. Experiments at 1350 °C were run for 120 h. Series A used the Diavik mixes, with an initial garnet CaO content of 5.3 wt.%, and was performed at 3.5 GPa. Series B was run on a carbonate-free basis, with the material including the Udachnaya garnet (6.3 wt.% CaO) and peridotite, along with

the Diavik clinopyroxene at 3.5 GPa. Series C used the same garnet and clinopyroxene mixes as series B, but had a carbonated peridotite mix, also performed at 3.5 GPa. Series D used the same mixes as series A, but was run at 5.5 GPa. Series E used the Diavik clinopyroxene and peridotite mixes, along with lower Ca Diavik garnet mix (3.3 wt.% CaO), and was performed at 3.5 GPa. Therefore series A, C and E examine the effect of CaO content of garnet; series A and D investigate how pressure affects the results; and series B and C look at the effects of carbonate, in conjunction with temperature. The role of carbonate in these experiments was to produce a small melt fraction, which should aid the attainment of equilibrium. Capsules were mounted in epoxy after quenching and were then polished to expose the charge, allowing for SEM and LA-ICP-MS analysis.

6.3 Analytical Methods

Initial examination and major element analysis of run products was performed using a JEOL 6400 scanning electron microscope (SEM) at the Centre for Advanced Microscopy, ANU. The accelerating voltage was 15 kV and the beam current of 1 nA. Major element compositions were determined using energy dispersive X-ray spectroscopy (EDS) with an acquisition time of 120 s. Crystalline phases were analysed using a focused beam with a 1 μm diameter, which has an excitation volume 3-5 μm in diameter. For the analysis of melt phases an area scan was used, which minimises the effect of heterogeneities in the melt, as well as Na loss. Detection limits for both methods are approximately 0.1-0.2 wt. %.

Table 6.2: Experimental run numbers and series label, compositions, and conditions, along with the phases observed in peridotite layers of the completed runs.

Series	Experiment Number	Temperature (°C)	Pressure (GPa)	Peridotite	Clinopyroxene	Garnet	Carbonate present?	Phases Observed in Peridotite Layers
A	GCC10	1050	3.5	Dvk Pdt 02	Diavik Cpx	Diavik Ga	Yes	Ga, Cpx, Opx, Ol
A	GCC08	1200	3.5	Dvk Pdt 02	Diavik Cpx	Diavik Ga	Yes	Ga, Cpx, Opx
A	GCC06	1250	3.5	Dvk Pdt 02	Diavik Cpx	Diavik Ga	Yes	Ga, Cpx, Opx, Ol
A	GCC09	1350	3.5	Dvk Pdt 02	Diavik Cpx	Diavik Ga	Yes	Ga, Cpx, Opx
B	GCC19	1050	3.5	UV45-03-2	Diavik Cpx	UV45-03 Ga	No	Ga, Cpx, Opx
B	GCC18	1150	3.5	UV45-03-2	Diavik Cpx	UV45-03 Ga	No	Ga, Cpx, Opx, Ol
B	GCC16	1250	3.5	UV45-03-2	Diavik Cpx	UV45-03 Ga	No	Ga, Cpx, Opx, Ol
B	GCC29	1350	3.5	UV45-03-2	Diavik Cpx	UV45-03 Ga	No	Ga, Cpx, Opx, Ol
C	GCC20	1050	3.5	UV45-03-3	Diavik Cpx	UV45-03 Ga	Yes	Ga, Cpx, Opx, Ol
C	GCC21	1150	3.5	UV45-03-3	Diavik Cpx	UV45-03 Ga	Yes	Ga, Cpx, Opx
C	GCC22	1250	3.5	UV45-03-3	Diavik Cpx	UV45-03 Ga	Yes	Ga, Cpx, Opx
C	GCC27	1350	3.5	UV45-03-3	Diavik Cpx	UV45-03 Ga	Yes	Ga, Cpx, Opx
D	GCC24	1050	5.5	Dvk Pdt 02	Diavik Cpx	Diavik Ga	Yes	Cpx, Opx, Ol
D	GCC25	1150	5.5	Dvk Pdt 02	Diavik Cpx	Diavik Ga	Yes	Ga, Cpx, Opx, Ol
D	GCC26	1250	5.5	Dvk Pdt 02	Diavik Cpx	Diavik Ga	Yes	Cpx, Opx, Ol
D	GCC28	1350	5.5	Dvk Pdt 02	Diavik Cpx	Diavik Ga	Yes	Ga, Cpx, Ol
E	GCC30	1050	3.5	Dvk Pdt 02	Diavik Cpx	Dvk 3% Ca Ga	Yes	Ga, Cpx, Opx, Ol
E	GCC31	1150	3.5	Dvk Pdt 02	Diavik Cpx	Dvk 3% Ca Ga	Yes	Ga, Cpx, Opx, Ol
E	GCC32	1250	3.5	Dvk Pdt 02	Diavik Cpx	Dvk 3% Ca Ga	Yes	Ga, Cpx, Opx, Ol, Melt
E	GCC33	1350	3.5	Dvk Pdt 02	Diavik Cpx	Dvk 3% Ca Ga	Yes	Ga, Cpx, Opx, Ol

Trace element concentrations were obtained using laser ablation-inductively coupled plasma-mass (LA-ICP-MS) spectrometry on the Agilent 7700 at RSES using an Excimer 193 nm laser to ablate the phases of interest. Analysis was performed using both single spots and linescans along the charge. Linescans were performed along the long axis of the experimental charge using a slit, which focuses the beam to a size of $100\text{ }\mu\text{m} \times 6\text{ }\mu\text{m}$. During a linescan the stage is moved a constant speed of $2\text{ }\mu\text{m/s}$ to scan along the length of the experimental charge; all linescans are oriented parallel to the long axis of the charge. A background signal is recorded with the laser for 30 s before and 10 s after the linescan. Due to the small crystal size in the peridotite layer, it was only possible to obtain reliable data for the garnet and clinopyroxene layers using the linescan mode. Spot analyses were performed on pooled melt fractions using a $105\text{ }\mu\text{m}$ diameter spot with a 100 s acquisition time, consisting of 30 s pre-ablation background (laser off), 60 s counting time (laser on) and 10 s post-ablation background. NIST612 glass was used as the reference standard and BCR2G was used as a secondary standard. EDS determined abundances of Si were used as the internal reference element for all phases, with the data reduced using the Iolite program (Paton et al., 2011), standard values were obtained from Jochum et al. (2011).

6.4 Results

6.4.1 Experimental Products

The layered nature of the experiments ensured that large amounts of garnet and clinopyroxene were present amongst the products of all experiments. The minerals observed in the peridotite layer for each experiment are shown in Table 6.2. Orthopyroxene and clinopyroxene were observed within the peridotite layer for all experiments, with garnet observed in all but two (GCC24, GCC26). Olivine was observed within the peridotite layers in only 11 of the 20 experiments, including all experiments at 5.5 GPa (GCC24-26, 28) and all experiments with the lowest Ca in garnet (GCC30-33). Pooled melt was only observed in one experiment (GCC32).

Figure 6.4a shows a polished cross-section of a completed experiment, with the layers of garnet, clinopyroxene and peridotite visible. Holes created by the removal of crystals during polishing were found in all clinopyroxene layers. At the interface between layers it was common to see some mingling of material, i.e. clinopyroxene crystals in the garnet layer, however this becomes less common towards the centre of the layer (Figure 6.4b-d). Very small grains ($\sim 5 \mu\text{m}$) of Cr-rich spinel were observed in a number of runs, however their size prevented quantification. Crystals in the peridotite layers are small (typically $< 50 \mu\text{m}$), and identification can be difficult as there is little difference in the appearance of orthopyroxene and olivine; or garnet and clinopyroxene (Figure 6.4d-e). A region of pooled melt was observed at the base of GCC32, with olivine being the most abundant mineral in the nearby peridotite (Figure 6.4f).

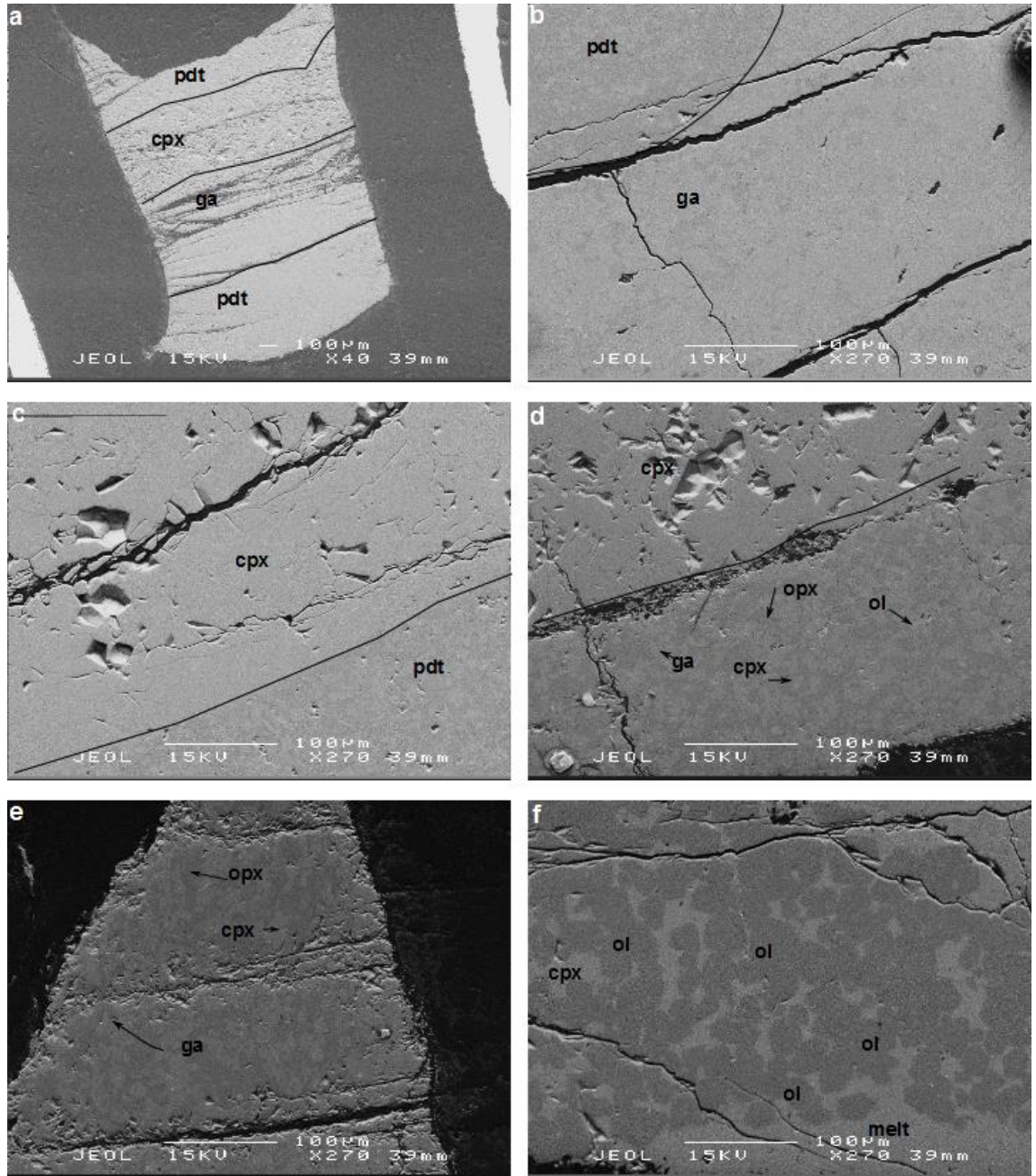


Figure 6.4: Backscattered electron images of the experimental products. Scale bar in all images is 100 μm long. (a) – GCC27, (b & c) – GCC33, (d & e) – GCC29, (f) – GCC32. ‘pdt’ = peridotite, ‘ga’ = garnet, ‘cpx’ = clinopyroxene, ‘opx’ = orthopyroxene, ‘ol’ = olivine.

6.4.2 Major Element Compositions

The compositions of the garnet and clinopyroxene layers, as well as averages of several crystals of garnet and clinopyroxene within the peridotite layers, are shown in Table 6.3. Garnet compositions are also shown on the garnet ternary diagram in Figure 6.5. Series A shows an increase in the grossular component for both the peridotite and

garnet layer, along with an increase in the pyrope component from the original composition (Diavik). The peridotite layer of Series B shows an increase in pyrope from the original UV45-03 composition. Meanwhile, the garnet layer shows an increase in both the grossular and almandine components for two experiments but an increase in pyrope for the other two. The garnet layer of Series C shows a trend to increasing pyrope composition, whilst the peridotite layer shows an increase in both pyrope and grossular. Both the peridotite and garnet layer from Series D show an increase in pyrope, but no change in grossular, excepting one unreacted peridotite data point. Series E shows an increase in grossular for both the layer and experiment, excepting one peridotite result that retains the original composition.

The pyroxene compositions are shown in Figure 5.6, as proportions of the relevant end-members. The starting clinopyroxene (Diavik) had an Mg-rich augite composition, whilst the run products exhibited a general decrease in Ca, moving towards a clinoenstatite composition. A high Mg# was observed in some clinopyroxene results, which indicates possible Fe-loss to the Pt capsule, however calculation of the structural formula indicated that the data was reliable, and that any Fe-loss was not substantial. The two orthopyroxene starting compositions (Diavik and UV45-03) were enstatitic with just under 10% $\text{Fe}_2\text{Si}_2\text{O}_6$ present, whilst the run products all showed an increase in the Ca component, with some crossing into the pigeonite field. Olivine exhibited a range in Mg# from 0.89 to 0.96. The FeO content of the olivine varies substantially with some runs having lower FeO than in the original mix and others showing a noticeable enrichment.

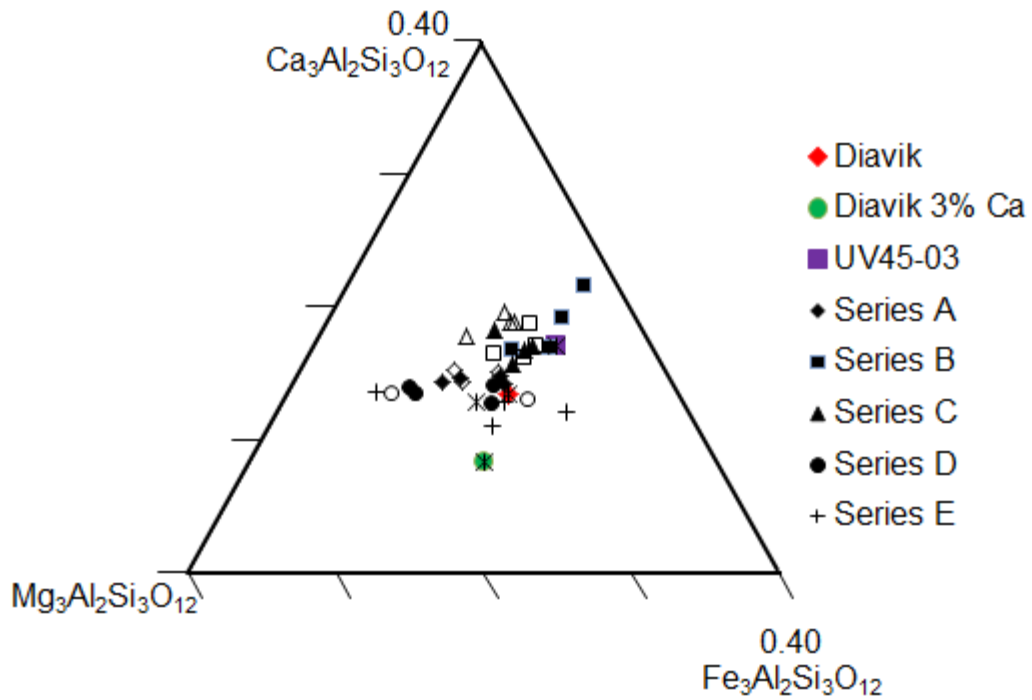


Figure 6.5: Composition of the garnet starting material and run products. For series A-D, black symbols indicate the 'layer' and open symbols the 'peridotite'; Series E is shown using '+' for the 'layer' and '*' for the 'peridotite'.

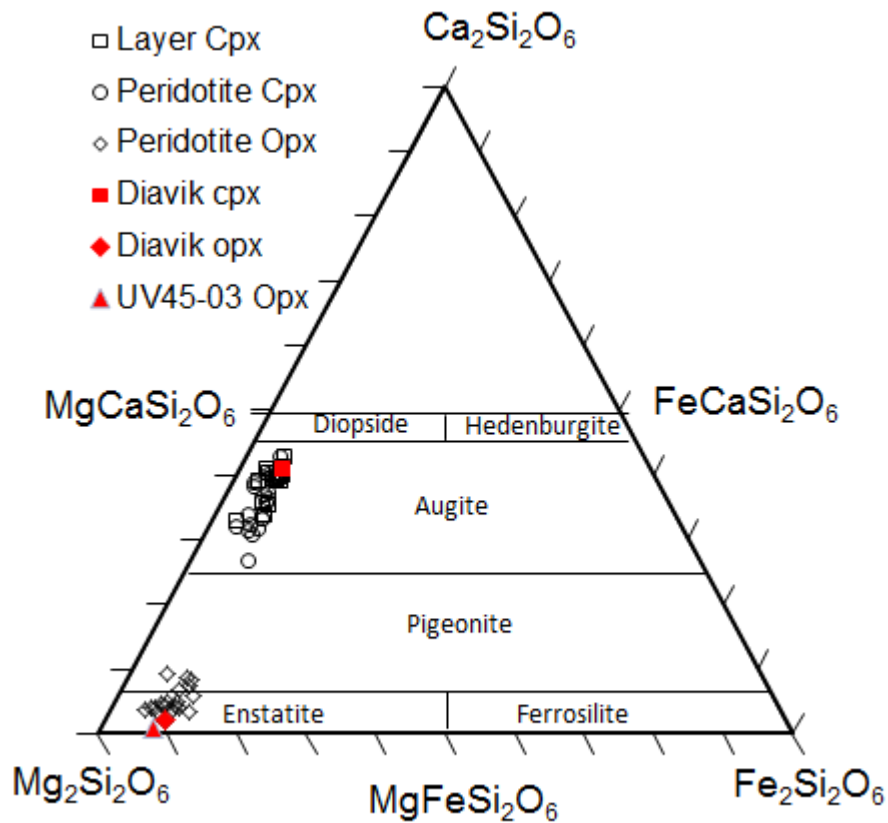


Figure 6.6: Pyroxene compositions for the starting material and run products.

Table 6.3: Average composition of the run products from each phase of the completed experiments. ‘bdl’ = below detection limit.

