

## Closure Temperature, Cooling Age and High Temperature Thermochemistry

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**Abstract:** The concept and analytical formulations of mean closure temperature ( $\bar{T}_c$ ) and closure temperature profile in cooling geochronological systems have been reviewed along with a discussion of their limitations. The conventional approach of retrieving the average cooling rate of a rock from  $\bar{T}_c$  vs cooling age data of multiple geochronological systems, which are applied to the same sample, suffers from the problem of circular logic in that the  $\bar{T}_c$  of a given decay system itself depends on the cooling rate, especially when it falls below 10°C/Myr for many systems. It is, however possible to retrieve cooling rate of a sample, without any knowledge of  $\bar{T}_c$ , directly from (a) the extent of resetting of average mineral age during cooling and (b) the difference between the average ages of a central segment of a mineral grain and the bulk grain itself, as determined by a specific decay system. On the other hand  $\bar{T}_c$  for a specific system, grain size and geometry can be retrieved from the inferred cooling rate. These recent developments between the cooling age and cooling rate relations are reviewed in this paper.

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## 5.1 Introduction

In a broad sense thermochronology refers to determination or constraining the thermal history of rocks within a framework of absolute time that is determined by dating rocks and minerals. Most thermochronological studies deal with relatively low temperature geological and planetary processes, typically below  $\sim 500^\circ\text{C}$ . A recent volume of *Reviews of Mineralogy and Geochemistry*, edited by Reiners and Ehlers (2005), provides a thorough overview of the subject of low-temperature thermochronology and its wide ranging applications.

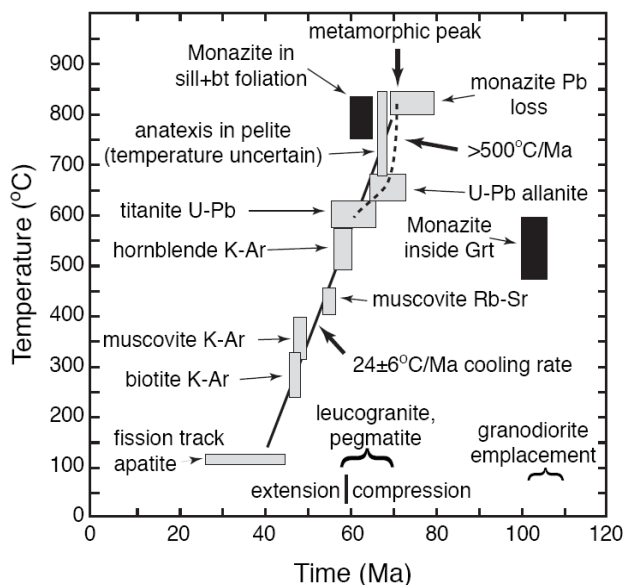
It is fair to say that quantitative thermochronological studies began with a seminal paper by Dodson (1973), which formally introduced the concept of closure temperature ( $T_c$ ) of a cooling geochronological system and provided a mathematical formulation for calculating the closure temperature on the basis of the geometry and size of the mineral grains used for dating, cooling rate of the host rock and diffusion kinetic properties of the geochronological system in the mineral of interest. The age of a mineral as determined by mineral-whole rock age or internal mineral isochron, is effectively the time lapse since the closure temperature of the mineral for the specific decay system. The mineral ages are, thus often referred to as cooling ages.

Since Dodson's paper, numerous studies have sought to constrain cooling rates of rocks on the basis of a  $T_c$  vs age

plot in which the different combinations of  $T_c$  and age, as determined by different decay systems in different minerals are collected together and fitted to obtain the average rate of change of temperature during cooling. An example of such approach is illustrated in Fig. 5.1 which is taken from Spear and Parrish (1996). An inherent circularity in this approach is that cooling rate is retrieved by assigning a  $T_c$  to a specific system in a mineral while  $T_c$  itself depends on cooling rate. Despite this circularity, cooling rate retrieved from closure temperature diagrams may provide a good first order approximation of the true cooling rate within the temperature interval encompassed by the closure temperatures, provided that several decay systems have been used to constrain it, the cooling is relatively rapid ( $>10^\circ\text{C}/\text{Myr}$ ) and sufficient uncertainties are assigned to the  $T_c$  values to reflect their variability in natural environments as function of different parameters that affect them, as discussed below. Ideally the  $T_c$  of each decay system should be recalculated using the initial value of the cooling rate and the process should be repeated until there is no significant change of the calculated  $T_c$  values for the different systems.

There are several simplifying assumptions in the Dodson (1973) formulation of closure temperature. One of the assumptions is that there is sufficient diffusive loss of the daughter product from the mineral so its concentration even at the core of the mineral is different from that at the peak thermal condition. For many geologically important systems, this "memory loss" condition is not satisfied. For example diffusivities of elements in minerals like garnet and pyroxene are too slow to affect the composition at the core during cooling unless the cooling rate is very slow and/or the grain size is very small (Ganguly et al. 1998). Ganguly and Tirone (1999) extended the Dodson formulation to include systems that did not suffer complete "memory loss" and also developed methods of determining cooling rate from cooling ages of minerals, without requiring any knowledge of their closure temperatures.

The purpose of this review is to provide a simple exposition of the concept of closure temperature in a cooling geochronological system and the methods by which one can retrieve cooling rate from knowing the average age loss of a decay system or its spatial variation within a single crystal. Within the framework of assumptions of the Dodson (1973) formulation of closure temperature, there is no formal restriction on the temperature range of application of these methods as long as the cooling is monotonic and follows a specific form. However if the average age loss is determined by such decay systems as Sm-Nd, Lu-Hf, Rb-Sr for which the parent and daughter nuclides effectively cease to diffuse at relatively high temperatures ( $>500^\circ\text{C}$ ), then one obtains cooling rates at temperatures between the peak temperature and the closure temperature of diffusion of the geochronological system. Thus the methods reviewed in this paper may be used to complement those of low temper-



**Fig. 5.1** Mineral closure temperature vs cooling age plot of a number of geochronological systems for samples from the Valhalla complex, British Columbia. The data are fitted to obtain an average cooling rate of  $24 \pm 6^\circ\text{C}/\text{Ma}$ . From Spear and Parrish (1995). With permission from J Pet (Oxford University Press)

ature thermochronology that typically yield cooling rates below 500°C.

