Pickles, J., Blundy, J., & Brooker, R. (2016). Trace element thermometry of garnet-clinopyroxene pairs. American Mineralogist, 101(6), 1438-1450. DOI: 10.2138/am-2016-5427

Trace Element Thermometry of Garnet-Clinopyroxene Pairs
Revision 1

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Abstract

We present major and trace element data on coexisting garnet and clinopyroxene from experiments carried out between 1.3 and 10 GPa and 970 and 1400 °C. We demonstrate that the lattice strain model, which was developed for applications to mineral-melt partitioning, can be adapted to garnet-clinopyroxene partitioning. Using new and published experimental data we develop a geothermometer for coexisting garnet and clinopyroxene using the concentration of rare earth elements (REE). The thermometer, which is based on an extension of the lattice strain model, exploits the tendency of minerals at elevated temperatures to be less discriminating against cations that are too large or too small for lattice sites. The extent of discrimination against misfit cations is also related to the apparent elasticity of the lattice site on which substitution occurs, in this case the greater stiffness of the dodecahedral X-site in garnet compared with the 8-fold M2-site in clinopyroxene. We demonstrate that the ratio of REE in clinopyroxene to that in coexisting garnet is particularly sensitive to temperature. We present a method by which knowledge of the major and REE chemistry of garnet and clinopyroxene can be used to solve for the equilibrium temperature. This method is applicable to any scenario in which the two minerals are in equilibrium, both above and below the solidus, and where the mole fraction of grossular in garnet is less than 0.4. Our method, which can be widely applied to both peridotitic and eclogitic paragenesis with particular potential for diamond exploration studies, has the advantage over commonly used Fe-Mg exchange thermometers in having a higher closure temperature because of slow interdiffusion of REE. The uncertainty in the calculated temperatures, based on the experimental data set, is less than ±80 °C.

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

Introduction

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 temperatures of coexisting garnet and clinopyroxene (Raheim and Green 1974; Ellis and Green 1979; Powell 1985; Ai 1994; Nakamura 2009; Sun and Liang 2015). The majority of these thermometers rely on Fe-Mg exchange between garnet and clinopyroxene. For example, the geothermometer of Ellis and Green (1979) utilizes the Fe-Mg exchange K_D ($K_D = \frac{(Fe^{2+}/Mg)^{gnt}}{(Fe^{2+}/Mg)^{cpx}}$) between garnet and clinopyroxene. This method is widely used but is susceptible to uncertainty in stoichiometrically-derived estimates of Fe^{3+} in the minerals that can arise from cumulative errors in electron microprobe analyses (EMPA). This has been clearly demonstrated by Li et al. (2005) who measured the Fe^{2+}:Fe^{3+} ratio with Mössbauer and compared this to the ratio calculated by stoichiometry using EMPA. They found that in every instance the ratios were different. However it should be noted that advances are being made to EMPA methodology (Matjuschkin et al. 2014) and increasingly XANES is being used to estimate garnet Fe^{2+}:Fe^{3+} ratios (Berry et al. 2010; Hanger et al. 2015).

Although there are alternative permutations to the thermometer of Ellis and Green (1979) most methods rely on the Fe-Mg K_D. A further limitation with this type of thermometer can arise through the relative ease of resetting of Fe-Mg exchange during cooling. For these reasons exchange of slow-diffusing trace elements between garnet and clinopyroxene has potential as a more reliable alternative geothermometer, e.g. Sun and Liang (2012, 2013, 2015). The trace element concentrations of garnet and clinopyroxene from eclogite and garnet peridotite are routinely measured (for example Harte and Kirkley (1997); Appleyard et al. (2007); Gréau et al. (2011)), often as an aspect of diamond exploration strategies. However, interpreting the trace element data is less routine (Griffin and Ryan 1995). Here we further explore the use of trace element contents of coexisting garnet and clinopyroxene as a geothermometer.

Theoretical Framework

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

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

Equation 1

Where D_i is the partition coefficient of element i between crystal and melt, D_o is the theoretical strain-free partition coefficient, E is the apparent Young's modulus of the lattice site, N_A is Avogadro's Number and r_o is the ideal cation size for the lattice site of interest. Based on this model Wood and Blundy (1997) give equations to predict each term for clinopyroxene-melt partitioning of rare earth elements (REE), van Westrenen et al. (1999) and van Westrenen and Draper (2007) give equivalent terms for garnet-melt partitioning of REE.

