Diffusion closure temperature and age of a mineral with arbitrary extent of diffusion: theoretical formulation and applications

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Abstract

The commonly used expression of the closure temperature, T_C, of a diffusing species in a mineral, as derived by M.H. Dodson [Contrib. Mineral. Petrol. 40 (1973) 259–264], is applicable only to systems which have undergone sufficient diffusion so that even the composition at the center of individual grains is significantly removed from that established at the onset of cooling. We have extended Dodson's formulation to include cases with arbitrarily small amount of diffusion, and applied it to calculate T_C and age profiles, which would develop in single crystals of different geometries. These results permit evaluation of the extent of resetting of mineral age and of ion exchange geothermometers during cooling. The measured age profile of a mineral can also be used to constrain its cooling rate. These applications have been illustrated for the cases of garnet–biotite Fe–Mg exchange geothermometer, and the cooling age and closure temperatures of the Sm–Nd and Lu–Hf decay systems in garnet. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: crystal chemistry; crystal zoning; geologic thermometry; garnet group; *P–T–t* paths; diffusion; age

1. Introduction

The closure temperature, T_C, of a diffusing species in a mineral undergoing cooling during its transport to the Earth's surface has been a topic of considerable interest among geochronologists and petrologists. The cooling rate of a regionally metamorphosed rock, which reflects its exhumation rate, is often derived from a plot of selected mineral ages vs the closure temperatures of the specific geochronological systems in the minerals (e.g. [1,2]). The answer to the question of whether a mineral age dated by a particular decay system corresponds to the peak metamorphic age or a cooling age rests

critically on the closure temperature of the system in the particular mineral. Further, the interpretation of geothermometry and geobarometry in terms of peak metamorphic versus cooling conditions of a rock depends on the closure temperature of the compositional properties of the minerals used for these purposes.

In a seminal contribution, Dodson [3] formalized the concept of closure temperature of a diffusing species in a mineral and derived an analytical solution for T_C. Subsequently, he [4] expanded the concept to address the problem of closure temperature of slowly diffusing species, which may develop a closure temperature profile, $T_C(x)$, and thus of related variables, because the equilibration of the core with the surrounding matrix may lag behind that of

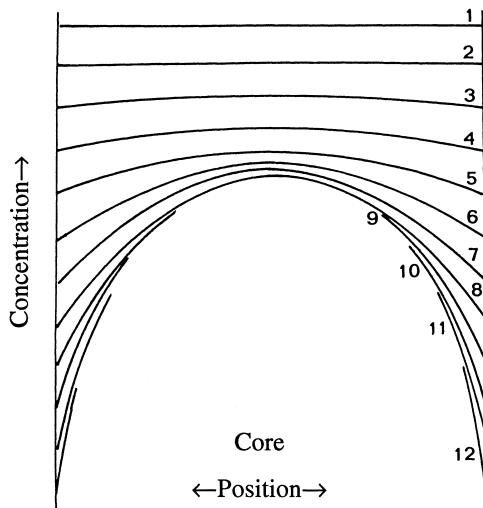* Corresponding author. E-mail: ganguly@geo.arizona.edu

Fig. 1. Successive concentration profiles in a mineral at different temperatures (*1–12*) during cooling (modified from Dodson [4]). The interface of the mineral is in equilibrium with the matrix at all stages. The increasing nonuniformity of the concentration profiles is a consequence of the time scale of diffusive homogenization in the mineral progressively lagging behind that of the change of interface composition during cooling. The quenched concentration profile preserves compositions that have developed in the mineral over a range of temperature (*8–12*).

the interface during cooling, as illustrated in Fig. 1. To simplify the derivation of analytical solutions, Dodson [3,4] assumed that the mineral of interest (a) is surrounded by a matrix which behaves as a homogeneous infinite reservoir of the diffusing species, (b) has achieved homogeneous concentration of the diffusing species at a temperature T_o at the onset of or during cooling, and (c) has a closure profile which is sufficiently removed at all points from the homogeneous state established at T_o (Fig. 1). The last assumption is implied by an imposed mathematical condition, as discussed below. In addition, the surface composition of the mineral was assumed to change linearly with time between T_o and T_C.

For a mineral such as garnet, which is the most extensively used mineral for the purpose of geothermobarometry and geochronology, the condition (c) is not usually satisfied because of its slow diffusion properties with respect to the elements that are used for these purposes [5–7]. Indeed, one often sees homogeneous core composition of the divalent cations like Fe and Mg and zoning only near the margin

in garnets exhumed from high grade metamorphic conditions (e.g. [8,9]) even when the garnet is in contact with biotite which has relatively much faster diffusion property so that the diffusion in garnet is effectively the rate-limiting step in the development of compositional zoning. For geologically reasonable cooling rates, this type of compositional zoning in a mineral with slow diffusion property implies preservation of the peak metamorphic composition at the core (cf. [10]).

