

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 across 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 Å) to La (1.032 Å) (in VI coordination) (Shannon, 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

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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. $150 \times 150 \times 100 \mu\text{m}$) 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.

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). 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 $180 \mu\text{m}$ 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).

Table 1

Sample characteristics.

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

Sample	Rock Type	Skaergaard Zone	Plagioclase An %	Olivine Mg#	Clinopyroxene En-Fs-Wo	T (°C) of crystallisation
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

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 20 kV was used with a beam current of 350 pA. A suite of appropriate mineral standards from the Smithsonian Institution (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 193 nm ATLex 300 ArF excimer laser and a HelEx II active two-volume ablation cell, and are coupled with a Thermo Scientific iCAP-Qc ICP-MS.

Olivine and clinopyroxene were analysed at a spot size of $85 \mu\text{m}$, 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 $150 \mu\text{m}$ spot size, at a laser repetition rate of 30 Hz and a shot count of 4000 for masses ²⁹Si, ²⁴Mg, ²⁷Al, ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴⁶Nd, ¹⁶⁰Gd, ¹⁶³Dy, ¹⁷²Yb, and ¹⁷⁵Lu, 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 by subtracting the gas blank. 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 5×5 mm, using a repetition rate of 60 Hz and a square beam diameter of 30 μ m. 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 20×20 μ m thanks to pooling data pixels into regions of interest (ROI). Precision increases for increasing number of pixels and errors reported here represent $2 \times$ 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 ~3000 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 Fig. 1.

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 Fig. 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 provided in Fig. 2 establish equilibrium between olivine and clinopyroxene for all seven samples.

In a next step, the empirical data were compared to predictions from 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 partition coefficients, $D_{ol/melt}$, 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 Fig. 3 (panels a–g). The errors shown in Fig. 3 are 1σ of measured replicates of olivines, which by far exceed those of clinopyroxene measurements and the uncertainties of the model $D_{cpx/melt}$.

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. 3a–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 Fig. 3 that the more forsteritic samples yield tighter parabolas than the more fayalitic

Table 2
Major element concentrations of olivine, clinopyroxene, and plagioclase.
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.’

	P16039						P16040						P16041					
	Olivine		1σ		Clinopyroxene		1σ		Plagioclase		1σ		Olivine		1σ		Clinopyroxene	
Na ₂ O	< d.l.				0.31	0.06	0.17	< d.l.	4.83	< d.l.	0.08	0.03	0.29	0.04	0.03	0.04	< d.l.	
MgO	28.9	15.1	0.3	0.34	15.1	0.34	0.98	14.1	< d.l.	0.08	0.08	0.2	10.9	0.2	0.2	16.4	< d.l.	
Al ₂ O ₃	< d.l.	2.54		0.2	2.54	0.2	0.85	< d.l.	30.1	< d.l.	0.18	0.06	1.23	0.2	0.31	33.2	< d.l.	
SiO ₂	35.9	50.9	0.29	0.54	50.9	0.54	0.85	32.5	54.1	0.18	0.18	0.06	51.2	0.29	0.08	< d.l.	< d.l.	
K ₂ O	< d.l.	< d.l.			< d.l.			< d.l.	0.33	< d.l.	0.01	0.02	< d.l.	0.08	0.01	< d.l.	< d.l.	
CaO	< d.l.	19.3		0.42	19.3	0.42	0.03	0.2	11	0.01	0.01	0.02	17	0.1	1.28	< d.l.	< d.l.	
TiO ₂	< d.l.	0.69		0.11	0.69	0.11		< d.l.	< d.l.			0.02	0.81	0.02	0.02	< d.l.	< d.l.	
MnO	0.54	0.25	0.05	0.04	0.25	0.04		< d.l.	< d.l.	0.04	0.04	0.02	0.5		0.02	0.86	0.86	
FeO	35.4	9.2	0.3	0.1	9.2	0.1	0	53.2	0.37	0.28	0.28	1.71	19.5	0.06	1.71	50.5	50.5	
Total	101	98.3			98.3			101	101			32.1	102			101	101	
Mg#	59.3															36.7	36.7	