Following the lattice strain model (illustrated schematically in Fig. 2 of Wood and Blundy (1997)) as the radius of the substituent cation, r_i, deviates from r_o so the partition coefficient decreases in a near–parabolic fashion. A large Young's Modulus, E, will narrow the parabola making it harder for the lattice to accommodate a misfit ion. Wood and Blundy (1997) showed that the parabola is both lattice site- and cation charge-dependent. The latter dependency arises because heterovalent substitutions in minerals (e.g. Nd^{3+} for Ca^{2+}) require charge-balancing coupled substitutions even when the mismatch between host and substituent ionic radii is very small (Wood and Blundy 2001). In most rock-forming minerals a wide range of charge-coupled substitutions is possible (e.g. $Nd^{3+} + Al^{3+} = Ca^{2+} + Si^{4+}$ or $Nd^{3+} + Na^{+} = 2Ca^{2+}$ in clinopyroxene; Wood and Blundy (1997)). The challenge is to find the substitution mechanism that is most energetically favorable and best suited to the bulk chemistry of the system.

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

The success of the lattice strain model for mineral-melt pairs lies primarily in the fact that the shear moduli of silicate melts are zero, hence $E^{melt}=0$. Consequently from a purely lattice strain point of view there is no mechanical energy associated with replacing one ion with another in a silicate melt. In reality this is unlikely to be true, especially as other factors influence trace element incorporation into melts, such as co-ordination environment, complexation, configurational entropy etc. Experimental studies of melt-melt partitioning (e.g. Watson (1976), Ryerson and Hess (1978), Schmidt et al. (2006)) reveal that elements in general partition unequally between melts of different composition reflecting the energetic preferences of ions with different charges and/or radii for melts with different compositions/structures. However, the magnitude of melt-melt partition coefficients is always smaller, by several orders of magnitude, than that of mineral-melt partition coefficients for the same range of ionic radii and charge, demonstrating that it is the energetics of trace ion incorporation into minerals that dominates the energetics of mineral-melt exchange equilibria. Moreover, atomistic simulations in which ions are substituted onto lattice sites and the resultant relaxation (strain) energies calculated (e.g. Allan et al. (2003)) corroborate the findings of mineral-melt partitioning studies.

Having established that it is the energetics of trace ion incorporation into crystals that dominates mineral-melt partitioning equilibria it is a simple matter to show that an understanding of mineral-melt partitioning for Mineral 1 and for Mineral 2 constitutes an approach to understanding trace element partitioning between Mineral 1 and Mineral 2. Here we explore the possibility of extending the lattice strain models for clinopyroxene-melt and garnet-melt towards a better understanding of garnet-clinopyroxene partitioning. Through experiments we investigate the mineral-mineral partitioning of elements, rather than mineral-melt. Lee et al. (2007) used this approach to develop a version of the lattice strain model that describes trace element partitioning between olivine and cpx, which we have modified here for the case of partitioning between garnet and cpx. As our reference element we have chosen Y instead of Lu, which was used by Lee et al. (2007), due to the greater availability of reliable Y data (Y has a natural abundance approximately 60 times greater the Lu). However, using any REE as a reference is valid.

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

Equation 2

By referencing the model to an element we obviate the need to explicitly evaluate the ratio of individual D_o parameters for garnet and cpx that appear in the mineral-melt formulations of the lattice strain model (Equation 1), thereby reducing the number of unknown parameters. Moreover, all of the parameters in the exponential on the right hand side of Equation 2 can be calculated for the P-T-X of interest thereby eliminating the need to know anything about the composition of any melt that may or may not have coexisted with the garnet and clinopyroxene.

To test our model we performed a series of experiments aimed at investigating the partitioning of trace elements, particularly the rare earth elements (REE) and Y, between garnet and clinopyroxene, using a flux, e.g. a silicate melt, to promote crystal growth. The new experimental dataset are augmented by published experimental data on garnet-clinopyroxene pairs. Conditions of the new experiments were designed so as to increase the coverage of P -T –X space. We will use our experimental dataset to (a) investigate extension of the Lee et al. (2007) approach to garnet and clinopyroxene (b) critically appraise the recent mineral-mineral partitioning work by Sun and Liang (2015, 2013, 2012) and (c) develop a REE geothermometer for coexisting garnet and cpx. We use experimental garnet and cpx from both eclogitic and peridotitic bulk compositions to increase the applicability of the models. In all cases the Nernst partition coefficient, D_i, is defined as the weight concentration of the element i in garnet divided by the concentration of i in cpx. Thus D_i is shorthand for $D^{grt/cpx}$.