In its commonly used forms, Dodson's formulations [3,4] will not be valid for the determination of closure temperatures of a diffusing species in a mineral which bear any signature of the composition developed at T_o in its quenched concentration profile. The purpose of this paper is to extend Dodson's formulations to include the case of arbitrarily limited diffusion, thus making them applicable to a wider range of petrological and geochronological problems, and then to apply the modified formulations to evaluate the closure temperatures of selected geo-thermometric and -chronological systems.

2. Review of Dodson's mathematical analysis

We start with a brief review of Dodson's [4] mathematical analysis of the closure temperature problem, retaining his symbols to facilitate comparison.

Combining eqs. 13, 14 and 15 of Dodson [4] one has:

$$Q(u, x) = 2 \sum_{n=1}^{\infty} \frac{\beta_n(x)}{\alpha_n} \left[\int_{b_n}^{\alpha_n^2(M-u)} \ln(v)\, e^{-v}\, dv \right.$$

$$\left. - \ln b_n \left(e^{-b_n} - e^{-\alpha_n^2(M-u)} \right) \right] \qquad (1)$$

where x is a normalized positional coordinate of the crystal (e.g. normalized radial distance of a spherical crystal), α_n and β_n are characteristic properties of the crystal geometry, u is a time variable defined as $u = M(1 - e^{-\Theta})$, where Θ is a dimensionless time and M is a dimensionless parameter as defined below, and $b_n = \alpha_n^2 M$. According to Dodson [4], α_n and β_n can be calculated as: (a) $\alpha_n = (n - \frac{1}{2})\pi$ and $\beta_n(x) = (-1)^{n+1} \cos(\alpha_n x)$ for plane sheet $(-1 < x < 1)$; (b) $\alpha_n \approx (n - \frac{1}{4})\pi$ and $\beta_n(x) = J_o(\alpha_n x) J_1(\alpha_n)$ for

cylinder ($J \equiv$ Bessel function); and (c) $\alpha_n = n\pi$ and $\beta_n(x) = (-1)^{n+1} \sin(\alpha_n x)$ for sphere.

For $t \to \infty$, $u \to M$, in which case the upper limit of the above integral becomes 0. Dodson [4] also showed that for $t \to \infty$, $Q = E/RT_C(x) - E/RT_o$, where E is the activation energy of diffusion. Thus, for $t \to \infty$, Eq. 1 reduces to:

$$\frac{E}{RT_C(x)} - \frac{E}{RT_o} = 2 \sum_{n=1}^{\infty} \frac{\beta_n(x)}{\alpha_n} \left[\int_{b_n}^{0} \ln(v)\, \mathrm{e}^{-v}\, \mathrm{d}v \right.$$
$$\left. + \ln b_n \left(1 - \mathrm{e}^{-b_n} \right) \right] \qquad (2)$$

At this point Dodson imposed the condition $M \gg 1$ (i.e. b_n very large) so that the integral in Eq. 2 effectively equals the Euler constant C (which is $0.5772157\ldots$), and the last exponential term becomes insignificant. Thus, one obtains:

$$\frac{E}{RT_C(x)} - \frac{E}{RT_o} = 2 \sum_{n=1}^{\infty} \frac{\beta_n(x)}{\alpha_n} \left(C + \ln \alpha_n^2 + \ln M \right) \qquad (3.1)$$

The dimensionless parameter M equals $D(T_o)\tau/a^2$, where $D(T_o)$ is the diffusion coefficient at T_o, a is characteristic dimension of the crystal (e.g. radius of a spherical or a cylindrical grain and half thickness of plane sheet), and τ is a characteristic time taken for D to diminish by a factor 'e' (i.e. by $\sim 2/3$) during cooling ($D = D_o\, \mathrm{e}^{-E/RT} \equiv D(T_o)\, \mathrm{e}^{-t/\tau}$, assuming a linear change of $1/T$ vs t, i.e. $E/RT = E/RT_o + t/\tau$ or $1/T = 1/T_o + \eta t$ with $\eta = R/E\tau$). The physical implication of the condition $M \gg 1$ can be understood by noting that, from its definition, $\sqrt{M}$ is of the order of the average distance the diffusing species would travel at T_o within the time scale τ relative to the characteristic dimension of the crystal. Thus, $M \gg 1$ implies a large enough extent of diffusion to significantly affect the core composition of the crystal.

Dodson [4] showed that $\sum \beta_n/\alpha_n = 0.5$. Thus, substituting:

$$\ln M = \ln \left(\frac{D(T_o)\tau}{a^2} \right) = \ln \left(\frac{D_o \tau}{a^2} \right) - \frac{E}{RT_o} \qquad (3.2)$$

Eq. 3.1 reduces to:

$$\frac{E}{RT_C(x)} = \ln \left(\frac{\tau D_o}{a^2} \right) + \left(C + 4 \sum_{n=1}^{\infty} \frac{\beta_n(x)}{\alpha_n} \ln \alpha_n \right) \qquad (4)$$

(which is Dodson's [4] eq. 19). The quantity within the last parentheses has been defined as the 'closure function', $G(x)$, by Dodson [4].

