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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  $CN_{\text{Lu-O}} = 8$  and bond distance  $r_{\text{Lu-O}} = 2.36 \text{ \AA}$  in the haplogranite melt, decreasing to  $CN_{\text{Lu-O}} = 6$  and  $r_{\text{Lu-O}} = 2.29 \text{ \AA}$  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  $CN_{\text{Lu-O}}$  and  $r_{\text{Lu-O}}$  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  $CN_{\text{Lu-O}}$  increasing from 6 to 8-fold and  $r_{\text{Lu-O}}$  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. Introduction

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

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

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

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

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

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

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

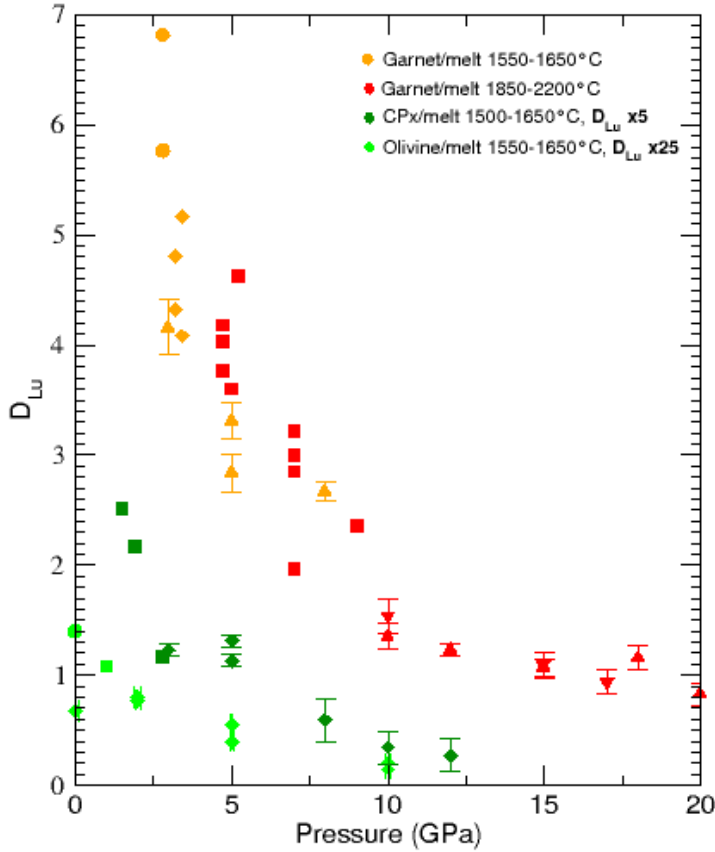


Figure 1: Mineral-melt partition coefficient data ( $D_{\text{Lu}}^{\text{min/melt}}$ ) for Lu with pressure. For the sake of inter-comparison,  $D_{\text{Lu}}^{\text{CPx/melt}}$  have been multiplied by 5, and  $D_{\text{Lu}}^{\text{Olivine/melt}}$  multiplied by 25. Data presented are from studies where the composition was consistent over all  $P$ - $T$  conditions, i.e. basaltic composition for garnet and clinopyroxene 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.

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

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

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 <sub>2</sub>	71.6 (7)	73.2 (4)	48.8 (5)	46.9 (7)
Al <sub>2</sub> O <sub>3</sub>	10.5 (3)	10.7 (1)	14.7 (2)	14.4 (4)
Na <sub>2</sub> O	3.3 (3)	3.6 (2)	-	-
K <sub>2</sub> O	3.7 (1)	3.8 (1)	-	-
MgO	-	-	10.2 (2)	14.2 (2)
CaO	-	-	22.7 (2)	21.6 (2)
Lu <sub>2</sub> O <sub>3</sub>	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