	P16042						P16043						P16044					
	Olivine		1σ		Clinopyroxene		1σ		Plagioclase		1σ		Olivine		1σ		Clinopyroxene	
Na ₂ O	< d.l.				0.47	0.04	0.04	< d.l.	7.38	< d.l.	0.06	0.07	0.07	0.03	0.03	0.03	0.03	0.27
MgO	0.25	0.31	0.02	0.12	0.31	0.12	0.01	0.43	< d.l.	0.01	0.01	0.04	< d.l.	4.2	0.25	0.25	4.88	
Al ₂ O ₃	1.3	0.1	0.1	0.28	1.3	0.28	0.18	< d.l.	25.7	0.03	0.03	0.03	25.7	0.08	0.03	0.03	0.94	
SiO ₂	0.16	0.77	0.07	0.04	0.77	0.04	0.04	29.3	60.3	0.03	0.03	0.03	60.3	30	0.18	0.18	48.6	
K ₂ O	< d.l.	< d.l.			< d.l.			< d.l.	0.57	< d.l.	0.07	0.07	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	
CaO	16	1.36	1.36	8.74	16	8.74	0.09	20.1	6.33	0.35	0.35	0.07	6.33	0.07	0.03	0.03	18.1	
TiO ₂	0.87	0.3	0.3	< d.l.	0.87	< d.l.		< d.l.	< d.l.			< d.l.	< d.l.	0.03	0.01	0.01	0.79	
MnO	0.04	0.06	0.06	< d.l.	0.06	< d.l.	0.02	1	< d.l.	0.12	0.12	0.02	< d.l.	1.25	0.03	0.03	0.54	
FeO	0.64	1.27	1.27	0.33	0.64	0.33	0.16	29.8	0.49	0.38	0.38	0.02	0.49	63.6	0.43	25.5	25.5	
Total	101	102			101			99.9	101				101	99.4		99.6	99.6	
Mg#								1.11						10.5				

	P16039						P16043						P16044					
	Clinopyroxene		1σ		Plagioclase		1σ		Olivine		1σ		Plagioclase		1σ		Olivine	
Na ₂ O	0.31	6.99	0.03	0.04	6.99	0.04	0.03	6.79	0.17	0.07	0.07	0.01	0.01	0.04	0.04	0.04	4.62	0.43
MgO	15.1	< d.l.	0.23	< d.l.	< d.l.	< d.l.	0.57	< d.l.	28	28	16.3	0.58	0.1	1.53	1.53	< d.l.	< d.l.	
Al ₂ O ₃	2.54	26.6	0.04	0.24	26.6	0.24	0.03	26	0.29	0.17	0.17	0.1	0.1	0.57	0.57	31.1	31.1	1.39
SiO ₂	50.9	58.8	0.36	0.2	58.8	0.2	1.47	56.7	0.73	35.8	52.5	0.36	0.36	1.2	1.2	53.9	53.9	0.75
K ₂ O	< d.l.	0.42		0.01	0.42	0.01		0.42	0.04	< d.l.	< d.l.	0.03	0.03	0.03	0.03	0.33	0.33	0.08
CaO	19.3	7.21	0.15	0.17	7.21	0.17	0.08	7.03	0.02	0.1	16.2	0.03	0.03	1.34	1.34	11.4	11.4	1.12
TiO ₂	0.69	< d.l.	0.02	< d.l.	< d.l.	< d.l.	0.01	< d.l.	0.04	0.04	0.68	0.02	0.02	0.15	0.15	< d.l.	< d.l.	
MnO	0.25	< d.l.	0.01	< d.l.	< d.l.	< d.l.	0.02	< d.l.	0.57	0.57	0.33	0.03	0.03	0.01	0.01	< d.l.	< d.l.	
FeO	9.2	0.43	0.38	0.04	0.43	0.04	0.06	0.4	36.8	36.8	12.4	0.18	0.18	0.14	0.14	0.34	0.34	0.04
Total	98.3	100			100			97.3	102	102	101			102	102	102	102	
Mg#									57.6									

Table 3
Trace element concentrations of olivine and clinopyroxene.
Trace element concentrations determined by LA-QICP-MS, given in ppm and ppb. Not analysed: n.a.

