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.

1 The closure temperature of an element in a mineral is the lower temperature limit
2 at which the element effectively stops diffusive exchange with its surrounding medium
3 during cooling. In geochronology, the closure temperature (T_A^c) corresponds to the
4 temperature at the apparent age (t_A^c) of an isotope system in mineral A , and depends on
5 the diffusion rate of the element, mineral grain size, and cooling rate (Dodson, 1973,
6 1986), viz.,

$$7 \quad \frac{E_A}{RT_A^c} = \ln \left[\frac{R(T_A^c)^2 D_A^0}{E_A d_A^2 \dot{s}} \right] + G, \quad (1)$$

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

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

8 Attempts have been made to investigate closure temperatures for cooling bi-
9 mineralic and poly-mineralic systems (e.g., Lasaga et al., 1977; Onorato et al., 1981;
10 Lasaga, 1983; Eiler et al., 1992; Ehlers and Powell, 1994; Jenkin et al., 1995; Powell and
11 White, 1995). However, the definitions of the closure temperature in these studies are
12 inconsistent. Giletti (1986) chose the lowest closure temperature of individual phases
13 derived from Dodson's equation as the closure temperature of bi-mineralic and poly-
14 mineralic systems. Jenkin et al. (1995) defined the closure time and hence the closure
15 temperature of the plagioclase-biotite bi-mineralic system through the apparent Sr
16 isochron; however, this approach is limited to radiogenic isotopes. Based on element
17 concentrations in the cores of two adjacent minerals, Ehlers and Powell (1994) calculated
18 an apparent temperature using temperature-dependent exchange coefficients, and defined
19 the invariant apparent temperature as the closure temperature of the bi-mineralic system.
20 Using results from numerical simulations of diffusive exchange between two minerals,
21 Ehlers and Powell (1994) empirically modified the Dodson's equation by including two

1 additional parameters: relative grain size of the two minerals and the effective exchange
2 coefficient. Powell and White (1995) further extended Dodson's equation to bi-mineralic
3 systems by analytically solving the underlying diffusion equations of Ehlers and Powell
4 (1994). In the empirical and analytical equations of Ehlers and Powell (1994) and Powell
5 and White (1995), closure temperatures for bi-mineralic systems depend only on
6 diffusion parameters of the mineral that has a slower diffusion rate for the element of
7 interest. In general, diffusive exchange of an element of interest between two minerals
8 depends on diffusion coefficients and partition coefficients of the element in the two
9 minerals, grain sizes and volume fractions of individual minerals (Lasaga et al., 1977;
10 Onorato et al., 1981; Eiler et al., 1992; Liang, 2014). Thus, one would expect that these
11 factors also affect the closure temperatures of bi-mineralic systems. However, some of
12 these factors are not considered in the aforementioned studies. As will be shown in this
13 study, the closure temperature equations of Ehlers and Powell (1994) and Powell and
14 White (1995) are not applicable to REE redistribution in cooling two-pyroxene bearing
15 systems.

16 In this study, we follow the basic idea of Dodson (1976) for closure temperature
17 and systematically examine the various definitions of the closure temperature for a trace
18 element in cooling bi-mineralic systems. We use a finite difference model to study
19 diffusive exchange of a trace element in a bi-mineralic system with temperature-
20 dependent diffusion coefficients and mineral-mineral partition coefficients (Section 3).
21 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 the Dodson's equation (e.g., Eq. 1), closure temperature is independent of C_A^0 and b . Due

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

18 The closure temperature defined by Dodson (1973, 1976) and illustrated in Figs.
 19 3a-3c can be easily implemented in numerical simulations of diffusive exchange between
 20 a mineral and its surrounding media, a method that we will adopt in the present study.
 21 Figure 3d shows one such example (red circles) where closure temperatures of REE in

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

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

18 where b' is a constant. For the purpose of demonstration, we choose a value of -4.3×10^3
 19 for b' , which gives the same amount of change in rim concentration as that from the
 20 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

