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Lutetium incorporation in magmas at depth: changes in melt local environment and the influence on partitioning behaviour

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Abstract

The structure of two Lu doped (4000 ppm) model end member silicate liquids, a highly polymerised haplogranite (Si-Al-Na-K-O) and a less polymerised anorthite-diopside (Si-Al-Mg-Ca-O), have been studied up to 8 GPa using *in situ* x-ray diffraction techniques. The results are the first to identify trace rare Earth element incorporation in silicate melts at high pressure. At pressures below 5 GPa, the bonding environment of Lu-O was found to be dependent on composition with coordination number $CN_{Lu-O} = 8$ and bond distance $r_{\rm Lu-O} = 2.36$ Å in the haplogranite melt, decreasing to $CN_{\rm Lu-O} = 6$ and $r_{\rm Lu-O} = 2.29 \,\text{\AA}$ in the anorthite-diopside melt. This compositional variance in coordination number at low pressure is consistent with observations made for Y-O in glasses at ambient conditions and is coincident with a dramatic increase in the partition coefficients previously observed for rare Earth elements with increasing melt polymerisation. With increasing pressure we find that CN_{Lu-O} and r_{Lu-O} remain constant in the haplogranite melt. However, an abrupt change in both Lu-O coordination and bond distance is observed at 5 GPa in the anorthite-diopside melt, with CN_{Lu-O} increasing from 6 to 8-fold and $r_{\rm Lu-O}$ from 2.29 to 2.39 Å. This occurs over a similar pressure range where a change in the P-dependence in the reported rare Earth element partition coefficients is observed for garnet-, clinopyroxene-, and olivine-melt systems. This work shows that standard models for predicting trace elements at depth must incorporate the effect of pressure-induced structural transformations in the melt in order to realistically predict partitioning behaviour.

1 1. Introduction

Trace elements are highly fractionated during planetary differentiation events, be-2 cause of differential partitioning between minerals, melts and metals at high pressures 3 (P) and temperatures (T). The resulting partition coefficients are used as key indicators 4 of depth, temperature, composition and potential age of melting events since planetary 5 formation (McIntire (1963)). Trace element partitioning behaviour at mantle pressures 6 is of particular interest for dating early crust formation on Earth and the Lu/Hf iso-7 tope system is regularly used to constrain early Earth melting processes (Guitreau et al. 8 (2012)). Many studies have shown that variables such as composition, P, T and oxygen g fugacity have a control on the mineral/melt partitioning of trace elements (see Wood 10 and Blundy (2013) and references within). Although it has long been recognised that 11 crystal chemistry and composition play a major role in controlling how elements parti-12 tion (Blundy and Wood, 1994), fewer studies have focused on the influence of the melt 13 structure due to the lack of systematic experimental data (Corgne et al., 2012). 14

Variations in the melt however do influence partitioning significantly, as first re-15 ported by several compositional studies, e.g. olivine/melt Ni partitioning (Hart and 16 Davis, 1978), rare earth elements (REEs) partitioning between granitic and gabbroic 17 melts (Ryerson and Hess, 1978; Schmidt et al., 2006), REE clinopyroxene/melt parti-18 tioning (Gaetani, 2004), titanite/melt trace element partitioning (Prowatke and Klemme. 19 2005), REE forsterite/melt partitioning (Evans et al., 2008). As the polymerisation of 20 the melt was increased, a two orders of magnitude increase in partition coefficient for 21 trivalent rare earth elements such as Lu, Y, La, is observed with high field strength 22 elements (HFSE) such as Hf and Zr unaffected (Prowatke and Klemme, 2005; Schmidt 23 et al., 2006). Prowatke and Klemme (2005) concluded that the polymerisation of the 24 melt reduces the number of non-bridging oxygens available to bond with the trivalent 25 cations, resulting in a preference for REEs to enter less polymerised melt structures. 26 This was confirmed by a molecular dynamic study of Y in silicate melts (Haigis et al., 27 2013), that demonstrated the greater affinity of Y for Ca than for Si or Al in depolymer-28 ized melts, due to the weaker nature of the Ca-O bond compared to the Si(Al)-O bonds, 29 resulting in more non-bridging oxygens being effectively available for Y. If pressure also 30 has a significant effect on the melt structure and influence the compatibility of ele-31 ments, then our current perception of how these element pairs behave at the conditions 32 of melting may be altered. 33

³⁴ To predict partitioning ratios, current models are based on experimental data for

partition coefficients measured within individual systems and extrapolated for different 35 size and charge of cations. One model that is frequently used to predict partitioning 36 ratios is the 'lattice strain model' (Blundy and Wood, 1994). This incorporates the 37 effect of ionic radius, charge and cation size in a model that links the parabolic relation 38 between the partition coefficient and ionic radius with the size of the ion and Young's 39 modulus or elasticity of the lattice site. No explicit term for the effect of melt structure 40 is included as it is assumed to be negligible and can be summarised within the initial 41 measured partitioning ratio D_0 , which normalises the partition coefficient of a chosen 42 cation with a specific melt composition. 43

Amongst the few existing studies on REE partitioning with pressure, only the gar-44 net/melt, clinopyroxene/melt and olivine/melt systems have been studied over a P-45 range large enough to cover most terrestrial magmatic processes i.e. up to 5-6 GPa, 46 other studies being restricted to below 3.5 GPa. The garnet/melt studies show a change 47 in the *P*-dependence of mineral/melt partitioning, with an initially large decrease in 48 partition coefficient and a compatibility plateau after 5 GPa. (Figure 1). For Hf and Zr 49 this trend was not observed and they were largely unaffected. This would suggest that at 50 P > 5 GPa partition coefficients between REE and 4+ cations may become similar. The 51 transition to majorite may be the cause of this change in REEs partitioning behaviour 52 (Draper et al., 2003), however, it does so at the cost of a reduced site elasticity and 53 reduced cation size which is incompatible with mineral physics rules. To solve inconsis-54 tencies in apparent site elasticity trends, van Westrenen and Draper (2007) introduced 55 corrections for T including an empirical correction for site elasticity by fitting a larger 56 set of garnet/melt partitioning data. Under increased T, $D^{\text{mineral/melt}}$ is expected to get 57 closer to unity due to the induced thermal disorder on crystal lattice sites. This better 58 parameterisation of the lattice strain model clearly improved its robustness, although 59 site elasticity values outside the 500-600 GPa range still cannot be reproduced. Be-60 sides, later datasets showed the strongest P-change of $D_{\rm Lu}^{\rm garnet/melt}$ between 3 and 8 GPa 61 (Figure 1), where data were collected over a 100 K T-range only (Suzuki et al., 2012). 62 Datasets collected on larger P-ranges (up to 17 GPa for (Corgne et al., 2012) and 20 63 GPa for Suzuki et al. (2012) vs up to 10 GPa for van Westrenen and Draper (2007)) 64 point out a worsening of the predictive value of the model at higher pressures. Clinopy-65 roxene/melt partitioning studies at P up to 3.5 GPa have been parameterized by Wood 66 and Blundy (1997) and subsequent papers. The exploration of a larger compositional 67 space at 1.5 GPa demonstrated the dependence of $D_{\rm REE}^{\rm CPx/melt}$ on melt polymerization 68