In the numerical simulation presented in Fig. 5.2,  $T_c$  varies as a function of the radial distance within the crystal in-

## 5.2 Closure Temperature and Mineral Age

### 5.2.1 General Concept

The concept of closure temperature is illustrated in Fig. 5.2 with a numerical simulation of the spatial variation of the compositional change during cooling in a spherical mineral surrounded by a homogeneous matrix of fixed composition. The mineral is assumed to have a radius of 1 mm and to have cooled from a peak temperature ( $T_0$ ) of 900°C following an asymptotic form given by the relation (Fig. 5.2a)

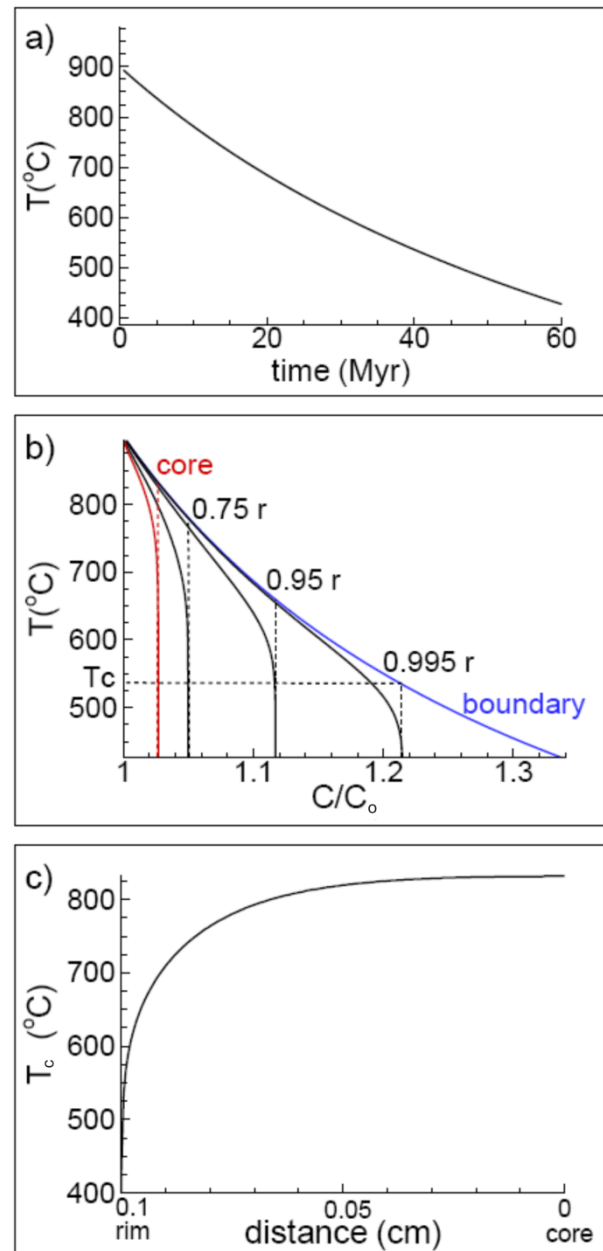
$$(1/T) = (1/T_0) + \eta t \quad (5.1a)$$

so that

$$(dT/dt) = -\eta T^2 \quad (5.1b)$$

where  $\eta$  is a cooling time constant with the dimension of  $K^{-1}t^{-1}$ . It is assumed to have a value of  $9.6 \times 10^{-6} \text{ Myr}^{-1}K^{-1}$ . As the mineral cools, a species  $i$  tends to diffuse into the mineral to maintain equilibrium with the matrix. It is assumed that the diffusion coefficient of  $i$  as a function of temperature is given by the Arrhenian relation  $D = D_0 e^{-E/RT}$ , where  $D_0 = 7.22 \times 10^{-4} \text{ cm}^2/\text{s}$  and  $E$  (activation energy) = 266 kJ/mol.

The surface composition ( $C_s$ ) of the mineral is assumed to maintain equilibrium with the matrix at all time following a prescribed relation,  $C_s/C_0 = 0.65e^{500/T}$ , where  $C_0$  is the initial concentration, which is homogeneous at  $T_0$ . However the compositional change within the interior of the grain progressively lags behind that required to maintain equilibrium with the matrix. Figure 5.2b shows the compositional change of the species within the crystal as a function of radial distance. At any given distance, the change of composition of  $i$  follows the equilibrium path up to a certain temperature, then falls off the equilibrium relation and ultimately quenches below a temperature ( $T_q$ ) where the diffusion coefficient is too small relative to the length scale of diffusion to cause any significant gain of the diffusing species (note that  $D$  decreases exponentially with temperature). The temperature corresponding to the projection of the quenched composition on to the line for equilibrium change of composition (given by  $C_s$  vs  $T$  relation) has been defined by Dodson (1973) as the closure temperature ( $T_c$ ) (Fig. 5.2b). It is different from  $T_q$ , but as long as the time interval between  $T_c$  and  $T_q$  is small, substitution of  $T_c$  for  $T_q$  does not cause any significant problem.