Methods

Experimental Methods

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

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

Trace elements were added to all starting materials as ICP-standard nitrate solutions using a micropipette and dried under a heat lamp. The doped mixtures were re-homogenized in an agate mortar and denitrified at 300 °C. As the BAS glass is natural and already contains a wide range of trace elements only 200 ppm of Li were added. JP1, ZrTi, AOB and NSR-16 had a complete suite of trace elements added. The trace element contents of all starting materials are given in Table S2. Following doping and denitrification starting materials JP1, ZrTi and AOB were melted and quenched in a controlled atmosphere, vertical quench furnace at an fO_2 equivalent to the nickel-bunsenite (NNO) buffer, between 1000 and 1520 °C. This fixes the Fe^{2+}:Fe^{3+} ratio in the starting material to match the relatively oxidized intrinsic fO_2 of the experimental apparatus (>NNO) and thereby minimizes redox reactions, mediated by H_2 diffusion, taking place during the experiments. NSR-16 was prepared as a hydrous glass, using $Al(OH)_3$ as a source of H_2O. Trace element-doped NSR-16 powder was loaded into an Au_{80}:Pd_{20} capsule and held at 0.22 GPa and 1000

°C for 2 hrs in a rapid-quench TZM cold-seal apparatus at NNO+1.

To minimize Fe loss during experiments we used Au_{80}:Pd_{20} capsules that were annealed and acid-cleaned before loading and welding. The outside diameter of the capsules was 2 mm and they ranged in length from 0.5 to 2 mm. Some experiments were run with two capsules each containing different starting materials in end-to-end configuration. Experimental run times were between 4 and 123 hours, see Table 1. We note that for the basanite runs these run durations are identical to those of Green et al. (2000) for the same starting materials and run conditions.

Experiments from 3.0 to 3.4 GPa pressure were carried out using 1/2" end-loaded piston cylinder apparatus at the University of Bristol. The pressure media were NaCl, Pyrex and crushable alumina with a graphite furnace. The experiments were pressurized and heated simultaneously with the pressure always being the final variable to be increased, i.e. hot piston-in technique. During the experiment pressure was maintained manually at the desired value and the temperature was measured using an axial $W_{95}Re_5$-$W_{75}Re_{25}$ thermocouple (not corrected for pressure) and regulated by a Eurotherm controller. The pressure correction of McDade et al. (2002b) was applied and verified by bracketing the quartz-coesite boundary. RB627 (1.3 GPa) was performed in a 3/4" talc/Pyrex assembly with a tapered graphite furnace and pressure-calibrated using the melting point of CsCI (see McDade et al. (2002a)).

Experiments above 3.4 GPa were carried out using a Walker-type multi-anvil apparatus at Bayerisches Geoinstitut (B.G.I.), University College London (U.C.L.) and the University of Bristol. In each case the pressure medium was precast MgO octahedra with truncations of varying length depending on the pressure required. Either an MgO or alumina spacer surrounded the capsule with a ZrO_2 insulator around the furnace. Experiments at B.G.I. used the 10/4 assembly with a $LaCrO_3$ furnace; at U.C.L. a 14/8 assembly with a graphite furnace; and at Bristol an 18/11 assembly with graphite furnace. The temperature was measured with a $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouple, inserted radially in U.C.L. experiments and axially at B.G.I. and Bristol. The experiments were pressurized over 3 hours and heated for between 6 and 8 hours. The pressure calibrations used the following phase changes: quartz-coesite, coesite-stishovite, Bi I-II, Bi III-V and $CaGeO_4$ (garnet to pervoskite). All experiments were ended by turning the power off to give quench times of less than 10 seconds to reach 300 °C.