136 The haplogranite (HPG) and anorthite-diopside (AnD) glasses were synthesised by  
137 mixing appropriate amounts of reagent grade oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO) and carbonates  
138 (K<sub>2</sub>CO<sub>3</sub>, Ca<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>) from Alfa Aesar (Table 1). The corresponding degree of  
139 polymerization as expressed by the NBO/T ratio is 0.4 for the HPG glass, and 1.28  
140 for the AnD glass. The mixed powders were ground in an agate pestle and mortar  
141 and decarbonated via a slow ramp for 12 hours at 1273 K, then fused at 1873 K in a  
142 platinum crucible for 1 hour. The molten glass was quenched by immediately placing  
143 the crucible into cold water. The glass was checked for homogeneity, crushed and re-  
144 ground under acetone and finally fused again three times. Lu was added in the form of  
145 high purity Lu<sub>2</sub>O<sub>3</sub> (>99.99%) at the desired concentration (Table 1) to a portion of the  
146 ground glass in order to have both a doped and plain sample of each composition for  
147 comparison. This glass was crushed, re-ground, re-melted at 1873 K and re-fused three  
148 times to ensure homogeneous distribution of Lu. All glasses were free from bubbles and  
149 contained no signs of crystallisation. The samples were crushed to a fine homogeneous  
150 powder before being loaded. The samples were free from iron to minimize the number of  
151 elements with bond lengths between 2.2-2.4 Å, as these overlap the Lu-O bond distance.



152 In order to lower the melting temperature of the haplogranite to temperatures  
153 achievable in a resistively heated diamond anvil cell (<1270 K), water was added to the  
154 sample through high pressure addition in a piston-cylinder press. Platinum capsules  
155 were welded containing finely ground haplogranite with 8-10 wt.% H<sub>2</sub>O and held for  
156 4 hours at 2 GPa and 1670 K to ensure full homogenisation. The samples were fast  
157 quenched by immediately cutting power to the press. Final totals of water were between  
158 6-8% over 4 runs as estimated from the recovered sample analysis (Section 2.3).

## 159 *2.2. X-ray Diffraction*

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

174 To create the high temperature conditions in the DAC, we have used the internal  
175 heating technique developed by Fei and Mao (1994) using a Pt wire. Sample was loaded  
176 into the 250  $\mu\text{m}$  hole of a rhenium gasket previously indented to 90  $\mu\text{m}$  thickness. In  
177 order to access the highest possible  $Q$ -range, we used 70° opening Boehler-Almax seats.  
178 Temperature was recorded by a K-type thermocouple placed on the very edge of the  
179 gasket indent as close to the sample chamber as possible. Thermocouples were previ-  
180 ously calibrated using materials of known melting temperature (Pb and Na<sub>2</sub>CO<sub>3</sub>) in  
181 order to constrain the error in temperature and the thermal gradient within the sample  
182 chamber. High energy x-rays (0.2637 Å wavelength) were used to achieve maximum  
183 signal intensity from the low scattering sample with a beam focussed to 70×70  $\mu\text{m}^2$ .  
184 Diffraction patterns were collected for the glass and melt for 60 s using a Perkin Elmer  
185 detector at each pressure point (Table 2), and a background dark image was collected

