

1 **Trace Element Thermometry of Garnet-Clinopyroxene Pairs**
2 **Revision 1**

3
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11 **Abstract**

12 We present major and trace element data on coexisting garnet and clinopyroxene for
13 experiments carried out between 1.3 and 10 GPa and 970 and 1400 °C. We demonstrate that the
14 lattice strain model, which was developed for applications to mineral-melt partitioning data,
15 can be adapted to garnet-clinopyroxene partitioning. Using new and published experimental
16 data we develop a geothermometer for coexisting garnet and clinopyroxene using the
17 concentration of rare earth elements (REE). The thermometer, which is based on an
18 extension of the lattice strain model, exploits the tendency of minerals at elevated
19 temperatures to be less discriminating against cations that are too large or too small for
20 lattice sites. The extent of discrimination against misfit cations is also related to the apparent
21 elasticity of the lattice site on which substitution occurs, in this case the greater stiffness of the
22 dodecahedral X-site in garnet compared with the 8-fold M2-site in clinopyroxene. We
23 demonstrate that the ratio of REE in clinopyroxene to that in coexisting garnet is
24 particularly sensitive to temperature. We present a method by which knowledge of the major
25 and REE chemistry of garnet and clinopyroxene can be used to solve for the equilibrium
26 temperature. This method is applicable to any scenario in which the two minerals are in
27 equilibrium, both above and below the solidus, and where the mole fraction of grossular in garnet

28 is less than 0.4. Our method, which can be widely applied to both peridotitic and eclogitic
29 paragenesis with particular potential for diamond exploration studies, has the advantage over
30 commonly used Fe-Mg exchange thermometers in having a higher closure temperature
31 because of slow interdiffusion of REE. The uncertainty in the calculated temperatures, based
32 on the experimental data set, is less than ± 80 °C.

33 **Keywords:** Lattice Strain Model, geothermometer, garnet, clinopyroxene, eclogite,
34 experimental petrology, REE

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Introduction

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Deciphering the pressure (P) and temperature (T) conditions of deep earth
processes using samples that are now exhumed to the surface requires a detailed
understanding of the high-pressure phases and their chemistry over a range of
relevant conditions. Such information has played an important role in the unraveling of
 P - T conditions during metamorphism and tectonic events. One industrial application
involves diamond exploration where a particular challenge is establishing whether
mantle-derived samples formed at P and T conditions conducive to diamond stability.
In this context, the paragenesis of garnet (grt) + clinopyroxene (cpx) in rocks of
mafic or ultramafic composition has focused attention on this mineral pair as potential
geothermometers and barometers. A number of models exist to estimate equilibrium

52 temperatures of coexisting garnet and clinopyroxene (Raheim and Green 1974; Ellis and
53 Green 1979; Powell 1985; Ai 1994; Nakamura 2009; Sun and Liang 2015). The majority of these
54 thermometers rely on the Fe-Mg exchange between the garnet and clinopyroxene. For
55 example, the geothermometer of Ellis and Green (1979) utilizes the Fe-Mg exchange K_D
56 ($K_D = \frac{(Fe^{2+}/Mg)^{gnt}}{(Fe^{2+}/Mg)^{cpx}}$) between garnet and clinopyroxene. This method is widely used but
57 is susceptible to stoichiometrically-derived estimates of Fe^{3+} in the minerals that can
58 arise from cumulative errors in electron microprobe analyses (EMPA). This has been
59 clearly demonstrated by Li et al. (2005) who measured the $Fe^{2+}:Fe^{3+}$ ratio with Mössbauer
60 and compared this to the ratio calculated by stoichiometry using EMPA. Li et al. (2005)
61 found that in every instance the ratios were different. However it should be noted that
62 advances are being made to EMPA methodology (Matjuschkin et al. 2014) and increasingly
63 XANES is being used to estimate garnet $Fe^{2+}:Fe^{3+}$ ratios (Berry et al. 2010; Hanger et
64 al. 2015). Although there are alternative permutations to the thermometer of Ellis and
65 Green (1979) most methods rely on the Fe-Mg K_D . A further limitation with this type
66 of thermometer can arise through the relative ease of resetting of this exchange
67 during cooling. For these reasons exchange of slow-diffusing trace elements
68 between garnet and clinopyroxene has potential as a more reliable alternative
69 geothermometer, e.g. (Sun and Liang 2012, 2013, 2015). The trace element
70 concentrations of garnet and clinopyroxene from eclogite and garnet peridotite are
71 routinely measured (for example Harte and Kirkley (1997); Appleyard et al. (2007); Gréau
72 et al. (2011)), often as an aspect of diamond exploration strategies. However,
73 interpreting the trace element data is less routine (Griffin and Ryan 1995). Here we further

74 explore the use of trace element contents of coexisting garnet and clinopyroxene as a
75 geothermometer.

76 Early work by Goldschmidt (1937) demonstrated that trace elements enter
77 specific mineral sites and he proposed that ionic charge and radius strongly influence
78 trace element uptake, as measured, for example, by the partition coefficient for a trace
79 element between coexisting phases. Based on the thermodynamic work of Nagasawa
80 (1966) and Brice (1975), Blundy and Wood (1994) and Wood and Blundy (1997)
81 developed the lattice strain model which allows for the prediction of trace element
82 partitioning between a mineral and melt as a function of temperature, pressure and
83 mineral composition (X). The model describes how readily an element, i , with a
84 known ionic radius, r_i , will be incorporated into a crystal lattice. Blundy and Wood
85 (1994) and Wood and Blundy (1997) describe the incorporation of trace ions into
86 crystal lattices via the lattice strain model:

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$$(2003) D_i = D_o \exp \left(\frac{-4\pi EN_A \left[\frac{r_o}{2} (r_i - r_o)^2 + \frac{1}{3} (r_i - r_o)^3 \right]}{RT} \right)$$

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Equation 1

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91 Where D_i is the partition coefficient of element i between crystal and melt, D_o is
92 the theoretical strain-free partition coefficient, E is the apparent Young's modulus of
93 the lattice site, N_A is Avogadro's Number and r_o is the ideal cation size for the lattice
94 site of interest. Based on this model Wood and Blundy (1997) give equations to

95 predict each term for clinopyroxene-melt partitioning of rare earth elements (REE),
96 and van Westrenen et al. (1997) and van Westrenen and Draper (1999) give
97 equivalent terms for garnet-melt partitioning of REE.

98 Figure 1, a schematic representation of the lattice strain model, shows that
99 as the cation radius, r_i , deviates from r_o so the partition coefficient decreases. A
100 large Young's Modulus, E , will narrow the parabola making it harder for the lattice to
101 accommodate a misfit ion. Wood and Blundy (1997) showed that the parabola is
102 lattice site- and cation charge-dependent. The latter dependency arises because
103 heterovalent substitutions in minerals (e.g. Nd^{3+} for Ca^{2+}) require charge-balancing
104 coupled substitutions even when the mismatch between host and substituent ionic
105 radii is very small (Wood and Blundy 2001). In most rock-forming minerals a
106 wide range of charge-coupled substitutions is possible (e.g. $\text{Nd}^{3+} + \text{Al}^{3+} = \text{Ca}^{2+} + \text{Si}^{4+}$
107 or $\text{Nd}^{3+} + \text{Na}^+ = 2\text{Ca}^{2+}$ in clinopyroxene; Wood and Blundy (1997)). The challenge is
108 to find the substitution mechanism that is most energetically favorable and best
109 suited to the bulk chemistry of the system.

110 Temperature and pressure also play a role in influencing the partition
111 coefficient. An increase in T and a decrease in P allow the crystal lattice sites to be
112 more flexible, i.e. reduce their effective E , which in turn allows them to accommodate
113 misfit cations more easily. Note also that T appears in the denominator to Equation 1
114 so that at very high temperatures all mineral-melt partition coefficients approach
115 unity.

116 The success of the lattice strain model for mineral-melt pairs, lies primarily
117 in the fact that the shear moduli of silicate melts are zero, hence $E^{\text{melt}}=0$.

118 Consequently from a purely lattice strain point of view there is no mechanical
119 energy associated with replacing one ion with another in a silicate melt. In reality
120 this is unlikely to be true, especially as other factors influence trace element
121 incorporation into melts, such as co-ordination environment, complexation,
122 configurational entropy etc. Experimental studies of melt-melt partitioning (e.g.
123 Watson (1976), Ryerson and Hess (1978), Schmidt et al. (2006)) reveal that elements
124 in general partition unequally between melts of different composition reflecting the
125 energetic preferences of ions with different charges and/or radii for melts with
126 different compositions/structures. However, the magnitude of melt-melt partition
127 coefficients is always smaller, by several orders of magnitude, than that of mineral-
128 melt partition coefficients for the same range of ionic radii and charge, demonstrating
129 that it is the energetics of trace ion incorporation into minerals that dominates the
130 energetics of mineral-melt exchange equilibria. Moreover, atomistic simulations in
131 which ions are substituted onto lattice sites and the resultant relaxation (strain)
132 energies calculated (e.g. Allan et al. (2003)) corroborate the findings of mineral-
133 melt partitioning studies.

134 Having established that it is the energetics of trace ion incorporation into
135 crystals that dominates mineral-melt partitioning equilibria it is a simple matter to
136 show that an understanding of mineral-melt partitioning for Mineral 1 and for
137 Mineral 2 constitutes an approach to understanding trace element partitioning
138 between Mineral 1 and Mineral 2. The object of this paper is to explore the possibility
139 of extending the lattice strain models for clinopyroxene-melt and garnet-melt towards
140 a better understanding of garnet-clinopyroxene partitioning. Through experiments we

141 investigate the mineral-mineral partitioning of elements, rather than mineral-melt. Lee
142 et al. (2007) used this approach to develop a version of the lattice strain model
143 that describes trace element partitioning between olivine and cpx, which we have
144 modified here for the case of partitioning between garnet and cpx. As our reference
145 element we have chosen Y instead of Lu, which was used by Lee et al. (2007), due
146 to the greater availability of reliable Y data (Y has a natural abundance
147 approximately 60 times greater than Lu).

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$$149 \quad D_i^{grt/cpx} = D_Y^{grt/cpx} \cdot \exp\left(\frac{-4\pi N_A}{RT} \left[\frac{1}{2}(r_Y^2 - r_i^2)(E_{grt}r_o^{grt} - E_{cpx}r_o^{cpx}) + \frac{1}{3}(r_i^3 - r_Y^3)(E_{grt} - E_{cpx}) \right]\right)$$

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Equation 2

151 By referencing the model to an element it obviates the need to explicitly evaluate the
152 ratio of D_o parameters for garnet and cpx that appear in the mineral-melt formulations of the
153 lattice strain model (Equation 1). Moreover, as all of the parameters in the exponential on the
154 right hand side of Equation 2 can be calculated for the P-T-X of interest using existing
155 models for cpx-melt and garnet-melt partitioning, so D_Y is a fit parameter for the experimental
156 data. To add to this current methods of calculating D_o require knowledge of the melt
157 composition and as D_o is not a true equilibrium constant we feel that this is a robust approach.

158 To test our model we performed a series of experiments aimed at
159 investigating the partitioning of trace elements, particularly the rare earth elements
160 (REE) and Y, between garnet and clinopyroxene, using a flux, e.g. a silicate melt, to
161 promote crystal growth. The new experimental dataset is augmented by published
162 experimental data on garnet-clinopyroxene pairs. Conditions of the new experiments

163 were designed so as to increase the coverage of P - T - X space. We will use our
164 experimental dataset to (a) investigate extension of the Lee et al. (2007) approach
165 to garnet and clinopyroxene (b) critically appraise the recent mineral-mineral
166 partitioning work by Sun and Liang (2015, 2013, 2012) and (c) develop a REE
167 geothermometer for coexisting garnet and cpx. We use experimental garnet and cpx
168 from both eclogitic and peridotitic bulk compositions to increase the applicability of the
169 models. In all cases the Nernst partition coefficient, D_i , is defined as the weight
170 concentration of the element i in garnet divided by the concentration of i in cpx. Thus
171 D_i is shorthand for $D_{grt/cpx}$.

172 **Methods**

173 **Experimental Methods**

174
175 Experimental starting materials (supplementary data table S1) consisted of
176 either a mechanical mixture of synthetic oxides (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO)
177 and carbonates (CaCO_3 , Na_2CO_3 , K_2CO_3) or a natural basanitic glass. Starting
178 materials were doped with trace elements chosen to represent the different
179 geochemical groups (HFSE, REE, LILE etc.) but also in a way that minimizes
180 analytical interferences during analysis. Analytical grade oxides of SiO_2 , MgO and
181 Al_2O_3 were dried at 1000 °C for 2 hours. Other oxides and carbonates were oven dried
182 at 200 °C for 24 hours. All oxides and carbonates were then stored either in a
183 desiccator or an oven at 110 °C prior to mixing. Reagents were mixed in appropriate
184 proportions and ground under acetone to homogenize and reduce the grain size.
185 The mixture was decarbonated at 600 to 1000 °C over a minimum of 12 hours.

186 Starting material JP 1 (Table S1) is based on analyses of an eclogite xenolith
187 from the Roberts Victor mine. A synthetic hydrous “rhyolite” flux, based on a partial
188 melt in equilibrium with an eclogitic residue at subduction zone conditions (Klimm et
189 al. 2008), was mixed with the synthetic garnet powder and synthetic cpx powder to
190 enhance the equilibration rates on the timescales of experiments. The use of a
191 fluxing agent has previously proven to be successful in the case of zircon-garnet
192 partitioning by Rubatto and Hermann (2007). The rhyolite flux was formulated
193 using dried oxides and carbonates, as above, but alkalis were added as natural albite
194 and K-feldspar. For experimental run temperatures below 1300 °C 10 wt.% deionized
195 water was added with a micro-syringe. Finally, the flux, the synthetic garnet and cpx
196 powders were mixed in the desired proportions and ground under acetone to
197 further homogenize. The weight proportions used for JP1 were 20:40:40,
198 flux:garnet:cpx. Of the other starting materials, ZrTi is a 25:25:50 mixture of
199 synthetic oxide mixes of grossular, pyrope and diopside, with extra Zr and Ti to
200 saturate with zircon and rutile, BAS is a natural basanitic glass used in experiments
201 by Green et al. (2000), AOB is a synthetic alkali olivine basalt based on previous
202 work by Withers (1997) and NSR-16 is a synthetic basaltic glass, similar in
203 composition to a 12.8 Ma transitional low-K basalt, from the Little North Santiam
204 River area of Oregon in the Western Cascades volcanic arc (R.M. Conrey, written
205 comm). Crystal seeds were not used in any experiments. These different starting
206 materials were chosen to generate garnet and cpx across a wide variation in bulk
207 composition.

208 Trace elements were added to all starting materials as ICP-standard nitrate

209 solutions using a micropipette and dried under a heat lamp. The doped mixtures
210 were re-homogenized in an agate mortar and denitrified at 300 °C. As the BAS glass
211 is natural and already contains a wide range of trace elements only 200 ppm of Li
212 were added. JP 1, ZrTi, AOB and NSR-16 had a complete suite of trace elements added.
213 The trace element contents of all starting materials are given in Table S2. Following
214 doping and denitrification starting materials JP 1, ZrTi and AOB were melted and
215 quenched in a controlled atmosphere, vertical quench furnace at an fO_2 equivalent
216 to the nickel-bunsenite (NNO) buffer, between 1000 and 1520 °C. This fixes the
217 $Fe^{2+}:Fe^{3+}$ ratio in the starting material to match the intrinsic fO_2 of the experimental
218 apparatus and thereby minimizes redox reactions, mediated by H_2 diffusion, taking
219 place during the experiments. The exact 'intrinsic' fO_2 of the various apparatus is
220 unknown but anecdotal evidence suggests it is above NNO. NSR-16 was prepared as
221 a hydrous glass, using $Al(OH)_3$ as a source of H_2O . This trace element-doped powder
222 was loaded into an Au80:Pd20 capsule and held at 0.22 GPa and 1000 °C for 2 hrs in a
223 rapid-quench TZM cold-seal apparatus at NNO+1. To minimize Fe loss during
224 experiments the capsule material was a gold palladium alloy (Au80:Pd20). All
225 capsules were annealed and acid-cleaned before loading and welding. The outside
226 diameter of the capsules was 2 mm and they ranged in length from 0.5 to 2 mm. Some
227 experiments were run with two capsules each containing different starting
228 materials in end-to-end configuration.

229 Experiments from 3.0 to 3.4 GPa pressure were carried out using 1/2" end-
230 loaded piston cylinder apparatus at the University of Bristol. The pressure media

231 were NaCl, Pyrex and crushable alumina with a graphite furnace. The experiments
232 were pressurized and heated simultaneously with the pressure always being the
233 final variable to be increased, i.e. hot piston-in technique. During the experiment the
234 pressure was manually maintained at the desired value and the temperature was
235 measured using an axial $W_{95}Re_5$ - $W_{75}Re_{25}$ thermocouple (not corrected for
236 pressure) and regulated by a Eurotherm controller. The pressure correction of
237 McDade et al. (2002b) was applied and verified by bracketing the quartz-coesite
238 boundary. RB627 (1.3 GPa) was performed in a 3/4" talc/Pyrex assembly with a
239 tapered graphite furnace and pressure-calibrated using the melting point of CsCl
240 (see McDade et al. (2002a)).

