

Rare earth elements in olivine: determination, occurrence and behaviour

Ph.D Thesis

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Clare V. Stead

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Abstract

Olivine is a widely occurring mineral that offers great potential for improving our understanding of geological processes. Olivine is present across a range of geologically significant settings, occurring in stony-iron meteorites, as inclusions in diamonds and as a dominant phase in upper mantle peridotite. The utility of the trace elements in olivine has been established through their application as geothermobarometers and as a tool for discrimination of mantle lithologies. The study of the rare earth elements (REE) in olivine has lagged behind that of the trace elements due to their ultra-low abundances. However, the value of REE studies has been proven through their application in minerals such as garnet, upon which the field of mantle metasomatism, for example, has rapidly expanded, as well as Ca perovskite, which has added much to our understanding of the differentiation in the early earth. With the precedent set and rapidly advancing analytical capabilities, the REE in olivine are in a prime position for geochemical exploration.

This thesis presents a novel analytical technique for determination of the REE in olivine using laser ablation quadrupole inductively coupled plasma mass spectrometry (LA-QICP-MS) and demonstrates the application of this technique for a global suite of olivine. Building upon this research, this thesis brings new insights into olivine-melt and olivine-mineral REE partitioning behaviour. Key findings from this aspect of the thesis are that: 1) the olivine Mg number (Mg#) exerts a strong control over REE partitioning via its influence over lattice elasticity; and 2) that the LREE in natural olivine may experience preferential diffusion of the light REE (LREE) from neighbouring phases or grain boundary fluids/melts. This work thus provides a framework within which the REE in olivine can be interpreted. With this framework established the final aspect of this thesis uses the study of the REE in olivine to assess the metasomatic model for Archaean peridotite. Mass balance modelling of the REE in olivine, orthopyroxene and garnet with a range of reasonable metasomatic agents has shown that the conventional metasomatic model cannot replicate all three phases. In doing so this work highlights the importance of analysing all the major phases in such studies. Furthermore this thesis has revealed olivine to be an important host of the REE in Archaean peridotite. This paves the way for future studies to exploit the REE contents of olivine and bolster geochemical studies of the sub-continental lithospheric mantle (SCLM).

“Scepticism is as much the result of knowledge, as knowledge is of scepticism. To be content with what we at present know, is, for the most part, to shut our ears against conviction; since, from the very gradual character of our education, we must continually forget, and emancipate ourselves from, knowledge previously acquired; we must set aside old notions and embrace fresh ones; and, as we learn, we must be daily unlearning something which it has cost us no small labour and anxiety to acquire.”

-Homer, The Iliad

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Chapter 1: Introduction to the thesis

1. Context of the thesis

Olivine is an important phase in upper mantle peridotite and one of the first crystallising phases in mafic magmas (Bowen, 1915). It also occurs in stony and stony-iron meteorites and as inclusions in diamonds (Sobolev et al., 2008), demonstrating the wide range of geological settings and processes to which olivine studies can be applied. Nonetheless, geochemical studies of trace elements, and in particular the rare earth elements (REE), in olivine are lagging behind those of phases such as garnet and clinopyroxene. Despite the control exerted by garnet and clinopyroxene over REE partitioning during mantle melting, the high modal abundance of olivine makes it a key factor in REE fractionation regardless of its low affinity for these elements (Sun and Liang, 2013). This low affinity has challenged the study of the REE in olivine through analytical difficulties associated with measuring elements at ultra-low concentrations. Olivine is a significant component of peridotite xenoliths, which are critical to our understanding of the evolution and alteration of the Earth's sub-continental lithospheric mantle (SCLM). Unravelling the history of the SCLM and the various melt depletion and enrichment events that may have affected it could therefore benefit from a more thorough geochemical understanding of the incompatible elements in olivine from mantle xenoliths.

Recent analytical advances have fostered the study of minor and trace elements in olivine, demonstrating that olivine geochemistry has great potential as a petrogenetic tool (De Hoog et al., 2010; Foley et al., 2013; Sanfilippo et al., 2014; Tollan et al., 2015). This thesis expands the study of incompatible elements in olivine with a novel analytical strategy for REE determination using laser ablation quadrupole inductively coupled plasma mass spectrometry (LA-QICP-MS), applying it to a global suite of olivines and using this data to advance the understanding of REE partitioning and behaviour in olivine (Chapter 2).

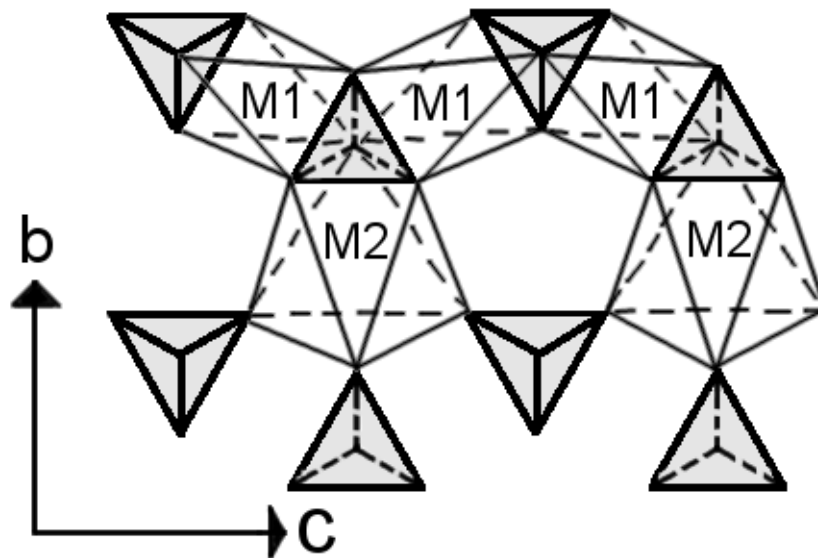


Figure 1: Projection down the *a* axis of the olivine lattice structure showing the octahedral M1 and M2 sites, with tetrahedral sites shown in grey. Arrows mark the orientations of the *b* and *c* axes. Drawing after Lumpkin and Ribbe (1983).

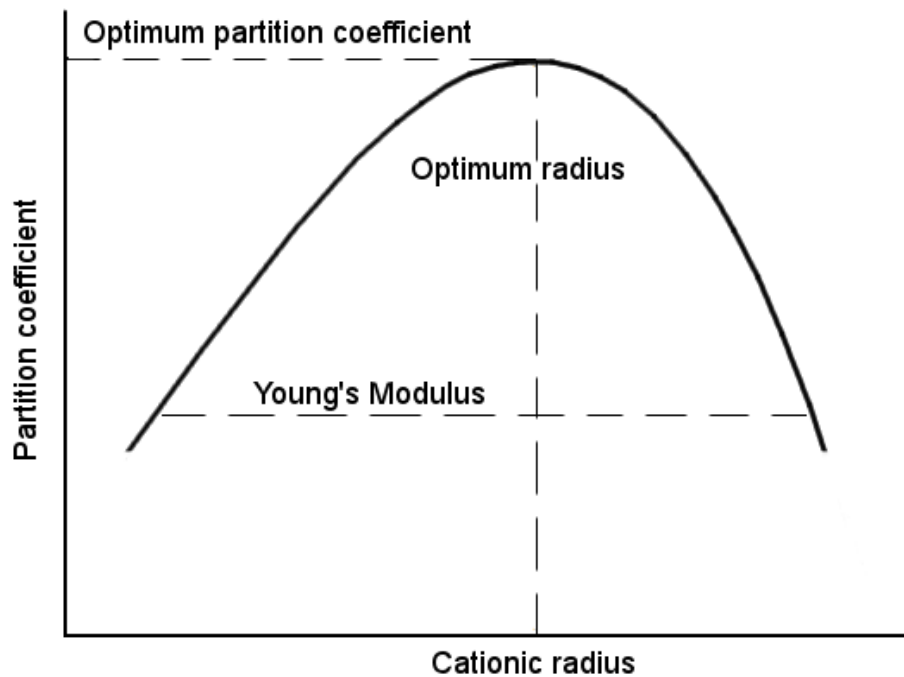


Figure 2: Schematic showing the parameters of the Brice Equation (1975), including the optimum partition coefficient and radius for the 'best-fit' ion. Schematic after Wood and Blundy (2003).

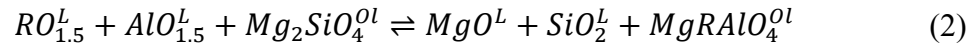
Olivine is an orthorhombic mineral consisting of individual SiO_4 tetrahedra (T sites) held together by six-fold coordinated divalent cations (M1 and M2 octahedral sites) (Birle et al., 1968; Burns, 1970) as shown in figure 1. The M1 and M2 sites are occupied primarily by the Mg and Fe cations, and it is typically presumed that the large cationic radii of the REE limit them to partitioning into the slightly larger M2 site (Evans et al., 2008). Many Mg,Fe olivines are disordered, as evidenced by the preference of the M2 site by Fe^{2+} in some instances while Fe^{2+} in the majority of Mg,Fe olivine is mostly contained in the M1 site (e.g. Lumpkin et al., 1983). It follows that this disorder may also play a small role the partitioning behaviour of the REE. In six-fold co-ordination the ionic radii of the REE are larger than the optimum cationic radius of olivine (0.81 Å), ranging from 0.861 Å for Lu to 1.032 Å for La.

Our understanding of trace element partitioning is built upon the foundation that the charge and size of both the trace ion and lattice site are the controlling variables over trace element ions entering specific sites (Goldschmidt, 1937). Although this is an oversimplification, failing to take into account other influential variables such as temperature and pressure, it nonetheless provided the theoretical framework from which lattice strain theory developed (Blundy and Wood, 2003; Blundy and Wood, 1994; Brice, 1975; Nagasawa, 1966; Onuma et al., 1968). Onuma (1968) measured partition coefficients between two pyroxenes and their host lava, plotting partition coefficients against ionic radius to create the ‘Onuma diagram’ that is now commonplace in partitioning studies. Brice (1975) describes lattice strain theory for substituting ions that are smaller or larger than the optimum radius of the site (r_o), showing the parabolic relationship between partition coefficients and ionic radii as shown in figure 2. The Brice equation that describes this relationship is as follows:

$$D_i = D_o \times \exp \left(\frac{-4\pi E_s N_A \left(\left(\frac{r_o}{2} \right) (r_o - r_i)^2 - \left(\frac{1}{3} \right) (r_o - r_i)^3 \right)}{RT} \right) \quad (1)$$

Where D_i is the partition coefficient for a given ion, D_o is the optimum partition coefficient, r_i is the cationic radius for a given ion, E_s is the effective Young’s modulus of the crystal site, N_A is Avogadro’s number, R is the Universal Gas Constant, and T is the temperature.

Trace element partitioning studies remained predominantly theoretical until trace element microbeam techniques triggered new experimental work, including work on the trace element partitioning systematics between olivine and silicate melts (Beattie, 1994). Beattie (1994) found that low concentration trivalent cations (i.e. the REE) conformed to Henry's law in olivine, demonstrating that the substitution of these cations into the olivine lattice cannot be charge balanced by the creation of vacancies or interstitials and instead local charge balance is maintained by paired substitution with Al for Si (Beattie, 1994; Colson et al., 1989) according to the following reaction (2):



where R is the trivalent cation (Beattie, 1994). Included in this study by Beattie (1994) was a comparison of REE partition coefficients (D values) to $D_{\text{olivine/melt}}$ from previous studies (Kennedy et al., 1993; Matsui et al., 1977; McKay, 1986; McKay and Weill, 1977; Schnetzler and Philpotts, 1970), finding consistent values for the heavy REE (HREE) but up to three orders of magnitude in variation amongst D values for the light REE (LREE).

This over-representation of LREE D values for olivine is commonplace throughout the literature, most notably amongst D values for phenocryst-matrix pairs (Lee et al., 2007), with variation observed not only for absolute values but also the relative behaviour of the LREE to the middle REE (MREE) and HREE. Typical $D_{\text{olivine/melt}}$ values for the HREE vary from 0.002 to 0.4, while those for the LREE vary from 0.00001 to 0.3 (Lee et al., 2007 and references therein). Abnormal LREE patterns in olivine are typically attributed to one or more of the following mechanisms:

- i) Analytical artefacts due either to the incorporation of glass during analysis or to problems associated with analysing elements at concentrations close to the limits of detection (LOD) (e.g. Beattie, 1994; Evans et al., 2008; McKay, 1986).
- ii) Contamination of analysed material from the surface, along grain boundaries and fractures, or through integration of fluid, melt, and/or mineral inclusions (e.g. Eggins et al., 1998; Lee et al., 2007).

- iii) The LREE not being structurally bound within the olivine lattice and consequently not constrained to behave according to lattice strain theory (Stosch, 1982).

Accurate interpretation of REE patterns in olivine requires an understanding of the nature and cause of LREE anomalies. Diffusion has been shown experimentally to affect trace elements and the REE in olivine (Cherniak, 2010; Cherniak and Liang, 2014; Jollands et al., 2016; Qian et al., 2010; Spandler and O'Neill, 2010). Within this thesis volume diffusion is presented as a further plausible cause of abnormal LREE patterns, and is examined alongside the three commonly cited mechanisms outlined above with the aim of improving the interpretation of REE patterns in olivine (Chapter 3). Diffusion of the REE in olivine is believed to be independent of crystallographic orientation (Cherniak, 2010; Spandler and O'Neill, 2010) and may operate according to a lattice bound mechanism (Spandler and O'Neill, 2010).

Studies of $D_{\text{olivine/melt}}$ have recognized a number of variables that influence REE partitioning in olivine. These variables include pressure (P), temperature (T), oxygen fugacity, and mineral and melt compositions (X) (Blundy and Wood, 2003; Blundy and Wood, 1994; Ford et al., 1983; Sun and Liang, 2013; Wood and Blundy, 2003). The effects of each of these variables are difficult to tease apart for natural magmatic systems, hence experimental work in low-variance systems have been important in assessing the influence of each variable (Blundy and Wood, 2003). It is well established that T plays an important role in olivine structure (Blundy and Wood, 2003; Heinemann et al., 2006; Heinemann et al., 2007; Heinemann et al., 1999; Redfern et al., 2000; Wood and Blundy, 2003), and has been shown to affect the distribution of the cations Mg and Fe between the cation sites within the mineral through changes to exchange enthalpy and entropy (Heinemann et al., 2007). Reports on the effect of T for the partitioning of the REE specifically, however, are conflicting. Blundy and Wood (2003) found a decrease in partition coefficients with increased T while Sun and Liang (2013) found no considerable T influence on partitioning of REE between olivine and melt. The basis for a P control over REE partitioning is due to the P dependency of the volume of fusion (e.g. Wood and Blundy, 2003). It has been suggested that the effects of both T and P may only be secondary factors, with melt composition as the dominant control (Sun and Liang, 2013). The influence of melt composition over REE

partitioning in olivine has been attributed to the charge balancing paired substitution between olivine and the melt according to equation (2).

Increasing melt MgO and SiO₂ have both been linked to decreases in REE *D* values (Bédard, 2005; Evans et al., 2008), while increasing olivine Al₂O₃ content has been associated with increases in REE partitioning (Sun and Liang, 2013). It should be noted, however, that the experimental range of Al₂O₃ that showed a positive correlation with *D* values (Sun and Liang, 2013) is greater than that observed in natural olivine at 0-0.4 wt%, and caution should be taken in using these results to draw conclusions for partitioning behaviour in natural olivine as the influence of Al₂O₃ is extremely limited within the natural concentration range for olivine. A prominent aspect of this thesis is to examine these factors affecting REE partitioning for olivine from natural systems, providing a dataset to compliment the established experimental work.

There is great potential to use REE patterns in olivine for the study of mantle metasomatism. Trace element systematics of olivine have already been successfully applied as a petrogenetic indicator for mantle lithologies (De Hoog et al., 2010; Foley et al., 2013). Olivine Zr and Sc contents, for example, can be used to distinguish between garnet- and spinel-bearing peridotites, while metasomatic and melting histories may be deduced using olivine TiO₂ and Cr# (molar ratio Cr/Cr + Al) (De Hoog et al., 2010). The low ppb concentrations of the REE in olivine have limited their use in mantle studies to date; the focus instead has been placed on garnet and clinopyroxene as they contain higher concentrations of the incompatible elements (e.g. Shimizu, 1975). In recent years the widespread application of LA-ICP-MS has opened the study of REE to the more REE-deprived orthopyroxene and olivine (Ashchepkov et al., 2017; Jean and Shervais, 2017). As olivine is the most abundant mineral in upper mantle peridotite it should be considered an important host for the REE, despite its low affinity for these elements (De Hoog et al., 2010; Foley et al., 2013; Lee et al., 2007). Understanding the distribution of REE in olivine and orthopyroxene becomes particularly important for making interpretations of clinopyroxene- and garnet free lithologies, and one could argue even more so for olivine inclusions in diamonds when no co-existing phases are available. Furthermore, the characteristic geochemical behaviour of the REE due to the lanthanide contraction provides unique insights into processes such as melt depletion and re-fertilisation.

Until 1973 the term metasomatism was used solely in relation to crustal processes. Mantle metasomatism was first identified by Lloyd and Bailey (1973). Subsequently, Harte et al. (1983) introduced the term “modal” mantle metasomatism to describe the addition of new mineral phases to the assemblage commonly found in peridotites, a concept labelled as ‘patent’ metasomatism by Dawson (1982). Dawson (1982) also introduced the term “cryptic” metasomatism to describe compositional changes of existing phases without the introduction of new phases. Although ‘patent’ and ‘modal’ metasomatism refer to the same process, it is ‘modal’ that is the more widely used term along with ‘cryptic’ to describe the two end-member types of metasomatism (O'Reilly and Griffin, 2013). Modal metasomatism is easily recognised by the introduction of secondary phases including hydrous minerals such as phlogopite (e.g. Franz et al., 2002). Other mineral phases that may be introduced in mantle peridotite include garnet and clinopyroxene (Franz et al., 2002). Mineralogically, the effects of this type of metasomatism on mantle xenoliths in kimberlites are similar to a suite of ‘mantle pegmatites’ consisting of the MARID suite (Mica Amphibole, Rutile, Ilmenite and Diopside) (Kramers et al., 1983), the origin of which is beyond the scope of this thesis. In contrast to the obvious changes seen with modal metasomatism, cryptic metasomatism is characterised by trace element enrichment of the ultramafic rocks without any visible mineralogical changes. The possibility that cryptic enrichment may occur outside the zone of modal metasomatism in the mantle complicates the unravelling of the cause of the chemical enrichment seen in peridotite xenoliths that are not accompanied by clear mineralogical changes (Gregoire et al., 2003). The sinusoidal REE patterns that are commonly observed in peridotitic garnet, for example, are typically attributed to interaction with a metasomatic agent (Griffin et al., 1999; Hoal et al., 1994; Shimizu and Richardson, 1987; Simon et al., 2007) and will be investigated in this thesis in chapter 4. The widespread occurrence of olivine means it has great potential to be used in deciphering cryptic metasomatic processes across a range of ultramafic rocks, including those that are not garnet-bearing. This thesis presents REE patterns for olivine and co-existing phases from garnet facies peridotite samples from the Kaapvaal Craton in South Africa to contribute to our understanding of the processes that have affected the REE systematics of the xenoliths from this craton.

2. Layout and themes of the thesis

This thesis is arranged to begin with the advancements of REE determination in olivine, followed by new insights into REE partitioning behaviour and diffusion in olivine, and concludes with the study of the REE in olivine from cratonic mantle.

Chapter 2 outlines the importance of the REE in olivine and summarises the analytical challenges of analysing at ultra-low concentrations as documented throughout the literature. The focus of this chapter is the description and evaluation of a novel analytical approach for the measurement of the REE in olivine. The technique is subsequently applied to determine REE concentrations across a global range of olivines spanning mantle, magmatic, meteoritic, and metamorphic sources. Finally, these data are used to calculate empirical partition coefficients (D values) for the REE between olivine and clinopyroxene and orthopyroxene.

Chapter 3 provides a comprehensive study of the partitioning behaviour of the REE in olivine. This chapter provides olivine REE data for natural samples to compliment, and expand upon, experimental data from the literature. Apparent D values and crystal lattice strain model parameters are calculated and examined in relation to temperature (T), melt SiO_2 , olivine Al content, and magnesium number (Mg#). This chapter also gives new insights into the LREE over-representation in olivine that is seen throughout the literature.

Chapter 4 presents trace and REE data for olivines from garnet-bearing peridotites from the Kaapvaal Craton, South Africa. Trace element data are presented here to compliment existing studies of the behaviour of these elements in olivine. The REE concentrations in olivine are discussed within the contexts of co-existing phases and potential processes that may have affected the xenoliths. In doing so, this chapter provides new insights from olivine for mantle peridotite geochemistry and demonstrates the great potential for use of olivine REE for further study in this field.

Chapter 5 is a synthesis of the principal findings of the research presented in this thesis and their context within the wider fields of olivine and mantle geochemistry.

3. Co-author statement

The core chapters (2-4) of this thesis are comprised of one published paper, one submitted manuscript, and one advanced manuscript draft. I am the lead author of these three manuscripts, all of which were produced during the duration of the thesis. As the lead author of these manuscripts I was responsible for sample preparation and analysis, data reduction and interpretation, and all stages of manuscript preparation including addressing reviewer/editor comments. The contributions from each co-author are outlined below.

Michael Babechuk and Cora McKenna provided guidance for sample preparation, analysis, data reduction, and editorial comments for the solution ICP-MS analyses presented in Chapter 2. Cora McKenna also provided assistance with the LA-ICP-MS measurements of Chapters 2 and 3.

Balz Kamber provided guidance and discussion for geochemical analysis and subsequent editorial comments for Chapters 2 and 3.

Emma Tomlinson, my PhD supervisor, was the main source of discussion and guidance throughout the thesis, including sample preparation/analysis, data reduction and interpretation, and editorial comments on each chapter.

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Chapter 2: REE determination in olivine by LA-QICP-MS: an analytical strategy and applications

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Abstract

Olivine offers huge, largely untapped, potential for improving our understanding of magmatic and metasomatic processes. In particular, a wealth of information is contained in rare earth element (REE) concentrations, which are well studied in other minerals. However, REE data for olivine are scarce, reflecting the difficulty associated with analysing concentrations in the low ppb range and with controlling the effects of LREE contamination. We report an analytical procedure for measuring REEs in olivine using LA-QICP-MS. We have achieved limits of determination at sub-ppb levels and accuracies of ~5-10%. Empirical partition coefficients (*D* values) calculated using the new olivine compositions agree with experimental values, indicating that the measured REEs are structurally bound in the olivine crystal lattice, rather than residing in micro-inclusions. We conducted an initial survey of REE contents of olivine from mantle, metamorphic, magmatic, and meteorite samples. REE concentrations vary from 0.1 to double-digit ppb levels, with low and restricted light REEs and more variable heavy REE concentrations. Heavy REE vary from low concentrations in meteoritic samples, through variably enriched peridotitic olivine to high concentrations in magmatic olivines, with fayalitic olivines showing the highest levels. The variable enrichment in HREE demonstrates that olivine REE patterns have petrologic utility.

1. Introduction

Olivine is the most abundant mineral in upper mantle peridotite. It is also present in stony and stony-iron meteorites and occurs as inclusions in diamonds (Sobolev et al. 2008). Despite its low affinity for the rare earth elements (REE), olivine's high modal abundance makes it an important contributor to heavy REE (HREE) fractionation (Sun and Liang 2013) in magmatic systems. Olivine is one of the first minerals to form in crystallising mafic magmas on both sides of the thermal divide that separates silica-saturated and silica-undersaturated fields at low pressures (Bowen, 1915). Without understanding the role of olivine, our comprehension of magmatic and metasomatic processes will remain incomplete. The isovalent REEs are particularly useful in petrogenetic studies, as they display characteristic partitioning behaviour linked to their ionic radii (Nagasawa 1966; Bau 1996). Many experimental studies have determined how the REE partition into rock forming minerals confirming the systematic behaviour

resulting from the small changes in ionic radii from Lu (0.977Å) to La (1.16Å) (in VIII coordination) (Shannon et al. 1976). For many silicate minerals, the HREE display stronger compatibility than both the middle and light REEs (MREE and LREE) (Onuma et al. 1968; Van Orman et al. 2001), although in detail this is dependent of the size of the site into which the REE are partitioning. To date there have been relatively few studies of minor and trace element characteristics in olivine (Lee et al. 2007; Spandler and O'Neill 2009; De Hoog et al. 2010; Foley et al. 2013) and even fewer have determined the REE (Eggins et al. 1998b; Zanetti et al. 2004; Lee et al. 2007). The scarcity of empirical REE data for olivine reflects, firstly, the analytical difficulty associated with analysing concentrations in the low ppb range, and, secondly, the obstacles of minimising the effects of LREE contamination on grain boundaries and from inclusions (Lee et al. 2007). Experimental work (McDade et al. 2003; Zanetti et al. 2004) and lattice strain modelling (Lee et al. 2007) indicate that olivine has a preference for HREE over the lighter rare earths, demonstrated, for example, by the olivine/clinopyroxene partition coefficients of the order of 10^{-2} for Yb and 10^{-5} for La (McDade et al. 2003; Zanetti et al. 2004).

In this contribution, we describe a new analytical approach using LA-QICP-MS as a macro-sampling tool (100-200 micron scale) to analyse REE in olivine. This approach offers a further step towards tapping into the wealth of information locked into olivine and could help unravel the often complex and multi-stage metasomatic histories in mantle rocks and improve our knowledge of mantle melting and magma generation. We present REE data for a selection of olivines across a range of lithologies, assessing REE variability in olivine. We use these data to investigate REE partitioning in olivine and discuss our findings in relation to previous experimental and theoretical work.

2. Sample Description

Olivines from 18 samples were handpicked and analysed in this study. The samples were chosen to represent a range of lithologies, localities, and forsterite (Fo) content. Samples are divided into four groups: mantle, magmatic, metamorphic, and meteorite.

Sample localities and characteristics are described in Table 1. Mantle olivines were selected from dunites, harzburgites and lherzolites, thus covering a wide range of apparent melt-depletion. Grain size varied from 1-5mm, and Fo ranged from 85-91% with NiO ranging from approx. 0.2-0.6 wt%. Samples originate from many localities including xenoliths from both shallow, spinel-facies lithospheric mantle, and from garnet-bearing lithospheric mantle.

Magmatic samples range from tholeiitic to basanitic, and include both intrusive and extrusive (porphyritic) representatives. Grain size varied from 1-7mm, and Fo ranged from 30-90%, encompassing forsteritic and fayalitic olivines. Average NiO content was lower than for mantle olivines, at approx. 0.2 wt%.

Two meteorite samples were analysed. Both of these are pallasitic, i.e. stony-iron meteorites. The Springwater meteorite olivines are fragments <0.5mm in diameter and were donated by the Smithsonian Institute, while the Jepara meteorite olivine grains range in size from 1-4mm. The Fo contents are 82-87% respectively.

A single metamorphic sample, a forsterite marble, was analysed. Average grain size was 2mm. During hand picking of this sample, discoloured and cloudy grains were found. These were avoided to minimise possible alteration effects. The Fo content was approx. 95%.

Individual olivine crystals from each sample were handpicked to optical purity, selected to be free from external contamination and inclusions, and wherever possible, broken internal fragments were chosen. Crystals were subsequently mounted in epoxy resin.

Name	Location	Source Rock	Source	Previous Publications
Magmatic				
P16029*	Margi, Cyprus	Volcanic - Picrite	TCD collection	
P16180	Waimarino, New Zealand	Mafic - Basalt	TCD collection	
P16034	Etna, Sicily	Mafic - Basalt	TCD collection	
Sk22	Skaergaard Layered Intrusion (UZb)	Hortonolite Ferrodiiorite	TCD collection	
Sk24	Skaergaard Layered Intrusion (UZa)	Hortonolite Ferrodiiorite	TCD collection	
Sk31	Skaergaard Layered Intrusion (LZb)	Olivine Hypersthene Gabbro	TCD collection	
P1655	Coverack, Cornwall	Gabbroic - Troctolite	TCD collection	
Mantle				
P16028	Dun, New Zealand	Ultramafic - Dunite	TCD collection	
P16030*	Meerfelder Maar	Ultramafic - Spinel Lherzolite	TCD collection	
P5372	Newlands Mine, SA	Ultramafic – Garnet Harzburgite	TCD collection	
P16032	Vulture, Italy	Ultramafic - Spinel Lherzolite	TCD collection	
P16031	Puerto del Carmen, Lanzarote	Ultramafic - Harzburgite	Ian Meighan	Published as ER63-33 (Roedder, 1965; Murek et al. 1978)
P16033	Hawaii		TCD collection	
P16035		Ultramafic - Spinel Lherzolite	TCD collection	
P32003	Tallante, Spain	Ultramafic - Spinel Lherzolite	TCD collection	
P5508	Mont. Briancon	Ultramafic - Spinel Lherzolite	TCD collection	
KH 96-21	Kilbourne Hole	Ultramafic - Spinel Harzburgite	Jason Harvey	Harvey et al. (2012)
NMNH	San Carlos, Arizona	Ultramafic - Lherzolite	Smithsonian Institute	
111312-44**				

Table 1: Sample Characteristics. * denotes in-house olivine standards ** denotes Smithsonian standards

Name	Location	Source Rock	Source	Previous Publications
Metamorphic				
P15759	Loch Duich, Scotland	Forsterite Marble	TCD collection	
Meteorite				
P16027	Indonesia	Pallasite Meteorite	Commercial	
USNM 2566**	Springwater	Pallasite Meteorite	Smithsonian Institute	

Table 1 cont.

3. Analytical Methods

3.1 Major Element EDS

Major elements were analysed by SEM-EDS (Scanning Electron Microscope Energy Dispersive Spectroscopy) at the Centre for Microscopy and Analysis (CMA) at Trinity College Dublin (TCD). The analysis was carried out using a Tescan Mira XMU, equipped with an 80mm² silicon drift energy dispersive detector, and the Oxford Inca X-ray microanalysis software. Accelerating voltage was 20kV, with a beam current of 1nA. The instrument was calibrated using a suite of appropriate mineral reference materials from the Smithsonian Institute (Jarosewich et al. 1980). Biases for MgO, SiO₂, and FeO for the reference materials NMNH 111312-44 (n=14) and USNM 2566 (n=10) were <2.7% relative to reported reference values (Jarosewich et al. 1980).

3.2 LA-QICP-MS

Rare earth element concentrations were determined in-situ by LA-QICP-QMS using a Teledyne Photon Machines Analyte Excite laser ablation system at Trinity College Dublin between February and September of 2015. The laser ablation system is equipped with a 193 nm ATLex 300 ArF excimer laser and a HeLex II two-volume ablation cell, and attached to a Thermo iCAP-Q ICP-MS.

In the earlier analytical sessions the collision cell was used in kinetic energy discrimination (KED) mode (employing grade 6.0N He as collision gas) for two reasons. Firstly, to reduce polyatomic interferences via collisions with the inherently larger polyatomic ions and secondly to suppress the signal in the low mass range and avoid exposing the detector to excessive signals from higher abundance elements such as Si. As the study progressed, the collision gas inlet developed a small air leak that led to increased oxide rates and suspected molecular interferences, affecting ⁴⁵Sc (e.g. ¹⁴N₂¹⁶O¹H⁺) and ⁷¹Ga (Cl and S oxides e.g. ³⁶S¹⁷O¹⁸O⁺).

Subsequent experiments were run in standard mode without the use of the collision cell to avoid interferences on ⁴⁵Sc and ⁷¹Ga. The REE data produced in both KED and

standard mode were scrutinised and found to be in complete agreement, showing that these elements were not affected by molecular interferences in the earlier experiments run using KED mode. Typical sensitivities measured for a tuning line (85 μm spot, 10 Hz repetition rate, 40 $\mu\text{m s}^{-1}$ scan speed) on NIST SRM 612 were as follows: ^7Li 53,000 cps, ^{140}Ce 300,000 cps, ^{172}Yb 120,000 cps, ^{232}Th 460,000 cps, ^{230}U 495,000 cps.

For olivine analysis, we used a very large spot size, high frequency and untypically long dwell times, as outlined in Table 2, to maximize the REE signal. Ablation sites were chosen away from external boundaries, and to avoid fractures that may introduce contamination. We used a spot size of 160 μm and a laser repetition rate of 30 Hz, which resulted in pit depths of 165 μm . This arrangement allowed for >3 replicates per grain in large grains. The volume of ablated material results in approximately 500 μg of olivine being carried to the plasma via an in house developed signal-smoothing device. Trials carried out at varying spot sizes (100 to 190 μm) and frequencies (5 to 40 Hz), and thus representing varying volumes of ablated material, do not indicate the presence of a mass or plasma loading effect from the large volume of ablated material.

Under these particular experimental conditions, oxide production can be higher than in normal laser ablation analysis due to the high ablation rate required to produce a detectable signal. The latter leads to lower plasma temperature and associated increased oxide rates. The ThO/Th^+ ratio was monitored for experiments run in both standard and KED mode and found to be consistently below 0.2% in standard mode and below 2% in KED mode. No correction for oxide interference was employed but possible analytical artefacts due to unaccounted oxide interference were tested by quantifying the data with two reference materials with very different relative REE abundance: BHVO-2G (Basalt, Hawaiian Volcanic Observatory, a natural reference material with Oddo-Harkins effect abundances) and NIST SRM 612 (an artificial equal atom reference material). The resulting REE patterns of samples were statistically not resolvable despite the very different relative production rates of LREE and MREE oxides from these reference materials, showing that oxide formation had a negligible effect on final measured values. The agreement between REE concentrations for those samples run in both standard and KED mode provides additional support for uncorrected oxide interferences. Finally, a SiC semiconductor wafer was analysed to investigate the effect

of high purity aerosol particles on measured backgrounds. The wafer background was found to be within uncertainty of the gas background for all REE (see Supplementary Table 4), showing that no scrubbing of elements from the sample cell or aerosol transfer path occurred.

The untypically long dwell times used here, up to 2.5 s for MREE, resulted in a long sweep time of ~8 s, with the high shot count (4200) allowing for 20 sweeps per analyte. Most analyses were performed with the ‘set A’ element dwell time configuration given in Table 2. This is a short analyte set, covering only a selection of REE across the mass range. Due to the long dwell time required and the maximum sweep time of the iCAP-Q we needed to run two analyses to obtain a more complete REE dataset. For this full REE characterisation we used configuration sets ‘B’ and ‘C’ in sequence, each targeting different analytes as outlined in Table 2, with overlaps at Ce and Yb to ensure comparability.

Data reduction was carried out using Iolite software v2.5 (Paton et al. 2011) and Si, known from major element analysis, was used as the internal standard using the trace element internal standard data reduction scheme (IS DRS). A gas blank subtraction was carried out using this DRS and the ‘mean no outlier reject’ setting, with typical background count rates provided in Supplementary Table 4. The resulting ^{29}Si signal on the QICP-MS was very large and in order to preserve detector lifetime, a very short (2 ms) dwell-time was employed. USGS reference glass BHVO-2G was used as the calibration reference material, while NIST SRM 616 and 612 and MPI-DING GOR132-G were used as quality control reference materials (Max Planck Institute-Dingwell) (Jochum et al. 2006; Jochum et al. 2011). Two samples, one magmatic and one mantle were chosen as in-house reference materials for this work (Table 1). These samples were selected due to their large exposed surface areas (>4 mm diameter) in the mounts, relatively high REE mass fractions, and high degree of homogeneity ($n=8-10$). Homogeneity of samples was previously determined using EDS transects across the mineral surface ($n=8$ spot analyses per transect), and was also demonstrated in replicate trace element analyses. Typical relative standard deviation (%RSD) for Mg and Si were <2%, while for Fe this was <3%.