rather than crystal composition (Gaetani, 2004), an effect restrained to compositions 69 closed to the lherzolite solidus. Higher P data collected up to 12 GPa (Suzuki et al., 70 2012) show an overall similar *P*-trend to the garnet/melt system (Figure 1). In the 71 case of olivine/melt data, the REE partition coefficients decrease with increasing silica 72 in the melt at room P (Evans et al., 2008). This is at odds with the main stream of 73 studies showing the opposite behaviour (Hart and Davis, 1978; Ryerson and Hess, 1978; 74 Prowatke and Klemme, 2005; Schmidt et al., 2006), and might be taken with caution as 75 the authors pointed out the poor fit statistics (Evans et al., 2008). Under high P, REE 76 partition coefficients between olivine and peridotitic melt for 3+ cations decrease with 77 increasing pressure between 2-10 GPa (Imai et al., 2012). As for garnet, the apparent 78 site elasticity behaves anomalously with P, decreasing by 200 GPa of which the T-effect 79 can only explain a maximum of 33 GPa. Instead, Imai et al. (2012) proposed that elas-80 ticity of the cation site in the melt affects partitioning as changes on the crystal lattice 81 alone would not produce a large enough effect. It is currently challenging to test this 82 hypothesis without a proper understanding of site elasticity in melts. It is nonetheless 83 true that the large compressibility difference between melts and crystals that exists at 84 ambient pressure largely diminishes with pressure (see Sanloup (2016) for a review and 85 references therein) as the melt becomes much harder to compress. Consequently, it 86 is expected that the strain energy resulting from the insertion of REE elements in the 87 melt ceases to be negligible. However, the fine P-mesh available for the Gt/melt system 88 implies that the strong change in *P*-dependence of $D_{Lu}^{Gt/melt}$ excludes a purely gradual 89 transformation, an effect that could be artificially smoothed for CPx/melt, Olivine/melt 90 systems due to the insufficient mapping of the P space. Rather, the observations on 91 garnet/melt, clinopyroxene/melt and olivine/melt systems, taken together, point to a 92 potential change in trace element local environment. As pointed out by Haigis et al. 93 (2013), if melt properties exert some control on element partitioning, their influence is 94 hidden in the adjustable parameters used in current lattice strain models, and as such. 95 cannot be predicted nor explained by the model. In their development of a predictive 96 mineral-melt partitioning model for clinopyroxene, Wood and Blundy (1997) assumed 97 that mineral-like trace element sites are present in silicate melt. However, if the nature 98 of the quasi-crystalline components changes, the energetics of partitioning are such that 99 partitioning should also change (van Westrenen et al., 2000). 100

Studies on silicate glasses, and more recently liquids, have shown that structural alterations do occur within the liquid with increasing pressure. For example, major



Figure 1: Mineral-melt partition coefficient data $(D_{Lu}^{\min/melt})$ for Lu with pressure. For the sake of intercomparison, $D_{Lu}^{CPx/melt}$ have been multiplied by 5, and $D_{Lu}^{Olivine/melt}$ multiplied by 25. Data presented are from studies where the composition was consistent over all *P*-*T* conditions, i.e. basaltic composition for garnet and clinoyroxene studies, and peridotitic composition for olivine studies. Other studies (i.e. van Westrenen et al. (1999)) have varying starting compositions that may mask any *P* effects; similarly, datasets have been limited to restricted *T*-range for Gt/melt and CPx/melt studies, which was not possible for olivine/melt due to the small number of studies available at high *P*. Symbols represent various studies; for Gt/melt (circles: Salters and Longhi (1999), diamonds: Salters et al. (2002), squares: Draper et al. (2003), up triangles: Suzuki et al. (2012), down triangles: Corgne et al. (2012)), for CPx/melt (squares: Salters and Longhi (1999), diamonds: Suzuki et al. (2012)), for Ol/melt (circle: Evans et al. (2008), squares: Salters et al. (2002), diamonds: Imai et al. (2012)). Error bars are taken from references where possible and for those not shown are smaller than the symbol size.

element coordination changes have been reported in silicate melts at high pressure, in-103 cluding Si-O coordination change from 4 to 6 above 15-35 GPa (Sanloup et al., 2013; 104 Sato and Funamori, 2010) and the change in Al-O coordination from fully 4-fold co-105 ordination to 50% 6-fold between 2-12 GPa (Drewitt et al., 2015; Yarger et al., 1995). 106 However as yet no minor element incorporation in silicate melts has been studied *in* 107 situ at high pressure. Simon et al. (2013) have investigated the local structural environ-108 ment of Y in silicate glasses using Extended X-ray Absorption Fine Structure (EXAFS) 109 at ambient conditions. They studied the bonding environment of Y within the same 110 glasses as Prowatke and Klemme (2005) and discovered that increasing melt polymeri-111 sation leads to an increase in Y coordination from 6 to 8, with a corresponding increase 112 in average bond distance from 2.28 Å to 2.38 Å. Ponader and Brown (1989) observed a 113 similar compositional variance for La with $CN_{\text{La}-\text{O}}$ increasing from 7 to 9 in the higher 114 polymerised melt, with $r_{\text{La}-\text{O}}$ also lengthening from 2.42 to 2.59 Å. In contrast, Farges 115 (1996) observed a constant CN of 6 for HFSE Zr in silicate glasses, at the exception 116 of a minor amount of octahedral Zr in their most polymerised rhyolitic composition. 117 All these studies suggest that an increase in REE coordination results in an increase in 118 bond length and indicate that important structural changes within the melt, not just 119 the crystal lattice, impact REE local structure and partitioning. Nevertheless, to date 120 all these studies have been carried out on quenched glass systems and not *in situ* at the 121 conditions of melt formation. 122