Analytical Methods

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

A Cameca IMS-4f ion-microprobe at the University of Edinburgh was used to measure trace elements in garnet and cpx of the experimental run products by secondary ion mass spectrometry (SIMS). All samples had a 20 nm gold coat applied under vacuum. A primary beam of $^{16}O^-$ with a net impact of energy of 15 keV was used. Positive secondary ions were accelerated to 4500 V with an energy offset of 75 eV and a window of 40 eV to minimize transmission of molecular ions. The beam current was varied as necessary to permit analysis of the smaller grains because, in general, beam diameter is a strong function of beam current, i.e. 30 μm beam diameter at 5 nA, 15 μm at 1.5 nA. All SIMS pits were examined subsequently by SEM to check that there was no visible overlap onto adjacent phases. Secondary ion yields were calibrated using standard glass NIST SRM 610 (Hinton 1990) and checked using secondary standards of garnets DD1 (Irving and Frey 1978), AP, SG and cpx SC8804 (van Westrenen 2000). The following positive secondary ion masses were analyzed and ratioed to ^{30}Si (as determined by electron microprobe): ^{7}Li, ^{11}B, ^{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, ^{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 ^{71}Ga was used for the NIST610 glass due to overlap on ^{69}Ga of ^{138}Ba, a species with negligible concentration in garnet and clinopyroxene.) The count times per cycle 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 ^{143}Nd and ^{149}Sm and 10 s for ^{178}Hf. The number of cycles was between 8 and 15 to produce statistically significant data, with low counting error. Isobaric oxide interferences were greatly minimized by the careful choice of elements, doping levels and energy filtering of secondary ions. The remaining molecular interferences, such as ^{29}Si^{16}O on ^{45}Sc, were removed by conventional peak-stripping. Overlap of LREE oxides on HREE was corrected using in-house REEO/REE values for cpx and values of van Westrenen (2000) for garnet. Analysis of secondary standards demonstrated that there was no significant secondary ion-yield differences between garnet and cpx thus D_i is taken to be the Si-normalized concentration of an element in garnet divided by that in cpx.

Results and Discussion

Experimental run conditions and major element mineral data measured by EMPA are presented in Table 1 and Table 2. Attainment of equilibrium in the new experiments is demonstrated through the homogeneity of the run products (**Figure 1**), the small standard deviation in the major element data, Table 1 and Table 2, and the shape of the parabolae of the REE data. The presented EMPA data for each experiment are a mixture of core and rim measurements, therefore any variability within a crystal, i.e. zoning, would result in a large standard deviation in the major element data. A total of 12 experiments contained garnet and cpx crystals between 20 and 100 μm that could be analysed by ion-microprobe. Occasionally garnets contained cpx inclusions, which were avoided during analysis. Areas of melt or quench crystals occurred in some experiments. The garnet and cpx end members were calculated using the methods of Deer et al. (1992) and Morimoto et al. (1988) respectively. SIMS trace element data for cpx are presented in Table 3 and for garnet in Table 4. Care was taken during data processing to check that there was no contamination by other phases during analysis. One clear indication of glass contamination is elevated concentrations of highly incompatible elements, such as U or Th. In some cases contamination only involved a few analytical cycles and these were eliminated during processing. In cases where there was persistent contamination throughout the analysis the trace element data were discarded.

The major element composition of garnet varies very little between each starting composition. All garnets are pyrope-rich (0.65-0.41 mol fraction) with lesser amounts of grossular (0.26-0.14 mol fraction) and almandine (0.32-0.07 mol fraction), where almandine was calculated from stoichiometric Fe^{2+}. The only experiment with a greater almandine than grossular content is RB627. The majority of the experimental cpx are Na-rich (omphacite following Morimoto et al. (1988)) with three being relatively Mg-rich and falling within the Ca-Fe-Mg quadrilateral. Al^{iv} ranges between 0.175-0.003 cations per formula unit (c.p.f.u.), Na 0.507-0.108 c.p.f.u., 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 concentration of Ca in both garnet and cpx increases with an increase in pressure, however the rate of change per GPa is greatest in garnet, which may have potential as a barometer, although this is not explored here.

The high Fe^{3+} content of the garnets and most cpx (Table 1 and Table 2) is consistent with the assumption of a run fO_2 above NNO. For instance, the average calculated garnet Fe^{3+}/Fe^{tot} is 26% (range 8-41%; See Table 2) which is closer to the $ReReO_2$ buffered runs (~NNO+2) of Matjuschkin et al. (2014) than the 5% Fe^{3+}/Fe^{tot} in garnets of the NNO runs of Rubatto & Hermann (2007). Note that at these high fO_2 values it is anticipated that >90% of the Eu can be considered as trivalent (see Burnham et al. (2015)).

Garnet-cpx trace element partition coefficient data, Figure 2, show that the differing starting compositions produce similar trends. In all experiments Sr has the smallest garnet-cpx partition coefficient. The absolute concentration of Sr increases greatly in both garnet and cpx with an increase in pressure, however the change in concentration is similar in both minerals resulting in only a modest increase in D_{Sr} with P. A comparable effect is seen in Li with P except that the concentration in garnet increases more quickly than cpx resulting in a potential barometer, as previously identified by Hanrahan et al. (2009, 2009b). Lutetium has the highest partition garnet-cpx coefficient in all experiments.

