

# High field strength element/rare earth element fractionation during partial melting in the presence of garnet: Implications for identification of mantle heterogeneities

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[1] Abstract: A synthesis of recent garnet-melt trace element partitioning data for key trace elements (Ti, Hf, Zr, U, Th, Sm, and Yb) is used to compare and contrast the trace element signatures imparted on mantle melts by garnets from peridotitic and eclogitic source rocks. Garnetmelt partition coefficients D<sup>Grt/Melt</sup> are very sensitive to changes in garnet major element composition. Specifically, high-pressure, high-temperature experimental studies show that high field strength elements (HFSE) Zr, Hf, and Ti are incompatible in garnets with  $<19 \pm 1$  mol% Ca on their X site, with  $D_{Ti} < D_{Zr} \le D_{Hf} < 1$ , while at higher Ca levels, all three become compatible with  $D_{Zr} > D_{Hf} > D_{Ti} > 1$ . U and Th also have higher partition coefficients at higher garnet Ca contents, while the amount of fractionation between the two decreases. In contrast, the heavy rare earth element partition coefficients  $D_{\text{HREE}}$  are hardly affected by a change in garnet Ca content. We provide a semiquantitative explanation for the behavior of the high field strength elements based on a crystal lattice strain model in which Zr and Hf are split between the X and Y sites in Ca-rich garnet and in which significant changes in garnet elasticity occur as a function of garnet composition. The large variations in both absolute  $D^{\text{Grt/Melt}}$  values and  $D^{\text{Grt/Melt}}$  ratios (e.g.,  $D_{Z_{1}}$  $D_{\gamma b}$ , in conjunction with compositional differences between natural peridotitic (Ca poor) and eclogitic (Ca richer) garnets, allow identification of trace element ratios that may best serve as a fingerprint for the presence of eclogitic garnet. We present simple batch melting calculations for two end-member melting scenarios (anhydrous garnet peridotite melting and anhydrous bimineralic eclogite melting). Our calculations show that near-uniform Zr/HREE and Hf/HREE as a function of melt fraction, in combination with Hf/Sm and Zr/Sm ratios that are smaller than the source ratio, could serve as fingerprints for the presence of Ca-rich garnet in the source of mantle melts. Our calculations show that it is impossible to define one unique "garnet signature" to determine the presence or absence of garnet in basalt sources but rather that different garnet-bearing sources are likely to produce distinctly different "garnet signatures."

Keywords: Partitioning; mantle heterogeneities; high field strength elements; garnet.

**Index terms:** Experimental mineralogy and petrology; igneous petrology; minor and trace element composition; physics and chemistry of magma bodies.



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### 1. Introduction

[2] Several lines of geophysical, geological, and geochemical evidence point to the presence of pockets or veins of recycled, garnet-bearing, pyroxene-rich lithologies (i.e., garnet pyroxenite and/or eclogite) in the source region of both mid-ocean ridge basalt (MORB) and oceanic island basalt (OIB) [e.g., Hofmann and White, 1982; Hirschmann and Stolper, 1996; Hofmann, 1997; Rehkämper and Hofmann, 1997; Lassiter et al., 2000; Sobolev et al., 2000]. Seismic tomography studies [e.g., Widyantoro and Van der Hilst, 1996; Ritsema et al., 1999] indicate that subducting slabs of oceanic basalt are currently being recycled into the upper and even lower mantle, and exposed sections of peridotitic mantle material are commonly heterogeneous on the centimeter to meter scale. Most pyroxene-rich rocks have a lower solidus than anhydrous peridotite [Hirschmann and Stolper, 1996], so that their contribution to derived melts will be relatively large, even if they form only a small volume of the overall source region. Evaluating the role of these lithologies in melting processes beneath mid-ocean ridges and oceanic islands is vital for the solution of several important geochemical and geodynamical problems. For example, partial melting of garnetbearing pyroxenite veins present at shallow levels in the upper mantle could obviate the need for MORB melting to start at high pressures, within the stability field of garnet lherzolite (>2.9 GPa [Robinson and Wood, 1998]).

[3] Both bulk and mineral compositions of these pyroxene-rich lithologies are different from those of the surrounding peridotitic mantle. This is illustrated in Figure 1, summarizing the major element composition (in terms of end-members) of garnets found in the Earth's mantle. Garnets from fertile peridotites have a fairly restricted compositional range, rich in pyrope (Py  $(Mg_3Al_2Si_3O_{12})$ ) and poor in almandine (Alm (Fe<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>)) and especially grossular (Gr (Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>)). Gr contents are generally between 6 and 16 mol %. On the other hand, group A eclogites (the group found as xenoliths in kimberlites and basalts or as cumulates in ultramafic rocks [see Coleman et al., 1965]) and pyroxenites, which can be formed through a variety of processes (e.g., metamorphism of basalt that may or may not have experienced alteration, high-pressure cumulate), show a far wider range of major element composition. These garnets generally contain significantly more Fe and Ca, with Gr contents in the range from 10 up to  $>60 \mod \%$ , averaging around 30 mol %.

