

Closure Temperature and Closure Pressure in Bi-Mineralic Systems
with Applications to REE-in-Two-Mineral Thermobarometers

by

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Introduction

Evolution of the planetary bodies is a dynamic process involving changes in thermal state and chemical composition on global, regional, and grain scales. Thus, understanding these thermochemical responses is fundamental in unraveling the dynamic evolution of the planets. On grain scales, equilibrium exchange of elements and isotope ratios of interest between coexisting minerals is a function of temperature, pressure, and mineral compositions and can be calibrated as thermobarometers to read temperature and pressure records in rock samples. However, chemical zoning is often observed in minerals from rocks that have experienced heating or cooling, which indicates that diffusive exchanges of the chemical species are also important. Dodson (1973) defined the chemical zoning as a closure profile that documents the chemical composition and temperature at the closure time of diffusive exchange with surroundings. He then derived a simple analytical equation relating the closure temperature to diffusion parameters, cooling rate and grain size. One may use Dodson's equation as a geospeedometer to estimate the rate of dynamic processes in a mineral grain given the diffusion data of the element. Yet Dodson's simple equation was derived for a mono-mineralic system with an infinite reservoir, which may not be applicable to major and trace element exchange in multi-mineralic systems. Numerical analysis of diffusive exchange of the elements in bi-mineralic and multi-mineralic systems is thus critical to constrain the temperature, pressure and rate of dynamic processes using geothermobarometers and

geospeedometers. Here I focused on bi-mineralic systems and built a finite difference code to model the diffusive re-distribution of major and trace elements for different thermal histories.

In Chapter 1, I systematically examined Dodson's definition of closure temperature for cooling mono-mineralic and bi-mineralic systems. Numerical simulations were performed to model trace element diffusive redistribution in bi-mineralic systems. Application to REE diffusion in two-pyroxene systems demonstrated that temperatures calculated using the REE-in-two-pyroxene thermometer are essentially the same as the average REE closure temperatures in the two-pyroxene system and practically independent of pyroxene modal abundances in the system. Closure curves were constructed using the closure temperatures of REE and major elements to estimate cooling rates for selected abyssal peridotites; however, the inferred cooling rates may strongly depend on the diffusion parameters.

In Chapter 2, I conducted numerical simulations of REE diffusive exchange between coexisting garnet and clinopyroxene along different P-T paths. The numerical results show that temperatures and pressures derived from the REE-in-garnet-clinopyroxene thermobarometer are equivalent to the average REE closure temperatures and pressures. The temperatures and pressures derived from the REE-in-garnet-clinopyroxene thermobarometer are consistent with the prescribed P-T paths. This

demonstrates that these temperatures and pressures can be used to estimate exhumation or subduction rates of garnet- and clinopyroxene-bearing rocks. The inferred cooling rates and exhumation rates are $10^{-1} - 10^2$ °C/Myr and 0.03 – 45 mm/yr, respectively, for selected garnet peridotites, granulites and eclogites that experienced exhumation. My preliminary calculations also suggest heating rates of 20 ~ 200 °C/Myr and convergence rates of 10 to 100 mm/yr for selected garnet- and clinopyroxene-bearing rocks from subduction environments.

In Chapter 3, I investigated the influence of major elements on REE redistribution among coexisting minerals in spinel peridotites under subsolidus conditions. The widely used thermodynamic software, THERMOCALC was used to constrain the redistribution of major elements in coexisting minerals. During subsolidus cooling, equilibrium redistribution of major elements and REE in the spinel peridotites results in a factor of two increase in heavy REE concentrations of clinopyroxene as temperature decreases from 1300 °C to 800 °C. This confirms that REE re-equilibration can give rise to false garnet signatures in clinopyroxene in abyssal peridotites, as suggested by Sun and Liang (2014). Diffusion modeling of major elements and REE in the two-pyroxene system demonstrates a later closure time of major elements due mainly to their faster diffusion rates. The decoupling in closure time between major elements and REE gives rise to up to $\pm 20^{\circ}\text{C}$ uncertainties in REE closure temperatures calculated using the REE-in-two-pyroxene thermometer

In Chapter 4, I present trace element partitioning experiments and a parameterized lattice strain model for REE partitioning between low-Ca pyroxene and basaltic melts. The model demonstrates that temperature and low-Ca pyroxene composition dominate REE partitioning. The competing effects between temperature and low-Ca pyroxene compositions result in nearly constant REE partition coefficients in orthopyroxene during adiabatic mantle melting when clinopyroxene is present in the system. When clinopyroxene is absent, REE partition coefficients of orthopyroxene vary significantly, indicating that the temperature and compositional dependences need to be considered during geochemical modeling of REE fractionation in clinopyroxene-free harzburgite. In addition, I showed that the low-Ca pyroxene-melt and high-Ca pyroxene-melt (Sun and Liang, 2012) REE partitioning models can reproduce orthopyroxene-clinopyroxene REE partition coefficients measured in well-equilibrated mantle xenoliths.

CHAPTER 1

Closure Temperature in Cooling Bi-Mineralic Systems: I. Definition and with Application to REE-in-Two-Pyroxene Thermometer

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Abstract

Closure temperature is an important concept to many diffusion related problems involving cooling. The basic idea and formulation were outlined in the seminal work of Dodson for cooling mono-mineralic systems. The Dodson's equation has been widely used to calculate closure temperatures for igneous and metamorphic rocks that contain more than one mineral. The purpose of this study is to examine closure temperatures in cooling bi-mineralic systems and to investigate the physical meaning of temperatures calculated using the REE-in-two-pyroxene thermometer. We conduct numerical simulations of diffusive redistribution of trace elements between two coexisting minerals under prescribed cooling using temperature-dependent diffusion coefficients and mineral-mineral partition coefficients. Following Dodson's treatment, the closure temperature in bi-mineralic systems can be defined by the evolution of either average trace element concentrations in the two minerals or their ratio. The latter defines an effective partition coefficient. Closure temperatures calculated based on the two definitions are compared for a range of cooling rates, grain sizes, mineral proportions, and temperature-dependent partition coefficients and diffusion coefficients. Temperatures defined by the effective partition coefficient are recommended. Application to diffusive redistribution of rare earth elements (REE) in orthopyroxene-clinopyroxene systems demonstrates that closure temperature differences among REE are small and hence their average value may be used as the closure temperature for the cooling two-pyroxene system. The average closure

temperature of REE in the two-pyroxene system is essentially the same as the temperature calculated using the REE-in-two-pyroxene thermometer and practically independent of pyroxene modal abundance in the system. Differences in temperatures calculated using the REE- and major element-based two-pyroxene thermometers can be used to infer cooling rate of two-pyroxene bearing mafic and ultramafic rocks.

1. Introduction

Geothermometers have played an important role in the interpretation of thermal history of igneous and metamorphic rocks (e.g., Putirka, 2008 and references therein). In a recent study, Liang et al. (2013) presented a REE-in-two-pyroxene thermometer for mafic and ultramafic rocks. This rare earth element (REE) based thermometer is derived from two independently calibrated lattice strain models for REE partitioning between high-Ca pyroxene and basaltic melt (Sun and Liang, 2012) and between low-Ca pyroxene and basaltic melt (Yao et al., 2012). For well-equilibrated peridotite xenoliths, these authors showed that temperatures calculated by the REE-in-two-pyroxene thermometer and those calculated by major element-based two-pyroxene thermometers are in excellent agreement. However, for abyssal peridotites and mafic cumulates, the temperatures calculated using the REE-in-two-pyroxene thermometer are systematically higher than those calculated using major element-based two pyroxene thermometers (Fig. 1). Liang et al. (2013) attributed the temperature differences to the differences in diffusion rates between trivalent REE and divalent Ca, Mg, and Fe in pyroxene, as closure temperatures for the divalent and trivalent cations are different for a given cooling rate (e.g., Dodson, 1973, 1986). The purposes of the present study are two folds: (1) to determine the physical meaning of the temperature derived from the REE-in-two-pyroxene thermometer (designated as T_{REE}), and (2) to examine the relationship between T_{REE} and the closure temperature of cooling two-pyroxene bearing systems.

The closure temperature of an element in a mineral is the lower temperature limit at which the element effectively stops diffusive exchange with its surrounding medium during cooling. In geochronology, the closure temperature (T_A^c) corresponds to the temperature at the apparent age (t_A^c) of an isotope system in mineral A , and depends on the diffusion rate of the element, mineral grain size, and cooling rate (Dodson, 1973, 1986), viz.,

$$\frac{E_A}{RT_A^c} = \ln \left[\frac{R(T_A^c)^2 D_A^0}{E_A d_A^2 \dot{s}} \right] + G, \quad (1)$$

where E_A and D_A^0 are the activation energy and pre-exponential factor for diffusion of the element of interest in mineral A , respectively; d_A is the effective diffusion radius; $\dot{s}$ is the cooling rate at the closure temperature; R is the gas constant; and G is the closure function. The closure function G “depends upon the geometry of the system, the equilibrium concentration-temperature relationship, and the shape of the cooling curve, and could be determined numerically where an analytical treatment is impossible (i.e., for most realistic systems)” (Dodson, 1986). Ganguly and Tirone (1999) made an important correction for the closure function G in Eq. (1) by adding an extra term to incorporate the effect of initial temperature for large crystals. Recently, Gardés and Montel (2009) and Watson and Cherniak (2013) expanded the Dodson’s equation to more general heating-cooling scenarios. The Dodson’s equation and its modifications have been widely used to study the closure temperature and the thermal evolution of igneous and metamorphic rocks from various tectonic settings. Since these equations are formulated for a single

mineral grain in an infinite reservoir, their application to bi-mineralic and poly-mineralic systems may cause inconsistency in closure temperature, and hence cooling rate calculations. For instance, in a two-pyroxene system we calculated REE closure temperatures in clinopyroxene (cpx) and orthopyroxene (opx) for a grain size of 1 mm and a cooling rate of 20 °C/Myr, using Eq. (1) and the diffusion coefficients of REE in diopside (Van Orman et al., 2001, 2002) and enstatite (Cherniak and Liang, 2007) (Fig. 2a). The calculated REE closure temperatures in cpx and opx can differ by 120 °C (Fig. 2b).

Attempts have been made to investigate closure temperatures for cooling bi-mineralic and poly-mineralic systems (e.g., Lasaga et al., 1977; Onorato et al., 1981; Lasaga, 1983; Eiler et al., 1992; Ehlers and Powell, 1994; Jenkin et al., 1995; Powell and White, 1995). However, the definitions of the closure temperature in these studies are inconsistent. Gilotti (1986) chose the lowest closure temperature of individual phases derived from Dodson's equation as the closure temperature of bi-mineralic and poly-mineralic systems. Jenkin et al. (1995) defined the closure time and hence the closure temperature of the plagioclase-biotite bi-mineralic system through the apparent Sr isochron; however, this approach is limited to radiogenic isotopes. Based on element concentrations in the cores of two adjacent minerals, Ehlers and Powell (1994) calculated an apparent temperature using temperature-dependent exchange coefficients, and defined the invariant apparent temperature as the closure temperature of the bi-mineralic system.

Using results from numerical simulations of diffusive exchange between two minerals, Ehlers and Powell (1994) empirically modified Dodson's equation by including two additional parameters: relative grain size of the two minerals and the effective exchange coefficient. Powell and White (1995) further extended Dodson's equation to bi-mineralic systems by analytically solving the underlying diffusion equations of Ehlers and Powell (1994). In the empirical and analytical equations of Ehlers and Powell (1994) and Powell and White (1995), closure temperatures for bi-mineralic systems depend only on diffusion parameters of the mineral that has a slower diffusion rate for the element of interest. In general, diffusive exchange of an element of interest between two minerals depends on diffusion coefficients and partition coefficients of the element in the two minerals, grain sizes and volume fractions of individual minerals (Lasaga et al., 1977; Onorato et al., 1981; Eiler et al., 1992; Liang, 2014). Thus, one would expect that these factors also affect the closure temperatures of bi-mineralic systems. However, some of these factors are not considered in the aforementioned studies. As will be shown in this study, the closure temperature equations of Ehlers and Powell (1994) and Powell and White (1995) are not applicable to REE redistribution in cooling two-pyroxene bearing systems.

In this study, we follow the basic idea of Dodson (1976) for closure temperature and systematically examine the various definitions of the closure temperature for a trace element in cooling bi-mineralic systems. We use a finite difference model to study

diffusive exchange of a trace element in a bi-mineralic system with temperature-dependent diffusion coefficients and mineral-mineral partition coefficients (Section 3). Motivated by the REE-in-two-pyroxene thermometer of Liang et al. (2013), we then explore diffusive exchange of REE between opx and cpx in a bi-mineralic system using published REE diffusion coefficients and partition coefficients and investigate the physical meaning of the temperature derived from the REE-in-two-pyroxene thermometer (Section 4). We show that temperature calculated by the REE-in-two-pyroxene thermometer is equivalent to the average closure temperature of REE for the cooling opx-cpx system. In Part II of this study, we will further expand the numerical model for REE diffusion by including major element exchange between the two pyroxenes and go on to develop a method that can be used to infer cooling rates of mafic and ultramafic rocks. To setup the stage for this study, we first review the definition of closure temperature for cooling mono-mineralic systems.

2. Closure temperature for cooling mono-mineralic systems

In Dodson's model (1973, 1976, 1986), the temperature (Fig. 3a) and mineral surface concentration (C_A^{rim} ; blue solid line in Fig. 3c) decreases following the prescribed expressions during cooling,

$$\frac{1}{T} = \frac{1}{T_0} + \eta t, \quad (2a)$$

$$C_A^{rim} = C_A^0 + bt, \quad (2b)$$

where T is temperature at a given time t , T_0 is the initial temperature; η is a constant related to the cooling rate; C_A^0 is the initial element concentration and b is a constant. In Dodson's equation (e.g., Eq. 1), closure temperature is independent of C_A^0 and b . Due to diffusive loss, grain-scale mineral composition systematically decreases during cooling and freezes at low temperatures (Fig. 3b). Thus the average (weighted mean) trace element concentration ($\bar{C}$; red solid line in Fig. 3c) across the mineral grain also decreases and approaches to a nearly constant value (green solid line in Fig. 3c). According to Dodson (1973, 1976), a closure temperature (T_A^c ; red circle in Fig. 3a) and closure time (t_A^c ; red circle in Fig. 3c) can be obtained by projecting the asymptotic value of average concentration back to the rim concentration (C_A^{rim}). It is important to note that the rim or surface concentration (blue solid line in Fig. 3c) is not necessarily tangent to the average concentration (red line in Fig. 3c) at $t = 0$. In more general cases, the evolution of C_A^{rim} could be defined by curves representing other choices of boundary conditions or cooling functions. For example, an exponential evolution of the rim concentration ($C_A^{rim'}$; blue dashed line in Fig. 3c) may lead to a different evolution of average concentration ($\bar{C}'$; red dashed line in Fig. 3c) and hence give rise to an earlier closure time ($t_A^{c'}$) and higher closure temperature ($T_A^{c'}$), even though the same amount of changes ($C_A^c - C_A^0$) happened during cooling. As pointed out by Dodson (1986) the closure temperature also depends on “the equilibrium concentration-temperature relationship” at the mineral surface.

The closure temperature defined by Dodson (1973, 1976) and illustrated in Figs. 3a-3c can be easily implemented in numerical simulations of diffusive exchange between a mineral and its surrounding media, a method that we will adopt in the present study. Figure 3d shows one such example (red circles) where closure temperatures of REE in opx derived from numerical experiments are compared with those calculated using Dodson's equation for a plane sheet (Eq. 1). In the numerical experiments, we use REE diffusion coefficients of Cherniak and Liang (2007), and choose the ranges of cooling rates from 1 to 80 °C/Myr and grain sizes from 0.5 to 5 mm, respectively. Without loss of generality, we set $C_A^0 = 1$ and use a small value of $b = -1.5 \times 10^{-3}/\text{Myr}$ that can guarantee positive concentration of C_A^{rim} during cooling in the numerical experiments. We derive the time interval from the given initial and final temperatures and cooling rate, and then calculate η from Eq. (2a). The 1-D diffusion equation is solved using finite difference method and the closure temperatures are calculated following the procedures illustrated in Figs. 3a-3c. The closure temperatures from our numerical simulation agree very well with those calculated using Dodson's equation (red circles; Fig. 3d). Small discrepancies at higher temperatures are mainly due to initial temperature effect on closure temperatures for large grain sizes and fast cooling rates that are not incorporated in Dodson's original equation (e.g., Ganguly and Tirone, 1999). For comparison, we also calculate closure temperatures numerically for the same ranges of cooling rates and grain sizes but using an exponential expression for the rim concentration, i.e.,

$$C_A^{rim} = C_A^0 \cdot \exp\left(\frac{b'}{T}\right) \quad (2c)$$

where b' is a constant. For the purpose of demonstration, we choose a value of -4.3×10^3 for b' , which gives the same amount of change in rim concentration as that from the linear relationship of Eq. (2b) during cooling. As expected, closure temperatures defined by the exponential boundary condition (green circles) are systematically higher than those defined by the linear equation of Dodson's (1973, 1986).

3. Closure temperature of a trace element in cooling bi-mineralic systems

Following the approach of Dodson (1973, 1976), we can define the closure temperature of a trace element in cooling bi-mineralic systems based on the evolution of the average concentration of the trace element in either of the two minerals. Further, we can also obtain a closure temperature based on the evolution of an effective partition coefficient, defined as the ratio of the average concentrations in the two minerals. In this section, we compare closure temperatures based on evolution of the average concentrations in the two minerals and the effective partition coefficient using a diffusive exchange model. Below we first outline the model setup.

3.1. Model setup

The basic model setup is illustrated in Fig. 4a. It is very similar to those of Lasaga et al. (1977), Onorato et al. (1981), Cherniak and Liang (2007, 2012), and Liang (2014)

for diffusive redistribution of a chemical component between two minerals. To focus on the definition of closure temperature for cooling bi-mineralic systems, we consider a simplified problem of a trace element diffusive exchange between two minerals (A and B) in a 1-D geometry subject to prescribed cooling (Eq. 2a). (In supplementary material S1, we also consider diffusive exchange between two spherical minerals.) Initially at temperature T_0 , minerals A and B are in chemical equilibrium, and the concentrations of the trace element in minerals A and B (C_A^0 and C_B^0 , respectively) are related to each other through a mineral-mineral partition coefficient $k_{AB}(T_0)$. During cooling, minerals A and B are out of chemical equilibrium except at their interface where their concentrations are related to each other by a temperature-dependent partition coefficient, k_{AB} ,

$$C_A^0|_{x=0^-} = k_{AB} \cdot C_B^0|_{x=0^+} . \quad (3a)$$

Across mineral A - B interface, the diffusive flux is continuous, viz.,

$$\frac{\phi_A}{d_A} D_A \frac{\partial C_A}{\partial x} \bigg|_{x=0^-} = \frac{\phi_B}{d_B} D_B \frac{\partial C_B}{\partial x} \bigg|_{x=0^+} , \quad (3b)$$

where ϕ_A and ϕ_B are volume fractions of minerals A and B in the bi-mineralic system, respectively; d_A and d_B are the half width or radius of minerals A and B ; D_A and D_B are trace element diffusion coefficients in minerals A and B ; C_A and C_B are trace element concentrations in minerals A and B ; and x represents the position away from the mineral A - B interface ($x = 0$). The partition coefficient k_{AB} takes on the usual form,

$$k_{AB}(T) = k_{AB}^0 \cdot \exp\left(-\frac{\Delta H}{RT}\right), \quad (4)$$

where the pre-exponential factor k_{AB}^0 and exchange enthalpy ΔH are functions of mineral compositions, ionic radius, and possibly pressure. For details regarding governing equations, initial and boundary conditions, numerical method, and assumptions used in the model setup, a reader is referred to the online supplementary material S1. It is worth noting that the partition coefficient (Eq. 4) is an exponential function, which is different from the linear relationship of Dodson (Eq. 2b). Hence a difference in closure temperature between Dodson's and this study is expected (cf. Fig. 3d). A detailed discussion is presented in the supplementary material (Figs. S1-S2).

Model parameters used in this study are as follows. Without loss of generality, we set $C_A^0 = 1$, $C_B^0 = 1/k_{AB}(T_0)$, $T_0 = 1400$ °C, $k_{AB}^0 = 4.5$ and $\Delta H = 7.1 \times 10^4$ J/mol in the simulations reported in this study. The partition coefficient at the onset of cooling $k_{AB}(T_0)$ is then 0.03, which is a typical value for incompatible trace elements such as middle REE between opx and cpx. To examine the effect of partition coefficient on closure temperature, we also chose a smaller value for ΔH ($= 3.6 \times 10^4$ J/mol), which leads to a larger $k_{AB}(T_0)$ ($= 0.34$). To explore the effect of diffusion coefficients in the two minerals on closure temperature, we consider three cases: (a) $D_B = D_A$, (b) $D_B = D_A/5$ and (c) $D_B = 5D_A$. We used the diffusion coefficients of REE in enstatite from Cherniak and Liang (2007) for mineral *A* [i.e., $D_A = 1.2 \times 10^{-7} \exp(-369 \times 10^3/R/T)$ m²/s]. Graphic illustrations of temperature-dependent diffusion coefficients and partition coefficients for the simulations reported in this study can be found in Fig. 5. We use the same grain sizes for mineral *A*

and B ($d_A = d_B$), and conducted 600 simulations in total (100 simulations for each combination of diffusion coefficient and partition coefficient). The 100 simulations cover a range of grain sizes from 0.5 to 5 mm, which are typical values for mantle xenoliths and abyssal peridotites. Cooling rates used in the simulations range from 1 to 80 °C/Myr. In Section 4, we also present simulations with different activation energies for diffusion and cooling rates up to 10^6 °C/Myr (Fig. 1). Details of the parameters used in each simulation are summarized in the online supplementary Table S1. The results of numerical simulations are shown in Figs. 4b, 6-7.

3.2. Model results and discussion

Figure 4b shows an example of the calculated concentration profiles of a trace element across minerals A ($-5 < x < 0$ mm) and B ($0 < x < 5$ mm) for the case of $D_B = D_A$ and the smaller k_{AB} [$k_{AB}(T_0) = 0.03$, Fig. 5b]. The grain size (half width) of this mineral pair is 5 mm and the cooling rate is 35 °C/Myr. During cooling, the trace element diffuses out of mineral A and into mineral B , increasing the concentration in the later (note different scales for C_A and C_B in Fig. 4b). Both concentrations approach closure profiles across the minerals at low temperatures (e.g., when $t > 15$ Myr). It is important to note that the relative changes of trace element concentration in minerals A (C_A) and B (C_B) are quite different during cooling. For example, the relative change at the A - B boundary is ~70% for C_A , but only ~5% for C_B at $t = 20$ Myr. Due to the very small value of k_{AB} ($\leq$

0.03), trace element concentration in mineral A is much smaller than that in mineral B , so that the same amount of mass transfer across A - B interface causes larger relative change in mineral A but much smaller variation in mineral B . Hence mineral A is more sensitive to temperature variation than mineral B so long as $k_{AB} \ll 1$. We will come back to this point in Section 4.

The average concentrations of the trace element across each mineral at a given time were calculated numerically using the trapezoidal rule. Figure 6 displays the evolutions of temperature, average concentrations in minerals A and B , and the effective partition coefficient for three choices of diffusion coefficients ($D_B = D_A$, $D_B = D_A/5$ and $D_B = 5D_A$). Again we used the smaller k_{AB} [$k_{AB}(T_0) = 0.03$], a grain size of 1 mm, and a cooling rate of 20 °C/Myr. The evolutions of rim concentrations are also shown in Fig. 6 (blue dashed lines). Note that the rim concentrations in minerals A and B are curvilinear (rather than straight lines as in Dodson's model) since the partition coefficients vary exponentially with temperature (Eq. 4). Similar to the average concentration in a mono-mineralic system, the average concentrations in mineral A ($\bar{C}_A$) and mineral B ($\bar{C}_B$) and the effective partition coefficient ($\bar{k}_{AB}$) approach asymptotic values ($\bar{C}_A^c$, $\bar{C}_B^c$ and $\bar{k}_{AB}^c$) as temperature decreases. Projecting these asymptotic values to the corresponding rim concentrations or partition coefficient (C_A^{rim} , C_B^{rim} or k_{AB}^{rim}), we obtain the closure times (t_A^c , t_B^c , t_{AB}^k) and closure temperatures (T_A^c , T_B^c , T_{AB}^k) defined by average concentrations or

effective partition coefficient (designated by superscript c or k). Interestingly, the three closure temperatures (or times) do not always agree with each other.

Figures 6a1-6a4 show that the closure times and closure temperatures defined by the three variables ($\bar{C}_A$, $\bar{C}_B$ and $\bar{k}_{AB}$) are identical for the case $D_B = D_A$. However, T_B^c is higher than T_A^c when $D_B < D_A$ (Figs. 6b1-6b3), and T_B^c is lower than T_A^c when $D_B > D_A$ (Fig. 6c1-6c3). It is interesting to note that the closure temperature defined by the effective partition coefficient T_{AB}^k is practically the same as T_A^c for the three choices of diffusion coefficients (Figs. 6a4, 6b4 and 6c4). To further examine the relationships among closure temperatures defined by the three variables, we compare T_A^c , T_B^c and T_{AB}^k from the numerical experiments for a range of cooling rates (1 - 80 °C/Myr) and grain sizes (0.5 - 5 mm) using the smaller k_{AB} . It is evident that T_B^c are the same as T_A^c when $D_A = D_B$. In Figs. 7a and 7c we compare the three closure temperatures for the case of $D_A \neq D_B$: T_B^c are higher than T_A^c when $D_B < D_A$ (Fig. 7a) and lower than T_A^c when $D_B > D_A$ (Fig. 7c). These systematic differences can be attributed to grain size and differences in diffusion rates between the two minerals. For large crystals that experienced fast cooling, the diffusion rate may not be high enough to cause sufficient changes in mineral core compositions. The closure temperatures of such samples are very close to the initial temperature. This explains the curved trends at high temperatures in Figs. 7a and 7c. Regardless of cooling rate, diffusion coefficients, and grain size, T_A^c and T_{AB}^k remain

consistent for the range of parameters explored. This conclusion holds true so long as $k_{AB} \ll 1$.

The difference between T_A^c and T_B^c for cases of different diffusivities in Figs. 6, 7a and 7c indicates that for a given grain size and cooling rate, diffusion rate plays an important role in constraining the closure temperatures defined by the average trace element concentrations in individual minerals. This is consistent with Dodson's model for mono-mineralic systems. However, in bi-mineralic systems diffusive exchange of trace element between the two minerals also depends on the partition coefficient and volume proportions of the two minerals (e.g., Onorato et al., 1981; Liang, 2014). As discussed above, trace element concentration in mineral A is much more sensitive to small changes in temperature than mineral B due to the very small partition coefficient of k_{AB} . This explains the nearly identical values in T_{AB}^k and T_A^c . Conversely, when k_{AB} is much greater than one, the relative variations in the abundance of trace element in mineral B will be more sensitive to temperature, and consequently T_{AB}^k and T_B^c will be the same. When k_{AB} is close to one, both minerals A and B may become important in affecting the effective partition coefficient. This can be further illustrated below.

In Figs. 7b and 7d, we compare T_A^c , T_B^c and T_{AB}^k from the numerical experiments for the case of a larger k_{AB} [$k_{AB}(T_0) = 0.34$, Fig. 5b]. Other parameters are the same as those used in Figs. 7a and 7c, respectively. Because the trace element of interest is still incompatible in mineral A relative to mineral B , the general relationships among T_A^c , T_B^c

and T_{AB}^k in this case (solid blue and red lines) are similar to those for the case of a smaller k_{AB} in Figs. 7a and 7c. The larger k_{AB} , however, reduces the differences in trace element concentration between minerals A and B , and hence the differences between T_B^c and T_A^c when $D_A \neq D_B$. Mineral B now has more influence on the effective partition coefficient than in the case of a smaller k_{AB} . Therefore, small but systematical deviations between T_{AB}^k and T_A^c (< 25 °C for the case of $D_B = D_A/5$, red solid line in Fig. 7b; < 15 °C for the case of $D_B = 5D_A$, red solid line in Fig. 7d) are observed. The values of T_{AB}^k are always between T_B^c and T_A^c (Figs. 7a-7d), indicating that T_{AB}^k encapsulates the effects of diffusion and partitioning in the bi-mineralic system. For this reason and also the REE-in-two-pyroxene thermometer, which will be discussed below, we use the closure temperature defined by the evolution of effective partition coefficients T_{AB}^k as the closure temperature for the cooling bi-mineralic systems.

In Figs. 7b and 7d, we also compare T_A^c , T_B^c and T_{AB}^k from the numerical experiments for the case of a larger k_{AB} [$k_{AB}(T_0) = 0.34$, Fig. 5b] with two other choices of mineral proportions: $\phi_A:\phi_B = 1:9$ (red and blue dashed lines) and $\phi_A:\phi_B = 9:1$ (red and blue dash-dotted lines). The cooling rates, grain sizes, and diffusion coefficients are the same as those used above. Similarly, T_B^c are higher than T_A^c when $D_B < D_A$ (Fig. 7b), and lower than T_A^c when $D_B > D_A$ (Fig. 7d). The closure temperatures of T_{AB}^k are nearly identical to T_A^c when mineral proportion is $\phi_A:\phi_B = 1:9$ (red dashed lines in Figs. 7b and 7d), whereas T_{AB}^k are much closer to T_B^c when modal abundances of mineral B is very

small (i.e., < 10%, dash-dotted lines in Figs. 7b and 7d). These results can be understood in terms of the relative equilibrium abundances of the trace element of interest in minerals A and B , $\phi_A k_{AB}/\phi_B$, and the relative diffusive time scales, $(d_A^2 / D_A^c) / (d_B^2 / D_B^c)$, for the two minerals (see Eq. 17 in Liang, 2014), where D_A^c and D_B^c are diffusion coefficients at the closure temperature. When $\phi_A k_{AB} \gg \phi_B$, mineral A is the larger reservoir for the trace element in the bi-mineralic system. The trace element in mineral B then is more sensitive to temperature change and becomes the major factor in affecting the closure temperature T_{AB}^k (blue dash-dotted line in Fig. 7b). The dominant effect of mineral B is subdued when trace element diffusion rate in mineral B is much faster than that in mineral A (blue dash-dotted line in Fig. 7d). According to the simple analysis of Liang (2014), mineral B is more important in determining the time-scale of diffusive re-equilibration, hence the closure temperature, for a bi-mineralic system than mineral A when

$$\phi_A k_{AB} \frac{d_A^2}{D_A^c} > \phi_B \frac{d_B^2}{D_B^c}. \quad (5)$$

4. Closure temperatures of REE in cooling two-pyroxene systems

Closure temperatures of REE in cooling two-pyroxene systems can be related to the temperature derived from the REE-in-two-pyroxene thermometer (Liang et al., 2013). To better understand the physical meaning of the latter, we apply the numerical model described in Section 3 to the two-pyroxene system for the same ranges of cooling rates

and grain sizes as those used to simulations shown in Fig. 7. In these numerical experiments, we incorporate experimentally determined REE diffusivities in pyroxenes (Van Orman et al., 2001, 2002; Cherniak and Liang, 2007) and the opx-cpx REE partition coefficients (Liang et al., 2013).

Figure 2a displays diffusion coefficients of REE in cpx (Van Orman et al., 2001, 2002) and opx (Cherniak and Liang, 2007) as a function of temperature. REE diffusion coefficients in cpx depend on REE ionic radius, and the diffusion coefficients decrease from Lu to La by one to four orders of magnitude as temperature decreases from 1400 °C to 800 °C. Pressure is set as a constant 1 GPa in the calculation of cpx REE diffusion coefficients of this study. REE diffusion coefficients in enstatite are not sensitive to ionic radii and can be represented by a single Arrhenius equation.

Figure 8 displays the calculated opx-cpx REE partition coefficients using the model of Liang et al. (2013). For purpose of demonstration, we used the major element compositions of cpx and opx in a well-equilibrated spinel lherzolite (sample 314-74 of Ionov et al, 2005). In general, REE are very incompatible in opx relative to cpx, and their compatibilities in opx decrease with the decrease of temperature (Fig. 8). According to our numerical simulations (Section 3.2), the closure temperatures of REE calculated from the opx-cpx effective partition coefficients are expected to be very similar to those derived from the average REE concentrations in opx.

In the numerical simulation of REE diffusion in the two-pyroxene system, differences between closure temperatures defined by the effective partition coefficients (T_{2pyx}^k) and those defined by the average REE concentrations in opx (T_{opx}^c) are indeed very small when modal abundances of opx and cpx are comparable to each other. The maximum difference between T_{2pyx}^k and T_{opx}^c is only ~ 11 °C when $\phi_{opx} = \phi_{cpx}$. As mineral proportion of opx decreases, the temperature differences between T_{2pyx}^k and T_{opx}^c become negligible (< 1.5 °C when $\phi_{opx}:\phi_{cpx} = 1:9$). As opx proportion increases, the differences between T_{2pyx}^k and T_{opx}^c also increase: the maximum is 45 °C for $\phi_{opx}:\phi_{cpx} = 9:1$ and 70°C when $\phi_{opx}:\phi_{cpx} = 98:2$. (For additional results and discussion, see supplementary Figs. S3 and S4). Hence, one can use REE as a group to define a closure temperature for the cooling opx-cpx systems, such as websterites, lherzolites and harzburgites with $\phi_{opx}:\phi_{cpx} < 9:1$. However, when the cpx volume proportion is very low, there might be larger derivations in the two closure temperatures. Again, since REE partition coefficients between opx and cpx vary exponentially with temperature (Fig. 8), opx closure temperatures from numerical experiments (T_{opx}^c) are different from those calculated by the Dodson's equation.

In Fig. 9 we further compare the two-pyroxene REE closure temperature T_{2pyx}^k with opx closure temperatures calculated using the modified Dodson's equation of Ganguly and Tirone (1999, designated as T_{opx}^{GT}). The temperature difference between T_{2pyx}^k and T_{opx}^{GT} is negligible for heavy REE and increases to ~ 25 °C for light REE when

opx and cpx proportions are the same (Fig. 9a). As opx proportion increases, the temperature difference between T_{2pyx}^k and T_{opx}^{GT} also increases: the maximum difference is ~ 50 °C for $\phi_{opx}:\phi_{cpx} = 9:1$ (from -30 °C for heavy REE to 50 °C for light REE in Fig. 9b), and ~ 70 °C for $\phi_{opx}:\phi_{cpx} = 98:2$ (from -70 °C for heavy REE to 65 °C for light REE Fig. 9c). Hence to a good approximation, one can use T_{opx}^{GT} to represent the closure temperature for middle REE or the average closure temperature for all the 14 REE in cooling two-pyroxene systems. However, large difference exists between T_{opx}^{GT} and closure temperature for light or heavy REE derived from the numerical simulation, especially when cpx proportion is very low in the two-pyroxene system (Fig. 9c). As cpx proportion is much higher than opx (e.g., $\phi_{opx}:\phi_{cpx} = 1:9$), the two-pyroxene closure temperatures T_{2pyx}^k are higher than T_{opx}^{GT} for all the REE. Since T_{2pyx}^k are practically identical to T_{opx}^c in the numerical simulations, the difference between T_{2pyx}^k and T_{opx}^{GT} is mainly due to the difference in the equilibrium concentration-temperature relationship at the mineral surface (cf. Fig. 3c).

REE concentrations in opx and cpx obtained from the numerical simulations can also be used to calculate temperatures for the two-pyroxene systems using the REE-in-two-pyroxene thermometer of Liang et al. (2013). The temperature inversion was based on the average REE concentrations in the two pyroxenes after establishment of the closure profiles (see Fig. S5 for details). In Figs. 10a and 10b, we compare the temperatures inverted by the REE-in-two-pyroxene thermometer (T_{REE}) with the average

REE closure temperatures defined by the effective partition coefficients of REE between opx and cpx ($\bar{T}_{2pyx}^k$) for both 1-D planar and 3-D spherical geometries. Overall, the differences between T_{REE} and $\bar{T}_{2pyx}^k$ are less than 5°C when $\phi_{\text{opx}}:\phi_{\text{cpx}} = 1:1$, less than 13 °C when $\phi_{\text{opx}}:\phi_{\text{cpx}} = 9:1$, and less than 17 °C when $\phi_{\text{opx}}:\phi_{\text{cpx}} = 98:2$. Figure 10c shows that the maximum difference in T_{REE} for different pyroxene proportions ($\phi_{\text{opx}}:\phi_{\text{cpx}}$) is generally less than $\pm 25^\circ\text{C}$ unless the cpx abundance is extremely low (i.e., $\phi_{\text{opx}}:\phi_{\text{cpx}} > 99:1$, Fig. S6). Hence temperatures calculated using the REE-in-two-pyroxene thermometer are essentially the same as the average closure temperatures of REE in the cooling two-pyroxene systems, and not very sensitive to pyroxene modal abundances.

Since closure temperature depends on the product of the cooling rate and the square of effective grain size (cf. $d^2\dot{s}$ in Eq. 1), the product, $d^2\dot{s}$, is eliminated in the temperature vs. temperature correlation diagram for two elements in the same mineral, defining a “closure curve” for the two elements. Dygert and Liang (2015) compared closure temperatures of REE in opx with closure temperatures for Ca-Fe-Mg diffusion in pyroxenes calculated using the formulation of Ganguly and Tirone (1999) and discussed their implications for cooling rates of ophiolitic and abyssal peridotites. In Fig. 1 we compare T_{REE} derived from the numerical simulations of this study with closure temperatures for Fe-Mg diffusion in pyroxenes (designated as $T_{\text{Fe-Mg}}$) calculated using the formulation of Ganguly and Tirone (1999) for a range of initial temperatures (1100-1400 °C), two choices of $\phi_{\text{opx}}:\phi_{\text{cpx}}$ (1:1, red solid curves; 98:2, blue dashed lines), and two

choices of Fe-Mg diffusion data. $T_{\text{Fe-Mg}}$ are calculated using the Fe-Mg interdiffusion coefficients in cpx from Dimanov and Wiedenbeck (2006) and Müller et al. (2013) in Figs. 1a and 1b, respectively. For purpose of illustration, contours of cooling rates for an effective grain size of 2 mm are shown as black dots connected by thin dashed black lines. As shown in Fig. 1, closure curves are very sensitive to the choice of Fe-Mg diffusion data but practically independent of pyroxene modal abundances. For an effective grain size of 2 mm, the inferred cooling rates for abyssal peridotites can differ by up to two orders of magnitudes (10^2 to 10^6 °C/Myr vs. 10 - 10^4 °C/Myr) due to the different choices of Fe-Mg diffusion coefficients. Nonetheless, the ranges of cooling rates are comparable to those of Oman ophiolites (10^{-1} to 10^5 °C/Myr) independently estimated based on Ca diffusion in olivine (Coogan et al., 2002; VanTongeren et al., 2008). The cooling curves in Fig. 1 also help to explain the observation made by Dygert and Liang (2015) that T_{REE} is not correlated with cpx abundance in ophiolitic peridotites from around the world (78 samples from 15 localities).

The preceding example demonstrated the potential advantage of the REE-in-two-pyroxene thermometer: It can be used as a geospeedometer when combined with the two-pyroxene thermometer of Brey and Köhler (1990). For purpose of demonstration, we used closure temperatures of Fe-Mg diffusion in cpx as proxies for T_{BKN} (additional examples with Fe-Mg diffusion in opx were presented in Dygert and Liang, 2015). To further quantify this new geospeedometry, one has to assess closure temperature of the

two-pyroxene thermometer of Brey and Köhler (1990). In a companion study, we will pursue this problem by considering diffusive exchange of major elements between opx and cpx and by coupling REE diffusion with major element diffusion in the pyroxenes.

5. Summary and further discussion

It is important to reiterate that both the closure temperature for REE in the cooling two-pyroxene system and the REE-in-two-pyroxene temperature are derived from effective partitioning coefficients of REE between opx and cpx using average mineral compositions. This is very similar to the treatment of Ehlers and Powell (1994) and Powell and White (1995), who defined a closure temperature for bi-mineralic system using an effective exchange coefficient calculated according to mineral core compositions. The exchange coefficients for two substituting cations are especially useful for major elements (e.g., Fe and Mg exchange between clinopyroxene and garnet). According to the analytical solution of Powell and White (1995), grain size (d_A), the diffusion parameters (D_A^0 and E_A) of the slower diffusing phase (say mineral A), cooling rate ($\dot{s}$), initial element concentrations in the two minerals, and the relative grain size collectively determine the closure temperature for the bi-mineralic system. Here we use the equation of Powell and White (1995) to calculate the REE closure temperatures in the two-pyroxene system for selected grain sizes and cooling rates (red: $d_{\text{opx}} = 0.5$ mm, $\dot{s} = 1$ °C/Myr; green: $d_{\text{opx}} = 2.5$ mm, $\dot{s} = 9$ °C/Myr; blue: $d_{\text{opx}} = 5$ mm, $\dot{s} = 80$ °C/Myr), and

compare them with the numerical results in Fig. 11. For simplicity, we set $d_{\text{cpx}} = d_{\text{opx}}$ and use the same diffusion parameters as in our simulations (Fig. 2a, Van Orman et al., 2001, 2002; Cherniak and Liang, 2007). In the 1-D model of Powell and White (1995), the ratio of mineral grain sizes between A and B was taken as the same as the ratio of mineral volume fraction. This, however, is only valid when the grain numbers of the two minerals are the same. In our formulation, we treat mineral grain size and volume fraction as two independent variables (e.g., Eqs. 3b). To compare with the results of Powell and White (1995), we set $\phi_{\text{opx}} = \phi_{\text{cpx}}$ in the examples below.

Since La, Ce, Nd and Sm diffuse slower in cpx than in opx (Fig. 2a), D_0 and E in cpx are used to calculate the closure temperature from La to Sm. Closure temperatures of Dy, Er and Yb are calculated using D_0 and E for opx. It is apparent that large differences (50-400 °C) exist between closure temperatures calculated using the model of present study (Eqs. S1a-S1h) and those calculated using the equation of Powell and White (1995) for elements La to Sm, and relatively small temperature differences (5-30 °C) are observed for elements Dy to Yb (Fig. 11). As grain size and cooling rate increase, the temperature difference becomes larger. In addition, the temperature differences from La to Yb are also distinct for the same grain size and cooling rate (e.g., 20-240 for grain size 0.5 mm and cooling rate 1 °C/Myr). The large variations of the temperature difference between these two studies are mainly caused by the simplifications in the model of Powell and White (1995). This indicates that Powell and White's model may not be

applicable to the calculation of closure temperature of a trace element, especially when its partition coefficient between the minerals A and B is (much) smaller than one and its diffusion rate in mineral B is slower than in mineral A .

To investigate the physical meaning of temperature calculated using the REE-in-two-pyroxene thermometer, we systematically examined various definitions of the closure temperature in cooling bi-mineralic systems following Dodson's original idea. For simplicity, we used a 1-D diffusive re-equilibration model with temperature-dependent partition coefficients and diffusion coefficients, and considered cases in which grain sizes of the two minerals are the same. In general, (average) grain sizes of the two minerals are different and grain shape is often treated as sphere in many diffusion related studies. Nonetheless, difference in grain size between the two minerals will not affect the conclusions drawn from the equal grain size simulations because the diffusion time scales with grain size and diffusivity, viz. d^2/D . This can be further demonstrated by two sets of simulations for diffusive re-equilibration between opx and cpx: one with $d_{\text{opx}} = 0.5d_{\text{cpx}}$ and the other with $d_{\text{opx}} = 2d_{\text{cpx}}$. Again, for simplicity we set mineral proportions of opx and cpx the same. As shown in supplementary Figs. S7-S8, the average REE closure temperatures based on the effective partition coefficients ($\bar{T}_{2\text{pyx}}^k$) and opx concentrations ($\bar{T}_{\text{opx}}^c$) are within 7 °C of temperatures derived from the REE-in-two-pyroxene temperatures for the two choices of grain size.

Figure 10 shows that the closure temperatures of REE in the opx-cpx bi-mineralic systems ($\overline{T}_{2_{pyx}}^k$) are also nearly identical to T_{REE} that derived from the REE-in-two-pyroxene thermometer using the 3-D spherical geometry for the two minerals (see also Fig. S9 for further comparison between T_{REE} and $\overline{T}_{2_{pyx}}^k$ for 3-D spherical simulations), so that conclusions drawn from the simulations with 1-D plane sheet also hold for 3-D spherical geometry. A further comparison of T_{REE} between 1-D and 3-D systems (Fig. S10a) shows that the temperature differences between the two geometries are 60-100 °C, which is consistent with the temperature difference for mono-mineralic systems (Fig. S10b) based on the Dodson's equation. The temperature differences indicate that mineral geometry is another important factor that can affect the value of T_{REE} .

Following Dodson (1973, 1976), we defined closure temperatures based on average or mean concentrations of the two minerals. It is possible to define closure temperatures based on mineral core concentrations for the cooling bi-mineral system (e.g., Ehlers and Powell, 1994). Closure temperatures calculated from the core concentrations should be systematically higher than those derived from the average mineral concentrations for systems experienced cooling. For the opx-cpx bi-mineralic system, this is indeed the case for REE: the former are 39-55°C higher than the latter (supplementary Fig. S11, $\phi_{\text{opx}}:\phi_{\text{cpx}} = 1:1$). In many practical applications, trace element abundances in a mineral grain are often measured at a few selected points (e.g., core, rim and a point in the middle). Average concentrations for the mineral grain can be derived from the three

points either by parabolic interpolation or numerical integration using the trapezoidal rule. A comparison of closure temperatures based on the 3-point average and the average concentrations shows that the former are 2-15°C lower than the latter (see also Fig. S11), which is within the range of uncertainties of the REE-in-two-pyroxene thermometer ($\pm 20\sim 50^\circ\text{C}$, Liang et al., 2013). The main conclusions of this study maybe summarized as follows:

1. Based on Dodson's concept (1976), closure temperature of a trace element in cooling bi-mineralic systems can be defined through (1) the evolution of average trace element concentrations in the two minerals, and (2) the evolution of the effective partition coefficient between the two minerals. We recommend the use of closure temperature defined by the effective partition coefficient for cooling bi-mineralic systems.

2. Results from numerical simulations demonstrate that closure temperatures defined by the effective partition coefficient are dominated by the mineral, in which the trace element is more incompatible in terms of mineral-mineral partitioning, less abundant, and has a slower diffusion rate. The mineral in which trace element is relatively compatible plays an important role in affecting effective partition coefficient as its volume proportion is very small and mineral-mineral partition coefficients increase.

3. Small but systematical differences exist in the closure temperatures between mono- and bi-mineralic systems, due to the equilibrium concentration-

temperature relationship at the mineral surface. As the partition coefficient decreases, the differences in closure temperature between mono- and bi-mineralic systems increase.

4. Application of the trace element diffusion model for bi-mineralic systems to REE diffusion between opx and cpx shows that REE have similar closure temperatures in most of the two-pyroxene systems, so that one can use REE as a group to define the closure temperature for cooling two-pyroxene systems. Temperatures derived from the REE-in-two-pyroxene thermometer are essentially the same as the average REE closure temperatures in the two-pyroxene systems and not very sensitive to pyroxene modal abundances. Given closure temperatures of major elements in the two pyroxenes, it is possible to infer cooling rates of mafic and ultramafic rocks based on temperature differences between the REE- and major element-based two-pyroxene thermometers.

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Figure Captions

Figure 1-1 Comparison between temperatures calculated using the REE-in-two-pyroxene thermometer of Liang et al. (2013, designated as T_{REE}) and those calculated using the two-pyroxene thermometer of Brey and Köhler (1990, T_{BKN}) for well-equilibrated mantle xenoliths (grey triangles) and abyssal peridotites (yellow dots). (a) Closure curves based on diffusive exchange of REE between orthopyroxene and clinopyroxene from this study and the closure temperature formulation of Ganguly and Tirone (1999) for Fe-Mg interdiffusion in clinopyroxene using data from Dimanov and Wiedenbeck (2006), all in spherical geometry. (b) Same as (a) except with Fe-Mg interdiffusion coefficients in clinopyroxene from Müller et al. (2013). Red solid lines represent orthopyroxene and clinopyroxene volume proportions $\phi_{\text{opx}}:\phi_{\text{cpx}} = 1:1$; blue dashed lines represent $\phi_{\text{opx}}:\phi_{\text{cpx}} = 98:2$. Initial temperatures (T_0) used in the model of Ganguly and Tirone (1999) are listed on the right of the grey 1:1 line. The black dots connected by thin dashed black lines are cooling rates (in $^{\circ}\text{C}/\text{Myr}$) for a grain size of 2 mm indicated by the numbers above. The data sources for well-equilibrated mantle xenoliths and abyssal peridotites are the same with those listed in Liang et al. (2013). A pressure of 1.5 GPa is assumed for the mantle xenoliths and 1.0 GPa for the abyssal peridotites in the two-pyroxene thermometer of Brey and Köhler (1990).

Figure 1-2 (a) Arrhenius plot showing variations of REE diffusion coefficients in enstatite (D_{opx}^{REE} , Cherniak and Liang, 2007) and diopside (D_{cpx}^{REE} , Van Orman et al., 2001, 2002). Pressure is set as a constant 1 GPa in the calculation of cpx REE diffusion coefficients. (b) Closure temperatures of REE in orthopyroxene (opx) and clinopyroxene (cpx) based on the Dodson's equation for plane sheet geometry. The grain sizes of opx and cpx are 1 mm, and the cooling rate is 20 °C/Myr. Parameters for REE diffusion (D_0 and E) in opx (enstatite) and cpx (diopside) are from the studies listed above.

Figure 1-3 Definition of closure temperature for a trace element in cooling mono-mineralic systems according to Dodson (1973, 1976). (a) Cooling path defined by Eq. (2a). (b) Evolution of the trace element concentration across the mineral during cooling. (c) Evolution of the rim (blue solid line, C_A^{rim} , linear) and average (red solid line, $\bar{C}$) concentrations of the trace element during cooling. Green line denotes asymptotic value of the average concentration (C_A^c), and the intercept of the green and blue dashed lines (red circle) represents the projection of constant average concentration to the rim concentration, which corresponds to the closure time (t_A^c) and closure temperature (T_A^c). For comparison, an exponential evolution of the rim concentration ($C_A^{rim'}$, blue dashed line,) and the corresponding average trace element concentration ($\bar{C}'$, red dashed line) are also shown. During cooling, $\bar{C}'$ experienced the same amount of variation with $\bar{C}$, so that green solid line also intercept $C_A^{rim'}$ at the magenta circle, which corresponds to the

closure time ($t_A^{c'}$; magenta circle in c) and closure temperature ($T_A^{c'}$; magenta circle in a). (d) Comparison between the closure temperatures defined by the numerical simulation and Dodson's formulation (Eq. 1), for a range of grain sizes (0.5 - 5 mm) and cooling rates (1 - 80 °C/Ma). Red circles are based on the linear boundary condition; green circles are based on the exponential boundary condition.

Figure 1-4 Diffusive re-equilibration between two minerals in a plane-sheet geometry: (a) model setup; (b) an example of calculated diffusing profiles in the two minerals at six selected times (note different scales in concentration in the two minerals). Grain sizes of the two minerals are 5 mm, and the cooling rate is 35 °C/Myr. See text for details.

Figure 1-5 Diffusion coefficients (a) and partition coefficients (b) used in the numerical simulation reported in Figs. 4, 6, 7 and supplementary Figs. S1-S2.

Figure 1-6 Definitions of closure temperature of a trace element in cooling bi-mineralic systems. (a1-a4) Case of $D_B = D_A$. (b1-b4) Case of $D_B = D_A/5$. (c1-c4) Case of $D_B = 5D_A$. Parameters used in these examples are grain size of 1 mm, cooling rate of 20 °C/Ma and partition coefficients with $k_{AB}(T_0) = 0.03$, (magenta circles, Fig. 5b). (a1)-(c1) The same prescribed cooling defined by Eq. (1). (a2)-(c2) Evolution of the rim (blue dashed lines, C_A^{rim}) and average (red lines, $\bar{C}_A$) concentrations of a trace element in mineral A. (a3)-

(c3) same as (a2)-(c2) but for mineral B. (a4)-(c4) Same as (a2)-(c2) but for the effective partition coefficient between minerals A and B. The intercepts (red circles) of the blue dashed line and the green line in (a2) to (c4) are projections of asymptotic values of the average trace element concentrations in minerals A and B or the effective partition coefficient to their rim values, which correspond to closure temperatures (T_A^c , T_B^c and T_{AB}^k , in a1-c1) and closure time (t_A^c in a2-c2, t_B^c in a3-c3, and t_{AB}^k in a4-c4).

Figure 1-7 Comparison of closure temperatures defined by the trace element concentrations (T_A^c for mineral A, T_B^c for mineral B) and the effective partition coefficients (T_{AB}^k) for different partition coefficients, diffusion coefficients and mineral proportions. The closure temperatures are for a set of grain sizes (0.5 to 5 mm), cooling rates (1 to 80 °C/Myr), and mineral proportions ($\phi_A:\phi_B = 1:1, 1:9$ and $9:1$). See text for discussion.

Figure 1-8 Variation of orthopyroxene and clinopyroxene REE partition coefficients ($k_{opx-cpx}^{REE}$) as a function of temperature based on the model of Liang et al. (2013).

Figure 1-9 Comparison of REE closure temperatures defined by effective partition coefficients between opx and cpx (T_{2pyx}^k) with the REE closure temperatures in opx calculated by the equation of Ganguly and Tirone (1999) (T_{opx}^{GT}) for four choices of

mineral proportions: (a), $\phi_{\text{opx}} : \phi_{\text{cpx}} = 1:1$; (b), $\phi_{\text{opx}} : \phi_{\text{cpx}} = 9:1$; (c), $\phi_{\text{opx}} : \phi_{\text{cpx}} = 98:2$; (d), $\phi_{\text{opx}} : \phi_{\text{cpx}} = 1:9$. The ranges of grain sizes and cooling rates are the same as those in Fig. 7. See text for discussion.

Figure 1-10 Comparison between temperatures calculated using REE-in-two-pyroxene thermometer (T_{REE}) and the average REE closure temperatures defined by their effective partition coefficient between opx and cpx ($\bar{T}_{2\text{pyx}}^k$) for 1-D plane sheet (a) and 3-D spherical geometry (b) and the differences in T_{REE} for different pyroxene abundances (c). Three choices of mineral proportions are shown as: $\phi_{\text{opx}} : \phi_{\text{cpx}} = 1:1$ (red circles); $\phi_{\text{opx}} : \phi_{\text{cpx}} = 9:1$ (green squares); $\phi_{\text{opx}} : \phi_{\text{cpx}} = 98:2$ (blue diamonds) in (a) and (b). $(\Delta T_{\text{REE}})_{\phi_{\text{opx}} : \phi_{\text{cpx}}}$ in (c) represents the temperature differences between T_{REE} for different mineral proportions (red for $\phi_{\text{opx}} : \phi_{\text{cpx}} = 9:1$; blue for $\phi_{\text{opx}} : \phi_{\text{cpx}} = 98:2$) with T_{REE} for $\phi_{\text{opx}} : \phi_{\text{cpx}} = 1:1$ of 1-D (solid lines) and 3-D (dashed lines) geometries. T_{REE} are calculated using the REE-in-two-pyroxene thermometer and the average concentrations of REE in two pyroxenes after the establishment of the closure profiles (for details, see supplementary Fig. S5). The ranges of grain sizes and cooling rates are the same as those in Fig. 7.

Figure 1-11 Comparison between closure temperatures of REE from this study and those calculated using the closure temperature model of Powell and White (1995) for cooling bi-mineralic systems. Grain sizes of two pyroxenes are the same. Diffusion coefficients

from Van Orman et al. (2002) and Cherniak and Liang (2007) are used for calculation.

Red dots represent grain size of 0.5 mm and cooling rate of 1 °C/Myr; green dots represent grain size of 2.5mm and cooling rate of 9 °C/Myr; blue dots of 5 mm and cooling rate of 80 °C/Myr.