X-ray diffraction at high pressure and temperature is a well-established technique 123 for studying silicate liquid structures in situ (see the initial study by Funamori et al. 124 (2004) to the current highest P-T range (Sanloup et al. (2013)) but has not previously 125 been applied to trace element studies due to the low concentrations of trace elements 126 (<0.1 wt%) required to represent natural systems. X-ray diffraction has the benefit of 127 providing information on both the short and medium range structure of the melt, includ-128 ing absolute distance and average coordination numbers, without relying on structural 129 models. In this study we employ two end member melt compositions, silicic haplogran-130 ite and a 'model basalt' iron-free anorthite-diopside to monitor structural changes at 131 high pressure and temperature that may affect the incorporation of Lu at 4000 ppm 132 concentration into the melt. 133

Table 1: Compositions from electron microprobe analysis of both initial and recovered samples. HPG (haplogranite) and AnD (anorthite-diopside) compositions given in wt.% oxide. Analyses are based on average of a minimum of 10 sample spots, standard deviations are shown in brackets. *The low totals for the HPG composition are due to the presence of water in the sample and correspond well with the amounts added during synthesis.

Oxide	HPG initial	HPG recovered	AnD Initial	AnD Recovered
SiO_2	71.6(7)	73.2(4)	48.8(5)	46.9(7)
Al_2O_3	10.5(3)	10.7(1)	14.7(2)	14.4(4)
Na_2O	3.3(3)	3.6(2)	-	-
K_2O	3.7(1)	3.8(1)	-	-
MgO	-	-	10.2(2)	14.2(2)
CaO	-	-	22.7(2)	21.6(2)
$\mathrm{Lu}_2\mathrm{O}_3$	3.9(1)	3.9(1)	3.6(1)	3.3(1)
Totals	93.0* (6)	$95.7^{*}(3)$	100.2~(6)	100.5~(6)

134 2. Experimental Methods

135 2.1. Glass Synthesis

The haplogranite (HPG) and anorthite-diopside (AnD) glasses were synthesised by 136 mixing appropriate amounts of reagent grade oxides (SiO₂, Al₂O₃, MgO) and carbonates 137 $(K_2CO_3, Ca_2CO_3, Na_2CO_3)$ from Alfa Aesar (Table 1). The corresponding degree of 138 polymerization as expressed by the NBO/T ratio is 0.4 for the HPG glass, and 1.28 139 for the AnD glass. The mixed powders were ground in an agate pestle and mortar 140 and decarbonated via a slow ramp for 12 hours at 1273 K, then fused at 1873 K in a 141 platinum crucible for 1 hour. The molten glass was quenched by immediately placing 142 the crucible into cold water. The glass was checked for homogeneity, crushed and re-143 ground under acetone and finally fused again three times. Lu was added in the form of 144 high purity Lu_2O_3 (>99.99%) at the desired concentration (Table 1) to a portion of the 145 ground glass in order to have both a doped and plain sample of each composition for 146 comparison. This glass was crushed, re-ground, re-melted at 1873 K and re-fused three 147 times to ensure homogeneous distribution of Lu. All glasses were free from bubbles and 148 contained no signs of crystallisation. The samples were crushed to a fine homogeneous 149 powder before being loaded. The samples were free from iron to minimize the number of 150 elements with bond lengths between 2.2-2.4 Å, as these overlap the Lu-O bond distance. 151

In order to lower the melting temperature of the haplogranite to temperatures achievable in a resistively heated diamond anvil cell (<1270 K), water was added to the sample through high pressure addition in a piston-cylinder press. Platinum capsules were welded containing finely ground haplogranite with 8-10 wt.% H₂O and held for 4 hours at 2 GPa and 1670 K to ensure full homogenisation. The samples were fast quenched by immediately cutting power to the press. Final totals of water were between 6-8% over 4 runs as estimated from the recovered sample analysis (Section 2.3).

159 2.2. X-ray Diffraction

Two experimental methods were used to obtain structural data at high pressure and 160 temperature conditions. 1) Measurements on HPG melts were carried out up to 8 GPa 161 and 1100 K using angle-dispersive x-ray diffraction in resistively heated diamond anvil 162 cells (DACs) on beamline I-15 at the Diamond Light Source (Harwell Campus, UK). 163 2) Experiments on the AnD melts up to 8 GPa and 2000 K were collected on beamline 164 16-BM-B, HP-CAT, at the Advanced Photon Source (Argonne National Laboratory, 165 USA) by energy-dispersive x-ray diffraction. High P-T conditions were generated by 166 use of a Paris-Edinburgh press. Ambient temperature AnD glass data were collected 167 using DACs on beamline 13-ID-D, GSECARS, at the Advanced Photon Source by 168 angle-dispersive x-ray diffraction to ensure that the obtained structural data are not 169 dependent on the type of pressure apparatus (Figure 4 top panel). Ambient pressure 170 AnD glass data were collected on the PSICHE beamline at Synchrotron Soleil, Paris, 171 France (for Lu doped AnD glass) and at P02.2 beamline at PETRA III synchrotron in 172 Hamburg, Germany (for plain AnD glass). 173

To create the high temperature conditions in the DAC, we have used the internal 174 heating technique developed by Fei and Mao (1994) using a Pt wire. Sample was loaded 175 into the 250 µm hole of a rhenium gasket previously indented to 90 µm thickness. In 176 order to access the highest possible Q-range, we used 70° opening Boehler-Almax seats. 177 Temperature was recorded by a K-type thermocouple placed on the very edge of the 178 gasket indent as close to the sample chamber as possible. Thermocouples were previ-179 ously calibrated using materials of known melting temperature (Pb and Na_2CO_3) in 180 order to constrain the error in temperature and the thermal gradient within the sample 181 chamber. High energy x-rays (0.2637 Å wavelength) were used to achieve maximum 182 signal intensity from the low scattering sample with a beam focussed to $70 \times 70 \, \text{um}^2$). 183 Diffraction patterns were collected for the glass and melt for 60 s using a Perkin Elmer 184 detector at each pressure point (Table 2), and a background dark image was collected 185

after each measurement in order to subtract the inherent electronic noise of the detector. Pressure was determined before each experiment by ruby fluorescence and at high temperature it was monitored by a Pt foil inserted into the sample chamber. Diffraction on the Pt calibrant was collected for 10 s at each pressure before and during heating. For each loading, measurements were collected on the samples, and afterwards the gasket was unloaded and replaced in the cell in order to collect the background scattering signal.