Laser parameters				
Fluence	4.87 Jcm-2			
Repetition rate	30 Hz			
Shot Count	4200			
Laser spot size	160 mm			
Average pit depth	165 mm			
He cell gas flow	0.65 Lmin-1			
N2 trace gas flow	6 ml min-1			
Sampling strategy	Spot			
Background measurement	60s			
ICP-MS parameters				
RF power	1550 W			
Mode	Collision Cell (CCTS) and Standard (STDS)			
Nebulizer gas flow	0.7032 l min-1			
Collision cell gas flow (He) in KED mode	5.3 ml min-1			
Dwell time (s) configurations and analytes	Element	Set A (s)	Set B (s)	Set C (s)
	29Si*	0.002	0.002	0.002
	45Sc		0.001	0.001
	71Ga		0.08	
	89Y	0.02	0.02	
	139La	0.35	0.4	
	140Ce	0.25	0.15	0.15
	141Pr		2.15	
	146Nd	2.5	2.5	
	147Sm			2.5
	153Eu			2.5
	160Gd	2.5	2	
	163Dy			2.5
	166Er	1	0.35	
	172Yb	0.35	0.35	0.35
	Total	6.972	8.003	8.003

Table 2: LA-QICP-MS Operating Parameters. * denotes the internal standard

3.3 Solution QICP-MS

Solution QICP-MS analysis was carried out on the in-house olivine reference material (P16029) using the same iCap-Q at Trinity College Dublin in November 2015 for comparison to the LA-Q-MS data. Three individual olivine crystals were broken from the hand specimen and aliquots from these were handpicked to select the clearest possible internal fragments. A range of aliquot sizes of around 20 to 50 mg was picked, where the smallest were expected to yield the purest olivine signature. Nevertheless, the mass of all aliquots could not be accurately determined on the balance and olivine grains were transferred to Teflon beakers without weighing.

In view of the widely acknowledged (e.g. Eggins et al. 1998, Lee et al. 2007) issue of alteration and concomitant contamination with incompatible trace elements, the aliquots were divided into two fractions, one to be cleaned by leaching, the other one to be left unleached. Leaching was carried out in three stages using a method adapted from Eggins et al. (1998) whereby grains were subjected to a 30 min leach in $\sim 2 \text{ mol l}^{-1}$ HCl, followed by a 15 min leach in $\sim 1 \text{ mol l}^{-1}$ HF, and a final overnight soak in boiling Milli-Q water. Unleached samples were rinsed in Milli-Q water only. All samples were then digested in a 4:1 HF- HNO_3 mixture. Sequential addition and removal of acid was necessary to fully digest the unmilled (higher mass) grain fragments, which proved to negatively impact the procedural blank and associated correction on all samples. Once digested, the solution and fluorides were evaporated, and the residue converted to nitrates using two stages of concentrated HNO_3 addition. All acids used were purified using in-house sub-boiling triple distillation.

One way to measure the very low REE concentrations in olivine is to co-precipitate and concentrate them after digestion. This helps to avoid matrix issues and boosts sensitivity for measurement (e.g. Qi et al. 2005). However, in order to overcome inherent blank issues, a reasonably large sample mass is required. Because of the very small aliquots hand-picked in this study, the co-precipitation step was not deemed appropriate. Instead, final solutions of relatively low dilution factors were prepared directly for analysis by dissolving the nitrate residue in 2mL of $\sim 0.3 \text{ mol l}^{-1}$ HNO_3 spiked with a mixed internal standard of ^6Li , Rh, Re, Bi, ^{235}U .

A sample volume of 1 mL was introduced into the QICP-MS using a microFast system coupled to an ESI SC-2 DX autosampler at a rate of 140 $\mu\text{L}/\text{min}$ (allowing for ca. 7 mins of data collection). Typical sensitivities (cps per ng g^{-1}) measured after tuning the QICP-MS were as follows: ^{59}Co 132,000 cps, ^{140}Ce 320,000 cps, ^{209}Bi 370,000 cps, ^{238}U 500,000 cps. Experiment set-up followed the approach of Eggins et al. (1997) with the modifications as outlined in later publications (e.g. Babechuk et al. 2010). Sample unknowns were preceded with blanks, multiple analyses of the calibration standard (USGS rock reference material W-2), and quality control reference materials (USGS rock reference material BIR-1) all spiked with the same internal standard mixture. Interleaved between these samples was a monitor solution (additional rock reference material) to correct for external drift. Beyond the REE+Y, a small suite of other elements (Al, Ca, Mn, Fe, Mg, Sc, Cr, Co, Ni, Rb, Zr and Th) was also analysed. Instrument intensities were corrected offline for internal and external drift, procedural blank, and isobaric interferences and calibrated using the preferred values of W-2 reported elsewhere (Kamber 2009).

The intensities of several of the high-field-strength elements (Zr, Th and Sc) showed excessive (up to 50 %) drift in some of the samples. The drift of all the other analytes was small (<5 %) and correlated exactly with the internal standard intensities. The difficulty in digesting the samples also manifested as residual solids (colloids) that remained and did not fully dissolve into $\sim 0.3 \text{ mol l}^{-1} \text{ HNO}_3$. Drifting elemental data for those samples are not reported. Nearly all REE intensities were above the background equivalent concentration (BEC) calculated from multiple measurements of the blank internal standard mixture. However, as expected, the sample signal intensities for the REE were low and progressively approached the levels of the procedural blank from the HREE to LREE. Accordingly, data for La to Nd were indeterminable above the blank. For the remaining REE, only the blank-corrected solution concentrations that exceeded the value of the procedural blanks by a factor of 2 were considered reliable. This is demonstrated in Supplementary Table 1 and Figure 1, where the latter shows the CI-chondrite normalised REE patterns of the BEC, procedural blanks, and screened sample concentrations as described above. These REE data are used for comparison to those obtained by the LA-ICP-MS method. Rubidium, analysed as a proxy for melt addition

or metasomatism, was only detectable in one sample. The lab is continuing to refine the technique for single-crystal shard analysis by S-QICP-MS.

The analysis of Fe and Mg was used to scale the measured FeO+MgO wt. % to a sum of 59 wt. % based on SEM EDS data that returned an average of 59.3 ± 0.3 . For unleached samples, the factor by which the abundances were scaled is an indirect measure of the measurement dilution factor, which ranged from c. 11,000 to 38,000 and corresponds to back-calculated olivine aliquot masses ranging from 0.05 to 0.18 mg. For leached samples, where an indeterminate amount of mass was lost, the scaling factor cannot provide a dilution factor. The scaled abundance data for leached and unleached samples are presented in Supplementary Table 1.

4. Results and Discussion

4.1 Downhole Fractionation during LA-QICP-MS analysis

Fractionation can lead to inaccurate measured values in data if there are differences between analyte behaviour of samples and the calibration reference materials. It is especially important to monitor such fractionation in view of the long dwell times used in this study. Many factors contribute towards different types of fractionation at all stages of analysis, such as during aerosol transport and during ionization in the plasma. At the laser ablation stage, the pit depth-diameter ratio has been identified as a key parameter in causing downhole fractionation (Eggins et al. 1998a), with aspect ratios >1 being unfavourable. Here we limited the overall analysis time and repetition rate to maintain an aspect ratio of ~ 1 .

Given the relatively large spot size and high frequency that were used in this study, we identified downhole fractionation as a potential issue. As such, downhole fractionation was monitored by calculation of the fractionation index relative to the internal standard ^{29}Si (FI_{29}) (Fryer et al. 1995). The fractionation index measures the relative change between analyte signal and the internal standard (^{29}Si) over the duration of the analysis, and is calculated as follows:

$$FI_{29} = \frac{(I_i/I_{IS})^{T_{0-64}}}{(I_i/I_{IS})^{T_{65-130}}} \quad (1)$$

Where I_i is the mean intensity of the analyte mass and I_{IS} is the mean intensity of ^{29}Si the internal standard, for the two halves of data acquisition (total ablation time of 130s per spot) where T is time in seconds. Where FI_{29} deviates from 1, fractionation has occurred. Fig. 1 shows FI_{29} for the in-house olivine (P16029, P16030), soda-lime glass (NIST SRM 612, NIST SRM 616) and basalt glass (BHVO-2G, KL2-G, GOR132-G) reference materials. Typically, FI_{29} clusters between 0.9 and 1.1, indicating that no systematic or significant fractionation took place, and additionally there was no difference in fractionation between the glass and olivine matrices. In view of the aim of the study – to determine measured values at very low concentrations with moderate precision – uncertainty introduced by fractionation was not significant during ablation, transport or detection, despite the high mass of sample material removed using this analytical set up.

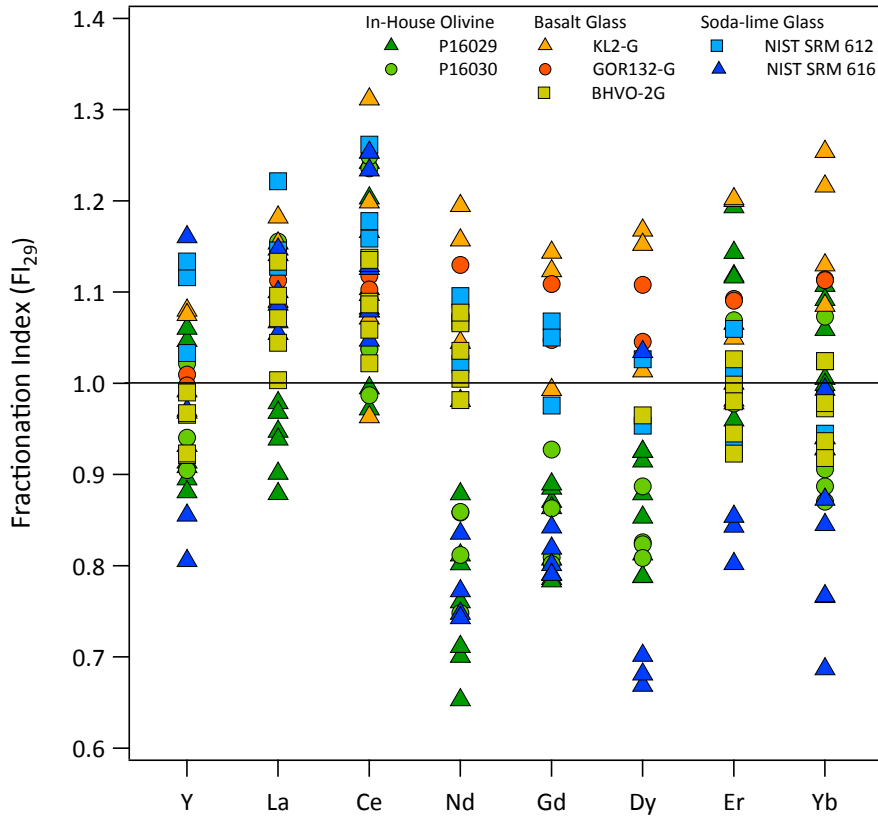


Figure 1: Variation of Fractionation Index (see text for definition) for glass- and in-house olivine reference materials for a typical experimental run (April 2015).

4.2 Data Quality and Comparison

4.2.1 Limits of Determination

We prefer the more conservative limits of determination (LOD) over limits of detection, i.e. using 6 times the standard deviation (σ) of the background rather than the standard 3σ , to ensure quantitative determinations. The LODs achieved using the LA-QICP-MS technique were sub-ppb, typically 0.2-0.4 ppb. The determined concentrations of REEs in the samples in this study were consistently above LOD, typically at least 10 times greater, with very few values falling below the limit. The two elements found most likely to fall below LOD were Pr and Sm, even though their dwell times are at or close to the maximum allowable duration (2.5 s).

4.2.2 Accuracy

Data trueness was assessed by calculation of relative bias (%bias) of reference materials. The %bias was determined for three reference materials: soda-lime glasses (NIST SRM 612, NIST SRM 616) (Jochum et al. 2011) and the basalt glass (GOR132-G) (Jochum et al. 2006) reference materials, and is shown in Fig. 2. A table of average concentrations is provided in Supplementary Table 2. The bias was typically 5-10% for both the NIST SRM and the MPI-DING reference material glasses, however there is a discrepancy for Ce values recorded for GOR132-G, averaging approx. 10% lower than the reference value. The raw Ce signals for all experiments involving GOR132-G were examined and it was determined that this offset was not due to a switch between analogue (BHVO-2G) and pulse count (GOR132-G) modes, as the offset remained even in runs where both signals were recorded in pulse count mode. Moreover, the CI-normalised REE pattern for our average GOR132-G values determined here is smooth and shows no negative Ce anomaly. In addition, lower than preferred Ce values have previously been reported in the literature for this reference material (e.g. Gibson et al., 2013). This may therefore reflect a problem with the GOR glasses themselves.

Regardless, the NIST SRM 616 measured values most closely resemble the levels in natural olivines and for this reference material we are able to achieve biases of $\pm 10\%$ (typically) similar to the results for our in house olivine reference materials, even at single digit ppb mass fractions.

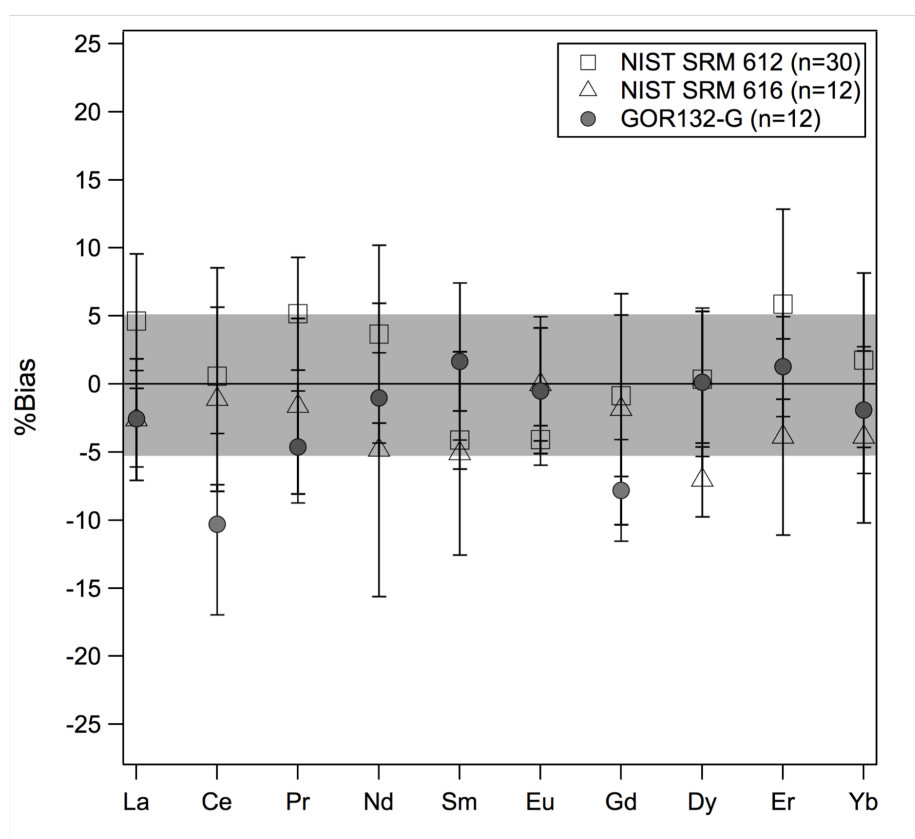


Figure 2: %Bias (see text for definition) for three reference materials that were used as quality monitors for all experiments (Feb-Sept 2015), plotted in order of atomic mass. Error bars represent 1s. For ease of comparison, an area has been shaded to highlight the data that is within the $\pm 5\%$ bias bracket.

4.2.3 Precision

To a first order, the measurement repeatability is a function of counting statistics, predicting that large signals can be measured with much better precision than tiny signals such as those obtained for REE in olivine. In our datasets, there is the expected

trend of increasing precision (expressed as relative standard deviation of Si-normalised analyte signals) with an increasing signal but only in the signal range of 10^0 to 10^4 cps (Fig. 3a). For signals $>10^4$ cps the expected further improvement of internal errors was not found. By contrast, in the few experiments where Al was also measured, Al-normalised signal internal errors were lower and improved to 1-3% for signals of ca. 10^6 cps (Fig. 3a). This discrepancy is explained with the irregularity of the Si signals in our experiments. At the chosen experimental conditions, the short dwell time for Si resulted in more irregular signals than those of comparably sized analyte signals (see Fig. 3b for an example). Thus, for high concentration samples, the irregular Si signal degraded the quality of the internal errors for high concentration analytes, and our method should not be used to analyse materials with higher REE concentrations such as garnet or clinopyroxene.

Figure 3c shows the external error of REE concentrations determined from repeat analyses of olivine, basalt and soda-lime glass reference materials, thus the measurement reproducibility of the method. When plotted against average analyte count rate, there is a general negative correlation across all matrix types. For very small signals, the measurement reproducibility approaches or is even lower than the internal error, which is a common observation for QICP-MS data, even in solution mode (see e.g. Ulrich et al. 2010). For reference material analytes that yield larger signals (i.e. $>10^4$ cps) the expected better intermediate precision was not observed, similar to the measurement repeatability (Fig. 3a). Therefore, for large signals, our method yields unfavorably large errors. However, in view of the analytical targets with expected REE concentrations of a few ppb, the measurement reproducibility is $<10\%$ (Fig. 3c).

Figure 3d shows %RSD variation with observed REE concentrations for two olivine in-house reference materials. This illustrates that to maintain an RSD of $<10\%$, the concentration should be above 10 ppb. From table 3 we know that the HREE for both mantle and magmatic olivines are present at concentrations >10 ppb, and thus the method should be able to achieve %RSD of better than 10%. The LREE are consistently lower in measured value and are therefore subject to higher %RSDs. Count rates, and thus measurement repeatability, for the LREE could be improved by using an even larger laser spot size.

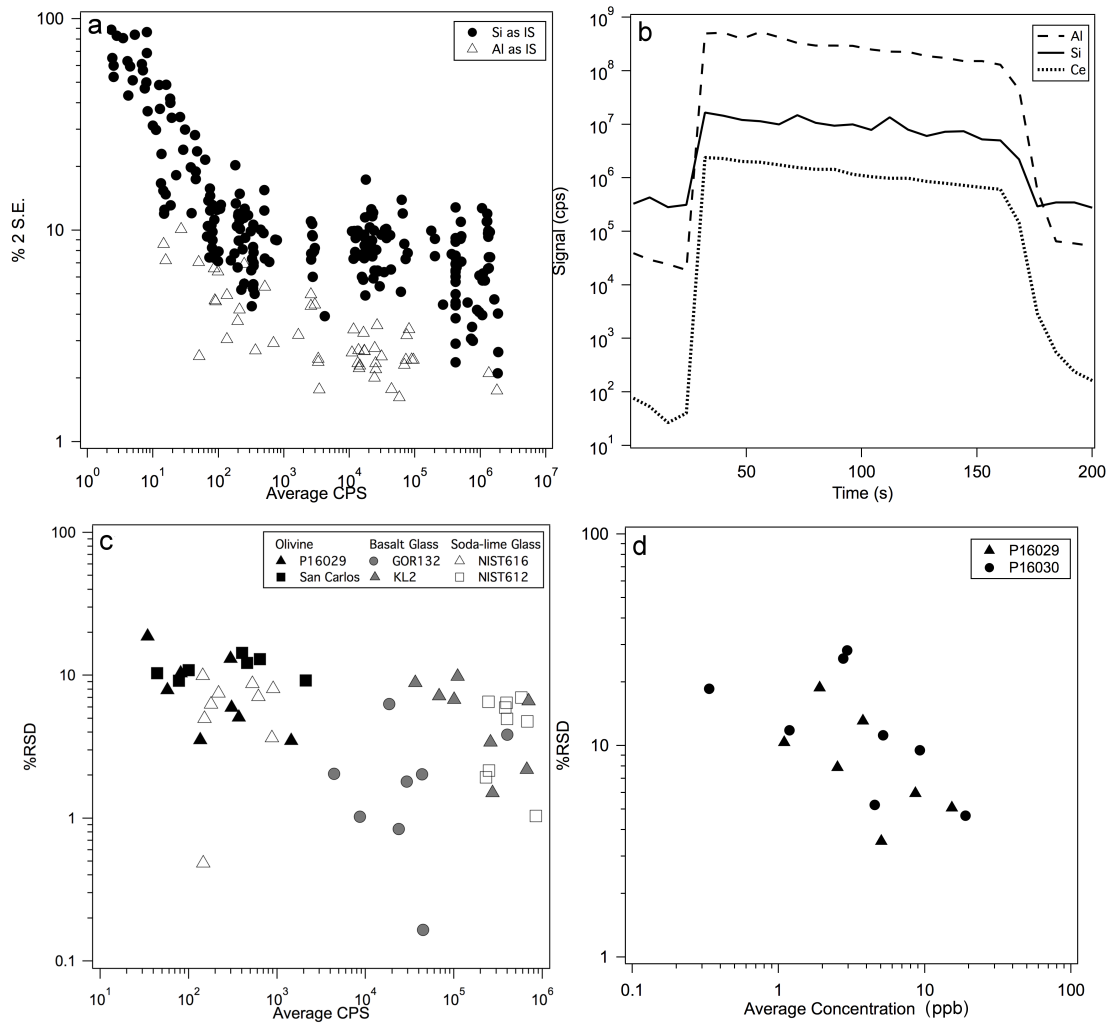


Figure 3: a) Measurement repeatability (% 2 Standard Error) plotted against average background corrected signal (cps) for representative analytical runs, using Si and Al as internal standards for calibration, between February and September 2015. Relative standard deviation (%RSD) was calculated for NIST SRM and MPI-DING reference material and an in-house olivine reference material (P16029) as follows:

$$\%RSD = 100 \times \left(\frac{\text{Standard deviation (counts)}}{\text{Average (counts)}} \right) \quad (2)$$

b) Typical signals (cps) for Al, Si, and Ce shown for a representative ablation of BHVO-2G. c) Relative standard deviation of determined concentrations against average count rate of replicate analyses of NIST SRM and MPI-DING reference materials and two olivine samples from analytical runs between February and September 2015. d) Relative standard deviation against average concentration of individual REEs in ppb for a picritic olivine (sample P16029) and a spinel lherzolite (sample P16030) from analytical runs between February and September 2015.

4.2.4 Comparison of LA-QICP-MS and Solution QICP-MS data

Comparing the concentrations between the leached and unleached aliquots of sample P16029 (see Supplementary Table 1), very good agreement is found for elements highly compatible in olivine: Co (146 ± 2 ppm leached and 147 ± 3 ppm unleached), Ni (2100 ± 36 ppm leached and 2093 ± 103 ppm unleached), and Mn (0.150 ± 0.002 wt. % leached and 0.153 ± 0.005 wt. % unleached). Chromium also produced agreement between the two populations within uncertainty (484 ± 69 ppm leached and 417 ± 55 ppm unleached), with one exception (CS47, with Cr 586 ppm). These Ni-Co-Cr values are within the range of values reported for other picritic olivines (e.g. Krishnamurthy et al. 2000 and Zhang et al. 2008) and is in agreement with an external measurement of Ni (2020 ± 470 ppm) determined via semi-quantitative SEM-EDS as outlined in section 3.1. Collectively, these observations confirm that the MgO+FeO g/100g scaling procedure produced reliable final abundances. Further, the quality of correspondence in Co-Ni-Cr demonstrates that metasomatism, if present, did not significantly affect these elements in the olivine. The low Al and undetectable Rb in all samples but one (see below) can also be considered evidence that initially selected aliquots of olivine were mostly free of other mineral contaminants or metasomatic alteration features. Finally, since the aliquots were picked from several separate grains, it can also be concluded that the grains are chemically homogenous and of only one generation.

Scandium was one of the elements that showed excessive drift in 5 of the 9 analysed aliquots and only data for the remaining 4 are reported. The average Sc content of the two leached aliquots is somewhat lower (6.4 ± 0.4 ppm) than for the unleached pair (9.1 ± 0.6 ppm).

Yttrium and the HREE (Dy to Lu) show a very strong agreement between the leached and unleached aliquots and within aliquots, with the exception of one leached sample (CS51) that records higher concentrations of all elements. The overall coherency between leached and unleached olivine shows that despite the very low concentrations of these elements in olivine, secondary processes did not significantly alter the absolute and relative abundances of the HREE. The MREE Sm to Eu were only quantifiable in a smaller subset of the leached and unleached samples and they show a wider range in concentrations. The LREE La to Nd were not quantifiable in any sample due to the

concentration of these elements in the procedural blank. The origin of the higher concentrations in leached sample CS51 is uncertain, but Rb was only detectable in this sample. If Rb is an appropriate proxy for alteration, this could indicate that the leaching step in this case did not successfully remove all traces of melt or altered olivine from cracks or grain boundaries. However, the Al content is the same as all other samples and it is noteworthy that the HREE pattern still parallels that of all other aliquots of P16029.

From the solution analyses, the mean REE values of both leached and unleached aliquots are compared to the laser-ablation data from the same sample. Figure 4a gives a comparison of CI-normalised REE patterns between the solution datasets for 3 olivine crystals (divided into 9 aliquots) and the average laser ablation determined concentrations for P16029 (n=10), while Fig. 4b gives a direct comparison between solution and laser ablation determined concentrations for the same sample. Figure 4a shows that the laser data plot close to the average solution data for Yb, Er and Dy, and within error of the leached average for Gd, resulting in comparable REE patterns for both datasets. There is also good agreement between absolute and relative HREE contents derived by solution and laser ablation, as shown in Fig. 4b. Most elements plot consistently within error of the 10% error bracket of the 1:1 line, with the exception of Gd, which plots below the 1:1 line, perhaps from a slight inaccuracy in isobaric (e.g., Dy) interference correction. The overall concordance indicates that the data obtained using our ablation strategy is consistent with the more classically applied grain digestion and solution analysis.

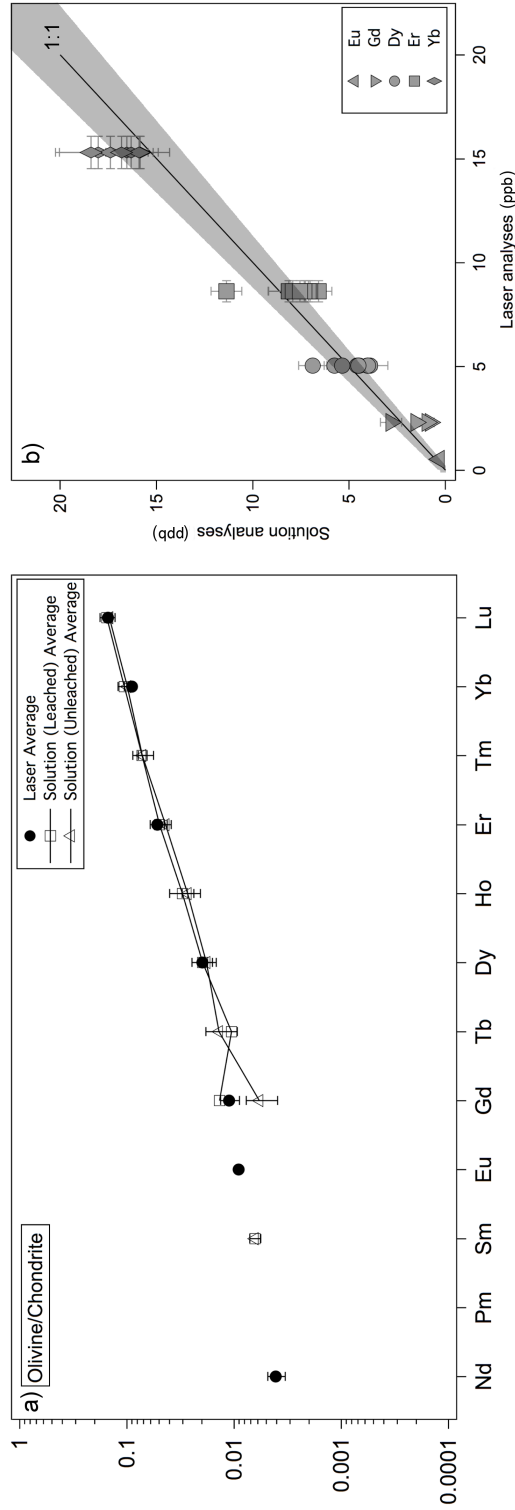


Figure 4: a) CI normalised (McDonough and Sun, 1995) partial REE patterns for average leached ($n=5$) and unleached ($n=4$) olivine groups (see Supplementary Table 1) by S-QICP-MS compared to the mean mass fraction determined for the same olivine by the LA-QICP-MS ($n=10$) method. Error bars represent the external 1σ standard error of the final concentration. CI-chondrite values are from McDonough and Sun (1995). b) Mean LA-ICP-MS concentrations determined for Eu, Gd, Dy, Er, and Yb compared to each analysis (leached and unleached) of the same elements determined by S-QICP-MS. Horizontal error bars represent the external 1σ standard error of the final concentrations (LA-QICP-MS), whereas vertical error bars represent internal 1σ standard error of the final intensity during measurement (S-QICP-MS). A dashed 1:1 line is given for ease of comparison, while the shaded area represents the $\pm 10\%$ error envelope.

4.3 REE contents of natural olivine

Concentration data for natural olivines are listed in Table 3 and range from 0.1 to double-digit ng g^{-1} , with HREE significantly more variable than LREE. CI chondrite-normalised rare earth element patterns are illustrated in Fig. 5. Notwithstanding this variation in the HREE, all REE patterns are relatively similar with only a few exceptions observed in meteorite olivines. Four olivine samples (P5372, P16027, P16031, and USNM 2566; 2 mantle and 2 meteorite) exhibited significantly lower than expected Y concentrations. This is most evident from the Y/Ho ratio. Assuming a smooth CI-normalised REE pattern between Dy_N and Er_N , the projected Ho_N position can be used to predict its concentrations in the olivine, since this element was not measured by the LA-ICP-MS technique. From these extrapolated Ho data, Y/Ho mass ratios for LA-ICP-MS Y data returns a mean of 23 ± 4.7 , with the exception of the 4 low Y samples that yield ratios from 1.2 to 2.4. Expressed another way, an assumed chondritic Y/Ho ratio of 28.8 (McDonough & Sun, 1995) can be used to calculate a predicted Y concentration for all samples. When the latter are compared to measured Y values (as shown in Supplementary Figure 2), most samples fall along the expected 1:1 line, with some increasing deviation at lower concentrations expected from the lower precision. However, the four samples identified as anomalous plot to clearly sub-chondritic Y values. These low Y values are apparently not an analytical artefact (Supplementary Figure 3) and it is noted that unusually low Y/Ho ratios have previously been reported for mantle samples associated with metasomatism (e.g. Grégoire et al 2000, Bodinier et al 2004). As the Y concentrations for these four samples were the lowest measured in this study, an analytical artefact should not be completely dismissed, although it is difficult to envisage an analytical process that would lead to specific suppression of only the Y signal. For comparison, the directly measured mean Y/Ho ratio for P16029 (leached and unleached S-QICPMS) is 27 ± 2.9 , similar to the extrapolated laser data.

Sample (average n)	Mantle	P16028 (7)	P5372 (10)	P16031 (8)	P16030 (8)	NMNH 111312- 44 (7)	P16033 (4)
wt%							
SiO ₂		41.00	40.80	40.89	40.67	41.31	40.21
MgO		49.78	50.10	49.59	48.58	48.37	45.23
FeO		8.72	8.53	9.06	10.21	9.80	14.08
Fo		91.05	91.28	90.70	89.45	89.79	85.13
ppb							
Sc			21700	21700	21650	20820	
<i>Iσ</i>			2121	707	919	7062	
Ga			40.10		105.70	91.00	
<i>Iσ</i>							
Y		37.93	1.28	0.96	45.29	44.28	85.00
<i>Iσ</i>		2.52	0.11	0.15	3.23	4.53	2.65
La		1.00	0.94	1.17	1.19	0.95	1.59
<i>Iσ</i>		0.08	0.11	0.22	0.14	0.18	0.07
Ce		3.14	3.57	3.89	4.56	3.89	5.28
<i>Iσ</i>		0.13	0.60	0.70	0.24	0.62	0.33
Pr			0.20	0.24	0.34		
<i>Iσ</i>			0.06	0.05	0.06		
Nd		2.05	2.18	2.11	2.95	1.84	3.39
<i>Iσ</i>		0.24	0.37	0.36	0.83	0.45	0.25
Sm							
<i>Iσ</i>							
Eu			0.41		0.57	0.34	
<i>Iσ</i>						0.20	
Gd		1.78	1.48	1.51	2.77	1.83	4.43
<i>Iσ</i>		0.13	0.18	0.14	0.71	0.19	0.44
Dy		3.15	1.31	1.16	5.20	4.11	9.03
<i>Iσ</i>		0.36	0.25	0.10	0.58	1.42	0.34
Er		8.95	2.28	2.36	9.25	6.91	14.70
<i>Iσ</i>		0.14	0.19	0.29	0.88	1.13	0.25
Yb		18.54	1.39	1.88	19.03	15.39	27.20
<i>Iσ</i>		0.59	0.30	0.21	0.89	3.41	1.21

Table 3: Major and Trace Olivine Compositions. Major element concentrations determined by SEM EDS and are given in weight %, trace element concentrations were determined by LA-ICP-MS and are given in ppb.

Sample (average n)	P16032 (7)	P16035(5)	P32003 (6)	P5508 (4)	KH 96-21 (4)	Magmat ic	P16029 (10)
wt%							
SiO ₂	40.50	40.86	40.43	40.49			40.35
MgO	48.10	49.73	48.64	48.66			47.87
FeO	10.99	8.96	10.45	10.45			11.44
Fo	88.64	90.83	89.25	89.25			88.18
ppb							
Sc							21300
<i>Iσ</i>							
Ga							
<i>Iσ</i>							
Y	54.51	13.65	28.25	22.75	24.25		41.99
<i>Iσ</i>	6.80	2.70	3.18	1.39	7.14		1.46
La	1.40	1.20	1.20	1.21	0.36		1.09
<i>Iσ</i>	0.31	0.06	0.15	0.09			0.11
Ce	4.84	4.01	4.12	4.76	0.35		3.78
<i>Iσ</i>	0.81	0.88	0.63	0.05	0.29		0.49
Pr					0.06		
<i>Iσ</i>					0.02		
Nd	2.72	1.88	2.04	2.09	0.42		1.91
<i>Iσ</i>	0.48	0.08	0.15	0.11	0.14		0.36
Sm					0.31		
<i>Iσ</i>					0.14		
Eu					0.16		0.53
<i>Iσ</i>					0.06		
Gd	3.94	1.72	1.82	1.93	0.88		2.30
<i>Iσ</i>	0.59	0.17	0.14	0.12	0.39		0.20
Dy	8.31	2.00	3.36		2.34		5.03
<i>Iσ</i>	0.21	0.16	0.03		1.06		0.18
Er	9.16	4.31	7.00	6.08	3.07		8.61
<i>Iσ</i>	1.32	0.36	0.61	0.24	1.11		0.51
Yb	14.49	7.66	16.23	12.31	7.32		15.31
<i>Iσ</i>	2.03	0.42	1.94	0.37	1.84		0.78

Table 3 cont.

