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# Garnet compositions as recorders of $P$ – $T$ – $t$ history of metamorphic rocks

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## ABSTRACT

On the basis of tests made in recent studies, we conclude that the simultaneous solutions of the equilibrium conditions of garnet–biotite Fe–Mg exchange and  $\text{Grs} = \text{Plag} + \text{Aluminosilicate} + \text{Qtz}$  (GASP) reactions, as formulated on the basis selected experimental data and well constrained thermodynamic mixing properties of garnet and plagioclase, offer robust estimates of  $P$ – $T$  conditions of metapelitic assemblages that consist of the above minerals. Additional calculations are presented to show the compatibility of the retrieved  $P$ – $T$  conditions of natural assemblages with the aluminosilicate phase diagram. We also calculate the minimum grain sizes of garnets that should be used for the calculation of the peak metamorphic  $P$ – $T$  ( $P_p$ ,  $T_p$ ) conditions, using reasonable initial guessed values of minimum cooling rate and maximum  $T_p$ . To retrieve the thermal history of metapelites, we have developed a finite difference scheme for modeling multicomponent diffusion profiles in garnet, incorporating provisions for continuous nucleation and growth. This has been interlinked with a genetic algorithm that permits retrieval of the temperature vs. time path of metapelites through modeling of the zoning profiles in garnets, keeping several model parameters as floating variables. The numerical code has been applied to retrieve the  $T$ – $t$  history of the low pressure–high temperature Royke metamorphic belt, Japan, by modeling the concentration profiles of Fe, Mn, Mg and Ca of garnets of different sizes that have been inferred to have developed by a process of continuous nucleation and growth.

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## 1. Introduction

Retrieval of pressure–temperature–time ( $P$ – $T$ – $t$ ) history of metamorphic rocks and the constraints that it imposes in the reconstruction of the tectono-metamorphic evolution of rocks in different tectonic regimes have been among the central themes of metamorphic petrology for a long time. Major efforts have thus been made, through systematic integration of experimental studies with thermodynamic and diffusion kinetic theories, towards the retrieval of the  $P$ – $T$ – $t$  records that are preserved in the compositional properties of minerals. Garnet has proved to be the single most important mineral from this perspective as it is stable over a wide range of metamorphic  $P$ – $T$  conditions and shows compositional response to the change of such condition, but without achieving complete equilibrium. Garnets in metamorphic rocks commonly show compositional zoning that preserve temporal records of the  $P$ – $T$  history of the host rocks, which could be retrieved if the diffusion kinetic data of the major divalent cations are available. Thus, there has been major effort over nearly the past 25 years to determine the diffusion kinetic parameters of the divalent cations in garnet (Loomis et al., 1985; Elphick et al., 1985; Chakraborty and Ganguly, 1991, 1992; Ganguly et al., 1998; Freer and Edwards, 1999; Carlson, 2006; Vielzeuf et al., 2007; Perchuk et al., 2009). On the other hand, because garnet is

stable over a wide range of metamorphic conditions, there are more thermobarometric formulations that are based on the equilibrium compositions of garnet and coexisting minerals than involving any other mineral group (e.g. Ganguly and Saxena, 1987).

The purpose of this paper is to (a) discuss thermobarometric methods for metapelitic assemblages involving garnet, and (b) present a new modeling protocol linked to a genetic algorithm that permits simulation of compositional zoning of major divalent cations in metapelitic garnets of different sizes to retrieve both pro- and retro-grade temperature–time paths.

## 2. Thermobarometry using garnet compositions

### 2.1. Formulations

Thermobarometric formulations require well constrained experimental phase equilibrium data on simplified model systems or thermodynamic properties of end-member phases together with activity composition ( $a$ – $X$ ) relations of the phases involved. Conventional thermobarometry involves use of selected cation exchange and breakdown equilibria in anhydrous (or volatile free) systems, and retrieval of the peak metamorphic  $P$ – $T$  condition of the host rock from the point or domain of intersection(s) of these equilibria in the  $P$ – $T$  space. An alternative method is to use a number of equilibria or all possible equilibria within a given mineral assemblage and find the statistically optimal  $P$ – $T$  condition that best satisfies the equilibria. The

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latter method, commonly referred to as the “average  $P$ - $T$  method”, is due to Powell and Holland (1994), and has been used extensively in metamorphic petrology literature. Gaides et al. (2008a) have developed a software package, THERIA\_G, which permits one to numerically compute garnet compositional profiles along a proposed  $P$ - $T$ - $t$  path and thus, in principle, could be used to infer thermobarometric and temporal conditions of evolution of metapelites by comparison with the observed compositional profiles of garnet.

The “average  $P$ - $T$  method” and the THERIA\_G software package represent important advancements towards constraining  $P$ - $T$  evolution of metamorphic rocks, but these also require much more data, especially reliable  $a$ - $X$  relations of minerals that are often complex solid solutions, than the conventional thermobarometric methods that use a limited number of equilibria. The main distinction between the “average  $P$ - $T$  method” and conventional thermo-barometry lies in the scope of the number of equilibria that are utilized for  $P$ - $T$  calculations. However, as remarked by Dasgupta et al. (2004), there is considerable gap in our knowledge of thermodynamic mixing properties of minerals to make the “average  $P$ - $T$  method” a robust approach at the current state for the determination of the  $P$ - $T$  condition of many metamorphic assemblages. Additionally, as pointed out by them, if devolatilization equilibria are used in the calculation of  $P$ - $T$  conditions, then it is necessary to have *a priori* knowledge of the fluid composition, a requirement that is very difficult to satisfy.

Dasgupta et al. (2004, 2009) have tested the results from the “average  $P$ - $T$  method” against independent phase equilibrium and observational constraints for the metamorphic rocks in the Sikkim Himalayas, and found that it gives erroneous results for some bulk compositions and mineral assemblages. Gaides et al. (2008b) also carried out comparisons of the predicted mineral assemblages, which form along  $P$ - $T$  paths that are required for the successful forward modeling of garnet compositional profiles, with the observed mineralogy. They noted several mismatches between the predicted and observed mineralogies and remarked on the problem with the thermodynamic database as a possible explanation for the discrepancies.

It was found that in contrast to the results from the “average  $P$ - $T$  method”, a software package of conventional thermobarometric formulations developed by J. Ganguly and W. Cheng ([ftp://ftp.geo.arizona.edu/pub/ganguly/P-T\\_Calc/](ftp://ftp.geo.arizona.edu/pub/ganguly/P-T_Calc/)), which, for metapelites, rely on the simultaneous solution of garnet–biotite Fe–Mg exchange equilibrium and  $\text{Gr}_5 = \text{Al}_2\text{SiO}_5 + \text{Plag} + \text{Qtz}$  equilibrium (acronym GASP), yield  $P$ - $T$  estimates for the Himalayan rocks in Sikkim that are in very good agreement with the independent constraints (Dasgupta et al., 2004, 2009). The data utilized in this package are the well reversed experimental data of Ferry and Spear (1978) for Fe–Mg exchange between garnet and biotite and Koziol and Newton (1989) for GASP, along with the garnet solution property of Ganguly et al. (1996), the mutually compatible biotite solution property therein, and plagioclase solution property by Elkins and Grove (1990). Holdaway (2004) has also presented formulations for the garnet–biotite and GASP equilibria, but we are unable to comment at this stage if these formulations work as well as or better than the Ganguly–Cheng formulation.