241 Experiments at pressures greater than 3.4 GPa were carried out using a Walker-
242 type multi-anvil apparatus at Bayerisches Geoinstitut (B.G.I.), University College
243 London (U.C.L.) and the University of Bristol. In each case the pressure medium
244 was precast MgO octahedra with truncations of varying length depending on the
245 pressure required. Either an MgO or alumina spacer surrounded the capsule with a
246 ZrO_2 insulator around the furnace. Experiments at B.G.I. used the 10/4 assembly with
247 a $LaCrO_3$ furnace, at U.C.L. a 14/8 assembly with a graphite furnace and at Bristol an
248 18/11 assembly with graphite furnace. The temperature was measured with a
249 $W_{97}Re_3$ - $W_{75}Re_{25}$ thermocouple, inserted radially in U.C.L. experiments and axially
250 at B.G.I. and Bristol. The experiments were pressurized over 3 hours and heated for
251 between 6 and 8 hours. The pressure calibrations used the following phase changes:
252 quartz-coesite, coesite-stishovite, Bi I-II, Bi III-V and $CaGeO_4$ (garnet to perovskite).
253 All experiments were ended by turning the power off to give quench times of less

254 than 10 seconds to reach 300 °C.

255 **Analytical Methods**

256 Major element data were collected using the Cameca SX100 electron
257 microprobe at the University of Bristol. For both garnet and cpx the beam
258 conditions were 20 kV, 20 nA beam and 1 μm spot size. Peak count times ranged
259 from 10 to 30 s depending on the concentration of the element of interest.

260 The Cameca IMS-4f ion-microprobe at the University of Edinburgh was used to
261 measure trace elements in garnet and cpx of the experimental run products by
262 secondary ion mass spectrometry (SIMS). All samples had a 20 nm gold coat applied
263 under vacuum. A primary beam of $^{16}\text{O}^-$ with a net impact of energy of 15 keV was
264 used. Positive secondary ions were accelerated to 4500 V with an energy offset of 75
265 eV and a window of 40 eV to minimize transmission of molecular ions. The beam
266 current was varied as necessary to permit analysis of the smaller grains because, in
267 general, beam diameter is a strong function of beam current, i.e. 30 μm beam
268 diameter at 5 nA, 15 μm at 1.5 nA. All SIMS pits were examined subsequently by
269 SEM to check that there was no visible overlap onto adjacent phases. Secondary ion
270 yields were calibrated using standard glass NIST SRM 610 (Hinton 1990) and
271 checked using secondary standards of garnets DD1 (Irving and Frey 1978), AP, SG
272 and cpx SC8804 (van Westrenen 2000). The following positive secondary ion masses
273 were analyzed and ratioed to ^{30}Si (as determined by electron microprobe): ^7Li , ^{11}B ,
274 ^{30}Si , ^{42}Ca , ^{44}Ca , ^{45}Sc , ^{47}Ti , ^{51}V , ^{59}Co , ^{69}Ga , ^{88}Sr , ^{89}Y , ^{90}Zr , ^{93}Nb , ^{138}Ba , ^{139}La , ^{140}Ce , ^{143}Nd ,
275 ^{149}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{267}Er , ^{171}Yb , ^{175}Lu , ^{178}Hf , ^{181}Ta , ^{208}Pb , ^{232}Th , ^{238}U . (Note that

276 ^{71}Ga was used for the NIST610 glass due to overlap on ^{69}Ga of ^{138}Ba , a species with
277 negligible concentration in garnet and clinopyroxene.) The count times per cycle
278 were 5 s for all isotopes, except: 2 s for Si and ^{42}Ca , 3 s for ^{140}Ce , ^{47}Ti and ^{88}Sr , 7 s for
279 ^{143}Nd and ^{149}Sm and 10 s for ^{178}Hf . The number of cycles was between 8 and 15 to
280 produce statistically significant data, with low counting error. Isobaric oxide
281 interferences were greatly minimized by the careful choice of elements, doping levels
282 and energy filtering of secondary ions. The remaining molecular interferences, such
283 as $^{29}\text{Si}^{16}\text{O}$ on ^{45}Sc , were removed by conventional peak-stripping. Overlap of LREE
284 oxides on HREE was corrected using in-house REEO/REE values for cpx and values of
285 van Westrenen (2000) for garnet. Analysis of secondary standards demonstrated that
286 there was no significant secondary ion-yield differences between garnet and cpx thus
287 D_i is taken to be the Si-normalized concentration of an element in garnet divided by
288 that in cpx.

289 **Results and Discussion**

290
291 Experimental run conditions and major element mineral data measured by EMPA are
292 presented in Table 1 and Table 2. Experimental runs times were between 4 and 123
293 hours, see Table 1. We note that for the basanite runs these run durations are identical to
294 those of Green et al (2000) for the same starting materials and run conditions. Attainment
295 of equilibrium in the new experiments is demonstrated through the homogeneity of the
296 SEM images (Figure 2) combined with the small standard deviation in the major element
297 data, Table 1 and Table 2, along with the shape of the parabolae of the REE data.
298 The presented EMPA data for each experiment is a mixture of core and rim measurements,
299 therefore any variability within a crystal, i.e. zoning, would result in a large standard

300 deviation in the major element data. A total of 12 experiments contained garnet and cpx
301 crystals between 20 and 100 μm that could be analysed by ion-microprobe.
302 Occasionally garnets contained cpx inclusions, which were avoided during analysis.
303 Areas of melt or quench crystals occurred in some experiments. The garnet and cpx
304 end members were calculated using the methods of Deer et al. (1992) and Morimoto et
305 al. (1988) respectively. SIMS trace element data for cpx are presented in Table 3 and
306 for garnet in Table 4. Care was taken during data processing to check that there was no
307 contamination by other phases during analysis. One clear indication of glass
308 contamination is elevated concentrations of highly incompatible elements, such as U or
309 Th. In some cases contamination only involved a few analytical cycles and these were
310 eliminated during processing. In cases where there was persistent contamination
311 throughout the analysis the trace element data were discarded.

312 The major element composition of garnet varies very little between each bulk
313 composition. All garnets are pyrope-rich (0.65-0.41 mol fraction) with lesser amounts
314 of grossular (0.26-0.14 mol fraction) and almandine (0.32-0.07 mol fraction), where
315 almandine was calculated from stoichiometric Fe^{2+} . The only experiment with a
316 greater almandine than grossular content is RB627. The majority of the experimental
317 cpx are Na-rich (omphacite following the classification of Morimoto et al. (1988)) with
318 three being relatively Mg-rich and falling within the Ca-Fe-Mg quadrilateral. Al^{iv}
319 ranges between 0.175-0.003 cations per formula unit (c.p.f.u.), Na 0.507-0.108 c.p.f.u.,
320 Ca 0.757-0.475 c.p.f.u., Mg 1.049-0.539 c.p.f.u. and Fe 0.375-0.069 c.p.f.u. The
321 concentration of Ca in both garnet and cpx increases with an increase in pressure,
322 however the rate of change per GPa is greatest in garnet, which may have potential

323 as a barometer, although this is not explored here.

324 The high Fe³⁺ content of the garnets and most cpx (Table 1 and Table 2) is
325 consistent with the assumption of a run fO_2 above NNO. For instance, the average
326 calculated garnet Fe³⁺/Fe^{tot} is 26% (range 8-41%; See Table 2) which is closer to the
327 ReReO₂ buffered runs (~NNO+2) of Matjuschkin et al. (2014) than the 5% Fe³⁺/Fe^{tot} in
328 garnets of the NNO runs of Rubatto & Hermann (2007). Note that at these high fO_2
329 values it is anticipated that >90% of the Eu can be considered as trivalent (see Burnham
330 et al. (2015)).

331 Garnet-cpx trace element partition coefficient data, Figure 3, show that the
332 differing bulk compositions produce similar trends. In all experiments Sr has the
333 smallest garnet-cpx partition coefficient. The absolute concentration of Sr increases
334 greatly in both garnet and cpx with an increase in pressure, however the change in
335 concentration is similar in both minerals resulting in a modest increase in D_{Sr} with
336 P . A comparable effect is seen in Li with P except that the concentration in garnet
337 increases more quickly than cpx resulting in a potential barometer. This effect has
338 been previously identified by Hanrahan et al. (2009, 2009b). Lutetium has the
339 highest partition coefficient in all experiments.

340

341 **Lattice Strain Model Applied to Garnet-Cpx Pairs**

342 Our new data on REE partitioning between the dodecahedral X-site in garnet and
343 the 8-fold M2 site in cpx are in agreement with previous studies. Figure 4 and Figure
344 5 show the partition coefficient plotted against the ionic radius of the cation in 8-
345 fold coordination, using ionic radii values from Shannon (1976). There is an

346 increase in concentration from La to Lu in both minerals, however the LREE have a
347 greater affinity for cpx than garnet, whereas HREE more readily enter garnet. The
348 change in the REE concentration in garnet, from LREE to HREE, is far greater than
349 that of cpx. The concentration of Sm is approximately equal in garnet and cpx,
350 resulting in a partition coefficient of around 1. Garnet-melt and cpx-melt data have
351 been shown to form parabolae by van Westrenen (2000) and Wood and Blundy
352 (1997) respectively. By combining the two mineral-melt parabolae, as we
353 effectively do here, we see an almost linear trend. This is in part because Sc is not
354 considered here as it enters the cpx M1 site rather than the M2 site which
355 accommodates the REE (Allan et al. 2003). Consequently, we only observe one limb
356 of what is still a parabola. One of the objectives of this paper is to investigate the
357 ability of the lattice strain model to describe partitioning between garnet and cpx.
358 To this end we have used the equations of Wood and Blundy (1997) and van
359 Westrenen and Draper (2007) to derive the lattice strain parameters r_0^{cpx} , E^{cpx} , r_0^{grt} ,
360 E^{grt} . We find that these parameters describe the data well. Figure 4 and Figure 5
361 show the curve of weighted best fit for the lattice strain model for the new
362 experimental data (Equation 2) having adopted the Wood and Blundy (1997) and
363 van Westrenen and Draper (2007) r_0 and E terms for cpx and garnet respectively.
364 As all variables are known, i.e. T , P and composition, this demonstrates the
365 agreement between theory and the experimental data and confers a self-consistency
366 between the published mineral-melt and the new mineral-mineral models.

367 To further investigate the lattice strain approach, garnet-cpx partitioning data
368 from other experimental studies were also considered (Table S3). These

369 experiments cover a wide range of $P - T$ conditions (1000 to 1750 °C and 1.5 to 7.0
370 GPa). As with our experiments, the weighted curve of best fit to the garnet-cpx REE
371 partition coefficients is calculated using Equation 2 with r_0 and E for cpx and garnet
372 calculated from Wood and Blundy (1997) and van Westrenen and Draper (2007)
373 respectively. Most data are well described by the lattice strain model and the
374 imposed lattice strain parameters (see Figure S1, Figure S2 and Figure S3). Poor
375 agreement between the model and the data can often be attributed to the quality of
376 the analyses. The experiments by Hauri et al. (1994) and Klein et al. (2000), for
377 example, show many inconsistencies with the other datasets, possibly due to
378 contamination by glass or cpx in the garnet analyses. For this reason these data
379 were not included in further analysis. The experiments by Kuzyura et al. (2010),
380 however, have small analytical uncertainties and no obviously anomalous results,
381 yet the model provides a poor fit to the data (Figure S2). The primary difference
382 between these experiments and all the others is that Kuzyura et al. (2010) used a
383 carbonate-silicate mix, as opposed to silicate only. This results in garnets with a
384 much greater Ca content (around 0.5 mole fraction grossular end-member as
385 opposed to between 0.1 and 0.2 in the other experiments). The effect of Ca on REE
386 partitioning was investigated by van Westrenen et al. (1999) who found that as the
387 grossular component in garnet increases E^{grt} decreases. van Westrenen and Draper
388 (2007) provide a correction for Ca in the r_0^{grt} term which is then used to calculate
389 E^{grt} . In many instances this is acceptable however in very Ca-rich garnets this
390 approach breaks down, as shown by the Kuzyura et al. (2010) experiments. As the
391 experiments by Kuzyura et al. (2010) are extreme in their Ca content they are not

392 included in the temperature comparisons in this study. We do suggest that further
393 work is required to fully quantify the effect of high-Ca on E^{grt} .

394 Sun and Liang (2012, 2013) present a model for garnet-cpx partitioning of
395 REE in which they define new terms for predicting E and r for both minerals. A
396 comparison of the $r_{\text{o}^{\text{cpx}}}$ and E^{cpx} values obtained by Sun and Liang (2012) to those
397 of Wood and Blundy (1997) shows very good agreement. However, for $r_{\text{o}^{\text{grt}}}$ the term
398 of Sun and Liang (2013) is calculated using only the Ca content of garnet and E^{grt}
399 is only dependent on $r_{\text{o}^{\text{grt}}}$. The result is that both parameters in garnet are defined
400 solely by the Ca content. Previous work by van Westrenen et al. (1999); van
401 Westrenen (2000); van Westrenen and Draper (2007) demonstrated that E^{grt} is
402 heavily dependent on a number of other garnet compositional terms, in addition to
403 T and P . Comparing the E^{grt} values calculated through the method of Sun and Liang
404 (2013) with those calculated with the method of van Westrenen and Draper (2007)
405 demonstrates little correlation between the values (Figure 6). The method of Sun
406 and Liang (2013) underestimates the majority of the E^{grt} by several hundred GPa
407 compared to the method of van Westrenen and Draper (2007). E^{grt} values from the
408 two experiments by Kuzyura et al. (2010) are overestimated by around 250 GPa.

409 Calculating E^{cpx} , $r_{\text{o}^{\text{cpx}}}$, E^{grt} and $r_{\text{o}^{\text{grt}}}$ using the method of Sun and Liang (2013,
410 2015) and comparing the fit to the experimental data, analogous to figures Figure 4
411 and Figure 5, demonstrates little correlation between the fit and the data. The
412 mismatch can be attributed entirely to the value of E^{grt} . Figure 6 indicates that using
413 only Ca in garnet to calculate both E^{grt} and $r_{\text{o}^{\text{grt}}}$ is not robust. Whilst the method
414 given by Sun and Liang (2013) aids in predicting temperature and pressure their

415 E_{grt} values are inconsistent with garnet-melt experimental data.

416 **Lattice Strain Model and Temperature**

417

418 The partitioning of trace elements between garnet and cpx given by Equation 2 has an
419 inherent T term. Based solely on Equation 2, a change in the partitioning with T is
420 predicted, both through its occurrence in the denominator of the exponential terms
421 and in its tendency to reduce E and increase r_o . In contrast, although pressure will
422 also affect E and r_o the magnitude of this effect is relatively small, compared to that of
423 temperature. The influence of temperature was confirmed by the work of Wood and
424 Blundy (1997) and van Westrenen and Draper (2007) who found that E in both cpx
425 and garnet has a quantifiable temperature dependence. Dohmen and Blundy (2014)
426 came to a similar conclusion from a study of plagioclase-melt trace element partitioning.
427 Figure 7 confirms the importance of T by displaying the change in the shape of the
428 parabola when all the terms are kept constant and only T is altered. Equation 2 can be
429 re-arranged to make T the dependent variable and therefore give a geothermometer
430 that can be applied to REE partitioning between coexisting garnet and cpx.

431

$$432 \quad D_i^{grt/cpx} = D_j^{grt/cpx} \cdot \exp\left(\frac{-4\pi N_A}{RT} \left[\frac{1}{2}(r_j^2 - r_i^2)(E_{grt} r_o^{grt} - E_{cpx} r_o^{cpx}) + \frac{1}{3}(r_i^3 - r_j^3)(E_{grt} - E_{cpx}) \right]\right)$$

433

$$T(K) = \frac{-4\pi N_A \left[\frac{1}{2}(r_j^2 - r_i^2)(E_{grt}r_o^{grt} - E_{cpx}r_o^{cpx}) + \frac{1}{3}(r_i^3 - r_j^3)(E_{grt} - E_{cpx}) \right]}{R \ln\left(\frac{D_i}{D_j}\right)}$$

435 Equation 3

436

437 Where j is any REE other than i . As three of the parameters in the lattice
 438 strain model (E^{cpx} , E^{grt} and r_o^{grt}) require temperature to be known an iterative
 439 approach was adopted to solve for the temperature. This negates the need for
 440 developing new, temperature-independent methods for calculating each of these
 441 variables and consequently compliments the mineral-melt partitioning work of
 442 previous studies. We consider it essential that any garnet-cpx partitioning model is
 443 consistent with garnet- and cpx-melt partitioning, rather than invoking a set of
 444 new, best-fit lattice strain parameters for one or both minerals.

445 To calculate temperature we use the partition coefficients of two rare earth
 446 elements (replacing i and j in Equation 3), Equation 3 and the lattice strain parameters
 447 as defined by Wood and Blundy (1997) and van Westrenen and Draper (2007). For
 448 clarity, the lattice strain terms given by Wood and Blundy (1997) and van Westrenen
 449 and Draper (2007), where P is in GPa and T is absolute temperature in Kelvin, are:

$$\begin{aligned} E^{cpx} &= 318.6 + 6.9P - 0.036T \\ r_o^{cpx} &= 0.974 + 0.067X_{Ca}^{M2} - 0.051X_{Al}^{M1} \\ r_o^{grt} &= 0.9302X_{Py} + 0.993X_{Gr} + 0.916X_{Alm} + 0.946X_{spes} + 1.05(X_{And} + X_{Uv}) \\ &\quad - 0.0044(P - 3) + 0.000058(T - 1818) \\ E^{grt} &= 2826(1.38 + r_o^{grt})^{-3} + 12.4P - 0.072T + 237(Al + Cr) \end{aligned}$$

450

451

452 Any two REE can be chosen to replace i and j in Equation 3 but it is preferable
453 to choose two elements that have a large relative difference in ionic radius and exist
454 in concentrations high enough to return accurate measurements. An important
455 consideration is the precision of the REE analysis. LREE are invariably in very low
456 concentration in natural garnet and subject to considerable analytical uncertainty. To
457 minimize the error in our temperature prediction we calculated the temperature
458 using multiple REE pairs and compared the weighted mean to the experimental
459 temperature. We assumed that calculating the temperature with multiple pairs
460 avoids too much weight being placed on one erroneous datum. The elements not used
461 in the temperature calculations are La and Ce as they are in very low concentration in
462 garnet and Tb, Dy and Ho as they are often not included in experimental charges.
463 For each temperature calculation the terms in the lattice strain model were
464 calculated with an initial best-guess temperature in order to derive the
465 temperature-dependent terms on the right hand side of Equation 3. The
466 temperature was then adjusted iteratively until the input and the calculated
467 temperature were the same to within 1 degree. The temperature for each element
468 pair, along with the error from the ion probe data, is used to calculate a weighted
469 mean for each experiment. This approach takes into account the uncertainty in the
470 trace element data. Calculated temperatures less than 600 or greater than 2000 °C
471 were assumed to be erroneous and removed from consideration. An excel
472 spreadsheet to perform these calculations is available from the first author.