GCC10							GCC08							GCC06						
Layers		Peridotite					Layers		Peridotite					Layers		Peridotite				
	Ga	Cpx	Ga	Cpx	Opx	Ol	Ga	Cpx	Ga	Cpx	Opx	Ga	Cpx	Ga	Cpx	Opx	Ol			
n	9	14	5	9	4	1	7	5	1	16	3	14	22	3	7	7	1			
Na ₂ O	bdl	0.67(8)	bdl	0.7(1)	0.2(1)	bdl	bdl	0.9(1)	bdl	0.68(8)	0.2(1)	0.03(5)	0.66(7)	0.06(1)	0.7(1)	0.22(6)	0.06			
SiO ₂	40.6(4)	53.0(3)	41.1(6)	52.9(4)	54(1)	40.04	41.7(2)	54.1(9)	41.49	53.7(4)	55.3(2)	42.0(5)	53.9(5)	42(1)	53.8(5)	55.8(5)	40.8			
Al ₂ O ₃	20.4(6)	3.1(3)	20(1)	3.3(2)	4(2)	0.07	21.1(3)	2.3(6)	22.16	2.8(7)	2.6(2)	21.2(4)	3.2(4)	20.6(3)	3.4(3)	3.3(3)	0.06			
MgO	19.7(3)	19.4(7)	20(2)	20(1)	29(1)	47.34	20.2(3)	18.2(6)	20.81	19.5(1)	31(2)	21.2(2)	20.0(4)	21.2(9)	21(2)	32.4(5)	49.5			
K ₂ O	bdl	0.01(2)	0.01(4)	0.01(2)	bdl	0.03	bdl	0.01(4)	bdl	0.01(3)	bdl	0.01(3)	bdl	0.01(4)	0.01(4)	bdl	bdl			
CaO	5.64(2)	16.5(9)	6.0(7)	15(1)	4(2)	0.24	5.5(3)	18(1)	5.57	17.2(2)	3(2)	5.8(3)	17.0(7)	6.0(3)	15(2)	2.3(6)	0.29			
Cr ₂ O ₃	3.31(6)	0.92(9)	3.0(3)	1.00(8)	0.9(3)	0.21	3.0(4)	0.9(1)	1.28	0.9(2)	0.8(1)	3.4(3)	1.0(1)	3.20(6)	1.0(1)	0.8(1)	0.1			
FeO	6.83(9)	3.9(3)	6.9(2)	4.0(3)	5.9(4)	9.45	7.2(3)	3.5(4)	5.69	3.7(3)	5.4(4)	5.7(3)	3.4(1)	5.3(3)	3.5(3)	4.5(3)	7.01			
NiO	0.01(9)	bdl	bdl	bdl	bdl	0.02	bdl	0.09(8)	0.02	0.08(9)	0.24(1)	0.03(6)	bdl	bdl	bdl	bdl	bdl			
P ₂ O ₅	0.03(6)	bdl	0.04(8)	bdl	bdl	bdl	0.02(6)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl			
MnO	0.35(8)	0.2(1)	0.33(8)	0.15(5)	0.21(4)	0.16	0.39(6)	0.18(9)	0.39	0.15(7)	0.13(5)	0.32(7)	0.16(8)	0.37(4)	0.14(4)	0.18(6)	0.16			
TiO ₂	0.66(7)	0.3(1)	0.7(2)	0.33(8)	0.32(7)	0.11	0.51(8)	0.23(4)	0.49	0.26(6)	0.23(6)	0.46(6)	0.22(8)	0.45(2)	0.21(9)	0.15(9)	bdl			
Total	97.6(8)	98.1(7)	98(1)	97.8(8)	99(1)	97.5	99.5(6)	99(2)	97.78	98.9(7)	99.1(2)	100(1)	99.5(8)	99(2)	99.2(9)	100(1)	97.9			
Mg#	83.7	89.9	83.9	89.9	89.9	89.9	83.3	90.4	86.7	90.4	90.3	87.0	91.3	87.7	91.6	92.2	92.6			

GCC09					GCC19					GCC18						
Layers		Peridotite			Layers		Peridotite			Layers		Peridotite				
	Ga	Cpx	Ga	Cpx	Opx	Ga	Cpx	Ga	Cpx	Opx	Ga	Cpx	Ga	Cpx	Opx	Ol
n	8	7	3	18	1	12	6	2	5	7	12	11	10	12		6
Na ₂ O	bdl	0.68(7)	bdl	0.7(1)	0.2	0.14(5)	0.79(6)	0.18(3)	0.67(9)	0.17(5)	0.11(9)	0.88(7)	0.08(5)	0.9(1)	0.3(6)	0.06
SiO ₂	41.1(9)	53.5(3)	42.6(1)	53.7(8)	54.9	41.2(7)	54.10(2)	42.0(3)	53.9(4)	56.4(6)	41.5(9)	54.1(6)	42(1)	54.0(5)	56(1)	40.7
Al ₂ O ₃	20.6(7)	2.1(3)	21.6(4)	3(1)	3.8	20(1)	1.4(2)	21(2)	1.6(2)	2.2(9)	19(1)	1.9(2)	20(2)	2.6(3)	3(1)	0.24
MgO	21.0(9)	18.6(5)	22.2(4)	19(2)	30.6	17(2)	17.8(1)	19.4(3)	18.1(3)	33.6(8)	18.0(6)	18.0(2)	19(1)	19(2)	31(2)	48.0
K ₂ O	0.01(3)	bdl	bdl	0.01(2)	bdl	bdl	0.01(2)	bdl	bdl	bdl	0.02(5)	0.02(2)	0.01(2)	bdl	bdl	bdl
CaO	5.5(2)	18.5(5)	5.51(5)	17(2)	4.52	8(1)	20.5(4)	7.5(2)	20.7(3)	1.0(3)	7.4(9)	19.4(4)	7(1)	18(2)	2(1)	0.19
Cr ₂ O ₃	3.3(4)	0.84(8)	3.2(3)	1.0(2)	0.94	6(2)	1.2(2)	2.6(7)	1.3(3)	1.2(2)	5(1)	1.0(1)	4(1)	1.6(3)	1.1(2)	0.16
FeO	5.0(5)	3.1(3)	4.2(1)	3.2(4)	3.4	8(1)	3.3(1)	7.0(4)	2.9(2)	5.8(5)	7.6(9)	3.4(2)	7.5(5)	3.5(3)	5.9(4)	9.69
NiO	bdl	0.10(7)	bdl	0.1(1)	0.09	bdl	0.11(6)	0.20(7)	0.07(8)	0.1(1)	bdl	0.1(1)	bdl	0.1(1)	0.2(1)	0.42
P ₂ O ₅	0.05(4)	bdl	0.02(5)	bdl	bdl	0.05(8)	bdl	0.07(1)	bdl	bdl	0.01(7)	bdl	0.05(6)	0.02(6)	bdl	bdl
MnO	0.3(1)	0.14(9)	0.30(1)	0.15(7)	0.28	0.7(1)	0.18(5)	0.61(3)	0.19(7)	0.23(6)	0.6(1)	0.14(8)	0.57(5)	0.19(6)	0.21(7)	0.27
TiO ₂	0.42(5)	0.22(4)	0.35(5)	0.21(7)	0.16	0.04(7)	0.14(6)	0.1(1)	0.11(5)	0.08(7)	0.09(5)	0.12(9)	0.08(6)	0.10(7)	0.02(5)	0.01
Total	97(2)	97.8(5)	100(1)	98(1)	98.8	101.0(8)	99.4(7)	100.7(0)	99.6(5)	100.6(7)	100.1(9)	99.0(1)	100.7(7)	99.8(5)	100(1)	99.7
Mg#	88.3	91.5	90.5	91.4	94.1	79.5	90.7	83.2	91.7	91.2	80.8	90.8	81.9	90.5	90.5	89.8

GCC16							GCC29					GCC20						
n	Layers		Peridotite			Ol	Layers		Peridotite			Ol	Layers		Peridotite			Ol
	Ga	Cpx	Ga	Cpx	Opx		Ga	Cpx	Ga	Cpx	Opx		Ga	Cpx	Ga	Cpx	Opx	
9	6	30	21	13	6	6	8	5	3	13	1	6	6	2	10	3	1	
Na ₂ O	0.13(3)	1.0(1)	0.13(8)	1.0(1)	0.4(1)	0.14(3)	0.08(5)	0.9(1)	0.09(6)	0.92(8)	0.27(3)	0.11	0.11(7)	0.68(9)	0.14(1)	0.8(2)	0.22(3)	
SiO ₂	41.0(5)	53.6(5)	41(1)	53.9(8)	55(2)	41(1)	41.3(4)	54.0(6)	41.6(6)	52.9(2)	55(1)	40.9	42.9(6)	53.0(9)	41(1)	52(1)	53.4(9)	
Al ₂ O ₃	19.4(6)	2.0(5)	20(2)	3.3(4)	4(2)	0.6(8)	19.4(6)	2.0(8)	20(2)	3.52(7)	4(1)	0.12	21(1)	4(1)	19.6(3)	4(1)	5.3(6)	
MgO	18.7(8)	18.5(7)	19.6(7)	20(2)	30(3)	46(1)	19.3(7)	18.6(9)	19.8(9)	20.8(1)	32(1)	49.5	20.0(8)	20(1)	19.0(1)	18(1)	29(1)	
K ₂ O	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.01(3)	0.01(1)	bdl	0.01(1)	0.04	bdl	bdl	0.01(4)	bdl	bdl	
CaO	6.6(6)	18.6(9)	6.4(8)	16(1)	4(3)	0.4(2)	6.5(6)	18(2)	6.4(6)	14.5(2)	2.5(5)	0.4	6.2(7)	15.9(9)	7.2(6)	18(1)	3(1)	
Cr ₂ O ₃	5.1(6)	0.9(2)	5(1)	1.7(2)	1.4(5)	0.3(1)	5(1)	1.1(3)	5(2)	1.8(1)	1.4(2)	0.25	2.3(8)	1.1(6)	5(2)	1.4(3)	1.0(1)	
FeO	7.9(3)	4.0(6)	7.30(7)	4.1(3)	6.1(5)	10.2(4)	6.6(4)	3.5(2)	6.1(7)	3.4(4)	4.8(6)	7.42	7.2(4)	4.1(5)	6.2(2)	3.3(4)	6.7(1)	
NiO	bdl	0.1(2)	bdl	0.1(1)	0.09(7)	0.12(9)	0.12(5)	0.08(7)	bdl	0.1(1)	0.1(1)	0.18	0.1(1)	0.1(1)	0.06(9)	0.05(7)	0.10(2)	
P ₂ O ₅	0.2(3)	bdl	0.3(3)	0.1(1)	0.1(2)	0.2(1)	0.03(5)	bdl	0.08(5)	0.03(2)	0.01(1)	bdl	0.08(5)	0.02(4)	0.01(4)	bdl	bdl	
MnO	0.5(4)	0.2(1)	0.3(2)	0.2(1)	0.1(1)	0.04(9)	0.56(9)	0.16(9)	0.5(1)	0.20(8)	0.25(8)	0.3	0.58(7)	0.3(1)	0.5(1)	0.27(8)	0.3(2)	
TiO ₂	0.05(6)	0.13(7)	0.10(6)	0.09(6)	0.07(8)	bdl	0.06(4)	0.1(1)	0.05(8)	0.07(7)	0.04(5)	bdl	0.14(6)	0.05(6)	0.09(7)	0.06(8)	0.12(2)	
Total	100(1)	98.9(8)	100(1)	100(1)	100.5(9)	100(1)	99.3(6)	98.9(5)	99(1)	98.2(1)	99.4(5)	99.22	100.2(8)	99.7(6)	98.5(2)	98.6(9)	99(1)	
Mg#	80.9	89.1	82.7	89.8	89.8	89.0	83.8	90.4	85.2	91.6	92.1	92.2	83.3	89.5	84.6	90.8	88.6	

GCC21					GCC22					GCC27								
n	Layers		Peridotite			Ol	Layers		Peridotite			Ol	Layers		Peridotite			Ol
	Ga	Cpx	Ga	Cpx	Opx		Ga	Cpx	Ga	Cpx	Opx		Ga	Cpx	Ga	Cpx	Opx	
16	16	8	7	9	16	6	7	10	8	6	20	3	24	1				
Na ₂ O	0.06(4)	0.89(9)	0.08(6)	0.87(9)	0.18(4)	0.10(4)	0.76(5)	0.09(4)	0.80(8)	0.22(6)	0.13(3)	1.1(1)	0.4(5)	1.1(1)	0.1			
SiO ₂	41.5(5)	54.1(5)	42.5(3)	54.6(8)	56.4(8)	41.4(3)	54.4(3)	42(1)	54.0(5)	55.6(6)	41.4(2)	54(1)	44(4)	53.3(6)	40.1			
Al ₂ O ₃	19(1)	2.6(2)	20(1)	2.8(4)	3.2(4)	19.5(9)	1.4(1)	19.2(6)	1.9(8)	2.9(4)	20.0(5)	2.0(5)	17(5)	4.3(5)	7.0			
MgO	19.4(7)	18.5(5)	20.3(4)	20(2)	33.3(8)	19(1)	18.5(2)	19(1)	18.7(9)	32(1)	19.0(6)	18(1)	20.2(5)	20.2(9)	37.5			
K ₂ O	bdl	0.01(2)	0.01(2)	bdl	bdl	bdl	bdl	bdl	bdl	0.01(3)	0.02(3)	bdl	0.03(3)	bdl	0.06			
CaO	7.0(8)	19.2(6)	7.0(3)	18(1)	1.9(3)	7(1)	19.3(3)	7.3(8)	19(2)	2.1(9)	6.5(4)	18.9(7)	8(3)	15(1)	2.0			
Cr ₂ O ₃	6(2)	1.8(2)	6(2)	1.8(2)	1.8(4)	5(1)	0.9(1)	5(2)	1.2(5)	1.3(1)	4.8(7)	0.9(2)	3.6(7)	1.7(2)	1.6			
FeO	5.8(8)	2.0(4)	5.0(4)	1.7(4)	3.3(5)	7.3(6)	3.2(1)	6.3(9)	3.1(2)	4.8(5)	7.1(9)	3.6(4)	6(1)	4.1(4)	9.0			
NiO	bdl	bdl	bdl	0.1(2)	0.1(1)	bdl	0.1(1)	bdl	0.1(1)	0.2(1)	bdl	0.1(1)	bdl	0.1(1)	0.20			
P ₂ O ₅	0.03(4)	bdl	0.02(5)	bdl	bdl	0.05(7)	bdl	0.06(2)	0.05(4)	bdl	0.06(7)	0.01(4)	0.10(8)	bdl	bdl			
MnO	0.6(1)	0.20(9)	0.47(4)	0.17(4)	0.23(6)	0.6(1)	0.16(7)	0.5(1)	0.18(7)	0.2(1)	0.56(6)	0.17(6)	0.4(2)	0.26(9)	0.35			
TiO ₂	0.04(5)	0.01(6)	0.04(5)	0.09(7)	0.02(8)	0.05(4)	0.11(7)	0.03(7)	0.12(8)	0.01(4)	bdl	0.23(7)	0.20(5)	0.07(7)	0.02			
Total	99.7(9)	99.3(8)	100.9(8)	100.2(9)	100.3(9)	99.6(7)	98.8(3)	99(1)	98.9(7)	99.1(8)	99.5(6)	99(2)	100(2)	99.6(7)	97.9			
Mg#	85.7	94.3	87.8	95.3	94.7	82.1	91.3	84.4	91.5	92.1	82.6	89.8	85.5	89.9	88.1			

GCC24						GCC25						GCC26					
n	Layers	Peridotite				Layers	Peridotite				Layers	Peridotite				n	Mg#
	Ga	Cpx	Cpx	Opx	Ol	Ga	Cpx	Ga	Cpx	Opx	Ol	Ga	Cpx	Cpx	Opx		
6	4	10	12	3	24	8	1	5	10	1	11	27	6	11	5		
Na ₂ O	0.14(4)	1.00(4)	1.0(1)	0.31(1)	0.14(6)	0.16(5)	1.1(1)	0.23	0.9(1)	0.25(5)	0.09	0.13(2)	1.2(2)	1.3(2)	0.31(3)	0.10(4)	
SiO ₂	42.3(4)	55.2(3)	54.6(6)	54(2)	44(2)	42.0(6)	54.9(5)	46.2	54.7(7)	58(1)	40.9	42.1(4)	54.4(5)	54.2(6)	56.4(7)	42.0(4)	
Al ₂ O ₃	20.6(7)	1.6(3)	2.2(7)	5(3)	0.4(2)	20.7(8)	1.7(2)	15.2	1.9(5)	1.4(3)	0.36	21.1(7)	2.7(8)	3.3(8)	2.7(9)	0.08(3)	
MgO	21.0(6)	18.3(4)	19(2)	30(2)	46(2)	20.8(8)	18.2(3)	24.3	19.3(3)	34(1)	50.6	22(1)	19.4(6)	21(1)	33.4(8)	53.5(6)	
K ₂ O	0.01(2)	0.02(2)	0.01(1)	0.01(1)	bdl	0.01(2)	bdl	bdl	0.03(3)	0.01(2)	bdl	0.01(3)	0.01(2)	0.01(1)	bdl	bdl	
CaO	5.1(7)	19.7(5)	19(2)	4(2)	1(1)	5.6(8)	19.6(7)	4.4	19(1)	1.7(7)	0.20	5.5(4)	18(1)	16(1)	2.0(3)	0.13(4)	
Cr ₂ O ₃	3.6(5)	0.91(8)	0.91(4)	0.9(4)	0.2(1)	3.5(7)	0.9(2)	bdl	0.83(8)	0.42(7)	0.07	4.6(7)	1.2(3)	1.4(2)	0.9(2)	0.1(1)	
FeO	7.2(3)	3.7(4)	3.3(2)	5.6(5)	8.4(5)	6.9(9)	3.3(7)	6.2	3(1)	4.7(7)	5.39	4(1)	2.1(8)	2.7(6)	4.1(7)	4.3(4)	
NiO	0.05(9)	0.17(8)	0.1(1)	0.1(1)	0.5(2)	bdl	0.1(1)	bdl	0.1(1)	0.2(1)	0.31	bdl	0.1(1)	bdl	0.1(1)	0.2(1)	
P ₂ O ₅	0.04(3)	0.03(3)	0.02(3)	0.03(4)	0.02(5)	0.05(7)	0.02(6)	0.07	0.01(6)	bdl	bdl	0.05(4)	bdl	0.06(6)	0.01(4)	bdl	
MnO	0.42(9)	0.10(6)	0.15(6)	0.19(7)	0.13(2)	0.39(9)	0.14(5)	0.38	0.17(6)	0.12(6)	0.17	0.4(1)	0.20(6)	0.23(7)	0.15(3)	0.03(7)	
TiO ₂	0.50(9)	0.22(8)	0.19(4)	0.17(9)	0.04(4)	0.7(2)	0.25(8)	0.6	0.19(8)	0.16(4)	0.14	0.3(1)	0.1(1)	0.1(1)	0.13(6)	0.08(5)	
Total	101.0(9)	100.8(5)	100(1)	101.4(5)	100.9(7)	100.9(7)	100.2(8)	99.8	100(1)	101(2)	98.14	100.6(7)	99.8(9)	100(1)	100.2(9)	100.5(9)	
Mg#	83.8	90.9	89.9	90.5	90.7	84.3	90.7	87.5	93.0	92.9	94.4	90.7	93.8	94.4	93.6	95.6	
GCC28						GCC30						GCC31					
n	Layers	Peridotite				Layers	Peridotite				Layers	Peridotite				n	Mg#
	Ga	Cpx	Ga	Cpx	Ol	Ga	Cpx	Ga	Cpx	Opx	Ol	Ga	Cpx	Ga	Cpx		
7	13	2	8	12	4	11	3	3	5	6	2	12	4	1	14	2	
Na ₂ O	0.14(4)	0.9(1)	0.13(2)	0.83(8)	0.12(5)	0.16(2)	1.1(2)	0.13(3)	0.89(5)	0.18(6)	0.07(4)	0.18(1)	1.1(1)	0.16(5)	0.73	0.23(8)	0.2(1)
SiO ₂	42.8(7)	54.8(5)	42.4(6)	54.6(7)	42.4(4)	40.8(3)	55.3(7)	43(1)	53(1)	56(2)	41(1)	41.6(3)	54.8(6)	40(1)	53.8	55(2)	42(1)
Al ₂ O ₃	21.2(9)	2.0(3)	19.5(9)	2.9(8)	0.2(2)	20.4(5)	2.2(9)	19(1)	4(1)	3.1(9)	0.1(1)	21.6(4)	1.7(2)	21.4(8)	4.31	4(2)	0.5(1)
MgO	22.5(9)	19.2(5)	20(2)	20.3(7)	54(1)	20.0(2)	19(1)	21.4(7)	19.7(8)	32(1)	48.5(9)	19.0(6)	18.0(4)	19.7(1)	22.4	32(2)	47(2)
K ₂ O	bdl	bdl	0.02(1)	0.01(2)	0.01(2)	0.01(3)	bdl	0.01(3)	bdl	bdl	bdl	0.01(1)	bdl	0.02(3)	bdl	bdl	0.04(2)
CaO	5.5(6)	19.6(6)	9(3)	18(1)	0.3(2)	5.0(5)	19(3)	5.6(3)	17(2)	1.8(6)	0.2(1)	4.7(7)	19.5(3)	5.1(2)	12.8	2.0(5)	1(1)
Cr ₂ O ₃	3.3(8)	1.0(1)	5(2)	1.0(2)	0.22(9)	3.3(5)	1.0(2)	3.3(3)	1.1(1)	0.7(2)	0.05(6)	2.8(3)	0.8(7)	3.3(6)	1.04	1.0(4)	0.26(5)
FeO	4.4(7)	2.6(7)	4(2)	2.1(3)	4(1)	7.4(4)	3.7(7)	6.6(3)	3.8(5)	5.9(2)	9.4(2)	9.8(3)	3.4(4)	8.1(4)	4.88	6.4(6)	9.3(6)
NiO	0.02(2)	0.1(1)	bdl	bdl	0.2(1)	0.05(5)	0.11(8)	0.1(2)	bdl	0.3(1)	0.4(1)	0.04(9)	0.1(2)	bdl	0.23	0.1(2)	0.4(1)
P ₂ O ₅	0.07(3)	0.01(5)	0.1(1)	0.01(5)	0.01(5)	0.01(6)	bdl	0.03(3)	0.04(6)	0.01(2)	bdl	0.1(1)	0.02(4)	0.07(6)	bdl	0.01(6)	bdl
MnO	0.23(5)	0.1(1)	0.2(2)	0.09(4)	0.09(6)	0.31(3)	0.09(8)	0.3(1)	0.21(9)	0.13(2)	0.15(8)	0.47(4)	0.16(9)	0.38(8)	0.2	0.18(9)	0.17(4)
TiO ₂	0.41(7)	0.14(7)	0.3(1)	0.11(8)	0.02(2)	0.73(8)	0.26(8)	0.9(1)	0.32(6)	0.28(9)	0.07(7)	0.49(9)	0.28(6)	1.2(7)	0.27	0.3(2)	0.07(5)
Total	101(1)	100.4(9)	100.2(5)	100.4(7)	101.1(9)	98.1(4)	101(1)	100.3(9)	100.4(7)	100(2)	100(1)	100.7(4)	100(1)	100(1)	100.6	101(1)	100.9(4)
Mg#	90.1	93.0	90.0	94.6	95.8	82.8	90.0	85.2	90.2	90.6	90.2	77.6	90.3	81.2	89.1	89.8	89.9