In this study, we have carried out additional tests to check the validity of the Ganguly–Cheng formulations of Grt–Bt and GASP equilibria by calculating the  $P$ - $T$  conditions of a large number of mineral assemblages containing garnet, aluminosilicate, plagioclase, biotite and quartz. The results are illustrated in Fig. 1 and compared with the stability fields of the aluminosilicate polymorphs, as determined by Holdaway and Mukhopadhyay (1993). These assemblages were used earlier by Ganguly and Saxena (1984) to test the validity of their garnet solution model and Grt–Bt plus GASP thermobarometric formulations. The compositional data of all but the Mt. Moosilauke assemblage (Hodges and Spear, 1982a,b) have been summarized by Newton and Haselton (1981). On the basis of the distribution of the aluminosilicate polymorphs, Hodges and Spear (1982a,b) concluded that the  $P$ - $T$

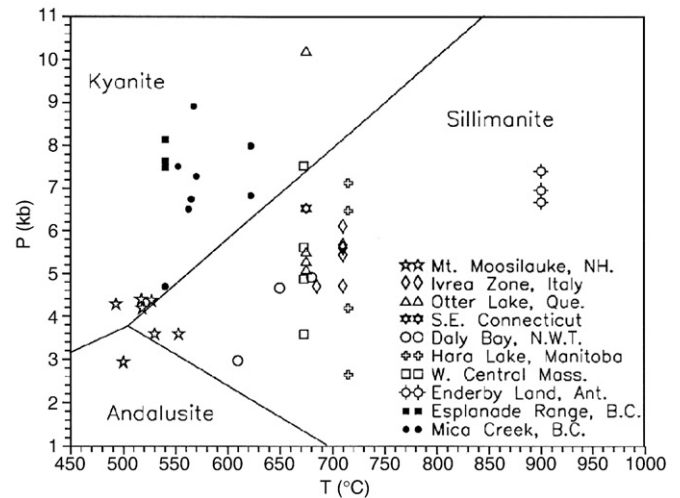


Fig. 1. Simultaneous solutions of pressure and temperature from the equilibrium conditions of garnet–biotite Fe–Mg exchange and garnet = plagioclase + aluminosilicate + quartz (GASP) reaction in metapelitic assemblages from different localities, as indicated in the figure. The filled and open symbols indicate presence of only kyanite and only sillimanite, respectively, whereas the stars indicate assemblages that have been independently inferred by Hodges and Spear (1982a,b) to have formed near the aluminosilicate triple point. The aluminosilicate phase diagram is from Holdaway and Mukhopadhyay (1993). All data except those indicated by stars are from Newton and Haselton (1981).

condition of the Mt. Moosilauke assemblages should be near the aluminosilicate triple point. The calculated  $P$ - $T$  conditions (star symbols) satisfy this requirement. Furthermore, except for one, the  $P$ - $T$  conditions calculated for all samples satisfy the constraints imposed by the nature of the aluminosilicate polymorphs in these assemblages.

## 2.2. Selection of composition in zoned garnets and resetting of garnet composition during cooling

Metapelitic garnets are almost invariably zoned. The selection of composition within a zoned garnet crystal that effectively represents the peak metamorphic composition, and the compositions of biotite and plagioclase grains that could be used in conjunction with the selected garnet composition to retrieve the peak metamorphic  $P$ - $T$  condition is a tricky issue. The problem has been discussed in detail by Ganguly et al. (2000) and Dasgupta et al. (2004, 2009). Regardless of what formulation or approach is issued to retrieve peak  $P$ - $T$  condition, it is imperative that one follows a well justifiable scheme, within the framework of diffusion kinetic analysis, for choosing equilibrium compositions of garnet and coexisting mineral phases that reflect peak  $P$ - $T$  condition.

If compositional zoning of garnet was only due to its growth up to the peak temperature and had not been significantly modified by diffusion, then the rim composition of garnet reflects its peak metamorphic composition. This is usually the case for rocks in the garnet grade and lower amphibolite facies conditions. For garnets subjected to granulite facies metamorphism, the compositional profiles often show flat core compositions along with zoning near the rim. This is due to the homogenization of growth zoning at the relatively higher temperature of granulite facies metamorphism and development of retro-grade zoning near the rim as a result of partial re-equilibration with the coexisting phases in response to changing  $P$ - $T$  condition. In these cases, use of rim compositions of garnet for thermobarometric purpose would yield  $P$ - $T$  conditions at which diffusion effectively ceased in the garnet grains. These diffusion closure temperatures tend to be  $\sim 500$  °C or even lower.

For garnet grains in granulite facies assemblages with the above characteristics, one needs to choose core compositions of large enough grains that could be expected to have preserved the peak metamorphic compositions, considering diffusive readjustments during cooling. If the

garnet is surrounded by biotite, then, as shown by Ganguly and Tirone (1999), the appropriate grain size could be selected by considering the value of a dimensionless parameter,  $M$ , which is defined as follows.

$$M = \frac{RD(T_p)T^2}{E(dT/dt)\mathfrak{R}^2} \quad (1)$$

where  $R$  is the gas constant,  $D(T_p)$  is the diffusion coefficient at the peak temperature ( $T_p$ ),  $E$  is the activation energy of diffusion,  $dT/dt$  is the cooling rate at  $T$  (appearing in the numerator) and  $\mathfrak{R}$  is the radius of the garnet crystal. Ganguly and Tirone (1999) showed that there is no significant resetting of garnet core composition for  $M \leq 0.1$  if  $T_p \leq 1000$  °C.

Using Eq. (1) and setting  $M=0.1$ , we have calculated the relationship between  $\mathfrak{R}$  vs.  $T_p$  for different initial cooling rates. The results are illustrated in Fig. 2. With initial guess of the maximum peak temperature and minimum cooling rate, this diagram may be used to select garnet crystals that may be used for thermobarometric studies to retrieve  $T_p$ . To calculate this diagram we have used the Fe–Mg interdiffusion coefficient at  $T_p$  and the activation energy for the interdiffusion. These values were calculated on the basis of the self-diffusion parameters of Fe and Mg, as determined by Ganguly et al. (1998), and the relationship between interdiffusion of two equally charged species and their self-diffusion coefficients (e.g. Ganguly, 2003).