473 Comparing the temperature calculated through our new method, which uses
474 the lattice strain parameters of Wood and Blundy (1997) and van Westrenen and
475 Draper (2007), with the experimental temperature shows very good agreement (Table
476 5 and Figure 8a). The mean absolute deviation between the temperatures, when the
477 high-Ca experiments by Kuzyura et al. (2010) are disregarded, is only 76 °C.
478 The broad range of bulk compositions for our validation experimental dataset
479 demonstrate that our approach can be applied to any coexisting garnet-cpx pairs.

480

481

482

Applications

483

484 Although the majority of the garnet-cpx geothermometers in common usage
485 utilize the major elements we believe that our rare earth element approach has a
486 number of advantages.

487

488 1) The use of rare earth elements as a geothermometer has an advantage
489 over the Fe-Mg exchange models as the slow diffusion of 3+ cations (van Orman et al.
490 2002) leads to a correspondingly higher closure temperature (Frost and Chacko
491 1989). Work by Pattison (1994) and others shows that the Fe-Mg exchange can
492 return differing temperatures that depend on the grain size of the minerals analyzed.
493 Pattison (1994) suggested that the Fe-Mg in granulites may record the temperature
494 at which inter granular exchange ceased in the rock. By using REE, which diffuse
495 much more slowly, the peak metamorphic temperature should be recovered. See Yao
496 and Liang(2015) and Sun and Liang (2015) for detailed discussion of closure
497 temperatures in bi-mineralic systems.

496 2) The REE geothermometer presented here is developed independently of
497 any other geothermometer. Other models, such as Witt-Eickschen and O'Neill
498 (2005), use natural xenoliths along with extant major element thermometers to
499 develop trace element geothermometers. Such models will therefore inherit any
500 inaccuracies from their "parent" model against which they are calibrated. This will
501 not be the case with our model as it has been developed independently of any pre-
502 existing geothermometer.

503 3) The thermometer developed here is entirely consistent with a
504 substantial body of garnet-melt and cpx-melt partitioning studies that have gone
505 some way to refining the key lattice strain parameters. We have not had to invoke
506 new lattice strain parameters for the specific purpose of recovering temperature
507 from garnet-cpx pairs.

508 4) Finally, the availability of a large number of REE data gives our
509 approach considerable flexibility in that different pairs of REE can be used,
510 according to data availability and precision. Through combining the temperature
511 predictions of multiple REE pairs the most accurate temperature can be estimated.

512 An enduring shortcoming of this and other thermometers is the need to
513 know the equilibrium pressure. Throughout this study where a pressure estimate
514 is required, such as in predicting E_{grt} , the experimental P has been used. Currently
515 the barometers of Simakov (2008) and Sun and Liang (2015) are available for
516 garnet-cpx pairs. Alternatively, many studies use an assumed pressure of 5 GPa to
517 compare data. To avoid including uncertainties inherent in the barometers and to
518 clearly display the error associated with our model we have only used experimental

519 pressures. An increase of 1 GPa in assumed pressure increases the temperature
520 estimate by, on average, 50 °C in our model irrespective of the REE pair chosen.

521 Our experiments show that the effect of pressure on rare earth element
522 partitioning in isothermal, isochemical experiments is not consistent enough to be used
523 as barometer. Comparing the isothermal experiments, Figure 9, for experiments
524 carried out at 1200 and 1400 °C shows that there is not a consistent effect of
525 pressure that can be used to solve for the pressure. The experiments carried out at
526 1200 °C, but variable pressure, are all within error of each other. The experiments
527 at 1400 °C appear to show a pressure effect, however, on closer inspection the effect
528 is not consistent.

529
530

Comparison to existing thermometers

531 The Fe-Mg exchange geothermometer of Ellis and Green (1979) is the most
532 widely used method of estimating temperature for garnet-clinopyroxene pairs. To
533 evaluate our new geothermometer we have calculated the temperature using the
534 method of Ellis and Green (1979), both with and without the calculation of Fe²⁺ by
535 stoichiometry. We have also calculated temperature for the same
536 experiments with the REE method of Sun and Liang (2015) and compared all
537 *T* estimates to the experimental temperature (Table 5). Points of note are that
538 temperature estimates for some of the experiments carried out during this study are
539 significantly over-estimated using the method of Ellis and Green (1979). Even when
540 the error associated with the Fe²⁺ calculation is removed ($T_{(EG)^*}$ in Table 5) the
541 temperature estimates are still several hundred degrees too high. This results in

542 a mean absolute deviation of 240 °C between the temperature calculated using the
543 method of Ellis and Green (1979) and the experimental temperature. The mean
544 absolute deviation between the experimental temperature and that calculated T using
545 the method of Sun and Liang (2014) is 174 °C. This value is compared with our
546 lattice strain approach which has an absolute mean deviation of only 76 °C when the
547 temperature is calculated using the mean of all REE pairs. (The highly discrepant
548 values for Kuzyura et al. (2010) data are not included in either of the REE models.)
549 This clearly demonstrates that not only can the lattice strain model be used to
550 estimate temperature but also the T is more accurate than the most commonly used
551 eclogitic geothermometer. It should be reemphasized that our formulation is not
552 calibrated on the experimental data presented in Table 5. We have simply
553 transferred the lattice strain parameters from garnet-melt and cpx-melt models and
554 applied them. Thus this is a fair test of all thermometers.

555

556

Implications

557 In this paper we explore the potential of the lattice strain model, as derived from studies
558 of mineral-melt partitioning, to be used as a geothermometer. By testing our approach
559 to estimating temperature with both eclogitic and peridotitic minerals we have
560 demonstrated the versatility of the lattice strain model as a thermometer for mantle
561 minerals. Through focusing on garnet and cpx, which are stable over a very wide range
562 of temperature and pressure conditions, we have developed a model that has very wide-
563 reaching applications, both in metamorphic geology, tectonic reconstructions and
564 diamond exploration. Whilst the focus of this paper is on the partitioning of garnet

565 and cpx the approach taken here can be applied to any coexisting mineral pair, as
566 long as a method exists to calculate E and r for the minerals of interest. In light of
567 recent predictive models for plagioclase-melt partitioning of trace elements
568 (Dohmen and Blundy 2014) the potential of cpx-plagioclase pairs as trace element
569 geothermometers would benefit from further evaluation. It also stands to reason
570 that this approach could be used to estimate T from mineral-melt partitioning data,
571 which can be applied to volcanic systems.

572

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Acknowledgements

576 JP is grateful to Rio Tinto for a PhD studentship at the University of Bristol, B.G.I. and
577 Dave Dobson for access to their multi-anvil apparatus and Richard Hinton for
578 assistance with the ion-microprobe analyses. JB acknowledges funding from ERC
579 Advanced Grant CRITMAG and a Royal Society Wolfson Research Merit Award. This
580 work has benefitted from discussion with Chris Smith, Russell Sweeney, John
581 Schumacher, Susanne Skora and Wim van Westrenen. We thank Yan Liang and an
582 anonymous reviewer for thoughtful reviews of our manuscript.

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767
768 **Figures**
769

770

771 **Figure 1.** Schematic representation of the terms in the lattice strain
772 model taken from Wood and Blundy (1997). The Nernst partition
773 coefficient describes the partitioning of an element between a mineral
774 and melt. The parameters are defined in the text.

775

776

777 **Figure 2.** SEM images of typical experimental run products demonstrating
778 homogenous grains, indicative of equilibrium. **a** is a piston cylinder experiment,
779 RD25, at 1200 °C and 3.4 GPa. **b** is a multi-anvil experiment, V545, at 1400 °C
780 and 10 GPa. The scale bar is 100 μm in both cases.

781

782

783 **Figure 3.** Spider diagram of partition coefficients between garnet and cpx for
784 trace element data generated in this research. **a** is JP1 starting composition, **b** is
785 BAS and **c** is the AOB, ZrTi and NSR-16 starting mixes.

786

787 **Figure 4.** Experimental REE partitioning between garnet and cpx as a function
788 of ionic radius of the element. The red line shows the weighted fit calculated
789 using Equation 2 with values of D and r calculated by the method of Wood and
790 Blundy (1997) and van Westrenen and Draper (2007). Error bars show 1
791 s.d. of the mean.

792

793 **Figure 5.** Experimental REE partitioning between garnet and cpx as a function of
794 ionic radius of the element. The red line shows the weighted fit calculated using
795 Equation 2 with values of D and r calculated by the method of Wood and Blundy
796 (1997) and van Westrenen and Draper (2007). Error bars show 1 s.d. of the
797 mean.

798

799 **Figure 6.** Comparison of values of E^{grt} calculated through the model of Sun and
800 Liang (2013) ($E_{\text{(S\&L)}}$) with those found with the model van Westrenen and
801 Draper (2007) ($E_{\text{(vW\&D)}}$) using the experimental the garnet-cpx data set.

802

803 **Figure 7.** The effect of change in T on the partitioning of REE. The black lines
804 use the same experimental data values for E and r and change only T from 800 to
805 1400 °C in 200 °C intervals.

806

807

808 **Figure 8. a.** Comparison of experimental temperature with T found through a
809 weighted mean of REE pairs, from Nd to Lu, and the lattice strain model, Equation
810 3. Error bars are shown where larger than symbol. The red circles are
811 experiments from this study and the black diamonds are those from the
812 literature, see Table 5. The mean absolute deviation is only 75 °C for all the data.
813 **b.** Comparison of calculated T using the weighted mean temperature using all

814 REE pairs lattice strain model ($T_{(JP)}$) with the T found using Ellis and Green
815 (1979) ($T_{(EG)}$) and Sun and Liang (2015) ($T_{(SL)}$), which have a mean absolute
816 deviation of 240 and 278 °C respectively. In both figures the black line shows the
817 1:1 relationship.

818
819 **Figure 9:** Comparison of isothermal, isochemical experiments to show the effect
820 of pressure. The temperature is the experimental T .

821
822 **Figure S1:** Graphs showing published data with red fit line calculated using the
823 methods of Wood and Blundy (1997) and van Westrenen and Draper (2007).
824 The superscript 1 denotes data are normalized to Yb, superscript 2 are
825 normalized to Eu and superscript 3 denotes Er, as opposed to Y, as no Y
826 partitioning data are available.

827
828 **Figure S2:** See **Figure S1** for explanation.

829
830
831 **Figure S3:** See **Figure S1** for explanation.

Table 1: Cpx wt% EMPA data

| Experiment | BL58 | RD25 | G21 | V547 | V546 | V545 | BL88 | RD56 | G25 | RD56 AOB | UCL3 | RB627 |
|--------------------------------|------------|-------------|-------------|------------|------------|------------|------------|------------|------------|-------------|------------|-------------|
| Starting Comp. | JP 1 | JP 1 | JP 1 | JP 1 | JP 1 | JP 1 | BAS | BAS | BAS | AOB | ZrTi | NSR- 16 |
| T | 1200 | 1200 | 1200 | 1400 | 1400 | 1400 | 1100 | 1200 | 1200 | 1200 | 1120 | 970 |
| P | 3.0 | 3.4 | 6.0 | 6.0 | 8.0 | 10.0 | 3.0 | 3.0 | 5.0 | 3.0 | 5.0 | 1.3 |
| t | 6 | 4 | 7 | 6 | 6 | 6 | 48 | 48 | 7 | 48 | 10 | 123 |
| n | 20 | 11 | 6 | 20 | 29 | 14 | 21 | 3 | 3 | 17 | 8 | 6 |
| SiO ₂ | 53.07 (32) | 54.75 (24) | 56.00 (76) | 54.21 (78) | 56.17 (37) | 56.55 (30) | 51.12 (66) | 50.27 (56) | 52.65 (42) | 51.01 (38) | 53.80 (36) | 48.4 (41) |
| TiO ₂ | 0.07 (2) | 0.05 (1) | 0.39 (57) | 0.06 (2) | 0.17 (1) | 0.14 (1) | 0.88 (22) | 0.70 (4) | 0.35 (3) | 0.44 (2) | 0.46 (10) | 1.21 (15) |
| Al ₂ O ₃ | 4.29 (40) | 3.49 (40) | 9.44 (107) | 9.18 (85) | 9.39 (78) | 8.84 (51) | 6.78 (67) | 7.65 (34) | 6.07 (62) | 5.61 (24) | 5.23 (31) | 8.14 (47) |
| Cr ₂ O ₃ | 1.11 (40) | 0.94 (41) | 0.44 (28) | 0.02 (2) | 0.68 (15) | 0.68 (8) | 0.07 (4) | 0.08 (2) | 0.08 (2) | 0.50 (14) | 0.03 (1) | |
| FeO | 3.77 (15) | 4.06 (27) | 3.17 (110) | 4.07 (27) | 4.60 (29) | 4.77 (19) | 6.06 (32) | 6.66 (27) | 4.81 (15) | 6.97 (30) | 5.45 (50) | 11.88 (155) |
| MnO | 0.10 (1) | 0.12 (1) | 0.05 (3) | 0.06 (2) | 0.04 (1) | 0.04 (1) | 0.11 (2) | 0.09 (1) | 0.07 (1) | 0.11 (1) | 0.13 (1) | 0.29 (6) |
| MgO | 17.79 (42) | 19.77 (76) | 11.17 (132) | 12.60 (45) | 10.69 (46) | 10.24 (27) | 12.87 (59) | 12.54 (20) | 13.66 (50) | 14.01 (30) | 15.03 (27) | 10.91 (89) |
| CaO | 17.87 (49) | 15.54 (136) | 14.39 (134) | 13.91 (50) | 13.00 (67) | 12.54 (42) | 19.28 (24) | 18.48 (26) | 18.32 (22) | 18.83 (33) | 16.97 (35) | 16.64 (110) |
| Na ₂ O | 1.54 (11) | 1.62 (12) | 5.67 (47) | 4.70 (36) | 5.52 (34) | 6.43 (25) | 2.19 (19) | 2.64 (10) | 3.25 (31) | 1.95 (14) | 2.04 (10) | 1.5 (41) |
| K ₂ O | b.d. | b.d. | b.d. | 0.66 (11) | 0.23 (2) | 0.35 (2) | b.d. | 0.01 (4) | b.d. | b.d. | b.d. | 0.01 (1) |
| ZrO ₂ | | | | | | | | | | | 0.02 (2) | |
| Total c.p.f.u. | 99.62 | 100.33 | 100.71 | 99.49 | 100.49 | 100.58 | 99.36 | 99.13 | 99.27 | 99.44 | 99.13 | 98.98 |
| Si | 1.91 | 1.95 | 1.97 | 1.93 | 1.99 | 2.00 | 1.87 | 1.84 | 1.91 | 1.87 | 1.96 | 1.82 |
| Al ^(iv) | 0.09 | 0.05 | 0.03 | 0.07 | 0.01 | 0.00 | 0.13 | 0.16 | 0.09 | 0.13 | 0.04 | 0.18 |
| Al ^(vi) | 0.10 | 0.09 | 0.37 | 0.32 | 0.39 | 0.37 | 0.17 | 0.17 | 0.16 | 0.11 | 0.19 | 0.19 |
| Ti | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.03 |
| Cr | 0.03 | 0.03 | 0.01 | 0.00 | 0.02 | 0.02 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 |
| Fe ³⁺ | 0.06 | 0.04 | 0.02 | 0.10 | 0.00 | 0.07 | 0.06 | 0.13 | 0.14 | 0.12 | 0.00 | 0.03 |
| Fe ²⁺ | 0.05 | 0.08 | 0.08 | 0.02 | 0.14 | 0.07 | 0.12 | 0.07 | 0.01 | 0.10 | 0.17 | 0.34 |
| Mn | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| Mg | 0.96 | 1.05 | 0.59 | 0.67 | 0.57 | 0.54 | 0.70 | 0.69 | 0.74 | 0.77 | 0.82 | 0.61 |
| Ca | 0.69 | 0.59 | 0.54 | 0.53 | 0.49 | 0.47 | 0.76 | 0.73 | 0.71 | 0.74 | 0.66 | 0.67 |
| Na | 0.11 | 0.11 | 0.39 | 0.32 | 0.38 | 0.44 | 0.16 | 0.19 | 0.23 | 0.14 | 0.14 | 0.11 |
| K | 0.00 | 0.00 | 0.00 | 0.03 | 0.01 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Zr | | | | | | | | | | | 0.00 | |

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Starting comp. refers to table S1, *T* is in °C, *P* is in GPa, *t* is in hours, *n* is the number of analyses, b.d. is below detection and the parentheses show one standard deviation, e.g. 53.07 (11) should read

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53.07 ±0.11, c.p.f.u. stands for cations per formula unit and are calculated based on 4 cations. The Fe³⁺ is calculated using the method of Schumacher (1991).

