

THERMAL HISTORY: A new software to interpret diffusive zoning profiles in garnet[☆]

Jörg Robl^{*}, Stefan Hergarten, Kurt Stüwe, Christoph Hauzenberger

Institut für Erdwissenschaften, Universität Graz, Heinrichstr. 26, A-8010 Graz, Austria

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Abstract

Mineral grains can record the cooling history of metamorphic terrains by preserving characteristic chemical zoning profiles caused by diffusion. A range of analytical and numerical models have been used to describe the relationship between the cooling rate and the shape of chemical zoning profiles. Most of these models are characterized by a deficit of usability to external users. This problem is overcome by the code THERMAL HISTORY presented here. The code is platform independent and runs without compilation or a hard disk install. Model results are stored in a basic database and displayed graphically. The code is controlled by an intuitive graphical user interface and uses a very fast diffusion algorithm. THERMAL HISTORY can be used to model zoning profiles as a function of a series of cooling histories, and is written so that it is particularly applicable for the Fe–Mg exchange between garnet and biotite. The code takes into account mass balance so that the volumetric ratio of garnet and biotite can be considered explicitly and it provides a facility to calculate sections through the grains. As some of these facilities have never been published before, the impact of cooling histories, mass balance and section position is explained in some detail. As an application example, THERMAL HISTORY is used to demonstrate that highly non-linear cooling histories, small biotite–garnet ratios and the section effect may result in zoning profiles that are misleading if interpreted in terms of the cooling history.

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1. Introduction

Diffusive chemical zoning profiles in mineral grains bear important information on the change of physical conditions like pressure and temperature during the evolution of a metamorphic terrain (e.g. Chakraborty, 2006). Such zoning profiles—if they

are caused by diffusion—may be interpreted in terms of the time–temperature evolution of the system. In particular the exchange of Fe and Mg between garnet and biotite has been recognized as geologically relevant and a number of studies have used this system to determine aspects of the cooling history of metamorphic rocks. For example Ehlers et al. (1994a,b) and Ganguly and Tirone (2002) determined cooling rates by employing the analytical solution of the diffusion equation by Dodson (1973, 1986), which describes the relationship between the grain size, closure temperature and

[☆] Code available from server at <http://www.iamg.org/CGEditor/index.htm>.

^{*} Corresponding author.

E-mail address: joerg.rob1@uni-graz.at (J. Robl).

the cooling rate for a specific set of boundary conditions. However, most geological relevant problems cannot be modeled with the restrictive boundary conditions used for this analytical solution. Accordingly, most studies that interpreted zoning profiles in terms of the cooling history of rocks have adopted numerical approaches to solve the diffusion equation: since the first numerical approach to model chemical zoning caused by diffusion (Anderson and Buckley, 1973) numerical interpretations of chemical zoning patterns in garnet have been performed with an increasing number of improvements (Lasaga and Richardson, 1975; Loomis, 1978a,b; Florence and Spear, 1991; Hauenberger et al., 2005).

One problem that is shared by all these sophisticated models is that they are characterized by a deficit of usability to external users: there is usually no graphical user interface (GUI), the numerical codes are dependent on a specific computer platform or they require the compilation of the source code by the user. In order to overcome these problems, the finite difference code THERMAL HISTORY is presented here as a tool to model and interpret chemical zoning profiles in minerals caused by diffusion. In particular, THERMAL HISTORY is designed to model diffusive zoning that arises from Fe–Mg exchange in garnet grains as a consequence of cooling. During cooling, the equilibrium coefficient K_d causes changes in the chemical

