Mineral-melt partition coefficients and the problem of multiple substitution mechanisms: insights from the rare earths in forsterite and protoenstatite

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Abstract

A trace element may substitute into a mineral by more than one substitution mechanism, complicating the thermodynamic description of its partition coefficients. In order to understand this phenomenon better, the mineral/melt partition coefficients for all 14 rare earth elements (REE) plus Y and Sc were measured experimentally for coexisting forsterite and protoenstatite in the system CaO-MgO-SiO_2±Al_2O_3±TiO_2 at 1406 °C and atmospheric pressure. For both phases, the results show these large trivalent cations (REE^{3+}) replace Mg^{2+} on octahedral sites, but with charge-balanced achieved by two different mechanisms: 1) cation vacancies (2 REE^{3+} + vacancy = 3 Mg^{2+}); and 2) substitution of Al for Si (REE^{3+} + Al^{3+} = Mg^{2+} + Si^{4+}). The overall REE partition coefficient is the sum of the partition coefficients for each substitution mechanism. Because the stoichiometric control is different for each mechanism, the relative importance of the mechanism varies with melt composition, including the activities of both silica and alumina in the melt ($a^{melt}_{SiO_2}$ and $a^{melt}_{AlO_{1.5}}$). The coexistence of forsterite and protoenstatite fixes the silica activity, allowing the effect of $a^{melt}_{AlO_{1.5}}$ to be separated from that of $a^{melt}_{SiO_2}$. The relative importance of the two mechanisms depends strongly on the identity of the REE for forsterite, but not for protoenstatite. The results are used to test the lattice strain model: the two substitution mechanisms in forsterite imply different values for the Young's modulus in the Brice equation, despite the fact that the REE^{3+} cations likely occupy the same crystallographic site in both mechanisms, casting doubt on the physical basis of the lattice strain theory. Comparison with literature data confirms earlier observations that the activity coefficients of REE_2O_3 in silicate melts decrease with increasing SiO_2 content of the melt, but the effect decreases with increasing atomic number, from La to Lu, and is almost negligible for Sc. The influence of melt composition should apply to the mineral/melt REE partition coefficients of all other minerals. Recognising that observed mineral/melt partition coefficients are often the sums of contributions from multiple substitution mechanisms, each with its own dependence on both crystal composition and the stoichiometric control from the melt composition, will improve parameterizations of the mineral/melt partition coefficients of other rock-forming minerals. Partition coefficients for Na, Al, Ca, Ti, and Zr are also reported.

Acknowledgements

We thank Jung-Woo Park for assistance with the LA-ICP-MS analyses, Chris Ballhaus for his editorial supervision and Raúl Fonseca for constructive comments on this and earlier drafts of the

manuscript. This work was supported by Australian Research Council Laureate Fellowship FL130100066 to HO'N.

1. Introduction

Mineral/melt partition coefficients are the enablers of the trace-element approach to understanding the petrogenesis of igneous rocks, through their use in mass-balance equations (e.g., Shaw 2006; Zou, 2007). They are defined as the concentration of an element in a mineral phase divided by its concentration in the melt, usually by weight. They depend on the valence state of the element, the compositions of both the mineral and the melt, and temperature and pressure, all of which may be elucidated from the thermodynamic description of the mineral-melt system. Partition coefficients are not, however, thermodynamic entities in themselves, except in special circumstances, as pointed out by Nernst (1890, 1891). Rather, the relationship of a partition coefficient to the thermodynamic description of the mineral-melt system begins with formulating the chemical equilibrium (colloquially, "reaction") between the relevant component containing the element in the mineral, and the components in the melt that add up to the same composition as the mineral component[1] (e.g., O'Neill and Eggins 2002). The essence of this concept may be explicated using the well-known example of the partitioning of Ni between olivine and melt, for which the reaction is:

$$\underset{\text{melt}}{NiO} + \tfrac{1}{2}\underset{\text{melt}}{SiO_2} = \tfrac{1}{2}\underset{\text{olivine}}{Ni_2SiO_4} \quad (1)$$

The equilibrium constant for this reaction is:

$$K_{Ni}^{ol/melt} = \frac{(a^{\text{ol}}_{\text{Ni}_2\text{SiO}_4})^{1/2}}{a^{\text{melt}}_{\text{NiO}} \cdot (a^{\text{melt}}_{\text{SiO}_2})^{1/2}} \quad (2)$$

where a_i^{phase} is the activity of component *i* in a phase. Since a main contribution to an activity is from the configurational entropy of mixing in the phase, which in crystals is related to atomic fractions on individual crystallographic sites, activities are usually evaluated from mole fractions. In this simple case, $a^{\text{ol}}_{\text{Ni}_2\text{SiO}_4} = (X^{\text{ol}}_{Ni} \cdot \gamma^{\text{ol}}_{Ni})^2$, where X^{ol}_{Ni} is the mole fraction of Ni in the octahedral sites of the olivine and γ^{ol}_{Ni} is the activity coefficient, which is a function of the major-element composition of the olivine. The exponent of 2 comes from the fact that Ni is considered to mix on two sites per formula

[1] The term "component" has a rigorously defined meaning: it is one of a set of compositional variables that together describe the composition of the phase of interest, whose amount can be varied in that phase independently of the amounts of the other components. The latter consideration means that there exists a well-defined quantity $(\partial G/\partial n_i)_{n_j}$, known as the chemical potential, where G is the Gibbs free energy of the phase, n_i is the amount of component *i* ($n_i \neq 0$), and n_j are the amounts of the other components in the phase. For example, in the case of Ni partitioning between Mg-rich olivine of general formula M_2SiO_4, where M stands for divalent cations, and silicate melt, the Ni component in olivine is Ni_2SiO_4, rather than NiO or Ni, because NiO and Ni cannot be varied independently in olivine without violating the constraints of stoichiometry and charge-balance, which are foundation assumptions in the thermodynamics of phase equilibria (e.g., Callen 1985). Point-defect thermodynamics, which describes excursions from these constraints, nevertheless confirms their essential validity in the phase-equilibrium context (e.g., Schmalzried 1995). The activity is intimately related to the chemical potential.

unit of olivine, although from a crystallographic perspective, this is not correct: Ni orders on to the M1 octahedral site of olivine (e.g., Boström 1989). The explanation lies in the playoff between the loss of configurational entropy because of ordering between sites and the enthalpy and other contributions gained from the ordering, which nearly cancel out to give the observed relationship (e.g., Seifert and O'Neill 1987). The mole fraction, X_{Ni}^{ol}, is proportional to the concentration of Ni in olivine by weight, to an excellent approximation in the trace-element concentration regime: $c_{Ni}^{ol} = k_{Ni}^{ol} X_{Ni}^{ol}$. The proportionality factor, k_{Ni}^{ol}, is, like γ_{Ni}^{ol}, also a function of the major-element composition of the olivine, so the two are sometimes combined into one term. Similar considerations apply to the components in the melt, here NiO and SiO_2.

The partition coefficient is defined as:

$$D_{Ni}^{ol/melt} = \frac{c_{Ni}^{ol}}{c_{Ni}^{melt}} \quad (3)$$

where c_M^{phase} is the weight concentration of element M in a phase. Combining these relationships and rearranging gives:

$$D_{Ni}^{ol/melt} = K_{Ni}^{ol/melt} \cdot \frac{\gamma_{NiO}^{melt} k_{NiO}^{melt}}{\gamma_{Ni}^{ol} k_{Ni}^{ol}} \cdot (a_{SiO_2}^{melt})^{1/2} \quad (4)$$

This emphasises that partition coefficients vary not only with the composition of the mineral (here, through $\gamma_{Ni}^{ol} k_{Ni}^{ol}$), but with melt composition, through two conceptually different and independently measurable factors, which in this case are $\gamma_{NiO}^{melt} k_{NiO}^{melt}$ and $a_{SiO_2}^{melt}$. Several studies have measured $\gamma_{NiO}^{melt} k_{NiO}^{melt}$ independently of $D_{Ni}^{ol/melt}$ (e.g. O'Neill and Eggins 2002) and found it to vary by about a factor of two in melts saturated in olivine at magmatic temperatures and atmospheric pressure. But quantitatively the more significant variable is $a_{SiO_2}^{melt}$, which may cover one to two orders of magnitude, depending on temperature, in systems containing olivine and silicate melt (e.g., see Fig. 3 of Zhukova et al. 2017). This is an example of the "stoichiometric control" on partition coefficients (Takahashi and Irvine 1981; O'Neill and Eggins 2002).