Spear (1991, 1995) considered the problem of resetting of garnet composition surrounded by a large matrix of biotite during cooling, assuming a homogeneous composition at the peak metamorphic condition. The grain sizes calculated by Spear (1991) to prevent resetting of the core composition of garnet at different cooling rates are much larger than those illustrated in Fig. 2. In their study of inverted metamorphic sequence of the Himalayan rocks in Nepal, Martin et al. (2009) used Eq. (1) to select appropriate grain sizes for the purpose of thermobarometric studies. They have also addressed the issue of the difference between the results obtained from Eq. (1) and Spear's analysis, and shown that the problem lies in the incorrect treatment of the Mg diffusion data. Spear (1991) used the  $D(\text{Mg})$  data of Cygan and Lasaga (1985), but without correcting for the effects of pressure and oxygen fugacity. The diffusion experiments carried out by these workers were at a pressure of 2 kb and  $f(\text{O}_2)$  close to the hematite–magnetite buffer whereas metapelitic assemblages typically reflect higher pressure (5–10 kb) and lower  $f(\text{O}_2)$ , usually near quartz–fayalite–magnetite or graphite buffers. Adjustments for  $D(\text{Mg})$  values for the metapelitic conditions significantly reduce the  $D(\text{Mg})$  value and thus the grain size requirement to prevent resetting of the core composition of garnet. Furthermore, Spear (1991) used Mg self-diffusion instead of Fe–Mg

interdiffusion data. Martin et al. (2009) showed that when the diffusion coefficient is corrected for the effects of pressure and  $f(\text{O}_2)$ , the numerical simulation of Spear (1991) yields essentially the same grain size as that obtained from Eq. (1) or Fig. 2.

### 3. Modeling partially modified growth zoning of garnets in metamorphic rocks

The pro-grade thermal history is usually erased from the compositional properties of garnets in the granulite facies rocks as these were completely homogenized at the peak metamorphic conditions. In contrast, garnets in medium grade metapelites show growth zoning that had been often modified by intracrystalline diffusion (e.g. Chakraborty and Ganguly, 1991; Florence and Spear, 1993; Okudaira, 1996; Faryad and Chakraborty, 2005; Ganguly, in press). These partially modified growth zoning profiles preserve the  $P$ – $T$ – $t$  records for both pro- and retro-grade cycles that may be retrieved by numerical modeling within the framework of diffusion kinetic, nucleation and crystal growth theories. We discuss below multicomponent diffusion modeling of partially modified growth zoning of garnets of different sizes to retrieve the pro- and retro-grade  $T$ – $t$  paths experienced by the low pressure Ryoke metamorphic rocks, Japan (see Brown, 2010–this issue, for a modern review of the geology). The purpose of this modeling is to explore the success of a finite difference scheme linked to a genetic algorithm (Haupt and Haupt, 1998; Deb, 2001) that permits treatment of a number of parameters required for such modeling, and usually difficult to constrain, as floating variables. To our knowledge, a modeling of this nature has not been attempted before.

#### 3.1. Simulation of garnet compositional zoning in Ryoke metamorphic belt

We first provide a brief review of the work of Okudaira (1996) and then discuss our approach of simulation of compositional profiles in garnets of Ryoke metamorphic belt. Using the diffusion data of Chakraborty and Ganguly (1992), Okudaira (1996) modeled zoning profiles of garnet crystals of different sizes from the Ryoke metamorphic rocks in south western Japan. As the Fe and Mn components of garnet constitute ~88% of garnet composition, Okudaira normalized the garnet composition to the Fe–Mn binary, and treated the diffusion problem as a quasibinary process between Fe and Mn. On the basis of observations of spatial distribution of garnet grains and crystal size distribution (CSD) analysis (Cashman and Ferry, 1988), Okudaira concluded that the garnet grains of 0.1–0.5 radii were formed by continuous nucleation and diffusion-controlled growth. Assuming that the width of depleted/enriched zone of components near a growing crystal surface, which typically develops during diffusion-controlled growth process, is large compared to the crystal radius ( $r$ ), it can be shown that under isothermal condition (Kretz, 1994)

$$r_i = k_1 \sqrt{D(t-t_{n(i)})} \quad (2)$$

where  $k_1$  is a dimensionless constant,  $D$  is the coefficient of intergranular diffusion through the matrix of the growing crystal ( $i$ ) and  $t_{n(i)}$  is the nucleation time of the crystal. The parameter  $k_1$  depends on the equilibrium fractionation of components at the crystal–matrix interface. It is assumed that a constant value of  $k_1$ , averaged over the temperature interval of interest, is adequate for the treatment of garnet growth problem.

The diffusion coefficient is expressed as a function of temperature according to the Arrhenius relation  $D = D_0 \exp(-E/RT)$ . Substituting this expression into Eq. (2), one obtains

$$r_i = k_2 \sqrt{\left(t-t_{n(i)}\right) \exp\left(-\frac{E}{RT}\right)} \quad (3)$$

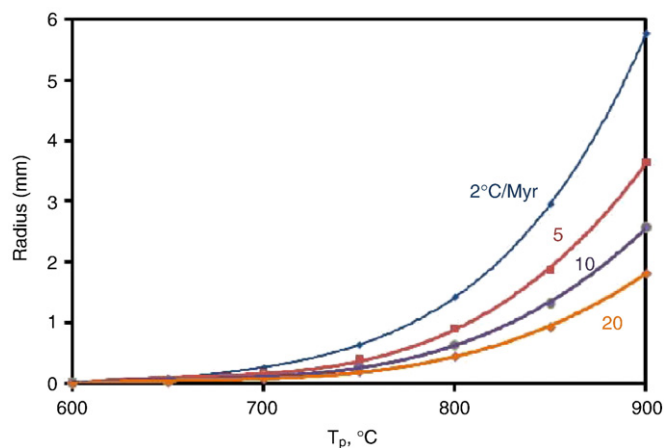


Fig. 2. Minimum grain size of spherical of garnet crystal surrounded by biotite (or homogeneous infinite matrix) that is required to preserve the peak metamorphic composition at the grain center.  $T_p$  stands for the peak temperature. The numbers beside the curves indicate cooling rates (°C per Myr).

where  $k_2 = k_1(D_0)^{1/2}$ . Okudaira (1996) assumed  $E$  to be 83.7 kJ/mol (Fisher, 1978), and derived a value of  $k_2$  of  $6.29 \times 10^{-8} \text{ m} / \sqrt{\text{s}}$  by assuming that the nucleation of the largest garnet grain (0.5 mm radius) commenced with the breakdown of muscovite plus quartz, presumably at 600 °C, and that the growth of the grain was continuous up to the peak temperature ( $T_p$ ) of 670 °C. He also assumed a linear relation between the surface concentration of Mn in garnet and temperature,

$$X_{\text{Mn}(s)} = c + m(T_p - T) \quad (4)$$

and retrieved the constants ( $c = 1.095$  and  $m = 1.0 \times 10^{-3} \text{ K}^{-1}$ ) by matching the highest and lowest values of  $X_{\text{Mn}}$  in the simulation of the growth and compositional change within the largest garnet crystal (0.5 mm radius) after 2 Myr to those observed in the natural crystal of the same size. Using these parameters and imposing the  $T$ - $t$  history of the metamorphic belt that was calculated previously (Okudaira et al., 1994) from the numerical solution of one dimensional heat transfer equation incorporating the effects of conduction and fluid advection, Okudaira (1996) was able to simulate the normalized Fe–Mn zoning profiles through approximately the central sections of garnets of 0.1–0.4 mm radius. However, there was a slight mismatch between the simulated and observed profiles for garnets with 0.5 mm radius, and a small adjustment of the  $T$ - $t$  path was needed to obtain a better agreement.