GCC32								GCC33						
Layers		Peridotite						Layers		Peridotite				
	Ga	Cpx	Ga	Cpx	Opx	Ol	Melt		Ga	Cpx	Ga	Cpx	Opx	Ol
n	7	9	2	11	3	14	12		6	14	3	5	10	6
Na ₂ O	0.20(1)	1.13(6)	0.07(5)	1.16(7)	0.27(2)	0.13 (5)	2.1(3)		0.13(5)	1.1(2)	0.10(5)	0.82(9)	0.3(1)	0.08(5)
SiO ₂	43(2)	53.3(6)	42.6(1)	53.3(7)	54(1)	41.8(5)	32(1)		41.2(4)	54.1(3)	42.3(3)	53.7(2)	55(1)	41.0(7)
Al ₂ O ₃	21(2)	4.4(6)	21.3(1)	4.6(3)	3.9(8)	0.2(2)	8.2(9)		21(1)	1.9(4)	20.9(3)	3.46(7)	3.3(3)	0.4(5)
MgO	23.4(3)	21.1(3)	22.6(5)	21.2(4)	34(3)	53(1)	19(4)		20.5(5)	17.9(8)	21.2(3)	21.5(9)	32.2(9)	48.2(7)
K ₂ O	bdl	bdl	0.04(3)	0.01(3)	0.02(2)	0.01(2)	0.67(7)		0.01(4)	0.01(2)	0.02(3)	bdl	bdl	0.01(2)
CaO	5(1)	15.2(5)	5.38(0)	14.7(5)	2.1(4)	0.4(6)	13(1)		4.3(5)	19(1)	5.1(1)	14.7(9)	2.2(4)	0.6(4)
Cr ₂ O ₃	3.9(6)	1.4(1)	3.3(1)	1.4(1)	1.0(1)	0.22(9)	0.30(7)		3.0(5)	0.9(1)	3.4(2)	0.97(8)	0.8(1)	0.1(1)
FeO	3.2(5)	1.9(3)	3.5(6)	2.1(4)	3.9(8)	3.6(3)	3.4(2)		7.5(5)	3.8(2)	6.7(3)	4.1(2)	6.0(5)	9.3(1)
NiO	bdl	bdl	0.01(8)	bdl	bdl	0.05(7)	0.03(9)		bdl	0.1(1)	0.05(6)	0.2(2)	0.1(1)	0.36(9)
P ₂ O ₅	0.04(8)	0.01(4)	0.06(1)	0.03(5)	bdl	bdl	0.27(5)		0.08(5)	bdl	0.02(6)	0.02(6)	bdl	bdl
MnO	0.32(7)	0.16(5)	0.23(5)	0.16(8)	0.17(2)	0.15(9)	0.20(9)		0.28(4)	0.18(6)	0.26(5)	0.17(9)	0.10(8)	0.17(7)
TiO ₂	0.39(7)	0.3(1)	0.4(1)	0.22(9)	0.15(6)	0.04(6)	1.6(2)		0.79(8)	0.30(8)	0.74(9)	0.33(5)	0.27(6)	0.06(6)
Total	100.1(5)	98.9(5)	99.6(4)	99.0(9)	100.0(6)	99.7(8)	80(3)		99.2(8)	98.9(5)	101.0(3)	100.0(3)	100.3(7)	100.2(5)
Mg#	93.0	95.1	91.9	94.7	94.0	96.4			83.1	89.2	84.9	90.3	90.6	90.6

6.4.3 Trace Element Compositions

The trace element concentrations of the garnet and clinopyroxene layers, taken as segments (20 – 30 μm wide) close to the interface between the layers, are shown in Table 6.4. It was decided to use the data from close to the interface as it is assumed that this region is likely to have most closely approached equilibrium. During investigation of the run products using SEM, it was observed that the centre of some garnet and clinopyroxene layers had different compositions to the edges, near the interface with the other layers; as such it was assumed that some experiments did not fully equilibrate throughout each layer. There is a substantial variation in concentrations between experiments; however the abundances of Ti, Mn and Ni are consistently higher than other elements in both garnet and clinopyroxene. Garnet is richer in U and Ta than clinopyroxene; whilst Ce, Pr, Nd and Sm are lower in garnet compared with clinopyroxene. As all trace elements were added to the mixture at relatively constant abundances, traditional methods for graphically displaying trace element abundances (e.g. REE plots, spider diagrams) do not realistically describe the data, as such the trace element data is best represented through partition coefficients.

Table 6.4: Trace element compositions (ppm) at the interface between the garnet and clinopyroxene layers, determined using LA-ICP-MS. “bdl” = below detection limit. Where no standard deviation (σ) is given only a single measurement was obtained.

	GCC10				GCC08				GCC06				GCC09				GCC19			
	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ
Sc	55	14	15.8	0.7	47	15	27	2	69	7	13.41	0.82	64	9	20	2	15	4	22	13
Ti	2905	459	2532	146	2618	638	1962	162	2630	181	1466	78	2295	274	1431	59	937	405	625	383
V	54	8	56.3	3.7	61	14	56	9	66	4	48	2	65	9	64	4	116	149	34	21
Mn	2069	363	1395	56	2440	672	1577	109	2435	180	1267	45	2257	268	1630	114	5813	987	1180	718
Co	45	9	47.5	0.8	60	15	60	6	41	3	37	1	41	7	52	5	36	8	30	18
Ni	102	42	324	64	218	33	699	342	35	4	185	26	68	27	406	138	269	111	468	290
Cu	14	13	9.6	3.0	32	32	15	11	24	11	13	5	5	2	10	6	28	32	6	4
Zn	59	15	71.0	3.0	82	36	69	8	39	6	48	3	37	5	60	15	42	13	12	7
Ga	53	12	52.1	2.3	56	19	45	4	49	4	40	2	46	5	53	4	34	6	18	11
Rb	1.57	0.49	0.16	0.04	0.22	0.09	0.15	0.07	0.50	0.07	0.06	0.03	0.19	0.06	0.10	0.01	0.13	0.12	0.04	0.05
Sr	20	2	94.9	2.7	9	5	102	10	5.0	1.0	40	1	3.0	1.5	57	2	6	5	53	33
Y	80	18	12.2	0.5	65	20	23.0	1.4	85	9	10.9	0.5	87	12	22	3	34	8	22	13
Zr	35	8	6.7	1.1	20	7	6.1	1.0	24	3	3.95	0.58	26	3	4.4	0.5	118	32	9	6
Nb	12.8	3.3	2.9	0.2	3.87	0.93	2.45	0.24	4.8	0.5	0.70	0.11	1.9	0.4	0.6	0.1	5.4	0.9	0.71	0.43
Cs	0.56	0.23	0.04	0.02	0.02	0.01	0.03	0.03	0.10	0.05	0.03	0.02	0.01	0.01	0.01	0.00	bdl		bdl	
Ba	10.7	3.1	1.15	0.33	0.42	0.43	0.58	0.14	2.4	0.5	0.20	0.14	0.2	0.1	0.3	0.1	bdl		bdl	
La	9.3	1.0	16.5	0.5	3.5	1.9	15.1	1.0	2.1	0.2	4.63	0.09	1.0	0.3	7.5	0.5	3.3	0.6	7	5
Ce	12.8	0.7	31.2	1.2	6.9	2.7	29	2	3.9	0.2	10.0	0.4	2.9	0.4	15.1	0.9	7.1	0.8	13	8
Pr	15.1	0.9	36.4	1.2	8.80	0.63	34	3	6.4	0.2	12.7	0.5	5.6	0.7	17.4	0.2	8	1	16	10
Nd	10.7	0.8	21.7	0.6	8.35	0.99	20.2	1.3	6.4	0.6	8.8	0.3	5.9	0.7	11.7	0.5	4.9	0.5	10	6
Sm	35.4	5.6	34.6	1.8	30	5	33	3	29	2	19	1	29	2	23.8	0.8	11	1	19	12
Eu	47	9	32.7	0.4	40	10	35	2	42	4	21	1	41	4	27.1	0.8	17	3	20	12
Gd	51	10	23.6	1.2	44	11	28	1	50	5	17.6	1.1	49	6	24.3	1.8	15	3	19	12
Tb	62	13	18.3	0.5	54	16	25	1	66	9	15.1	0.6	61	7	22.6	1.1	19	3	20	12
Dy	72	18	15.1	0.3	61	17	23.4	0.5	77	10	13.1	0.6	76	9	21.5	1.6	25	5	20	12
Ho	77	19	11.8	0.5	66	20	21.0	0.7	83	9	10.5	0.4	80	10	19.1	1.3	27	5	18	11
Er	85	21	10.0	0.6	72	21	20.3	0.8	91	9	8.8	0.5	90	11	17.9	1.5	31	7	18	11
Tm	87	20	8.79	0.43	75	23	18.9	0.3	96	11	7.8	0.5	95	11	16.8	1.6	37	9	18	11
Yb	93	22	8.17	0.73	80	27	19	3	102	11	7.0	0.5	102	10	15.9	1.8	41	9	17	10
Lu	90	20	7.29	0.57	76	24	17.6	0.5	99	10	5.9	0.6	99	12	14.5	1.2	40	10	16	9
Hf	54	13	19.9	1.9	34	10	19.0	1.1	40	5	11.3	0.9	37	4	12.1	0.8	13	2	10	6
Ta	12.8	3.5	3.85	0.42	5.7	1.5	3.46	0.23	5.9	0.5	0.92	0.03	2.1	0.3	0.69	0.05	9	3	1.6	1.0
U	12.2	2.9	3.41	0.27	5.6	1.3	2.93	0.45	5.8	0.6	1.05	0.11	3.6	0.7	0.94	0.26	6.13	1.10	0.88	0.55

	GCC18				GCC16				GCC29				GCC20				GCC21			
	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ
Sc	15	4	21	3	12.12	8.35	17	4	14	2	22.0	1.7	5.7		19.3		27	6	6	1
Ti	649	172	692	37	537	153	634	64	621	79	739	35	247		741		396	66	236	12
V	27	7	37	4	24.74	5.57	34	1	28	5	40.65	8.10	22		42		36	8	29	1
Mn	4558	1402	1575	72	4114	1252	1921	71	4655	281	1577	56	1735		3496		3733	972	1461	91
Co	25	7	33	7	20	4	27.6	1.3	22	2	34.18	2.98	15		30		16	3	12	2
Ni	154	51	1040	1157	153	44	496	75	156	43	559	8	318		577		59	8	220	29
Cu	35	35	169	88	7	4	9	3	1.39	0.69	3.29	1.38	1.83		6.0		3	1	7	8
Zn	62	32	43	5	55	267	48	6	31	9	25.05	0.97	46		59		11	4	15	8
Ga	28	8	27	2	22	4	29	3	24	3	27.68	1.56	13		30		14	2	10	1
Rb	0.14	0.04	0.17	0.05	0.14	0.14	0.09	0.06	0.10	0.06	0.07	0.03	0.06		0.10		0.09	0.06	0.09	0.04
Sr	8	8	78	1	12	11	111	5	2.35	0.29	64.10	1.75	16		64		3.4	1.5	23	1
Y	40	13	19	2	27	13	16	2	40.9	0.4	22.28	1.60	8		20		40	12	3.3	0.2
Zr	113	36	14	3	122	49	20	2	128	11	12.78	1.62	43		25		56	17	6	2
Nb	1.50	0.19	0.80	0.23	2.91	0.68	1.38	0.30	1.62	0.42	0.65	0.10	1.6		3.0		0.81	0.36	0.20	0.17
Cs	0.01	0.02	0.01	0.02	0.02	0.03	0.01	0.01	0.01	0.01	0.00	0.00	0.00		0.01		0.02	0.03	bdl	
Ba	0.15	0.18	0.25	0.26	0.64	0.80	0.42	0.36	0.61	0.67	0.29	0.13	0.16		0.36		0.90	1.24	0.39	0.40
La	1.2	0.6	8.2	0.3	1.87	1.06	11.4	1.0	0.89	0.19	7.71	0.57	1.85		7.93		0.53	0.25	0.99	0.11
Ce	2.7	1.0	15.6	0.5	3.94	1.38	20.2	1.7	2.07	0.20	13.2	0.7	3.39		14		1.06	0.24	1.99	0.09
Pr	4.1	1.1	17.4	0.6	5.49	1.04	19.7	1.5	3.27	0.28	14.7	0.5	3.99		15		1.47	0.21	2.85	0.19
Nd	3.7	0.6	10.5	0.7	3.86	0.79	11.2	0.7	3.43	0.28	9.8	0.5	2.51		9.3		1.44	0.28	2.06	0.29
Sm	13	3	18	1	12	4	15.5	0.7	11.9	1.3	17.8	0.7	5.81		18		7.3	2.0	5.02	0.45
Eu	18	5	19	1	15	5	16.0	1.2	16.4	1.7	19.4	0.9	6.41		19		12	3	5.91	0.15
Gd	20	6	18	2	16	7	13.9	1.5	18.1	1.8	18.0	0.8	5.82		18		16	4	5.20	0.32
Tb	24	7	17	2	18	9	13.9	1.1	223	2	18.1	0.8	5.86		17		22	6	4.38	0.69
Dy	30	10	17	1	22	12	13.6	1.4	28	2	18.8	0.6	6.43		17		29	7	3.61	0.71
Ho	32	10	16	1	22	13	13.3	1.8	30	1	18.0	1.3	6.07		16		32	8	2.83	0.57
Er	36	11	17	2	24	16	13.0	1.6	35	2	17.6	1.0	6.01		16		35	10	2.47	0.49
Tm	40	12	15	2	27	18	12.8	2.0	39	3	17.6	1.0	6.19		16		39	12	1.98	0.60
Yb	46	12	15	2	29	21	12.9	2.2	42	5	17.4	1.8	6.42		16		41	12	1.77	0.66
Lu	44	13	14	3	27	20	12	3	40.	6	16.4	1.2	5.80		15		40	12	1.53	0.58
Hf	18	5	12	1	19	6	14.13	2.45	18	1	10.2	0.6	5.98		12		7.1	1.8	2.20	0.26
Ta	2.9	0.7	1.13	0.27	4.3	1.0	2.47	0.58	3.23	0.48	0.81	0.16	2.56		3.21		1.28	0.60	0.20	0.12
U	2.62	0.52	1.12	0.43	4.9	1.0	1.74	0.30	2.78	0.31	0.79	0.10	2.10		3.06		0.82	0.46	0.19	0.17