Figures

Figure 1-1

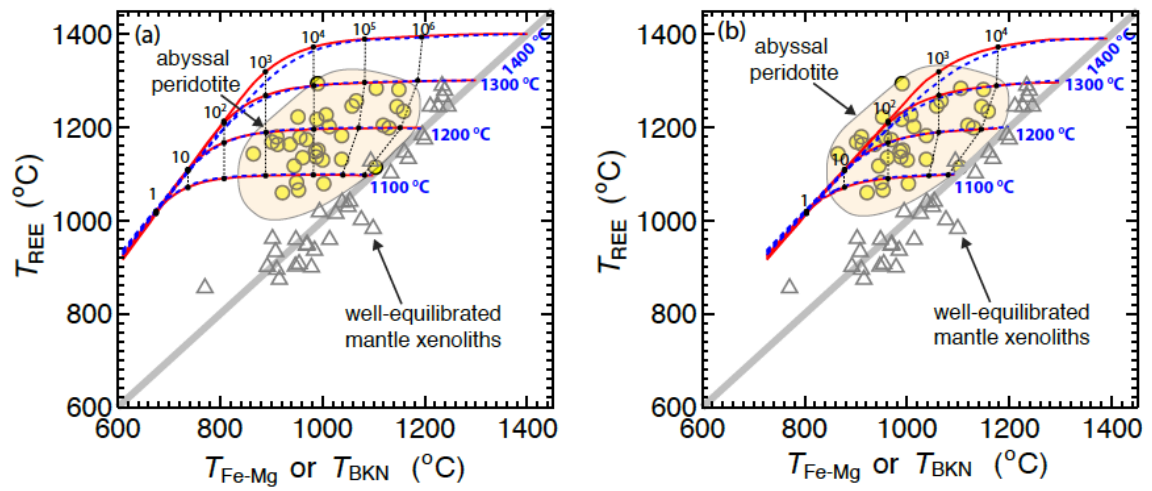


Figure 1-2

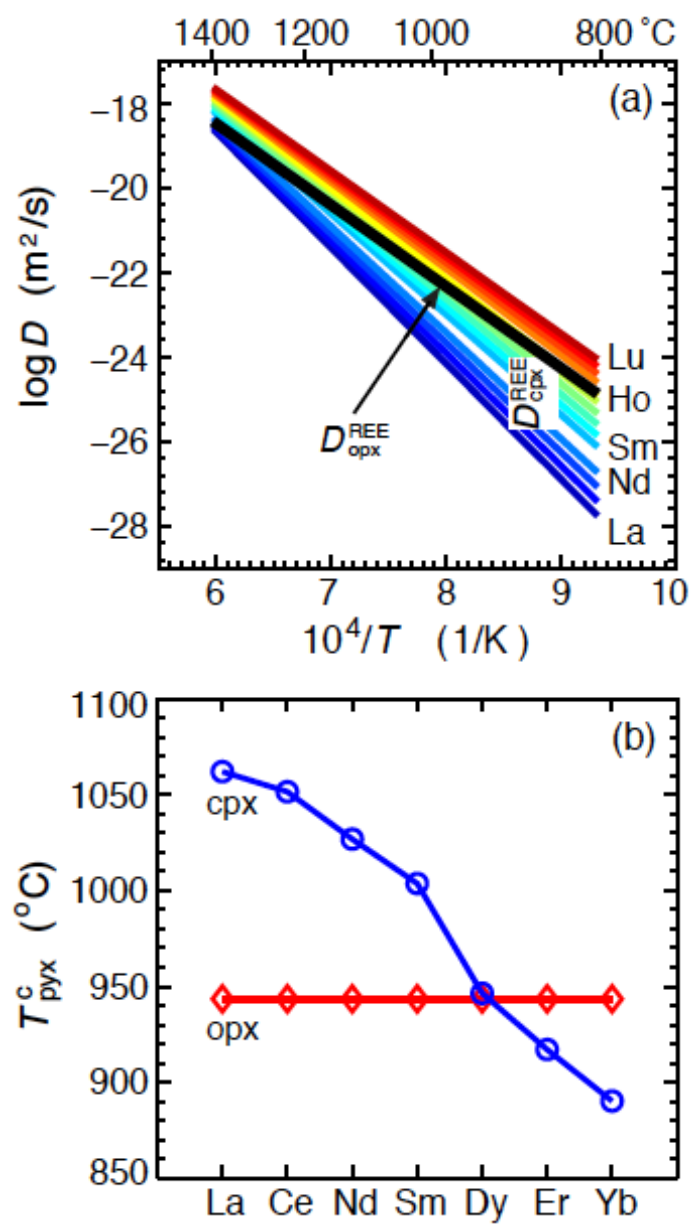


Figure 1-3

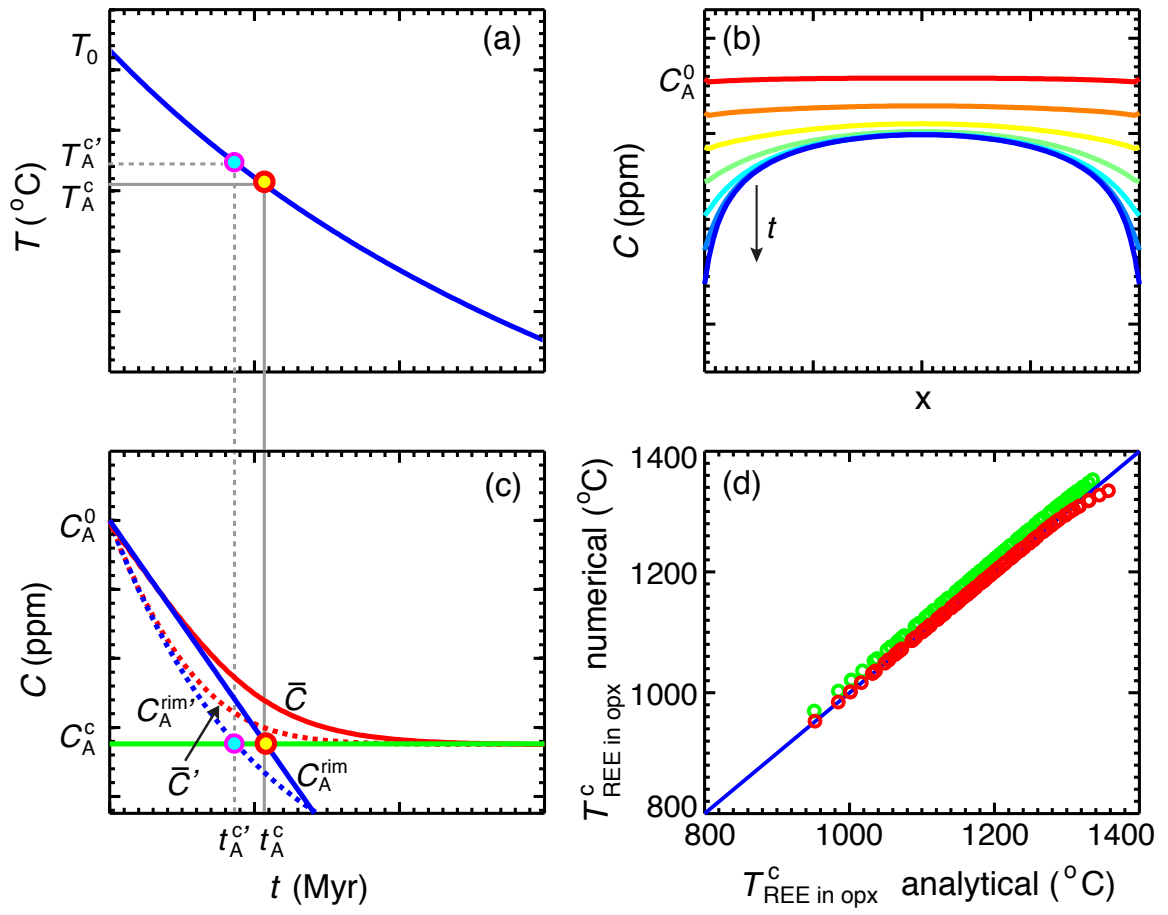


Figure 1-4

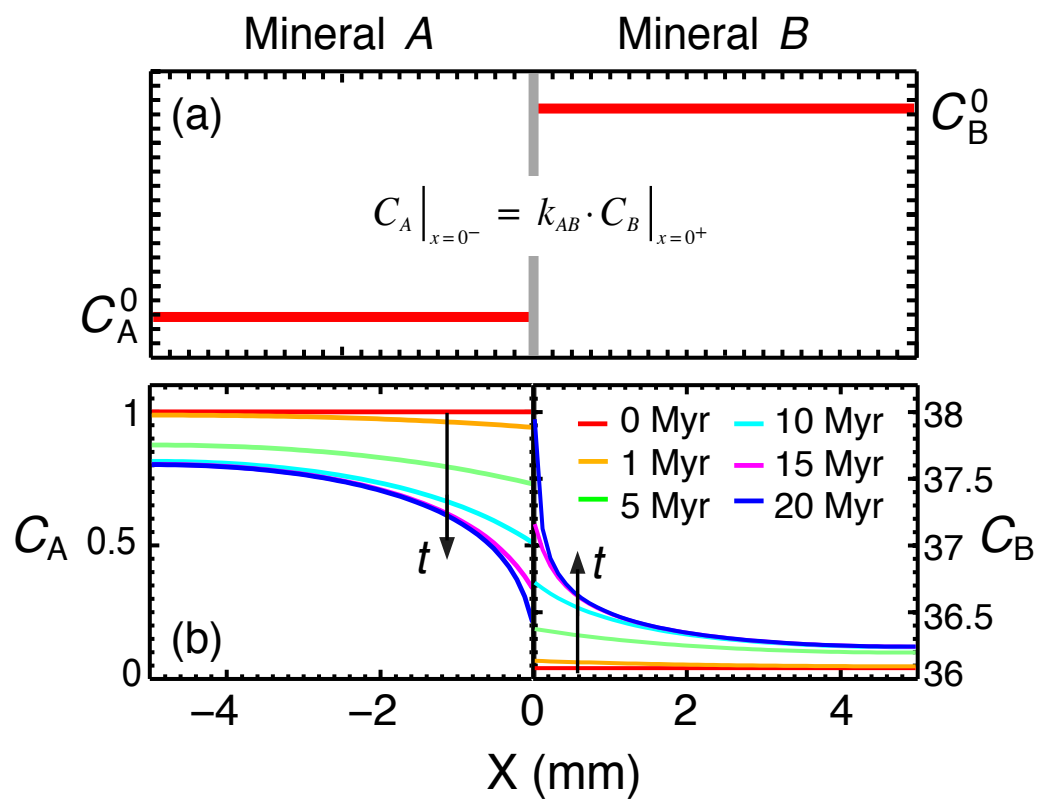


Figure 1-5

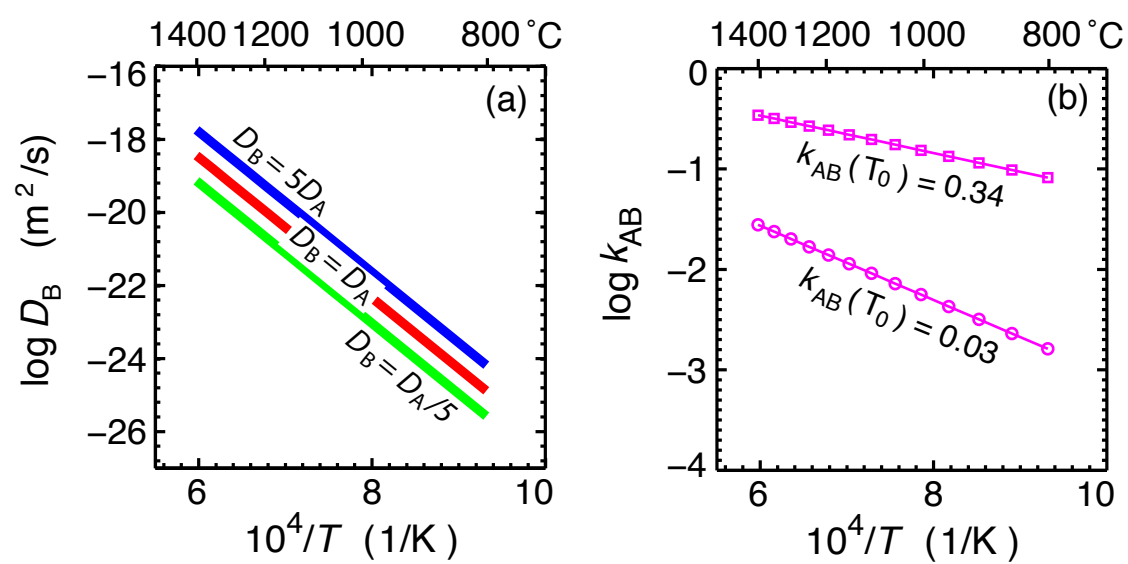


Figure 1-6

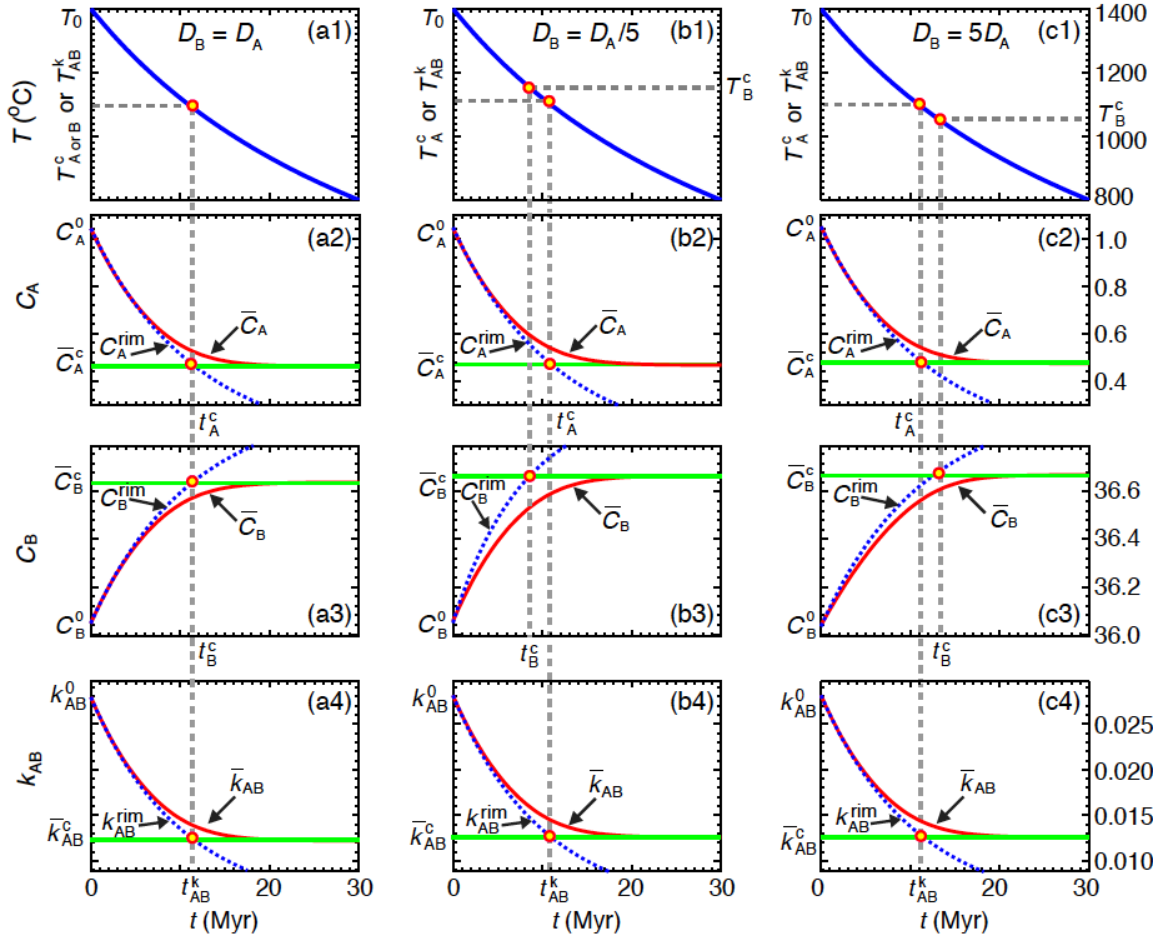


Figure 1-7

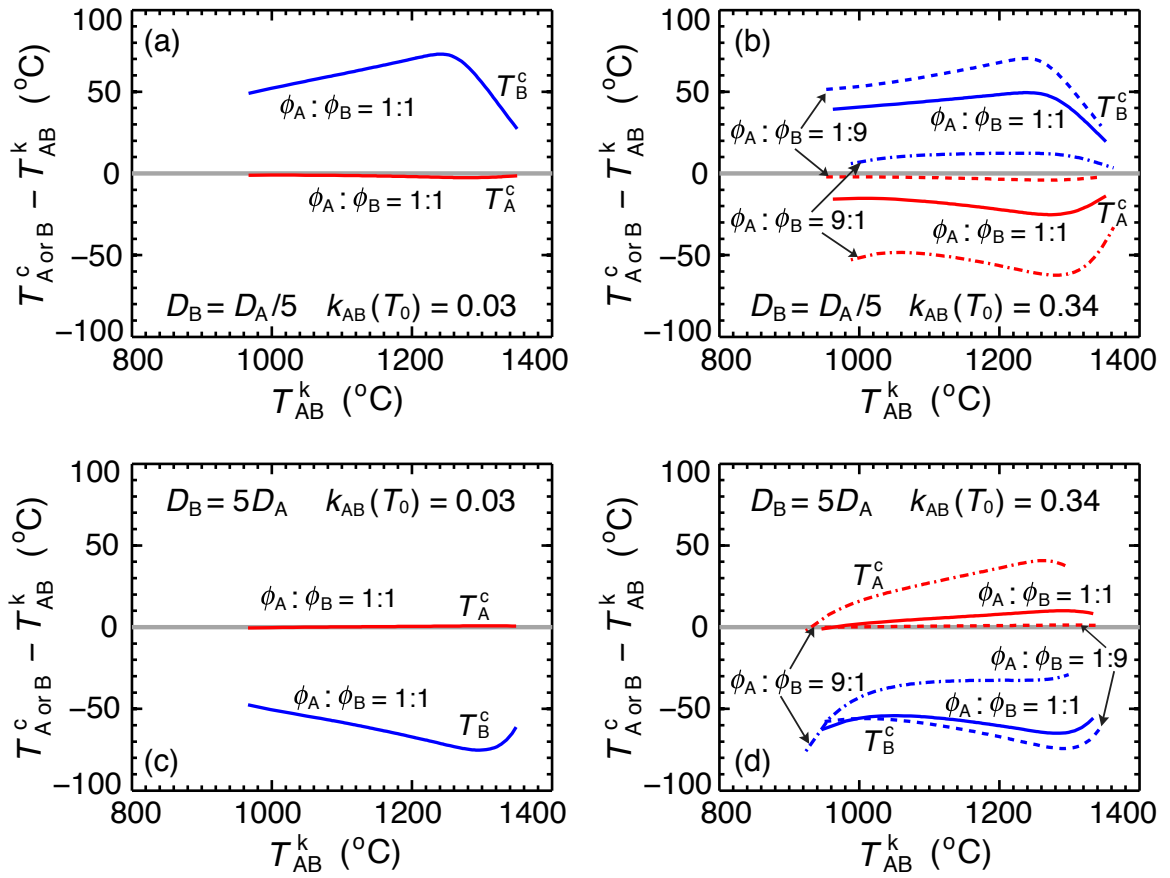


Figure 1-8

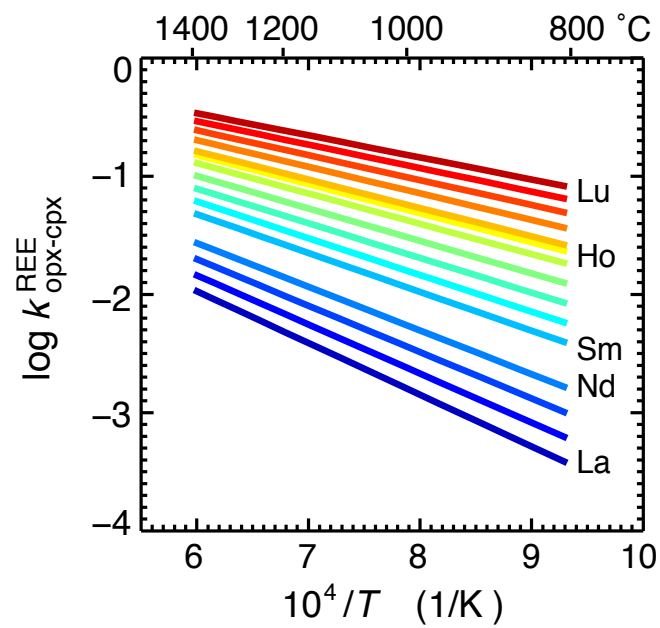


Figure 1-9

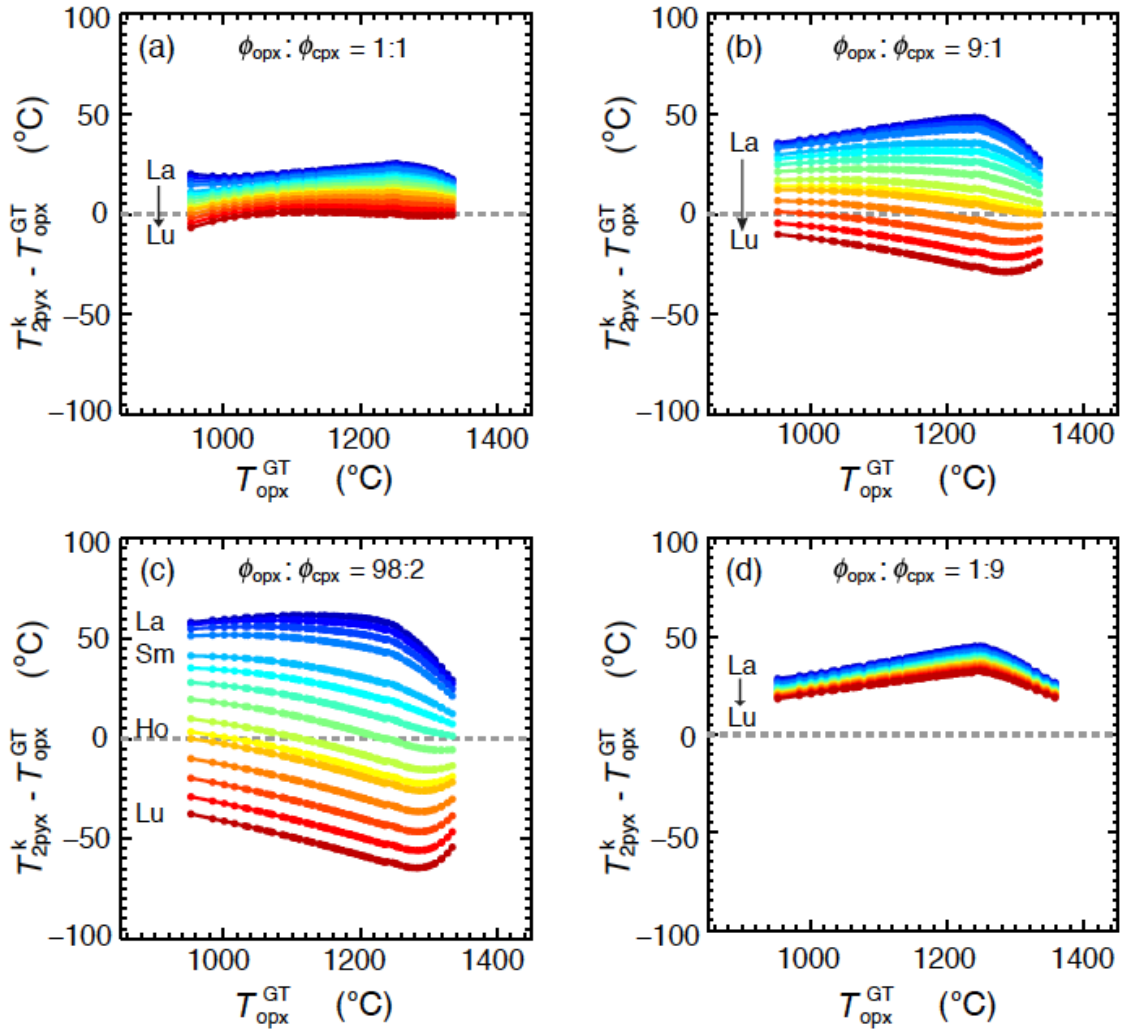


Figure 1-10

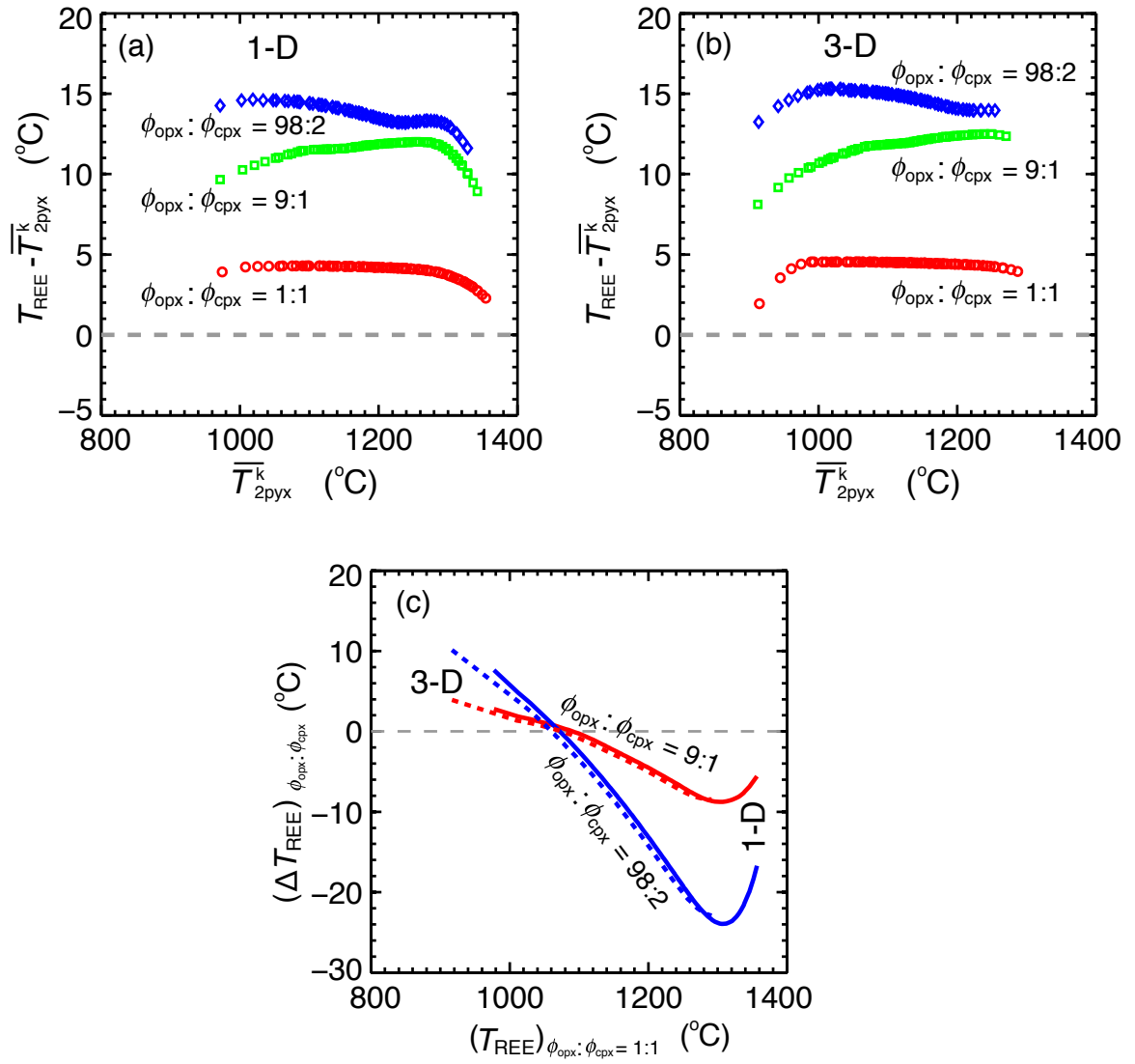
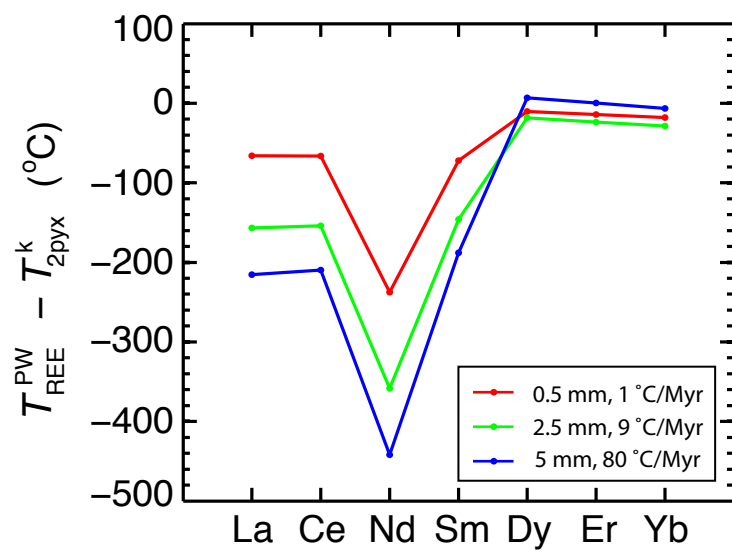


Figure 1-11



Supplementary Material

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Supplementary Material S1

Model setup

The basic setup of our simple model is illustrated in Fig. 4a. We consider diffusive exchange of a trace element in a cooling bi-mineralic system that consists of mineral A (volume fraction ϕ_A) and mineral B (volume fraction ϕ_B). Initially at a high temperature, concentrations of the trace element are homogeneous in minerals A and B (concentrations C_A^0 and C_B^0) and they are related to each other through a mineral-mineral partition coefficient. During cooling the trace element concentrations in minerals A and B are related through a temperature-dependent partition coefficient at the A-B interface. The governing diffusion equations for plane sheet or axisymmetric cylindrical or spherical geometry are:

$$\frac{\partial C_A}{\partial t} = D_A \left(\frac{\alpha}{x} \cdot \frac{\partial C}{\partial x} + \frac{\partial^2 C}{\partial x^2} \right), \quad d_A < x < 0, \quad (\text{S1a})$$

$$\frac{\partial C_B}{\partial t} = D_B \left(\frac{\alpha}{x} \cdot \frac{\partial C}{\partial x} + \frac{\partial^2 C}{\partial x^2} \right), \quad 0 < x < d_B, \quad (\text{S1b})$$

where $\alpha = 0$ for plan sheet geometry (1-D); $\alpha = 1$ for cylindrical geometry (2-D), and $\alpha = 2$ for spherical geometry (3-D). d_A and d_B represent the average or mean radius or half width of minerals A and B, respectively.

Initial conditions are:

$$C_A|_{t=0} = C_A^0, \quad d_A < x < 0, \quad (\text{S1c})$$

$$C_B|_{t=0} = C_B^0, \quad 0 < x < d_B, \quad (\text{S1d})$$

Boundary conditions are:

$$\left. \frac{\partial C_A}{\partial x} \right|_{x=-d_A} = 0, \quad (\text{S1e})$$

$$\left. \frac{\partial C_B}{\partial x} \right|_{x=d_B} = 0, \quad (\text{S1f})$$

$$C_A|_{x=0^-} = k_{AB} \cdot C_B|_{x=0^+}, \quad (\text{S1g})$$

$$\frac{\phi_A}{d_A} D_A \left. \frac{\partial C_A}{\partial x} \right|_{x=0^-} = \frac{\phi_B}{d_B} D_B \left. \frac{\partial C_B}{\partial x} \right|_{x=0^+}, \quad (\text{S1h})$$

where ϕ_A and ϕ_B are model abundances of minerals A and B , respectively. Eqs. S1a-1h are solved numerically using the Crank-Nicolson finite difference method (Crank, 1975). To reduce numerical errors, we used a second order asymmetric finite difference scheme to approximate the diffusive fluxes (Eqs. S1h) at the A - B interface.

Assumptions and simplifications

Several assumptions are made in the model simulations, including, (1) divalent major elements reach instantaneous equilibrium between the two minerals as the system cools; (2) partition coefficients of the trace element between the two minerals depend only on temperature; and (3) grain boundary diffusion is much faster than volume diffusion. The first assumption may not be true at very low temperatures but is a reasonable approximation for temperatures greater than 800°C because diffusivities of divalent Ca, Mg, and Fe are generally over two orders of magnitude greater than those of REE (Cherniak and Dimanov, 2010 and references therein). Although trace element partitioning between minerals also depends on mineral composition (e.g., Witt-Eickschen and O'Neill, 2005; Lee et al., 2007; Liang et al., 2013), the compositional effect is generally small for a given sample. To focus on definition of closure temperature, we

used the same effective grain size for the two minerals in most of our simulations reported in this study.

Supplementary Table 1-S1

Parameters used for numerical simulation

Parameters	Unit	Value
D_A	m^2/s	$1.2 \times 10^{-7} \times \exp(-369 \times 10^3 / R/T)$
D_B (case 1)	m^2/s	D_A
D_B (case 2)	m^2/s	$D_A/5$
D_B (case 3)	m^2/s	$5 \times D_A$
k_{AB}^1 (small)	-	$4.5 \times \exp(-7.1 \times 10^4 / R/T)$
k_{AB}^2 (large)	-	$4.5 \times \exp(-3.6 \times 10^4 / R/T)$
d	mm	0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5
$\dot{s}$	$^{\circ}\text{C}/\text{Ma}$	1, 2.5, 4, 6, 9, 14, 20, 35, 50, 80

The total number of numerical simulations:

$$3 \text{ (\# of } D_B) \times 2 \text{ (\# of } k_{AB}) \times 10 \text{ (\# of } d) \times 10 \text{ (\# of } \dot{s}) = 600.$$

Supplementary Material S2

Comparison of closure temperatures between mono- and bi-mineralic systems

Since the closure temperature for bi-mineralic systems depends on diffusivities, mineral-mineral partition coefficient of the trace element of interest and mineral proportions, in addition to cooling rate and grain size, it is instructive to compare closure temperatures for mono- (Dodson, 1973 and 1986) and bi-mineralic systems. An important difference between mono- and bi-mineralic systems is how the trace element concentrations at the mineral boundaries evolve during cooling. Trace element evolutions at the rim of minerals *A* and *B* are curvilinear (blue dashed lines in Fig. 6). On the other hand, trace element concentration varies linearly as a function of time at the rim of mono-mineralic system (Fig. 3c). Hence a difference in closure temperature between Dodson's and this study is expected. Since the initial temperatures affect the closure temperatures for large grain sizes and fast cooling rates, we use the modified version of Dodson's equation from Ganguly and Tirone (1999) to calculate the closure temperatures for minerals *A* and *B*, respectively. Figure S1 shows that the maximum temperature difference between bi- and mono-mineralic systems is ~ 25 °C for minerals *A* and *B*. A similar comparison of closure temperatures for spherical geometry shows that a maximum of ~ 35 °C exists between bi- and mono-mineralic systems (Fig. S2). The smaller the k_{AB} , the larger the difference in closure temperatures between the two systems is (Figs. S1-S2). These temperature differences demonstrate the subtle effect of “the equilibrium concentration-temperature relationship” at the mineral surface on the closure temperature, as Dodson's pointed earlier (1986).

Supplementary Figure 1-S1

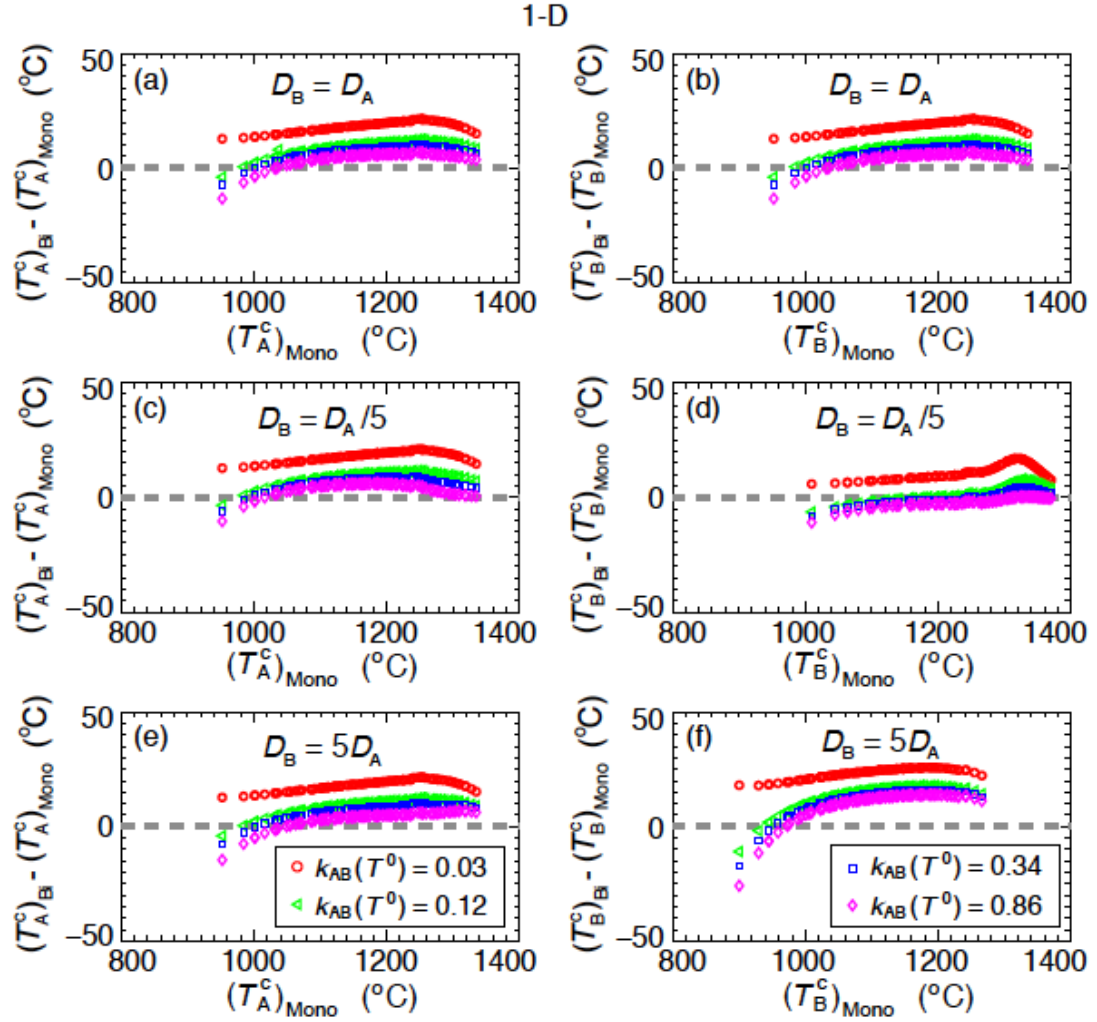


Figure 1-S1. Comparison of closure temperatures for minerals *A* (a, c, e) and *B* (b, d, f) between bi-mineralic [$(T^c)_{Bi}$ and $(T^c)_{Bi}$] and mono-mineralic [$(T^c)_{Mono}$ and $(T^c)_{Mono}$] systems for $\phi_{\text{opx}}:\phi_{\text{exp}} = 1:1$. Closure temperatures for bi-mineralic systems are calculated using results from numerical simulations. Closure temperatures for the mono-mineralic systems are calculated using modified Dodson's equation from Ganguly and Tirone (1999), and diffusion parameters (*E* and *D*₀) used in the analytical calculation are the same as those used in Fig. 7.

Supplementary Figure 1-S2

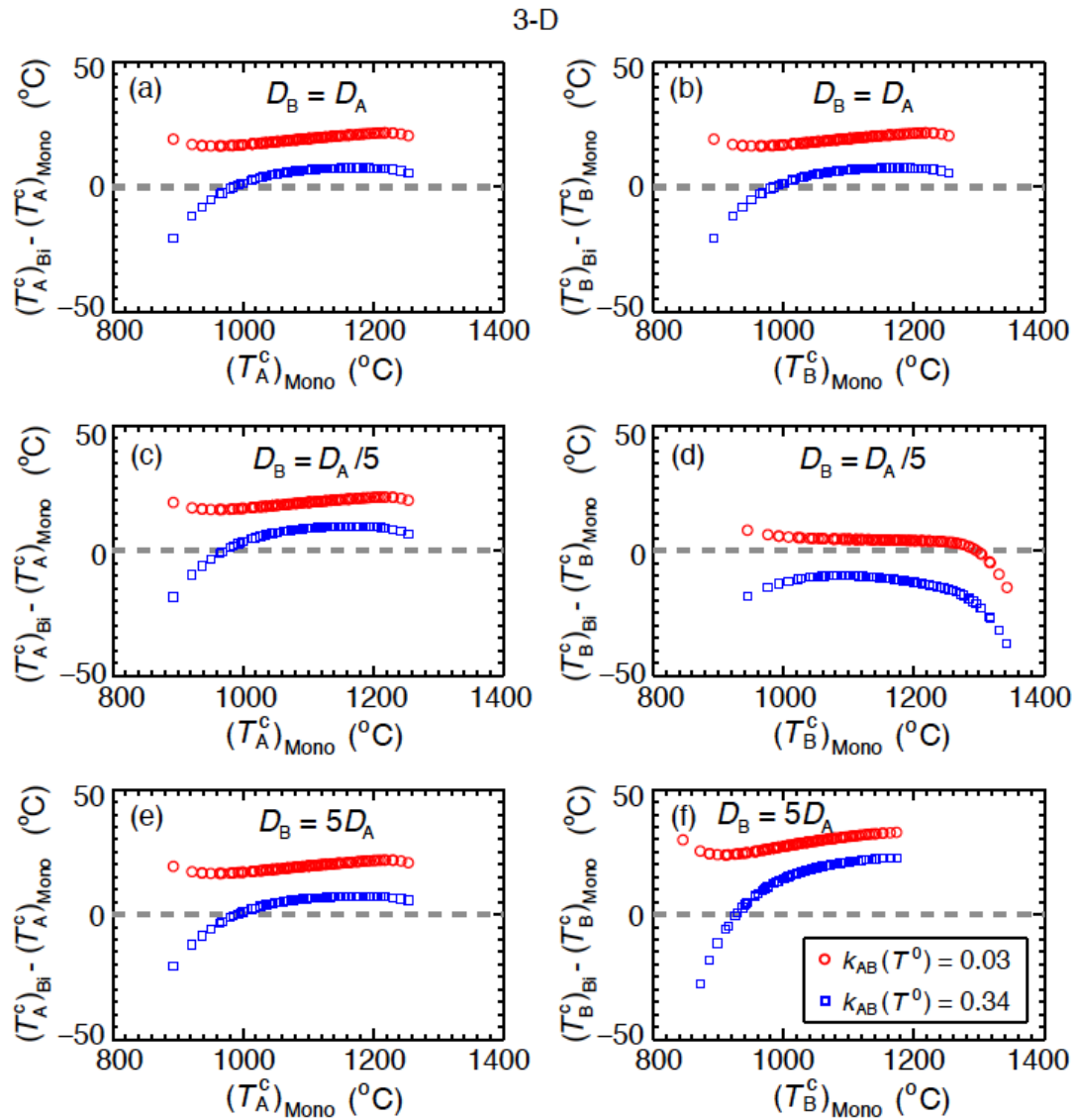


Figure 1-S2. Same as Fig. S1 but for 3-D simulations.

Supplementary Figure 1-S3

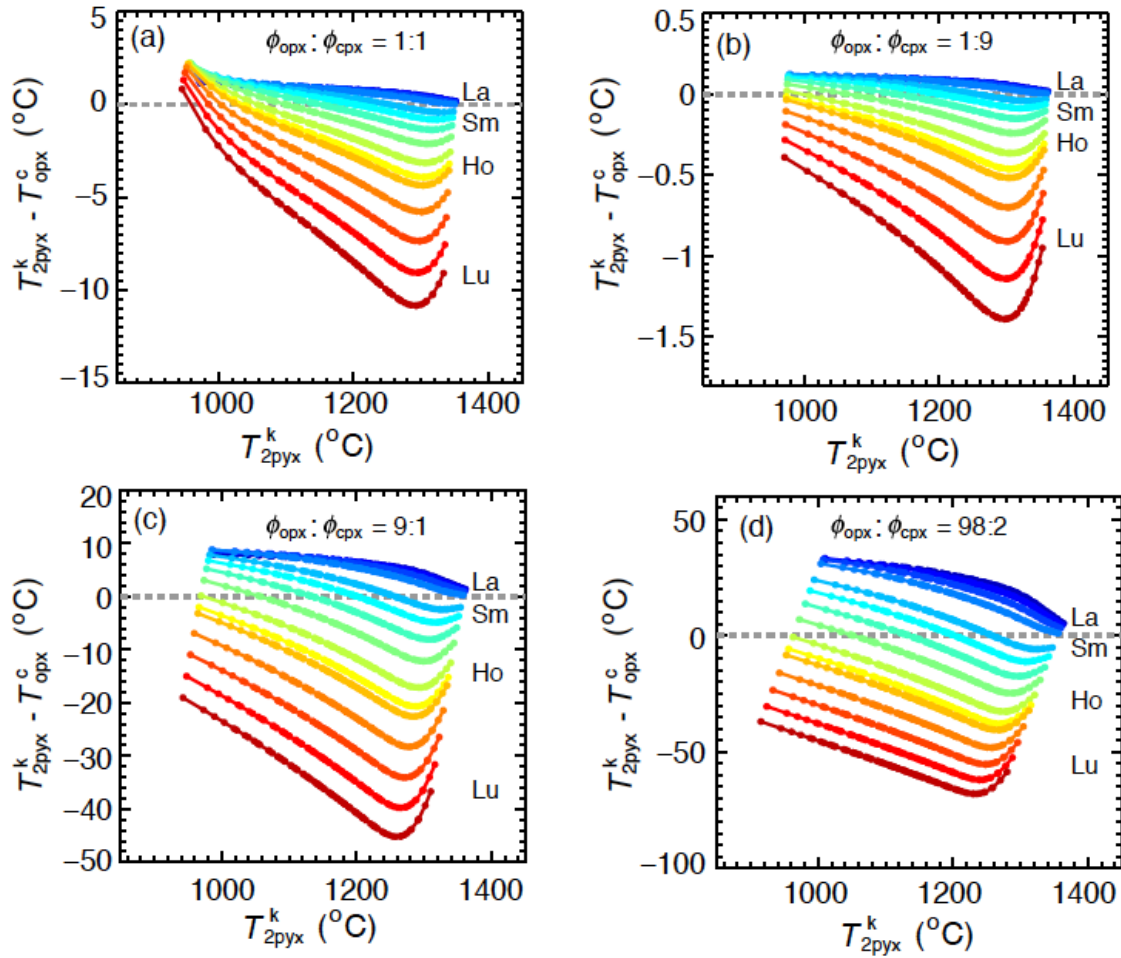


Figure 1-S3. Comparison of REE closure temperatures defined by effective partition coefficients between opx and cpx (T_{2pyx}^k) with those defined by the REE concentrations in opx (T_{opx}^c). T_{2pyx}^k and T_{opx}^c are both from numerical simulation. The opx-cpx REE partition coefficients (Liang et al., 2013) and REE diffusion coefficients in enstatite and diopside (Cherniak and Liang, 2007; Van Orman et al., 2002) are used in the numerical simulations. The ranges of grain size and cooling rate are the same as those in Fig. 7.

Supplementary Figure 1-S4

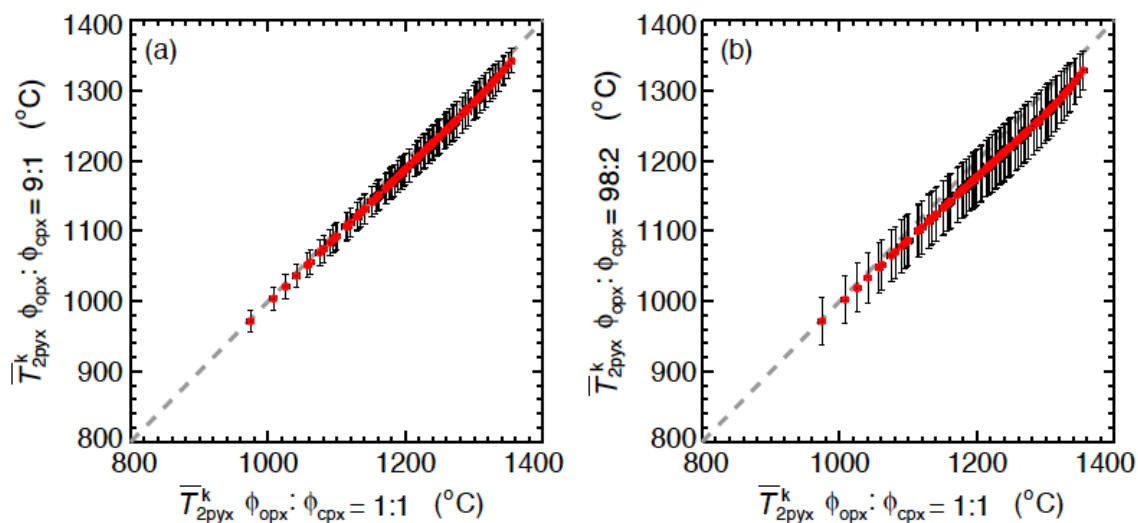


Figure 1-S4. Comparison of average REE closure temperatures defined by effective partition coefficients between opx and cpx ($\bar{T}_{2pyx}^k$) with different proportions of opx and cpx. Error bars represent one-sigma standard derivations of the average REE closure temperatures. As shown, when $\phi_{\text{opx}}:\phi_{\text{cpx}} = 1:1$ (x-axes in both a and b), the standard derivations are negligible (smaller than mark size); when $\phi_{\text{opx}}:\phi_{\text{cpx}} = 9:1$ (y-axis in a), the standard derivations increase due to the increased differences in closure temperatures from La to Lu (Fig. S3c); when $\phi_{\text{opx}}:\phi_{\text{cpx}} = 98:2$ (y-axis in b), the standard derivations increase dramatically as well since even larger differences exist among REE (Fig. S3d). However, the average REE closure temperatures are close to 1:1 line with different mineral proportions of opx and cpx.

Supplementary Figure 1-S5

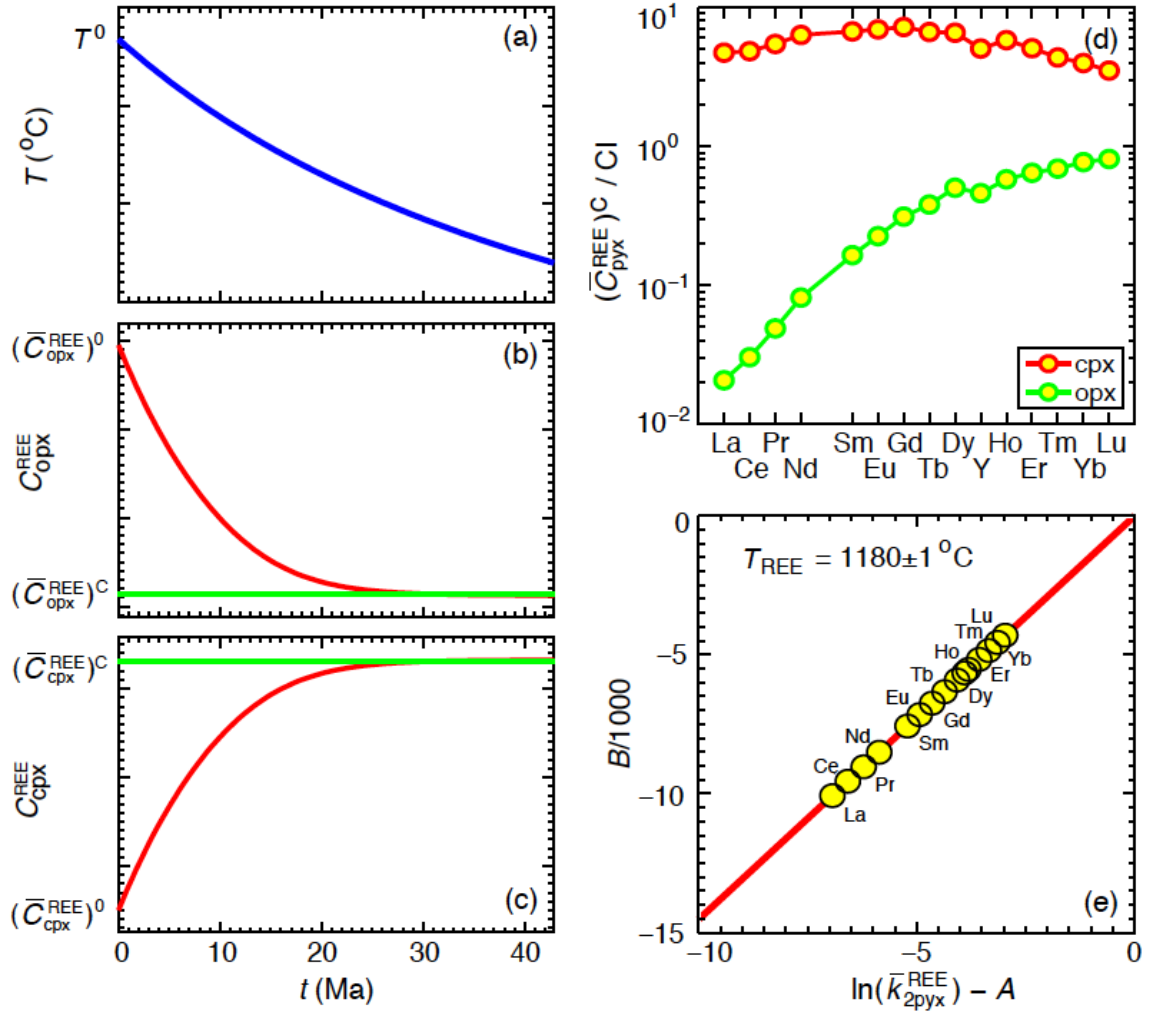


Figure 1-S5. An example showing the derivation of REE-in-two-pyroxene temperature (T_{REE}) for a grain size of 2 mm and cooling rate of $14^{\circ}\text{C}/\text{Ma}$. (a) Cooling path defined by Eq. (2a). (b, c) The average concentration evolution of Yb in opx ($\bar{C}_{\text{opx}}^{\text{REE}}$) and cpx ($\bar{C}_{\text{cpx}}^{\text{REE}}$), respectively. Subscripts 0 and c represent initial and close values, respectively. $(\bar{C}_{\text{opx}}^{\text{REE}})^c$ and $(\bar{C}_{\text{cpx}}^{\text{REE}})^c$ are asymptotic values. (d) CI chondrite normalized concentration of $(\bar{C}_{\text{opx}}^{\text{REE}})^c$ and $(\bar{C}_{\text{cpx}}^{\text{REE}})^c$ after the closure time. (e) Temperature inversion (T_{REE}) based on the average REE concentrations in two pyroxenes $(\bar{C}_{\text{opx}}^{\text{REE}})^c$ and $(\bar{C}_{\text{cpx}}^{\text{REE}})^c$ in (d) and REE-in-two-pyroxene thermometer of Liang et al. (2013).

Supplementary Figure 1-S6

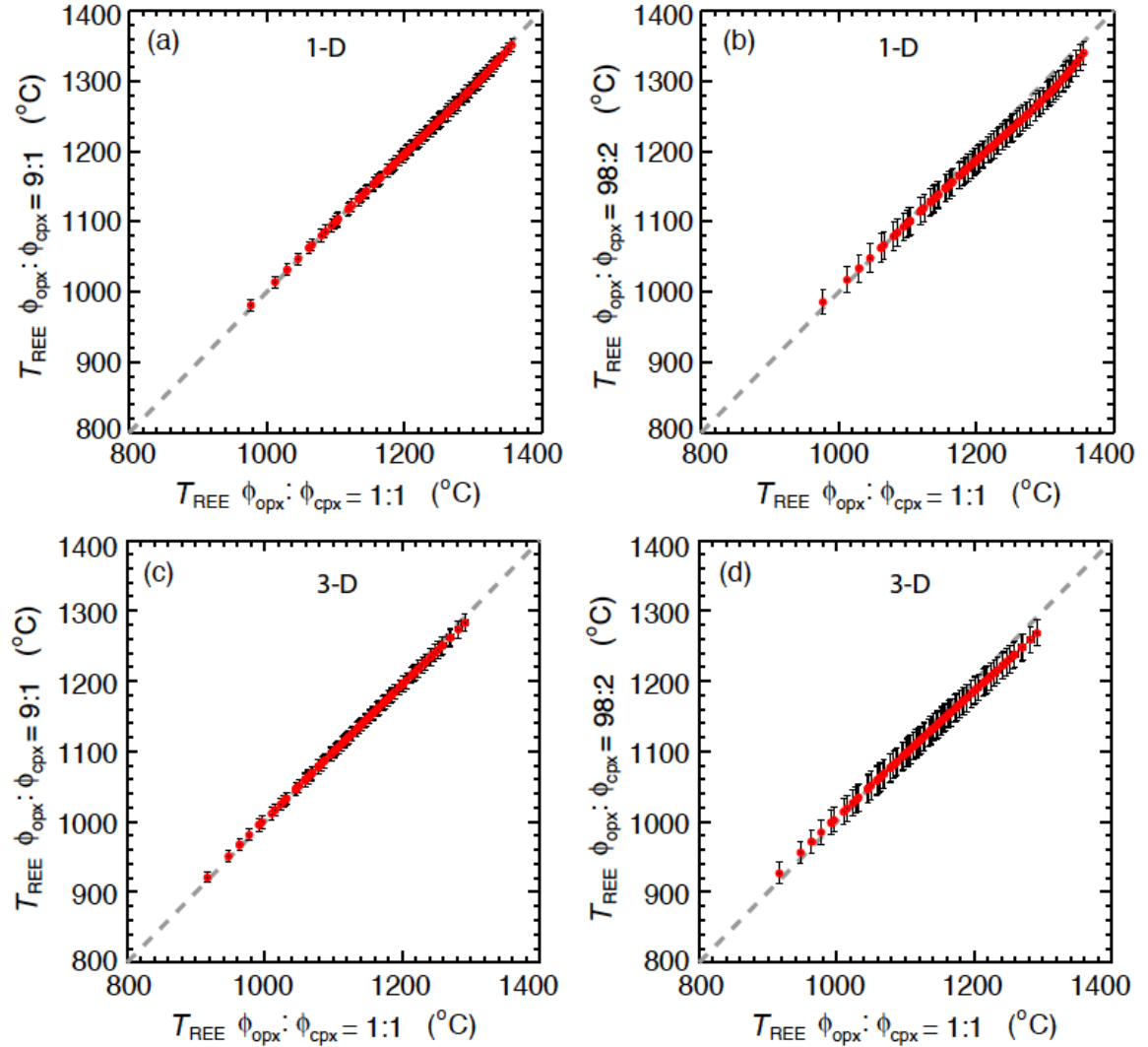


Figure 1-S6. Comparison of T_{REE} with different mineral proportions of opx and cpx for 1-D (a,b) and 3-D (c,d) geometries. Error bars represent one-sigma standard derivations from the temperature inversion. As shown, when $\phi_{\text{opx}}:\phi_{\text{cpx}} = 1:1$, the standard derivations are negligible (x-axes of the above figures, smaller than mark size); when $\phi_{\text{opx}}:\phi_{\text{cpx}} = 9:1$ (y-axes in a and c), the standard derivations increase due to the increased differences in closure temperatures from La to Lu (e.g., Fig. S3c); when $\phi_{\text{opx}}:\phi_{\text{cpx}} = 98:2$ (y-axes in b and d), the standard derivations increase dramatically as well since even larger differences exist among REE (e.g., Fig. S3d). However, the average T_{REE} are close to 1:1 line with different mineral proportions of opx and cpx.