**Fig. 5.2** Numerical simulation of (a) cooling of a system following an asymptotic  $T$ - $t$  relation (Eq. 5.1a) with  $\eta = 9.6 \times 10^{-6} \text{ Myr}^{-1}K^{-1}$ , (b) spatial variation of change of concentration of a species during cooling within a spherical grain of 1 mm radius and (c) corresponding closure temperature profile within the crystal. The diffusion coefficient of the species is given by  $D = 7.22 \times 10^{-4} \exp(-E/RT)$  with  $E$  (activation energy) = 266 kJ/mol. The panel (b) illustrates the formal definition of closure temperature ( $T_c$ ) at any radial distance within the crystal.  $C_0$  stands for the initial concentration that is established at the peak temperature

creasing smoothly towards the center (Fig. 5.2c). Thus instead of a discrete closure temperature, there is a closure temperature profile,  $T_c(x)$ . The magnitude of change of  $T_c(x)$  as function of distance depends on the factors that control the diffusive loss of the species of interest from the mineral, namely  $D$ , grain size,  $T_0$  and cooling rate. One can also speak of mean closure temperature,  $\bar{T}_c$  which represents a weighted average of  $T_c(x)$ .

If the diffusing species represent the parent and daughter nuclides of a decay system (e.g. Sm-Nd system), then the age of a mineral effectively represents the elapsed time since the average closure temperature,  $\bar{T}_c$  of the system in the mineral. If there is significant variation of closure temperature as function of distance within a mineral, then there is also a corresponding age profile, in which case the age of a mineral determined by thermal ionisation mass spectrometry represents its average age.

### 5.2.2 Dodson Formulation

Dodson (1973) derived an expression for the weighted average of the closure temperatures,  $\bar{T}_c$  of a geochronological system as

$$\frac{E}{R\bar{T}_c} = \ln \left( - \frac{AR\bar{T}_c D_0}{Ea^2 (dT/dt)_{@T_c}} \right) \quad (5.2)$$

where  $a$  is a characteristic grain dimension (radius for sphere and cylinder, and half-length for a plane sheet),  $R$  is the gas constant,  $D_0$  is the pre-exponential factor in the Arrhenian expression of diffusion coefficient and  $A$  is a geometric factor that is given by

$$A = e^G \quad (5.2')$$

where  $G = 4.0066$  for sphere,  $3.29506$  for cylinder and  $2.15821$  for plane sheet.

It is, however often overlooked that the cooling rate in the above expression refers to that at  $\bar{T}_c$ . It can be replaced by cooling rate at any other temperature,  $T'$ , by replacing  $\bar{T}_c$  with  $T'$  on the right hand side. (According to Eq. 5.1b) the cooling rates (CR) at any two temperatures, say  $T_0$  and  $T'$  are related according to the square of their ratio, e.g.  $(CR)_{@T_0}/(CR)_{@T'} = (T_0/T')^2$ . Subsequently Dodson (1986) derived an expression of closure temperature profile, which is discussed below along with a modification of his formulation.

The important assumptions underlying Dodson's formulations of closure temperature (Dodson 1973, 1986), which is restricted to minor or trace components (a condition that is satisfied by a geochronological system) are:

(a) The mineral of interest has a homogeneous distribution of the parent and daughter nuclides at the peak thermal condition

(b) It is surrounded by a sufficiently large mass of fast diffusing matrix so that the composition of the matrix remains effectively homogeneous and fixed

(c) The surface composition of the mineral is in equilibrium with the matrix during cooling and changes uniformly with time

(d) The cooling is monotonic and follows the form of Eq. 5.1

(e) The mineral is isotropic with respect to diffusion and, as mentioned above

(f) The mineral has suffered a complete "memory loss" of its concentration of radiogenic daughter product established at  $T_0$ .

The last assumption makes the closure temperature independent of  $T_0$ . This critical assumption underlying Dodson (1973, 1986) formulation has, however been overlooked in numerous applications of his formulation (Eq. 5.2) to calculate  $\bar{T}_c$  of a geochronological system.

In order to discuss further developments, it is convenient at this stage to introduce a dimensionless parameter,  $M$ , the square root of which may be viewed as the diffusion distance within a grain, normalised by the grain size. The original expression of  $M$  given by Dodson (1973) may be recast in the following form (Ganguly and Tirone, 1999).

$$M = - \frac{RD(T_0)T^2}{Ea^2 (dT/dt)_{@T}} = \frac{RD(T_0)}{E\eta a^2} \quad (5.3)$$

where  $D(T_0)$  is the diffusion coefficient at  $T_0$ .

The closure temperature formulation of Dodson (1973) is valid only for a sufficiently large value of  $M$  so that the original concentration of the daughter product at the peak temperature is not preserved even at the core of the mineral grains. Ganguly and Tirone (1999) showed that the threshold values of  $M$  are  $\sim 0.3$  for sphere,  $\sim 0.5$  for cylinders and  $\sim 1.1$  for plane sheet. Thus one needs to evaluate if the system has an  $M$  value greater or equal to the appropriate threshold value if the average closure temperature is to be determined from Eq. 5.2. Also, in as much as the common practice is to determine cooling rate from  $\bar{T}_c$  vs cooling age data of multiple geochronological systems applied to the same rock (Fig. 5.1), one should at least evaluate  $M$  from the retrieved cooling rate to test if it has a value greater than the appropriate threshold value given above, if  $\bar{T}_c$  values are calculated according to Eq. 5.1.