	GCC22				GCC27				GCC24				GCC25				GCC26			
	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ
Sc	13	3	24	2	6	1	21	3	82	18	30	1	52	12	23	3	81	9	21	2
Ti	644	76	570	46	532	18	876	77	3400	347	1254	96	3540	314	1478	187	3005	325	1146	93
V	34	13	42	4	24	7	37	3	108	6	62	20	86	14	50	3	86	22	56	4
Mn	5012	454	1674	187	3268	588	1847	87	3571	120	1533	129	2995	269	1302	50	2845	291	1038	128
Co	27	5	38	4	15	1	28	3	96	9	58	10	65	6	50	4	42	9	27	6
Ni	166	44	596	113	55	18	335	59	686	137	932	401	281	85	692	107	270	222	515	209
Cu	7.33	5.12	21.26	12.63	10	6	7	5	37	21	36	22	17	11	17	1	2.0	1.6	1.2	0.3
Zn	87	28	41	6	23	2	23	3	158	30	63	7	44	7	36	7	19	6	18	5
Ga	30	6	26	4	21	4	31	2	85	17	38	5	73	9	39	2	50	10	31	8
Rb	0.18	0.08	0.07	0.03	0.71	0.12	0.22	0.10	1.00	0.26	0.32	0.05	0.36	0.08	0.34	0.10	1.04	0.31	0.28	0.25
Sr	2.3	1.9	44	1	34	7	131	10	3.5	1.6	74.9	0.9	7	3	110	8	10	4	71	4
Y	39	11	19	1	18	5	23	3	120	26	34	4	103	16	40	17	154	33	45	16
Zr	121	25	7	2	128	21	28	5	46	8	8.3	1.3	44	7	9	3	59	3	12	4
Nb	4.6	0.8	0.20	0.02	16	3	3.9	1.8	12	2	3.47	0.40	4.9	0.6	1.7	0.3	8	2	1.94	1.99
Cs	0.04	0.04	0.01	0.01	0.18	0.05	0.04	0.06	0.44	0.13	0.15	0.04	0.06	0.07	0.06	0.03	0.29	0.11	0.07	0.06
Ba	0.31	0.67	0.07	0.13	16	2	3.7	3.1	7.5	2.8	2.11	0.36	1.2	0.4	1.3	0.2	6.5	3.6	2.5	3.3
La	0.93	0.41	2.97	0.17	11	3	23	3	5.3	0.9	15	1	3.4	0.6	18	1	8.9	4.3	22	4
Ce	2.83	0.45	6.8	1.0	13	3	31	3	7.8	1.0	25	1	6.1	0.9	30	2	7.3	2.5	23	2
Pr	4.6	0.7	9.0	0.8	10	1	27	3	10	1	26	1	9.7	0.4	32	2	9.1	1.4	23	3
Nd	4.1	0.6	6.2	0.3	6.6	0.8	15	2	9.3	0.4	15	1	9.3	0.4	21	3	9.0	1.0	18	1
Sm	14	2	14.5	0.9	11	1	23	3	41	4	28	1	35	3	33	1	33	2	26	2
Eu	18	3	16.7	1.0	13	0	23	3	52	4	31	1	47	2	35	1	43	4	27	3
Gd	19	3	17.0	1.0	11	1	21	3	70	3	30	2	53	2	29	2	56	8	25	1
Tb	25	4	17.0	1.1	12	1	20	2	89	10	30	2	63	5	26	2	70	8	22	2
Dy	30	6	17.7	1.0	12	1	20	2	112	17	31	2	76	8	26	3	94	11	23	1
Ho	32	6	17.1	0.9	12	2	19	2	116	21	29	2	80	9	23	3	100	13	19	1
Er	37	8	17.2	0.7	12	2	20	3	130	29	30	2	87	12	24	4	124	16	18	1
Tm	40	9	17.0	0.7	13	3	20	3	139	31	29	2	91	17	23	4	127	15	15	2
Yb	44	12	16.7	1.1	14	3	20	4	150	34	30	2	97	19	23	4	145	21	15	1
Lu	43	11	15.8	0.8	12	3	18	3	145	36	29	2	94	19	21	4	136	17	13	1
Hf	21	7	7.5	1.1	13	0	20	4	59	7	19	1	50	7	15	2	44	6	9.8	1.0
Ta	8.2	2.8	0.31	0.11	20	3	5.6	2.6	14	2	4.0	0.5	6.1	0.5	2.0	0.2	8.8	2.1	2.0	2.1
U	7.0	1.5	0.21	0.03	21	2	5.0	2.6	16	1	4.0	1.2	7.4	0.5	3.0	0.9	9.5	1.5	3.4	1.5

	GCC28				GCC30				GCC31				GCC32				GCC33			
	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ	Garnet	σ	Cpx	σ
Sc	26	31	22	3	43	13	35	5	59	38	35	4	40	10	19	1	44	29	41	6
Ti	993	1245	913	94	4040	912	1998	208	3788	1426	1983	205	1973	591	2124	860	3595	864	2385	193
V	39	28	53	7	52	4	52	18	64	10	45	5	43	8	57	1	69	35	43	3
Mn	1233	980	914	136	1944	309	1260	36	2267	704	1345	73	1398	397	1187	86	2063	697	1286	50
Co	38	15	25	7	57	9	51	2	82	21	55	4	18	6	17	1	89	37	55	3
Ni	854	672	501	121	229	40	698	137	304	111	953	491	20	8	23	5	228	81	594	152
Cu	1.7	1.5	1.5	0.6	2.2	1.5	9.4	3.9	30.60	20.25	59.65	50.65	10	6	4.2	1.7	8	5	21	14
Zn	33	18	19	10	43	5	34	1	77	25	40	4	30	14	32	4	95	47	78	8
Ga	26	33	29	5	54	7	44	4	71	30	45	3	24	7	28	4	66	28	53	8
Rb	0.16	0.10	0.16	0.05	0.48	0.05	0.43	0.13	15.7	8.6	1.7	0.8	7	3	9	8	1.16	0.81	1.00	0.35
Sr	26	16	123	6	52	16	131	9	47	17	127	7	45	18	93	46	29	9	197	10
Y	38	49	24	2	57	13	42	5	52	22	43	3	70	13	48	4	48	24	39	1
Zr	20	24	7.3	0.7	129	15	30	4	124	58	35	3	205	72	227	147	110	40	45	10
Nb	0.9	0.9	0.48	0.07	115	31	5	1	33	24	7	1	28	13	37	31	11	5	6	2
Cs	0.04	0.04	0.05	0.01	0.23	0.09	0.14	0.05	6.4	3.2	0.86	0.57	2.7	1.4	3.8	3.3	0.76	0.62	0.41	0.26
Ba	1.2	1.0	1.0	0.3	2.8	0.9	2.9	0.8	36	17	11	5	42	21	63	53	5	3	6	2
La	2.2	0.8	9.9	0.9	17	4	31	1	23	11	34	6	27	12	44	28	9	1	51	3
Ce	3.3	0.7	14	1	30	7	48	2	28	12	47	5	26	10	46	26	16	1	75	6
Pr	3.5	0.7	14	2	35	7	48	5	30	11	49	5	22	8	40	20	20	2	73	6
Nd	3.5	1.6	11	1	22	4	27	2	18	5	27	2	14	5	26	11	14	2	38	3
Sm	10	11	18	3	45	2	41	3	38	13	44	3	24	7	36	11	37	10	52	3
Eu	13	16	19	3	51	5	44	3	46	16	46	2	29	8	37	11	45	15	53	2
Gd	16	21	18	3	47	6	37	2	46	18	42	2	30	7	32	8	43	17	44	2
Tb	20	28	17	2	50	8	36	1	48	20	40	2	35	9	28	6	48	21	39	1
Dy	26	39	17	2	55	12	36	2	56	24	40	3	42	11	28	5	55	26	40	2
Ho	27	40	15	2	57	12	35	1	55	25	39	2	44	12	23	4	55	30	38	2
Er	32	47	15	2	59	13	35	1	61	27	39	3	50	13	23	3	55	31	38	2
Tm	33	49	13	2	64	15	35	1	63	31	40	3	53	14	20	3	56	31	37	1
Yb	36	53	13	2	66	17	37	2	71	39	40	3	61	17	19	2	70	56	39	5
Lu	35	51	12	2	62	14	34	1	60	29	38	2	55	14	16	2	53	31	37	3
Hf	14	20	6.1	0.6	51	3	34	4	42	15	34	4	30	10	32	17	37	13	43	8
Ta	1.3	1.4	0.57	0.10	121	32	5.8	1.6	29	21	8	1	27	13	36	29	16	7	8	3
U	1.3	1.4	0.98	0.12	28	5	7.7	0.6	29	15	12	3	23	11	33	27	13	6	6	1

6.5 Discussion

6.5.1 Equilibrium within Experiments

Conventional peridotite thermobarometry techniques were used to assess whether the phases in the experimental runs had achieved equilibrium, by comparing the calculated temperature with the run temperature (Table 6.5). Temperatures were calculated for two parts of each experiment: ‘layer’ which used compositions of the garnet and clinopyroxene layers, along with orthopyroxene from the peridotite layer; and ‘peridotite’ which was used the compositions of garnet, clinopyroxene and orthopyroxene from the peridotite layer. Average EDS determined values for the relevant phase were used in this calculation. An experiment was assessed as having closely approached equilibrium if the calculated temperature was within 100 °C of the run temperature, this threshold was chosen as it matched the temperature difference between experiments and was also substantially above the uncertainty of most thermometers (typically 50 °C). The temperature was calculated using a variety of two-pyroxene (T[BKN] - Brey and Köhler, 1990, T[TA98] - Taylor, 1998), clinopyroxene (T[NTcpx] - Nimis and Taylor, 2000) and garnet-clinopyroxene (T[EG] - Ellis and Green, 1979) thermometers, and the results of these were compared with each other. Ultimately, the two-pyroxene thermometers were considered, as they gave comparable results, which indicated that the same experiments had approached equilibrium. Figure 6.7 shows the difference between T[BKN] and T[TA98] and the nominal experimental temperature against this experimental temperature.

Table 6.5: Difference in temperature (ΔT) from the experimental temperature, as calculated using T[BKN], T[TA98], T[NTcpx] and T[EG]. ‘Y’ in column ‘Model’ denotes which experiments were used in the development of multivariate algorithm. ‘NA’ = not applicable.

Sample	Phases	Temperature/ C	Pressure/ GPa	$\Delta T/^{\circ}\text{C}$				Model
				[BKN]	[TA98]	[NTcpx]	T [EG]	
GCC10	layer	1050	35	290	296	267	275	
GCC08	layer	1200	35	72	53	29	104	Y
GCC06	layer	1250	35	99	75	74	169	Y
GCC09	layer	1350	35	-33	-63	-107	-105	Y
GCC19	layer	1050	35	76	72	56	349	Y
GCC18	layer	1150	35	56	54	24	216	Y
GCC16	layer	1250	35	-3	0	-50	374	Y
GCC29	layer	1350	35	-83	-96	-127	85	Y
GCC20	layer	1050	35	285	329	305	148	
GCC21	layer	1150	35	103	91	68	22	
GCC22	layer	1250	35	-23	-30	-52	-58	Y
GCC27	layer	1350	35	-158	-99	-175	-152	
GCC24	layer	1050	55	216	257	151	233	
GCC25	layer	1150	55	99	73	44	113	Y
GCC26	layer	1250	55	59	67	29	17	Y
GCC28	layer	1350	55	NA	NA	-109	-56	
GCC30	layer	1050	35	187	168	151	277	
GCC31	layer	1150	35	27	37	-5	168	Y
GCC32	layer	1250	35	135	113	116	-179	
GCC33	layer	1350	35	-123	-143	-171	-266	
GCC10	peridotite	1050	35	314	315	296	212	
GCC08	peridotite	1200	35	129	111	102	-29	
GCC06	peridotite	1250	35	140	114	125	214	
GCC09	peridotite	1350	35	17	-19	-50	-68	
GCC19	peridotite	1050	35	76	81	67	NA	
GCC18	peridotite	1150	35	141	135	125	224	
GCC16	peridotite	1250	35	103	106	86	30	
GCC29	peridotite	1350	35	39	30	33	-1	
GCC20	peridotite	1050	35	189	240	187	NA	
GCC21	peridotite	1150	35	152	139	130	245	
GCC22	peridotite	1250	35	8	-2	-18	134	
GCC27	peridotite	1350	35	-10	44	12	152	
GCC24	peridotite	1050	55	252	300	205	290	
GCC25	peridotite	1150	55	122	117	94	84	
GCC26	peridotite	1250	55	161	154	135	-22	
GCC28	peridotite	1350	55	NA	NA	-24	-314	
GCC30	peridotite	1050	35	268	250	249	310	
GCC31	peridotite	1150	35	248	247	259	244	
GCC32	peridotite	1250	35	147	124	128	57	
GCC33	peridotite	1350	35	24	7	18	-78	

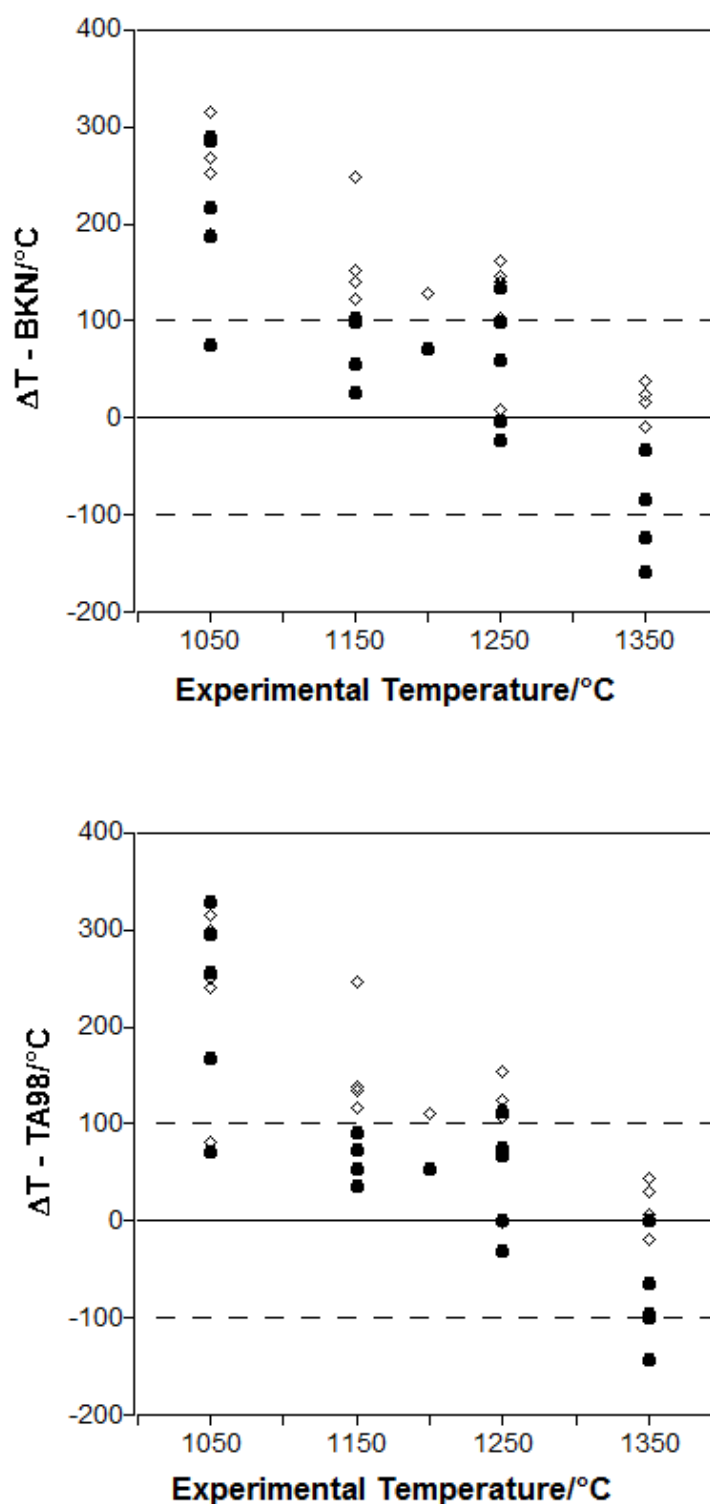


Figure 6.7: Experimental temperature (°C) against the difference between the equilibrium temperature calculated and the experimental temperature (ΔT), for both T[BKN] and T[TA98]. Dark circles are the calculations using average clinopyroxene analyses from the layers and open diamonds are the results of calculations using average mineral compositions from the peridotite layers. The dotted lines indicate ± 100 °C of the experimental temperature, which the criteria used for equilibrium.

Based on this test, experiments at the lowest temperature (1050 °C) were the least equilibrated, with only the carbonate free run, GCC19, meeting the criteria for equilibrium. At temperatures between 1150 and 1250 °C, the calculated ‘layer’ temperatures agree with the run temperatures for most experiments (except GCC32) whilst the calculated ‘peridotite’ temperature did not always indicate equilibrium. In all runs at 1350 °C the peridotite layer attained equilibrium, however the garnet and clinopyroxene layers did not show equilibrium with each other or the peridotite layer in runs GCC32 and GCC33. Series A, B and C recorded acceptable temperature for at the 3 of the 4 experiments, whilst series D and E only recorded equilibrium for two experiments.

6.5.2 Elemental Partitioning

Partition coefficients for garnet over clinopyroxene ($D_{\text{Ga/Cpx}}$) are shown in Table 6.6; calculated from the average concentration determined for each layer in each experiment. Elements such as Cr, Mn, Y, Zr, Nb, and U partition into garnet in most cases; whilst clinopyroxene is the preferred host of Ni and Sr. Some transition metals, such as Sc, Ti, V, Co and Cu display a range of partition coefficients, indicating that their favoured phase varies depending on other conditions, or that they did not equilibrate during the experiments. Partition coefficients for the primitive mantle normalised REE (REE_N) are shown in Figure 6.8. This shows that the LREE partition strongly into clinopyroxene, with $D_{\text{Ga/Cpx}}$ ranging from 0.1 to 1. Sm, Eu and Gd show variable partitioning depending on the experiment, with $D_{\text{Ga/Cpx}}$ of 0.8 to 1.2. The HREE, from Tb onwards, partition into garnet strongly for most experiments, with $D_{\text{Ga/Cpx}}$ up to 12. Two experiments (GCC21 and GCC27), which had an initial garnet CaO content of 6.3 wt.% and were conducted at 1050 and 1350 °C respectively did not show any partitioning of REEs into

garnet, despite the REEs being detectable in garnet, indicating that they may not have been mobilised during the experiment. The temperature series with an initial garnet CaO content of 3.2 wt.% showed only a small degree of partitioning into garnet with a maximum $D_{\text{Ga/Cpx}}$ of 1.3. A number of experiments showed a slightly higher partition coefficient for La relative to Ce, despite being lighter. When $\log D_{\text{Ga/Cpx}}$ was plotted relative to the ionic radii of the REE, a relatively smooth relationship was observed for the vast majority of experiments. The partitioning behaviour observed is similar to that previously observed in xenoliths from kimberlites, including Finsch (Lazarov et al., 2012) and Diavik (Yaxley et al, in preparation), however, these experiments show a smaller spread of values, with the HREE and LREE being less strongly partitioned into garnet and clinopyroxene respectively.

6.5.3 Effects of Temperature

The distribution of Fe and Mg between garnet and clinopyroxene can be quantified as the distribution coefficient, $K_D^{\text{Fe-Mg}}$, which is calculated using:

$$K_D^{\text{Fe-Mg}} = (X_{\text{Fe}}/X_{\text{Mg}})^{\text{Ga}} (X_{\text{Mg}}/X_{\text{Fe}})^{\text{Cpx}} \quad (6.1)$$

Where X_{Fe} and X_{Mg} are the mole fractions of Fe or Mg in garnet (Ga) or clinopyroxene (Cpx), assuming ideal solid solutions exist (Ellis and Green, 1979). Most experiments show no substantial difference in $K_D^{\text{Fe-Mg}}$ between the garnet-clinopyroxene layers or the peridotite, with the largest variations being ~ 0.2 ln units. When compared with temperature, it was found that this distribution coefficient decreases as temperature increases (Figure 6.9a). Runs at 1050 °C deviate from this trend, though this can be explained their lack of chemical equilibrium.