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

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

### 206 *2.3. Recovered Sample Analysis*

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

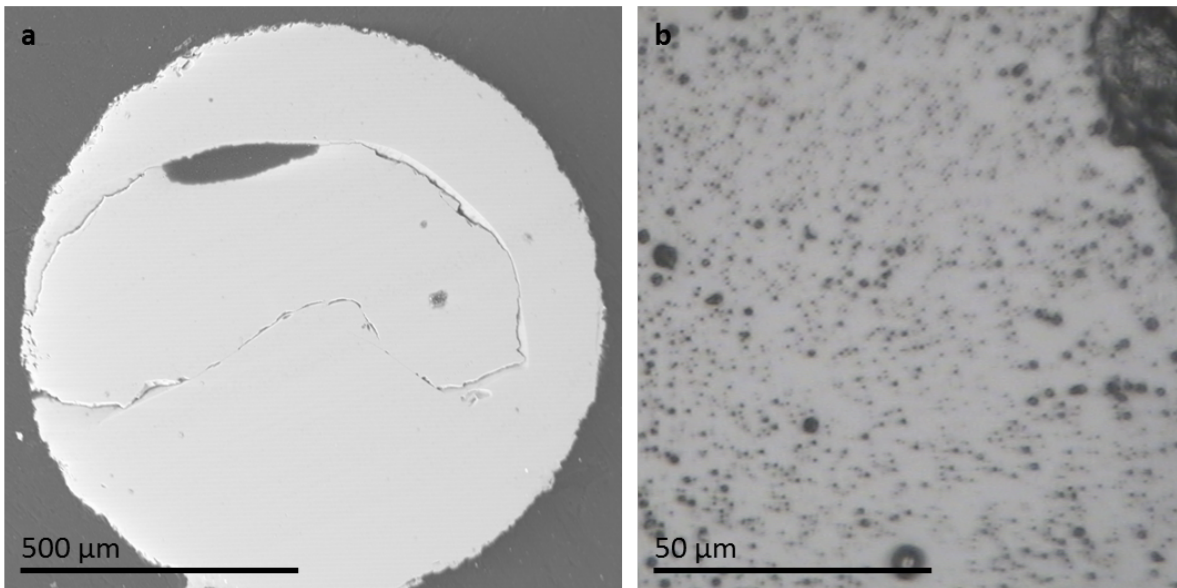


Figure 2: Left: Recovered sample from AnD experiment A8-a using a Paris-Edinburgh press. Right: Recovered sample from HPG experiment D8 from resistive heated DAC polished within Re gasket. Spots are bubbles within the hydrous sample.

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

#### 222 2.4. Data Processing

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

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

230 where  $I_s(Q)$  represents the scattering from the sample containing only structural  
 231 information, and  $I_{inc}(Q)$  represents the incoherent scattering from the atoms, arising  
 232 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  
 233  $c_{\alpha}$  is the concentration of species  $\alpha$ . The values for the self and Compton scattering

234 amplitudes are documented by Hajdu (1972); Hubbell et al. (1975). The Faber-Ziman  
 235 total structure factor,  $S(Q)$ , (Faber and Ziman (1965)) is then determined by;

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

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

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

240 where  $n_0$  is the atomic density in atoms per  $\text{\AA}^3$  and the experimental values are listed  
 241 in Table 2. The densities were estimated by fixing  $CN_{\text{Si-O}} = 4$  and  $d_{\text{Si-O}} = 1.61 \text{\AA}$  and  
 242 integrating under the Si-O contribution for each run (cf section 3.2 and Table 2), as  
 243 well as applying self-consistency checks. These included ensuring the  $S(Q)$  followed the  
 244 sum rule  $\int_0^{\infty} [S(Q) - 1] Q^2 dQ = -2\pi n_0$ , and that at low- $r$  any unphysical oscillations  
 245 were minimised as  $G(r = 0) = 0$  (Zeidler et al. (2009); Drewitt et al. (2013)).

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

257 For the sake of comparison between EDX and ADX data, all  $S(Q)$  were cut at  
 258  $12 \text{\AA}^{-1}$  in order to have the same spatial resolution in the direct space on obtained  
 259  $G(r)$ .

Table 2:  $P$ - $T$  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)	$n_0$ ( $\text{\AA}^{-3}$ )	$G(r)$ positions ( $\text{\AA}$ )	
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 (†)	0	290	0.081	1.62	2.41
Amb2	AnD + Lu (‡)	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