A detailed description of the Paris-Edinburgh press experimental techniques and cell 193 design can be found in Kono et al. (2014). The experimental conditions are detailed in 194 Table 2 with pressure determined from the cell-volume change of the pressure transmit-195 ting medium in the form of an MgO cylinder. Temperature was estimated by previous 196 power calibrations using this cell assembly (Kono et al. (2014)). This calibration also 197 accounts for the effect on pressure of the distance between the sample and MgO ring at 198 high temperature using the P-V-T relation of MgO and elastic wave velocity measure-199 ments (Kono et al. (2010)). Diffraction patterns on the MgO were collected at room 200 temperature and above the melting temperature. X-ray diffraction was collected for 201 2 hours using an energy-dispersive germanium solid-state detector at ten 2θ angles (2°, 202 $2.7^{\circ}, 3.5^{\circ}, 5^{\circ}, 7^{\circ}, 10^{\circ}, 15^{\circ}, 20^{\circ}, 27^{\circ}, 35^{\circ}$) enabling coverage up to 20 Å^{-1} in reciprocal 203 space with $Q = 4\pi E \sin \theta / 12.398$, where E is the energy of the x-rays in keV up to 204 >100 keV.205

206 2.3. Recovered Sample Analysis

Recovered HPG quenched samples were polished for electron microprobe analysis 207 at the EMMAC (The Edinburgh Materials and Micro-Analysis Centre), University of 208 Edinburgh. Analyses were carried out using a CAMECA SX100 electron microprobe 209 with an accelerating voltage of 15 keV and 8 µm beam size. Where glass was recovered 210 the samples retained a stoichiometry nearly identical to their starting compositions 211 (Table 1); therefore it is unlikely the samples underwent any major chemical change 212 during the experiments and no loss of Lu. Back scattered electron images taken of 213 the sample show no evidence for quench crystallisation and the sample appears glassy 214 (Figure 2b). Bubbles are present in the HPG which is probably due to exsolution 215 of water during quenching indicating that water remained in the sample during the 216 experiment. The low microprobe totals (Table 1) for the HPG composition are due 217 to the presence of water in the sample. Quenched AnD samples were analysed at the 218 Centre de Microanalyse Camparis, University Pierre and Marie Curie. These results 219



Figure 2: Left: Recovered sample from AnD experiment A8-a using a Paris-Edinburgh press. Right: Recovered sample from HPG experiment D8 from resistive heated DAC polished within Re gasket. Spots are bubbles within the hydrous sample.

(Table 1) show that when the sample quenched to a glass (Figure 2a) the composition after the experiment was nearly identical.

222 2.4. Data Processing

Angle-dispersive diffraction patterns were radially integrated using FIT2D (Hammersley (1996)), with a mask applied to crystalline Bragg peaks that arise from diffraction of the single crystal diamond anvils. The measured experimental intensity, I(Q), contains scattering by both the sample and background contributions, where $Q = \frac{4\pi}{\lambda} \sin \theta$ and λ is the x-ray beam wavelength. In order to isolate the intensity that contains only the structural information, corrections for background intensity, $I_B(Q)$, and attenuation, A(Q), from the sample must be made to the measured intensity given by

$$I(Q) = I_s(Q) + A(Q)I_B(Q) + I_{inc}(Q),$$
(1)

where $I_s(Q)$ represents the scattering from the sample containing only structural information, and $I_{inc}(Q)$ represents the incoherent scattering from the atoms, arising from the sum of the self $\sum_{\alpha} c_{\alpha} f_{\alpha}(Q)^2$ and Compton scattering $\sum_{\alpha} c_{\alpha} C_{\alpha}(Q)$, where c_{α} is the concentration of species α . The values for the self and Compton scattering amplitudes are documented by Hajdu (1972); Hubbell et al. (1975). The Faber-Ziman total structure factor, S(Q), (Faber and Ziman (1965)) is then determined by;

$$S(Q) - 1 = \frac{K[I_s(Q) - A(Q)I_B(Q)] - I_{inc}(Q)}{\langle f^2(Q) \rangle},$$
(2)

where K is required to normalise the data to the incoherent scattering profile and the total structure factor is normalised to the average scattering $\langle f^2(Q) \rangle = (\sum_{\alpha} c_{\alpha} f_{\alpha}(Q))^2$. The radial distribution functions, G(r), are then obtained from a Fourier transform of the S(Q) as:

$$G(r) - 1 = \frac{1}{2\pi^2 r n_0} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ,$$
(3)

where n_0 is the atomic density in atoms per Å³ and the experimental values are listed in Table 2. The densities were estimated by fixing $CN_{\rm Si-O} = 4$ and $d_{\rm Si-O} = 1.61$ Å and integrating under the Si-O contribution for each run (cf section 3.2 and Table 2), as well as applying self-consistency checks. These included ensuring the S(Q) followed the sum rule $\int_0^{\infty} [S(Q) - 1]Q^2 dQ = -2\pi n_0$, and that at low-*r* any unphysical oscillations were minimised as G(r = 0) = 0 (Zeidler et al. (2009); Drewitt et al. (2013)).

For the energy dispersive x-ray diffraction data collected on HP-CAT, Bragg peaks 246 arising from the diffraction of graphite in the cell assembly, and fluorescence of indium 247 on the detector and Lu were removed at each angle. If peaks were at >30% concentra-248 tion between the energies of interest (25 to 55 keV) the data were discarded. Where 249 required, fits were made to the data to extrapolate the signal after the Bragg peaks were 250 removed. The aEDXD program developed by Changyong Park (see Kono et al. (2014)) 251 was then used to scale the primary beam by least squares fitting at the highest 2θ angle. 252 and an evenly spaced S(Q) function was produced by error weighted spline smoothing 253 of the merged data in Q-space. This technique is based on the highest diffraction angle 254 oscillating around 1 because as $Q \to \infty$, $S(Q) \to 1$. The G(r) was then obtained by 255 Fourier Transform of the spline smoothened S(Q) (Equation 3). 256

For the sake of comparison between EDX and ADX data, all S(Q) were cut at 12 Å⁻¹ in order to have the same spatial resolution in the direct space on obtained G(r).