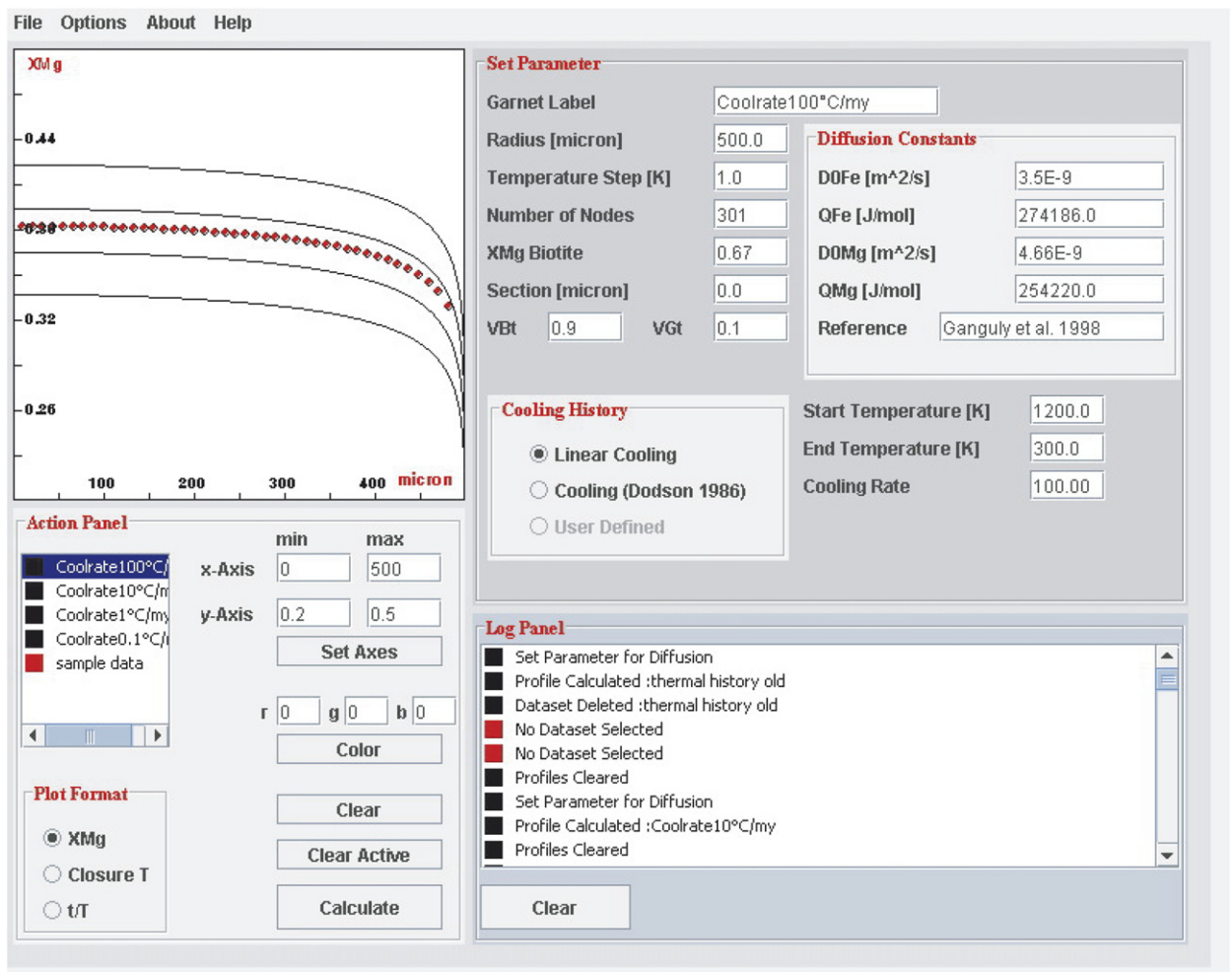


Fig. 1. Screenshot of finite difference diffusion code THERMAL HISTORY. Solid lines in canvas window upper left show modeled diffusion profiles. Diamonds indicate imported sample data of a measured diffusion profile. Upper right window accommodates Set Parameter panel, which allows defining model parameters. Action Panel at lower left window determines appearance of canvas window and objects therein. Log Panel at lower right records all operations and informs about failures.

composition of the garnet. Because of the exponentially decreasing diffusivity, the rate of these changes becomes successively sluggish and ultimately a chemical zoning profile is preserved as the frozen record of cooling (Tracy, 1982; Stüwe, 1999). This process is modeled with the software presented here. THERMAL HISTORY is available as a java applet on the internet (Fig. 1).¹ The code is platform independent and it does not require compilation or a hard disk install. A modern GUI allows to set model parameters and to observe the result of the calculation as graphical output. Moreover, the code THERMAL HISTORY allows a series of processes to be modeled that few studies have previously investigated, for example arbitrary cooling histories, concentration-dependent diffusion, mass balance and sectioning effects.

2. Physics

For the modeling of diffusion profiles that evolved during cooling of a metamorphic realm with THERMAL HISTORY we use the mineral garnet as an example. For this we make the following assumptions but note that many of these assumptions can easily be relaxed by inserting new subroutines. Interested users are invited to suggest further improvements on the code. We assume that garnet crystals are spherical objects and completely surrounded by a rim of biotite and that chemical equilibrium between the two is reached by binary exchange of two cations namely Fe and Mg. The garnet is assumed to be an almandine–pyrope solid solution, which means that no further cross terms of multi component diffusion are considered. The garnet crystal is assumed to have no zoning at the peak temperature. The amount of garnet and biotite remains constant during the complete cooling path and the size of the garnet grain does not change: growth and resorption are not considered. We further assume that diffusion within the biotite is infinitely fast, so that there is no chemical zoning within the biotite. The modeling of chemical zoning profiles in garnet is performed by solving the time-dependent radial symmetrical diffusion equation of the form:

$$\frac{\partial C(r, t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D(r, t) \frac{\partial C(r, t)}{\partial r} \right), \quad (1)$$

where C stands for the concentration, t for time and r for the radial coordinate of the mineral grain. The temperature dependence of the diffusivity, D , was calculated using the Arrhenius relationship:

$$D = D_0 e^{-Q/RT(t)}, \quad (2)$$

where R is the gas constant and $T(t)$ is the absolute temperature at time t . D_0 and Q are the pre-exponent diffusivity and the activation energy, respectively. The concentration dependence of D in the garnet is assumed to depend on the concentration of Fe and Mg according to

$$D = \frac{D_{\text{Mg}} D_{\text{Fe}}}{X_{\text{Mg}} D_{\text{Mg}} + X_{\text{Fe}} D_{\text{Fe}}} \quad (3)$$

(Florence and Spear, 1995; Ganguly et al., 1998). D_{Mg} and D_{Fe} are the temperature-dependent diffusivities of Fe and Mg as calculated from Eq. (2). X_{Mg} and X_{Fe} represent the concentration ratios of Mg and Fe in the form: $X_{\text{Mg}} = C_{\text{Mg}}/(C_{\text{Mg}} + C_{\text{Fe}})$ and $X_{\text{Fe}} = 1 - X_{\text{Mg}}$. As $C_{\text{Mg}} + C_{\text{Fe}}$ is constant, Eq. (1) can be directly written in terms of X_{Mg} instead of C_{Mg} .

The equations above represent the classical set of assumptions made to interpret zoning profiles (Stüwe, 1999; Chakraborty, 2006). Because of the strong temperature dependence of D (Eq. (2)), the length scale of diffusion decreases during cooling. Dependent on the grain size, there will be a certain temperature for each mineral grain, where the length scale of diffusion becomes smaller than the radius of the mineral grain. Then the chemical equilibrium of the grain core will lag behind the ongoing equilibration of the grain margin. With decreasing temperature the core of the grain is successively closed towards diffusive equilibration, while the outer parts begin to lag behind the equilibration of the very grain margin. This process is going on until the complete mineral grain is closed for diffusion. This stepwise closure of the mineral grain leads ultimately to a curved zoning profile that bears information on the experienced thermal history. In this study the term “closure interval” is used for the temperature span between the temperature of the first disequilibrium within the garnet grain and the temperature where diffusion across the entire grain is negligible on the scale on which it might be resolvable by microprobe analysis. As such, the “closure interval” is different from “closure temperature”, which is defined as the temperature that can be extracted from the non-equilibrium composition of the frozen diffusion

¹http://wegener.uni-graz.at/thermal_history/index.html.

profile, in particular that of the grain core (Ehlers and Powell, 1994; Ehlers et al., 1994a). The cooling history dependence of the zoning profile is modeled through the time-dependent temperature in Eqs. (2) and (4). For the boundary conditions to Eq. (1) we assume that the garnet surface is always in equilibrium with the adjacent biotite at $T(t)$ and controlled by the K_d . The K_d is calculated using the thermometer equation of Ferry and Spear (1978):

$$K_d = \exp\left(\frac{-\Delta H + T(t)\Delta S}{3RT(t)}\right). \quad (4)$$

In Eq. (4) ΔH and ΔS stand for the change of enthalpy and entropy, respectively. Values of $\Delta H = 52107.536 \text{ J}$ and $\Delta S = 19.506 \text{ J K}^{-1}$ are hard-wired in the code. We note that the original formulation also includes a P -dependent term, which is neglected here. Since the garnets are often pure almandine–pyrope solid solutions, the activity model of Ferry and Spear (1978) describes sufficiently the non-ideal behavior of mixing. The surface concentration of the modeled garnet is calculated from Eq. (4) and the K_d expression between garnet and biotite:

$$K_d = \frac{X_{\text{Mg}}^{\text{Grt}} X_{\text{Fe}}^{\text{Bt}}}{X_{\text{Fe}}^{\text{Grt}} X_{\text{Mg}}^{\text{Bt}}} = \frac{X_{\text{Mg}}^{\text{Grt}}(1 - X_{\text{Mg}}^{\text{Bt}})}{(1 - X_{\text{Mg}}^{\text{Grt}})X_{\text{Mg}}^{\text{Bt}}};$$

$$X_{\text{Mg}}^{\text{Grt}(\text{surface})} = \frac{K_d \times X_{\text{Mg}}^{\text{Bt}}}{1 - X_{\text{Mg}}^{\text{Bt}} + K_d \times X_{\text{Mg}}^{\text{Bt}}}. \quad (5)$$