Supplementary Figure 1-S7

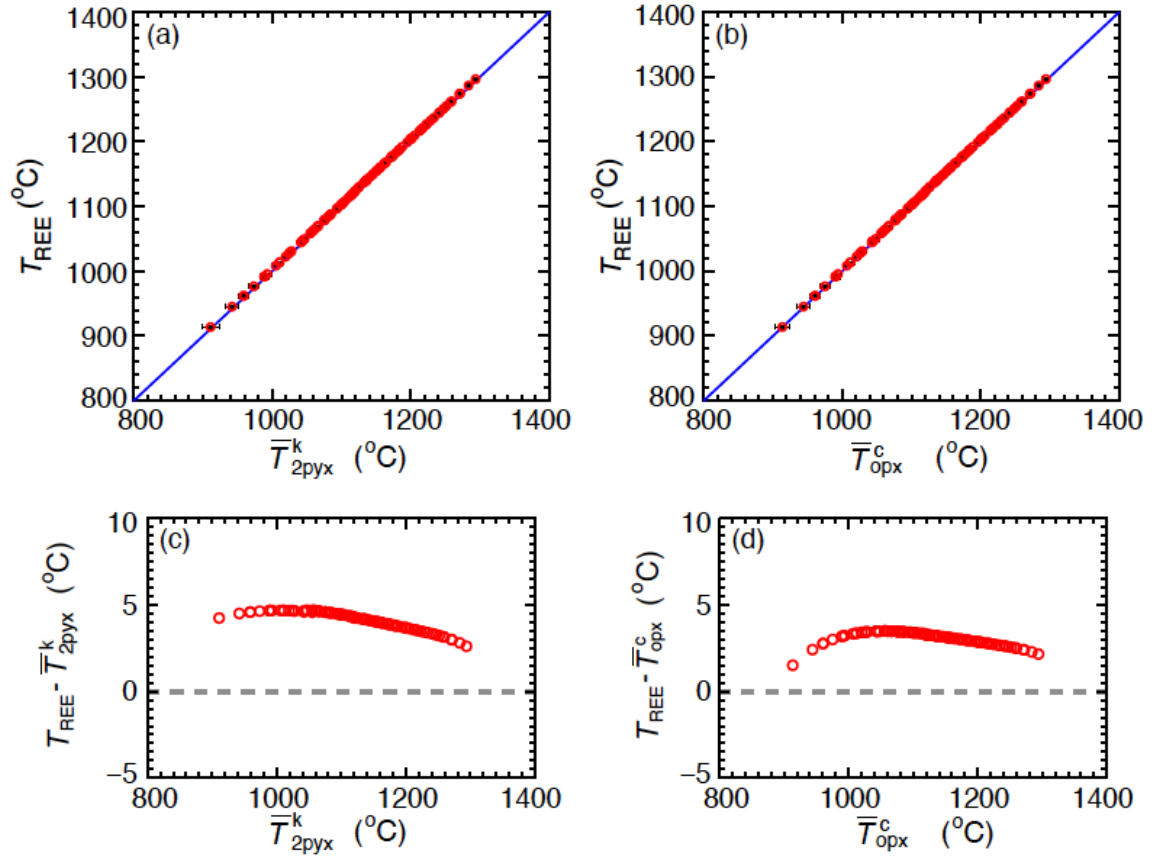


Figure 1-S7. Effect of grain size on closure temperatures. Comparison of closure temperatures defined by the effective partition coefficients of REE ($\bar{T}_{2\text{pyx}}^k$ in a and c) and average concentrations of REE in opx ($\bar{T}_{\text{opx}}^c$ in b and d) with temperature calculated using the REE-in-two-pyroxene thermometer for $d_{\text{opx}} = 0.5d_{\text{cpx}}$.

Supplementary Figure 1-S8

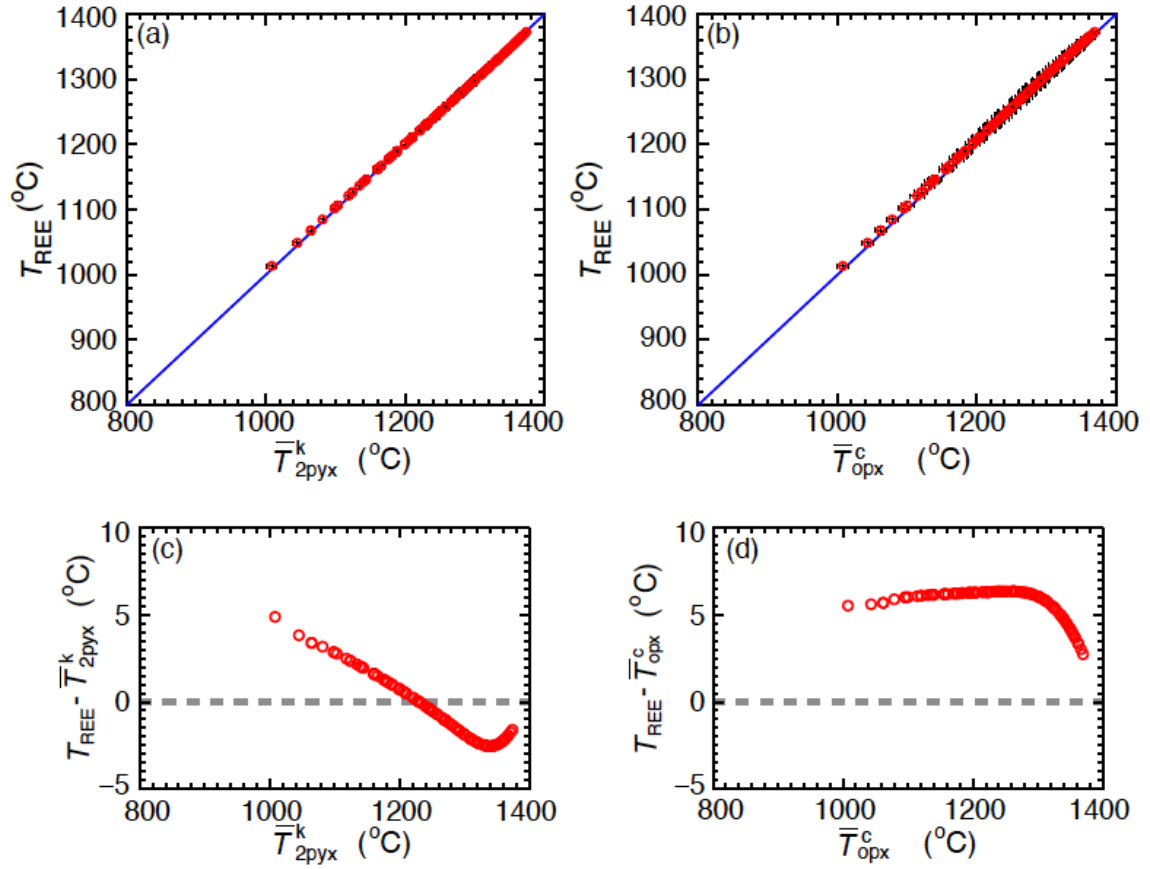


Figure 1-S8. Effect of grain size on closure temperatures. Comparison of closure temperatures defined by the effective partition coefficients of REE ($\bar{T}_{2\text{pyx}}^k$ in a and c) and average concentrations of REE in opx ($\bar{T}_{\text{opx}}^c$ in b and d) with temperature calculated using the REE-in-two-pyroxene thermometer for $d_{\text{opx}} = 2d_{\text{cpx}}$. Results from Figs. S7 and S8 demonstrate that T_{REE} is equivalent to the REE closure temperature in the cooling two-pyroxene systems.

Supplementary Figure 1-S9

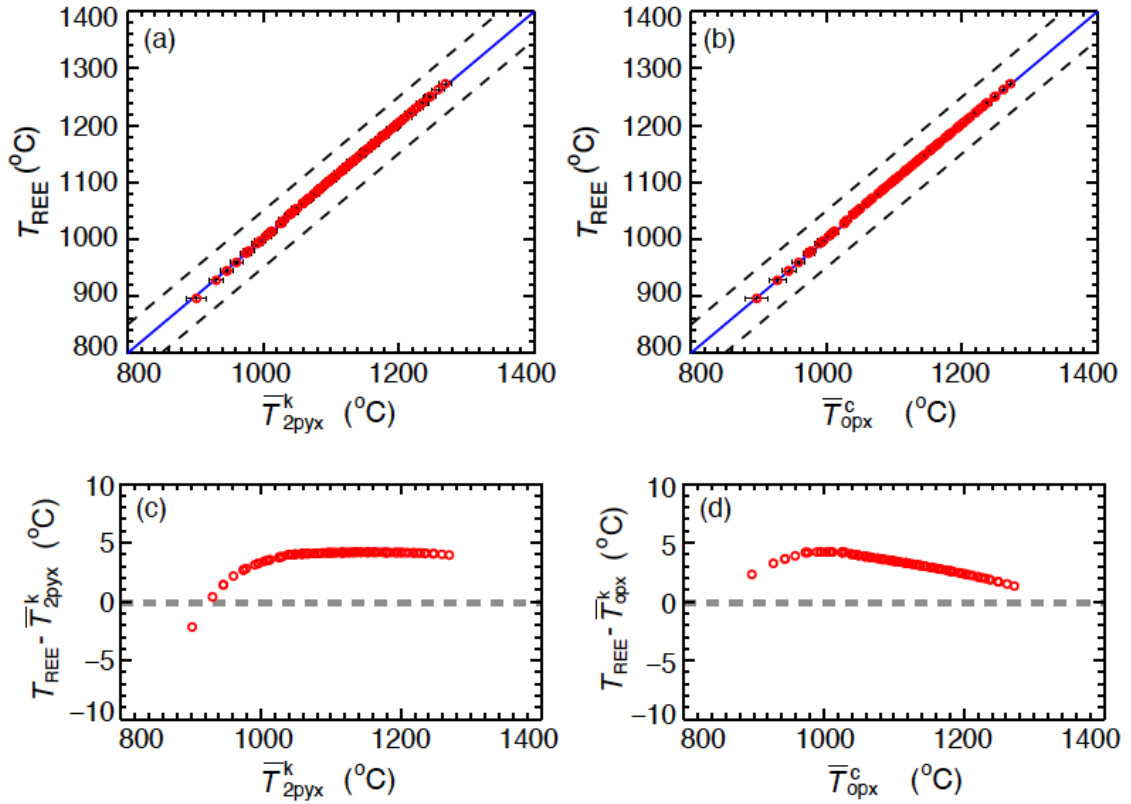


Figure 1-S9. Comparison of closure temperatures defined by the effective partition coefficients of REE ($\bar{T}_{2\text{pyx}}^k$ in a and c) and average concentrations of REE in opx ($\bar{T}_{\text{opx}}^c$ in b and d) with temperature calculated using the REE-in-two-pyroxene thermometer and results from simulations in 3-D spherical geometry. The small differences between REE closure temperature and T_{REE} indicate that T_{REE} can also represent the closure temperature of REE in 3-D systems.

Supplementary Figure 1-S10

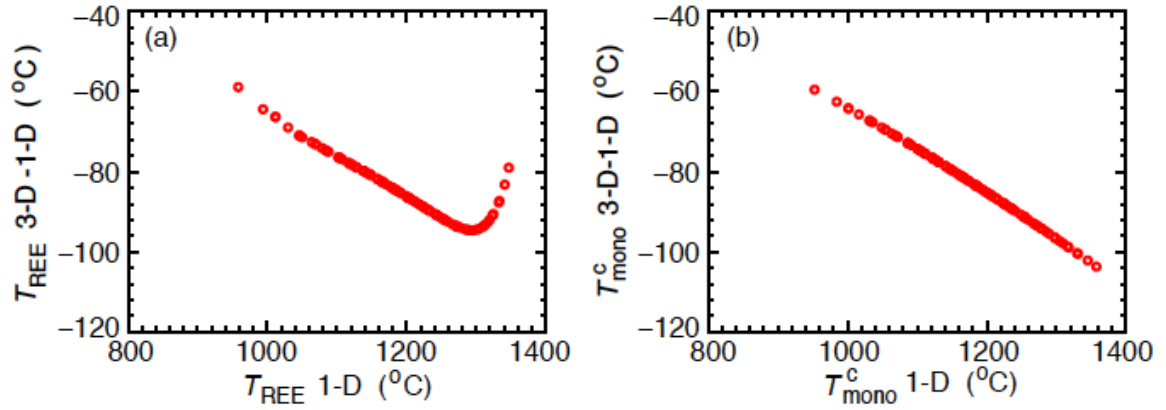


Figure 1-S10. Comparison of closure temperatures between 1-D and 3-D geometries for bi-mineralic (a, T_{REE} 1-D and 3-D) and mono-mineralic systems (b, $T_{\text{mono}}^{\text{c}}$ 1-D and 3-D). The closure temperatures for bi-mineralic systems are from 1-D planar and 3-D spherical simulations. The closure temperatures for mono-mineralic systems are calculated using Dodson's equation. The ranges of grain sizes and cooling rates are the same as those in Fig. 7.

Supplementary Figure 1-S11

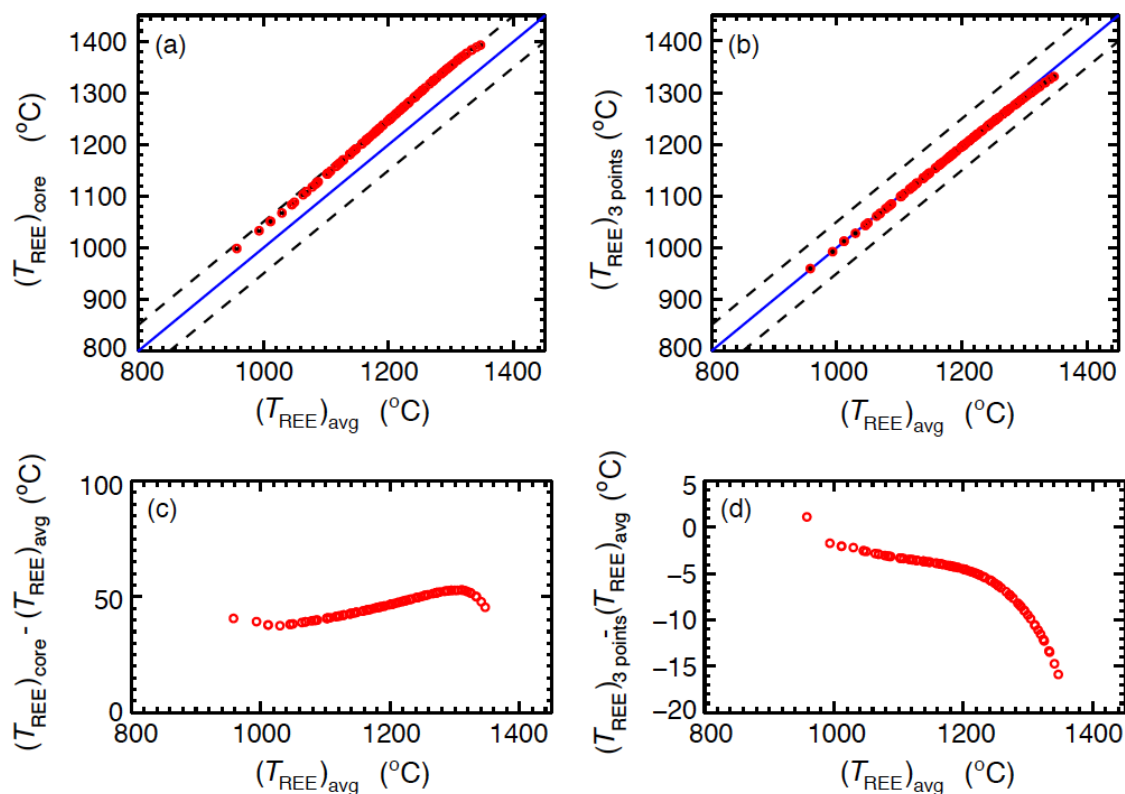


Figure 1-S11. Comparison of T_{REE} calculated using the average REE concentrations in two pyroxenes [$(T_{\text{REE}})_{\text{avg}}$] with those calculated using the core concentrations [$(T_{\text{REE}})_{\text{core}}$, a and c] or the 3-point averages [$(T_{\text{REE}})_{\text{3 points}}$, b and d]. $(T_{\text{REE}})_{\text{avg}}$ are the same as those used in Fig. 10. The core concentrations of REE after closure time are used in the calculation of $(T_{\text{REE}})_{\text{core}}$. $(T_{\text{REE}})_{\text{3 points}}$ are calculated using the average REE concentrations through the integration of parabolic interpolation of three points (core, rim and a point in the middle) across the REE diffusion profiles after closure time.

CHAPTER 2

Cooling and Heating Paths of Mafic and Ultramafic Rocks as Derived from the REE-in-Garnet-Clinopyroxene Thermobarometer

Abstract

Thermobarometers have played an important role in the understanding of the thermal state and thermal evolution of lithosphere. The calculation of equilibrium pressure for garnet- and clinopyroxene-bearing rocks has been relying on the assistance of extra phases or local geotherms. However, large uncertainties exist in the pressure estimation, resulting in inconsistent results in the temperature calculation. Recently, Sun and Liang (2015) developed a REE-in-garnet-clinopyroxene thermobarometer that can be used to derive temperature and pressure simultaneously by analyzing REE and major element concentrations in coexisting garnet and clinopyroxene. In order to understand the physical meanings of temperature and pressure calculated using the REE-in-garnet-clinopyroxene thermobarometer, we conduct numerical simulations of REE diffusive exchange between coexisting garnet and clinopyroxene along different temperature-pressure paths. We find that temperatures and pressures derived from the REE-in-garnet-clinopyroxene thermobarometer are equivalent to the average REE closure temperatures and closure pressures defined by the effective partition coefficients of REE between garnet and clinopyroxene. The correlation between temperatures and pressures calculated using the REE-in-garnet-clinopyroxene thermobarometer are consistent with prescribed temperature-pressure paths, which indicates that these temperatures and pressures can be used to derive temperature-pressure paths and possibly upwelling or downwelling rates for garnet- and clinopyroxene-bearing rocks once their cooling rates are obtained. As examples of geological applications, we derive cooling rates of $10^{-1} \sim 10^2$ °C/Myr for garnet peridotites, granulites and eclogites that experienced exhumation using closure curves constrained by REE and major element closure temperatures. We further estimate

exhumation rates of 0.03 to 45 mm/yr for these samples based on the correlation between REE temperatures and pressures, which are consistent with those derived by isotopic dating. We also estimate heating rates of 20 ~ 200 °C/Myr and convergence rates of 10 to 100 mm/yr for garnet- and clinopyroxene-bearing rocks from subduction environments. However, large uncertainties may exist in the estimation of heating/subduction histories for these rocks due to the complex thermal structure in subduction zones.

1. Introduction

Thermobarometers have played a central role in the interpretation of the thermal state and thermal history recorded in igneous and metamorphic rocks. For example, equilibrium temperatures and pressures derived from thermobarometers for well-equilibrated garnet peridotites and pyroxenites from lithospheric mantle have been used to construct local geotherms (e.g., O'Reilly & Griffin, 1985; Pearson et al., 1995; Rudnick et al., 1998; Rudnick and Nyblade, 1999; Kopylova et al., 1999; Chen et al., 2001; Ionov, 2002; Downes et al., 2004; Lehtonen et al., 2004; McKenzie et al., 2005; Mather et al., 2011; Su et al., 2011). When thermobarometry studies are coupled with isotopic dating (e.g., Sm-Nd, Lu-Hf) or element zoning, metamorphic rocks from active tectonic regions, such as eclogites and granulites from subduction zones and orogenic terranes, can also be used to construct P-T-t trajectories of tectonic events (e.g., Harley, 1985; Scott & St-Onge, 1995; Spear & Parrish, 1996; O'Brien, 1997; Rubatto & Hermann, 2001; Tirone & Ganguly 2010; Müller et al., 2015).

The Fe-Mg exchange between garnet and clinopyroxene has been calibrated as thermometers for garnet- and clinopyroxene-bearing rocks (e.g., Råheim & Green, 1974; Ellis & Green, 1979; Ganguly, 1979; Saxena, 1979; Powell, 1985; Krogh, 1988; Ai, 1994; Ravna, 2000; Nakamura, 2009). However, these thermometers require an independent estimation of pressure, which can be realized through application of another thermobarometer (e.g., the garnet-orthopyroxene thermobarometer) or a local geotherm. Recently, Sun and Liang (2015) developed a REE-in-garnet-clinopyroxene thermobarometer based on REE partitioning between garnet and clinopyroxene (Sun and Liang, 2012, 2013, 2014), which can be used to calculate equilibrium or apparent

temperature and pressure simultaneously. Application of the new thermobarometer to well equilibrated experimental and natural samples leads to consistent temperatures and pressures when compared with known values (experimental) or those derived from widely used major element based thermometers (e.g., Ellis & Green, 1979; Krogh, 1988; Ravna, 2000; Nakamura, 2009). Application of the new thermobarometer to garnet- and clinopyroxene-bearing rocks from active tectonic environments generates systematically higher temperatures than those calculated using Fe-Mg exchange thermometers (e.g., Krogh, 1988) for samples that experienced cooling, and lower for samples that experienced heating. Sun and Liang (2015) attributed the systematic temperature differences to the different diffusion rates between the trivalent REE and divalent Fe and Mg in garnet and clinopyroxene. They suggested that temperature (T_{REE}) and pressure (P_{REE}) derived from the REE-in-garnet-clinopyroxene thermobarometer can be used to study thermal history of mafic and ultramafic rocks when coupled with temperatures derived from Fe-Mg thermometers. This raises two important questions: (1) what are the physical meanings of temperature and pressure derived from the REE-in-garnet-clinopyroxene thermobarometer? and (2) how are T_{REE} and P_{REE} related to the P-T path(s) experienced by the garnet- and clinopyroxene-bearing rocks?

In a recent study, Yao and Liang (2015) conducted numerical simulations of trace element diffusive redistribution between two coexisting minerals to examine the closure temperature in cooling bi-mineralic systems and demonstrated that temperatures calculated using the REE-in-two-pyroxene thermometer (Liang et al., 2013) are essentially the same as the average REE closure temperatures in two-pyroxene systems.

In this study, we use a similar finite difference model to study REE diffusive exchange between garnet and clinopyroxene using temperature- and pressure-dependent REE diffusion coefficients in garnet and clinopyroxene and garnet-clinopyroxene REE partition coefficients (Section 2), and to investigate the physical meanings of the temperature and pressure derived from the REE-in-garnet-clinopyroxene thermobarometer and their correlation (Section 3). We conduct further numerical simulations to quantify the cooling (exhumation) or heating (subduction) rates for garnet- and clinopyroxene-bearing rocks (Section 4).

2. REE diffusion in cooling garnet-clinopyroxene systems

In Yao and Liang (2015), we systematically examined Dodson's definition of closure temperature for cooling mono-mineralic and bi-mineralic systems. We used a diffusion model similar to those of Lasaga et al. (1977), Onorato et al. (1981), Cherniak and Liang (2007, 2012) and Liang (2014) to study trace element redistribution in cooling bi-mineralic system and applied it to REE diffusion in two-pyroxene system in both planar and spherical geometries. In this study, we conduct numerical simulations of REE distribution between garnet and clinopyroxene and derive REE closure temperature and closure pressure through the numerical results. Here we briefly describe the model setup and assumptions. For more details regarding governing equations, initial and boundary conditions, numerical method, and assumptions, a reader is referred to the supplementary material S1 in Chapter 1 of this dissertation.

2.1. Model setup, assumptions and boundary conditions

We consider diffusive reequilibration of REE in a bi-mineralic system consisting of garnet (volume fraction ϕ_{gt}) and clinopyroxene (volume fraction ϕ_{cpx}). Initially at temperature T_0 and pressure P_0 , REE in garnet and clinopyroxene are in chemical equilibrium, and their concentrations are related to each other through partition coefficients k_{gt-cpx}^{REE} at T_0 and P_0 . During cooling, REE are out of equilibrium between garnet and clinopyroxene except at their interface where REE concentrations are related to each other through the simple partitioning relation,

$$C_{gt}\Big|_{r=0^-} = k_{gt-cpx}^{REE}(T, P) \cdot C_{cpx}\Big|_{r=0^+} \quad (1a)$$

Across garnet-clinopyroxene interface, the diffusive flux is continuous, viz.,

$$\frac{\phi_{gt}}{d_{gt}} D_{gt} \frac{\partial C_{gt}}{\partial r} \Big|_{r=0^-} = \frac{\phi_{cpx}}{d_{cpx}} D_{cpx} \frac{\partial C_{cpx}}{\partial r} \Big|_{r=0^+}, \quad (1b)$$

where d_{gt} and d_{cpx} are the effective or average radii of garnet and clinopyroxene, respective; D_{gt} and D_{cpx} are REE diffusion coefficients in garnet and clinopyroxene; C_{gt} and C_{cpx} are REE concentrations in garnet and clinopyroxene and r represents the position away from the garnet-clinopyroxene interface ($r = 0$). The partition coefficient of (k_{gt-cpx}^{REE}) and diffusion coefficient (D) take on the usual form,

$$k_{gt-cpx}^{REE}(T, P) = k_{gt-cpx}^{REE,0} \cdot \exp\left(-\frac{\Delta H + P \cdot \Delta V}{RT}\right), \quad (1c)$$

$$D = D_0 \cdot \exp\left(-\frac{E_a + P \cdot \Delta V}{RT}\right), \quad (1d)$$

where the pre-exponential factor $k_{gt-cpx}^{REE,0}$ and the exchange energy ΔH are functions of mineral compositions and ionic radius. The expression of k_{gt-cpx}^{REE} , which is a

parameterized lattice strain model, can be found from the REE partitioning and thermobarometry studies of Sun and Liang (2014, 2015). D_0 and E_a are the pre-exponential factor and activation energy for REE diffusion. ΔV is the partitioning exchange volume; and V_a is activation volume for diffusion. To focus on the physical meanings of temperature and pressure derived by the REE-in-garnet-clinopyroxene thermobarometer, we consider cooling or heating along a prescribed P-T-t path. For simplicity, we use the expression of Dodson (1973, 1986) for temperature variation,

$$\frac{1}{T} = \frac{1}{T_0} + \eta t \quad (1e)$$

where T is the temperature at a given time t , T_0 is the initial temperature; η is a constant related to the cooling rate. Without loss of generality, we make pressure vary with temperature along a continent lithospheric geotherm of Pollack and Chapman (1977). The latter is derived from simplified steady state heat conduction equation and can be written as,

$$T = C_1 P^2 + C_2 P \quad (1f)$$

where C_1 is a constant related to local heat production rate and heat conductivity; and C_2 is a constant related to heat conductivity and surface heat flow Q . Larger Q value represents warmer continent and smaller dP/dT slope (Fig. 1). In this study we choose $Q = 50 \text{ mWm}^{-2}$ and 90 mWm^{-2} (green and red solid lines in Fig. 1, designated as Geotherm50 and Geotherm90, respectively hereafter) to represent two geotherms and examine REE variations between garnet and clinopyroxene along them.

For simplicity, we assume (1) divalent major element reach instantaneous equilibrium between the garnet and clinopyroxene on the time scales of REE diffusion in garnet and clinopyroxene; (2) we only consider the effects of temperature and pressure on

REE partitioning during cooling; (3) grain boundary diffusion is much faster than volume diffusion so that REE reach instantaneous equilibrium at the interface of garnet and clinopyroxene within a representative element volume. For the purpose of demonstration, we use the major element compositions of garnet and clinopyroxene in a well-equilibrated eclogite (sample JDE 03 of Smart et al., 2009) to calculate REE partition coefficients as a function of temperature and pressure. Figure 2 displays the calculated garnet-clinopyroxene partition coefficients for selected REE using the model of Sun and Liang (2014, 2015) along Geotherm50 (solid lines) and their comparison with those along Geotherm90 (dashed lines). In general, light REE (LREE) are very incompatible in garnet relative to clinopyroxene and their compatibility in garnet increase from LREE to heavy REE (HREE). For LREE and middle REE, their compatibilities in garnet decrease with the decrease of temperature and pressure. For HREE Tm, Yb and Lu, their compatibilities in garnet increase slightly when temperature and pressure decrease along geotherms. For Er, its compatibilities in garnet increase slightly at the beginning of cooling and decrease afterwards along Geotherm50.

2.2. Choices of diffusion coefficients

Van Orman et al. (2001, 2002a) measured diffusion coefficients of La, Ce, Nd, Dy, and Yb in natural diopside (with 0.70 wt% FeO) from 1050 to 1450 °C, and found systematic dependence of diffusion coefficients on REE ionic radius and pressure. Figure 3a presents diffusion coefficients of REE in clinopyroxene as a function of temperature along Geotherm50 with diffusivities of other REE interpolated or extrapolated according to ionic radius and the data of Van Orman et al. (2001, 2002a). REE diffusion

coefficients in clinopyroxene decrease from Lu to La by one to five orders of magnitude as temperature decreases from 1400 °C to 700 °C.

Direct measurement of REE diffusion coefficients in garnet began from the study of Ganguly et al. (1988) for Sm and Nd diffusion in almandine-pyrope garnet. Their experiments were performed at 777-827 °C and 1 bar with oxygen fugacity (f_{O_2}) buffered at the iron-wüstite (IW), and produced diffusion coefficients similar to that of Mg, and about an order of magnitude higher than that of Fe. Van Orman et al. (2002b) determined tracer diffusion coefficients of Ce, Sm, Dy and Yb in a natural pyrope garnet at 28 kbar and 1200-1450 °C, using Pt capsules and graphite powder inside the capsules to buffer the f_{O_2} conditions. The data of Van Orman et al. (2002b), when extrapolated to the temperature of Ganguly et al. (1988), are several orders of magnitude smaller. Tirone et al. (2005) conducted experiments to study the diffusion of Nd, Gd and Yb in natural pyrope and almandine garnets at 1 bar, 777-927 °C and f_{O_2} of IW buffer, and re-examined some samples from the study of Ganguly et al. (1988). Studies from Van Orman et al. (2002b) and Tirone et al. (2005) both showed that REE diffusion coefficients depend weakly on ionic radius (Fig. 2b). However, after considering the effects of mineral composition, f_{O_2} and pressure, REE diffusion coefficients from Tirone et al. (2005) are still about one and a half orders of magnitude higher than those of Van Orman et al. (2002). Cherniak (2005) examined diffusion of Y and Yb in grossular garnet at 700-1000 °C, 1 bar, and f_{O_2} buffered by either IW or the quartz-fayalite-magnetite (QFM) equilibrium. The measured diffusivities are comparable to those of Van Orman et al. (2002). Recently, Carlson (2012) used numerical simulation to study the stranded diffusion profiles in partially resorbed garnet crystals from the aureole of Makhavinekh

Lake Plution, Labrador, and estimated diffusion coefficients of REE at 700-900 °C and 5.3 kbar. REE diffusion coefficients of Carlson (2012) are close to the values of Van Orman et al. (2002) and Cherniak (2005). Most recently, Bloch et al. (2015) measured Lu diffusion coefficient in natural almandine and spessartine garnets over a range of T-P- f_{O_2} conditions, and found good agreement with Yb diffusivity determined by Van Orman et al. (2002b) when both data sets are normalized to the same pressure. The reason for the significant higher diffusivities reported by Tirone et al. (2005) is still unknown. In this study, we use REE diffusion coefficients of Van Orman et al. (2002b) to calculate diffusion profiles in garnet and clinopyroxene. We discuss the difference caused by using REE diffusion coefficients of Tirone et al. (2005) in supplementary Fig. S3.

2.3. Model results and discussion

Figure 4 shows an example of the calculated concentration profiles of La (a) and Lu (b) across garnet ($-2 < r < 0$ mm) and clinopyroxene ($0 < r < 2$ mm) interface. The grain sizes of garnet and clinopyroxene are the same (2 mm), the cooling rate is 50 °C/Myr along Geotherm50, and the volume proportion of garnet to clinopyroxene is 1:1. La and Lu concentrations in the two minerals are normalized to their initial concentrations in garnet, so that their initial abundances in clinopyroxene are the reciprocals of their partition coefficients ($1/k_{gt-cpx}^{REE}$) at 1400 °C. Since LREE are more incompatible in garnet and the compatibility decreases with temperature, La diffuses out of garnet and into clinopyroxene during cooling. In contrast, HREE are more compatible in garnet and their compatibility increases with temperature, so that Lu diffuses out of clinopyroxene and into garnet. La and Lu concentrations in both garnet and

clinopyroxene approach closure profiles across the minerals at low temperatures (e.g., > 18 Myr for La in clinopyroxene; >22 Myr for Lu in both garnet and clinopyroxene). It is worth noting that the relative changes of La and Lu in garnet and clinopyroxene are quite different (e.g., ~70% La change in garnet with only ~35% La change in clinopyroxene; ~10% Lu change in garnet with ~ 55% Lu change in clinopyroxene) during cooling. This is due to the combined effects of grain size, mineral proportion, and temperature and pressure dependent REE partition coefficients and diffusion coefficients (For a detailed discussion, see Section 3.2 in Yao and Liang, 2015, Chapter 1 of this dissertation).

Following the same procedures of Yao and Liang (2015), we calculate REE closure temperatures based on the evolution of REE effective partition coefficient (T_{gc}^k , see details in supplementary Fig. S1). Pressures that correspond to the closure temperatures on geotherms are defined as closure pressures (P_{gc}^k).

3. Physical meanings of T_{REE} and P_{REE}

In order to investigate the physical meanings of the temperatures and pressures derived from the REE-in-garnet-clinopyroxene thermobarometer, we calculate T_{REE} and P_{REE} by substituting an effective garnet-clinopyroxene partition coefficient into the REE-in-garnet-clinopyroxene thermobarometer of Sun and Liang (2015). The effective or apparent garnet-clinopyroxene REE partition coefficient is defined by the average REE concentrations in garnet and clinopyroxene after REE closure profiles are established. We then compare T_{REE} and P_{REE} with the average REE closure temperatures ($\bar{T}_{gc}^k$) and pressures ($\bar{P}_{gc}^k$) for grain sizes from 0.5 – 5 mm, cooling rates from 1 – 1000 °C/Myr and mineral proportions of $\phi_{gt} : \phi_{cpx} = 1:1$, $\phi_{gt} : \phi_{cpx} = 1:9$ and $\phi_{gt} : \phi_{cpx} = 9:1$, and found that

T_{REE} and P_{REE} are essentially the same as the average REE closure temperature ($\overline{T}_{gc}^k$) and pressure ($\overline{P}_{gc}^k$) in the garnet and clinopyroxene systems (see detailed comparisons in supplementary Fig. S2). The maximum differences between T_{REE} and P_{REE} versus $\overline{T}_{gc}^k$ and $\overline{P}_{gc}^k$ are 60 °C and 0.4 GPa, respectively, when garnet and clinopyroxene proportion is 9:1, which are equivalent to the deviations caused by 20% analytical errors in REE measurements. This indicates that T_{REE} and P_{REE} can be used to define a P-T path and to constrain cooling (or heating) history of garnet- and clinopyroxene-bearing rocks. This is demonstrated below.

Figure 5 compares T_{REE} and P_{REE} derived from numerical simulations for the same ranges of model parameters as mentioned above (grain size: 0.5 – 5 mm; cooling rate: 1 – 1000 °C/Myr; volume proportions: $\phi_{\text{gt}}: \phi_{\text{cpx}} = 1:9, 1:1$ and 9:1) with the prescribed cooling paths of Geotherm50 and Geotherm90, respectively. It is apparent that the correlation between T_{REE} and P_{REE} are very consistent with the cooling curves Geotherm50 and Geotherm90, especially when garnet proportion is close to or smaller than clinopyroxene proportion (red circles and blue crosses). When garnet proportion increases to $\phi_{\text{gt}}: \phi_{\text{cpx}} = 9:1$ (green diamonds), T_{REE} and P_{REE} deviate from the cooling paths with the maximum values of 20 °C and 0.2 GPa, respectively, which are equivalent to the discrepancies caused by 10% analysis errors in REE measurement (Fig. 11 of Sun and Liang, 2015). Therefore, T_{REE} and P_{REE} derived from the REE-in-garnet-clinopyroxene thermobarometer can provide reasonable estimates on the thermal history of garnet-clinopyroxene bearing rocks that experienced cooling (or heating).

4. Geological applications

Since closure temperature is closely related to cooling rate, grain size and element diffusion coefficient (e.g., Dodson, 1973; 1986; Ganguly & Tirone, 1999; Gardés and Montel 2009; Watson & Cherniak, 2013; Liang 2014), we used closure curves defined by the REE and major element closure temperatures (T_{REE} vs. $T_{\text{Fe-Mg}}$) to estimate cooling rates for two-pyroxene bearing rocks in recent studies (Dygert and Liang, 2015; Wang et al., 2015; Yao and Liang, 2015). One of the main objects of the thermobarometry study of garnet- and clinopyroxene-bearing samples is to examine the pressure change associated with the temperature variation during thermal evolution. Here we conduct numerical simulations along different thermal evolution paths (exhumation and subduction) to calculate the T_{REE} and P_{REE} for coexisting garnets and clinopyroxenes, to estimate cooling or heating rates, and to further acquire the changing rates of pressure (depth) according to the correlation between T_{REE} and P_{REE} for garnet- and clinopyroxene-bearing rocks from active environments. As discussed in Section 3, volume proportion does not affect T_{REE} and P_{REE} significantly as long as garnet proportion is not extremely high. In the examples given below, we use results from numerical simulations with $\phi_{\text{gt}}: \phi_{\text{cpx}} = 1:1$.

4.1. Granulites, eclogites and peridotites from cooling tectonic settings

Sun and Liang (2015, and references therein) compiled major and trace element data for 27 garnet- and clinopyroxene-bearing samples (garnet peridotites, granulites and eclogites) that experienced cooling during exhumation processes. Based on the correlation between T_{REE} and P_{REE} calculated using the REE-in-garnet-clinopyroxene

thermobarometer and difference between T_{REE} and temperatures calculated using major element based thermometer of Krogh (1988, designated as T_{K88} hereafter), they discussed cooling and exhumation histories of these samples. Here we conduct numerical simulations along possible exhumation paths to derive T_{REE} and P_{REE} , and quantify the cooling and exhumation rates for these samples.

Grasemann et al. (1998) discussed different types of temperature evolution during the exhumation of ultra-high pressure rocks in the framework of dynamic simulations that incorporate geothermal gradient change. According to Grasemann et al. (1998), geothermal gradient can become steeper or gentler during exhumation, which can cause a phenomenon that rocks seem to upwell and cool across geotherms. The most common situation is when the geothermal gradient is colder than steady state during exhumation and relaxes towards the higher temperature with the instantaneous temperature change rate that is still positive. In this case, a rock appears to exhume from colder geotherms toward warmer geotherms (e.g., Fig. 6a). A less common situation is when geothermal gradient is hotter than steady state and relaxes toward lower temperatures, and this situation applies to exhumation after magmatism or where fast exhumation is followed by slower exhumation. In this case, a rock appears to exhume from warmer geotherms toward colder geotherms (e.g., magenta dashed line in Fig. 6b). Here we focus on the more common situation and run numerical simulations to derive T_{REE} and P_{REE} along two sets of apparent upwelling paths from colder to warmer geotherms. One set (paths a, Fig. 6a) is from a colder geotherm with surface heat flux of 40 mWm^{-2} (blue solid line labeled as Geotherm40) to a warmer geotherm with surface heat flux of 90 mWm^{-2} (red solid line labeled as Geotherm90). The other set (paths b, Fig. 6b) is from a geotherm with surface

heat flux of 50 mWm^{-2} (green solid line labeled as Geotherm50) to Geotherm90 (red solid line). The black dashed lines in Fig. 6 represent the apparent exhumation paths of the eclogites. Initial (peak) temperatures and pressures are labeled along the colder geotherms, and the target (final) temperature ($600 \text{ }^{\circ}\text{C}$) and pressure (0.82 GPa) is labeled on Geotherm90. For comparison, we also derived T_{REE} and P_{REE} along a third exhumation path from the hotter Geotherm90 to the colder Geotherm50 (path c in Fig. 6b).

Temperatures (T_{REE}) and pressures (P_{REE}) from aforementioned numerical simulations are calculated using the REE-in-garnet-clinopyroxene thermobarometer and plotted in Fig. 7a. Paths (a), (b) and (c) correspond to those labeled in Fig. 6. Each curve represents numerical simulations of grain sizes from 0.5 to 5 mm and cooling rates from 1 to $1000 \text{ }^{\circ}\text{C/Myr}$. The grey area outlines the general exhumation trend of the natural samples (yellow diamonds, Sun and Liang, 2015 and references listed in the caption of Fig. 7). The exhumation trends of the numerical simulations, especially paths (a), are consistent with exhumation trend defined by the natural samples. An exhumation rate can be calculated for these samples according to the relationship between T_{REE} and P_{REE} given the cooling rate experienced by the samples. Samples with pressures of lower than 1 GPa , especially those outlined in light grey area may experience an exhumation path from hotter geotherm to colder geotherm when comparing with path (c), but different initial and final temperatures and pressures. Alternatively, these samples could also be interpreted as being affected later processes that resulted in rotation in the inversion diagram, which causes underestimation of pressure (see details in the supplementary materials of Sun and Liang, 2015).

In order to estimate cooling rates for the garnet- and clinopyroxene-bearing rocks, we follow a method similar to that described in Dygert and Liang (2015) and Yao and Liang (2015) by constructing closure curves defined by REE and major element closure temperatures. In Fig. 7b, we plot closure curves (red lines) of T_{REE} versus Fe-Mg closure temperatures (designated as $T_{\text{Fe-Mg}}$) over the garnet- and clinopyroxene-bearing samples to derive their cooling rates. T_{REE} are results of numerical simulations of paths (a), from Geotherm40 to Geotherm90. $T_{\text{Fe-Mg}}$ are calculated using the modified Dodson's equation that incorporates the relationship between temperature and pressure (Eq. 2, Liang, 2015, personal communication) and Fe-Mg inter-diffusion coefficients. The expression of the modified Dodson's equation is,

$$\frac{\alpha R(T_A^c)}{d_A^2 \dot{s}} D_A^{T_A^c} = E_{a,A} + \left(P_A^c - \frac{dP_A}{dT_A} T_A^c \right) V_{a,A}, \quad (2a)$$

where α is the same geometric factor as the exponential of G in Dodson's equation (1973, 1986); $D_A^{T_A^c}$ is the diffusion coefficient of the element of interest at its closure temperature; d_A is the effective diffusion radius; $\dot{s}$ is the cooling rate at the closure temperature; R is the gas constant; T_A^c and P_A^c are the closure temperature and closure pressure of the element of interest, respectively; $E_{a,A}$ is the diffusion activation energy; $V_{a,A}$ is the diffusion activation volume of the mineral of interest; dP_A/dT_A is the slope of the P-T paths. Along a linear cooling path, temperature and pressure are related through,

$$P_A = P_A^c + \frac{dP_A}{dT_A} (T_A - T_A^c). \quad (2b)$$

Clinopyroxene is likely the rate-limiting mineral in the garnet-clinopyroxene systems, so that we choose Fe-Mg inter-diffusion coefficients of clinopyroxene (Müller et

al., 2013) in the calculation of $T_{\text{Fe-Mg}}$. Initial temperatures (900 – 1200 °C) are labeled as blue at the right of the 1:1 grey line, and each of the red curves represents grain sizes from 0.5 to 5 mm and cooling rates from 1 to 1000 °C/Myr. For the purpose of illustration, contours of cooling rates for an effective grain size of 2 mm are plotted as black dots connected by dashed black lines. For an effective grain size of 2 mm, the inferred cooling rates for these garnet peridotites, granulites and eclogites are $\sim 10^{-1}$ to 10^2 °C/Myr, which correspond to exhumation rates of 0.03 to 45 mm/yr. These exhumation rates are consistent with those derived by isotopic dating and petrographic studies for garnet- and clinopyroxene-bearing rocks from orogenic terranes (e.g., Rubatto and Hermann, 2001; Carswell et al., 2003).

4.2. Granulites, eclogites and peridotites from thermally perturbed settings

Sun and Liang (2015) also applied the REE-in-garnet-clinopyroxene thermobarometer to rocks that experienced heating, such as subduction, delamination or magmatic heating. They predicted the subduction trend for 37 representative granulites, eclogites and peridotites around the world (Sun and Liang, 2015 and references therein), based on the difference between T_{REE} and major element temperatures (T_{K88}) and the correlation between T_{REE} and P_{REE} . However, T_{REE} and P_{REE} distributions of these garnet- and clinopyroxene-bearing samples are relatively scattered, which may suggest different heating processes due to the complex thermal structure of the arc lithosphere and subduction trajectories (e.g., Peacock 1996; Kelemen et al., 2004; Arcay et al., 2007; Syracuse et al., 2010; Hacker et al., 2011). Thermal structure of a subduction zone depends on many parameters, including but are not limited to, age of the incoming

lithosphere, convergence rate, geometry of subduction slab, radioactive heating, convection in the overlying mantle wedge, shear heating along the subduction zone, mantle viscosity, and hydrothermal circulation. In order to calculate heating and subduction rates for samples from subduction environments, more detailed investigations into the thermal structure of different subduction zones incorporating these important parameters are needed. For the purpose of demonstration, we examine the variation of T_{REE} and P_{REE} along representative temperature-pressure (P-T) paths along the subducting slab as follows.

Here, we run numerical simulations along two selected subduction zone P-T paths (Fig. 8) from Peacock (1996) to examine the evolution of T_{REE} and P_{REE} , and derive the preliminary information about heating and subduction rates for these rocks. Red and blue solid lines in Fig. 8 represent the P-T conditions on the surface of the subducting slab along subduction zones with convergence rates of 10 and 100 mm/yr, respectively (Peacock, 1996). The subduction angle is fixed at 26.6° , and therefore the heating rates along these P-T paths are ~ 20 and 200°C/Myr , respectively. The age of the incoming lithosphere is 50 Ma, the shear stress is a constant 100 MPa, and values for other parameters can be found in Peacock (1996). There is difficulty in selecting initial conditions. Here, we choose a lowest possible temperature of 800°C at which eclogites are formed as the initial temperature, and pressures that correspond to the initial temperature on the P-T paths as the initial pressure. The initial and selected possible peak temperatures and pressures are labeled along the P-T paths. Since major elements diffuse much faster than REE, we assume that they reach instantaneous equilibrium during

heating. We use the temperatures at the rim of the coexisting garnet and clinopyroxene (T_{REE}^{rim}) to represent major element based temperatures (T_{K88}) during heating.

We plot P_{REE} versus T_{REE} from the aforementioned numerical simulations in Fig. 9a and T_{REE} versus T_{REE}^{rim} in Fig. 9b. The symbols in Fig. 9 are garnet- and clinopyroxene-bearing samples compiled by Sun and Liang (2015). In Fig. 9a, orange area outlines a general subduction trend, and the pink area covers majoritic garnets from Western Gneiss Region in Norway, which involved deep subduction during the orogenic process (Scambelluri et al., 2008). The light grey area circles garnet peridotite xenoliths from Prahuanieyu that have been perturbed by high-temperature events (Bjerg et al., 2009). The exceptionally low pressures in these samples may result from the rotation in T_{REE} and P_{REE} inversion diagram (Sun and Liang, 2015). Red and blue lines are correlations between T_{REE} and P_{REE} from numerical simulations corresponding to the P-T paths in Fig. 8. The correlation between T_{REE} and P_{REE} can reproduce the general subduction trend estimated by the nature samples and enclose a wide range of the samples. The heating rates for these samples are $\sim 20 - 200$ °C/Myr or higher according to the correlation of T_{REE} and P_{REE} and the subduction angle 26.6 °C. However, some of the samples cannot be explained by T_{REE} and P_{REE} derived from the simple subduction scenarios (e.g., majoritic garnets from Norway).

As first order approximation, we also estimate heating rate for these garnet- and clinopyroxene-bearing samples through the temperature differences between T_{REE} and T_{REE}^{rim} in Fig. 9b. Lines of the given convergence rates (10 and 100 mm/yr) for an effective grain size of 2 mm are plotted as red dots connected by solid red lines, and the same convergence rates for an effective grain size of 0.5 mm are plotted as green dots and

green lines. For convergence rates of 10 and 100 mm/yr, the effective grain sizes of 0.5 – 2 mm can only enclose a small proportion of the natural samples. One of the reasons that cause the large discrepancies may be our overestimation of major element temperatures using T_{REE}^{rim} to represent T_{K88} . Another possible reason is that these garnet- and clinopyroxene-bearing rocks are formed at different starting temperatures and pressures. To resolve this problem, detailed examination on the subducting paths of the rocks, a well-constrained closure temperature equation, and model for Fe-Mg exchange during heating processes are needed. Again, since samples have experienced complex thermal histories at subduction zones, there may be large uncertainties in the estimated heating or subduction rates.

5. Summary

To investigate the physical meaning of temperature (T_{REE}) and pressure (P_{REE}) calculated using the REE-in-garnet-clinopyroxene thermobarometer, we conduct numerical simulations of REE diffusive redistribution between coexisting garnet and clinopyroxene. We show that T_{REE} and P_{REE} represent the average REE closure temperature and pressure of the garnet and clinopyroxene system. The correlation between T_{REE} and P_{REE} are consistent with the given cooling paths (Geotherm50 and Geotherm90 in Fig. 5), which indicates that an upwelling or downwelling rate of pressure (depth) can be derived based on the correlation between T_{REE} and P_{REE} once a cooling or heating rate is specified.

We derive cooling rates of 10^{-1} to 10^2 °C/Myr for garnet- and clinopyroxene-bearing samples that experienced upwelling and cooling, using closure curves constrained by REE and major element closure temperatures (Fig. 7b). Based on the correlation between T_{REE} and P_{REE} (Fig. 7a), we further estimate exhumation rates of ~ 0.03 to 45 mm/yr for these samples, which are consistent with those derived from isotopic dating studies for samples from orogenic terranes. We use a similar method to derive heating rates of $\sim 20 - 200$ °C/Myr and convergence rates of $\sim 10 - 100$ mm/yr for selected garnet- and clinopyroxene-bearing rocks that experienced subduction or heating events (Fig. 9). However, relatively large uncertainties may exist in the heating and subduction rates estimation due to the complex thermal structure at subduction environments. More detailed investigations about the T_{REE} and P_{REE} evolutions at subduction zone are needed.

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Figure Captions

Figure 2-1 Representative geotherms from Pollack and Chapman (1977). Geotherm40 (blue), Geotherm50 (green) and Geotherm90 (red) represent continent lithospheric geotherms with the surface heat flow $Q = 40, 50$ and 90 mWm^{-2} and 50 mWm^{-2} , respectively.

Figure 2-2 Variations of REE partition coefficients between garnet and clinopyroxene (k_{gt-cpx}^{REE}) as a function of temperature based on the model of Sun and Liang. (2014) and temperature and pressure variation along Geotherm50 (solid lines) and Geotherm90 (dashed lines) for selected REE. Major element concentrations of garnet and clinopyroxene from a well-equilibrated eclogite JDE 03 (Smart et al., 2009) are used in the calculation.

Figure 2-3 (a) Arrhenius plot of REE diffusion coefficients in diopside (Van Orman et al., 2001). (b) Arrhenius plot of REE diffusion coefficients in garnet (Van Orman et al., 2002; Tirone et al., 2005). Pressure effects are both considered for REE diffusivities in garnet and clinopyroxene, and pressure varies with temperature along Geotherm50.

Figure 2-4 An example of calculated diffusing profiles of La (a) and Lu (b) in the coexisting garnet and clinopyroxene at selected times (note the different scales of the element concentrations in the two minerals). Grain sizes of garnet and clinopyroxene are 2 mm, and the cooling rate is $20 \text{ }^{\circ}\text{C/Ma}$. See text for details.

Figure 2-5 Correlation between T_{REE} and P_{REE} for three choices of mineral proportions (red circles: $\phi_{\text{gt}}: \phi_{\text{cpx}} = 1:1$; blue crosses: $\phi_{\text{gt}}: \phi_{\text{cpx}} = 1:9$; green diamonds: $\phi_{\text{gt}}: \phi_{\text{cpx}} = 9:1$), overlying the prescribed cooling path Geotherm50 (grey solid line) and Geotherm90 (darker grey solid line).

Figure 2-6 Apparent exhumation P-T paths of garnet- and clinopyroxene-bearing rocks. Geotherms are the same with those in Fig. 1. Black dashed lines represent the apparent exhumation paths of the rocks.

Figure 2-7 Correlation between P_{REE} and T_{REE} (a) derived from exhumation paths in Fig. 6 and closure curves constrained by T_{REE} and major element closure temperatures ($T_{\text{Fe-Mg}}$, b) overlying representative granulites, eclogites and garnet peridotites from cooling environments. a. Paths (a) are derived from exhumation paths from Geotherm40 to Geotherm90 in Fig. 6a, paths (b) are derived from exhumation paths from Geotherm50 to Geotherm90 in Fig. 6b, path (c) is derived from exhumation path from Geotherm90 to Geotherm50 of Fig. 6b (magenta dashed line). b. Red curves represent closure curves constrained by T_{REE} and $T_{\text{Fe-Mg}}$, which represent the major element closure temperature of the garnet and clinopyroxene system. $T_{\text{Fe-Mg}}$ are calculated using a modified Dodson's closure temperature formulation of Liang (in prep.) that incorporate the relationship between temperature and pressure and the Fe-Mg inter-diffusion in clinopyroxene of Müller et al. (2013). Initial temperatures (T_0) are listed on the right of the grey 1:1 line. Each curve in (a) and (b) represents closure temperatures or pressures for a range of simulations of grain sizes from 0.5 to 5 mm and cooling rates from 1 to 1000 °C/Myr.

The black dots connected by thin dashed black lines are cooling rates (in °C/Myr) indicated by the numbers above for a grain size of 2 mm. The garnet- and clinopyroxene-bearing rocks are from: Koreshkova et al. (2011), Nehring et al. (2010), Tang et al. (2007), Spengler et al. (2006), Chin et al. (2012).

Figure 2-8 Selected subduction P-T paths on the surface of the subducting slab from Peacock (1996).

Figure 2-9 Correlation between P_{REE} and T_{REE} (a) derived from subduction paths in Fig. 8 and contours of convergence (heating) rates constrained by T_{REE} and T_{REE}^{rim} (b). Red curves are contours of convergence (heating) rates (in mm/yr, indicated by the numbers in blue boxes) for grain size of 2 mm, and green curves are those for a grain size of 0.5 mm. The granulites, eclogites and garnet peridotites are from: Jacob and Foley (1999), Shatsky et al. (2008), Jacob et al. (2009), Smart et al. (2009), Scambelluri et al. (2008), Gysi et al. (2011) and Bjerg et al. (2009).