Thus the thermodynamic description of element partitioning between mineral and melt is founded on being able to identify the relevant component in the mineral, and then evaluating the form of its configurational entropy of mixing. In the example of $D_{Ni}^{ol/melt}$, it is obvious from crystal-chemical considerations that the relevant component for Ni in olivine is Ni_2SiO_4, and it is unsurprising that the simple substitution of Ni for Mg (or Fe^{2+}) in the olivine structure should give the $a_{Ni_2SiO_4}^{ol} \propto (X_{Ni}^{ol})^2$ relationship. But elsewhere identifying substitution mechanisms and their configurational entropies may be more difficult, especially where the substituting element requires charge-balancing. Here again, olivine/melt partitioning can provide an instructive example, this time of the Rare Earth Elements (REE). The REE form 3+ cations that are too large to substitute for Si in the tetrahedral site of olivine, and therefore replace Mg, a divalent cation, in octahedral coordination, probably on the M2

94 octahedral site, which favours larger cations like Ca (e.g., Blasse and Bril, 1967). For charge-
95 balancing this substitution, there are several possibilities. The most often suggested is by octahedral-
96 site vacancies (Colson et al. 1989; Nielsen et al. 1992; Evans et al. 2008), making the relevant
97 thermodynamic component $REE_{4/3}\square_{2/3}SiO_4$, where the symbol □ stands for a vacancy. (The
98 component could be written $MgREE_{2/3}\square_{1/3}SiO_4$, which in the present context comes to the same thing,
99 see Evans et al. 2008). The partitioning equilibrium is:

$$\underset{\text{melt}}{REEO_{1.5}} + \tfrac{3}{4}\underset{\text{melt}}{SiO_2} = \tfrac{3}{4}\underset{\text{olivine}}{REE_{4/3}\square_{2/3}SiO_4} \quad (5)$$

100

101 which gives the stoichiometric control as $D_{\mathrm{REE}}^{\mathrm{ol/melt}} \propto (a_{\mathrm{SiO_2}}^{\mathrm{melt}})^{3/4}$ (Evans et al. 2008).
102 A different possibility would be charge-balancing with tetrahedral-site vacancies, which would give
103 the component as $MgREESi_{3/4}\square_{1/4}O_4$. The partitioning equilibrium would then be:

$$\underset{\text{melt}}{REEO_{1.5}} + 1/4\,\underset{\text{melt}}{SiO_2} + \tfrac{1}{2}\,\underset{\text{olivine}}{Mg_2SiO_4} = \underset{\text{olivine}}{MgREESi_{3/4}\square_{1/4}O_4} \quad (6)$$

104

105 and the stoichiometric control would have $D_{\mathrm{REE}}^{\mathrm{ol/melt}} \propto (a_{\mathrm{SiO_2}}^{\mathrm{melt}})^{1/4}$. It may look as though it should be
106 possible experimentally to distinguish between these alternatives by measuring the dependence of
107 $D_{\mathrm{REE}}^{\mathrm{ol/melt}}$ on $a_{\mathrm{SiO_2}}^{\mathrm{melt}}$, but in practice the relationship is obscured by the dependence of $D_{REE}^{ol/melt}$ on
108 $\gamma_{\mathrm{REEO_{1.5}}}^{\mathrm{melt}}$, the activity coefficient of the $REEO_{1.5}$ component in the silicate melt, because the latter is a
109 strong function of the SiO_2 content of the melt (Evans et al. 2008), and therefore also of $a_{\mathrm{SiO_2}}^{\mathrm{me*lt}}$. That
110 the substitution mechanism is by charge-balancing by octahedral-site vacancies (Eq. 5) and not
111 tetrahedral-site vacancies (Eq. 6) is now based on inference from hydroxylation spectroscopy (Berry
112 et al. 2007), and this assignment will be assumed in the rest of this paper.
113 But even for the relatively simple case of $D_{\mathrm{REE}}^{\mathrm{ol/melt}}$ there are more options, because of charge-
114 balancing by coupled substitution with other elements. Several authors have proposed charge-
115 balancing of the REE substitution in olivine by coupled substitution of Al^{3+} replacing Si^{4+} on
116 tetrahedral sites (Beattie 1994; Taura et al. 1998). This gives the component $REEMgAlO_4$, for which
117 the partitioning equilibrium is:

$$\underset{\text{melt}}{REEO_{1.5}} + \underset{\text{melt}}{AlO_{1.5}} + \tfrac{1}{2}\,\underset{\text{olivine}}{Mg_2SiO_4} = \underset{\text{olivine}}{REEMgAlO_4} + \tfrac{1}{2}\,\underset{\text{melt}}{SiO_2} \quad (7)$$

118 In this case the stoichiometric control predicts $D_{\mathrm{REE}}^{\mathrm{ol/melt}} \propto (a_{\mathrm{SiO_2}}^{\mathrm{melt}})^{-1/2}$, hence this substitution would
119 be favoured by lower $a_{\mathrm{SiO_2}}^{\mathrm{melt}}$, but is obviously only possible if there is alumina in the system.
120
121 This example of the partitioning of the REEs between olivine and melt brings another issue into
122 focus: there is no reason to suppose, *a priori*, that any one substitution mechanism dominates to the
123 exclusion of all the others. This possibility has been noted by most previous workers, but has not been
124 quantitatively explored.

Here we report an experimental study of this problem, in which we investigate how the partitioning of REE between olivine and melt changes as a function of Al_2O_3 in the melt, while holding temperature, pressure and $a_{SiO_2}^{melt}$ constant. The buffering of $a_{SiO_2}^{melt}$ was achieved with coexisting protoenstatite, $Mg_2Si_2O_6$; serendipitously, this mineral shows the same two substitution mechanisms for REE as forsterite (i.e., the components $REE_{4/3}\square_{2/3}Si_2O_6$ and $REEMgSiAlO_6$), allowing the same phenomenon to be compared side-by-side in different minerals. The partition coefficients of all 14 REEs plus Y and Sc were determined, to see whether the two mechanisms affect the REE differently, with implications for the use of lattice strain theory in modelling trace element partitioning. We also included a melt composition rich in TiO_2 in order to change melt composition independently of olivine composition and alumina activity. Our aim is to obtain quantitative information on an example of the phenomenon of multiple substitution mechanisms in trace-element partitioning, which will be of heuristic value in refining the way mineral/melt trace-element partition coefficients in general are parameterized. The example of REE partitioning between olivine and melt was chosen for this purpose not only to build on the previous experimental and theoretical work reviewed above, but also because Mg_2SiO_4-rich forsterite provides a compromise between simplicity of composition and crystal structure, while still having the complexity to exhibit multiple substitution mechanisms.

2. Methods

A base composition in the system CaO-MgO-SiO_2 designed to crystallize approximately 15% each of protoenstatite and forsterite was prepared by combining weighed proportions of SiO_2, MgO, $CaCO_3$, the REE oxides (all REE_2O_3 apart from CeO_2, Pr_6O_{11} and Tb_4O_7) and Sc_2O_3 under acetone using an agate pestle and mortar. We used a high level of doping in light REE to achieve good precision in the partition coefficients, based on the experience of Evans et al. (2008). Because the REEs are heavy elements, these high levels translate to a sum of mole fractions of the REE oxide components ($\sum XREEO_{1.5}$) of 0.029 to 0.056, compared to 0.012 to 0.015 in the study of Evans et al. (2008). Thus although large on a weight-percent basis, the doping levels may be considered modest in terms of mole fractions, and are not expected to have a significant effect on the results, as discussed below. The amounts of REE oxides added varied with the incompatibility of the REE, from approximately 2% for La and Ce to 0.02 wt% for Sc and some of the heavy REEs, totalling 6.9 wt%. Three further compositions were prepared by adding 2 wt% Al_2O_3, 5 wt% Al_2O_3 and 5 wt% TiO_2 to the base mix. Three elements, Na, Zr and Y, occur as impurities in the starting chemicals at sufficiently high concentrations to be analysed profitably in the run products, as does Ti in the three compositions nominally free of this element. The prepared powders were affixed to Pt wire loops using polyethylene oxide solution and, after drying, were run simultaneously in a vertical Gero tube furnace at 1406 °C (loaded at 600 °C and heated to the target at 6 °C/min, monitored using a Type B

thermocouple) for 20 days under flowing CO_2 ($fO_2 = 10^{-3.05}$ bars) before being dropped into water to quench.

The resulting beads were mounted in epoxy, ground and polished. Electron probe microanalysis (EPMA) of the glass, forsterite and protoenstatite was performed using a Cameca SX-100 electron probe at the Research School of Earth Sciences (Australian National University). The elements analysed, the standards used, analysing crystal and the background positions were Si Kα (quartz, TAP, –600, +500), Ti Kα (rutile, PET, –500, +600), Al Kα (K412 glass, TAP, –500, +500), Mg Kα (San Carlos olivine, TAP, –800, +600), Ca Kα (K412 glass, PET, –500, +400), La Lα ($LaPO_4$, PET, –400, +400), Ce Lα ($CePO_4$, PET, n/a, +500), Pr Lβ ($PrPO_4$, –460, +330), Nd Lβ ($NdPO_4$, LLIF, –350, n/a), Sm Lβ ($SmPO_4$, LLIF, n/a, +370), Eu Lβ ($EuPO_4$, LLIF, –350, +465) and Gd Lβ ($GdPO_4$, LLIF, –442, +420). The REE phosphate standards (Jarosewich and Boatner, 1991) were measured using the same analytical routine and the results used to correct the glass analyses. Only La_2O_3, Eu_2O_3 and Gd_2O_3 required a correction of >0.01 %. The REEs were below the limits of detection in the protoenstatite and forsterite; the reason for analysing them in the glasses by EPMA was to provide the correction factors for the other major elements, and to check that analytical totals were near 100%. Precise trace-element analyses of the glass, forsterite and protoenstatite were obtained by laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) using a 193 nm excimer laser in a HelEx ablation cell coupled to an Agilent 7700 quadrupole mass spectrometer. The spot size was 28 μm and fluence was 3 – 4 J cm^{-2} at a pulse rate of 5 Hz, with counting times 20 s on background and 45 s on glass or crystal. For each experiment, seven spots were taken on the glass and between six and 17 on the crystals. For the crystals, the laser ablated through to glass during the 45 s of the analysis on many occasions. Where this occurred during the first 25 s or so of ablation, the analysis was abandoned, otherwise the contaminated part was excised during data processing. Approximately half the protoenstatite analyses and a quarter of the forsterite were affected. NIST 610 glass was used as the external standard with concentrations of all elements from Jochum et al. (2011), and ^{29}Si was used as the internal standard, referenced to Si concentrations measured by EPMA. The isotopes measured were ^{23}Na, ^{27}Al, ^{29}Si, ^{43}Ca, ^{45}Sc, ^{49}Ti, ^{89}Y, ^{90}Zr, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb and ^{175}Lu. The ablation data were reduced using an in-house spreadsheet, which permitted thorough checking of the time-resolved signals to exclude contamination from melt, including melt inclusions, and to eliminate the occasional electronic blip. Following Jenner and O'Neill (2012) we determined the interference of $^{29}Si^{16}O$ on ^{45}Sc using an in-house San Carlos olivine standard with 2.32±0.02 ppm Sc, and used the SiO^+/Si^+ production rate to subtract the interference, approximately 0.5 ppm, from the olivine and glass data. This correction was never larger than 3% relative for the data presented here.