Lattice Strain Model Applied to Garnet-Cpx Pairs

Our new data on REE partitioning between the dodecahedral X-site in garnet and the 8-fold M2 site in cpx are in agreement with previous studies. Figure 3 shows the partition coefficient plotted against the ionic radius of the cation, using 8-fold ionic radii values from Shannon (1976). There is an increase in concentration from La to Lu in both minerals, however the LREE have a greater affinity for cpx than garnet, whereas HREE more readily enter garnet. The change in the REE concentration, from LREE to HREE, is far greater for garnet than for cpx. The concentration of Sm is approximately equal in garnet and cpx, resulting in $D_{Sm}\approx1$. Garnet-melt and cpx-melt data have been shown to form parabolae by van Westrenen (2000) and Wood and Blundy (1997) respectively. By combining these two mineral-melt parabolae we see an almost linear trend. This is in part because Sc is not considered here as it enters the cpx M1 site rather than the M2 site which accommodates the REE (Allan et al. 2003). Consequently, we only observe one limb of what is still a parabola.

One of the objectives of this paper is to investigate the ability of the lattice strain model to describe partitioning between garnet and cpx. To this end we have used the equations of Wood and Blundy (1997) and van Westrenen and Draper (2007) to derive the lattice strain parameters r_o^{cpx}, E^{cpx}, r_o^{grt}, E^{grt}. We find that these parameters describe the garnet-cpx partitioning data well. Figure 3 shows the curve of weighted best fit for the lattice strain model for the new experimental data (Equation 2) having adopted the Wood and Blundy (1997) and van Westrenen and Draper (2007) r_o and E terms for cpx and garnet respectively. As all variables that influence E and r_o parameters are known, i.e. *T, P* and mineral composition, there is evidently a self-consistency between the published mineral-melt and the new mineral-mineral models.

To further investigate the lattice strain approach, garnet-cpx partitioning data from other experimental studies were also considered (Table S3). These experiments cover a wide range of *P* – *T* conditions (1000 to 1750 ^{o}C and 1.5 to 7.0 GPa). As with our experiments, the weighted curve of best fit to the garnet-cpx REE partition coefficients is calculated using Equation 2 with r_o and E for cpx and garnet calculated from Wood and Blundy (1997) and van Westrenen and Draper (2007) respectively. Most data are well described by the lattice strain model and the imposed lattice strain parameters (see Figure S1, Figure S2 and Figure S3). Poor agreement between the model and the data can often be attributed to the quality of the analyses. The experiments by Hauri et al. (1994) and Klein et al. (2000), for example, show many inconsistencies with the other datasets, possibly due to contamination by glass or cpx in the garnet analyses. For this reason these data were not included in further analysis. The experiments by Kuzyura et al. (2010), however, have small analytical uncertainties and no obviously anomalous results, yet the model provides a poor fit to their data (Figure S2). The primary difference between these experiments and all the others is that Kuzyura et al. (2010) used a carbonate-silicate mix, as opposed to silicate only. This results in garnets with a much greater Ca content (around 0.5 mole fraction grossular end-member as opposed to between 0.1 and 0.2 in the other experiments). The effect of Ca on REE partitioning was investigated by van Westrenen et al. (1999) who found that as the grossular component in garnet increases E^{grt} decreases. van Westrenen and Draper (2007) provide a correction for Ca in the r_o^{grt} term which is then used to calculate E^{grt}. It would appear that in the case of Kuzyura et al.'s (2010) unusually Ca-rich garnets this approach breaks down. For this reason those experiments are not considered further in our study, pending further work to better quantify the effect of high-Ca on E^{grt}.

Sun and Liang (2012, 2013) present a model for garnet-cpx partitioning of REE in which they define new terms for predicting E and r for both minerals. A comparison of the r_o^{cpx} and E^{cpx} values obtained by Sun and Liang (2012) to those of Wood and Blundy (1997) shows very good agreement. However, for r_o^{grt} the term of Sun and Liang (2013) is calculated from the Ca content alone, and E^{grt} depends only on r_o^{grt}. The result is that both parameters in garnet are defined solely by its Ca content. Previous work by van Westrenen et al. (1999); van Westrenen (2000); van Westrenen and Draper (2007) demonstrated that E^{grt} is heavily dependent on a number of other garnet compositional terms, in addition to *T* and *P*. Comparing the E^{grt} values calculated through the method of Sun and Liang (2013) with those calculated with the method of van Westrenen and Draper (2007) demonstrates little correlation between the values (Figure 4). The method of Sun and Liang (2013) underestimates the majority of the E^{grt} by several hundred GPa compared to the method of van Westrenen and Draper (2007). E^{grt} values from the two experiments by Kuzyura et al. (2010) are overestimated by around 250 GPa. These mismatches have consequences for garnet-cpx partitioning. Calculating E^{cpx}, r_o^{cpx}, E^{grt} and r_o^{grt} using the method of Sun and Liang (2013, 2015) and comparing the fit to the garnet-cpx experimental data, analogous to Figure 3, demonstrates little correlation between the fit and the data. We attribute this mismatch to the values of E^{grt}, which cannot be calculated solely from Ca in garnet. Whilst the method given by Sun and Liang (2013) is useful for estimating temperature and pressure their E^{grt} values are inconsistent with garnet-melt experimental data.

