A simple model for closure temperature of a trace element in cooling bi-mineralic systems

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ABSTRACT

Closure temperature is defined as the lower temperature limit at which the element of interest effectively ceases diffusive exchange with its surrounding medium during cooling. Here we generalize the classic equation of Dodson (1973) for cooling mono-mineralic systems to cooling bi-mineralic aggregates by considering diffusive exchange of a trace element between the two minerals in a closed system. We present a simple analytical model that includes key parameters affecting the closure temperature of a trace element in cooling bi-mineralic systems: cooling rate, temperature-dependent diffusion coefficients for the trace element in the two minerals, temperature-dependent partition coefficient of the trace element between the two minerals, effective grain sizes of the two minerals, and volume proportions of the minerals in the system. We show that closure temperatures of a trace element in cooling bi-mineralic systems are bounded by the closure temperatures of the trace element in the two mono-mineralic systems and that our generalized model reduces to Dodson's equation when one of the mineral serves as "an effective infinite" reservoir to the other mineral. Application to closure temperatures of REE in orthopyroxene and clinopyroxene bi-mineralic systems highlights the importance of REE diffusion and partitioning in the pyroxenes as well as clinopyroxene modal abundance and grain size in the systems. Closure temperatures for REE in two-pyroxene bearing equigranular rocks are controlled primarily by diffusion in orthopyroxene unless the modal abundance of clinopyroxene is very small. This has important bearings on the interpretation of temperatures derived from the REE-in-two-pyroxene thermometer.

1. INTRODUCTION

Closure temperature is an important topic to many diffusion related problems involving changes in temperature during the course of diffusive exchange between a mineral grain and its surrounding medium (e.g., Crank, 1975; Albarède, 1995; Lasaga, 1998; Zhang, 2008). It is defined as the lower temperature limit at which the element of interest effectively ceases diffusive exchange with its surrounding medium during cooling. The original formulation of closure temperature was rigorously derived by Dodson (1973, 1976, 1983) for cooling mono-mineralic systems by considering analytical solutions to diffusion equations with temperature- or time-dependent diffusion coefficient. According to Dodson (1973), closure temperature (T_c) for an element in a mineral grain depends on diffusion parameters of the element and decreases with the decrease of the product of cooling rate and the square of effective diffusion radius (d_A). It is given by Dodson's equation

$$\frac{E_A}{RT_c} = G + \ln \frac{D_A^0 RT_c^2}{E_A \dot{s} d_A^2}, \quad (1a)$$

where G is the closure function, depending on geometry of the system; E_A and D_A^0 are the activation energy and pre-exponential factor for diffusion of the element of interest; $\dot{s}$ is the cooling rate at the closure temperature; and R is the gas constant. Eq. 1a can also be written in terms of the diffusion coefficient evaluated at the closure temperature, D_A^c , viz.,

$$\frac{E_A \dot{s}}{RT_c^2} \frac{d_A^2}{D_A^c} = \exp(G), \quad (1b)$$

where terms on the left hand side of Eq. 1b represent a measure of diffusion time relative to cooling time at the closure temperature (see Section 2.1. below). The geometry function, G , in Dodson's equation was modified by Ganguly and Tirone (1999) to include the "memory effect"

1 that arises from situations when diffusion has not affected the center of the crystal (i.e., cases of
2 fast cooling and large grain size). Dodson's equation and its modification (e.g., Ganguly and
3 Tirone, 1999; Gardés and Montel, 2009; Watson and Cherniak, 2013) have been widely used to
4 study the closure temperature and thermal history of igneous and metamorphic rocks (e.g.,
5 Giletti, 1986; Ganguly et al., 2007).