3. Results

198 The experiments quenched to homogeneous glasses with crystals of forsterite and protoenstatite (up to
199 60 μm) as the liquidus phases. The protoenstatite crystals were commonly cracked, which is attributed
200 to the orthorhombic to monoclinic transition during cooling (Kamenetsky et al., 2006). Major-element
201 compositions by EPMA are given in Table 1 and minor and trace elements by LA-ICP-MS are given
202 in Table 2. The analyses for forsterite and protoenstatite are in good agreement with the expected
203 stoichiometries of these phases. A comparison of data for the elements analysed by both EPMA and
204 LA-ICP-MS in the glasses indicates that the LA-ICP-MS values for Mg and Ca were both too low
205 relative to the EPMA data by 13 % on average, with the exception of the high-Ti glass. The EPMA
206 data for Eu are, for unknown reasons, on average about 40% lower than the LA-ICP-MS values. The
207 LA-ICP-MS data are much more precise and were used for calculating the partition coefficients for all
208 elements. Although there may be some systematic errors in absolute values reported due to matrix
209 effects, as indicated by the different ways in which the count rates for different elements change with
210 depth during ablation between the NIST 610 glass and the forsterite, protoenstatite and experimental
211 glasses (e.g., Jenner and O'Neill, 2012), these largely cancel out in the comparisons between REEs,
212 and between the different experiments. Any errors in the reported reference concentrations of
213 elements in the NIST 610 standard cancel out completely when calculating partition coefficients.
214
215 The trace elements studied are all incompatible in protoenstatite and forsterite (Table 3), with
216 protoenstatite/melt partition coefficients ranging from $D_{La} = 1.6(2) \times 10^{-5}$ in the Al-free composition
217 to $D_{Sc} = 0.25(1)$ in the most Al-rich composition. Forsterite/melt partition coefficients are mostly
218 within a factor of three of the corresponding protoenstatite/melt partition coefficients, with the
219 exception of Al, Ti and Na, which are more compatible in protoenstatite than in forsterite (Fig. 1). In
220 the base composition, protoenstatite is more accommodating of the light REEs, but forsterite has a
221 slightly higher preference for the heavy REEs and Sc (Fig. 1).
222
223 The relative standard deviations (RSDs) of the trace elements in the glasses are nearly all in the range
224 1 to 3% (Table 2). The results from the crystals are quite different. The RSDs for the undoped
225 elements (Na, Ti, Y and Zr) in the crystals are large because their low concentrations approach the
226 limits of detection. The limit of detection, calculated after Longerich et al. (1996), is different for each
227 analysis but typical values lie in the range 5 - 10 ppm Na, 630 – 710 ppb Ti, 2 – 10 ppb Y, 5 – 15 ppb
228 Zr. Another explanation must be sought where the REEs have high RSDs, as all REEs are well above
229 the limit of quantification. The distinction between the two causes of high RSDs is well illustrated by
230 comparing the RSDs of Y with those of La. In the protoenstatite of the low-Al experiment, the RSD
231 of Y is 23%, but its concentration is only 0.03 ppm, very close to the limit of detection, whereas for
232 La the RSD is 44%, although present at the much healthier concentration of 3.4 ppm. On the other
233 hand, La and Yb have a similar number of counts per time slice in the LA-ICP-MS analyses, La in

protoenstatite, with an RSD of ~ 45%, is much more inhomogeneous than Yb, with RSDs of ~ 2%. The effect is much larger in protoenstatite than forsterite. We propose that the elevated standard deviations of the more incompatible REEs in protoenstatite are due to undetected contamination by glass in the ablated volume. This phenomenon is particularly severe for highly incompatible elements, as can be seen by the following thought experiment. Where the mineral analysis includes a mass fraction x of glass, then an apparent partition coefficient D^* results:

$$D^* = \frac{(1-x)c^{xtl}+xc^{melt}}{c^{melt}} \quad (8)$$

which simplifies to $D^* = D + x$ for small values of x. Hence, the relative importance of any non-zero value of x is inversely proportional to D. In Fig. 2 we compare partition coefficients for all REE in protoenstatite in the two Al-free compositions. The partition coefficients differ considerably for the light REE (La to Nd) but are more closely correlated for the heavy REE, conforming to the pattern we would expect for melt contamination. Although it is not possible to know *a priori* how the partition coefficients will vary due to the presence of TiO_2 in one of the experiments, a value of $x = 0.00003$ (i.e., 30 parts per million) results in a straight-line correlation between ($D^* - x$) for the low-Al series and D for the Al-series. Such small volumes would not be observable optically, and if diffusely distributed would not be evident in the time-resolved signal of the ICP-MS. The forsterite analyses also show an increase of RSD with incompatibility, but more muted, and we have no reason to suppose that in forsterite the effect is not simply that expected from the counting statistics. Protoenstatite may be more susceptible to contamination if the cracks in the crystals, which we attribute to the volume change caused by the inversion to the monoclinic pyroxene during quenching, provide pathways for insertion of melt, although we avoided visible cracks during analysis. As Fig. 2 shows, the putative contamination becomes insignificant for REE heavier than Nd.

4. Discussion

4.1 REE oxidation states

Two of the REE (Ce and Eu) are known to exist in oxidation states other than 3+ in geological materials, but in these experiments their partition coefficients are not noticeably anomalous relative to the neighbouring elements (La and Pr, and Sm and Gd, respectively). This is in qualitative agreement with the small amounts of Eu^{2+} and Ce^{4+} expected under the experimental conditions: we calculate that only 2 to 4% % of the Eu in the melt was Eu^{2+} (Burnham et al., 2015), while 4 to 5% of the Ce was Ce^{4+} (Burnham and Berry, 2014). The optical basicities of the REE needed for these calculations were taken from Duffy (2005). The partitioning data of Leitzke et al. (2017) indicate that the presence of Eu^{2+} should give rise to a negative Eu anomaly in the partition coefficients, which is not observed in the present study; similarly, neither Eu nor Ce anomalies occurred in the forsterite/melt partitioning experiments of Evans et al. (2008), which were performed in air. Hence all Ce and Eu were considered to be trivalent in the following discussion.

4.2 Major-element relations

The coexistence of nearly pure forsterite (fo) and protoenstatite (prEn) fixes the activities of both MgO and SiO_2 each at nearly the same values in all four compositions. In detail, the deviations from the pure components Mg_2SiO_4 and $Mg_2Si_2O_6$ with the minor substitutions of Ca and Al almost cancel out as Al increases and Ca decreases in the base, lo-Ti and hi-Ti compositions, making this an excellent approximation. Since $a_i^{melt} = X_i^{melt}\gamma_i^{melt}$, where a_i^{melt} are activities, X_i^{melt} are mole fractions, and γ_i^{melt} are activity coefficients, the fact that $X_{SiO_2}^{melt}$ and X_{MgO}^{melt} hardly change when Al_2O_3 is added to the base composition means that $\gamma_{SiO_2}^{melt}$ and γ_{MgO}^{melt} stay almost constant, because $a_{SiO_2}^{melt}$ and a_{MgO}^{melt} are constant on the fo+prEn cotectic. By contrast, adding TiO_2 causes a marked decrease of $X_{SiO_2}^{melt}$, hence an increase in $\gamma_{SiO_2}^{melt}$. These major-element systematics are qualitatively similar to those noted by Kushiro (1975) from the loci of the fo+prEn cotectics in CaO-free ternary $MgO\text{-}SiO_2\text{-}XO_n$ systems, where XO_n is a third major-element oxide component. An advantage of the $CaO\text{-}MgO\text{-}SiO_2\text{-}XO_n$ systems is that the cotectic may be followed along paths of increasing XO_n isothermally. Although an increase of about 20% in $D_{Ca}^{prEn/melt}$ and $D_{Ca}^{fo/melt}$ may be resolved with increasing X_{CaO}^{melt} (Fig. 3), and hence a decrease by this amount in γ_{CaO}^{melt}, the magnitude is relatively small, and as a first approximation we propose to treat it as constant. For Al, it is the square root of its concentration in both protoenstatite and forsterite that varies with $X_{AlO_{1.5}}^{melt}$, which is thought to be due to short-range order between octahedral and tetrahedral Al, rather than any change of $\gamma_{AlO_{1.5}}^{melt}$ (Evans et al., 2008; Burnham and O'Neill, 2016). With $\gamma_{SiO_2}^{melt}$, γ_{MgO}^{melt}, γ_{CaO}^{melt} and probably $\gamma_{AlO_{1.5}}^{melt}$ all close to constant in the compositions studied, it seems plausible from the Gibbs-Duhem relation ($\sum X_i d(\ln\gamma_i) = 0$) for the activity coefficients of the other components, $\gamma_{REEO_{1.5}}^{melt}$, etc., also to be constant over this range of melt compositions (quasi-ideal mixing). The approximation of constant activity coefficients in melts on the fo+prEn cotectic will be invoked in the modelling below.