The closure temperature T_C defined earlier by Dodson [3] is simply a weighted average of $T_C(x)$ so that:

$$\frac{E}{RT_C} = \ln \left(\frac{\tau D_o}{a^2} \right) + G \qquad (5)$$

where G is the spatially weighted average of $G(x)$. The $G(x)$ and G values are given in [4] for plane sheet, cylinder and sphere. Defining now $A = \mathrm{e}^G$, Eq. 5 becomes the classic Dodson [3] equation for closure temperature (eq. 23).

3. Extension of Dodson formulation to include systems with arbitrarily small amount of diffusion

In order to develop a general formulation of T_C which is valid for any M (i.e. arbitrary extent of diffusion), we need to add a 'correction' closure function, $g(x)$, to the right hand side of Eq. 4 so that the general expression of T_C, given by Eq. 2, is recovered. It is easy to see that this correction term must be:

$$g(x) = -2 \sum_{n=1}^{\infty} \frac{\beta_n(x)}{\alpha_n} \left[\int_{\infty}^{b_n} \ln(v)\, \mathrm{e}^{-v}\, \mathrm{d}v + \mathrm{e}^{-b_n} \ln(b_n) \right] \qquad (6)$$

The integral in Eq. 6 can be expressed as:

$$\int_{\infty}^{b_n} \ln(v)\, \mathrm{e}^{-v}\, \mathrm{d}v = \int_{\infty}^{0} \ln(v)\, \mathrm{e}^{-v}\, \mathrm{d}v + \int_{0}^{b_n} \ln(v)\, \mathrm{e}^{-v}\, \mathrm{d}v$$
$$= C + \int_{0}^{b_n} \ln(v)\, \mathrm{e}^{-v}\, \mathrm{d}v \qquad (7)$$

The last integral can be evaluated as follows (e.g. [11], eqs. 522 and 524):

$$\int_{0}^{b_n} \ln(v)\, \mathrm{e}^{-v}\, \mathrm{d}v = \left[-\mathrm{e}^v \ln v \right]_{0}^{b_n} + \int_{0}^{b_n} \mathrm{e}^{-v}\, \mathrm{d}\ln v \qquad (8)$$

and:

$$\int_0^{b_n} e^{-v} \, d\ln v = \left[\ln v - v + \frac{v^2}{2(2!)} - \frac{v^3}{3(3!)} + \dots \right]_0^{b_n}$$

$$= \left[\ln v + \sum_{m=1}^{\infty} \frac{(-v)^m}{m(m!)} \right]_0^{b_n} \qquad (9)$$

Combining Eqs. 8 and 9, we have:

$$\int_0^{b_n} \ln(v) \, e^{-v} \, dv = \left[\ln v(1 - e^{-v}) + \sum_{m=1}^{\infty} \frac{(-v)^m}{m(m!)} \right]_0^{b_n} \qquad (10.1)$$

The first term within the square bracket can be evaluated for $v = 0$ as follows:

$$\ln v(1 - e^{-v}) = -\frac{1 - e^{-v}}{\ln v}$$

Using L'Hôpital's rule:

$$\lim_{v \to 0} -\frac{1 - e^{-v}}{\ln v} = \lim_{v \to 0} -v \, e^{-v} = 0 \qquad (10.2)$$

Thus:

$$\int_0^{b_n} \ln(v) \, e^{-v} \, dv = \ln b_n(1 - e^{b_n}) + \sum_{m=1}^{\infty} \frac{(-b_n)^m}{m(m!)} \qquad (10.3)$$

which leads to:

$$g(x) = -2 \sum_{n=1}^{\infty} \frac{\beta_n(x)}{\alpha_n} \left[C + \ln b_n + \sum_{m=1}^{\infty} \frac{(-b_n)^m}{m(m!)} \right] \qquad (11)$$

This expression of $g(x)$ is to be substituted in the following expression to calculate $T_C(x)$:

$$\frac{E}{RT_C(x)} = \ln \left(\frac{\tau D_o}{a^2} \right) + G(x) + g(x)$$

$$= \ln M + \frac{E}{RT_o} + G(x) + g(x) \qquad (12)$$

For large values of b_n (corresponding to large values of M since $b_n = \alpha_n^2 M$), the convergence of the series in Eq. 11 requires extremely large number of terms causing computational problems. In evaluating the series, we have truncated the value of b_n at 10. The residual value of the series for $b_n > 10$ is negligible. This can be easily demonstrated