1 temperature T_0 , minerals A and B are in chemical equilibrium, and the concentrations of
 2 the trace element in minerals A and B (C_A^0 and C_B^0 , respectively) are related to each other
 3 through a mineral-mineral partition coefficient $k_{AB}(T_0)$ (C_A^0 / C_B^0). During cooling,
 4 minerals A and B are out of chemical equilibrium except at their interface where their
 5 concentrations are related to each other by a temperature-dependent partition coefficient,
 6 k_{AB} ,

$$7 \quad C_A^0 \Big|_{x=0^-} = k_{AB} \cdot C_B^0 \Big|_{x=0^+} . \quad (3a)$$

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

$$9 \quad \frac{\phi_A}{d_A} D_A \frac{\partial C_A}{\partial x} \Big|_{x=0^-} = \frac{\phi_B}{d_B} D_B \frac{\partial C_B}{\partial x} \Big|_{x=0^+} , \quad (3b)$$

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

$$15 \quad k_{AB}(T) = k_{AB}^0 \cdot \exp\left(-\frac{\Delta H}{RT}\right) , \quad (4)$$

16 where the pre-exponential factor k_{AB}^0 and activation enthalpy ΔH are functions of mineral
 17 compositions, ionic radius, and possibly pressure. For details regarding governing
 18 equations, initial and boundary conditions, numerical method, and assumptions used in
 19 the model setup, a reader is referred to the online supplementary material S1. It is worth
 20 noting that the partition coefficient (Eq. 4) is an exponential rather linear function, which

1 is different from the linear relationship of Dodson (Eq. 2b). Hence a difference in closure
2 temperature between Dodson's and this study is expected (cf. Fig. 3d). A detailed
3 discussion is presented in the supplementary material (Figs. S1-S2).

4 Model parameters used in this study are as follows. Without loss of generality, we
5 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
6 simulations reported in this study. The partition coefficient at the onset of cooling $k_{AB}(T_0)$
7 is then 0.03, which is a typical value for incompatible trace elements such as middle REE
8 between opx and cpx. To examine the effect of partition coefficient on closure
9 temperature, we also chose a smaller value for ΔH ($= 3.6 \times 10^4$ J/mol), which leads to a
10 larger $k_{AB}(T_0)$ ($= 0.34$). To explore the effect of diffusion coefficients in the two minerals
11 on closure temperature, we consider three cases: (a) $D_B = D_A$, (b) $D_B = D_A/5$ and (c) $D_B =$
12 $5D_A$. We used the diffusion coefficients of REE in enstatite from Cherniak and Liang
13 (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
14 temperature-dependent diffusion coefficients and partition coefficients for the simulations
15 reported in this study can be found in Fig. 5. We use the same grain sizes for mineral A
16 and B ($d_A = d_B$), and conducted 600 simulations in total (100 simulations for each
17 combination of diffusion coefficient and partition coefficient). The 100 simulations cover
18 a range of grain sizes from 0.5 to 5 mm, which are typical values for mantle xenoliths and
19 abyssal peridotites. Cooling rates used in the simulations range from 1 to 80 °C/Myr. In
20 Section 4, we also present simulations with different activation energies for diffusion and
21 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} (≤ 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 concentration 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 concentration 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

1 among closure temperatures defined by the three variables, we compare T_A^c , T_B^c and T_{AB}^k
 2 from the numerical experiments for a range of cooling rates (1 - 80 °C/Myr) and grain
 3 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
 4 $D_A = D_B$. In Figs. 7a and 7c we compare the three closure temperatures for the case of D_A
 5 $\neq D_B$: T_B^c are higher than T_A^c when $D_B < D_A$ (Fig. 7a) and lower than T_A^c when $D_B > D_A$.
 6 These systematic differences can be attributed to grain size and differences in diffusion
 7 rates between the two minerals. For large crystals that experienced fast cooling, the
 8 diffusion rate may not be high enough to cause sufficient changes in mineral core
 9 compositions. The closure temperatures of such samples are very close to the initial
 10 temperature. This explains the curved trends at high temperatures in Figs. 7a and 7c.
 11 Regardless of cooling rate, diffusion coefficients, and grain size, T_A^c and T_{AB}^k remain
 12 consistent for the range of parameters explored. This conclusion holds true so long as k_{AB}
 13 $\ll 1$.