6 Most petrologic systems are polycrystalline, consisting of more than one mineral. Closure
7 temperatures for bi-mineralic or poly-mineralic systems were investigated in a number of studies
8 through numerical simulations or analytical solutions of the diffusion equations (e.g., Lasaga et
9 al., 1977; Onorato et al., 1981; Lasaga, 1983; Spear, 1991; Eiler et al., 1992; Jenkin et al., 1994,
10 1995; Ehlers and Powell, 1994; Powell and White, 1995). Although significant progress has been
11 made in understanding closure temperature for cooling bi-mineralic systems through these
12 studies, algebraic equations for closure temperatures were either not available or obtained under
13 simplified settings. For example, the equation of Powell and White (1995) was obtained under
14 the assumption that cation diffusion in one mineral is significantly faster than that in the other
15 (see also Ehlers and Powell, 1994). Application of the equation of Powell and White (1995) to
16 REE in cooling diopside-enstatite systems leads to inconsistent results (Yao and Liang, in press)
17 as diffusion coefficients of light REE in diopside are smaller than those in enstatite, whereas
18 diffusion coefficients of heavy REE in diopside are larger than those in enstatite (Fig. 1a, Van
19 Orman et al., 2001; Cherniak and Liang, 2007; but see also Sano et al., 2011).

20 In general, diffusive re-equilibration of a trace element between two minerals in a closed
21 system depends on mineral-mineral trace element partition coefficient, diffusion coefficients for
22 the trace element in the two minerals, grain sizes of the two minerals, as well as volume
23 proportions of the minerals in the system (e.g., Lasaga et al., 1977; Lasaga, 1983; Liang, 2014).

The main objective of this study is to quantify the relationships among the aforementioned parameters for the closure temperature of a trace element in cooling bi-mineralic systems. A simple algebraic expression will be very useful for assessing the relative roles of the various parameters in controlling closure temperatures. As will be shown in this study, the closure temperature of a trace element in cooling bi-mineralic system is bounded by the closure temperatures of the trace element in the two mono-mineralic systems and that mineral-mineral trace element partition coefficient and modal abundances are also important in determining closure temperatures for the bi-mineralic systems.

2. CLOSURE TEMPERATURE AND TIME SCALES FOR DIFFUSION AND COOLING

We consider diffusive exchange of a trace element in a cooling bi-mineralic aggregate consisting of minerals A and B of average half sizes or radii d_A and d_B and volume fractions ϕ_A and ϕ_B , respectively, in a representative elementary volume or REV. For simplicity, we assume that (1) diffusion in the minerals is isotropic; (2) the two minerals are in local equilibrium at their interfaces; (3) grain boundary diffusion is much faster than volume diffusion in the two minerals, so that mass exchanges freely along grain boundaries among minerals within the REV (e.g., Eiler et al., 1992); and (4) grain growth is negligible during the course of diffusive exchange. The temperature-dependent diffusion coefficients for the trace element of interest in the two minerals take on the usual expressions:

$$D_A(T) = D_A^0 \exp\left(-\frac{E_A}{RT}\right), \quad (2a)$$

$$D_B(T) = D_B^0 \exp\left(-\frac{E_B}{RT}\right), \quad (2b)$$

where subscripts A and B refer to the two minerals. Assumption (2) allows us to relate concentrations of a trace element at the surfaces of mineral A and mineral B through a mineral-mineral partition coefficient, k_{AB} , which is a function of temperature, pressure, and mineral compositions. For simplicity, we use the Arrhenius expression in the present study

$$k_{AB}(T) = k_{AB}^0 \exp\left(-\frac{E_k}{RT}\right), \quad (2c)$$

where E_k and k_{AB}^0 are the exchange energy and pre-exponential factor for the partitioning of a trace element between mineral A and mineral B. Physically, E_k is a sum of two parts: (1) the change in internal energy for strain-free exchange of the trace element of interest between mineral A and mineral B, and (2) the difference in lattice strain energy for the substitution of the trace element in the two minerals (see Eq. 2 in Sun and Liang, 2014).

Standard analysis of closure temperature in cooling mono-mineralic or bi-mineralic systems involves analytical or numerical solutions of diffusion equations subject to prescribed cooling. Although the governing diffusion equations and the initial and boundary conditions for the bi-mineralic system are well known (e.g., Lasaga et al., 1977; Onorato et al., 1981; Eiler et al., 1992; Ehlers and Powell, 1994), their mathematical analyses are considerably more difficult without further simplification (e.g., Powell and White, 1995). To include all the key features of the closure temperature for the cooling bi-mineralic system, here we carry out an order of magnitude analysis by comparing an effective diffusion time scale with the cooling time scale. This method, which we will briefly review below, has been successfully used to elucidate closure temperatures for cooling mono-mineralic systems (e.g., Dodson, 1976; Albarède, 1995).