### 5.2.3 Extension of Dodson Formulation by Ganguly and Tirone

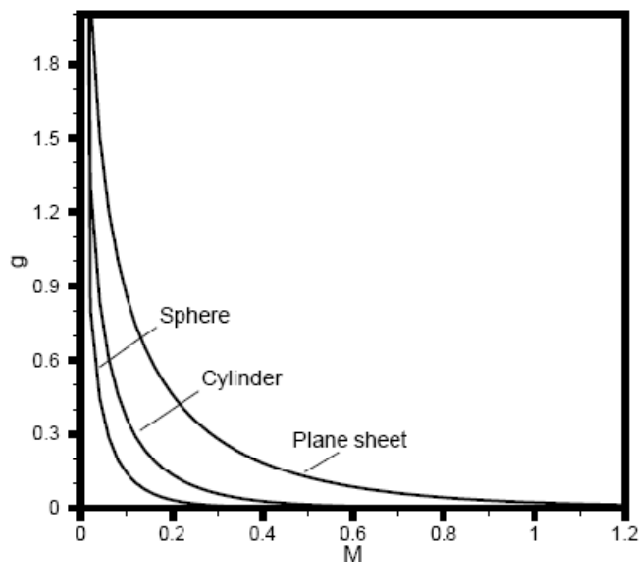
When the concentration of a species established at  $T_0$  is preserved within a mineral grain, which is a quite common situation both in terrestrial and planetary samples, the classic Dodson formulation would yield erroneously high value of  $\bar{T}_c$ . As stated by Dodson (personal communication) "... calculated closure temperatures which come out close to the peak metamorphic temperatures are bound to be in error to some extent." Many closure temperature calculations in the literature are indeed erroneously too high because these were calculated on the basis of Dodson (1973) formulation without regard to the condition of critical diffusive loss of the daughter product, as discussed above.

Ganguly and Tirone (1999) modified the Dodson (1973) formulation so that it becomes applicable to any system regardless of the extent of diffusive loss of daughter products. They showed that the desired modification results in the replacement of the geometric term  $A$  in Dodson's formulation (Eq. 5.2) by  $A'$  that is given by  $A' = e^{G+g}$ . The term  $g$ , which we would refer to as a "memory function", depends on both  $M$  and the shape or geometry of the mineral grains (Fig. 5.3). In other words  $g$  depends on size and geometry of the grain, cooling rate,  $T_0$  and the volume diffusion property of the species of interest. In terms of  $M$ , one can express the closure temperature at a given position within a mineral grain,  $T_c(x)$  (Fig. 5.2), according to Ganguly and Tirone (1999),

$$E/[RT_c(x)] = \ln M + (E/RT_0) + G(x) + g(x) \quad (5.4)$$

where  $G(x)$  and  $g(x)$  are respectively, a spatially dependent geometric term called "closure function" by Dodson (1986) and a spatially dependent "memory function". Values for  $G(x)$  within a single crystal as function of distance normalised by the grain size, as well as their mean values, are given by Dodson (1986) for spherical, plane sheet and cylindrical geometries. Note from the last expression that incorporation of the "memory effect" has introduced a dependence of  $T_c$  on  $T_0$ , which is unlike the expression of  $T_c$  in the classic Dodson (1973) formulation (Eq. 5.2). The expression of  $T_c(x)$  derived by Dodson (1986) is the same as the last expression except that it does not have the  $g(x)$  term.

If the mean value of the "memory function" is negligible, then combination of Eqs. (5.3) and (5.4) and substitution of mean  $G$  for  $G(x)$  yield the general form of the classic Dodson (1973) expression for  $\bar{T}_c$  (Eq. 5.2). In this case, the cooling rate on the right is defined at any arbitrary temperature,  $T'$  that appears in the right hand numerator instead of  $\bar{T}_c$ . Dodson (1973) specialised the general expression by substituting  $\bar{T}_c$  for  $T'$ .

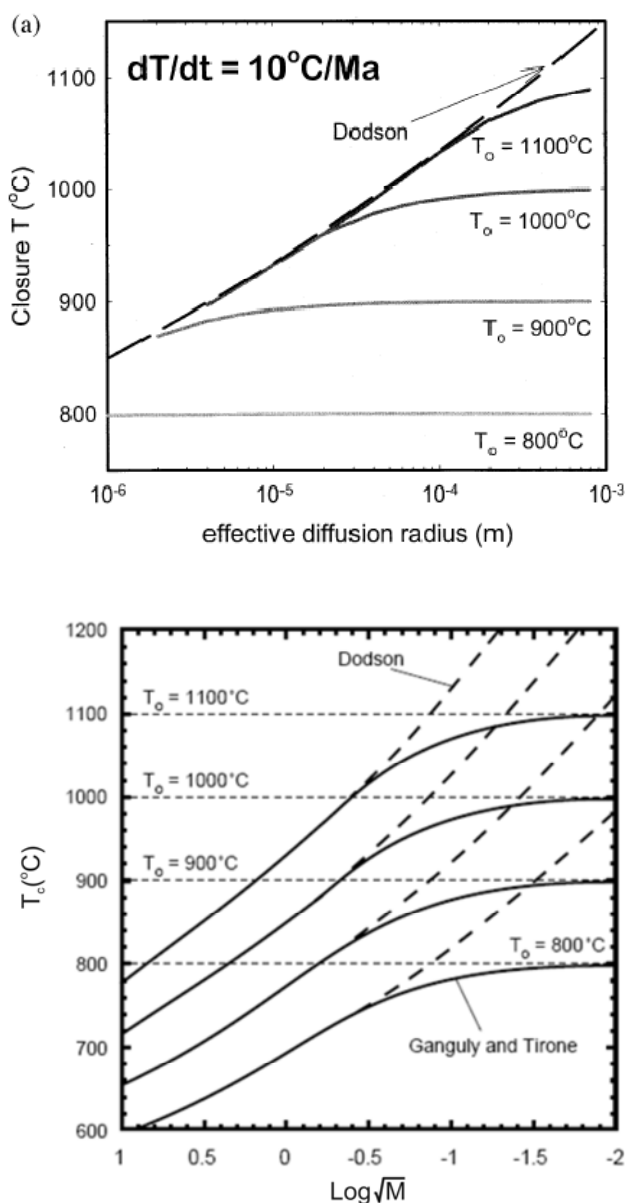


**Fig. 5.3** Variation of the "memory function"  $g$  used in the modification of Dodson (1973) formulation of closure temperature as function of the dimensionless parameter  $M$  (Eq. 5.3) and grain geometry. From Ganguly and Tirone (1999). With permission from EPSL (Elsevier)

Ganguly and Tirone (1999) derived an analytical expression for  $g(x)$ . Using that formulation, Ganguly and Tirone (2001) calculated values of  $g(x)$  that are averaged over normalised distances of 0.25, 0.5 and 1.0 from the center of a crystal of a specific geometry (sphere, cylinder and plane sheet) and presented the data in tabular form as function of  $M$ .