Figures

Figure 2-1

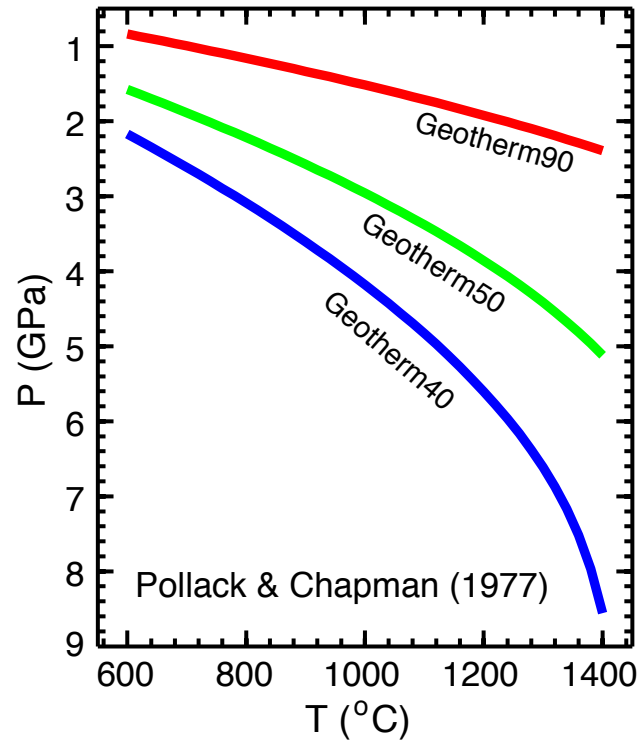


Figure 2-2

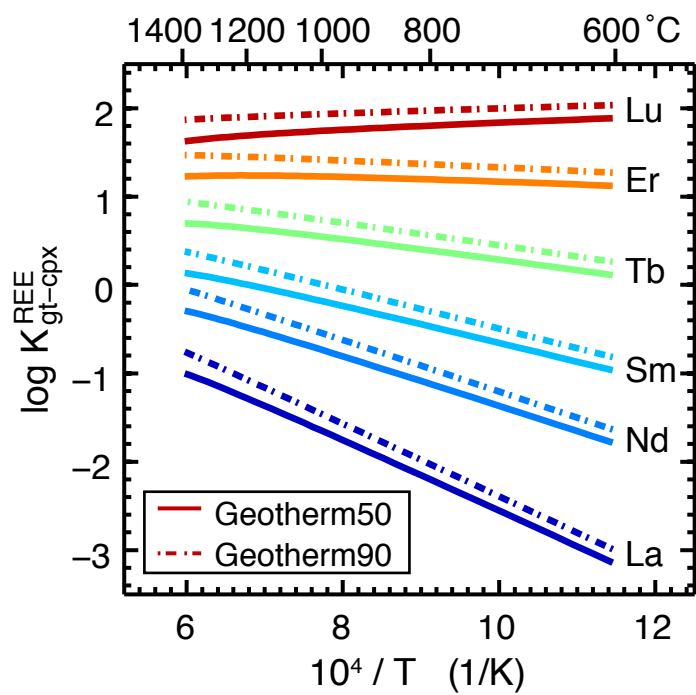


Figure 2-3

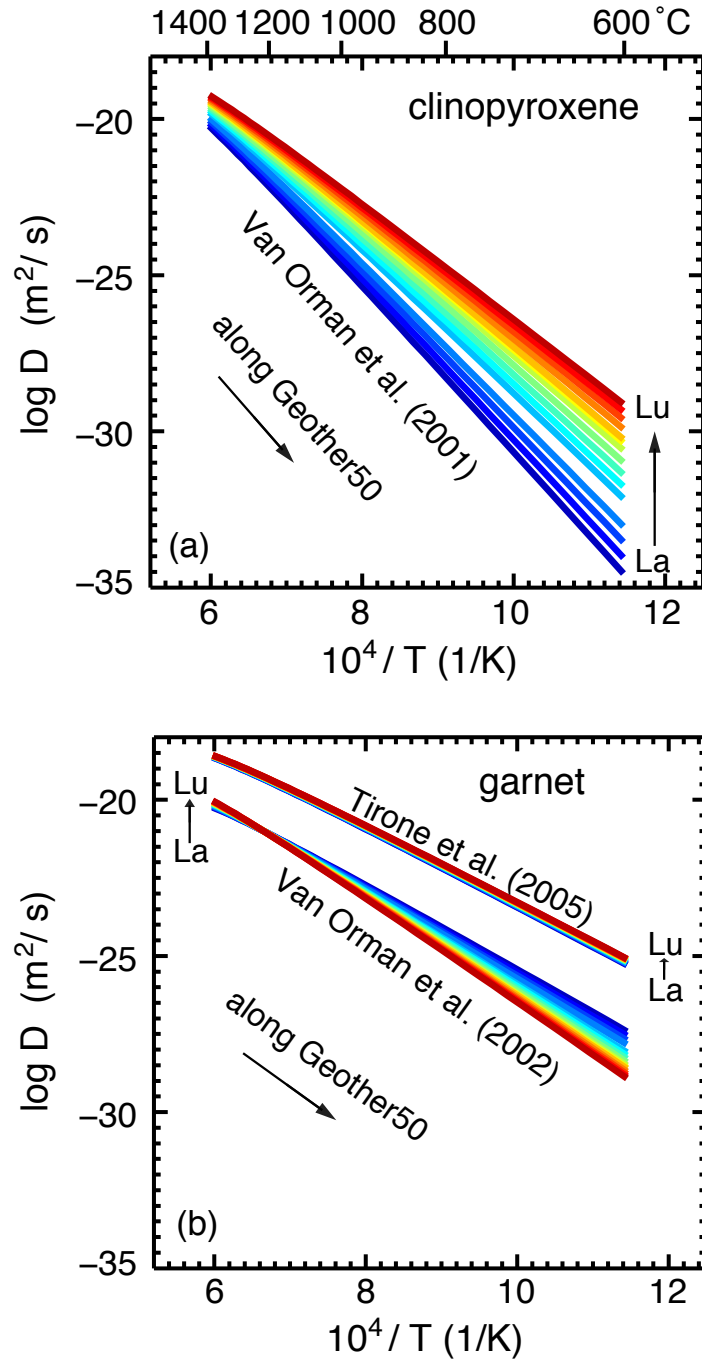


Figure 2-4

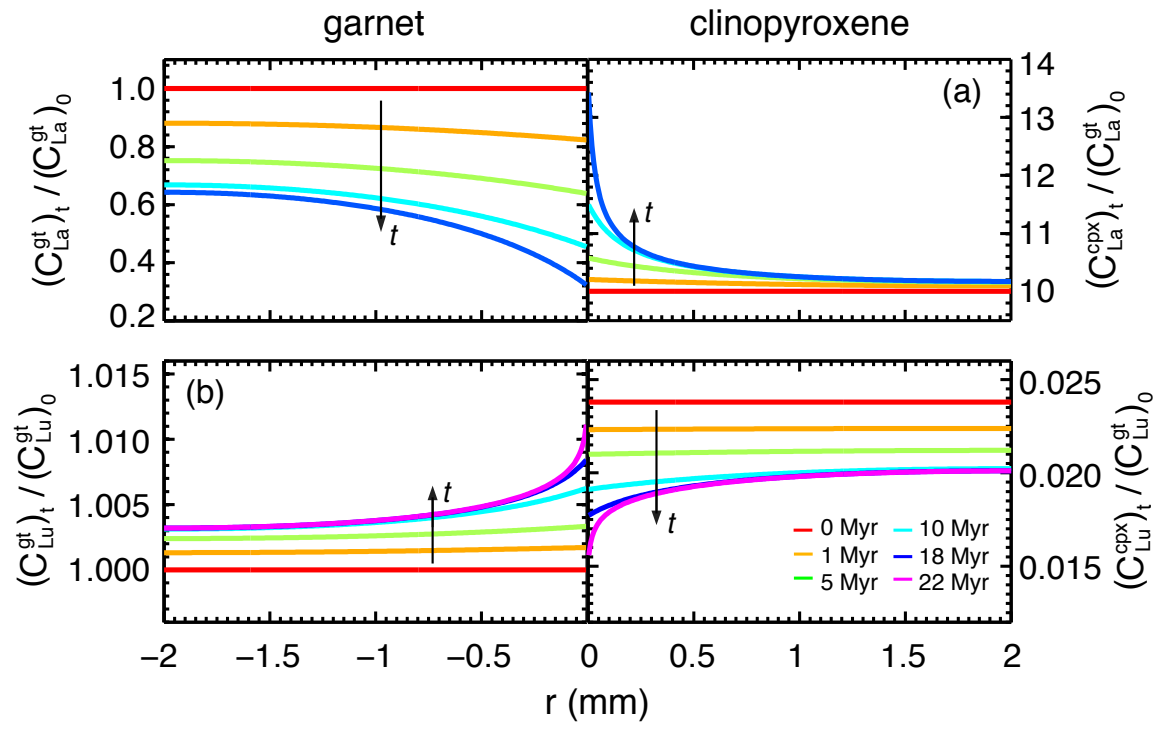


Figure 2-5

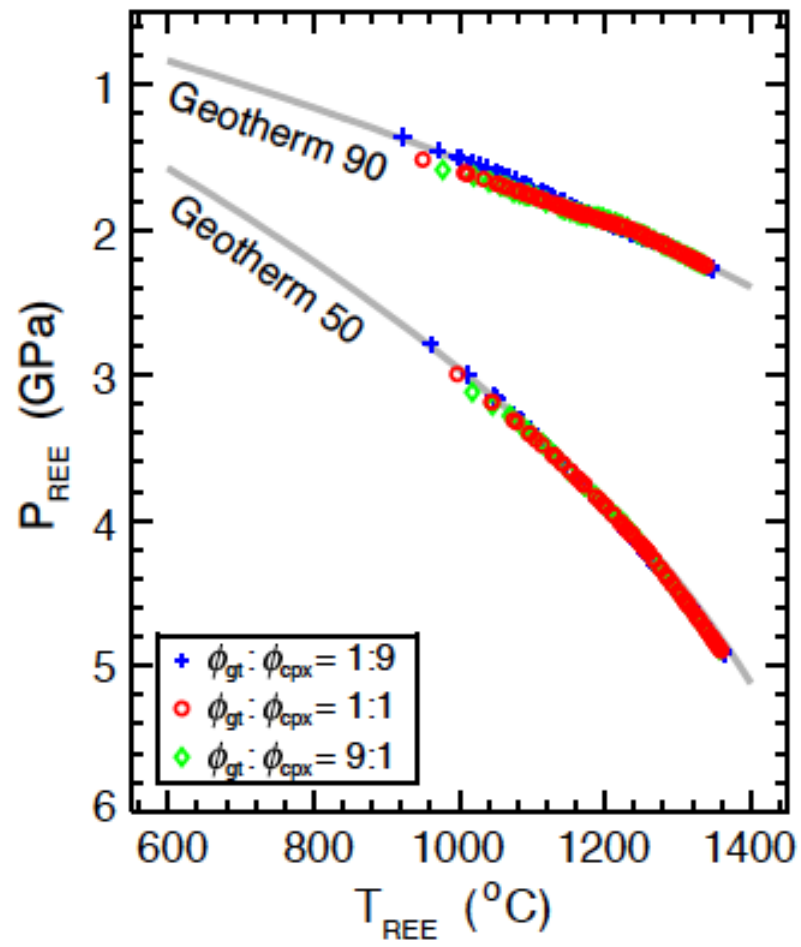


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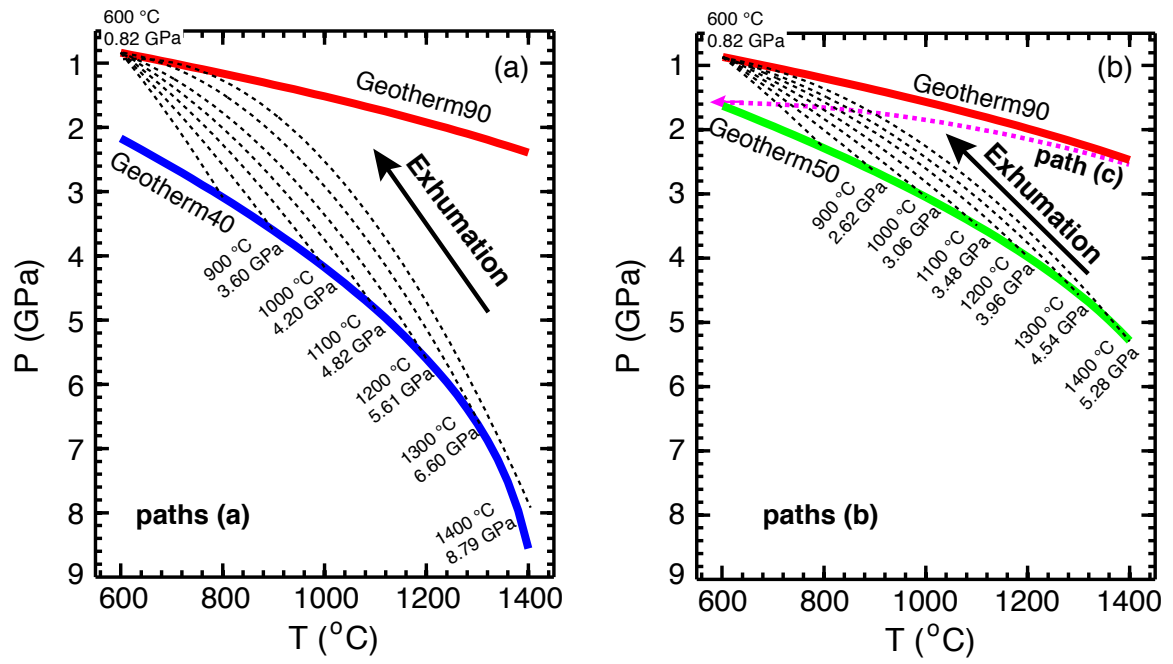


Figure 2-7

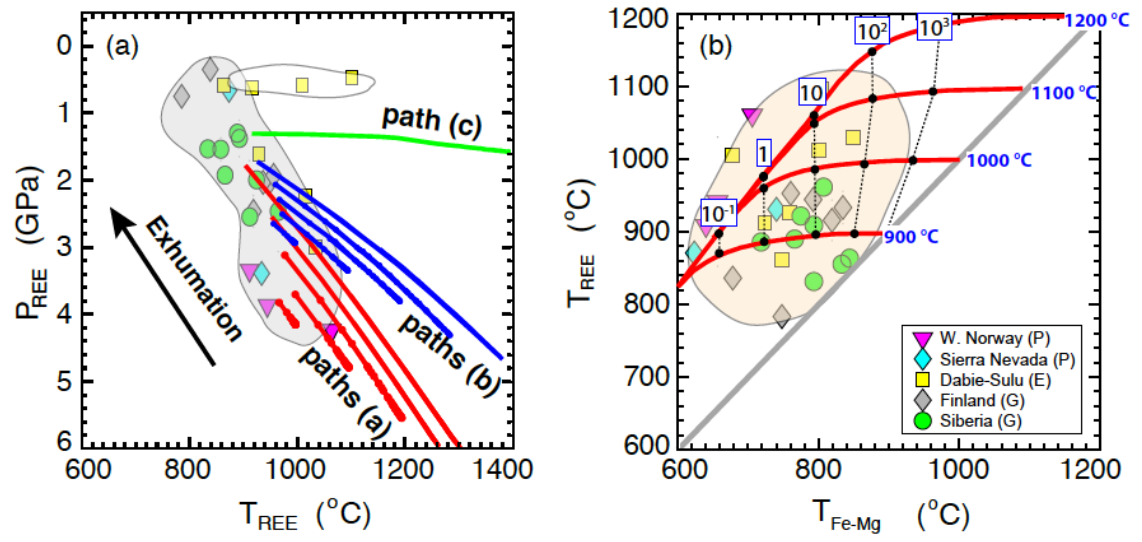


Figure 2-8

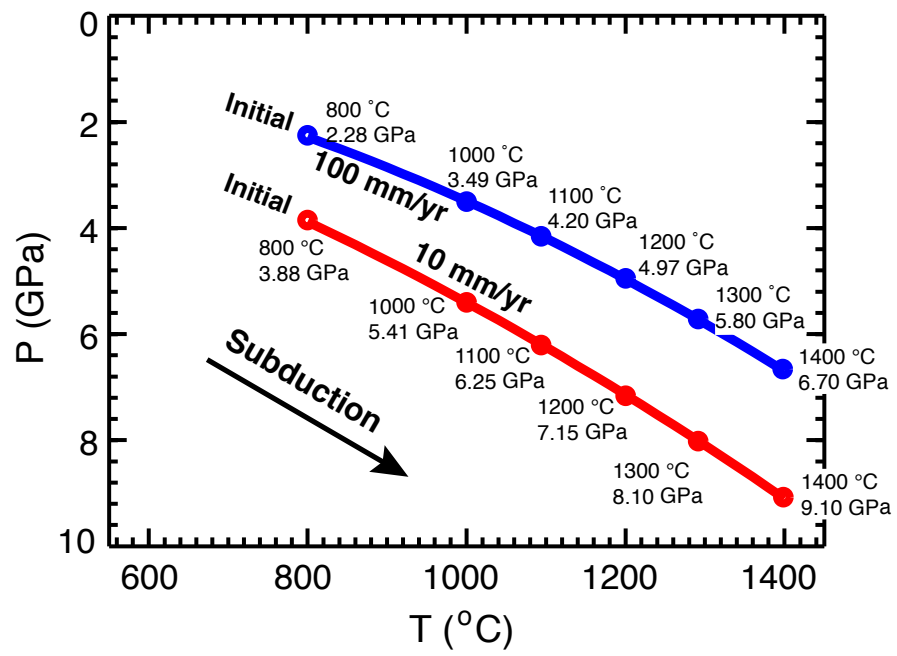
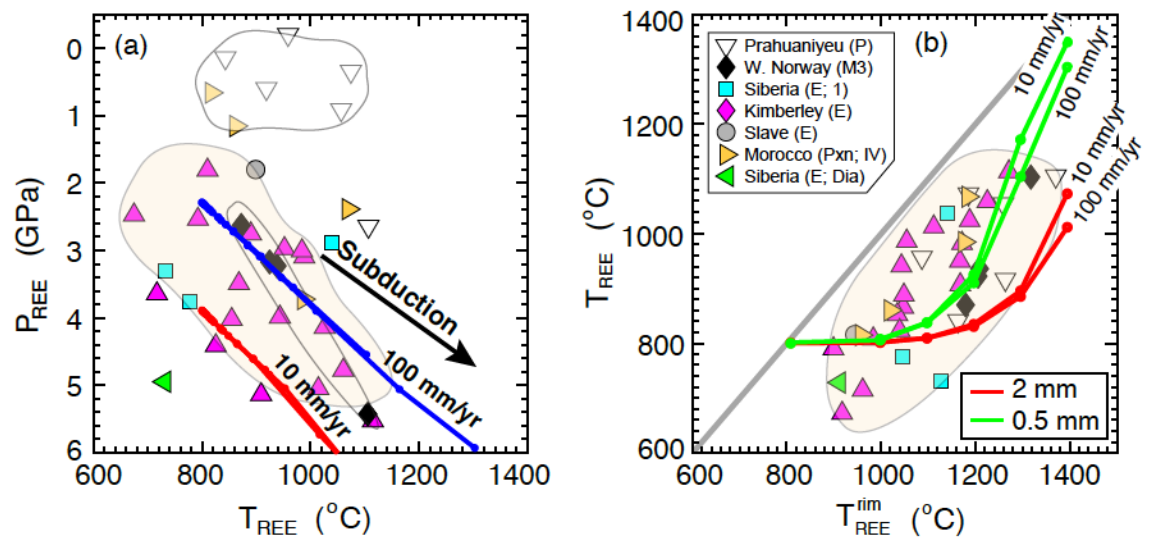


Figure 2-9



Supplementary Material

Table of Contents	
Figure 2-S1	Derivation of La and Lu closure temperatures in garnet and clinopyroxene system
Figure 2-S2	Comparison between T_{REE} and P_{REE} and the average REE closure temperatures and pressures defined by Fig. S1
Figure 2-S3	Effect of REE diffusion coefficients in garnet on T_{REE}

Supplementary Figure 2-S1

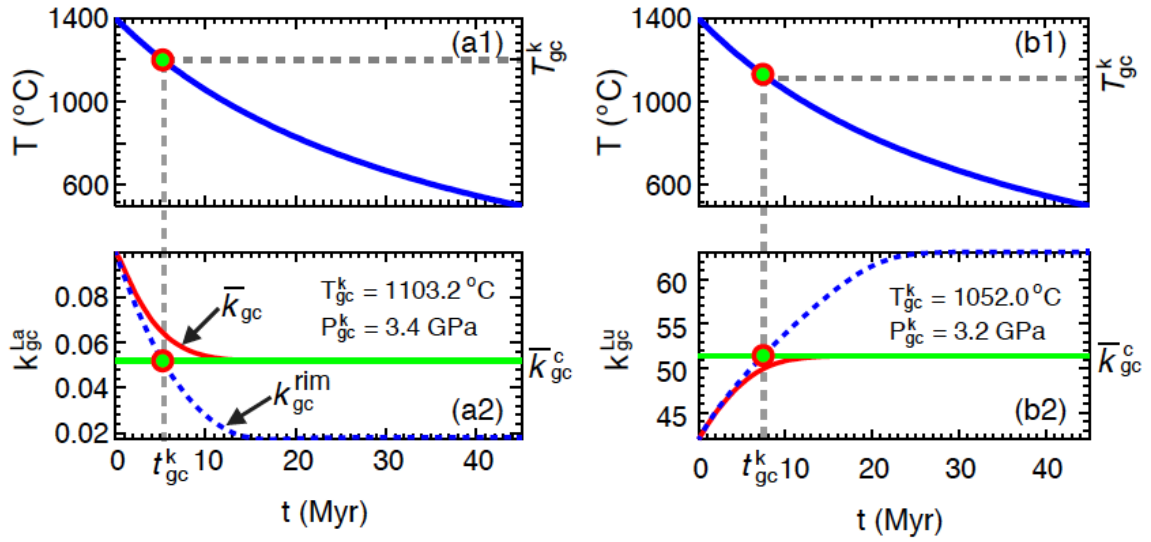


Figure 2-S1. Derivation of closure temperatures for La (a1-a2) and Lu (b1-b2) based on the evolutions their effective partition coefficients in the cooling garnet-clinopyroxene system. Grain size in this example is 2 mm and cooling rate is 20 °C/Myr along Geotherm50. (a1)-(b1) Cooling curves as prescribed by Eq. 1d. (a2)-(b2) Evolution of the rim (blue dashed lines, k_{gc}^{rim}) and average (red lines, $\bar{k}_{gc}^c$) effective partition coefficients of La and Lu between garnet and clinopyroxene. The intercepts (cyan dots) of the blue dashed line and the green line in (a2) to (b2) are projections of asymptotic effective partition coefficients of La and Lu to their rims, which correspond to closure temperatures (T_{gc}^k in a1 and b1) and closure time (t_{gc}^k in a2-c2). The closure pressures (P_{gc}^k) are obtained by projecting closure temperatures to the cooling path which is Geotherm50 in Fig. 1.

Supplementary Figure 2-S2

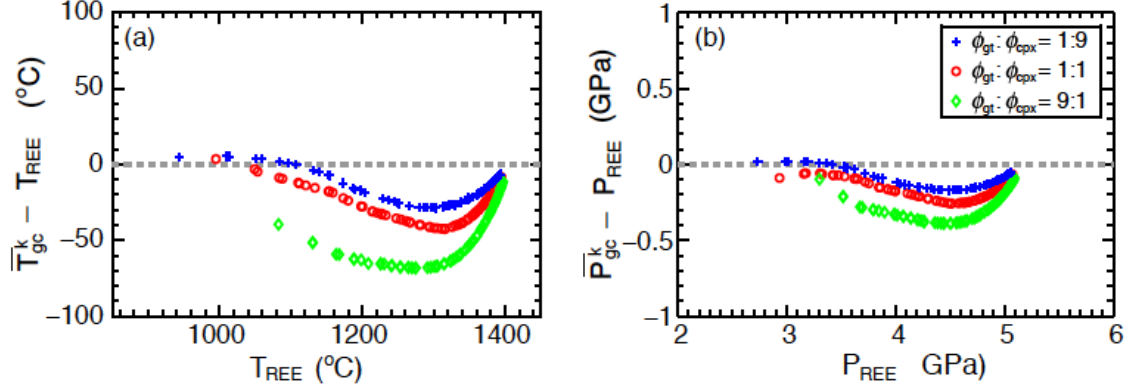


Figure 2-S2. Comparison between temperatures (a) and pressures (b) calculated using REE-in-garnet-clinopyroxene thermobarometer (T_{REE} and P_{REE}) and the average REE closure temperatures and pressures defined by their effective partition coefficient between opx and cpx ($\bar{T}_{gc}^k$ and $\bar{P}_{gc}^k$) for three choices of mineral proportions: $\phi_{gt} : \phi_{cpx} = 1:1$ (red circles); blue crosses for $\phi_{gt} : \phi_{cpx} = 1:9$; and green diamonds for $\phi_{gt} : \phi_{cpx} = 9:1$. T_{REE} and P_{REE} are calculated using the REE-garnet-clinopyroxene thermobarometer and the average concentrations of REE in garnet and clinopyroxene after the establishment of the closure profiles. Since REE closure temperatures are not linearly related with REE ionic radii, we calculate their average closure temperatures ($\bar{T}_{gc}^k$) and pressures ($\bar{P}_{gc}^k$) through trapezoidal rule over REE ionic radii. The ranges of grain sizes are 0.5 – 5 mm and cooling rates are 1 to 1000 °C/Myr. The difference between $\bar{T}_{gc}^k$ and T_{REE} is increases as garnet proportion increases, and the maximum difference is ~ 70 °C as garnet proportion increases to $\phi_{gt} : \phi_{cpx} = 9:1$. The maximum difference between $\bar{P}_{gc}^k$ and P_{REE} is ~ 0.4 GPa. The maximum differences between T_{REE} and P_{REE} and $\bar{T}_{gc}^k$ and $\bar{P}_{gc}^k$ are less than those caused by 20% REE analysis error during T_{REE} and P_{REE} inversion (see Fig. 11 of Sun and Liang, 2015). Accordingly, the T_{REE} and P_{REE} can represent the average REE closure temperatures and pressures for most of the eclogites, granulites and garnet peridotites.

Supplementary Figure 2-S3

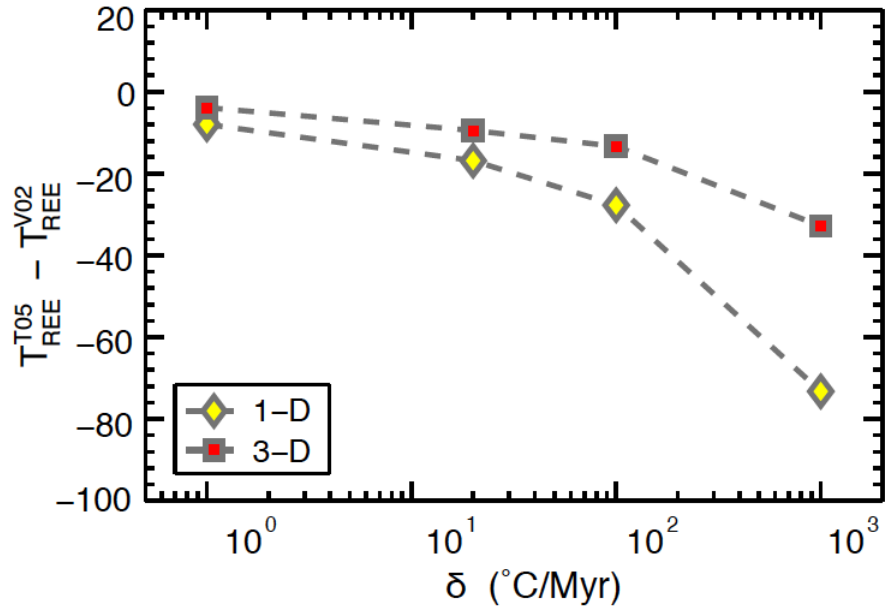


Figure 2-S3. Comparison of REE closure temperatures between those calculated using REE diffusion coefficients of Van Orman et al. (2002, $T_{\text{REE}}^{\text{V02}}$) and those using REE diffusion coefficients of Tirone et al. (2005, $T_{\text{REE}}^{\text{T05}}$) for a grain size of 0.5 mm and cooling rates as plotted. The higher REE diffusion coefficients of Tirone et al. (2005) cause $T_{\text{REE}} \sim 35^{\circ}\text{C}$ lower at most. The maximum difference for the whole ranges of cooling rates and grain size described in this study is $\sim 40^{\circ}\text{C}$, which corresponds to a pressure of ~ 0.2 GPa at most along the three geotherms (Geotherm40, Geotherm50 and Geotherm90). These differences are smaller than those caused by 20 % analysis errors, and can only cause overestimation in cooling or heating rates by a factor of less than two.

CHAPTER 3

Closure Temperature in Cooling Bi-Mineralic Systems: II. Subsolidus Major Element Redistribution and Its Effect on REE Redistribution and Closure Temperature in Two-Pyroxene Systems

Abstract

Subsolidus redistribution plays an important role in altering the original major and trace element compositions in coexisting mantle minerals. In two recent studies, Sun and Liang (2014) and Yao and Liang (2015) assessed equilibrium and diffusive redistribution of REE among coexisting mantle minerals during subsolidus cooling. The analyses are simplified by assuming constant mineral major element compositions and proportions during cooling. However, major elements redistribute during subsolidus reequilibration, which may significantly affect REE partitioning between coexisting minerals. In the first part of this study, we investigate major element redistribution among coexisting minerals in spinel peridotites through thermodynamic calculation, and examine their effect on REE re-equilibration during subsolidus cooling. Incorporating the effect of major element redistribution on REE partition coefficients between different minerals, we found that heavy REE concentrations in clinopyroxene can increase by a factor of two when temperature decreases from 1300 to 800 °C. This extent of increase is smaller than those calculated by considering temperature effect only. The increased heavy REE contents in clinopyroxene can generate a wide range of increased $(Yb)_N$ and decreased $(Sm/Yb)_N$ values, which has been interpreted as a garnet signature in the mantle source for abyssal peridotites. This is consistent with what has been suggested by Sun and Liang (2014) that REE re-equilibration can give rise to false garnet signatures in the mantle source for abyssal peridotites. In the second part of this study, we conduct numerical simulations of major elements and REE diffusive redistribution between coexisting orthopyroxene and clinopyroxene to examine the major element effect on REE closure temperature. Major elements close at a later stage of cooling than REE due to their faster diffusion rates. The

decoupling in closure times between major elements and REE can result in ± 20 °C uncertainties in REE closure temperatures calculated using the REE-in-two-pyroxene thermometer. Major element closure temperatures are systematically higher than those calculated using Dodson's equation and Fe-Mg inter-diffusion coefficients. The maximum difference can be 120 °C. However, the major element redistributions are calculated based on the thermodynamic software THERMOCALC, which has not considered the effects of minor elements on major element redistribution, so that these calculations can only be taken as semi-quantitative.

1. Introduction

The compositional information recorded in the rocks from the lower crust and uppermost mantle is important to understand the melting processes of the interior of the Earth and its dynamic evolution. However, during subsolidus re-equilibration, major, minor, and trace element compositions in minerals redistribute, which has been used as thermobarometers (e.g., Brey and Köhler, 1990; Krogh, 1988; Nimis and Taylor, 2000). In a recent study, Sun and Liang (2014) assessed the effect of subsolidus re-equilibration on REE redistribution between a pair of major mantle minerals in spinel and garnet peridotites based on internally consistent lattice strain models for REE partitioning among mantle minerals. According to Sun and Liang (2014), subsolidus redistribution can increase heavy and middle REE abundances in clinopyroxene (cpx) by a factor of three in spinel peridotite, which can give rise to a false garnet signature in residual peridotites. In their study, Sun and Liang (2014) focused on the effect of temperature on REE re-distribution among mantle minerals. However, major elements play an important role in affecting REE partitioning (Liang et al., 2013; Sun and Liang, 2014), and their redistribution also affects REE re-equilibration substantially.

In a recent study, we developed a REE-in-two-pyroxene thermometer (Liang et al., 2013) for mafic and ultramafic rocks based on independently calibrated lattice strain models for REE partitioning between high-Ca pyroxene and basaltic melt and between low-Ca pyroxene and basaltic melt (Sun and Liang, 2012; Yao et al., 2012). Application of this thermometer to abyssal peridotites and mafic cumulates that experienced cooling reveals systematically higher temperatures than those derived from major element based thermometers (e.g., Brey and Köhler, 1990; Putirka 2008). This temperature difference is

attributed to different diffusion rates between trivalent REE and divalent Ca, Mg, and Fe in pyroxenes. In order to develop a method to estimate cooling rate for mafic and ultramafic rocks, we examined the physical meaning of temperature derived from the REE-in-two-pyroxene thermometer (T_{REE}) through numerical simulations of REE diffusive redistribution in two-pyroxene systems (Yao and Liang, 2015), and demonstrated that T_{REE} are essentially the same as average REE closure temperatures in the cooling two pyroxene systems. Therefore we can use closure curves constructed by T_{REE} and major element closure temperatures to estimate cooling rates for mafic and ultramafic rocks (ophiolites, Dygert and Liang, 2015; abyssal peridotites, Yao and Liang, 2015; mantle xenoliths from North China Craton, Wang et al., 2015). To focus on the definition of closure temperature in bi-mineralic systems and the physical meaning of T_{REE} , we only considered temperature variations during cooling.

In the first part of this study, we investigate the major element redistribution under subsolidus conditions in spinel peridotites through widely used thermodynamic software and its effect on REE redistribution between coexisting cpx and orthopyroxene (opx). In the second part of this study, we will investigate the major element diffusive redistribution between coexisting opx and cpx and their effects on REE redistribution and closure temperatures using a finite difference method.

2. Equilibrium re-distribution of major elements in spinel peridotites

Here we use thermodynamic software to calculate the major element compositions for coexisting minerals at given temperatures and pressures. The most widely used thermodynamic modeling programs include THERMOCALC (e.g., Powell et al., 1998, Holland et al., 2013), Perple_X (e.g., Connolly, 1990; Connolly 2009) and Theriak-

Domino (e.g., de Capitani and Pertrakakis, 2010; Duesterhoeft and de Capitani, 2013). The current databases of Perple_X and Theriak-Domino are originated from the thermodynamic database of THERMOCALC (Holland and Powell, 1998 or updated 2002) and their own revisions. THERMOCALC is based on a nonlinear equation solver by considering the solid solution models for coexisting minerals, stoichiometric relations in the minerals and equilibrium Fe-Mg exchange coefficients. Perple_X and Theriak-Domino are based on Gibbs free energy minimization method, without considering stoichiometric constraint or Fe-Mg exchange.

2.1. Evaluation of thermodynamic programs

These aforementioned thermodynamic programs can all generate correct chemical trends for natural rocks (e.g., Klemme et al., 2009; Perkins and Anthony, 2011; Holland et al., 2013). However, when calculating element variations, Perple_X and Theriak-Domino can give rise to unreasonable results due to the lack of stoichiometric and equilibration constraints. For example, we use the updated THERMOCALC (Holland et al. 2013), Perple_X (Zibera et al. 2013 and database updated in March, 2014) and Theriak-Domino (Perkins and Anthony, 2011, with Cr₂O₃ update) to calculate mineral major element compositions over a range of temperatures using bulk compositions (Table 1) of a well-equilibrated spinel lherzolite (Mo22 from Witt-Eickschen and O'Neill, 2005) and a well-equilibrated spinel harzburgite (MM1213 from Witt-Eickschen and O'Neill, 2005). Figure 1 displays the calculated Mg# (molar percent of $100 \times \text{Mg}/(\text{Mg} + \text{Fe})$) in cpx as a function of temperature. The calculations of THERMOCALC are plotted as solid lines, calculations of Perple_X are plotted as dash-dotted lines, and calculations of

Theriak-Domino are plotted as dashed lines. It is evident that Mg# of cpx derived from Theriak-Domino and Perple_X are too high for a peridotite. The kinks in Perple_X results are due mainly to the appearance of a Cr-enriched liquid. THERMOCALC generates the most reasonable Mg# in cpx. A caveat in the application of THERMOCALC to spinel peridotite is the lack of Cr₂O₃ in its database. THERMOCALC (database of 2013 for mafic rocks) has been developed to study phase equilibria down to the uppermost lower mantle for pressures from 4 GPa and higher, so that it is not very sensitive to the pressure of spinel peridotite stability field. Both Cr₂O₃ and pressure may affect Al₂O₃ substitution in pyroxenes (e.g., Gasparik and Newton, 1984; Brey et al., 1999; Girnis and Brey, 1999; Liu and O'Neill, 2004; Klemme and O'Neill, 2000; Klemme 2004, 2009), which is an important element in affecting REE partitioning between opx and cpx. In the absence of a more accurate thermodynamic model for major elements, we use THERMOCALC as an approximation to explore the effects of major element redistribution during cooling on REE partitioning between opx and cpx in spinel peridotites.

2.2. Variation of mineral abundances in spinel peridotites

For the purpose of demonstration, we choose the same starting compositions as above (Sp Lh Mo22 and Sp Hz MM1213), which were also used in Sun and Liang (2014), to investigate major element variations in coexisting pyroxenes during subsolidus re-equilibration. A comparison of Fe-Mg exchange coefficients between THERMOCALC calculation and well-equilibrated phase equilibria experiments (Brey and Köhler, 1990) is presented in Fig. S1. They show consistent trend, but the absolute

values are slightly off, so that temperatures calculated using major element concentrations from THERMOCALC and the two-pyroxene thermometer of Brey and Köhler (1990) are not quite consistent with the given temperatures of THERMOCALC (Figs. S6-S9). Figure 2 shows the variations of mineral volume proportions in the two samples during isobaric (1 GPa) cooling. Mineral abundances in the spinel lherzolite (Sp Lh: Mo22) vary more significantly than in the spinel harzburgite (Sp Hz: MM1213). In Fig. 2a, cpx abundance decreases from 22% to 16%, opx abundance increases from 20% to 26%, olivine abundance decreases slightly from 56% to 54%, and spinel abundance increases from 1% to 3% during cooling. In Fig. 2b, mineral abundances only change slightly (to within 1%). Pyroxene proportions, especially cpx, from THERMOCALC are relatively high and olivine proportions are relatively low than those from natural samples. This may be caused in part by the lack of minor element (e.g., Cr_2O_3 , TiO_2 or NiO) in the thermodynamic dataset in THERMOCALC. Nevertheless, the overall trends and magnitudes of mineral volume variation are reasonable.

2.3. Variation of major element compositions in pyroxenes

According to THERMOCALC, Al distributes in opx in the form of Ca-Tschermak (CaAlAlSiO_6), and substitutes into cpx in the form of Ca-Tschermak and jadeite ($\text{NaAlSi}_2\text{O}_6$) components. The presence of jadeite component in cpx involves coupled substitution of Al and Na. Calcium is in the M2 (Ca^{M2}) sites of opx and cpx, and Na is in the M2 sites of cpx. Fe and Mg distribute in the M1 (Fe^{M1} and Mg^{M1}) and M2 (Fe^{M2} and Mg^{M2}) sites of opx and cpx randomly according to their $\text{Mg}^{\#}$'s. Therefore major element contents, including Ca, Mg, Fe, Al and Na, in opx and cpx follow the stoichiometric

constrains as shown in Fig. 3. Accordingly, we can calculate Al contents in M1 (Al^{M1}) and tetrahedral (Al^{T}) sites of opx and cpx using the following expressions:

$$(\text{Ca}^{\text{M2}} + \text{Fe}^{\text{M1+M2}} + \text{Mg}^{\text{M1+M2}} + \text{Al}^{\text{M1}})_{\text{opx}} = 2 \quad (1a)$$

$$(\text{Al}^{\text{T}})_{\text{opx}} = (\text{Al}^{\text{M1}})_{\text{opx}} \quad (1b)$$

$$(\text{Na}^{\text{M2}} + \text{Ca}^{\text{M2}} + \text{Fe}^{\text{M1+M2}} + \text{Mg}^{\text{M1+M2}} + \text{Al}^{\text{M1}})_{\text{cpx}} = 2 \quad (1c)$$

$$(\text{Al}^{\text{T}})_{\text{cpx}} = (\text{Na}^{\text{M2}} + \text{Al}^{\text{M1}})_{\text{cpx}} \quad (1d)$$

where cations in the above expressions are defined as molar fraction per 6 oxygen.

According to the parameterized lattice strain models of Sun and Liang, (2012) and Yao et al. (2012), partition coefficients of REE between cpx and basaltic melt are mainly affected by Mg^{M2} , Al^{T} and Al^{M1} in cpx, while partition coefficients of REE between opx and basaltic melt are affected by Al^{T} , Ca^{M2} and Mg^{M2} in opx through the following expressions,

$$k_0^{\text{cpx-melt}} = -7.14(\pm 0.53) + \frac{7.19(\pm 0.73) \times 10^4}{RT} + 4.37(\pm 0.47) X_{\text{Al}}^{\text{T}} + 1.98(\pm 0.36) X_{\text{Mg}}^{\text{M2}} \quad (2a)$$

$$r_0^{\text{cpx}} = 1.066(\pm 0.007) - 0.104(\pm 0.035) X_{\text{Al}}^{\text{M1}} - 0.212(\pm 0.033) X_{\text{Mg}}^{\text{M2}} \quad (2b)$$

$$k_0^{\text{opx-melt}} = -5.37(\pm 0.49) + \frac{3.87(\pm 0.74) \times 10^4}{RT} + 3.54(\pm 0.61) X_{\text{Al}}^{\text{T}} + 3.56(\pm 1.02) X_{\text{Ca}}^{\text{M2}} \quad (2c)$$

$$r_0^{\text{opx}} = 0.693(\pm 0.055) + 0.432(\pm 0.147) X_{\text{Ca}}^{\text{M2}} + 0.228(\pm 0.056) X_{\text{Mg}}^{\text{M2}} \quad (2d)$$

where $k_0^{\text{min-melt}}$ is the mineral-melt partition coefficient for the strain-free substitution that dominates the magnitude of REE partition coefficients; r_0^{min} is ideal lattice site for strain-free substitution that determines the distributional shape of REE partition coefficients.

For more complete expressions of the lattice strain models, a reader is referred to the references above.

In Fig. 4 we present the variations of Mg^{M2} , Al^{T} and Al^{M1} in cpx and Ca^{M2} , Al^{T} , and Mg^{M2} in opx as a function of temperature for the spinel lherzolite (red lines) and spinel harzburgite (green lines). Other pyroxene components can be found in the supplementary Figs. S2-S5. For the variations of major elements in weight percent, a reader is referred to online supplementary materials S6-S9. Magnesium concentration in M2 site ($X_{\text{Mg}}^{\text{M2}}$, Fig. 4a) and Al concentration in tetrahedral site (X_{Al}^{T} , Fig. 4b) of cpx decrease during cooling, which will result in a decrease of the partitioning of REE in cpx (Eq. 2a). Calcium concentration in M2 site ($X_{\text{Ca}}^{\text{M2}}$, Fig. 4d) and X_{Al}^{T} (Fig. 4e) of opx also decrease during cooling, which will decrease the REE partition coefficients in opx. However, REE partition coefficients of opx may decrease more strongly than cpx due to the larger coefficients of $X_{\text{Ca}}^{\text{M2}}$ and X_{Al}^{T} in REE partitioning model of opx (Eq. 2c). The decrease of $X_{\text{Ca}}^{\text{M2}}$ and Al content in M1 site ($X_{\text{Al}}^{\text{M1}}$, Fig. 4c) will increase the r_0 in cpx (Eq. 2b). The competing effect between the increase of $X_{\text{Mg}}^{\text{M2}}$ (Fig. 4f) and decrease of $X_{\text{Ca}}^{\text{M2}}$ (Fig. 4d) may affect r_0 little in opx. It is important to note that there is no melt in this system, so that REE partition coefficients discussed here are hypothetical values for the purpose of elucidating the temperature and composition dependent opx-cpx REE partitioning to be present in next section.

3. REE re-equilibration

To investigate the effects of major element redistribution and mineral abundance variation on REE re-equilibration, here we first calculated the hypothetical REE partition

coefficients in opx, cpx and olivine using the mineral-melt lattice strain models (Sun and Liang, 2012; Yao et al., 2012; Sun and Liang, 2013) and mineral compositions shown in Figs. 4 and S2-S5. We then derive REE partition coefficients between the coexisting minerals (cpx, opx and olivine), and calculate the REE abundance in the minerals based on mass balance equations.

3.1. REE partition coefficients in opx and cpx

Figure 5 displays the variations of REE partition coefficients in cpx (solid lines, Figs. 5a and 5b) and opx (solid lines, Figs. 5c and 5d) with variable major element (labeled as vX) for the aforementioned spinel peridotites. For comparison, we plot the variations of REE partition coefficients calculated with constant major element (Sun and Liang, 2014, labeled as cX) as dashed line in this figure. As expected, REE partition coefficients decrease for both cpx (Figs. 5a and 5b) and opx (Figs. 5c and 5d) comparing with those calculated using constant major elements (dashed lines) for both spinel peridotites. r_0 increases significantly in cpx due to the decrease of X_{Ca}^{M2} and X_{Al}^{M1} , which corresponds to the reductions in heavy REE partition coefficients (Figs. 5a and 5b). There are not obvious rotations between the REE partition coefficients calculated with variable major element and those calculated using constant major elements in opx (Figs. 5c and 5d).

3.2. REE partition coefficients between opx and cpx

In Fig. 6, we compare the REE partition coefficients between opx and cpx at three selected temperatures from this study (solid lines) with those only considered temperature

effects of Sun and Liang (2014, dashed lines). REE partition coefficients from this study are lower than those from Sun and Liang (2014) for light REE but slightly higher for heavy REE. The rotations between the two studies are due mainly to the major element effects on r_0 of cpx as discussed above. This difference of REE partition coefficients may result in substantial difference in the temperature inversion of REE-in-two-pyroxene thermometer, which will be discussed in Section 4.

3.3. Variation of REE concentrations in cpx and opx

The mineral-mineral REE partitioning models developed by Liang et al. (2013) and Sun and Liang (2014) can reproduce REE partitioning among coexisting minerals in well-equilibrated mafic and ultramafic rocks. The internal consistency of these mineral-mineral REE partitioning models allows us to assess the extent of REE re-distribution among mantle minerals during subsolidus cooling. Sun and Liang (2014) calculated variations of REE abundances in coexisting minerals using constant bulk REE concentrations and temperature dependent REE partitioning models. Neglecting contribution of spinel to the REE budget in peridotites, REE concentration in cpx can be calculated using the mass balance equation,

$$C_{cpx} = \frac{C_{bulk}}{p_{cpx} + p_{opx} \cdot k_{opx-cpx}^{REE} + p_{ol} \cdot k_{ol-cpx}^{REE}} \quad (3)$$

where, C_{cpx} and C_{bulk} are REE concentrations in cpx and whole rock, respectively; p_{cpx} , p_{opx} and p_{ol} are mineral modal abundances; and $k_{opx-cpx}^{REE}$ and k_{ol-cpx}^{REE} are mineral-mineral REE partition coefficients. Here we consider variations in mineral proportion and major element compositions during subsolidus re-equilibration and calculate REE abundances

in coexisting minerals for the spinel lherzolite and spinel harzburgite at selected temperatures.

Figure 7 displays the normalized REE abundances in cpx (Figs. 7a and 7b) and opx (Figs. 7c and 7d) at selected temperatures from this study (solid lines) and those calculated by considering constant major elements (dashed lines; Sun and Liang, 2014). Heavy REE concentrations in cpx can increase by a factor of 1.2 to 2 (solid lines in Figs. 7a and 7b) when temperature decreases to 1200 – 800 °C, but lower than those of Sun and Liang (2014, dashed lines in Figs. 7a and 7b) by about one factor. The decrease of X_{Mg}^{M2} and X_{Al}^{M1} in cpx results in an increase in r_0 of cpx, leading to a plateau at the transition of middle to heavy REE. REE concentrations in opx from this study are generally lower than those of Sun and Liang (2014) for light REE and slightly higher than the latter for heavy REE for the two samples (Figs. 7c and 7d). The rotation in opx (Figs. 7c and 7d) is mainly caused by the large shift of r_0 for cpx (Figs. 5a and 5b). In THERMOCALC, olivine solid solution only includes the forsterite (Mg_2SiO_4) fayalite (Fe_2SiO_4) end members, and olivine abundance does not change significantly (Fig. 2). Major element re-distribution barely affect REE concentrations in olivine, and their variations are identical to those only consider temperature effect from Sun and Liang (2014), which will not be presented here.

3.4. Garnet signature

As shown in Figs. 7a and 7b, subsolidus re-distribution can increase heavy and middle REE abundances in cpx, which may give rise to a false garnet signature in residual peridotites as discussed by Sun and Liang (2014). When major element

redistribution and mineral abundance variation are considered, the increase of heavy and middle REE in cpx are less strong. In Fig. 8, we re-examine the variations of Yb_N and $(Sm/Yb)_N$ in cpx by including the major element redistribution and mineral volume variation with a DMM starting composition and pMELTS calculation for melting trends (for details, see Sun and Liang, 2014). Results of Sun and Liang (2014) are shown as thin dotted lines. Including major element variations in pyroxenes, subsolidus distribution of REE can still reproduce most of the garnet signatures (Hellebrand et al. 2002 and references therein). As expected, the range of Yb_N and $(Sm/Yb)_N$ distribution of this study is narrower than those of Sun and Liang (2014) due to the effects of major element distribution. To generate a range as wide as those from Sun and Liang (2014), a lower temperature or different starting composition is needed. However, this is a preliminary calculation based on THERMOCALC. As discussed in Section 2, the effects of minor elements in the THERMOCALC database are not included, and the database was designed to calculate phase equilibration for pressures of 4 GPa and higher so that these results cannot totally reproduce the major element redistribution in natural samples, especially for samples at spinel stability fields. We can take these results as semi-quantitative.

4. Closure temperatures of major elements (Ca, Mg, Fe and Al) and REE in cooling two-pyroxene systems

As discussed above, major element redistribution affects REE partitioning in pyroxenes in spinel peridotites (Fig. 6), so that it may affect the temperature inversion of the REE-in-two-pyroxene thermometer (Liang et al., 2013). In Yao and Liang (2015), we

demonstrated that temperatures calculated using the REE-in-two-pyroxene thermometer (T_{REE}) are essentially the same as the average REE closure temperatures, and used the closure curves constructed by T_{REE} and major element closure temperatures ($T_{\text{Fe-Mg}}$) to estimate cooling histories for abyssal peridotites. To focus on the definition of REE closure temperature, we only examined the temperature effect on REE partition coefficients in our numerical simulations. Here we use a similar method to investigate major element and REE diffusion between opx and cpx, incorporating the THERMOCALC constraints on major elements and their effects on REE partition coefficients.

4.1. Major element diffusion and choices of diffusion coefficients

We consider diffusive redistribution of major elements (Ca, Fe, Mg, and Al) in pyroxenes in a framework of multicomponent diffusion. We choose Al as the dependent component and assume multicomponent diffusion occurs in the M1 and M2 sites between opx and cpx. We calculate X_{Al}^{M1} through the stoichiometric relations of Eqs. (1a) and (1c), and X_{Al}^T through Eqs. (1b) and (1d). Monovalent cation Na diffuses much faster than divalent (Fe, Mg and Ca) and trivalent cations (Al), so that we assume Na can reach instantaneous equilibrium in cpx during cooling. We calculate the diffusion coefficients of the major elements in opx and cpx through the [D] matrix of Lasaga (1979),

$$D_{ij} = D_i^* \delta_{ij} - \frac{D_i^* z_i z_j X_i}{\sum_{k=1}^n D_k^* z_k^2 X_k} (D_j^* - D_n^*) \quad (4)$$

where δ_{ij} is the Kronecker delta ($\delta_{ij} = 1$ when $i = j$ and $\delta_{ij} = 0$ when $i \neq j$), z_i is the valence of the cation, D_i^* and X_i are the self-diffusion coefficient and mole fraction of

the species *i*, respectively. Due to the lack of activity-composition models for pyroxene and the possible errors caused by the approximations of self-diffusion coefficients (Fe and Ca diffusion coefficients in opx) in the simulation, we treat pyroxenes as ideal solutions in our diffusion matrices calculations.

We select the self-diffusion coefficients of Ca, Mg and Fe in cpx from the literature, and present them as a function of temperature in Fig. 9. Ca diffusion in diopside has been investigated by Dimanov and Ingrin (1995), Dimanov et al. (1996), Dimanov and Jaoul (1998), and recently by Zhang et al. (2010). All studies measured ⁴⁴Ca tracer diffusion at 0.1 MPa. However, in the earlier experiments (Dimanov and Ingrin, 1995; Dimanov et al., 1996; Dimanov and Jaoul, 1998), diopside exhibits different extents of early partial melting and experiments of Dimanov and Ingrin (1995) were performed on synthetic iron-free diopside. Here we choose Ca self-diffusion coefficients along c-axes (green solid line) from Zhang et al. (2010). Mg self-diffusion coefficients along c-axes (blue solid line) are from the same experiments as Ca in Zhang et al. (2010) in our simulations. Fe self-diffusion coefficients (red solid line) for cpx are from Azough and Freer (2000). There are not many studies of major element self-diffusion in opx, and the only available data are Mg self-diffusions in enstatite (cyan solid line) from Schwandt et al. (1998). Since diffusion coefficients are generally correlate with their ionic radii for elements of the same charge on the same site of mineral structures (e.g., Koker and Stixrude, 2010), we assume diffusion coefficients of Ca, Mg and Fe in opx display the same correlation as those in cpx. Based on the ratios of Ca, Mg and Fe self-diffusion coefficients in cpx and Mg self-diffusion coefficient in opx, we estimate self-diffusion coefficients of Ca and Fe in opx, shown as dark green and dark red

dash-dotted lines, respectively, in Fig. 9. There has not been any systematic study of Al diffusion in pyroxenes. Sautter et al. (1988) measured Al diffusion coefficient at 1180 °C, 0.1 MPa and $pO_2 = 10^{-4}$ MPa and obtained a value of 0.32×10^{-20} m²/s. Jaoul et al. (1991) conducted further diffusion experiments at 1100 and 1000 °C and obtain an activation energy of 273 kJ/mol and a pre-exponential factor of 2.11×10^{-11} m²/s (magenta dashed line Fig. 9). Here, we choose the diffusion coefficients from the combined study of Sautter et al. (1988) and Jaoul et al. (1991) as Al self-diffusion coefficients in both cpx and assume Al diffusion coefficients in opx the same as in cpx.

We consider diffusive redistribution of major elements in a cooling bi-mineralic system consisting of opx (volume fraction ϕ_{opx}) and cpx (volume fraction ϕ_{cpx}). We use the general diffusion models described in Chapters 1 and 2 to model major element distribution. Initial and boundary conditions at the center of the coexisting opx and cpx are consistent with those described before. Major elements at the interface of the coexisting opx and cpx are constrained by continuous fluxes and major element concentrations (Figs. 4 and S2-S5) from THERMOCALC. However, continuous flux of an element is not only constrained by itself but also constrained by other elements in the multicomponent system. For example, assuming Mg is the first element in the diffusive matrix and Ca, Fe, Al are the second, third and forth elements, respectively, continuity of the diffusive flux of Mg across the opx-cpx interface can be described as:

$$\begin{aligned} & \frac{\phi_{\text{opx}}}{d_{\text{opx}}} \left[D_{11}^{\text{opx}} \frac{\partial C_{\text{opx}}^{\text{Mg}}}{\partial r} + D_{12}^{\text{opx}} \frac{\partial C_{\text{opx}}^{\text{Ca}}}{\partial r} + D_{13}^{\text{opx}} \frac{\partial C_{\text{opx}}^{\text{Fe}}}{\partial r} + D_{14}^{\text{opx}} \frac{\partial C_{\text{opx}}^{\text{Al}}}{\partial r} \right] \Bigg|_{r=0^-} \\ &= \frac{\phi_{\text{cpx}}}{d_{\text{cpx}}} \left[D_{11}^{\text{cpx}} \frac{\partial C_{\text{cpx}}^{\text{Mg}}}{\partial r} + D_{12}^{\text{cpx}} \frac{\partial C_{\text{cpx}}^{\text{Ca}}}{\partial r} + D_{13}^{\text{cpx}} \frac{\partial C_{\text{cpx}}^{\text{Fe}}}{\partial r} + D_{14}^{\text{cpx}} \frac{\partial C_{\text{cpx}}^{\text{Al}}}{\partial r} \right] \Bigg|_{r=0^+} \quad (5a) \end{aligned}$$

where d_{opx} and d_{cpx} are the effective or average radii of opx and cpx, respective; and ∇_i are the element concentration gradients; D_{ij}^{opx} and D_{ij}^{cpx} are diffusion coefficients calculated according to [D] matrix of Eq. (4) for opx and cpx, respectively. For simplicity, we use the expression of Dodson (1973, 1986) for temperature variation for both major elements and REE,

$$\frac{1}{T} = \frac{1}{T_0} + \eta t \quad (5b)$$

where T is the temperature at a given time t , T_0 is the initial temperature; η is a constant related to the cooling rate. Below we briefly describe the model setup and assumptions. For more details regarding governing equations, initial and boundary conditions, and numerical method, a reader is referred to the supplementary material S1 in Chapter 1.

4.2. Model setup, assumptions and boundary conditions

We consider diffusive redistribution of REE also in a cooling bi-mineralic system consisting of opx (volume fraction ϕ_{opx}) and cpx (volume fraction ϕ_{cpx}). Initially at temperature T_0 and pressure P_0 , major element and REE in opx and cpx are in chemical equilibrium, and REE concentrations are related to each other through partition coefficients $k_{\text{opx-cpx}}^{\text{REE}}$ at T_0 and P_0 . During cooling, major elements and REE in opx and cpx are out of equilibrium except at their interface, where their concentrations are constrained by thermodynamic equilibration for major elements (Figs. 4 and S2-S5) and partition coefficients for REE, respectively. For REE at the opx-cpx interface, we have

$$C_{\text{opx}} \Big|_{r=0^-} = k_{\text{opx-cpx}}^{\text{REE}}(T) \cdot C_{\text{cpx}} \Big|_{r=0^+} , \quad (6a)$$

Across opx-cpx interface, the diffusive flux is continuous, viz.,

$$\left. \frac{\phi_{opx}}{d_{opx}} D_{opx} \frac{\partial C_{opx}}{\partial r} \right|_{r=0^-} = \left. \frac{\phi_{cpx}}{d_{cpx}} D_{cpx} \frac{\partial C_{cpx}}{\partial r} \right|_{r=0^+}, \quad (6b)$$

where d_{opx} and d_{cpx} are the effective or average radii of opx and cpx, respective; D_{opx} and D_{cpx} are REE diffusion coefficients in opx and cpx; C_{opx} and C_{cpx} are REE concentrations in opx and cpx; and r represents the position away from the opx-cpx interface ($r = 0$). The partition coefficient of ($k_{opx-cpx}^{REE}$) and diffusion coefficients (D) take on the usual forms,

$$k_{opx-cpx}^{REE}(T) = k_{opx-cpx}^{REE,0} \cdot \exp\left(-\frac{\Delta H}{RT}\right), \quad (6c)$$

$$D = D_0 \cdot \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (6d)$$

where the pre-exponential factor $k_{opx-cpx}^{REE,0}$ and the exchange energy ΔH are functions of mineral compositions and ionic radius. The expression of $k_{opx-cpx}^{REE}$, which is a parameterized lattice strain model, and values of coefficients can be found from the REE-in-two-pyroxene thermometry study of Liang et al. (2013). D_0 and ΔH_a are the pre-exponential factor and activation energy of diffusion. For REE diffusion coefficients, we choose REE diffusion coefficients of Cherniak and Liang (2007) for opx and Van Orman et al. (2001, 2002) for cpx in our simulation. Since $k_{opx-cpx}^{REE}$ is not sensitive to the change of pressure, we consider an isobaric cooling and set the pressure to 1 GPa. For simplicity, we assume (1) grain boundary diffusion is much faster than volume diffusion so that major element and REE reach instantaneous equilibrium at the interface of opx and cpx within a representative element volume. (2) We calculate REE partition coefficients using the given temperature and major element concentrations in opx and cpx at their interface during cooling.