2.1. Closure temperature for cooling mono-mineralic systems

The time scale of diffusive re-equilibration is a useful concept. To within a constant factor, Dodson's equation can be obtained by comparing an accumulated mean square diffusive penetration distance with the square of an effective grain radius (e.g., Taylor et al., 1975; Lasaga, 1998; Cherniak and Watson, 2007; Zhang, 2008; Watson and Cherniak, 2013) or by comparing a diffusion time scale with a cooling time scale (e.g., Dodson, 1976; Albarède, 1995). If D_A is the temperature-dependent diffusion coefficient for an element in mineral A, the characteristic diffusion time is given by the usual expression

$$t_D = \frac{3\beta d_A^2}{D_A}, \quad (3)$$

where β is a constant, depending on mineral shape and boundary condition. It takes on values of 1, 4, or 5 for diffusion in plane sheet of half-length d_A , cylinder or sphere of radius d_A , respectively (Liang, 2014). For mineral aggregates, the β may take on a range of values (1~5), depending on mineral shape and grain size distribution. The cooling time scale or constant (τ), according to Dodson (1973), is defined as the time it takes to decrease D_A by a factor of e or 63%, viz.,

$$\tau = -\frac{d \ln D_A}{dt} = \frac{RT_c^2}{E_A \dot{s}}, \quad (4)$$

where t is time. The mineral is effectively closed to diffusive exchange with its surrounding when the cooling time is shorter than the diffusion time. At closure temperature T_c , Eqs. 3 and 4 differ by a constant factor A' , viz.

$$\frac{3\beta d_A^2}{D_A^c} = A' \frac{RT_c^2}{E_A \dot{s}}, \quad (5)$$

where D_A^c is diffusion coefficient at the closure temperature T_c . Eq. 5 is the same as Dodson's equation for closure temperature (Eq. 1b) when the geometry function $G = \ln(A'/3\beta)$.

2.2. Closure temperature for cooling bi-mineralic systems

The approach outlined above can also be used to obtain an equation for closure temperature for cooling bi-mineralic systems. According to the analysis of Liang (2014), the diffusive re-equilibration time for a trace element in a bi-mineralic aggregate is a weighted sum of characteristic diffusion times for the trace element in the two minerals and takes on the simple expression

$$t_D = \frac{\phi_B}{\beta(\phi_A k_{AB} + \phi_B)} \frac{d_A^2}{D_A} + \frac{\phi_A k_{AB}}{\beta(\phi_A k_{AB} + \phi_B)} \frac{d_B^2}{D_B}, \quad (6)$$

where β is a constant depending on geometry of the mineral grain; and ϕ again is the volume fraction of mineral A or mineral B. The bulk or effective diffusive exchange rate between mineral A and mineral B in the REV, α , is inversely proportional to t_D , viz.,

$$\alpha = \frac{3\beta(\phi_A k_{AB} + \phi_B)}{\phi_B \frac{d_A^2}{D_A} + \phi_A k_{AB} \frac{d_B^2}{D_B}}. \quad (7)$$

Eqs. 6 and 7 were obtained from approximate solutions to the diffusion equations governing diffusive exchange between minerals A and B in the bi-mineralic aggregate with effective diffusion radii of d_A and d_B using the method of parabolic approximation (for details see Liang, 2014). Similar to Dodson (1973), we introduce a cooling time constant τ , defined as the time it takes to reduce the effective diffusive exchange rate α by a factor of e , viz.

$$\alpha = \alpha_0 \exp\left(-\frac{t}{\tau}\right), \quad (8a)$$

which can also be written as

$$\frac{1}{\tau} = - \frac{d \ln \alpha}{dt} . \quad (8b)$$

Upon differentiation of Eq. 7, we obtain the cooling time constant for the bi-mineralic system,

$$\tau = - \frac{(\phi_A k_{AB} + \phi_B) \left(\phi_B \frac{d_A^2}{D_A} + \phi_A k_{AB} \frac{d_B^2}{D_B} \right) RT^2}{\phi_B \phi_A k_{AB} E_k \left(\frac{d_A^2}{D_A} - \frac{d_B^2}{D_B} \right) + (\phi_A k_{AB} + \phi_B) \left(\phi_B E_A \frac{d_A^2}{D_A} + \phi_A k_{AB} E_B \frac{d_B^2}{D_B} \right)} \frac{dT}{dt} . \quad (9)$$

The cooling bi-mineralic system is effectively closed to diffusive mass transfer when the characteristic cooling time is considerably smaller than the diffusive exchange time, i.e., $\tau < t_D$.