Figure 5.4a shows  $\bar{T}_c$  vs grain size for a cooling rate of  $10^\circ\text{C}/\text{Myr}$  (at  $\bar{T}_c$ ) for Pb diffusion on monazite, as calculated by Cherniak et al. (2004) using both Dodson (1973) formulation, and its extension by Ganguly-Tirone (1999), which may be referred to as Dodson-Ganguly-Tirone or DGT formulation. Figure 5.4b shows a comparison of the  $\bar{T}_c$  - s of spherical grains according to the two formulations as function of the dimensionless variable  $M$  (Ito and Ganguly, 2005). From the latter diagram one can calculate  $\bar{T}_c$  for any geochronological system for any combination of grain size and cooling rate, provided that the  $T_0$  values correspond to those used in the calculations.

To reiterate, in general  $T_c$  depends on  $T_0$ . However  $T_c$  becomes independent of  $T_0$  (Fig. 5.4a) when the system has suffered a critical amount of diffusive loss of the daughter product. In Fig. 5.4, the domain of validity of the Dodson (1973) formulation is restricted to grain size or  $M$  values below those marking the points of its divergence from the modified formulation by Ganguly and Tirone (1999). Note



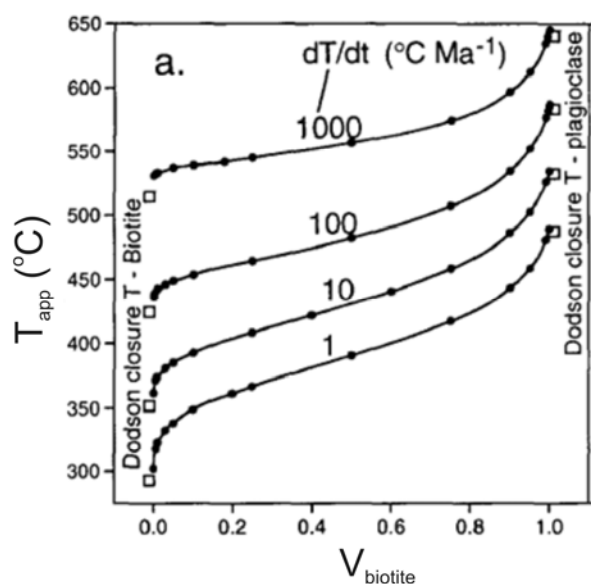
**Fig. 5.4** Comparison of average closure temperatures according to the conventional Dodson (1973) formulation with the modified formulation by Ganguly and Tirone (1999). (a) Pb diffusion in monazite for a fixed cooling rate of 10°C/Myr and different initial temperatures,  $T_o$  (from Cherniak et al. 2004); (b)  $T_c$  vs the dimensionless variable,  $M$  (Eq. 5.3) (from Ito and Ganguly, 2006). The domain of validity of the Dodson (1973) formulation is restricted to (a) grain size or (b)  $M$  values marking the point of divergence from the modified formulation by Ganguly and Tirone (1999). With permission from EPSL (Elsevier)

that the Dodson closure temperatures exceed  $T_o$  at grain size and  $M$  values somewhat above the threshold values. Values of  $T_c$  greater than  $T_o$  were erroneously calculated by some workers in the literature (Ganguly and Tirone 2001, for discussion of the results of Göpel et al. 1994).

### 5.2.4 Effects of Modal Abundance and Nature of Matrix Phase

As stated above the closure temperature formulation of Dodson (1973) and its subsequent modification by Ganguly and Tirone (1999, 2001) assume that the matrix is homogeneous and effectively infinite. Analytical formulation of  $\bar{T}_c$  under condition of a homogeneous but finite matrix (i.e. matrix of limited mass but sufficiently rapid diffusion property so that it changes composition during cooling, but remains homogeneous) has not been developed yet. However Jenkin et al. (1995) explored the problem numerically for a biotite-plagioclase assemblage and showed that the  $\bar{T}_c$  for the Rb-Sr system changes non-linearly between the Dodson  $\bar{T}_c$ 's of the two minerals as function of their modal abundances (Fig. 5.5). Since the system consists of only two minerals, there is only one  $\bar{T}_c$ , denoted as  $T_{app}$ , since both minerals must close simultaneously (in a binary system, the composition of a mineral cannot change if the other phase is closed). In the limits of biotite surrounded by a semi-infinite matrix of plagioclase ( $V_{biotite} \sim 0$ ) and the reverse ( $V_{biotite} \sim 1$ ),  $T_{app}$  approaches  $\bar{T}_c$  (biotite) and  $\bar{T}_c$  (plagioclase) of Dodson (1973), respectively.

The expected effect of the nature of matrix phase on closure temperature has been demonstrated by Burton et al. (1995) in their geochronological study of a garnet bearing coronite from Gaupås in the Bergen Arcs, western Norway.



**Fig. 5.5** Variation of Rb-Sr closure temperature in an assemblage consisting of biotite and plagioclase as function volume fraction of biotite,  $V_{biotite}$  and cooling rate, as calculated numerically by Jenkin et al. (1995)

They showed that the Sm-Nd ages of different parts of a garnet crystal are different, depending on the nature of the adjacent matrix phases, which implies that closure temperature for Nd diffusion within garnet depends on the nature of matrix phase, as expected.