14 The difference between T_A^c and T_B^c for cases of different diffusivities in Figs. 6,
 15 7a and 7c indicates that for a given grain size and cooling rate, diffusion rate plays an
 16 important role in constraining the closure temperatures defined by the average trace
 17 element concentrations in individual minerals. This is consistent with Dodson's model for
 18 mono-mineralic systems. However, in bi-mineralic systems diffusive exchange of trace
 19 element between the two minerals also depends on the partition coefficient and volume
 20 proportions of the two minerals (e.g., Onorato et al., 1981; Liang, 2014). As discussed
 21 above, trace element concentration in mineral A is much more sensitive to small changes

1 in temperature than mineral B due to the very small partition coefficient of k_{AB} . This
 2 explains the nearly identical values in T_{AB}^k and T_A^c . Conversely, when k_{AB} is much greater
 3 than one, the relative variations in the abundance of trace element in mineral B will be
 4 more sensitive to temperature, and consequently T_{AB}^k and T_B^c will be the same. When k_{AB}
 5 is close to one, both minerals A and B may become important in affecting the effective
 6 partition coefficient. This can be further illustrated below.

7 In Figs. 7b and 7d, we compare T_A^c , T_B^c and T_{AB}^k from the numerical experiments
 8 for the case of a larger k_{AB} [$k_{AB}(T_0) = 0.34$, Fig. 5b]. Other parameters are the same as
 9 those used in Figs. 7a and 7c, respectively. Because the trace element of interest is still
 10 incompatible in mineral A relative to mineral B , the general relationships among T_A^c , T_B^c
 11 and T_{AB}^k in this case (solid blue and red lines) are similar to those for the case of a smaller
 12 k_{AB} in Figs. 7a and 7c. The larger k_{AB} , however, reduces the differences in trace element
 13 concentration between minerals A and B , and hence the differences between T_B^c and T_A^c
 14 when $D_A \neq D_B$. Mineral B now has more influence on the effective partition coefficient
 15 than in the case of a smaller k_{AB} . Therefore, small but systematical deviations between
 16 T_{AB}^k and T_A^c (< 20 °C for the case of $D_B = D_A/5$, red solid line in Fig. 7b; < 15 °C for the
 17 case of $D_B = 5D_A$, red solid line in Fig. 7d) are observed. The values of T_{AB}^k are always
 18 between T_B^c and T_A^c (Figs. 7a-7d), indicating that T_{AB}^k encapsulates the effects of
 19 diffusion and partitioning in the bi-mineralic system. For this reason and also the REE-in-
 20 two-pyroxene thermometer, which will be discussed below, we use the closure

1 temperature defined by the evolution of effective partition coefficients T_{AB}^k as the closure
 2 temperature for the cooling bi-mineralic systems.

3 In Figs. 7b and 7d, we also compare T_A^c , T_B^c and T_{AB}^k from the numerical
 4 experiments for the case of a larger k_{AB} [$k_{AB}(T_0) = 0.34$, Fig. 5b] with two other choices
 5 of mineral proportions: $\phi_A:\phi_B = 1:9$ (red and blue dashed lines) and $\phi_A:\phi_B = 9:1$ (red and
 6 blue dash-dotted lines). The cooling rates, grain sizes, and diffusion coefficients are the
 7 same as those used above. Similarly, T_B^c are higher than T_A^c when $D_B < D_A$ (Fig. 7b), and
 8 lower than T_A^c when $D_B > D_A$ (Fig. 7d). The closure temperatures of T_{AB}^k are nearly
 9 identical to T_A^c when mineral proportion is $\phi_A:\phi_B = 1:9$ (red dashed lines in Figs. 7b and
 10 7d), whereas T_{AB}^k are much closer to T_B^c when modal abundances of mineral B is very
 11 small (i.e., $< 10\%$, dash-dotted lines in Figs. 7b and 7d). These results can be understood
 12 in terms of the relative equilibrium abundances of the trace element of interest in
 13 minerals A and B , $\phi_A k_{AB}/\phi_B$, and the relative diffusive time scales, $(d_A^2/D_A^c)/(d_B^2/D_B^c)$,
 14 for the two minerals (see Eq. 17 in Liang, 2014), where D_A^c and D_B^c are diffusion
 15 coefficients at the closure temperature. When $\phi_A k_{AB} \gg \phi_B$, mineral A is the larger
 16 reservoir for the trace element in the bi-mineralic system. The trace element in mineral B
 17 then is more sensitive to temperature change and becomes the major factor in affecting
 18 the closure temperature T_{AB}^k (blue dash-dotted line in Fig. 7b). The dominant effect of
 19 mineral B is subdued when trace element diffusion rate in mineral B is much faster than
 20 that in mineral A (blue dash-dotted line in Fig. 7d). According to the simple analysis of
 21 Liang (2014), mineral B is more important in determining the time-scale of diffusive re-