To be consistent with Dodson's formulation, we set

$$\frac{\exp(G)}{\beta} \tau = t_D , \quad (9)$$

where G again is the geometry function as in Dodson's equation (Eq. 1). From Eqs. 6 and 9, we have an algebraic equation for closure temperature for a cooling bi-mineralic system

$$\frac{\phi_B E_A \frac{d_A^2 \dot{s}}{D_A^c} + \phi_A k_{AB}^c E_B \frac{d_B^2 \dot{s}}{D_B^c}}{(\phi_A k_{AB}^c + \phi_B) RT_c^2} + \frac{\phi_B \phi_A k_{AB}^c E_k}{(\phi_A k_{AB}^c + \phi_B)^2 RT_c^2} \left(\frac{d_A^2 \dot{s}}{D_A^c} - \frac{d_B^2 \dot{s}}{D_B^c} \right) = \exp(G) , \quad (10)$$

where the cooling rate $\dot{s}$, diffusion coefficients (D_A^c and D_B^c) and partition coefficient (k_{AB}^c) are all evaluated at the closure temperature T_c .

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3. DISCUSSION

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Eq. 10 encapsulates all the relevant parameters for closure temperature for cooling bi-mineralic systems: cooling rate, diffusion coefficients, mineral-mineral partition coefficient, activation energies for diffusion, exchange energy for trace element partitioning, effective grain sizes, and modal abundances. The first three parameters are evaluated at the closure temperature

T_c and hence may be taken as extrinsic, whereas the last three parameters are intrinsic to the bi-mineralic system. The first term on the left hand side of Eq. 10 accounts for the temperature- or time-dependent diffusion coefficients, whereas the second term on the left hand side of Eq. 10 arises from the temperature-dependent partition coefficient, as $d \ln k_{AB} / dt = E_k / RT^2$. The activation energies for cation diffusion in silicate minerals are typically larger than the exchange energy for mineral-mineral partitioning. For example, the exchange energies for REE partitioning between orthopyroxene and clinopyroxene (83~38 kJ/mol, from La to Yb, according to the model of Liang et al., 2013) are 3~10 times smaller than the activation energies for REE diffusion in diopside (530~400 kJ/mol, from La to Yb in cpx, Van Orman et al., 2001) and Mg-rich orthopyroxene (369 kJ/mol for REE, Cherniak and Liang, 2007; 218-262 kJ/mol for Nd, Sano et al., 2011). This situation is also true for a number of trace elements in the pyroxenes (e.g., Ti, Hf, U, Th, Sr, Pb, Sc, Cr, and Mn) according to the published diffusion and partitioning data (Sneeringer et al., 1984; Seitz et al., 1999; Van Orman et al., 1998; Witt-Eickschen and O'Neill, 2005; Dimanov and Wiedenbeck, 2006; Ganguly et al., 2007; Cherniak and Liang, 2012; Block and Ganguly, 2014). Hence the second term in Eq. 10 is negligible in many practical applications. The second term also vanishes when the differences in diffusion time between mineral A and mineral B at the closure temperature is very small, i.e., $d_A^2 / D_A^c \approx d_B^2 / D_B^c$.

An important property of Eq. 10 is that it reduces to Dodson's equation (Eq. 1b) when one of the minerals serves as "an effective infinite" reservoir to the other mineral. This can be achieved under two limiting conditions or through their combination. Let w_A^{e-c} and w_B^{e-c} be the equilibrium mass fractions of the element of interest in minerals A and B relative to their total mass in the REV at the closure temperature T_c ,

$$w_A^{e-c} = \frac{\phi_A \bar{C}_A^{e-c}}{\phi_A \bar{C}_A^{e-c} + \phi_B \bar{C}_B^{e-c}} = \frac{\phi_A k_{AB}^c}{\phi_A k_{AB}^c + \phi_B}, \quad (11a)$$