P16039										P16040				P16041				P16042			
										Olivine		Clinopyroxene		1σ		Olivine		Clinopyroxene		1σ	
ppm	Al	77	34	19,000	270	90	9	6500	150	86	150	1700	3800	7100	520	120	6700	3800	120		
	Ca	590	39	220,000	4700	1800	110	130,000	4	1900	4	14	9.5	140	3	9.5	140	3	9.5		
	Sc	7.3	0.2	150	8	11	0	120	5	44	5	64	68	590	0	34	590	0	34		
	Ti	21	2	980	30	42	3	590	1	240	7	79	240	72	0	240	240	0	240		
	Co	260	2	86	1	240	7	3.6	0.3	20	0.3	79	6500	140	370	370	6500	140	370		
	Ni	950	3	290	7	12	0	6300	79	160	79	6500	140	6500	140	370	6500	140	370		
ppb	Ga	200	61	9840	610	140	6	33	4	480	4	360	1300	< 9.1	1300	2300	1300	2300	2300		
	Rb	60		26	7	26		22,000	1200	1100	1100	1100	1900	26,000	1900	13,000	26,000	1900	13,000		
	Sr	280	110	25,000	530	15	31	20,000	1100	1500	1100	1100	1600	23,000	3800	1600	23,000	3800	1600		
	Y	490	62	20,000	970	860	110	22,000	5	6.7	5	32	1	32	1	36	23,000	3800	1600		
	Zr	270	0.3	130	11	1.8		37	5	6.7	5	32	1	32	1	36	23,000	3800	1600		
	Nb	2.7	8	4200	420	12	1	1100	42	15	42	39	620	3100	620	39	3100	620	39		
	La	26	14	13,000	1600	36	7	5100	180	30	180	2600	150	11,000	2600	150	11,000	2600	150		
	Ce	33	6	1900	210	n.a.		1200	45	n.a.	45	400	n.a.	1900	400	n.a.	1900	400	n.a.		
	Pr	n.a.		9400	870	28	3	8100	290	10	290	530	160	8700	530	160	8700	530	160		
	Nd	14		3200	160	n.a.		3400	190	n.a.	190	790	n.a.	3900	790	n.a.	3900	790	n.a.		
	Sm	n.a.		970	27	n.a.		950	31	n.a.	31	45	n.a.	960	45	n.a.	960	45	n.a.		
	Eu	n.a.		3800	170	22	3	4400	230	21	230	110	470	4400	110	470	4400	110	470		
	Gd	9.0	2.0	4300	180	82	8	4700	250	89	250	340	1500	5500	340	1500	5500	340	1500		
	Dy	42	5	830	30	n.a.		900	51	n.a.	51	120	n.a.	1100	120	n.a.	1100	120	n.a.		
	Ho	n.a.		2200	58	170	11	2400	18	220	18	41	n.a.	430	41	n.a.	430	41	n.a.		
	Er	100	7	310	20	n.a.		330	20	n.a.	20	270	3000	2700	270	3000	2700	270	3000		
	Tm	n.a.		2000	98	440	16	2100	120	490	120	39	570	380	39	570	380	39	570		
	Yb	310	13	270	16	94	3	310	37	44	37	9	35	900	9	35	900	9	35		
	Lu	73	2	910	1	14	1	860	0.1	< 73	0.1	< 2.5	< 2.5	3.0	0.1	< 2.5	3.0	0.1	< 2.5		
	Hf	9.0		13	1	< 1.3		3.5	0.1	< 73	0.1	< 2.5	< 2.5	3.0	0.1	< 2.5	3.0	0.1	< 2.5		
	Ta	< 1.5																			

P16042										P16043				P16044				P16045			
										Olivine		Clinopyroxene		1σ		Olivine		Clinopyroxene		1σ	
ppm	55	3700	1100	130	n.a.	n.a.	150	23	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.		
	1100	150,000	13,000	n.a.	n.a.	n.a.	n.a.	1	n.a.	n.a.	n.a.	210	100	n.a.	100	n.a.	n.a.	n.a.	n.a.		
	0.3	81	1	13	240	7	18	1	210	3	210	48	59	0.4	59	3	7.4	100	9		
	6	140	11	n.a.	n.a.	n.a.	n.a.	12	n.a.	n.a.	n.a.	48	59	5	59	3	n.a.	n.a.	n.a.		
	3	17	1	100	44	2	130	0.02	0.12	0.01	0.12	0.12	190	38	190	4	250	190	4		
	< 0.91	< 0.91	0.01	0.07	0.096	0.012	0.14	0.02	n.a.	n.a.	n.a.	n.a.	n.a.	0.1	n.a.	n.a.	780	n.a.	n.a.		
ppb	58	8700	670	39	31	31	33	5	8.6	1.1	8.6	26,000	760	0.1	760	1300	2.3	760	1300		
	12	1200	110	n.a.	29,000	980	160	40	990	990	990	19,000	18,000	10.9	18,000	1500	7.7	18,000	1500		
	1900	22,000	450	320	20,000	980	2500	350	19,000	1000	19,000	1700	16,000	62	16,000	570	490	16,000	570		
	1400	170,000	8600	3600	20,000	2200	1500	420	19,000	1700	19,000	280	25,000	280	25,000	7800	1100	25,000	7800		
	290	19,000	1000	2100	21,000	9	5.2	1.5	40	2	40	1300	390	5.7	390	270	5.9	390	270		
	15	550	6	120	52	57	50	8	6300	83	6300	2500	2500	0.010	2500	61	0.68	2500	61		
	24	4500	120	57	1500	450	170	6	n.a.	370	1300	6400	6400	0.4	6400	610	1.8	6400	610		
	110	20,000	510	130	6600	450	49	8	n.a.	0.28	6300	n.a.	n.a.	0.4	n.a.	0.28	0.28	n.a.	n.a.		
	4300	4300	93	25	n.a.																