### 5.2.5 Effect of Diffusion Anisotropy

Diffusion in non-cubic minerals is expected to be anisotropic and has indeed been found to have significant dependence on crystallographic orientation of diffusion direction in a number of anisotropic minerals (e.g. Chakraborty [1997]; Ito and Ganguly [2004, 2006]; Ganguly et al. [2007]). Ito and Ganguly (2006) and Ganguly et al. (2007) have shown variation of closure temperature as a function of crystallographic orientation of the direction of diffusive loss in olivine and orthopyroxene, respectively. In general, however the Dodson (1973) or the DGT (1999, 2001) formulation is inadequate to treat the problem of bulk closure temperature for minerals with significant diffusion anisotropy. It is anticipated that such a formulation would not only involve grain size, but also an aspect ratio. Diffusion may be very fast in one direction compared to that in other directions, but the diffusive loss in the fast direction may be small because of relatively much larger length scale for diffusive loss along that direction.

## 5.3 Thermochronology

### 5.3.1 Resetting of Bulk Mineral Age

Equation (5.4) enables one to calculate cooling rate of a mineral from knowledge of the difference between

(a) Its bulk cooling age, as determined by a specific decay system, and age at the peak thermal condition (Ganguly et al. [1998]; Ganguly and Tirone [2001]) or

(b) Its core and bulk ages (Ganguly and Tirone [2001]; Ducea et al. [2003]).

These methods, which have been developed by Ganguly and Tirone (1999, 2001) are presented below. As noted above, these methods are not restricted to any particular range of temperature, and thus may be used to fill the gap of thermochronological methods in the high temperature domain if these are used for decay systems with relatively slow diffusion property.

From Eq. 5.4, we have

$$\frac{E}{R} \left( \frac{1}{\bar{T}_c} - \frac{1}{T_o} \right) = \ln M + G + g \quad (5.5)$$

where the geometric term  $G$  and the “memory function”  $g$ , are for the bulk crystals of specific geometries. The bulk values of  $G$  for crystals of three different geometries, namely, spherical, cylindrical and plane sheet are given above (Eq. 5.2’), whereas those of  $g$  for the bulk crystal are given by Ganguly and Tirone (2001) as function of  $M$  for the same geometrical shapes.

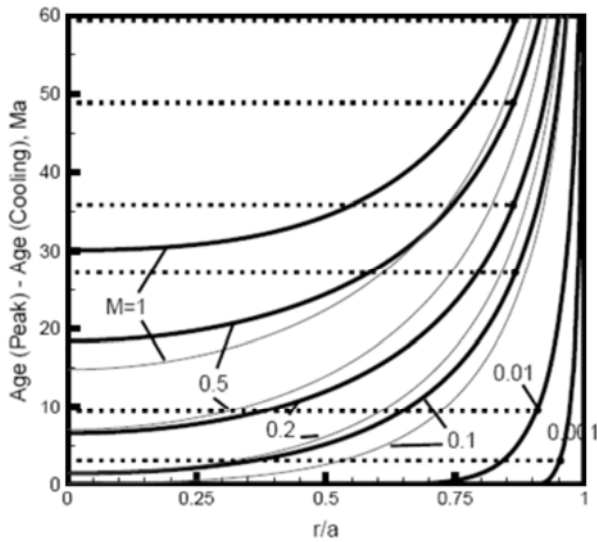
If  $\Delta t$  represents the extent of resetting of a bulk mineral age (i.e. the time lapse between  $T_o$  and  $\bar{T}_c$ ), as determined by a specific decay system, then we can write  $\Delta t = \text{Age}$  since  $T_o - \text{Age}$  since  $\bar{T}_c$ . Thus using Eq. 5.1a, the above expression may be written as

$$\Delta t = R/\eta E [\ln M + G + g] \quad (5.6)$$

Note that  $M$  is a function of the cooling time constant  $\eta$  (Eq. 5.3), whereas  $g$  is a function of  $M$ . If the peak temperature,  $T_o$ , grain size and diffusion kinetic properties determining the closure of the decay system in the mineral of interest are known, then both  $M$  and  $g$  can be determined by specifying  $\eta$  and crystal geometry, according to Eq. 5.3 and the tabulation of bulk  $g$  values as function of  $M$  and grain geometry given by Ganguly and Tirone (2001). If  $\Delta t$  for a specific decay system and mineral is known (e.g. for Sm-Nd age of garnet in a given rock), then one can determine  $\eta$  numerically by varying its value until the right hand side of the above equation yields the estimated value of  $\Delta t$ . This method has been applied (e.g. Ganguly et al. [1998]; Ito and Ganguly [2006]; Ganguly et al. [2007]; Shearer et al. [2000]) to determine the cooling rates of both terrestrial and planetary samples at relatively high temperatures. In this approach, one needs to know the age since the peak temperature from either whole rock age or mineral age by using another geochronological system, such as U-Pb system, that is characterised by very slow diffusion kinetic property leading to its closure at nearly the peak thermal condition.

### 5.3.2 Spatial Variation of Age Within a Crystal

In the absence of any knowledge of age since  $T_o$ , one can retrieve the cooling rate from the spatial variation of age or age profile, within a single crystal. The assumptions behind this approach are the same as for Dodson (1973, 1986) formulations, as summarised above, except that it does not require the condition of critical “memory loss” (condition (f)). An example of such age profiles as function of the dimensionless parameter  $M$  in crystals with spherical and plane sheet geometries (Ganguly and Tirone, 1999), is



**Fig. 5.6** Simulated cooling age profiles within single crystals of spherical (heavy black lines) and plane sheet (light blue lines) geometries as function of the dimensionless variable,  $M$  (Eq. 5.3) and normalised distance from the center. The cooling age profiles are relative to the age at the thermal peak. From Ganguly and Tirone (1999). With permission from EPSL (Elsevier)

shown in Fig. 5.6. The activation energy ( $E$ ) for diffusion is assumed to be 260 kJ/mol, which is approximately that for Nd diffusion in garnet (Ganguly et al. 1998). The mean ages corresponding to different age profiles for spherical geometry are shown by horizontal dashed lines.