Sample (average n)	Sk 22 (3)	Sk31 (4)	Sk24 (3)	P1655 (1)	SF39 (4)	P16180 (4)
wt%						
SiO ₂	31.46				38.98	40.66
MgO	13.28				41.31	48.95
FeO	54.59				19.43	9.87
Fo	30.26				79.12	89.84
ppb						
Sc	15100					
<i>1σ</i>	2121					
Ga	168.0					
<i>1σ</i>						
Y	515.0	500.5	1525	55.00	120.70	20.53
<i>1σ</i>	7.07	50.20	261.6		6.35	1.69
La	21.25	0.57	275.1	1.61	1.85	2.48
<i>1σ</i>	5.59	0.13	346.3		0.14	1.16
Ce	56.33	1.48	319	4.95	6.34	4.45
<i>1σ</i>	26.76	0.26	459.9		0.33	0.61
Pr	9.10	0.28	37.05		0.50	
<i>1σ</i>	3.82	0.02	43.77		0.03	
Nd	46.50	1.70	131.9	2.22	3.61	4.02
<i>1σ</i>	9.19	0.09	147.2		0.25	1.52
Sm	7.60	1.19	6.3			
<i>1σ</i>		0.06				
Eu	3.63	0.54	4.665			
<i>1σ</i>		0.01	2.60			
Gd	24.00	6.47	29.1	1.96	7.67	2.55
<i>1σ</i>	0.28	0.07			0.24	0.51
Dy	51.50	31.6	102	3.92	15.18	3.46
<i>1σ</i>	13.44	1.27			0.67	0.57
Er	81.50	85.35	226	13.00	19.05	4.84
<i>1σ</i>	7.78	3.32	56.57		0.74	0.20
Yb	223.3	248	503	42.70	28.90	7.48
<i>1σ</i>	43.75	19.32	104.7		2.31	0.50

Table 3 cont.

Sample (average n)	Meteorite	P16027 (4)	USNM 2566 (3)	Metamorphic	P15759 (4)
wt%					
SiO ₂		40.03	39.70		41.66
MgO		47.02	43.17		53.54
FeO		12.76	16.93		4.60
Fo		86.79	81.97		95.40
ppb					
Sc					
<i>1σ</i>					
Ga					2.01
<i>1σ</i>					
Y		1.47	0.97		
<i>1σ</i>					
La		1.33	1.68		2.04
<i>1σ</i>		0.02	0.10		1.22
Ce		3.92	4.84		5.46
<i>1σ</i>		0.10	0.21		1.23
Pr		0.24			
<i>1σ</i>					
Nd		1.81	2.31		2.41
<i>1σ</i>		0.12	0.21		0.45
Sm					
<i>1σ</i>					
Eu					
<i>1σ</i>					
Gd		1.63	2.02		1.27
<i>1σ</i>		0.03	0.33		0.11
Dy		1.92	2.64		0.98
<i>1σ</i>		0.22	0.42		
Er		2.96	2.99		1.61
<i>1σ</i>		0.06	0.27		0.18
Yb		2.80	1.72		1.11
<i>1σ</i>		0.05	0.39		0.22

Table 3 cont.

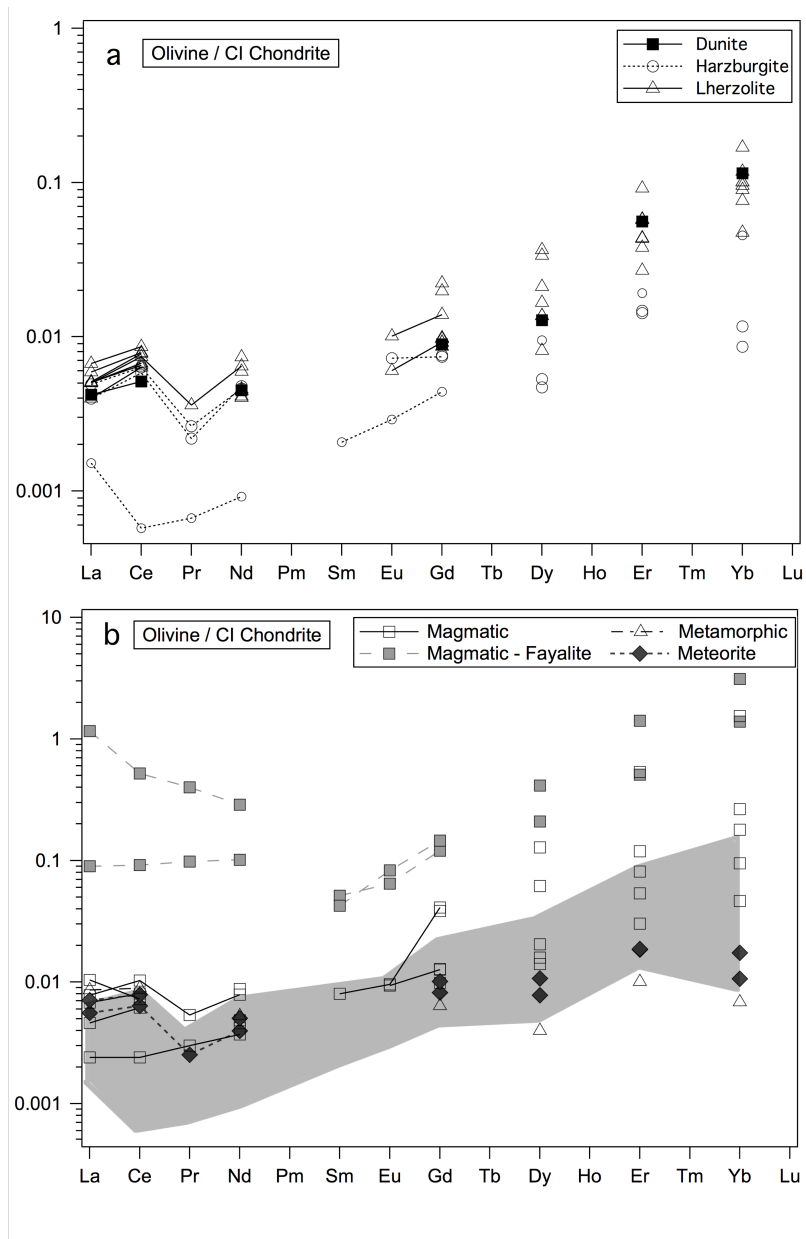


Figure 5: CI normalised (McDonough and Sun, 1995) REE patterns in olivine, arranged by atomic mass. a) Olivine/chondrite patterns for all mantle olivine samples in this study. b) Olivine/chondrite patterns for magmatic, meteorite and metamorphic olivine samples for this study with a grey field representing the mantle samples.

4.3.1 Mantle olivines

With a total abundance of approx. $\geq 60\%$, olivine is the dominant mineral in upper mantle peridotite, the majority of it lying between Fo₈₉ and Fo₉₄ (Deer et al. 1997). These olivines have a very low affinity for REEs, with concentrations estimated at low ppb level.

The CI-normalised REE patterns (Fig. 5a) show that mantle olivines range from low to high La/Yb ratios (0.002 to 1.8). The variability in La/Yb is mainly caused by relative HREE abundance. The LREE are typically 100-1,000 times lower than chondrite, while HREE show greater variation from as little as 10 times lower than chondrite. There is only limited petrological control over REE behaviour. Harzburgitic samples presented here display a wide range in La/Yb ratios, while the dunite and lherzolites all show consistently higher ratios (Fig. 5a) and similar patterns. Melt extraction to some degree is considered to be ubiquitous among peridotites (Walter, 1981). This extraction process results in the depletion of REEs in olivine due to their incompatibility, preferentially removing the larger cations (LREE), causing a positive slope in the REE pattern. The resulting low REE concentrations in olivine mean that the mineral can in essence be described as a 'blank slate' upon which metasomatic enrichment patterns might be over-printed. This metasomatic enrichment generally adds LREE, and so may result in the flattening out of a positive slope, or causing a slight U-shaped pattern. Different metasomatic agents induce different REE patterns, for example the normalized La/Yb ratios of clinopyroxenes are known to be much lower for those affected by silicate metasomatism than by carbonatitic metasomatism (Coltorti et al. 1999). It follows that the expected trends would show greater variation amongst the LREE than the HREE, as those elements are more strongly affected by metasomatism. The data presented here however show greater variation amongst the HREE, with a trend for decreasing variability tapering across the mass range from the heavy to light REE.

4.3.2 Magmatic olivines

Magmatic olivines exhibit the highest HREE concentrations, clearly shown in Fig. 5b. The LREE are typically 100 times lower than chondrite, while HREE are between 10-100 times lower. This variation in enrichment can be quantified by $\text{La}_\text{N}/\text{Yb}_\text{N}$ ratios, which range from 0.001 to 0.37. Magmatic olivines overlap with those mantle olivines that have more elevated REE contents, but also extend to higher absolute REE concentrations. Much of the variation seen amongst the magmatic olivines is due to the higher REE concentrations of two samples from Skaergaard which contain higher fayalite contents, as can be seen in figure 5b.

4.3.3 Meteorite olivines

Both meteorite-derived olivines analysed in this study display flatter REE patterns than the magmatic and mantle groups, with $\text{La}_\text{N}/\text{Yb}_\text{N}$ ratios of 0.32 and 0.66, and concentrations approx. 100 times lower than chondrite. These patterns are flatter than the v-shaped patterns typically reported for pallasite olivines in the literature, such as those abundances reported for the Brenham olivine by Masuda (1968). More recent work by Minowa and Ebihara (2002) on olivine from the same Brenham pallasite determined REE abundances after leaching, finding much flatter patterns than those previously reported by Masuda (1968) and others. The v-shaped patterns reported elsewhere for pallasite olivines are instead suggested to be the result of terrestrial contamination (Minowa and Ebihara 2002). The patterns presented here show a slight up-turn at the LREEs. Terrestrial alteration/contamination cannot be excluded as a reason for the LREE upturn, although the in-situ nature of our data certainly lowers this prospect compared to bulk digestion data.

4.4. REE Partitioning in olivine

The olivine structure has two octahedral cation sites, M1 and M2. The M1 site is smaller than M2, and it is generally assumed that the large cationic radii of REEs limit their partitioning into the larger M2 site (Evans et al. 2008). The optimum cationic radius (r_O) in olivine ($0.81 \text{ \AA}$) is smaller than even the heaviest REEs, and the elastic modulus prevents significantly larger (i.e. LREE) cations from successful substitution. There are several reports of apparent partition coefficients for REE into olivine in the literature and these vary by more than two orders of magnitude not only in absolute but also relative behavior of the REE (e.g. Stosch et al. 1982; Eggins et al. 1998; McDade et al. 2003; Lee et al. 2007; Evans et al. 2008; Sun and Liang 2013). It is suspected that a lot of this variation likely results from analytical difficulties including concentrations approaching detection limits and uncorrected contamination from inclusions and grain boundaries (Lee et al. 2007). Recognising these limitations, attempts have been made to predict the partitioning behavior of REEs in olivine with the lattice strain model and temperature correction equations (Witt-Eickschen and O'Neill, 2005; Lee et al. 2007).

Here we calculate apparent empirical REE partition coefficients for olivine using data from our in-situ LA-QICP-MS technique and present them within the context of theoretical models, experimental, and other empirically determined values from the literature. For a few samples it was possible to obtain apparent partition coefficients by dividing the olivine REE concentrations with those in co-existing clinopyroxene and orthopyroxene, yielding Dol/cpx and Dol/opx. For other (mineral separate) samples, where no suitable clinopyroxene or orthopyroxenes were available for analysis, REE concentrations for the pyroxene phases were taken from the literature. This included peridotite olivines from San Carlos (NMNH 111312-44), Tallante (P32003) and Kilbourne Hole (KH 96-21) (Lee et al. 2007; Rampone et al. 2009; Harvey et al. 2012). These Dol/cpx and Dol/opx values are plotted in Figs. 6a and 6b against effective cationic radii (Onuma et al. 1968; Lee et al. 2007). For comparison the figure also shows theoretical and experimental data from literature (Stosch 1982; Eggins et al. 1998b; McDade et al. 2003; Lee et al. 2007).

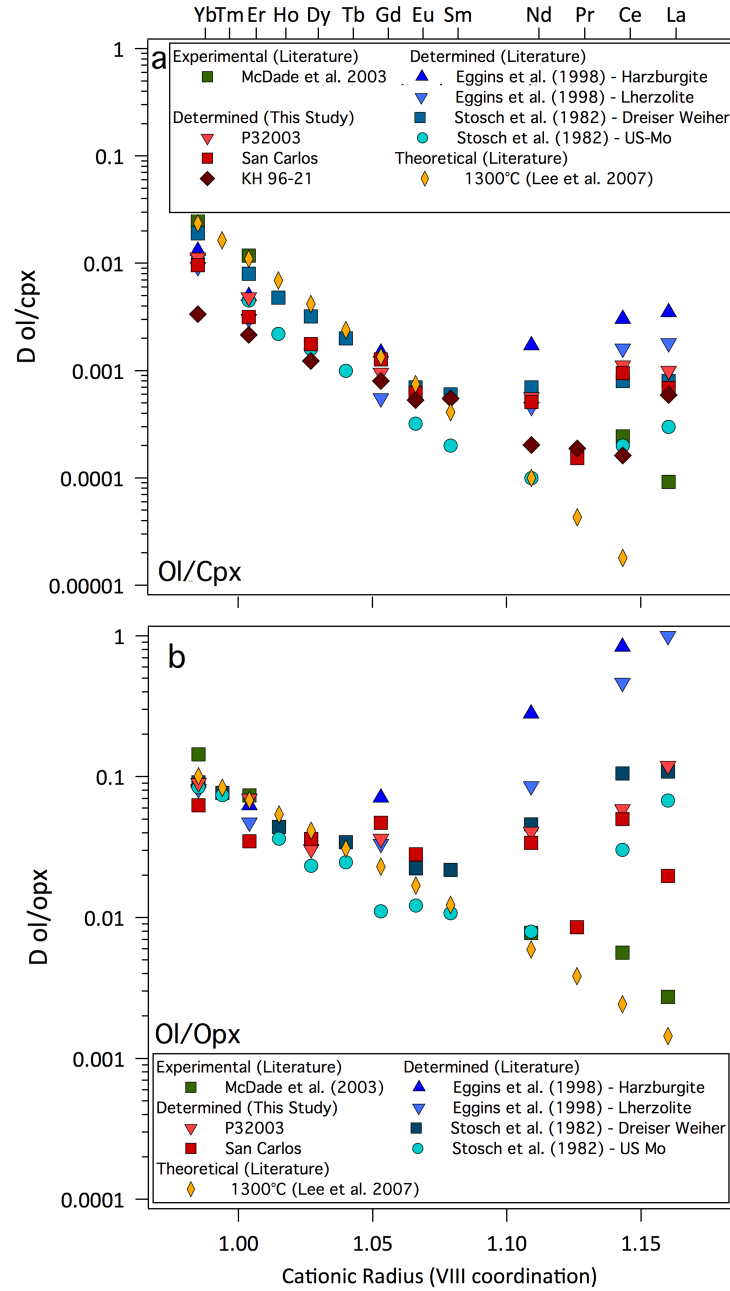


Figure 6: a) $D_{ol/cpx}$ for empirically determined, experimental and theoretical data plotted against cationic radius. Samples shown from this study are San Carlos (NMNH 111312-44) and a spinel lherzolite (P32003). Cationic radii are in 8-fold coordination (Shannon et al., 1976). b) $D_{ol/opx}$ for empirically determined, experimental and theoretical data plotted against cationic radius. Samples shown from this study are San Carlos (NMNH 111312-44) and a spinel lherzolite (P32003). Cationic radii are in 8-fold coordination (Shannon et al., 1976).

There is a strong negative correlation between $D_{\text{ol/cpx}}$ and $D_{\text{ol/opx}}$ and cationic radius for HREEs and MREEs, with a close agreement between empirical, experimental (Eggins et al. 1998b; McDade et al. 2003) and theoretical values (Lee et al. 2007) providing additional confidence in the LA-QICP-MS method. The correlation between $D_{\text{ol/mineral}}$ and cationic radius suggests that the REEs are structurally bound within the lattice rather than being present as micro-inclusions in olivine. The trends deviate towards the LREEs, where we see increasingly diverging variation from Nd to La in the literature data. This variation has been previously noted, for example by Stosch et al (1982) who suggested that the concentration of LREE in olivine might not be governed by lattice-strain effects, and as such LREE might not be structurally bound in the olivine lattice. Instead the apparent concentration of these elements could be dominated by fluid inclusions or as surface contamination (Lee et al. 2007). While surface contamination should not be an issue using this laser ablation strategy, the effect of fluid inclusions cannot be excluded. Although common, this discrepancy at the LREE is not ubiquitous throughout the literature, with La contamination instead being attributed to analysis of small amounts of glass (McKay 1986; Beattie 1994; Evans et al. 2008). The close agreement between theoretical and experimental data suggests that the ‘true’ LREE concentrations are those predicted by lattice strain theory, and that the variation amongst natural samples in the literature is due to contamination. The greater degrees of contamination observed for the LREE in comparison to the HREE are likely to be due to the lower LREE concentrations in olivine, making them more susceptible to overprinting than the HREE.

5. Conclusions

The LA-QICP-MS technique described in this contribution has successfully determined REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb) and Y concentrations in olivines from a global range, with observed absolute concentrations from 0.1 to double-digit ppb levels. The REE Sm to Lu and Y were determined in one in-house olivine (P16029) with a S-QICP-MS technique for comparison and yielded results within 10% of LA-QICPMS values. The LREE were unquantifiable by S-QICP-MS due to the high procedural blank for these elements. More detailed low-blank solution work, possibly including a pre-concentration stage, is required to reinforce the authenticity of the observed LREE enrichment in the LA-QICP-MS data. Calculation of $D_{\text{ol/cpx}}$ and $D_{\text{ol/opx}}$ suggests that the REEs are structurally bound in the olivine lattice, with HREEs and MREEs agreeing closely with experimental and theoretical values from the literature, suggesting a successful application of this LA-QICP-MS technique. While this method has been developed for the analysis of REE in olivine, it may also be applied to other low abundance elements and to other minerals. Limited spatial resolution is a disadvantage with the technique however it may be used as a macro-sampling method with the potential for widespread application.

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P16029							
Leached							
	CS47	CS48	CS49	CS50	CS51	Average	1σ
Dilution Factor	39070	4950	29920	34270	16870		
wt%							
Al ₂ O ₃	0.034	0.038	0.035	0.030	0.040	0.035	0.004
FeO	9.69	9.52	9.74	9.70	9.69	9.67	0.084
MnO	0.152	0.148	0.15	0.149	0.150	0.150	0.002
MgO	49.6	49.8	49.6	49.6	49.6	49.6	0.085
CaO	0.210	0.195	0.185	0.210	0.209	0.202	0.011
ppb							
Sc	n.r.	6110	n.r.	n.r.	6630	6370	368
Cr	586000	461000	450000	463000	404000	473000	67500
Co	141000	141000	141000	143000	147000	143000	2590
Ni	2100000	2020000	2050000	2093000	2010000	2050000	35030
Rb	b.d.	b.d.	b.d.	b.d.	57	57	
Y	35.8	42.5	31.3	36.3	74.3	44.0	17.4
Sm	2.21	b.d.	b.d.	0.725	b.d.	1.47	1.05
Eu	b.d.	b.d.	b.d.	b.d.	b.d.		
Tb	b.d.	b.d.	0.165	b.d.	b.d.	0.165	
Gd	b.d.	b.d.	b.d.	b.d.	2.32	2.32	
Dy	3.49	3.97	3.47	4.87	6.45	4.45	1.26
Ho	1.38	1.38	1.25	1.44	2.58	1.61	0.55
Er	6.32	7.07	7.67	7.51	11.0	7.91	1.79
Tm	1.43	1.58	1.61	1.87	2.43	1.78	0.39
Yb	15.0	16.0	17.0	16.4	21.7	17.2	2.60
Lu	3.36	3.43	3.22	3.84	4.76	3.721	0.63

Supplementary Table 1: Major and Trace Olivine Compositions from Solution QICP-MS.

Major and trace element concentrations for P16029, a picritic olivine, determined by Solution QICP-MS and given in wt% and ppb respectively. Concentrations are given for both leached and unleached grains. “b.d.” notes elements which were below detection, “n.r.” notes elements which were not reported due to signal instability.

	Unleached					
	CS57	CS58	CS59	CS60	Average	<i>1σ</i>
Dilution Factor	18870	11140	21640	37830		
wt%						
Al ₂ O ₃	0.037	0.035	0.025	0.026	0.031	<i>0.006</i>
FeO	9.63	9.43	10.1	10.0	9.80	<i>0.32</i>
MnO	0.151	0.148	0.157	0.157	0.153	<i>0.005</i>
MgO	49.7	49.9	49.2	49.3	49.5	<i>0.32</i>
CaO	0.21	0.189	0.232	0.193	0.207	<i>0.02</i>
ppb						
Sc	n.r.	8720	9510	n.r.	9110	<i>561</i>
Cr	458000	450000	360000	362000	408000	<i>54000</i>
Co	141000	141000	147000	145000	143000	<i>3020</i>
Ni	2130000	2120000	1940000	1970000	2040000	<i>101000</i>
Rb	b.d.	b.d.	b.d.	b.d.		
Y	43.0	39.6	40.0	41.3	41.0	<i>1.52</i>
Sm	b.d.	1.17	b.d.	b.d.	1.17	
Eu	0.364	0.316	b.d.	b.d.	0.340	<i>0.04</i>
Tb	0.380	0.290	0.215	0.463	0.337	<i>0.11</i>
Gd	1.29	0.555	0.548	1.04	0.858	<i>0.37</i>
Dy	4.70	3.86	4.58	3.15	4.07	<i>0.72</i>
Ho	1.68	1.36	1.58	1.24	1.46	<i>0.20</i>
Er	7.29	7.13	7.55	8.17	7.53	<i>0.4</i>
Tm	1.77	1.56	1.92	1.93	1.80	<i>0.170</i>
Yb	16.	15.9	17.2	19.5	17.4	<i>1.55</i>
Lu	3.60	3.59	3.49	3.41	3.521	<i>0.09</i>

Supplementary Table 1 cont.

	NIST612	NIST616	KL2	GOR132-G
ppm				
Sc	43.6	n.a.	31.6	n.a.
<i>1σ</i>	<i>1.6</i>		<i>0.71</i>	
Ga	36.2	n.a.	20.3	n.a.
<i>1σ</i>	<i>0.7</i>			
Y	45.0	0.031	26.8	14.03
<i>1σ</i>	<i>2.1</i>	<i>0.003</i>	<i>1.68</i>	<i>0.56</i>
La	37.7	0.029	13.1	0.082
<i>1σ</i>	<i>1.9</i>	<i>0.001</i>	<i>0.28</i>	<i>0.003</i>
Ce	38.6	0.029	32.4	0.347
<i>1σ</i>	<i>3.1</i>	<i>0.002</i>	<i>1.21</i>	<i>0.023</i>
Pr	39.9	0.015	4.69	0.085
<i>1σ</i>	<i>1.7</i>	<i>0.001</i>	<i>0.06</i>	<i>0.004</i>
Nd	36.8	0.022	21.4	0.682
<i>1σ</i>	<i>2.4</i>	<i>0.002</i>	<i>0.68</i>	<i>0.023</i>
Sm	36.2	0.016	6.14	0.516
<i>1σ</i>	<i>0.8</i>	<i>0.001</i>	<i>0.09</i>	<i>0.030</i>
Eu	34.2	0.015	2.05	0.254
<i>1σ</i>	<i>0.4</i>	<i>0.001</i>	<i>0.14</i>	<i>0.014</i>
Gd	37.0	0.016	5.90	1.10
<i>1σ</i>	<i>2.4</i>	<i>0.002</i>	<i>0.46</i>	<i>0.05</i>
Dy	35.6	0.016	5.45	2.15
<i>1σ</i>	<i>1.8</i>	<i>0.001</i>	<i>0.48</i>	<i>0.12</i>
Er	40.2	0.015	2.55	1.58
<i>1σ</i>	<i>2.8</i>	<i>0.001</i>	<i>0.17</i>	<i>0.06</i>
Yb	39.9	0.016	2.08	1.58
<i>1σ</i>	<i>2.6</i>	<i>0.001</i>	<i>0.16</i>	<i>0.07</i>

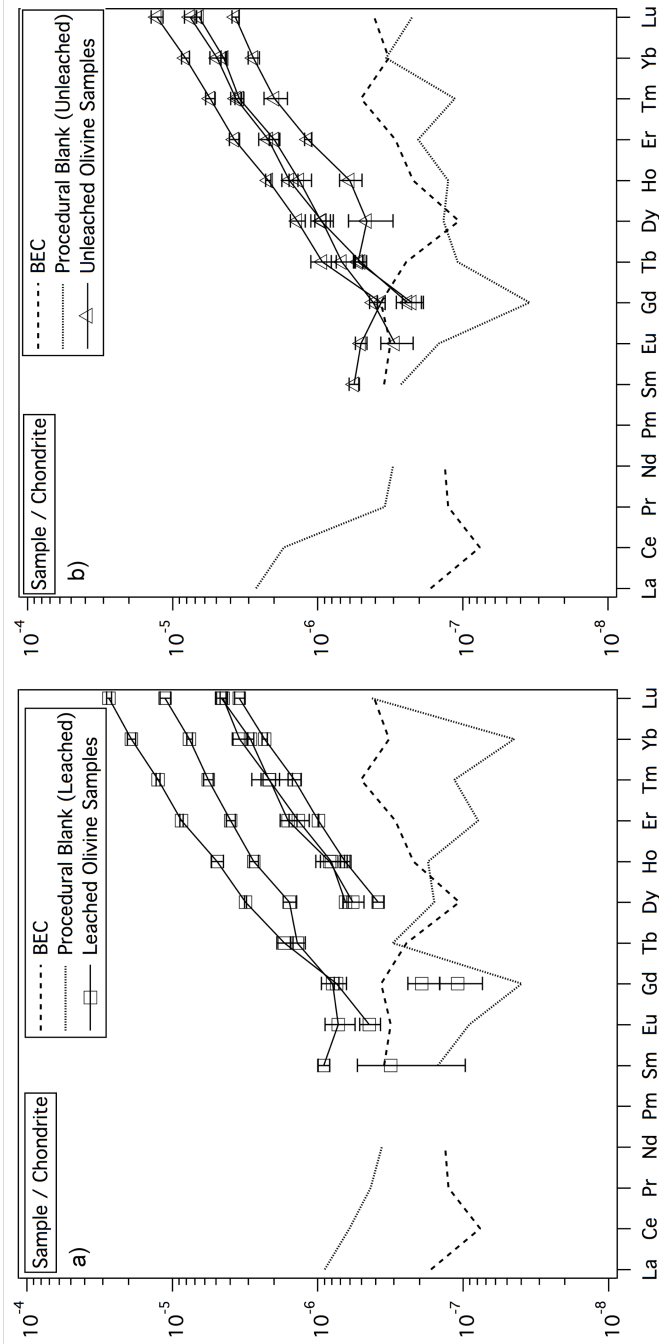
Supplementary Table 2: Trace Compositions of Reference Materials determined by LA-QICP-MS. Average trace element compositions and associated standard deviations for four reference materials (NIST612, NIST616, KL2, and GOR132), determined by LA-QICP-MS and given in ppb.

ppt	BEC
Sc	20073
Ti	19491
V	1928
Cr	22252
Co	1960
Ni	45625
Rb	3426
Sr	735190
Y	24.3
La	39.7
Ce	42.6
Pr	12.0
Nd	62.3
Sm	53.7
Eu	18.3
Tb	8.3
Gd	75.6
Dy	27.1
Ho	12.5
Er	48.6
Tm	12.9
Yb	55.2
Lu	11.1

Supplementary Table 3: Background Equivalent Concentrations (BEC). Background Equivalent Concentrations are given in ppt for solution QICP-MS analyses.

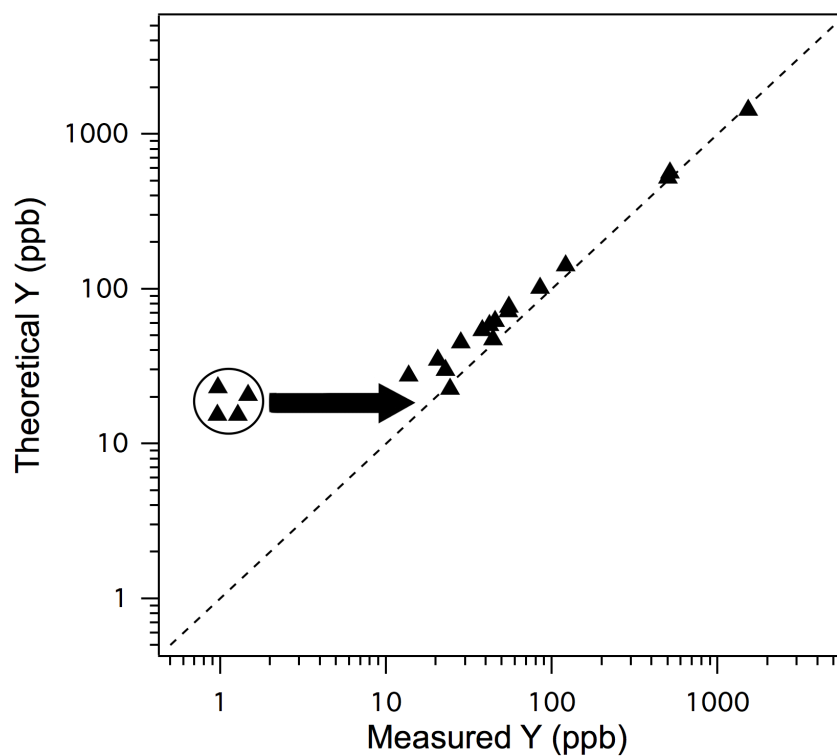
	SiC semiconductor wafer		Gas Background		Typical Olivine
	cps	2 σ	cps	2 σ	cps
Y	3.83	4.50	2.60	3.60	820.14
La	5.48	3.33	2.78	1.62	395.87
Ce	8.03	5.29	6.52	3.42	660.50
Pr	4.42	3.08	54.76	1.34	70.89
Nd	4.25	3.32	4.68	4.37	60.69
Sm	2.14	1.19	2.33	0.50	5.81
Eu	3.93	3.03	2.16	0.89	12.00
Gd	1.93	1.19	1.67	0.45	12.32
Dy	1.94	1.34	2.15	0.46	25.67
Er	2.02	1.11	1.76	1.71	70.40
Yb	1.88	2.80	1.90	1.55	85.06

Supplementary Table 4: Trace element background rates. Trace element count rates and associated 2 sigma errors are shown for a SiC semiconductor wafer and gas background, as well as count rates for a typical olivine, determined by LA-ICP-MS from a typical experimental run.

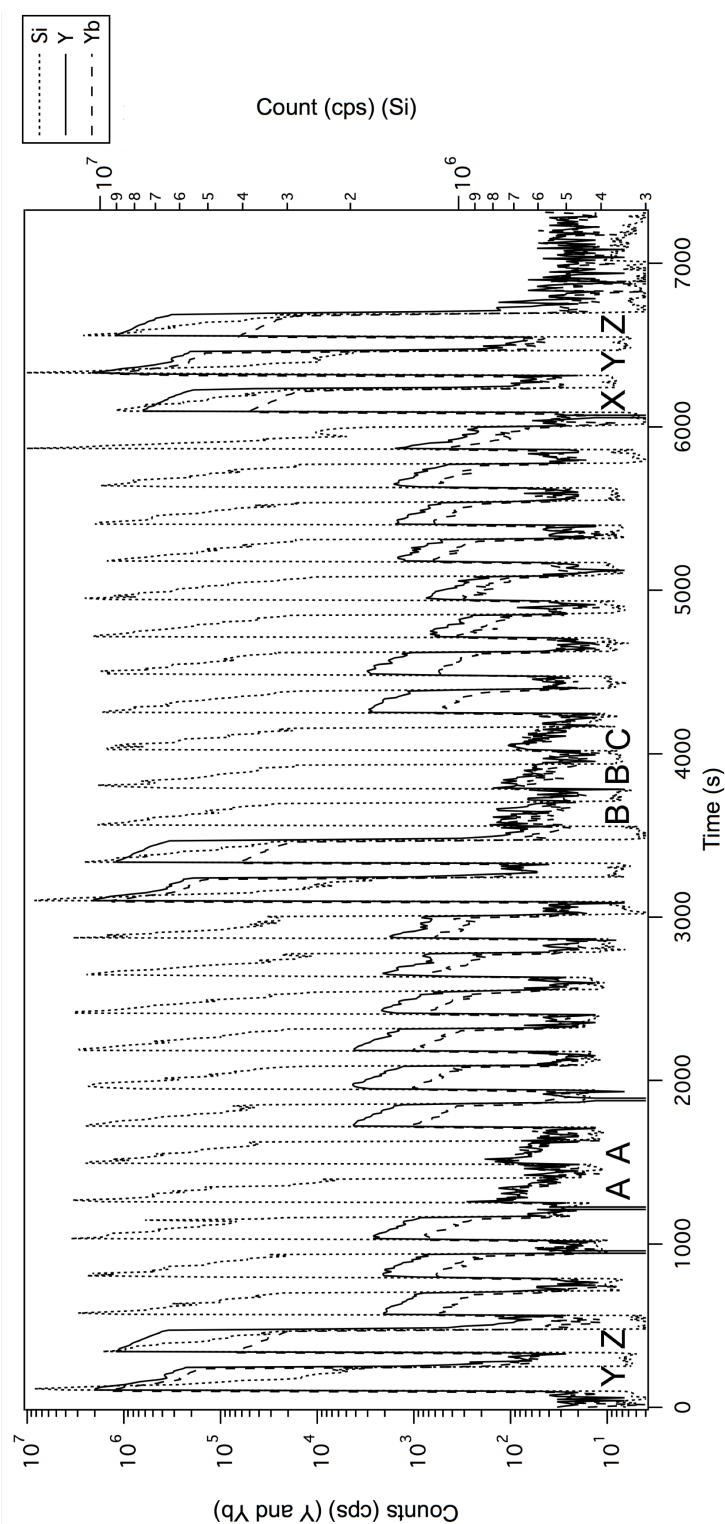


Supplementary Figure 1

CI-chondrite normalised REE patterns for all S-QICP-MS measured concentrations in the (a) leached and (b) unleached P16029 olivines, in addition to the procedural blank for each method and the BEC from the experiment. Error bars on each sample REE determination represent the internal 1σ standard deviation of the mean intensity during measurement. CI-chondrite values are from McDonough and Sun (1995).