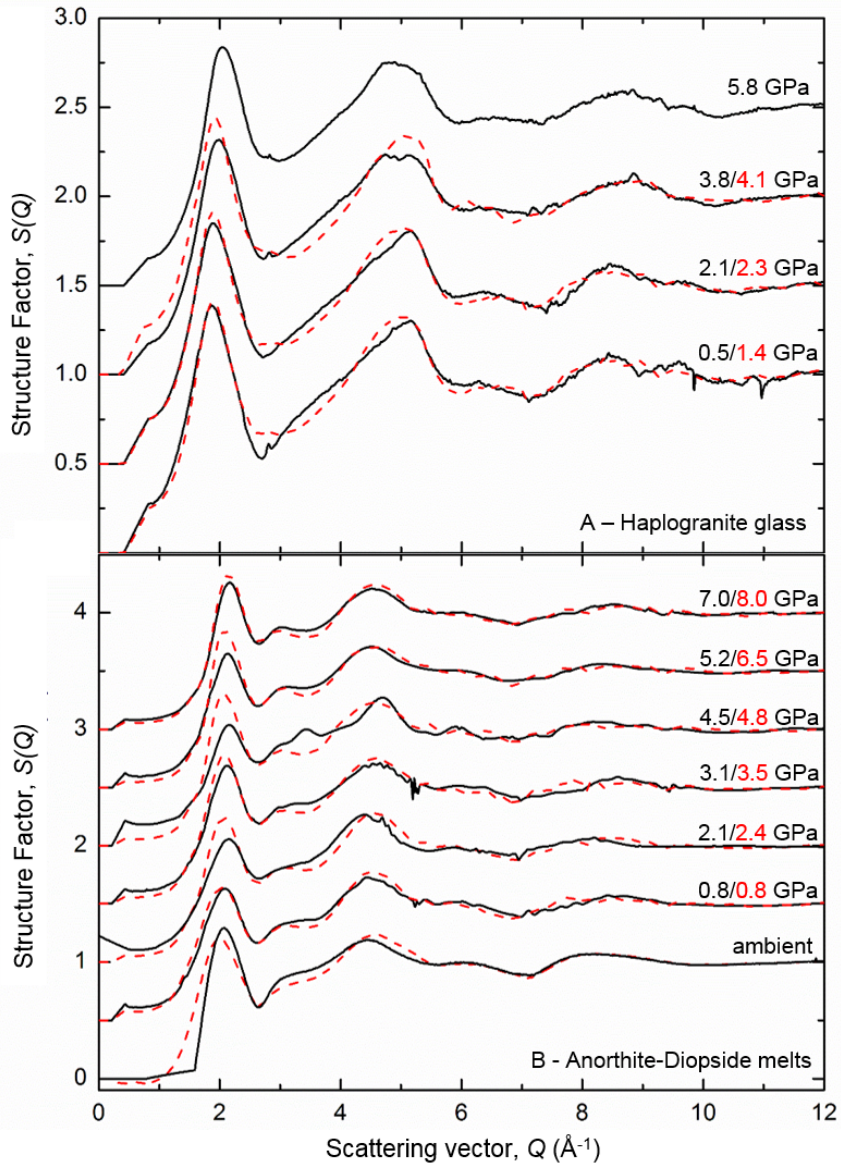


Figure 3:  $S(Q)$  for samples listed in Table 2. Black solid lines show Lu doped samples and red dashed curves are the undoped samples at similar pressures. Top panel (A) shows HPG data with pressures shown for the Lu-doped measurements, and undoped glass spectra within 0.5 GPa of these. Glass measurements 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

262 Ambient and high temperature data were collected on Lu-doped and undoped sam-  
263 ples at similar pressure points and when possible, quench measurements were taken on  
264 all runs (Table 2). The  $S(Q)$  and  $G(r)$  are shown in Figures 3 and 4. During heating  
265 HPG samples, at temperatures  $>850$  K the samples either recrystallised or remained  
266 amorphous due to the strong glass forming nature of  $\text{SiO}_2$ -rich liquids. On these time  
267 scales ( $>1$  hour) recrystallization would be expected to occur above the glass transi-  
268 tion temperature at  $\sim 850$  K (Dingwell, 1998). Therefore, if recrystallization did not  
269 occur at these temperatures, the samples were in the super-cooled liquid state. Two  
270 experiments (D2 and D7) were conducted at  $T$  exceeding the liquidus temperature for  
271 haplogranite (Holtz et al. (1992)). From our results, the local environment of Lu in the  
272 melt phase and the ambient temperature glass phase are identical as no changes were  
273 observed in the corresponding  $G(r)$  (grey and red solid lines on Figure 4). In Figure  
274 3A the first sharp diffraction peak (FSDP) is seen at  $1.98 \text{ \AA}^{-1}$  at 0.5 GPa-room  $T$  with  
275 little change over the  $P$ -range presented here (up to  $2.01 \text{ \AA}^{-1}$  at 5.8 GPa-room  $T$ ). This  
276 is higher than in the dry HPG glass where the FSDP is at  $1.67 \text{ \AA}^{-1}$  and reflects the  
277 depolymerisation of the glass induced by water (Anderson et al., 2014), an effect also  
278 reported by forsterite-enstatite melts (Yamada et al., 2007). Alteration to the  $S(Q)$   
279 from the scattering of Lu is seen in the 2nd peak between  $3\text{-}5 \text{ \AA}^{-1}$ , where the peak  
280 appears less broad in the Lu-doped case with slightly greater intensity on the upward  
281 slope at  $3\text{-}4 \text{ \AA}^{-1}$ .