While Okudaira (1996) demonstrated that the normalized compositional profiles of garnets of 0.1–0.5 mm radius may be satisfactorily explained in terms of the  $T$ - $t$  path of the Ryoke metamorphic belt that was previously calculated, it is, in general, of greater interest to explore if metamorphic  $T$ - $t$  paths could be retrieved from modeling the compositional profiles of garnet (e.g. Florence and Spear, 1993; Faryad and Chakraborty, 2005; Gaides et al., 2008b). To this end we explore, using the data of Okudaira (1996), a modeling strategy of diffusion profiles in garnet to retrieve metamorphic  $T$ - $t$  path as it affords an opportunity for comparison with a  $T$ - $t$  path that was calculated independently, and consequently, provides a test of the validity of the method developed in this study. However, unlike Okudaira (1996), we have modeled the compositional profiles of all major divalent cations, namely Fe, Mn, Mg and Ca, using full multicomponent diffusion formalism, since the sum of the atomic fractions of Fe and Mn is not effectively a constant from the core to rim of a single garnet crystal. In addition, we did not fix the growth constant ( $k_2$ ) for the garnet (Eq. (3)) and assign any specific values to the parameters governing the presumed linear change of surface concentration vs. temperature of a component.

As discussed by Carlson (1989), the growth constant may vary as a function of grain size, degree of supersaturation and time (the time dependence of the growth constant comes primarily from the temperature dependence of  $k_1$ ). Additionally, the Arrhenian parameters ( $D_0$  and  $E$ ) for intergranular diffusion may also have spatial variability. However, likewise Carlson (1989) and Okudaira (1996), we have treated  $k_2$  and the Arrhenian parameters as constants. Thus, the value that we retrieve for  $k_2$  by treating it as a floating parameter should be regarded as a spatially and temporally averaged value of the growth constant. For  $E$ , we have used the same value ( $8.37 \times 10^4 \text{ J/mol}$ ) as Okudaira (1996), and this value of  $E$  should also be regarded as its spatially averaged value. In general, treating  $k_2$  and  $E$  as constants may be over simplification. However, for any given case, the degree of success in modeling multicomponent compositional profiles in garnet crystals of different sizes provides a test of the validity of the assumptions. We want to emphasize that our approach is not restricted to the treating  $k_2$  and  $E$  as constants, and that we can incorporate additional floating parameters (e.g. different growth constant for different garnet crystals in the chosen set), but in keeping with the general philosophy of modeling, we preferred not to make the modeling framework any more complicated than it needs to be for the solution of the problem in hand.

We also retained the linear form of the change of surface concentration of the components vs. time, Eq. (4), but treated the constant parameters,  $m$  and  $c$ , as floating parameters for all (independent)

components. In general, the surface concentration is a nonlinear function of time (e.g. Ganguly et al. 2000) and may even have temporal discontinuities. Thus, our simulations represent linear approximations to a nonlinear problem. As with the growth model, the degree of success of our simulation of garnet compositional profiles provides a test for the extent of validity of the linear approximation of the change of boundary condition.

### 3.2. Retrieval of $T$ - $t$ path of Ryoke metamorphic belt from garnet compositional zoning: imposed conditions and floating parameters

In our study, the  $T$  vs.  $t$  relation is represented by a parabolic equation

$$T = T_0 - (T_p - T_0) \left( \frac{t}{t_p} \right)^2 + 2(T_p - T_0) \left( \frac{t}{t_p} \right) \quad (5a)$$

in the pro-grade path, where  $T_0$ ,  $T_p$  and  $t_p$  are the initial temperature, peak temperature and the time to the peak temperature, respectively, and by

$$T = T_p - b \ln \left( \frac{t}{t_p} \right) \quad (5b)$$

in the retro-grade path, where  $b$  is a positive constant. The pro- and retro-grade  $T$ - $t$  relations conform to the form of the thermal model used by Okudaira (1996).

The parameters ( $T_p$ ,  $t_p$ ,  $b$ ) governing the quantitative  $T$ - $t$  relations in the pro- and retro-grade paths were treated as unknowns in our study. In addition, we also treated the growth constant,  $k_2$  (Eq. (3)), and the constants in Eq. (4) that define the change of surface compositions of garnets vs. temperature of the independent components as unknowns (since there are four components in garnet, Fe, Mn, Mg and Ca, the composition at any point of only three components are independent, that of the fourth component being determined by the stoichiometric constraint,  $\sum X_i = 1$ , where  $X_i$  is the mole fraction of the component  $i$ ). Thus, there are 10 unknowns in our simulation of garnet zoning. We simulated the compositional zoning of five garnet crystals of radius 0.10, 0.20, 0.32, 0.43 and 0.49 mm. These are the same crystals that Okudaira (1996) used in his study.

### 3.3. Multicomponent diffusion simulation: mathematical formalisms and numerical scheme

In multicomponent diffusion, the flux of a component depends not only on its own concentration gradient, but also on those of the gradients of all other independent components. In the domain of validity of linear irreversible thermodynamics that holds for diffusion problems, the relationship between the flux of a component and the concentration gradients is linear. This is known as the Ficks–Onsager relation (Onsager, 1945). The consequent diffusion equation in a spherical coordinate, which is appropriate for the selected garnet crystals, and volume fixed reference frame, takes the form:

$$\frac{\partial X_i}{\partial t} = \frac{1}{\mathfrak{R}^2} \frac{\partial}{\partial r} \sum_{j=1}^{n-1} D_{i-j} \mathfrak{R}^2 \frac{\partial X_j}{\partial r} \quad (6)$$

where  $X_i$  is the atomic fraction of an independent component,  $n$  is the total number of diffusing species,  $r$  and  $\mathfrak{R}$  are the radial distance and radius, respectively, and  $D_{i-j}$  is an element in the matrix of diffusion coefficients that is related to the self or tracer diffusion coefficients of the components according to (Lasaga, 1979):

$$D_{i-j} = D_i \delta_{ij} - \frac{D_i X_i z_i z_j}{\sum_{l=1}^n z_l^2 D_l X_l} (D_j - D_k) \quad (7)$$

where  $D_i$  and  $D_j$  are the self-diffusion coefficients of the components  $i$  and  $j$ , respectively,  $D_k$  is that of the dependent component  $k$ ,  $z$  is the number of charges on the diffusing species and  $\delta_{ij}$  is the Kronecker delta.