Lattice Strain Model and Temperature

The partitioning of trace elements between garnet and cpx given by Equation 2 has an inherent T term; a change in D_i with T is predicted, both through its occurrence in the denominator of the exponential terms and in its tendency to reduce E and increase r_o. In contrast, although pressure will also affect E and r_o the magnitude of this effect is small relative to that of temperature. The influence of temperature was confirmed by the work of Wood and Blundy (1997) and van Westrenen and Draper (2007) who found that E in both cpx and garnet has a quantifiable temperature dependence. Dohmen and Blundy (2014) came to a similar conclusion from a study of plagioclase-melt trace element partitioning. Figure 5 confirms the importance of T by displaying the change in the shape of the parabola when all the lattice strain terms are kept constant and only T is altered. Equation 2 can be re-arranged to make T the dependent variable and therefore yield a geothermometer that can be applied to REE partitioning between coexisting garnet and cpx.

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

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

Equation 3

Note that, in contrast to Equation 2, the reference element is no longer Y, but any REE, where $j \neq i$. As three of the parameters in the lattice strain model (E^{cpx}, E^{grt} and r_o^{grt}) require temperature to be known an iterative approach was adopted to solve for the temperature. This negates the need for developing new, temperature-independent methods for calculating each of these variables and consequently compliments the mineral-melt partitioning work of previous studies. We consider it essential that any garnet-cpx partitioning model is consistent with garnet- and cpx-melt partitioning, rather than invoking a set of new, best-fit lattice strain parameters for one or both minerals. Moreover, our approach obviates the need to select, arbitrarily any particular REE as a reference element.

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

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

Although any two REE can be chosen to replace i and j in Equation 3 but it is preferable to choose two elements that have a large relative difference in ionic radius and exist in concentrations high enough to return accurate measurements. An important consideration is the precision of the REE analysis. LREE are invariably in very low concentration in natural garnet and subject to considerable analytical uncertainty. To minimize the error in our temperature prediction we calculated the temperature using all possible REE pairs and compared the weighted mean to the experimental temperature. We assumed that calculating the temperature with multiple pairs avoids too much weight being placed on one erroneous datum. We found that the following elements should not be used to calculate T: La and Ce as they are in very low concentration in garnet; Tb, Dy and Ho as they are often not included in experimental charges. For each temperature calculation the terms in the lattice strain model were calculated with an initial best-guess temperature to derive the temperature-dependent terms on the right hand side of Equation 3. The temperature was then adjusted iteratively until the input and the calculated temperature were the same to within 1 degree. The temperature for each element pair, along with the error on D_i from the ion probe data, allow a weighted mean to be calculated for each experiment. This approach means that the mean temperature can be screened for analyses with a large error. Calculated temperatures less than 600 or greater than 2000 ^{o}C were assumed to be erroneous and removed from consideration. An excel spreadsheet to perform these calculations is available from the first author.

Comparing the temperature calculated through our new method, which uses the lattice strain parameters of Wood and Blundy (1997) and van Westrenen and Draper (2007), with the experimental temperature shows very good agreement (Table 5 and Figure 6a). The mean absolute deviation between the temperatures, when the high-Ca experiments by Kuzyura et al. (2010) are disregarded, is only 76 °C. The broad range of bulk compositions for our validation experimental dataset demonstrate that our approach can be applied to any coexisting garnet-cpx pairs.

Applications

Although the majority of the garnet-cpx geothermometers in common usage utilize major elements we believe that our rare earth element approach offers a number of benefits.