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Table 2: Garnet wt% EMPA data

| Experiment | BL58 | RD25 | G21 | V547 | V546 | V545 | BL88 | RD56 | G25 | RD56 AOB | UCL3 | RB627 |
|--------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-------------|-------------|------------|
| Starting Comp. | JP 1 | JP 1 | JP 1 | JP 1 | JP 1 | JP 1 | BAS | BAS | BAS | AOB | ZrTi | NSR- 16 |
| T | 1200 | 1200 | 1200 | 1400 | 1400 | 1400 | 1100 | 1200 | 1200 | 1200 | 1120 | 970 |
| P | 3.0 | 3.4 | 6.0 | 6.0 | 8.0 | 10.0 | 3.0 | 3.0 | 5.0 | 3.0 | 5.0 | 1.3 |
| <i>n</i> | 30 | 4 | 12 | 25 | 13 | 13 | 12 | 20 | 12 | 20 | 21 | 4 |
| SiO ₂ | 41.82 (28) | 41.48 (38) | 42.60 (50) | 42.39 (46) | 42.74 (29) | 43.45 (33) | 39.56 (51) | 40.58 (38) | 39.56 (51) | 40.24 (38) | 41.04 (45) | 38.61 (34) |
| TiO ₂ | 0.16 (12) | 0.27 (2) | 0.24 (21) | 0.11 (2) | 0.36 (4) | 0.44 (4) | 0.78 (18) | 0.61 (12) | 0.78 (18) | 0.51 (5) | 1.46 (54) | 0.94 (37) |
| Al ₂ O ₃ | 21.38 (53) | 20.71 (96) | 22.60 (58) | 21.91 (47) | 21.30 (28) | 20.23 (36) | 21.98 (40) | 21.86 (39) | 21.98 (40) | 21.11 (28) | 21.03 (65) | 21.29 (20) |
| Cr ₂ O ₃ | 2.24 (83) | 4.35 (105) | 1.21 (77) | 1.23 (41) | 1.02 (27) | 0.89 (15) | 0.19 (4) | 0.26 (11) | 0.19 (4) | 0.92 (20) | 0.91 (71) | |
| FeO | 6.56 (79) | 7.81 (15) | 8.03 (35) | 6.63 (29) | 7.71 (28) | 7.45 (12) | 12.26 (32) | 12.65 (14) | 12.26 (32) | 13.15 (15) | 7.97 (159) | 19.4 (66) |
| MnO | 0.26 (2) | 0.25 (2) | 0.24 (3) | 0.22 (1) | 0.22 (1) | 0.23 (4) | 0.34 (2) | 0.40 (2) | 0.34 (2) | 0.40 (2) | 0.29 (3) | 1.07 (14) |
| MgO | 21.05 (75) | 19.28 (31) | 18.79 (48) | 20.10 (40) | 18.52 (51) | 17.76 (36) | 13.69 (58) | 14.94 (20) | 13.69 (58) | 15.49 (24) | 20.00 (189) | 11.77 (31) |
| CaO | 6.51 (54) | 6.96 (50) | 7.31 (57) | 7.43 (18) | 8.67 (72) | 9.86 (44) | 10.91 (64) | 9.05 (34) | 10.91 (64) | 8.16 (28) | 6.34 (132) | 6.45 (60) |
| Na ₂ O | 0.03 (2) | 0.03 (1) | 0.14 (9) | 0.18 (14) | 0.30 (3) | 0.56 (4) | 0.15 (2) | 0.11 (2) | 0.15 (2) | 0.04 (5) | 0.12 (3) | 0.06 (7) |
| K ₂ O | b.d. | b.d. | b.d. | 0.01 (1) | 0.01 (1) | 0.01 (1) | 0.01 (3) | b.d. | 0.01 (3) | b.d. | b.d. | b.d. |
| ZrO ₂ | | | | | | | | | | | 0.17 (6) | |
| Total c.p.f.u. | 100.01 | 101.14 | 101.16 | 100.21 | 100.86 | 100.88 | 99.88 | 100.45 | 99.88 | 100.02 | 99.33 | 99.59 |
| Si | 2.96 | 2.95 | 3.00 | 2.99 | 3.02 | 3.08 | 2.90 | 2.95 | 2.90 | 2.94 | 2.95 | 2.91 |
| Al | 1.78 | 1.74 | 1.88 | 1.82 | 1.78 | 1.69 | 1.90 | 1.87 | 1.90 | 1.82 | 1.78 | 1.89 |
| Ti | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.02 | 0.04 | 0.03 | 0.04 | 0.03 | 0.08 | 0.05 |
| Cr | 0.13 | 0.24 | 0.07 | 0.07 | 0.06 | 0.05 | 0.01 | 0.01 | 0.01 | 0.05 | 0.05 | 0.00 |
| Fe ³⁺ | 0.16 | 0.10 | 0.04 | 0.13 | 0.12 | 0.14 | 0.23 | 0.17 | 0.23 | 0.2 | 0.13 | 0.19 |
| Fe ²⁺ | 0.23 | 0.37 | 0.44 | 0.26 | 0.34 | 0.31 | 0.53 | 0.60 | 0.53 | 0.61 | 0.35 | 1.03 |
| Mn | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.07 |
| Mg | 2.22 | 2.04 | 1.98 | 2.12 | 1.95 | 1.88 | 1.50 | 1.62 | 1.50 | 1.69 | 2.14 | 1.32 |
| Ca | 0.49 | 0.53 | 0.55 | 0.56 | 0.66 | 0.75 | 0.86 | 0.70 | 0.86 | 0.64 | 0.49 | 0.52 |
| Na | 0.00 | 0.00 | 0.02 | 0.03 | 0.04 | 0.08 | 0.02 | 0.02 | 0.02 | 0.01 | 0.02 | 0.01 |
| K | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

837 ^{Zr} Abbreviations are the same as table 1 and calculations are based on 8 cations. 0.01

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Table 3: Cpx trace element data measured by SIMS

| Sample | BL58 | RD25 | G21 | V547 | V546 | V545 | BL88 | RD56 | G25 | RD56 AOB | UCL3 | RB627 |
|----------|----------|-----------|----------|----------|----------|----------|------------|------------|------------|-------------|------------|-------------|
| <i>n</i> | 4 | 4 | 2 | 4 | 4 | 2 | 4 | 3 | 1 | 3 | 5 | 1 |
| Li | 10.8 (6) | 24 (4) | 30.2 (1) | 17.8 (4) | 33 (2) | 35 (3) | 28 (2) | 25 (1) | 15 (3) | 44 (1) | 417 (20) | 24 (5) |
| B | 0.99 (7) | 1.3 (2) | 3.2 (6) | 1.1 (2) | 9 (1) | 15.6 (6) | 1.8 (4) | 0.1 (1) | 1.8 (4) | 1.7 (5) | 28 (3) | 5.4 (11) |
| Sc | 14.2 (7) | 16 (1) | 6.7 (7) | 6.8 (9) | 6.3 (2) | 5.0 (5) | 21 (2) | 21.54 (8) | 12 (4) | 74 (7) | 131 (6) | 232 (46) |
| Ti | 336 (10) | 380 (173) | 382 (33) | 267 (13) | 835 (19) | 790 (98) | 5667 (801) | 3582 (125) | 1832 (366) | 2881 (773) | 2053 (291) | 5422 (1084) |
| V | 20.4 (5) | 64 (14) | 40.1 (5) | 23 (1) | 33 (2) | 34.9 (1) | 309 (17) | 135 (10) | 243 (49) | 67 (4) | 72 (7) | 534 (107) |
| Co | 54 (2) | 54 (6) | 27.6 (1) | 39 (1) | 37 (2) | 33 (2) | 49 (3) | 49 (3) | 31 (6) | 231 (7) | 5.1 (6) | na |
| Ga | 50 (9) | na | na | 68 (2) | 77 (12) | 93 (12) | na | na | na | na | na | na |
| Sr | 9 (1) | 7 (1) | 19.0 (5) | 15.7 (8) | 77 (1) | 96 (22) | 169 (7) | 163 (2) | 142 (28) | 70 (6) | 76 (8) | 14.3 (29) |
| Y | 2.2 (9) | 1.5 (2) | 0.8 (1) | 1.03 (7) | 1.11 (8) | 0.9 (2) | 4.8 (9) | 4.41 (1) | 2.3 (5) | 9 (3) | 10 (3) | 111 (22) |
| Zr | 0.7 (1) | 1.0 (5) | 17 (22) | 0.5 (1) | 1.5 (2) | 4.6 (17) | 48 (7) | 27 (1) | 22 (4) | 5 (2) | 134 (30) | 91 (18) |
| Nb | 0.16 (6) | 0.4 (2) | 0.7 (5) | 0.18 (6) | 1.2 (5) | 4 (5) | 0.5 (2) | 0.26 (4) | 0.25 (5) | 14 (15) | 0.11 (3) | 5.2 (10) |
| Ba | 0.14 (7) | 0.06 (6) | 3.4 (1) | 0.5 (4) | 2.1 (14) | 0.44 (6) | 0.7 (3) | 0.4 (3) | 2 (4) | 2 (1) | 0.04 (4) | 12.4 (25) |
| La | 2.1 (4) | 1.0 (3) | 1.0 (3) | 0.15 (5) | 0.4 (2) | 0.8 (8) | 4.2 (5) | 3.4 (1) | 1.8 (4) | 11 (3) | 5 (1) | 47.1 (94) |
| Ce | 1.4 (1) | 0.8 (2) | 2.7 (9) | 0.9 (2) | 2.7 (2) | 3.4 (8) | 14 (1) | 10.1 (4) | 6 (1) | 30 (6) | 17 (6) | 22.9 (46) |
| Pr | na | na | na | na | na | na | 2.5 (3) | 1.79 (8) | 1.1 (2) | 0.04 (4) | na | na |
| Nd | 1.9 (3) | 1.1 (3) | 3.15 (2) | 1.0 (3) | 2.6 (4) | 3 (1) | 15 (2) | 10.6 (6) | 6 (1) | 39 (3) | 27 (9) | 53 (11) |
| Sm | 2.2 (9) | 0.03 (2) | 1.2 (5) | 1.1 (3) | 3.1 (5) | 2.1 (4) | 4.0 (5) | 2.8 (4) | 1.5 (3) | 12.7 (8) | 11 (3) | 79 (16) |
| Eu | 6.7 (6) | 3.7 (6) | 2.9 (1) | 2.7 (4) | 5.9 (4) | 4.2 (6) | 1.3 (1) | 0.78 (2) | 0.7 (1) | 27 (2) | 26 (8) | 90 (18) |
| Gd | 7.7 (10) | 3.6 (9) | 2.4 (4) | 3.1 (4) | 3.9 (3) | 4 (1) | 3.9 (6) | 1.9 (6) | 2.0 (4) | 29 (3) | 27 (8) | 115 (23) |
| Tb | b.d. | b.d. | b.d. | b.d. | b.d. | b.d. | 0.48 (8) | 0.33 (3) | 0.23 (5) | b.d. | b.d. | na |
| Dy | na | na | na | na | na | na | 2.8 (3) | 1.7 (3) | 1.3 (3) | 2.6 (4) | na | na |
| Ho | na | na | na | na | na | na | 0.28 (3) | 0.21 (1) | 0.17 (3) | 0.08 (5) | na | na |
| Er | 4.2 (5) | 2.9 (6) | 2.3 (5) | 2.1 (6) | 1.8 (3) | 0.77 (3) | b.d. | 0.5 (2) | 0.36 (7) | 22 (7) | 20 (5) | 74 (15) |
| Yb | 4.6 (4) | 3.3 (8) | 1.3 (1) | 2.1 (6) | 1.9 (6) | 1.6 (3) | 0.4 (2) | 0.4 (2) | 0.5 (1) | 28 (15) | 19 (4) | na |
| Lu | 67 (7) | 5.6 (3) | 1.8 (3) | 3.3 (6) | 3.1 (6) | 3.1 (4) | 0.12 (3) | 0.03 (2) | 0.02 (3) | 43 (16) | 24 (5) | 23.4 (47) |
| Hf | 0.9 (4) | 1.0 (5) | 1.5 (3) | 0.6 (2) | 1.7 (2) | 1.6 (6) | 2.1 (3) | 0.8 (4) | 0.9 (2) | 6 (1) | 0.5 (2) | 45 (9) |
| Ta | 0.14 (7) | 0.7 (3) | 1.0 (9) | 0.2 (7) | 0.7 (7) | 2 (3) | 0.35 (4) | b.d. | 0.21 (4) | 7.3 (7) | 0.12 (4) | 1.8 (4) |
| Pb | 5 (1) | na | na | 0.07 (4) | 42 (16) | 29.1 (6) | na | na | na | na | na | na |

| | | | | | | | | | | | | | | | | | | | | | | | |
|----|------|-----|-----|-----|-----|-----|------|-----|-----|------|-----|-----|------|-----|------|-----|------|-----|---|-----|------|-----|----|
| Th | 0.13 | (3) | 0.1 | (1) | 1 | (1) | 0.09 | (4) | 2.2 | (16) | 11 | (1) | 0.23 | (3) | 0.3 | (3) | 0.17 | (3) | 8 | (5) | 0.4 | (2) | na |
| U | 0.09 | (5) | 0.1 | (1) | 0.2 | (3) | 0.07 | (4) | 0.4 | (3) | 0.4 | (3) | 0.21 | (5) | b.d. | | 0.15 | (3) | 5 | (4) | 0.15 | (7) | na |

840 All values are the mean of *n* in ppm, *n* is the number of analyses. Where the number of grains analyzed is one then the S.D. is 20% of the measured value.

841 **Table 4:** Garnet trace element data measured by SIMS

| Sample | BL58 | RD25 | G21 | V547 | V546 | V545 | BL88 | RD56 | G25 | RD56 | AOB | UCL3 | RB627 |
|----------|-----------|------------|----------|-----------|-----------|-----------|------------|------------|------------|------------|------------|------------|-------|
| <i>n</i> | 3 | 5 | 2 | 4 | 3 | 3 | 5 | 1 | 4 | 4 | 4 | 5 | 1 |
| Li | 0.41 (9) | 1.17 (4) | 3.9 (5) | 1.9 (1) | 6.6 (1) | 11.3 (6) | 5 (1) | 2.9 (6) | 2.1 (3) | 5 (1) | 81 (11) | 2.3 (5) | |
| B | 0.28 (4) | 0.22 (3) | 2 (3) | 0.3 (2) | 1.1 (2) | 4 (2) | 0.8 (6) | b.d. | 0.4 (5) | 0.4 (1) | 6 (8) | 0.42 (8) | |
| Sc | 72 (3) | 112 (11) | 44 (6) | 48 (4) | 47 (7) | 40 (1) | 84 (12) | 71 (14) | 51 (2) | 268 (9) | 604 (18) | 702 (140) | |
| Ti | 578 (4) | 1621 (221) | 746 (5) | 480 (25) | 1752 (50) | 2119 (1) | 3629 (615) | 2951 (590) | 2951 (278) | 2990 (511) | 6641 (1) | 3191 (638) | |
| V | 60 (2) | 113 (3) | 74 (5) | 57 (1) | 62 (2) | 63 (1) | 247 (9) | 105 (221) | 171 (20) | 78 (4) | 98 (10) | 343 (69) | |
| Co | 97 (3) | 101 (5) | 88 (2) | 95 (1) | 128 (18) | 104 (3) | 75 (2) | 97 (19) | 76 (3) | 408 (9) | 10.8 (6) | na | |
| Ga | 53 (5) | na | na | 64 (4) | 114 (6) | 114 (2) | na | na | na | na | na | na | |
| Sr | 0.4 (3) | 0.32 (7) | 1 (2) | 0.39 (8) | 2.0 (4) | 3.5 (7) | 1.5 (3) | 1.1 (2) | 2.0 (9) | 3 (4) | 1 (1) | 0.31 (6) | |
| Y | 22 (1) | 35 (3) | 14 (3) | 15.0 (6) | 19.4 (3) | 15.4 (4) | 72 (10) | 62 (12) | 39 (1) | 98 (7) | 50 (8) | 1078 (216) | |
| Zr | 5.2 (9) | 10.4 (9) | 5 (1) | 3.1 (4) | 11 (2) | 13 (3) | 92 (21) | 90 (18) | 61 (8) | 14 (3) | 1492 (410) | 87 (17) | |
| Nb | b.d. | 1.0 (3) | b.d. | 0.18 (5) | 0.46 (3) | 1.1 (9) | 0.29 (9) | 0.21 (4) | 0.3 (2) | b.d. | 0.46 (6) | 1.1 (2) | |
| Ba | b.d. | 0.04 (2) | b.d. | 0.1 (2) | 1.1 (5) | 0.6 (5) | 0.5 (4) | 0.06 (1) | 0.7 (6) | 0.3 (1) | 0.1 (1) | 0.83 (17) | |
| La | 0.2 (2) | 0.09 (3) | 1.6 (-) | 0.020 (1) | 0.10 (2) | 0.3 (2) | 0.19 (5) | 0.15 (3) | 0.2 (1) | 0.3 (1) | 0.3 (4) | 1.0 (2) | |
| Ce | 0.04 (16) | 0.19 (6) | 2 (2) | 0.11 (6) | 0.9 (2) | 2 (1) | 1.0 (2) | 0.8 (2) | 0.7 (3) | 1.69 (9) | 1.1 (1) | 0.6 (1) | |
| Pr | na | na | na | na | na | na | 0.4 (1) | 0.3 (1) | 0.29 (8) | 0.02 (1) | na | na | |
| Nd | 0.6 (3) | 1.0 (3) | 1.7 (3) | 0.6 (1) | 2.2 (3) | 2.3 (2) | 4.4 (6) | 4 (1) | 3.2 (7) | 20 (10) | 4 (1) | 5.3 (11) | |
| Sm | 2.0 (17) | 54 (2) | 7 (1) | 2.0 (4) | 7.3 (2) | 6 (1) | 3.6 (4) | 3.3 (7) | 2.7 (5) | 17 (4) | 5 (1) | 29 (6) | |
| Eu | 11 (3) | 15 (3) | 7 (1) | 7.2 (4) | 19.7 (6) | 16 (2) | 1.9 (4) | 2.15 (4) | 1.6 (1) | 56 (11) | 16 (4) | 67 (13) | |
| Gd | 19 (5) | 22 (3) | 9.8 (9) | 12.4 (7) | 20 (7) | 17 (4) | 7 (1) | 5 (1) | 5.3 (4) | 88 (12) | 26 (6) | 146 (29) | |
| Tb | b.d. | 0.02 (1) | b.d. | b.d. | b.d. | b.d. | 1.8 (2) | 1.6 (3) | 1.0 (2) | b.d. | 0.03 (2) | na | |
| Dy | na | na | na | na | na | na | 13 (2) | 10 (2) | 8 (1) | 1.3 (7) | na | na | |
| Ho | na | na | na | na | na | na | 3.0 (4) | 2.6 (5) | 1.72 (8) | 0.2 (2) | na | na | |
| Er | 57 (2) | 90 (9) | 30 (7) | 25 (21) | 45 (3) | 22 (3) | b.d. | 8 (2) | 4.9 (6) | 252 (20) | 128 (17) | 1131 (226) | |
| Yb | 103.3 (9) | 176 (23) | 49 (9) | 64 (4) | 75 (3) | 47 (5) | 10 (1) | b.d. | 5 (1) | 445 (30) | 269 (29) | na | |
| Lu | 228 (10) | 379 (59) | 103 (21) | 136 (9) | 149 (11) | 113.0 (3) | 12 (3) | 8 (2) | 1.0 (1) | 767 (56) | 491 (41) | 1131 (211) | |
| Hf | 1.8 (9) | 4.4 (6) | 1.72 (8) | 1.9 (3) | 6 (1) | 7 (2) | 4 (1) | 2.2 (4) | 2.1 (4) | 11 (3) | 2.1 (6) | 18.2 (36) | |
| Ta | 0.6 (5) | 3.7 (4) | 4 (6) | 0.11 (5) | 0.3 (1) | 0.9 (6) | 2.6 (5) | 0.6 (1) | 0.5 (2) | 0.5 (2) | 0.3 (1) | 0.7 (1) | |
| Pb | 5.08 (4) | na | na | 5 (2) | 18 (7) | 5 (4) | na | na | na | na | na | na | |