$$w_B^{e-c} = \frac{\phi_B \bar{C}_B^{e-c}}{\phi_A \bar{C}_A^{e-c} + \phi_B \bar{C}_B^{e-c}} = \frac{\phi_B}{\phi_A k_{AB}^c + \phi_B}, \quad (11b)$$

where $\bar{C}_A^{e-c}$ and $\bar{C}_B^{e-c}$ are the equilibrium concentrations for the trace element in minerals A and B in the REV at T_c , respectively. The equilibrium concentrations are related to each other through the mineral-mineral partition coefficient, i.e., $k_{AB}^{e-c} = \bar{C}_A^{e-c} / \bar{C}_B^{e-c}$. Eq. 10 then takes on a simpler form,

$$w_B^{e-c} \frac{E_A \dot{s}}{RT_c^2} \frac{d_A^2}{D_A^c} + w_A^{e-c} \frac{E_B \dot{s}}{RT_c^2} \frac{d_B^2}{D_B^c} + w_A^{e-c} w_B^{e-c} \frac{E_k \dot{s}}{RT_c^2} \left(\frac{d_A^2}{D_A^c} - \frac{d_B^2}{D_B^c} \right) = \exp(G). \quad (12)$$

Eq. 12 recovers Dodson's equation for mineral A (Eq. 1b) when $w_A^{e-c} \rightarrow 0$. That is when the volume fraction of mineral A is much smaller than mineral B ($\phi_A \ll \phi_B$) and/or when the mineral A-B partition coefficient at the closure temperature is much smaller than one (i.e., $k_{AB}^c \ll 1$). Similarly, Eq. 12 reduces to Dodson's equation for mineral B when $w_B^{e-c} \rightarrow 0$. In this latter case, mineral A effectively serves as an infinite sink for diffusant of interest initially in mineral B, as the equilibrium concentration in mineral A is much larger than that in mineral B (i.e., $k_{AB}^c \gg 1$). This buffering effect is referred to as "minor's rule" in Liang (2014) for diffusive re-equilibration in bi-mineralic systems, viz., the mineral that contains lesser amount of the trace element of interest in the bi-mineralic system contributes more to the overall diffusive re-equilibration time. As a corollary of minor's rule, we can make the following general statement: closure temperatures for cooling bi-mineralic systems are bounded by the closure temperatures for the trace element in the two mono-mineralic systems consisting of mineral A and mineral B, respectively.

Minor's rule is particularly useful in situations when abundance of the element of interest is much smaller in one mineral relative to the other. Some examples for crustal rocks include the Ti-in-quartz, Ti-in-zircon, and Zr-in-rutile thermometers of Watson and coworkers that are based on the temperature dependent Ti solubility in quartz or zircon coexisting with rutile (or Zr solubility in rutile coexisting with zircon) (Watson and Harrison, 2005; Wark and Watson, 2006; Watson et al., 2006; Thomas et al., 2010). Similar examples for mafic rocks include the Mg-in-plagioclase thermometer of Faak et al. (2013) and the Al-in-olivine thermometer of Coogan et al. (2014). The former is based on the temperature sensitive Mg partitioning between plagioclase and clinopyroxene, while the latter is based on the temperature dependent Al partitioning between olivine and spinel. Here Mg is a minor element in plagioclase but a major element in clinopyroxene; Al is a trace element in olivine but a major element in spinel. According to minor's rule, temperatures derived from the Ti-in-quartz thermometer, the Mg-in-plagioclase thermometer, and the Al-in-olivine thermometer should correspond to the closure temperatures of Ti diffusion in quartz, Mg diffusion in plagioclase, and Al diffusion in olivine, respectively, independent of Ti diffusion in rutile (Cherniak et al., 2007), Mg diffusion in clinopyroxene (Faak et al., 2014), and Al diffusion in spinel.

The characteristic diffusion time t_D in Eq. 6 (hence the effective diffusive exchange rate α in Eq. 7) was obtained by approximating diffusion profiles in minerals A and B at a given time as functions of second order polynomials (Liang, 2014). Since the parabolic approximation is applicable only when diffusion has already penetrated into the mineral cores (e.g., Goodman, 1964; Hill, 1987; Bodinier et al., 1990; Liang, 2003), Eqs. 10 and 12 are valid under conditions similar to that of Dodson's (Eqs. 1a and 1b) and hence may be taken as a generalization of Dodson's equation to cooling bi-mineralic systems. However, these equations are not applicable

1 to situations where diffusion has not affected mineral core concentrations, as discussed in the
2 model of Ganguly and Tirone (1999).