Supplemental Figure 2: Measured Y (ppb) plotted against theoretically predicted Y (ppb) calculated based on the measured D_y and E_r values and the relationship between Y and H_o . Most samples plot as expected on the 1:1 dashed line. There are four outliers, namely USNM 2566, P16027, P5372, and P16031, which are circled in the plot with an arrow indicating where they should lie based on predicted values. These four samples show lower Y than predicted. These low values are not believed to be caused by any analytical artefact, as Y values are low even in the raw data as shown in supplemental figure 3.



Supplementary Figure 3: Raw counts vs time shown for three elements (Si, Y and Yb) for a typical analytical run (April 2015). Letters A, B, and C identify the position of the samples USNM 2566, P5372, and P16031 respectively within the run. It is clear from the Y trace that the low Y values displayed by these samples are due not an analytical artefact as they are clearly present in the raw data. Letters X, Y, and Z identify samples GOR132-G, NIST SRM 612, and BHVO-2G respectively.

Chapter 3: Rare Earth Element Partitioning and Subsolidus Exchange Behaviour in Olivine

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Abstract

The systematics of the rare earth element (REE) abundances in olivine are poorly understood and this undermines their usefulness in deciphering petrogenetic processes. Here we report a novel REE dataset for olivine spanning a wide range in Mg number (Mg# 1-59) from the Skaergaard Layered Intrusion.

Olivine La and Lu concentrations vary from 0.68 to 56 ppb and 66 to 571 ppb, respectively. Apparent olivine/melt partition coefficients for the heavy to middle REE define near-symmetrical parabolas, consistent with lattice strain theory, indicating that these elements are structurally bound within the olivine lattice. The parabolas define peaks with variable optimal radii (r_o). This suggests that the Fe-content of olivine exerts a strong influence on REE partitioning, as fayalitic olivines display more open parabolas (higher apparent Young's modulus, E) than forsteritic olivines. The greater site elasticity is manifest as higher REE concentrations in the fayalitic samples. The observation that E and r_o are not constant accross a range of Mg# has implications for predictive models for olivine REE.

The CI chondrite-normalised olivine REE patterns show smooth trends from the heavy to the middle REE, with greater variation amongst the light REE (LREE). Variation and enrichment of the LREE are ubiquitous within published data for natural olivine, yet are not predicted by experimental results. This study also presents two-dimensional REE maps illustrating the behaviour of the REE in olivine in unprecedented detail. Mapping of magnesian olivine shows core to rim increase in Al, LREE, and Eu and the development of a positive Eu anomaly in olivine, resulting from solid-state, likely diffusive re-equilibration with adjacent plagioclase. We propose that secondary redistribution is the principal cause of elevated LREE patterns in natural olivine.

The results from the present investigation show that from a petrological point of view, MREE to HREE systematics of olivine hold promise for study of olivine petrogenesis and that the LREE in olivine may be further developed to understand diffusion time scales and cooling rates in magmatic systems.

1. Introduction

Olivine is one of the earliest crystallising minerals in mafic and ultramafic magmas and the most common upper mantle peridotite phase, and thus, its geochemistry is crucial to our understanding of magmatic processes. Olivine has a low affinity for the REE, however, due to its high modal abundance in magmatic systems it can still contribute significantly to bulk heavy REE (HREE) fractionation (Sun and Liang, 2013). The REEs are of particular use in petrogenetic studies due to their systematic partitioning behaviour, which is strongly linked to variations in their ionic radii (Bau, 1996; Nagasawa, 1966), from Lu ($0.861\text{\AA}$) to La ($1.032\text{\AA}$) (in VI coordination) (Shannon et al., 1976). Experimental work (Beattie, 1994; Evans et al., 2008; Imai et al., 2012; McDade et al., 2003; Zanetti et al., 2004) and lattice strain modelling (Lee et al., 2007) indicate that the HREE are much more compatible in olivine than the LREE.

Mineral-melt partition coefficients are typically dependent on pressure, temperature, and both mineral and melt compositions. The effects of temperature (T) and pressure (P) are expressions of the enthalpy and volume of fusion respectively (Wood and Blundy, 2003). Although difficult to de-convolute from the effects of T and P , melt composition (X) has also been experimentally shown to influence partition coefficients (Colson et al., 1988; Evans et al., 2008). For example, Evans et al. (2008) found that forsterite REE partition coefficients decrease as melt SiO_2 increases.

Only very few authors have reported REE data for natural olivine (e.g. Eggins et al., 1998b; Lee et al., 2007; Zanetti et al., 2004). The scarcity of studies primarily reflects the difficulty associated with analysing concentrations in the low ppb range. Apparent olivine REE partition coefficient values reported in the literature vary in absolute terms and also in relative behaviour of the REE, most notably for the LREE, by over two orders of magnitude. The deviation of LREE from lattice strain predictions has been attributed to analytical artefacts and contamination from LREE-rich inclusions and grain boundary films (Lee et al., 2007). Similar deviations from expected LREE concentrations have also been reported in other minerals with very low LREE abundances e.g. zircon (Hanchar and Van Westrenen, 2007; Whitehouse and Kamber, 2002) and garnet (e.g. Fulmer et al., 2010).

In a recent study from our laboratory, Stead et al. (2016) proposed a macro-analytical strategy for analysing the REE with laser ablation quadrupole inductively-coupled-plasma mass spectrometry (LA-QICP-MS), enabling REE determination down to single-digit ppb concentrations. In minerals that preserve sufficiently large (ca. 150 x 150 x 100 μm) portions of optically clean material, this method minimises the grain boundary contamination that is prevalent in solution analysis of olivine (Stead et al., 2016). In this contribution, we have applied this strategy to produce trace and REE data for olivine from seven samples of the Skaergaard Layered Intrusion to examine elemental partitioning in olivine. We also applied a novel 2-dimensional LA-QICP-MS mapping approach (Petrus et al., 2017) to document the spatial distribution of REE in olivine and bordering phases to further investigate the cause of the observed LREE patterns in olivine and assess their utility for petrogenetic modelling.

Sample	Rock Type	Skaergaard Zone	Plagioclase An %	Olivine Mg#	Clinopyroxene En - Fs - Wo	T (°C) of crystallisation (ol, cpx)
P16039	Hypersthene olivine gabbro	Lower zone b	67.1	59.25	30.3 - 23.8 - 45.9	1141
P16040	Hortonolite ferrodiorite	Upper zone b	51.5	32.10	19.4 - 44.7 - 35.9	1084
P16041	Hortonolite ferrodiorite	Upper zone a	56.1	36.67	21.6 - 44.1 - 34.3	1101
P16042	Fayaltie ferrodiorite	Upper zone c	43.2	1.11	0.7 - 61.3 - 38	1055
P16043	Fayaltie ferrodiorite	Upper zone c	48.2	10.54	8.2-55.5-36.3	1073
P16044	Ferrohortonolite ferrodiorite	Upper zone c	48.3	14.98	11.3-52.2-36.5	1073
P16045	Olivine hypersthene gabbro	Lower zone b	68.8	57.57	31.7-31.0-37.3	1147

Table 1: Sample Characteristics

Olivine, clinopyroxene, plagioclase, and magnetite are represented by 'ol', 'cpx', 'pl', and 'mg' respectively.

2. Sample Description

The Skaergaard Layered Intrusion in East Greenland was chosen for this study because it crystallised a wide range of olivine compositions, ranging from forsterite content (Fo) close to 70 in the Lower Zone to the more unusual fayalites (with Fo as low as 0) in the Upper Zone. It is clear that this suite of olivines is less magnesian than most common olivines in peridotites and mantle melt. Nevertheless, it was anticipated that these natural olivines could represent an empirical laboratory to study the effects of mineral chemistry as well as temperature on REE partitioning.

The Skaergaard Intrusion was emplaced approximately 55 Ma ago, involving the intrusion of moderately evolved tholeiitic magma into Archean gneisses and Tertiary basalts (McBirney, 1996). It is believed that the Skaergaard Intrusion is a closed system having been subjected to only one pulse of magma, which was intruded during the opening of the North Atlantic (Schwarz et al., 1979), and has been subjected to fractional crystallisation and magma convection. Magma crystallisation during cooling resulted in three sequences of layered cumulates: the Layered Series; the Marginal Series; and the Upper Border Series which crystallised from the roof downwards (Wager and Deer, 1939). Pressures of formation at the roof of the intrusion ranged from ~ 0.7 kbar for the Lower Zone a (LZa) to ~ 3 kbar for the Sandwich Horizon (SH) (Larsen and Tegner, 2006). Olivine Mg numbers (Mg#) in the Skaergaard Intrusion range from 0 to 68 (Ariskin, 2002). Seven samples from different layers within the intrusion were selected to reflect this wide Mg# range (Mg# range from 1 to 59). The samples were prepared as 180 μm thick polished sections. This permits selection of best-possible analytical sites within the olivine via inspection in transmitted light. Sample characteristics are provided in Table 1. In limiting the study to samples from one intrusion, the melt source and pressure were kept relatively constant, reducing the number of variables that may have controlled the REE abundances in olivine. Temperatures (T) were calculated using the plagioclase anorthite content (mol %) thermometer of Thy et al. (2009).

3. Methods

3.1 Major Element EDS

Major element concentrations were determined at the iCRAG lab at Trinity College Dublin (TCD) by Field Emission Gun Scanning Electron Microscopy Energy Dispersive Spectroscopy (FEG SEM EDS). Measurements were conducted using a Tescan Mira XMU equipped with an XMAX 150mm² silicon drift energy dispersive detector, with the Oxford Inca X-ray microanalysis software. An accelerating voltage of 20kV was used with a beam current of 350pA. A suite of appropriate mineral standards from the Smithsonian Institute (Jarosewich et al., 1980) was used to calibrate the instrument for quantitative analyses. Accuracies for San Carlos olivine NMNH 111312-44 (n=6) for MgO, SiO₂, and FeO were <1.6% relative to reported reference values (Jarosewich et al., 1980).

3.2 LA-QICP-MS

Trace element concentrations were determined by LA-QICP-MS at TCD using either a Teledyne Photon Machines Analyte Excite laser ablation system for spot analyses, or a Teledyne Photon Machines Analyte G2 laser ablation system utilising the Aerosol Rapid Introduction System (ARIS; Van Malderen et al., 2015; Van Acker et al., 2016) for mapping experiments. Both systems are equipped with a 193nm ATLex 300 ArF excimer laser and a HelEx II active two-volume ablation cell, and are coupled to a Thermo Scientific iCAP-Qc ICP-MS.

Olivine and clinopyroxene were analysed at a spot size of 85 µm, at a laser repetition rate of 8 Hz, and a shot count of 320, giving 40 s of drill time. Analyses were preceded by 80 s counting time on the gas blank (background). Masses ²⁴Mg, ²⁷Al, ⁴⁴Ca, ⁴⁵Sc, ⁴⁸Ti, ⁵⁹Co, ⁶⁰Ni, ⁷¹Ga, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁶⁰Gd, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, and ¹⁸¹Ta, were analysed. Olivine REE were additionally analysed using a high resolution-long dwell time method, with a larger 150 µm spot size, at a laser repetition rate of 30Hz and a shot count of 4000 for

masses ^{29}Si , ^{24}Mg , ^{27}Al , ^{89}Y , ^{139}La , ^{140}Ce , ^{146}Nd , ^{160}Gd , ^{163}Dy , ^{172}Yb , and ^{175}Lu , as described in Stead et al. (2016).

The Iolite software v2.5 (Paton et al., 2011) was used for data reduction using the trace element internal standard data reduction scheme (IS DRS). Previously determined Si was used as the internal standard for all olivine-only experimental runs, while Mg was used as the internal standard for the broader elemental suite applied in olivine and pyroxene experimental runs.

Background signals were corrected for by subtracting the gas blank, though this may not be the most appropriate method at such extremely low count rates as, for example, low-level molecular interferences may not be detected. Blanks were previously determined using this method for a SiC wafer, finding no difference for the REE (see Chapter 2); however, the SiC matrix is still relatively simple in comparison to olivine. Experimental runs were bracketed with USGS reference glass BHVO-2G, which was used as the calibration standard, and SRM NIST 612, which was used as a quality control standard. Three other quality control standards were analysed: SRM NIST 616, MPI-DING GOR132-G, and KL2 (Max Planck Institute-Dingwell) (Jochum et al., 2006; Jochum et al., 2011). Accuracies for these reference materials are typically better than $\pm 7\%$.

In addition to spot analyses, 2-dimensional REE maps were made across olivine-bearing areas on three samples (P16042, P16043, and P16045). Mapping was carried out on areas of approximately 5 x 5mm, using a repetition rate of 60 Hz and a square beam diameter of 30 μm . The Aerosol Rapid Introduction System ARIS (Van Malderen et al., 2015) was used to connect the laser cell to the ICP-MS torch. Quantitative REE concentrations from the 2-dimensional maps were extracted from the maps using a new add-in in Iolite's trace element data reduction scheme (Woodhead et al., 2007) called Monocle (Petrus et al., 2017). Petrus et al. (2017) have demonstrated that accurate single digit ppb concentrations can be analysed with laser spot sizes as small as 20 x 20 μm (30 x 30 μm spots were used in this study) thanks to pooling data pixels into regions of interest (ROIs). Pooling data into ROIs using pixels produced at small laser spot sizes reduces spatial resolution but allows bespoke areas of analysis to be chosen;

for example, ROIs can be created to allow analysis of areas containing fractures or inclusions that would have been impossible to avoid at a large spot size. Precision increases for increasing number of pixels and errors reported here represent 2x standard error.

4. Results & Discussion

4.1 Major and Trace Element Concentrations

Major element concentrations for all olivine and clinopyroxene samples are listed in Table 2. Olivines and clinopyroxenes vary in MgO and FeO across the seven samples, the most fayalitic sample, P16042, has a Mg# of 1, while the most forsteritic P16039 has a Mg# of 59. For ease of comparison, samples may be referred to by their Mg# from here onwards, e.g. P16039_{Mg59} refers to sample P16039. Clinopyroxene enstatite content varies from 0.7 to 31.7 mol per cent.

Trace element concentration data for the Skaergaard olivines and clinopyroxenes are listed in Table 3. Olivine Al and Sc contents range from 77 to 115 ppm and 7.3 to 13.7 ppm, respectively, with REE concentrations ranging from single digit ppb levels to ~3,000 ppb. Absolute concentrations of La and Lu vary from 0.68 to 56 ppb and 66 to 571 ppb, respectively. CI chondrite-normalised REE patterns are shown for olivines and clinopyroxenes in figure 1.

P16039				P16040				P16041			
Ol	1 σ	Cpx	1 σ	Plag	1 σ	Ol	1 σ	Pl	1 σ	Ol	1 σ
Na ₂ O	<d.l.	0.31	0.06	4.83	0.17	<d.l.	<d.l.	6.66	0.04	<d.l.	<d.l.
MgO	28.9	15.1	0.34	<d.l.	<d.l.	14.1	0.08	<d.l.	<d.l.	16.4	0.25
Al ₂ O ₃	<d.l.	2.54	0.2	30.1	0.98	<d.l.	<d.l.	27.7	0.2	<d.l.	1.3
SiO ₂	35.9	50.9	0.54	54.1	0.85	32.5	0.18	59	0.29	33.2	0.16
K ₂ O	<d.l.	<d.l.	<d.l.	0.33	<d.l.	<d.l.	<d.l.	0.46	0.08	<d.l.	<d.l.
CaO	<d.l.	19.3	0.42	11	0.03	0.2	0.01	7.91	0.1	<d.l.	16
TiO ₂	<d.l.	0.69	0.11	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	0.87
MnO	0.54	0.05	0.04	<d.l.	<d.l.	0.9	0.04	<d.l.	<d.l.	0.86	0.04
FeO	35.4	0.3	0.1	0.37	0	53.2	0.28	1.71	0.06	50.5	0.64
Total	101	98.3	101	101	101	101	102	102	101	101	101
Mg#	59.3	66.6				32.1	50		36.7		53
Cations											
Si	0.99	1.92	2.43		0.99	0.99	1.95	2.59	0.99	0.99	1.94
Al		0.11	1.59				0.06	1.43			0.06
Ti		0.02					0.02				0.03
Mg	1.19	0.85				0.64	0.62		0.73	0.73	0.68
Fer	0.82	0.29				1.35	0.62		1.26	1.26	0.60
Mn	0.01	0.01				0.02	0.02		0.02	0.02	0.02
Ca		0.78	0.53				0.69	0.37			0.66
Na		0.02	0.42				0.02	0.57			0.02
K			0.02					0.03			
Total	3.01	4.00	4.99		3.01	4.00	4.00	4.98	3.01	4.00	4.00

Table 2: Major element concentrations and stoichiometry of olivine (Ol), clinopyroxene (Cpx), and plagioclase (Plag).

Major element concentrations were determined by SEM EDS and given in wt %. Concentrations < 0.2 wt % were deemed below acceptable limits of accuracy for this work and are denoted by '< d.l.'. Stoichiometry for olivine, clinopyroxene, and plagioclase were calculated on the basis of 4, 6, and 8 oxygens, respectively.

	P16041			P16042			P16043			P16044		
	Plag	1 σ	Ol	1 σ	Ol	1 σ	Plag	1 σ	Ol	1 σ	Plag	1 σ
Na ₂ O	6.16	0.05	<d.l.				7.38	0.06	0.1	0	6.99	0.04
MgO	<d.l.		0.43	0.01	0.47	0.04	<d.l.		4.2	0.25	<d.l.	
Al ₂ O ₃	28.6	0.12	<d.l.		0.28	0.03	25.7	0.08	0.08	0.03	26.6	0.24
SiO ₂	57.7	0.07	29.3	0.18	48.2	0.03	60.3	0.19	30	0.18	58.8	0.2
K ₂ O	0.39	0.04	<d.l.		<d.l.		0.57	0.07	<d.l.		0.42	0.01
CaO	8.74	0.09	<d.l.		20.1	0.35	6.33	0.07	0.07	0.03	7.21	0.17
TiO ₂	<d.l.		<d.l.		<d.l.		<d.l.		0.03	0.01	<d.l.	
MnO	<d.l.		1.64	0.02	1	0.12	<d.l.		1.25	0.03	<d.l.	
FeO	0.33	0.07	68.6	0.16	29.8	0.38	0.49	0.02	63.6	0.43	0.43	0.04
Total	102		99.9		99.9		101		99.4		100	
Mg#			1.11		2.7				10.5		25.4	
Cations												
Si	2.54		0.99		2.00		2.67		0.99		2.62	
Al	1.49				0.01		1.34				1.40	
Ti					0.00				0.21			
Mg			0.02		0.03				0.29			
Fer			1.94		1.03				1.76			
Mn			0.05		0.04				0.04			
Ca	0.41				0.89		0.30				0.34	
Na	0.53				0.00		0.63				0.60	
K	0.02						0.03				0.02	
Total	4.99		3.01		4.00		4.98		3.00		4.98	

Table 2 cont.

P16044				P16045						
	Cpx	1σ	Plag	1σ	Ol	1σ	Cpx	1σ	Plag	1σ
Na ₂ O	0.28	0.03	6.79	0.17	0.07	0.01	0.3	0.04	4.62	0.43
MgO	6.6	0.57	<d.l.		28	0.58	16.3	1.53	<d.l.	
Al ₂ O ₃	1.04	0.03	26	0.29	0.17	0.1	2.17	0.57	31.1	1.39
SiO ₂	49.4	1.47	56.7	0.73	35.8	0.36	52.5	1.2	53.9	0.75
K ₂ O	<d.l.		0.42	0.04	<d.l.		<d.l.		0.33	0.08
CaO	18	0.08	7.03	0.02	0.1	0.03	16.2	1.34	11.4	1.12
TiO ₂	0.79	0.01	<d.l.		0.04	0.02	0.68	0.15	<d.l.	
MnO	0.5	0.02	<d.l.		0.57	0.03	0.33	0.01	<d.l.	
FeO	23.6	0.06	0.4	0.04	36.8	0.18	12.4	0.14	0.34	0.04
Total	100		97.3		102		101		102	
Mg#	33.2				57.6		70.2			
Cations										
Si	1.96		2.60		0.99		1.94		2.40	
Al	0.05		1.41				0.09		1.63	
Ti	0.02						0.02			
Mg	0.39				1.15		0.90			
Fe	0.78				0.85		0.38			
Mn	0.02				0.01		0.01			
Ca	0.76		0.35				0.64		0.54	
Na	0.02		0.60				0.02		0.40	
K			0.02						0.02	
Total	4.00		4.98		3.01		4.00		4.99	
Table 2 cont.										

Table 2 cont.

		P16039				P16040			
		Olivine	1 σ	Clinopyroxene	1 σ	Olivine	1 σ	Clinopyroxene	1 σ
ppm	Al	77	34	19000	270	90	9	6500	150
	Ca	590	39	220000	4700	1800	110	130000	1700
	Sc	7.3	0.2	150	8	11	0	120	4
	Ti	21	2	980	30	42	3	590	5
	Co	260	2	86	1	240	7	79	1
	Ni	950	3	290	7	12	0	3.6	0.3
ppb	Ga	200	61	9840	610	140	6	6300	79
	Rb	60		26	7	26		33	4
	Sr	280		25000	530	15		18000	360
	Y	490	110	20000	970	860	31	22000	1200
	Zr	270	62	22000	1300	460	110	20000	1100
	Nb	2.7	0.3	130	11	1.8		37	5
	La	26	8	4200	420	12	1	1100	42
	Ce	33	14	13000	1600	36	7	5100	180
	Pr	n.a.		1900	210	n.a.		1200	45
	Nd	14	6	9400	870	28	3	8100	290
	Sm	n.a.		3200	160	n.a.		3400	190
	Eu	n.a.		970	27	n.a.		950	31
	Gd	9.0	2.0	3800	170	22	3	4400	230
	Dy	42	5	4300	180	82	8	4700	250
	Ho	n.a.		830	30	n.a.		900	51
	Er	100	7	2200	58	170	11	2400	150
	Tm	n.a.		310	20	n.a.		330	18
	Yb	310	13	2000	98	440	16	2100	120
	Lu	73	2	270	16	94	3	310	20
	Hf	9.0		910	1	14	1	860	37
	Ta	<1.5		13	1	<1.3		3.5	0.1

Table 3: Trace element concentrations of olivine and clinopyroxene

Trace element concentrations determined by LA-QICP-MS, given in ppm and ppb. Errors are given in 1 σ , calculated as one standard deviation of measured replicates. Not analysed: n.a.

Chapter 3

		P16041				P16042			
		Olivine	1σ	Clinopyroxene	1σ	Olivine	1σ	Clinopyroxene	1σ
ppm	Al	86	12	7100	520	120	55	3700	1100
	Ca	1900	280	120000	3800	6700	1100	150000	13000
	Sc	14	0	140	3	9.5	0.3	81	1
	Ti	44	0	590	64	68	6	140	11
	Co	240	5	72	0	34	3	17	1
	Ni	20	1	5.7	0	<0.78		<0.91	
ppb	Ga	160	13	6500	140	370	58	8700	670
	Rb	480	90	<9.1		37	12	1200	110
	Sr	380	8	16000	1300	2300	1900	22000	450
	Y	1100	150	26000	1900	13000	1400	170000	8600
	Zr	1500	99	23000	3800	1600	290	19000	1000
	Nb	6.7	0.2	32	1	36	15	550	6
	La	15	10	3100	620	39	24	4500	120
	Ce	30	20	11000	2600	150	110	20000	510
	Pr	n.a.		1900	400	n.a.		4300	93
	Nd	10	5	8700	530	160	97	30000	500
	Sm	n.a.		3900	790	n.a.		13000	450
	Eu	n.a.		960	45	n.a.		2600	250
	Gd	21	0.0260	4400	110	470	170	20000	620
	Dy	89	17	5500	340	1500	360	28000	1600
	Ho	n.a.		1100	120	n.a.		6600	190
	Er	220	14	3100	350	1900	350	21000	520
	Tm	n.a.		430	41	n.a.		3200	180
	Yb	490	29	2700	270	3000	380	20250	2080
	Lu	100	6	380	39	570	59	3500	270
	Hf	44	4	900	9	35	1	530	38
	Ta	<73		3.0	0.1	<2.5		38	3

Table 3 cont.

Chapter 3

		P16043				P16044			
		Olivine	1σ	Clinopyroxene	1σ	Olivine	1σ	Clinopyroxene	1σ
ppm	Al	130	100	n.a.		150	23	n.a.	
	Ca	n.a.		n.a.		n.a.		n.a.	
	Sc	13	2	240	7	18	1	210	3
	Ti	n.a.		n.a.		n.a.		n.a.	
	Co	100	4	44	2	130	12	48	1
	Ni	0.07	0.01	0.096	0.012	0.14	0.02	0.12	0.01
ppb	Ga	n.a.		n.a.		n.a.		n.a.	
	Rb	39	7	31	31	33	5	8.6	1.1
	Sr	320	21	29000	980	160	40	26000	990
	Y	3600	870	20000	980	2500	350	19000	1000
	Zr	2100	310	21000	2200	1500	420	19000	1700
	Nb	120	40	52	9	5.2	1.5	40	2
	La	57	14	1500	57	50	8	1300	83
	Ce	130	56	6600	450	170	6	6300	370
	Pr	25	15	n.a.		49	8	n.a.	
	Nd	150	44	8800	520	230	37	8300	650
	Sm	68	7	3700	200	79	14	3600	160
	Eu	45	17	n.a.		48	37	n.a.	
	Gd	250	83	4400	200	130	13	4400	160
	Dy	540	150	4200	220	270	44	4000	150
	Ho	n.a.		n.a.		n.a.		n.a.	
	Er	730	160	2000	82	480	20	2000	91
	Tm	n.a.		n.a.		n.a.		n.a.	
	Yb	1500	220	1900	48	1100	62	1900	37
	Lu	330	19	340	17	230	8	320	12
	Hf	54	15	920	88	29.	2	850	59
	Ta	0.01	4.0	4.2	0.7	<0.5		3.7	0.3

Table 3 cont.

P16045					
		Olivine	1σ	Clinopyroxene	1σ
ppm	Al	n.a.		n.a.	
	Ca	n.a.		n.a.	
	Sc	7.4	0.4	100	9
	Ti	n.a.		n.a.	
	Co	250	5	59	3
	Ni	780	38	190	4
ppb	Ga	n.a.		n.a.	
	Rb	2.3	0.1	760	1300
	Sr	7.7	10.9	18000	1500
	Y	490	62	16000	570
	Zr	1100	280	25000	7800
	Nb	5.9	5.7	390	270
	La	0.68	0.010	2500	61
	Ce	1.8	0.4	6400	610
	Pr	0.28		n.a.	
	Nd	1.4	0.4	6300	370
	Sm	1.2	0.0	2227	133.7
	Eu	0.54		n.a.	
	Gd	5.1	1.5	3000	130
	Dy	34	5	3300	120
	Ho	n.a.		n.a.	
	Er	87	9	1700	78
	Tm	n.a.		n.a.	
	Yb	270	29	1500	60
	Lu	66	5	210	9
	Hf	36	5	1000	100
	Ta	0.03		21	9

Table 3 cont.

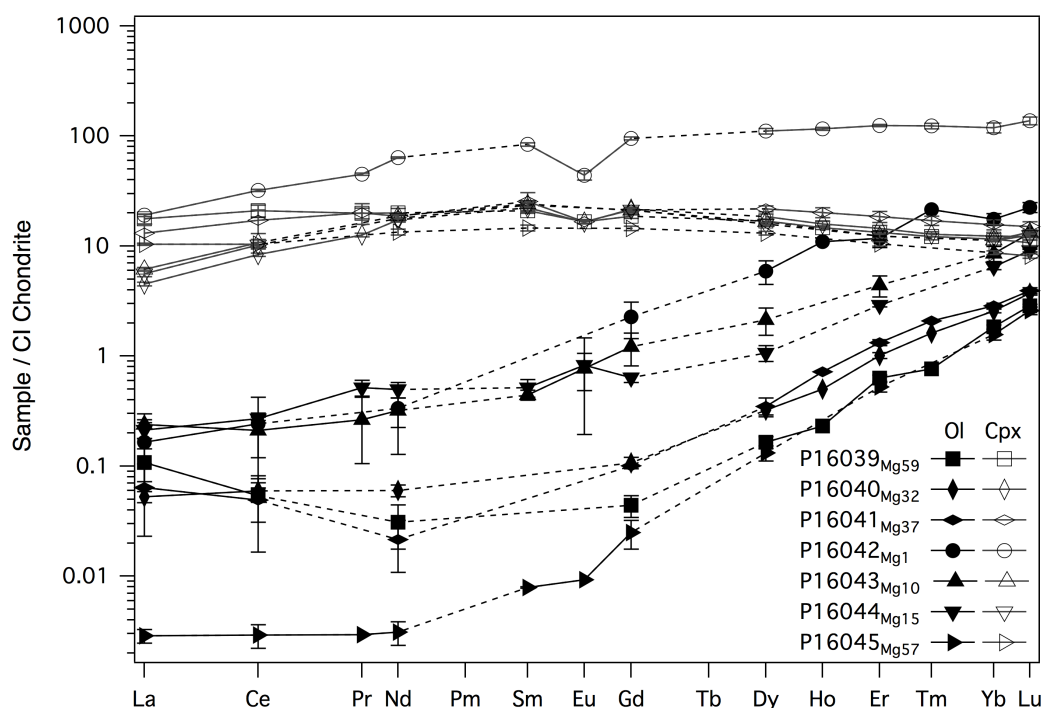


Figure 1. CI chondrite-normalised (McDonough and Sun, 1995) REE patterns in olivines (closed symbols) and clinopyroxenes (open symbols) from samples P16039_{Mg59}, P16040_{Mg32}, P16041_{Mg37}, P16042_{Mg1}, P16043_{Mg10}, P16044_{Mg15}, and P16045_{Mg57}. Errors are 1 σ of measured replicates. Elements are spaced according to VI-fold coordination ionic radii.

The CI chondrite-normalised REE patterns in the Skaergaard olivine samples show a smooth and consistent trend from the HREE to the middle REE (MREE). There is little variation in the normalised MREE/HREE ($MREE_N/HREE_N$) ratios amongst the samples, with Gd_N/Lu_N values ranging from ~ 0.01 to ~ 0.10 , resulting in broadly parallel trends. In contrast, the LREE are much more variable with La_N/Lu_N values ranging from ~ 0.001 to ~ 0.04 .

The highest REE concentrations were found in the three most fayalitic olivines, i.e. P16042_{Mg1}, P16043_{Mg10}, and P16044_{Mg15}, while the lowest are seen in the most forsteritic samples, with particularly low LREE in P16045_{Mg57}. The magnitude of difference between fayalitic and forsteritic samples is greatest around the MREE, which can be quantified by comparing the normalised Gd (Gd_N) and Lu (Lu_N) ratios between sample P16045_{Mg57} and P16042_{Mg1}. Sample P16042_{Mg1} shows Gd_N values >50 times greater than P16045_{Mg57}, while Lu_N is <10 times greater in this sample.

Clinopyroxene shows more limited variation in REE, with the exception of sample P16042_{Mg1}. As with the olivine REE patterns, the clinopyroxene from this sample also shows significantly higher MREE and HREE values. All other clinopyroxenes show very similar MREE/HREE trends, with Gd_N/Lu_N varying from 1.4 to 1.8 only. Variation amongst the LREE is only marginally greater, with La_N/Lu_N ranging from 0.4 to 1.7. Clinopyroxene REE patterns also show a negative Eu anomaly. This is consistent with the textural observation that plagioclase was the earliest crystallising phase. Under most petrological conditions, Eu is present both as divalent Eu (Eu^{2+}) and trivalent Eu (Eu^{3+}), resulting in its preferential incorporation into plagioclase (e.g. Weill and Drake, 1973), leaving residual liquid and later crystallising phases with an Eu deficit.

4.2 Olivine/Clinopyroxene and Olivine/Melt REE Partition Coefficients

The extent of equilibrium between olivine and clinopyroxene was tested by comparing the apparent measured olivine-clinopyroxene partition coefficients ($D_{ol/cpx}$) for five minor and trace elements (Y, Sc, Mn, Co, and Ni) with predicted values from the literature (Laubier et al., 2014), including partition coefficients corresponding to the respective zone of each sample in the Skaergaard Layered Series for Sc and Ni (McBirney, 1998). Apparent measured and predicted D values are shown in figure 2. Elements Sc, Ni, and Mn show very close agreement (within error) with the idealised (equilibrium) line, but there is a noticeable deviation for the most fayalitic samples (P16042_{Mg1}, P16043_{Mg10}, and P16044_{Mg15}) in Y. This deviation most likely reflects the inappropriateness of applying published $D_{ol/melt}$ values derived from magnesian systems to fayalite. Taking this into consideration, the minor and trace element data, excluding Y, provided in figure 2 establish equilibrium between olivine and clinopyroxene for all seven samples. The correlation between the Mg# of olivine and clinopyroxene also provides good corroborating evidence for equilibrium between these phases. The disparity between measured and predicted Y values highlights a potential issue with the application of published $D_{ol/melt}$ values derived from magnesian systems to fayalite. As such, the Y data is not considered for establishing equilibrium for these samples; and furthermore, the appropriateness of applying such $D_{ol/melt}$ models to olivine of varying forsterite content is explored in detail later in this section (4.2). Figures 3a-g show

apparent and predicted $D_{ol/cpx}$ values for the REE including Y. Predicted $D_{ol/cpx}$ values were calculated using the excel programs CalCpxKd v.1.0, of C. Sun (Sun and Liang, 2012) and CalOIKd v.1.0 (Sun and Liang, 2013; Sun and Liang, 2014). Figure 3 shows a close agreement between predicted and observed D values for the MREE and HREE, especially for the more forsteritic samples (e.g. Fig 3a,b). There is a deviation from predicted D values around Sm that grows in magnitude towards the lighter REE. Furthermore, the most fayalitic samples (Fig 3e,f,g) plot further from predicted values around the MREE than the more forsteritic samples, which is indicative that application of such partitioning models may not be wholly appropriate for fayalitic olivine.