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|----|-----|-----|------|-----|------|------|------|-----|-----|-----|-----|-----|------|-----|------|------|-----|-----|-----|-----|-----|-----|----|
| Th | 0.2 | (3) | 0.07 | (3) | 4.16 | (-) | 0.05 | (2) | 1 | (1) | 6 | (8) | 0.9 | (2) | b.d. | 0.16 | (7) | 0.4 | (1) | 0.5 | (8) | na | |
| U | 0.2 | (2) | 0.7 | (3) | 0.9 | (10) | 0.12 | (7) | 0.2 | (1) | 0.7 | (3) | 0.23 | (5) | 0.06 | (1) | 0.2 | (1) | 0.5 | (2) | 0.4 | (4) | na |

842 All values are the mean of n in ppm, n is the number of analyses. Where the number of grains analyzed is one then the S.D. is 20% of the measured value.

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Table 5: Temperature calculations

| Sample | $P_{(exp)}$ | $T_{(exp)}$ | $T_{(JP)}$ | $\sigma T_{(JP)}$ | $\Delta T_{(JP)}$ | $T_{(EG)}$ | $\Delta T_{(EG)}$ | $T_{(EG^*)}$ | $\Delta T_{(EG^*)}$ | $T_{(SL)}$ | $\Delta T_{(SL)}$ |
|---------------------------|-------------|-------------|------------|-------------------|-------------------|------------|-------------------|--------------|---------------------|------------|-------------------|
| BL58 | 3 | 1200 | 1188 | 31 | 12 | 1220 | 20 | 966 | 234 | 813 | 387 |
| RD25 | 3.4 | 1200 | 1141 | 30 | 59 | 1166 | 34 | 1051 | 149 | 1202 | 2 |
| G21 | 6 | 1200 | 1377 | 29 | 177 | 1487 | 287 | 1427 | 227 | 1502 | 302 |
| V547 | 6 | 1400 | 1362 | 38 | 38 | 1037 | 363 | 886 | 514 | 1381 | 19 |
| V546 | 8 | 1400 | 1456 | 28 | 56 | 2646 | 1246 | 2165 | 765 | 1505 | 105 |
| V545 | 10 | 1400 | 1538 | 47 | 138 | 2066 | 666 | 1716 | 316 | 1737 | 337 |
| BL88 | 3 | 1100 | 1038 | 23 | 62 | 1345 | 245 | 1149 | 49 | 1297 | 197 |
| RD56 | 3 | 1200 | 960 | 16 | 240 | 1005 | 195 | 914 | 286 | 1300 | 100 |
| G25 | 5 | 1200 | 1231 | 31 | 31 | | | | | | |
| RD56 AOB | 3 | 1200 | 1382 | 64 | 182 | 1076 | 124 | 958 | 242 | 1370 | 170 |
| UCL3 | 5 | 1120 | 1237 | 34 | 117 | 2144 | 1024 | 1758 | 638 | 1194 | 74 |
| RB627 | 1.3 | 970 | 971 | 16 | 1 | 1392 | 442 | 1275 | 325 | 946 | 24 |
| Adam and Green (2006) | 3.5 | 1180 | 1253 | 39 | 73 | 1166 | 14 | 1112 | 68 | 1129 | 51 |
| Bennett et al. (2004) | 3 | 1330 | 1413 | 73 | 83 | | | | | | |
| Green et al. (2000) | 4 | 1100 | 1178 | 20 | 78 | 1081 | 19 | 929 | 171 | 1276 | 176 |
| Green et al. (2000) | 3 | 1160 | 1077 | 17 | 83 | 1047 | 113 | 905 | 255 | 1125 | 35 |
| Green et al. (2000) | 4 | 1200 | 1121 | 9 | 79 | 1246 | 46 | 1160 | 40 | 1109 | 91 |
| Klemme et al. (2002) | 3 | 1400 | 1334 | 49 | 66 | | | | | | |
| Kuzyura et al. (2010) | 7 | 1265 | 1579 | 52 | 314 | 1461 | 196 | 1470 | 205 | -162 | 1427 |
| Kuzyura et al. (2010) | 7 | 1265 | 1474 | 39 | 209 | 1633 | 368 | 1618 | 353 | -255 | 1520 |
| McDade (unpublished) | 3 | 1495 | 1537 | 29 | 42 | 1583 | 88 | 1395 | 100 | 1908 | 413 |
| Salters and Longhi (1999) | 2.8 | 1537 | 1591 | 64 | 54 | 1563 | 1 | 1425 | 137 | 1927 | 390 |
| Salters and Longhi (1999) | 2.8 | 1530 | 1493 | 49 | 37 | 1486 | 44 | 1367 | 163 | 1668 | 138 |
| Salters and Longhi (1999) | 2.8 | 1525 | 1502 | 53 | 23 | 1613 | 63 | 1389 | 161 | 1713 | 188 |
| Salters et al. (2002) | 2.8 | 1650 | 1581 | 125 | 69 | 1444 | 206 | 1015 | 635 | 1804 | 154 |
| Tuff and Gibson (2007) | 3 | 1475 | 1405 | 24 | 70 | 1385 | 90 | 1414 | 61 | 1779 | 304 |
| Tuff and Gibson (2007) | 3 | 1425 | 1487 | 27 | 62 | 1458 | 33 | 1373 | 52 | 1643 | 218 |
| Tuff and Gibson (2007) | 7 | 1750 | 1780 | 34 | 30 | 1489 | 261 | 1611 | 139 | | |

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|----------------|---|------|------|----|----|------|-----|------|-----|------|-----|
| Withers (1997) | 3 | 1470 | 1410 | 16 | 60 | 1416 | 54 | 1375 | 95 | 1607 | 137 |
| mean | | | | | 88 | | 240 | | 245 | | 278 |

844 $T_{(exp)}$ is the experimental temperature, $T_{(jp)}$ is the weighted mean temperature found iteratively using Equation 3 with multiple REE pairs. The error, σT , is
 845 propagated from the standard deviation of the ion probe data. In each case ΔT is the mean absolute difference between the experimental T and the calculated T .
 846 $T_{(EG)}$ is the temperature calculated with the method of Ellis and Green (1979), $T_{(EG^*)}$ is the method of Ellis and Green (1979) where Fe valence is not considered and
 847 $T_{(SL)}$ is the temperature calculated with the method of Sun and Liang (2015). Gaps in the table are a result of the models being unable to calculate a temperature or
 848 the necessary data not being available. The mean value shows the mean temperature deviation of all the experiments, including Kuzyura et al. (2010).
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857 **Table S1:** Experimental starting compositions

| | JP1 | BAS | AOB | ZrTi | NSR-16 |
|--------------------------------|-------|-------|--------|--------|--------|
| SiO ₂ | 51.66 | 44.82 | 44.68 | 44.95 | 51.70 |
| TiO ₂ | 0.34 | 2.5 | 2.48 | 11.20 | 1.30 |
| Al ₂ O ₃ | 13.85 | 14.73 | 14.46 | 12.22 | 19.52 |
| FeO | | 11.03 | | | 9.46 |
| Fe ₂ O ₃ | 6.34 | | 15.41 | 6.80 | |
| MnO | 0.15 | 0.19 | 0.18 | 0.16 | 0.26 |
| MgO | 13.74 | 9.69 | 10.21 | 13.07 | 5.40 |
| CaO | 9.94 | 10.05 | 9.00 | 7.43 | 8.61 |
| Na ₂ O | 2.69 | 4.01 | 2.58 | 0.83 | 3.35 |
| K ₂ O | 0.66 | 1.85 | 0.77 | 0.03 | 0.24 |
| Cr ₂ O ₃ | 0.62 | | 0.25 | 0.59 | |
| P ₂ O ₅ | | 0.94 | | | 0.17 |
| ZrO ₂ | | | | 3.69 | |
| Total | 99.99 | 99.81 | 100.02 | 100.97 | 100.01 |

JP1 is a synthetic oxide mix, BAS is a natural basanite glass, from Green et al. (2000), AOB is a synthetic alkali olivine basalt and NSR-16 a synthetic basaltic glass.

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889 **Table S2:** Trace elements and amount added to starting compositions.

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| | JP1 | BAS* | AOB | ZrTi | NSR-16 |
|-----------|-----|------|-----|------|--------|
| | ppm | ppm | ppm | ppm | ppm |
| Zn | 250 | - | 250 | 250 | - |
| Ni | 250 | - | 250 | 250 | - |
| Co | 250 | - | 250 | - | - |
| Cr | 250 | - | 250 | - | - |
| V | 100 | - | 100 | 100 | 300 |
| Sc | 100 | - | 100 | 300 | 150 |
| Ti | 100 | - | 100 | - | - |
| Y | 50 | 33 | 50 | 50 | 300 |
| La | 50 | 54 | 150 | 150 | 200 |
| Ce | 200 | 110 | 300 | 300 | 50 |
| Nd | 100 | 42 | 200 | 200 | 50 |
| Sm | 50 | 8.7 | 50 | 50 | 60 |
| Eu | 100 | 2.6 | 100 | 100 | 80 |
| Gd | 100 | - | 100 | 100 | 100 |
| Er | 100 | - | 100 | 100 | 250 |
| Yb | 150 | 2.2 | 150 | 150 | - |
| Lu | 250 | 0.3 | 250 | 250 | 200 |
| Nb | 200 | - | 200 | 200 | - |
| Ta | 200 | 5 | 300 | 300 | 50 |
| Zr | 50 | 286 | 50 | - | 150 |
| Hf | 50 | 5.3 | 50 | 50 | 50 |
| Th | 200 | - | 300 | 300 | - |
| U | 200 | - | 200 | 200 | - |
| Pb | 200 | - | 200 | 200 | - |
| Sr | 400 | 1094 | 400 | 400 | 100 |
| Ga | 100 | 18 | 100 | 100 | - |
| Li | 100 | 200 | 300 | 500 | 10 |
| Ba | - | - | - | - | 400 |
| B | - | - | - | - | 10 |

* trace elements in BAS are those measured by Green et al. (2000)
 except Li which was added for this study.

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898 **Table S3:** List of published experimental studies included in our thermometer
899 evaluation with T , P and starting composition of data

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| Author | T (°C) | P (GPa) | Bulk |
|---------------------------|----------|-----------|--------------------|
| Adam and Green (2006) | 1180 | 3.5 | lherzolite |
| Bennett et al. (2004) | 1330 | 3 | CMAS eclogite |
| Green et al. (2000) | 1200 | 4 | tholeiite |
| Green et al. (2000) | 1100 | 3 | basanite |
| Green et al. (2000) | 1160 | 4 | tholeiite |
| Hauri et al. (1994) | 1430 | 2.5 | high Al basalt |
| Klein et al. (2000) | 1100 | 1.5 | granulite xenolith |
| Klein et al. (2000) | 1050 | 1.5 | granulite xenolith |
| Klemme et al. (2002) | 1400 | 3 | eclogite |
| Kuzyura et al. (2010) | 1265 | 7 | silicocarbonatite |
| Kuzyura et al. (2010) | 1265 | 7 | silicocarbonatite |
| McDade (unpublished) | 1495 | 3 | Garnet-Peridotite |
| Salters and Longhi (1999) | 1537 | 2.8 | MORB |
| Salters and Longhi (1999) | 1530 | 2.8 | MORB |
| Salters and Longhi (1999) | 1525 | 2.8 | MORB |
| Salters et al. (2002) | 1600 | 2.8 | MORB |
| Tuff and Gibson (2007) | 1475 | 3 | ferropicrite |
| Tuff and Gibson (2007) | 1425 | 3 | ferropicrite |
| Tuff and Gibson (2007) | 1750 | 7 | ferropicrite |
| Withers (1997) | 1470 | 3 | basalt |
| Withers (1997) | 1487 | 3 | basalt |