282 The measured  $S(Q)$  for the Lu doped AnD compositions are shown in the lower  
283 panel (B) of Figure 3 along with undoped samples for comparison. The FSDP shows a  
284 gradual increase from  $2.05$  to  $2.1 \text{ \AA}^{-1}$  from ambient conditions to 7 GPa. An increase in  
285 the FSDP has been seen for other silicate glass and melt compositions and is attributed  
286 to the collapse of open cages in the  $\text{SiO}_2$  network (Benmore et al. (2010); Meade et al.  
287 (1992)). A similar increase in intensity between  $3\text{-}4 \text{ \AA}^{-1}$ , as observed in the HPG, is  
288 seen in the Lu-doped AnD  $S(Q)$ .

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

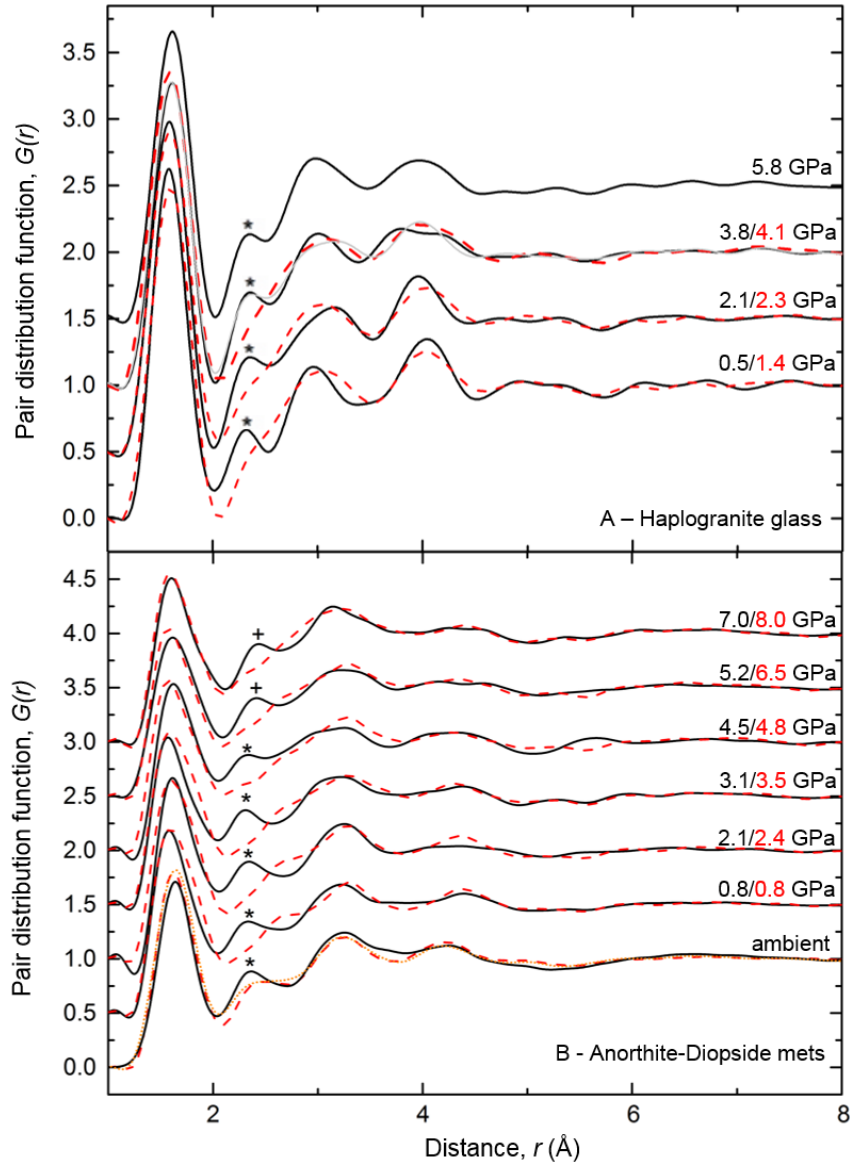


Figure 4: Radial distribution functions from the  $S(Q)$  shown in Figure 3 and detailed in Table 2. Black solid lines are Lu-doped and red dashed are undoped samples as described in Figure 3. In the HPG (A) grey solid line was collected at high- $T$  and show the similarity between molten high  $P$  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.