[4] Our objective is to identify trace elements whose garnet/melt partition coefficients are sensitive to the range of garnet compositions shown in Figure 1. Abundance ratios involving such elements would provide criteria for distinguishing melts in equilibrium with different garnet compositions. We particularly evaluate whether trace element compositions of melts in equilibrium with grossular-rich garnets, typical





**Figure 1.** Compositional range of mantle garnets in terms of end-members pyrope (Py  $(Mg_3Al_2Si_3O_{12}))$ , grossular (Gr  $(Ca_3Al_2Si_3O_{12})$ ), andradite (And  $(Ca_3Fe_2Si_3O_{12})$ ), uvarovite (Uv  $(Ca_3Cr_2Si_3O_{12})$ ), almandine (Alm  $(Fe_3Al_2Si_3O_{12})$ ), and spessartine (Spes  $(Mn_3Al_2Si_3O_{12})$ ). Data (n = 390) are taken from *Boyd and Nixon* [1972], *Irving* [1974], *Bodinier et al.* [1987], *Sen and Leeman* [1991], *Bell and Rossman* [1992], *Beard et al.*, [1992], *O'Reilly and Griffin* [1995], *Harte and Kirkley* [1997], *Brenker and Brey* [1997], *Stachel et al.* [1998], *Robinson and Wood* [1998], *Matsyuk et al.* [1998], and *MacKenzie and Canil* [1999]. Note the large spread in iron and, particularly, calcium contents of eclogitic and pyroxenitic garnets compared with peridotitic garnets. High-pressure, high-temperature garnet-melt partition coefficients left and right of the dashed line drawn at a constant (Gr + And + Uv) content of 19% are markedly different, as discussed in the text. Solid circles along the bottom axis show garnet compositions from *van Westrenen et al.* [1999] for which garnet-melt partitioning data are shown in Figure 2.

of eclogites/pyroxenites, can be distinguished from melts in equilibrium with pyrope-rich garnets, typical of fertile peridotites.

## 2. Garnet-Melt Trace Element Partitioning Data

<sup>[5]</sup> The aluminosilicate garnets (general formula is  $X_3^{\text{VIII}}\text{Al}_2^{\text{VIS}}\text{Si}_3^{\text{IV}}\text{O}_{12}$ , where  $X = \text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , or  $\text{Mn}^{2+}$  and Roman numerals denote coordination numbers) can incorporate a wide range of elements [e.g., *Novak and Gibbs*, 1971]. Many geochemically important trace elements (e.g., the rare earth elements (REE), Y, U, and Th) are known to substitute for major divalent cations in the large dodecahedral garnet X site, with a smaller number of elements (e.g., Zr and Hf) believed to enter the octahedral Y site by replacing Al. Recently, we studied the effect of garnet major element composition on  $D^{\text{Grt/Melt}}$  through experiments in the simple systems CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

![](_page_3_Picture_1.jpeg)

![](_page_3_Figure_2.jpeg)

**Figure 2.** Spidergram comparing  $D^{\text{Grt/Melt}}$  for three different experiments conducted at constant pressures and temperatures using different starting materials (data are from *van Westrenen et al.* [1999]). Note large variations in both absolute  $D^{\text{Grt/Melt}}$  and general trace element patterns as a function of garnet major element composition. Shading shows elements discussed in text.

(CMAS [van Westrenen et al., 1999]) and FeO-CMAS (FCMAS [van Westrenen et al., 2000]). All experiments were performed in a piston cylinder apparatus at the same constant pressure of 3 GPa and temperatures spanning a very small range ( $1545^{\circ} \pm 15^{\circ}$ C) but using a wide range of starting compositions.  $D^{\text{Grt/Melt}}$ , measured using secondary ion mass spectrometry (SIMS), are plotted in Figure 2 for three experiments in the CMAS system producing aluminosilicate garnets with widely different X site major element compositions [van Westrenen et *al.*, 1999], shown as solid circles along the bottom axis of Figure 1. The pattern defined by the data for  $Py_{84}Gr_{16}$  (circles), a garnet with a composition that is the CMAS equivalent of typical peridotitic garnets, is broadly consistent with other garnet-melt partitioning data obtained at similar temperatures and pressures on garnets with comparable compositions [e.g., *Shimizu and Kushiro*, 1975; *LaTourrette et al.*, 1993; *Johnson*, 1998; *Salters and Longhi*, 1999]: U is retained preferentially over Th by a factor of 3-5;  $D_{Nb}$  is equal within error to

 $D_{Ta}$ , Zr, Hf, and Ti are incompatible with  $D_{Ti} < D_{Zr} < D_{Hf}$ . The light REE (LREE) are very incompatible with  $D^{\text{Grt/Melt}} < 0.01$ , and the heaver REE (HREE) are compatible with  $D_{\text{HREE}} \sim 4$ . HREE/LREE fractionation is large ( $\sim 10^3$ ), a feature that distinguishes garnet patterns from those generated by clinopyroxene [e.g., *Hart and Dunn*, 1993; *Blundy et al.*, 1998; *Salters and Longhi*, 1999].

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[6] This pattern is in sharp contrast with the data for Py<sub>60</sub>Gr<sub>40</sub> (squares in Figure 2), a garnet in which the X site contains 40 mol % Ca and 60 mol % Mg, placing it within the range of eclogitic garnets (Figure 1) but outside the range of garnet compositions found in peridotites and pyroxenites. Values of  $D^{\text{Grt/Melt}}$  are clearly very different, and as all experiments for which data are shown in Figure 1 were performed at essentially identical pressure P and temperature T, the observed differences must be compositional in origin. In  $Py_{60}Gr_{40}$ ,  $D_U$  still exceeds  $D_{Th}$ , but the partition coefficients are an order of magnitude higher, and U / Th fractionation is almost half the value observed in  $Py_{84}Gr_{16}$ .