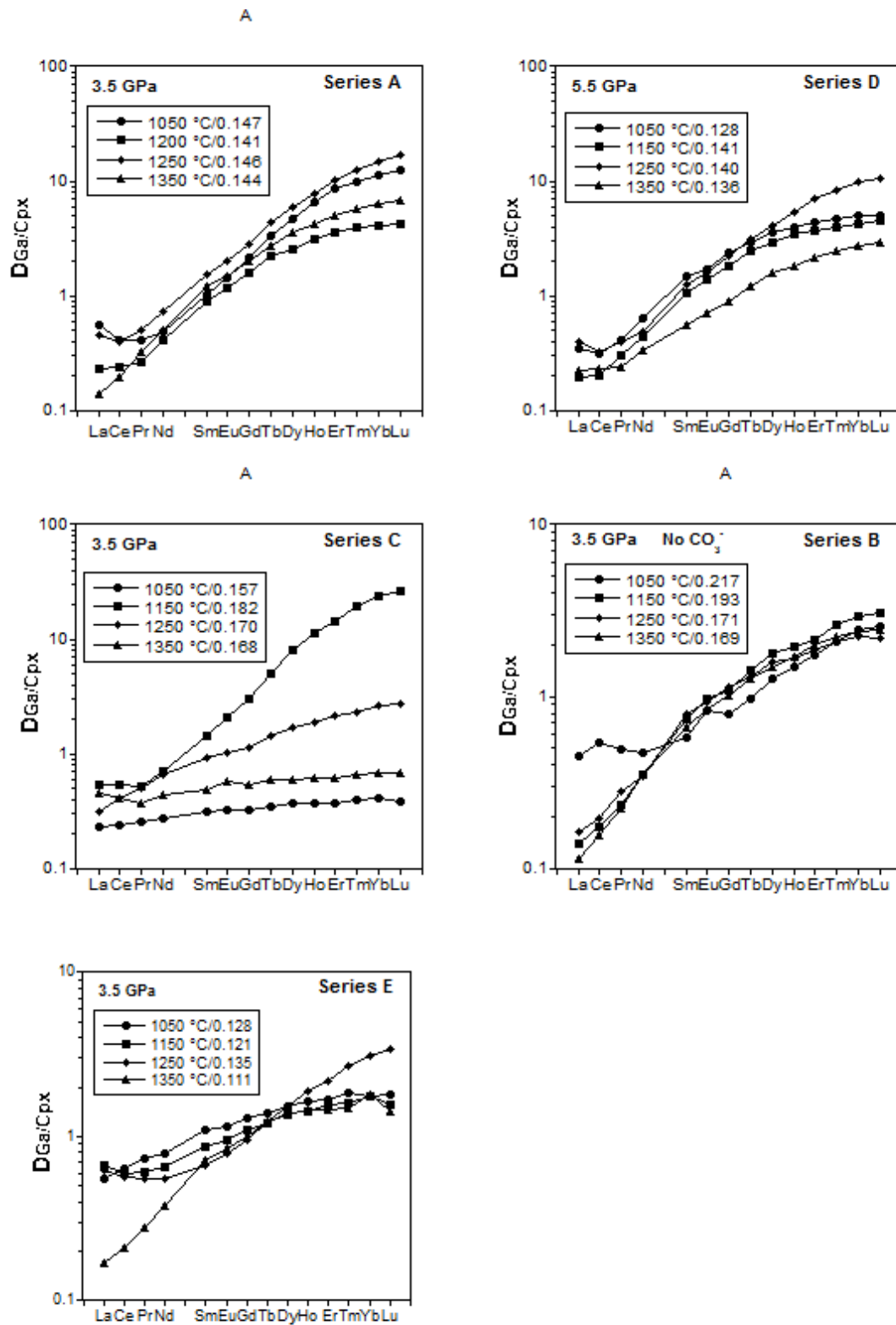


Figure 6.8: REE partition coefficients ($D_{Ga/Cpx}$) for each series of experiments. X_{Ca}^{Ga} of the completed experiments is given after the temperature of each run in the legend.

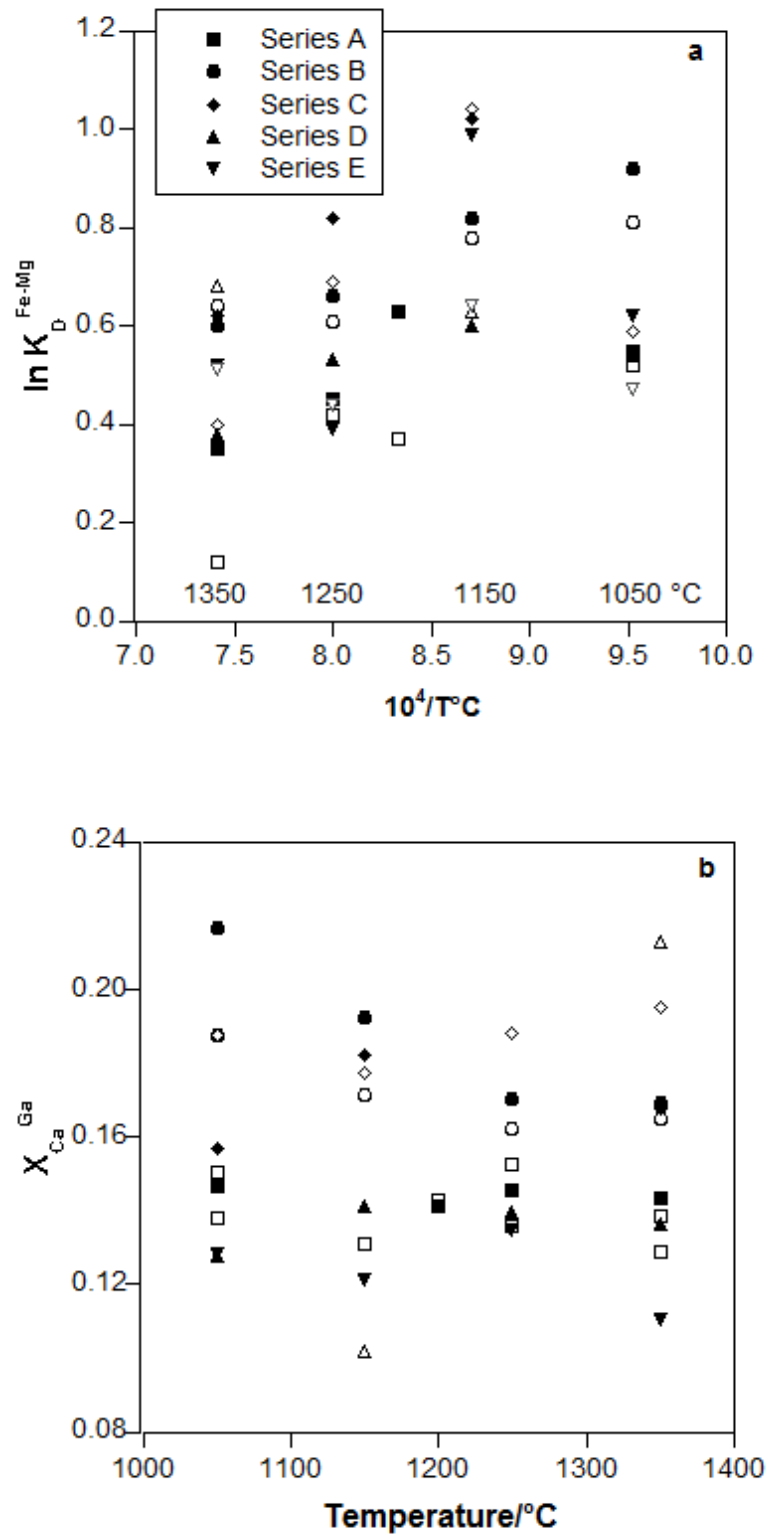


Figure 6.9: Compositional variations with temperature. a) $\ln K_D^{\text{Fe-Mg}}$ against $10^4/T$ and b) $X_{\text{Ca}}^{\text{Ga}}$ vs T. Filled symbols indicate the layer compositions, whilst open symbols indicate the peridotite compositions.

Table 6.6: Partition coefficients ($D_{\text{Ga/Cpx}}$) for garnet over clinopyroxene. Where no value is given, that element was not detectable in at least one phase.

	GCC10	GCC08	GCC06	GCC09	GC19	GCC18	GCC16	GCC29	GCC20	GCC21	GCC22	GCC27	GCC24	GCC25	GCC26	GCC28	GCC30	GCC31	GCC32	GCC33
Cr₂O₃	3.60	3.53	3.43	3.95	4.75	5.73	5.78	4.97	2.03	3.16	5.88	5.36	3.95	3.86	3.51	3.32	3.43	3.29	2.80	3.55
Sc	3.47	1.76	5.13	3.24	0.67	0.72	0.70	0.65	0.29	4.64	0.54	0.29	2.70	2.22	3.86	1.16	1.22	1.69	2.07	1.09
Ti	1.15	1.33	1.79	1.60	1.50	0.94	0.85	0.84	0.33	1.68	1.13	0.61	2.71	2.40	2.62	1.09	2.02	1.91	0.93	1.51
V	0.95	1.10	1.35	1.03	3.43	0.72	0.72	0.70	0.53	1.22	0.80	0.64	1.76	1.72	1.53	0.75	1.01	1.42	0.76	1.61
Mn	1.48	1.55	1.92	1.38	4.93	2.89	2.14	2.95	0.50	2.55	2.99	1.77	2.33	2.30	2.74	1.35	1.54	1.69	1.18	1.60
Co	0.94	0.99	1.09	0.80	1.20	0.76	0.74	0.66	0.50	1.28	0.71	0.54	1.65	1.31	1.55	1.51	1.11	1.50	1.08	1.61
Ni	0.32	0.31	0.19	0.17	0.57	0.15	0.31	0.28	0.55	0.27	0.28	0.16	0.74	0.41	0.52	1.71	0.33	0.32	0.88	0.38
Cu	1.49	2.16	1.88	0.48	4.91	0.21	0.76	0.42	0.30	0.41	0.34	1.54	1.03	0.98	1.75	1.16	0.24	0.51	2.26	0.37
Zn	0.84	1.19	0.81	0.61	3.67	1.44	1.15	1.25	0.77	0.75	2.13	1.01	2.52	1.24	1.09	1.71	1.27	1.93	0.96	1.23
Ga	1.02	1.25	1.21	0.88	1.83	1.02	0.76	0.88	0.45	1.36	1.14	0.66	2.22	1.85	1.63	0.90	1.21	1.59	0.87	1.24
Rb	9.91	1.47	8.10	1.79	3.70	0.79	1.48	1.44	0.54	0.98	2.51	3.27	3.09	1.07	3.67	1.02	1.11	9.47	0.73	1.16
Sr	0.21	0.09	0.12	0.05	0.12	0.10	0.11	0.04	0.25	0.15	0.05	0.26	0.05	0.07	0.14	0.21	0.39	0.37	0.48	0.15
Y	6.60	2.80	7.80	4.03	1.57	2.11	1.68	1.84	0.38	12.14	2.03	0.77	3.54	2.56	3.40	1.58	1.35	1.20	1.46	1.24
Zr	5.04	3.24	6.04	6.22	13.58	7.99	6.44	10.14	1.73	9.49	19.50	4.40	5.65	4.87	4.90	2.76	4.33	3.53	0.91	2.47
Nb	4.45	1.58	6.78	3.23	7.58	1.87	2.10	2.51	0.57	4.05	23.51	4.14	3.36	2.91	4.06	1.79	22.08	4.71	0.74	1.76
Cs	13.45	0.53	3.70	2.37	-	1.08	2.61	3.53	0.45	-	8.07	4.66	2.84	1.10	4.04	0.89	1.65	7.40	0.71	1.84
Ba	9.33	0.72	11.49	0.72	-	0.62	1.52	2.09	0.45	2.27	4.62	4.27	3.56	0.88	2.56	1.11	0.95	3.24	0.67	0.85
La	0.56	0.23	0.45	0.14	0.45	0.14	0.16	0.12	0.23	0.54	0.31	0.46	0.35	0.19	0.40	0.22	0.55	0.67	0.62	0.17
Ce	0.41	0.24	0.39	0.19	0.55	0.18	0.20	0.16	0.24	0.53	0.42	0.42	0.31	0.20	0.33	0.23	0.64	0.60	0.56	0.21
Pr	0.42	0.26	0.50	0.32	0.50	0.24	0.28	0.22	0.26	0.52	0.50	0.38	0.41	0.30	0.40	0.24	0.74	0.61	0.55	0.28
Nd	0.49	0.41	0.73	0.51	0.47	0.35	0.34	0.35	0.27	0.70	0.66	0.44	0.63	0.44	0.49	0.33	0.79	0.65	0.55	0.38
Sm	1.02	0.89	1.53	1.21	0.57	0.74	0.79	0.67	0.32	1.45	0.93	0.49	1.46	1.07	1.26	0.56	1.10	0.88	0.66	0.71
Eu	1.42	1.17	2.03	1.49	0.83	0.94	0.94	0.84	0.34	1.98	1.06	0.58	1.69	1.35	1.60	0.71	1.15	0.98	0.79	0.85
Gd	2.18	1.57	2.85	2.02	0.80	1.08	1.13	1.01	0.33	3.03	1.14	0.54	2.37	1.82	2.20	0.90	1.28	1.09	0.96	0.99
Tb	3.38	2.19	4.36	2.71	0.96	1.41	1.31	1.26	0.35	5.01	1.44	0.59	2.96	2.44	3.17	1.20	1.37	1.21	1.24	1.22
Dy	4.76	2.59	5.91	3.52	1.27	1.76	1.59	1.48	0.37	7.92	1.68	0.60	3.63	2.87	4.03	1.58	1.53	1.38	1.53	1.35
Ho	6.55	3.14	7.84	4.20	1.49	1.95	1.66	1.71	0.37	11.37	1.88	0.61	3.98	3.42	5.39	1.82	1.64	1.42	1.90	1.47
Er	8.53	3.53	10.35	4.99	1.75	2.15	1.88	1.99	0.37	14.35	2.15	0.62	4.32	3.69	6.99	2.15	1.66	1.56	2.18	1.46
Tm	9.91	3.97	12.35	5.67	2.09	2.62	2.08	2.22	0.39	19.71	2.33	0.66	4.75	4.01	8.34	2.49	1.82	1.59	2.69	1.49
Yb	11.42	4.15	14.58	6.42	2.43	2.95	2.22	2.41	0.41	23.50	2.66	0.67	4.93	4.25	9.73	2.76	1.78	1.74	3.14	1.78
Lu	12.38	4.30	16.92	6.84	2.57	3.04	2.18	2.44	0.39	26.05	2.71	0.67	4.97	4.48	10.62	2.94	1.82	1.58	3.45	1.42
Hf	2.70	1.79	3.51	3.11	1.29	1.50	1.34	1.72	0.53	3.25	2.75	0.65	3.18	3.31	4.48	2.28	1.51	1.25	0.93	0.86
Ta	3.32	1.66	6.40	3.03	5.66	2.57	1.74	4.01	0.80	6.43	26.04	3.48	3.56	3.06	4.51	2.19	20.70	3.90	0.75	1.96
U	3.57	1.90	5.55	3.79	6.95	2.34	2.83	3.52	0.69	4.21	33.19	4.29	3.98	2.51	2.75	1.31	3.66	2.39	0.71	2.35

When the Ca content of the garnet, expressed as the mole fraction of grossular (X_{Ca}^{Ga}), is compared with temperature, there are some visible trends (Figure 6.9b). Series A shows little variation with temperature; however, the peridotite and layers values are closer at high temperatures. Series B shows a decrease in Ca from 1050 to 1250 °C, before levelling off at 1350 °C. Series C shows a slight increase from 1050 to 1150 °C before levelling in the layers, whilst the peridotite increases with temperature. Series D is relatively constant in the layers; however the peridotite shows a dramatic increase between the runs at 1150 and 1350 °C. Series E shows a relatively constant relationship between X_{Ca}^{Ga} and temperature, with a small range of 0.111 to 0.135.

The partitioning of the REEs between garnet and clinopyroxene is shown in Figure 6.4. In all but Series C the smallest partition coefficients for La and Ce are observed at 1350 °C. The largest partition coefficients for the HREEs are generally observed at the intermediate temperatures (1150 – 1250 °C).

6.5.4 Effect of Pressure

Two series of experiments with the same initial composition (CaO in garnet of 5.3 wt.%) were performed, one at 3.5 GPa (series A) and the other at 5.5 GPa (series D). In the high pressure series, only the experiments at 1150 and 1250 °C reached an acceptable state of equilibrium, and such they will be compared with the runs at 1200 and 1250 °C from the low pressure series. The Mg# and Cr₂O₃ concentration of the high pressure experiments is consistently higher for garnet and clinopyroxene in both the layers and the peridotite. Na₂O and CaO also show an increase in concentration with temperature in clinopyroxene and garnet respectively. There is no substantial difference in the partition coefficient of garnet/clinopyroxene due to pressure.

6.5.5 Effects of Carbonate

The effects of carbonate on the partitioning behaviour within peridotite were examined by performing two temperature series (series B and C) at the same conditions with similar mixtures, excepting for the presence of carbonate in the peridotite. The silicate composition of the peridotite used in both series was the same, however, series C contained ~5 wt.% dolomite. The same garnet (UV45-03) and clinopyroxene (Diavik) mixes were used in both series. The two experiments at 1050 °C were not considered as they did not reach an acceptable state of chemical equilibrium. Garnet from the carbonate-bearing experiments had a higher Mg# in the layer and the peridotite, compared to the carbonate-free experiments. The partition coefficients show that the LREE have a stronger affinity for clinopyroxene in the carbonate free series. The HREE show a more varied behaviour with clinopyroxene being the preferred host in the carbonate-bearing experiment at 1350 °C, whilst garnet is preferred for the carbonate-free experiment. Garnet is the preferred host of the HREE at in both systems at 1150 and 1250 °C, however there is a much stronger affinity for garnet observed in the carbonate-bearing system at 1250 °C (Figure 6.8), which may be related to the higher X_{Ca}^{Ga} observed in this run.

6.5.6 Effect of Ca in Garnet

Three of the experimental series (A, C, E) can be used to examine the effect of Ca in garnet on the partitioning of the REE. Series C has the highest Ca, followed by series A and series E which has the lowest. The variation in partition coefficient for three elements (Ce, Eu, Lu) with X_{Ca}^{Ga} at the four different temperature intervals is shown in Figure 6.10. Of the three experiments at 1050 °C, none reached an acceptable level of chemical equilibrium so no clear conclusions can be obtained from them. The experiments performed at 1150 and 1200 °C, which are considered together for this

analysis, show a systematic increase in the compatibility of the HREE in garnet with increasing X_{Ca}^{Ga} , with series C (high X_{Ca}^{Ga}) having values for $D_{Ga/Cpx}$ up to an order of magnitude larger than series E (low X_{Ca}^{Ga} - Figure 6.10b). For all other temperatures the strongest partitioning of the HREE into garnet is observed in the experiments with intermediate X_{Ca}^{Ga} (Series A). At 1250 °C, the experiment with low X_{Ca}^{Ga} did not achieve chemical equilibrium, and the remaining experiments showed a decrease in $D_{Ga/Cpx}$ with increasing X_{Ca}^{Ga} . The amount of partitioning observed at 1350 °C was less than at lower temperatures, with the HREE from series C (high X_{Ca}^{Ga}) favouring clinopyroxene not garnet, suggesting that the REE were not mobilised in this experiment. Once again stronger partitioning into garnet is observed at the intermediate X_{Ca}^{Ga} than at the low value.