4.3. Closure temperatures of major elements and REE

We conducted numerical simulations for a range of cooling rates from 1 to 1000 °C/Myr, grain sizes from 0.5 to 5 mm and initial temperatures from 1400 to 1000 °C, and used a method similar method to Yao and Liang (2015) to calculate closure temperatures for major elements and REE. We first calculate the average concentrations of each element through trapezoidal method, and plot the average concentrations versus time. We then substitute the average concentrations of REE and major elements after closure profiles are established into the REE-in-two-pyroxene thermometer and major element based two-pyroxene thermometer of Brey and Köhler (1990, designated as T_{BKN}) to calculate REE and major element closure temperatures in the two-pyroxene system. Since major elements diffuse faster than REE, they close at a later time than REE. For example, in Fig. 10 we plot the evolutions of average concentrations of Ca and Sm in opx from the simulations of the same grain size (1.0 mm) and cooling rate (100 °C/Myr). There is obvious decoupling in closure time and closure temperature between Sm and Ca. Due to the decoupling, there is ubiquitous rotation in the T_{REE} inversion diagram, and therefore larger uncertainties may be generated due to this reason (Fig. S10). This partly explains the rotation in T_{REE} inversion diagrams for some natural samples (Liang, et al., 2013). However, since the decoupling mainly occurs at the late stage of cooling, during which major elements only vary for small amounts, no large errors in the T_{REE} inversion are expected.

In Fig. 11, we compare T_{REE} calculated using major element compositions at the time when REE closed and those calculated using major elements after they are closed

for the two spinel peridotites ($T_0 = 1400$ °C; grain size, 0.5 – 5 mm; and cooling rate, 1 – 1000 °C/Myr). There are maximum ± 20 °C differences between these two sets of calculations. Again, these calculations are based on THERMOCALC, which can be only taken as semi-quantitative.

Since major element temperatures T_{BKN} deviate systematically from those given by THERMOCALC (Figs. S6-S9), we make simple correction for T_{BKN} according to their correlation with the given THERMOCALC temperatures in Fig. 12. This is an interim solution that allows us to correct or adjust for the incomplete thermodynamic data of THERMOCALC for spinel peridotites (e.g., no data for Cr_2O_3). The adjusted T_{BKN} are compared with Fe-Mg closure temperatures ($T_{\text{Fe-Mg}}$ in Fig. 1b of Yao and Liang, 2015) calculated using modified Dodson's equation (Ganguly and Tirone, 1999) and Fe-Mg exchange coefficients in cpx from Müller et al. (2013) in Fig. 12 ($T_0 = 1400$ °C; grain size, 0.5 – 5 mm; and cooling rate, 1 – 1000 °C/Myr). T_{BKN} from this study are systematically higher than $T_{\text{Fe-Mg}}$ used by Yao and Liang (2015). These differences may be caused by the under estimation of major element closure temperature by Dodson's equation or the semi-quantities of THERMOCALC in calculating major element re-distribution. Major element self-diffusion coefficients are also important factors that can affect the difference (e.g., Ca, Fe diffusion coefficients in opx are estimated).

4.4. Cooling rates of abyssal peridotites

Following our previous studies (Yao and Liang, 2015), we plot TREE against the adjusted T_{BKN} of this study with different initial temperatures (1100 to 1400 °C) to construct closure curves (red solid lines) to estimate cooling rates for abyssal peridotites in Fig. 14. We connect different cooling rates for a grain size of 2 mm by black dotted

lines. Cooling rates of $1 - 10^5$ °C/Myr can explain a significant fraction of the observed data. This range of cooling rates is one order of magnitude larger than those ($10 - 10^4$ °C/Myr) estimated by TREE of constant major elements and $T_{\text{Fe-Mg}}$ in Fig. 1b of Yao and Liang (2015) and could be two orders of magnitude different from those ($10^3 - 10^6$ °C/Myr) estimated using the Fe-Mg diffusion coefficients of Dimanov and Wiedenbeck (2006) in Fig. 1a of Yao and Liang (2015), which underscores the importance of the major element variation in the partitioning and diffusion of REE between opx and cpx during subsolidus re-equilibration.

We notice that there are large ranges of two-pyroxene bearing samples that experienced cooling and that cannot be covered by the closure curves of this study (e.g. some abyssal peridotites in Fig. 14 and some ophiolites from Dygert and Liang., 2015). One possible reason is that the closure curves of this study are limited to the choices of the certain group of diffusion coefficients, especially for major elements (Fig. 9). Larger diffusion coefficients of major elements will generate lower T_{BKN} , and hence wider closure curves in Fig. 14. To explain the cooling histories for two-pyroxene bearing rocks, more careful examination of major element diffusion coefficients is needed. More importantly, these calculations are based on THERMOCALC, which does not consider minor elements effect and maybe not quite applicable to major element variations in spinel stability field, so that these calculations can only be taken as semi-quantitative

5. Summary

In order to investigate the effect of major element redistribution on REE re-equilibration during subsolidus cooling, we calculated the variations of major elements

and volume proportions of the coexisting minerals (cpx, opx olivine and spinel) in a spinel lherzolite (Mo22) and a spinel harzburgite (MM1213) using the thermodynamic software THERMOCALC. We perform similar calculation as in Sun and Liang (2014) to quantify REE abundances in the coexisting minerals using internally consistent mineral-mineral REE partitioning models and mass balance constraint. We considered the effects of major element redistribution and mineral abundance variation derived from THERMOCALC. We found that heavy REE contents in cpx can increase by a factor of two in the spinel harzburgite when temperature decreases to 800 °C during subsolidus re-equilibration, which is smaller than that caused by considering constant major element concentrations (Figs. 7a and 7b). We also calculated REE concentrations in cpx during subsolidus cooling through Eq. (2). The increased heavy REE concentration from our modeling can still reproduce a wide range of increased $(Yb)_N$ and decreased $(Sm/Yb)_N$ values, which has been suggested as a garnet signature in the mantle source for abyssal peridotites. This result confirms the suggestion of Sun and Liang (2014) that subsolidus re-equilibration of REE may give rise to false garnet signatures in the mantle source of abyssal peridotites.

In order to evaluate the major element effect on REE closure temperatures, we conduct numerical simulations of major elements and REE diffusive redistribution in coexisting opx and cpx, incorporating the THERMOCALC constraints on major elements and REE partition coefficients involving major element variations. Major elements close at a later stage than REE during cooling due to their faster diffusion rates, which can cause $\pm 20^\circ\text{C}$ uncertainties in the calculations of T_{REE} . Major element closure

temperatures are systematically higher than those calculated using Dodson's equation and Fe-Mg inter-diffusion coefficients

However, these calculations are all based on the thermodynamic software THERMOCALC, the database of which was designed for mafic rocks at pressure of 4 GPa and above. In addition, some important mineral elements, such as Cr_2O_3 , TiO_2 , NiO that can significantly affect major element distributions are not considered in this system. These results can only be taken as semi-quantitative

Acknowledgements

We thank Chenguang Sun for useful discussion. This work was supported in part by NSF grant EAR-1220076 and NASA grant NNX13AH07G.

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Figure Captions

Figure 3-1 Variation of Mg# in cpx during isobaric cooling calculated using THERMOCALC, Perplex and Theriak-Domino. Mg# is the molar percent of $\text{Mg}/(\text{Mg}+\text{Fe}) \times 100\%$. The bulk rock compositions of the spinel peridotites are from Witt-Eickschen and O'Neill (2005). Pressure is set as 1 GPa in the calculation.

Figure 3-2 Variations of coexisting mineral abundances in a spinel lherzolite Mo22 (a) and a spinel harzburgite MM1213 (b) during isobaric (1 GPa) cooling according to THERMOCALC. Bulk compositions of Mo22 and MM1213 can be found in Table 1.

Figure 3-3 Stoichiometric constraints on major elements in opx (a) and cpx (b) according to THERMOCALC.

Figure 3-4 Major element variations in the form of molar percent per 6-oxygen in cpx (a-c) and opx (d-f) during isobaric (1 GPa) cooling for the spinel lherzolite Mo22 (red lines) and spinel harzburgite MM1213 (green lines), according to THERMOCALC.

Figure 3-5 Variations of REE partition coefficients in cpx (a and b) and opx (c and d) for the spinel lherzolite Mo22 (a and c) and the spinel harzburgite MM1213 (b and d) calculated by Eq. (Sun and Liang, 2012; Yao et al., 2012).

Figure 3-6 REE partition coefficients between opx and cpx calculated from the values of Fig. 3-5.

Figure 3-7 REE concentrations in cpx (a and b) and opx (c and d) for the spinel lherzolite Mo22 (a and c) and the spinel harzburgite MM1213 (b and d). The REE in mineral concentrations are calculated by using Eq. (3) and REE partition coefficients with major element (Fig. 4) and model abundance (Fig. 2) variations considered in the calculation.

Pressure is 1 GPa. The concentrations are all normalized to their initial concentrations at 1300 °C.

Figure 3-8 Variations of Yb_N and $(Sm/Yb)_N$ in clinopyroxene from abyssal peridotites. The subscript N denotes that Sm and Yb abundances are normalized by CI chondrite of Anders and Grevesse (1989). The grey filled shows the compilation of global abyssal peridotites in Hellebrand et al. (2002; see their Fig. 8). Red curve shows the calculation results of near fractional melting of a spinel lherzolite mantle. Curves marked with temperatures (1200 °C, 1000 °C, and 800 °C) represent results of subsolidus corrections through Eq. (2). For detailed calculation, a reader is referred to Sun and Liang (2014).

Figure 3-9 Arrhenius plot showing variations of major element self-diffusion coefficients in opx and cpx. Ca (green line) and Mg (blue line) diffusion coefficients in cpx are from Zhang et al. (2010). Fe self-diffusion coefficients (red solid line) for cpx are from Azough and Freer (2000). Mg self-diffusions in opx (cyan solid line) are from Schwandt et al. (1998). Al diffusion coefficients in cpx (magenta dashed line) are from Sautter et al. (1988) and Jaoul et al. (1991). Ca (dark green dot-dashed line) and Fe (dark red dot-dashed line) are estimated based on the ratios of Ca, Mg and Fe self-diffusion coefficients in cpx and Mg self-diffusion coefficients in opx.

Figure 3-10 Differences in closure times and closure temperatures for Ca and Sm in an orthopyroxene.

Figure 3-11 Comparison between TREE calculated using the major element concentrations at the time when REE closed [(TREE)REE-C] only and those calculated using major elements after they are closed [(TREE)ME-C].

Figure 3-12 Correlation between the THERMOCALC temperatures ($T_{\text{THERMOCALC}}$ or T_{ThC}) and those calculated using the major element based two-pyroxene thermometer of Brey and Köhler (1990, designated as T_{BKN}) for the spinel lherzolite Mo22 (a) and the spinel harzburgite MM1213 (b). Blue circles are direction calculation results, and solid lines (red in a and green in b) are numerical interpolations and extrapolations.

Figure 3-13 Comparison between the adjusted TBKN and TFe-Mg for the spinel lherzolite (red) and spinel harzburgite (green) for a range of grain sizes from 0.5 to 5 mm and a range of cooling rates from 1 to 1000 °C/Myr. TBKN are calculated using the thermometer of Brey and Köhler (1990) and the closure concentrations of the major elements in this study, and adjusted by the correlations with THERMOCALC temperatures in Fig. 12. TFe-Mg are calculated using the modified Dodson's equation of Ganguly and Tirone (1999) and the Fe-Mg inter-diffusion coefficients of Müller et al. (2013). The initial temperatures are 1400 °C for the two sets of closure temperatures.

Figure 3-14 Closure temperatures of major elements (TBKN) and REE (TREE) of this study overlying abyssal peridotites that experienced cooling (yellow dots). Initial temperatures (T_0) are listed on the right of the grey 1:1 line. The black dots connected by thin dashed black lines are cooling rates (in °C/Myr) for a grain size of 2 mm indicated by

the numbers above. The data sources for the abyssal peridotites are the same with those listed in Liang et al. (2013).

Figures

Figure 3-1

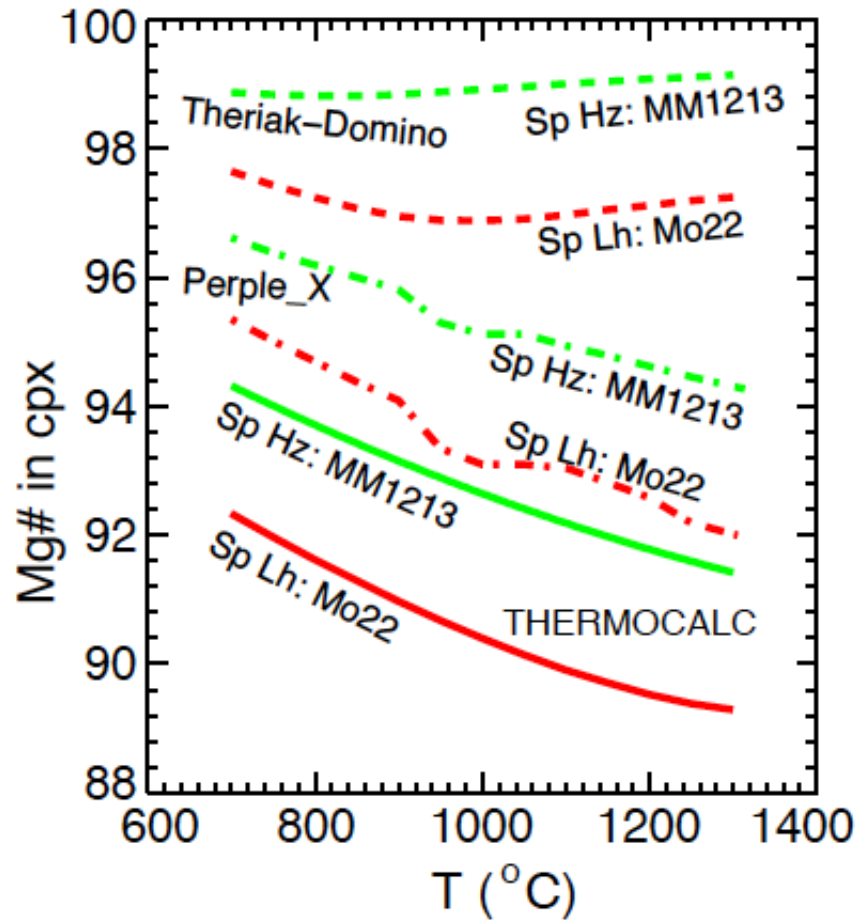


Figure 3-2

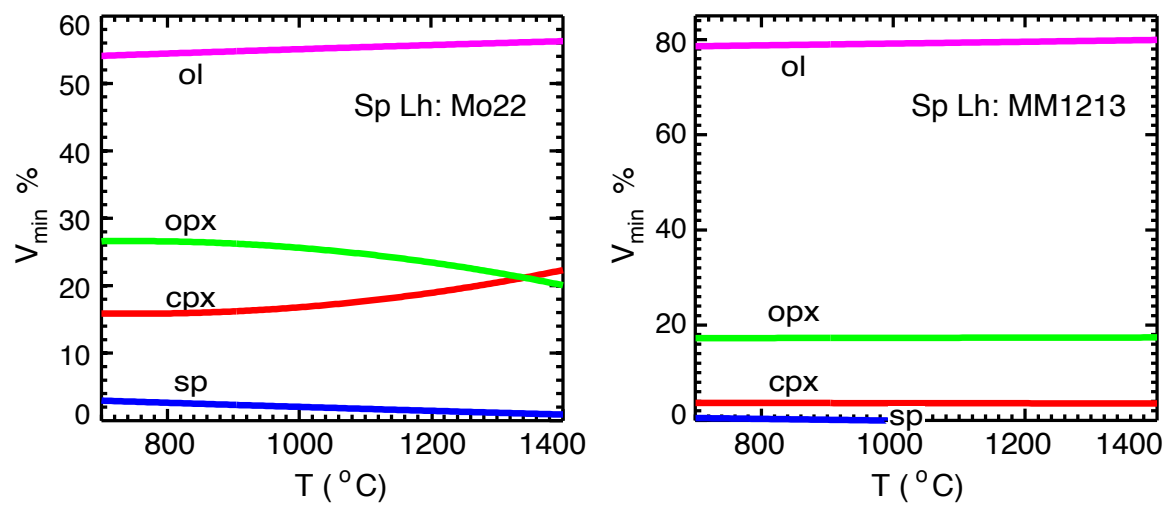


Figure 3-3

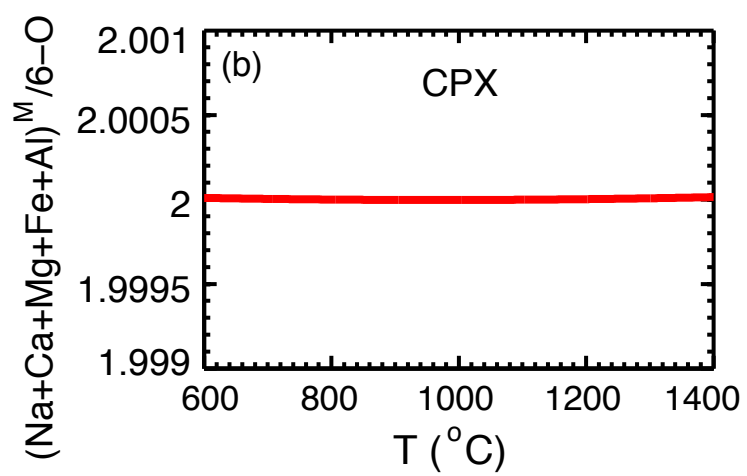
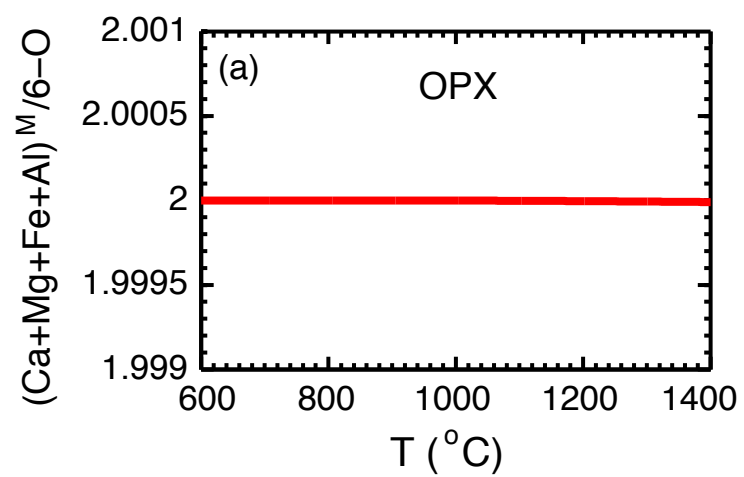


Figure 3-4

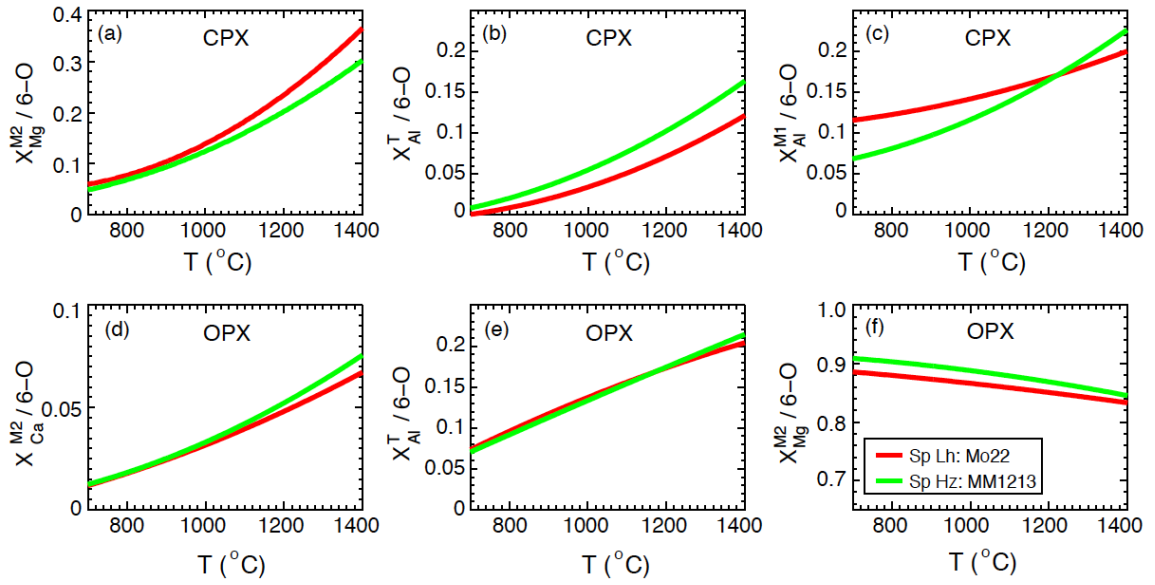


Figure 3-5

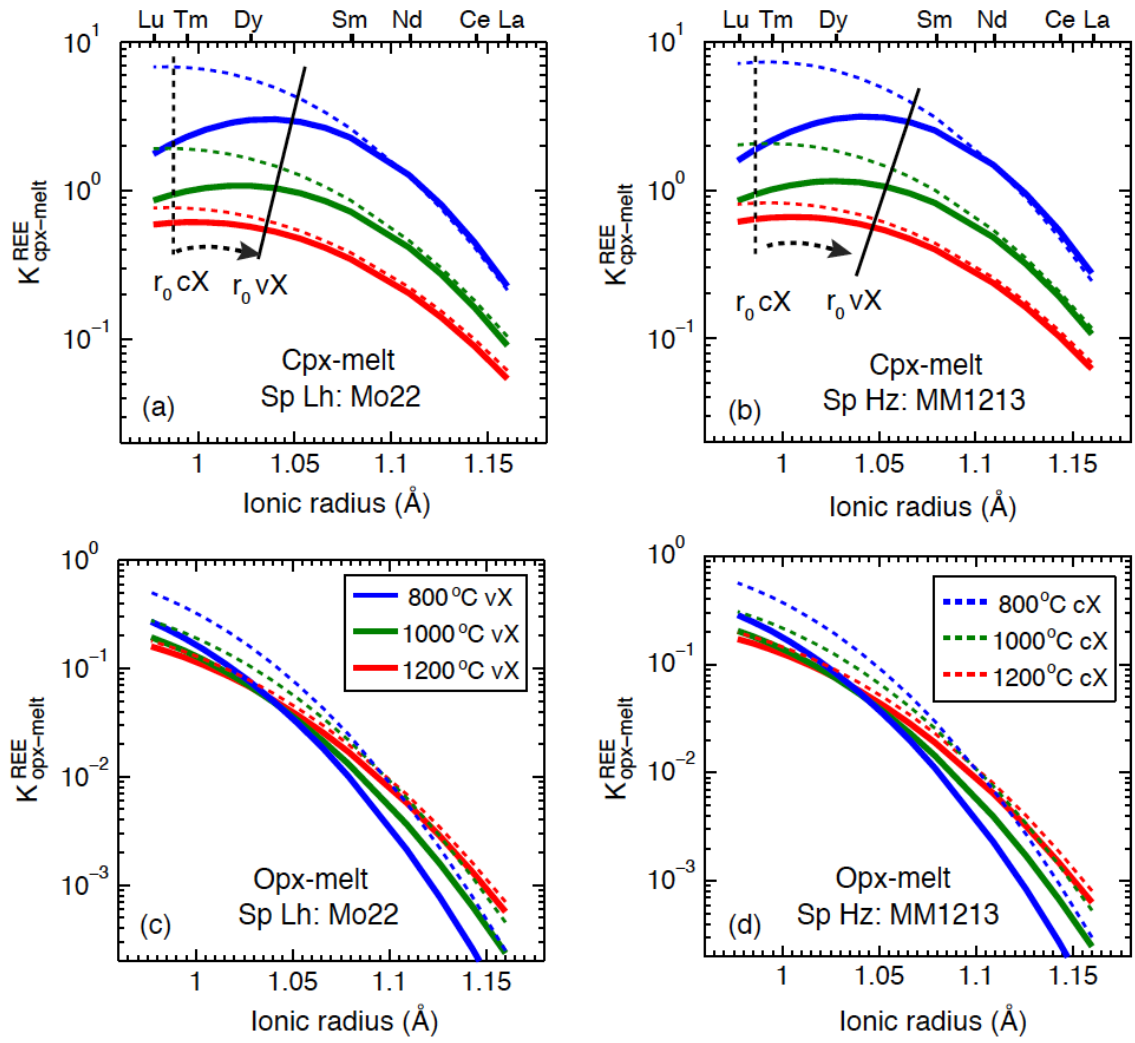


Figure 3-6

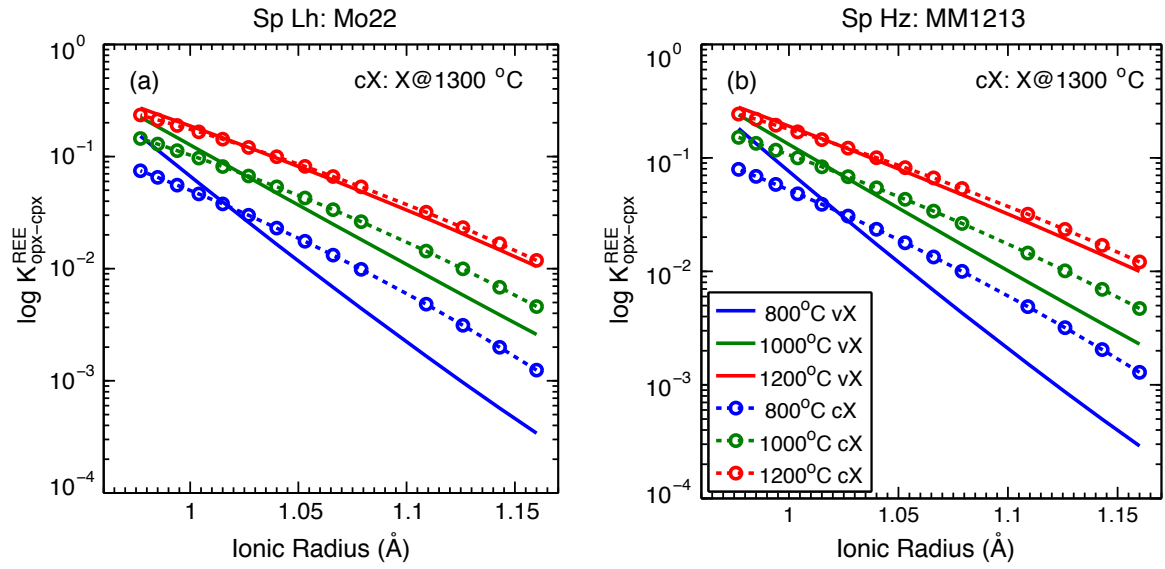


Figure 3-7

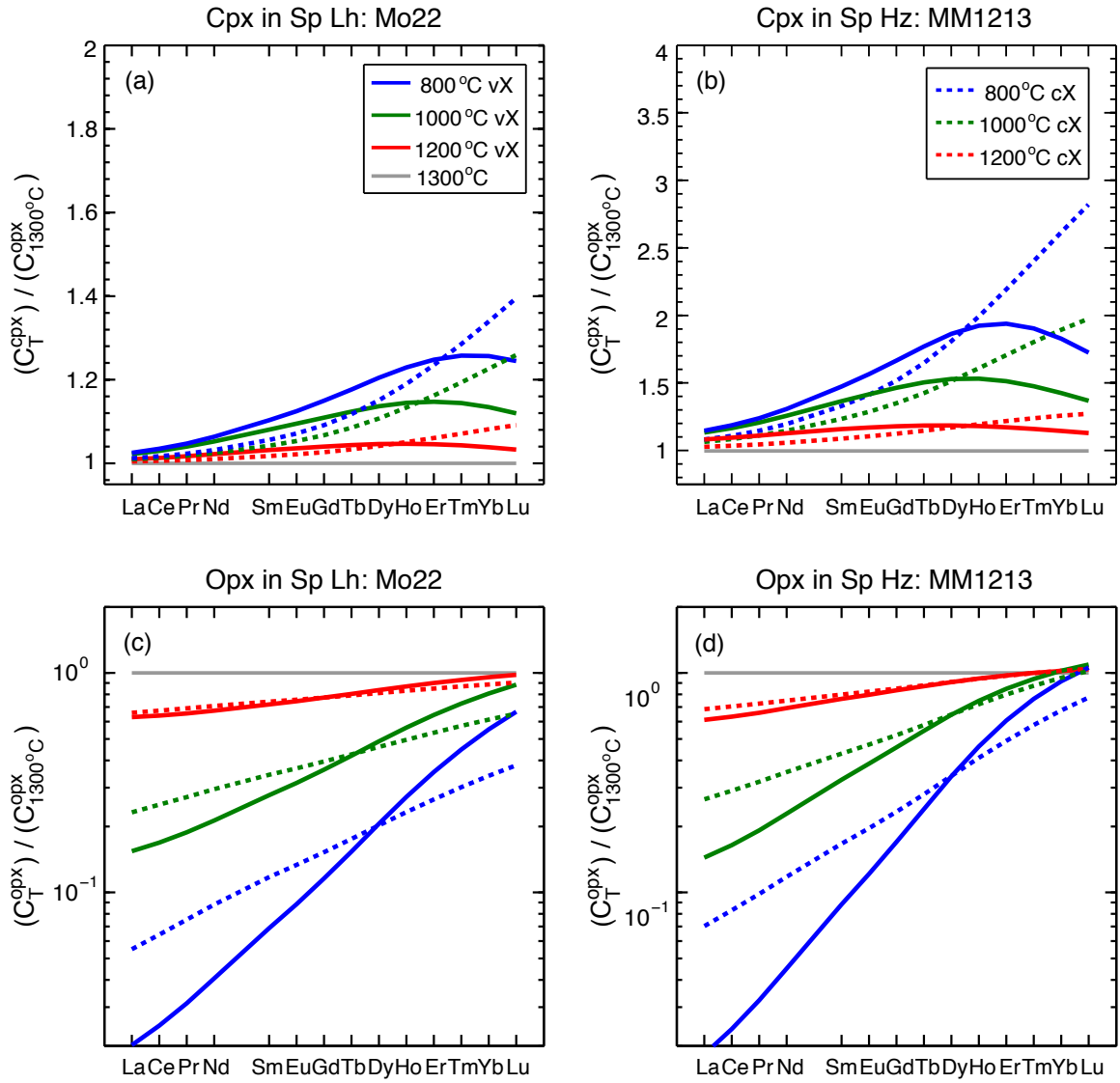


Figure 3-8

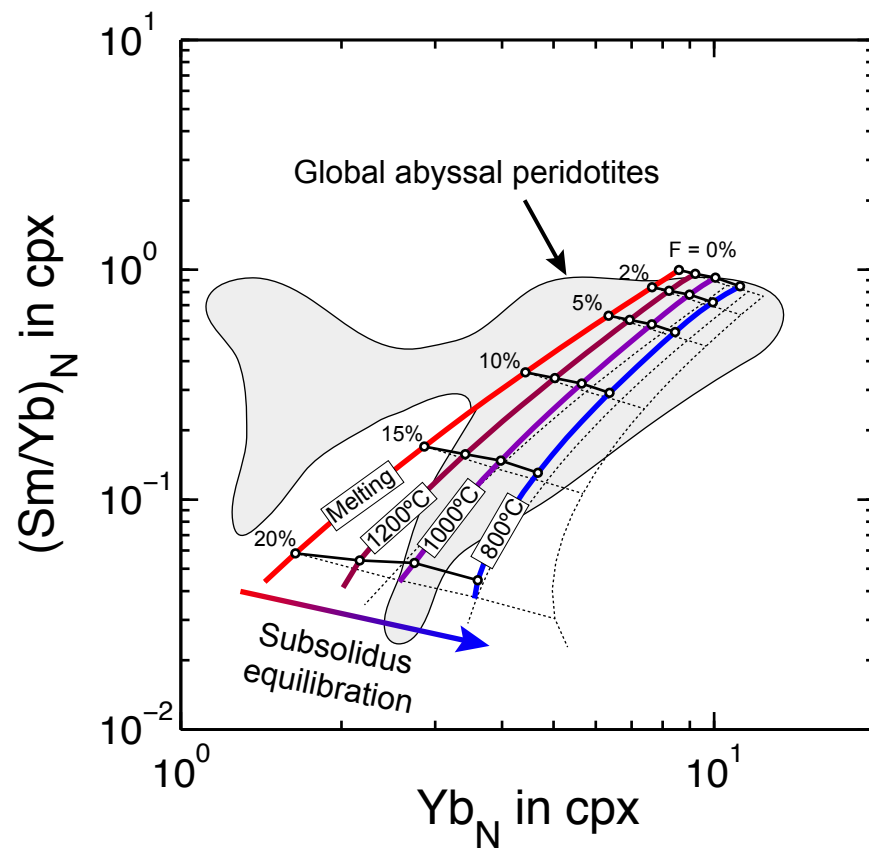


Figure 3-9

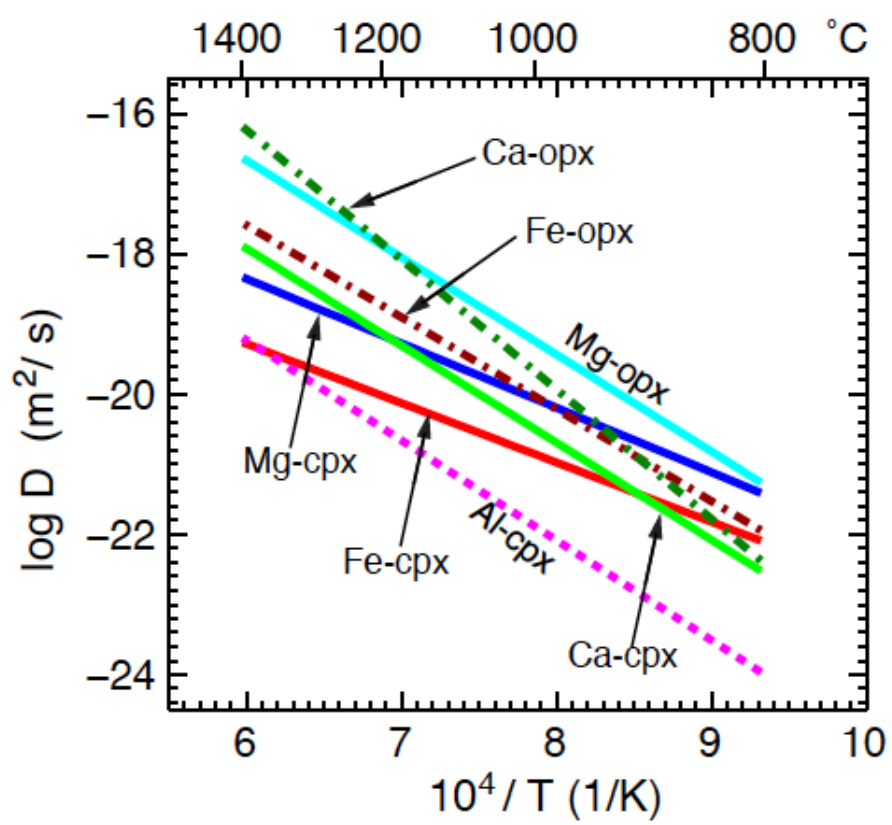


Figure 3-10

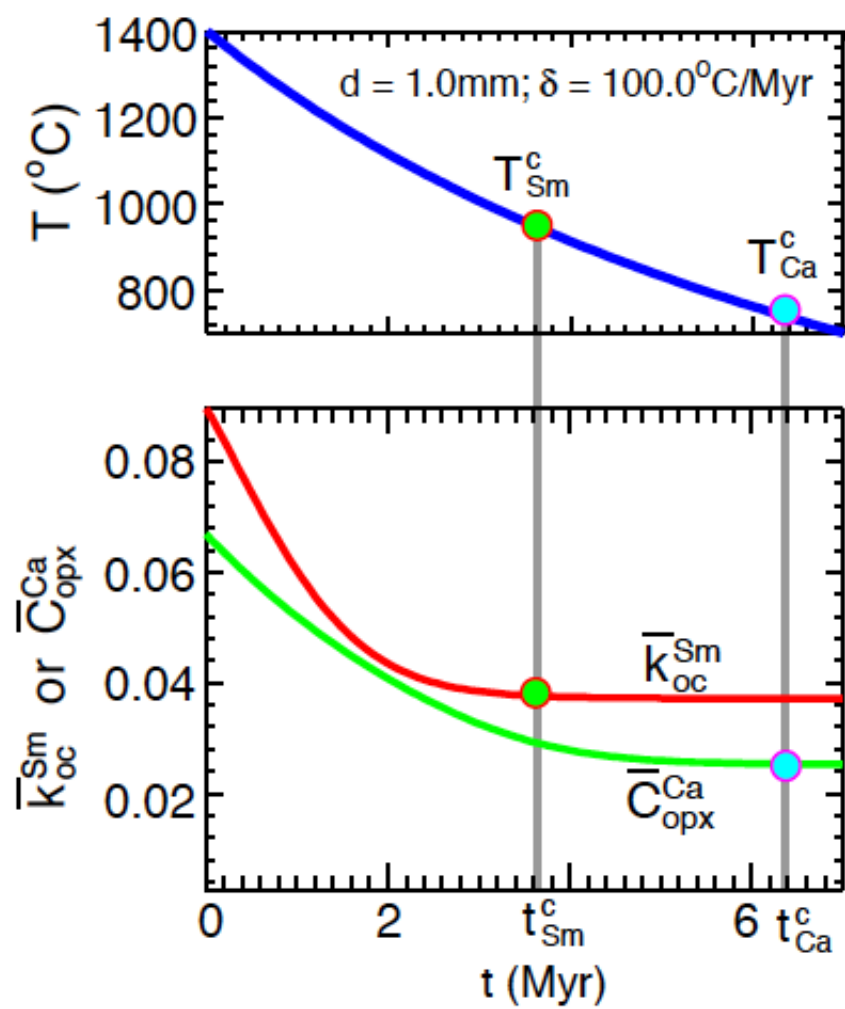


Figure 3-11

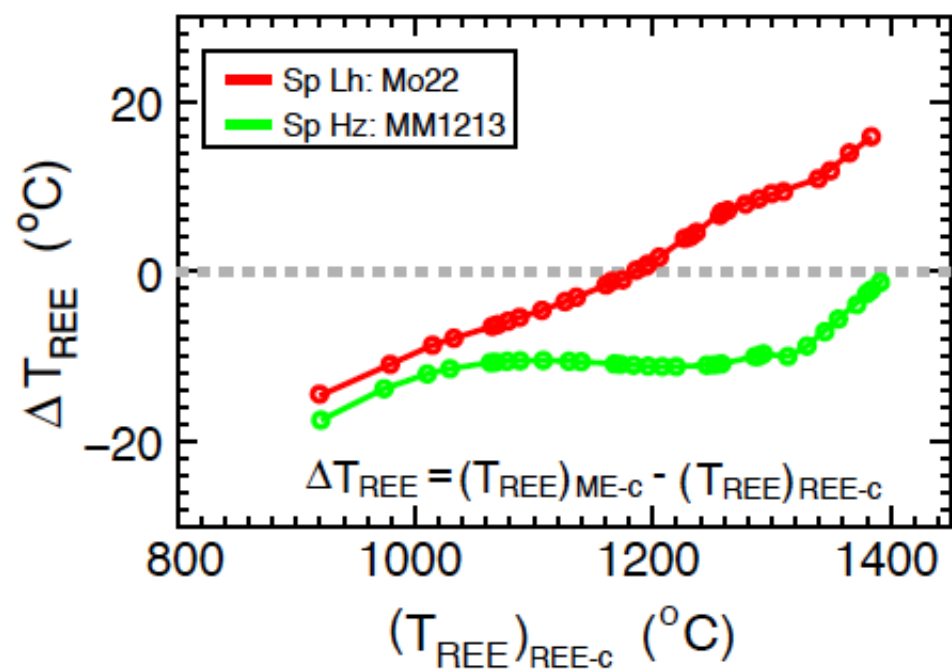


Figure 3-12

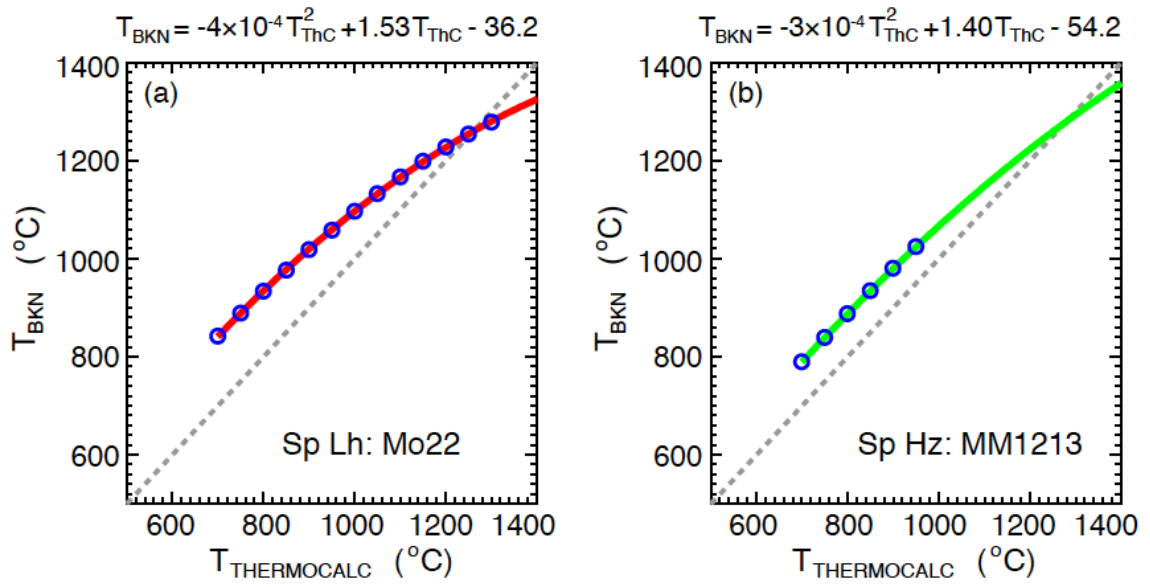


Figure 3-13

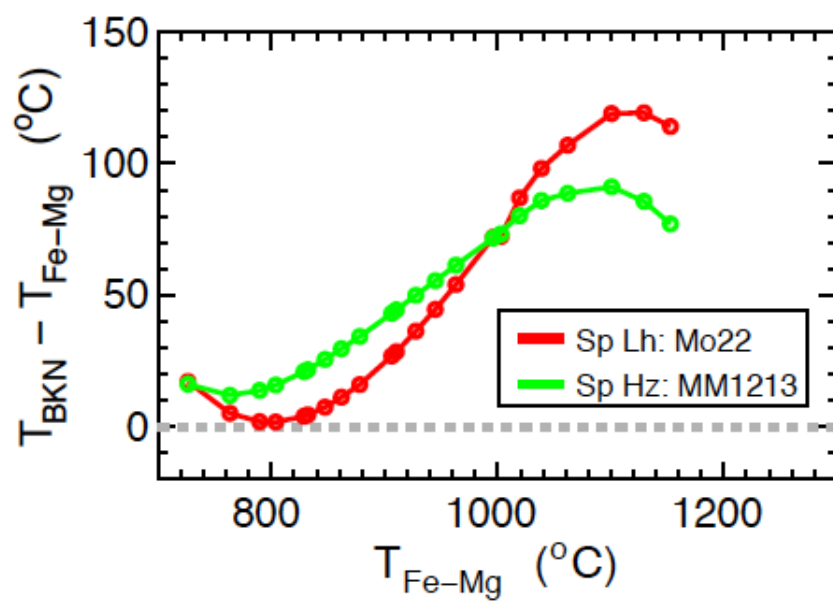
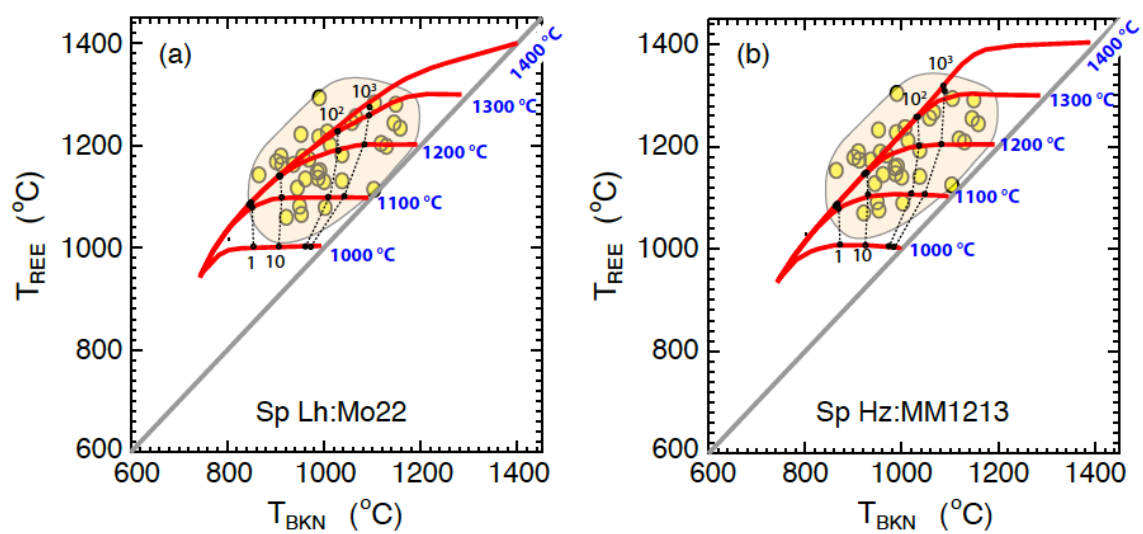


Figure 3-14



Tables

Table 3-1 Compositions of the spinel peridotites

Sample	Reference	Mode				Bulk rock composition (wt%)									
		ol	opx	cpx	sp	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	NiO	CaO	Na ₂ O
MM1213	W&N (05)	84	13	2	1	43.48	0.01	0.93	0.62	7.38	0.12	47.48	0.37	0.72	0.03
Mo22	W&N (05)	63	21	14	3	44.46	0.12	3.87	0.55	8.45	0.03	40.22	0.29	2.88	0.21
DMM	W&H (05)	57	28	13	2	44.71	0.13	3.98	0.57	8.18	0.13	38.73	0.24	3.17	0.28

Supplementary Figure 3-S1

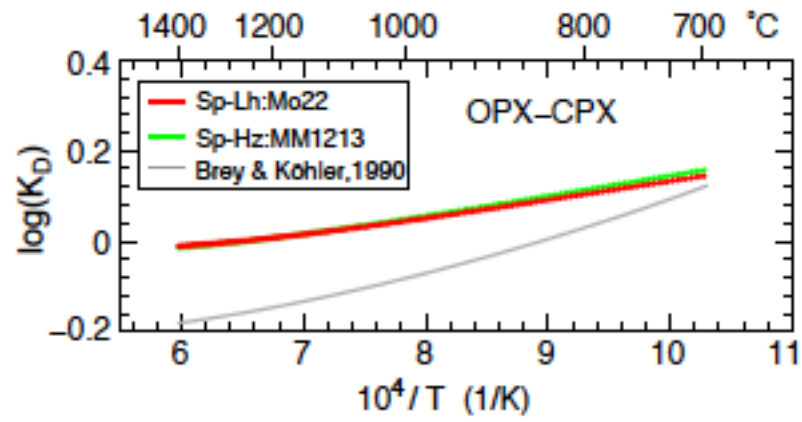


Figure 3-S1. Comparison in Fe-Mg exchange coefficients between THERMLCALC calculation and those from well equilibrated phase equilibria experiments.

Supplementary Figure 3-S2

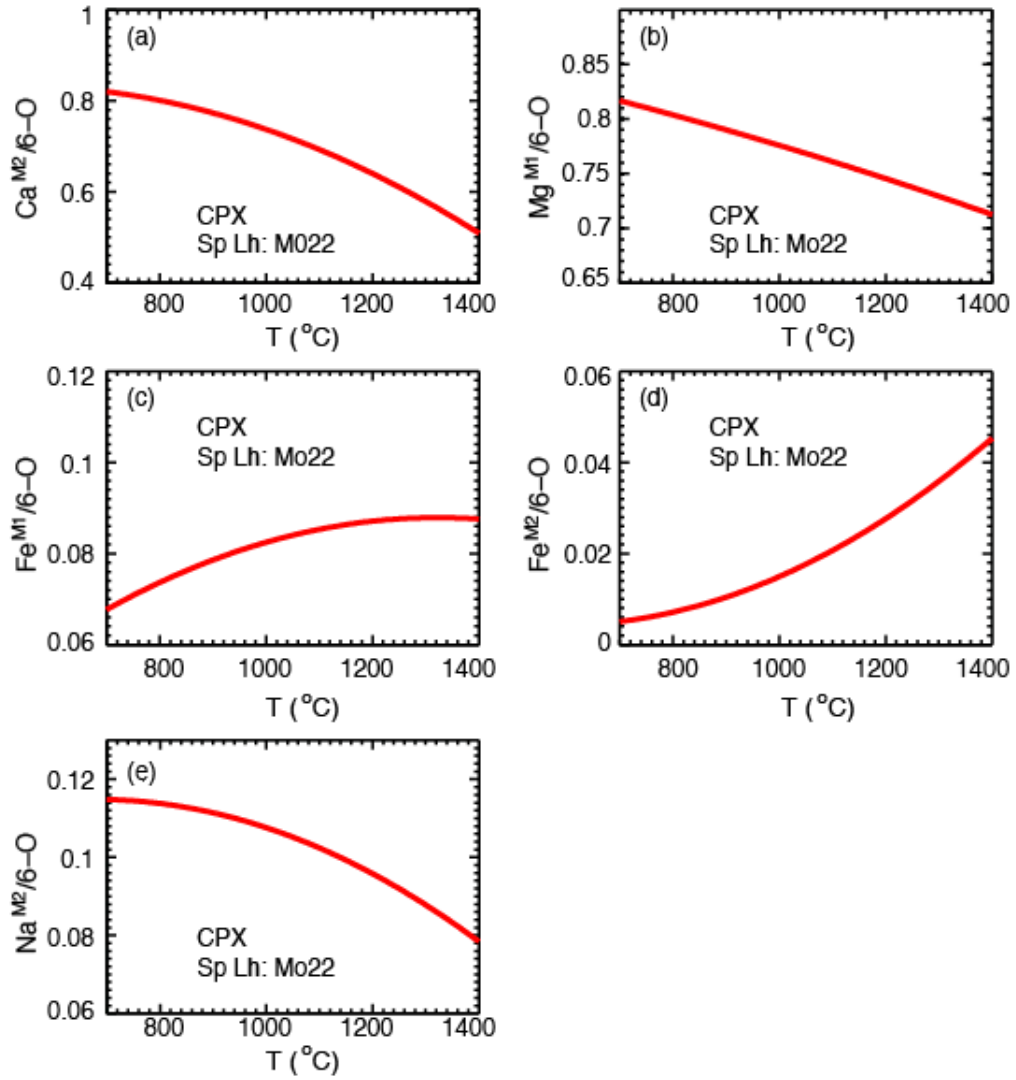


Figure 3-S2. Major element variation in cpx calculated by THERMOCALC for spinel hercynite Mo22.

Supplementary Figure 3-S3

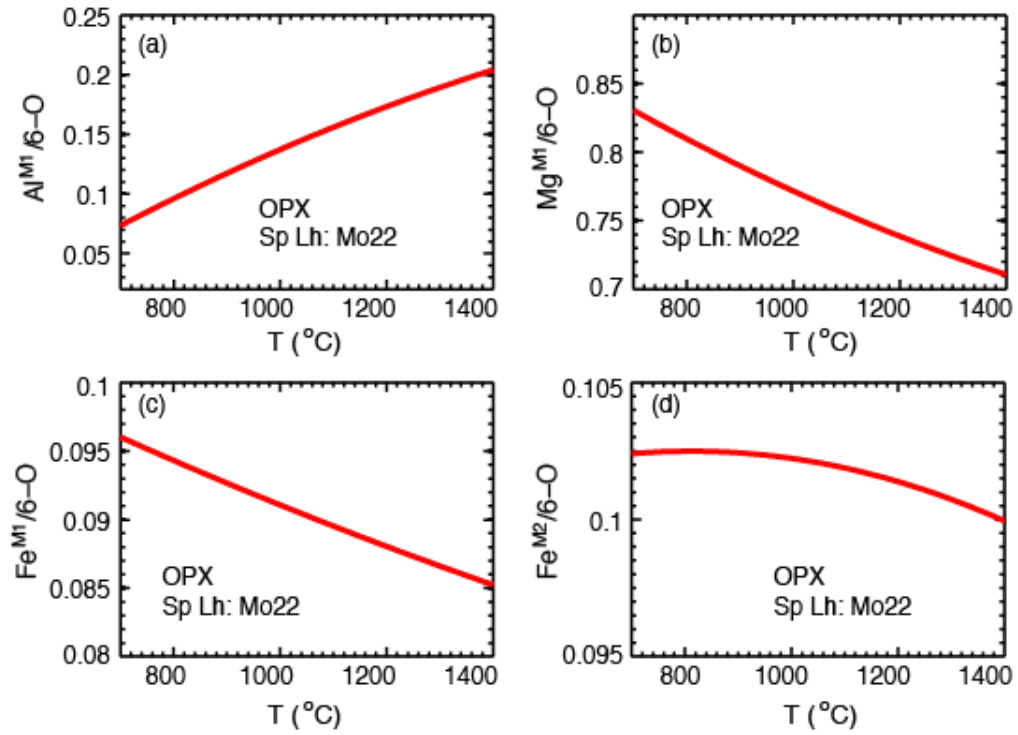


Figure 3-S3. Major element variation in opx calculated by THERMOCALC for spinel hercynite Mo22.

Supplementary Figure 3-S4

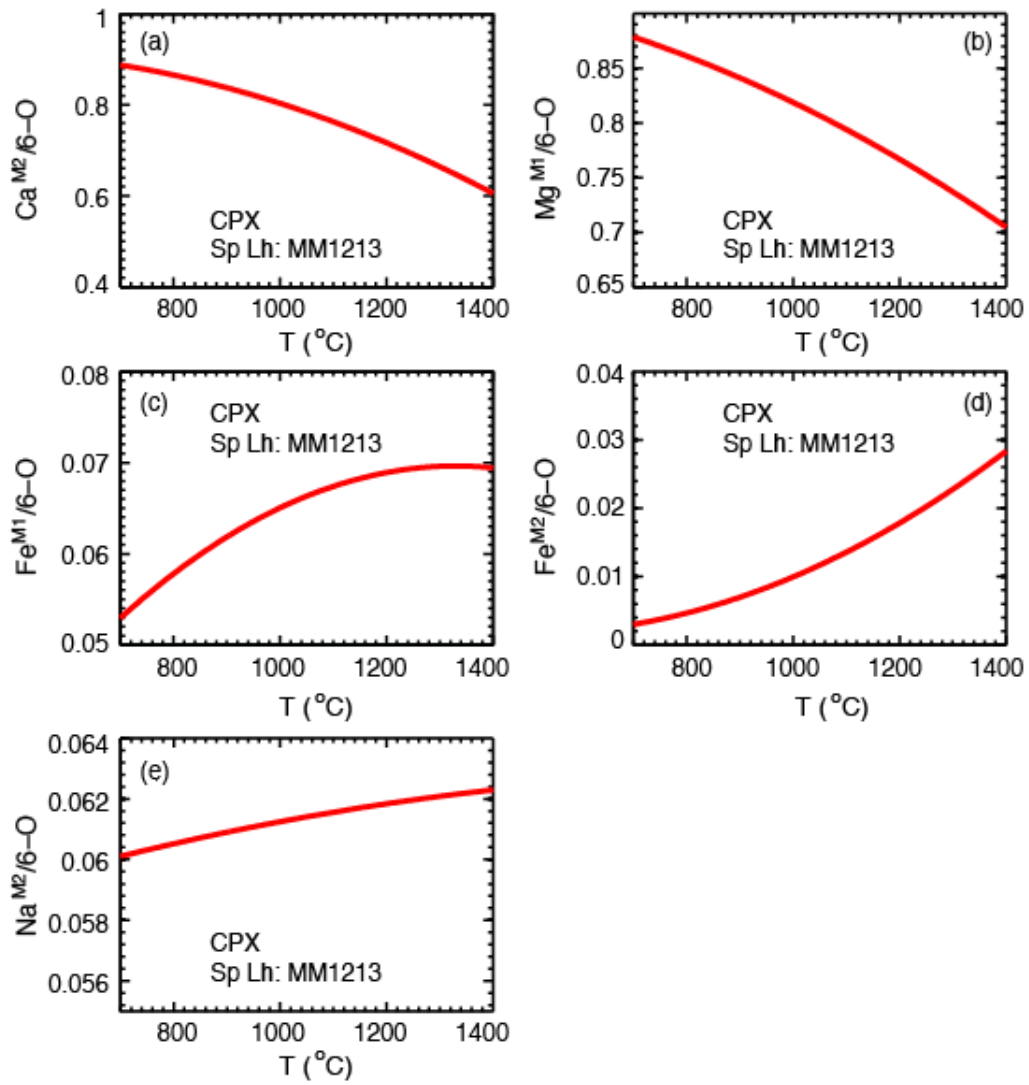


Figure 3-S4. Major element variation in cpx calculated by THERMOCALC for spinel harzburgite MM1213.