[7] These data are consistent with the assertion by Stracke et al. [1999] that  $D_U/D_{Th}$  for pyroxenitic garnets is smaller than  $D_U/D_{Th}$  for peridotitic garnets. However, Stracke et al. [1999] also claim that U and Th partition coefficients are lower for Ca-rich garnets (i.e., eclogitic and pyroxenitic garnets) than for Ca-poor garnets (i.e., peridotitic garnets). The results shown in Figure 2 clearly show the opposite. Stracke et al.'s conclusion was drawn from a comparison of a variety of experimental results obtained for a range of T, P, and X (composition) conditions [Salters and Longhi, 1999; Hauri et al., 1994]. As discussed in more detail in section 3, garnet fractionation of U and Th is clearly a complex function of temperature, pressure, and composition. The conclusion of Stracke et al. [1999] thus seems premature, and further experiments

are needed to determine how the partitioning behavior of U and Th differs between peridotitic and pyroxenitic melting.

<sup>[8]</sup>  $D_{Nb}$  and  $D_{Ta}$  remain equal within error in Py<sub>60</sub>Gr<sub>40</sub>, although again absolute  $D^{\text{Grt/Melt}}$  values for these elements are significantly higher.  $D_{\text{LREE}}$  and  $D_{Sr}$  are 1–2 orders of magnitude higher in Py<sub>60</sub>Gr<sub>40</sub> than in Py<sub>84</sub>Gr<sub>16</sub>. In contrast, the HREE show relatively little change, so that HREE/LREE fractionation is significantly decreased. Strikingly, Ti, Zr, and Hf are all compatible in this calcic garnet. In fact, Zr is the most compatible trace element out of all those plotted in Figure 2. Additionally, Zr/Hf fractionation is reversed compared to the data for pyrope-rich garnet, while at the same time Zr/Ti fractionation is increased.

<sup>[9]</sup> It is interesting to compare these observations with mineral-melt partitioning data for clinopyroxene (Cpx), the other main component of eclogitic and pyroxenitic lithologies. Cpx from these rocks is generally richer in Ca and Al than Cpx from peridotite [e.g., Salters and Longhi, 1999], and there is a comparatively large database on  $D^{Cpx/Melt}$  variations as a function of Cpx CaTs (CaAl<sub>2</sub>SiO<sub>6</sub>) component [e.g., Lundstrom et al., 1998; Hill et al., 2000; Wood and Trigila, 2001]. In clinopyroxene, Zr and Hf enter the small M1 site commonly occupied by Mg. With increasing CaTs content both Zr and Hf become increasingly compatible, but the ratio  $D_{Zr}/D_{Hf}$  remains close to 0.5 across the range of Cpx compositions likely to be present in the mantle [e.g., Hill et al., 2000]. Figure 2 shows that at low Ca contents, garnet fractionates Zr from Hf in the same way as pyroxene (i.e., with  $D_{Zr} < D_{Hf}$ ) but that at higher Ca contents, garnet prefers Zr to Hf.

<sup>[10]</sup> Finally, triangles in Figure 2 show data for a garnet of composition Py<sub>9</sub>Gr<sub>91</sub>. This composition is very rare in the mantle, but the data

![](_page_5_Figure_2.jpeg)

**Figure 3.** Variation of experimentally determined garnet-melt partition coefficients with garnet grossular content (data are from *Nicholls and Harris* [1980], *Hauri et al.* [1994], *Johnson* [1998], *Salters and Longhi*, [1999], A. C. Withers et al. (manuscript in preparation, 2001), and *van Westrenen et al.* [1999, 2000]). Note that data for garnets containing more than  $\sim$ 19 mol % Ca on their X sites show distinctly different partition coefficients from garnets containing less than that amount.

illustrate how unusual the partitioning behavior of "eclogitic" garnet is. In  $Py_9Gr_{91}$ , Zr is less compatible than Hf, and Ti is slightly incompatible, as in the very pyrope-rich garnets (e.g.,  $Py_{84}Gr_{16}$ ). Furthermore, Sr, Cd, Zr, Hf, Ti, and Li are all more compatible in  $Py_{60}Gr_{40}$  than in either Mg-rich or Ca-rich garnets.

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[11] A compilation of available high-pressure, high-temperature garnet-melt partitioning data for basaltic rocks shows that the unexpected behavior shown in Figure 2 and discussed above is very sensitive to garnet composition. Figure 3 shows published experimental  $D^{\text{Grt/}}$ <sup>Melt</sup> obtained in the pressure range of 2.5–3 GPa and at temperatures between 1380° and 1565°C, plotted against garnet Gr content. As no isobaric, isothermal data are available for partitioning into this wide range of garnet compositions under hydrous conditions, only experiments performed under anhydrous conditions were considered here.