6.5.7 Multivariate Effects on Garnet/Clinopyroxene Partitioning

The earlier results show that garnet-clinopyroxene trace element partitioning behaviour is controlled by several variables, namely run temperature, equilibrium X_{Ca}^{Ga} and pressure. Therefore, the experimentally determined partition coefficients were used to derive an empirical relationship between run temperature and pressure, X_{Ca}^{Ga} , ionic radii and the partition coefficient ($D_{Ga/Cpx}^{REE}$). The partition coefficients used to produce this model were those obtained from close to the interface between the garnet and clinopyroxene layers, as listed in Table 6.5, for only the 11 experiments that achieved an acceptable level of chemical equilibrium, as indicated in Table 6.6. X_{Ca}^{Ga} was obtained as the average of multiple EDS analyses on the garnet layer. Multivariate non-linear regression was used to generate parameters for the following empirical equation, which was based upon that used by Witt-Eickschen and O'Neill (2005):

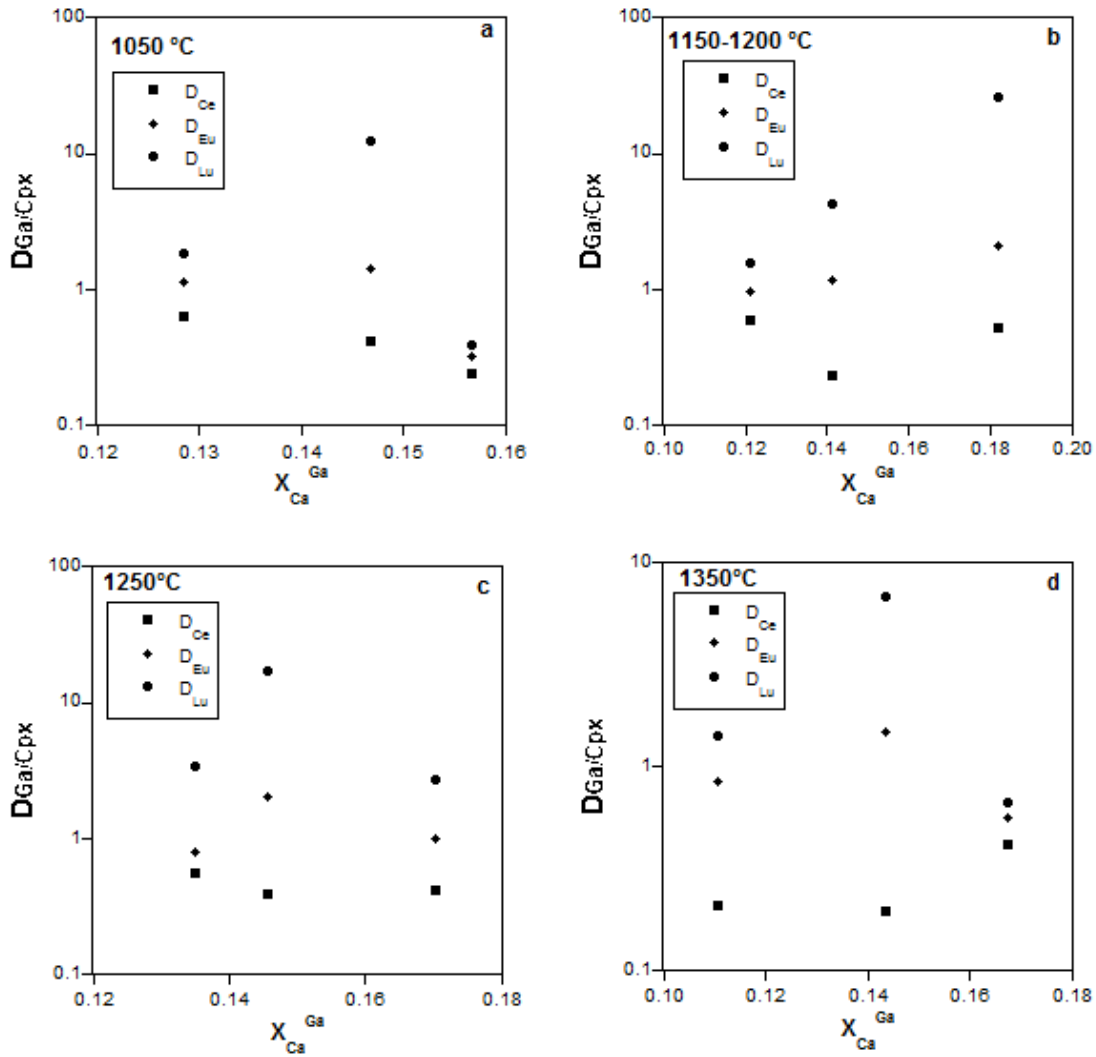


Figure 6.10: Selected REE partition coefficients ($D_{\text{Ga/Cpx}}$) against $X_{\text{Ca}}^{\text{Ga}}$ for each of the for temperature intervals, a) 1050 °C, b) 1150-1200 °C, c) 1250 °C and d) 1350 °C.

$$\ln D_{\text{Ga/Cpx}}^{\text{REE}} = A_0 + A_1 r_i + B_0/T + B_1 r_i/T + C_0 X_{\text{Ca}}^{\text{Ga}} + C_1 X_{\text{Ca}}^{\text{Ga}} r_i + E_0 P/T \quad (6.1)$$

where $D_{\text{Ga/Cpx}}^{\text{REE}}$ is the partition coefficient for any particular REE; A_0 , A_1 , B_0 , B_1 , C_0 , C_1 and E_0 are fitting parameters determined by regression; r_i is the ionic radius of the specified REE in Å, in an eight-fold coordination environment (Shannon, 1976); T is temperature in K; $X_{\text{Ca}}^{\text{Ga}}$ is the CaO concentration of garnet in wt.%; and P is pressure in GPa. These variables were chosen as they were changed and controlled during the

experimental program. The regression-determined parameters yield the following equation:

$$\begin{aligned} \ln D_{\text{Ga/Cpx}}^{\text{REE}} = & 54.972 - 50.052r_i - 22395.4/T + 21651r_i/T - 128.64 X_{\text{Ca}}^{\text{Ga}} \\ & + 109.06 X_{\text{Ca}}^{\text{Ga}} r_i - 0.16 P/T \end{aligned} \quad (6.2)$$

The reduced chi-squared (χ^2) value was used to determine how well the equation fits the data, and was found to be 2.71, which indicates a good fit to the model. In order to obtain a reasonable result, the standard deviation (σ) for each experimentally determined coefficient was set to a minimum of 20% of the partition coefficient, as a very small standard deviation on any one value would yield an unrealistically high level of control on the model.

This algorithm was then used to model the variation in partitioning observed with changes in P, T and $X_{\text{Ca}}^{\text{Ga}}$, whilst $D_{\text{Ga/Cpx}}$ is always higher for elements with smaller ionic radii (HREE). When pressure was increased from 2.5 to 7 GPa, at 1150 °C and $X_{\text{Ca}}^{\text{Ga}} = 0.15$, it was found that $D_{\text{Ga/Cpx}}$ for any REE decreased by less than 0.01, indicating that its effect is minimal over the pressure range relevant to the cratonic mantle. Figure 6.11a shows the variation in $D_{\text{Ga/Cpx}}$ as temperature increased from 1000 to 1400 °C, at 4.0 GPa and $X_{\text{Ca}}^{\text{Ga}} = 0.15$. It was found that the HREE (e.g. Lu) show an increase in $D_{\text{Ga/Cpx}}$ with temperature, whilst the LREE (e.g. Ce) show a decrease. When $X_{\text{Ca}}^{\text{Ga}}$ is increased from 0.10 to 0.19, at 1150 °C and 4.0 GPa, all the REE show a decrease in $D_{\text{Ga/Cpx}}$ (Figure 6.11b).

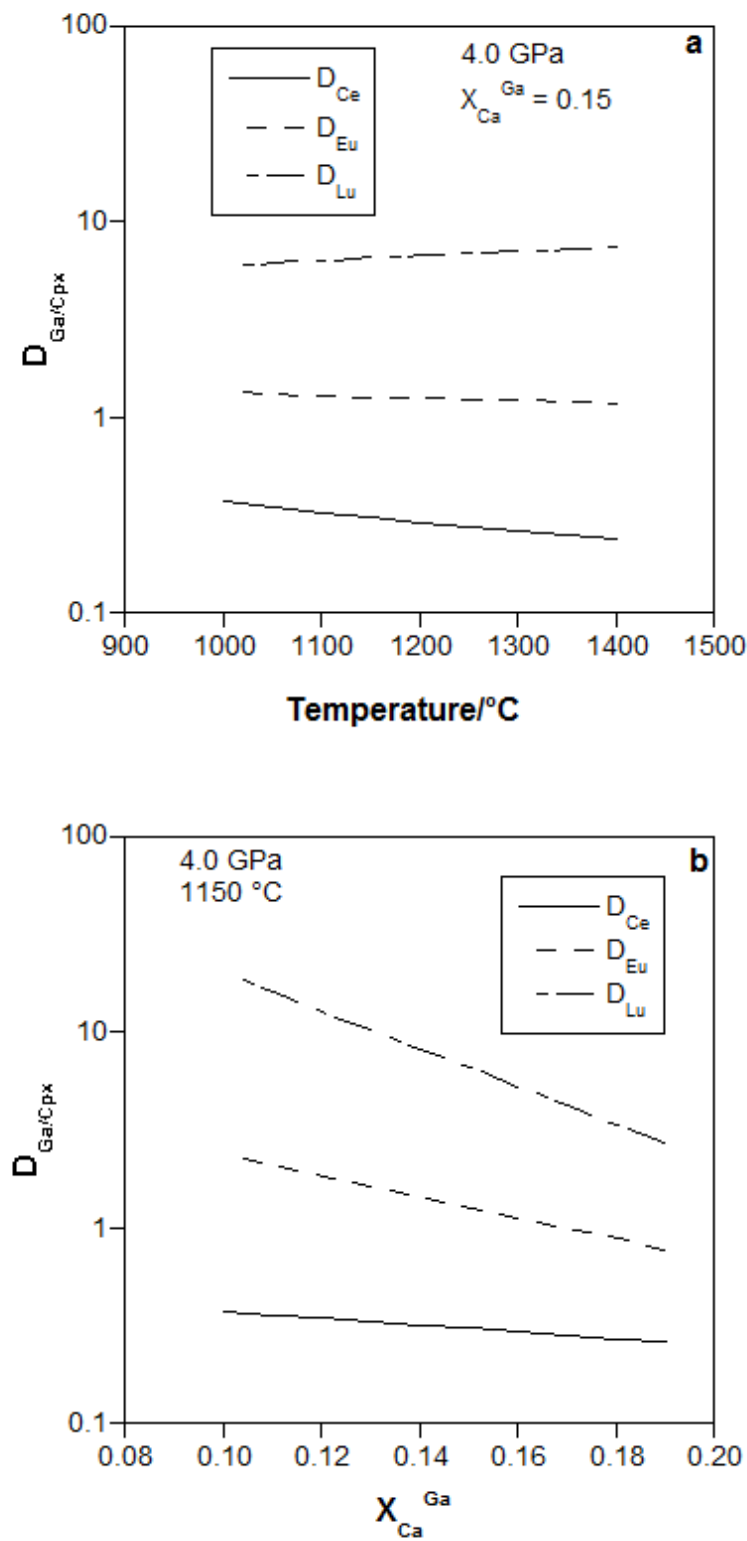


Figure 6.11: Modelled garnet/clinopyroxene partition coefficients for selected elements with varying temperature (a) and $X_{\text{Ca}}^{\text{Ga}}$ (b). See text for details regarding the modelling process and variable range.

Whilst this model is useful in predicting the changes to $D_{\text{Ga/Cpx}}$ when T , P and $X_{\text{Ca}}^{\text{Ga}}$ are changed, it still has limitations. Its ability to predict the REE_N patterns that will be observed in garnet or clinopyroxene, at different conditions, is limited, because knowledge of the pattern for one phase is required for calculating the pattern for the other phase. For example, if the chosen clinopyroxene REE_N pattern was originally associated with a sinusoidal garnet REE_N pattern, then this model will always produce a sinusoidal pattern. To truly understand how the REE pattern for one phase (e.g. garnet) varied with changes to T or $X_{\text{Ca}}^{\text{Ga}}$, you would also need to know how the total abundance of each REE varied in the system, which is independent of the partition coefficient. At high temperatures, REE partitioning between clinopyroxene and orthopyroxene or olivine may be significant (Witt-Eickschen and O'Neill, 2005), therefore the system becomes more complex than this model as you approach magmatic temperatures. Further investigation into the distribution of rare-earth elements in all phases of garnet peridotite assemblages is needed to develop a better understanding of partitioning as magmatic temperatures are approached.

6.6 Conclusion

The partitioning of the REEs between garnet and clinopyroxene in a carbonate-bearing peridotite has been investigated through high temperature and pressure experiments. The experiments showed that the LREE partition into clinopyroxene whilst the HREE favour garnet. The results were used to develop a multivariate algorithm to incorporate the effects of temperature, pressure, ionic radius and $X_{\text{Ca}}^{\text{Ga}}$ content. It was found that $D_{\text{Ga/Cpx}}$ is highest for elements with smaller ionic radii, whilst it decreases when $X_{\text{Ca}}^{\text{Ga}}$ increases. As temperature increases $D_{\text{Ga/Cpx}}$ increases for the HREE and decreases for the LREE. This indicates that there will be a redistribution of the REE in peridotite

systems as they cool from magmatic temperatures to the temperature recorded by the xenolith, however this process may be complicated if orthopyroxene or olivine also host REE at magmatic temperatures.

6.7 Acknowledgements

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Chapter 7: Thesis Overview and Future Directions

7.1 Thesis Overview

This thesis has investigated the redox conditions within the cratonic mantle and examines the links between oxidation state and metasomatism. This has been achieved through a number of studies into kimberlite-borne garnet peridotite xenoliths, which are the major source of cratonic mantle samples. Links between metasomatism and redox state have been recognised in samples from one location in the Kaapvaal cratonic mantle (Wesselton), but were not recognised in samples from a second locality (Kimberley), indicating that metasomatism and associated changes in the redox state may be highly localised events.

Through the study of garnet peridotite xenoliths from the Wesselton kimberlite, evidence for at least one metasomatic event was observed, particularly through the presence of compositionally zoned garnets (Chapter 2). The survival of this zonation suggested that this metasomatic event occurred at the same time as or very shortly before entrainment in the erupting kimberlite. Fe K-edge XANES spectroscopy was used on these samples, allowing for the determination of a redox profile through the sampled cratonic lithosphere. The rims of the zoned garnets were found to be substantially more oxidised than the cores, which, when combined with the enrichment observed in metasomatic indicator elements, such as Ti, Y and Zr, infers that this oxidation may be linked to metasomatism. More reduced samples from this suite did not show evidence of metasomatism. The more oxidised rims are consistent with the stability of carbonate melts, however, if diffusive re-equilibration had occurred, removing these rims, then the observed fO_2 would have been somewhere between that

of the rim and the core, inconsistent with carbonate melt stability. Therefore, metasomatism may have been more oxidising than previously thought, as diffusive re-equilibration of samples would lead to the observation of an intermediate fO_2 , which is a weighted average of the original material and the metasomatic agent, rather than recording the fO_2 of the metasomatic agent.

The discovery of the zoned garnet crystals in the Wesselton peridotite suite presented a unique opportunity to map the distribution of $Fe^{3+}/\Sigma Fe$ of the garnet using Fe K-edge XANES spectroscopy, producing the first ever fully quantitative maps of this distribution in garnet (Chapter 3). The distribution observed in this map was similar to that expected from stoichiometry and produced further evidence that this zonation was caused by metasomatism close to the time of eruption, as the crystals had not been subjected to significant diffusive re-equilibration.

The compositional profiles observed in the zoned garnets from the Wesselton kimberlite were examined in detail using both EPMA and NanoSIMS, in order to further investigate the timing of the formation of these features relative to entrainment in the erupting kimberlite (Chapter 4). By modelling the profiles as a diffusive process, it was determined that they formed in less than ten years based upon the diffusivity of Ca. These compositional profiles were also used to determine diffusion coefficients for a variety of major and minor elements relative to Ca, including Na, Cr, Mn, Fe, Ti and Y. These are the first determinations of the diffusivity of Na, Cr, Ti and Y in peridotitic garnet. The mixing behaviour between the core and rim material was modelled by

examining changes in REE_N profiles and it was found that as little as eight percent of rim material is required to remove the depleted HREE_N signal observed in the core.

Examination of a suite of garnet peridotite xenoliths, some of which also contained phlogopite, from the Kimberley pipe revealed evidence for two generations of metasomatic activity (Chapter 5). One metasomatic event is responsible for the formation of secondary clinopyroxene and associated phlogopite, whilst the other event is related to coarse grained clinopyroxene and a fluid metasomatism signature in garnet. The redox state recorded by these samples was within the range observed at this pressure for other studies of the Kaapvaal and around the world, however there was no evidence linking the metasomatic events to any oxidative event.

An experimental study into the partitioning of the rare earth elements between garnet and clinopyroxene in carbonated peridotite was performed (Chapter 6). These experiments confirmed that the LREE preferentially partition into clinopyroxene, whilst the HREE favour garnet. It was found that the partition coefficients (for garnet over clinopyroxene) are highest for elements with smaller ionic radii. It was found that pressure has little effect on the partitioning whilst a decrease in the partition coefficient was observed with increasing Ca content in garnet. As temperature increased, it was found that the HREE partition more strongly into garnet whilst the LREE favour clinopyroxene. This indicates that there will be a redistribution of the REE in peridotite systems as they cool from magmatic temperatures to the temperature recorded by the xenolith, however this process may be complicated if orthopyroxene or olivine also host REE at magmatic temperatures.

7.2 Future Directions

As much as this thesis has identified some of the relationships between redox conditions and metasomatism in the cratonic mantle, it has also exposed more questions regarding these processes. Oxidation trends at high pressure in the Wesselton samples could be easily linked to metasomatic activity; however, a similar trend across small garnet crystals at a lower pressure could not be attributed to metasomatism. As such we must ask how it is possible for garnet crystals within 20 mm of each other to show dramatically different oxygen fugacities, yet lack evidence of any metasomatic activity. It may be that this variation is related to the size of the crystals and that the redox state is a weighted average of the original crystal and the contribution of a past metasomatic event, evidence of which has been obscured by diffusive re-equilibration.

Another question of interest is the mechanisms responsible for the zoned garnet observed in the Wesselton suite. Why do only a small number of garnets show this zoning? Do all metasomatised garnets originally show such clear compositional zoning? If so, why do we not find it more often, is it lost to diffusive re-equilibration, or to the kelyphitic alteration rims that are common on so many peridotitic garnets?

As has been demonstrated, Fe K-edge XANES spectroscopy provides a robust technique for the determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnet, and the subsequent calculation of the oxygen fugacity in garnet-bearing assemblages. However, current methods for the in-situ determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ on spinel, using EPMA, depend on stoichiometric calculations, limiting the ability to perform a similar investigation of the redox state of the shallow cratonic mantle. Development of a similar empirical calibration for the application of Fe K-edge XANES to spinel would improve our ability to study the upper

cratonic mantle with respect to its oxidation state, using a technique that is dependent only on standards, not assumed or calculated stoichiometry.

There is also scope for significant experimental investigations into the signatures of metasomatism that commonly used, such as the partitioning of rare earth elements. Whilst this study began to look at the effects of pressure, temperature and garnet Ca content, there remains much more to be done. It would also be desirable to further investigation the concentrations and partitioning of the REE in all phases of garnet peridotite as magmatic temperatures are approached, so that the impacts of partitioning into orthopyroxene and olivine can be considered. Investigation of a wider pressure and compositional range would also be beneficial to improve the empirical model that has been developed.

In short, the cratonic mantle is a very complex part of the earth, which plays host to a wide variety of processes. It is also slow to give up its secrets and will be a fertile field of fascinating study for years to come, and I hope to be part of this future work.