Eq. (5) only defines a unique boundary condition to Eq. (1) if X^{Bt} is known and constant. This is only

3. Program design

Designing the code THERMAL HISTORY we have emphasized usability, but have also optimized for calculation speed and functionality. The code consists of a set of fast libraries for the numerical solution of the diffusion equation and for the required physics and an intuitively arranged GUI that allows application to a variety of diffusion problems. The code is provided as a java applet so that every geologist can easily model zoning profiles in garnet, without coding experience, or the mathematical background of how to solve the diffusion equation. The source code for the applet is freely available (published under GPL) on the server.²

3.1. Numerical approach

Except for the treatment of the boundary in case of finite biotite volume, when mass balance must be a boundary condition, standard methods can be used for solving the radial symmetric diffusion equation. A number n of nodes $r_0 \dots r_{n-1}$ is defined according to $r_i = (1 + \frac{1}{2}) \delta r$ where $\delta r = r/(n - \frac{1}{2})$ and Θ is the grain radius. With respect to the boundary conditions, the outermost node is placed at the grain boundary, while the innermost node is $\delta r/2$ away from the center.

Except for the boundary node, i.e., for $i \neq n-1$, the diffusion equation (Eq. (1)) can be discretized in a straightforward way:

$$\frac{\partial}{\partial t} X_i^{\text{Grt}} = \frac{r_{i+1/2}^2 D_{i+1/2} ((\partial/\partial r) X^{\text{Grt}})_{i+1/2} - r_{i-1/2}^2 D_{i-1/2} ((\partial/\partial r) X^{\text{Grt}})_{i-1/2}}{r_i^2 \delta r}$$

$$= \frac{r_{i+1/2}^2 D_{i+1/2} (X_{i+1}^{\text{Grt}} - X_i^{\text{Grt}}) - r_{i-1/2}^2 D_{i-1/2} (X_i^{\text{Grt}} - X_{i-1}^{\text{Grt}})}{r_i^2 \delta r^2}, \quad (6)$$

given if the biotite volume is infinite (> 3 times the garnet volume according to Ehlers and Powell, 1994). Then, X^{Bt} is constant, so that Eq. (5) provides an explicit boundary condition for X^{Grt} at the grain boundary. In contrast, if only a finite amount of biotite is available, then the X_{Mg} in biotite changes as a function of the flux of Fe and Mg between garnet and biotite, which in turn, is governed by the size of the available reservoir. Mass balance needs to be considered. A numerical treatment of this phenomenon is presented in the following section.

where quantities with the index $i + \frac{1}{2}$ refer to the point in the middle between i and $i+1$. The diffusivities at this point are obtained by averaging.

The boundary node $i = n-1$ is treated in a different way. Let us imagine a spherical shell around this node which contains both garnet and biotite. To be more precise, its inner part ranges from $\Theta - \delta r/2$ to Θ and consists of garnet, while the outer part contains the entire volume of biotite. This simplification can be made since chemical zoning in

²wegener.uni-graz.at/thermal_history/source/.

biotite is negligible. Using Eq. (5) and regarding the mass densities and molar weights of garnet and biotite, the total amount of Mg contained in this cell can be computed as a function of X_{n-1}^{Grt} . Then, the mass balance for this cell is stated (regarding diffusion between the nodes $n-2$ and $n-1$).

After some straightforward calculus, the following equation for the time derivative of X_{n-1}^{Grt} emerges:

$$c \frac{\partial X_{n-1}^{\text{Grt}}}{\partial t} = \frac{r_{n-3/2}^2 D_{n-3/2} (X_{n-2}^{\text{Grt}} - X_{n-1}^{\text{Grt}})}{r_{n-1}^2 \delta r^2} + \left(c - \frac{1}{2} \right) X_{n-1}^{\text{Grt}} (1 - X_{n-1}^{\text{Grt}}) \frac{\partial \log K_d}{\partial t}, \quad (7)$$

where

$$c = \frac{1}{2} + \frac{M^{\text{Grt}} \rho^{\text{Bt}} V^{\text{Bt}}}{M^{\text{Bt}} \rho^{\text{Grt}} 4\pi R^2 \delta r} \frac{K_d}{(X_{n-1}^{\text{Grt}} + K_d(1 - X_{n-1}^{\text{Grt}}))^2} \quad (8)$$

and $M^{\text{Grt/Bt}}$, $\rho^{\text{Grt/Bt}}$, V^{Bt} stand for molar weights, mass densities and volume of biotite, respectively. c can be seen as some kind of storage capacity. The first term on the right-hand side of Eq. (7) describes the flux between the nodes $n-2$ and $n-1$, while the second term describes the effect of temporal changes in K_d which finally drives diffusion. In sum, Eqs. (6) and (7) constitute a tridiagonal set of equations for the evolution of the variables X_i through time. The time discretization was made in such a way that the terms with the strongest variation are discretized implicitly in order to allow time steps of arbitrary size, while some other terms are discretized explicitly in order to avoid non-linearity of the resulting system of equations. In Eq. (6), the variables X_{i-1}^{Grt} , X_i^{Grt} and X_{i+1}^{Grt} were discretized implicitly, while diffusivities were discretized explicitly. In Eq. (7) the variables $X_{n-2}^{\text{Grt}} - X_{n-1}^{\text{Grt}}$ and the first factor of the product $X_{n-1}^{\text{Grt}}(1 - X_{n-1}^{\text{Grt}})$ were discretized implicitly, while all other terms were discretized explicitly. The discretization results in a tridiagonal linear system which can easily be solved and turned out to be stable even for large time steps.

3.2. Description of the GUI

The GUI consists of several panels and subpanels so that parameters that belong together are clearly arranged (Fig. 1). THERMAL HISTORY is built with default values (see Appendix A) that represent a typical garnet–biotite couple in an upper amphi-

bolite or granulite facies rock containing garnet porphyroblasts and biotite. As such, the program will run and produce a zoning profile as soon as the “Calculate” button at the bottom left (see screen shot in Fig. 1) is pressed. Every calculation is immediately shown graphically on the canvas panel. A description explaining all parameters goes beyond the scope of this study and we restrict the description below to the general meaning of the different panels, subpanels and menus of the applet. For a detailed description of all buttons and parameters we refer to the tutorial about practical work with the diffusion code THERMAL HISTORY which is available online at wegener.uni-graz.at/thermal_history/tutorial/.