by referring to Eq. 6 and noting that the value of the function $\ln(v) \, e^{-v}$ essentially vanishes for large values of v. The value of the integral $\int \ln(v) \, e^{-v} \, dv$ from $b_n = 10$ to infinity is $\sim 10^{-4}$, as evaluated numerically. Comparing Eqs. 6 and 11, the numerical magnitude of the series in Eq. 11 at $b_n = 10$ is given by:

$$g(x) = -2 \sum_{n=1}^{\infty} \frac{\beta_n(x)}{\alpha_n} \left[\int_\infty^{b_n} \ln(v) \, e^{-v} \, dv + e^{-b_n} \ln(b_n) \right]$$

$$= -2 \sum_{n=1}^{\infty} \frac{\beta_n(x)}{\alpha_n} \left[-10^{-4} + e^{-10} \ln(10) \right]$$

$$\approx -10^{-4}$$

Thus, no significant error is introduced in the evaluation of $g(x)$ by truncating the series at $b_n = 10$.

We have evaluated $g(x)$ as a function of M for three different geometries, namely sphere, cylinder and plane sheet, using the expressions of α_n and β_n for these geometries. The spatially weighted mean of $g(x)$ for each geometry, denoted by g, is illustrated in Fig. 2 as a function of M. It is evident that in order for the commonly used Dodson [3] formulation of T_C to be valid, the dimensionless term M should be greater than 0.3 for sphere, 0.6 for cylinder and 1.2
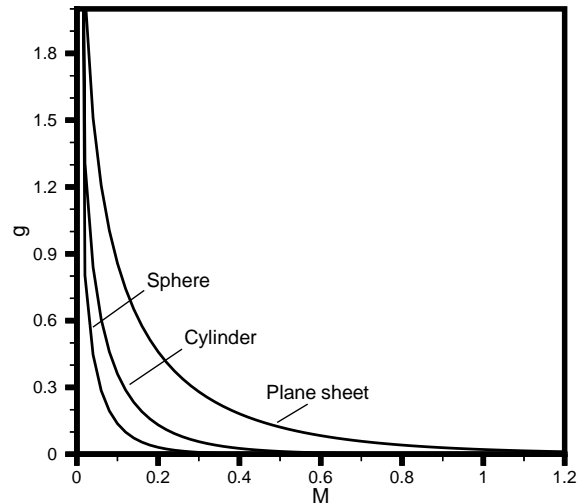

Fig. 2. Behavior of the 'correction term' g vs the dimensionless parameter M for sphere, cylinder and plane sheet. g is the spatially weighted mean of the correction closure function, $g(x)$ (Eqs. 6 and 11).
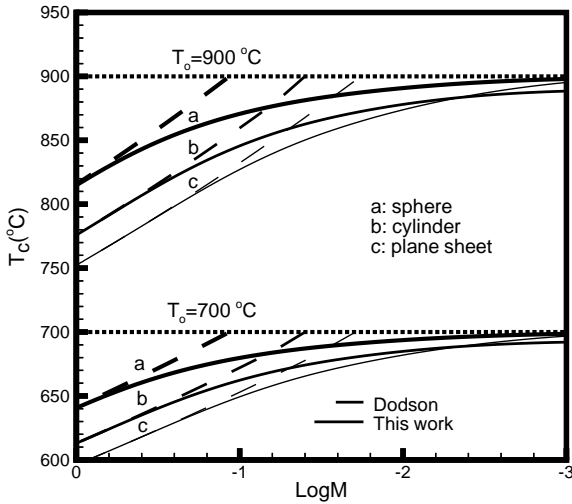
Fig. 3. The mean closure temperature, T_C, for grains with (a) spherical (heavy line), (b) cylindrical (medium solid line) and (c) plane sheet (light solid line) geometries vs $\log M$, and the commonly used form of T_C due to Dodson [3,4] (dashed lines).

for plane sheet. However, even though we demonstrate that Dodson's [3,4] specialized equations for T_C are valid for much smaller values of M than what he had originally stipulated, the composition of a crystal must still be significantly removed, even at its core, from the initial homogeneous composition established at T_o, as demonstrated later.

Using Eq. 12, we have calculated the spatially weighted mean closure temperatures for sphere, cylinder and plane sheet as functions of M and T_o. The results are illustrated in Fig. 3 for T_o of 900° and 700°C using a logarithmic scale of M. Also shown for comparison are the T_C vs $\log M$ for each geometry using the commonly used formulation of Dodson [3]. To get a feeling for the value of M in geological problems, let us consider a 2 mm diameter spherical garnet crystal which had achieved homogeneous composition at 700°C (T_o), and was then subjected to cooling at a rate of 25°C/Ma near T_o. This scenario is within the range of peak metamorphic and exhumation conditions of granulite facies rocks. If the initial T–t path of the rock conforms to a linear relation of $1/T$ vs t (in which case $\tau = -RT^2/E(dT/dt)_T$), then one obtains from the definition of M (Eq. 3.2):

$$M = -\frac{RD(T_o)T^2}{E(dT/dt)_T a^2} = \frac{RD(T_o)}{E\eta a^2} \tag{13}$$

Using the diffusion data [7] for Sm and Nd in garnet ($D_{Sm} \approx D_{Nd} = 1.79 \times 10^{-4} e^{-31039/T}$ cm^2/s), and $T \leq T_o$, we get $\log M \leq -2.0$. If the grain size increases by a factor of 2, then $\log M$ decreases by 0.60, and vice versa.