Table 2: $P \cdot T$ conditions of each experimental run as well as estimated densities and results on positions of the first two peaks in the G(r), r_{1-2} . Errors for P and T shown in brackets. Experiment 1 on HPG was carried out on I-15 at the Diamond Light Source. Where both glass and high T data were collected, the density in [] is from the melt. Peak positions are shown only for high T phases unless none were collected. * on temperature indicates where the thermocouple failed during the run and a minimum T was estimated from recrystallisation of Pt and previous thermocouple calibrations. Experiment 2: Collected on HP-CAT at the Argonne Photon Source in june 2014 (-a) and February 2016 (-b). ! represents where the 2nd peak arises from the O-O contribution producing a shoulder on the r_3 peak. † denotes collection at synchrotron Soleil, PSICHE. ‡ denotes collection at Petra P.02 DESY.

Run no.	Comp.	P (GPa)	T (K)	$n_0 ({\rm \AA}^{-3})$	G(r) positions (Å	
Exp. 1					r_1	r_2
D1	HPG	1.4(2)	290	0.07	1.6	-
D2	HPG	2.3(3)	920(50)	$0.075 \ [0.067]$	1.6	-
D3	HPG	4.1(3)	390	0.077	1.62	-
D4	HPG + Lu	0.5(2)	910* (50)	$0.069 \ [0.066]$	1.59	2.33
D5	HPG + Lu	2.1(3)	900* (50)	[0.071]	1.6	2.37
D6	HPG + Lu	2.5(3)	290	0.073	1.59	2.36
D7	HPG + Lu	3.8(2)	973~(40)	$0.079\ [0.078]$	1.6	2.36
D8	HPG + Lu	5.8(4)	1073 (40)	$0.083 \ [0.082]$	1.59	2.35
Exp. 2						
Amb1	AnD (\dagger)	0	290	0.081	1.62	2.41
Amb2	$AnD + Lu (\ddagger)$	0	290	0.081	1.62	2.36
A1-b	AnD	0.8(3)	1570(50)	0.082	1.59	2.78 !
A2-b	AnD	2.4(2)	1670(50)	0.084	1.61	2.76!
A3-b	AnD	3.5(3)	1720(50)	0.087	1.59	2.76!
A4-b	AnD	4.8(3)	1770(50)	0.09	1.59	-
A5-b	AnD	6.5(3)	1870(50)	0.092	1.60	-
A6-b	AnD	8.0(4)	2070~(60)	0.092	1.61	-
A7-b	AnD + Lu	0.8(3)	1570(50)	0.082	1.59	2.34
A8-a	AnD + Lu	2.1(3)	2020 (80)	0.084	1.61	2.34
A9-b	AnD + Lu	3.1(3)	1570(50)	0.09	1.59	2.32
A10-b	AnD + Lu	4.2(3)	1750(50)	0.091	1.62	2.32
A11-a	AnD + Lu	5.2(3)	1850(50)	0.094	1.62	2.41
A12-b	AnD + Lu	7.0(3)	2120(50)	0.093	1.61	2.43



Figure 3: S(Q) for samples listed in Table 2. Black solid lines show Lu doped samples and red dashed curves are the undoped samples at similar pressures. Top panel (A) shows HPG data with pressures shown for the Lu-doped measurements, and undoped glass spectra within 0.5 GPa of these. Glass measurements are shown due to a lack of high-T data at each P, however as discussed in Section 3.1, the HPG glass is analogous to the melt. Lower Panel (B) shows AnD melt experiments at >1500 K and undoped samples are within 1 GPa of given P.

260 3. Results

261 3.1. Overall structural description

Ambient and high temperature data were collected on Lu-doped and undoped sam-262 ples at similar pressure points and when possible, quench measurements were taken on 263 all runs (Table 2). The S(Q) and G(r) are shown in Figures 3 and 4. During heating 264 HPG samples, at temperatures $> 850 \,\mathrm{K}$ the samples either recrystallised or remained 265 amorphous due to the strong glass forming nature of SiO_2 -rich liquids. On these time 266 scales (>1 hour) recrystallization would be expected to occur above the glass transi-267 tion temperature at ~ 850 K (Dingwell, 1998). Therefore, if recrystallization did not 268 occur at these temperatures, the samples were in the super-cooled liquid state. Two 269 experiments (D2 and D7) were conducted at T exceeding the liquidus temperature for 270 haplogranite (Holtz et al. (1992)). From our results, the local environment of Lu in the 271 melt phase and the ambient temperature glass phase are identical as no changes were 272 observed in the corresponding G(r) (grey and red solid lines on Figure 4). In Figure 273 3A the first sharp diffraction peak (FSDP) is seen at 1.98 Å⁻¹ at 0.5 GPa-room T with 274 little change over the *P*-range presented here (up to 2.01 Å⁻¹ at 5.8 GPa-room *T*). This 275 is higher than in the dry HPG glass where the FSDP is at 1.67 Å^{-1} and reflects the 276 depolymerisation of the glass induced by water (Anderson et al., 2014), an effect also 277 reported by forsterite-enstatite melts (Yamada et al., 2007). Alteration to the S(Q)278 from the scattering of Lu is seen in the 2nd peak between $3-5 \text{ Å}^{-1}$, where the peak 279 appears less broad in the Lu-doped case with slightly greater intensity on the upward 280 slope at $3-4 \text{ Å}^{-1}$. 281

The measured S(Q) for the Lu doped AnD compositions are shown in the lower panel (B) of Figure 3 along with undoped samples for comparison. The FSDP shows a gradual increase from 2.05 to 2.1 Å⁻¹ from ambient conditions to 7 GPa. An increase in the FSDP has been seen for other silicate glass and melt compositions and is attributed to the collapse of open cages in the SiO₂ network (Benmore et al. (2010); Meade et al. (1992)). A similar increase in intensity between 3-4 Å⁻¹, as observed in the HPG, is seen in the Lu-doped AnD S(Q).

The resulting real space distribution functions, G(r), are shown in Figure 4B. The main peak positions, atomic densities and uncertainties in real space for each data point are detailed in Table 2. In both compositions the first peak in the G(r), r_1 , is attributed to the $d_{\text{Si}-\text{O}}$ at 1.61(2) Å with 4-fold coordination as shown in other silicate glass, liquid and crystalline structures (Sato and Funamori (2010); Meade et al. (1992)).