The panel “Set Parameter” contains all physical and numerical parameters that control the boundary conditions, the diffusion process within the grain and the section of the modeled garnet grain. Defining a unique “Garnet Label” allows easily identifying each modeled garnet in the case that several model runs are performed at one session. By setting the physical properties “Radius”, “XMg Biotite”, “VBt” and “VGt”, the size of the garnet grain, the X_{Mg} of the adjacent biotite and the volumetric ratio of biotite (V_{Bi}) and garnet (V_{Grt}), are determined. If the modeled diffusion profile is to be viewed at a section position through the garnet crystal that goes not through its center, the distance of the section plane to the center of the grain can be inserted with the “Section” parameter. Resolution in space and time is controlled by setting the “Number of Nodes” and the “Temperature Step”, where equidistant temperature steps are recalculated to time steps, so that for non-linear cooling histories, time segments with higher cooling rates are characterized by smaller time steps and vice versa. The default values render a resolution that is within the resolution of a microprobe, but these values can be experimented with. The numerical solution is unconditionally stable for all spatial resolutions.

The subpanel “Diffusion Constants” allows defining parameters like the activation energy Q and the pre-exponential coefficient D_0 for both minerals involved in the exchange process. As default values we inserted the most modern estimate for the Fe–Mg exchange between garnet and biotite (Ganguly et al., 1998) but we note that a variety of other diffusion constants were published over the past 20 years (Cygan and Lasaga, 1985; Loomis et al., 1985; Chakraborty and Ganguly, 1992).

The subpanel “Cooling History” allows defining the relationship between time and temperature of the model run. The buttons “Linear Cooling”, “Cooling (Dodson, 1986)” and “User Defined” determine the general shape of the cooling history. The parameters to the right of this subpanel control the quantitative placing of the chosen general shape in temperature–time space. Linear cooling is implemented in the code in the form:

$$T(t) = T_i - st, \quad (9)$$

where the initial temperature T_i (“Start Temperature [K]” in Set Parameter Panel) and the cooling rate s can be defined with the parameters “Start Temperature” and “Cooling Rate” (in °C per million year). The last parameter (“Cooling Rate at K”) is only required if “Cooling (Dodson, 1986)” is set. That cooling function sets a cooling curve of the form:

$$T(t) = \frac{T_i}{1 + s_i t / T_i}, \quad (10)$$

where $T(t)$ stands for the temperature at time t , T_i and s_i are the initial temperature and initial cooling rate at T_i . A cooling curve of this form is linear in $1/T$ and was used by Dodson (1973, 1986) to derive an analytical solution of Eq. (1). As such, this cooling curve can be used to compare modeled zoning profiles directly with their analytical solution. Moreover, such a cooling history is typical for cooling following contact metamorphism. When “Cooling (Dodson, 1986)” is set, the quantitative placing of the cooling curve also requires to define “Cooling Rate at K” which allows to set a temperature where the cooling rate has the value defined in the text field “Cooling Rate”. The parameter “End Temperature” defines the temperature where the code stops the diffusion model. For complete closure profiles, this parameter should be set to a temperature where diffusion becomes insignificant. However, using larger values allows observing the evolution of diffusion profiles along the time–temperature history.

The radio button “User Defined” is set inactive as default and becomes active at the moment a user defined cooling history is imported using the file menu at the top left corner of the applet. A user defined cooling history is an ASCII table with a time and a temperature column where time is in million years and temperature in K. To fulfill the time step requirements defined by the parameter “Temperature Step” a linear interpolation algorithm is used to

increase the number of time steps, while the user defined time–temperature couples remain unchanged. Examples for user defined cooling histories can be found at: wegener.uni-graz.at/thermal_history/coolinghistory/.

The “Action Panel” allows starting the model run with the “Calculate” button, deleting a single profile by hitting the “Clear Active” button or deleting all calculated or imported profiles with the “Clear All” button. Already calculated profiles are shown by their “Garnet Label” in the profile list top left in the “Action Panel”. Activating a profile in the profile list updates the “Parameter Panel” with the parameters used for the calculation of the activated profile. The “Color” button and the three text fields labeled with “r”, “g” and “b” that stand for red, green and blue, respectively, allow to define the plot color for the profiles, that are shown in the canvas located top left in the applet. The “Set Axes” button and the four text fields above allow determining the plot area, which allows zooming in and zooming out. Profiles are scaled automatically to the correct zoom factor. The “Plot Format” subpanel enables switching between the output modes “XMg”, “Closure Temperature” and “ t/T ” represented by radio buttons. By activating one of these radio buttons the canvas is updated by the correct curves, axes are rescaled to the default values for the different output modes and the axes labels show the correct units.

The File menu located at the very top of the applet allows exporting the modeled data as csv-spreadsheet or eps-graphics. The exported data correspond to the data shown on the canvas, which means that zoning profiles, closure profiles or time–temperature histories are exported depending on the active radio button of the “Plot Format” subpanel. The “File” menu also allows importing measured diffusion profiles from garnet crystals and user defined cooling histories from your hard disk to the applet.

4. Application

The diffusion code THERMAL HISTORY allows to model zoning profiles in spherical crystals in equilibrium with a faster diffusing mineral and to import measured zoning profiles so that the modeled zoning profile can be compared with a measured profile as they can be plotted in the canvas of the applet. Aside from being able to model zoning profiles (a) in grains of different size,

(b) in grains in equilibrium with different concentration of the faster diffusing phase, (c) using different diffusion constants, the applet also allows to explore three additional aspects of zoning profiles, namely: (i) defining arbitrary time–temperature curves, (ii) specifying a volumetric ratio between the spherical grain and the mineral in contact and (iii) calculating section profiles. Each of these three facilities is introduced here by applying it to some specific scenarios. The general design of the code is not restricted to garnet–biotite couples, but might be used for spherical minerals that show diffusional zoning profiles at the contact to a faster diffusing phase. However, all application presented below describe aspects of diffusion profiles in garnet crystals at the contact to biotite.