In this study, we assumed Ca to be the dependent component ( $k$ ). Thus, according to Eq. (6), the diffusion equation for the independent component Fe is given by

$$\begin{aligned} \frac{\partial X_{Fe}}{\partial t} = & \frac{\partial D_{Fe-Fe}}{\partial r} \frac{\partial X_{Fe}}{\partial r} + D_{Fe-Fe} \left( \frac{2}{r} \frac{\partial X_{Fe}}{\partial r} + \frac{\partial^2 X_{Fe}}{\partial r^2} \right) + \frac{\partial D_{Fe-Mn}}{\partial r} \frac{\partial X_{Mn}}{\partial r} \\ & + D_{Fe-Mn} \left( \frac{2}{r} \frac{\partial X_{Mn}}{\partial r} + \frac{\partial^2 X_{Mn}}{\partial r^2} \right) + \frac{\partial D_{Fe-Mg}}{\partial r} \frac{\partial X_{Mg}}{\partial r} \\ & + D_{Fe-Mg} \left( \frac{2}{r} \frac{\partial X_{Mg}}{\partial r} + \frac{\partial^2 X_{Mg}}{\partial r^2} \right) \end{aligned} \quad (8)$$

Two additional equations of the above form are introduced in our model for the two other independent components, Mn and Mg.

The boundary conditions are defined as follows: (a)  $\partial X/\partial r = 0$  at the core because the concentration profiles show extrema at this point of a crystal (which implies that there is no flux across the center of a garnet grain); (b) rim or surface compositions of the diffusing species follow the relations defined by Eq. (4). The diffusion equation for each independent component is numerically discretized using Crank–Nicolson finite difference method (Crank, 1975). This method is known to be stable regardless of the spatial and temporal step sizes. For a particular time step, the set of three equations of the form of Eq. (8) is solved by iteration. The concentration of the component on the left side of these three equations is the only unknown, while the concentration of the other components is held fixed until the next iteration. Only the left hand side and the first two terms in the right hand side of Eq. (8) contain the unknown quantity  $X_{Fe}$  while the components in all the other terms are taken from the solution of the diffusion equation similar to Eq. (8) in which these components appear on the left side. Usually, no more than 3–4 iterations are necessary to reach convergence for a particular time step. The numerical procedure for each diffusion equation builds a tridiagonal system of linear equations for which very efficient solution methods are available (Press et al., 1992).

Crystal growth is implemented in the diffusion equation by defining the time step to be equal to the time interval required to add exactly one grid point to the crystal size. In this way spacing is kept fixed ( $\Delta r = 0.0003$  cm) while the time step ( $\Delta t$ ) is variable during growth that is terminated at the peak condition.

To obtain the optimal combination of the values of the floating parameters that minimizes the differences between the computed and observed zoning profiles of the five selected crystals, we used a genetic algorithm (Haupt and Haupt, 1998; Deb, 2001) that represents a basic tool of a wide range of evolutionary schemes. The optimization procedure is described briefly in the Appendix. The quality of the match between the calculated and observed profiles is defined by an objective function,  $f$  (Eq. (A.2)). The robustness of the numerical program to retrieve the correct values of the floating parameters has been checked by first creating a set of synthetic multicomponent profiles in garnet using fixed values of the 10 model parameters summarized above, and then modeling the synthetic profiles keeping these parameters floating. We found no significant difference between the input and retrieved values of the model parameters.

The self-diffusion data of Fe, Mn and Mg have been taken from the experimental studies of Chakraborty and Ganguly (1992). As reviewed recently by Ganguly (in press), the diffusion parameters for Ca are still poorly constrained, especially in relatively Mn rich compositions, as in the samples selected in the present study. Following the suggestion of Loomis et al. (1985), we assumed  $D(\text{Ca}) = 0.5D(\text{Fe})$ . This suggestion was also followed by Florence and Spear (1993). However, we tested the

sensitivity of the modeling results by reducing  $D(\text{Ca})$  to  $0.1D(\text{Fe})$ , but found no significant effect in either the quality of the fits of the concentration profiles and the retrieved  $T$ – $t$  path.

#### 3.4. Best fits to the concentration profiles, optimized model parameters and $T$ – $t$ path

Fig. 3 shows the best fits ( $f = 0.074$ ) to the concentration profiles of five crystals of 0.1 to 0.5 mm radii that have been selected by CSD analysis (Okudaira, 1996) as having formed by continuous nucleation and growth process. The retrieved values of the floating or model parameters are summarized in Table 1. The values of the growth constant ( $k_2$ ),  $T_p$  and  $t_p$ , as retrieved in this study, are also compared with those imposed by Okudaira (1996) in his quasibinary modeling of the compositional profiles of Mn and Fe of the same crystals. While Okudaira (1996) set the nucleation time of the largest garnet grain to the time of attainment of the presumed breakdown temperature of muscovite plus quartz, we treated the nucleation time (and temperature) of all garnet grains as dependent function of the floating variables  $k_2$ ,  $T_p$  and  $t_p$ .