4.3 Henry's Law

Henry's Law describes the situation where the activity coefficient of a component in a phase does not vary with the concentration of that component in that phase. It does not address the change of activity coefficients with other components, as discussed in the previous section. In the context of trace-element partitioning studies, an element *i* is said to follow Henry's Law if D_i is independent of the concentration of *i* in the system, implying that Henry's Law is followed in both phases.

In previous work, McKay (1986) showed in his study of olivine/melt partitioning of Sm, Gd and Yb, that Henry's Law was followed to concentrations of 5 wt% of individual REE_2O_3 in the melt. In the case of Yb, the level of doping in the olivines in the experiments of McKay (1986) extended up to 800

ppm, which compares with a maximum concentration in olivine for any REE in this study of 18 ppm (for Er), see Table 2. Total REE, Y and Sc concentrations do not exceed 100 ppm. This constancy of partition coefficients independent of concentration was assumed in subsequent parameterizations of experimental data that have combined results from studies that used different composition ranges (e.g., Beattie 1994; Sun and Liang 2013). The present results contain several observations that reinforce this finding. Despite the greater uncertainties caused by its lower concentrations, the partition coefficients for Y for both protoenstatite/melt and forsterite/melt fall consistently between those of Ho and Er, and closer to the former, as expected from the close coherence of these elements in most rocks (Pack et al., 2007). The Y concentrations are approximately 150 times less than those of Ho and 500 times less than those of Er in three of the four compositions (for unknown reason, Y levels are about 5 times higher in the phases in the base composition experiment), showing that there is no significant deviation from Henry's law over this range, which may allay fears about the high doping levels of the experiments. The same conclusion may be drawn from noting that the values of the partition coefficients of REEs with adjacent atomic numbers but different doping levels fall on the same smooth curves of $D_{REE}^{fo/melt}$or $D_{REE}^{prEn/melt}$ versus ionic radii (see Section 4.7 below); this is best exemplified by the adjacent pair Er (Z = 68) and Tm (Z=69), whose doping levels differ in the experimental melts by an order of magnitude. These smooth curves for $D_{REE}^{fo/melt}$ versus atomic number are effectively identical in shape to those of Di Stefano et al. (2018) for Fe-containing olivine, allowing for the differences in the olivine composition and the major-element melt composition, despite the ratios of REE concentrations differing by factors from 10^{-3} to 20 between the two sets of experiments, as shown in Fig. 4. The present data are also in agreement with the results of Evans et al. (2008; see Section 4.3 below for a more detailed comparison), in which the REE concentrations in the melt totalled ~ 4 % REE_2O_3. Taken together, all this evidence suggests that olivine/melt partition coefficients are independent of concentration from a few ppm to over 10 % REE_2O_3 in the melt. This observation joins an increasing body of evidence showing that high concentrations of incompatible elements in silicate melts do not by themselves lead to significant deviations from Henry's Law. For example, Schoneveld and O'Neill (2019) report partition coefficients for the REE between anorthite and melt that do not vary over an order of magnitude, with total doping of $\sum REE_2O_3$ from 2 to 11 wt%. Jollands et al. (2014) found constant partition coefficients of Zr and Hf into forsterite from a few parts per million up to zircon/hafnon saturation, at which the Zr or Hf concentration in the melt approaches 10 wt%. In the same vein, $D_{Ti}^{prEn/melt}$ (the partition coefficient for Ti between protoenstatite and melt) in the nominally Ti-free base composition is only ~ 25% higher than that in the high-Ti composition with 9 wt% TiO_2 in the melt, despite the ratio of concentrations being nearly 10^3; similar constancy of $D_{Ti}^{fo/melt}$ was observed by Leitzke et al. (2016) with TiO_2 in the melt ranging from 1 to 18 %. Another test of Henry's law for protoenstatite is that the experimental values of D_{Ti}, D_{Sc} and D_Y are in good agreement with the values for natural samples, despite large differences in concentration,

as are those for D_{Ca} (Yurimoto and Sueno, 1987). The concentrations of the REEs, Y and Sc in the protoenstatites of this study are similar to those in the coexisting forsterites (Table 2).

4.4 Two substitution mechanisms for REE in forsterite in CMAS

The results from the base composition support the inference of Evans et al. (2008) and previous workers (e.g., Colson et al. 1986; Nielsen et al. 1992; Beattie 1994) that the REE can substitute into olivine by a vacancy-coupled mechanism (Eq. 5). With the addition of alumina, values of $D_{REE}^{fo/melt}$ increase linearly with $X_{AlO_{1.5}}^{melt}$ (Fig. 5). Under our assumption that $\gamma_{AlO_{1.5}}^{melt}$ is constant, this means that $D_{REE}^{fo/melt}$ is linearly dependent on $a_{AlO_{1.5}}^{melt}$. Hypothetically, this might be ascribed to an increase in $\gamma_{REEO_{1.5}}^{melt}$with added alumina, but this would change $D_{REE}^{fo/melt}$ and $D_{REE}^{prEn/melt}$ identically for all REE, which is not the case: another advantage of these doubly-saturated experiments.

Instead, our preferred explanation is as follows. The equilibrium constant for reaction (5) and (7) are:

$$K_{(fo,\ vac)} = \frac{\left(a_{REE_{4/3}SiO_4}^{fo}\right)^{3/4}}{a_{REEO_{1.5}}^{melt}\left(a_{SiO_2}^{melt}\right)^{3/4}} = \exp\{-\Delta G^{o}_{(fo,\ vac)}/RT\} \quad (9)$$

and

$$K_{(fo,\ Al)} = \frac{a_{REEMgAlO_4}^{fo}\left(a_{SiO_2}^{melt}\right)^{1/2}}{a_{REEO_{1.5}}^{melt}a_{AlO_{1.5}}^{melt}} = \exp\{-\Delta G^{o}_{(fo,\ Al)}/RT\} \quad (10)$$

From which, using the assumptions about configurational entropy outlined in Appendix A, the partition coefficients are:

$$D_{REE(vac)}^{fo/melt} = K_{(fo,\ vac)}\left(\gamma_{REEO_{1.5}}^{melt}/\gamma_{REE_{4/3}SiO_4}^{fo}\right)\left(a_{SiO_2}^{melt}\right)^{3/4} \quad (11)$$

and

$$D_{REE(Al)}^{fo/melt} = K_{(fo,\ Al)}\left(\gamma_{REEO_{1.5}}^{melt}/\gamma_{REEMgAlO_4}^{fo}\right)a_{AlO_{1.5}}^{melt}\left(a_{SiO_2}^{melt}\right)^{-1/2} \quad (12)$$

From $c_{REE}^{fo} = c_{REE(vac)}^{fo} + c_{REE(Al)}^{fo}$, it follows that $D_{REE}^{fo/melt} = D_{REE(vac)}^{fo/melt} + D_{REE(Al)}^{fo/melt}$. Then, by combining Eqns. 11 and 12:

$$D_{REE}^{fo/melt} = \gamma_{REEO_{1.5}}^{melt}\left[K'_{(fo,\ vac)}\left(a_{SiO_2}^{melt}\right)^{3/4} + K'_{(fo,\ Al)}\left(X_{AlO_{1.5}}^{melt}\gamma_{AlO_{1.5}}^{melt}\right)\left(a_{SiO_2}^{melt}\right)^{-1/2}\right] \quad (13)$$

Here we have changed the standard state of $REE_{4/3}SiO_4$ and $REEMgAlO_4$ from the pure endmember component to that of the component at unit concentration but exhibiting infinite-dilution behaviour, by putting $K'_{(fo,\ vac)} = K_{(fo,\ vac)}/\gamma_{REE_{4/3}SiO_4}^{fo}$ and $K'_{(fo,\ Al)} = K_{(fo,\ Al)}/\gamma_{REEMgAlO_4}^{fo}$. The change of standard state is conducive to clarity because the dependences of $\gamma_{REE_{4/3}SiO_4}^{fo}$ or $\gamma_{REEMgAlO_4}^{fo}$ on the identity of the REE cannot be separated from those of $K_{(fo,\ vac)}$ or $K_{(fo,\ Al)}$ without further information of a kind beyond the reach of this study (e.g., from calorimetry).

In the present experiments, $a^{melt}_{SiO_2}$ is constant (fixed by the coexistence of fo and prEn), and, as discussed previously, we propose that values of $\gamma^{melt}_{REEO_{1.5}}$ and are also constant along the fo+prEn cotectic as the alumina content increases. With this latter assumption, Eq. 12 predicts that a plot of $D^{fo/melt}_{REE}$ against $X^{melt}_{AlO_{1.5}}$ should yield a straight line, as observed. The intercept is$D^{fo/melt}_{REE(vac)}$ (which is given by $\gamma^{melt}_{REEO_{1.5}} K'_{(fo, vac)} (a^{melt}_{SiO_2})^{3/4}$, see Eq. 11), and the slope is $[\gamma^{melt}_{REEO_{1.5}} K'_{(fo, Al)} \gamma^{melt}_{AlO_{1.5}} (a^{melt}_{SiO_2})^{-1/2}]$. For the lightest REE (La and Ce), the line is horizontal, hence $D^{fo/melt}_{REE(Al)}$ cannot be distinguished from zero, but a non-zero slope is resolvable for the heavy REE, and the slope is even larger for Sc (Fig. 5). Equation 12 shows that the linear relationship between $D^{fo/melt}_{REE}$ and $X^{melt}_{AlO_{1.5}}$ would not have been so apparent without $a^{melt}_{SiO_2}$ being kept constant. The complications expected from not fixing $a^{melt}_{SiO_2}$ extend beyond the effects explicit from the $a^{melt}_{SiO_2}$ terms in Eq. 12, because $\gamma^{melt}_{REEO_{1.5}}$ also varies strongly with $a^{melt}_{SiO_2}$, as will be shown in the next section, where we discuss the results of Evans et al. (2008) in the light of the new results presented here. Our thermodynamic analysis makes a general theoretical point: there are pitfalls to inferring the stoichiometry of the of a trace-element substitution from correlations with major elements.