Table 3 (continued)

	P16042			P16043			P16044			P16045		
	1σ	Clinopyroxene	Olivine	1σ	Clinopyroxene	Olivine	1σ	Clinopyroxene	Olivine	1σ	Clinopyroxene	Olivine
	97	30,000	150	500	8800	230	37	8300	650	1.4	6300	370
		13,000	68	450	3700	79	14	3600	160	1.2	2227	133.7
		2600	45	250	n.a.	48	37	n.a.	160	0.54	n.a.	
	170	20,000	250	620	4400	130	13	4400	160	1.5	3000	130
	360	28,000	540	1600	4200	270	44	4000	150	5	3300	120
		6600	n.a.	190	n.a.	n.a.		n.a.	91	n.a.	n.a.	
	350	21,000	730	520	2000	480	20	2000	37	9	1700	78
		3200	n.a.	180	n.a.	1100	62	1900	12	n.a.	n.a.	
	380	20,250	1500	2080	1900	230	8	320	59	29	1500	60
	59	3500	330	270	340	29	2	850	5	5	210	9
	1	530	54	38	920	< 0.5		3.7	36	5	1000	100
			0.01	3	4.2				21	0.03		9

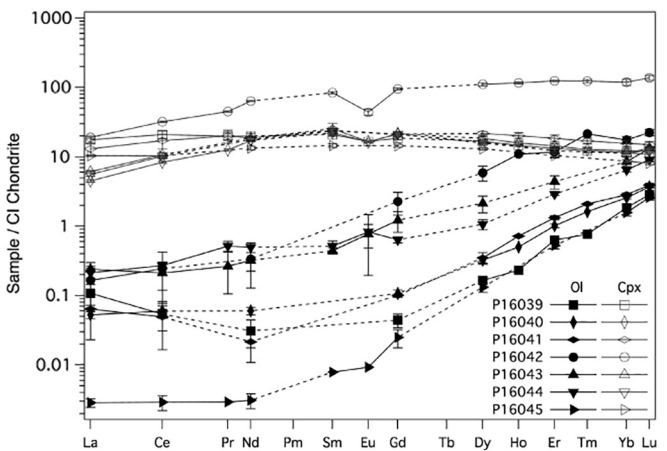


Fig. 1. CI chondrite-normalised (McDonough and Sun, 1995) REE patterns in olivines (closed symbols) and clinopyroxenes (open symbols) from samples P16039_{Mg59}, P16040_{Mg32}, P16041_{Mg37}, P16042_{Mg1}, P16043_{Mg10}, P16044_{Mg15}, and P16045_{Mg57}. Errors are 1σ of measured replicates. Elements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

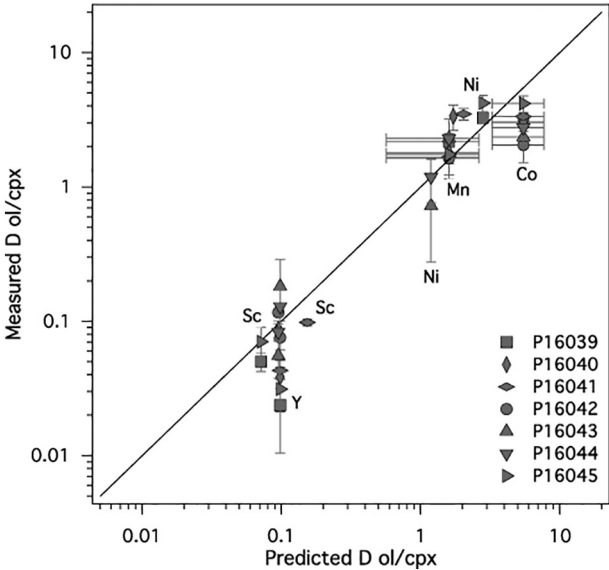


Fig. 2. Predicted vs measured $D_{ol/cpx}$ values for Y, Sc, Mn, Co, and Ni. The line represents the ideal 1:1 ratio. Predicted D values from Laubier et al. (2014) (Co, Mn, and Y), McBirney (1998) (Ni and Sc for the respective Skaergaard Zones). Errors are 2σ.