4.1. Cooling curves

The cooling histories of most metamorphic rocks are not linear but are characterized by a change of cooling rate over time. This has been documented by a number of field studies (e.g. Harris et al., 2004: Himalaya; Brouwer et al., 2004: Western Alps), but has also been predicted for different tectonic scenarios. For example, England and Thompson (1984) have already shown that—in regional metamorphic terrains—cooling rates increase with decreasing temperature, while Harrison and Clark (1979) show that contact metamorphism is followed by cooling rates that decrease with decreasing temperature. For that reason the THERMAL HISTORY accepts both linear cooling functions and user defined cooling histories (Fig. 2a). For the purpose of comparison four zoning profiles that result from four different time–temperature cooling

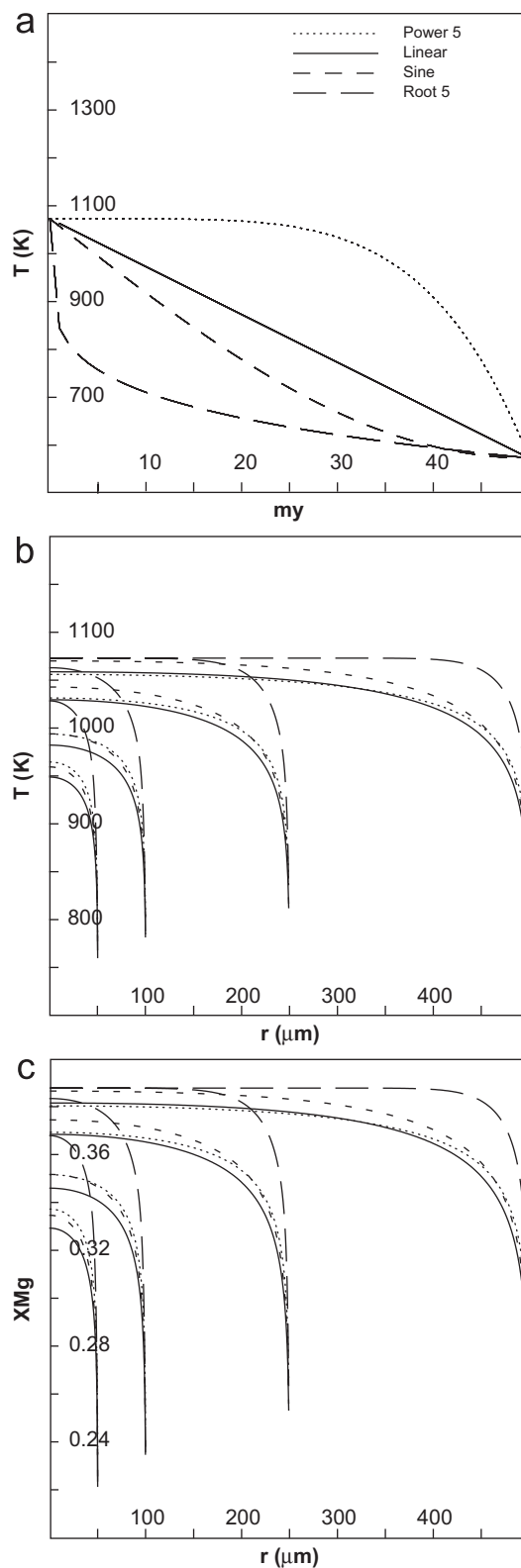


Fig. 2. Influence of cooling histories on diffusion and closure profiles. (a) The four time–temperature paths are characterized by same average cooling rate of $10\text{ }^{\circ}\text{C my}^{-1}$, a peak temperature of 1073 K ($800\text{ }^{\circ}\text{C}$), a duration of cooling of 50 my and a final temperature of 573 K ($300\text{ }^{\circ}\text{C}$). Four different cooling histories are user defined time–temperature tables and available at: wegener.uni-graz.at/thermal_history/coolinghistory/. The cooling paths are characterized as follows: Power5 ($T = 1073 - (t/50)^5 \times 500$), Linear ($T = 1073 - t \times 10$), Sine ($T = 1073 - \sin(t/50 \times \pi/2) \times 500$) and Root5 ($T = 1073 - (t/50)^{0.2} \times 500$) and presented as dotted, solid, short dashed and long dashed line, respectively. (b) Closure profiles modeled with four different cooling histories shown in (a) and for four different grain sizes. The line style of curves corresponds to cooling histories presented in (a). (c) Corresponding chemical zoning profiles to closure profiles shown in (b).

curves were modeled. The cooling curves have the same average cooling rate of $10^{\circ}\text{C my}^{-1}$ but are characterized by different cooling rates within the closure interval. Garnet crystals in the size range of 50–500 μm were explored. All cooling curves shown in Fig. 2 were discretized into tT -pairs and imported to thermal THERMAL HISTORY using the File menu and the user defined cooling history option.

The sine-shaped cooling curve (Fig. 2a dotted line) is characterized by a similar cooling rate within the closure interval compared to the linear cooling path, but starts with higher cooling rates near the peak temperature (Start Temperature), and lower cooling rates at a temperature where most of the garnet grain is already closed for diffusion. A similar shape to the sine-shaped cooling path is given by the “root5”-shaped cooling path that represents the concave end member of a time–temperature history. The temperature decreases with the fifth root of time (Fig. 2a long dashed line). Such a cooling curve is characterized by extremely rapid cooling from the peak temperature at 1073–800 K, a sudden change in the cooling rate at about 800 K and very slow cooling below. The “power5” time–temperature path (Fig. 2a dotted line) represents the convex end member of possible cooling paths, where the cooling rate is small ($\ll 10^{\circ}\text{C my}^{-1}$) at the peak temperature and increases slowly with time until 1000 K is reached. At about 1000 K the cooling rate changes dramatically to high values ($\gg 10^{\circ}\text{C my}^{-1}$).

As shown in Fig. 2b and c, the modeled diffusion profiles with non-linear time–temperature histories deviate significantly from diffusion profiles with an applied constant cooling rate (Fig. 2b and c solid line). It can also be shown that non-linear cooling paths influence the chemical zoning of garnet crystals in dependence of the grain size.

Applying a sine-shaped cooling curve it can be shown that for garnet crystals in the size range between 250 and 500 μm the closure- and chemical zoning profiles deviate only slightly (Fig. 2b and c short dashed line). Garnet crystals below 250 μm behave more sensitive to the sine-shaped cooling path. It can be shown that profiles modeled with a sine-shaped cooling path have a significantly higher closure temperature and higher values of X_{Mg} . Using a “root5” cooling history chemical zoning profiles of grains larger than 250 μm are flat, as this part of the profile has been frozen near the peak temperature (Fig. 2b and c long dashed line). Only the outer rim of the profiles has been affected by

diffusion. Garnet crystals below 250 μm are characterized by lower X_{Mg} values in the core, compared to larger grains modeled with the same cooling history. This indicates that a considerable amount of Mg has lost the garnet grain caused by diffusion. However, the X_{Mg} value in the core of even small grains is sizable larger than in equally sized garnet grains modeled with a linear cooling history but the same average cooling rate of $10^{\circ}\text{C my}^{-1}$. As we can see from the modeled chemical zoning and the closure profiles, the fast cooling from peak temperature down to about 800 K determines the shape of the diffusion profiles, while the slow cooling below does not effect the diffusion profiles at all.