Values of $D^{fo/melt}_{REE(vac)}$ and of $D^{fo/melt}_{REE(Al)}$ extrapolated to $X^{melt}_{AlO_{1.5}} = 0.15$ for all REE from least-squares fitting of the data are shown in Fig. 6 as a function of ionic radius in 6-fold coordination (our revised values; Table 3); the value of $X^{melt}_{AlO_{1.5}} = 0.15$ was chosen for illustrative purposes because this is typical of basaltic melt compositions. The relative importance of the Al-substitution mechanism increases smoothly with decreasing ionic radius, being negligible for the light REE, but for Sc, $D^{fo/melt}_{Sc(Al)}$ becomes comparable to $D^{fo/melt}_{Sc(vac)}$.

4.5 Activity coefficients of $REEO_{1.5}$ in silicate melts: re-evaluating the results of Evans et al. (2008)

Distinguishing and separating out the two substitution mechanisms allows the cause of the variation of $D^{fo/melt}_{REE}$ with composition observed by Evans et al. (2008) to be reassessed, and the changes in $\gamma^{melt}_{REEO_{1.5}}$for the different REE to be quantified more exactly. The results of the present study (which, unlike the former study, is saturated in forsterite and protoenstatite and hence has equal silica activities for all four compositions) allow us to disambiguate the effect of the Al-substitution in the forsterite from that of changes in $\gamma^{melt}_{REEO_{1.5}}$, due, for example, to $REEO_{1.5}$-SiO_2 interactions. To re-evaluate the data of Evans et al. (2008), which did not fix $a^{melt}_{SiO_2}$, we applied a correction for the expected dependence of $D^{fo/melt}_{REE}$ on this variable by normalising to $\gamma^{melt, f+p}_{REEO_{1.5}}$, the activity coefficients of $REEO_{1.5}$ in a melt on the forsterite + protoenstatite cotectic (Reaction 1 and Eq. 2; for details see

Appendix B). Values of $\gamma^{melt}_{REEO_{1.5}}/\gamma^{melt,\,f+p}_{REEO_{1.5}}$ calculated from the results of Evans et al (2008) show an exponentially shaped decrease with $X^{melt}_{SiO_2}$, which becomes less pronounced from La through to Lu, extrapolating to hardly any change in $\gamma^{melt}_{ScO_{1.5}}/\gamma^{melt,\,f+p}_{ScO_{1.5}}$ (Fig. 8). Part of the scatter around these trends was found to be correlated with X^{melt}_{CaO}, hence the data were parameterized with an extra term in this variable that vanished for the fo+prEn compositions (for internal consistency), to give:

$$\ln\left(\gamma^{melt}_{REEO_{1.5}}/\gamma^{melt,\,f+p}_{REEO_{1.5}}\right) = \left(X^{melt}_{SiO_2} - 0.52\right)\left(23.7 - 22.5 r^{VIII}_{REE} - 52.4\, X^{melt}_{CaO}\right) \qquad (14)$$

where r^{VIII}_{REE} is the ionic radius in Å of the REE^{3+} cation in 8-fold coordination from Shannon (1976). The composition DFA-a from Evans et al. (2008), which was noted to be anomalous in that study, could not be well fitted, and was not used in the final parameterization. The problem is mainly with the well-determined heavy REE and Sc, so it is unlikely to be an analytical mishap, rather a failure of the model. The data for two elements were omitted from this treatment: Y, which was imprecisely determined, and Gd, for which we noticed a small but systematic discrepancy in the values of Evans et al., possibly due to an interference of $^{141}Pr^{16}O$ on ^{157}Gd, as the Gd/Pr ratio used in those experiments was only 0.03, versus 0.4 in this study. For the fitted data (12 compositions and 11 elements including Sc) the standard deviation implied from the fit is 10% relative.

In summary, the activity coefficients of the $REEO_{1.5}$ components in silicate melts change with melt composition, especially with silica content, $X^{melt}_{SiO_2}$ (as distinct from silica activity, $a SiO_2$, which affects partitioning separately via the stoichiometric control $REEO_{1.5} + ¾\ SiO_2 = ¾\ REE_{4/3}\square_{2/3}SiO_4$). The decrease of $\gamma^{melt}_{REEO_{1.5}}$ with increasing silica is largest for La, being approximately a factor of three over the range of melt compositions studied by Evans et al. (2008), and becomes less pronounced with increasing atomic number of the REE (or decreasing ionic radius). It is almost negligible for Sc. These conclusions are robust against the assumptions and approximations used in the above discussion, which affect all the REE in the same way, but the details of the compositional dependence implied in our parameterization of $\gamma^{melt}_{REEO_{1.5}}/\gamma^{melt,\,f+p}_{REEO_{1.5}}$ (Eq. 14) is less certain, because it is not completely insensitive to these assumptions and approximations. We also emphasise that the parameterization only addresses the small range of melt compositions in CMAS that are in equilibrium with forsterite at 1400ºC and atmospheric pressure. It is offered as a counter to the default assumption that is sometimes invoked in applying lattice strain theory, that variations in $\gamma^{melt}_{REEO_{1.5}}$ with melt composition are negligible. We envisage that Eq. 14 could be used to estimate the magnitude of likely variations in $\gamma^{melt}_{REEO_{1.5}}$in a given context, to see if they are significant against other uncertainties and approximations.

4.6 Comparison of $D_{REE}^{prEn/melt}$ with $D_{REE}^{fo/melt}$

The relationship of $D_{REE}^{prEn/melt}$ with $X_{AlO_{1.5}}^{melt}$ (e.g., Fig. 8) shows that the REE^{3+} cations substitute into protoenstatite in the CMAS system by the same two mechanisms as in forsterite: that is, vacancy-coupled ($MgREE_{2/3}\square_{1/3}Si_2O_6$), and charge-balanced by Al ($MgREEAlSiO_6$). The stoichiometric controls should be the same, and the relationship between the activities of these two components and REE concentrations (c_{REE}^{prEn}) are also likely similar. Although the substitution of Al^{3+} for Si^{4+} occurs over two equivalent tetrahedral sites per formula unit, the relationship between c_{Al}^{prEn} and $X_{AlO_{1.5}}^{melt}$ shows that tetrahedral and octahedral Al are also short-range ordered, as in forsterite (Evans et al. 2008).

There are some salient differences, however (Fig. 6). Whereas the two mechanisms are of subequal importance in forsterite over basaltic ranges of alumina contents, with the vacancy mechanism slightly dominant, in protoenstatite the vacancy mechanism would not be resolvable in melt compositions with natural levels of alumina. Moreover, the slopes of $D_{REE(vac)}^{fo/melt}$ and $D_{REE(Al)}^{fo/melt}$ vs. r_{REE}^{VIII} are different, but the slopes of $D_{REE(vac)}^{prEn/melt}$ and $D_{REE(Al)}^{prEn/melt}$ vs. r_{REE}^{VIII} are about the same.

Zr also becomes more compatible in protoenstatite with increasing $X_{AlO_{1.5}}^{melt}$ (Fig. 8), implying substitution as $ZrMgAl_2O_6$. A similar increase in the compatibility of Zr in forsterite with increasing $X_{AlO_{1.5}}^{melt}$ (Fig. 9) suggests the component $Mg_{1/2}\square_{1/2}ZrAlO_4$ or perhaps $Zr_{5/4}\square_{3/4}AlO_4$, in addition to the $Zr\square SiO_4$ component already identified in Al-free systems (Jollands et al., 2014). The former seems more likely, because it allows the substitution of Al^{3+} for Si^{4+} in the tetrahedral site to lower the octahedral-site vacancy concentration needed for charge-balancing more effectively, resulting in a more even distribution of positive charge over the volume of the crystal lattice in the neighbourhood of the Zr^{4+} impurity.

4.7 The effect of Ti

Since the hi-Ti and base composition experiments are at the same activity of silica, and neither contain Al, the ratios of $D_{REE}^{fo/melt}$ and $D_{REE}^{prEn/melt}$ between these two compositions (i.e., $[D_{REE}^{fo/melt}]_{hi\text{-}Ti}/[D_{REE}^{fo/melt}]_{base}$ and $[D_{REE}^{prEn/melt}]_{hi\text{-}Ti}/[D_{REE}^{prEn/melt}]_{base}$) should both be equal to the ratio of activity coefficients in the melt, $[\gamma_{REEO_{1.5}}^{melt,\ hi\text{-}Ti}/\gamma_{REEO_{1.5}}^{melt,\ base}]$. The two ratios are indeed close to each other, if we allow for probable glass contamination of the light REE determinations of $D_{REE}^{prEn/melt}$ as discussed above, but in detail $[D_{REE}^{prEn/melt}]_{hi\text{-}Ti}/[D_{REE}^{prEn/melt}]_{base}$ is consistently about 10% higher than $[D_{REE}^{fo/melt}]_{hi\text{-}Ti}/[D_{REE}^{fo/melt}]_{base}$. The Ti content of the protoenstatite, although considerably greater than that of the forsterite, is equivalent to a mole fraction of only 0.005 of the $Mg_2Ti_2O_6$ component, which hardly

seems sufficient to change $[D_{REE}^{prEn/melt}]_{hi\text{-}Ti}/[D_{REE}^{prEn/melt}]_{base}$ by as much as 10%. No explanation is at present apparent.