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, Fig. 3 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 ($r_o = 0.695 \text{ \AA}$) 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

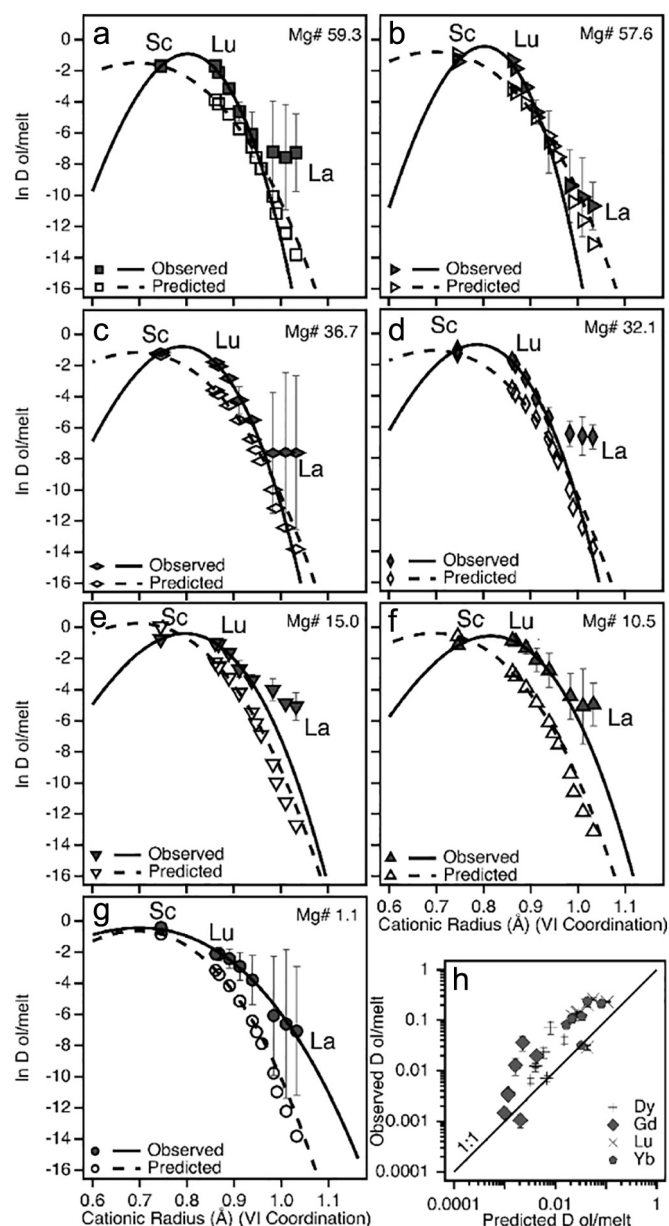


Fig. 3. (a)–(g): Apparent and predicted olivine/melt partition coefficients for the REE and Sc plotted as $\ln D_{ol/melt}$ vs. cationic radius in VI coordination (Shannon, 1976) for a) P16039_{Mg59}, b) P16045_{Mg57}, c) P16041_{Mg37}, d) P16040_{Mg32}, e) P16044_{Mg15}, f) P16043_{Mg10}, and g) P16042_{Mg1}. 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.

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.

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. 4a), but not with D_o or r_o . 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. 3), 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. 4b). 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. 4c), which is the opposite of what is expected if T were controlling site elasticity (Smyth, 1975).

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 $T > 600$ °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 and Wood, 1994; Wood and Blundy, 1997).

Several mechanisms have been proposed to explain the overabundance of LREE in olivine. Stosch (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