From Eq. 12, the expression for *mean closure temperature* can be written in the commonly used form of Dodson's equation ([3], eq. 23) as:

$$\frac{E}{RT_C} = \ln\left(-\frac{A'RT_C^2 D_o}{E(dT/dt)_{T_C} a^2}\right) \tag{14}$$

where $A' = e^{G+g}$. The values of G, as given in [4], are 4.0066 for sphere, 3.29506 for cylinder and 2.15821 for plane sheet (Dodson, [3] gave the values for e^G as A), while those of g can be read off Fig. 2.

4. Closure temperatures, cooling rates and geothermometry

Using Eq. 12, one can now calculate the closure temperature profile ($T_C(x)$) of a single crystal and the weighted mean closure temperature (T_C) as a function of M, T_o, and the normalized distance. Fig. 4 illustrates the results of calculations for grains with spherical and plane sheet geometries and with $T_o = 700°C$, 900°C and 1100°C. The resetting of the central composition of a garnet crystal as a function of T_o and M is illustrated in Fig. 5. As evident from Fig. 3, the T_C for a cylindrical grain will be intermediate between these two cases. The activation energy used for this calculation has been chosen to be that for Fe–Mg interdiffusion in a binary garnet with Fe/(Fe + Mg) = 0.75. The interdiffusion coefficient, D(Fe–Mg), has been calculated according to:

$$D(\text{Fe–Mg}) = \frac{D_{Fe} D_{Mg}}{X_{Fe} D_{Fe} + X_{Mg} D_{Mg}} \tag{15}$$

where D_{Fe} and D_{Mg} are the self diffusion coefficients of Fe and Mg, respectively. These self diffusion values for garnet are taken from Ganguly et al. [6], which yield $D(\text{Fe–Mg}) = 7.22 \times 10^{-5} e^{-E/RT}$ cm^2/s with $E = 266.5$ kJ/mol at 7 kbar and $X_{Fe} = 0.75$. In Fig. 4, the weighted mean closure temperature, T_C, corresponding to each $T_C(x)$ profile for spherical geometry is shown by a connected dashed line.
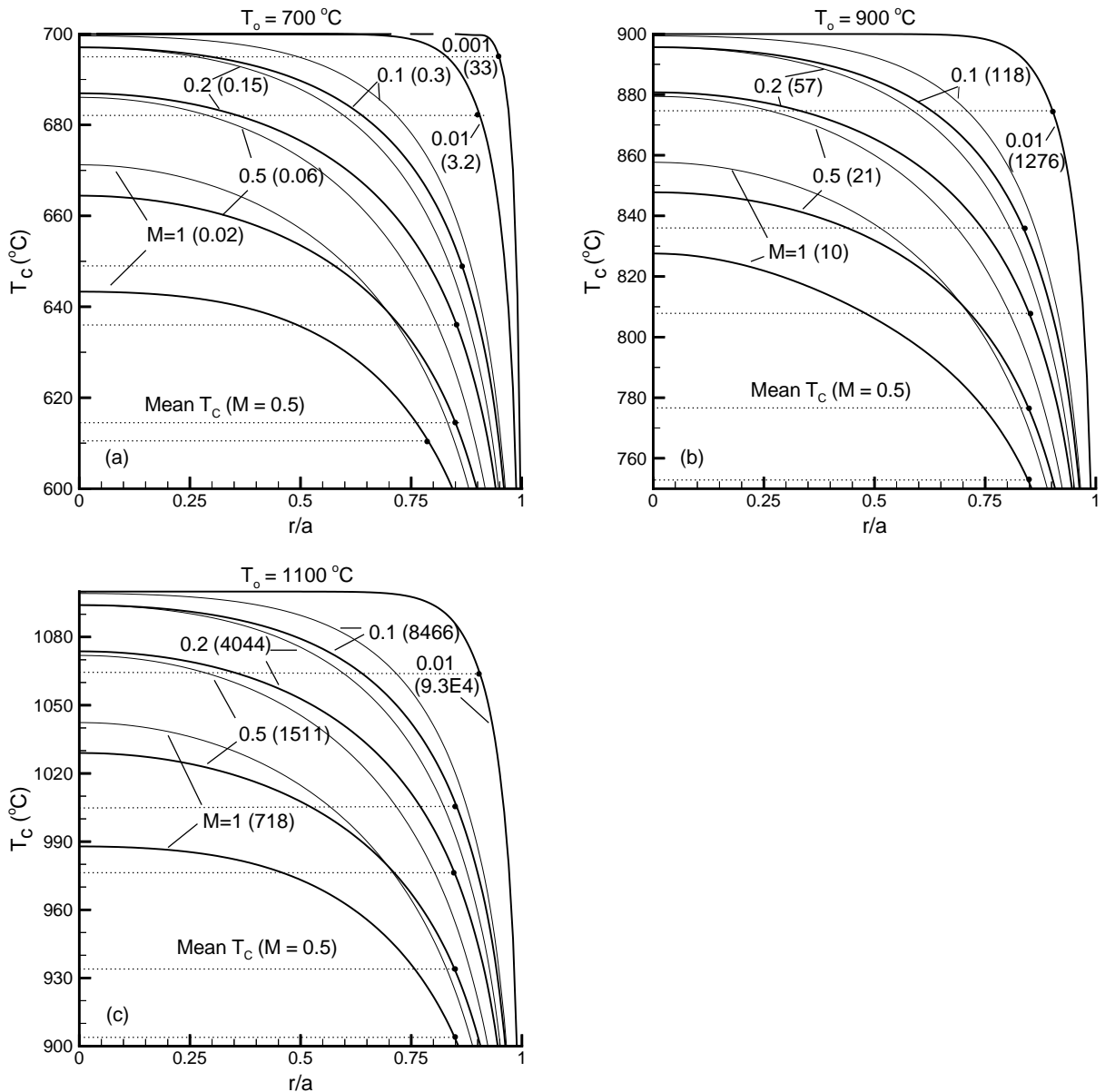
Fig. 4. Closure temperature profiles (solid lines) and weighted mean closure temperatures (dashed line) as function of M and dimensionless distance for (a) $T_o = 700$°C, (b) $T_o = 900$°C and (c) $T_o = 1100$°C for mineral with $E = 266$ kJ/mol. The closure temperature profiles for the sphere and plane sheet are illustrated by heavy and light solid lines (those for cylinder should be intermediate between these two cases). Only heavy lines are shown where these are almost indistinguishable from the light lines for a given M. The mean $T_C - s$ are only for spheres. Each mean T_C corresponds to the T_C profile to which it is connected by a heavy dot. The cooling rate (K/Ma) at the mean T_C of a spherical 2 mm diameter crystal corresponding to a specific value of M is shown in the parentheses. The cooling rate for a different grain size can be calculated from these data by noting that it varies as $1/a^2$ for a given value of M.