The observed decrease in $\gamma_{REEO_{1.5}}^{melt}$ with added TiO_2 is opposite to that indicated by Eq. 14, if the effect of adding TiO_2 was simply to lower $X_{SiO_2}^{melt}$ by dilution. For example, for La, $\gamma_{LaO_{1.5}}^{melt,\ hi\text{-}Ti}/\gamma_{LaO_{1.5}}^{melt,\ base}$ is 0.82, whereas Eq. 14 would predict $\gamma_{LaO_{1.5}}^{melt,\ hi\text{-}Ti}/\gamma_{LaO_{1.5}}^{melt,\ base} = 1.36$. The effect decreases with decreasing ionic radius, and is insignificant for Sc. The qualitative conclusion is that there are significant interactions between the light REE^{3+} cations and Ti^{4+} in silicate melts, at least for melts with high TiO_2.

5. Comparison with previous work

5.1 Identifying substitution mechanisms

Olivine is not a major repository of REEs, but its relatively simplicity of composition and stoichiometry gives it theoretical interest, which may explain why the partitioning of the REE between olivine and melt has been the object not only of many experimental studies, but also of computational simulations (Purton et al. 1997; Zhang and Wright 2005). While some studies have debated the substitution mechanism, others focussed on the empirical results only, without discussing the mechanisms. Such studies will not be considered further.

Of the experimental studies that have discussed substitution mechanisms, Nielsen et al. (1992) concluded that the REE^{3+} substituted by vacancy-coupling only, based on the lack of correlation between $D_{REE}^{ol/melt}$ and $X_{AlO_{1.5}}^{melt}$, as did Grant and Wood (2010) for Sc partitioning, from the lack of correlation between $D_{Sc}^{ol/melt}$ and $X_{AlO_{1.5}}^{melt}$. Evans et al. (2008) argued that the vacancy mechanism was predominant with only a "minor proportion" of $REEMgAlO_4$. The conclusions of Evans et al. (2008) were compromised by the fact that although *T* and *P* were kept constant between all samples in these experiments, $a_{SiO_2}^{melt}$ was not, causing increasing $X_{AlO_{1.5}}^{melt}$ to be correlated with decreasing $X_{SiO_2}^{melt}$, hence also decreasing $a_{SiO_2}^{melt}$. We can now see from the results of this study that resolving the effect of alumina is only possible when $a_{SiO_2}^{melt}$ is kept constant.

Beattie (1994) favoured $REEMgAlO_4$ on statistical thermodynamic grounds. Observing that the values of $D_{REE}^{fo/melt}$ followed Henry's Law, he reasoned that this could be best explained if REE^{3+} were charge-balanced by tetrahedral Al with short-range order, such that $a_{REEMgAlO_4}^{fo} \propto c_{REE}^{fo}$. While we agree with this latter assignment (see Eqns. 7, 10, 12), our results show that his next assumption, that the vacancies in the $REE_{4/3}\square_{2/3}SiO_4$ component contribute to configurational entropy, is not warranted.

Instead, ordering of vacancies adjacent to the REE^{3+} cations that they charge-balance produces $(a^{fo}_{REE_{4/3}SiO_4})^{3/4} \propto c^{fo}_{REE}$, and Henry's Law is maintained (Appendix A). Both mechanisms are consistent with Henry's Law, which cannot be used to discriminate between them.

Colson et al. (1989), in their evaluation of experiments previously reported in Colson et al. (1988), also noted the possibility of both substitution mechanisms operating in combination in olivine, but concluded that "the larger cations in olivine (Sc, Yb) are charge-balanced primarily by (octahedral site vacancies)". They did not attempt to quantify "primarily", partly due to their precision being limited by their reliance on electron microprobe analyses at trace concentrations, but also because the experiments of Colson et al. (1988) encompass two additional variables: a large range of Mg/Fe in olivine, and temperatures varying from 1169 to 1414ºC. Colson et al. (1989) contrasted their conclusion that the REE and Sc substituted in olivine charge-balanced by vacancies against their evidence that Sc substituted into what they called "low-Ca pyroxene" in their experiments by charge-balancing with tetrahedral Al. This "low-Ca pyroxene" is unlikely to be protoenstatite, at least in most of their experiments, because this phase is not stable at the low Mg/Fe of their compositions (see, for example, Ohi and Miyake 2016 and references therein).

5.2 Implications for lattice strain models

Lattice strain theory proposes that mineral/melt partition coefficients among a suite of cations of the same charge and with spherically symmetric electron configurations, such as the REEs, vary with their ionic radii. Several formulations of this concept have been proposed since the fundamentals of the idea were introduced by Mott and Littleton (1938), among which one due to Brice (1975) has come to dominate in the Earth sciences literature following the demonstration of its usefulness by Blundy and Wood (1994). Note, however, that Beattie (1994) applied a different formulation, after Nagasawa (1966), to fit his REE olivine/melt partitioning data. The Brice equation is:

$$\ln D_{REE} = \ln D_0 - \frac{4\pi E N_A}{RT}\left(\frac{r_0}{2}(r_{REE} - r_0)^2 + \frac{1}{3}(r_{REE} - r_0)^3\right) \quad (15)$$

where D_0 is the partition coefficient for a hypothetical 3+ cation of ionic radius r_0, E is the Young's modulus of the cation site, and N_A is Avogadro's number. Comparison with the thermodynamic formulation (e.g., Eqns. 11 or 12) shows that the second term on the right-hand side is equivalent to $\ln\gamma^{fo}_{REE_{4/3}SiO_4}$ or $\ln\gamma^{fo}_{REEMgAlO_4}$, respectively, which leaves D_0 to incorporate three quantities: the equilibrium constant (that is, a ΔG^o term), $\gamma^{melt}_{REEO_{1.5}}$, and the stoichiometric control. The presumption has been that the three contributions to D_0 are not functions of the cation's identity (hence of r_{REE}), therefore the variation of ln D_{REE} with r_{REE} is entirely due to the lattice strain term, which has a very specific shape: that of a slightly asymmetric parabola.

As shown in Section 4.5 and Fig. 7, this cannot be correct in detail, because the sensitivity of $\gamma^{melt}_{REEO_{1.5}}$ to melt composition depends on the REE, hence r_{REE} (Eqn. 14). Furthermore, if we apply Eqn. (15) to each of the two substitution mechanisms in forsterite (Fig. 6a), we find differences in their E and r_0, despite the probability that the REEs occupy the same crystallographic site in both substitution mechanisms. The curve for $D^{fo/melt}_{REE(vac)}$ versus r_{REE} gives E_{vac} = 415(19) GPa and $r_{0,vac}$ = 0.713(7) Å, while that for $D^{fo/melt}_{REE(Al)}$ versus r_{REE} gives E_{Al} = 625(28) GPa and $r_{0,Al}$ = 0.740(4) Å. An explanation is that $\Delta G^{o}_{(fo,\ vac)}$ and $\Delta G^{o}_{(fo,\ Al)}$ are, firstly, functions of r_{REE}, and, secondly, different functions of r_{REE}. There is no theoretical reason that such quantities as $\Delta G^{o}_{(fo,\ vac)}$ and $\Delta G^{o}_{(fo,\ Al)}$ would vary with r_{REE} according to the same slightly asymmetric parabolic shape as that deduced by Brice (1975) for lattice strain in Eq. (15). Of the three thermodynamic factors listed above as contributing to D_0, only one, the stoichiometric control, is expected not to vary with r_{REE}.

A literal interpretation of the lattice strain models of Nagasawa (1966) or Brice (1975) also encounters the problematic nature of the concept of ionic radii. Ionic radii could in principle be derived from interatomic distances in crystals by splitting up that part of the electron density associated with the cation from that associated with the anion (e.g., Gibbs et al. 2013). In practice the splitting-up is not done, and instead a fictive radius is assigned to the anion (here, O^{2-}) and the cation's radius is then found by subtracting the anion's fictive radius from the interatomic distance (Shannon, 1976). So by "ionic radius" what is really meant is interatomic distance. Except in geometrically simple, high-symmetry crystal structures like halite, the interatomic distances defining a coordination polyhedron often vary considerably. The M2 site in forsterite, which is probably the site that hosts the REE, like in (Li,Na)$REESiO_4$ olivine (Blasse and Bril 1967) and is the site occupied by similarly sized Ca^{2+} in $CaMgSiO_4$, e.g., Lumpkin and Ribbe 1983) has been identified as an egregious example of a site whose distortion from regular geometry is so profound that it is difficult to parameterize (Dollase 1974). The second problem is specific to the radii of the REE in six-fold coordination (r^{VI}_{REE}), which Eq.(15) would seem to require to best match the relevant cation sites in both forsterite and protoenstatite. The values of $D^{fo/melt}_{REE}$ and $D^{prEn/melt}_{REE}$ are smooth functions of atomic number (Z), as are the more widely used radii in eight-fold coordination from Shannon (1976) to 0.001Å (r^{VIII}_{REE}), but r^{VI}_{REE}, from the same source are not. We take this to be a deficiency in the latter, since there is no conceivable physical explanation for such a difference. The values from Shannon (1976) are essentially those of Shannon and Prewitt (1970) except for La and Pr. The revision to Pr appears anomalous; it may be a typographical error (0.99 for 0.997). Part of the difficulty is that crystal data for the light REE in 6-fold coordination are relatively few. Evans et al. (2008) noticed the lack of smoothness in the values of r^{VI}_{REE}, and allowed their values to vary in their regressions of $D^{fo/melt}_{REE}$ vs. r^{VI}_{REE}, but in so far as their refined values still do not eliminate the lack of smoothness, that approach may have been too conservative.