1 equilibration, hence the closure temperature, for a bi-mineralic system than mineral A
2 when

$$3 \quad \phi_A k_{AB} \frac{d_A^2}{D_A^c} > \phi_B \frac{d_B^2}{D_B^c}. \quad (5)$$

4

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

6 Closure temperatures of REE in cooling two-pyroxene systems can be related to
7 the temperature derived from the REE-in-two-pyroxene thermometer (Liang et al., 2013).
8 To better understand the physical meaning of the latter, we apply the numerical model
9 described in Section 3 to the two-pyroxene system for the same ranges of cooling rates
10 and grain sizes as those used to simulations shown in Fig. 7. In these numerical
11 experiments, we incorporate experimentally determined REE diffusivities in pyroxenes
12 (Van Orman et al., 2002; Cherniak and Liang, 2007) and the opx-cpx REE partition
13 coefficients (Liang et al., 2013).

14 Figure 2a displays diffusion coefficients of REE in cpx (Van Orman et al., 2002)
15 and opx (Cherniak and Liang, 2007) as a function of temperature. REE diffusion
16 coefficients in cpx depend on REE ionic radius, and the diffusion coefficients decrease
17 from Lu to La by one to four orders of magnitude as temperature decreases from 1400 °C
18 to 800 °C. REE diffusion coefficients in enstatite are not sensitive to ionic radii and can
19 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

1 between opx and cpx vary exponentially with temperature (Fig. 8), opx closure
2 temperatures from numerical experiments (T_{opx}^c) are different from those calculated by
3 the Dodson's equation.

4 In Fig. 9 we further compare the two-pyroxene REE closure temperature T_{2pyx}^k
5 with opx closure temperatures calculated using the modified Dodson's equation of
6 Ganguly and Tirone (1999, designated as T_{opx}^{GT}). The temperature difference between
7 T_{2pyx}^k and T_{opx}^{GT} is negligible for heavy REE and increases to ~ 25 °C for light REE when
8 opx and cpx proportions are the same (Fig. 9a). As opx proportion increases, the
9 temperature difference between T_{2pyx}^k and T_{opx}^{GT} also increases: the maximum is ~ 50 °C
10 for $\phi_{opx}:\phi_{cpx} = 9:1$ (from -30 °C for heavy REE to 50 °C for light REE in Fig. 9b), and $\sim$
11 70 °C for $\phi_{opx}:\phi_{cpx} = 98:2$ (from -70 °C for heavy REE to 65 °C for light REE Fig. 9c).
12 Hence to a good approximation, one can use T_{opx}^{GT} to represent the closure temperature for
13 middle REE or the average closure temperature for all the 14 REE in cooling two-
14 pyroxene systems. However, large difference exists between T_{opx}^{GT} and closure
15 temperature for light or heavy REE derived from the numerical simulation, especially
16 when cpx proportion is very low in the two-pyroxene system (Fig. 9c). As cpx proportion
17 is much higher than opx (e.g., $\phi_{opx}:\phi_{cpx} = 1:9$), the two-pyroxene closure temperatures
18 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
19 the numerical simulations, the difference between T_{2pyx}^k and T_{opx}^{GT} is mainly due to the
20 difference in the equilibrium concentration-temperature relationship at the mineral
21 surface (c.f. 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 ($\bar{T}_{2\text{pyx}}^k$) for both 1-D plane sheet and 3-D spherical geometries. Overall, the differences between T_{REE} and $\bar{T}_{2\text{pyx}}^k$ 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 (in review) 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