3 Another simplification in the derivation of the diffusion time t_D in Eq. 6 is the use of effective
4 diffusion radii d_A and d_B , which is a standard practice in diffusion modeling of poly-mineralic
5 systems. In real rocks, mineral grain size and surface area vary within REV and grain size
6 distribution may also play an important role in determining closure temperatures: consider a rock
7 with bi-modal grain size distribution or log-normal grain size distribution. Such more
8 complicated but real cases can be treated numerically. Nonetheless, the key factors controlling
9 closure temperatures for cooling bi-mineralic systems identified through the simple analysis
10 present in this study likely remain valid.

12 **4. CLOSURE TEMPERATURES OF REE IN PYROXENES**

13 To further illustrate the key features of Eq. 10, we consider closure temperatures of REE in
14 an effective bi-mineralic system that consists of orthopyroxene (opx) and clinopyroxene (cpx).
15 These two pyroxenes are frequently observed in ultramafic and mafic rocks. [Figure 1a](#) displays
16 REE diffusion coefficients in cpx and opx as a function of temperature. Van Orman et al. (2001)
17 demonstrated that diffusion rates of REE in diopside depend strongly on their ionic radii (green
18 to yellow lines in [Fig. 1a](#)), whereas Cherniak and Liang (2007) showed that diffusion rates of
19 REE in enstatite are not sensitive to their ionic radii (red dashed line). Orthopyroxene-
20 clinopyroxene REE partition coefficients depend primarily on temperature, ionic radius, and
21 pyroxene compositions (e.g., Stosch, 1982; Witt-Eickschen and O'Neill, 2005; Lee et al., 2007;
22 Liang et al. 2013). [Figure 1b](#) displays opx-cpx REE partition coefficients for three choices of
23 temperature using the model of Liang et al. (2013) which was derived from pyroxene-basalt REE

partitioning models (Sun and Liang, 2012; Yao et al., 2012) and validated by well-equilibrated spinel lherzolite xenoliths. Relative to cpx, light REE are considerably more incompatible in opx ($k_{AB} \sim 0.002 - 0.04$, where A = opx, B = cpx) than heavy REE in opx ($k_{AB} \sim 0.1 - 0.4$). During subsolidus re-equilibration, REE are strongly and preferentially partitioned into cpx relative to opx. Hence, according to minor's rule, cpx may serve as a sink for REE redistribution in opx when cpx modal abundance in the opx-cpx aggregate is not too small.

Figures 2a-2c display closure temperatures for REE in cpx + opx aggregates as a function of effective diffusion radius for a cooling rate of 10°C/Myr and for three choices of opx:cpx volume proportions using REE diffusion data of Van Orman et al. (2001) for cpx and Cherniak and Liang (2007) for opx. In each case, closure temperatures for Ce and Yb in mono-mineralic cpx and REE in mono-mineralic opx, calculated using Dodson's equation (Eq. 1a), are also shown for reference. For purpose of illustration, we first consider cases with equal grain size ($d_{opx} = d_{cpx}$). For two-pyroxene aggregates with more than 20% cpx, the closure temperature is determined primarily by that of opx, because of the lower abundances of REE in opx in the REV (or very small REE opx-cpx partition coefficients) (cf. Fig. 1b and Eq. 12). Clinopyroxene in this case serves effectively as a large reservoir for REE redistribution in opx (Fig. 2a). The buffering role of cpx has been demonstrated in the numerical simulations of Cherniak and Liang (2007) who examined diffusive re-distribution of REE between opx and cpx (in 1:1 volume proportion) under a prescribed cooling rate. They showed that large differences in diffusive and partitioning behaviors of REE between opx and cpx result in very large relative core-to-rim compositional variations in opx, but very small relative compositional variations in cpx (see their Fig. 11).

However, when cpx modal abundance decreases, the equilibrium mass fractions of REE in cpx, w_{cpx}^{e-c} , also decreases. According to Eq. 12, clinopyroxene eventually becomes the minor

1 component for REE in the orthopyroxenite (or harzburgite). Figures 2b and 2c show that cpx
2 becomes important when its volume fraction is less than 5%. Both lherzolite and harzburgite
3 contain significant amount of olivine. Clinopyroxene is important in determining closure
4 temperatures for REE between opx and cpx in these natural rocks only when its modal
5 abundance is less than 1~2% (e.g., in a depleted harzburgite).