![](_page_6_Picture_1.jpeg)

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[13] The threshold value of  $19 \pm 1 \mod \%$  exceeds the upper boundary of peridotitic garnet compositions, but more calcic garnets are found in pyroxenites and especially eclogites (Figure 1). It follows that the trace element signature imposed by eclogitic garnets can be significantly different from the signature imposed by peridotitic garnet. In sections 3 and 4, we first attempt to provide a physical explanation for the anomalous partitioning behavior of calcic garnets and then report results of simple batch melting models to quantify the maximum effects of these contrasting D values on the trace element composition of mantle melts. We concentrate on the HFSE elements Ti, Zr, and Hf; for a discussion of the effects on rare earth elements the reader is referred to our earlier papers [van Westrenen et al., 1999, 2000].

## **3. A Semiquantitative Model for Anomalous Partitioning of the HFSE**

<sup>[14]</sup> The large variations observed particularly for Zr and Hf in Figures 2 and 3 may seem surprising, considering that Zr and Hf have the same charge (4+) and very similar ionic radii (72 and 71 pm in sixfold coordination, respectively [*Shannon*, 1976]). Zr and Hf therefore used to be considered as inseparable during magmatic processes, and until recently, it was assumed that the Zr/Hf ratios in unaltered MORB and OIB were constant at  $36 \pm 3$ [e.g., *McDonough and Sun*, 1995]. With the advent of more accurate analytical techniques and new experimental data, these notions are being challenged on several fronts.

[15] First, experimental amphibole-melt and clinopyroxene-melt partitioning data have shown that Zr and Hf can be fractionated from each other [e.g., Brenan et al., 1995; Dalpé et al., 1995; Lundstrom et al., 1998; Hill et al., 2000]. These partitioning data have been used to argue for clinopyroxene control on observed variations in Zr/Hf ratios in seamount basalts [e.g., Lundstrom et al., 1998] and peridotites [e.g., Takazawa et al., 2000]. Second, Fujinawa and Green [1997] point out that Zr/Hf ratios in the range 16-105 have been measured in metasomatised mantle bulk rock [e.g., Dupuy et al., 1992; Rudnick et al., 1993; Stein and André, 1995] and mineral separate analyses [Ionov and Hofmann, 1995]. Third, new high-precision

![](_page_7_Picture_1.jpeg)

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[16] Here we describe a semiquantitative model for garnet fractionation of the HFSE and for the reversal of Zr/Hf fractionation as garnet Gr contents exceed  $19 \pm 1 \mod \%$  (Figure 3). As a framework for the interpretation of  $D^{\text{Grt/Melt}}$ data we use the mineral-melt partitioning model of *Blundy and Wood* [1994], based on lattice strain theory [*Brice*, 1975], which describes partitioning of an element *i* with radius  $r_i$  in terms of (1) the effective radius  $r_0$  of the site on which partitioning takes place, (2) the strain-free partition coefficient  $D_0$  for an element with "ideal" radius  $r_0$ , and (3) the compressibility of the site, given by its apparent Young's modulus *E*:

$$D_{i}^{\text{Grt/Melt}} = D_{0}^{\text{Grt/Melt}} \times \exp\left(\frac{-4\pi E N_{A} \left[\frac{r_{0}}{2} (r_{i} - r_{0})^{2} + \frac{1}{3} (r_{i} - r_{0})^{3}\right]}{RT}\right),$$
(1)

where  $N_A$  is Avogadro's number and R is the gas constant. According to this model, a series of elements of the same charge entering a single crystallographic site will define a parabolic trend in plots of  $\log(D_i)$  versus  $r_i$  (so-called Onuma diagrams [Onuma et al., 1968]).

[17] Our model for HFSE partitioning into garnet is based upon fits to (1) of  $D^{\text{Grt/melt}}$ data for the 3+ cations entering the eightfold coordinated garnet X site (REE, Sc, Y, and In<sup>3+</sup>) [*van Westrenen et al.*, 1999, 2000, 2001]. For these elements, fits of the partitioning data to (1) give values of  $r_0(3+)$  for the X site varying linearly from 93.5 ± 0.4 pm in Py<sub>84</sub>Gr<sub>16</sub> to 99 ± 1 pm for Py<sub>9</sub>Gr<sub>91</sub>, a trend consistent with variations in the size of the X site as a function of Ca content. On the other hand, fitted values of the apparent Young's modulus of the X site ( $E_X$ ) for 3+ cations show nonlinear dependence on Ca content. The lowest fitted  $E_X$  (3+) for garnets in the CMAS system is 257 ± 20 GPa for Py<sub>60</sub>, lower than both values of 590 ± 40 GPa for Py<sub>84</sub> and 347 ± 20 GPa for Py<sub>9</sub>.

[18] These anomalously low E values point to an anomalous softness of the garnet structure at intermediate Ca contents, causing trace elements that are very incompatible in pyrope-rich garnets, such as the LREE, Sr, Nb, and Ta, to be more readily incorporated in calcic garnets (Figures 2 and 3). The anomalously low Evalues could be due to the softening of the garnet structure due to the proximity of a phase transition, possibly manifested by Ca/Mg ordering (W. van Westrenen et al., manuscript in preparation, 2001). Work in progress to further study this hypothesis includes trying to measure the elasticity of intermediate Py-Gr garnets and computer simulations of trace element incorporation into Py-Gr solid solutions.