Assuming a linear change of $1/T$ vs t between T_o and T_C, the cooling rate corresponding to a given value of M can be calculated from Eq. 13 if the grain size is specified. As examples we have shown the cooling rates corresponding to a 1 mm characteristic length (radius for a spherical or cylindrical
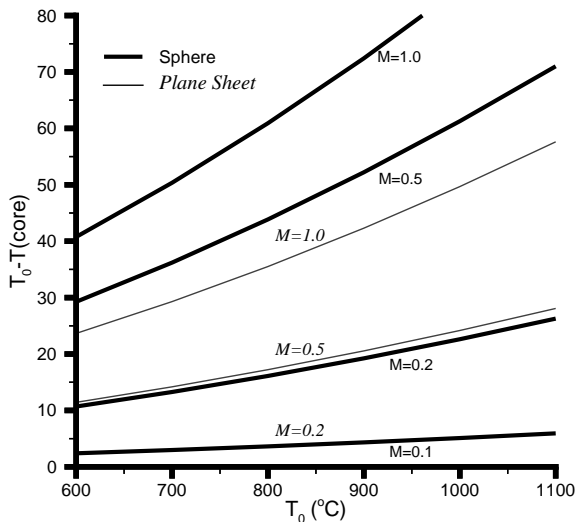
Fig. 5. Resetting of the core temperature of grains with spherical (thick lines) and plane sheet (thin lines) geometries as function of T_o and M. The activation energy of diffusion is 266 kJ/mol, which is typical of garnet in metamorphic rocks. The curves for $M = 0.1$ for sphere and $M = 0.2$ for plane sheet are overlapping. The curve for $M = 0.1$ for plane sheet grazes the horizontal axis, and is, thus, omitted from the figure.

grain and half-thickness for a plane sheet) within the parentheses beside each value of M. The cooling rate for any other grain size can be readily determined from these data noting that, according to Eq. 13, $(dT/dt)_T \alpha 1/a^2$ for a given value of M.