1) The use of rare earth elements as a geothermometer has an advantage over the Fe-Mg exchange models as the slow diffusion of 3+ cations (van Orman et al. 2002) leads to a correspondingly higher closure temperature (Frost and Chacko

1989). Work by Pattison (1994) and others shows that the Fe-Mg exchange can return differing temperatures that depend on the grain size of the minerals analyzed, a hallmark of a diffusion-controlled process. Pattison (1994) suggested that the Fe-Mg in granulites may record the temperature at which inter granular exchange ceased in the rock. By using REE, which diffuse much more slowly, the peak metamorphic temperature should be recovered. See Yao and Liang (2015) and Sun and Liang (2015) for detailed discussion of closure temperatures in bi-mineralic systems.

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

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

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

be estimated.

An enduring shortcoming of this and other thermometers is the need to know the equilibrium pressure. Throughout this study where a pressure estimate is required, such as in predicting E^{grt}, the experimental *P* has been used. Currently the barometers of Simakov (2008) and Sun and Liang (2015) are available for garnet-cpx pairs. Alternatively, many studies use an assumed pressure of 5 GPa to compare data. To avoid amplifying uncertainties inherent in the barometers and to clearly display the error associated with our model we have only used experimental pressures. An increase of 1 GPa in assumed pressure increases the temperature estimate by, on average, 50 ^{o}C in our model irrespective of the REE pair chosen.

Our experiments show that the effect of pressure on rare earth element partitioning in isothermal, isochemical experiments is not consistent enough to be used as barometer. Comparing isothermal series of experiments carried out at 1200 and 1400 ^{o}C (Figure 7) shows that there is no consistent effect of pressure that can be used to solve for the pressure. The experiments carried out at 1200 ^{o}C, but variable pressure, are all within error of each other, whereas the experiments at 1400 ^{o}C appear to show a pressure effect, which on closer inspection is found to be not consistent.

Comparison to existing thermometers

The Fe-Mg exchange geothermometer of Ellis and Green (1979) is the most widely used method of estimating temperature for garnet-clinopyroxene pairs. To evaluate our new geothermometer we have calculated the temperature using the method of Ellis and Green (1979), both with and without the calculation of Fe^{2+} by stoichiometry. We have also calculated temperature for the same experiments with the REE method of Sun and Liang (2015) and compared all T estimates to the experimental temperature (Table 5 and Figure 6b). Points of note are that temperature estimates for some of our new experiments are significantly over-estimated using the method of Ellis and Green (1979). Even when the error associated with the Fe^{2+} calculation is removed ($T_{(EG^*)}$ in Table 5) the temperature estimates are still several hundred degrees too high. This results in a mean absolute deviation of 240 °C between the temperature calculated using the method of Ellis and Green (1979) and the experimental temperature. The mean absolute deviation between the experimental temperature and that calculated T using the method of Sun and Liang (2014) is 174 °C. These values can be compared with our lattice strain approach which has an absolute mean deviation of only 76 °C when the temperature is calculated using the mean of all REE pairs. (The highly discrepant values for Kuzyura et al. (2010) data are not included in either of the REE temperature estimates.) This clearly demonstrates that not only can the lattice strain model be used to estimate temperature but also the T may be more accurate than the most commonly used eclogitic geothermometer. It should be reemphasized that our temperature formulation is not calibrated on the experimental data presented in Table 5. We have simply transferred the lattice strain parameters from garnet-melt and cpx-melt models and applied them the case of garnet-cpx partitioning. Thus this is a fair test of all thermometers.

Implications

In this paper we explore the potential of the lattice strain model, as derived from studies of mineral-melt trace element partitioning, to be used as a mineral-mineral geothermometer. By testing our approach to estimating temperature with both eclogitic and peridotitic minerals we have demonstrated the versatility of the lattice strain model as a thermometer for mantle minerals. Through focusing on garnet and cpx, which are stable over a very wide range of temperature and pressure conditions, we have developed a model that has very wide-reaching applications, both in metamorphic geology, tectonic reconstructions and diamond exploration. Whilst the focus of this paper is on the partitioning of garnet and cpx the approach taken here can be applied to any coexisting mineral pair, as long as a method exists to calculated E and r for the minerals of interest, ideally from mineral-melt partitioning studies. In light of recent predictive models for plagioclase-melt partitioning of trace elements (Dohmen and Blundy 2014) the potential of cpx-plagioclase pairs as trace element geothermometers would benefit from further evaluation.

Acknowledgements

JP is grateful to Rio Tinto for a PhD studentship at the University of Bristol, B.G.I. and

Dave Dobson for access to their multi-anvil apparatus and Richard Hinton for assistance with the ion-microprobe analyses. JB acknowledges funding from ERC Advanced Grant CRITMAG and a Royal Society Wolfson Research Merit Award. This work has benefitted from discussion with Chris Smith, Russell Sweeney, John Schumacher, Susanne Skora and Wim van Westrenen. We thank Yan Liang and an anonymous reviewer for thoughtful reviews of our manuscript.