[19] Early work by Milton et al. [1961] and Ito and Frondel [1967] showed that Zr, Hf, and Ti can enter the octahedral garnet Y site (occupied mainly by Al in natural mantle garnets, together with usually small quantities of  $Fe^{3+}$  and  $Cr^{3+}$ ). If this were the case, only small variations in the extent of fractionations between these three elements would be expected as a function of garnet Ca content: although Ca has a large effect on the X site radius of garnets, the Y site radius is far less sensitive to compositional variations on the X site. Average Mg-O distances in pyrope are 227 pm [Armbruster et al., 1992], compared to the average Ca-O distance in grossular of 241 pm [Ganguly et al., 1993]. In contrast, average Al-O distances only vary from 189 pm in Py to 192 pm in Gr [Armbruster et al., 1992; Ganguly et al., 1993], which assum-

![](_page_8_Figure_1.jpeg)

![](_page_8_Figure_2.jpeg)

Figure 4. A model of Zr, Hf, and Ti partitioning into garnet, illustrated using the experimental data from van Westrenen et al. [1999, 2000]. (a) Onuma diagram for Zr, Hf, and Ti, assuming sixfold ionic radii [Shannon, 1976]. (b and c) Possible model for Zr and Hf entering both X and Y sites in garnets that contain between 19 and at least 40 mol % grossular. Lines are weighted least squares fits to data using the summation of two separate Onuma curves (equation (1)); see Table 2 for best fit parameters.

ing an  $O^{2-}$  radius of 138 pm, translates to Y site radii of 51 and 54 pm, respectively.

[20] Figure 4a shows an Onuma diagram for Zr, Hf, and Ti partitioning data in simple systems of van Westrenen et al. [1999, 2000]. Data for the three garnets, which contain  $\leq 18$ mol % Ca on their X site, and for the extremely calcic composition Py<sub>9</sub>Gr<sub>91</sub> are consistent with all Ti, Zr, and Hf occupying the garnet Y site. Their  $\log (D)$  values lie along a single smooth parabolic curve as a function of their radii, and in all cases,  $D_{\text{Ti}} < D_{\text{Zr}} < D_{\text{Hf}}$ . The optimum radius for this site for the 4+ cations necessarily has to lie between the ionic radii of Ti and Hf. Shown in Figure 4a are weighted, nonlinear, least squares fits to (1) of the data for these four experiments, using the uncertainties in the measured D values as weights. Resulting values of  $r_0(4+)$ ,  $E_Y(4+)$ ,

![](_page_9_Figure_1.jpeg)

![](_page_9_Figure_2.jpeg)

and  $D_0(4+)$  are given in Table 1. For individual experiments we would not have great confidence in fitting only three data points to (1) (as it has three adjustable parameters). Small uncertainties in measured *D* values and even small errors in ionic radii can translate into large errors in fit parameters. For example, measured *D* values for garnet composition  $Gr_{18}$  have relatively large error bars, which translates into large errors, especially for the apparent site elasticity  $E_{Y}$  (4+) (Table 1).

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<sup>[21]</sup> However, remarkably, all fits to the experiments that are consistent with all Ti, Zr, and Hf occupying the Y site give identical values within error for the optimal size  $r_0$  of the garnet Y site for 4+ cations ( $r_0$  (4+) = 67 ± 1 pm). This is entirely consistent with abovementioned observation that the Y site size is relatively insensitive to variations in garnet X site composition. Additionally, apart from the garnet with 13 mol % Ca, which has a very large error associated with it, the apparent elasticity of the garnet Y site  $E_Y$  (4+) appears to decrease from Ca-poor garnets to the most Ca-rich composition Py<sub>9</sub>Gr<sub>91</sub>, which is consistent with mineral physics data [e.g., *Hazen and Finger*, 1979] and with the trends seen in our fitted values for 3+ cations entering the X site [*van Westrenen et al.*, 2000]. These observations

![](_page_10_Figure_2.jpeg)

greatly increase our confidence in the validity of the fits shown in Figure 4a.

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<sup>[22]</sup> In contrast, garnets with Gr contents of 19–40 mol % show a very different pattern on the Onuma diagram in Figure 4a. Hf, Zr, and Ti all become compatible in these garnets, with  $D_{Ti}$  smaller than the *D* values for Zr and Hf. However,  $D_{Zr}$  becomes equal to or significantly larger than  $D_{Hf}$ . This combination of observations cannot possibly be reconciled with these three elements exclusively entering the garnet Y site. A single site with a radius between the ionic radii of Ti and Hf could never lead to  $D_{Zr}$ >  $D_{Hf}$ , and it is therefore impossible to fit Ti, Zr, and Hf data by a single parabolic curve describing partitioning on a single garnet (Y) site. Zr will have to partially reside on a site larger than the Y site in garnet, and because of the small size difference between Zr and Hf it is highly likely that Hf enters this site as well. The only crystallographic site in garnet bigger than the Y site is the X site, on which the large 4+ cations U and Th are known to reside. Our data for the garnets with intermediate Ca contents points to Zr and Hf entering both the X site and the Y site. It is important to note that this seems to occur even though the X site radius (and hence the X site  $r_0$  (4+)) increases significantly from low-Ca to intermediate-Ca contents and

![](_page_11_Picture_1.jpeg)

Percent Gr	<i>r</i> <sup>0</sup> (4+), pm	$\sigma(r_0 (4+))$	$E_Y$ (4+), GPa	$\sigma(E_Y\left(4+\right))$	$D_0$ (4+)	$\sigma(D_0 (4+))$	References <sup>t</sup>
13	67	1	1648	1596	0.6	0.4	1
16	67	1	3273	546	1.7	0.5	2
18	67	1	2776	457	1.2	0.3	2
91	67	1	1211	129	1.8	0.1	2

**Table 1.** Fits of Selected Zr, Ti, and Hf Garnet-Melt Partitioning Data to Equation (1) in Simple Systems CMAS and FCMAS<sup>a</sup>

<sup>a</sup>The 1  $\sigma$  errors are determined using uncertainties in D values.