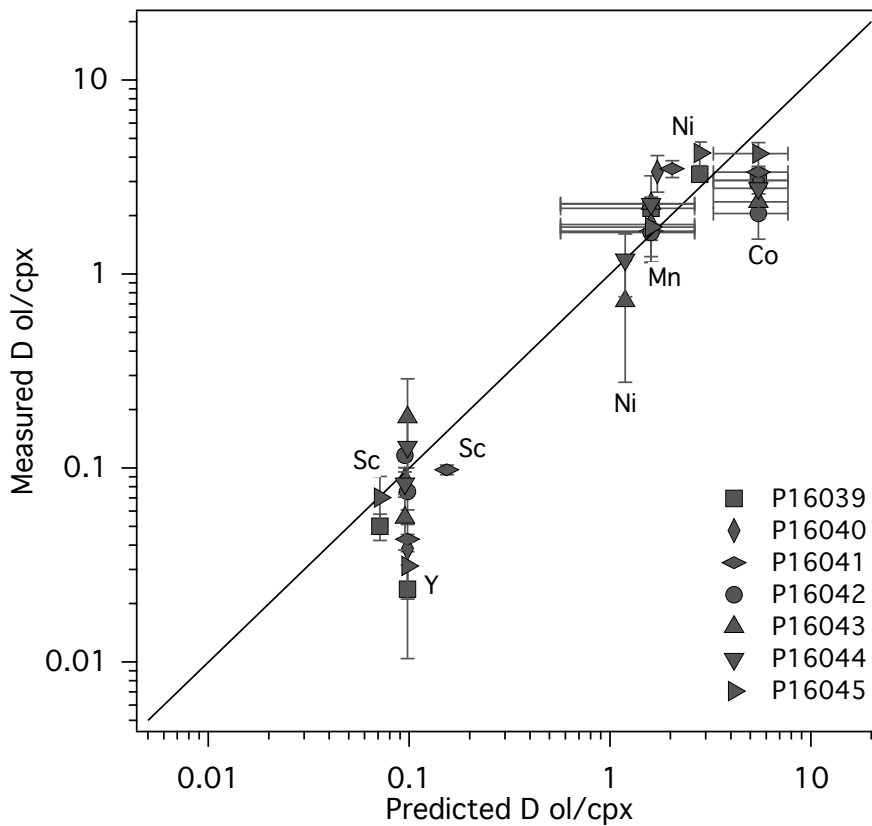


Figure 2. Predicted vs measured $D_{ol/cpx}$ values for Y, Sc, Mn, Co, and Ni. The line represents the ideal 1:1 ratio. Predicted D values from Laubier et al. (2014) (Co, Mn, and Y), McBirney and (1998) (Ni and Sc for the respective Skaergaard Zones). Errors are 2σ .

In a next step, the empirical data were compared to predictions from mineral-melt partitioning models. For this purpose, apparent partition coefficients ($D_{ol/melt}$) were calculated in a three step process: 1) Appropriate $D_{cpx/melt}$ were calculated for the observed clinopyroxene compositions using the excel program CalCpxKd v.1.0, of C. Sun (Sun and Liang, 2012). As the CalCpxKd program does not calculate $D_{cpx/melt}$ values for Sc, these were calculated using the program BIGD of Nielsen (1992) using

the temperatures and compositions of liquids for each zone of the Layered Series from McBirney and Naslund (1990). 2) Calculated $D_{cpx/melt}$ values were then combined with measured clinopyroxene trace element concentrations to calculate the composition of the equilibrium melt. 3) The equilibrium melt composition was then combined with the measured olivine trace element data to calculate olivine/melt REE partition coefficients ($D_{ol/melt}$). Apparent $D_{ol/melt}$ for the HREE are consistently around 10^{-1} while the MREE range from 10^{-2} to 10^{-3} , and are plotted in Onuma diagrams (Onuma et al. 1968) in figure 4 (panels a-g). The errors shown in figure 4 are 1σ of measured replicates of olivines, which by far exceed those of clinopyroxene measurements and the uncertainties of the model $D_{cpx/melt}$. Average errors for the LREE, MREE, and HREE are ~35%, ~20%, and ~10%, respectively.

Apparent $D_{ol/melt}$ values for each sample outline the shape of a parabola in the Onuma diagrams. The parabolic shape is best defined by Sc, the HREE and the MREE, whereas the LREE typically plot at $D_{ol/melt}$ above the right-hand side limb of the parabola. The extent of mismatch of the LREE is greatest for La and diminishes with decreasing ionic radius until Gd. The issue of LREE mismatch in natural olivines is well established in the literature and the exclusion of these data for the calculations will be justified in more detail in section 4.4. Therefore, the Brice equation (Brice, 1975; LaTourette and Burnett, 1992; Wood and Blundy, 1997) was used to calculate crystal lattice strain parameters from Sc+HREE-MREE (Gd to Lu), but omitting the REE lighter than Gd. It is necessary to include Sc to constrain the low-radius limb of the parabola, even though the exact partitioning mechanism of this element in olivine is not fully understood. It has been suggested that Sc may obey a different partitioning mechanism to that of the lanthanides whereby Sc, with an ionic radius close to that of Mg^{2+} , may occupy both the M2 and M1 sites (Evans et al., 2008). Regardless, Sc in our datasets appears to fall on the same parabola as the REE and earlier studies have also included it for determining crystal lattice strain parameters (e.g. Evans et al. 2008; Spandler and O'Neill, 2010, Imai et al 2012). Until the behaviour of Sc in olivine is fully understood, the lattice parameters calculated here should be considered as indicative.

The calculated parabolas fit the input data very well for all seven samples (Fig. 4a-g). The parabolas are approximately symmetrical and consistent with the trend predicted from lattice strain theory when partition coefficients are plotted against cationic radii

(Blundy and Wood 1994). This supports the notion that the MREE-HREE are structurally incorporated in the olivine crystal lattice, rather than being present in micro-inclusions. A very important observation from this study is that the parabolas define optimal radii (r_o) from 0.70 to 0.82 Å and corresponding optimum partition coefficients (D_o) ranging from 0.40 to 0.67. Furthermore, it is noticeable from figure 3 that the more forsteritic samples yield tighter parabolas than the more fayalitic olivines. This is expressed by the calculated values for the apparent Young's Modulus (E), which represents the rigidity of the lattice site, varying from 200 to 1200 GPa.

For comparison, figure 4 also shows the $D_{ol/melt}$ values predicted by the lattice strain model of Sun and Liang (2013), calculated for the same olivine Mg# contents using the excel program CalOLKd v.1.0 (Sun and Liang, 2013; Sun and Liang, 2014). The parameterised lattice strain model is based on 177 experiments from 6 studies spanning a range of pressure and temperature conditions. Importantly, however, olivine composition in these experiments is limited to >60 Mg# (Sun and Liang 2013). The predicted $D_{ol/melt}$ values are consistently lower than the apparent $D_{ol/melt}$ values (Fig. 3h). As with the apparent $D_{ol/melt}$ values, crystal lattice strain parameters were calculated using Sc+HREE-MREE. Relative to the apparent empirical values, the predicted $D_{ol/melt}$ values define a constant optimal radius ($r_o = 0.695$ Å) and higher optimal partition coefficients (D_o ranging from 0.25 to 1.43). The predicted $D_{ol/melt}$ values define rigid parabolas ($E = 350$, note this is lower than the value of 442 calculated using the REE+Y+Sc, Sun and Liang, 2013) of constant shape. The mismatch between E for the observed and predicted parabolas is most pronounced for the most fayalitic samples, decreasing for the higher Mg# samples. This strongly suggests that constant E and r_o values may not be appropriate for olivine. Certainly, applying such models outside their calibrated range (i.e. to lower forsterite contents Mg#<60) can result in erroneous predictions.

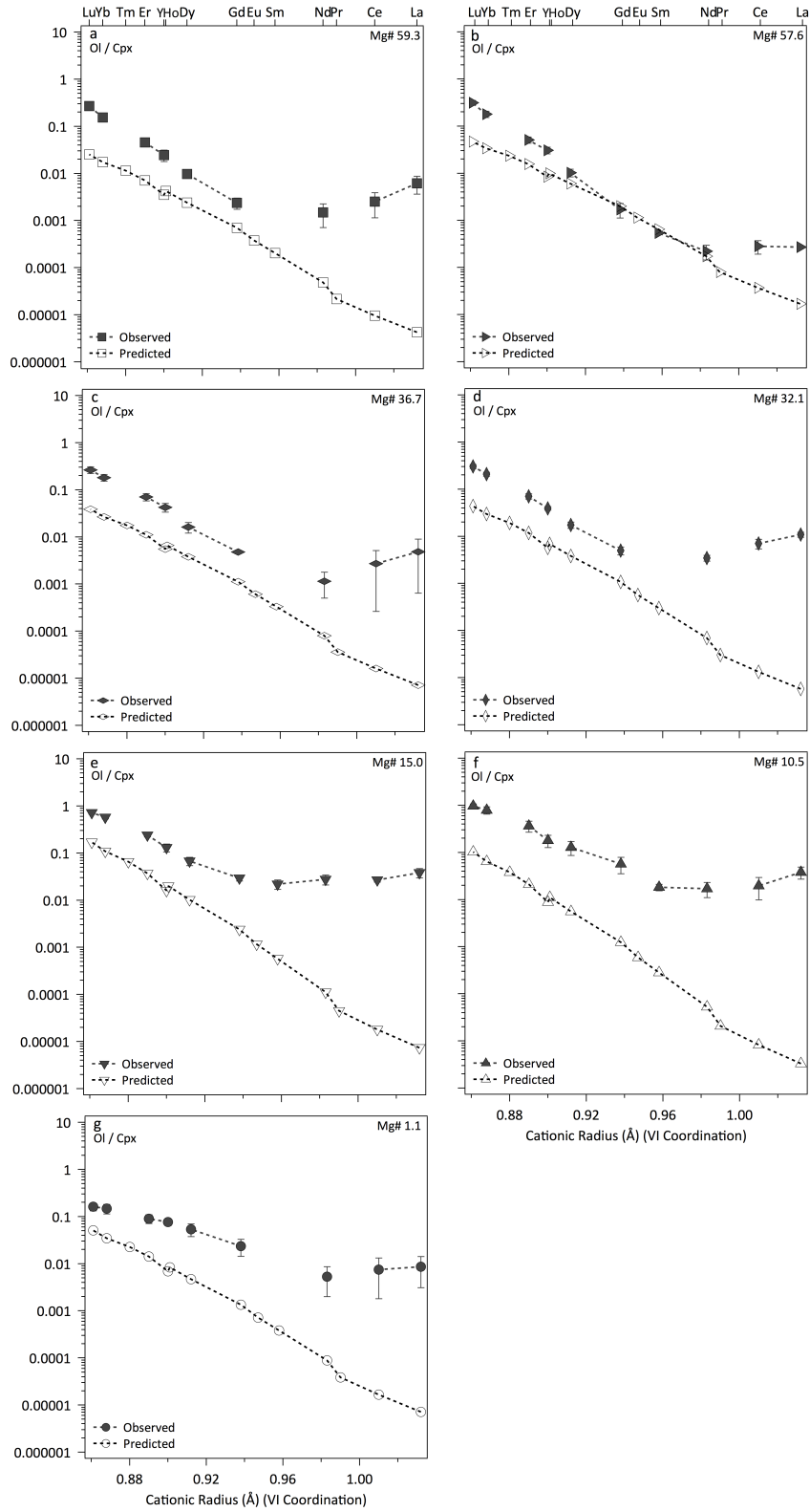


Figure 3. (a)-(g): Apparent and predicted olivine/melt partition coefficients for the REE and Sc plotted as $\ln D_{ol/cpx}$ vs cationic radius in VI coordination (Shannon et al., 1976) for a) P16039_{Mg59}, b) P16045_{Mg57}, c) P16041_{Mg37}, d) P16040_{Mg32}, e) P16044_{Mg15}, f) P16043_{Mg10}, and g) P16042_{Mg1}. Panels are ordered according to Mg# from highest (a) to lowest (g) and are annotated with each sample's respective Mg#. Predicted values were calculated using the models of Sun and Liang (2013; 2014). Errors are 1σ of measured replicates.

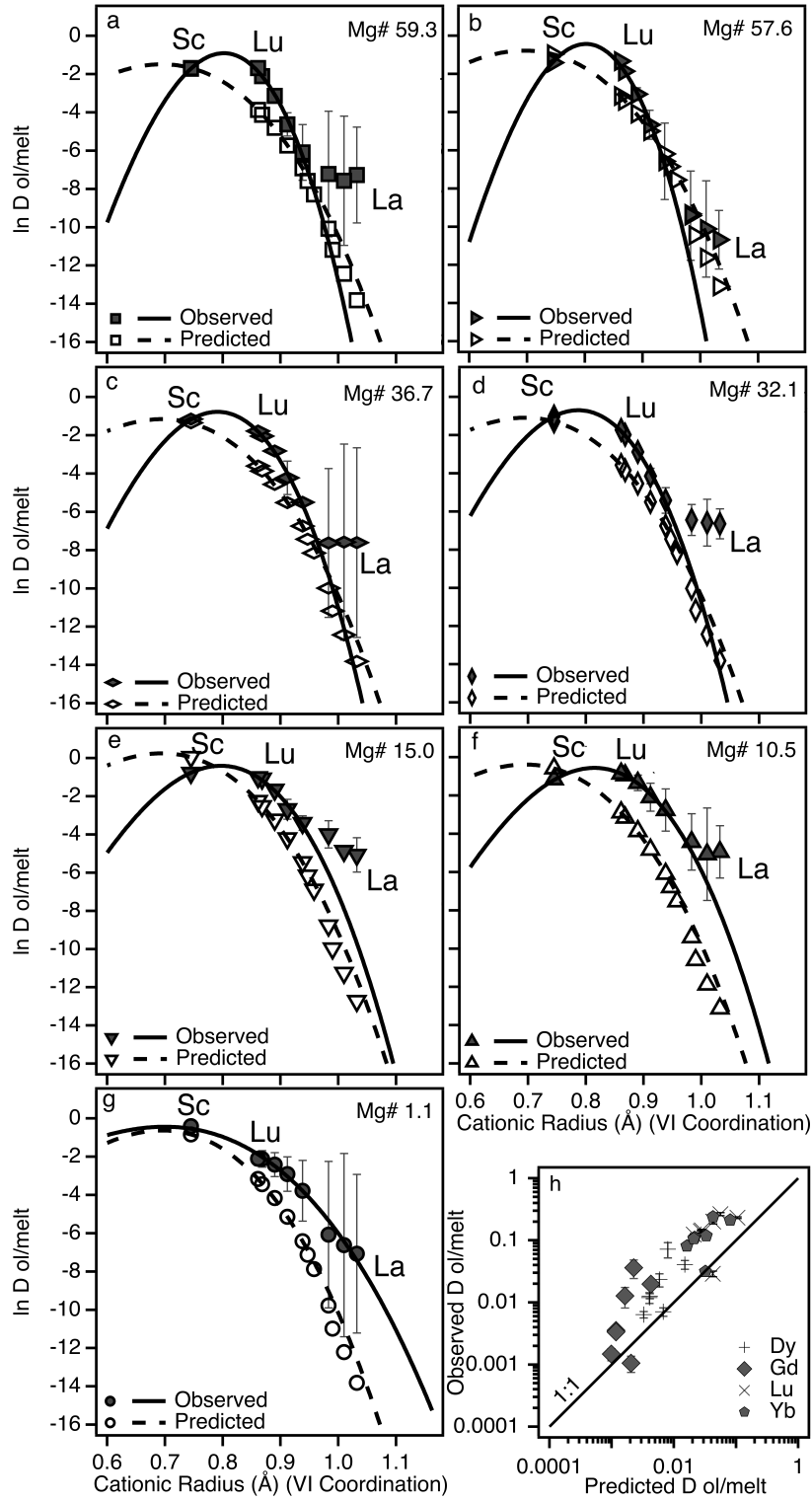


Figure 4. (a)-(g): Apparent and predicted olivine/melt partition coefficients for the REE and Sc plotted as $\ln D_{ol/melt}$ vs cationic radius in VI coordination (Shannon et al., 1976) for a) P16039_{Mg59}, b) P16045_{Mg57}, c) P16041_{Mg37}, d) P16040_{Mg32}, e) P16044_{Mg15}, f) P16043_{Mg10}, and g) P16042_{Mg1}. Parabolas were calculated with the elements Gd-Lu and Sc using the Brice Equation (Brice, 1975; LaTourette and Burnett, 1992; Wood and Blundy, 1997). Panels are ordered according to Mg# from highest (a) to lowest (g) and are annotated with each sample's respective Mg#. (h): Predicted vs observed $D_{ol/melt}$ values for Dy, Gd, Yb, and Lu; line represents the ideal 1:1 ratio. Predicted values were calculated using the model of Sun and Liang (2013; 2014). Errors are 1σ of measured replicates.

4.3 Effect of Fe on REE partitioning in olivine

Previous work has identified the dependency of cation partitioning in olivine on P , T , mineral and melt compositions (X), and oxygen fugacity (Blundy and Wood, 2003; Ford et al., 1983; Sun and Liang, 2013;). The four factors that have been identified as most strongly governing partitioning are: T (Blundy and Wood, 1994; Colson et al., 1988; Wood and Blundy, 2003); olivine Al content (Beattie, 1994; Sun and Liang, 2013); olivine Mg# (Sun and Liang, 2013); and melt SiO_2 (Evans et al., 2008). Significantly, the samples examined in this study span only a restricted range in P (~ 0.7 to ~ 3 kbar), T (1320-1420°C) and Al content (0.015-0.023 wt%) and no correlations were found between these factors and the calculated crystal lattice strain parameters.

By contrast, there is a strong correlation between forsterite content (olivine Mg#) and E (Fig. 5a), but not with D_0 or r_0 . The increase in elasticity seen with decreasing olivine Mg# suggests that the rigidity of the crystal lattice, but not necessarily the size of the lattice site, may be affected by the iron content of olivine. This change in lattice rigidity associated with the lower Mg# manifests as a broader parabola (Fig. 4), where the D for the HREE close to the apex of the parabola remain largely unchanged, but the MREE display higher D values in comparison to their more magnesian counterparts (Fig. 5b). It should be noted that there is also a positive correlation between T and E , however, this is likely due to the covariance of T with Mg#, because site elasticity decreases with increasing T (Fig. 5c), which is the opposite of what is expected if T were controlling site elasticity (Smyth, 1975).

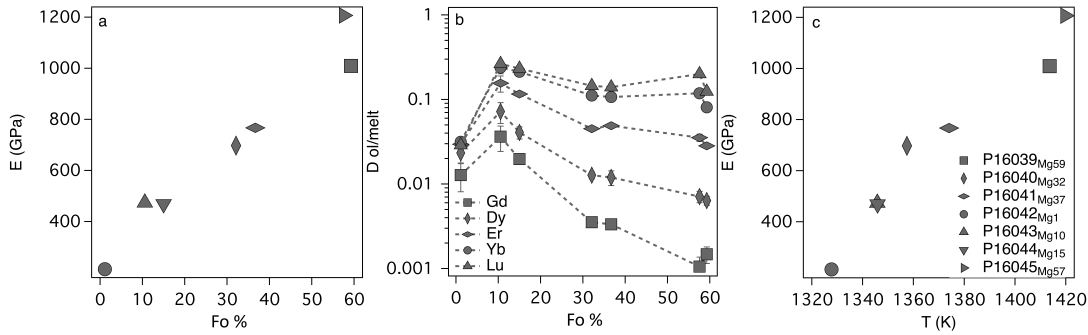


Figure 5. a) Olivine Fo% vs apparent Young's Modulus (E) (GPa), b) olivine Fo% vs $D_{ol/melt}$ for Gd, Dy, Er, Yb, and Lu, and c) T (K) vs E (GPa). Symbol keys for panels a and c are shown in panel c.

The link between olivine Fe content and crystal structure has previously been studied in some detail (Hazen, 1977; Heinemann et al., 2006; Heinemann et al., 2007; Smyth, 1975). Olivine has two octahedral lattice sites, M1 and M2, into which the cations Fe^{2+} and Mg partition. The REE are expected to favour the larger M2 site over M1 due to their relatively large ionic radii. Although the larger Fe^{2+} should also favour the M2 site, for $T > 600^\circ\text{C}$ the Fe^{2+} cation progressively disorders into the M1 octahedra towards a state of anti-order (Heinemann et al., 2006; Smyth, 1975), resulting in distortions to the octahedral site (Heinemann et al., 2006). It follows that olivine with higher Fe content may experience greater distortions of the M1 and M2 octahedral lattice sites, increasing their elasticity (lowering E) and allowing the greater accommodation of the larger MREE.

4.4 Spatial distribution of REE in olivine and the origin of anomalous LREE enrichment

Published partition coefficients for the LREE in olivine vary significantly, not only in absolute values but also in relative behaviour to the MREE and HREE (Beattie, 1994; Eggins et al., 1998a; Eggins et al., 1998b; Evans et al., 2008; Lee et al., 2007; McDade et al., 2003; McKay, 1986; Stead et al., 2016; Stosch, 1982; Sun and Liang, 2013). When plotted against cationic radius, it is frequently observed that the mineral/melt LREE partition coefficients derived from empirical samples deviate generally well

above the expected parabolic distribution that is predicted by lattice strain theory (Blundy, 1994; Wood and Blundy, 1997).

Several mechanisms have been proposed to explain the overabundance of LREE in olivine. Stosch et al. (1982) suggested that the LREE may not be structurally bound within olivine, and therefore their abundance would not be governed by lattice strain theory. Another commonly cited explanation for the LREE overabundance is that it reflects analytical artefacts (e.g. Beattie, 1994; Evans et al., 2008; McKay, 1986) due to problems with analysing elements that occur close to the limits of detection (LODs). In the present study, this explanation appears unlikely because the LODs of the applied method (Stead et al., 2016) are typically sub-ppb for the REE, with LODs for La and Ce both <0.5 ppb. This is significantly below the predicted abundance of LREE of the studied olivines. Alternatively, anomalous LREE enrichment has also been attributed to contamination of the analysed material, either at the surface, along grain boundaries and fractures or through incorporation of melt, fluid, and/or mineral inclusions (e.g. Lee et al., 2007). Attempts to minimise contamination in analyses from digested olivine involve careful selection of optically pure mineral separates and acid leaching (e.g. Eggins et al., 1998b; Fulmer et al., 2010). However, even the most meticulous procedures have not succeeded in eliminating the LREE over-enrichment. Indeed, anomalous LREE patterns persist even when olivines are analysed in-situ by laser ablation ICP-MS (Stead et al., 2016, this study), and when analysis sites are carefully selected under transmitted light, allowing internal grain fractures and inclusions to be avoided. The final plausible explanation for overabundance of LREE in olivine is sub-solidus re-equilibration with neighbouring phases that have substantially higher LREE concentrations (e.g. clinopyroxene, plagioclase, melt). For example, sub-solidus re-equilibration is known to cause redistribution of the REE among mantle minerals, including olivine (Sun and Liang, 2014). If sub-solidus re-equilibration at least in part occurred as volume diffusion, a concentric rim-core structure in LREE content could be expected if the LREE $D_{ol/neighbouring\ phase}$ decreased with T .

In an attempt to distinguish between these possibilities, a 2-D laser trace element mapping technique was deployed to visualise the REEs in olivine and surrounding phases of three samples (P16042₁, P16043₁₀, and P16045_{Mg57}). They represent nearly the full spectrum of Mg# in our sample suite and because of the systematic relaxation of

E with decreasing Mg#, there is also a strong trend in the extent of apparent over-enrichment in the LREE, from highest in P16045₅₇ (Fig. 4) to lowest in P16042₁. All elemental maps showed similar systematics but for the purpose of illustration, the trace element maps (3 x 3 mm area; Fig. 6b) for the most pronounced example (on P16045_{Mg57}) are shown for Al, Lu, La, and Eu. The back-scattered electron (BSE) image of this area on the thin section (Fig. 6a) shows a central olivine crystal enclosed on three sides by plagioclase and on one by clinopyroxene/ilmenite. The olivine in question is ~630µm in diameter but its extension and neighbouring phases in the third dimension are unknown.

The most important observation from the map is that there are clear core-rim structures in the concentrations of Al, La, and Eu in olivine, with contents increasing in a concentric fashion towards the rim. The rim-core concentration ratios for these elements analysed away from the grain boundary are all very high ($Al_{rim}/Al_{core} = 48.9$, $La_{rim}/La_{core} = 49.9$, $Eu_{rim}/Eu_{core} = 36.7$), showing that there is a very strong concentration gradient. The increase in Al, La and Eu concentration towards the grain boundary is not an artefact of signal smearing from resampling of ejecta from adjacent plagioclase because it is seen around the entire grain. Resampling artefacts lead to horizontal streaks in the direction of travel (left to right in this case) and can be readily exposed on maps (e.g. Petrus et al., 2017). It is also clear from comparison of the La and Eu maps, that La apparently has a wider and more pronounced rim of increased concentration. Lutetium, by contrast, does not show a concentration structure within the olivine.

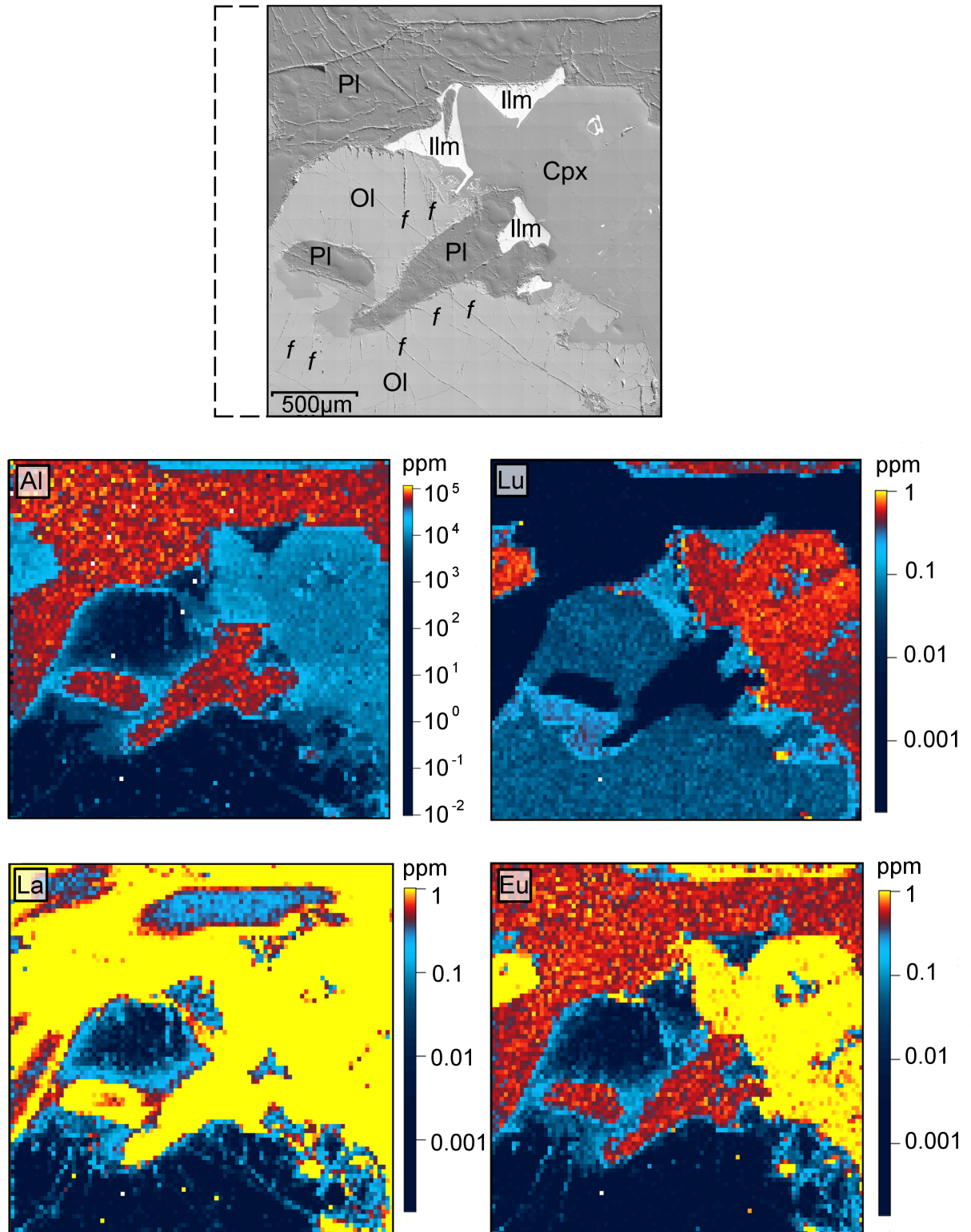


Figure 6. a) Annotated back-scattered electron (BSE) image with dashed line to represent the area mapped using the laser and b-e) semi-quantitative element maps of Al, Lu, La, and Eu, respectively, obtained on a $\sim 3 \times 3$ mm area of P16045_{Mg57}. In the BSE image plagioclase, olivine, clinopyroxene, and ilmenite are labelled with 'Pl', 'Ol', 'Cpx', and 'Ilm', respectively, while *f* represents the major fractures in the olivine. The two light-grey BSE grains to the south of the small plagioclase on the left hand side of the map are Ca-poor pyroxene.

The maps of La and Al (Fig.6) clearly also show that elevated concentrations are found along the most prominent fractures in olivine. However, there are clearly recognisable additional fractures on the BSE image that do not appear to be elevated in LREE or Al content. Thus, fracture-controlled contamination does occur but can be avoided (with transmitted light inspection during LA-ICP-MS analysis) and is not the cause of the LREE excess observed in the analysis of this study. The La map also exposes single pixels of abnormally high concentration (mainly in the olivine crystal at the bottom of the map). Where they correlate with similar pixels of other elements (e.g. the example Al) they likely represent inclusions. Very few of these were found, implying that accidental ablation of them in spot analysis mode is not the likely explanation for the observed consistent LREE excess.

The core to rim variations on the selected semi-quantitative concentration maps instead suggest that the REE inventory of the olivine are not the result of contamination or 'metasomatism' via fractures and other imperfections. To further evaluate the cause of the spatial distribution of LREE enrichment, the maps were inspected in Monocle using an interactive loupe tool (Petrus et al. 2017). Supplementary Material 1 contains a brief video recording of the user panning the loupe from the core of the olivine across the plagioclase boundary, into the plagioclase and back. The data contained in the pixels under the loupe are used to display a real-time CI-normalised REE pattern. By simultaneously tracking of the position of the loupe and the shape of the REE pattern, it becomes evident that the rim areas of the olivine have a pronounced positive Eu anomaly. This feature strongly argues in favour of sub-solidus re-equilibration between plagioclase and olivine. Theoretically, it could be possible that the increase in LREE towards the olivine rim could have resulted from crystallisation of a residual very LREE-enriched melt. However, the early crystallisation of cumulus plagioclase left evolved liquids of the Skaergaard Layered Intrusion with a relative Eu-deficit (evident also in the spot analyses of cpx and ol from this study; Fig. 1).

To test the possibility of solid-state diffusive re-equilibration, a fully quantitative elemental concentration traverse across the plagioclase-olivine interface was constructed. Readers are reminded that, because of the very low concentrations of the LREE in olivine and the HREE in plagioclase, a simple LA-QICP-MS line scan would

yield data with so much scatter that trends would be substantially compromised. Instead, the profile was constructed from the map data. This was achieved by defining a series of 14 polygons (ROI) drawn parallel to the grain boundaries (Fig. 7a) with the software tool Monocle (Petrus et al., 2017). The ROIs are drawn on a semi-quantitative element map of choice (in this case Al), and the software tool then pools the data of all pixels under the area for all elements analysed, including the internal standard (in this case Si), which can subsequently be used to obtain quantitative concentrations (listed in Table 4). The 14 ROIs represent plagioclase (3 x) and an olivine traverse (11 x) from the rim to the core, towards the opposite rim, adjacent to a separate plagioclase neighbour. The compositional traverse for the elements shown on the maps in figure 6 is illustrated on figure 7b (note log scale of y-axis). This reveals four features. Firstly, the three elements that are in much higher concentration in the plagioclase (Al, La, and Eu) show smooth and sharply decaying concentration gradients away from the plagioclase grain boundary towards the centre of the grain and then begin to increase again towards the opposite rim. Secondly, no concentration plateau is found within the olivine for any of the three elements, suggesting that re-equilibration progressed right into the core of the grain. Thirdly, Lu displays a nice plateau concentration across the entire olivine but then an exponential decrease within the plagioclase. We note that the concentration gradient of Lu within plagioclase runs against the stage travel direction used in mapping and cannot be an artefact of resampling ejecta. Finally, the software tool permits users to avoid extracting data from the grain boundary itself (Fig. 7a, see spacing of ROIs 3 and 4) thus only considering concentrations in the two phases of interest.

Concentration data from ROIs 4 (olivine near grain boundary), and 8 (olivine away from grain boundary) are also shown as CI-normalised REE patterns in figure 7d alongside co-existing plagioclase (concentrations extracted from the map using criteria $Al > 20,000$ ppm; $Sc < 5$ ppm), clinopyroxene (concentrations extracted from the map using criterion $Lu > 0.4$ ppm), and the most LREE-depleted olivine data obtained using spot analysis for P16045_{Mg57}. The comparison of patterns clearly shows the transitional nature of the REE patterns between plagioclase and olivine, including the presence of a positive Eu anomaly in olivine rims, and the distinctively different pattern for clinopyroxene with its mild negative Eu anomaly.

Chapter 3

ROI		1		2		3		4		5		6		7	
	Phase	Plagioclase	Int2SE	Plagioclase	Int2SE	Plagioclase	Int2SE	Olivine	Int2SE	Olivine	Int2SE	Olivine	Int2SE	Olivine	Int2SE
ppm	Al	210000	13000	220000	9600	230000	11000	18000	4200	4200	670	1900	320	1100	240
ppb	Sc	1900	380	1600	120	2000	130	7100	660	6900	250	7800	370	7700	320
	Y	540	76	490	54	650	75	290	59	240	18	270	24	290	24
	La	8100	2400	8200	1800	10000	1600	520	130	130	32	51	17	30	8.9
	Ce	13000	2200	14000	2700	17000	2600	790	160	190	41	110	27	46	12
	Pr	1100	120	1200	190	1400	180	66	14	17	4.1	6.6	2.2	4.3	1.9
	Nd	2500	310	2700	450	3200	290	140	30	47	11	16	6.3	9.3	6.1
	Sm	410	78	460	71	610	79	24	6.4	5.7	3.2	3.2	3	3.9	3.2
	Eu	2000	130	2100	96	2300	130	100	20	30	6.8	17	4.9	8.5	3.1
	Gd	270	68	320	52	360	35	19	5.8	6.3	3.6	8.2	4.1	3.5	2.9
	Tb	31	9	32	4.6	36	5.3	2.3	0.8	1.8	0.6	0.7	0.5	1.8	0.8
	Dy	130	25	90	17	130	19	18	5	15	3.7	16	4	18	4.1
	Ho	21	6.4	17	4.2	27	6	10	1.6	8.7	1.5	8.4	2.1	10	2.3
	Er	91	34	51	13	86	20	81	12	78	10	86	11	100	12
	Tm	7	4.6	4.5	2	3.7	1.4	12	1.6	11	1.6	12	1.8	12	1.5
	Yb	59	35	28	11	39	13	200	17	210	14	240	30	250	24
	Lu	7.2	5.6	1.7	1.3	1.8	1.2	51	3.7	50	3.8	59	4.5	61	4.8

Table 4: Trace element data for regions of interest (ROI) extracted from plagioclase and olivine.

Errors are reported as internal 2 x standard error.