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

### 308 3.2. Fit of the Lu-O contribution

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

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

312 where;

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

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

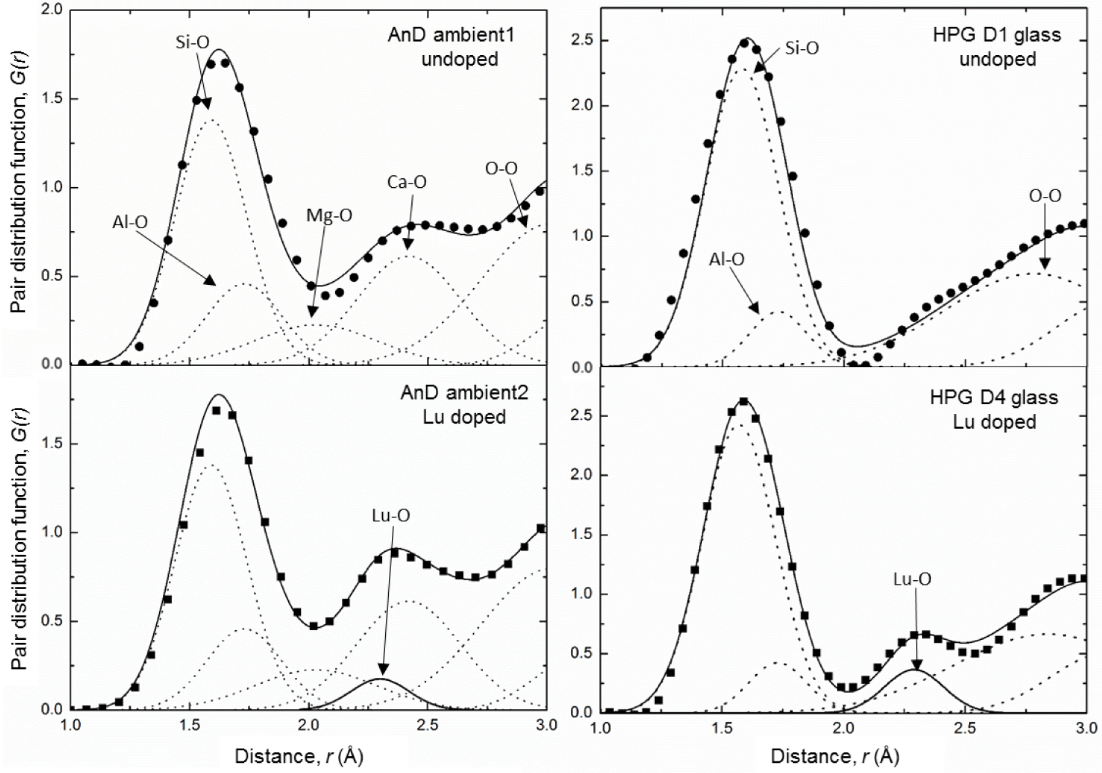


Figure 5: Measured  $G(r)$  (black markers) from Figure 4 shown with Gaussian fits to both the plain (upper panels) and doped (lower panels) samples. Individual Gaussians,  $g_{\text{ind}}(r)$ , for ion-ion contributions are labelled (dotted lines) along with the total sum of Gaussians (solid black line). 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,  $g(r)_{\text{ind}}$  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  $\pm 0.3$  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						
P	Al-O		P	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)	-