The temperature dependence of the Fe–Mg distribution coefficient between garnet and coexisting minerals such as biotite, orthopyroxene and clinopyroxene, constitutes some of the most widely used geothermometers [12]. However, recently questions have been raised if the Fe–Mg exchange geothermometers record peak metamorphic temperatures of high grade metamorphic rocks even when one uses the compositions around the center of a mineral grain [13,14]. The calculations presented in Figs. 4 and 5 permit us to address this problem to some extent. A garnet surrounded by biotite would effectively satisfy the condition that the crystal is surrounded by a homogeneous infinite reservoir, since D(biotite) $\gg$ D(garnet) (biotite is never zoned), and the mass of the surrounding biotite is often large enough to remain at a fixed concentration. Now, if the peak metamorphic temperature was $\sim$900°C, then a 2 mm

diameter spherical garnet crystal surrounded by biotite would not preserve the compositional signature of that temperature even at the core unless the rock had a cooling rate greater than 100°C/Ma (Fig. 4), which is unusual for a metamorphic rock. However, for $T_o \sim 700$°C, the record of the peak temperature would be preserved at the core of a similar garnet grain, even when it was subjected to extremely slow cooling. If the concentration profile of garnet were measured normal to a straight edge which is much longer compared to the length of the diffusion profile, then the proper approximation of geometry is a plane sheet, for which T_C would be somewhat higher for a given value of M and T_o (Fig. 4).

It should be noted that the retrograde adjustment of garnet composition illustrated in Figs. 4 and 5 represents the maximum possible adjustment for a given set of conditions (T_o, E and M), as the surrounding matrix has been assumed to have a diffusion coefficient of the species that is much larger than that of garnet. When a garnet is in contact with a mineral like ortho- or clino-pyroxene, in which D(Fe–Mg) is at least as slow as in garnet [15,16], the composition of garnet will readjust much more slowly for a given M. Thus, the Fe–Mg exchange thermometry using core compositions of garnet–orthopyroxene and garnet–clinopyroxene pairs may, in some cases, yield higher temperatures than those obtained from the garnet–biotite pairs in the same rock, especially if the rock had a relatively high peak metamorphic temperature. On the other hand, if it can be independently established that the temperature obtained from the garnet–biotite pair is lower than the peak metamorphic temperature (T_o), then the cooling rate of the rock can be readily obtained from the value of the dimensionless parameter M corresponding to the extent of resetting of temperature, as illustrated in Figs. 4 and 5.

Following Lasaga [10], a value of 10 for a dimensionless parameter, γ', has been assumed in some earlier studies [17,18] as the minimum value at which the initial composition would be preserved at the core of a mineral grain. The parameter γ', as defined in [10], is the inverse of the parameter M of Dodson [3,4]. The results summarized in Fig. 5 support the above assumption for the retention of core temperature in minerals with $E \approx 65$ kcal/mol.
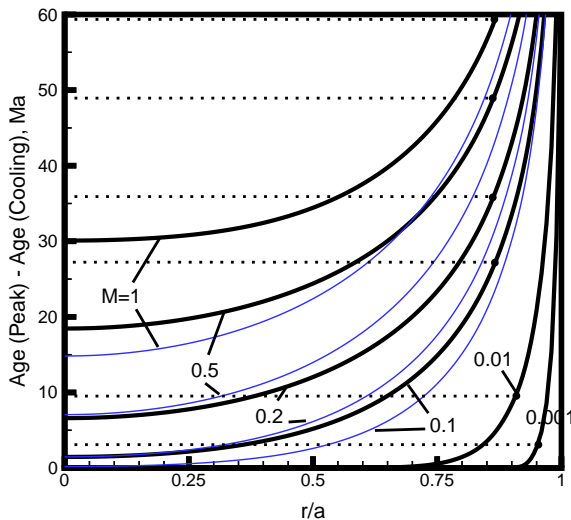
Fig. 6. Resetting of the age of crystals (Δt) with spherical (heavy solid lines) and plane sheet (light solid lines) geometries during cooling as a function of the dimensionless variable M and normalized distance for a T–t path defined by an asymptotic cooling model ($1/T = 1/T_o + \eta t$) with $\eta = 2.11 \times 10^{-6}$ K^{-1} Ma^{-1}, which corresponds to a cooling rate of 2 K/Ma at 973 K. Doubling of cooling rate causes the Δt to reduce by the same factor for a fixed M. The activation energy (E) used in these calculations is 26 kJ/mol. For a geochronological system with different activation energy (E_i) of diffusion, the value of η is given by $0.1447/E_i$.