Chapter 3

ROI		8		9		10		11		12		13		14	
	Phase	Olivine	Int2SE	Olivine	Int2SE	Olivine	Int2SE	Olivine	Int2SE	Olivine	Int2SE	Olivine	Int2SE	Olivine	Int2SE
ppm	Al	1100	380	560	110	510	160	820	210	1800	590	3200	920	5500	1400
ppb	Sc	8200	400	7600	490	7800	680	8100	610	7500	320	7100	390	7100	350
	Y	270	22	290	17	310	21	310	27	250	25	240	21	190	9.6
	La	23	10	13	4.1	12	5.4	26	9.5	63	23	120	38	230	58
	Ce	29	12	24	7.4	25	7.7	56	20	100	39	210	88	370	98
	Pr	2.3	2	1.3	0.8	1.8	0.7	1.9	1.3	8.4	2.9	14	4	34	7.6
	Nd	4.7	2.8	5.3	2.6	2.8	2.5	14	7.9	29	12	46	16	78	26
	Sm	0	0	0.9	1.8	4.5	4.1	0	0	3.8	3.5	8.7	4.8	14	5.7
	Eu	9.7	3.8	5.4	2.8	3.6	1.9	6.4	2.6	15	6.4	21	9.2	73	21
	Gd	4.5	3.6	5.6	4.8	5.1	4	0	0	3.6	3.3	6.9	3.2	6.5	4.4
	Tb	2	1.3	1.4	0.6	1.8	0.9	1.6	1	1.7	0.8	1.3	0.6	1	0.5
	Dy	17	4.9	23	4.3	18	7.2	18	5	20	5.6	14	4.3	15	3.8
	Ho	9.9	2.6	11	2.2	10	1.9	12	1.9	7.6	1.7	9	1.5	6.4	1.4
	Er	84	14	100	11	110	13	96	18	100	6.7	88	13	73	13
	Tm	14	2.9	13	1.7	13	1.7	11	1.9	12	2	10	1.6	10	1.8
	Yb	260	27	240	21	270	28	220	24	210	24	200	23	200	19
	Lu	61	6.4	66	5.5	54	5.5	58	6	59	5.9	54	3.7	50	4.2

Table 4 cont.

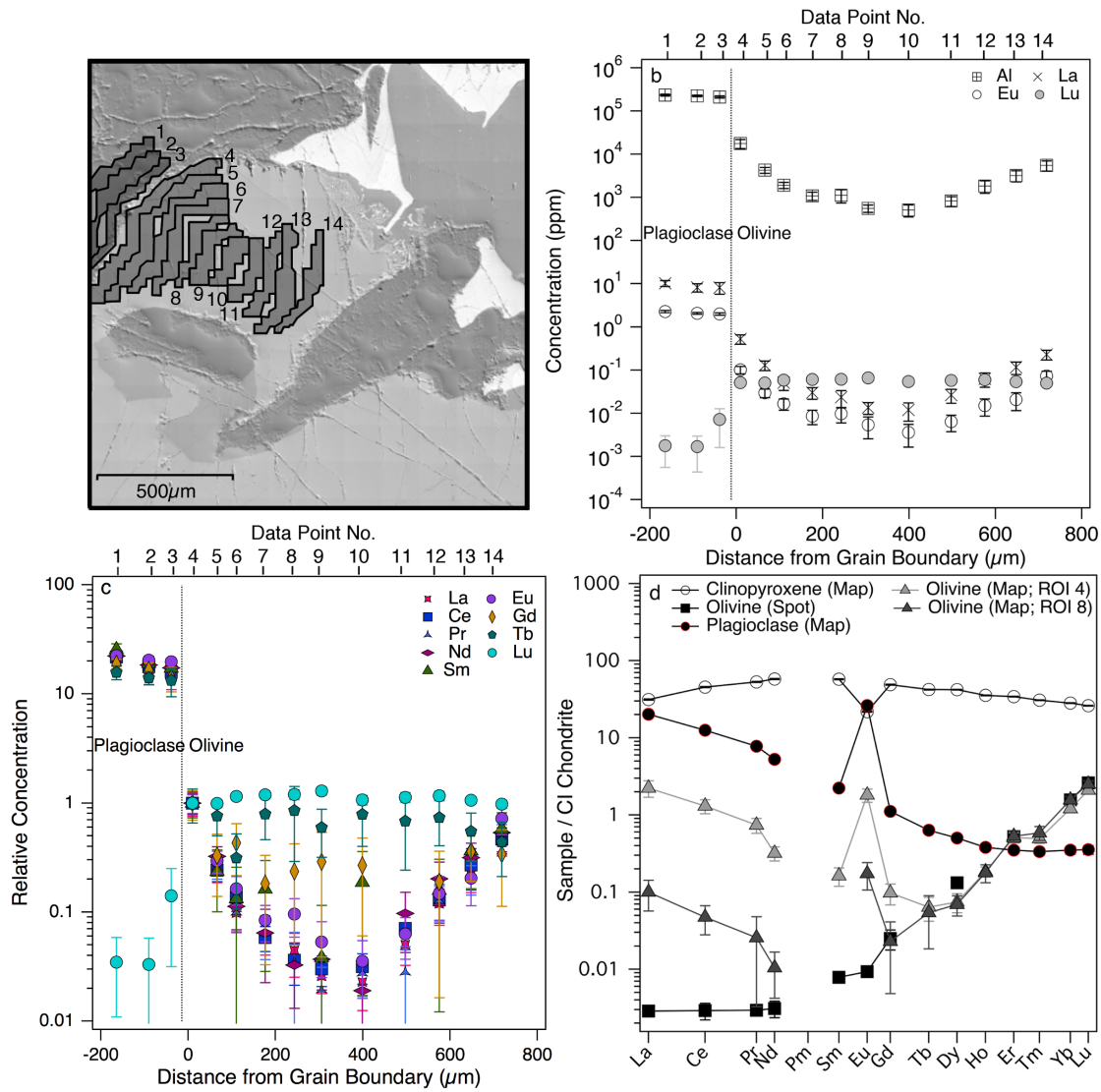


Figure 7. a) BSE image of a sub-section of sample P16045_{Mg57}, as shown in Figure 6a, annotated with the 14 ROIs from which data were extracted using Monocle to create the diffusion profiles in b) for Al, La, Eu, and Lu along a transect through plagioclase (-200 to 0 μm) and olivine (0 to 800 μm) with 2SE error bars, and in c) for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Lu along the same transect with 2SE error bars. Relative concentration contrast profiles are shown for data normalised to constant assumed olivine rim concentrations of 1 ppm. Data extraction areas (i.e. ROIs) were selected from the Al semi-quantitative map to represent zones of approximately equal concentration at intervals of $\sim 50 \mu\text{m}$ across a transect through plagioclase and olivine. d) CI chondrite-normalised (McDonough and Sun, 1995) REE patterns of olivine (both spot analyses and map ROI data), clinopyroxene (mapped concentrations extracted using monocle according to the criterion $\text{Lu} > 0.4 \text{ ppm}$), and plagioclase (mapped concentrations extracted using monocle according to the criteria $\text{Al} > 20,000 \text{ ppm}$; $\text{Sc} < 5 \text{ ppm}$) from sample P16045_{Mg57}. Errors are 1σ of measured replicates for spot analyses and 2SE for map data.

Figure 7c shows traverses of relative concentrations of the elements La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, and Lu. To aid comparison of elemental behaviours, absolute concentrations were normalised for each element to a nominal olivine edge content of 1 ppm. This shows that Tb has a flat traverse across both minerals. By contrast, Lu shows evidence of transport from olivine into plagioclase whereas the lighter REE show migration from plagioclase into olivine. The heaviest element for which this behaviour can be demonstrated is Eu, which has a much higher concentration contrast than its neighbours Sm and Gd due to the plagioclase's very pronounced Eu anomaly. The abundance of Gd is less affected in the core of the olivine and may approach that of the original concentrations dictated by olivine/melt partitioning.

With reference to the CI-normalised REE patterns of plagioclase and least re-equilibrated olivine (Fig. 7d), it can be seen that $D_{\text{ol/plag}}$ for Er and Ho is ca. 1, explaining the lack of evidence for re-equilibration. The original concentration contrast for Lu was ca. 7 in favour of olivine whereas the original concentration contrast in La was at least 7,000 in favour of plagioclase. The observation thus is that the larger the individual REE concentration contrast between olivine and plagioclase, the more pronounced the extent of sub-solidus re-equilibration. The T dependence of $D_{\text{plag/solid}}$ at subsolidus T for the REE is unknown (e.g. Bedard, 2006; Bindemann et al., 1998) but the shape of the concentration profiles (Figs. 7b,c) suggests that solid-state diffusion between these two phases may lead to attenuation of originally greater concentration contrasts. The close match in concentration gradients between Al and the LREE is consistent with a charge balanced Al, Si⁻¹ paired substitution for the REE in olivine. Cherniak (2010) determined REE diffusivities in olivine in both synthetic forsterite and natural olivine, finding them to be an order of magnitude faster than those in enstatite and diopside under most conditions. Olivine is thus more likely to display REE signatures that have been affected by diffusion than orthopyroxene or clinopyroxene (Cherniak, 2010). Neither the ionic radii of the REE nor the crystallographic orientation of natural olivine were found to influence diffusivity in olivine, with La, Dy, and Yb diffusing at similar rates to each other and along both [010] and [001] orientations (Cherniak, 2010).

The findings from olivine REE mapping are in agreement with the more general observation (from figure 4 and crystal lattice strain modelling) that Gd-Lu define the

expected parabolic relationship in the Onuma diagram but the lighter REE always deviate towards higher apparent D_s . Because olivine is always the phase with the lowest original LREE in common igneous rocks, it is exposed to the greatest LREE concentration gradients during subsolidus cooling. Fayalitic olivine, with its broader parabola and inherently higher LREE is less susceptible than forsterite, which experiences a greater concentration contrast in LREE. We therefore conclude that incorporation of LREE, likely in part via diffusion, is a common major cause in LREE over-reporting in many empirical datasets of samples that were not quench-cooled. The compilation of literature data for olivine/melt REE partitioning by Lee et al. (2007) shows that LREE over-enrichment is significantly more prevalent for natural samples (Fujimaki et al., 1984; Larsen, 1979; Matsui et al., 1977; Schnetzler and Philpotts, 1970) than for experimental run products (Kennedy et al., 1993; McDade et al., 2003; McKay, 1986), with the exception of only two experimental studies that show elevated LREE $D_{ol/melt}$ values (McKay and Weill, 1977; Shimizu et al., 1982). The experimental works of both Beattie (1994) and Evans et al. (2008) for the system CaO-MgO-Al₂O₃-SiO₂ (CMAS) also produced LREE that conform to lattice strain theory. As experimental studies occur at higher cooling rates (hundreds of degrees per minute), and typically lack a co-existing high REE phase such as plagioclase, experimental olivine REE data are expected to be less susceptible to re-equilibration effects than olivine in natural samples.

Light REE diffusion into the studied olivine was pervasive, likely due to the combination of the small crystal size, the low original LREE content, and the large surface area it shares with plagioclase. This unfortunately rules out calculation of cooling rates from the shape of the concentration profiles (Fig. 7b). It proved impossible to find any remaining optically clean, larger similar olivines in our samples for further study of diffusion time scales but the data presented here suggest that REE mapping in olivine may hold promise for reconstructing cooling histories of mafic to ultramafic igneous rocks. Nonetheless, the diffusional profile for this sample was used in conjunction with the activation energy and diffusion parameters from Cherniak (2010) to estimate the closure temperature for the system. With an initial crystallisation temperature of ~1085°C of the Skaergaard intrusion, diffusion into and from olivine would have occurred over a wide T interval of ~400°C to the REE closure temperature of ~650-700°C as the closed system of the Skaergaard Intrusion cooled. The textural

evidence of Skaergaard cumulates support a very slow cooling rate (Holness et al., 2007), suggesting the potential for prolonged re-equilibration. Diffusional length was calculated using diffusivity values for La, Dy, and Yb in olivine from Cherniak (2010) and a cooling time of 130,000 yrs (Norton and Taylor, 1979). Resulting diffusion lengths were 0.20, 0.18, and 0.11m for La, Dy, and Yb, respectively.

The pervasive nature of diffusion into the studied olivine may also be linked to the depth at which the section cuts through the grain. If the section cut through a shallow area of the original grain, exposing an area that isn't close to the true grain core, then you would expect to observe a greater degree of diffusion than that observed at the core. This would explain the difference in the extent of diffusion between the studied olivine and the olivine present at the bottom of the map in figure 6. This second, larger olivine shows less extensive diffusion from the rim, indicating that the section through this olivine may be closer to the core of the grain.

In summary, the REE mapping of a fairly magnesian olivine ($Fo\ 57$) showed that cracks and inclusions can lead to apparent elevated LREE. However, the mapping clearly exposes the extent of this type of problem, suggesting that it is not the major cause of the widespread over-estimates of LREE concentration in olivine. Rather, maps and a quantitative traverse (extracted from the map) across an olivine show pervasive uptake of LREE from neighbouring plagioclase, including its characteristic Eu anomaly, which is much higher in original LREE concentration. This explains why extensive leaching and etching does not solve the problem. The extent of redistribution is likely to be influenced by the mineralogy of the co-existing phases, whereby the chemical disequilibrium that drives diffusion will vary between olivine and different minerals as the values of $D_{min/ol}$ with changing T are not constant. Although the diffusivity in olivine is similar across the REE (Cherniak, 2010), the same may not be true for the neighbouring crystals such that REE diffusivity in them may also control the extent of alteration of the original REE inventory in olivine.

The smooth and coherent concentration profile across the mapped olivine also suggests that LREE in olivine are in fact lattice bound, contrary to the proposal of Stosch (1982). However, considering the extremely low $D_{ol/melt}$ for the common forsteritic olivines

(due to the rigidity of the lattice), it may prove difficult to isolate areas in grains that preserve the original igneous inventory.

Conclusions

Rare earth element concentrations were determined for olivine and clinopyroxene from seven samples from the Skaergaard Layered Intrusion, over an olivine Mg# range of 1 to 59. Olivine La and Lu concentrations vary from 0.68 to 56 ppb and 66 to 571 ppb, respectively, with highest REE concentrations observed in the most fayalitic olivines.

There are systematic variations between olivine Mg#, apparent partition coefficients and crystal lattice strain model parameters. Olivine/melt partitioning parabolas define peaks with r_o from 0.70 to 0.82 Å. Significantly, there is systematic variation in the tightness of the parabolas, whereby the rigidity of the lattice site (E) is apparently dominantly influenced by the Mg# of the olivine. The fayalitic olivine display more relaxed parabolas and therefore greater accommodation of the MREE and LREE than forsteritic olivine.

To a first order, the results of this study confirm that the REE in olivine behave according to the crystal lattice strain theory and that experimental $D_{ol/melt}$ published by Sun and Liang (2013; 2014), Beattie (1994), and Evans et al. (2008) are appropriate for modelling HREE and MREE behaviour during mantle melting and appear to be the most appropriate $D_{ol/melt}$ values for modelling LREE behaviour. However, in detail, widely used predictive models for olivine REE $D_{ol/melt}$ (e.g. Sun and Liang, 2013) with constant crystal lattice parameters are likely in need of refinement, even over narrower ranges of Mg# and T . This conclusion arises from the insight gained from the studied olivines, which are much more Fe-rich than mantle olivine or olivine crystallising from typical mantle melts. They show systematic variation of E with Mg#, which is significant to interpretations of REE patterns for this phase in general.

An important discovery of this study is that REE concentrations in olivine were affected by subsolidus, solid-state re-equilibration with an adjacent more enriched phase, in this case plagioclase. This was documented with 2-D elemental mapping and has caused

core to rim increases in Al, LREE, and Eu in magnesian olivine. The discovery that LREE enrichment is accompanied by a positive Eu anomaly points to uptake of REE from neighbouring plagioclase. The distribution of LREE concentration profiles and the coupling with Al, suggest that uptake may have occurred via diffusion. In the case of La, the original concentration contrast between plagioclase and olivine was in excess of 7,000. The extent of concentration contrast apparently influenced the extent to which original REE systematics in olivine were subject to re-distribution.

In natural olivine, solid-state redistribution of the REE, and especially the LREE, should be considered a common process (see also Sun and Linag, 2014). It is proposed that secondary redistribution is a major reason for the elevated LREE $D_{ol/melt}$ values reported throughout the literature for natural olivines. The nature of the process likely involves volume diffusion but may be aided by other parameters such as the micro-structure of adjacent crystals.

Regardless of process, the results of this study argue against the analysis of olivine crystals that neighbour higher REE phases with $D_{min/ol}$ that create a chemical disequilibrium (such as clinopyroxene) in holocrystalline rocks and favour targeting grain interiors of optically pure crystals that are free of fractures and inclusions for pheno- or antecrysts in volcanic samples.

Although REE analysis in olivine remains technically challenging, the possibility of systematic diffusive redistribution of the LREE into olivine has potential for future use of olivine to illuminate interesting geological processes, including particularly study of cooling rates in magmatic systems.

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Oxide wt%	USNM111312		USNM143968		USNM122142	
	San Carlos Olivine	1s	Kakanui Pyrope	1s	Kakanui Augite	1s
Na ₂ O					1.34	0.07
MgO	50.16	0.55	19.14	0.2	16.48	0.15
Al ₂ O ₃			24.31	0.42	8.67	0.16
SiO ₂	40.34	0.57	41.36	0.4	50.21	0.48
CaO			4.94	0.06	15.6	0.14
TiO ₂			0.39	0.05	0.77	0.08
MnO			0.34	0.05		
FeO	9.7	0.05	10.62	0.1	6.38	0.09
NiO	0.38	0.02				
Total	100.99	1.03	101.28	1.06	99.82	0.98
Si	0.98		2.92		1.82	
Ti			0.02		0.02	
Al			2.02		0.37	
Cr						
Fer	0.20		0.63		0.19	
Mn			0.02			
Mg	1.82		2.01		0.89	
Ca			0.37		0.61	
Na					0.09	
tot. cat.	3.00		8.00		4.00	

Supplementary Table 1: FEG SEM EDS standard data for three USNM mineral standards. Errors are reported as 1 standard deviation (1s). Stoichiometry for olivine, pyrope, and augite was calculated based on 4, 12, and 6 oxygens, respectively.

ppm	NIST 616	1s	BHVO 2-G	1s	KL 2-G	1s	GOR 132-G	1s
Mg	36.2	0.2	47200	1410	47910	1120	148000	6370
Al	11300	251	78100	2610	77100	1690	63200	2250
Ca	85300	3450	83600	2000	79900	354	63300	2690
Sc	3.45	0.10	33.3	1.8	34.1	3.7	39.1	3.1
Ti	39.6	1.7	1890	84	1720	48	233	9
Co	<0.3	0.1	45.0	3.0	46.0	3.5	99.2	4.4
Ni	<0.43	0.25	123	3	116	3	1266	54
Ga	0.427	0.011	20.4	0.5	21.0	0.2	10.7	0.3
Rb	0.110	0.011	9.18	0.10	8.95	0.11	2.14	0.07
Sr	41.9	1.8	347	6	321	9	15.5	0.5
Y	0.029	0.007	23.5	1.2	25.0	1.3	13.4	0.2
Zr	0.094	0.028	158	10	146	8	10.5	0.5
Nb	0.025	0.006	18.4	0.4	15.2	0.2	0.059	0.001
La	0.030	0.004	15.6	0.6	13.7	0.9	0.086	0.007
Ce	0.030	0.005	38.7	1.4	34.4	2.3	0.388	0.041
Pr	0.021	0.004	5.35	0.16	4.71	0.00	0.089	0.004
Nd	0.022	0.007	25.1	1.1	22.3	1.8	0.707	0.042
Sm	0.017	0.008	6.10	0.13	5.74	0.07	0.542	0.028
Eu	0.015	0.003	2.02	0.08	1.91	0.00	0.266	0.011
Gd	0.017	0.007	5.94	0.35	5.83	0.56	1.19	0.10
Dy	0.016	0.005	5.32	0.32	5.40	0.53	2.10	0.22
Ho	0.016	0.005	0.926	0.046	0.939	0.048	0.525	0.035
Er	0.015	0.002	2.51	0.18	2.58	0.26	1.54	0.19
Tm	0.012	0.001	0.319	0.013	0.337	0.005	0.241	0.004
Yb	0.017	0.003	2.05	0.14	2.12	0.21	1.56	0.19
Lu	0.013	0.002	0.278	0.023	0.289	0.032	0.230	0.029
Hf	0.014	0.006	4.04	0.24	3.84	0.24	0.353	0.008
Ta	0.030	0.005	1.16	0.05	0.956	0.020	0.029	0.000

Supplementary Table 2: LA-QICP-MS data for standards NIST SRM 616, BHVO 2-G, KL 2-G, and GOR 132-G. Errors are reported as 1 standard deviation (1s).

Chapter 4: REE enrichment in the Kaapvaal craton: insights from olivine

Target Journal: *Geochimica et Cosmochimica Acta*

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1. Introduction

The Earth's cratonic subcontinental lithospheric mantle (C-SCLM) was formed between 4 and 2.4 Ga ago and is composed predominantly of ultramafic rocks, and underneath Archaean cratons is typically ~210 km deep. Peridotite xenoliths from the C-SCLM may be entrained in kimberlites or alkali basalts and undergo rapid exhumation to the surface. These xenoliths offer precious insight into the processes that have affected the C-SCLM over time, such as melt depletion and enrichment events (e.g. Gibson et al., 2008) as well as craton formation and stabilisation. The C-SCLM is extremely depleted in Al_2O_3 , CaO , and FeO . Olivine from the C-SCLM is characterised by high Mg# and Ni contents which are considered to reflect high degrees of melting (~40%) (Boyd, 1989), as these elements are compatible during mantle melting. The Mg# of olivine is primarily a reflection of the degree of melt depletion, though metasomatism by silicate and carbonatitic melts can lower and raise the Mg# of olivine respectively (Ionov et al., 1993).

Though the C-SCLM composition is characterised by a depleted major and minor element chemistry, it often has been superimposed by conspicuous trace element enrichments that are most evident in garnet. Archaean mantle garnets typically exhibit sinusoidal or humped REE signatures despite their otherwise depleted nature (e.g. Burgess, 2004; Gibson et al., 2008; Harte and Hawkesworth, 1989; Menzies et al., 1987; Shimizu, 1975; Stachel et al., 1998; Viljoen et al., 2009). These REE patterns are widely attributed to metasomatic enrichment of an ultra-depleted precursor through interaction with LREE-enriched fluids (Stachel et al., 2004; Stachel et al., 1998), as depicted in Figure 1. Such metasomatism should also result in enrichment of H_2O and heat producing elements such as K, Th, and U, as these are associated with silicic fluids and melts, which is not seen in mantle xenoliths (Russell et al., 2001).

Much of the focus on humped REE signatures has thus far been on garnet and clinopyroxene (Burgess, 2004; Simon, 2003; Viljoen et al., 2009). Nevertheless the metasomatic processes that affected these garnets should also be evident in the other phases present. The history recorded by all phases should be consistent both in fluid composition and degree of fluid interaction. In this contribution, we test the metasomatic model on olivine and orthopyroxene in addition to garnet, using in-situ

methods developed for the analysis of REE in olivine (Stead et al., 2016). The partitioning behaviour of the REE in olivine and orthopyroxene are very similar to that of these elements in garnet, with partition coefficients (KDs) increasing by 4-5 orders of magnitude between La and Lu for each phase (e.g. Sun and Liang, 2013; Wood and Blundy, 2003). While the overall behaviour of the REE should be similar in these phases, the lower REE contents of olivine should make this mineral more susceptible to alteration and metasomatic overprinting relative to garnet and thus potentially more useful in deciphering metasomatic processes than the established method of REE analysis in garnet. The occurrence of olivine across the wide array of peridotite lithologies suggests there is also great potential for this mineral to be used more broadly in the assessment of metasomatic processes in garnet-free lithologies.

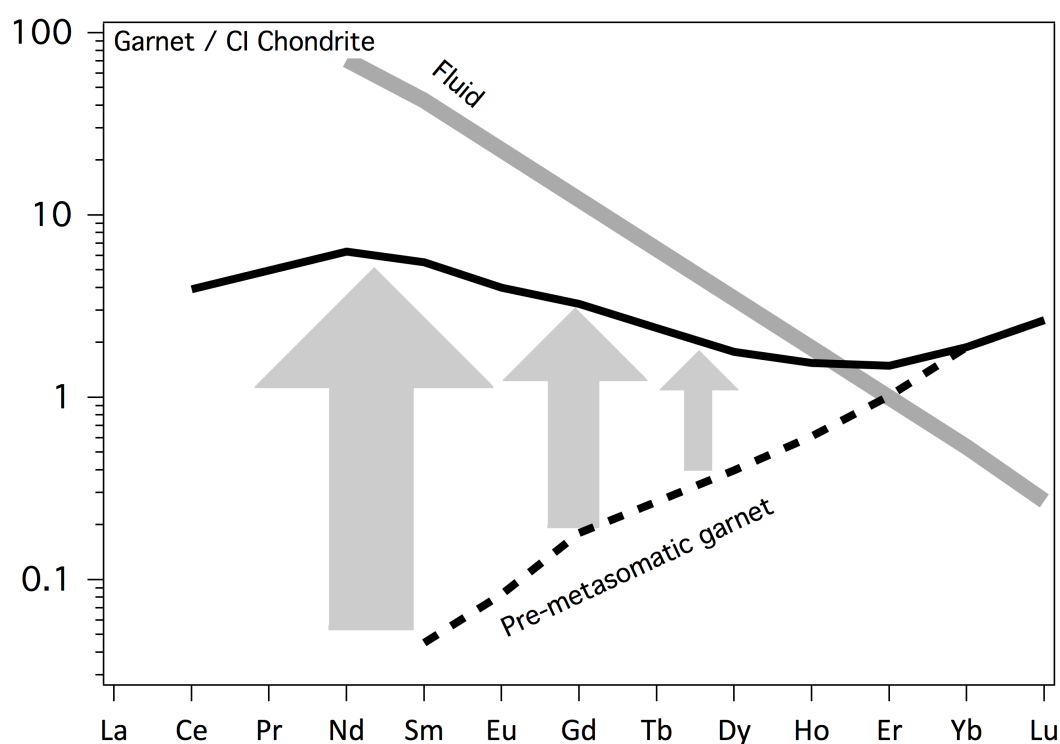


Figure 1: Schematic illustration of the metasomatic model modified from Stachel et al. (2004) for harzburgitic garnets. The ultra-depleted pre-metasomatic garnet is represented by a dashed black line, the continuous black line represents average garnet compositions of Stachel et al. (2004), the grey line represents a possible REE pattern for the metasomatic agent. Arrows indicate degree of enrichment. Chondrite-normalisation factors are from McDonough & Sun (1995).

2. Sample Description

Four peridotite xenoliths from the 86 Ma (Allsopp and Barrett, 1975) Kimberley kimberlite cluster in South Africa were chosen for this study. Garnets with sinusoidal REE patterns were first described from the Kimberley region (Richardson et al., 1984). The peridotite would have originated as the residua of a melt extraction event in which basalt or komatiite was extracted from a source that is typically thought to be of pyrolitic primitive mantle composition (Boyd, 1989, Boyd and Mertzman, 1987). It is generally thought that the peridotite subsequently experienced several enrichment events (e.g. Richardson et al., 1984, Shimizu and Richardson, 1987). The presence of garnet at proportions of ~5-10% in depleted cratonic peridotites is paradoxical, as garnet should have been removed during melting (e.g. Walter, 1998), and is typically attributed to metasomatism (e.g. Stachel, 1998) or exsolution (e.g. Cox et al., 1987, Canil, 1991).

Xenolith samples were selected based on the presence of large areas of unbroken, optically clear areas of olivine, and to include both normal and sinusoidal REE garnet compositions. Samples are coarse granular peridotites composed predominantly of anhedral olivine, orthopyroxene, and garnet. Clinopyroxene and phlogopite abundances are low to absent. Modal abundances were calculated by point counting (1,000 points per sample) and are listed in Table 1. Serpentinisation is present at low to moderate degrees in the samples. Samples are classified as garnet harzburgites or garnet lherzolites, along with their garnet G-number nomenclature according to Figure 1 (e.g. G9 lherzolite and G10 harzburgite (Grutter et al., 2004)). Samples were prepared as 180 μm thick polished sections. Key sample information is outlined in Table 1 and representative areas for each sample are shown in Figure 2.

Sample	Texture	Classification*	Modal Mineralogy (%)					T (°C) (ol)	T (°C) (opx)	P (kbar)
			Ol	Opx	Grt	Cpx	Phl			
P16046	Coarse granular	G9 Lherzolite	57.3	36.2	5.4	1.1		981	969	39.7
P16047	Coarse granular	G10 Harzburgite	56.2	33.2	5.5	2	3.1	1009	956	38.3
P16048	Coarse granular	G10 Harzburgite	66	32.1	1.9			1028	940	40.0
P16049	Coarse granular	G10 Harzburgite	49.3	46.1	4.6			973	892	46.0

Table 1: Key sample information including modal proportions of olivine (ol), orthopyroxene (opx), garnet (grt), clinopyroxene (cpx), and phlogopite (phl). Calculated temperatures (T) (°C) using Al-in-olivine (De Hoog et al. 2010) and Ca-in-orthopyroxene (Brey and Köhler, 1990), and pressures (P) (kbar) using Al-in-orthopyroxene (Brey and Köhler, 1990) are listed.

*Classification based on the G9/G10 plot of Grütter et al. (2004).

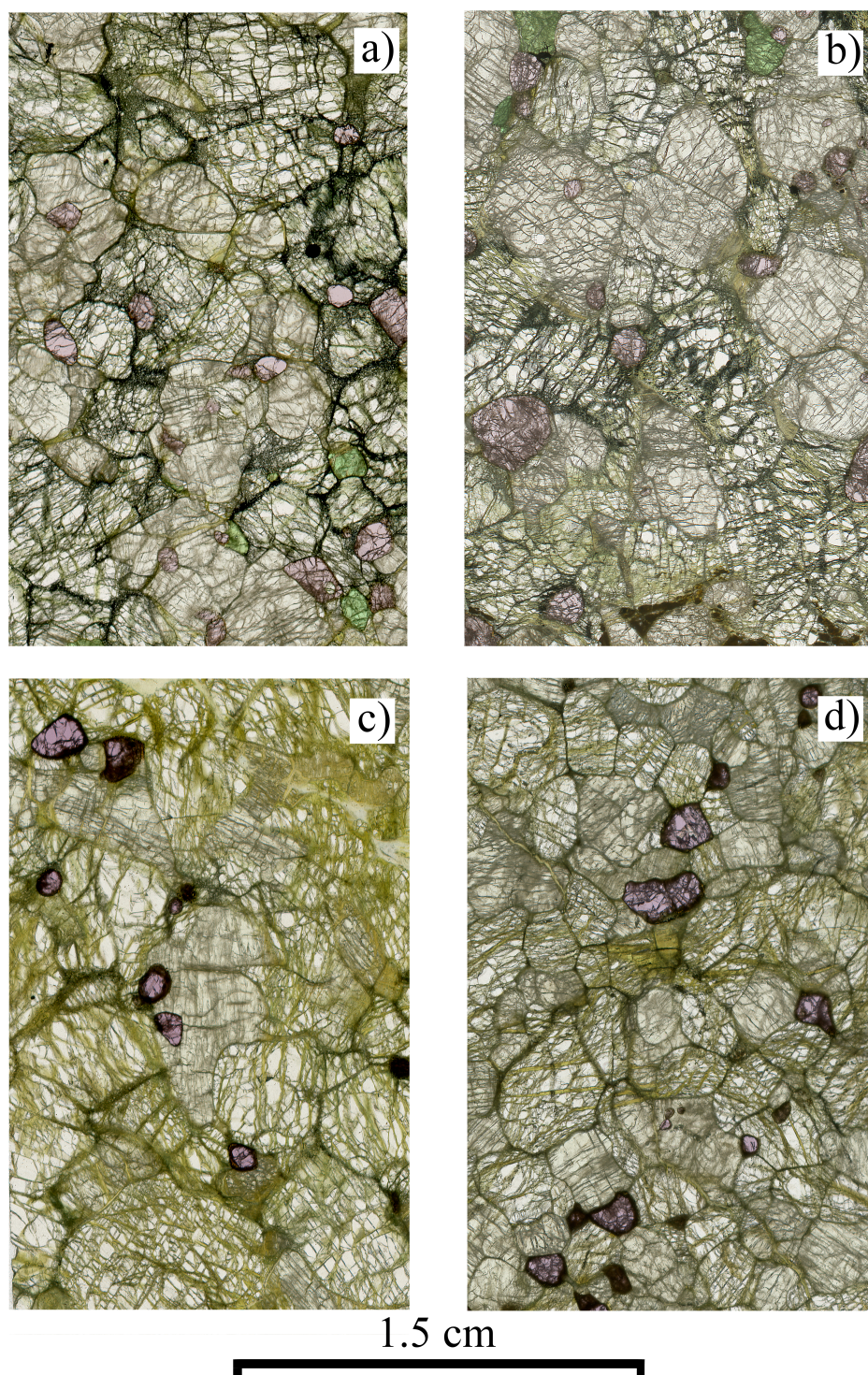


Figure 2: Thin section scans for representative areas of a) P16046, b) P16047, c) P16048, and d) P16049. Scale bar shown represents 1.5cm.

3. Methods

3.1 Major Element EDS

Field Emission Gun Scanning Electron Microscopy Energy Dispersive Spectroscopy (FEG SEM EDS) was undertaken at the iCrag lab at Trinity College Dublin (TCD) to determine major element concentrations. The instrument used was a Tescan Mira XMU, equipped with an XMAX 150mm² silicon drift energy dispersive detector and using the Oxford Aztec X-ray microanalysis software. An accelerating voltage of 20kV was used with a beam current of 300pA. The instrument was calibrated using a suite of appropriate mineral standards from the Smithsonian Institute (Jarosewich et al., 1980). Olivine (USNM 111312, n=9) and diopside (NMNH 117733, n=10) reference materials were assessed for accuracy. Major element concentrations for these reference materials are listed in Supplementary Table 1. Accuracies for Si, Fe, and Ca for both reference material were <1.8% relative to reported reference values (Jarosewich et al., 1980). Accuracies for Mg were <1.5% and <3% for olivine and diopside respectively (Jarosewich et al., 1980).

3.2 LA-QICP-MS

Trace element concentrations were determined in-situ by LA-QICP-MS at TCD using a Teledyne Photon Machines Analyte G2 laser ablation system, equipped with a 193nm ATLex 300 ArF excimer laser and a HeLex II two-volume ablation cell. The system is coupled with a Thermo iCAP-QICP-MS and utilised the Aerosol Rapid Introduction System (ARIS, Van Acker et al., 2016).

Mineral grains were inspected under transmitted light to select the optimum areas for analysis at a spot size of 156 µm. Analyses were carried out at a laser repetition rate of 60 Hz with a shot count of 2700, resulting in 45 s counting time, and were preceded by 80 s counting time on the gas blank (background). Masses ²³Na, ²⁴Mg, ²⁷Al, ⁴⁴Ca, ⁴⁵Sc, ⁵¹V, ⁵²Cr, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁸⁹Y, and ⁹⁰Zr were analysed. Olivine REE were additionally analysed the high resolution-long dwell time method outlined in Stead et

al. (2016) for masses ^{29}Si , ^{89}Y , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{160}Gd , ^{163}Dy , ^{166}Er , ^{172}Yb , and ^{175}Lu using a laser repetition rate of 80 Hz with a shot count of 2900.

Data reduction was carried out using the trace element internal standard data reduction scheme (IS DRS) using the Iolite software v2.5 (Paton et al., 2011). Mg (previously determined) was used as the internal standard for the broader elemental suite runs, while Si was used as the internal standard for the REE experimental runs.