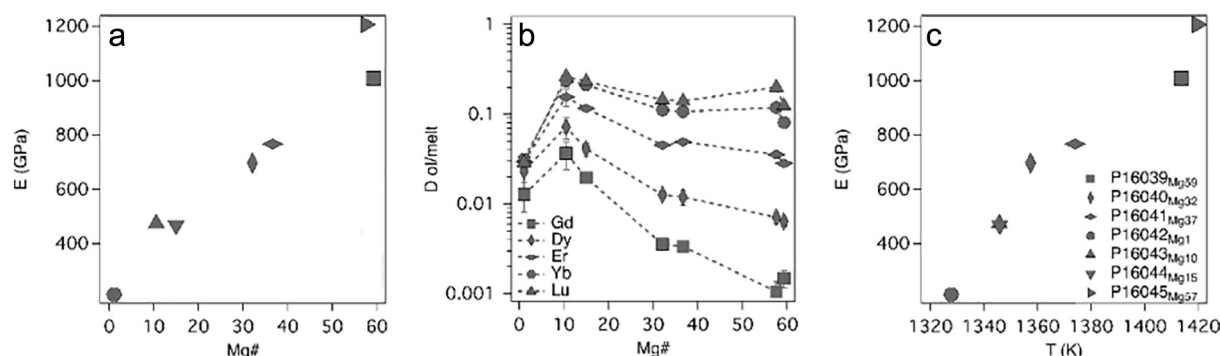


Fig. 4. a) Olivine Mg# vs apparent Young's Modulus (E) (GPa), b) olivine Mg# vs $D_{ol/melt}$ for Gd, Dy, Er, Yb, and Lu, and c) T (K) vs E (GPa). Symbol keys for panels a and c are shown in panel c.

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 amongst 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. 3) to lowest in P16042₁. All elemental maps showed similar systematics but for the purpose of illustration, the trace element maps (3×3 mm area; Fig. 5b) 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. 5a) shows a central olivine crystal enclosed on three sides by plagioclase and on one by clinopyroxene/ilmenite. The olivine in question is ~ 630 μ m 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.

The maps of La and Al (Fig. 5) 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. 6a) 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 ($3 \times$) and an olivine traverse ($11 \times$) 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 Fig. 5 is illustrated on Fig. 6b (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