6 In many peridotite samples, the average grain size of cpx is smaller than that of opx. At
7 constant volume proportion, the effect of a smaller cpx grain size is to further reduce the role of
8 cpx in controlling the closure temperature for the two-pyroxene system, as the characteristic
9 diffusion time for cpx scales with its grain size to the squares, i.e., d_{cpx}^2 / D_{cpx}^c in Eq. 12. Figures
10 3a and 3b show that the smaller cpx grain size effect is especially stronger for the light to middle
11 REE.

12 Sano et al. (2011) examined Nd diffusion in Mg-rich opx along three crystallographic
13 directions and noted some anisotropy. Although their measured diffusivities agree fairly well
14 with data reported in Cherniak and Liang (2007, normal to (210)) at temperatures above 1050°C,
15 their measurements at 975°C and 1025°C appear higher than trend established by the latter data
16 (see supplementary Figure S1 for a detailed comparison of the two studies). Consequently,
17 activation energies for Nd diffusion in opx reported in Sano et al. (216~269 kJ/mol) are
18 considerably smaller than values presented in Cherniak and Liang (321~384 kJ/mol) (for a
19 graphic comparison see Supplementary Figure S2). [Interestingly, nine out of 10 measured
20 diffusivities along b direction in Sano et al. (2011) agree very well with data reported in
21 Cherniak and Liang (2007, normal to (210)), see supplementary Figure S1.] Figures 4a-4c are
22 similar to Figs. 2a-2c except the Arrhenius relation of Sano et al. (2011) for Nd diffusion along c
23 direction in opx was used to calculate the closure temperatures. A larger diffusivity and smaller

activation energy for REE diffusion in opx (hence the smaller ratio E_A/D_A^c in Eq. 12) expand the role of cpx (mineral B in Eq. 12) and lower the closure temperatures for the cpx + opx bi-mineralic aggregates (cf. Figs. 2 and 4). More study is needed to further resolve REE diffusion in opx at low temperatures.

In a recent study, Liang et al. (2013) developed a REE-in-two-pyroxene thermometer (with temperature designated as T_{REE}) that is based on temperature sensitive REE partitioning between coexisting opx and cpx. Through both numerical simulations (Yao and Liang, in press) and theoretical analysis (Liang, 2014), they showed that for cooling opx-cpx systems, T_{REE} is equivalent to the average closure temperature of REE in two-pyroxene dominant rocks. As applications of this new thermometer, T_{REE} for abyssal peridotites (Liang et al., 2013), peridotites from mantle sections of ophiolites around the world (Dygert and Liang, 2015), and selected peridotite xenoliths from the North China Craton (Wang et al., 2015) were calculated. Results from these studies showed that T_{REE} for the peridotites are 50-300°C higher than temperatures derived from the major element based two-pyroxene thermometer of Brey and Köhler (1990, T_{BKN}) for the same samples (Fig. 5). This difference in temperature ($\Delta T = T_{REE} - T_{BKN}$) can be understood in terms of differences in closure temperature between the trivalent REE and divalent Fe-Mg (and Ca) in the pyroxenes. The large range in temperature difference may be attributed in part to variations in cpx modal abundance and grain size in the peridotites, and possibly REE diffusivities in opx, as demonstrated in Figs. 2-4. With a better understanding of closure temperatures in cooling bi-mineralic systems, it is possible to develop a quantitative model that can be used to infer cooling rates of mafic and ultramafic rocks based on temperatures and temperature differences derived from major element and REE based two-pyroxene thermometers (Dygert and Liang, 2015; Wang et al., 2015; Yao et al., in press).