5. Closure ages, cooling rates and geochronology

Using the relation $1/T = 1/T_o + \eta(\Delta t)$, where Δt is the elapsed time from T_o to T, Eq. 12 can be rewritten as:

$$\Delta t(x) = \frac{R}{\eta E} \left[\ln M + G(x) + g(x) \right] \qquad (16)$$

This expression permits calculation of the resetting of mineral age during cooling, as determined by a specific geochronological system. (It is interesting to note that the extent of resetting does not depend explicitly on T_o and grain size; these effects have been absorbed in M.) As an example, we have illustrated in Fig. 6 the Sm–Nd age profiles of a spherical garnet crystal relative to its homogenization age at T_o, using the available diffusion data of these elements [7], and $\eta = 2.11 \times 10^{-6}$ K^{-1} Ma^{-1}, which corresponds to a cooling rate of 2 K/Ma at 973 K ($dT/dt = -\eta T^2$). A horizontal dashed line indicates

the mean age of the grain corresponding to the age profile to which it is connected. The age profiles for a grain with the plane sheet geometry, but with the same value of activation energy as that of Nd in garnet (∼26 kJ/mol at 7 kbar, graphite buffer [7]), are also shown for comparison. Those for cylinder will be intermediate between the spherical and plane sheet geometries.

With the increased sophistication of analytical techniques, we may hope to be able to determine age profiles in the not too distant future, either by isotope dilution and thermal ionization mass spectrometry of very small quantities of samples drilled from different portions of the same grain or by SHRIMP (sensitive high resolution ion microprobe) or by laser ablation in ICP–MS (inductively coupled mass spectrometer). The cooling rate of a crystal can be determined by comparing the measured and calculated age profiles. Fig. 6 can be used for any system by noting that the calculated age profiles relate only to specific values of M and ηE. The value of ηE used in calculating Fig. 6 is 0.1447. Thus, the appropriate value of η corresponding to the age profiles in Fig. 6 for a mineral with different activation energy, E_i, is given by $0.1447/E_i$.

A further potential application of Eq. 16 and Fig. 5 lies in its usefulness in the determination of whether an average mineral age determined by isotope dilution of separated mineral grains from a rock according to a specific decay system corresponds to its metamorphic age or cooling age, if the appropriate kinetic properties and the grain size are known and one has an idea of the probable limits of the cooling rate. For example, let us consider the garnet–whole rock age of the eclogites from Dora Maira, Italy, determined recently by the Lu–Hf decay system by thermal ionization mass spectrometry [19]. There are no available diffusion data for either Lu or Hf in garnet, but our on-going study of the REE diffusion in garnet as a function of ionic size suggests that D(Lu) should be around a factor of 2 larger than that of D(Nd). The T_C for the Lu–Hf decay system in garnet should be controlled by the diffusivity of Lu as it should have a larger diffusion coefficient between the two species owing to its smaller charge, which is most unlikely to be counterbalanced by its slightly larger radius in the eight-fold coordination (Lu^{3+} = 0.848 Å; Hf^{4+} = 0.83 Å;

[20]). Thus, using the Nd diffusion data from [7] and $D(\text{Lu}) \approx 2D(\text{Nd})$, we obtain $D(\text{Lu}) \approx 5 \times 10^{-18}$ cm^2/s at the estimated $T_o = 700$ºC [19]. The average radius of garnet crystals in the Dora Maira eclogites is $\sim$2.5 mm [Duchêne, pers. comm.]. Thus from Eq. 13 we get $M \approx 0.005/(\mathrm{d}T/\mathrm{d}t)$, where the cooling rate is in the unit of K/Ma at 973 K.

Owing to the preservation of coesite inclusions in pyrope, the Dora Maira rocks are generally believed to have exhumed very rapidly. Chopin et al. [21] estimated a cooling rate of 7–15ºC/Ma at the onset of exhumation of the Dora Maira rocks. Using Eq. 13, one would, thus, estimate a value of $M < 0.001$ for these rocks. This implies (Fig. 6) a resetting of less than 3 Ma of the mean Lu–Hf age of the garnets in the Dora Maira eclogites, corroborating the independent conclusion of Duchêne et al. [19] that the mean Lu–Hf age of garnets from the Dora Maira eclogites essentially dates the high pressure metamorphic event.

6. Note

Computer programs to carry out the calculations illustrated in Figs. 4–6 are available, on request, from the authors.

Acknowledgements

Appendix A. List of symbols

C	Euler constant (0.5772157...)
D	Diffusion coefficient expressed as $D = D_o\, e^{-E/RT} = D(T_o)\, e^{-t/\tau}$ assuming $E/RT = E/RT_o + t/\tau$
E	Activation energy of diffusion
$G(x)$ and G	The closure function and the mean weighted closure function of Dodson [4]
$g(x)$ and g	The correction closure function and the mean weighted correction closure function
M	A dimensionless parameter relating cooling rate, diffusion properties and grain size, Eq. 3.2 and Eq. 13
T_o	The temperature at which a mineral has achieved homogeneous composition of the diffusing species at the onset of or during cooling
$T_C(x)$ and T	The closure temperature profile of a diffusing species in a single crystal and the mean weighted closure temperature
τ	A characteristic time by which the diffusion coefficient decreases by a factor of 'e' (i.e. by $\sim$2/3) during cooling
η	A cooling time constant (K^{-1} t^{-1}) relating time linearly to $1/T$ ($1/T = 1/T_o + \eta t$)

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