<sup>b</sup>References are as follows: 1, van Westrenen et al. [2000]; 2, van Westrenen et al. [1999].

should therefore becomes less attractive for the relatively small trace elements Zr and Hf.

[23] Again, anomalous softness leading to low apparent Young's moduli can be invoked to explain this apparent discrepancy. A softening of the X site could counteract the increase in X site  $r_0$  values. The high absolute  $D^{\text{Grt/Melt}}$  values for U and Th, which are too large to enter the garnet Y site and always reside in the X site, as well as the significantly lower U/Th fractionations are all consistent with low values of  $E_X(4+)$ for these garnet X sites compared to values for pyropic garnets. We therefore attempted to fit Ti, Zr, Hf, Th, and U to a two-site Blundy and Wood [1994] model, making the following assumptions: (1)  $r_0$  (4+) for the garnet Y site in eclogitic garnets is 67 pm, as fitted for garnets with both higher and lower Ca content (Figure 4a). (2) Their apparent Young's moduli  $E_{y}(4+)$  for intermediate garnet compositions are assumed to be smaller than  $E_Y(4+)$  for  $Py_9Gr_{91}$  by the same factor as observed previously for the apparent Young's moduli for 3+ cations entering the X site [van Westrenen et al., 1999]. (3) Ionic radii for  $Hf^{4+}$  and  $Zr^{4+}$  in eightfold coordination are 83 and 84 pm, respectively [Shannon, 1976]. After fixing  $r_0$  (4+) and  $E_Y$ (4+) through assumptions 1 and 2, measured values of  $D_{Ti}$  are used together with equation (1) to predict the partition coefficients for Zr and Hf entering the sixfold coordinated garnet Y site ( $D_{Hf(VI)}$  and  $D_{Zr(VI)}$ ). It is then straightforward to calculate the partition coefficients  $D_{\text{Hf(VIII)}}$  and  $D_{\text{Zr(VIII)}}$  for eightfold coordinated Zr and Hf entering the garnet X site.

Combining the latter values with assumption 3 and data on  $D_U$  and  $D_{Th}$  provides constraints on the partitioning parabola (described by equation (1)) for 4+ cations entering the garnet X site. Resulting fits of the data for Py65Gr35 and Py<sub>60</sub>Gr<sub>40</sub> are shown in Figure 4b, and fit parameters are given in Table 2. Fits give good agreement with measured data, although Th partition coefficients are underestimated. Fitted values for  $r_0$  (4+) for the X site (91 ± 10 pm) are smaller than previously published  $r_0$  (3+) values for the same site by 4-5 pm [van Westrenen et al., 1999], which in turn have been shown to be consistently  $\pm 5$  pm smaller than fitted values for divalent cations. Fitted values for  $E_{\chi}(4+)$  are the same within error and significantly larger than  $E_{X}(3+)$  for the same experiments, as expected from theory.

[24] In Figure 4c we have applied our simple model to the experiment of Hauri et al. [1994], which was performed at 2.5 GPa and 1430°C, i.e., lower pressure and temperature than the data used in the derivation of our model. The Hauri et al. [1994] data show  $D_{Zr} > D_{Hf}$  in a garnet with an X site containing 24 mol % Ca (overall composition Py<sub>52</sub>Gr<sub>24</sub>Alm<sub>24</sub>). Best fit parameters for this case are given in Table 2. Fitted  $D_0$  (4+) for the garnet Y site in this case is comparable to the values obtained at higher P and T. Best fit values for  $r_0$  (4+) in the X site are  $\sim 2$  pm lower than those obtained for Py<sub>65</sub>Gr<sub>35</sub> and Py<sub>60</sub>Gr<sub>40</sub>, which is expected as this garnet contains slightly less Ca. Compared with the more calcic garnets shown in Figure 4b, formed at higher P and T,

![](_page_12_Picture_1.jpeg)

**Table 2.** Results of Fitting of Zr, Ti, Hf, U, and Th Partitioning Data for  $Py_{65}Gr_{35}$ ,  $Py_{60}Gr_{40}$ , and the Experiment of *Hauri et al.* [1994] to Equation (1) Assuming Two-Site Distribution of Zr and Hf<sup>a</sup>

<sup>a</sup>The 1  $\sigma$  errors are determined using uncertainties in D values.

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the best fit value for the X site  $D_0$  (4+) is a factor of 3 lower, while  $E_X$  (4+) is ~8% higher. The combination of these two effects, which in turn must be the result of the combined effects of *P*, *T*, and *X*, leads to predicted  $D_U$  and  $D_{Th}$  values for the *Hauri et al.* [1994] experiment that are close to the observed values and therefore about an order of magnitude lower than  $D_U$  and  $D_{Th}$ predicted at higher *P* and *T*. This illustrates the huge effect that a combination of *P*, *T*, and *X* changes can have on highly charged, large misfit cations like U and Th in garnet. Our data and model do suggest unequivocally that U and Th are more compatible in a Ca-rich garnet than in a Ca-poor garnet at the same *P* and *T* conditions.