Supplementary Figure 3-S5

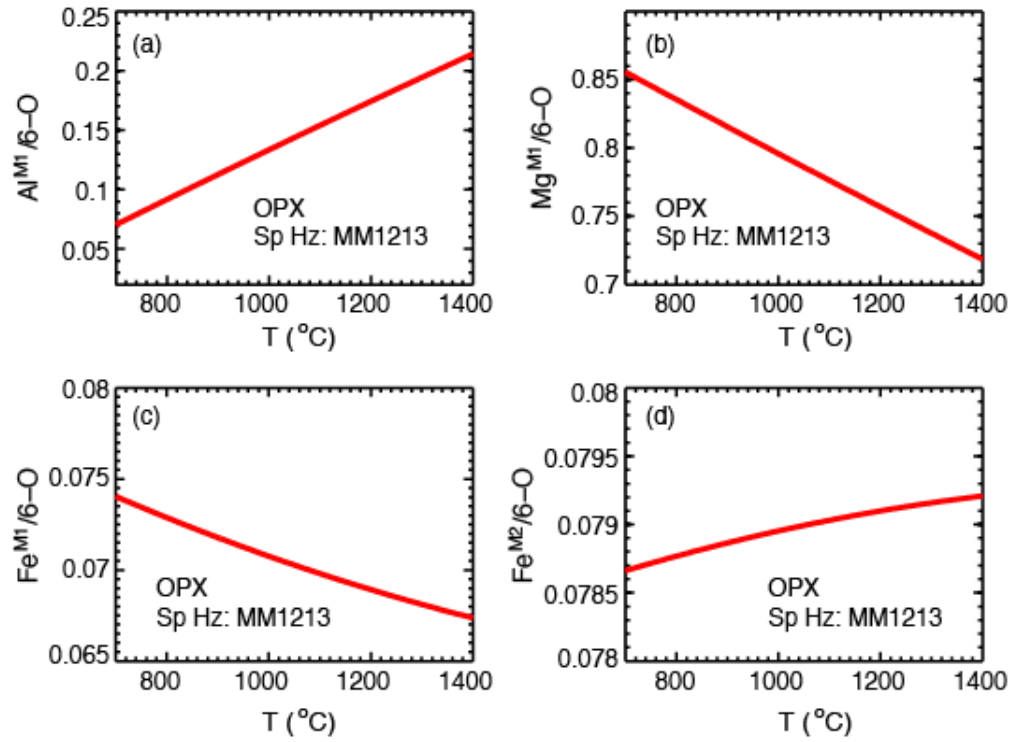


Figure 3-S5. Major element variation in opx calculated by THERMOCALC for spinel harzburgite MM1213.

Supplementary Figure 3-S6

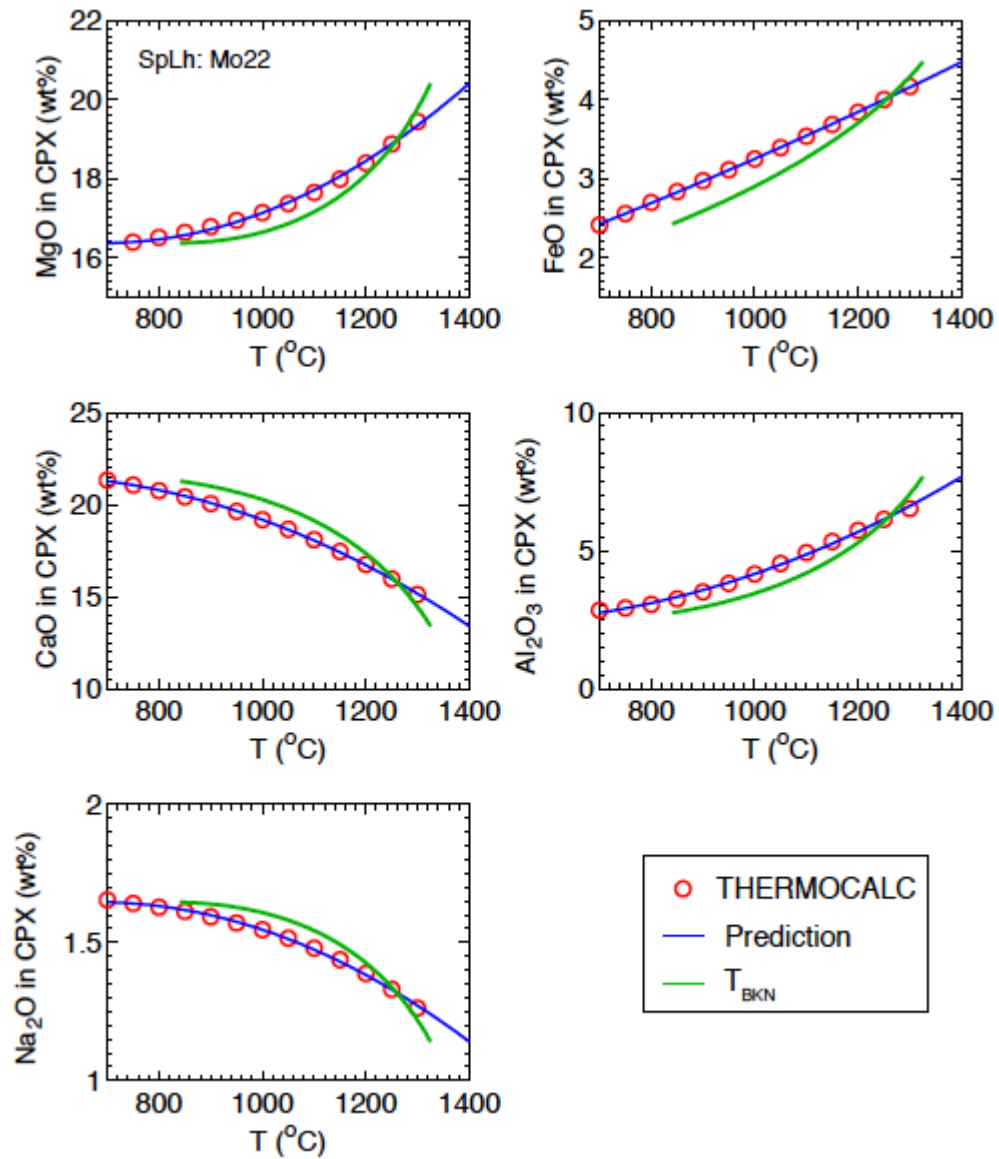


Figure 3-S6. Major element variations of cpx in weight percent. T_{BKN} are calculated using the two-pyroxene thermometer of Brey and Köhler (1990) and the major element concentrations as plotted in the figures above and Fig. 3-S7.

Supplementary Figure 3-S7

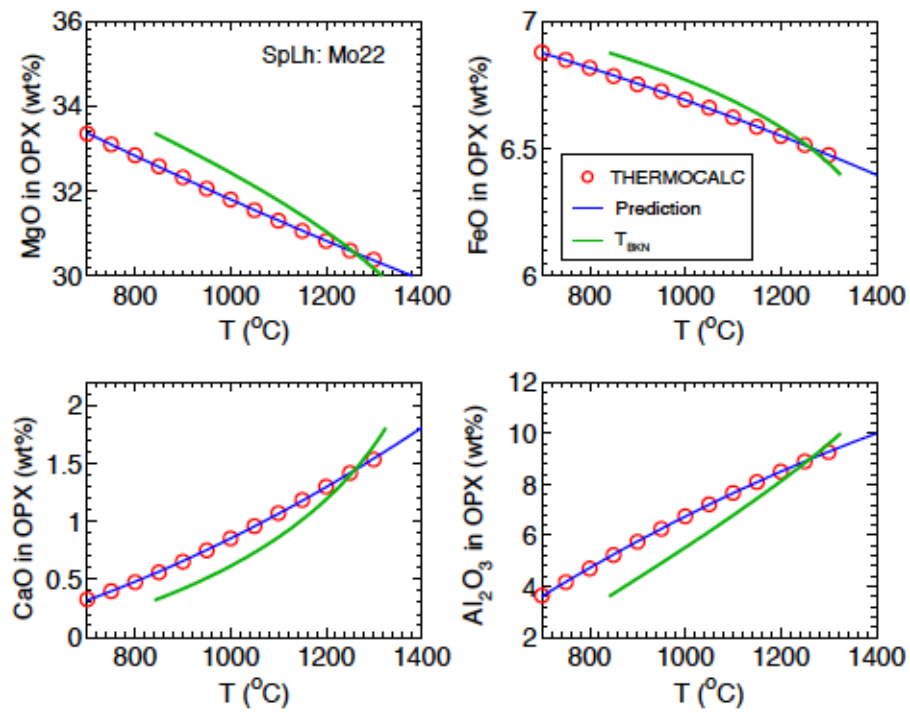


Figure 3-S7. Major element variations of opx in weight percent. T_{BKN} are calculated using the two-pyroxene thermometer of Brey and Köhler (1990) and the major element concentrations as plotted in the figures above and Fig. 3-S6.

Supplementary Figure 3-S8

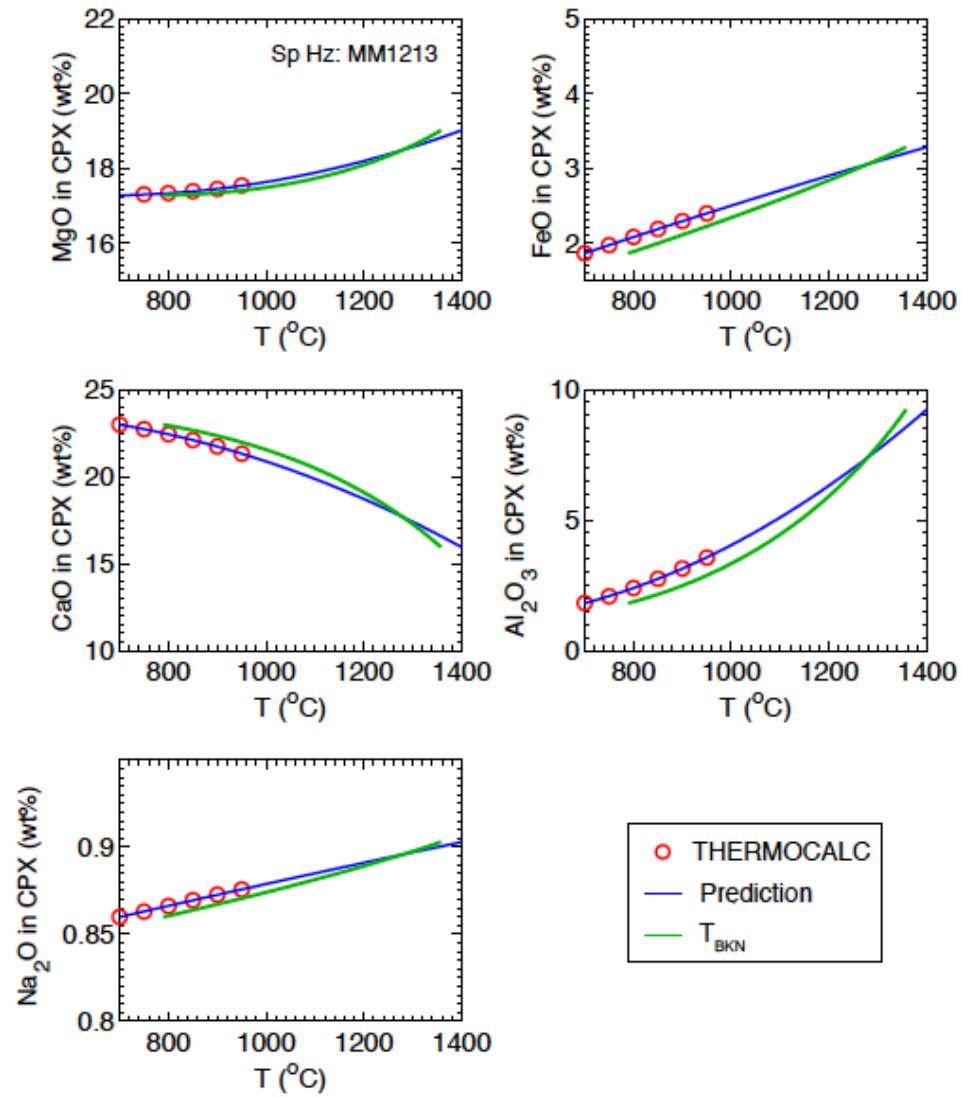


Figure 3-S8. Major element variations of cpx in weight percent. T_{BKN} are calculated using the two-pyroxene thermometer of Brey and Köhler (1990) and the major element concentrations as plotted in the figures above and Fig. 3-S9.

Supplementary Figure 3-S9

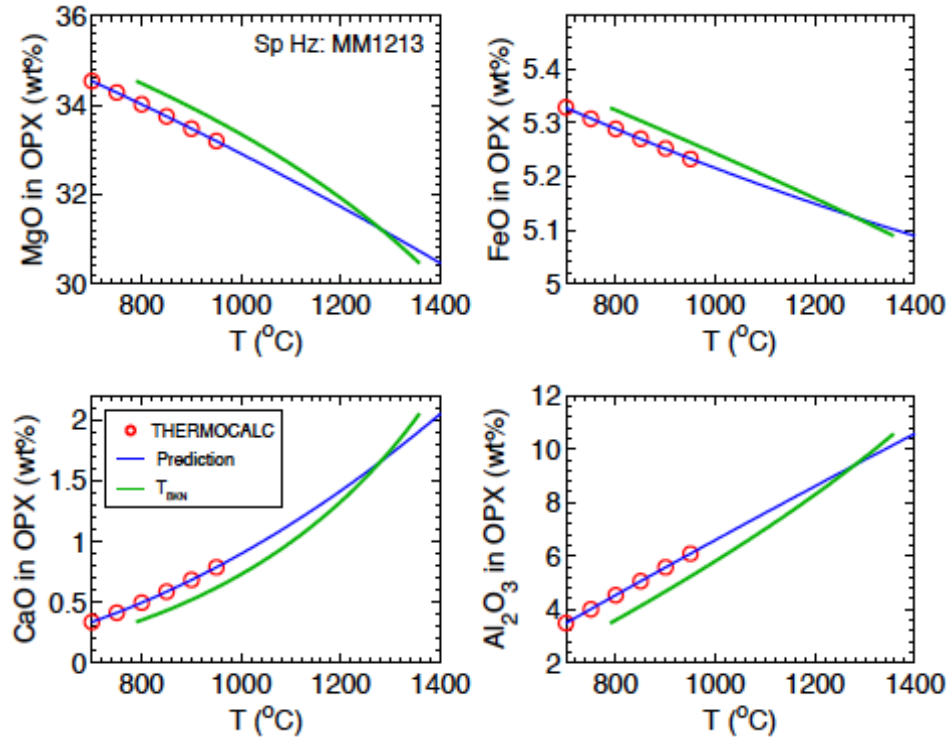


Figure 3-S9. Major element variations of opx in weight percent. T_{BKN} are calculated using the two-pyroxene thermometer of Brey and Köhler (1990) and the major element concentrations as plotted in the figures above and Fig. 3-S8.

Supplementary Figure 3-S10

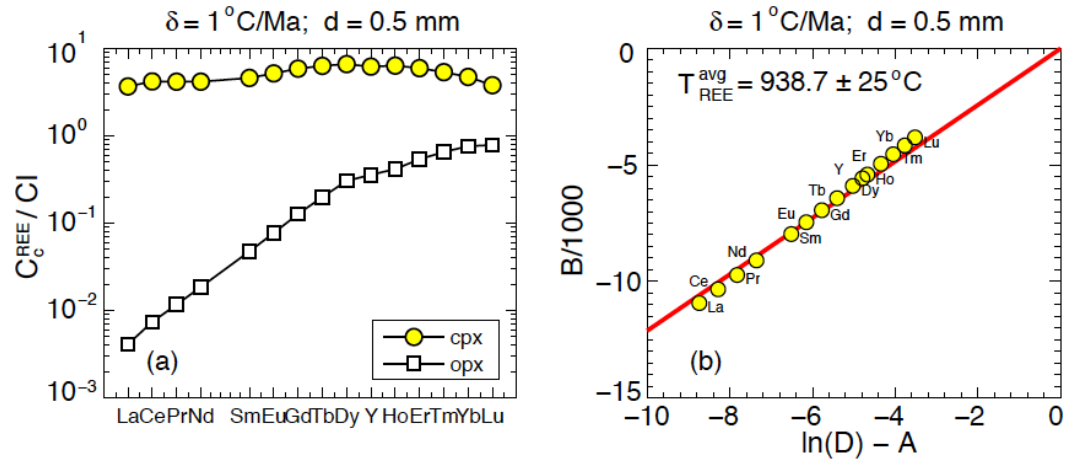


Figure 3-S10. Large uncertainty in T_{REE} inversion caused by the disequilibrium of major elements and REE.

CHAPTER 4

A Parameterized Model for REE Distribution between Low-Ca Pyroxene and Basaltic Melts with Applications to REE Partitioning in Low-Ca Pyroxene along a Mantle Adiabatic and during Pyroxenite-Derived Melt and Peridotite Interaction

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Abstract

Low-Ca pyroxenes play an important role in mantle melting, melt-rock reaction, and magma differentiation processes. In order to better understand REE fractionation during adiabatic mantle melting and pyroxenite-derived melt and peridotite interaction, we developed a parameterized model for REE partitioning between low-Ca pyroxene and basaltic melt. Our parameterization is based on the lattice strain model and a compilation of published experimental data, supplemented by a new set of trace element partitioning experiments for low-Ca pyroxenes produced by pyroxenite-derived melt and peridotite interaction. To test the validity of the assumptions and simplifications used in the model development, we compared model-derived partition coefficients with measured partition coefficients for REE between orthopyroxene and clinopyroxene in well-equilibrated peridotite xenoliths. REE partition coefficients in low-Ca pyroxene correlate negatively with temperature and positively with both calcium content on the M2 site and aluminum content on the tetrahedral site of pyroxene. The strong competing effect between temperature and major element compositions of low-Ca pyroxene results in very small variations in REE partition coefficients in orthopyroxene during adiabatic mantle melting when diopside is in the residue. REE partition coefficients in orthopyroxene can be treated as constants at a given mantle potential temperature during decompression melting of lherzolite and diopside-bearing harzburgite. In the absence of diopside, partition coefficients of light REE in orthopyroxene vary significantly, and such variations should be taken into consideration in geochemical modeling of REE fractionation in clinopyroxene-free harzburgite. Application of the parameterized model to low-Ca pyroxenes produced by reaction between pyroxenite-derived melt and

peridotite revealed large variations in the calculated REE partition coefficients in the low-Ca pyroxenes. Temperature and composition of starting pyroxenite must be considered when selecting REE partition coefficients for pyroxenite-derived melt and peridotite interaction.

1. Introduction

The Earth's upper mantle is mainly composed of olivine and pyroxene. Due to their relative high affinity for incompatible trace elements, clinopyroxene (cpx) and orthopyroxene (opx) play an important role in trace element fractionation during partial melting and melt migration in the upper mantle. Pyroxene-melt trace element partition coefficient is a key parameter for constraining these processes. Considerable progress has been made in understanding trace element partitioning between cpx and basaltic melts (e.g. Wood and Blundy 2003 and references therein). However, orthopyroxene becomes the dominant phase to fractionate incompatible trace elements when cpx is consumed during late stage melting of a peridotite or during melting of a lunar cumulate mantle composed of olivine and opx (e.g. Snyder et al. 1992). Furthermore, an opx-rich lithology can also be formed during melting of a marble cake mantle that consists of pyroxenite embedded in a lherzolite host at high pressure. During mantle upwelling, pyroxenite starts to melt at greater depth than peridotite (e.g. Takahashi and Nakajima 2002; Pertermann and Hirschmann 2003a; Hirschmann et al. 2003; Spandler et al. 2008). In general, pyroxenite-derived melts are more silica-rich and, when reacting with their surrounding lherzolite, can produce low-Ca pyroxene-enriched lithologies such as orthopyroxenite and harzburgite (Yaxley and Green 1998; Takahashi and Nakajima 2002; Morgan and Liang 2005; Lo Cascio and Liang 2007; Lo Cascio 2008). The low-Ca pyroxene includes both opx and subcalcic augite and is produced at the expense of cpx and olivine in the lherzolite. Compared with opx in the unreacted lherzolite, this layer of low-Ca pyroxene has higher Ca and Al contents and a lower Mg# ($100 \times \text{Mg}/(\text{Mg} + \text{Fe})$, in molar fraction). These low-Ca pyroxenes could have different trace element partition

coefficients (D) from opx in the unreacted lherzolite given the distinct chemical compositions. One of the main objectives of this study is to determine the partition coefficients of trace elements in the low-Ca pyroxenes derived from the melt-rock reaction.

In general, mineral-melt trace element partition coefficients (D_j) from a given partitioning experiment vary systematically as a function of their ionic radii and temperature, and can be quantitatively described by the lattice strain model (Brice 1975; Blundy and Wood 1994; Wood and Blundy 1997):

$$D_j = D_0 \cdot \exp \left\{ \frac{-4\pi E N_A}{RT} \left[\frac{r_0}{2} (r_j - r_0)^2 + \frac{1}{3} (r_j - r_0)^3 \right] \right\} \quad (1)$$

where D_0 is the mineral-melt partition coefficient for the strain-free substitution; r_0 is the radius of a hypothetical cation that substitutes into the site with zero strain; r_j is the ionic radius of the element of interest; E is the effective Young's modulus for the lattice site; N_A is Avagadro's number; R is the gas constant; and T is temperature in Kelvin. Applications of the lattice strain model to rare earth element (REE) partitioning between cpx and basaltic melt have been summarized in Wood and Blundy (1997, 2002), and a recent update can be found in Sun and Liang (2012).

Compared with cpx, there are considerably fewer trace element partitioning data for low-Ca pyroxenes. Of the published low-Ca pyroxene partitioning data, there are large variations in selected trace elements (e.g. $D_{La} = 0.00004$ -0.054, $D_{Nd} = 0.0005$ -0.114, $D_{Yb} = 0.0202$ -0.449; sources of data are given in Table 3 plus those from Colson et al. 1988; Kennedy et al. 1993; Klemme et al. 2006). It is not clear which set of the published partition coefficients one should use for low-Ca pyroxene when modeling adiabatic mantle melting or melt-rock reaction. Based on the published experimental data and the

lattice strain model, Wood and Blundy (2003) proposed a preliminary model to describe REE partitioning between opx and melt. Due to the limited partitioning data they set the effective Young's modulus E to a constant value of 360 GPa and D_0 a factor of five lower than that in cpx. Their model generally underestimates the REE partition coefficients in well-equilibrated opx by a factor of up to 5 and cannot be applied to subcalcic augite (Fig. 1a). Bédard (2007) compiled published opx partition coefficients from both partitioning experiments and natural samples. Based on linear regression analyses, he suggested that $\ln(D)$ for a given REE could be calculated using the $\ln(\text{MgO})$ of the melt, the Mg# of opx, the SiO_2 content in the melt, or a combination of these variables. Bédard (2007) provided five different partitioning models for each element, of which a linear function based on the $\ln(\text{MgO})$ of the melt and another based on the Mg# of opx appear to give better predictions of D_{REE} . We compared these two models and found that the linear function based on $\ln(\text{MgO})$ of the melt (Fig. 1b) generated better predictions than those based on the Mg# of opx (Fig. 1c); however, neither model is applicable to REE partitioning in subcalcic augite (Fig. 1b and 1c). Witt-Eickschen and O'Neill (2005) and Lee et al. (2007) developed models for REE partitioning between opx and cpx in peridotite. Orthopyroxene-melt partition coefficients may be deduced from their models given cpx-melt partition coefficients. However, their models were based on the analysis of peridotite xenoliths that were equilibrated at subsolidus conditions, and extrapolation to magmatic conditions needs further examination. Hence, an accurate model is needed to quantitatively describe REE partitioning in low-Ca pyroxenes.

Sun and Liang (2012) developed a new parameterized lattice strain model for REE and Y partitioning between cpx and basaltic melt. Instead of using all or most of the

published cpx-melt partitioning data in the literature, they selected a subset of data from 43 partitioning experiments (a total of 344 data) that show no obvious signs of chemical disequilibrium and that were analyzed by either ion probe or laser ablation inductively coupled mass spectrometry (LA-ICP-MS). They then systematically examined the effects of temperature (T), pressure (P), and mineral and melt compositions (X) on REE and Y partitioning in cpx. Through an extensive search of various permutations of the composition variables, they found that Mg content on the M2 site (X_{Mg}^{M2}) and Al content on the tetrahedral site (X_{Al}^T) in cpx, the molar fraction of water in the melt ($X_{H_2O}^{melt}$), and T were the primary variables determining D_0 . X_{Mg}^{M2} and Al content on the M1 site (X_{Al}^{M1}) in cpx are the main factors affecting r_0 . They showed, through a simultaneous inversion of the 344 filtered partitioning data, that the following expressions for the lattice strain parameters gave an excellent fit to the observed data:

$$\ln D_0 = -7.14(\pm 0.53) + \frac{7.19(\pm 0.73) \times 10^4}{RT} + 4.37(\pm 0.47) X_{Al}^T + 1.98(\pm 0.36) X_{Mg}^{M2} - 0.91(\pm 0.19) X_{H_2O}^{melt} \quad (2)$$

$$r_0 = 1.066(\pm 0.007) - 0.104(\pm 0.035) X_{Al}^{M1} - 0.212(\pm 0.033) X_{Mg}^{M2} \quad (3)$$

$$E = [2.27(\pm 0.44) r_0 - 2.00(\pm 0.44)] \times 10^3 \quad (4)$$

where $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$; numbers in parenthesis are two standard deviations calculated directly from the inversion. Using residual cpx compositions calculated along a mantle adiabat derived from pMELTS (Ghiorso et al. 2002) and Eqs. (1)-(4), they demonstrated that competing effects between temperature and cpx compositions gave rise to nearly constant partition coefficients for REE and Y in residual cpx in spinel lherzolite

stability field along a mantle adiabat (see also supplementary Fig. S1). The modeling and conclusions from Sun and Liang (2012) are intriguing and raise two broader questions: (1) can a similar approach be used for modeling REE and Y partitioning in low-Ca pyroxenes? and (2) do similar partitioning behaviors exist in the low-Ca pyroxenes during adiabatic mantle melting?

There are considerably fewer REE and Y partitioning data for low-Ca pyroxene than those for cpx. In this study, we report new trace element partitioning data for low-Ca pyroxenes produced by reactions between pyroxenite-derived melt and lherzolite at 1340-1425°C and 2 GPa. Following a procedure similar to that of Sun and Liang (2012), we then develop a parameterized lattice strain model for REE and Y partitioning in low-Ca pyroxenes. As an independent test of our new parameterization, we compute the REE partition coefficients between opx and cpx in peridotite xenoliths using major element compositions reported in the literature, and the REE partitioning models for cpx in Sun and Liang (2012) and low-Ca pyroxenes in this study. There is an excellent agreement between our model-derived opx-cpx partition coefficients for REE and those directly measured by LA-ICP-MS. As examples of geochemical application, we investigate the variation of REE and Y partitioning in low-Ca pyroxenes produced by pyroxenite-derived melt and peridotite interaction using major element compositions of the minerals reported in the melt-rock reaction experiments. Finally, we show that variations of opx-melt partition coefficients for REE are relatively small during adiabatic mantle melting and that constant partition coefficients can be used in studies of decompressional melting of lherzolite and cpx-bearing harzburgite.

2. Experiment

2.1. Experimental strategy and setup

Partial melting and melt-rock reaction experiments have shown that major element compositions of pyroxenite-derived melt vary considerably (grey fields in Fig. 2) and overlap with a significant number of low-Ca pyroxene-melt partitioning experiments (orange squares in Fig. 2). To further expand the database for trace element partitioning in low-Ca pyroxene, we conducted a set of pyroxenite-derived melt and peridotite reaction experiments. These experiments produced large, low-Ca pyroxene crystals that are well suited for partitioning studies. Figure 3 shows the experimental setup that consists of a melt layer (basaltic andesite or diorite) at the top, a layer of melt-lherzolite mixture in the middle, and a lherzolite layer at the bottom, in volume proportions of approximately 2:2:1. The mixture consists of two parts of melt and one part of lherzolite. Based on the basaltic andesite and lherzolite dissolution experiments of Morgan and Liang (2005) and Lo Cascio (2008), the reaction between lherzolite and a silica-saturated melt at temperatures above the solidus of lherzolite results in the dissolution of cpx and olivine and the precipitation of low-Ca pyroxene. The mixed layer in the middle helps to establish full contact between melt and lherzolite, facilitating the melt-peridotite reaction. If the temperature at the top of the reaction couple is slightly colder than that in the middle of the charge, which is normally achieved in a piston cylinder apparatus, large low-Ca pyroxene crystals will precipitate at the cold end of the capsule. Dissolution, precipitation, and reprecipitation in a nearly homogeneous melt along a small temperature gradient led to the formation of a few large pyroxene crystals near the top of the reaction couple.

2.2. Starting materials

Natural sample powders were used in our experiments for both melt and lherzolite. Based on the earlier work of Morgan and Liang (2005) and Lo Cascio (2008), we chose a basaltic andesite (Mont 147) and a diorite (FS3-1) to represent pyroxenite-derived melts (blue and red stars in Fig. 2, respectively). Sample Mont 147 (provided by Dr. J.D. Devine) is from Montserrat and used by Morgan and Liang (2005) in their studies of melt-lherzolite reactions at 1300°C and 1 GPa. Sample FS3-1 (provided by Dr. W. Xu) is from a diorite intrusion in the North China craton. The starting lherzolite powder (KBH-1Y) was created by mixing fine grained optically clean diopside (15wt%), opx (30%), olivine (52%), and spinel (3%) that are from a spinel lherzolite xenolith from Kilbourne Hole, NM (sample KBH-1 used in Morgan and Liang 2005). The mixtures were crushed in an agate mortar and ground under ethanol twice for 40 minutes each and then stored in an oven at 110°C to minimize the adsorption of water. Major element compositions of the starting materials are listed in Table 1.

2.3. Experimental procedure

Experiments were performed in a 19.05 mm piston-cylinder apparatus at Brown University. The experimental assembly consisted of a salt-Pyrex[®] sleeve, a straight-wall graphite furnace, and internal spacers of crushable MgO. Of the five experiments reported in this study, four were run using a graphite-lined molybdenum (Mo) capsule and one using a graphite capsule. The length of the capsules varies from ~ 5 mm to ~10 mm. The furnace assembly was vacuum dried at 200°C overnight and stored at 110°C.

Experiments were conducted using the “hot piston-in” technique. To start an experiment, we first pressurized the charge to a pressure that is slightly below 2 GPa. The temperature was then increased to the target temperature at a rate of 75°C per minute while slowly increasing the pressure to the target pressure. The run was held at the specified temperature and pressure for 48-72 hours before quenching to room temperature (Table 2). The retrieved capsule was sectioned longitudinally, mounted in epoxy, and polished to a 1 mm to finish.

The nominal pressure was not corrected for friction. No pressure correction was applied to the measured electromotive force (*e.m.f.*). Temperature was measured using a W₉₇Re₃–W₇₅Re₂₅ thermocouple and controlled with a Eurotherm 818. Uncertainties in temperature measurements are about ±10°C. The oxygen fugacity of the experimental conditions is estimated to be close to or slightly more reducing than the carbon-carbon monoxide (CCO) buffer (Médard et al. 2008).

2.4. Analytical techniques

Major element compositions of the crystal and melt were analyzed using a Cameca SX100 electron microprobe at Brown University. For the glasses, we used an accelerating voltage of 15 kV, a beam current of 15 nA, and a beam size of 5 μm for samples BA1LH2-T4 and BA1LH2-T6, and we used an accelerating voltage of 20 kV, a beam current of 25 nA, and a beam size of 20 μm for the other samples. For the minerals, we used an accelerating voltage of 20 kV, a beam current of 25 nA, and a beam size of 5 μm. Counting times were 10-30 s for peak and 10-15 s for background positions. Natural mineral standards were used, and the ZAF matrix correction was employed.

Trace element concentrations in crystals and glasses were measured *in situ* using a Thermo X-Series 2 quadrupole ICP-MS in conjunction with a New Wave UP 213 nm Nd-YAG laser-ablation system at the University of Rhode Island. The diameter of the laser beam was set to 60 μm for crystal and melt in run BA1LH2-T6 and crystal in run BA1LH2-T4, and 40 μm for crystals and melts in the other samples. Samples were ablated with an output energy of ~ 0.3 mJ at a frequency of 10 Hz. For each analysis, elements were analyzed in the mass spectrometer for a total time of 120 s. The background was measured for 30 s, and the signals were acquired for approximately 60 s by a laser firing. The gas mixture used during each analysis consisted of pure helium, which was used in the sample cell and later mixed downstream with pure argon. External standards used in the analyses include NIST-610 from Pearce et al. (1997), BCR-2g, BHVO-2g, BIR-1g from Kelley et al. (2003), and GOR132, StH1s, T1, ML3B, KL2 from Jochum et al. (2006). Since MgO is the predominant major oxide in low-Ca pyroxene, and its abundance is high in the reacted melt (Fig. 2), we used MgO as the internal standard. Electron microprobe analyses of MgO were chosen from points close to the spots analyzed by LA-ICP-MS. The detection limit for each analysis was estimated at 3 times or higher than the standard deviation of the background.

2.5. Experimental results

The experimental conditions and run products are summarized in Table 2, and representative back-scattered electron (BSE) images of the experimental charges are shown in Fig. 4 (BSE images showing the entire sectioned charges of selected runs can

be found in supplementary Fig. S2). Subcalcic augites are observed in run DR1LH-T2 (Figs. 4e and 4f), whereas opx crystals are present in the other four runs. The experiments generally form a few large crystals on the top and along the sidewall of the graphite inner capsule (Fig. 4). The crystals are 300-1500 μm in size. The Low-Ca pyroxenes possess no obvious zoning or melt inclusions. Run FS3-1-T1 also has tiny opx crystals smaller than 10 μm in the lower part of the melt.

Major and trace element compositions of melt and pyroxenes are listed in supplementary Tables S1 and S2, respectively. Melt from each experiment is relatively homogeneous; based on 9-17 spot analyses, standard deviations are smaller than the marker size in Fig. 2 for most experiments. There is some variation in Al_2O_3 content in melt of runs BA1LH2-T5 and BA1LH2-T6, which may be attributed to the thermal gradient within the charges. Major element compositions of pyroxene crystals are relatively homogeneous in each run.

The average trace element concentrations (weight percent) in both the melt (C_j^{melt}) and the crystals (C_j^{crystal}) for each experiment (4-7 spots) are used to calculate partition coefficients:

$$D_j^{\text{crystal}} = \frac{C_j^{\text{crystal}}}{C_j^{\text{melt}}} \quad (5)$$

Partition coefficients are listed in Table 2 and graphically displayed according to element groups with increasing compatibility in Fig. 5. The partition coefficients of Sr fall in the range of published data, although D_{K} and D_{Pb} of subcalcic augite (DR1LH2-T2) have not been reported before. The partition coefficients of REE and Y show a systematic increase in compatibility with decreasing ionic radii. The small negative Eu anomalies presumably

result from the reducing environment imposed by the Mo-graphite capsule. The partition coefficients of the high field strength elements (HFSE) and most of the transition metals (TM) in low-Ca pyroxene also show systematic variations in their compatibility and are comparable to the published data. The exception is D_{Cu} in opx, which is not within the range of the published data (Fig. 5). This may be attributed to either a paucity of published data, of which there are only two D_{Cu} values reported for opx, or a difference in the oxidation state. One D_{Cu} value for opx is from Adam and Green (2006), who reported a value of 2.8 in a hydrous garnet lherzolite. The other D_{Cu} value is from Klemme et al. (2006), who reported a value of 0.22 for enstatite in a simple system that is Ca-free. These two values may not adequately define the range of D_{Cu} for opx in the upper mantle. Alternatively, our experimental environment may be too reducing (c.f. Eu in Fig. 5), which results in a large fraction of Cu cations in the monovalent state (Cu^+). Six-fold coordinated Cu^+ has an ionic radius of 0.77 Å (Shannon 1976), which is larger than the M1 site of low-Ca pyroxene (ionic radius of Mg^{2+} is 0.72 Å), while Cu^{2+} (ionic radius of 0.73 Å) would be expected in Earth mantle. Overall, our measured trace element partition coefficients expand the range of low-Ca pyroxene trace element partition coefficients reported in the literature (Fig. 5).

REE and Y partitioning in pyroxene is mainly caused by substitution of the trivalent cations into the M2 site of pyroxene. For a given partitioning experiment, REE and Y partition coefficients generally follow a parabolic pattern in an Onuma diagram and can be described by the lattice strain model (Eq. 1). Here, we apply the lattice strain model to REE and Y partitioning data to obtain key parameters (D_0 , r_0 , and E in Eq. 1) for each experiment. For reasons outlined in the first section in Discussion below, we

used the 8-fold coordinated ionic radii of REE and Y from Shannon (1976) to fit the measured data while excluding Eu in the nonlinear regression analysis because of the possible presence of Eu^{2+} in our charges. The fitting results are summarized in Fig. 6, where data used in each regression analysis are shown as red circles. (In supplementary Fig. S3, we also show the fit to our experimental data using 6-fold coordinated ionic radii and the lattice strain model.) The derived D_0 (0.248-0.658) from our experiments ranges to higher values than that we recalculated from the published partitioning experiments using 8-fold coordinated ionic radii (0.05-0.464, except for D_0 of Green et al. 2000, which has a surprisingly high value of 3.27). The derived r_0 (0.781-0.984 Å) and E (152-292 GPa) from our experiments show relatively small variations than those we recalculated from the literature data ($r_0 = 0.705$ -1.001 Å, and $E = 110$ -427 GPa). Variations in the lattice strain parameters are due to variations in P - T - X , which we will discuss in the next section.

3. A parameterized model for REE and Y partitioning in low-Ca pyroxene

To better understand the P - T - X dependence of REE and Y partitioning in low-Ca pyroxene, we developed a parameterized model. Our parameterization is based on the lattice strain model using a subset of published partitioning data and follows the methodology of Sun and Liang (2012) for REE and Y partitioning between cpx and basaltic melts.

3.1. Data compilation

Although there is a fairly large database for REE and Y partitioning in low-Ca pyroxene from natural samples and experiments in the literature (see Bédard 2007 for a recent compilation), the quality of the published data is not uniform. Some data filtering is necessary to ensure the accuracy of the model. We compiled experimentally determined partition coefficients between low-Ca pyroxene and basaltic melt from the past two decades, to which we added the low-Ca pyroxene partitioning data from this study and the opx partitioning data for the lunar green, orange, and red picritic glass melts from Sun and Liang (manuscript in preparation, see also Sun et al. 2011). These data have been filtered on the basis of attainment of equilibrium (e.g. absence of core to rim variation, sector zoning in major elements, or melt inclusions, run duration), misfit or outlier with reference to the lattice strain model (e.g. Eu anomaly), and method of chemical analysis (LA-ICP-MS and ion probe), similar to the rational adopted by Sun and Liang (2012). REE and Y abundances in low-Ca pyroxenes are, in general, lower than those in cpx and hence more difficult to analyze using an electron microprobe, so we only considered data analyzed by ion probe or LA-ICP-MS in our parameterization. We obtained 344 data from 38 partitioning experiments for low-Ca pyroxene (29 for opx and 9 for subcalcic augite; 3 of the 29 opx experiments are conducted under hydrous conditions, Table 3), including 63 data from 5 experiments in the present study, and 66 data from 6 experiments of Sun and Liang (in preparation). The size of the database is similar to that used by Sun and Liang (2012) for REE and Y partitioning in cpx (43 experiments and 344 data). In the online supplementary Figs. S4-S6 we show Onuma

diagrams for the 38 experiments as well as those that were analyzed by either ion probe or LA-ICP-MS but excluded from our filtered database.

The 38 selected partitioning experiments cover a wide range of pressures (1 atm to 3.4 GPa) and temperatures (1080-1660°C). These experiments produced low-Ca pyroxene and melt with large variations in composition (e.g. Ca content on the M2 site $X_{Ca}^{M2} = 0.025-0.408$, Mg# = 70-100 in pyroxene; Mg# = 41-100 in melt, SiO₂ = 39.0-60.6 wt.% in melt; see Table 3 for details), and partition coefficients (e.g. $D_{La} = 0.0004-0.0268$, $D_{Nd} = 0.0016-0.114$, $D_{Yb} = 0.034-0.449$).

3.2. Parameterization method

To develop a parameterized model for REE and Y partitioning between low-Ca pyroxene and basaltic melt, we conducted a multivariable nonlinear least squares analysis. Here, we followed the same procedure as described in Sun and Liang (2012) for the least squares analysis of REE and Y partitioning in cpx. The analysis involves two steps: (1) identification of the key parameters that affect D_0 , r_0 , and E in the lattice strain model through least squares analysis of individual experiments; and (2) simultaneous inversion of all the filtered experimental data using the primary parameters identified in step (1).

As D_0 is the partition coefficient for strain-free substitution of the M2 site, we assume that D_0 has the same form used by Sun and Liang (2012, their Eq. 2), and that r_0 is a function of pyroxene compositions. Based on Monte Carlo simulations, Sun and Liang (2012) showed that E is positively correlated with r_0 . We find three subparallel trends of E and r_0 for opx (squares), subcalcic augite (diamonds), and cpx (circles, Sun

and Liang 2012) derived from regression analysis of individual partitioning experiments and the lattice strain model (Fig. 7). E and r_0 values of each pyroxene are positively correlated, which agrees with the Monte Carlo simulations of Sun and Liang (2012). The distribution of E and r_0 among the three subgroups of pyroxene reveals that E also correlates with pyroxene composition (e.g. Ca content on the M2 site, X_{Ca}^{M2} , and/or Mg content on the M2 site, X_{Mg}^{M2}). Accordingly, we assume E as a linear function of r_0 , mineral and/or melt compositions.

Through an extensive search of various permutations of the composition variables, we find that X_{Ca}^{M2} and X_{Al}^T in low-Ca pyroxene and T are the primary variables that determine D_0 , X_{Ca}^{M2} and X_{Mg}^{M2} are the main factors affecting r_0 , and that E can be described by a linear combination of r_0 and X_{Ca}^{M2} . Expressions for D_0 , r_0 , and E take the linear forms:

$$\ln D_0 = a_0 + \frac{a_1}{RT} + a_2 X_{Ca}^{M2} + a_3 X_{Al}^T \quad (6)$$

$$r_0 = a_4 + a_5 X_{Ca}^{M2} + a_6 X_{Mg}^{M2} \quad (7)$$

$$E = a_7 + a_8 r_0 + a_9 X_{Ca}^{M2} \quad (8)$$

where $a_0, a_1, \dots, a_9$ are constant coefficients determined by stepwise multiple linear regression analyses of the lattice strain parameters (D_0 , r_0 , and E); X_{Ca}^{M2} , X_{Al}^T , and X_{Mg}^{M2} are cation numbers (per 6 oxygen) on respective sites in pyroxene.

To better constrain the low-Ca pyroxene-melt partitioning model for REE and Y, we substituted Eqs. (6)-(8) back into Eq. (1) and used the lattice strain model and our filtered partition coefficients to invert for the 10 fitting parameters, $a_0, a_1 \dots a_9$,

simultaneously through a global nonlinear least squares analysis (e.g. Seber and Wild 1989). To carry out the global inversion, we used the coefficients from the stepwise multiple linear regressions as initial values in the nonlinear least squares analysis and minimize the chi-square as defined below:

$$\chi^2 = \sum_{j=1}^N \left(\ln D_j - \ln D_j^m \right)^2, \quad (9)$$

where D_j is defined by Eq. (1) for element j , D_j^m is the measured opx-melt partition coefficient for element j , $N (= 344)$ is the total number of measured partitioning data used in this study. Logarithmic normalized partition coefficients are used in the chi-square calculation because the absolute values of D are different from one element to another, and systematic variations in REE abundances and partition coefficients are usually examined in normalized semi-log spider diagrams. Although convenient in nonlinear regression analysis, the absolute values of the chi-square defined in Eq. (9) depend on the number of data points used in the inversion and hence are not statistically meaningful. To quantitatively evaluate the goodness of the fit, we calculate the Pearson's chi-square for the estimation using the expression:

$$\chi_P^2 = \sum_{j=1}^N \frac{\left(D_j - D_j^m \right)^2}{D_j}, \quad (10)$$

A better predictive model should produce a smaller χ_P^2 . The results are shown in Fig. 8 and discussed below.

3.3. Model results

Results of the global fit to the 344 partitioning data from the 38 experiments (Table 3) using 8-fold coordinated ionic radii from Shannon (1976) are as follows:

$$\ln D_0 = -5.37(\pm 0.49) + \frac{3.87(\pm 0.74) \times 10^4}{RT} + 3.56(\pm 1.02) X_{Ca}^{M2} + 3.54(\pm 0.61) X_{Al}^T \quad (11)$$

$$r_0 = 0.69(\pm 0.05) + 0.43(\pm 0.15) X_{Ca}^{M2} + 0.23(\pm 0.06) X_{Mg}^{M2} \quad (12)$$

$$E = [-1.37(\pm 0.47) + 1.85(\pm 0.52) r_0 - 0.53(\pm 0.11) X_{Ca}^{M2}] \times 10^3 \quad (13)$$

where numbers in parenthesis are two standard deviations calculated directly from the simultaneous inversion. As D_0 determines the peak value of the parabola defined by Eq. (1), to the first order, the REE partition coefficients increase with increasing X_{Ca}^{M2} and X_{Al}^T in low-Ca pyroxene but decrease with increasing temperature. In general, REE partition coefficients in subcalcic augite are larger than those in opx at a similar temperature and Al_2O_3 content.

4. Discussion

Combined with Eq. (1), equations (11)-(13) provide a simple empirical model for REE and Y partitioning between low-Ca pyroxene and basaltic melt. Figure 8 compares the predicted D values for REE and Y using Eqs. (1), (11)-(13) with the experimentally measured values. Almost all of the low-Ca pyroxene data fall between the 1:2 and 2:1 correlation lines (dashed lines in Fig. 8), including experimental results from the present study (stars). The small χ_p^2 ($= 1.30$) between observed and predicted D values suggests an excellent agreement between partitioning experiments and our model predictions. The

χ_p^2 value provided by our model is much smaller than that calculated using the preliminary model of Wood and Blundy (2003, $\chi_p^2 = 59.81$, Fig. 1a) and the values derived from the models of Bédard (2007, $\chi_p^2 = 58.17$ in Fig. 1b; and $\chi_p^2 = 92.99$ in Fig. 1c), which is indicative of the significant improvement of our new model for the prediction of REE and Y partitioning in low-Ca pyroxenes. In supplementary Fig. S4, we further compare our global model with each partitioning experiments in Omuna diagrams.

4.1. Six-fold vs. eight-fold coordinated ionic radii of REE

The use of 8-fold coordinated ionic radii in our application of the lattice strain model needs an explanation. Orthopyroxene has a larger 6-fold M2 site and a smaller 6-fold M1 site. REE and Y preferentially substitute into the M2 site of opx. Six-fold coordinated ionic radii have been used in the application of the lattice strain model to REE³⁺ and Y³⁺ partitioning in opx (e.g. Wood and Blundy 2003; Frei et al. 2009), a choice that we also made initially in this study. In the supplementary Figs. S3 and S7, we show that indeed 6-fold coordinated ionic radii work very well for both our measured partitioning data and the global fit to our filtered 344 data. However, when comparing our low-Ca partitioning model (Eqs. 1, S1-S3) with the cpx model of Sun and Liang (2012), it became clear that the 6-fold coordinated ionic radius of Pr reported in Shannon (1976) might not be as accurate as it should be. This is shown in Fig. 9 where Pr appears to deviate slightly from the nearly linear trend defined by the rest of REE and Y. According to Shannon (1976), ionic radius of 6-fold Pr is an interpreted value based on an approximately linear correlation between ionic volumes (r^3) and unit cell volumes (V) of

isotypic series of oxides and fluorides. Although the small deviation of the 6-fold ionic radius of Pr does not affect the overall quality of the fits to the lattice strain model for low-Ca pyroxene (Figs. S3 and S7), it does result in an unphysical kink in the calculated REE opx-cpx partition coefficients in the otherwise smooth spider diagram (see supplementary Fig. S9). One way to resolve this inconsistency is to use 8-fold coordinated ionic radii of REE and Y reported in Shannon (1976) as proxies for the 6-fold coordinated ionic radii in the lattice strain model for low-Ca pyroxene. This does not imply that REE is in 8-fold coordination in the M2 site of low-Ca pyroxene, but an interim solution to this peculiar problem. Given the nearly linear correlation between the two sets of ionic radii (Fig. 9), the use of 8-fold coordinated ionic radii merely results in a change in numerical values of the fitting parameters in the lattice strain model (c.f. Eqs. 11-13 and Eqs. S1-S3). The unphysical kink in the spider diagram disappeared (c.f. Figs. 14 and S9) when 8-fold coordinated ionic radii were used.

4.2. Composition dependence of REE partitioning in pyroxene

Our model indicates that REE and Y partition coefficients strongly depend on both temperature and X_{Ca}^{M2} and X_{Al}^T in low-Ca pyroxene. Temperature and pyroxene composition have opposite or competing effects (Eq. 11), a point that will be discussed in a later section. According to Eq. (2), REE partitioning in cpx is controlled primarily by X_{Al}^T and X_{Mg}^{M2} in cpx. Figures 10a-10i compare Ce, Nd, and Yb partitioning coefficients as functions of X_{Al}^T , X_{Ca}^{M2} , and X_{Mg}^{M2} in pyroxenes from the filtered data of Sun and Liang (2012, blue circles) and those used in the present study (red squares for opx and green diamonds for subcalcic augite). The effects of X_{Al}^T on REE partitioning are similar among

the three pyroxenes (i.e. similar slopes in Figs. 10a-10c), while the effect of X_{Ca}^{M2} appears more important in low-Ca pyroxene than in cpx. This is consistent with the large coefficient of X_{Ca}^{M2} in Eq. (11). The partition coefficients for low-Ca pyroxene negatively correlate with X_{Mg}^{M2} (Figs. 10g-10i), which may be explained by the complementary relationship between X_{Ca}^{M2} and X_{Mg}^{M2} on the M2 site. REE and Y partition coefficients are inversely correlated with temperature, but not explicitly dependent on pressure or melt composition (c.f. Eq. 11). Since the major element compositions of low-Ca pyroxene and melt vary systematically as a function of pressure and temperature, pressure (and melt compositions) can indirectly affect the partition coefficients of REE and Y between pyroxene and melt through the mineral compositions. The strain-free lattice size (r_0) increases with the increase of X_{Ca}^{M2} and X_{Mg}^{M2} in low-Ca pyroxene according to Eq. (12). The factors are different from those for cpx where r_0 decreases with increasing X_{Al}^{M1} and X_{Mg}^{M2} in cpx (c.f. Eqs. 3 and 12). This difference may account for the X_{Ca}^{M2} dependence of E , which is absent in the cpx model of Sun and Liang (2012, c.f. Eqs. 4 and 13).

4.3. The effect of water on REE partitioning in low-Ca pyroxene

Partitioning studies have indicated that presence of water in the melt hinders REE partitioning in cpx and garnet (Wood and Blundy 2003; Green et al. 2000; Adam and Green 2006; Sun and Liang 2012). To investigate the effect of water on REE partitioning in low-Ca pyroxene, we incorporated water in our parameterization following the procedure of Sun and Liang (2012). A preliminary model incorporating water effect can be found in the supplementary material (Fig. S8). The preliminary hydrous model has a

χ_p^2 value of 1.31 (1.30 for anhydrous model). Hence including water as an additional variable does not improve the goodness of the fit. The very small coefficient of water (an order of magnitude smaller than the coefficients of X_{Ca}^{M2} and X_{Al}^T) and large standard deviation (>100%) also suggest that the effect of water on REE partitioning in low-Ca pyroxene is insignificant. Since only three partitioning experiments in our compiled dataset were conducted under hydrous conditions (Green et al. 2000; McDade et al. 2003b; Adam and Green 2006), water effect may not be fully quantified in our preliminary model. Additional hydrous partitioning experiments are needed to further investigate the effect of water on trace element partitioning in low-Ca pyroxene.

4.4. REE and Y partitioning between sub-solidus opx and cpx: a field test

The excellent agreement between partition coefficients for REE and Y in low-Ca pyroxene calculated using our parameterized model and experimentally measured values from the filtered dataset is very encouraging (Fig. 8). To further test the validity of the assumptions and approximations used in our model development, we conducted a field test. Witt-Eickschen and O'Neil (2005) and Witt-Eickschen et al. (2009) measured the abundance of REE and other trace elements in cpx and opx from two suites of well-equilibrated spinel lherzolite xenoliths (866-1262°C) using LA-ICP-MS. They showed that opx-cpx partition coefficients for REE and Y vary systematically as a function of temperature and mineral compositions. To independently test our parameterized models for REE and Y partitioning in low-Ca pyroxene and high-Ca pyroxene, we calculated opx-cpx partition coefficients for REE and Y using the major element compositions reported in Witt-Eickschen and O'Neil (2005) and Witt-Eickschen et al. (2009), and our

low-Ca and high-Ca pyroxene partitioning models (Eqs. 1-4, 11-13). The equilibrium temperatures were calculated using the cpx-opx geothermometry of Brey and Köhler (1990). Figure 11 shows very good to excellent agreements between our model-derived opx-cpx partition coefficients and those reported in Witt-Eickschen and O'Neil (2005) and Witt-Eickschen et al. (2009). The deviation of some D_{La} from the main trend (two from Witt-Eickschen and O'Neil 2005 and five from Witt-Eickschen et al. 2009) is possibly due to the very low abundances of La in opx and large analytical uncertainties. Figure 11 also compares the model calculated and LA-ICP-MS measured opx-cpx partition coefficients of REE and Y between coexisting opx and cpx in a lherzolite and a harzburgite reported by Eggins et al. (1998). Again, there is an excellent agreement between our model results and the measured data.

It is worth noting that the application of our parameterized models to REE partitioning between opx and cpx in peridotite xenoliths is an *extrapolation*, as these models were calibrated at magmatic conditions. The very good to excellent agreement between the model predicted and observed values for the subsolidus peridotites demonstrates the internal consistency between the partitioning models for REE and Y in low-Ca pyroxene (this study) and high-Ca pyroxene (Sun and Liang 2012), and further justifies the assumptions and simplifications made in our parameterization and the lattice strain model. The model validations presented above and discussed in Sun and Liang (2012) give additional assurance in their applications to REE fractionation during mantle melting, melt-rock interaction, and magma differentiation processes. To apply our two-pyroxene partitioning models to subsolidus samples, two conditions must be met: (1) peridotite samples must be well equilibrated and free of secondary processes; (2) the

temperature of equilibration is calculated using the cpx-opx thermometer of Brey and Köhler (1990). Application of the Ca-in-opx thermometer of Brey and Köhler (1990) results in an overestimation of opx-cpx partition coefficients for REE and Y. This may be due to the differences between the two thermometers, as the Ca-in-opx thermometer tends to give lower temperature (up to 20-100°C) than the cpx-opx thermometer. For well-equilibrated mafic and ultramafic samples, our two-pyroxene partitioning models may be used as a thermometer, a topic that will be explored in the future.

5. Applications

As shown in Figs. 5 and 10, REE and Y partition coefficients in low-Ca pyroxene vary considerably. In this section, we examine the importance of these variations in relation to geochemical modeling of adiabatic mantle melting and pyroxenite-derived melt and peridotite interaction in the mantle.