If it is possible to determine age profile within a mineral grain, then one can calculate the value of  $M$  corresponding to the observed profile, and from that the cooling rate according to Eq. 5.3. However determination of age profile within a mineral does not seem to be a realistic goal within foreseeable future. It is more practical to determine the average age of a central segment and the average bulk age of a mineral using a single geochronological system. These ages can be used to derive cooling rate of a mineral as follows. Indeed Dodson (1986) suggested this possibility, but required a knowledge of  $E$  and  $\bar{T}_c$ . However as discussed below, the cooling rate can be determined from the difference between average core and average bulk ages without any knowledge of  $\bar{T}_c$ .

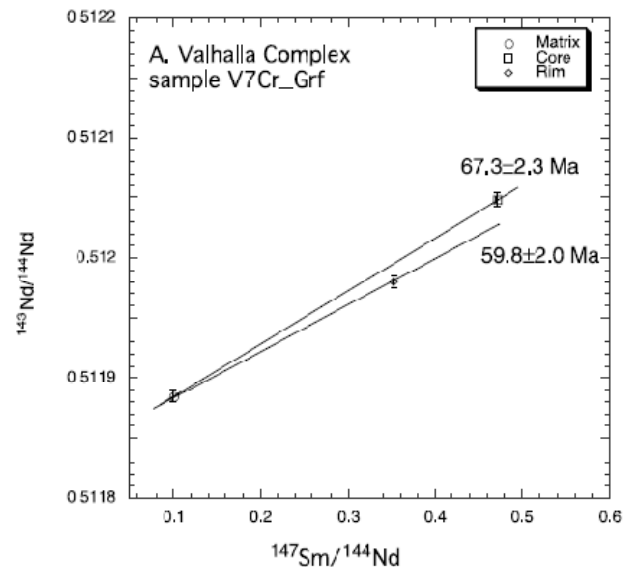
From Eqs. (5.1) and (5.5), the difference between the average central segment and bulk ages,  $\Delta\Gamma$ , is given by (Ganguly and Tirone, 2001)

$$\Delta\Gamma = -(R/\eta E) (\Delta G + \Delta g) \quad (5.7)$$

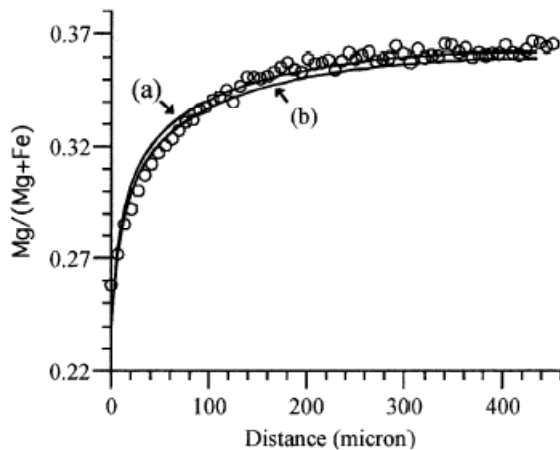
where  $\Delta$  stands for the difference of the specified quantity between its weighted average value at a central domain

of known dimension and for the bulk crystal (e.g.  $\Delta\Gamma = \text{average Age [central segment]} - \text{average Age [bulk grain]}$ ). The values of  $G$  and  $g$ , averaged over specified central dimensions and for the bulk crystal of different geometries (sphere, cylinder and plane sheet), are given by Ganguly and Tirone (2001). As for Eq. 5.6, the above equation is solved for  $\eta$  by successive approximations so that the right hand quantity equals the observed difference between the central and bulk age of a single crystal, as determined by a single geochronological system.

Ducea et al. (2003) applied the above method to determine the cooling rate of the granulite facies rocks from the metamorphic core complex in Valhalla, British Columbia. The cooling rate of these rocks were determined earlier by Spear and Parrish (1996) using the conventional  $\bar{T}_c$  vs mineral age relations of multiple geochronological systems (Fig. 5.1). Ducea et al. (2003) selected a large garnet crystal and drilled from it a circular central segment of normalised radius of 0.4 for mass spectrometric analyses of  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  isotopic ratios. The data, which are illustrated in Fig. 5.7, yield a central segment-whole rock age of 67.3 ( $\pm 2.3$  Ma). In contrast, the rim-whole rock and bulk crystal-whole rock Sm-Nd ages were found to be 59.8 ( $\pm 2.0$ ) and 60.9 ( $\pm 2.1$ ) Ma, respectively. Using the difference between the central segment-whole rock and bulk crystal-whole rock ages ( $6.4 \pm 3.1$  Myr) and the appropriate data for the spatially averaged values of  $\Delta G$  and  $\Delta g$  from Ganguly and Tirone (2001),  $T_o = 820^\circ\text{C}$ , as determined from geothermometry (Spear and Parrish, 1996)



**Fig. 5.7** Whole rock matrix, core and rim Sm-Nd ages of a garnet single crystal from the Valhalla complex, British Columbia (From Ducea et al. 2003). With permission from EPSL (Elsevier)



**Fig. 5.8** Compositional zoning (circles) of Mg in a garnet crystal from the Valhalla complex, British Columbia, which was subjected to core-rim Sm-Nd dating (Fig. 5.7). The solid lines are fits to the measured zoning profile assuming that the profiles developed during cooling from a peak temperature of 830°C at 8 kbar pressure. Curve (a) is an optimised fit to the data according to the numerical solution of the diffusion equation incorporating the effect of changing interface equilibrium during cooling, and assuming a non-linear cooling model (Eq. 5.1). The curve (b) is calculated by forcing the profile to better fit the data near the interface. With permission from EPSL (Elsevier)

and Nd diffusion data in almandine garnet (Ganguly et al. 1998), Ducea et al. (2003) solved Eq. 5.7 to obtain a value of  $\eta = (5.1-8.3) \times 10^{-6} \text{ K}^{-1}\text{Myr}^{-1}$ . Using Eq. 5.1 and assuming a monotonic cooling, one can now calculate a T-t path or cooling rate as a function of temperature. The initial cooling rate is found to be 6–10°C/Myr.