In summary, the Brice equation and similar equations (e.g., Nagasawa 1966) that actualize the concept of ionic radii are only approximations. For REE mineral/melt partition coefficients, the Brice equation has been useful in identifying aberrant data, and interpolating between measured D_{REE} to obtain partition coefficients for REE that were not measured. Whether it has predictive power is more contentious. For example, Evans et al. (2008) noted that fitting $D_{\mathrm{REE}}^{\mathrm{fo/melt}}$ to the lattice strain model did not predict $D_{\mathrm{Sc}}^{\mathrm{fo/melt}}$ well, which they ascribed to Sc substituting in both the M1 and M2 sites, whereas the REEs may substitute only into M2 (like Ca). Our present results add other possibilities to account for this predictive failure.

Despite the dubious theoretical justification for the Brice equation, Sun and Liang (2013) assumed its validity as the starting point for their parameterization of some experimental determinations of REE olivine/melt partition coefficients. A comparison between $D_{\mathrm{REE}}^{\mathrm{fo/melt}}$ measured in the present study and the predictions from the parameterization of Sun and Liang (2013) is presented in Fig. 10. Most partition coefficients are reproduced to within ± 30%, but there are systematic offsets caused by the flaws in their approach. With increasing $\mathrm{X}_{\mathrm{AlO_{1.5}}}^{\mathrm{melt}}$ the mismatch for the heavy REE and Sc increases, because their parameterization does not account for the competing effects of $\mathrm{X}_{\mathrm{AlO_{1.5}}}^{\mathrm{melt}}$ and $a_{\mathrm{SiO_2}}^{\mathrm{melt}}$, using only $\mathrm{X}_{\mathrm{AlO_{1.5}}}^{\mathrm{melt}}$ as a variable. Moreover, with increasing $\mathrm{X}_{\mathrm{AlO_{1.5}}}^{\mathrm{melt}}$ the mismatch with our data develops a dependence on ionic radius for the heavy REE and Sc because their model assumes a constant *E* parameter for forsterite, in contrast to our observation of a narrower parabola for the $\mathrm{REEMgAlO_4}$ substitution.

Parameterizing mineral/melt partition coefficients of the REEs as a function of their ionic radii is useful for petrological modelling (e.g., O'Neill 2016). Insofar as such parameterizations aim to fit the data as faithfully is possible, there is no compelling need to force them into the form of the Brice equation, or other models that have limited theoretical validity. To emphasise this point, we show that an empirical parameterization that is more faithful to the experimental results may be obtained by avoiding the Brice equation, simply by fitting values of $D_{\mathrm{REE}}^{\mathrm{fo/melt}}$ to polynomials in $r_{\mathrm{REE}}^{\mathrm{VIII}}$. We use $r_{\mathrm{REE}}^{\mathrm{VIII}}$ rather than $r_{\mathrm{REE}}^{\mathrm{VI}}$ in deference to the deficiency in physical reality that the concept of ionic radii has for distorted coordination polyhedra like the M2 site of olivine, and the uncertainty surrounding Shannon's values for $r_{\mathrm{REE}}^{\mathrm{VI}}$. Each set of $D_{\mathrm{REE}}^{\mathrm{fo/melt}}$ values from Evans et al. (2008) and this study (14 sets) was fitted to the orthogonal polynomials of O'Neill (2016):

$$\ln D_{\mathrm{REE}}^{\mathrm{fo/melt}} = \sum_n \delta_n f_{orth}^n \qquad (16a)$$

The advantage of the orthogonal polynomials lies with each term being independent of the others. Hence each term can be fitted to an expression for melt composition, using the insights gained from this study:

$$\delta_n = a_0 + a_{Si}\left(\mathrm{X}^{\mathrm{melt}}_{\mathrm{SiO_2}} - 0.52\right) + a_{Al}\mathrm{X}^{\mathrm{melt}}_{\mathrm{AlO_{1.5}}} + a_{Ca}\mathrm{X}^{\mathrm{melt}}_{\mathrm{CaO}} + a_{Ti}\mathrm{X}^{\mathrm{melt}}_{\mathrm{TiO_2}} \quad (16b)$$

The results of this fit with the orthogonal polynomial truncated at $n = 2$ is shown for comparison with the Sun and Liang model in Fig. 10. Even with only a second order polynomial, much of the systematic error caused by applying the Brice equation is eliminated. Adding in the next term in the orthogonal polynomial ($n = 3$) improves the fit further, but is not warranted given the precision of the data.

The requirements of any parameterization centre around the need to represent data to within their uncertainties as exactly as possible. Because the lattice strain theory due to Brice (1975) is based on simplifying assumptions that cannot be true in detail, it is unrealistic to expect that it would fulfil such an obligation. As shown for the example of REE olivine/melt partition coefficients here, it may generally be expected that better representations of partition data can be achieved without imposing the constraints inherent in the Brice equation. Against the empirical approach is the loss of predictive power for other trivalent cations (e.g., Sc), which can be resolved by using both approaches according to context.

6. Conclusions

The aim of the present study is to demonstrate a general principle that needs to be explicitly acknowledged in parameterizations of trace-element partition coefficients, namely that multiple substitution mechanisms for the same element in the same mineral may occur. Substitution of the REE^{3+} into both forsterite and protoenstatite by a combination of vacancy- and Al-balanced mechanisms are examples of a phenomenon that is likely important elsewhere in trace-element geochemistry. For example, at least three charge balance mechanisms are known for REE in zircon (Burnham and Berry, 2017). We suspect that the operation of multiple mechanisms is probably more the rule than the exception in minerals of interest to igneous petrologists.

For olivine and probably also pyroxenes, additional mechanisms include those where REE^{3+} is coupled with univalent cations ($2Mg^{2+} = M^{+} + REE^{3+}$, where M^{+} is H^{+}, Li^{+} or Na^{+}, e.g. Purton et al., 1997). The hydrous component, $REE\square SiO_4(OH)$, has been demonstrated by Berry et al. (2007.The orthosilicate $LiScSiO_4$ is a stable, olivine-structured endmember of this substitution type (Steele et al. 1978), but $LiREE^{3+}SiO_4$ components are unlikely to be a significant in natural basaltic systems, where the low availability of Li is the limiting factor. Because of the much higher abundance of Na in

basalts, $NaREE^{3+}SiO_4$ may be more significant, albeit offset by the lower compatibility of Na in olivine. The reaction for this would be:

$$\underset{\text{melt}}{REEO_{1.5}} + \underset{\text{melt}}{NaO_{0.5}} + \underset{\text{melt}}{SiO_2} = \underset{\text{olivine}}{NaREESiO_4} \quad (17)$$

and the stoichiometric control indicates $D_{\mathrm{REE}}^{\mathrm{ol/melt}} \propto a_{\mathrm{SiO_2}}^{\mathrm{melt}}$. This putative substitution requires experimental investigation, as does the potential for Na-REE interactions to lead to changes in $\gamma_{\mathrm{REEO_{1.5}}}^{\mathrm{melt}}$ (Michely et al., 2017). For this reason it would be premature to attempt another parameterization of REE olivine/melt partitioning. Whether the substitution $2Mg^{2+} = M^{+} + R^{3+}$ is significant in protoenstatite is unknown; it does not appear to matter in enstatite, at least with Li^{+} as M^{+} (van Kan Parker et al. 2011).

Another conclusion from this study is that unless ways can be found to achieve a satisfactory isolation of variables, it will be difficult to infer substitution mechanisms from mineral/melt partition coefficients reliably. This difficulty may be anticipated to be greater in crystals with more complex stoichiometry and composition than forsterite (i.e., most rock-forming minerals), and independent evidence from spectroscopy and computational studies may be needed. In particular, the slopes of the correlation between mineral/melt partition coefficients and major-element oxide components cannot be used to infer substitution stoichiometries (cf. Lundstrom et al., 1994), because these depend on both the free energy of the partitioning reaction and the activity coefficient of the oxide species in the melt, as well as the stoichiometric control. For example, see Eqn. 14, which summarizes the reasons why the slopes of $D_{\mathrm{REE}}^{\mathrm{fo/melt}}$ versus $X_{\mathrm{AlO_{1.5}}}^{\mathrm{melt}}$ differ among the REEs (Fig. 5), despite the substitution mechanism being identical for all REE.

Apart from the issues of multiple substitution mechanisms and their stoichiometric controls, this study also confirms the finding of Evans et al. (2008) that the activity coefficient of $REEO_{1.5}$ components in silicate melts vary as a function of melt composition, particularly silica content, and this variation differs systematically among the REE as a function of ionic radius. Here we also show that even at constant silica activity other aspects of melt composition can affect $\gamma_{\mathrm{REEO_{1.5}}}^{\mathrm{melt}}$ and hence partitioning, for example the REE-Ti interactions implied by the difference between D_{REE} in the base and high-Ti compositions. Note that factors affecting $\gamma_{\mathrm{REEO_{1.5}}}^{\mathrm{melt}}$ are common to all REE mineral/melt partition coefficients, and need to be included in any parameterization, whatever the mineral.