<sup>[25]</sup> Our model provides a simple explanation for the observed variations in partitioning data shown in Figure 2. The model is not fully quantitative, as the available data are still too scarce to quantify the variations in especially  $D_0$  (4+) and E (4+) for both the X and Y sites discussed above. An important additional source of error lies in the uncertainties in the trace element ionic radii. The tightness of the X site Onuma curves in Figure 4b is largely determined by the differences in ionic radii between Zr and Hf and Th and U, respectively. It is clear from Figure 4b that if the difference between the radii of Zr and Hf in eightfold coordination is slightly larger than quoted by Shannon [1976] (i.e., >1 pm), a better fit could be obtained to the Th partitioning data. A larger size difference would also result in lower fitted values of  $D_0$  (4+) and  $E_X$  (4+). Wood et al. [1999] have shown that the ionic radii of  $U^{4+}$ and Th<sup>4+</sup> coordinated by oxygen are likely to deviate slightly from the values quoted by Shannon [1976], derived from uranium and thorium fluorides. Unfortunately, we were not able to derive more applicable ionic radii for Zr<sup>4+</sup> and Hf<sup>4+</sup> in eight-fold coordination from crystallographic data on simple oxides, as no crystallographic information appears to be available on cubic HfO<sub>2</sub>.

<sup>[26]</sup> More experimental data will be needed to confirm our hypothesis about softening sites in intermediate garnets. It also remains to be explained why the change from "normal" to "anomalous" elasticity appears to occur over a narrow compositional range. There is, however, no doubt that our data and model show that garnet is capable of causing significant trace element fractionations during partial melting. Furthermore, because of a subtle interplay between the apparent elasticity and optimum radii of garnet X and Y sites these fractionations are a nonlinear function of garnet Ca content. In section 4 we discuss the implications of this for melting of garnet-bearing pyroxene-rich lithologies in the mantle, using batch melting models.

## 4. Melting Models

[27] Two simple end-member partial melting scenarios were studied, covering the range of current hypotheses regarding the possible role(s) of garnet in basalt genesis: (1) anhydrous melting of garnet peridotite and (2) anhydrous Ca-rich eclogite melting. Sourcenormalized trace element concentrations for Nb, Ta, Zr, Hf, Sm, and Yb were calculated as a function of melt fraction for eclogitic and peridotitic source rocks to identify which trace element ratios are most sensitive to changes in garnet source compositions. Input parameters for simple batch melting models are given in Table 3. Garnet peridotite mineral proportions and melting mode were taken from Salters [1996]. For eclogite we assumed modal melting of a 50:50 garnet:clinopyroxene mixture. Mineral-melt partition coefficients for garnet were those from *van Westrenen et al.* [1999]:  $Py_{84}Gr_{16}$  data for peridotitic models and  $Py_{65}Gr_{35}$  data for eclogitic garnet. The latter was chosen deliberately to be able to model the end-member scenario, in which the threshold garnet Gr content (19 mol %) discussed is exceeded. Olivine-melt partition coefficients were all assumed negligibly small.  $D^{Cpx/Melt}$ and  $D^{Opx/Melt}$  for peridotite were taken from *Salters and Longhi* [1999], and  $D^{Cpx / Melt}$  data for eclogitic pyroxenes are from Withers et al. (manuscript in preparation, 2001).

<sup>[28]</sup> In Figure 5 our most important findings are summarized. Figure 5a shows data for Nb and Ta. We evaluated these elements to show a clear example of element ratios that are not affected by the type of garnet that is present in the source. Nb/Ta ratios show no measurable deviation from the source ratio of 17 (taken from *Sun and McDonough* [1989]). Hf/Sm ratios and Zr/Sm ratios (which show virtually

			Eclogite			
	D <sup>Ol/Melt</sup>	D <sup>Grt/Melt</sup>	D <sup>Cpx/Melt</sup>	D <sup>Opx/Melt</sup>	D <sup>Grt/Melt</sup>	D <sup>Cpx/Melt</sup>
	Value	Value <sup>a</sup>	Value <sup>b</sup>	Value <sup>c</sup>	Value <sup>d</sup>	Value <sup>e</sup>
		F	Partition Coefficien	ts		
Zr	0	0.4	0.027	0.036	3.6	0.081
Hf	0	0.68	0.049	0.08	2.4	0.182
Nb	0	0.03	0.008	0	0.2	0.00318
Та	0	0.032	0.008	0	0.13	0.0106
Sm	0	0.28	0.07	0.039	1	0.205
Yb	0	3.3	0.174	0.227	2.9	0.306
		Mod	e and Melting Rea	<i>ction</i> <sup>f</sup>		
Rock mode	0.53	0.05	0.38	0.04	0.5	0.5
Melting reaction	0.05	0.13	1.31	-0.49	0.5	0.5

Table 3. Input Parameters for Batch Melting Models

<sup>a</sup>From van Westrenen et al. [1999], data for Py<sub>84</sub>Gr<sub>16.</sub>

<sup>b</sup>From Salters and Longhi [1999] experiment TM694-6, assuming  $D_{Ta} = D_{Nb}$ .