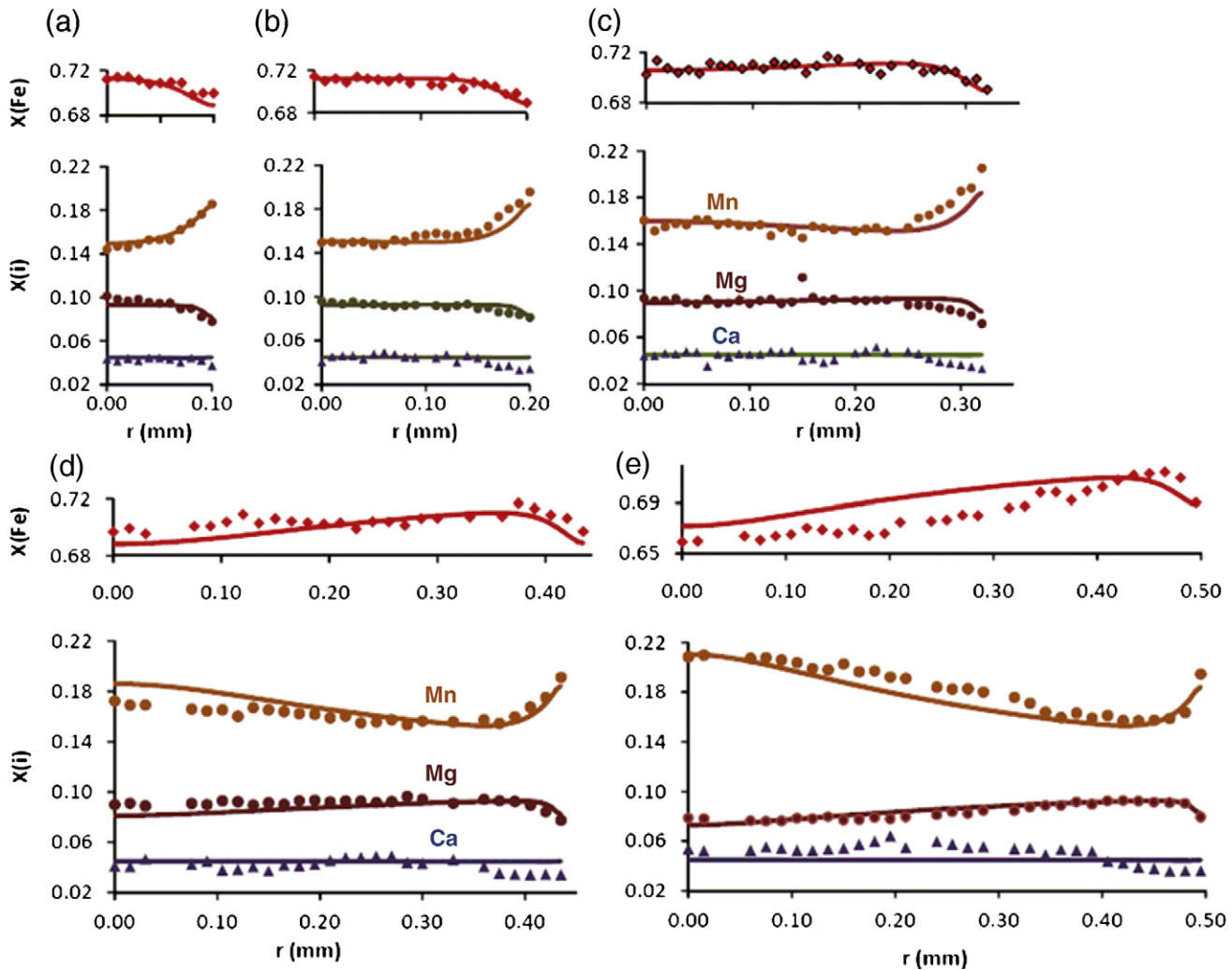
Fig. 4 shows the temperature–time path of the Ryoke metamorphic belt, as retrieved from numerical modeling of the garnet zoning profiles (solid line), with those calculated by Okudaira et al. (1994) from 1-D thermal modeling and modified to better reproduce the observed Mn profile of the 0.5 mm garnet. (The general form of the  $T$ – $t$  path determined from thermal modeling was subsequently confirmed by Okudaira et al. (2001) by geochronological data.) There is very good match between our calculated pro-grade path with the  $T$ – $t$  paths of Okudaira et al. (1994) and Okudaira (1996). We re-emphasize that our modeling was unconstrained with respect to both the peak temperature and the time to achieve the peak condition. However, there is mismatch between the retro-grade path retrieved by us and that calculated by Okudaira et al. (1994) from thermal modeling. We have also modeled the garnet zoning profiles by imposing Okudaira's  $T$ – $t$  path, keeping free all other model parameters discussed above. The overall quality of the fits is somewhat worse ( $f = 0.085$ ) than that illustrated in Fig. 3 ( $f = 0.074$ ), especially near the rims of the grains.

We have terminated the duration of the simulations at different times and found that the best match (minimum  $f$  value) between the calculated and observed profiles is obtained by restricting the termination between 1.5 and 2.0 Myr. Extending the simulation much beyond 2 Myr causes a decline in the overall quality of the fits to the observed data. This is the result of progressive homogenization of the zoning profiles for longer annealing time at nearly the same temperature. Thus, to preserve the best match between the observed and calculated profiles, our simulation requires sufficiently rapid drop of temperature (such as by exhumation of the rock) after 1.5–2 Myr since the time for the beginning of our simulation (set at 500 °C) so that there is no significant retro-grade adjustment of the garnet composition near the rims.

Our simulations suggest that the reported rim compositions of garnet reflect a temperature of around 600 °C. This prediction may be verified by determining the compositions of coexisting biotites and applying the Grt–Bt thermometric formulation discussed above. Our experience suggests that the composition of garnet change rapidly within the first 5–7  $\mu\text{m}$  from the rim (Ganguly et al., 2000) and that the true rim composition may be determined by analyzing the zoning profiles at  $\sim 1$ –2  $\mu\text{m}$  step near the rim and then extrapolating the data to the grain boundary. The 5  $\mu\text{m}$  step size used by Okudaira (1996) may be too coarse for determining the garnet rim compositions with the desired level of accuracy.

#### 4. Toward a robust approach for the retrieval of $T$ – $t$ path of metapelite using garnet compositional zoning

From comparison of the  $T$ – $t$  relations obtained from thermal modeling and simulation of garnet zoning profiles, it appears that a good approach to the retrieval of the  $T$ – $t$  relation would be to constrain



**Fig. 3.** Numerical simulation (solid lines) and measured data (symbols) of the multicomponent zoning profiles in garnets of different sizes (0.1–0.5 mm radii) that formed by a process of continuous nucleation and growth. The natural data are from Okudaira (1996 and pers. com.).

the temperature reflected by the garnet rim composition and terminating the simulation when that temperature is attained. Of course, additional reliable constraints such as cooling rate, which is

often determined from the geochronological constraints and modeling retro-grade zoning of garnets with homogeneous cores (e.g. Ganguly et al., 2000; Hauenberger et al., 2005), would be of added benefit to

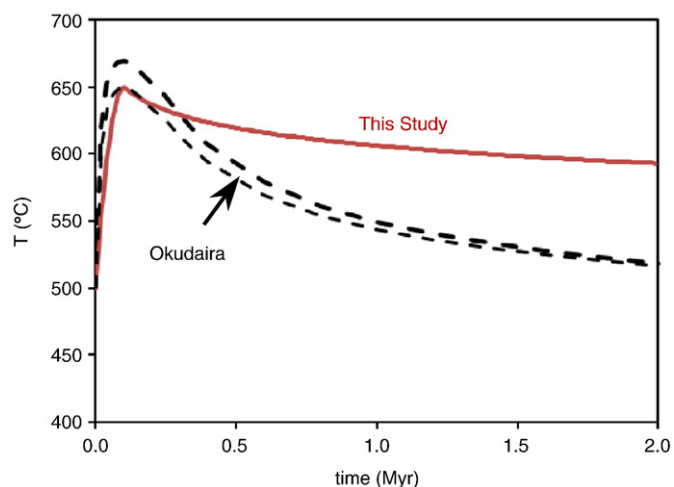
**Table 1**  
Summary of the model parameters retrieved from the simulation of compositional zoning of garnets of different sizes from the Ryoke metamorphic belt, Japan, and comparison with those imposed/retrieved by Okudaira (1996) to model garnet zoning profiles.