1 their implications for cooling rates of ophiolitic and abyssal peridotites. In Fig. 1 we
 2 compare T_{REE} derived from the numerical simulations of this study with closure
 3 temperatures for Fe-Mg diffusion in pyroxenes (designated as T_{Fe-Mg}) calculated using the
 4 formulation of Ganguly and Tirone (1999) for a range of initial temperatures (1100-1400
 5 °C), two choices of $\phi_{\text{opx}}:\phi_{\text{cpx}}$ (1:1, red solid curves; 98:2, blue dashed lines), and two
 6 choices of Fe-Mg diffusion data. T_{Fe-Mg} are calculated using the Fe-Mg interdiffusion
 7 coefficients in cpx from Dimanov and Wiedenbeck (2006) and Müller et al. (2013) in
 8 Figs. 1a and 1b, respectively. For purpose of illustration, contours of cooling rates for an
 9 effective grain size of 2 mm are shown as black dots connected by thin dashed black lines.
 10 As shown in Fig. 1, closure curves are very sensitive to the choice of Fe-Mg diffusion
 11 data but practically independent of pyroxene modal abundances. For an effective grain
 12 size of 2 mm, the inferred cooling rates for abyssal peridotites can differ by up to two
 13 orders of magnitudes (10^2 to 10^6 °C/Myr vs. 10 - 10^4 °C/Myr) due to the different choices
 14 of Fe-Mg diffusion coefficients. Nonetheless, the ranges of cooling rates are comparable
 15 to those of peridotites from Oman (10^{-1} to 10^5 °C/Myr) independently estimated based on
 16 Ca diffusion in olivine (Coogan et al., 2002; VanTongeren et al., 2008). The cooling
 17 curves in Fig. 1 also help to explain the observation made by Dygert and Liang (in review)
 18 that T_{REE} is not correlated with cpx abundance in ophiolitic peridotites from around the
 19 world (78 samples from 15 localities).

20 The preceding example demonstrated the potential advantage of the REE-in-two-
 21 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 closer 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, in review). 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: $d_{\text{opx}} = 0.5 \text{ mm}$, $\dot{s} = 1 \text{ }^{\circ}\text{C/Myr}$; green: $d_{\text{opx}} = 2.5 \text{ mm}$, $\dot{s} = 9 \text{ }^{\circ}\text{C/Myr}$; blue: $d_{\text{opx}} = 5 \text{ mm}$, $\dot{s} = 80 \text{ }^{\circ}\text{C/Myr}$), 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., 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 temperature of Dy, Er and Yb are calculated using D_0 and E for opx. It is apparent that large differences (50-400 $^{\circ}\text{C}$) 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 $^{\circ}\text{C}$) 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 $^{\circ}\text{C/Myr}$). The large variations of the temperature difference

1 between these two studies are mainly caused by the simplifications in the model of
2 Powell and White (1995). This indicates that Powell and White's model may not be
3 applicable to the calculation of closure temperature of a trace element, especially when its
4 partition coefficient between the minerals *A* and *B* is (much) smaller than one and its
5 diffusion rate in mineral *B* is slower than in mineral *A*.

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

Figure 10 shows that the closure temperatures of REE in the opx-cpx bi-mineralic systems ($\bar{T}_{2pyx}^k$) 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 $\bar{T}_{2pyx}^k$ 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, $\phi_{opx}:\phi_{cpx} = 1:1$). 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

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

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

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

17 3. Small but systematical differences exist in the closure temperatures
18 between mono- and bi-mineralic systems, due to the equilibrium concentration-
19 temperature relationship at the mineral surface. As the partition coefficient decreases, the
20 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.