<sup>c</sup>From Salters and Longhi [1999] exp. TM295-4, assuming  $D_{Ta} = D_{Nb}$ .

<sup>d</sup>From van Westrenen et al. [1999], data for Py<sub>65</sub>Gr<sub>35</sub>.

<sup>e</sup>From A. C. Withers et al. (manuscript in preparation, 2001).

<sup>f</sup>Peridotite data from *Salters* [1996].

![](_page_13_Picture_14.jpeg)

![](_page_14_Picture_2.jpeg)

## Trace element concentration ratios in melts derived from peridotitic versus eclogitic source rocks

![](_page_14_Figure_4.jpeg)

**Figure 5.** Variations of trace element ratios as a function of melt fraction for partial batch melting of garnet peridotite (solid lines) and bimineralic eclogite (dashed lines). (a) Nb/Ta, (b) Hf/Sm, (c) Zr/Hf, and (d) Zr/Yb. For details of model and input parameters, see Table 3.

identical trends with varying melt fraction) should be slightly more sensitive to the presence of eclogitic garnets in the source of mantle melts, as illustrated for Hf/Sm in Figure 5b. Our model predicts that the Hf/Sm and Zr/Sm ratio will remain indistinguishable from the source ratio (taken to be equal to the chondritic ratio of 0.78 after *Sun and McDonough* [1989]) in the case of garnet peridotite melting. Significantly, these ratios should become lower than the source ratio if significant amounts of eclogite melting are involved. Our end-member model predicts a Hf/Sm ratio of 0.4 at 10% partial melting of pure garnet:clinopyroxene eclogite. It is well known that the Hf/Sm ratio in basaltic rocks is generally constant and near the chondritic ratio [e.g., *Blichert-Toft and Albarède*, 1999], but subtle changes in this VAN WESTRENEN ET AL.: MANTLE HETEROGENEITIES

ratio could be a first indication of eclogite melt involvement in certain cases.

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[29] Figure 5c shows the variations in Zr/Hf ratios as a function of melt fraction. The large variations seen for garnet peridotite melting are largely attributable to clinopyroxene, which holds back Hf preferentially to Zr. Garnets, although of minor importance for the Zr/Hf budget in peridotites, also retain Hf preferentially to Zr, so that the effects of garnet and clinopyroxene are additive. Lundstrom et al. [1998] and Takazawa et al. [2000] use models like those presented for garnet peridotite melting in Figure 5c to show clinopyroxene control to explain observed Zr/Hf variations in peridotites and seamount basalt.

[30] Because of the large changes in  $D_{Zr}$  and  $D_{Hf}$ and particularly  $D_{Zr}/D_{Hf}$  discussed in section 3, variations in Zr/Hf ratios due to clinopyroxene are counteracted by garnet during eclogite melting. In combination with the much higher proportion of garnet in eclogites and pyroxenites compared to peridotites, there is no resulting variation in Zr/Hf ratios as a function of melt fraction F in the case of eclogite melting.

[31] Unlike Zr and Hf, the HREE remain approximately equally compatible at higher garnet Ca contents (Figure 2). Additionally, the HREE budget of mantle melts is largely controlled by garnet. Therefore both Hf/HREE and Zr/HREE ratios could be particularly sensitive to the presence of Ca-rich garnet, as illustrated for Zr/Yb in Figure 5d. At low melt fractions, Hf/ HREE and Zr/HREE ratios should vary with melt fraction in case of peridotite melting, while these ratios should remain virtually constant with F in case of eclogite melting.

[32] The melt model results we have presented are end-member scenarios. Figure 1 shows that garnets in eclogite suites generally span a range of compositions, with both Gr contents <19

mol % and >19 mol % present. A mixture of calcic and more Py-rich garnets in eclogites will lead to a dilution of the Ca-rich eclogite signatures we describe, as will a mixture of peridotitic and eclogitic melts. As illustrated by our discussion of U and Th partition coefficients, the pressure and temperature dependencies of these variations are still largely unknown. This could be important for garnets in eclogites, which will start melting at lower temperatures than peridotites. Nevertheless, our analysis points to hitherto unknown and unused trace element ratios that could be used as a fingerprint for partial melts derived from eclogitic lithologies. Specifically, we expect Hf/Sm and Zr/Sm ratios that are smaller than the source ratio as well as uniform Zr/HREE and Hf/HREE patterns if significant amounts of partial melt derived from eclogite are present.

## 5. Conclusions

[33] Garnet-melt partition coefficients for some trace elements (high field strength elements and LREE) show extreme nonlinear variations with garnet Ca content. Both absolute partition coefficients and ratios of garnet-melt D values for key trace elements change significantly as a function of source garnet composition. As a result, garnet signatures from eclogites and garnet peridotites differ significantly. Zr and Hf partitioning into garnet can be explained by these elements entering both the garnet X site and Y site at garnet X site Ca contents >19 mol %. Batch melting model calculations show that it is not possible to define one unique "garnet signature" to determine the presence or absence of garnet in basalt sources but rather that different garnet-bearing sources produce distinctly different "garnet signatures." We predict that a combination of low Hf/Sm ratios and Zr/HREE and Hf/HREE patterns that are independent of melt fraction F can be indicative for the involvement of eclogitic rocks in the source of mantle melts.

![](_page_15_Picture_9.jpeg)

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