5.1. Partitioning of REE in low-Ca pyroxene during pyroxenite-derived melt and peridotite interaction

Reaction between pyroxenite-derived melt and peridotite can generate low-Ca pyroxenes. This process is particularly effective at depths just above the peridotite solidus where melt derived from pyroxenite can readily infiltrate into partially molten lherzolite (Lo Cascio 2008). Depending on the reacting melt composition, major element compositions of the reacted low-Ca pyroxene can vary considerably (see inset to Fig. 12). Partitioning of REE in low-Ca pyroxene during pyroxenite-derived melt and peridotite interaction is likely a function P - T - X , a topic that has not been examined previously. To

investigate the variation of REE partitioning in low-Ca pyroxenes produced by melt-rock reaction, we calculated REE partition coefficients using temperature and major element compositions of the pyroxene reported in the melt-rock reaction experiments and our parameterized lattice strain model (Eqs. 1, 11-13), with the results shown in Fig. 12. Partitioning values for these pyroxenes, especially those of light REE (LREE), are distributed over a relatively wide range, suggesting a strong dependence on temperature and pyroxene composition. In general, predicted LREE partition coefficients in subcalcic augite from high-pressure experiments of Yaxley (2000) are more than an order of magnitude higher than those of opx. However, not all pyroxenes formed via melt-rock reaction have higher partition coefficients, examples being those low partition coefficients derived from three experiments of Rapp et al. (1999, dashed black lines in Fig. 12). Exceptionally low Ca and Al abundances in opx in the latter study ($\text{CaO} = 0.17\text{--}0.68\%$; $\text{Al}_2\text{O}_3 = 0.33\text{--}2.25\%$, compared with the general range of $\text{CaO} = 1.5\text{--}2.7\%$; $\text{Al}_2\text{O}_3 = 3.3\text{--}9.0\%$) are the main reason. Hence the composition of the (starting) pyroxenite or eclogite is important in determining the composition of low-Ca pyroxene which, in turn, controls REE partitioning in opx or subcalcic augite at a given temperature and pressure. As will be further demonstrated below, partition coefficients of REE in opx derived from pyroxenite-derived melt and peridotite interactions can be significantly different from those in opx in lherzolite along a mantle adiabat.

5.2. REE partitioning in orthopyroxene along mantle adiabats

During adiabatic mantle melting, both temperature and pyroxene composition vary systematically as a function of pressure or depth. Here, we examine variations in REE

partition coefficients between opx and basaltic melts during adiabatic mantle melting. We consider three cases of different potential temperature (T_P) using either the depleted MORB mantle (DMM) of Workman and Hart (2005) or an enriched mantle (EM) composed of 90% DMM and 10% N-MORB (composition from Hofmann 1988) as our starting mantle compositions: (1) $T_P = 1300^\circ\text{C}$ and DMM source (Fig. 13a-13c); (2) $T_P = 1400^\circ\text{C}$ and DMM source (Fig. 13d-13f); and (3) $T_P = 1350^\circ\text{C}$ and EM source (Fig. 13g-13i). Similar to Sun and Liang (2012), we calculated the compositions of residual opx using pMELTS (Ghiorso et al. 2002) and partition coefficients using Eqs. (1), (11)-(13). Figure 13 summarizes the calculated opx compositions and REE partition coefficients. (A similar figure showing the variations of major element compositions and REE partition coefficients for coexisting cpx can be found in supplementary Fig. S1.)

For the case of $T_P = 1300^\circ\text{C}$ and DMM, melting begins in the spinel lherzolite stability field. As the temperature decreases, X_{Ca}^{M2} in opx increases, whereas X_{Al}^T in opx decreases (Fig. 13a). According to Eq. (11), X_{Al}^T has a competing effect with X_{Ca}^{M2} and temperature on REE partitioning in opx in the spinel lherzolite. Since the decrease of X_{Al}^T is larger than the increase of X_{Ca}^{M2} in opx, the net result is a relatively constant partition coefficient for REE along the 1300°C adiabat (Fig. 13b). After cpx has been consumed, both X_{Ca}^{M2} and X_{Al}^T in opx decrease with decreasing temperature, so that temperature now has a competing effect with both X_{Ca}^{M2} and X_{Al}^T in opx on REE partitioning. The net effect is a very small decrease in REE partition coefficients along the cpx-free portion of the adiabat. The overall effect of changing temperature, X_{Ca}^{M2} and X_{Al}^T in opx along the

1300°C mantle adiabat is very small, so that variations in REE partition coefficients in opx are in a very small range over the entire melting range (Fig. 13c).

For the case of $T_P = 1400^\circ\text{C}$ and DMM, melting starts in the garnet stability field. Figures 13d and 13e show variations of X_{Mg}^{M2} , X_{Ca}^{M2} , and X_{Al}^T in opx and partition coefficients along the mantle adiabat. Before garnet has been consumed, as temperature decreases, X_{Al}^T increases while X_{Ca}^{M2} remains approximately constant, so that the effects of temperature and X_{Al}^T effectively cancel out. Variations of partition coefficients after garnet is consumed behave the same way as those in spinel lherzolite and cpx-bearing harzburgite as discussed in the first example. To a good approximation, partition coefficients of REE in opx in the garnet and spinel lherzolite and cpx-bearing harzburgite can be taken as constants along this mantle adiabat. However, after cpx has been consumed, both X_{Ca}^{M2} and X_{Al}^T in opx decrease with decreasing temperature. The decrease is more significant than those in case (1), so larger variations in REE partition coefficients are observed, especially in LREE (Fig. 13e and 13f). REE partition coefficients in opx in cpx-free harzburgite cannot be taken as constants in this latter case.

For the case of $T_P = 1350^\circ\text{C}$ and EM, melting also begins in the garnet stability field. Figures 13g-13i show that opx composition and calculated REE partition coefficients fall in between values from cases (1) and (2). This simulation shows that the starting lherzolite composition has only a very small effect on the calculated REE partition coefficients in the garnet and spinel lherzolite and cpx-bearing harzburgite.

In summary, partition coefficients of REE in opx can be treated as constants along a mantle adiabat at a given potential temperature and mantle source composition as long as cpx is present in the residue and the major element composition of opx calculated from

pMELTS can be treated as accurate. Variations of REE partition coefficients in opx (green fields in Figs. 13c, 13f, and 13i) happen predominantly in the cpx-free harzburgite and have to be taken into consideration in trace element modeling of mantle melting and melt migration. For convenience, we list our recommended opx-melt and cpx-melt partition coefficients along three different mantle adiabats in Table 4, which are the average values for garnet and spinel lherzolites and cpx-bearing harzburgite. The average partition coefficients of opx and those of cpx from Table 4 are used to calculate opx-cpx partition coefficients along two mantle adiabats ($T_p = 1300^\circ\text{C}$ and 1400°C , DMM). Figure 14 compares our calculated REE opx-cpx partition coefficients along the two mantle adiabats with the recommended values of Lee et al. (2007) for isothermal mantle melting at 1300°C and 1400°C . The most important difference between adiabatic and isothermal cases is in the LREE: During adiabatic mantle melting, orthopyroxene is likely to play a greater role in fractionating LREE than commonly believed.

6. Conclusions

Partition coefficients for trace elements in low-Ca pyroxene produced by pyroxenite-derived melt and peridotite interactions were determined experimentally at $1340\text{--}1425^\circ\text{C}$ and 2 GPa. Based on a combination of these new partitioning results and a subset of published low-Ca pyroxene partitioning data, we developed a parameterized lattice strain model for REE and Y partitioning between low-Ca pyroxene and basaltic melt over a large range of P - T - X . By combining our model with a recent model for REE and Y partitioning in high-Ca pyroxene that was calibrated using a similar method (Sun and Liang 2012), we demonstrated very good to excellent agreement between the model-

derived and independently measured opx-cpx partition coefficients for REE and Y in well-equilibrated peridotite xenoliths. This agreement not only justifies the assumptions and simplifications made in the development of our model but also lends added assurance to the model applications to REE fractionation during mantle melting, melt-rock interaction, and magma differentiation processes. The main conclusions of this paper are as follows:

1. Partition coefficients of REE and Y in low-Ca pyroxene are positively correlated to X_{Ca}^{M2} and X_{Al}^T in pyroxene but inversely correlated with temperature, giving rise to a strong competing effect between temperature and low-Ca pyroxene compositions.

2. Partition coefficients of REE and Y in low-Ca pyroxene produced by pyroxenite-derived melt and peridotite interaction span almost the entire range defined by the published low-Ca pyroxene partitioning data. Major element compositions of pyroxenite and temperature must be considered when selecting REE partition coefficients for low-Ca pyroxenes derived from melt-rock reaction.

3. In the presence of cpx, the competing effect between temperature and opx composition results in very small variations in REE and Y partition coefficients in opx along a mantle adiabat. Constant partition coefficients can be used for REE and Y in opx during decompression melting of lherzolite and cpx-bearing harzburgite. However, in the absence of cpx, partition coefficients of LREE vary considerably and the variations should be taken into consideration when modeling REE fractionation during high-degree melting of cpx-free harzburgite.

4. The very good to excellent agreement between the model-derived and independently measured opx-cpx partition coefficients for REE and Y in the three suites of well-equilibrated peridotite xenoliths suggests that our two-pyroxene REE partitioning models may be used as a thermometer.

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Figure Captions

Figure 4-1 Comparison between model-predicted low-Ca pyroxene partition coefficients and observed values. Observed values are from partitioning experiments listed in Table 3. Predicted values are calculated using the preliminary model of Wood and Blundy (2003, **a**), and two models from Bédard (2007) based on $\ln(\text{MgO})$ of melt (**b**) and $\text{Mg\#}$ of opx (**c**). The solid line represents 1:1 ratio and dashed lines represent 2:1 and 1:2 ratios, respectively. χ_P^2 is the Pearson's chi-square calculated according to Eq. (10). Circles and squares are the published data; stars are new experimental results of this study.

Figure 4-2 Compositions of melt from pyroxenite and eclogite partial melting studies and low-Ca pyroxene partitioning experiments (**a-c**), and quadrilateral projection of the low-Ca pyroxene compositions in the corresponding partitioning experiments (**d**). The gray fields in (**a**)-(c) are the melt compositions from selected pyroxenite and eclogite melting studies (Takahashi et al. 1998; Yaxley and Green 1998; Rapp et al. 1999; Klemme et al. 2002; Takahashi and Nakajima 2002; Kogiso et al. 2003; Hirschmann et al. 2003; Petermann and Hirschmann 2003b; Keshav et al. 2004; Kogiso and Hirschmann 2006; Spandler et al. 2008; Yaxley and Sobolev 2007; Lambart et al. 2009). Orange squares represent melts from low-Ca partitioning experiments (sources of data are listed in Table 3 plus those from Colson et al., 1988; Kennedy et al. 1993; Klemme et al. 2006). Larger symbols in (**a**)-(c) represent melt compositions from this study: Stars are starting compositions of FS3-1 (red), basaltic andesite Mont 147 (blue), and FS3-1-T1 (green, estimated, a mixture of FS3-1 and Mont 147). Circles are the compositions of melt from runs BA1LH2-T4 (cyan), BA1LH2-T5 (blue), BA1LH2-T6 (magenta), FS3-1-T1 (green), and DA1LH2-T2 (red) in this study. Dashed lines connect the starting and final melt compositions.

Figure 4-3 Schematic diagram showing the reaction couple setups. Graphite-lined molybdenum double capsules (**a**) were used for run BA1LH2-T5, BA1LH2-T6, FS3-1-T1, and DR1LH2-T2; and a graphite capsule (**b**) was used for run BA1LH2-T4. The volume proportion of the three layers is approximately 2:2:1, from top to bottom. Lh stands for lherzolite; Mix is the mixture of basaltic melt and lherzolite.

Figure 4-4 Back-scattered electron images of the experimental charges showing large opx (**a-d**) or subcalcic augite (**e**) crystals. A close up view of a subcalcic augite crystal from (**e**) is shown in (**f**). Medium gray layers around crystals in (**b**)-(d) are quench growth. Expanded views of selected runs are shown in supplementary Fig. S2.

Figure 4-5 Measured trace element partition coefficients, arranged in geochemical groups with increasing compatibility. LILE stands for large ion lithophile element; HFSE stands for high field strength element; TM stands for transition metal. The gray field represents the range of published partitioning data for opx; the light blue field represents the range of published partitioning data for subcalcic augite (sources of data are given in Table 3 plus those from Colson et al. 1988; Kennedy et al. 1993; Klemme et al. 2006). The inset shows compositions of the low-Ca pyroxenes in the pyroxene quadrilateral.

Figure 4-6 Onuma diagrams showing the measured REE and Y partition coefficients between low-Ca pyroxene and melt as a function of ionic radii (**a-e**), and their corresponding major element projections in the pyroxene quadrilateral (**f**). Red circles in (**a-e**) are partitioning data used in the regression analyses; blue circles are Eu and excluded from the fit. Error bars represent one standard derivation of analyzed partitioning data. The solid lines in (**a-e**) represent the best-fit parabolas to the trivalent REE and Y in the M2 sites of pyroxene using Eq. (1). Dashed lines represent 95% confidence intervals of the fit. Symbols in (**f**) are the same as those used in Fig. 5. For reasons outlined in the **Discussion**, eight-fold coordinated ionic radii from Shannon

(1976) are used here. Similar Onuma diagrams using 6-fold coordinated ionic radii are shown in the supplementary Fig. S3.

Figure 4-7 Correlation between E and r_0 for the trivalent cations on the M2 site of pyroxenes. Each pair of E and r_0 is obtained by fitting REE and Y data from a partitioning experiment using the lattice strain model. Partitioning experiments for clinopyroxene are from the compilation of Sun and Liang (2012). Eight-fold coordinated ionic radii from Shannon (1976) are used for both high-Ca and low-Ca pyroxenes.

Figure 4-8 Comparison between predicted partition coefficients calculated using the parameterized lattice strain model of Eqs. (1), (11)-(13) and the experimentally measured values. Data source and symbols are the same as those in Fig. 1.

Figure 4-9 Correlation between 6-fold and 8-fold coordinated ionic radii (r^{VI} and r^{VIII}) for REE and Y. Ionic radii are from Shannon (1976).

Figure 4-10 Variation of selected REE partition coefficients in low-Ca and high-Ca pyroxenes as functions of Al content on the tetrahedral site (X_{Al}^T), and Ca and Mg abundances on the M2 site (X_{Ca}^{M2} and X_{Mg}^{M2} , respectively) of pyroxene. Data source and symbols are the same as those in Fig. 7.

Figure 4-11 Comparison between model-derived and observed REE partition coefficients for opx-cpx. Observed data are from well-equilibrated spinel lherzolite and harzburgite

xenoliths of Witt-Eickschen and O’Neil (2005), Witt-Eickschen et al. (2009), and Eggins et al. (1998). Trace element abundances in these xenoliths were analyzed by LA-ICP-MS. Predicted values are calculated using Eqs. (1)-(4), (11)-(13).

Figure 4-12 Model-predicted REE partition coefficients for low-Ca pyroxenes produced by pyroxenite-derived melt and peridotite interactions. Partition coefficients are calculated using Eqs. (1), (11)-(13), and experimental temperatures and major element compositions from the references listed in the legend. Major element compositions of the pyroxenes from selected publications are shown in the inset of the pyroxene quadrilateral. The grey field represents the range of REE partitioning data for opx, and the light blue is the range of subcalcic augite, both of which are defined by the filtered data listed in Table 3.

Figure 4-13 Variations of X_{Ca}^{M2} , X_{Al}^T , and X_{Mg}^{M2} and calculated REE partition coefficients in opx along three mantle adiabats ($T_p = 1300^\circ\text{C}$, 1350°C , and 1400°C) and for two choices of starting mantle composition (DMM and EM). T_p is the mantle potential temperature; DMM is the depleted MORB mantle from Workman and Hart (2005); EM is an assumed enriched mantle composition that consists of 90% DMM + 10% N-MORB. Composition of N-MORB is from Hofmann (1988). Orthopyroxene compositions were calculated using pMELTS (Ghiorso et al. 2002) and the corresponding REE partition coefficients were calculated using our parameterized lattice strain model for low-Ca pyroxene (Eqs. 1, 11-13). Grey fields in (c), (f), and (i) represent the ranges of measured

REE partition coefficients defined by the filtered data (Table 3). See text for discussion. gt in the legend represents garnet.

Figure 4-14 REE opx-cpx partition coefficients along two mantle adiabats ($T_p = 1300^\circ\text{C}$ and 1400°C with DMM mantle source, solid lines). For comparison, REE opx-cpx partition coefficients from Lee et al. (2007) at constant temperatures of 1300°C and 1400°C are also shown (dashed lines). $D_{\text{opx-cpx}}$ along the two mantle adiabats are calculated using the recommended values for DMM listed in Table 4.

Figures

Figure 4-1

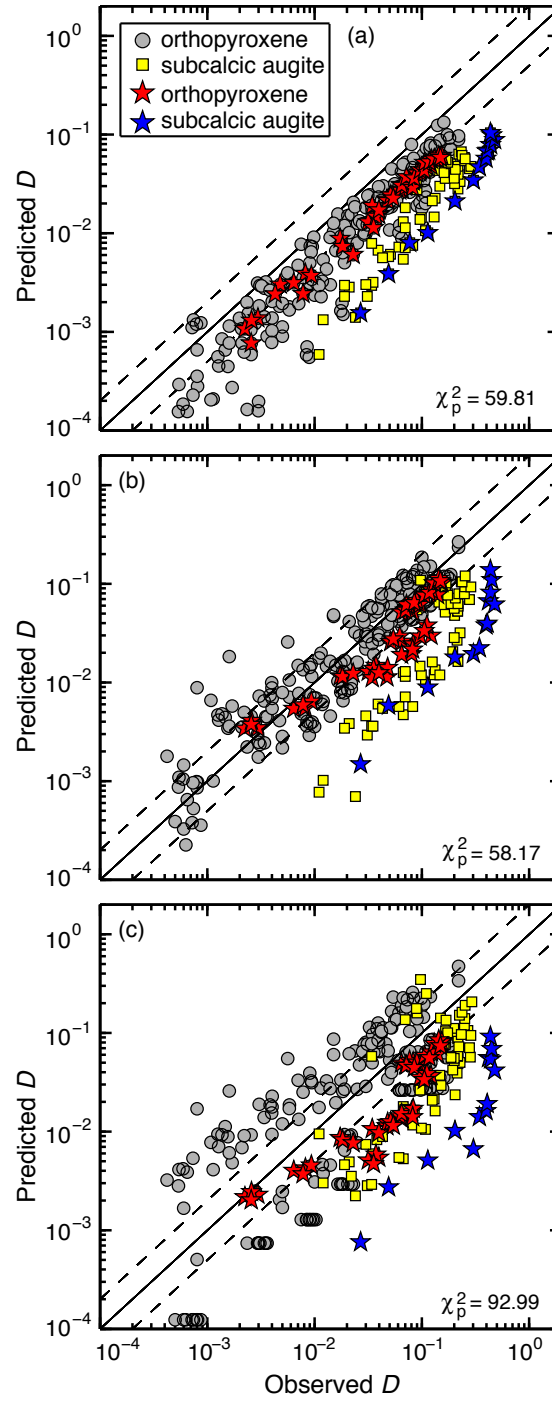


Figure 4-2

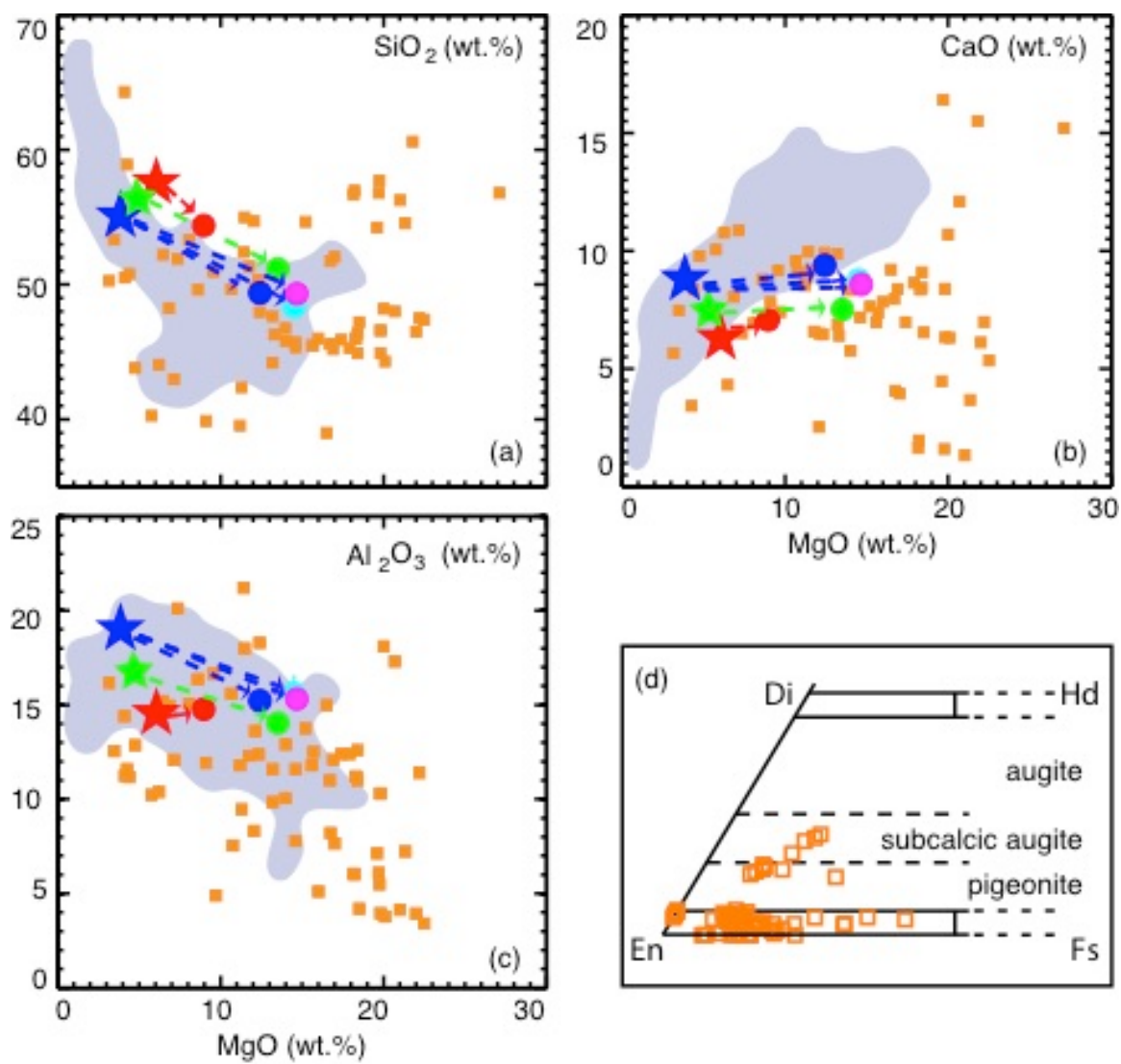


Figure 4-3

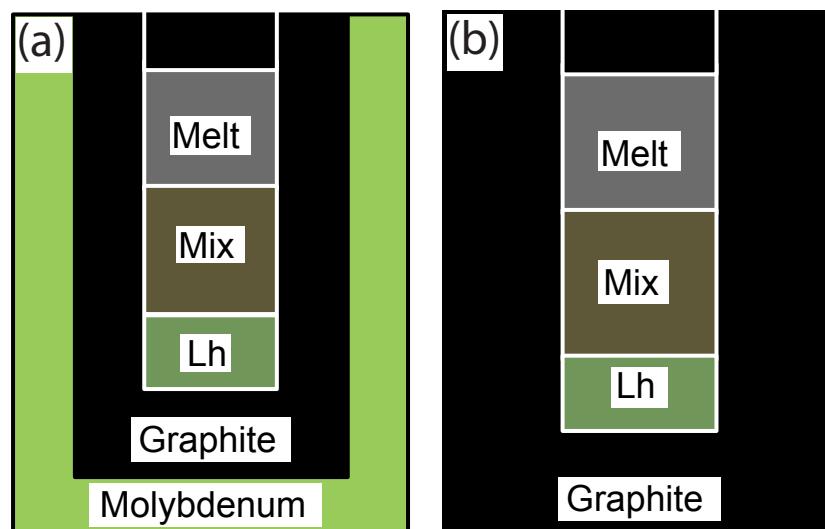


Figure 4-4

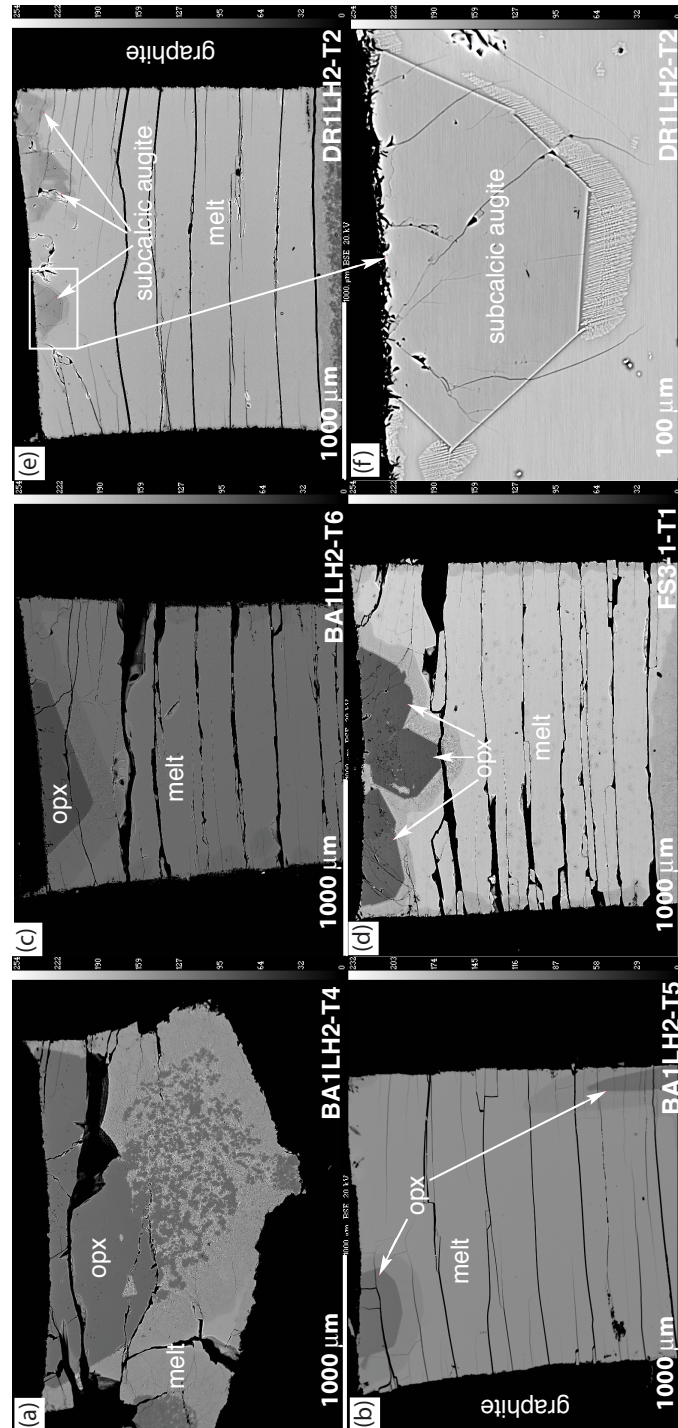


Figure 4-5

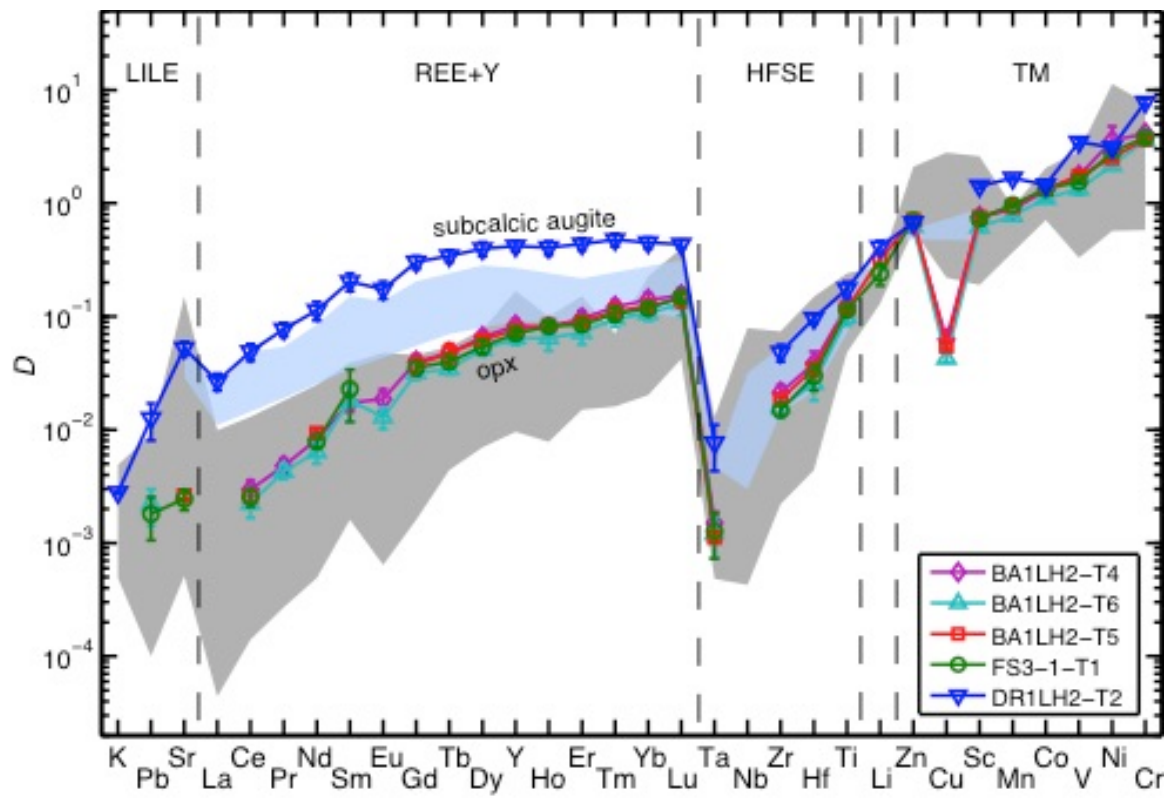


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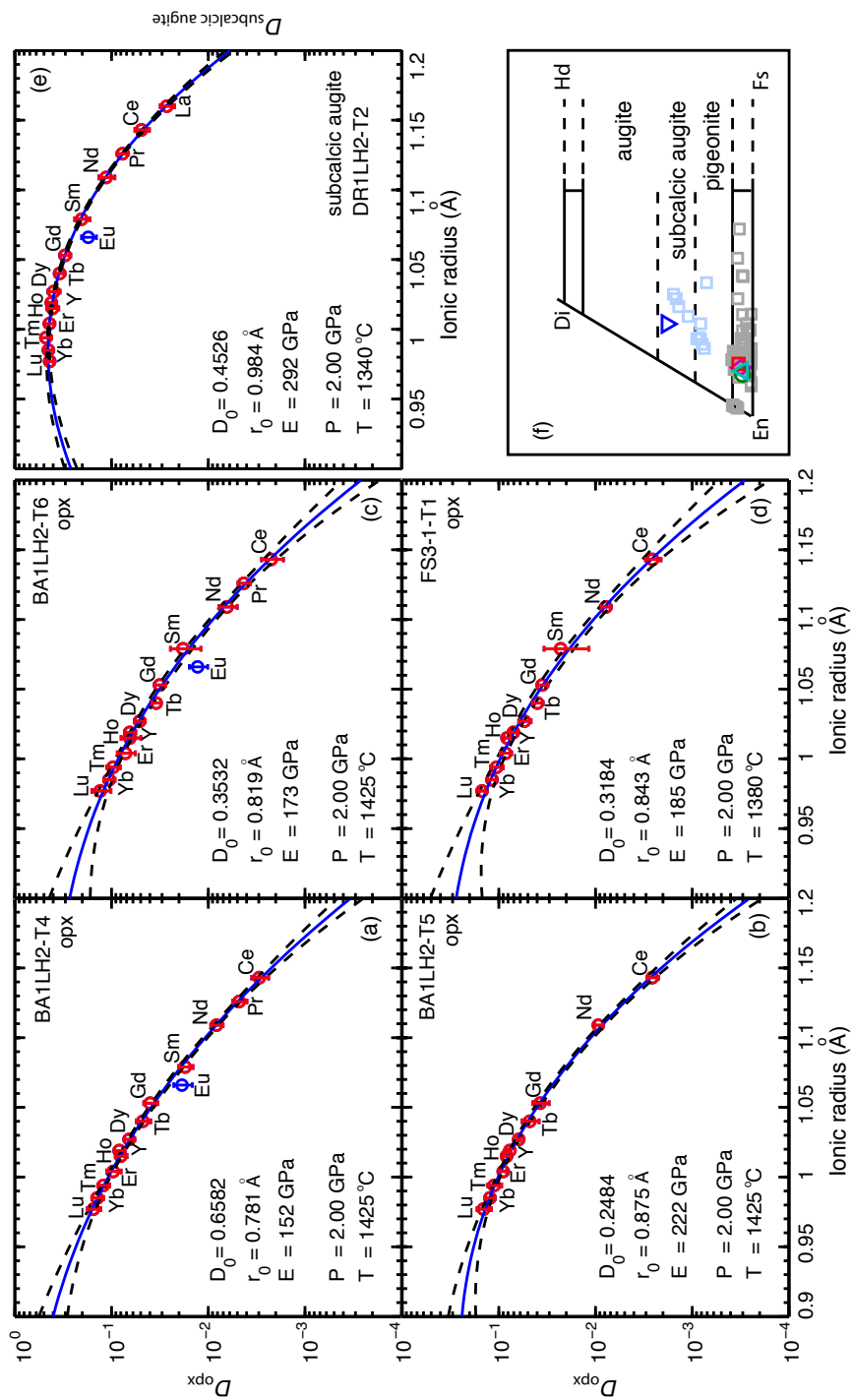


Figure 4-7

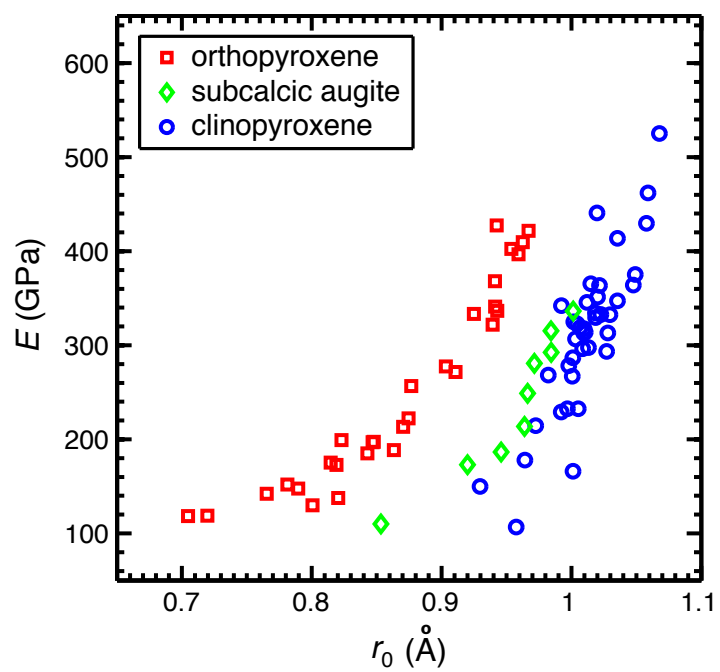


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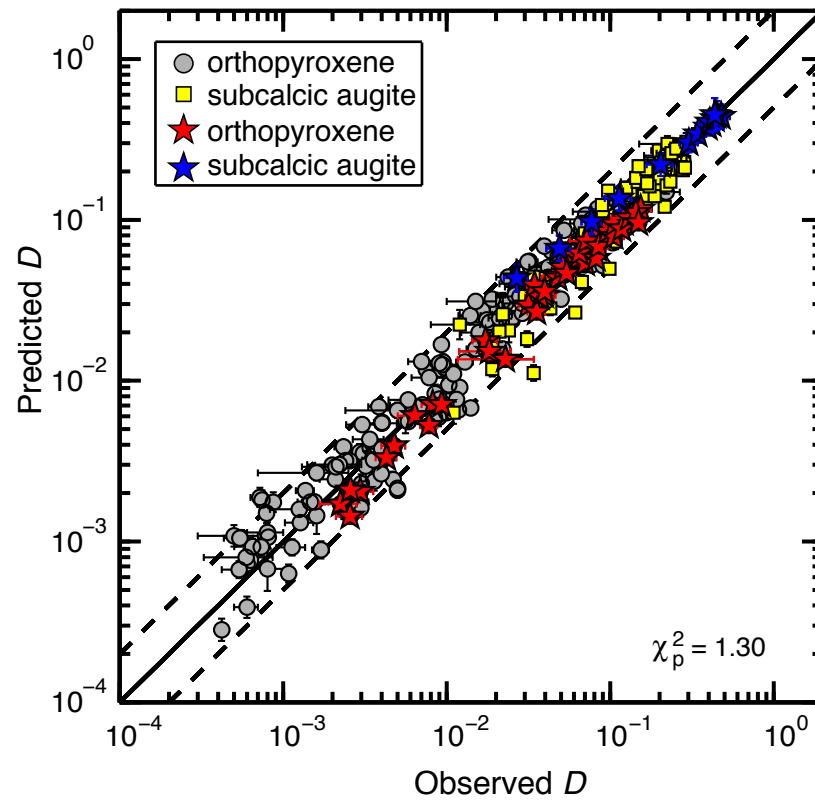


Figure 4-9

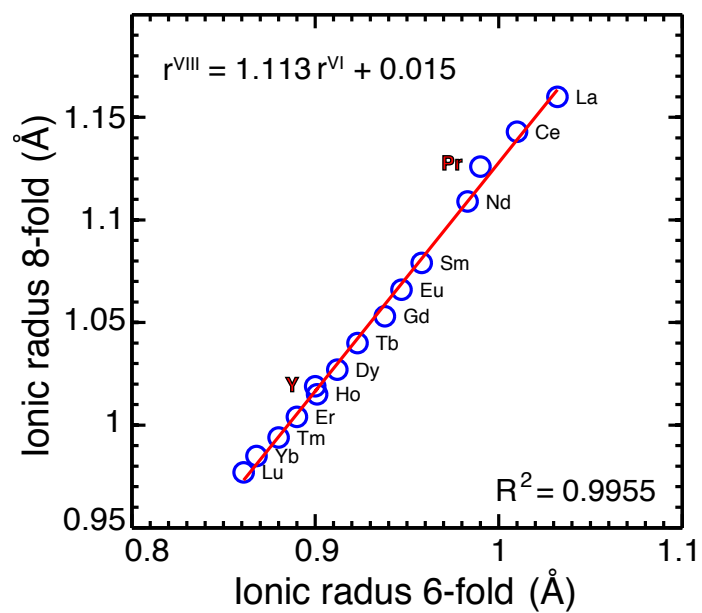


Figure 4-10

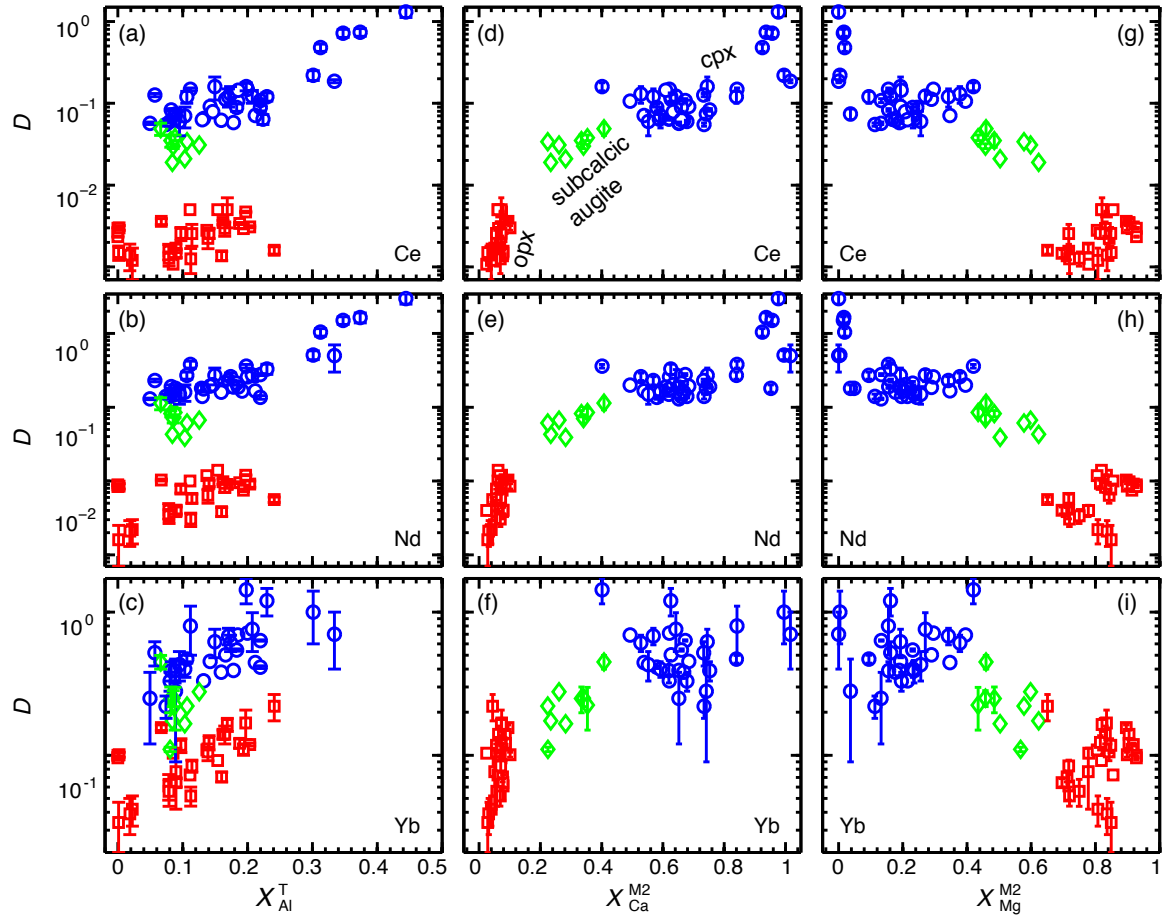


Figure 4-11

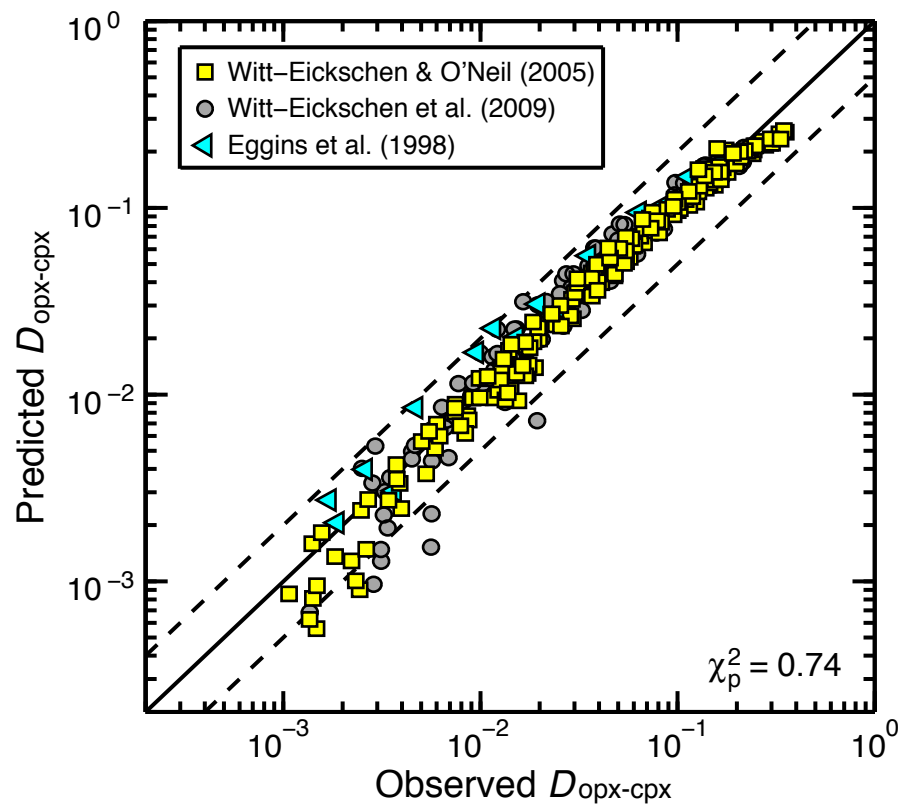


Figure 4-12

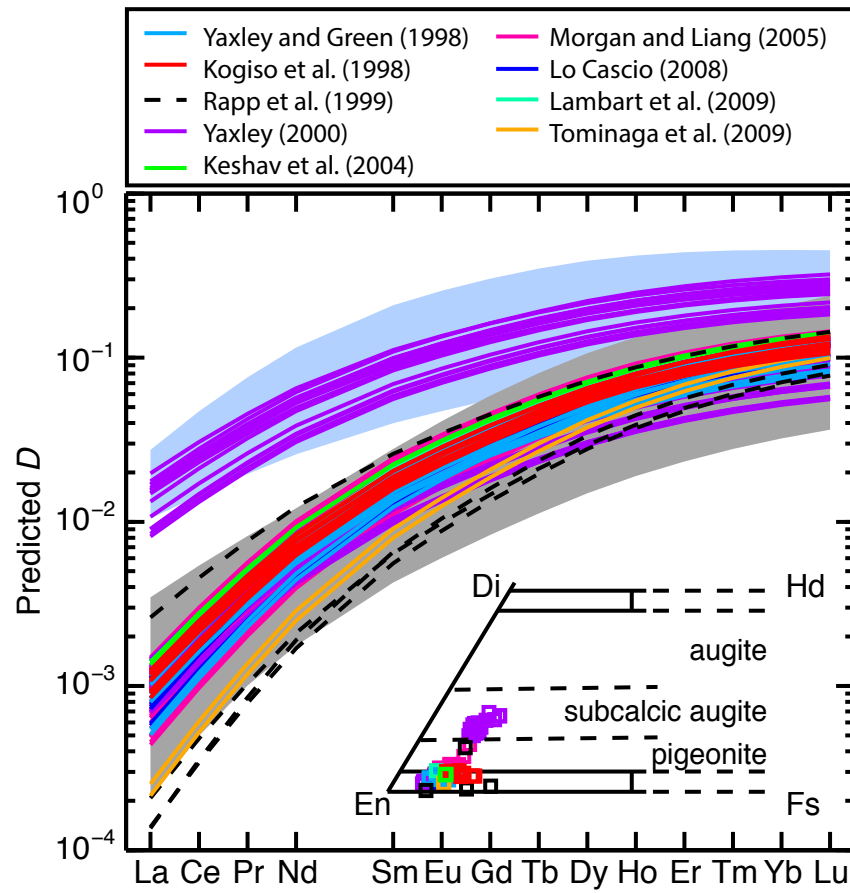


Figure 4-13

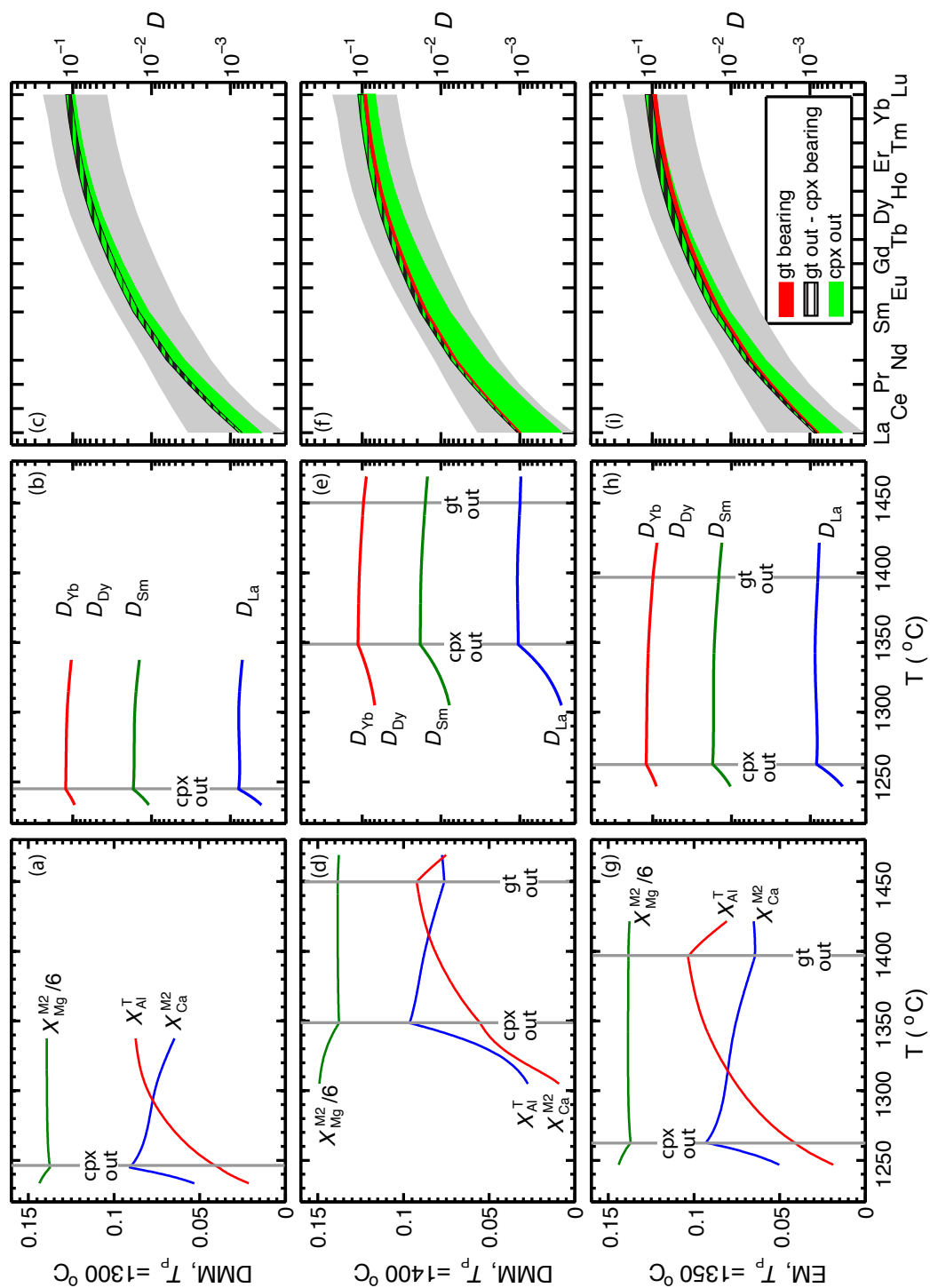
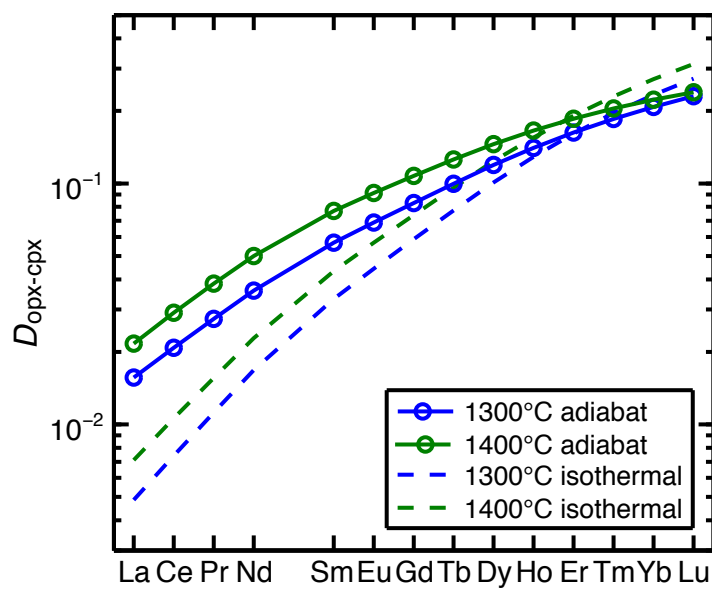


Figure 4-14



Tables

Table 4-1 Major element composition of the starting materials for the partitioning experiments

Oxide	basaltic andesite ^a	diorite ^b	olivine ^c	orthopyroxene ^c	clinopyroxene ^c	spinel ^c
SiO ₂ (wt.%)	55.09	57.55	40.47	54.25	51.82	0.09
TiO ₂	0.79	0.47	0.01	0.11	0.29	0.15
Al ₂ O ₃	19.03	14.54	0.1	5.43	6.98	57.88
Cr ₂ O ₃	n.a.	n.a.	0.06	0.56	0.91	10.87
FeO*	8.42	6.38	9.21	5.57	3.42	10.44
NiO	n.a.	n.a.	0.23	0.09	0.05	n.a.
MnO	0.22	0.1	0.14	0.13	0.11	0.12
MgO	3.86	6.06	49.8	32.87	18.76	21.21
CaO	8.8	6.29	0.2	1.58	16.94	n.a.
Na ₂ O	2.97	4.19	0.01	0.16	1.07	n.a.
K ₂ O	0.71	2.37	n.a.	n.a.	n.a.	n.a.
P ₂ O ₅	0.13	0.21	n.a.	n.a.	n.a.	n.a.
Total	100.01	99.54	100.22	100.75	100.35	100.86
Mg#	44.96	64.19	90.61	91.32	90.72	78.53

^a Mont 147, provided by Dr. J.D. Devine, used in Morgan and Liang (2005).

^b FS3-1 from North China craton, provided by Dr. W. Xu.

^c composition from Lo Cascio (2008).

n.a. not analyzed.

FeO* total Fe in FeO

Table 4-2 Pyroxene-melt partition coefficients calculated from LA-ICP-MS analysis

Run No.	BA1LH2-T4	BA1LH2-T5	BA1LH2-T6	FS3-1-T1	DR1LH2-T2
P (GPa)	2	2	2	2	2
T (°C)	1425	1425	1425	1380	1340
Dur (hr)	48	48	77	48	48
<i>D</i>	opx/melt	opx/melt	opx/melt	opx/melt	sub. aug/melt
Na	0.087(12)	0.096(2)	0.078(3)	0.064(5)	0.246(17)
P	0.090(26)	-	0.0812(47)	-	-
K	-	-	-	-	0.0028(1)
Li	-	0.379(23)	-	0.286(49)	0.415(44)
Sc	0.76(7)	0.752(39)	0.619(49)	0.728(49)	1.42(7)
Ti	0.124(15)	0.117(5)	0.098(14)	0.114(8)	0.175(27)
V	1.74(16)	1.74(11)	1.34(15)	1.55(7)	3.47(21)
Cr	4.13(35)	3.68(14)	3.58(38)	3.80(25)	7.8(5)
Mn	0.86(8)	0.934(17)	0.776(18)	0.964(32)	1.67(8)
Co	1.30(12)	1.333(43)	1.105(23)	1.341(36)	1.45(7)
Ni	4(1)	2.52(11)	2.17(9)	2.85(19)	3.13(21)
Cu	-	0.0547(34)	0.0426(29)	-	-
Zn	0.65(9)	0.72(2)	0.63(3)	0.704(36)	0.677(43)
Sr	-	0.00263(18)	-	0.0025(5)	0.053(7)
Y	0.083(11)	0.0769(26)	0.065(8)	0.071(6)	0.419(44)
Zr	0.0212(35)	0.0186(11)	0.0158(31)	0.0149(15)	0.048(8)
La	0.00165(46)	-	-	-	0.0268(45)
Ce	0.0030(6)	0.00258(35)	0.0022(6)	0.00257(47)	0.049(8)
Pr	0.0048(8)	-	0.0043(6)	-	0.077(10)
Nd	0.0082(12)	0.0093(9)	0.0064(14)	0.0078(9)	0.114(21)
Sm	0.0173(29)	-	0.018(6)	0.023(11)	0.204(36)
Eu	0.0187(40)	-	0.0129(28)	-	0.174(31)
Tb	0.047(8)	0.01(1)	0.0345(36)	0.040(5)	0.344(41)
Gd	0.040(7)	0.037(7)	0.0316(42)	0.0355(44)	0.303(39)
Dy	0.066(8)	0.0622(27)	0.051(7)	0.054(8)	0.40(6)
Ho	0.080(11)	0.083(8)	0.065(15)	0.082(6)	0.41(6)
Er	0.096(16)	0.090(7)	0.072(15)	0.085(11)	0.44(5)
Tm	0.122(17)	0.112(18)	0.096(15)	0.105(16)	0.48(6)
Yb	0.140(20)	0.123(14)	0.106(14)	0.117(13)	0.45(5)
Lu	0.153(24)	0.144(24)	0.131(29)	0.149(11)	0.435(35)
Hf	0.039(11)	0.0348(49)	0.026(7)	0.030(8)	0.097(9)
Ta	0.00150(38)	0.00112(6)	0.00121(47)	0.0013(5)	0.0077(34)
Pb	-	-	0.0022(8)	0.0018(8)	0.013(5)

Numbers in parenthesis represent one standard deviation.

opx, orthopyroxene.

sub. aug, subcalcic augite.