Bibliography

- BELONOSHKO, A. B. & SAXENA, S. K. 1992. A unified equation of state for fluids of C-H-O-N-S-Ar composition and their mixtures up to very high temperatures and pressures. *Geochimica et Cosmochimica Acta*, 56, 3611-3626.
- BERG, J. 1977. Dry granulite mineral assemblages in the contact aureoles of the Nain complex, Labrador. *Contributions to Mineralogy and Petrology*, 64, 33-52.
- BERRY, A. J., DANYUSHEVSKY, L. V., O'NEILL, H. S. C., NEWVILLE, M. & SUTTON, S. R. 2008. Oxidation state of iron in komatiitic melt inclusions indicates hot Archaean mantle. *Nature*, 455, 960-963.
- BERRY, A. J., O'NEILL, H. S. C., JAYASURIYA, K. D., CAMPBELL, S. J. & FORAN, G. J. 2003. XANES calibrations for the oxidation state of iron in a silicate glass. *American Mineralogist*, 88, 967-977.
- BERRY, A. J., O'NEILL, H. S. C., SCOTT, D. R., FORAN, G. J. & SHELLEY, J. 2006. The effect of composition on Cr²⁺/Cr³⁺ in silicate melts. *American Mineralogist*, 91, 1901-1908.
- BERRY, A. J., YAXLEY, G. M., HANGER, B. J., WOODLAND, A. B., DE JONGE, M. D., HOWARD, D. L., PATERSON, D. & KAMENETSKY, V. S. 2013. Quantitative mapping of the oxidative effects of mantle metasomatism. *Geology*, 41, 683-686.
- BORFECCHIA, E., MINO, L., GIANOLIO, D., GROPPPO, C., MALASPINA, N., MARTINEZ-CRIADO, G., SANS, J. A., POLI, S., CASTELLI, D. & LAMBERTI, C. 2012. Iron oxidation state in garnet from a subduction setting: a micro-XANES and electron microprobe ("flank method") comparative study. *Journal of Analytical Atomic Spectrometry*, 27, 1725-1733.
- BREY, G. P. & KÖHLER, T. 1990. Geothermobarometry in four-phase lherzolites II. New thermobarometers, and practical assessment of existing thermobarometers. *Journal of Petrology*, 31, 1353-1378.

- BREY, G. P., KÖHLER, T. & NICKEL, K. G. 1990. Geothermobarometry in four-phase Iherzolites I. Experimental results from 10 to 60 kb. *Journal of Petrology*, 31, 1313-1352.
- CANIL, D. 1994. An experimental calibration of the "Nickel in Garnet" geothermometer with applications. *Contributions to Mineralogy and Petrology*, 117, 410-420.
- CARLSON, W. D. 2006. Rates of Fe, Mg, Mn, and Ca diffusion in garnet. *American Mineralogist*, 91, 1-11.
- CARLSON, W. D. 2012. Rates and mechanism of Y, REE, and Cr diffusion in garnet. *American Mineralogist*, 97, 1598-1618.
- CHAKRABORTY, S. & BORINSKI, S. 2010. Ca Diffusion in Garnet: A Tale of Two Sites. Geological Society of America Annual Meeting. Denver.
- CHAKRABORTY, S. & GANGULY, J. 1992. Cation diffusion in aluminosilicate garnets: experimental determination in spessartine-almandine diffusion couples, evaluation of effective binary diffusion coefficients, and applications. *Contributions to Mineralogy and Petrology*, 111, 74-86.
- CHAKRABORTY, S. & RUBIE, D. C. 1996. Mg tracer diffusion in aluminosilicate garnets at 750-850° C, 1 atm. and 1300° C, 8.5 GPa. *Contributions to Mineralogy and Petrology*, 122, 406-414.
- CHAKRABORTY, S. 2008. Diffusion in Solid Silicates: A Tool to Track Timescales of Processes Comes of Age. *Annual Review of Earth and Planetary Sciences*, 36, 153-190.
- CHERNIAK, D. J., WATSON, E. B. & LIANG, Y. 2012. Diffusion of highly charged cations in olivine, Abstract MR22A-07. 2012 Fall Meeting, AGU. San Francisco, Calif.
- CREIGHTON, S., STACHEL, T., EICHENBERG, D. & LUTH, R. 2010. Oxidation state of the lithospheric mantle beneath Diavik diamond mine, central Slave craton, NWT, Canada. *Contributions to Mineralogy and Petrology*, 159, 645-657.

- CREIGHTON, S., STACHEL, T., MATVEEV, S., HÖFER, H., MCCAMMON, C. & LUTH, R. 2009. Oxidation of the Kaapvaal lithospheric mantle driven by metasomatism. *Contributions to Mineralogy and Petrology*, 157, 491-504.
- CYGAN, R. T. & LASAGA, A. C. 1985. Self-diffusion of magnesium in garnet at 750 degrees to 900 degrees C. *American Journal of Science*, 285, 328-350.
- DASGUPTA, R., MALLIK, A., TSUNO, K., WITHERS, A. C., HIRTH, G. & HIRSCHMANN, M. M. 2013. Carbon-dioxide-rich silicate melt in the Earth's upper mantle. *Nature*, 493, 211-215.
- DAWSON, J. B. & SMITH, J. V. 1977. The MARID (mica-amphibole-rutile-ilmenite-diopside) suite of xenoliths in kimberlite. *Geochimica et Cosmochimica Acta*, 41, 309-323.
- DE ANDRADE, V., SUSINI, J., SALOMÉ, M., BERALDIN, O., RIGAUULT, C., HEYMES, T., LEWIN, E. & VIDAL, O. 2011. Submicrometer hyperspectral X-ray imaging of heterogeneous rocks and geomaterials: Applications at the Fe K-edge. *Analytical Chemistry*, 83, 4220-4227.
- DELANEY, J. S., DYAR, M. D., SUTTON, S. R. & BAJT, S. 1998. Redox ratios with relevant resolution: Solving an old problem by using the synchrotron microXANES probe. *Geology*, 26, 139-142.
- EGGINS, S. M., RUDNICK, R. L. & MCDONOUGH, W. F. 1998. The composition of peridotites and their minerals: a laser-ablation ICP-MS study. *Earth and Planetary Science Letters*, 154, 53-71.
- ELLIS, D. J. & GREEN, D. H. 1979. An experimental study of the effect of Ca upon garnet-clinopyroxene Fe-Mg exchange equilibria. *Contributions to Mineralogy and Petrology*, 71, 13-22.
- ETSCHMANN, B. E., RYAN, C. G., BRUGGER, J., KIRKHAM, R., HOUGH, R. M., MOORHEAD, G., SIDONS, D. P., DE GERONIMO, G., KUCZEWSKI, A., DUNN, P., PATERSON, D., DE JONGE, M. D., HOWARD, D. L., DAVEY, P. & JENSEN, M. 2010. Reduced As components in highly oxidized environments: Evidence from full spectral XANES imaging using the Maia massively parallel detector. *American Mineralogist*, 95, 884-887.

- FOLEY, S. F. 2011. A reappraisal of redox melting in the Earth's mantle as a function of tectonic setting and time. *Journal of Petrology*, 52, 1363-1391.
- FROST, B. R. 1991. Stability of oxide minerals in metamorphic rocks. *Reviews in Mineralogy and Geochemistry*, 25, 469-488.
- FROST, D. J. & MCCAMMON, C. A. 2008. The Redox State of Earth's Mantle. *Annual Review of Earth and Planetary Sciences*, 36, 389-420.
- GANGULY, J. 2010. Cation diffusion kinetics in aluminosilicate garnets and geological applications. *Reviews in Mineralogy and Geochemistry*, 72, 559-601.
- GANGULY, J., CHENG, W. & CHAKRABORTY, S. 1998. Cation diffusion in aluminosilicate garnets: experimental determination in pyrope-almandine diffusion couples. *Contributions to Mineralogy and Petrology*, 131, 171-180.
- GANGULY, J., CHENG, W. & O'NEILL, H. S. C. 1993. Syntheses, volume, and structural changes of garnets in the pyrope-grossular join: Implications for stability and mixing properties. *The American mineralogist*, 78, 583-593.
- GANGULY, J., TIRONE, M. & HERVIG, R. L. 1998. Diffusion kinetics of Samarium and Neodymium in garnet, and a method for determining cooling rates of rocks. *Science*, 281, 805-807.
- GEIGER, C. A. & FEENSTRA, A. 1997. Molar volumes of mixing of almandine-pyrope and almandine-spessartine garnets and the crystal chemistry and thermodynamic-mixing properties of the aluminosilicate garnets. *American Mineralogist*, 82, 571-581.
- GIBSON, S. A., MALARKEY, J. & DAY, J. A. 2008. Melt depletion and enrichment beneath the western Kaapvaal Craton: evidence from Finsch peridotite xenoliths. *Journal of Petrology*, 49, 1817-1852.
- GREEN, T. H., BLUNDY, J. D., ADAM, J. & YAXLEY, G. M. 2000. SIMS determination of trace element partition coefficients between garnet, clinopyroxene and hydrous basaltic liquids at 2–7.5 GPa and 1080–1200°C. *Lithos*, 53, 165-187.

- GRÉGOIRE, M., BELL, D. & LE ROEX, A. 2002. Trace element geochemistry of phlogopite-rich mafic mantle xenoliths: their classification and their relationship to phlogopite-bearing peridotites and kimberlites revisited. *Contributions to Mineralogy and Petrology*, 142, 603-625.
- GRÉGOIRE, M., BELL, D. R. & LE ROEX, A. P. 2003. Garnet lherzolites from the Kaapvaal Craton (South Africa): Trace element evidence for a metasomatic history. *Journal of Petrology*, 44, 629-657.
- GRIFFIN, W. L. & RYAN, C. G. 1995. Trace elements in indicator minerals: area selection and target evaluation in diamond exploration. *Journal of Geochemical Exploration*, 53, 311-337.
- GRIFFIN, W. L., COUSENS, D. R., RYAN, C. G., SIE, S. H. & SUTER, G. F. 1989. Ni in chrome pyrope garnets: a new geothermometer. *Contributions to Mineralogy and Petrology*, 103, 199-202.
- GRIFFIN, W. L., FISHER, N. I., FRIEDMAN, J., RYAN, C. G. & O'REILLY, S. Y. 1999. Cr-pyrope garnets in the lithospheric mantle. I. Compositional systematics and relations to tectonic setting. *Journal of Petrology*, 40, 679-704.
- GRIFFIN, W. L., GURNEY, J. J. & RYAN, C. G. 1992. Variations in trapping temperatures and trace elements in peridotite-suite inclusions from African diamonds: evidence for two inclusion suites, and implications for lithosphere stratigraphy. *Contributions to Mineralogy and Petrology*, 110, 1-15.
- GRIFFIN, W. L., O'REILLY, S. Y., NATAPOV, L. M. & RYAN, C. G. 2003. The evolution of lithospheric mantle beneath the Kalahari Craton and its margins. *Lithos*, 71, 215-241.
- GRIFFIN, W. L., SHEE, S. R., RYAN, C. G., WIN, T. T. & WYATT, B. A. 1999. Harzburgite to lherzolite and back again: metasomatic processes in ultramafic xenoliths from the Wesselton kimberlite, Kimberley, South Africa. *Contributions to Mineralogy and Petrology*, 134, 232-250.

- GRIFFIN, W. L., SMITH, D., BOYD, F. R., COUSENS, D. R., RYAN, C. G., SIE, S. H. & SUTER, G. F. 1989. Trace-element zoning in garnets from sheared mantle xenoliths. *Geochimica et Cosmochimica Acta*, 53, 561-567.
- GRIFFIN, W. L., SMITH, D., RYAN, C. G., O'REILLY, S. Y. & WIN, T. T. 1996. Trace-element zoning in mantle minerals; metasomatism and thermal events in the upper mantle. *The Canadian Mineralogist*, 34, 1179-1193.
- GRÜTTER, H. S., GURNEY, J. J., MENZIES, A. H. & WINTER, F. 2004. An updated classification scheme for mantle-derived garnet, for use by diamond explorers. *Lithos*, 77, 841-857.
- GUDMUNDSSON, G. & WOOD, B. 1995. Experimental tests of garnet peridotite oxygen barometry. *Contributions to Mineralogy and Petrology*, 119, 56-67.
- HANGER, B. J., YAXLEY, G. M., BERRY, A. J., KAMENETSKY, V. S., PATERSON, D. & HOWARD, D. L. 2013. Oxygen Fugacity in the Kaapvaal Cratonic Lithosphere – Evidence from Fe XANES Measurements of Fe³⁺ in Garnet from the Kimberley Pipe. *Mineralogical Magazine*, 77, 1253.
- HARTE, B. 1977. Rock nomenclature with particular relation to deformation and recrystallisation textures in olivine-bearing xenoliths. *Journal of Geology*, 85, 279-288.
- HERMANN, J., RUBATTO, D. & TROMMSDORFF, V. 2006. Sub-solidus Oligocene zircon formation in garnet peridotite during fast decompression and fluid infiltration (Duria, Central Alps). *Mineralogy and Petrology*, 88, 181-206.
- HÖFER, H. E. & BREY, G. P. 2007. The iron oxidation state of garnet by electron microprobe: Its determination with the flank method combined with major-element analysis. *American Mineralogist*, 92, 873.
- HOLLAND, T. J. B. & POWELL, R. 2011. An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids. *Journal of Metamorphic Geology*, 29, 333-383.

- JAROSEWICH, E., NELEN, J. A. & NORBERG, J. A. 1980. Reference Samples for Electron Microprobe Analysis*. *Geostandards Newsletter*, 4, 43-47.
- JOCHUM, K. P., WEIS, U., STOLL, B., KUZMIN, D., YANG, Q., RACZEK, I., JACOB, D. E., STRACKE, A., BIRBAUM, K., FRICK, D. A., GÜNTHER, D. & ENZWEILER, J. 2011. Determination of Reference Values for NIST SRM 610–617 Glasses Following ISO Guidelines. *Geostandards and Geoanalytical Research*, 35, 397-429.
- JOHNSON, K. T. M. 1998. Experimental determination of partition coefficients for rare earth and high-field-strength elements between clinopyroxene, garnet, and basaltic melt at high pressures. *Contributions to Mineralogy and Petrology*, 133, 60-68.
- JONES, R. A. 1987. Strontium and neodymium isotopic and rare earth element evidence for the genesis of megacrysts in kimberlites of southern Africa. In: NIXON, P. H. (ed.) *Mantle xenoliths*. Chichester: J. Wiley & Sons.
- KENNEDY, C. S. & KENNEDY, G. C. 1976. The equilibrium boundary between graphite and diamond. *Journal of Geophysical Research*, 81, 2467-2470.
- KOHN, M. J. 2004. Oscillatory- and sector-zoned garnets record cyclic (?) rapid thrusting in central Nepal. *Geochemistry, Geophysics, Geosystems*, 5, Q12014.
- KRAMERS, J. D. & SMITH, C. B. 1983. A feasibility study of U-Pb and Pb-Pb dating of kimberlites using groundmass mineral fractions and whole-rock samples. *Chemical Geology*, 41, 23-38.
- KUSHIRO, I. & YODER, H. S. 1966. Anorthite—forsterite and anorthite—enstatite reactions and their bearing on the basalt—eclogite transformation. *Journal of Petrology*, 7, 337-362.
- LAZAROV, M., BREY, G. P. & WEYER, S. 2012/2012a. Evolution of the South African mantle—a case study of garnet peridotites from the Finsch diamond mine (Kaalpvaal craton); Part 2: Multiple depletion and re-enrichment processes. *Lithos*, 154, 210-223.

- LAZAROV, M., BREY, G. P. & WEYER, S. 2012b. Evolution of the South African mantle — A case study of garnet peridotites from the Finsch diamond mine (Kapaal craton); part 1: Inter-mineral trace element and isotopic equilibrium. *Lithos*, 154, 193-209.
- LAZAROV, M., WOODLAND, A. B. & BREY, G. P. 2009. Thermal state and redox conditions of the Kapaal mantle: A study of xenoliths from the Finsch mine, South Africa. *Lithos*, 112, Supplement 2, 913-923.
- LOOMIS, T., GANGULY, J. & ELPHICK, S. 1985. Experimental determination of cation diffusivities in aluminosilicate garnets. *Contributions to Mineralogy and Petrology*, 90, 45-51.
- LUTH, R. W. 1993. Diamonds, eclogites, and the oxidation state of the Earth's mantle. *Science*, 261, 66-68.
- LUTH, R. W., VIRGO, D., BOYD, F. R. & WOOD, B. J. 1990. Ferric iron in mantle-derived garnets. *Contributions to Mineralogy and Petrology*, 104, 56-72.
- MATJUSCHKIN, V., BREY, G., HÖFER, H. & WOODLAND, A. 2014. The influence of Fe³⁺ on garnet–orthopyroxene and garnet–olivine geothermometers. *Contributions to Mineralogy and Petrology*, 167, 1-10.
- MCCAMMON, C. & KOPYLOVA, M. G. 2004. A redox profile of the Slave mantle and oxygen fugacity control in the cratonic mantle. *Contributions to Mineralogy and Petrology*, 148, 55-68.
- MCCAMMON, C. A., GRIFFIN, W. L., SHEE, S. R. & O'NEILL, H. S. C. 2001. Oxidation during metasomatism in ultramafic xenoliths from the Wesselton kimberlite, South Africa: implications for the survival of diamond. *Contributions to Mineralogy and Petrology*, 141, 287-296.
- MCFARLANE, C. R. M., CARLSON, W. D. & CONNELLY, J. N. 2003. Prograde, peak, and retrograde P–T paths from aluminium in orthopyroxene: High-temperature contact metamorphism in the aureole of the Makhavinekh Lake Pluton, Nain Plutonic Suite, Labrador. *Journal of Metamorphic Geology*, 21, 405-423.

- MCGUIRE, A., DYAR, M. D. & NIELSON, J. 1991. Metasomatic oxidation of upper mantle peridotite. *Contributions to Mineralogy and Petrology*, 109, 252-264.
- MÉTRICH, N., BERRY, A. J., O'NEILL, H. S. C. & SUSINI, J. 2009. The oxidation state of sulfur in synthetic and natural glasses determined by X-ray absorption spectroscopy. *Geochimica et Cosmochimica Acta*, 73, 2382-2399.
- MORIOKA, M. 1980. Cation diffusion in olivine—I. Cobalt and magnesium. *Geochimica et Cosmochimica Acta*, 44, 759-762.
- MUÑOZ, M., DE ANDRADE, V., VIDAL, O., LEWIN, E., PASCARELLI, S. & SUSINI, J. 2006. Redox and speciation micromapping using dispersive X-ray absorption spectroscopy: Application to iron in chlorite mineral of a metamorphic rock thin section. *Geochemistry, Geophysics, Geosystems*, 7, Q11020.
- NICKEL, K. G. & GREEN, D. H. 1985. Empirical geothermobarometry for garnet peridotites and implications for the nature of the lithosphere, kimberlites and diamonds. *Earth and Planetary Science Letters*, 73, 158-170.
- NIMIS, P. & GRÜTTER, H. 2010. Internally consistent geothermometers for garnet peridotites and pyroxenites. *Contributions to Mineralogy and Petrology*, 159, 411-427.
- NIMIS, P. & TAYLOR, W. R. 2000. Single clinopyroxene thermobarometry for garnet peridotites. Part I. Calibration and testing of a Cr-in-Cpx barometer and an enstatite-in-Cpx thermometer. *Contributions to Mineralogy and Petrology*, 139, 541-554.
- NIXON, P., ROGERS, N., GIBSON, I. & GREY, A. 1981. Depleted and fertile mantle xenoliths from southern African kimberlites. *Annual Review of Earth and Planetary Sciences*, 9, 285.
- O'NEILL, H. S. C. & WALL, V. J. 1987. The olivine-orthopyroxene-spinel oxygen geobarometer, the nickel precipitation curve, and the oxygen fugacity of the Earth's upper mantle. *Journal of Petrology*, 28, 1169-1191.