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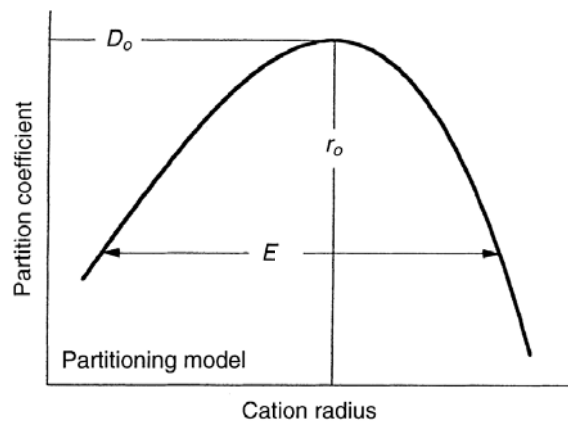
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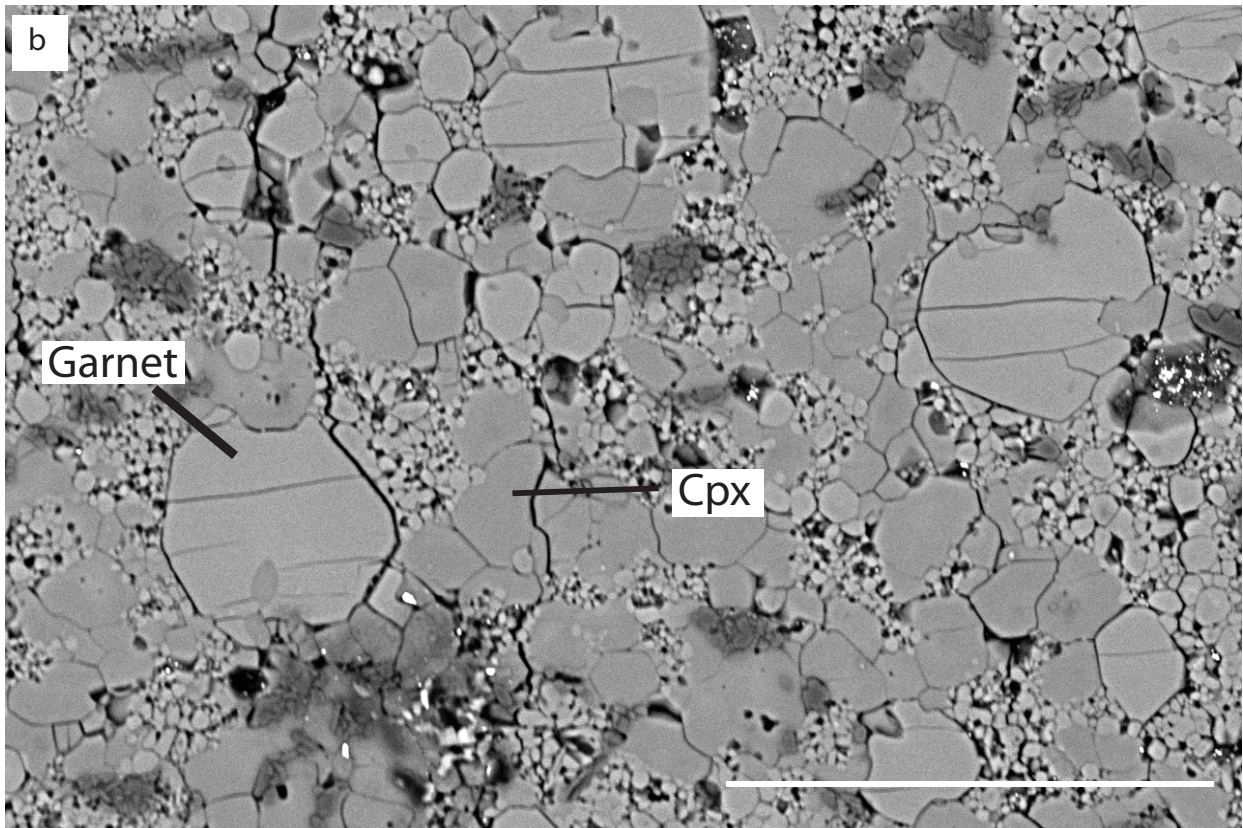
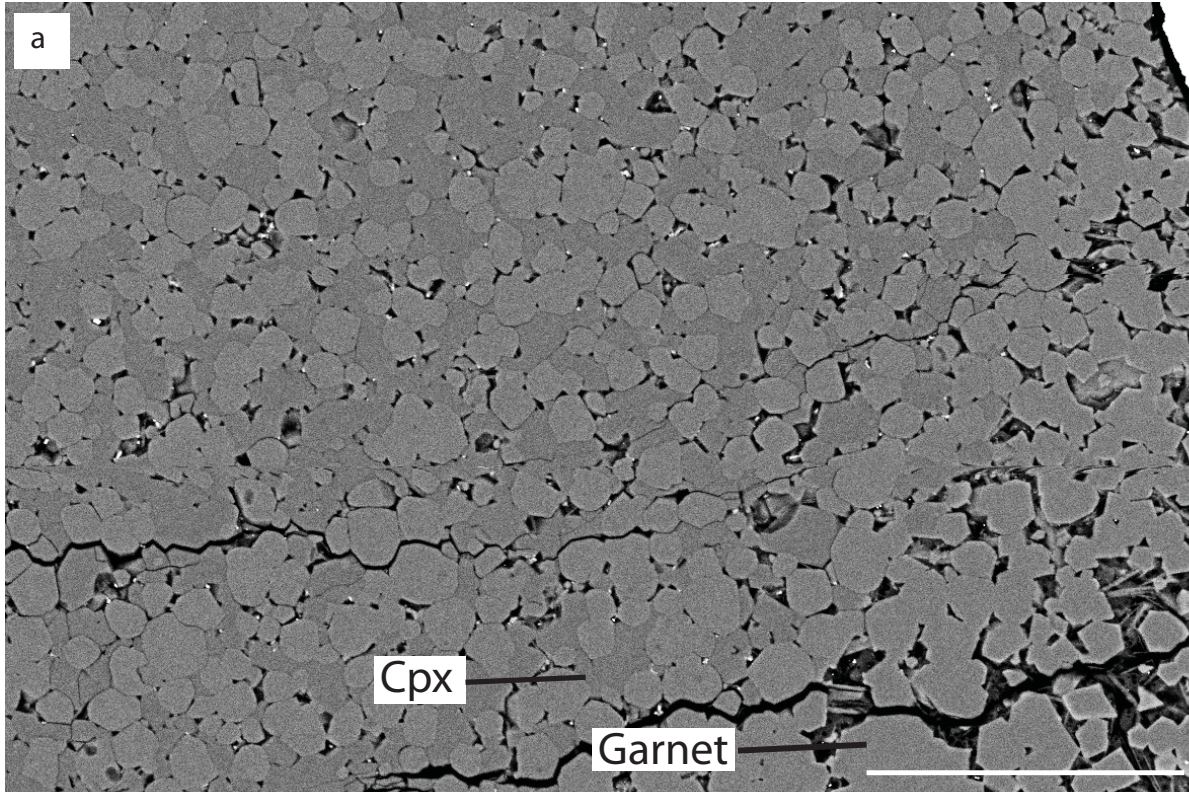
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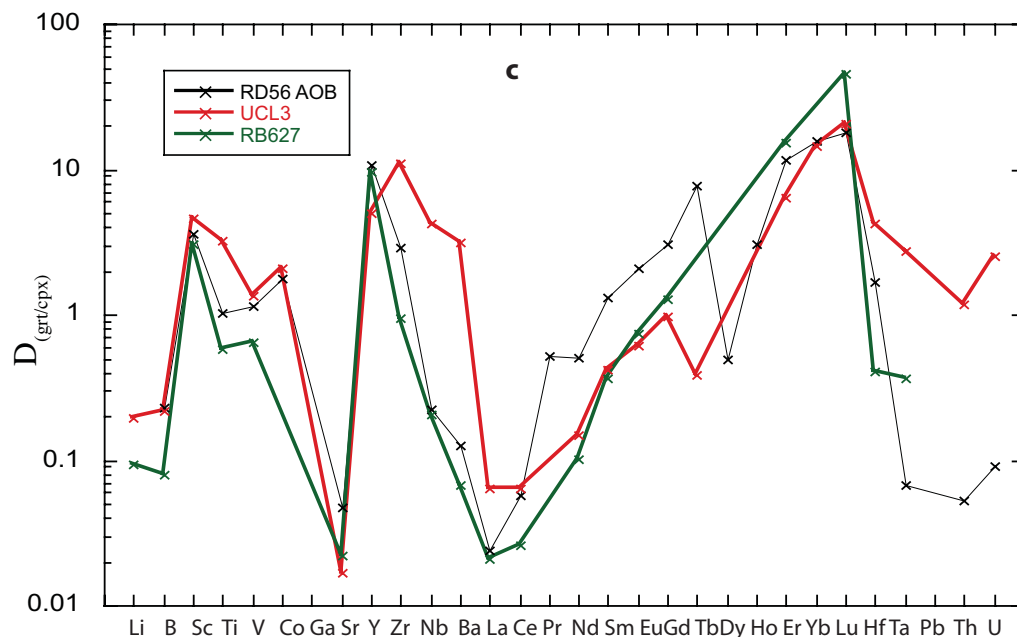
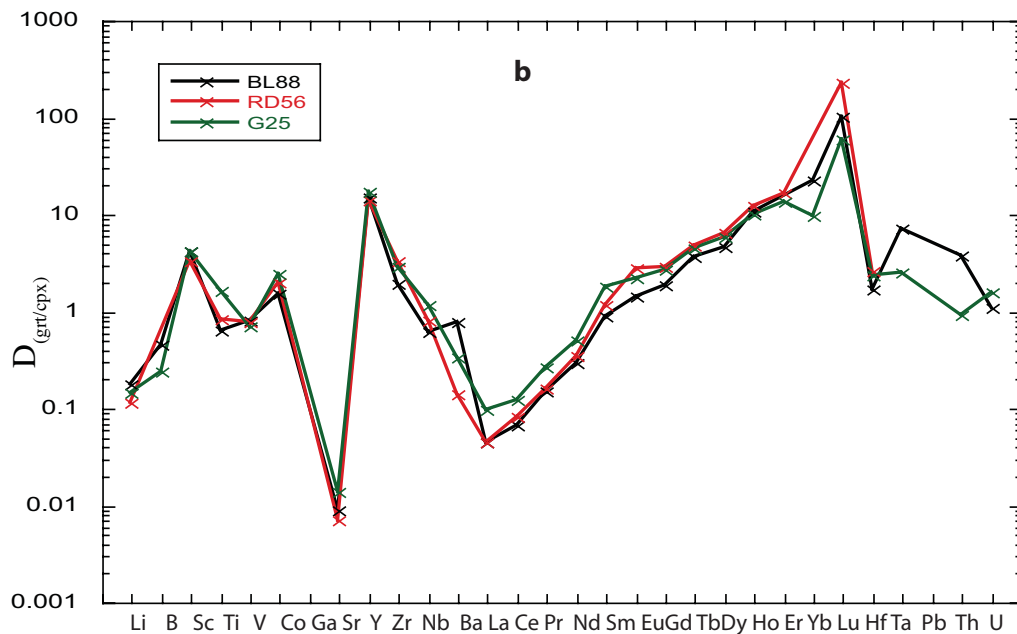
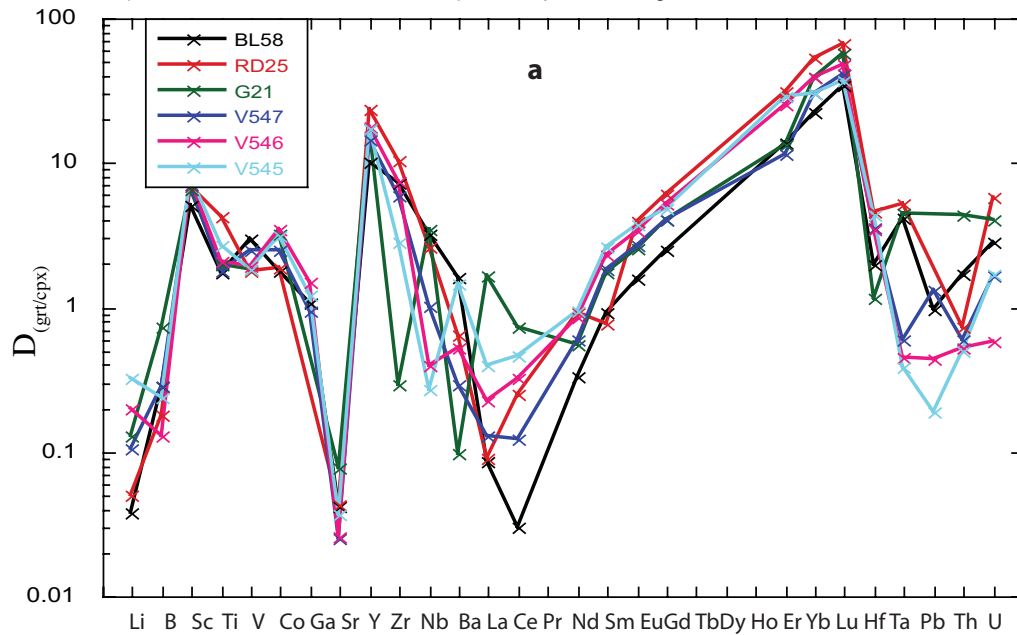
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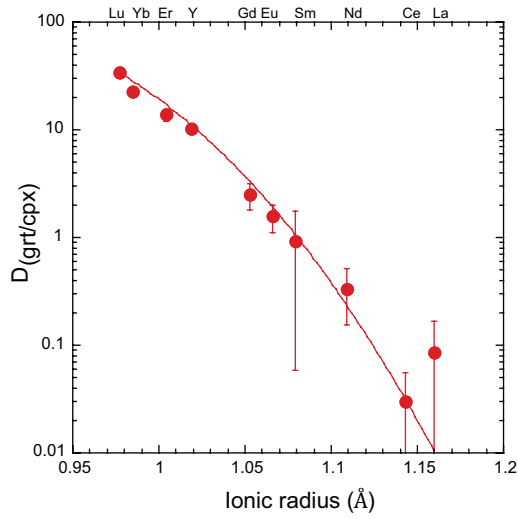
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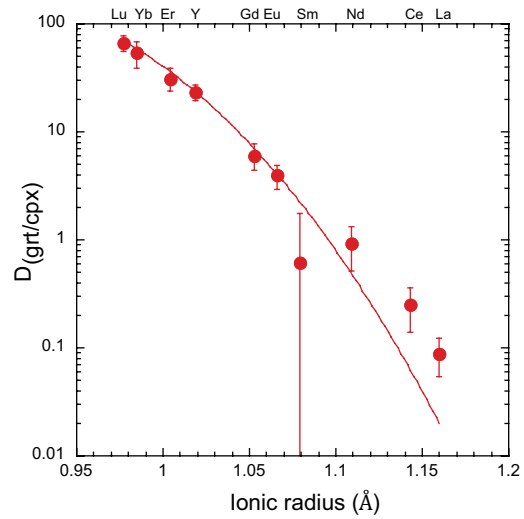




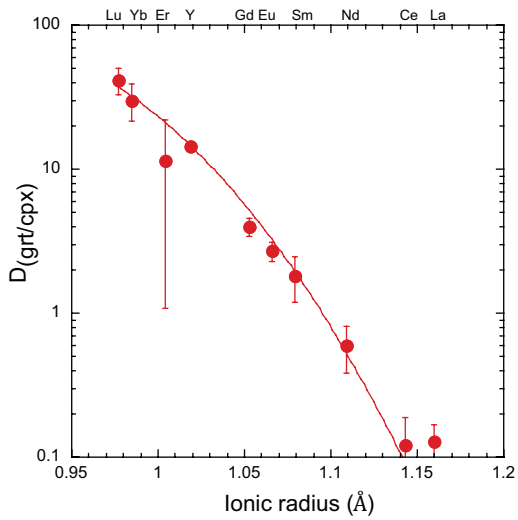
BL58



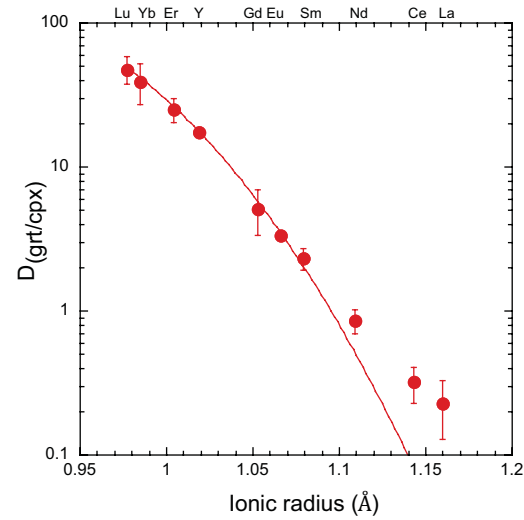
RD25



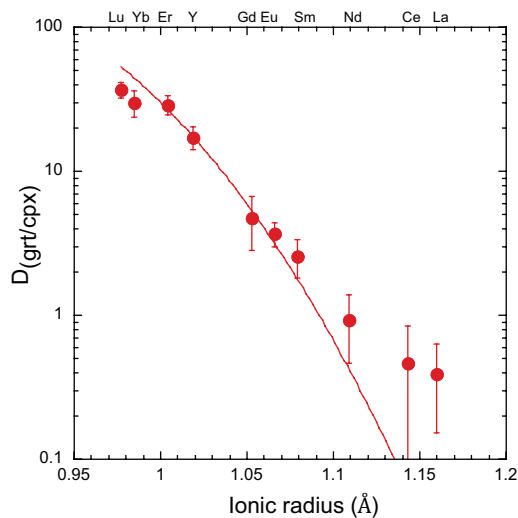
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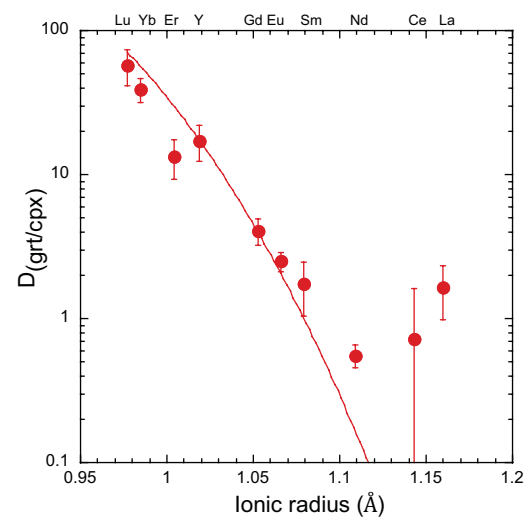
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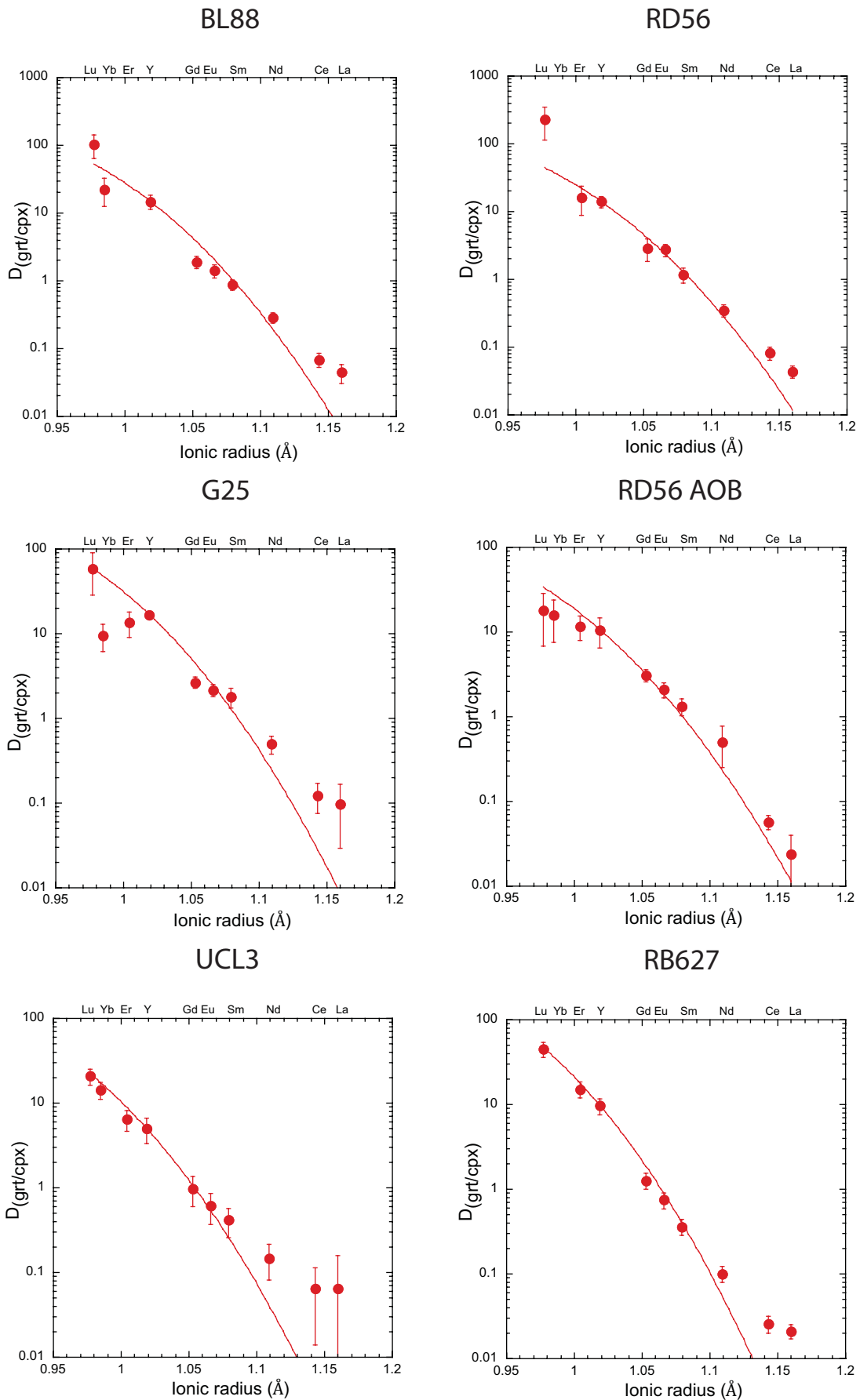