Parameter:	$T_p$ , °C	$t_p$ (Myr)	$k_2$ (cm/ $\sqrt{s}$ ) (growth const)	$b$ , °C (cooling const)
This study	650	0.1	$7.1 (10^{-6})$	19.07
Okudaira	650–670	0.1	$6.29 (10^{-6})$	
Parameter*:		$t_i$ (Myr)		$T_i$ , °C
This study		0.097(0.1), 0.087(0.2), 0.065(0.3) 0.036(0.4), 0.017(0.5)		650(0.1), 647(0.2), 632(0.3), 588(0.4), 545(0.5)
Okudaira		<i>*0.097(0.1), 0.086(0.2), 0.069(0.3)</i> <i>0.046(0.4), 0.015(0.5)</i>		600(0.5)
Parameter <sup>++</sup> :		$m_{Fe}$ (°C <sup>-1</sup> )	$m_{Mn}$ (°C <sup>-1</sup> )	$m_{Mg}$ (°C <sup>-1</sup> )
This study		$4.20 (10^{-4})$	$-6.17 (10^{-4})$	$1.99 (10^{-4})$
Okudaira			$-1.00 (10^{-3})$	
Parameter <sup>+++</sup> :		$c_{Fe}$	$c_{Mn}$	$c_{Mg}$
This study		0.713	0.149	0.093
Okudaira			1.095	

\*Time ( $t_i$ ) of nucleation of garnet of radius (mm) specified within the parentheses after the beginning of simulation at 500 °C, and the corresponding temperatures ( $T_i$ ).

<sup>++</sup>Parameters governing change of surface composition; see Eq. (4).

<sup>+++</sup>Italics indicate parameters retrieved by Okudaira (1996).



**Fig. 4.** Comparison of the temperature–time path of Ryoke metamorphic belt, south western Japan, as retrieved in this study (solid line), with those calculated by Okudaira et al. (1994) from 1-D thermal modeling (thick dashed line) and modified (thin dashed line) by Okudaira (1996) to yield a better match of the calculated Mn zoning profile of the 0.5 mm radius garnet crystals with the measured data. Our model requires that the temperature drops below the close temperature of cation diffusion in garnet (~500 °C) sufficiently rapidly after 1.5–2.0 Myr such that there are no further diffusive adjustments of garnet compositions.

the retrieval of the overall  $T$ – $t$  path of metamorphic rocks through the pro- and retro-grade regimes. The most reliable  $T$ – $t$  path is not necessarily retrieved by keeping as many model parameters floating as possible, but restricting those that may be reliably constrained to vary within limited intervals (as determined by the uncertainties of the constrained parameters), and optimizing the other floating parameters to obtain the best match between the measured and simulated compositions. The genetic algorithm that we have used in this study offers a powerful tool for the optimization of parameters. It is satisfying to note that despite the rather large number of free parameters (a total of 10) that we used in this study, we were able to retrieve the pro-grade path and peak temperature that match the results of independent thermal modeling (Okudaira et al., 1994; Okudaira, 1996). If the rock indeed had followed a monotonic retro-grade  $T$ – $t$  path shown by the results of thermal modeling, then we believe that with a reliable constrain on the temperature of equilibration of garnet rim, we would have also been able to retrieve a retro-grade path matching the result of thermal modeling.

## 5. Summary and comments

In this study we have (a) critically discussed the thermobarometric methods and calculated the grain sizes of garnets that may be used to constrain the peak  $P$ – $T$  conditions of metapelitic assemblages consisting of garnet, biotite, aluminosilicate and quartz, and (b) presented a modeling protocol utilizing the optimization methods of genetic algorithm to determine the best match between calculated and measured compositional profiles of multicomponent garnets to retrieve the pro- and retro-grade  $T$ – $t$  paths of the Ryoke metamorphic belt.

For the determination of the  $P$ – $T$  condition, the best approach, in our judgment, is to combine garnet–biotite Fe–Mg exchange geothermometry with GASP equilibrium instead of using multiple mineral equilibria as these conventional thermo-barometers are based on a large body of experimental data of high quality for the determination of equilibrium conditions in the simple system and translating those to complex natural systems through the use of well constrained thermodynamic solution properties. The use of multiple mineral equilibria, although a very good approach in principle, often suffers in practice from the problem of lack of adequate constraints on the thermodynamic mixing properties of minerals that frequently involve multisite mixing

and lack of independent constraint on the activity of volatile species when the set of equilibria contains devolatilization (typically dehydration) equilibria. We also discuss evidence from recent literature where the alternative approaches have been compared against independent constraints and that suggest the superiority of the approach recommended in this study. In particular, the formulations developed by Ganguly and Cheng incorporating the garnet mixing property of Ganguly et al. (1996) have been found to be the most robust; software for these thermobarometric formulations may be downloaded using the link given in Section 2.1 or obtained on request from J. Ganguly.

We presented a method of modeling multicomponent compositional zoning in garnet, incorporating the effects of nucleation, growth and diffusion, to retrieve both pro- and retro-grade temperature–time history of metamorphic rocks. The method is based on Crank–Nicolson finite difference scheme to model the multicomponent diffusion process and a genetic algorithm to simultaneously retrieve a  $T$ – $t$  path and a number of model parameters that are usually constrained *a priori* in other works aimed at retrieving  $T$ – $t$  history of metapelites. The method has been applied to retrieve the pro- and retro-grade  $T$ – $t$  paths of the low pressure Ryoke metamorphic belt and compared with the results of independent thermal model. From the results of this comparison, we recommend practical methods that may be used to further improve the retrieval of  $T$ – $t$  history of metapelites from modeling compositional zoning of garnets. In the present problem, we have treated garnet grains that developed by a process of continuous nucleation and growth so that the numerical simulation requires only one growth constant. CSD analysis may be used to choose an appropriate set of such crystals, as has been done for the garnet samples in Ryoke metamorphic belt by Okudaira (1996). We hope to be able to expand the scope of the numerical model in future to be able to deal with more complicated problems.

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Thanks are due to Drs. Gaides and Okudaira for constructive reviews of the manuscript. We are especially grateful to Dr. T. Okudaira for providing us with the full data of the garnet compositions that have been modeled in this study as well as the table of temperature vs. time path that he used for quasibinary modeling of the Fe–Mn zoning profiles of the same samples. Thanks are due to Prof. M. Santosh for his invitation to contribute a paper in the special volume in honor of the late Prof. Akiho Miyashiro, who has left a lasting and major influence on the development of the subject of petrology.