- PALME, H. & O'NEILL, H. S. C. 2007. Cosmochemical estimates of mantle composition. In: HEINRICH, D. H. & KARL, K. T. (eds.) *Treatise on Geochemistry*. Oxford: Pergamon.
- PATERSON, D., DE JONGE, M. D., HOWARD, D. L., LEWIS, W., MCKINLAY, J., STARRITT, A., KUSEL, M., RYAN, C. G., KIRKHAM, R., MOORHEAD, G. & SIDDONS, D. P. 2011. The X-ray fluorescence microscopy beamline at the Australian Synchrotron. *AIP Conference Proceedings*, 1365, 219-222.
- PATON, C., HELLSTROM, J., PAUL, B., WOODHEAD, J. & HERGT, J. 2011. Iolite: Freeware for the visualisation and processing of mass spectrometric data. *Journal of Analytical Atomic Spectrometry*, 26, 2508-2518.
- PEARSON, D. G., CANIL, D. & SHIREY, S. B. 2003. Mantle samples included in volcanic rocks: xenoliths and diamonds. In: HEINRICH, D. H. & KARL, K. T. (eds.) *Treatise on Geochemistry*. Oxford: Pergamon.
- PICKERING, I. J., PRINCE, R. C., SALT, D. E. & GEORGE, G. N. 2000. Quantitative, chemically specific imaging of selenium transformation in plants. *Proceedings of the National Academy of Sciences*, 97, 10717-10722.
- POLLACK, H. N. & CHAPMAN, D. S. 1977. On the regional variation of heat flow, geotherms, and lithospheric thickness. *Tectonophysics*, 38, 279-296.
- RINGWOOD, A. E. 1977. Synthesis of pyrope-knorringite solid solution series. *Earth and Planetary Science Letters*, 36, 443-448.
- RUSSELL, J. K., PORRITT, L. A., LAVALLEE, Y. & DINGWELL, D. B. 2012. Kimberlite ascent by assimilation-fuelled buoyancy. *Nature*, 481, 352-356.
- SALTERS, V. J. M., LONGHI, J. E. & BIZIMIS, M. 2002. Near mantle solidus trace element partitioning at pressures up to 3.4 GPa. *Geochemistry, Geophysics, Geosystems*, 3, 1-23.
- SHANNON, R. D. 1976. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*, 32, 751-767.

- SMITH, C. B., ALLSOPP, H. L., KRAMERS, J. D., HUTCHINSON, G. & RODDICK, J. C. 1985. Emplacement ages of Jurassic-Cretaceous South African kimberlites by the Rb-Sr method on phlogopite and whole-rock samples. *South African Journal of Geology*, 88, 249.
- SMITH, D. & BOYD, F. 1987. Compositional heterogeneities in a high-temperature lherzolite nodule and implications for mantle processes. In: NIXON, P. H. (ed.) *Mantle xenoliths*. New York: Wiley.
- SMITH, D. & EHRENBERG, S. 1984. Zoned minerals in garnet peridotite nodules from the Colorado Plateau: implications for mantle metasomatism and kinetics. *Contributions to Mineralogy and Petrology*, 86, 274-285.
- SMITH, D. 1988. Implications of zoned garnets for the evolution of sheared lherzolites: Examples From Northern Lesotho and the Colorado Plateau. *Journal of Geophysical Research: Solid Earth*, 93, 4895-4905.
- SPANDLER, C. & O'NEILL, H. C. 2010. Diffusion and partition coefficients of minor and trace elements in San Carlos olivine at 1,300°C with some geochemical implications. *Contributions to Mineralogy and Petrology*, 159, 791-818.
- STACHEL, T., AULBACH, S., BREY, G. P., HARRIS, J. W., LEOST, I., TAPPERT, R. & VILJOEN, K. S. 2004. The trace element composition of silicate inclusions in diamonds: a review. *Lithos*, 77, 1-19.
- STACHEL, T., HARRIS, J. & BREY, G. Year. REE patterns of peridotitic and eclogitic inclusions in diamonds from Mwadui (Tanzania). In: *Proceedings of the Seventh International Kimberlite Conference*, 1999.
- STACHEL, T., VILJOEN, K. S., BREY, G. & HARRIS, J. W. 1998. Metasomatic processes in lherzolitic and harzburgitic domains of diamondiferous lithospheric mantle: REE in garnets from xenoliths and inclusions in diamonds. *Earth and Planetary Science Letters*, 159, 1-12.
- STAGNO, V. & FROST, D. J. 2010. Carbon speciation in the asthenosphere: Experimental measurements of the redox conditions at which carbonate-bearing melts coexist with graphite or diamond in peridotite assemblages. *Earth and Planetary Science Letters*, 300, 72-84.

- STAGNO, V., OJWANG, D. O., MCCAMMON, C. A. & FROST, D. J. 2013. The oxidation state of the mantle and the extraction of carbon from Earth's interior. *Nature*, 493, 84-88.
- STAGNO, V., OJWANG, D. O., MCCAMMON, C. A. & FROST, D. J. 2013. The oxidation state of the mantle and the extraction of carbon from Earth's interior. *Nature*, 493, 84-88.
- SUTTON, S. R., BAJT, S., DELANEY, J., SCHULZE, D. & TOKUNAGA, T. 1995. Synchrotron x-ray fluorescence microprobe: Quantification and mapping of mixed valence state samples using micro-XANES. *Review of Scientific Instruments*, 66, 1464-1467.
- TAYLOR, W. R. & GREEN, D. H. 1987. The petrogenetic role of methane: effect on liquidus phase relations and the solubility mechanism of reduced C-H volatiles. *Magmatic Processes: Physicochemical Principles*, 121-138.
- TAYLOR, W. R. & GREEN, D. H. 1988. Measurement of reduced peridotite-C-O-H solidus and implications for redox melting of the mantle. *Nature*, 332, 349-352.
- TAYLOR, W. R. 1998. An experimental test of some geothermometer and geobarometer formulations for upper mantle peridotite with application to the thermobarometry of fertile lherzolite and garnet websterite. *Neues Jahrbuch für Mineralogie Abhandlungen*, 172, 381-408.
- TUFF, J. & GIBSON, S. A. 2007. Trace-element partitioning between garnet, clinopyroxene and Fe-rich picritic melts at 3 to 7 GPa. *Contributions to Mineralogy and Petrology*, 153, 369-387.
- VAN ACHTERBERGH, E., GRIFFIN, W. & STIEFENHOFER, J. 2001. Metasomatism in mantle xenoliths from the Letlhakane kimberlites: estimation of element fluxes. *Contributions to Mineralogy and Petrology*, 141, 397-414.
- VAN ORMAN, J., GROVE, T. & SHIMIZU, N. 2001. Rare earth element diffusion in diopside: influence of temperature, pressure, and ionic radius, and an elastic

- model for diffusion in silicates. *Contributions to Mineralogy and Petrology*, 141, 687-703.
- VAN WESTRENEN, W., BLUNDY, J. & WOOD, B. 1999. Crystal-chemical controls on trace element partitioning between garnet and anhydrous silicate melt. *American Mineralogist*, 84, 838-847.
- WILKE, M., FARGES, F., PETIT, P.-E., BROWN, G. E. & MARTIN, F. 2001. Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study. *American Mineralogist*, 86, 714-730.
- WINTERBURN, P. A., HARTE, B. & GURNEY, J. J. 1990. Peridotite xenoliths from the Jagersfontein kimberlite pipe: I. Primary and primary-metasomatic mineralogy. *Geochimica et Cosmochimica Acta*, 54, 329-341.
- WITT-EICKSCHEN, G. & O'NEILL, H. S. C. 2005. The effect of temperature on the equilibrium distribution of trace elements between clinopyroxene, orthopyroxene, olivine and spinel in upper mantle peridotite. *Chemical Geology*, 221, 65-101.
- WOODLAND, A. B. & KOCH, M. 2003. Variation in oxygen fugacity with depth in the upper mantle beneath the Kaapvaal craton, Southern Africa. *Earth and Planetary Science Letters*, 214, 295-310.
- WOODLAND, A. B., BAUER, M., BALLARAN, T. B. & HANRAHAN, M. 2009. Crystal chemistry of $\text{Fe}_{32}+\text{Cr}_2\text{Si}_3\text{O}_{12}$ – $\text{Fe}_{32}+\text{Fe}_{23}+\text{Si}_3\text{O}_{12}$ garnet solid solutions and related spinels. *American Mineralogist*, 94, 359-366.
- ALLSOPP, H. L. & BARRETT, D. R. 1975. Rb/Sr age determinations on South African kimberlite pipes. *Physics and Chemistry of the Earth*, 9, 605-617.
- YANG, P. & RIVERS, T. 2001. Chromium and manganese zoning in pelitic garnet and kyanite: Spiral, overprint, and oscillatory (?) zoning patterns and the role of growth rate. *Journal of Metamorphic Geology*, 19, 455-474.
- YAXLEY, G. M., BERRY, A. J., KAMENETSKY, V. S., WOODLAND, A. B. & GOLOVIN, A. V. 2012. An oxygen fugacity profile through the Siberian Craton — Fe K-edge XANES determinations of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in garnets in

peridotite xenoliths from the Udachnaya East kimberlite. *Lithos*, 140–141, 142-151.

YAXLEY, G. M., GREEN, D. H. & KAMENETSKY, V. 1998. Carbonatite metasomatism in the southeastern Australian lithosphere. *Journal of Petrology*, 39, 1917-1930.

YOKOYAMA, T. & NAKAMURA, E. 2002. Precise determination of ferrous iron in silicate rocks. *Geochimica et Cosmochimica Acta*, 66, 1085-1093.

Appendices

Appendix A – Chapter 3

Appendix B – Chapter 5

Appendix A

Appendix A is the published article upon which Chapter 3 is based, “*Quantitative mapping of the oxidative effects of mantle metasomatism*”. This was published in *Geology* (Vol. 41, No. 6, p. 683-686) in June 2013. Authors were Andrew J. Berry, Gregory M. Yaxley, **Brendan J. Hanger**, Alan B. Woodland, Martin D. de Jonge, Daryl L. Howard, David Paterson and Vadim S. Kamenetsky.

Due to copyright restrictions the published article can't be included in this online version of my thesis. It can be found at [doi: 10.1130/G34119.1](https://doi.org/10.1130/G34119.1), or a copy can be obtained from the author at brendan.hanger@gmail.com.

Appendix B

Appendix to Chapter 5.

Appendix B1 – EPMA primary standards

Appendix B2 – EPMA secondary standards

Appendix B3 – LA-ICP-MS secondary standards

Appendix B4 – Fe K-edge XANES standards

Appendix B1

Analysis and standard conditions for each element during EPMA analysis. The counting time was equal for both the peak and background measurements.

Element	Line	Crystal	PHA Mode	Counting Time (s)	Standard	Reference	Source
Na	K α	TAP	Integral	10	K-anorthoclase	1	Kakanui, New Zealand, USNM 133868
Si	K α	TAP	Integral	10	Clinopyroxene	2	Delegate, NSW
Al	K α	TAP	Integral	10	Plagioclase	1	Lake County, OR, USNM 115900
Mg	K α	TAP	Integral	10	Olivine	1	San Carlos, Gila Co., AZ, USNM 111312/244
K	K α	PET	Integral	10	Microcline	1	location unknown, USNM 143966
Ca	K α	PET	Integral	10	Clinopyroxene	2	Delegate, NSW
Fe	K α	LLIF	Integral	10	Hematite		Astimex Scientific
P	K α	LPET	Integral	50	Apatite	2	Durango, Mexico
Cr	K α	LLIF	Integral	20	Chromite	1,3	Tiebaghi Mine, New Caledonia, USNM 117075
F	K α	PCO	Differential	50	Topaz	2	Mati Raudsepp, Uni of British Columbia, S473, Topaz Valley Utah, Eugene Foord
Mn	K α	LLIF	Integral	10	Bustamite		Astimex Scientific
Ti	K α	PET	Integral	20	Rutile		Astimex Scientific

References

- 1– Jarosewich E, Nelen JA, Norberg JA (1980): Geostandards Newsletter 4(1) 43-47
- 2 – University of Tasmania – Central Science Laboratory
- 3 – Barnes SJ, (1998): Journal of Petrology 39(10) 1689-1720

Appendix B2

Secondary standards used in the calibration of the EPMA analysis, including the standard value, and determined mean, standard deviation, minimum and maximum values from the analysis (wt.%). These standards were only used as secondary standards for elements that were not used as primary standards for.

	Na ₂ O	SiO ₂	Al ₂ O ₃	MgO	K ₂ O	CaO	FeO	P ₂ O ₅	Cr ₂ O ₃	F	MnO	TiO ₂	Total
San Carlos Mg-Olivine													
Standard	-	40.80	-	49.43	-	<0.05	9.55	0.00	-	-	0.14	-	100.29
Mean	0.02	40.50	0.03	49.10	-0.01	0.10	9.95	0.00	0.02	-0.01	0.14	0.01	99.86
σ	0.06	0.19	0.02	0.25	0.02	0.02	0.13	0.01	0.03	0.02	0.06	0.03	0.37
Minimum	-0.05	40.15	0.01	48.60	-0.06	0.07	9.76	-0.02	-0.02	-0.06	0.05	-0.04	99.22
Maximum	0.22	40.80	0.08	49.51	0.03	0.13	10.17	0.01	0.05	0.02	0.25	0.08	100.41
Delegate Clinopyroxene													
Standard	0.89	51.00	5.50	16.08	0.00	21.06	4.01	-	0.68	-	0.08	0.52	99.82
Mean	0.79	51.06	5.36	15.74	0.00	21.23	4.12	0.01	0.68	0.00	0.11	0.53	99.62
σ	0.09	0.28	0.07	0.20	0.03	0.17	0.08	0.01	0.05	0.03	0.07	0.07	0.41
Minimum	0.65	50.70	5.22	15.35	-0.05	20.90	4.02	-0.01	0.61	-0.04	-0.01	0.44	98.85
Maximum	0.99	51.83	5.48	16.02	0.05	21.54	4.25	0.03	0.75	0.07	0.24	0.69	100.43
Kakanui Hornblende													
Standard	2.60	40.37	14.90	12.80	2.05	10.30	7.95	-	-	-	0.09	4.72	100.02
Mean	2.58	40.16	14.53	12.69	2.10	10.33	10.84	0.02	0.00	0.20	0.08	4.90	98.43
σ	0.20	0.22	0.12	0.12	0.11	0.12	0.19	0.01	0.02	0.04	0.02	0.19	0.50
Minimum	2.12	39.70	14.27	12.40	1.91	10.14	10.53	0.00	-0.04	0.15	0.05	4.58	96.98
Maximum	3.01	40.57	14.71	12.97	2.35	10.53	11.22	0.05	0.02	0.29	0.11	5.28	99.10

Appendix B3

Average values of 'n' analyses for the secondary standard (BCR-2G) used in LA-ICP-MS analysis for the three routines used – Cpx/Opx/Ga; Olivine and phlogopite. Standard values and uncertainties from Jochum et al. (2011).

	Standard		Cpx/Opx/Ga		Olivine		Phlogopite	
	Value	Uncertainty	Average	σ	Average	σ	Average	σ
n			16		10		5	
Li 7	9	1			9.28	0.39		
Be 9	2.3	0.4			2.26	0.21		
B 10	6	1			12.11	1.01		
B 11					12.75	1.27		
Sc 45	33	2	33.46	1.12	35.37	2.25	35.65	1.22
Ti 49	14100	1000	14120	5663	15226	474	14762	297
V 51	425	18	29.54	1719.1	418.7	6.62	366.4	3.04
Cr 53	17	2					12.72	0.55
Mn 55	1550	70					1375	18.48
Co 59	38	2	35.75	4.13	37.91	2.40	32.41	0.14
Ni 60	13	2	10.30	32.59	11.77	0.31	10.34	0.16
Cu 65	21	5			17.50	0.47	14.86	0.20
Zn 66	125	5					135.64	4.00
Ga 71	23	1	21.19	1.07	21.59	0.41	18.57	0.10
Rb 85	47	0.5	46.42	2.70	47.40	1.09	40.02	0.23
Sr 88	342	4	322.1	38.57	342.7	11.59	333.8	5.51
Y 89	35	3	30.83	1.20	32.64	2.35	33.31	1.20
Zr 90	184	15	165.3	16.16	178.6	12.61	182.9	7.81
Zr 91							182.3	7.48
Nb 93	12.5	1	12.43	0.33	12.83	0.40	12.66	0.19
Cs 133	1.16	0.07					0.96	0.02
Ba 138	683	7	668.8	24.98	694.8	15.47	667.9	10.25
La 139	24.7	0.3	23.83	0.61	24.89	1.05	24.81	0.65
Ce 140	53.3	0.5	50.39	2.52	52.10	0.57	48.07	0.57
Pr 141	6.7	0.4	6.25	0.14	6.50	0.21	6.28	0.10
Nd 146	28.9	0.3	27.35	0.70	28.53	1.04	28.38	0.79
Sm 147	6.59	0.07	6.36	0.16	6.61	0.36	6.63	0.19
Eu 151							1.91	0.05
Eu 153	1.97	0.02	1.86	0.04	1.92	0.07	1.93	0.03
Gd 157	6.71	0.07	5.97	0.18	6.37	0.43	6.43	0.23
Tb 159	1.02	0.08	0.90	0.02	0.96	0.06	0.97	0.03
Dy 163	6.44	0.06	5.91	0.20	6.28	0.46	6.36	0.21
Ho 165	1.27	0.08	1.18	0.04	1.25	0.09	1.27	0.04
Er 166	3.7	0.04	3.33	0.13	3.56	0.27	3.64	0.16
Tm 169	0.51	0.04	0.48	0.02	0.50	0.03	0.52	0.02
Yb 172	3.39	0.03	3.17	0.12	3.38	0.24	3.42	0.13
Lu 175	0.503	0.005	0.45	0.02	0.48	0.04	0.50	0.02
Hf 178	4.84	0.28					4.60	0.21
Ta 181	0.78	0.06	7.92	5.19			0.82	0.03
Pb 208	11	1	7.10	2.34	10.70	0.25	9.43	0.14
Th 232	5.9	0.3	2.89	1.91	5.90	0.35	6.01	0.22
U 238	1.69	0.12	1.49	0.05	1.61	0.04	1.40	0.02

Appendix B4

Mössbauer determined $\text{Fe}^{3+}/\Sigma\text{Fe}$ for the garnets used as standards for XANES, along with the XANES intensity at 7138.4 eV. Samples denoted ‘let’ and ‘kim’ are from Lesotho and Kimberley, respectively (Woodland & Koch 2003), whilst ‘dvk’ samples are from Diavik (Yaxley et al. unpublished).

Sample	$\text{Fe}^{3+}/\Sigma\text{Fe}$	Intensity
let1	0.043	0.746
let1	0.043	0.748
let39	0.051	0.748
let14	0.048	0.734
let21	0.045	0.731
let9-2	0.095	0.78
let9-1	0.095	0.777
let12-1	0.122	0.791
let6-1	0.043	0.739
let7-1	0.048	0.743
dvk7-1	0.101	0.792
dvk7-2	0.101	0.78
dvk8-2	0.098	0.78
dvk8-1	0.098	0.783
dvk9-3	0.07	0.769
dvk10-3	0.06	0.76
dvk1-1	0.105	0.783
dvk2-1	0.022	0.724
dvk3-1	0.105	0.775
dvk4-1	0.076	0.771
dvk5-1	0.099	0.771
dvk5-2	0.099	0.784
dvk6-5	0.066	0.758
dvk6-5	0.066	0.759
dvk6-5	0.066	0.759
let6-1-round	0.043	0.736
kim44-1	0.069	0.758
kim30-1	0.052	0.75
kim13-1	0.068	0.752
kim1-1	0.054	0.748
kim22-1	0.04	0.754
kim17-1	0.064	0.753
kim25-1	0.053	0.754
kim24-1	0.065	0.753
kim35-1	0.06	0.74