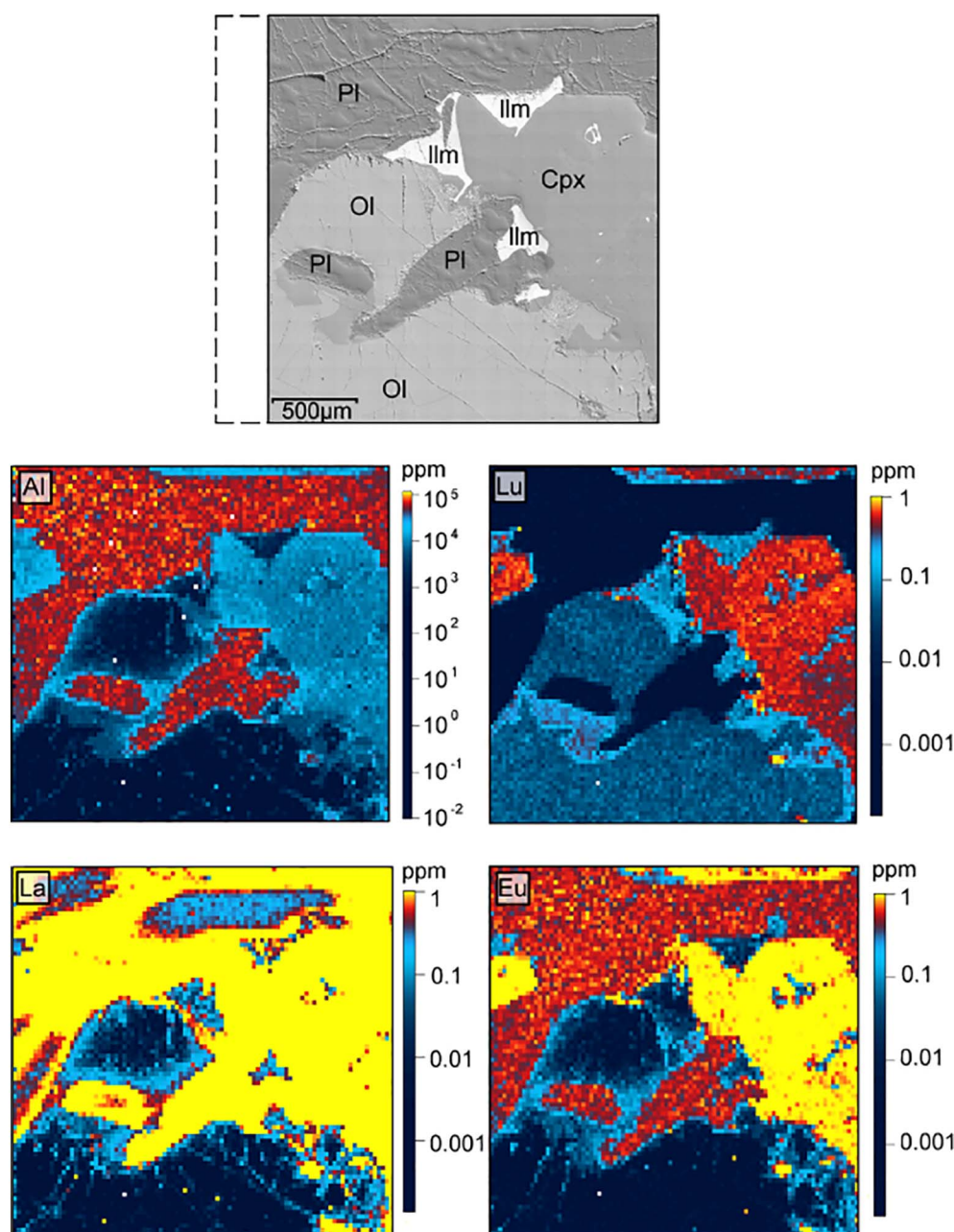


Fig. 5. a) Annotated back-scattered electron (BSE) image with dashed line to represent the area mapped using the laser and b-e) semi-quantitative element maps of Al, Lu, La, and Eu, respectively, obtained on a $\sim 3 \times 3$ mm area of P16045_{Mg57}. In the BSE image plagioclase, olivine, clinopyroxene, and ilmenite are labelled with 'Pl', 'Ol', 'Cpx', and 'Ilm', respectively. 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.

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. 6a, 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 Fig. 6d alongside co-existing plagioclase (concentrations extracted from the map using criteria $\text{Al} > 20,000$ ppm; $\text{Sc} < 5$ ppm), clinopyroxene (concentrations extracted from the map using criterion $\text{Lu} > 0.4$ 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.