## Appendix A.

### Genetic algorithm

The genetic algorithm (e.g. Haupt and Haupt, 1998; Deb, 2001) is a natural optimization method that permits exploration of a parameter space by maximizing or minimizing the value of a desired (*cost*) function. The method was originally inspired by problems in natural selection and natural genetics (Holland, 1975), but has been applied to a wide variety of scientific problems. The primary advantages of this algorithm are: (a) it permits optimization of parameters using complex cost function, (b) it does not require derivative of any function, and (c) it deals simultaneously with large number of parameters spanning different dimensional scales.

The main steps of the genetic algorithm with continuous parameters are described here within the context of the present problem. Here we tried to retrieve the thermal history of the Ryoke metamorphic belt by simulating the concentration profiles of Fe, Mn, Mg and Ca in metapelitic garnet grains of different radii. The free parameters are the growth constant ( $k_2$ ; Eq. (3)), two parameters for the function describing the concentration change at the boundary of a grain for each independent component ( $m_i$ ,  $c_i$ ; Eq. (4)), peak temperature and time to peak temperature ( $T_p$ ,  $t_p$ , respectively; Eq. (5a)) and a constant defining the

cooling path (b; Eq. (5b)). Thus, a total of ten free parameters were to be optimized.

A set of values for the free parameters yields a *chromosome* that may be represented as:

$$\text{chromosome} : [k_2, t_p, T_p, b, m_{Fe}, c_{Fe}, m_{Mn}, c_{Mn}, m_{Mg}, c_{Mg}] \quad (\text{A.1})$$

Each chromosome is created by choosing random values of the parameters within their respective specified upper and lower bounds. A set of even number of chromosomes is formed in this manner. Then each chromosome within the set is ranked on the basis of the value of a cost function,  $f$ , which for our problem is defined as follows.

$$f = \sum_{\text{core}}^5 \sum_{\text{rim}}^{n-1} \sum_{\text{point}}^1 \frac{|x_i^{\text{meas}} - x_i^{\text{calc}}|}{n_p} \quad (\text{A.2})$$

where the numerator within the first summation sign denotes the magnitude of the difference between the measured (meas) and calculated (calc) values of a component at a specific point within a grain,  $n_p$  is the number of points analyzed in the grain,  $n$  in the first summation sign denotes the total number of components, the second summation is for all data points from core to rim, and the number 5 in the third summation stands for the number of garnet crystals considered in this study. The lower the value of  $f$ , the higher is the ranking of a chromosome. A process of *natural selection* is then applied to the population and half of the chromosomes are selected and paired to form *parents* for the production of *offspring*s. The rest of the chromosomes are discarded.

The following procedure is applied to choose each parent. First, a cost weighted probability parameter,  $P_l$ , is defined as follows.

$$P_l = \frac{N-l+1}{\sum_{l=1}^N 1} \quad (\text{A.3})$$

where  $N$  is the total number of chromosomes and  $l$  is a running index. The latter is related to the cost function, being assigned a value of 1 for the best cost function, 2 for the second best cost function, and so on up to  $N$ . Let us now consider an example with  $N=8$ . In this case, the cost weighted probabilities are:  $P_1=0.222$ ,  $P_2=0.194$ ,  $P_3=0.167$ ,  $P_4=0.139$ ,  $P_5=0.111$ ,  $P_6=0.083$ ,  $P_7=0.056$ ,  $P_8=0.028$ . The cost weighted probability is defined such that the sum of the cost weighted probabilities is unity ( $\sum_{l=1}^N P_l = 1$ ).

A cumulative cost weighted probability (CWP) is now defined as  $\sum_{l=1}^m P_l$ , where  $m$  ranges between 1 and  $N$ . Thus, the successive CWP values are:  $\text{CWP}_{(m=1)} = P_1 = 0.222$ ;  $\text{CWP}_{(m=2)} = P_1 + P_2 = 0.416$ ;  $\text{CWP}_{(m=3)} = P_1 + P_2 + P_3 = 0.583$ , and so on. If a generated random number ( $r-n$ ) between 0 and 1 is  $\leq 0.222$ , then the first chromosome is chosen as the first parent, whereas if  $0.416 \leq r-n < 0.583$ , then the third chromosome is chosen as the first parent, and so on. After a chromosome is chosen as the first parent, it is removed from the set of available chromosomes, and the chromosome for the second parent is chosen following the same procedure according to the CWP value. For example, if the third chromosome is chosen as the first parent and in the next cycle,  $r-n \leq 0.222$ , then the first chromosome is chosen as the second parent and a couple is formed by the third and first chromosomes. Successive pairs of parents are paired to form couples.

The *mating* process within a couple involves a recombination of the chromosomes from the two parents to generate two offspring. The offspring can form in several different ways. Here we used a combination of extrapolation and crossover. A random number from 1 to the total number of parameters is generated, for instance let us say 6. Then the sixth parameter ( $c_{Fe}$ ) for the two offspring are:

$$\begin{aligned} c_{Fe}^1 &= c_{Fe}^{p1} - \beta(c_{Fe}^{p1} + c_{Fe}^{p2}) \\ c_{Fe}^2 &= c_{Fe}^{p2} + \beta(c_{Fe}^{p2} + c_{Fe}^{p1}) \end{aligned} \quad (\text{A.4})$$

where  $\beta$  is a random between 0 to 1 and  $p1$  and  $p2$  stand for first and second parent, respectively. The rest of the parameters from 7 to 10

are then crossed over to generate the full set of chromosomes for the two offspring, as follows:

$$\begin{aligned} \text{Chromosome}(\text{offspring}^1) &= [k_2^{p1}, t_{peak}^{p1}, T_{peak}^{p1}, b^{p1}, m_{Fe}^{p1}, c_{Fe}^{p1}, m_{Mn}^{p2}, c_{Mn}^{p2}, m_{Mg}^{p2}, c_{Mg}^{p2}] \\ \text{Chromosome}(\text{offspring}^2) &= [k_2^{p2}, t_{peak}^{p2}, T_{peak}^{p2}, b^{p2}, m_{Fe}^{p2}, c_{Fe}^{p2}, m_{Mn}^{p1}, c_{Mn}^{p1}, m_{Mg}^{p1}, c_{Mg}^{p1}] \end{aligned} \quad (\text{A.5})$$

In this way a population of offspring is generated so that the original population of chromosomes is restored. For example, with 8 chromosomes in the original selected set ( $N=8$ ), there will be 4 parents or 2 couples and 4 offspring so that in the end the number of 8 chromosomes (4 parents + 4 offspring) will be maintained.

The last stage allows for a small percentage of *mutations*. In this stage, we have replaced values of approximately 4% of the parameters with new ones that are selected randomly from the specified upper and lower bounds of each parameter. A new cycle starts over by computing new cost functions for the new population of chromosomes and repeating all the steps from creating parents to mutation until the values of the cost function does not decrease anymore. The domain of permissible variation of a parameter is successively refined or restricted by choosing the permissible domain in a given iteration around the value of the parameter found in a previous iteration.

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