Modeling diffusion profiles with a “power5” cooling history the X_{Mg} values and the closure temperatures in the core of garnet crystals larger 250 μm are slightly below or in the same range than garnet grains modeled with a linear cooling path (Fig. 2b and c dotted line). In contrary grains below 250 μm show significantly higher X_{Mg} values and closure temperatures compared to equal sized grains modeled with a linear cooling history. Because of the slow cooling rate at the peak temperature and the small increase of the cooling rate with time until 30 my of cooling, the complete garnet grains were open for diffusion over a long time span at high temperatures leading to low X_{Mg} -values in the core. At about 30 my of slow cooling the cooling rate increases rapidly causing the fast closure of the complete garnet. Therefore the profiles are characterized by increased X_{Mg} -values and higher closure temperatures at the rim of the garnet grains compared to garnet grains modeled with a linear cooling path. As the closure interval for smaller grains shifts to lower temperatures, zoning profiles of garnet grains with a size of 250 μm and below show higher X_{Mg} -values, as the cooling rate within the closure interval was above $10^{\circ}\text{C my}^{-1}$ and increases with increasing temperature.

4.2. Influence of mass balance

The analytical solution of Dodson (1986) and several numerical codes assume an infinite reservoir of the equilibrium partner mineral (biotite), so that the chemical composition of this mineral remains constant during the entire cooling path. Ehlers et al. (1994a) have shown that this assumption is valid, if the volumetric ratio of biotite to garnet is greater than three. However, this ratio is lower in many metamorphic rocks and may be different for every

single garnet grain within one sample, if the diffusion along the grain boundaries is limited as observed in granulite facies rocks (O'Brien and Finch, 1999; Hauzenberger et al., 2005). Then, the compositional changes of both minerals in the diffusion couple must be considered, and the resulting zoning profile may look substantially different (see Eq. (5)). The influence of finite size of both diffusing minerals was studied by Ehlers and Powell (1994). Their empirical solution can be tested using THERMAL HISTORY.

At a garnet–biotite ratio of 100 (Fig. 3) the amount of available Fe from the biotite reservoirs is extremely small, so that only the outer rim of the garnet crystal is affected by diffusion while the core remains unchanged. Even at a garnet–biotite ratio of 10, that may be geologically relevant, the impact of diffusion to form a chemical zoning profile is negligible. Significant changes in the core composition caused by diffusion can be observed at a garnet–biotite ratio of 1 for realistic garnet sizes. For garnet–biotite ratios smaller than 0.1 the difference in the closure profiles compared to closure profiles modeled under the assumption of an infinite biotite reservoir is negligible and within the noise of a microprobe analysis.

Only the determination of the exact garnet–biotite ratio and considering mass balance enables the modeling of cooling histories with garnet crystals. The example in Fig. 4 points out possible misleading

interpretation by neglecting mass balance between garnet and biotite. For garnet–biotite ratios of 10 or larger and a constant cooling rate of $10^{\circ}\text{C my}^{-1}$, diffusion is very limited (Fig. 4a fat solid line). In that case modeling closure profiles for a garnet crystal of the same size, but assuming an infinite biotite reservoir, the interpreted cooling rate will be two orders of magnitude higher than the actual one. The shape of the profile is very similar to profiles modeled with an assumed root5 cooling history shown in Fig. 2. Even at a garnet–biotite ratio of 1, the error in modeling cooling rates without considering mass balance amounts one order of magnitude (Fig. 4b). The numerical model shows that for a garnet–biotite ratio of 0.33, which was assumed as the cut of ratio where mass balance is negligible (Ehlers et al., 1994a), the error is still large (Fig. 4c) and becomes insignificant at a garnet–biotite ratio of 0.1 or smaller.

4.3. Sections

With respect to the petrological problem of determining cooling rates from closure temperatures, several studies have discussed the sectioning effect (e.g. Ehlers et al., 1994a; Powell et al., 1995). These studies show that the highest closure temperature measured at the apparent core of the garnet crystals indicates the garnet that is cut through the center, while lower closure temperatures in crystals

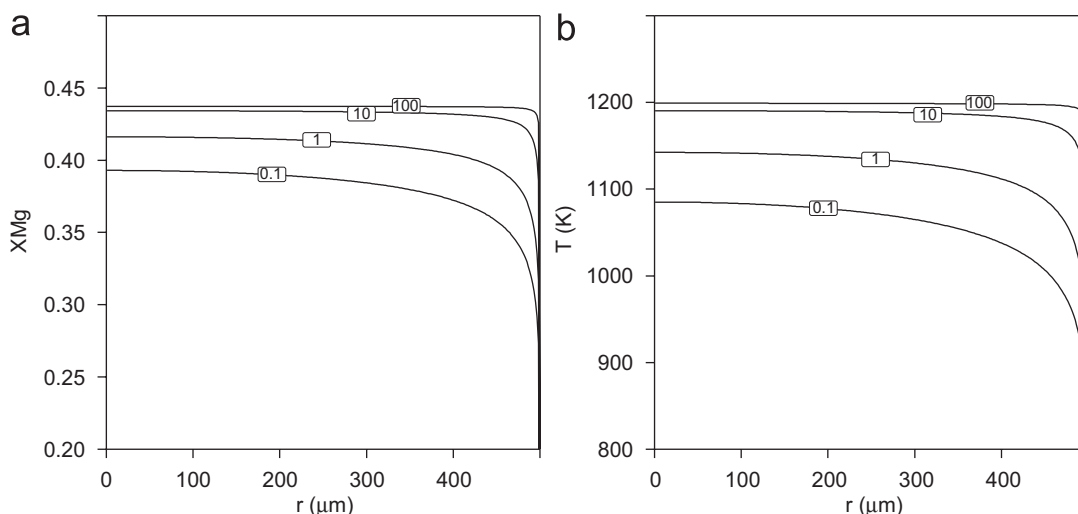


Fig. 3. Modeled diffusion (a) and closure (b) profiles show impact of mass balance for four different garnet–biotite ratios. Default parameters (see Appendix A) are used for diffusion modeling except the amount of garnet and biotite, which is expressed by garnet–biotite ratio indicated by numbers in boxes. The profiles are plotted from core ($0\ \mu\text{m}$) to rim ($500\ \mu\text{m}$).