Table 4-3 Data source and experimental run conditions

Reference	N(n) ^a	P (GPa)	T (°C)	Dur (hr)	Pyx	Pyx Mg#	Ca ^{M2} /6-O ^b	Melt Mg#	Melt SiO ₂ (wt.%)
Ion probe analysis									
Frei et al. (2009)	5(35)	1.1-3.2	1230-1535	24-144	opx	100	0.072-0.095	100	39.0-55.0
van Kan Parker et al. (2010)	3(21)	0.0001	1326-1390	60	opx	100	0.072-0.101	100	56.8-60.6
Green et al. (2000)	1(13)	2	1080	46	opx	70	0.044	41	50.28
McDade et al. (2003a)	1(8)	1.5	1315	48	opx	91	0.074	83	47.95
McDade et al. (2003b)	1(6)	1.3	1245	49	opx	90	0.073	72	49.67
Schwandt & McKay (1998)	1(8)	0.0001	1210	120	opx	80	0.025	53	53.31
Salter & Longhi (1999)	2(14)	2.4-2.8	1540-1555	48	opx	90	0.062-0.067	72-73	45.9-46.3
Salter et al. (2002)	1(7)	3.4	1660	19	opx	93	0.061	81	47.5
Salter & Longhi (1999)	3(21)	2.8	1515-1547	48	sub	84-88	0.224-0.283	62-73	44.2-45.8
Salter et al. (2002)	1(7)	2.8	1580	20.7	sub	88	0.261	73	45.2
Van Westrenen et al. (2000)	1(8)	3	1538	21.5	sub	73	0.225	55	47.6
Tuff and Gibson (2007)	3(39)	3	1475-1525	24	sub	79-82	0.334-0.354	49-62	39.54-46.77
Subtotal range	23(187)	0.0001-3.4	1080-1660	19-144		70-100	0.025-0.354	41-100	39.0-60.6
LA-ICP-MS									
Adam and Green (2006)	1(10)	2.7	1160	48	opx	84	0.051	64	39.88
Van Kan Parker et al. (2011)	3(18)	1.1-2.1	1430-1550	23-24	opx	84-87	0.028-0.040	62-70	46.0-47.4
Unpublished from C. Sun	6(66)	2-2.1	1340-1450	48-50	opx	77-81	0.058-0.079	48-56	32.57-45.33
This study	4(49)	2	1380-1425	48-77	opx	90-91	0.056-0.072	73-77	48.36-51.15
This study	1(14)	2	1340	48	sub	89	0.408	72	54.39
Subtotal range	15(157)	1.1-2.7	1160-1450	23-77		77-91	0.028-0.408	48-77	32.57-54.39
Total range	38(344)	0.0001-3.4	1080-1660	19-144		70-100	0.025-0.408	41-100	32.57-60.6

^a N stands for the number of experiments from the reference, and n in the parenthesis stands for the total number of elements from the experiments.

^b Molar content of Ca on the M2 site of pyroxene per six oxygen.

Dur run duration.

Pyx pyroxene.

opx orthopyroxene.

sub. aug subcalcic augite.

Table 4-4 Recommended REE partition coefficients for adiabatic melting of clinopyroxene-bearing peridotite

T_p D	DMM ^a				EM ^b	
	1300°C		1400°C		1350°C	
	opx ^c	cpx ^d	opx ^c	cpx ^d	opx ^c	cpx ^d
La	0.0007	0.0466	0.001	0.0449	0.0008	0.0484
Ce	0.0015	0.0733	0.0019	0.0666	0.0016	0.0741
Pr	0.003	0.1093	0.0036	0.0947	0.0032	0.1081
Nd	0.0055	0.1544	0.0065	0.1291	0.0058	0.1505
Sm	0.0143	0.2510	0.0156	0.2023	0.0146	0.2415
Eu	0.0204	0.2952	0.0217	0.2367	0.0206	0.2841
Gd	0.0281	0.3377	0.0293	0.2710	0.0282	0.3258
Tb	0.0376	0.3758	0.0383	0.3035	0.0374	0.3647
Dy	0.0487	0.4071	0.0487	0.3329	0.0481	0.3987
Ho	0.0601	0.4283	0.0591	0.3560	0.0592	0.424
Er	0.0714	0.4402	0.0692	0.3729	0.0699	0.441
Tm	0.0819	0.4443	0.0784	0.3842	0.0800	0.4508
Yb	0.0913	0.4426	0.0865	0.3909	0.0891	0.4548
Lu	0.0995	0.4368	0.0935	0.3939	0.0969	0.4545

^a DMM is the depleted MORB mantle source from Workman and Hart (2005).

^b EM is an assumed composition that is composed of 90% DMM and 10% N-MORB in major element compositions, and N-MORB is from Hofmann (1988).

^c opx partition coefficients are the average values of those from garnet lherzolite to spinel lherzolite and cpx-bearing harzburgite stability field during adiabatic melting.

^d cpx partition coefficients for the DMM source are from Sun and Liang (2012), or average values calculated using Eqs. (1)-(4) for the EM source along the 1350°C adiabat in the spinel stability field.

Supplementary Material

Supplementary Figure 4-S1

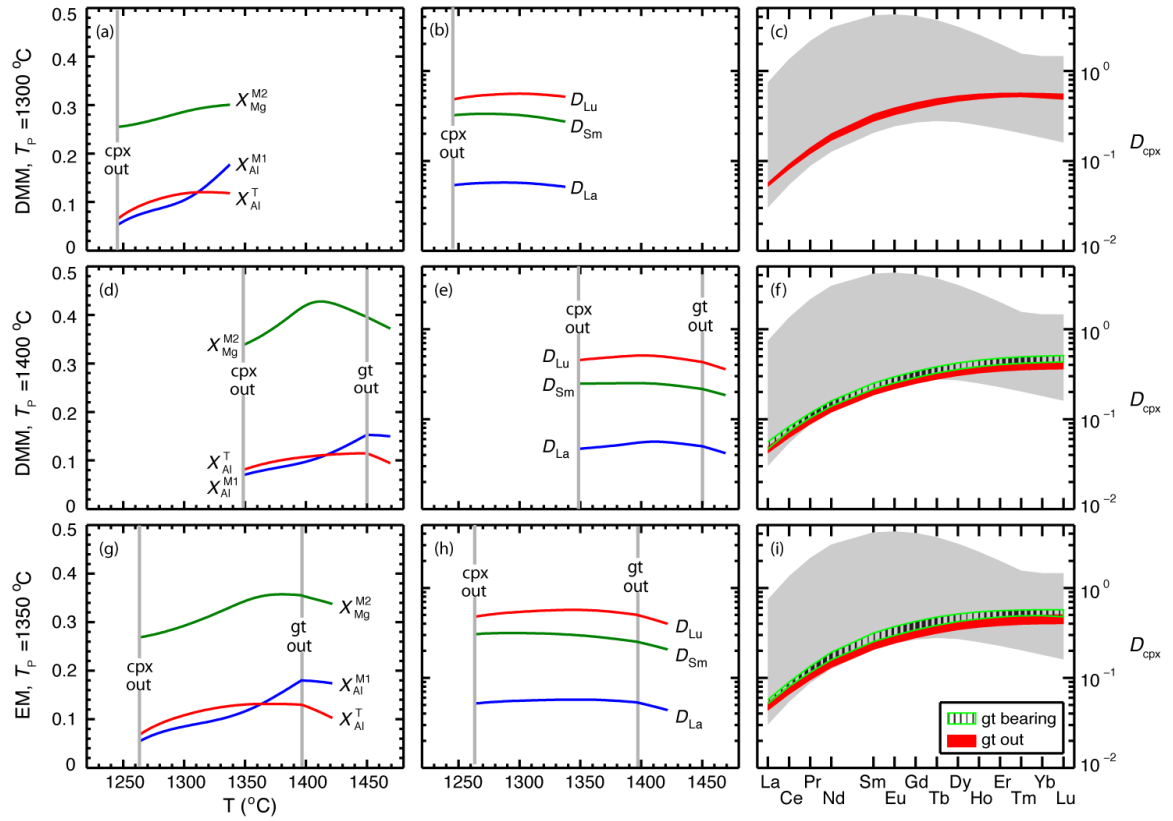


Figure 4-S1. Variations of $X_{\text{Ca}}^{\text{M2}}$, X_{Al}^{T} , and $X_{\text{Mg}}^{\text{M2}}$ and calculated REE partition coefficients in clinopyroxene along three mantle adiabats ($T_p = 1300^\circ\text{C}$, 1350°C , and 1400°C) and for two choices of starting mantle composition (DMM and EM). See caption to Fig. 13 for details.

Supplementary Figure 4-S2

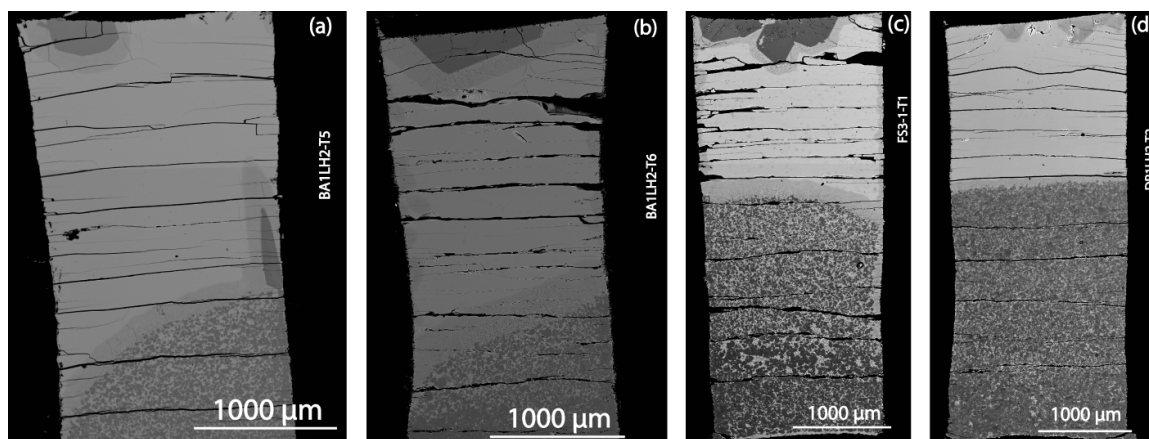


Figure 4-S2. Back-scattered electron (BSE) images of runs BA1LH2-T5, T6, FS3-1-T1, and DR1LH2-T2. See also Fig. 4 for close up views of selected samples.

Supplementary Figure 4-S3

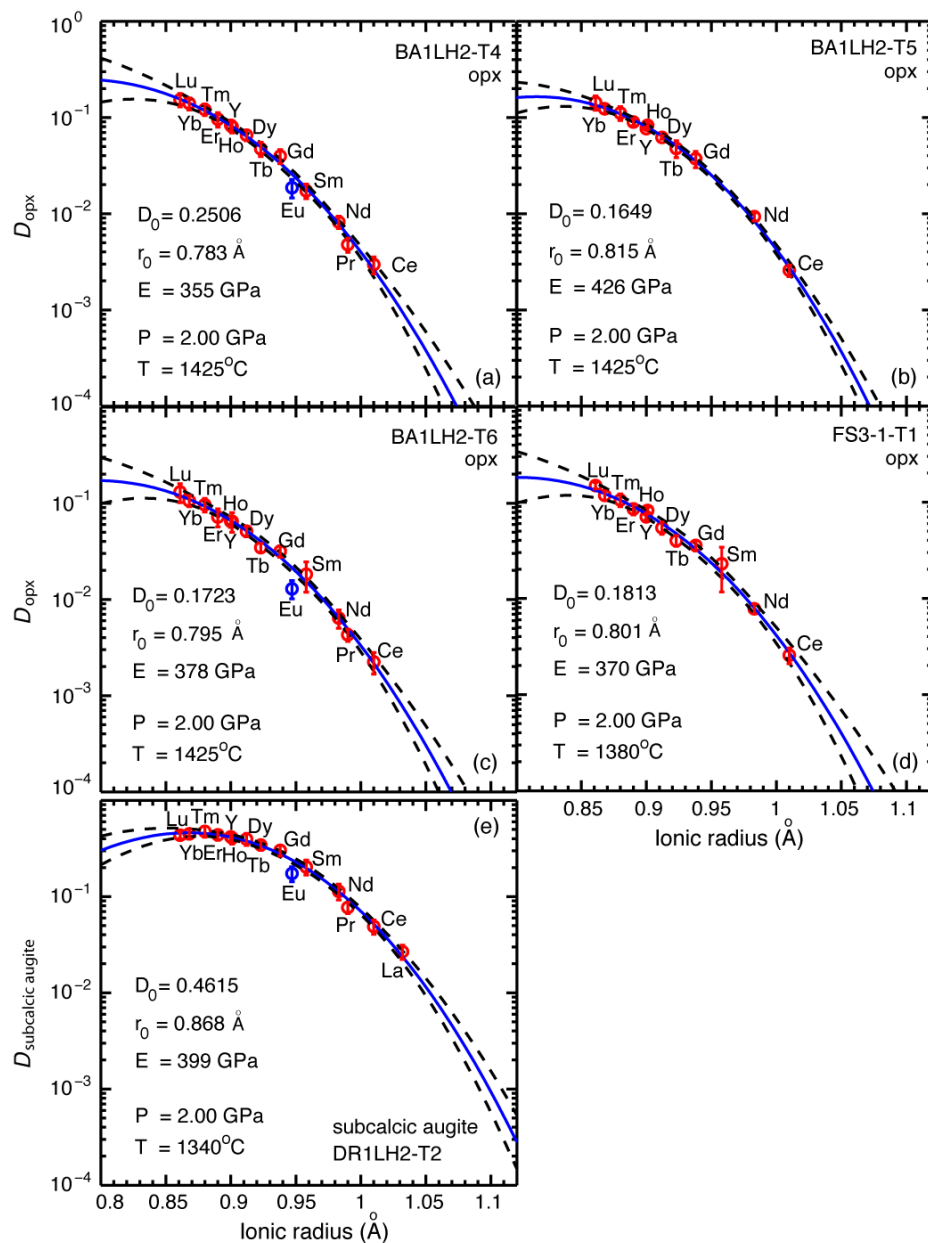


Figure 4-S3. Onuma diagrams showing the measured REE and Y partition coefficients between low-Ca pyroxene and melt as a function of 6-fold coordinated ionic radii of Shannon (1976). Both 6-fold and 8-fold coordinated ionic radii work equally well in the parabolic fit to the lattice strain model (c.f. Fig. 6 in the main text).

Supplementary Figure 4-S4 Plate (a)

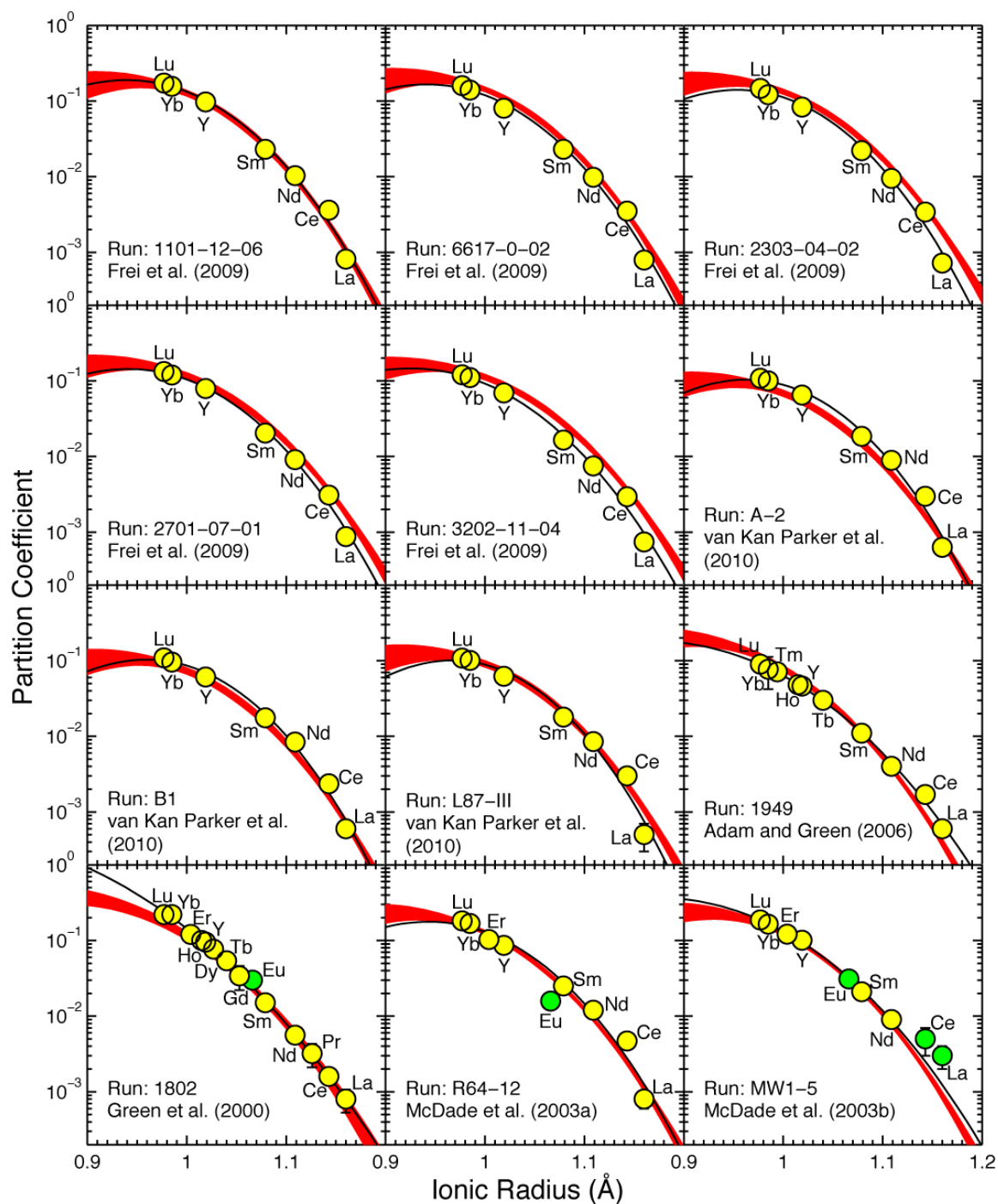
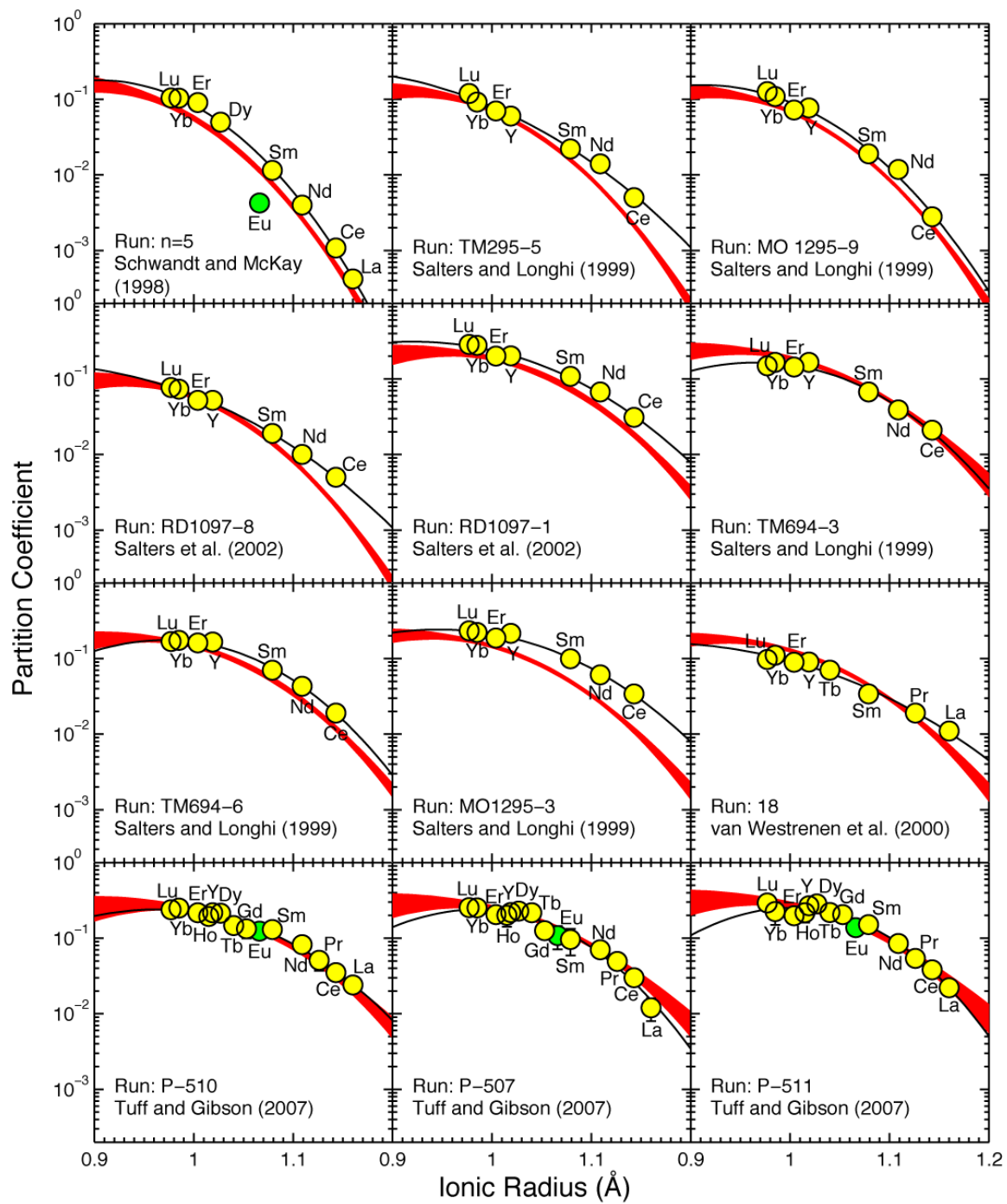
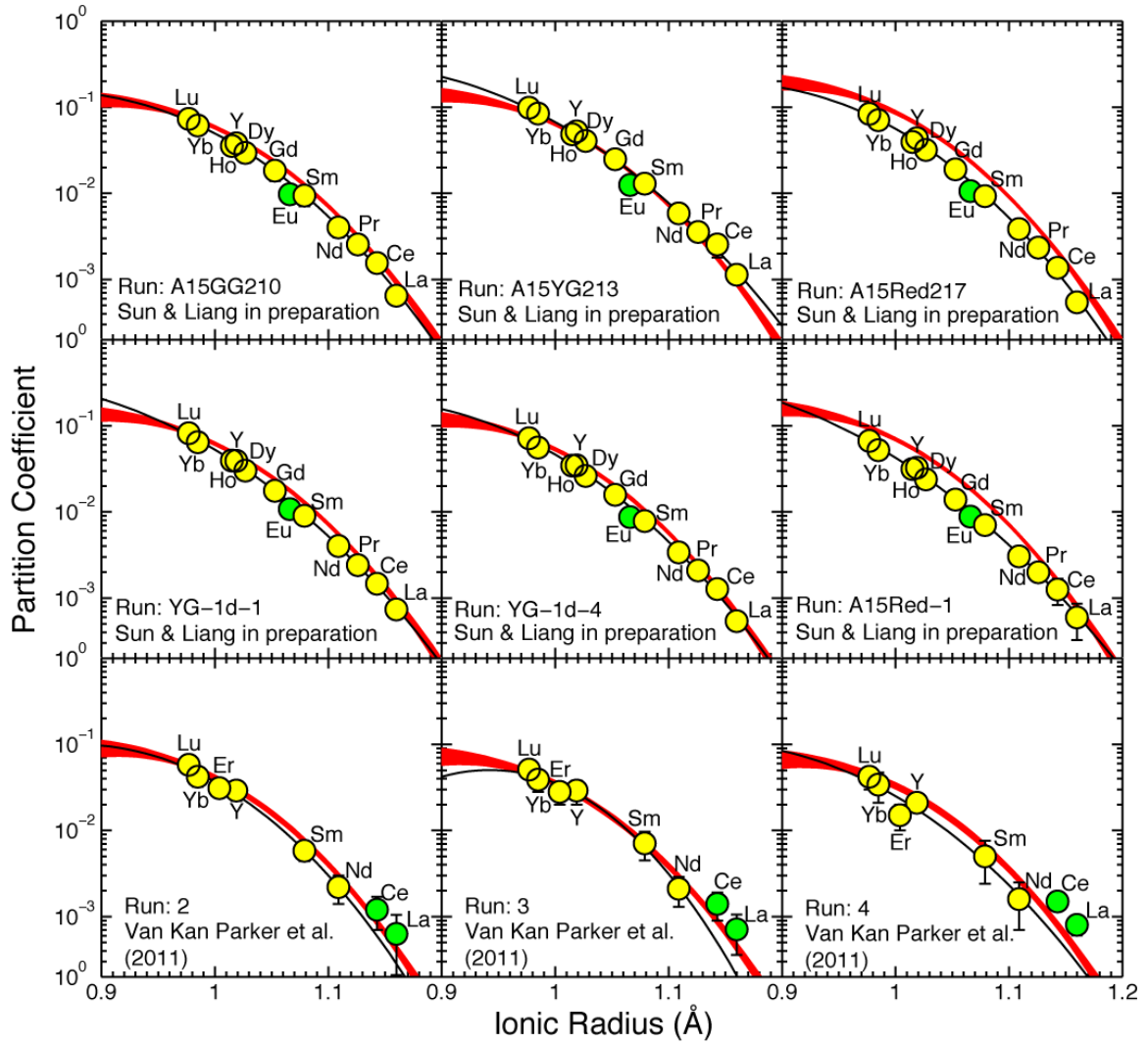


Figure 4-S4. Onuma diagrams showing REE and Y partition coefficients as a function of 8-fold coordinated ionic radii of Shannon (1976) in individual low-Ca pyroxene samples used in the parameterization (Table 3). Additional information is provided below Plate (c) on page 6 below.

Supplementary Figure 4-S4 Plate (b)



Supplementary Figure 4-S4 Plate (c)



Yellow circles are the measured partition coefficients that were used to the fit of the lattice strain model. Green circles are measured partition coefficients for Eu, La, or Ce that were excluded in the regression analysis. Eu may be divalent and La and Ce concentrations in some low-Ca pyroxenes may be close to detection limits. Black lines are fits from the lattice strain model (Eq. 1 in the main text). Red fields are the predicted results from Eqs. (1), (11)-(13), with 95% confidence intervals. In general, our parameterized lattice strain model reproduces the filtered partition coefficients (yellow circles) very well.

Supplementary Figure 4-S5 Plate (a)

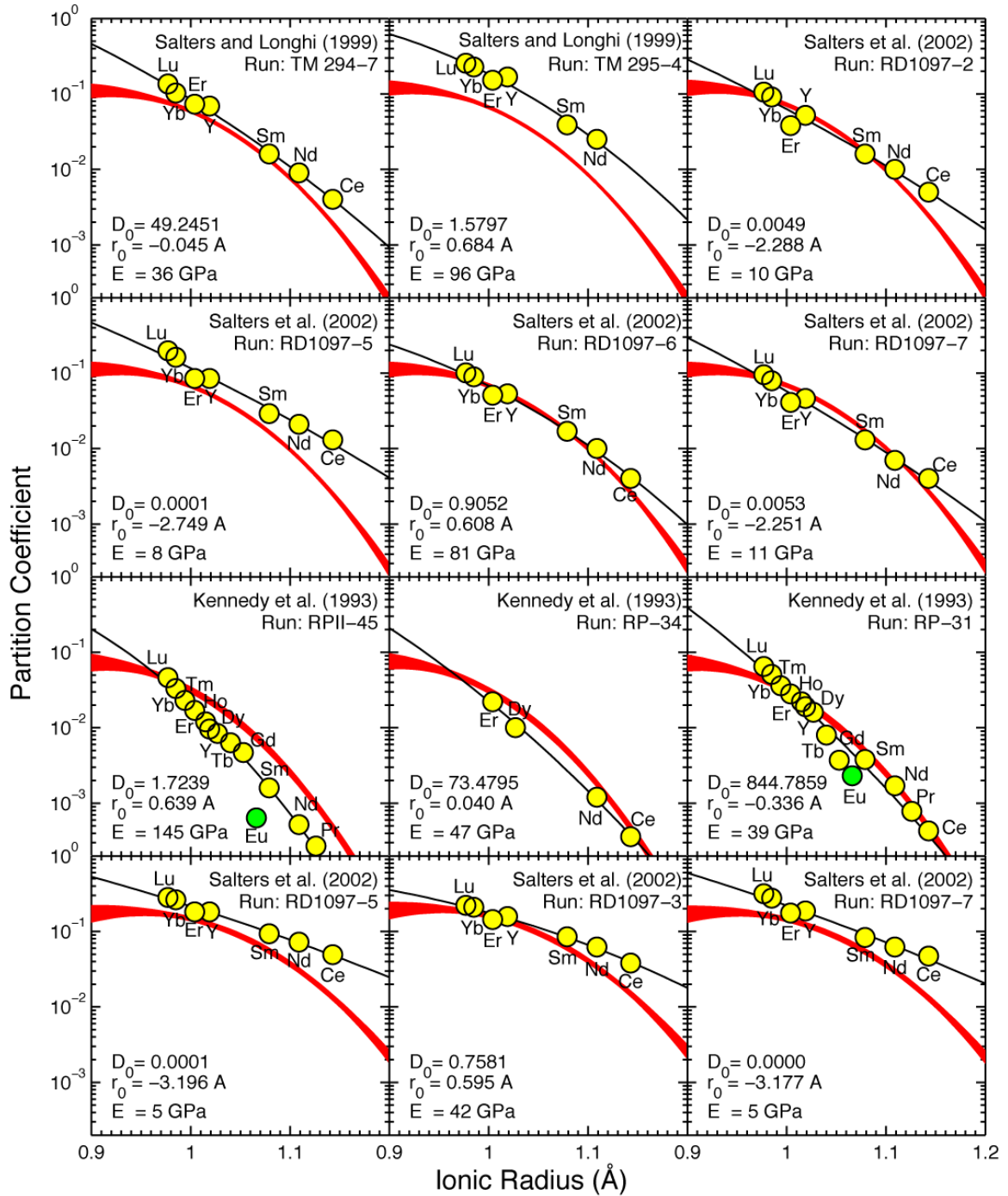
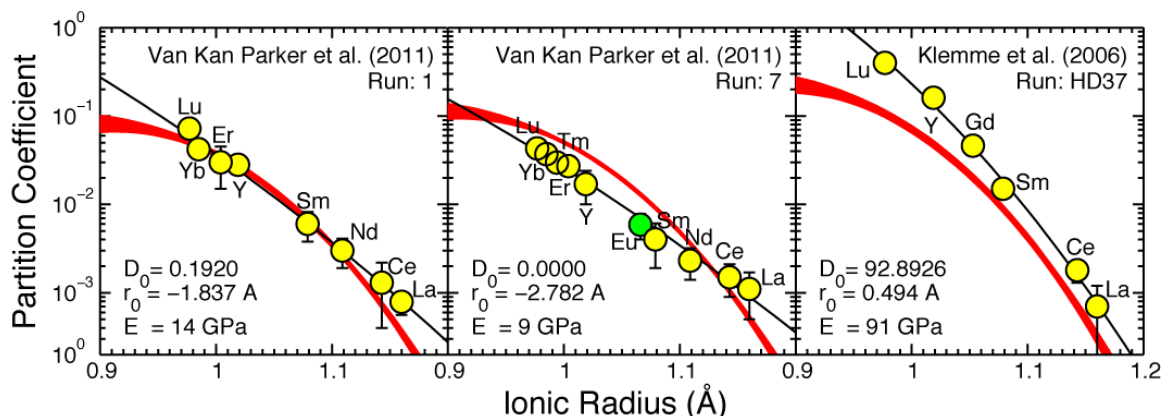


Figure 4-S5. Onuma diagrams showing REE and Y partition coefficients in individual low-Ca pyroxene samples that were excluded in this study. In contrast to the filtered data shown in Fig. S4, partition coefficients from these studies follow linear or nearly linear trends such lattice strain parameters (D_0 , r_0 , and E) are not well defined. Eight-fold coordinated ionic radii from Shannon (1976) are used.

Supplementary Figure 4-S5 Plate (b)



Symbols are the same as those used in Fig. S4. Data that were excluded in this study include: (1) Runs S1295, S1300, S1330, and P-529 from Tuff and Gibson (2007). REE abundances in crystals in P-529 were probably affected by melt contamination as noted by the authors. (2) Runs 5 and 6 from van Kan Parker (2011) were excluded because the run durations are too short (< 10 hrs). (3) Runs 117a, 117b, 118a, 118b and 120a from Colson et al. (1988) were excluded not only because REE were analyzed by EMP, but also only 1-3 REE were analyzed for each sample, which prevented us from an independent check of their data using the lattice strain model. Additionally, Ca content was not analyzed for most of the samples. (4) Runs RP-41, RP-33, RP-37, RP-40 from Kennedy et al. (1993) and RD1099-1 from Salters et al. (2002) cannot be fit by the lattice strain model. In addition, run HD37 from Klemme et al. (2006) was excluded not only because it cannot be fit by the lattice strain model, but also it was conducted in a Ca-free simple system, which may favor a different substitution mechanism for REE.

Supplementary Figure 4-S6 Plate (a)

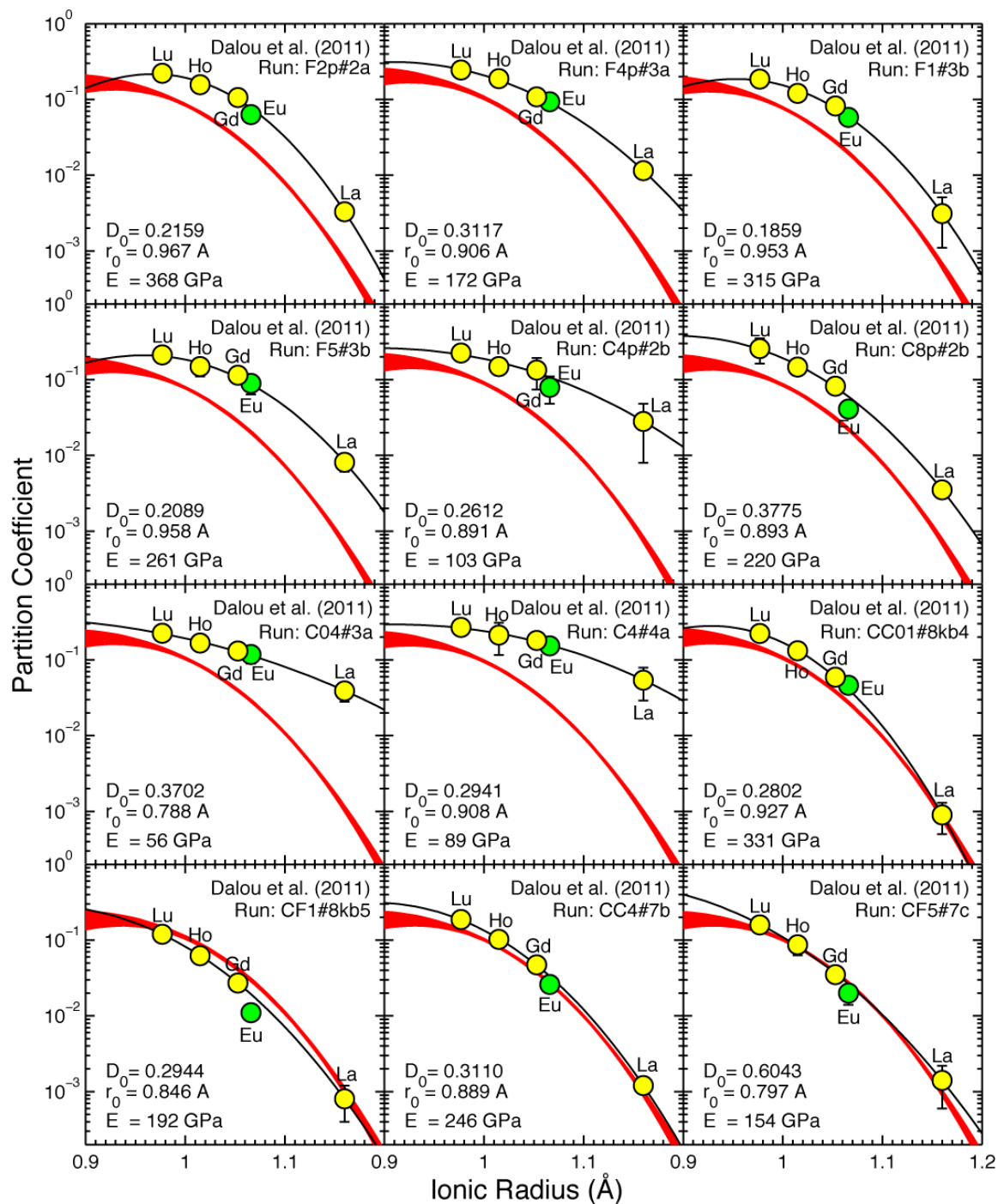
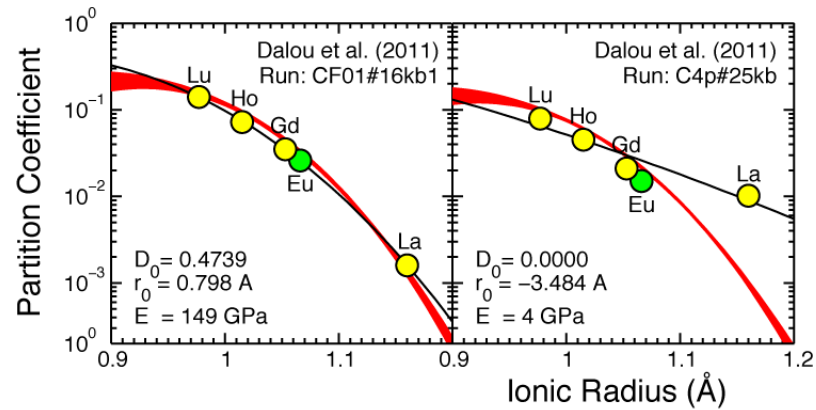


Figure 4-S6. Onuma diagrams showing REE and Y partition coefficients in experiments from Dalou et al. (2011). Symbols are the same as those used in Fig. S4.

Supplementary Figure 4-S6 Plate (b)



Dalou et al. (2011) recently reported a set of trace element partitioning experiments between pyroxenes and basaltic melts that are enriched in F, Cl, and H₂O. Here, we compare calculated REE partition coefficients derived from the global model (Eqs. 1, 11-13) with their measured data (lattice strain parameters derived from least squares fits to individual experiments using Eq. 1 are listed in each figure). As shown above, our low-Ca pyroxene model can only reproduce 4 out of their 14 reported experiments. The misfit samples appear to have larger D_0 (hence D) than that derived from our global model. The misfits persist even after we recalibrated our global model by including their measured partitioning data as part of the filtered database. It is not clearly if the misfits can be attributed to the effect(s) of volatile elements in their experiments. In this study, we exclude Dalou et al.'s data in our global inversion.

Dalou C, Koga KT, Shimizu N, Boulon J, Devidal J (2011) Experimental determination of F and Cl partitioning between lherzolite and basaltic melt. Contrib Mineral Petrol, DOI 10.1007/s00410-011-0688-2

Supplementary Figure 4-S7

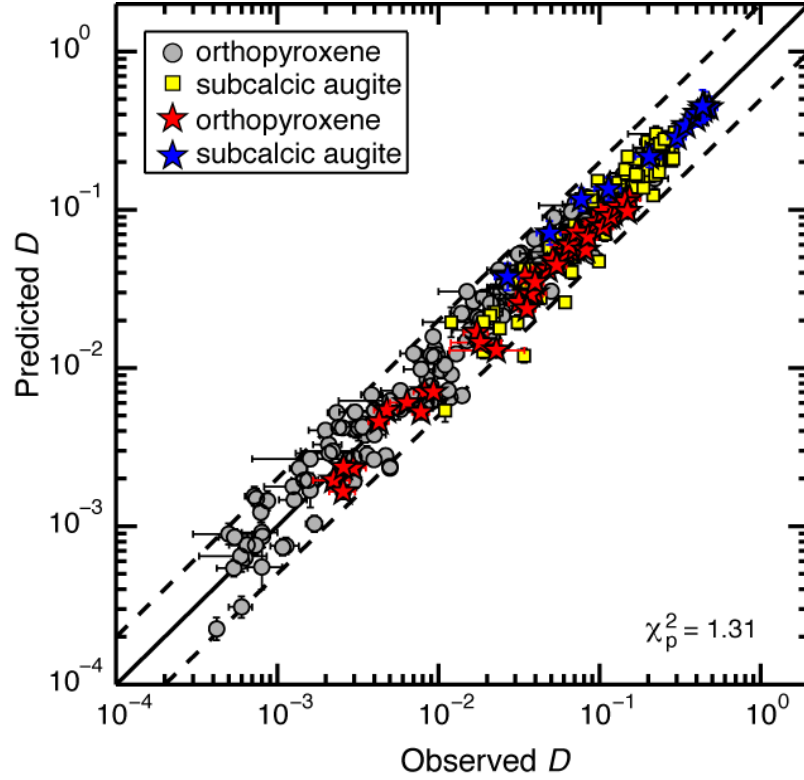


Figure 4-S7. Comparison between predicted partition coefficients calculated using the parameterized lattice strain model of Eqs. (1), (S1)-(S3) and the experimentally measured values. Data source and symbols are the same as those in Fig. 1. Six-fold coordinated ionic radii for REE and Y (Shannon 1976) are used in this model. A simultaneous inversion of the 344 low-Ca partitioning data using 6-fold coordinated ionic radii results in the following expressions for the lattice strain model:

$$\ln D_0 = -5.47(\pm 0.48) + \frac{3.87(\pm 0.69) \times 10^4}{RT} + 3.82(\pm 0.86) X_{Ca}^{M2} + 3.51(\pm 0.59) X_{Al}^T \quad (S1)$$

$$r_0 = 0.62(\pm 0.04) + 0.38(\pm 0.11) X_{Ca}^{M2} + 0.21(\pm 0.05) X_{Mg}^{M2} \quad (S2)$$

$$E = [-2.10(\pm 0.61) + 3.16(\pm 0.76) r_0 - 0.77(\pm 0.15) X_{Ca}^{M2}] \times 10^3 \quad (S3)$$

The slight differences between the χ_p^2 values (1.30 and 1.31 for a total of 344 data) and the excellent agreement between observed and predicted partition coefficients indicate that 6-fold and 8-fold coordinated ionic radii work equally well for the global fit.

Supplementary Figure 4-S8: Hydrous Model

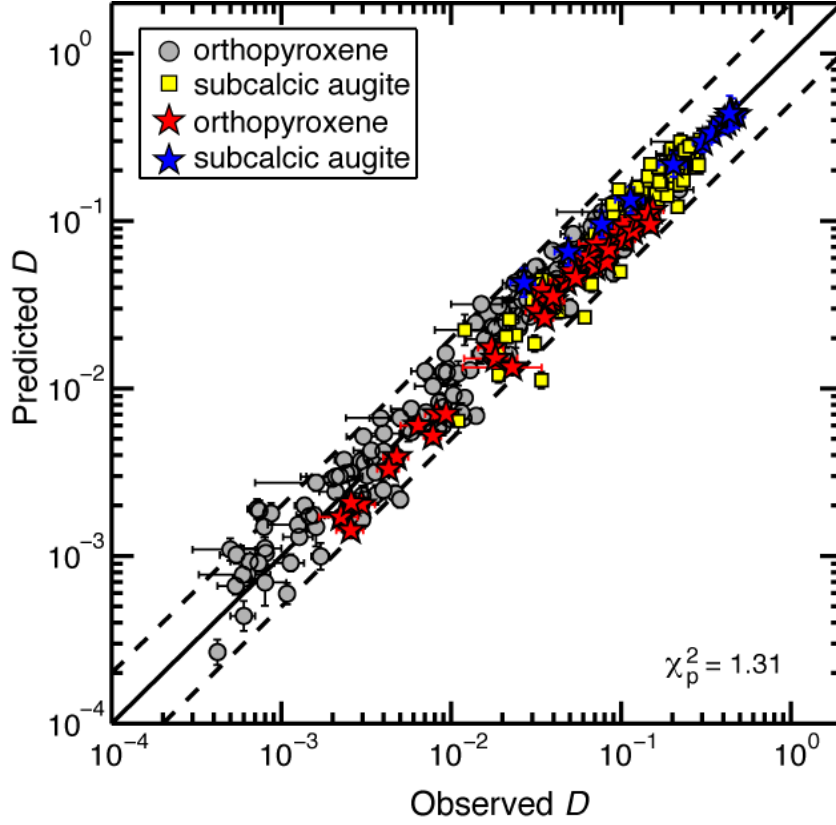


Figure 4-S8. Comparison between predicted partition coefficients calculated using a preliminary hydrous model (Eqs. 1, S4-S6) and the experimentally measured values. The hydrous model is obtained by a simultaneous inversion of the 344 filtered low-Ca pyroxene data while including molar fraction of water in the melt ($X_{H_2O}^{melt}$) as one of the independent variables. Parameters for the lattice strain model using 8-fold coordinated ionic radii are:

$$\ln D_0 = -5.03(\pm 0.64) + \frac{3.42(\pm 0.92) \times 10^4}{RT} + 3.51(\pm 1.02)X_{Ca}^{M2} + 3.47(\pm 0.62)X_{Al}^T + 0.31(\pm 0.37)X_{H_2O}^{melt} \quad (S4)$$

$$r_0 = 0.69(\pm 0.06) + 0.44(\pm 0.15)X_{Ca}^{M2} + 0.23(\pm 0.06)X_{Mg}^{M2} \quad (S5)$$

$$E = [-1.32(\pm 0.46) + 1.80(\pm 0.51)r_0 - 0.52(\pm 0.11)X_{Ca}^{M2}] \times 10^3 \quad (S6)$$

Except the extra water term in Eq. (S4), the preliminary hydrous model has the same function forms as the anhydrous model (Eqs. 11-13) with coefficients taking on slightly different values. The slightly increased χ_p^2 value (from 1.30 to 1.31) indicates that the inclusion of water as an additional variable cannot improve the fit to the observed data. The small coefficient of water with a large standard deviation (Eq. S4) suggests that the effect of water on REE partitioning for low-Ca pyroxene cannot be well constrained based on the present database.

Supplementary Figure 4-S9

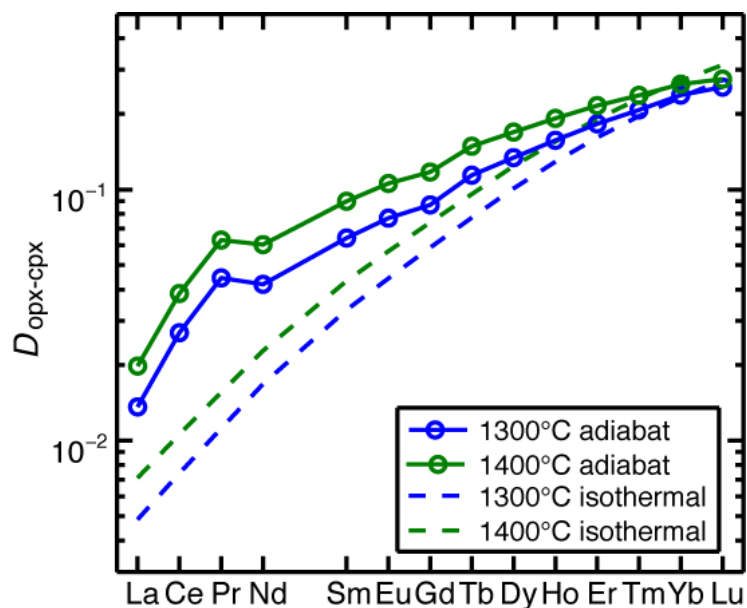


Figure 4-S9. REE opx-cpx partition coefficients along two mantle adiabats ($T_p = 1300^\circ\text{C}$ and 1400°C , solid lines). $D_{\text{opx-cpx}}$ values were calculated using the same procedure as described in the main text, but using 6-fold coordinated ionic radii for opx (Eqs. 1, S1-S3). For comparison, REE opx-cpx partition coefficients from Lee et al. (2007) at constant temperatures of 1300°C and 1400°C are also shown (dashed lines). Note the kink in Pr, which likely results from the small deviation in ionic radius shown in Fig. 9.

Supplementary Table 4-S1

Major and trace element composition of the melt

Run No.	BA1LH2-T4	BA1LH2-T5	BA1LH2-T6	FS3-1-T1	DR1LH2-T2
P (GPa)	2	2	2	2	2
T (°C)	1425	1425	1425	1380	1340
<i>EMP</i>	n=9	n=10	n=11	n=17	n=11
SiO ₂ (wt.%)	48.4(6)	49.37(15)	49.33(41)	51.15(28)	54.39(26)
TiO ₂	0.64(2)	0.62(1)	0.61(3)	0.47(1)	0.48(1)
Al ₂ O ₃	15.60(92)	15.22(9)	15.31(15)	14.03(29)	14.76(28)
Cr ₂ O ₃	0.20(1)	0.20(1)	0.23(2)	b.d.	b.d.
FeO	8.78(23)	8.14(7)	8.54(12)	7.30(7)	6.11(14)
MnO	0.18(3)	0.17(2)	0.17(3)	0.14(2)	0.11(1)
MgO	14.51(37)	12.42(13)	14.67(7)	13.51(27)	8.97(35)
CaO	8.77(37)	9.38(6)	8.58(13)	7.52(7)	7.07(12)
Na ₂ O	2.15(49)	2.52(5)	2.26(7)	3.03(7)	4.34(8)
K ₂ O	0.60(20)	0.61(2)	0.56(2)	1.54(4)	2.65(8)
P ₂ O ₅	0.13(3)	0.11(3)	0.10(3)	0.16(2)	0.22(2)
Total	99.9(9)	98.77(25)	100.39(34)	98.85(39)	99.10(22)
<i>LA-ICP-MS</i>	n=6	n=7	n=6	n=7	n=6
Na ₂ O (wt.%)	2.34(22)	2.71(3)	2.47(4)	3.34(8)	4.55(16)
K ₂ O	b.d.	0.65(1)	b.d.	1.76(3)	2.95(10)
P ₂ O ₅	0.101(9)	0.103(2)	0.103(3)	0.154(6)	0.191(6)
MnO	0.192(16)	0.210(2)	0.214(2)	0.167(4)	0.121(3)
Li (ppm)	b.d.	8.58(31)	b.d.	10.6(7)	12.56(44)
Sc	20(2)	23.65(38)	22.96(28)	24.7(8)	20.50(49)
Ti	0.594(60)	0.629(4)	0.657(18)	0.491(11)	0.494(12)
V	94(8)	124(2)	124(2)	114(4)	92(2)
Cr	1188(85)	1326(26)	1527(21)	1552(61)	409(12)
Co	77(6)	83(1)	89(1)	65(1)	40(1)
Ni	88(8)	319(12)	413(9)	445(22)	398(16)
Cu	44(8)	413(16)	557(23)	20(1)	10(1)
Zn	88(9)	89(2)	91(3)	64(3)	43(1)
Sr	b.d.	263(3)	b.d.	567(11)	852(10)
Y	17(2)	19.86(24)	18.0(7)	14.64(13)	13.35(21)
Zr	70(8)	84.3(9)	76(3)	95(1)	117(2)
Nb	11(1)	13.25(16)	12.11(34)	7.35(17)	6.75(18)
La	5.78(65)	7.21(10)	6.38(19)	19.52(29)	28.9(6)
Ce	14(1)	15.40(16)	15.25(33)	33.7(8)	48(1)
Pr	1.96(20)	2.16(4)	2.13(6)	3.77(6)	5.20(10)
Nd	10(1)	11.08(21)	10.36(38)	16.00(20)	21.2(7)

Sm	2.62(32)	2.94(12)	2.84(17)	3.26(6)	3.90(26)
Eu	0.92(11)	1.100(28)	0.978(33)	1.193(41)	1.488(36)
Tb	0.47(5)	0.540(13)	0.481(19)	0.430(17)	0.423(17)
Gd	2.87(37)	3.24(9)	3.08(11)	2.86(8)	3.10(12)
Dy	3.14(28)	3.50(4)	3.30(17)	2.65(6)	2.52(8)
Ho	0.67(6)	0.764(17)	0.689(32)	0.552(21)	0.522(26)
Er	1.94(22)	2.15(7)	2.08(9)	1.48(6)	1.344(43)
Tm	0.291(30)	0.323(10)	0.288(9)	0.223(14)	0.188(9)
Yb	2.09(21)	2.31(11)	2.26(12)	1.55(8)	1.38(8)
Lu	0.316(25)	0.359(15)	0.329(20)	0.243(8)	0.228(6)
Hf	2.04(24)	2.36(8)	2.17(10)	2.49(9)	3.06(6)
Ta	20(2)	26.90(28)	23.9(9)	6.04(15)	0.345(15)
Pb	9.0(9)	12.82(24)	8.79(41)	11.02(40)	7.15(35)

- EMP stands for electron microprobe analysis.
- LA-ICP-MS stands for laser ablation inductively coupled mass spectrometry analysis.
- b.d. below detection limit.
- n number of analysis.
- Numbers in parenthesis represent one standard deviation.

Supplementary Table 4-S2

Major and trace element composition of the pyroxene crystals

Run No.	BA1LH2-T4	BA1LH2-T5	BA1LH2-T6	FS3-1-T1	DR1LH2-T2
P (GPa)	2	2	2	2	2
T (°C)	1425	1425	1425	1380	1340
Pyx	opx	opx	opx	opx subcalcic	augite
<i>EMP</i>	n=11	n=10	n=9	n=28	n=40
SiO ₂ (wt%)	53.36(43)	54.24(42)	53.95(64)	55.22(30)	54.94(49)
TiO ₂	0.07(1)	0.07(1)	0.06(1)	0.05(1)	0.09(2)
Al ₂ O ₃	7.55(36)	7.1(7)	6.4(11)	4.43(31)	4.44(48)
Cr ₂ O ₃	0.78(3)	0.73(5)	0.81(10)	0.84(4)	0.49(4)
FeO	5.96(9)	6.22(9)	5.73(8)	5.46(6)	5.27(22)
MnO	0.15(2)	0.16(1)	0.14(1)	0.12(2)	0.15(2)
MgO	31.01(37)	30.47(38)	31.49(39)	32.40(28)	23.4(9)
CaO	1.72(10)	1.96(4)	1.52(4)	1.54(6)	10.8(8)
Na ₂ O	0.18(1)	0.23(1)	0.16(1)	0.17(1)	1.04(6)
Total	100.78(33)	101.14(33)	100.29(31)	100.23(27)	100.63(55)
<i>LA-ICP-MS</i>	n=6	n=7	n=6	n=5	n=6
Na ₂ O (wt.%)	0.203(19)	0.260(4)	0.192(6)	0.214(15)	1.12(6)
P ₂ O ₅	0.0090(25)	b.d.	0.0083(4)	b.d.	b.d.
MnO	0.170(5)	0.196(3)	0.166(3)	0.161(3)	0.203(9)
Li (ppm)	b.d.	3.25(16)	b.d.	3.02(48)	5.2(5)
Sc	15.2(6)	17.8(9)	14(1)	18(1)	29(1)
Ti	0.074(5)	0.074(3)	0.064(9)	0.056(4)	0.087(13)
V	165(7)	217(13)	166(19)	176(4)	317(17)
Cr	4903(232)	4877(163)	5472(568)	5898(313)	3195(188)
Co	100(5)	110(3)	98(2)	87(1)	58(2)
Ni	315(102)	803(18)	896(31)	1268(58)	1245(68)
Cu	b.d.	23(1)	24(1)	b.d.	b.d.
Zn	57(6)	63(1)	57(2)	45(1)	29(2)
Sr	b.d.	0.69(5)	b.d.	1.39(29)	45(6)
Y	1.40(11)	1.53(5)	1.16(14)	1.03(8)	5.6(6)
Zr	1.48(17)	1.57(9)	1.20(23)	1.41(14)	5.6(9)
La	0.0095(24)	b.d.	b.d.	b.d.	0.77(13)
Ce	0.040(7)	0.040(5)	0.034(9)	0.086(16)	2.34(39)
Pr	0.0093(12)	b.d.	0.0091(13)	b.d.	0.40(5)
Nd	0.079(8)	0.103(10)	0.066(14)	0.125(15)	2.41(44)
Sm	0.045(5)	b.d.	0.052(18)	0.075(36)	0.79(13)
Eu	0.017(3)	b.d.	0.0126(27)	b.d.	0.259(45)
Tb	0.022(3)	0.0259(52)	0.0166(16)	0.0171(21)	0.146(16)

Gd	0.114(12)	0.121(23)	0.098(13)	0.102(12)	0.94(11)
Dy	0.206(19)	0.218(9)	0.169(20)	0.144(21)	1.00(14)
Ho	0.054(6)	0.063(6)	0.045(10)	0.0452(31)	0.212(27)
Er	0.186(24)	0.193(14)	0.150(31)	0.126(16)	0.59(7)
Tm	0.0354(33)	0.036(6)	0.0278(44)	0.0235(32)	0.089(11)
Yb	0.292(29)	0.285(29)	0.239(29)	0.182(18)	0.62(6)
Lu	0.049(7)	0.052(8)	0.043(9)	0.0362(25)	0.099(8)
Hf	0.079(19)	0.082(11)	0.056(16)	0.074(19)	0.296(27)
Ta	0.031(7)	0.0302(16)	0.029(11)	0.0077(33)	0.0027(12)
Pb	b.d.	b.d.	0.019(7)	0.020(8)	0.090(32)

- opx orthopyroxene.
- EMP stands for electron microprobe analysis.
- LA-ICP-MS stands for laser ablation inductively coupled mass spectrometry analysis.
- b.d. below detection limit.
- n number of analysis.
- Numbers in parenthesis represent one standard deviation.