Acknowledgments

We thank Chenguang Sun, Nick Dygert, Amanda Getsinger and Colin Jackson for useful comments and suggestions to earlier versions of this manuscript. The manuscript benefited from thoughtful review comments from two anonymous reviewers and the associate editor Wim van Westrenen. This work was supported in part by NSF grant EAR-1220076 and NASA grant NNX13AH07G.

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Figure caption

Figure 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 °C/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).

1

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

8

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

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

6

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

11

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

14

15 Figure 6. Definitions of closure temperature of a trace element in cooling bi-mineralic
16 systems. (a1-a4) Case of $D_B = D_A$. (b1-b4) Case of $D_B = D_A/5$. (c1-c4) Case of $D_B = 5D_A$.
17 Parameters used in these examples are grain size of 1 mm, cooling rate of 20 °C/Ma and
18 partition coefficients with $k_{AB}(T_0) = 0.03$, (magenta circles, Fig. 5b). (a1)-(c1) The same
19 prescribed cooling defined by Eq. (1). (a2)-(c2) Evolution of the rim (blue dashed lines,
20 C_A^{rim}) and average (red lines, $\bar{C}_A$) concentrations of a trace element in mineral A. (a3)-
21 (c3) same as (a2)-(c2) but for mineral B. (a4)-(c4) Same as (a2)-(c2) but for the effective

1 partition coefficient between minerals A and B . The intercepts (red circles) of the blue
2 dashed line and the green line in (a2) to (c4) are projections of asymptotic values of the
3 average trace element concentrations in minerals A and B or the effective partition
4 coefficient to their rim values, which correspond to closure temperatures (T_A^c , T_B^c and
5 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).

6

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

13

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

16

17 Figure 9. Comparison of REE closure temperatures defined by effective partition
18 coefficients between opx and cpx (T_{2pyx}^k) with the REE closure temperatures in opx
19 calculated by the equation of Ganguly and Tirone (1999) (T_{opx}^{GT}) for four choices of
20 mineral proportions: (a), $\phi_{opx}:\phi_{cpx} = 1:1$; (b), $\phi_{opx}:\phi_{cpx} = 9:1$; (c), $\phi_{opx}:\phi_{cpx} = 98:2$; (d),

1 $\phi_{\text{opx}} : \phi_{\text{cpx}} = 1:9$. The ranges of grain sizes and cooling rates are the same as those in Fig. 7.

2 See text for discussion.

3

4 Figure 10. Comparison between temperatures calculated using REE-in-two-pyroxene

5 thermometer (T_{REE}) and the average REE closure temperatures defined by their effective

6 partition coefficient between opx and cpx ($\bar{T}_{2\text{pyx}}^k$) for 1-D plane sheet (a) and 3-D

7 spherical geometry (b) and the differences in T_{REE} for different pyroxene abundances (c).

8 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 $= 9:1$ (green squares); $\phi_{\text{opx}} : \phi_{\text{cpx}} = 98:2$ (blue diamonds) in (a) and (b). (ΔT_{REE}) $\phi_{\text{opx}} : \phi_{\text{cpx}}$ in

10 (c) represents the temperature differences between T_{REE} for different mineral proportions

11 (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

12 (solid lines) and 3-D (dashed lines) geometries. T_{REE} are calculated using the REE-in-

13 two-pyroxene thermometer and the average concentrations of REE in two pyroxenes after

14 the establishment of the closure profiles (for details, see supplementary Fig. S5). The

15 ranges of grain sizes and cooling rates are the same as those in Fig. 7.

16

17 Figure 11. Comparison between closure temperatures of REE from this study and those

18 calculated using the closure temperature model of Powell and White (1995) for cooling

19 bi-mineralic systems. Grain sizes of two pyroxenes are the same. Diffusion coefficients

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

21 Red dots represent grain size of 0.5 mm and cooling rate of 1 °C/Myr; green dots

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

Figure 1

Figure 2

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