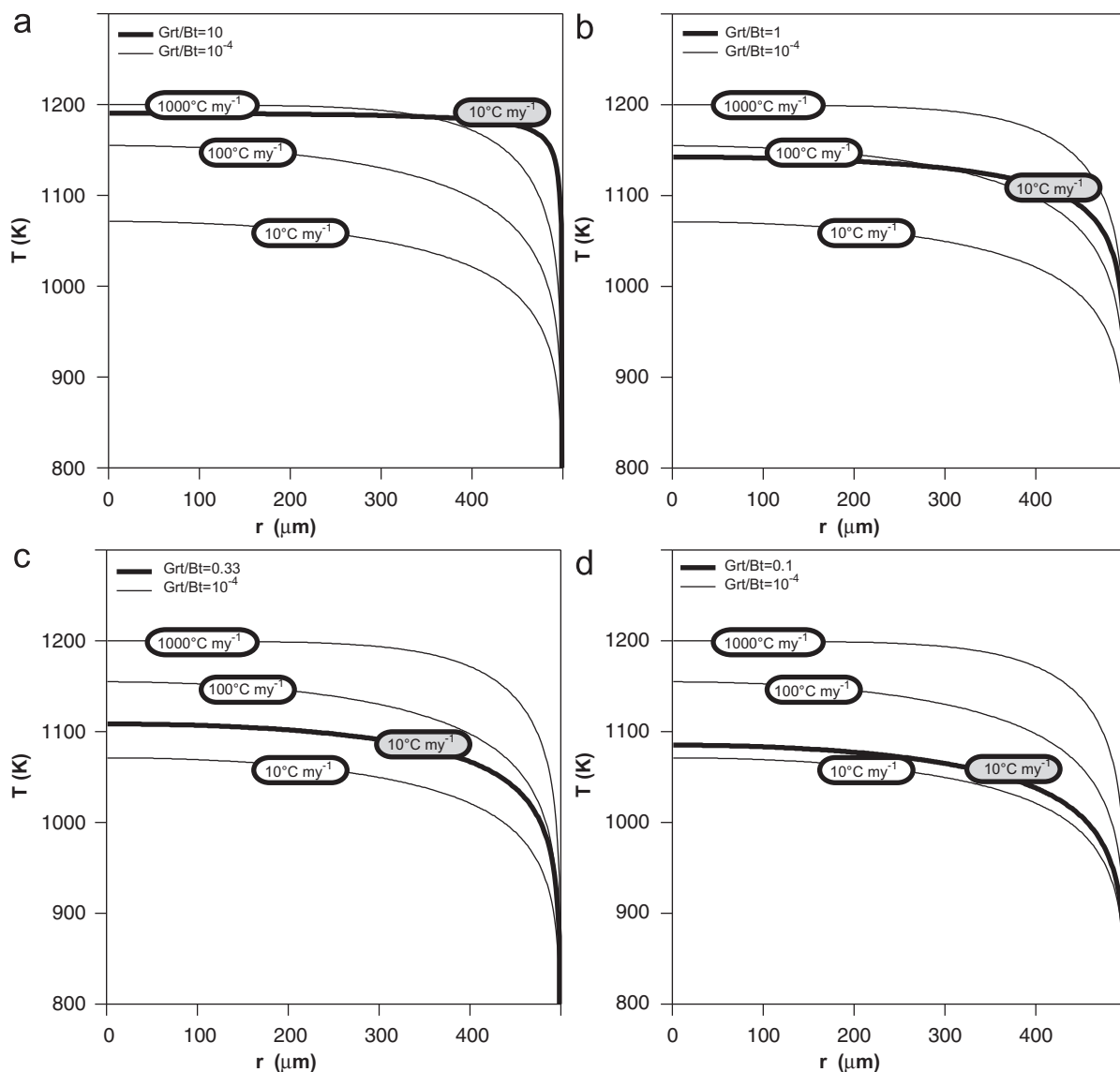


Fig. 4. Possible misinterpretation of closure profiles in terms of cooling rates by not considering mass balance. Fat black line shows a closure profile with a limited reservoir of biotite and a constant cooling rate of $10\text{ }^{\circ}\text{C my}^{-1}$. Garnet–biotite ratio was defined as (a) 10, (b) 1, (c) 0.33, (d) 0.1. Thin solid lines show closure profiles with a nearly infinite large reservoir of biotite ($\text{Grt/Bt} = 10^{-4}$) and are modeled for three different constant cooling rates indicated by numbers on curves.

with the same section radius are an evidence for a greater distance of the section plane to the core of the garnet. Fig. 5 shows four diffusion profiles with the same size that might be observed within one thin section (solid lines).

Keeping in mind that the diffusion profile showing the highest closure temperature (greatest value for X_{Mg}) in the center of the grain will be the grain which section is the nearest to the center, an

interpretation in terms of cooling rates is straightforward. However, in general we will hardly find several garnets showing exactly the same section radii and the interpretation of the cooling history might shift to too low cooling rates caused by the sectioning effect. Such a possible misinterpretation is pointed out by the three modeled zoning profiles is pointed out by the three modeled zoning profiles with an actual radius of $250\text{ }\mu\text{m}$ but with constant cooling rates of 10, 1 and $0.1\text{ }^{\circ}\text{C my}^{-1}$. It can be