Fig. 6c 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

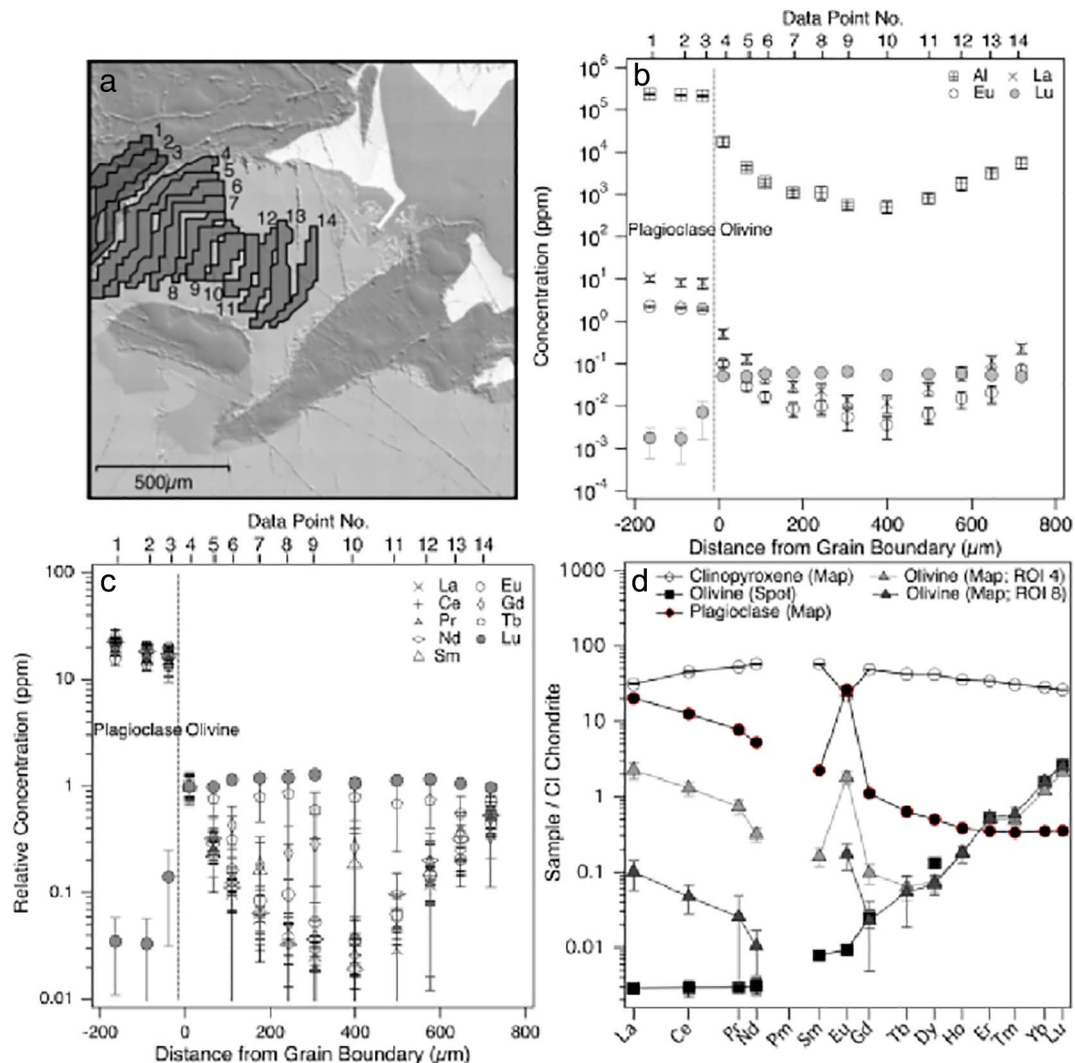


Fig. 6. a) BSE image of a sub-section of sample P16045_{Mg57}, as shown in Fig. 5a, annotated with the 14 ROIs from which data were extracted using Monocle to create the diffusion profiles in b) for Al, La, Eu, and Lu along a transect through plagioclase (–200 to 0 μm) and olivine (0 to 800 μm) with 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 ~50 μm 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 Lu > 0.4 ppm), and plagioclase (mapped concentrations extracted using monocle according to the criteria Al > 20,000 ppm; Sc < 5 ppm) from sample P16045_{Mg57}. Errors are 1σ of measured replicates for spot analyses and 2SE for map data.

least re-equilibrated olivine (Fig. 6d), it can be seen that $D_{ol/plag}$ 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 7000 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 $D_{plag/solid}$ at subsolidus T for the REE is unknown (e.g. Bedard, 2006; Bindeman et al., 1998) but the shape of the concentration profiles (Fig. 6b,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, Si¹ 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). 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. The textural evidence of Skaergaard cumulates support a very slow cooling rate (Holness et al., 2007), suggesting the potential for prolonged re-equilibration.

The findings from olivine REE mapping are in agreement with the more general observation (from Fig. 3 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

Table 4
Trace element data for regions of interest (ROI) extracted from plagioclase and olivine.
Errors are reported as internal $2 \times$ standard error.

ROI	1	2	3	4	5	6	7
Phase	Plagioclase	Int2SE	Plagioclase	Int2SE	Olivine	Int2SE	Olivine
ppm	Al	210,000	13,000	220,000	9600	230,000	11,000
ppb	Sc	1900	380	1600	120	2000	130
	Y	540	76	490	54	650	75
	La	8100	2400	8200	1800	10,000	1600
	Ce	13,000	2200	14,000	2700	17,000	2600
	Pr	1100	120	1200	190	1400	180
	Nd	2500	310	2700	450	3200	290
	Sm	410	78	460	71	610	79
	Eu	2000	130	2100	96	2300	130
	Gd	270	68	320	52	360	35
	Tb	31	9	32	4.6	36	5.3
	Dy	130	25	90	17	130	19
	Ho	21	6.4	17	4.2	27	6
	Er	91	34	51	13	86	20
	Tm	7	4.6	4.5	2	3.7	1.4
	Yb	59	35	28	11	39	13
Lu	7.2	5.6	1.7	1.3	1.8	1.2	
7	8	9	10	11	12	13	14
Int2SE	Olivine	Int2SE	Olivine	Int2SE	Olivine	Int2SE	Olivine
ppm	240	1100	380	560	110	510	820
	320	8200	400	7600	490	7800	8100
	24	270	22	290	17	310	310
	8.9	23	10	13	5.4	4.1	12
	12	29	12	24	7.4	25	56
	1.9	2.3	2	1.3	0.8	1.8	1.9
	6.1	4.7	2.8	5.3	2.6	2.8	14
	3.2	0	0	0.9	1.8	4.5	0
	3.1	9.7	3.8	5.4	2.8	3.6	6.4
	2.9	4.5	3.6	5.6	4.8	5.1	0
	0.8	2	1.3	1.4	0.6	1.8	1.6
	4.1	17	4.9	23	4.3	18	18
	2.3	9.9	2.6	11	2.2	10	12
	12	84	14	100	11	110	96
	1.5	14	2.9	13	1.7	13	11
24	260	27	240	21	270	220	
4.8	61	6.4	66	5.5	54	58	

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. 6b). 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.

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 overestimates 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 neighbouring minerals with high REE contents will have a stronger influence on the olivine than those with low levels of REE. Equally, transfer of LREE from neighbouring phases with strongly developed twinning, cleavage and other micro-textural complexities may aid migration over slower volume-diffusion (e.g. Wartho et al., 1999). 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.

5. 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_0 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 REE behaviour during mantle melting. 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 7000. The extent of concentration contrast apparently influenced the extent to which original REE systematics in olivine were subject to redistribution.

In natural olivine, solid-state redistribution of the REE, and especially the LREE, should be considered a common process (see also Sun and Liang, 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 (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.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2017.10.020>.

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