Ducea et al. (2003) also determined the cooling rate of the sample by modelling the retrograde Fe-Mg zoning that developed in the same garnet crystal (Fig. 5.8). They found that the measured zoning profiles could be fitted very well using  $\eta = (3.6-4.8) \times 10^{-6} \text{ K}^{-1}\text{Myr}^{-1}$  that yields initial cooling rate of 4–6°C/Myr. These results are in agreement with the cooling rate retrieved from the Sm-Nd age data of the garnet crystal.

The numerical programme used to fit the data allows for the effect of changing interface equilibrium during cooling. In addition, the programme allows for the effect of crystallisation/resorption of the mineral during cooling through an interlinked optimisation programme that permits variation of crystal size during cooling, along with a prescribed uncertainty of the initial composition of the crystal, which is assumed to be homogeneous. It is found that the best match to the observed retrograde profile is obtained with a fixed crystal size and initial concentration given by the quenched core composition of the garnet crystal.

Using an error of  $\pm 30^\circ\text{C}$  for  $T_0$ , the range of initial cooling rate inferred from the core and bulk Sm-Nd age data of garnet expands to 4–13°C/Myr, whereas that inferred from retrograde zoning to 2–13°C/Myr. These cooling rates are slower than that ( $24 \pm 6^\circ\text{C/Myr}$ ) deduced by Spear and Parrish (1996) from the closure temperature vs cooling age relations (Fig. 5.1). These workers have also discussed the tectonic implication of the relatively rapid cooling rate that they have deduced. As suggested by Ducea et al. (2003), a consensus temperature of 15–20°C/Myr would seem to roughly satisfy the cooling rates inferred by Ducea et al. (2003) and Spear and Parrish (1996), and would not affect the tectonic scenario presented by Spear and Parrish (1996). However in view of good agreement between the relatively slower cooling rates derived by two independent methods, namely spatial variation of Sm-Nd age of garnet and retrograde Fe-Mg zoning of the same crystal, further study of the cooling rate of Valhalla complex seems warranted.

## 5.4 Selection of Mineral Grains for Dating

For constraining cooling rate from mineral ages, whether it is from the conventional  $T_c$  vs cooling relation (Fig. 5.1) or from the thermochronological methods described above, one must ensure that (a) the mineral had a homogeneous composition of the daughter product at the peak temperature, (b) the only process significantly affecting the mineral age was cooling and (c) there was no significant growth/resorption or recrystallisation of the mineral grains. Conventional age determination by isotopic analyses of crushed mineral grains in a thermal ionisation mass spectrometer cannot, however serve these objectives. However the crystallisation/resorption history of the mineral may be understood by taking compositional profiles of major (Fig. 5.8) and/or minor elements in an electron microprobe. If the compositional maps show complex compositional patterns of the elements forming a decay system, or of major elements when mapping of the desired minor elements is not feasible, then the crystals may not be suitable for the determination of cooling age that can be related to a closure temperature, as calculated from the Dodson (1973) formulation or its extension (Ganguly and Tirone, 1999).

Geochronologists should keep track of the size of the mineral grains that are used to determine average mineral ages. The closure temperature must always be calculated from the average grain size of the minerals. Geochronologists should also carefully examine the nature and abundance of the matrix phases of the target mineral that is being dated.

In summary, age determination should be preceded by a careful examination of the target mineral and its surroundings by optical microscope and electron microprobe. In this connection it should be noted that even if a target mineral is

not surrounded by minerals with very fast volume diffusion properties, the condition of a fast diffusing matrix may be satisfied when the matrix phases are fine grained because of rapid grain boundary diffusion and small length scale of volume diffusion required for the homogenisation of the matrix grains (e.g. Liermann and Ganguly, 2001; Ganguly et al. 2001).

## 5.5 Conclusions

For minerals that have not suffered a critical amount of diffusive loss of the daughter product, which needs to be determined from calculation of the dimensionless parameter,  $M$ , as discussed above, calculation of closure temperature according to the classic Dodson (1973) formulation would yield erroneously high values (Fig. 5.4), the extent of which depends on the value of the dimensionless variable,  $M$  (Eq. 5.3), and crystal geometry (Ganguly and Tirone [1999, 2001]).

In addition to cooling rate, grain size and diffusion kinetic property of the decay system, which have been considered explicitly in the Dodson formulation, the bulk closure temperature of a mineral also depends on the nature and modal abundance of the matrix phases, and diffusion anisotropy in non-cubic minerals.

## 5.6 References

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The cooling rate of a rock can be deduced from the cooling age of a mineral without requiring any knowledge of its closure temperature, thus avoiding the circular logic inherent in the use of  $\bar{T}_c$  vs cooling age data to retrieve cooling rate. The cooling rates can be determined from the bulk cooling age of a mineral if the age since the peak temperature of the rock is known or from the difference between average core and bulk ages of a single crystal, as determined by a single decay system. However using Eq. 5.1a, the closure temperature of a sample for a decay system may be calculated from the cooling rate data and resetting of age of the decay system during cooling. In this procedure, one needs to simply replace  $T$  by  $T_c$  and  $t$  by  $\Delta t$  (i.e. time lapse between  $T_o$  and  $T_c$ ) in Eq. 5.1a and solve for  $T_c$  using the inferred  $\eta$  value.

It is important to carry out careful optical microscopic examination of the rock sample and electron microprobe analysis of the target mineral to ensure that various assumptions that underlie the closure temperature and thermochronology formulations are approximately satisfied.

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