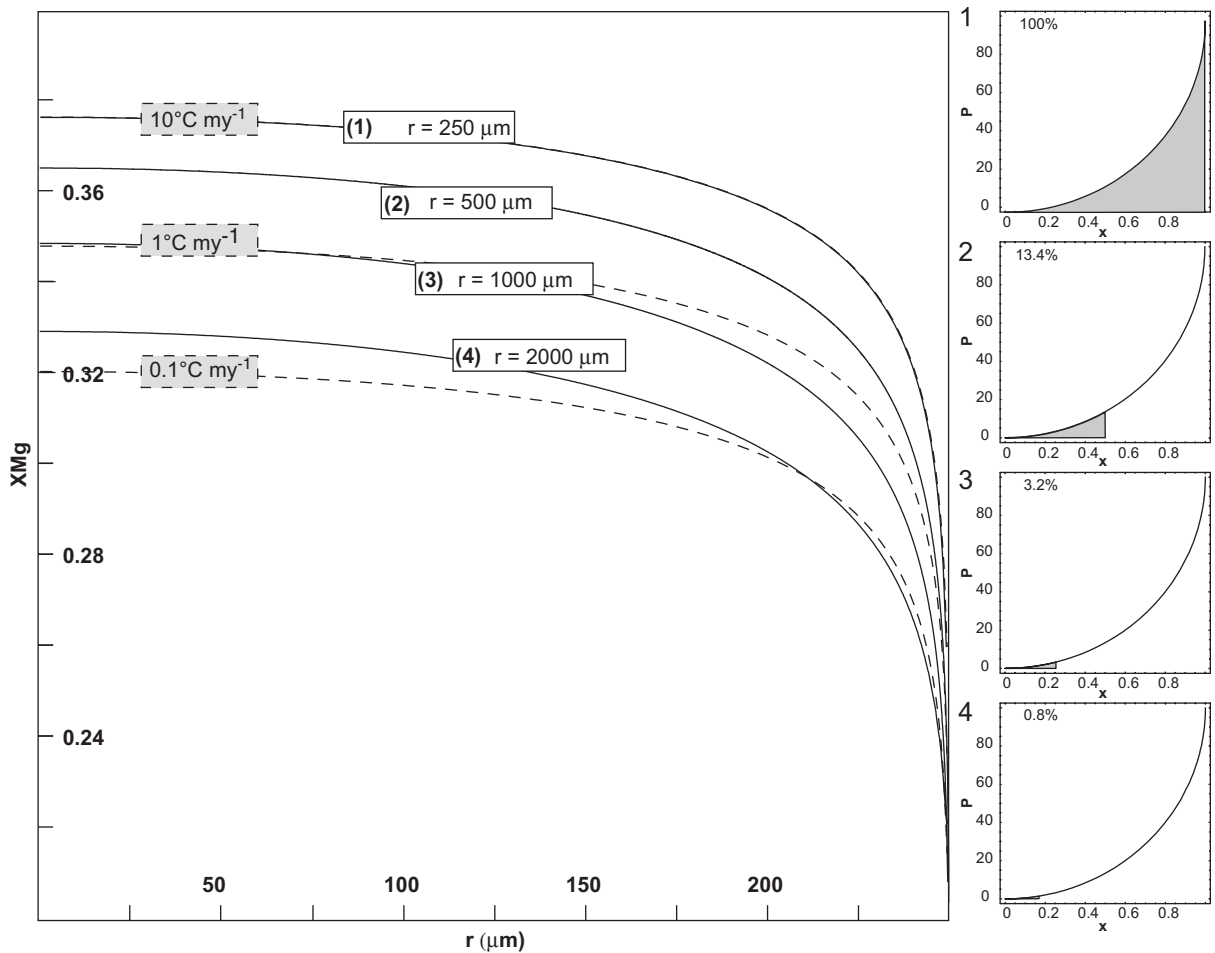


Fig. 5. The impact of sectioning effect on chemical zoning profiles is illustrated by four equally sized section profiles ($l = 250 \mu\text{m}$) from four differently sized garnet crystals (solid lines). Actual grain radius of garnet crystals is shown in boxes on top of curves. Equally sized section profiles were calculated using the relationship of Pythagoras by defining distance of section plane to core as follows: (1) $r = 250 \mu\text{m}$, $d = 0 \mu\text{m}$; (2) $r = 500 \mu\text{m}$, $d = 433 \mu\text{m}$; (3) $r = 1000 \mu\text{m}$, $d = 968 \mu\text{m}$; (4) $r = 2000 \mu\text{m}$, $d = 1984 \mu\text{m}$. Possible misinterpretation in terms of cooling rates is indicated by dashed lines. Dashed lines show zoning profiles with sections through center, but with different cooling rates as indicated in boxes. The numbers on solid lines link to insets explaining section probability. P stands for probability and x for radius normalized to 1. Area below curves is normalized to 1% or 100% as actual radius of four garnet grains is normalized to one. Gray shaded area below curves visualizes probability of a section of this size or smaller and corresponds to percentage on top left of insets.

shown that the modeled cooling rate of a diffusion profile of a $1000 \mu\text{m}$ large garnet crystal that is cut at the rim, so that the section radius amounts to $250 \mu\text{m}$ is lowered by about one order of magnitude. This effect increases with increasing distance of the section plane to the core and amounts about two orders of magnitude for a $2000 \mu\text{m}$ large garnet crystal and a section radius of $250 \mu\text{m}$. However, the probability of such a section at the outermost rim is very small as indicated by the four diagrams on left-hand side of Fig. 5. These diagrams show the probability that a garnet crystal with the grain size indicated by the box over the solid lines is sectioned

by the way that the section radius is $250 \mu\text{m}$ or smaller. By this definition a garnet crystal with an actual grain size of $250 \mu\text{m}$ with a section radius of $250 \mu\text{m}$ or smaller has the probability of 1 or 100%. A $250 \mu\text{m}$ or smaller section radius of 500 , 1000 and $2000 \mu\text{m}$ sized garnet show a probability of appearance of 0.134, 0.032 and 0.008, respectively. Because of the small probability of sectioning a garnet crystal at the outermost rim, the error caused by the section effect in the interpretation of zoning profiles in terms of cooling rates should be below one order of magnitude as long as a large number of garnet crystals is used for the modeling.

5. Conclusions

The diffusion code THERMAL HISTORY is a new software that can be used to model diffusive zoning profiles in minerals. In particular, it was coded to model garnet in equilibrium with biotite. The code offers an intuitively arranged GUI to control a fast spherical diffusion code. Platform independence is guaranteed by coding a java applet, which does not require compilation or a hard disk install by the user. The data exchange is menu driven. Data output in form of ready to publish eps-graphics or as csv-spreadsheet leads to greatest possible compatibility to vector graphic and spreadsheet software for post-processing. The import of measured diffusion profiles allows direct comparison between measured and modeled zoning profiles within the applet. As the applet allows setting user defined diffusion constants the code is not limited to garnet and biotite but can be used for all comparable diffusion problems, where a spherical mineral grain exchanges cations with a faster diffusing phase. THERMAL HISTORY is open for all kinds of cooling histories, it can be used to consider mass balance and investigate sectioning effects. The possibility to model zoning profiles using of non-linear cooling paths can help to avoid misleading interpretations in terms of cooling rates.

Application of the software to garnet–biotite equilibria shows that ignoring mass balance can cause dramatically wrong interpretations in terms of the cooling rate. We also apply the applet to different sections through the garnet grain as the determination of cooling histories from closure temperatures is typically plagued by the sectioning effect, as the section position of a particular mineral grain is in general unknown. As all mineral grains within a sample have recorded the same cooling history, apparently misleading results (e.g. different cooling rates for different grains) can be explained by calculating sections from a modeled diffusion profile.

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Appendix A. Default parameters

Parameter name	Default value
Garnet Label	garnet 0
Radius (μm)	500
Temperature Step (K)	1
Number of Nodes	301
XMg Biotite	0.67
Section (μm)	0
VBt	0.9
VGt	0.1
Diffusion Constants	
$D_0\text{Fe}$ (m^2/s)	3.50E–9
QFe (J/mol)	274186
$D_0\text{Mg}$ (m^2/s)	4.66E–9
QMg (J/mol)	254220
Reference	Ganguly et al. (1998)
Cooling History	
Linear Cooling	Default
Cooling (Dodson, 1986)	Optional
User Defined	Optional
Start Temperature (K)	1200
End Temperature (K)	300
Cooling Rate (K/my)	10
Cooling Rate at K (K)	873

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