APPENDIX A. The relationship between concentration and activity for the REE in forsterite

There are two separate issues: one is the relationship between concentration and mole fraction, which in the case of the crystalline phase is needed to evaluate site occupancies hence configurational entropies of mixing; the other is allowing for contributions to the activity that are additional to the

configurational entropy, through activity coefficients. For trace elements, concentrations are simply proportional to mole fractions, and defining activity coefficients in terms of concentrations bypasses the step of explicitly relating concentrations to mole fractions and site occupancies. Thus, in the present example, the activity of the REE^{3+} component, $a^{fo}_{REE_{4/3}SiO_4}$ (Eq. 2), should depend on c^{fo}_{REE} raised to some power that depends on the configurational entropy of mixing, that is, mixing of REE^{3+}, Mg^{2+} and the vacancies on the octahedral sites of forsterite. The experimental observation is that $D^{fo/melt}_{REE}$ is constant over a substantial range of concentrations (Henry's law), implying that $(a^{fo}_{REE_{4/3}SiO_4})^{3/4} = c^{fo}_{REE}\gamma^{fo}_{REE_{4/3}SiO_4}$, while $a^{melt}_{REEO_{1.5}} = c^{melt}_{REE}\gamma^{melt}_{REEO_{1.5}}$, where $\gamma^{fo}_{REE_{4/3}SiO_4}$ and $\gamma^{melt}_{REEO_{1.5}}$ are the activity coefficients defined in terms of concentration with respect to the standard state of infinite dilution. Substituting these relations into Eq. 2 and rearranging gives:

$$D^{fo/melt}_{REE} = K_{(fo,\ vac)}\,(\gamma^{melt}_{REEO_{1.5}}/\gamma^{fo}_{REE_{4/3}SiO_4})(a^{melt}_{SiO_2})^{3/4}$$

$$= \exp\{-\Delta G^{o}_{(fo,\ vac)}/RT\}(\gamma^{melt}_{REEO_{1.5}}/\gamma^{fo}_{REE_{4/3}SiO_4})(a^{melt}_{SiO_2})^{3/4} \quad (680)$$

Similarly, without experiment or the equivalent atomistic calculations, it is ambiguous how $a^{fo}_{REEMgAlO_4}$ (Eq. 5) relates to the concentration of Al in the forsterite, c^{fo}_{Al}. One conceptual possibility is that the configurational entropy of the substitution comes from mixing of REE^{3+} with Mg^{2+} on the octahedral sites happening independently of the mixing of Al^{3+} with Si^{4+} on the tetrahedral sites, in which case $a^{fo}_{REEMgAlO_4} \propto (c^{fo}_{REE}c^{fo}_{Al^{[4]}})$. But experimental evidence indicates a high degree of short-range order between octahedral and tetrahedral Al in forsterite (Evans et al., 2008; Burnham and O'Neill, 2016), suggesting that the charge-balancing of REE^{3+} by tetrahedral Al is also short-range ordered, and hence $a^{fo}_{REEMgAlO_4} \propto c^{fo}_{REE}$ is more likely. With this latter mechanism:

$$D^{fo/melt}_{REE} = K_{(fo,\ Al)}\,(\gamma^{melt}_{REEO_{1.5}}/\gamma^{fo}_{REEMgAlO_4})\,a^{melt}_{AlO_{1.5}}\,(a^{melt}_{SiO_2})^{-1/2}$$

$$= \exp\{-\Delta G^{o}_{(fo,\ Al)}/RT\}(\gamma^{melt}_{REEO_{1.5}}/\gamma^{fo}_{REEMgAlO_4})\,a^{melt}_{AlO_{1.5}}\,(a^{melt}_{SiO_2})^{-1/2}$$

APPENDIX B. Calculation of $\gamma^{melt}_{REEO_{1.5}}$ for the data of Evans et al. (2008)

Values of $D^{fo/melt}_{REE(vac)}$ may be related to those on the fo+prEn cotectic ($D^{fo/melt,\ f+p}_{REE(vac)}$) at the same temperature (≈ 1400 °C) and pressure (1 bar) by:

$$D^{fo/melt}_{REE(vac)} = D^{fo/melt,\ f+p}_{REE(vac)}\,(\gamma^{melt}_{REEO_{1.5}}/\gamma^{melt,\ f+p}_{REEO_{1.5}})(a^{melt}_{SiO_2}/a^{melt,\ f+p}_{SiO_2})^{3/4} \quad (B.1)$$

To apply this relationship to the results of Evans et al. (2008), we make the enabling assumption that $\gamma^{melt}_{SiO_2}$ remains constant (as it did on the forsterite-protoenstatite cotectic), such that $a^{melt}_{SiO_2}/a^{melt,\,f+p}_{SiO_2} \approx X^{melt}_{SiO_2}/X^{melt,\,f+p}_{SiO_2}$. Hence:

$$D^{fo/melt}_{REE(vac)} \approx D^{fo/melt,\,f+p}_{REE(vac)} \left(\gamma^{melt}_{REEO_{1.5}}/\gamma^{melt,\,f+p}_{REEO_{1.5}}\right)\left(X^{melt}_{SiO_2}/X^{melt,\,f+p}_{SiO_2}\right)^{3/4} \quad \text{(B.2)}$$

For the Al-substitution mechanism, we also need to make the analogous enabling assumption that $\gamma^{melt}_{AlO_{1.5}}$ is constant. This allows us to work in terms of $X^{melt}_{AlO_{1.5}}$:

$$D^{fo/melt}_{REE(Al)} \approx \frac{dD^{fo/melt,\,f+p}_{REE(Al)}}{dX^{melt}_{AlO_{1.5}}} X^{melt}_{AlO_{1.5}} \left(\gamma^{melt}_{REEO_{1.5}}/\gamma^{melt,\,f+p}_{REEO_{1.5}}\right)\left(X^{melt}_{SiO_2}/X^{melt,\,f+p}_{SiO_2}\right)^{-1/2} \quad \text{(B.3)}$$

Summing $D^{fo/melt}_{REE(vac)}$ and $D^{fo/melt}_{REE(Al)}$, and rearranging, gives:

$$\gamma^{melt}_{REEO_{1.5}}/\gamma^{melt,\,f+p}_{REEO_{1.5}} \approx D^{fo/melt}_{REE} / \left[D^{fo/melt,\,f+p}_{REE(vac)} \left(X^{melt}_{SiO_2}/X^{melt,\,f+p}_{SiO_2}\right)^{3/4} + \frac{dD^{fo/melt,\,p+f}_{REE(Al)}}{dX_{AlO_{1.5}}} \frac{dD^{fo/melt,\ f+p}_{REE(Al)}}{dX^{melt}_{AlO_{1.5}}} X^{melt}_{AlO_{1.5}} \left(X^{melt}_{SiO_2}/X^{melt,\,f+p}_{SiO_2}\right)^{-1/2}\right] \quad \text{(B.4)}$$

where $X^{melt,\,f+p}_{SiO_2}$ is taken as 0.52.

Figure Captions

Fig. 1 Comparison of protoenstatite/melt and forsterite/melt partition coefficients from the base composition (solid symbols) except where elements were below the detection limit in forsterite: Ti (values from the high-Ti composition), Al (values are averages of the low- and high-Al compositions, with the range shown by the error bar) and Na (protoenstatite D_{Na} is an average of all other compositions; forsterite D_{Na} is from composition AB011 of Burnham and O'Neill, 2016). The 1:1 line is shown for reference.

Fig. 2 A comparison of protoenstatite/melt partition coefficients for the REE and Y in the base and high-Ti compositions, showing La, Ce, Pr and Nd deviating from a linear correlation between the two datasets, inferred to be due to melt contamination (see text for discussion). Errors are 1σ of replicate analyses.

Fig. 3 Dependence of D_{Ca} on X_{CaO} of the melt for protoenstatite (solid symbols) and forsterite (open symbols). Errors are 1σ of replicate analyses.

Fig. 4 Comparison of c^{melt}_{REE} and $D^{fo/melt}_{REE}$ of the high-Al composition of this study with experiment MMC-2 of Di Stefano et al. (2018). The concentrations of the REE vary by over four orders of magnitude between the two experiments but this variation results in negligible deviation from a 1:1 correlation (dashed line), attesting to the validity of Henry's Law.

Fig. 5 Dependence of forsterite/melt partition coefficients on $X^{melt}_{AlO_{1.5}}$ with the linear best fits to the data. Y and Ho have a consistent relationship to each other despite a factor of 150 difference in doping concentrations, suggesting little deviation from Henry's Law. Errors are 1σ of replicate analyses; the data for Y in panel (c) are offset to slightly higher $X^{melt}_{AlO_{1.5}}$ for clarity.

Fig. 6 Mineral/melt partition coefficients for a) forsterite, and b) protoenstatite, split into the separate contributions from the vacancy and Al-coupled mechanisms. The latter are calculated at $X^{melt}_{AlO_{1.5}}$ = 0.15, a typical value for basaltic liquids. The curves are the fits to Eq. 15.

Fig. 7 Calculated $\gamma^{melt}_{MO_{1.5}}/\gamma^{melt,\ f+p}_{MO_{1.5}}$ as a function of $X^{melt}_{SiO_2}$ in CMAS compositions at ~ 1400ºC from Evans et al. (2008) and this study, showing the greater sensitivity to melt composition of the light REE (here exemplified by La) compared to the heavy REE (Lu) and Sc.

Fig. 8 Dependence of protoenstatite/melt partition coefficients on $X^{melt}_{AlO_{1.5}}$ and the linear best fits to the data; unlike for forsterite/melt the dependence on $X^{melt}_{AlO_{1.5}}$ is approximately the same for all trivalent cations.

Fig. 9 Dependence of $D^{fo/melt}_{Zr}$ on $X^{melt}_{AlO_{1.5}}$ for the present study (solid symbols) and Evans et al. (2008). The rate of variation is greater for Zr than a REE of similar incompatibility.

Fig. 10 The ratios of D_{REE} predicted using the model of Sun and Liang (2013) to the results of the present study, as a function of ionic radius (solid circles), for a) the base composition, b) the low-Al composition, c) the high-Al composition and d) the high-Ti composition. For comparison, the fit to an empirical equation (Eqn. 16 in the text) is also shown (open circles).

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