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Figures

Figure 1. SEM images of typical experimental run products demonstrating homogenous grains, indicative of equilibrium. **a** piston cylinder experiment, RD25, at 1200 °C and 3.4 GPa. **b** multi-anvil experiment, V545, at 1400 °C and 10 GPa. The scale bar is 100 µm in both cases.

Figure 2. Spider diagram of partition coefficients between garnet and cpx for trace element data presented in this paper. **a** experiments using JP1 starting composition, **b** BAS starting composition and **c** is the AOB, ZrTi and NSR-16 starting compositions.

Figure 3. Experimental REE partitioning between garnet and cpx as a function of ionic radius of the element. The red line shows the weighted fit calculated using **Equation 2** with values of E and r_o for cpx and garnet calculated by the method of Wood and Blundy (1997) and van Westrenen and Draper (2007) respectively. Error bars show 1 s.d. of the mean.

Figure 4. Comparison of values of E^{grt} calculated through the model of Sun and Liang (2013) ($E_{(S\&L)}$) with those found with the model van Westrenen and Draper (2007) ($E_{(vW\&D)}$) using the experimental the garnet-cpx data set.

Figure 5. The effect of change in *T* on the partitioning of REE. The black lines use the same experimental data values for E and r and change only *T* from 800 to 1400 °C in 200 °C intervals.

Figure 6. a. Comparison of experimental temperature with *T* found through a weighted mean of REE pairs, from Nd to Lu, and the lattice strain model, **Equation 3**. Error bars are shown where larger than symbol. The red circles are experiments from this study and the black diamonds are those from the literature, see **Table 5**. The mean absolute deviation is only 75 °C for all the data. b. Comparison of calculated *T* using the weighted mean temperature using all REE pairs lattice strain model ($T_{(JP)}$) with the *T* found using Ellis and Green (1979) ($T_{(EG)}$) and Sun and Liang (2015) ($T_{(SL)}$), which have a mean absolute deviation of 240 and 278 °C respectively. In both figures the black line shows the 1:1 relationship.

Figure 7: Comparison of isothermal, isochemical experiments to show the effect of pressure. The temperature is the experimental *T*.

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

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

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_2O_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_2O_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_2O	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_2O	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	99.62		100.33		100.71		99.49		100.49		100.58		99.36		99.13		99.27		99.44		99.13		98.98	
c.p.f.u.																								
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			

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 53.07 ±0.11, c.p.f.u. stands for cations per formula unit and are calculated based on 4 cations. The Fe^{3+} is calculated using the method of Schumacher (1991).

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	
n	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_2O_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_2O_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_2O	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_2O	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	100.01		101.14		101.16		100.21		100.86		100.88		99.88		100.45		99.88		100.02		99.33		99.59	
c.p.f.u.																								
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	

Zr	0.01

Abbreviations are the same as table 1 and calculations are based on 8 cations.

Table 3: Cpx trace element data measured by SIMS

Sample	BL58		RD25		G21		V547		V546		V545		BL88		RD56		G25		RD56 AOB		UCL3		RB627	
n	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	

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.

Table 4: Garnet trace element data measured by SIMS

Sample	BL58		RD25		G21		V547		V546		V545		BL88		RD56		G25		RD56 AOB		UCL3		RB627	
n	3		5		2		4		3		3		5		1		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	(154)	1621	(221)	746	(105)	480	(25)	1752	(50)	2119	(131)	3629	(615)	2951	(590)	2951	(278)	2990	(511)	6641	(1521)	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)	0.0254	(2)	2.177	(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	

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

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.

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		

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

$T_{(exp)}$ is the experimental temperature, $\mathrm{T}_{(\mathrm{JP})}$ is the weighted mean temperature found iteratively using Equation 3 with multiple REE pairs. The error, σT, is 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. $T_{(EG)}$ 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 $T_{(SL)}$ 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 the necessary data not being available. The mean value shows the mean temperature deviation of all the experiments, including Kuzyura et al. (2010).

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_2O_3	13.85	14.73	14.46	12.22	19.52
FeO		11.03			9.46
Fe_2O_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_2O	2.69	4.01	2.58	0.83	3.35
K_2O	0.66	1.85	0.77	0.03	0.24
Cr_2O_3	0.62		0.25	0.59	
P_2O_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.

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

	JP1 ppm	BAS* ppm	AOB ppm	ZrTi ppm	NSR-16 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.

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

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