The gas blank was subtracted to correct for the background signal. Experimental runs were bracketed with NIST 612 reference material, which was used as the calibration standard. Three quality control standards were also analysed: NIST 616, MPI-DING GOR 128-G and KL 2-G (Max Planck Institute-Dingwell) (Jochum et al., 2006; Jochum et al., 2011). Accuracies for these reference materials are typically within $\pm 10\%$. Trace element concentrations for these reference materials are listed in Supplementary Table 2.

4. Results and Discussion

4.1 Major and Trace Element Concentrations

Geothermobarometry was carried out using the Al-in-olivine thermometer of De Hoog et al. (2010), the Ca-in-orthopyroxene thermometer of Brey and Köhler (1990), and the Al-in-orthopyroxene barometer of Brey and Köhler (1990). There is good agreement between the Al-in-olivine and Ca-in-orthopyroxene thermometers, particularly for those clinopyroxene-bearing lithologies. Calculated equilibration temperatures are 973-1030°C, at pressures of 40.0-43.2 kbar.

Average major element concentrations for olivines, orthopyroxenes, garnets, and clinopyroxenes are provided in Table 2. All phases are typical of Kimberley garnet peridotites (e.g. Boyd and Mertzman, 1987; Griffin et al., 1999; Simon, 2003; Simon et al., 2007). Trace element concentrations for olivines, orthopyroxenes, and garnets, are listed in Table 3.

Garnets from samples P16046 and P16047 show lower chromium numbers (Cr#, molar ratio $\text{Cr}/(\text{Cr} + \text{Al})$) at 0.19 and 0.18 compared to the garnets from clinopyroxene-free lithologies (P16048 and P16049) with Cr# of 0.28 and 0.23. Garnet CaO (wt%) and Cr_2O_3 (wt%) are plotted in a classification diagram of G-number nomenclature after Grütter et al. (2004) in Figure 3 alongside garnet data for the Kaapvaal craton from the literature. The garnet lherzolite plots within the G9 field, while all other samples plot within the G10 field, though all four fall in close proximity to the G9/G10 boundary and are typical of garnets from Kaapvaal. Garnet Ni, Co, and Sc contents are ~30-50 ppm, ~25-50 ppm and ~95-150 ppm, respectively.

Orthopyroxenes are Al-poor ($\text{Al}_2\text{O}_3 < 1$ wt%) enstatites and show slightly higher CaO and Al_2O_3 contents in the lherzolites than the harzburgites. They are typical of orthopyroxenes from Archaean garnet facies peridotites (e.g. Gibson et al., 2008; Gregoire et al., 2003; Simon, 2003) and display high Ni (~750-780 ppm), Co (~44-51 ppm), and V (~23-35 ppm) contents, with low Sc (<6 ppm). Where present, clinopyroxene is Cr-diopside, as indicated by its Cr_2O_3 contents of 1.98 – 2.14 wt% (Stephens and Dawson, 1977).

The olivine is highly forsteritic, ranging from Mg# of 92.6 to 93.7, with slightly higher Mg# observed for the olivines from clinopyroxene-bearing lithologies than those co-existing with clinopyroxene. Olivines contain considerable amounts of Ni (~3000-3560 ppm) and Co (~100-130 ppm). Olivine Al and Na contents range from ~23-33 ppm and ~25-65 ppm respectively. Scandium is present in low concentrations in olivine (<2.5 ppm). Olivine Sc and Zr contents are shown in Figure 4 in a discrimination plot for mantle lithologies after De Hoog et al. (2010). Olivines from all four garnet peridotites from this study plot within the garnet peridotite field as defined by De Hoog et al., providing further support for the utility of these trace elements in discriminating between mantle lithologies.

Oxide wt%	Olivine				Orthopyroxene				Garnet				Clinopyroxene	
	P16046 (n=4)	P16047 (n=4)	P16048 (n=4)	P16049 (n=4)	P16046 (n=4)	P16047 (n=4)	P16048 (n=4)	P16049 (n=4)	P16046 (n=4)	P16047 (n=4)	P16048 (n=4)	P16049 (n=4)	P16046 (n=3)	P16047 (n=3)
Na ₂ O													2.33	3.15
MgO	52.1	52.1	52.3	52.1	36.7	36.4	36.9	36.8	21.8	22	21.6	21.8	16.7	15.7
Al ₂ O ₃					0.91	0.98	0.84	0.77	21.9	22	20.4	20.6	2.85	3.86
SiO ₂	40.9	40.7	41	40.7	57.9	57.5	57.8	57.4	41.8	41.6	41.6	41.8	55.1	54.7
CaO					0.42	0.39	0.33	0.33	4.63	4.15	4.63	4.72	18.7	16.9
Cr ₂ O ₃					0.31	0.32	0.36	0.33	4.09	3.77	6.02	4.42	1.98	2.14
FeO	7.38	7.1	6.68	6.25	4.49	4.32	4.11	3.82	6.87	6.61	6.43	6.17	2.27	2.45
NiO	0.43	0.44	0.44	0.4										
Total	100.8	100.3	100.4	99.5	100.7	99.9	100.3	99.5	101.1	100.1	100.7	99.5	99.9	98.9
Mg#	92.6	92.9	93.3	93.7										
Si	0.99	0.98	0.99	0.99	27.06	26.88	27.02	26.83	2.93	2.94	2.95	2.98	1.98	1.98
Al					0.48	0.52	0.44	0.41	1.81	1.83	1.70	1.73	0.12	0.16
Cr					0.21	0.22	0.25	0.23	0.23	0.21	0.34	0.25	0.06	0.06
Mg	1.87	1.88	1.88	1.89	22.13	21.95	22.25	22.19	2.28	2.32	2.28	2.32	0.89	0.85
Fet	0.15	0.14	0.13	0.13	3.49	3.36	3.19	2.97	0.40	0.39	0.38	0.37	0.07	0.07
Ni	0.01	0.01	0.01	0.01										
Ca					0.30	0.28	0.24	0.24	0.35	0.31	0.35	0.36	0.72	0.65
Na													0.16	0.22
Total cations	3.01	3.02	3.01	3.01	4.01	4.01	4.01	4.01	8.00	8.00	8.00	8.00	4.00	4.00

Table 2: Major element concentrations and stoichiometry for olivine, orthopyroxene, garnet, and clinopyroxene for four garnet peridotites. Stoichiometry for olivine, orthopyroxene, garnet, and clinopyroxene was calculated based on 4, 6, 12, and 6 oxygens, respectively.

Olivine								
	P16046	<i>1s</i>	P16047	<i>1s</i>	P16048	<i>1s</i>	P16049	<i>1s</i>
<i>ppm</i>								
Na	44	8	66	5	26	1	40	2
Al	24	4	28	3	33	1	23	2
Ca	89	25	91	13	130	6	110	13
Sc	1.3	0.2	2.5	0.2	0.95	0.13	1.3	0.1
V	3.2	0.2	2.4	0.2	3.7	0.2	3.8	0.3
Cr	120	18	140	13	130	4	110	12
Co	130	20	120	14	110	5	100	10
Ni	3100	240	3000	360	3000	32	3600	280
Cu	0.53	0.11	0.22	0.05	0.72	0.08	0.23	0.04
Zn	57	9	46	7	42	4	40	4
<i>ppb</i>								
Y	1.8	0.7	4.0	0.8	0.13	0.07	0.36	0.05
Zr	440	60	320	46	59	3	180	46
La	0.43	0.01	0.83	0.21	0.54	0.43	0.41	0.11
Ce	1.6	0.8	3.4	2.1	2.2	2.7	2.2	0.9
Pr	n.a		n.a		n.a		n.a	
Nd	2.9	0.2	3.1	1.1	2.9	1.5	3.4	0.1
Sm	0.84	0.36	0.95	0.51	0.91	0.15	1.1	0.6
Eu	n.a		n.a		n.a		n.a	
Gd	0.50	0.11	0.98	0.26	0.44	0.01	0.49	0.08
Dy	0.54	n.a	1.2	0.0	0.49	0.44	0.39	0.04
Ho	n.a		n.a		n.a		n.a	
Er	0.34	0.05	0.74	0.28	0.37	n.a	0.33	0.09
Yb	0.40	n.a	1.1	0.1	0.42	0.22	0.48	0.04
Lu	n.a		n.a		n.a		n.a	

Table 3: Trace element concentrations of olivine, orthopyroxene, and garnet. Trace element concentrations were determined by LA-QICP-MS. Errors are reported as 1s standard deviations, except in cases where only one value was above the LOD, in which case ‘*n.a*’ is noted in the 1s column.

Orthopyroxene								
	P16046	<i>Is</i>	P16047	<i>Is</i>	P16048	<i>Is</i>	P16049	<i>Is</i>
<i>ppm</i>								
Na	670	13	1100	10	290	4	630	84
Al	2700	230	3300	150	3500	130	3300	200
Ca	1900	190	2000	85	2100	99	2000	160
Sc	2.4	0.3	5.4	0.4	1.6	0.0	2.2	0.1
V	29	2	23	2	31	1	35	3
Cr	1900	130	1900	62	2100	160	1900	110
Co	51	2	48	1	46	1	44	3
Ni	750	85	750	24	780	58	780	40
Cu	0.33	0.09	0.16	0.02	0.42	0.01	0.19	0.06
Zn	32	4	31	4	27	1	27	2
<i>ppb</i>								
Y	64	2	77	4	46	<i>n.a</i>	11	2
Zr	860	110	850	33	83	1.4	320	33
La	5.8	1.1	5.0	0.6	27	<i>n.a</i>	8.3	3.1
Ce	39	8	32	3	110	<i>n.a</i>	40	4
Pr	8.6	<i>n.a</i>	6.6	1.3	30	<i>n.a</i>	13	3
Nd	60	8	52	9	200	<i>n.a</i>	85	5
Sm	22	0	19	2	38	<i>n.a</i>	32	12
Eu	10	0	7.1	0.2	20	<i>n.a</i>	9.1	0.8
Gd	24	2	21	5	11	<i>n.a</i>	18	7
Dy	18	1	21	5	5.3	<i>n.a</i>	9.3	4.3
Ho	<i>n.a</i>		<i>n.a</i>		<i>n.a</i>		<i>n.a</i>	
Er	4.9	0.9	9.2	0.4			2.4	1.6
Yb	2.3	0.4	11	1	1.2	<i>n.a</i>	1.1	0.2
Lu	<i>n.a</i>		<i>n.a</i>		<i>n.a</i>		<i>n.a</i>	

Table 3 cont.

Garnet								
	P16046	<i>I_s</i>	P16047	<i>I_s</i>	P16048	<i>I_s</i>	P16049	<i>I_s</i>
ppm								
Na								
Al							130000	3100
Ca							40000	980
Sc	83	18	160	30	110	3	120	4
V	230	1	130	15	230	20		
Cr								
Co	25	1	45	0	38	6	49	3
Ni	28	0	51	1	40	9	48	0
Cu	0.29	0.34	0.03	0.01	0.53	0.67		
Zn								
ppb								
Y	2300	95	23000	11000	570	49	2600	100
Zr	1800	190	170000	17000	22000	2500	55000	1400
La	2.5	2.5	12	3	80	13	84	8
Ce	20	10	220	51	1400	290	2200	210
Pr	10	3	130	40	81	130	950	80
Nd	130	25	2000	540	8900	210	8000	460
Sm	66	3	2000	230	2000	42	3200	460
Eu	20	2	970	42	410	28	940	40
Gd	50	3	3900	180	670	54	2200	140
Dy	31	3	4400	1400	170	12	1100	60
Ho	4.6	0.2	800	330	21	2	130	17
Er	14	1	2600	1200	57	5	190	16
Yb	18	1	2500	1500	130	10	160	15
Lu	3.2	0.0	370	210	29	1	35	8

Table 3 cont.

Clinopyroxene			
	P16046 (<i>n=1</i>)	P16047	<i>1s</i>
<i>ppm</i>			
Na	n.a	n.a	
Al	n.a	n.a	
Ca	n.a	n.a	
Sc	10	81	<i>4</i>
V	250	270	<i>9.9</i>
Cr	n.a	n.a	
Co	14	16	<i>1</i>
Ni	350	320	<i>9</i>
Cu	1.6	0.70	<i>0.10</i>
Zn	n.a	n.a	
<i>ppb</i>			
Y	400	5300	<i>230</i>
Zr	900	160000	<i>2800</i>
La	120	3200	<i>520</i>
Ce	550	13000	<i>1500</i>
Pr	120	2700	<i>260</i>
Nd	730	16000	<i>2500</i>
Sm	140	4400	<i>450</i>
Eu	30	1400	<i>170</i>
Gd	56	3500	<i>400</i>
Dy	11	1800	<i>180</i>
Ho	1.0	220	<i>24</i>
Er	1.4	480	<i>29</i>
Yb	0.50	230	<i>28</i>
Lu	0.10	25	<i>0.3</i>

Table 3 cont.

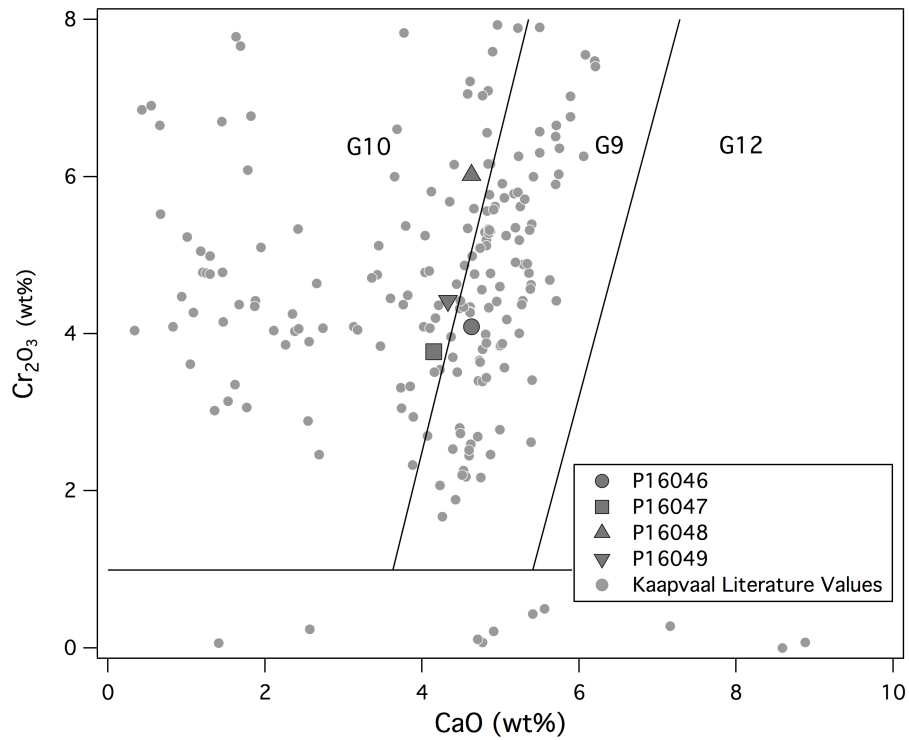


Figure 3: Classification diagram for G-number nomenclature after Grütter et al. (2004) using CaO (wt%) and Cr₂O₃ (wt%). Lines represent boundaries between G9, G10, and G12 categories. Dark grey symbols represent samples from this study. Light grey symbols represent values for garnets from Kaapvaal from the literature (Creighton et al., 2009; Gregoire et al., 2003; Lazarov et al., 2009a; Lazarov et al., 2012; Lazarov et al., 2009b; Peslier et al., 2012; Schmadicke et al., 2015; Shu and Brey, 2015; Simon et al., 2007; Wasch et al., 2009).

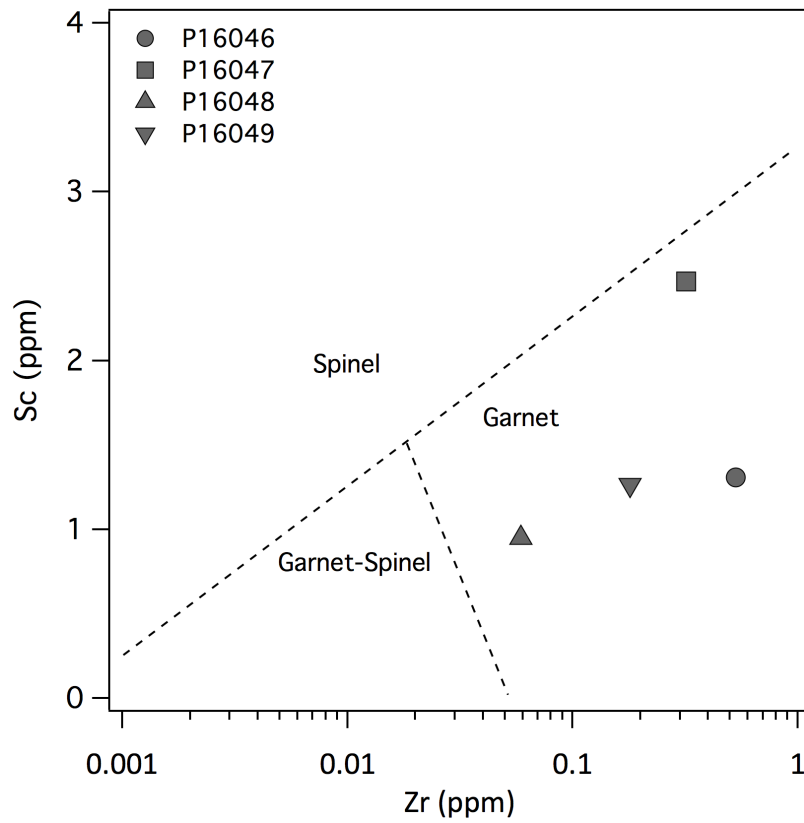


Figure 4: Discrimination plot for mantle lithologies using Zr and Sc in olivine after De Hoog et al. (2010), including the garnet peridotites from this study. Dashed lines show boundaries between spinel-, garnet-, and garnet-spinel lithologies.

CI chondrite-normalised (McDonough and Sun, 1995) REE patterns are shown for olivine, orthopyroxene, garnet, clinopyroxene, and whole rock (as reconstructed using the modal mineralogy presented in Table 1) in Figure 5. Garnet, clinopyroxene, and orthopyroxene REE patterns are typical of peridotites from the Kaapvaal craton (e.g. Simon, 2003). Three of the four samples show the sinusoidal REE patterns in garnet that are frequently observed in Kaapvaal peridotites, with only one showing a more ‘normal’ signature, with absolute concentrations of REE in garnet ranging from ~2.5 (La) to ~8700 ppb (Nd). For clarity, as the REE patterns appear to be independent of lherzolite and harzburgite classification (both petrological and using CaO-Cr₂O₃ contents), throughout this manuscript samples will henceforth be referred to as ‘sinusoidal’ (P16046, P16048, P16049) and ‘normal’ (P16047) on the basis of their garnet REE patterns. The difference between sinusoidal and normal REE patterns can be examined through normalised ratios of Sm and Er (Sm_N/Er_N), whereby $Sm_N/Er_N > 1$ indicates elevated MREE relative to the HREE. Garnets from the sinusoidal samples show Sm_N/Er_N of ~5-36, clearly demonstrating that these samples have greater MREE than HREE contents. In contrast, the Sm_N/Er_N of the normal garnet is only ~1. The sinusoidal garnet REE patterns show maxima around Nd and Sm and minima at La.

Absolute concentrations of the REE in olivine range from ~0.3 (Er) to ~3.4 ppb (Ce, Nd). Olivine from the sinusoidal samples show humped REE patterns, with maxima around Nd and Sm and minima at La and Lu. The olivine REE patterns are remarkably similar to those observed in their corresponding garnets, showing the same trough and subsequent levelling off to slight increase between Dy to Yb. The trough varies slightly between olivine and garnet, with the trough closer to Dy in olivine but Er in garnet. Olivine from the ‘normal’ sample display a Sm_N/Er_N value of ~1, this is lower than those from the sinusoidal samples which show Sm_N/Er_N of ~3-4.

Orthopyroxene REE concentrations range from ~1 to ~200 ppb. Similarly to the olivines, the orthopyroxenes from the sinusoidal samples show humped REE patterns, with maxima around Nd and Sm and minima at La and Lu. Orthopyroxenes from the sinusoidal samples show Sm_N/Er_N of ~5-14, which is greater than that of the normal sample with Sm_N/Er_N of only ~2, again illustrating the difference in relative enrichment between the MREE and the HREE for sinusoidal and normal samples.

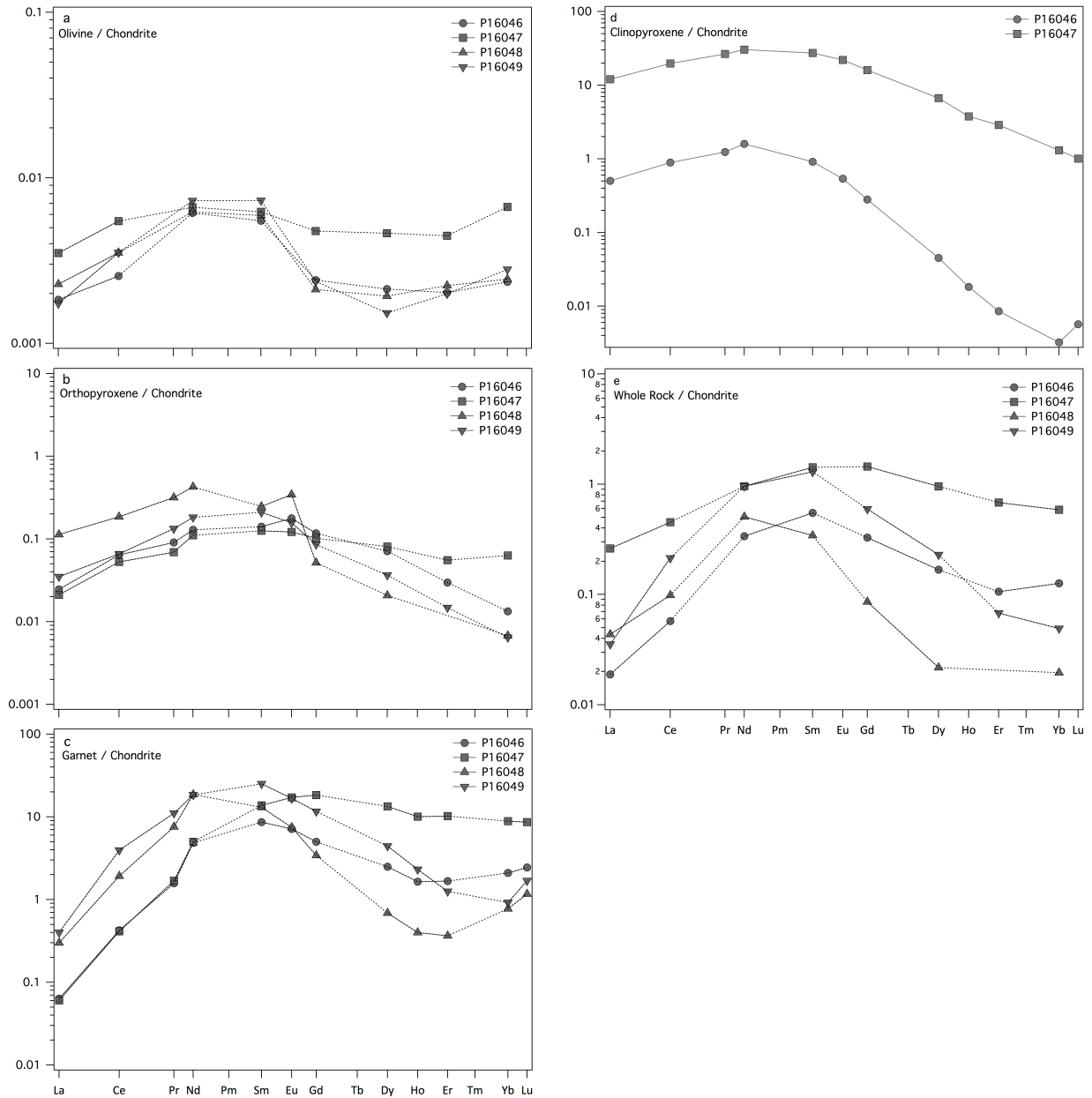


Figure 5. Chondrite-normalised (McDonough and Sun, 1995) REE patterns for a) olivine, b) orthopyroxene, c) garnet, d) clinopyroxene, and e) reconstructed whole rock values calculated using the modal mineralogy in Table 1. Elements spaced by cationic radii (VI coordination) (Shannon et al., 1976). P16046 is a G9 lherzolite; P16047, P16048 and P16049 are G10 harzburgites.

Figure 6 shows predicted and observed partition coefficients (D values) for olivine/orthopyroxene, orthopyroxene/garnet, and olivine/garnet. Predicted $D_{\text{olivine/orthopyroxene}}$ values are from Lee et al. (2007), while predicted $D_{\text{orthopyroxene/garnet}}$ and $D_{\text{olivine/garnet}}$ values combine $D_{\text{orthopyroxene/melt}}$ and $D_{\text{olivine/melt}}$, respectively, from Lee et al (2007) with $D_{\text{garnet/melt}}$ calculated using the programme CalGrtKd v1.0 (Sun and Liang 2013, 2014). Figure 6a shows good agreement between predicted and observed $D_{\text{olivine/orthopyroxene}}$ values for the HREE and MREE, with a deviation at the LREE such that La-Sm $D_{\text{olivine/orthopyroxene}}$ values are greater than predicted. This deviation is also observed in Figure 6c for $D_{\text{olivine/garnet}}$ values. In both cases the deviation is progressively greater towards the lightest REE. This deviation above predicted D values for the LREE in olivine may be due to a diffusion effect as outlined in Chapter 3. This LREE diffusion into olivine is unlikely to be from garnet, as the LREE plot above the predicted garnet D values which are representative of the conditions of equilibrium which should have been reached considering the long timescales (Ga) of cooling. Rather, this diffusion may instead be from grain boundary fluids or melts. Regardless of the cause of the elevated LREE concentrations in olivine, Figure 6 indicates that the ‘true’ LREE contents of the olivine in these samples are likely to be lower than those observed values.

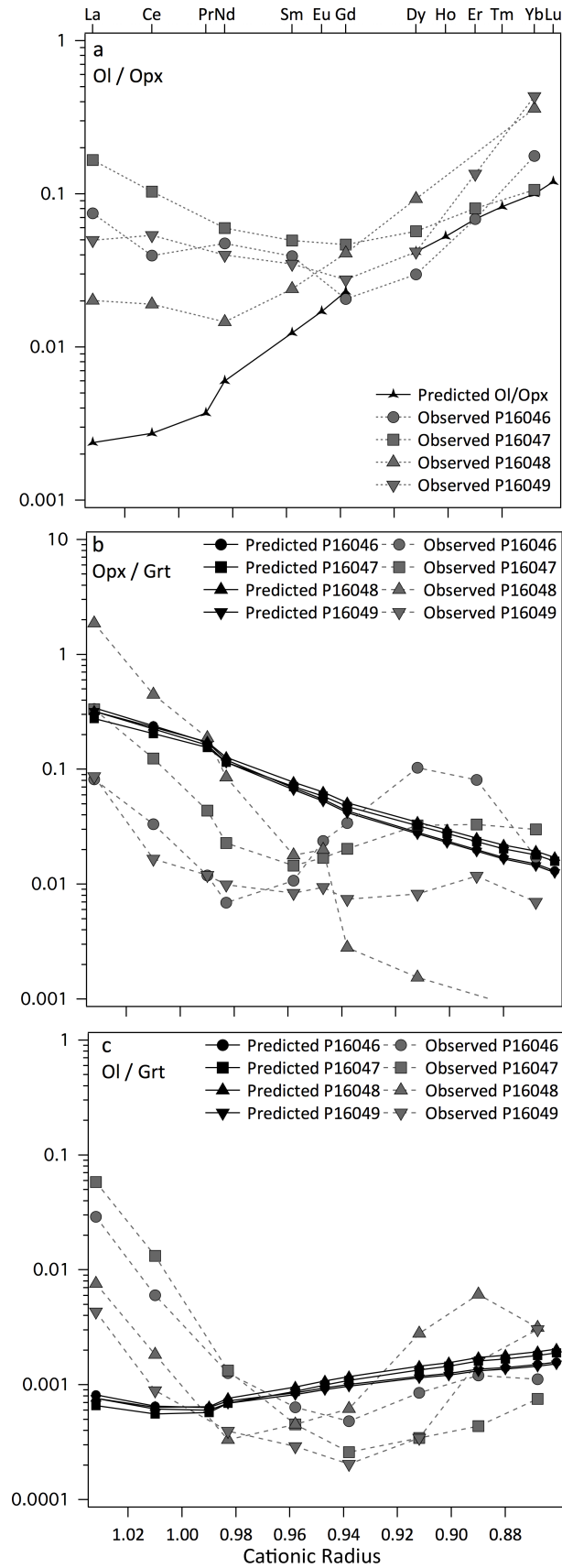


Figure 6. Partition coefficients (D values) for a) olivine / orthopyroxene, b) orthopyroxene / garnet, and c) olivine / garnet. Predicted olivine / orthopyroxene D values from Lee et al. (2007). Predicted orthopyroxene / garnet and olivine / garnet D values combine $D_{\text{orthopyroxene/melt}}$ and $D_{\text{olivine/melt}}$, respectively, from Lee et al (2007) with $D_{\text{garnet/melt}}$ calculated using the programme CalGrTKd v1.0 (Sun and Liang 2013, 2014). Cationic radii in VI coordination from Shannon (1976).

4.2 Assessing Potential Metasomatic Input

Metasomatism of the depleted SCLM is believed to be ubiquitous (e.g. Dawson, 1984) and due to both ancient and recent processes (e.g. Gregoire et al., 2003; Richardson et al., 1984). The differences between ‘sinusoidal’ and ‘normal’ REE patterns in garnets are attributed to metasomatic processes throughout the literature. The process that caused the sinusoidal REE in garnet must be ancient as such patterns are present in garnets included in diamonds (e.g. Shimizu and Richardson, 1987; Stachel and Harris, 1997; Stachel et al., 1998). Stachel et al. (1998) first proposed a metasomatic enrichment model for REE overprinting of an ultra-depleted precursor by a fluid with a very high LREE/HREE ratio to produce the typical harzburgitic garnets. In this model, lherzolitic garnets that show more normal REE patterns have been affected by a subsequent metasomatic event involving silicate melt that re-enriched the MREE and HREE, which was not experienced by the harzburgitic garnets (Stachel et al., 2004; Stachel et al., 1998). Figure 1 shows a schematic illustration of the model from Stachel et al. (2004). The schematic shows the highly fractionated LREE/HREE nature of the fluid suggested to produce the relative enrichment of the LREE, and to a lesser extent the MREE, relative to the HREE. The metasomatic model is widely accepted (e.g. Bell et al., 2005; Creighton et al., 2009; Griffin et al., 1999; Stachel et al., 2004; Stachel et al., 1998), but despite limited testing of this model (Gibson et al., 2013; Shu and Brey, 2015; Stachel et al., 2004; Ziberna et al., 2013), it has yet to be rigorously assessed.

Three of the samples in this study show garnets with sinusoidal REE patterns. According to the metasomatic model these REE patterns are the result of enrichment of an ultra-depleted precursor by an LREE-enriched fluid. The sinusoidal REE patterns that are observed in garnet are mirrored as humped patterns in olivine and orthopyroxene of other ‘depleted’ peridotites, both in this study and in the literature (Simon, 2003; Simon et al., 2007). Garnet from the remaining sample from this study shows a more normal REE pattern that would typically be explained by an additional metasomatic event involving a silicate melt to ‘flatten’ the MREE and HREE. The observed REE patterns for all present phases should therefore be the product of metasomatic overprinting of their ultra-depleted starting compositions. Hypothetical versions of such ultra-depleted starting compositions can therefore be calculated and consequently used to model and assess metasomatic input. These hypothetical

precursors were calculated for each sample (Fig. 7b) using measured Yb concentrations and partition coefficients from Lee et al. (2007) and Green et al. (2000) on the assumption that the partition coefficients for all REE in a pre-metasomatic mineral should follow the parabolic distribution of the Brice equation (Brice, 1975).

In order to assess the validity of a metasomatic origin for the REE patterns observed in this study, mass-balance calculations were carried out for olivine, orthopyroxene, and garnet with three potential metasomatic agents using the following equation:

$$XC_{o(f\text{fluid})} + (1 - X)C_{o(mineral)} = XC_{f(f\text{fluid})} + (1 - X)C_{f(mineral)} \quad (1)$$

Where X is the weight fraction of a given element in the fluid or mineral, and C_o and C_f are the initial and final concentrations. This equation can be rearranged with the introduction of partition coefficients (D), where D is equal to $C_{f(mineral)} / C_{f(f\text{fluid})}$, to isolate $C_{f(mineral)}$ as follows:

$$\begin{aligned} XC_{o(f\text{fluid})} + (1 - X)C_{o(mineral)} &= XC_{f(f\text{fluid})} + (1 - X)C_{f(mineral)} \\ Sum &= XC_{f(f\text{fluid})} + (1 - X)C_{f(mineral)} \\ &= X \frac{C_{f(mineral)}}{D} + (1 - X)C_{f(mineral)} \\ &= C_{f(mineral)} \left(\frac{X}{D} + (1 - X) \right) \\ \frac{Sum}{\left(\frac{X}{D} + (1 - X) \right)} &= C_{f(mineral)} \end{aligned} \quad (2)$$

Mineral/melt partition coefficients for olivine and pyroxene are from Lee et al. (2007) and garnet/melt partition coefficients are from Brey et al. (2008). The metasomatic agents chosen for these calculations are a carbonatitic fluid from Coltorti et al. (1999), a kimberlitic melt of Le Roex (k8/10) (2003), and high density silicic C-O-H fluid trapped as inclusions in a fibrous diamond from Kankan, Slave craton (Weiss et al., 2009). These three agents represent fluids and melts that are typically cited as causing the enriched REE profiles in garnet peridotites. CI normalised REE patterns for these

three agents are shown in Figure 7a, with all three fluids showing a high LREE/HREE ratio. Mass-balance calculations were undertaken for ten weight fraction input values, ranging from $X = 0.00001$ to $X = 0.1$, and are presented for olivine (Fig. 8), orthopyroxene (Fig. 9), and garnet (Fig. 10) alongside hypothetical pre-metasomatic olivine, orthopyroxene, and garnet are shown in Figure 7b. If the REE patterns for these samples are the result of metasomatic enrichment it should be expected that all three phases be satisfied by input from consistent fluid proportions and nature, i.e. consistent X and fluid type. Mass-balanced interactions between olivine and carbonatitic fluid, kimberlitic melt, and C-O-H fluid are shown in Figures 8 a-d, e-h, and i-l respectively.