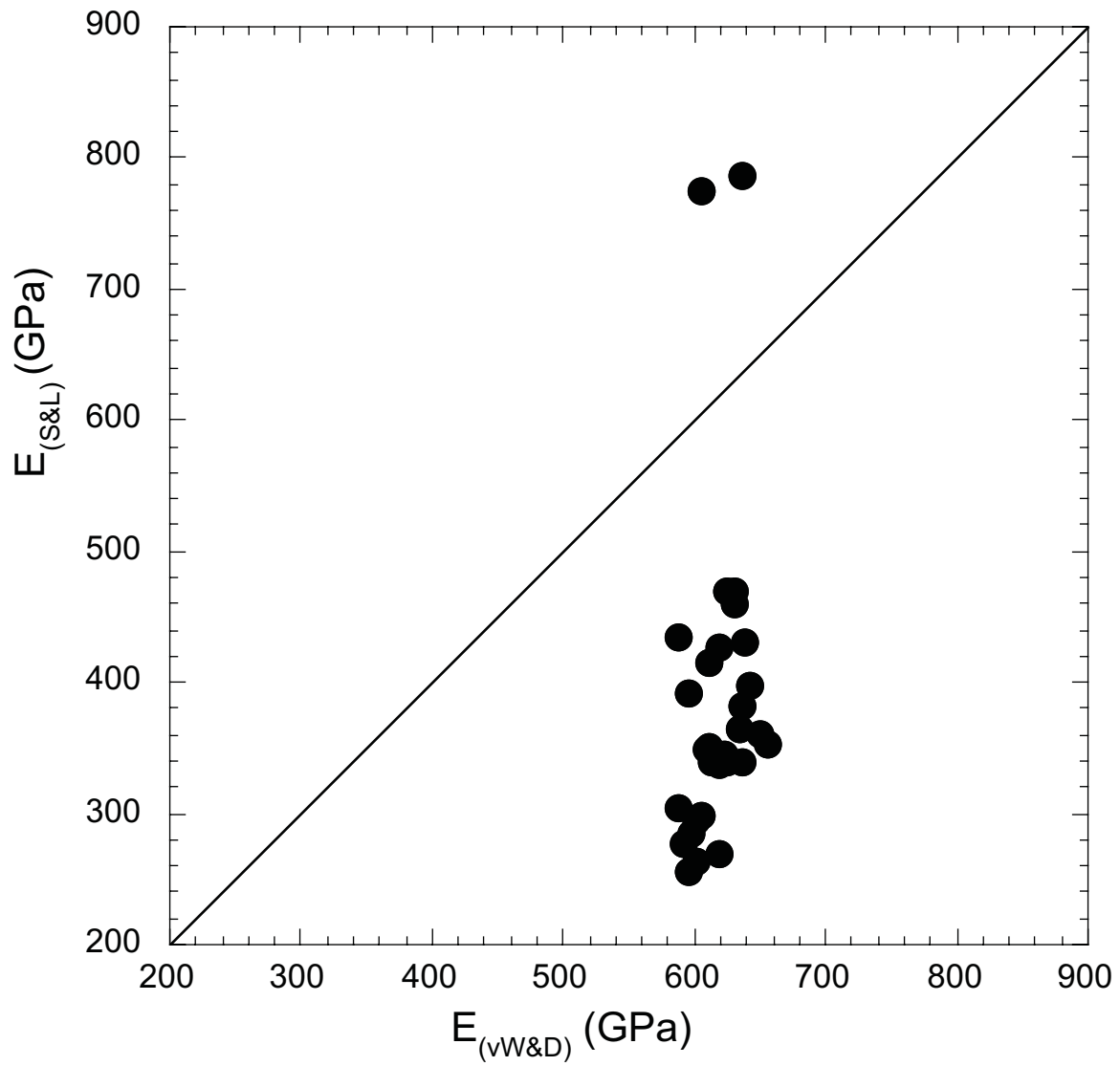
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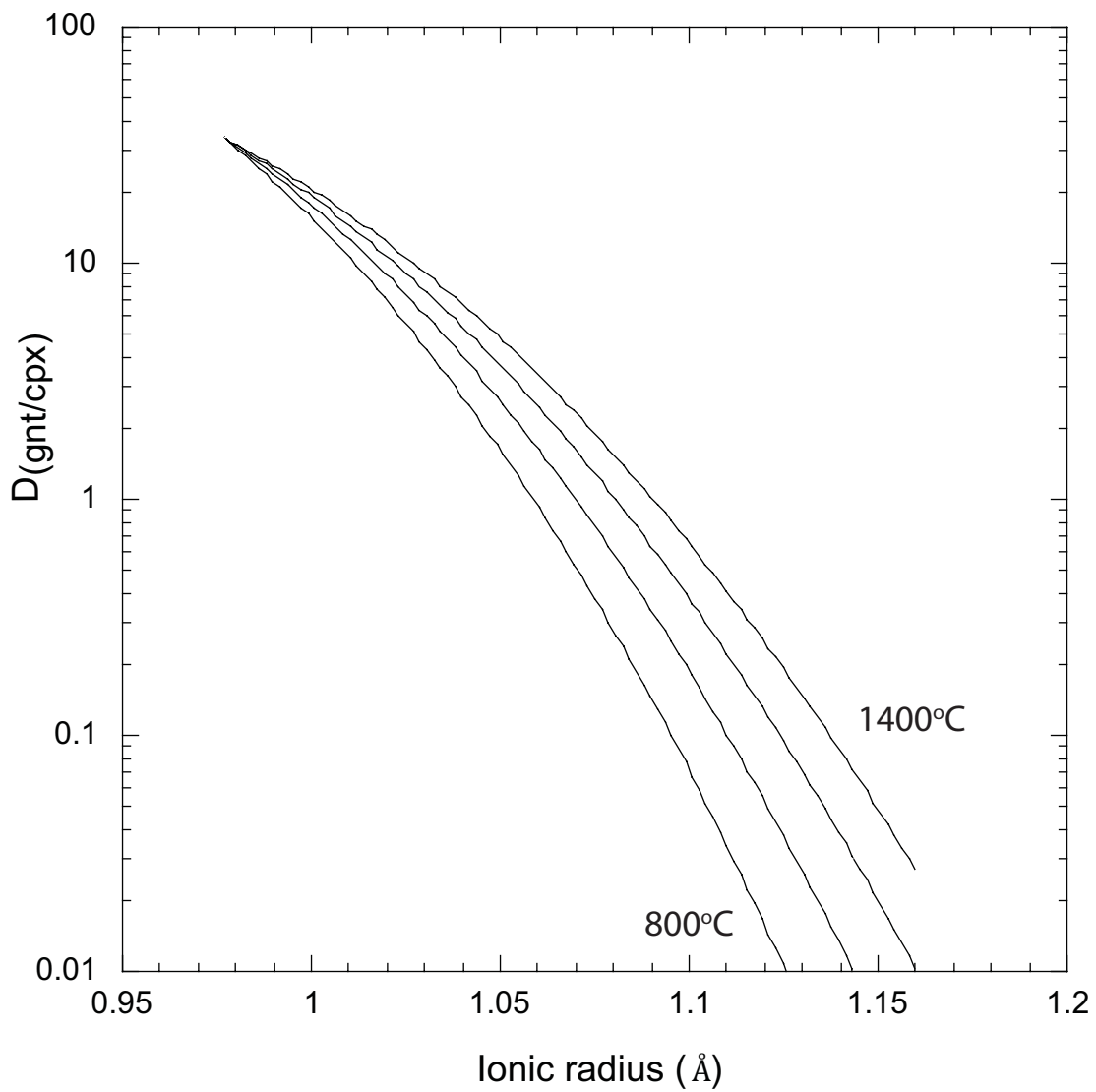


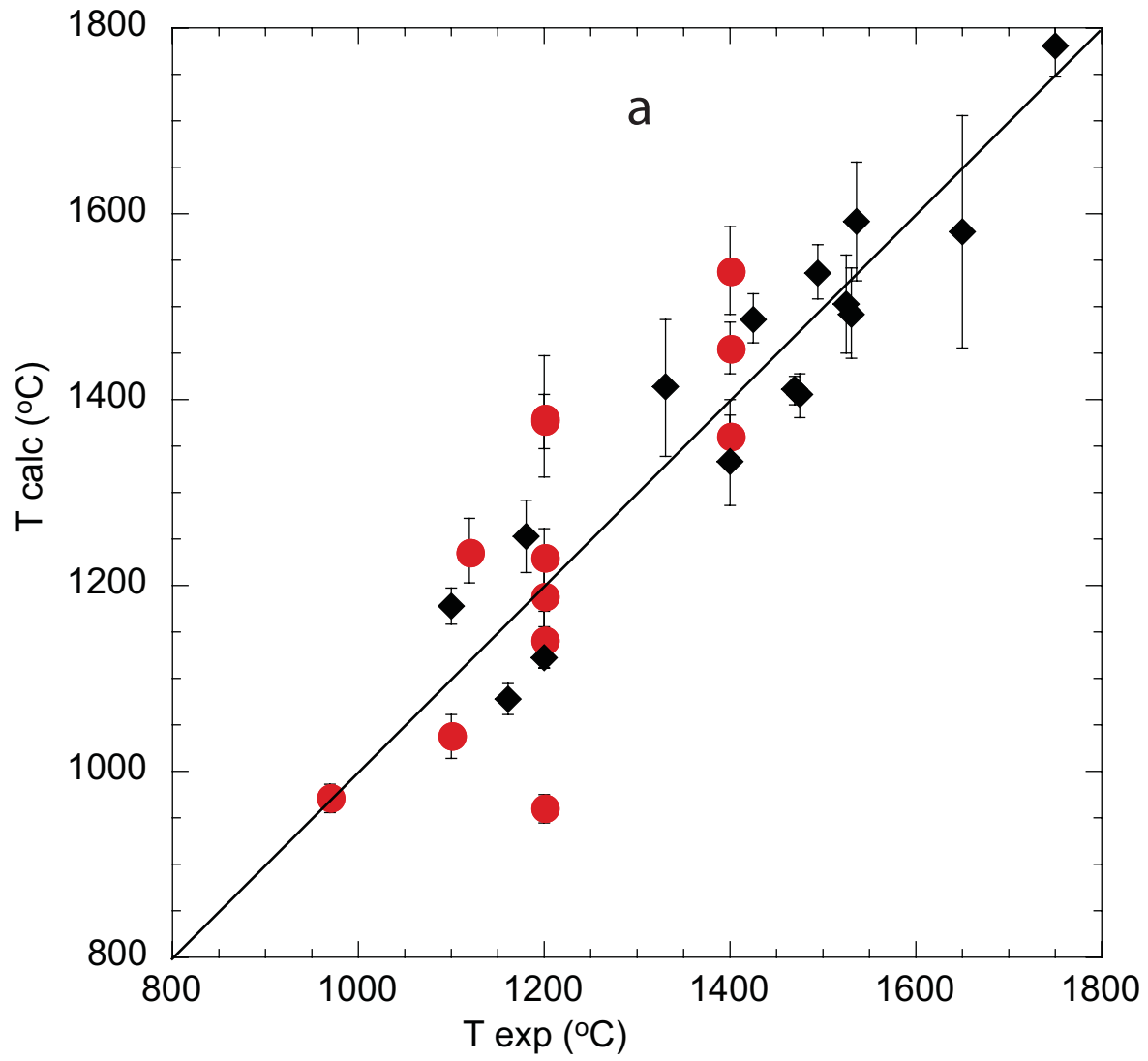
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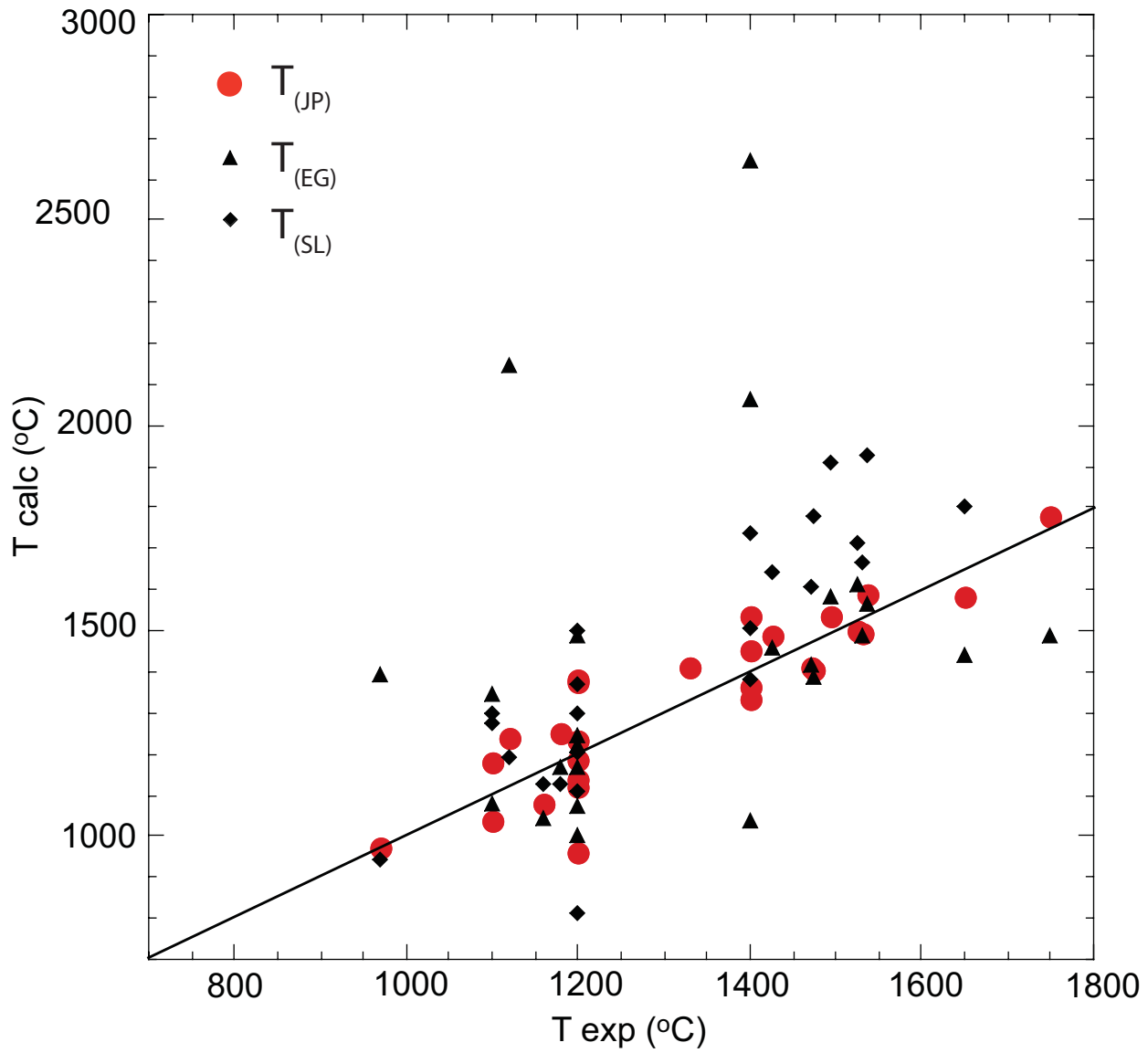


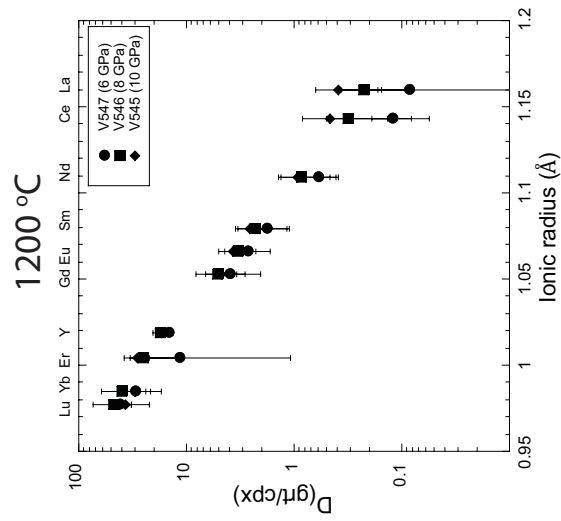
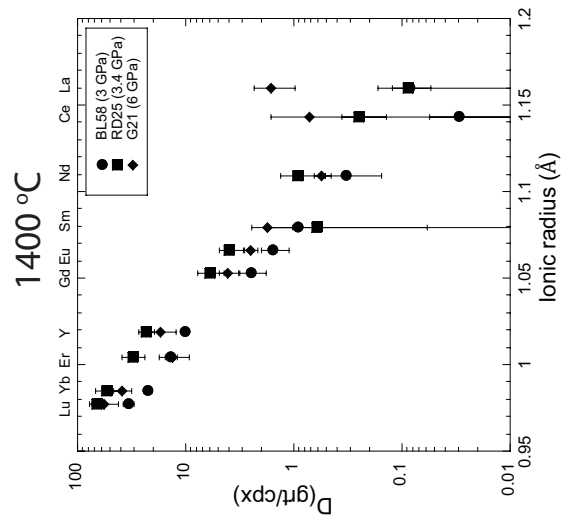