322 and Sator (2007a,b); Sun et al. (2011); Drewitt et al. (2015), and listed in Table 3). Na  
323 contribution is insignificant to the total  $G(r)$  due to its light scattering so is not shown  
324 here, as in rhyolitic  $G(r)$  models by Vuilleumier et al. (2009). Bond distances above  
325 3 Å (e.g. K-O, Si-Si) do not contribute to the signal below the Lu-O contribution and  
326 were fitted as a single contribution.

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

### 334 3.3. Lutetium incorporation

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

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

## 359 4. Discussion

360 To our knowledge this is the first experimental study of its kind to identify the  
361 structural incorporation of trace elements *in situ* within a silicate melt structure at  
362 high pressure, previous EXAFS data having been measured on glasses at ambient con-  
363 ditions. As the ambient pressure results presented for  $CN_{\text{Lu-O}}$  in glasses corroborate  
364 coordinations and bond lengths of Y, a geochemical proxy for Lu but with a lower  
365 absorption K-edge energy that makes it suitable for EXAFS analysis (Simon et al.,  
366 2013), this method appears to provide a reliable tool for determining REE speciation

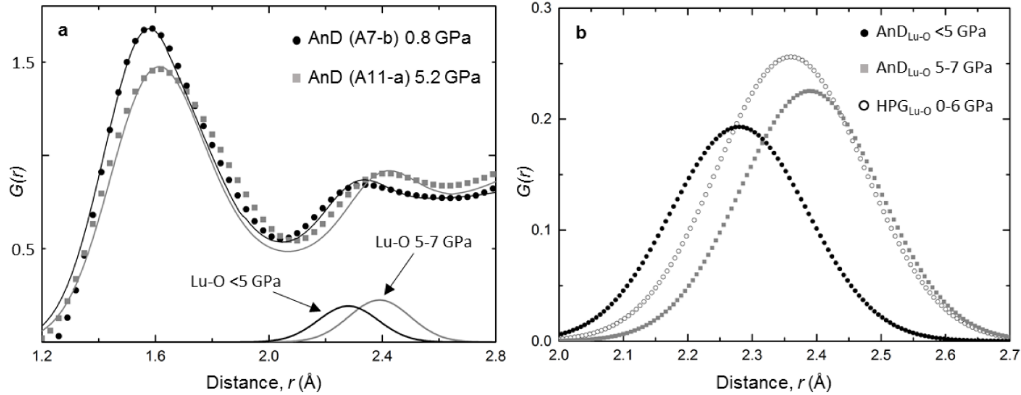


Figure 6: a) Change in fits for Lu-O in AnD with  $P$  increase above 5 GPa.  $G(r)$  for a low  $P$  AnD melt (black circles) and high  $P$  AnD melt above the Lu-O coordination change (grey squares) and their respective fits (solid lines) are shown. Individual  $g(r)_{\text{Lu-O}}$  are marked with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

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

#### 379 4.1. Compositional effect

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

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

#### 398 4.2. Pressure effect

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

419 minerals, where REE<sup>3+</sup> 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

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

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

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

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

## 465 5. Conclusions

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

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

479 Overall these results indicate that not only composition but also pressure induces  
480 structural changes in the melt that underpin drastic changes in REE partitioning, and  
481 subsequently cause distinct changes in the predicted Lu/Hf ratios from deep magmas.  
482 As the melt structure changes with pressure, using a single melt term to normalise the  
483 effects of melt on trace element partitioning will not accurately predict partitioning  
484 behaviour at depth during magma formation or differentiation. In order to fully under-  
485 stand 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 REE  
487 sites within the melt network with varying pressure.

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