Figure 4: Radial distribution functions from the S(Q) shown in Figure 3 and detailed in Table 2. Black solid lines are Lu-doped and red dashed are undoped samples as described in Figure 3. In the HPG (A) grey solid line was collected at high-T and show the similarity between molten high P HPG samples and their respective glass. * highlights the effect of Lu-O on the G(r) and r_2 position. In the AnD (B), at >5 GPa, the + marks where the peak shifts to higher r. In the AnD (B) dotted orange line was collected using a DAC at room T and is similar to the G(r) obtained using a PE cell.

In the HPG, the second peak, r_2 , only appears within the doped samples (D4-D8) at 294 2.36 (3) Å and is attributed to the Lu-O bond distance. In the undoped AnD, the 295 second contribution arises from the Ca-O correlations at ~ 2.4 Å and overlaps the Lu-296 O distance. However the r_2 peak in the doped AnD can be clearly seen to increase 297 in intensity and shift to lower r with the introduction of Lu in the ambient samples 298 (Figure 4B). The correlations observed at 3.0(2) Å in the HPG and 3.2(3) Å in the 299 AnD are attributed to the sum of the O-O and Si-Si contributions and match well with 300 G(r) observed in other studies (Crépisson et al. (2014); Sanloup et al. (2013)) and with 301 MD simulations by Vuilleumier et al. (2009) on similar compositions. In the HPG, 302 this correlation sharpens in the presence of Lu, potentially reflecting increased ordering 303 of the Si-Si distribution, an effect not observed for the AnD melts within the noise 304 level. In the HPG a fourth correlation is visible at 4 Å, this can be attributed to the 305 2nd interaction of Si-O and is much more pronounced in the HPG due to the higher 306 concentration of SiO_2 . 307

308 3.2. Fit of the Lu-O contribution

The radial distribution function G(r) is the sum of all the individual ion-ion interactions within the sample, where each individual Gaussian, $g(r)_{ind}$, represents a single ion-ion contribution. This was fit using the following relations:

$$G(r) = \sum g(r)_{\text{ind}} = \frac{1}{n_0 S_\infty} \sum_i \frac{x_i A_i}{\sigma_i \sqrt{2\pi}} exp\left(\frac{-(r-d_i)^2}{2\sigma_i^2}\right),\tag{4}$$

312 where;

$$A_i = \frac{CN_i}{\int \frac{4\pi r^2}{\sigma_i \sqrt{2\pi}} exp - \left(\frac{(r-d_i)^2}{2\sigma_i^2}\right) dr}.$$
(5)

The coordination number for the individual ion-ion contributions, CN_i , is related 313 to the integral under each individual Gaussian by the density, n_0 , and concentration, 314 x_i , of the species. The interatomic distance is d_i and $\sigma_i = k\sqrt{d_i}$ defines the width of the 315 Gaussian using an adjustable parameter k (Hosemann and Bagchi (1962)), with values 316 ranging from 0.07 to 0.2 depending on the ion-ion contribution. Over this pressure and 317 temperature range it is assumed that the Si-O coordination, CN_{Si-O} , of 4 and bond 318 length, $r_{\rm Si-O}$, of 1.61 Å remain unchanged (Benmore et al. (2010); Sanloup et al. (2013); 319 Sato and Funamori (2010)). Other known peak positions, i.e. Al-O for HPG and Al-O, 320 Mg-O and Ca-O for AnD, and coordination numbers are taken from literature (Guillot 321



Figure 5: Measured G(r) (black markers) from Figure 4 shown with Gaussian fits to both the plain (upper panels) and doped (lower panels) samples. Individual Gaussians, $g_{ind}(r)$, for ion-ion contributions are labelled (dotted lines) along with the total sum of Gaussians (solid black line). Left panels show the AnD compositions and right panels, the HPG. Lu-O contributions are shown in the doped figures by a thick black line and are labelled as Lu-O. Major element fit parameters are identical between the doped and undoped samples using parameters described in Table 3.

Table 3: Ion-ion contributions used to model individual Gaussians, $g(r)_{ind}$ for both compositions. * indicates values taken from references cited in the text, all others are fitted. The coordination numbers obtained for Lu are an average over a minimum of 10 fits with error of ± 0.3 for each final value. $d_i =$ bond length, $CN_i =$ coordination of individual bond. '-' indicates that the value is identical to above mentioned.

<i>P</i> -independent contributions									
HPG				AnD					
	Si-O		Lu-O			Si-O		Mg-O	
	d_i	CN_i	d_i	CN_i		d_i	CN_i	d_i	CN_i
	1.6(2)	4*	2.36(3)	8.1		1.6(2)	4*	2.00(5)	5^*
<i>P</i> -dependent contributions									
HPG			AnD						
Р	Al-O		Р	Al-O		Ca-O		Lu-O	
(GPa)	d_i	CN_i	(GPa)	d_i	CN_i	d_i	CN_i	d_i	CN_i
0.5	1.73(1)	4.1*	0.8	1.73(1)	4.3^{*}	2.40(2)	7^*	2.29(2)	6.2
2.1	-	4.1^{*}	2.1	-	4.5^{*}	-	7.2^{*}	2.32(2)	-
2.5	-	4.2^{*}	3.1	-	4.5^{*}	-	7.4^{*}	2.30(2)	-
3.8	-	4.4^{*}	4.5	-	4.6^{*}	-	7.6^{*}	2.32(2)	-
5.8	-	4.6^{*}	5.2	-	4.7^{*}	-	8.2^{*}	2.39(2)	7.9
			7.8	-	4.9^{*}	-	8.3^{*}	2.41(2)	-

and Sator (2007a,b); Sun et al. (2011); Drewitt et al. (2015), and listed in Table 3). Na contribution is insignificant to the total G(r) due to its light scattering so is not shown here, as in rhyolitic G(r) models by Vuilleumier et al. (2009). Bond distances above 3^{A} (e.g. K-O, Si-Si) do not contribute to the signal below the Lu-O contribution and were fitted as a single contribution.

Initially the undoped data for each pressure are fitted with a sum of Gaussians to obtain interatomic distances for major element ion-ion contributions at r < 2.5 Å along with the O-O contribution (Figure 5), and the same parameters are used to fit the Ludoped data. This results in the isolation of the fit parameters required for $CN_{\rm Lu-O}$ and $d_{\rm Lu-O}$ (Table 3 and Figure 5). This technique limits the uncertainty that arises from fitting complex pair distribution functions but errors in the average coordination arise from the asymmetry of the real $g(r)_{\rm ind}$ correlations and their high r oscillations.