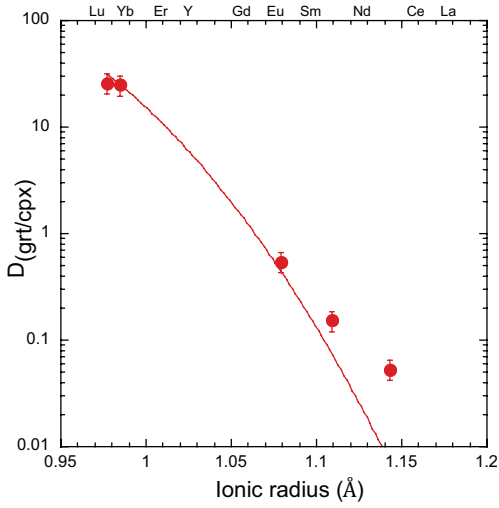




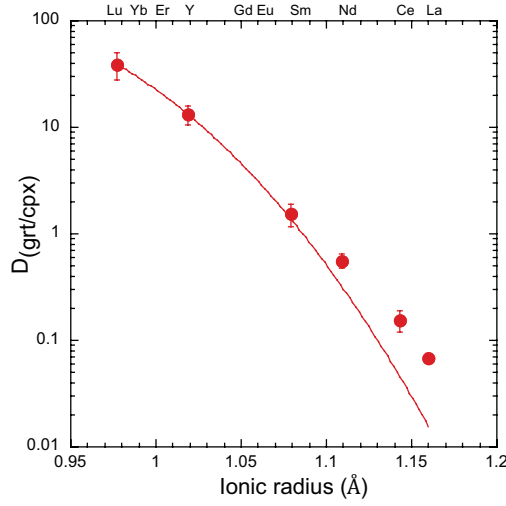




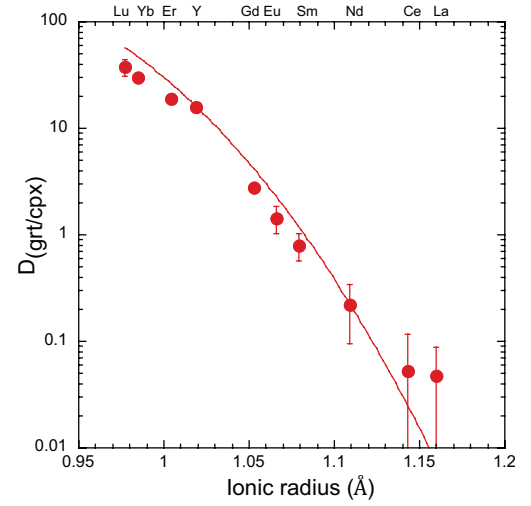
Adam and Green (2006)¹



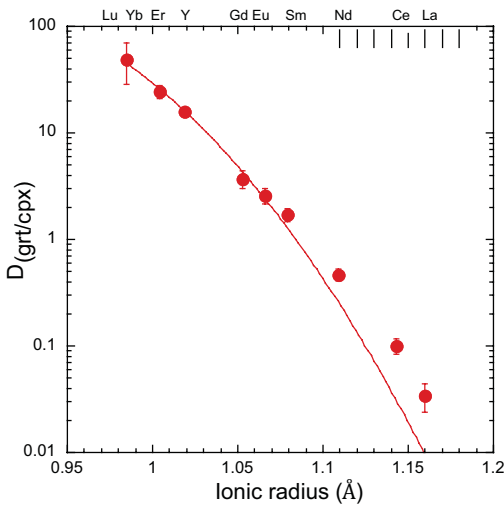
Bennett et al. (2004)



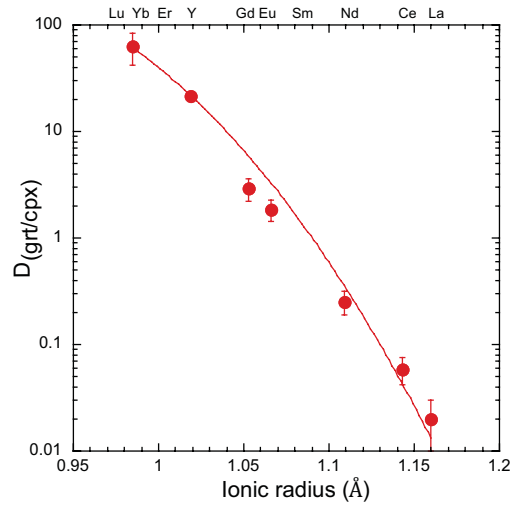
Green et al. (2000)
1787



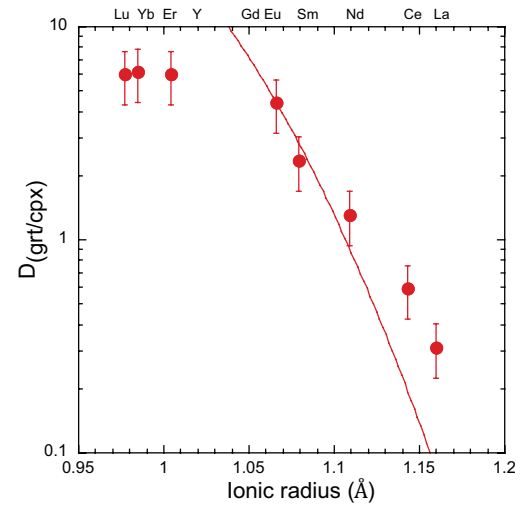
Green et al. (2000)
1798



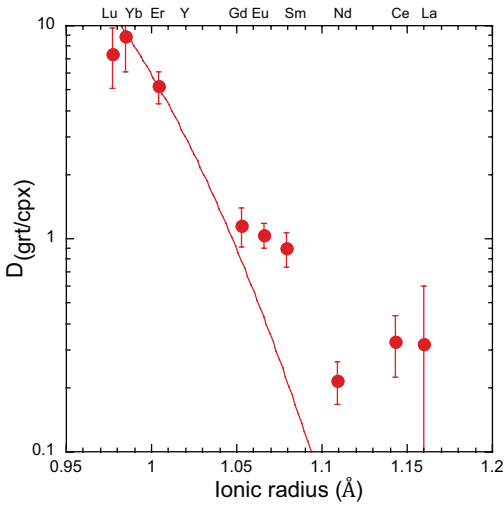
Green et al. (2000)
1807



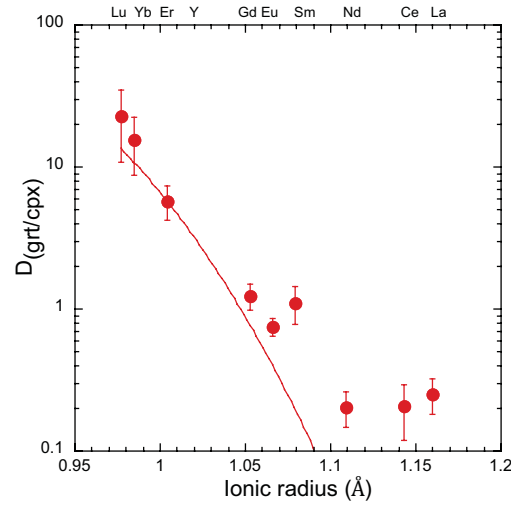
Hauri et al. (1994)²



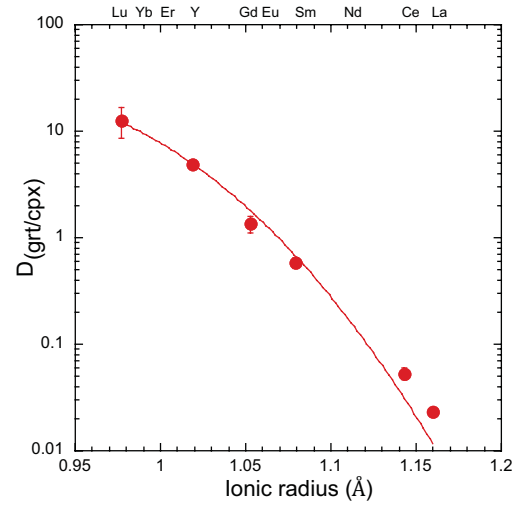
Klein et al. (2000)
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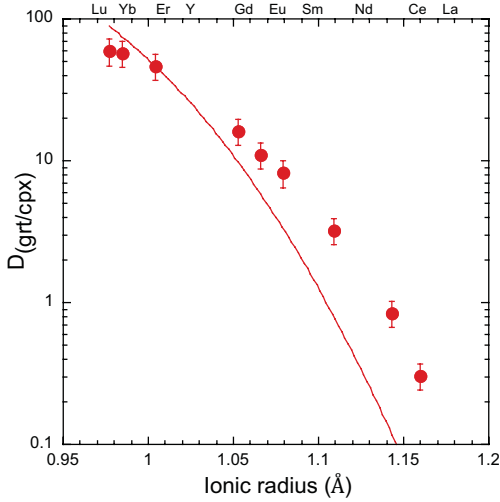
Klein et al. (2000)
1050



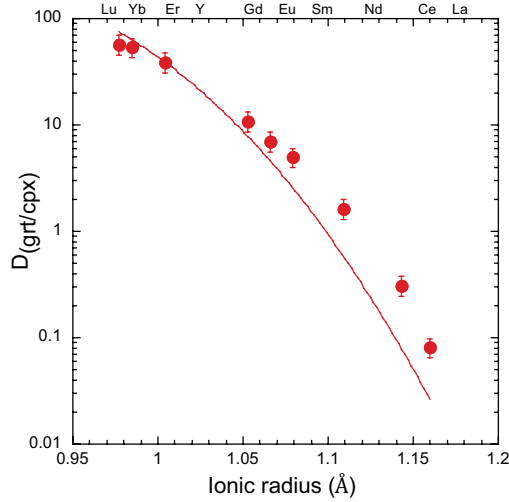
Klemme et al. (2002)



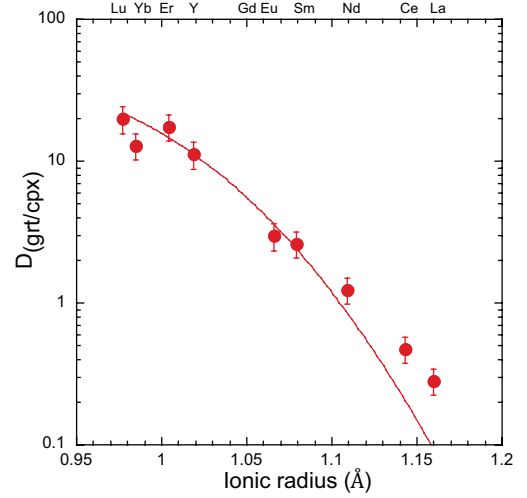
Kuzyura et al. (2010)³
2/1789a



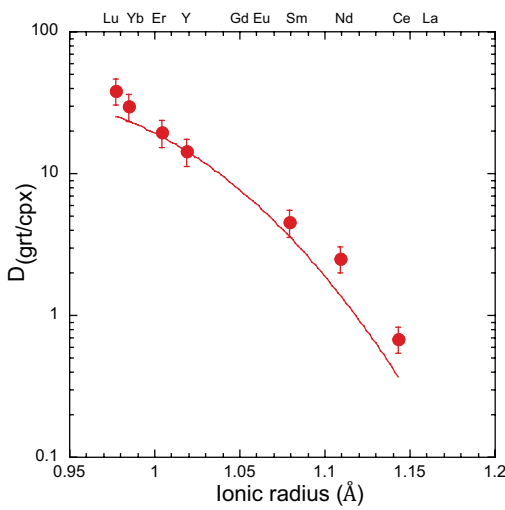
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2/17789b



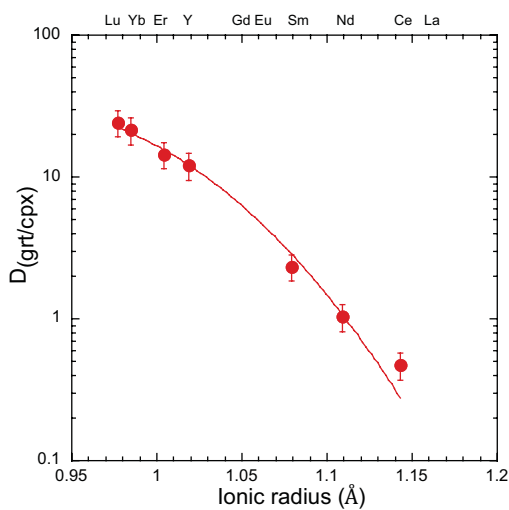
McDade



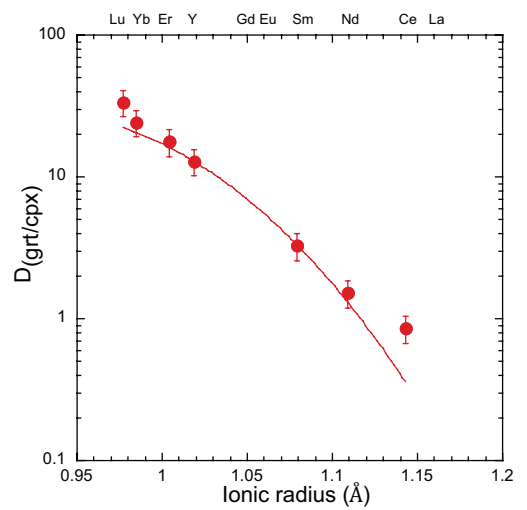
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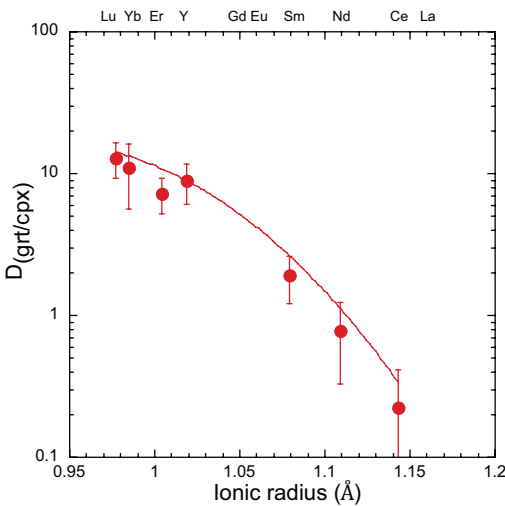
Salter and Longhi (1999)
M01295-3



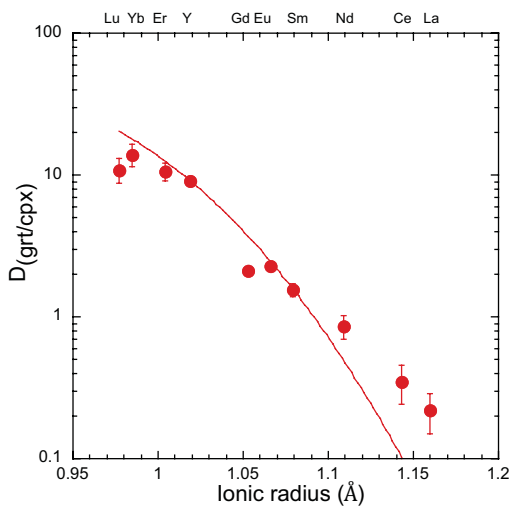
Salter and Longhi (1999)
TM694-3



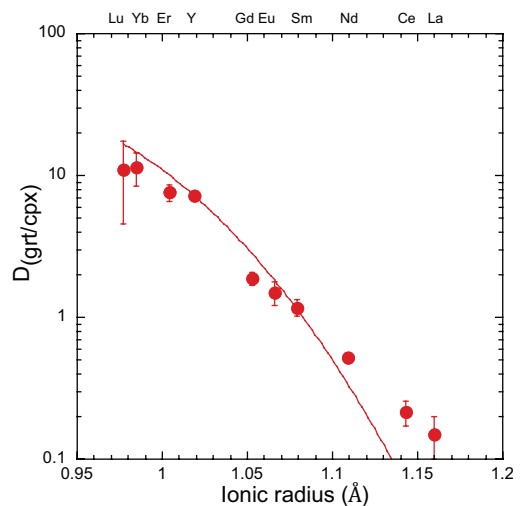
Salters et al. (2002)



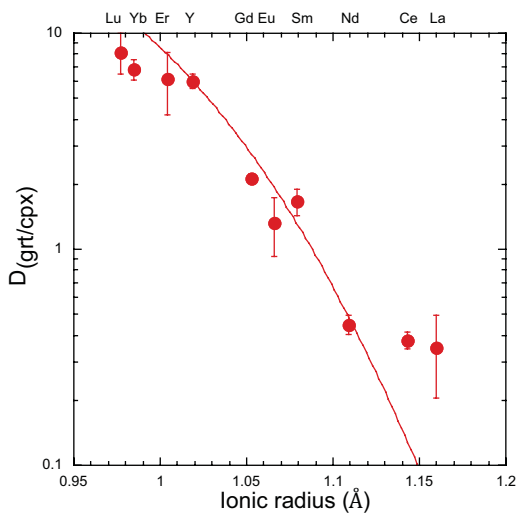
Tuff and Gibson (2007)
P511



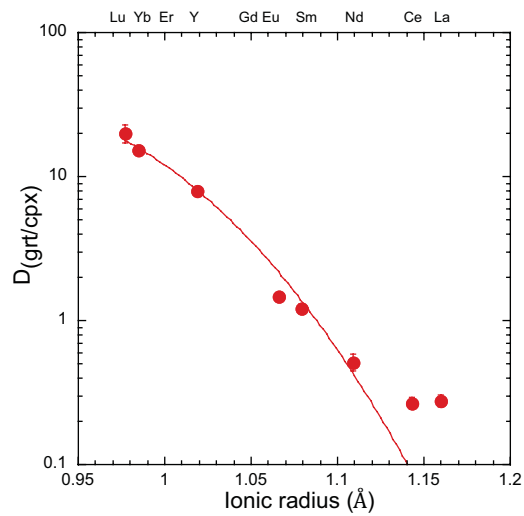
Tuff and Gibson (2007)
P529



Tuff and Gibson (2007)
S1330



Withers (1997)



Withers (1997)