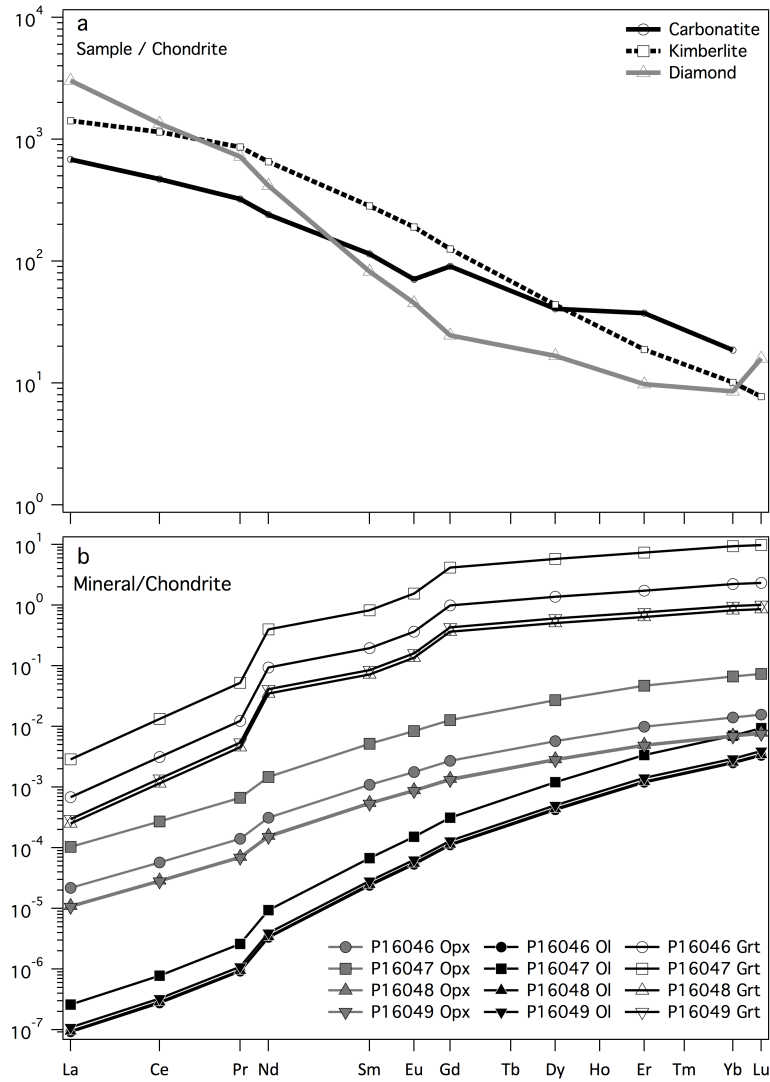


Figure 7: a) Chondrite normalised (McDonough and Sun, 1995) REE patterns for the carbonatitic fluid of Coltorti et al. (1999), kimberlitic melt of Le Roex (k8/10) (2003), and high density silicic C-O-H fluid trapped as inclusions in a fibrous diamond from Kankan, Slave craton (Weiss et al., 2009). These fluid and melt compositions were used to model metasomatic interactions with the minerals in this study. b) hypothetical pre-metasomatic (ultra-depleted) minerals that were calculated for each sample using measured Yb concentrations and partition coefficients from Lee et al. (2007) and Green et al. (2000). Elements spaced by cationic radii (VI coordination) (Shannon et al., 1976).

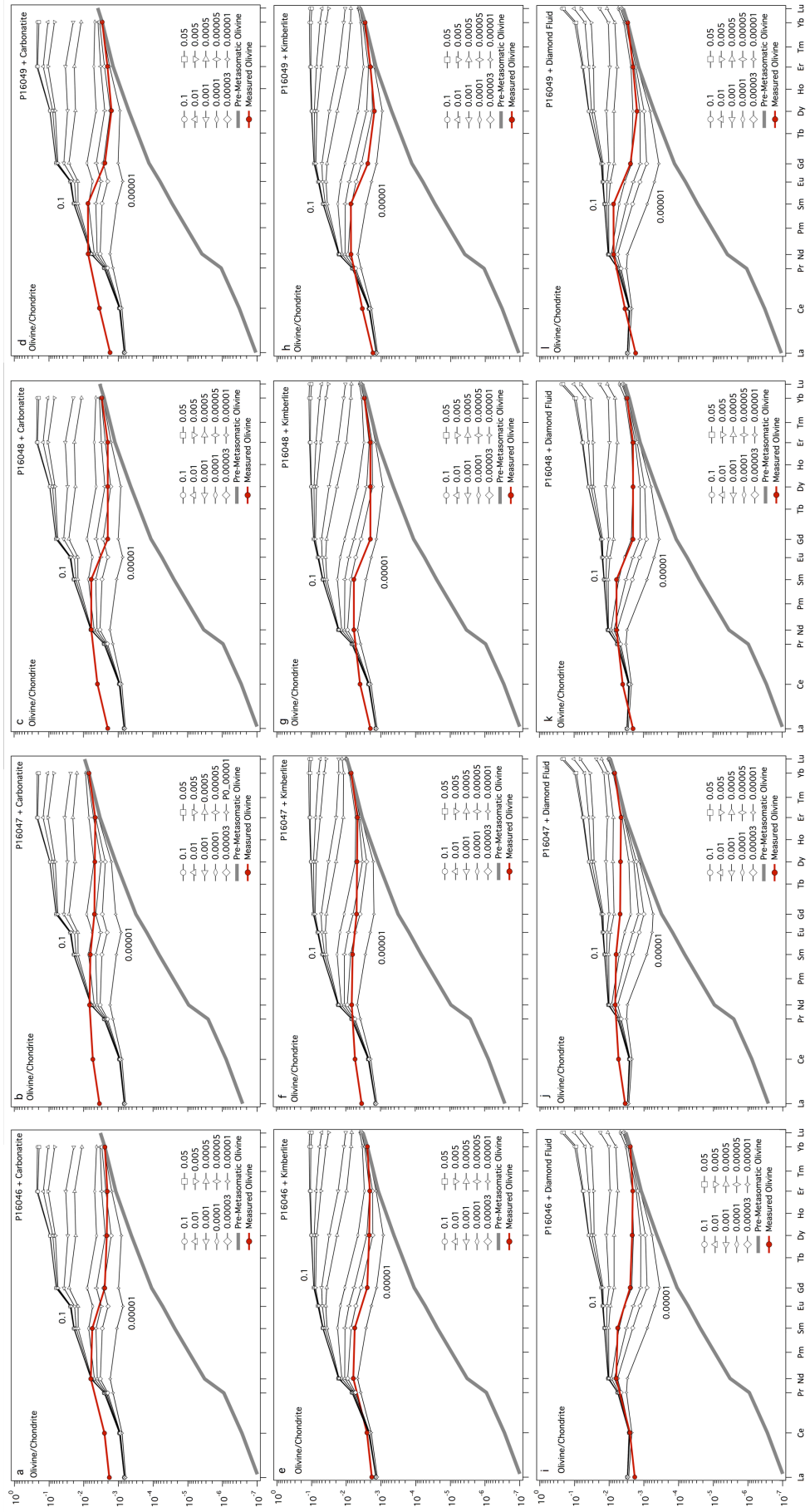


Figure 8: Chondrite-normalised REE patterns for olivines from P16046 (a,e,i), P16047 (b,f,j), P16048 (c,g,k), and P16049 (d,h,l). Red lines represent measured values, grey lines represent pre-metamorphic values, and black lines represent varying degrees of input from a carbonatic fluid (Coltorti et al., 1999) (a-d), kimberlitic melt (Le Roex et al., 2003) (e-h), and diamond C-O-H fluid (Weiss et al., 2009) (i-l). Chondrite-normalisation factors are from McDonough & Sun (1995).

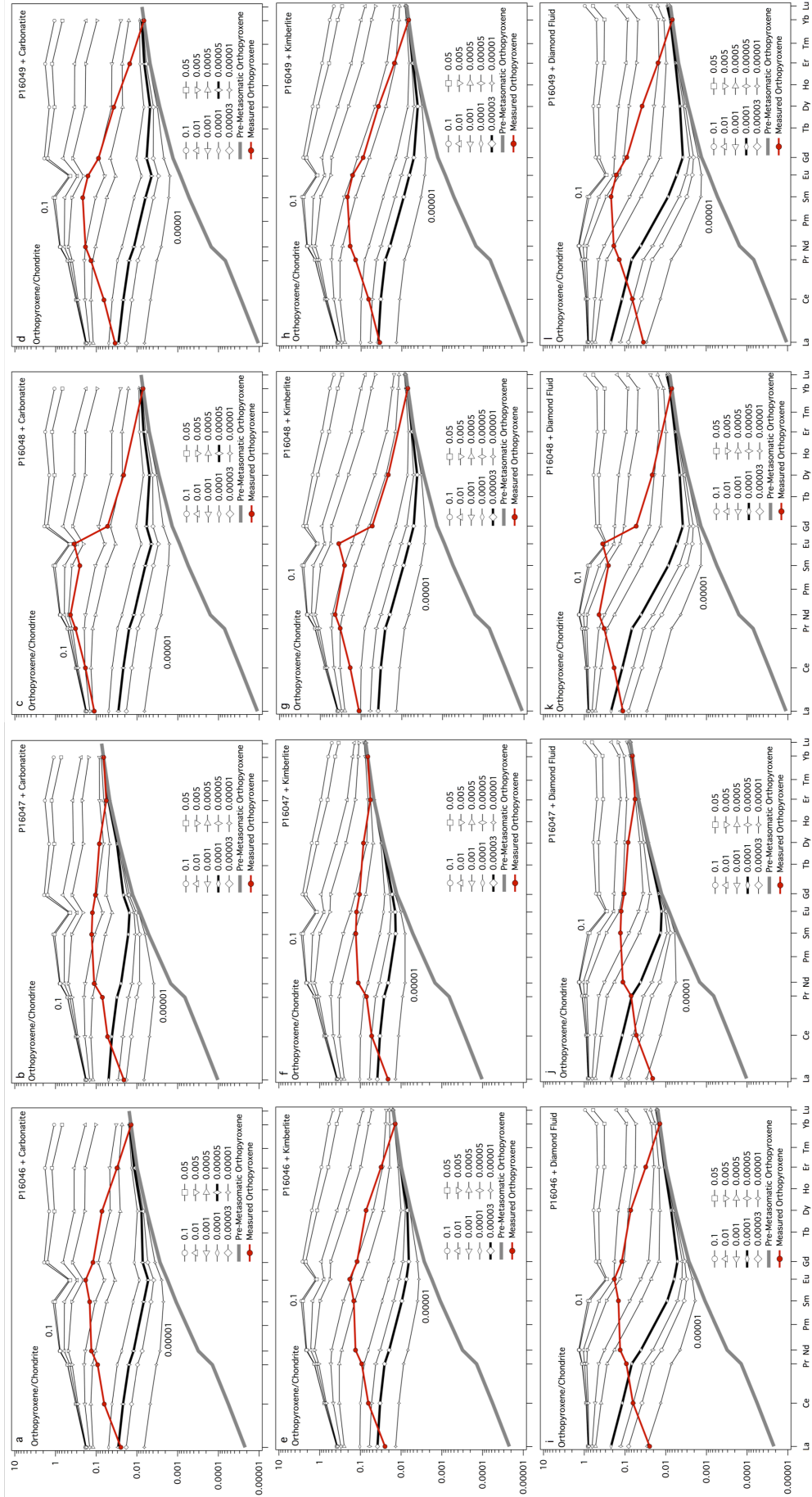


Figure 9: Chondrite-normalised REE patterns for orthopyroxenes from P16046 (a,e,i), P16047 (b,f,j), P16048 (c,g,k), and P16049 (d,h,l). Red lines represent measured values, grey lines represent pre-metasomatic values, and black lines represent varying degrees of input from a carbonatic fluid (Coltorti et al., 1999) (a-d), kimberlitic melt (Le Roex et al., 2003) (e-h), and diamond C-O-H fluids (Weiss et al., 2009) (i-l). Bold black lines represent X_{Opl} , the fluid input proportions deemed a 'best fit' for modelling metasomatic interaction with olivine from Figure 8. Chondrite-normalisation factors are from McDonough & Sun (1995).

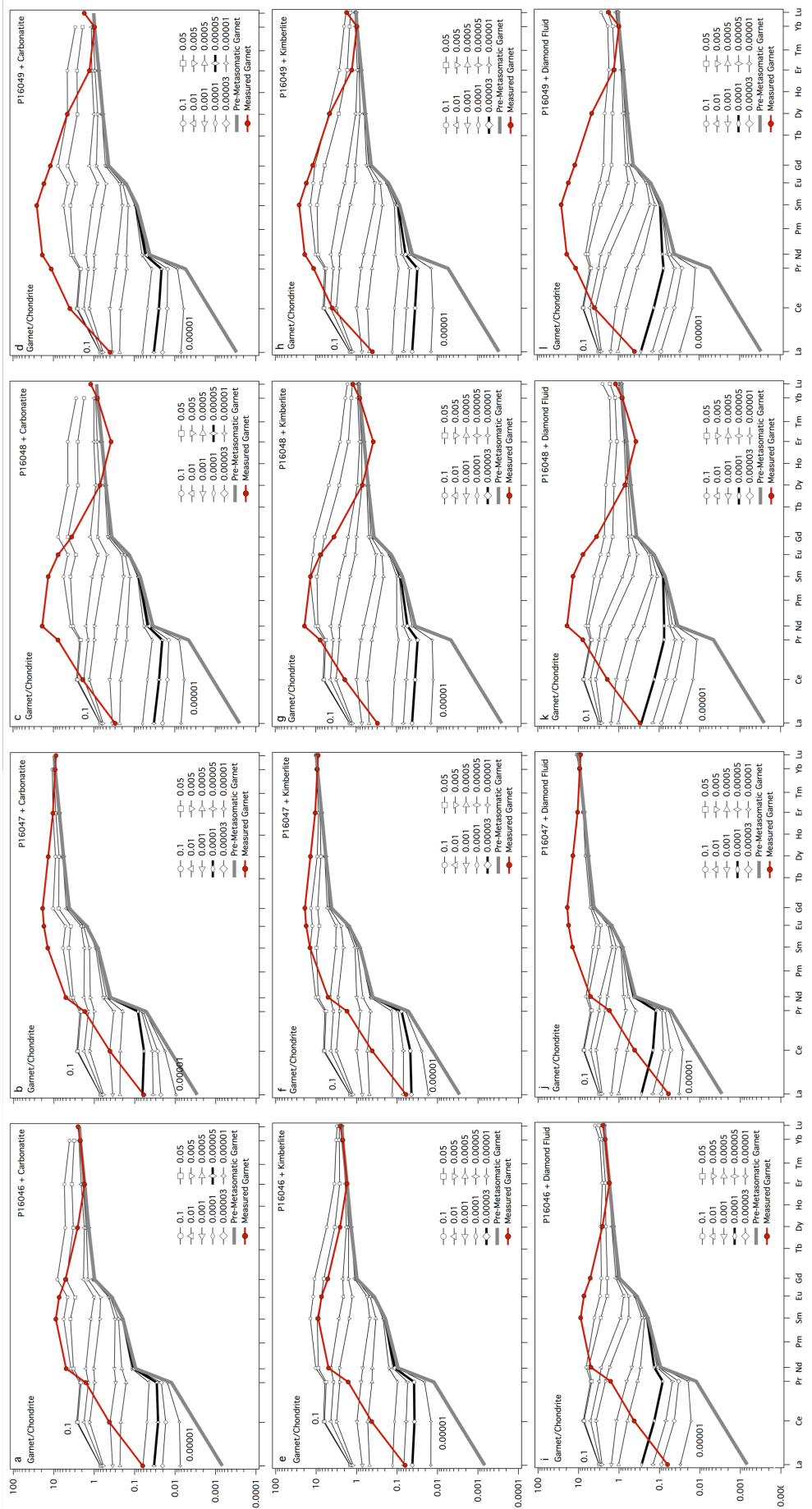


Figure 10: Chondrite-normalised REE patterns for garnets from P16046 (a,e,i), P16047 (b,f,j), P16048 (c,g,k), and P16049 (d,h,l). Red lines represent measured values, grey lines represent pre-metamorphic values, and black lines represent varying degrees of input from a carbonatitic fluid (Coltorti et al., 1999) (a-d), kimberlitic melt (Le Roex et al., 2003) (e-h), and diamond C-O-H fluids (Weiss et al., 2009) (i-l). Bold black lines represent X_{Opx} , the fluid input proportions deemed a ‘best fit’ for modelling metasomatic interaction with olivine from Figure 8. Chondrite-normalisation factors are from McDonough & Sun (1995).

4.2.1 Olivine Modelling

Of the three fluids used in this modelling, the carbonatite displays the gentlest REE trend, with a $\text{La}_\text{N}/\text{Yb}_\text{N}$ of ~ 35 compared to ~ 140 and ~ 355 for the kimberlitic melt and C-O-H fluid, respectively. This suggests that the carbonatite fluid has the least potential for enrichment of LREE relative to HREE.

From Figure 8 a-d it is clear that the interaction between a pre-metasomatic olivine and a carbonatitic fluid cannot recreate the observed REE patterns in any of the four samples presented here. In all cases the LREE in the observed olivine far exceed those achievable within the parameters that could produce the correct magnitudes for the MREE and HREE, with $X_{\text{opt}} = 0.00005$ to $X_{\text{opt}} = 0.0001$ producing MREE and HREE of similar magnitudes to the observed olivine. Though the LREE are enriched through interaction with the carbonatitic fluid they are not enriched to the same degree as present in the observed olivines. Modelled REE profiles have flat MREE to HREE for moderate degrees of fluid interaction, to a positive MREE to HREE slope at higher volumes. The observed REE patterns in the olivines presented here therefore cannot be produced through metasomatic interaction with a carbonatitic fluid.

The kimberlite melt and especially C-O-H fluids have steeper REE trends, giving rise to greater potential for LREE enrichment than the carbonatitic fluid. Figure 8e-l shows that both of these fluids produce LREE concentrations that are comparable to the observed olivine. This is clearest for the olivine from sinusoidal samples, with the least comparable LREE contents modelled for olivine from the normal sample. Enrichment of the hypothetical, depleted pre-metasomatic olivine by both of these agents can successfully replicate humped patterns across the REE with a step down from the MREE to the HREE. The best-fit for kimberlite melt and C-O-H fluids are at $X_{\text{opt}} = 0.00003$ to $X_{\text{opt}} = 0.0001$, respectively, i.e. very low melt proportions ($<0.01\%$). These best-fit values represent the olivine models that most closely match the measured olivine, and were determined visually from the range of fluid input models presented in Figure 8.

Olivine mass balance models demonstrate that the olivine compositions are therefore consistent with metasomatism of depleted olivine by either kimberlitic melt or C-O-H fluid.

4.2.2 Orthopyroxene and Garnet Modelling

The effect of mass balance modelling using carbonatite, kimberlite, and C-O-H fluids are presented for orthopyroxene and garnet in Figures 8 and 9 respectively. To aid comparison of fluid input between phases, the X input that is deemed the most appropriate fit for the measured olivines in Figure 8, referred to here as optimum X (X_{opt}), are represented by bold black lines in the figures for their corresponding orthopyroxenes (Fig. 9) and garnets (Fig. 10).

It is clear from Figure 9 that input from all three fluids at low fluid volumes produces concave downward REE patterns for the modelled orthopyroxene, with peaks at La and Lu and minima at Eu-Gd. This concave shape is most exaggerated with input from the C-O-H fluid, and is weakly developed with the carbonatitic and kimberlitic fluids. As you increase the input volume of fluids, the concave REE pattern transitions to a flat (C-O-H fluid), positive (carbonatitic fluid), or convex upward (kimberlite) REE pattern. The positive REE pattern that develops with a carbonatitic input is due to the gentler REE slope of the fluid, resulting in greater enrichment of the HREE relative to the MREE. The convex pattern developed when using the kimberlite melt, with its peak at Eu and minima at La and Lu, is similar to the observed orthopyroxene. However, the fluid volumes required to achieve this pattern in orthopyroxene are >100x times higher than the fluid volumes required to model the observed olivine REE patterns. The modelled olivines are a good match for the observed olivines at X_{opt} of 0.00003 (kimberlite) and 0.0001 (C-O-H fluid), however at these fluid volumes the modelled orthopyroxene has a strongly concave downward REE pattern with minima at Eu-Gd which is precisely the position of the maxima in the observed orthopyroxene. It follows that the REE patterns observed in the measured orthopyroxene cannot be reconciled by metasomatic input from any of the three fluids.

Figure 10 shows that modelled garnet REE patterns behave in a fashion to those seen in the modelled orthopyroxene with input from all three fluids. The resulting REE patterns at low fluid volumes show a slight ‘spoon-shape’ with peaks at Lu, which transitions to a more concave downward REE pattern at moderate fluid volumes with peaks at La and Lu. As observed in the orthopyroxene, this is most extreme for garnet that has been modelled with the C-O-H fluid. With increased fluid input the REE patterns become flat (C-O-H fluid), positive (carbonatitic fluid), or convex upward (kimberlite).

Similar to the modelled orthopyroxene, garnets modelled with kimberlitic melt produce convex upward patterns with minima at La and Lu, though the peak of the humped patterns sits at Sm rather than Eu. This pattern is similar to observed garnets for the normal sample and two of the sinusoidal samples between Nd and Lu, however this requires fluid volumes >100x times greater than those required to model the observed olivine at X_{opt} values. Furthermore, modelled La and Ce are greater than an order of magnitude lower in all observed garnets and this model cannot recreate the more extreme sinusoidal pattern of one of the sinusoidal samples (P16048). Modelled garnets with fluid input volumes of the olivine model X_{opt} display slightly ‘spoon shaped’ REE patterns with minima around Pr, yet for the observed garnets Pr is close to the maxima. As with orthopyroxene, the observed garnet REE patterns can therefore not be produced with metasomatic input from any of these fluids.

4.2.3 Review of the Metasomatic Model for Sinusoidal REE

In summary, mass-balance modelling of carbonatitic fluid, kimberlitic melt, and diamond-trapped C-O-H fluids with pre-metasomatic olivine, orthopyroxene, and garnet have shown that the humped REE patterns for these phases cannot be replicated by metasomatism of an ultra-depleted precursor by a single fluid at a consistent volume. Though we cannot exclude the possibility that late-stage interaction with kimberlite has modified the REE patterns of the studied phases, e.g. causing an upward flick of the LREE profiles of the observed phases particularly for olivine and orthopyroxene, our modelling suggests that fluid interaction is not responsible for the overall shape of the REE profiles observed in peridotitic xenoliths from the SCLM.

Mass Balance modelling was used by Gibson et al. (2013), who successfully replicate the LREE enrichment of an ultra-depleted, but non-sinusoidal garnet from Lashaine, Tanzania using the same C-O-H fluid (Weiss et al., 2009) as used in this study. However, the classic harzburgitic sinusoidal REE patterns with the hump at Nd-Eu have not been successfully reproduced. Shu and Brey (2015) apply mass balance modelling to harzburgitic garnets from Kaapvaal using hypothetical carbonatite melt. The chondrite-normalised pattern of the hypothetical carbonatite melt used by Shu and Brey (2015) varies from La to Lu by almost six orders of magnitude, this is in stark contrast to the calculated carbonatite compositions of Coltorti et al. (1999) that were used in the model in this study which vary by less than two orders of magnitude from La to Lu. Furthermore, the hypothetical carbonatite has an artificially humped REE pattern. Using this hypothetical carbonatite, Shu and Brey (2015) are able to model the composition of their garnet, however, the garnet in question does not represent typical sub-calcic garnets however, as the maxima falls closer to the LREE (around Ce-Nd) than is commonly observed for such garnets in the literature. Wider application of this model is problematic as the low LREE contents of Archaean garnets throughout the literature are inconsistent with interaction with a fluid as LREE-enriched as the hypothetical carbonatite of Shu and Brey (2015). Furthermore, as analytical quality continues to improve it has become even more apparent that the LREE of these garnets are extremely low, as seen in recent studies (e.g. Gibson et al., 2013; Luchs et al., 2013; Shu and Brey, 2015). Therefore these low LREE contents are a persistent problem with the model for metasomatism via LREE-enriched fluids.

The humped REE patterns observed in garnet, orthopyroxene and olivine cannot be produced by single-stage modelling of an ultra-depleted precursor composition. There are two possible explanations as to why mass balance modelling of metasomatism was not successful. The first scenario is that metasomatism occurs over several episodes, however none of the candidate fluids were able to replicate the sinusoidal and humped profiles seen in garnet and orthopyroxene. The second scenario is that the REE profile of the starting composition already has a humped pattern, whereby the hypothetical ultra-depleted 'precursor' flattens the REE profile. Since metasomatism serves to increase the LREE, this humped precursor would require even lower LREE contents and an even steeper dipped LREE-MREE trend. Thus, we suggest that the humped REE

patterns are an inherent characteristic of cratonic garnet peridotites, related to their primary formation.

Conclusions

In this contribution we present the first multi-phase REE dataset for peridotites to include REE data for Archaean olivine. Mass balance calculations have clearly demonstrated that the conventional metasomatic model is not capable of replicating the sinusoidal REE patterns of typical Archaean garnets. Regardless of the putative fluid used in the model it does not work for the full phase suite; to assess this further the model could be tested for a wider suite of trace elements. The disparity between modelling of olivine, orthopyroxene, and garnet has highlighted the importance of analysing all the major phases in order to investigate the geochemical, petrographic and metasomatic history of such samples. In particular this study emphasises the value of the REE in olivine and orthopyroxene, which are often overlooked. These phases span a wider depth range than the classically favoured garnet as they are present in even the shallowest portion of the mantle, and as such have great potential in further studies of Archaean peridotite and the processes that have affected the SCLM.

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San Carlos Olivine, USNM111312			Diopside, NMNH 117733	
Oxide wt%	(n=9)		(n=10)	
	Measured	Known	Measured	Known
MgO	50.1	49.4	18.3	17.8
<i>1s</i>	0.5		0.2	
SiO ₂	40.4	40.8	55.3	55.8
<i>1s</i>	0.3		0.4	
CaO			25.6	25.3
<i>1s</i>			0.3	
FeO	9.71	9.55	0.49	0.25
<i>1s</i>	0.13		0.03	
NiO	0.4	0.37		
<i>1s</i>	0.01			
Total	101.45	100.12	100.58	99.15
Mg#	90.19	90.22	98.52	99.21
Si	0.99	1.00	2.00	2.02
Mg	1.82	1.80	0.99	0.96
Fe _t	0.20	0.20	0.01	0.01
Ni	0.01	0.01		
Ca			0.99	0.98
Total Cations	3.01	3.00	4.00	3.98

Supplementary Table 1: Major element concentrations (oxide wt %) and stoichiometry for reference materials USNM 111312 and NMNH 117733. Standard deviations are given as 1s. Known concentrations are from Jarosewich et al. (1980). Stoichiometry for olivine and diopside was calculated based on 4 and 6 oxygens, respectively.

NIST SRM 616				GOR 128 -G			KL 2 -G		
ppm	Measured	1s	Known	Measured	1s	Known	Measured	1s	Known
Na	94925	15297	101635	3873	277	4258	14722	558	16800
Al	10380	1040	10532	49760	5984	52449	66133	8631	69300
Ca	85183	7768	84334	38400	3594	44597	67900	1435	77200
Sc	0.984	0.079	0.026	27.97	2.79	32.10	29.40	2.79	32.3
V	0.213	0.020	0.228	169.4	13.0	189.0	287.2	13.5	309
Cr	0.254	0.006	0.400	1986	88	2272	257.6	7.7	294
Co	0.039	0.002	0.051	84.46	10.01	92.40	38.67	1.85	42.0
Ni	0.239	0.039	0.435	1055	130	1074	101.9	8.4	116
Cu	1.64	0.13	0.70	57.28	6.15	63.80	79.1	4.8	87.9
Zn	1.26	0.23	1.33	77.07	9.38	74.70	110.1	14.5	110
Y	0.031	0.001	0.029	12.47	1.90	11.80	24.74	3.09	26.8
Zr	0.090	0.005	0.095	8.69	0.64	10.00	137.9	14.5	159
La	0.033	0.003	0.030	0.122	0.021	0.121	14.08	2.41	13.2
Ce	0.031	0.003	0.029	0.452	0.095	0.450	33.90	3.83	33
Nd	0.020	0.002	0.023	0.768	0.136	0.784	22.43	2.56	21.7
Sm	0.017	0.003	0.016	0.563	0.086	0.525	6.08	0.24	6
Gd	0.015	0.002	0.016	1.24	0.30	1.17	6.34	0.70	6.1
Dy	0.017	0.004	0.017	2.32	0.46	1.98	6.24	0.15	5
Er	0.017	0.003	0.016	1.67	0.21	1.40	2.97	0.45	2.6
Yb	0.017	0.002	0.017	1.53	0.38	1.41	2.33	0.29	2

Supplementary Table 2: Trace element concentrations (ppm) for reference materials NIST 616, GOR 128-G, and KL 2-G. Standard deviations are given as 1s. Known values from Jochum et al. (2006) (GOR 128-G and KL 2-G), and Jochum et al. (2011) (NIST SRM 616).

Chapter 5: Synthesis

Olivine has great potential as a geochemical tool thanks to its abundance and widespread occurrence. In recent years analytical advances have paved the way for the trace element contents of olivine to be explored and applied to geochemistry and geothermometry (De Hoog et al., 2010; Foley et al., 2013; Sanfilippo et al., 2014; Tollan et al., 2015). Partitioning of trace elements such as Ca, Al, Ti, and Sc between olivine and other minerals has received significant attention, particularly within the field of geothermometry (e.g. De Hoog et al., 2010; Finnerty and Boyd, 1978; Kohler and Brey, 1990; Stosch, 1981). Furthermore, trace element pairs such as Sc-Zr and Al-Mn in olivine can be used to discriminate between mantle lithologies (De Hoog et al., 2010). The utility of trace elements in olivine is therefore firmly established within the literature.

The rare earth elements (REE) in olivine have received less attention than the wider suite of trace elements because of their ultra-low abundances in olivine (down to single digit ppb). Despite the challenges associated at measuring elemental concentrations in the low ppb range, limited studies have determined the REE in natural olivine (Eggins et al., 1998; Lee et al., 2007; Zanetti et al., 2004). Given the significance of the REE in other minerals, such as garnet, within the context of assessing metasomatic enrichment of the subcontinental lithospheric mantle (SCLM), it follows that a better understanding of the REE contents of a mineral as prevalent throughout the mantle as olivine could further our comprehension of the widely cited metasomatic processes. This thesis has advanced the study of the REE in olivine through the analytical strategies for determination of these elements and an evaluation of their partitioning behaviour within the olivine crystal lattice. This provides a framework within which olivine REE contents can be assessed for a compositional range of natural olivines. Additionally, this thesis has presented olivine REE contents of mantle olivine to compliment REE data for co-existing orthopyroxene and garnet. In doing so, this work has provided new insights into the influence of metasomatic agents within the SCLM. The principal contributions and conclusions of this thesis in the context of olivine geochemistry can be summarised as three core findings:

Finding 1: The magnesium number (Mg#) of olivine exerts a strong control over the partitioning of the REE through its influence over the elasticity of the crystal lattice site.

Investigation of the partitioning behaviour for the REE in natural olivine over a Mg# range of 1 to 59 showed that with increasing Mg content in olivine, the Young's Modulus (E) of the olivine lattice showed a positive correlation. This increase in E represents a decrease in the elasticity of the crystal lattice, such that the lattice is less accommodating to the REE. This effect is observed to the greatest degree around the middle REE (MREE), with more fayalitic olivine (lower Mg#) showing broader REE partitioning parabolas and significantly higher absolute concentrations of the MREE relative to more forsteritic olivines. The identification of the Mg# as the primary influence over partitioning of the REE in olivine is significant to the application of REE in olivine as a petrogenetic tool. For samples with similar Mg#, such as peridotitic olivine, it can therefore be assumed that the observed REE patterns reflect external factors such as metasomatic enrichment or diffusion from neighbouring phases. This finding thus supports the use of REE in olivine as a geochemical tool for unravelling metasomatic processes within the mantle.

Finding 2: Natural olivine may experience preferential diffusion of the light REE (LREE) from neighbouring phases or grain boundary fluids/melts.

Application of a two-dimensional laser mapping technique to a natural olivine sample has revealed concentric core to rim increases in Al and the LREE, resulting from solid-state diffusive re-equilibration with the adjacent more-enriched plagioclase. Crucially, the REE heavier than Eu did not exhibit the same diffusional behaviour in olivine despite similar concentration gradients with the adjacent plagioclase. This finding is an important contribution to the study of olivine REE as it provides reasoning for the over-representation of LREE in natural relative to experimental olivine throughout the literature, and furthermore can offer recommendations for how achieving the optimal conditions for REE analysis in olivine (e.g. by avoiding small olivine grains that are in contact with high REE phases such as plagioclase). Acknowledging the potential for some REE diffusion is also an important factor when trying to reconstruct the original REE inventory in olivine. While this finding is important for understanding how best to

avoid analysing olivine that have been affected by diffusion of the LREE, it is also important to note that there is great potential to use REE diffusion profiles in studying the rates of cooling in igneous systems and diffusion timescales.

Finding 3: The REE in olivine from garnet peridotites from Kaapvaal show a humped pattern similar to that of co-existing garnet and orthopyroxene but these cannot be explained by consistent metasomatic input.

The REE contents of olivine, orthopyroxene, and garnet from garnet peridotites were determined and shown to exhibit sinusoidal and humped REE patterns, with one garnet lherzolite displaying more normal REE patterns. Sinusoidal REE patterns are consistently attributed to metasomatic enrichment events throughout the literature (e.g. Bell et al., 2005; Gibson et al., 2008; Griffin et al., 1999; Stachel et al., 1998). Through mass-balance modelling with three potential metasomatic agents, this thesis has demonstrated that the REE patterns of the three phases cannot be successfully reconstructed with consistent input of either carbonatite fluid, kimberlite melt, or diamond-trapped high-Mg carbonatitic high-density fluids (HDFs) despite their wide acceptance as metasomatic agents responsible for the observed sinusoidal REE patterns. Uncovering the true origin of such REE patterns is beyond the scope of this thesis, however the finding of olivine REE patterns that display similar sinusoidal patterns to their garnet counterparts lends great support to the use of REE in olivine to assess potential metasomatic input in garnet-free mantle lithologies.

These three findings demonstrate that the REE in olivine can now be successfully determined and assessed to provide a wealth of information for different geological settings. This thesis has advanced our understanding of the behaviour of the REE in olivine and provides support for wider application. It is hoped that this may spark new discussion within the field of mantle geochemistry in particular, as the REE in olivine have been overlooked to date. In recognising the utility of the REE in olivine, a new avenue is opened for exploration that could have great consequences for mantle geochemistry.

In looking forward, this thesis has highlighted many potential areas for further study. Firstly, the relationship between Mg# and E could be expanded beyond the Mg# 1 to 59 range that was covered in Chapter 3 of this thesis. It would be beneficial to cover the full compositional range of natural olivine to permit global application, especially to include mantle olivine compositions at the highly forsteritic end of the spectrum. Secondly, there is clearly a lot of work that could be done to better comprehend the diffusion of the LREE in olivine in order to use this for assessing rates of cooling and extracting original REE patterns. This should be carried out for natural olivines complementarily to existing experimental studies of REE diffusion in olivine (Cherniak, 2010; Spandler and O'Neill, 2010). Finally, determination of REE contents in mantle olivine should be expanded to cover the full array of mantle lithologies. This would allow potential enrichment processes to be compared across both depth and spatial contexts, with the prospect of a more comprehensive understanding of the processes that have affected the SCLM.

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