334 3.3. Lutetium incorporation

In the HPG melt, a bond distance $r_{Lu-O} = 2.36(3)$ Å was observed and found to be 335 invariable with pressure within the accuracy of this technique. The average $CN_{\rm Lu-O}$ 336 was determined to be 8.1(3) at all pressure and temperature conditions. For the AnD 337 a CN_{Lu-O} of 6.2 (3) and a r_{Lu-O} of 2.29 (2) Å were determined for the lowest pressure 338 data (< 5 GPa) and the ambient doped glass. The higher pressure points show a clear 339 shift in fit correlation to a higher r_{Lu-O} of 2.40 (3) Å and an estimated CN_{Lu-O} of 7.9 340 (3) (Table 3, Figure 6). This change appears to be abrupt, occurring within 1 GPa 341 (from the accuracy of our data points), and it only affects the Lu-O contribution. This 342 is unlike major element coordination changes which undergo a transition over a broad 343 pressure range (Sato and Funamori (2010); Drewitt et al. (2015); Yarger et al. (1995)). 344 At two pressure points data were also collected at three temperatures over a 400 K345 range (Supplementary Material). The Lu-O contribution in AnD seems unaffected by 346 T at least within the uncertainties of the method, i.e. 0.2 Å on bond length and 0.2 on 347 the coordination number. 348

Crystalline oxide bond lengths for Lu-O are in good agreement with the distance of 349 the r_2 correlation at ambient pressure. Six-fold coordinated Lu-O in oxides is reported 350 to be 2.24 Å and 8-fold coordinated Lu-O at 2.32 Å which agree with tabulated ionic 351 radii by Shannon (1976). Studies on other REE glasses, e.g. YbSiAlO/N, have found 352 similar parameters with Yb-O coordination at 6 and a bond length of 2.22 Å (Uhlig 353 et al. (1998)). Other REE-O such as Dy and La in sodium silicates show decreasing 354 bond length with atomic radii due to the lanthanide contraction, with 6-fold Dy-O at 355 2.29 Å and La-O at 2.48 Å. In this study, a coordination CN_{Lu-O} of 6 gives rise to a 356 bond distance of 2.29 Å, and CN_{Lu-O} of 8 gives 2.36-2.4 Å, as might be expected in the 357 liquid this distance is slightly longer than those of the solids. 358

359 4. Discussion

To our knowledge this is the first experimental study of its kind to identify the structural incorporation of trace elements *in situ* within a silicate melt structure at high pressure, previous EXAFS data having been measured on glasses at ambient conditions. As the ambient pressure results presented for CN_{Lu-O} in glasses corroborate coordinations and bond lengths of Y, a geochemical proxy for Lu but with a lower absorption K-edge energy that makes it suitable for EXAFS analysis (Simon et al., 2013), this method appears to provide a reliable tool for determining REE speciation



Figure 6: a) Change in fits for Lu-O in AnD with P increase above 5 GPa. G(r) for a low P AnD melt (black circles) and high P AnD melt above the Lu-O coordination change (grey squares) and their respective fits (solid lines) are shown. Individual $g(r)_{Lu-O}$ are marked with a clear shift to higher rseen above 5 GPa. b) Individual $g(r)_{Lu-O}$ for low P AnD (black circles), high P AnD (grey squares) and average for HPG (high silica) over the P range studied (open circles).

within silicate melts. A major consideration for this technique is that it is reliant on 367 the applicability of Henry's law as in order to use trace elements in models it is as-368 sumed that the activity, and hence partitioning of trace elements, is independent of 369 concentration below a given limit. This is because at such low concentrations they 370 form an insignificant structural part of a phase and do not alter the thermodynamics 371 of the system. Although Lu here is not at natural levels of concentration (<2 ppm), 372 in this system we propose that Henry's law is still obeyed as: 1) At concentrations of 373 4000 ppm Lu ions are highly unlikely to interact with each other. 2) Many studies 374 on partitioning of trace elements have shown that Henry's law is still obeyed even at 375 several wt. % concentration of trace elements (Beattie (1993); Prowatke and Klemme 376 (2006)). 3) There is a close similarity here with other results on REE (La, Gd and Yb) 377 at much lower concentrations (Ponader and Brown, 1989). 378

379 4.1. Compositional effect

At low pressure, <5 GPa, the results presented show an increase in Lu coordination from 6 to 8 with increasing silica content of the melt, from AnD to HPG, coincident with an increase in bond length of 0.07 (3) Å (Figure 6b). This is consistent with observations on Y-O in silicate and aluminosilicate glasses at ambient conditions (Simon et al. (2013)), and MD calculations on Y-O in aluminosilicate melts (Haigis et al., 2013).

As discussed in the introduction, this compositional effect is attributed to the higher 385 availability of non-bridging oxygens in the basaltic network due to the presence of oxy-386 gens weakly bonded to Ca atoms (Haigis et al., 2013). This is reflected in the narrower 387 distribution around a shorter mean Lu-O distance calculated for less polymerised melts 388 (Haigis et al., 2013) and observed in the present work (Figure 6b and width parameters 389 reported in Table 3). The results for the HPG presented here are all for a hydrous com-390 position. We measure the same Lu-O coordination number in our hydrous composition 391 than reported in dry silicate glasses for Y (Simon et al., 2013). This indicates that 392 the absence of water would not affect our results. Since water de-polymerises the melt 393 structure (Mysen et al., 1980) as can been seen by the shift of the first sharp diffraction 394 peak to high Q-values initially reported for hydrous forsterite-enstatite melts (Yamada 395 et al., 2007) and observed here as well (cf section 3.1), this in turn implies that Lu does 396 not enter the ring structure as expected from its large size. 397