5. SUMMARY

A simple model for closure temperature of a trace element in cooling bi-mineralic aggregates is obtained by comparing the characteristic diffusion time and an effective cooling time for the bi-mineralic systems. These time scales were obtained by solving grain-scale diffusion equations using the polynomial approximation that is valid when diffusion has already penetrated into the cores of the crystals. The model presented in this study is physically intuitive and helps to elucidate key parameters affecting closure temperature for a trace element in cooling bi-mineralic systems. In general, the mineral that has higher activation energy for diffusion, larger diffusion time (d^2/D) and smaller equilibrium mass fraction of the trace element in the system (w^{c-e}) contributes more to the closure temperature for the cooling bi-mineralic system (Eq. 12). The effects of mineral proportion and mineral-mineral trace element partition coefficient are encapsulated in a single parameter, the equilibrium mass fraction of the trace element in the system. The latter helps to explain the buffering effect of the second mineral during diffusive exchange and the minor's rule. The closure temperatures for a trace element in cooling bi-mineralic systems are bounded by the closure temperatures for the trace element in the two mono-mineralic systems.

Application to closure temperatures of REE in opx and cpx bi-mineralic systems highlights the importance of the minor's rule. Closure temperatures for REE in two-pyroxene bearing rocks are controlled primarily by REE diffusion in opx unless the modal abundance of cpx is very small or/and the effective grain size of cpx is considerably larger than that of opx. The latter has important implications for the interpretation of temperatures derived from the REE-in-two-pyroxene thermometer.

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Figure Captions

Figure 1. REE diffusion coefficients and partition coefficients used in model calculations. (a) Arrhenius plot showing variations of REE diffusion coefficients in diopside and enstatite (Van Orman et al., 2001; Cherniak and Liang, 2007). (b) Partition coefficients of REE between orthopyroxene (opx) and clinopyroxene (cpx) at three selected temperatures (Liang et al., 2013). Modified after Liang (2014).

Figure 2. Variations of closure temperatures for REE in two-pyroxene aggregates as a function of effective diffusion radius at a cooling rate of 10°C/Myr and for three choices of orthopyroxene-clinopyroxene volume proportions. (a) $\phi_{opx} : \phi_{cpx} = 50 : 50$; (b) $\phi_{opx} : \phi_{cpx} = 80 : 20$; and (c) $\phi_{opx} : \phi_{cpx} = 95 : 5$. For simplicity, effective grain sizes of the two pyroxenes are set the same. Closure temperatures of Ce and Yb in clinopyroxene (dashed blue lines) and REE in orthopyroxene (heavy black line) are also shown. REE diffusion data are from Van Orman et al. (2001) for clinopyroxene and Cherniak and Liang (2007) for orthopyroxene. See text for further discussion.

Figure 3. Variations of closure temperatures for REE in two-pyroxene aggregates as a function of effective diffusion radius of orthopyroxene at a cooling rate of 10°C/Myr and for two choices of clinopyroxene grain sizes. (a) $d_{cpx} = d_{opx} / 2$; and (b) $d_{cpx} = d_{opx} / 4$. The orthopyroxene-clinopyroxene volume proportion is fixed at 95:5. Symbols are the same as those used in Fig. 2.

Figure 4. Variations of closure temperatures for REE in two-pyroxene aggregates as a function of effective diffusion radius at a cooling rate of 10°C/Myr and for three choices of orthopyroxene-clinopyroxene volume proportions. (a) $\phi_{opx} : \phi_{cpx} = 50 : 50$; (b) $\phi_{opx} : \phi_{cpx} = 80 : 20$; and (c) $\phi_{opx} : \phi_{cpx} = 95 : 5$. For simplicity, effective grain sizes of the two pyroxenes are set the same. Closure temperatures of Ce and Yb in clinopyroxene (dashed blue lines) and REE in orthopyroxene (heavy black line) are also shown. REE diffusion data are from Van Orman et al. (2001) for clinopyroxene and Sano et al. (2011) for orthopyroxene.

Figure 5. Comparison between temperatures derived from the REE-in-two-pyroxene thermometer (T_{REE}) and those calculated using the major element based two-pyroxene thermometer of Brey and Köhler (1990, T_{BKN} , assuming a pressure of 1 GPa) for abyssal and ophiolitic peridotites. For clarity, temperature ranges for abyssal peridotites reported in Liang et al. (2013) are shown as orange field. Color-coded symbols are peridotites with supra-subduction zone (SSZ), mid-ocean ridge (MOR), or subcratonic (SC) affinity. Modified from Dygert and Liang (2015)

Figure 1R

Figure 2

Figure 3

Figure 4

Figure 5