398 4.2. Pressure effect

Within the HPG there is no observable pressure effect on Lu incorporation within 399 the melt structure up to 8 GPa. Silica rich melts are predominantly comprised of 400 interconnected rings of tetrahedra that form cages (Kohara et al., 2011). As pressure 401 increases these collapse as the network is compressed and reaches a packing limit around 402 5 GPa (Wang et al., 2014). However as Lu is unlikely to be accommodated within the 403 cages there is little compressional effect on its speciation within the melt. Within the 404 AnD, however, an increase in P causes an abrupt coordination increase between 4-405 $5 \,\mathrm{GPa}$, accompanied by an increase in the bond length from 2.29 to 2.40 Å (Figure 6). 406 Therefore above 5 GPa the CN_{Lu-O} and r_{Lu-O} are similar to that of the HPG. At high 407 pressures, as the packing limit of the melt is reached, Lu is forced onto 'crystal-like' 408 sites and coordination increases. The presence of these 'crystal-like' sites in the melt 409 was suggested by van Westrenen et al. (2000), who suggested that oxide like, J_2O_3 , and 410 garnet like, $J_3Al_5O_{12}$, sites might exist in the melt structure and influence partition 411 coefficients due to the site elasticity and radii. van Westrenen et al. (2000) showed that 412 partitioning behaviour between silicate melt and garnets could be better explained by 413 the presence of $J_3Al_5O_{12}$ sites with 8-fold coordination within the melt, rather than 6-414 fold J_2O_3 sites. As pressure increases and the melt is packed more closely together it is 415 likely that more 'crystal-like' sites are created within the melt with a higher coordination 416 environment. These have a similar bonding environment to sites within minerals such as 417 garnet and therefore a reduction at high P in partition coefficient between the melt and 418

⁴¹⁹ minerals, where REE³⁺ are usually compatible, would be expected. It is also interesting ⁴²⁰ to note that Ca atoms, that constitute the second shell of neighbours around Lu after ⁴²¹ O atoms in depolymerised melts (Haigis et al., 2013), get progressively bonded to more ⁴²² O atoms in the 0-10 GPa interval with a Ca-O coordination number increasing from 7

423 to 9 (Guillot and Sator, 2007a; Sun et al., 2011; Drewitt et al., 2015).

424 4.3. Impact on Partition Coefficients

The coordination change from 6 to 8 as melt polymerisation increases (i.e. from 425 the AnD to the HPG) corresponds with results presented by Prowatke and Klemme 426 (2005) and Schmidt et al. (2006) on the dramatic increase in REE partition coefficients 427 with melt polymerisation. This increase in compatibility and preference to incorporate 428 in the mineral as polymerisation of the melt increases has been proposed to be due 429 to the energetics associated with bonding to predominantly bridging oxygens. In de-430 polymerised melts the large sites and freely available non-bridging oxygens mean that 431 at lower P the REEs can more easily incorporate into the melt structure than in the 432 crystal lattice. Although we find that Lu has the same coordination in polymerised 433 melts as the basaltic melts at >5 GPa, existing partitioning studies would suggest that 434 the site or mechanism for Lu incorporation in these melts is different as opposite par-435 titioning behaviour is observed (between low pressure basaltic and granitic melts an 436 increase in D_{Lu} is witnessed, but a decrease in D_{Lu} between low pressure and >5 GPa 437 basaltic melts). 438

From these results we propose that in basaltic systems, the melt has a much stronger 439 influence on $D^{\min/\text{melt}}$ with pressure than previously expected. The observed decrease 440 in compatibility with P (Figure 1) could occur in relation with the observed change of 441 local structural environment of Lu in the melt. The coordination change in the melt 442 at 5 GPa results in the plateauing of the $D_{\text{REE}}^{\text{min/melt}}$ as there is little preference for either 443 the mineral or melt at this pressure. This change of local structural environment most 444 likely implies a variation of the volume change of the partitioning reaction between 445 mineral and melt. This is consistent with the previous findings from Corgne et al. 446 (2012) who attributed the factor of 2 mismatch between their measured $D_{\rm REE}^{\rm garnet/melt}$ and 447 those predicted by the van Westrenen&Draper (2007) model to the P-dependence of 448 the reaction volume change that is not accounted for. 449

In other words, the change of local environment of Lu in melts implies that both the pre-exponential term, D_0 , and site elasticity terms be revised in the lattice strain models to explicitly model not only the crystal part but also the melt contribution to element

partitioning. Structural changes in the melts have been advocated to explain the abrupt 453 changes in the *P*-dependence of $D^{\text{magma/metal}}$ for Ni, Co, W circa 5 GPa (Kegler et al., 454 2008; Cottrell et al., 2009; Keppler and Rubie, 1993; Sanloup et al., 2011) and 35 GPa 455 (Sanloup, 2016). The observed change of P-dependence of $D^{\text{magma/metal}}$ for Ni, Co, 456 W, of $D_{\rm Lu}^{\rm mineral/melt}$ for garnet, clinopyroxene and olivine/melt systems above 5 GPa 457 can either be a mere coincidence, or suggest instead an important structural control 458 from the silicate melt. The comparison of molten basalt density with crystalline basalt 459 (i.e. eclogite) density shows that the large crystal-melt density difference at room P460 is divided by 3 at 5 GPa, and almost vanishes above 50 GPa (Sanloup, 2016). The 461 structural control of magmas on element partitioning may thus occur through both 462 abrupt changes of coordination number as reported here for Lu, and through large 463 changes of melt compressibility. 464

465 5. Conclusions

This study shows that x-ray diffraction techniques can be used to study trace ele-466 ment incorporation in liquids at high pressure and can reliably determine the nearest-467 neighbour bond distances for minor elements. Our results show an increase in coordi-468 nation from 6 to 8 of Lu with increasing polymerisation of the melt, consistent with 469 an increase in the $D^{\text{mineral/melt}}$ partitioning ratio from <1 to >100. These results are 470 consistent with other studies carried out on Y, Zr, Th and La with changing glass 471 polymerisation. This data suggest that the coordination of REE in highly polymerised 472 compositions is similar in the glass and melt and also remains constant up to 6 GPa. 473

An abrupt coordination increase from 6 to 8 is observed at 4-5 GPa in less polymerised systems. This coordination change suggests that at >5 GPa compression of the melt results in the formation of 'crystal like' sites that accommodate Lu at high pressure. This change in Lu incorporation is likely to strongly affect the partitioning of Lu at depth, as is the increased stiffness of magmas at high pressures.

Overall these results indicate that not only composition but also pressure induces structural changes in the melt that underpin drastic changes in REE partitioning, and subsequently cause distinct changes in the predicted Lu/Hf ratios from deep magmas. As the melt structure changes with pressure, using a single melt term to normalise the effects of melt on trace element partitioning will not accurately predict partitioning behaviour at depth during magma formation or differentiation. In order to fully understand how partitioning is affected by melt structural changes, standard models should ⁴⁸⁶ be implemented with detailed insight into the exact geometry and elasticity of the REE⁴⁸⁷ sites within the melt network with varying pressure.

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