論文 **Original Paper**

Forward Calculation of the Formation of Chemical Zoning in Garnet

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Abstract: Garnet porphyroblasts in metamorphic rocks are often used to deduce the pressure-temperature paths of the metamorphism. Differential thermodynamic method is commonly applied to calculate the *P–T* changes during garnet growth. However, in the differential thermodynamic method, equations are solved using only the first term in Taylor's series expansion. Besides, it is difficult to estimate the change of amount of minerals. It is desirable to develop a means to predict the garnet formation mechanism, involving all available properties of mineral behaviors. Forward model was proposed to reconstruct the formation of normal chemical zoning in garnet consuming chlorite, based on the latest thermodynamic data set of minerals. Growth and chemical composition change of garnet were calculated quantitatively, through straightforward iterative algorithm. Dependence of enthalpy on temperature, and non-ideal mixing property were also considered. Estimated *P–T* path in the pelitic schists of the Sambagawa metamorphic belt, central Shikoku, Japan, was used for the case study. Though the predicted composition did not coincide well with natural samples, the overall shape and trend of chemical zoning of garnet were reproduced. The growth of ternary garnet was explained by the relationship of two pseudobinary loops.

Keywords: garnet, chemical zoning, *P–T* path, forward modeling, Sambagawa metamorphic belt

INTRODUCTION

Chemical zoning retained in rock forming minerals is one of the most important clues for the condition history of the rock. Garnet porphyroblasts in metamorphic rocks are commonly used to deduce the pressure-temperature paths of the metamorphism. It is widely accepted that garnet grows in thermodynamic equilibrium with other minerals during prograde metamorphism, gradually changing its composition in response to changing conditions. Due to the small chemical diffusion rate in garnet, the inner part of the grain is isolated from the reaction, being covered by the new growth surface. Changing chemical compositions retained in garnet from the core to the rim represent the chemical compositions that were in equilibrium with the matrix minerals at each stage of the garnet growth. It is possible to obtain the time series of pressure and temperature conditions, if other conditions are adequately constrained.

Differential thermodynamic method is often applied to estimate the *P–T* changes during garnet growth (Spear 1993). The relationship between the mineral compositions in the rocks is expressed by equations of thermodynamic equilibrium. The total rock system has certain number of thermodynamic variance, which is equal to the number of independent variables. The system can be solved if the independent variables are given value. Garnet is usually a four components solid solution, which provides three independent variables. When the thermodynamic variance of the rock in interest is less than four, the total rock system can be solved using only the garnet composition. The equation of thermodynamic equilibrium is highly nonlinear. The differential thermodynamic method enables to solve the simultaneous equations by applying Taylor's series expansion. Using only the linear terms, the equations are transformed into a set of simultaneous linear equations. Given the composition "changes" of garnet, the changes of all other conditions including the intensive variables can be calculated. If absolute pressure and temperature are known at certain point during the crystal growth, mostly at the rim of the grain, the whole history can be deduced by calculating back the *P–T* changes toward the garnet core.

However, there are several weaknesses in the differential thermodynamic method. First, it requires the exact starting conditions to begin with. The starting conditions are the absolute pressure, temperature, and the equilibrium mineral compositions under the *P–T*. They must be determined by other geothermobarometers, which may be inconsistent. Secondly, it is difficult to estimate if garnet grows or decomposes during the calculated *P–T* path. This information is desirable since it confirms the calculation result. It is possible to include volume changes of minerals

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as additional constraints. In this case, however, it is even more difficult to define the starting conditions concerning the molar amount of each mineral. Thirdly, equations are solved by using only the linear term in Taylor's series expansion. The ignored terms might cause difference to the results.

One way to solve the problem is to check the calculation results by forward modeling. Forward models concerning garnet growth were proposed by several authors (Hollister 1966; Banno *et al.*, 1986). Thermodynamic properties of minerals have been significantly refined since. The aim of this study is to construct a new forward growth model of Mg–Fe–Mn garnet using the latest thermodynamic property data of minerals. In addition, with the development of computers, it has become possible to solve the total system without linearization. Case study was performed using the *P–T* path of the Sambagawa metamorphic rocks in central Shikoku, southwest Japan, which was calculated using differential thermodynamic method (Inui & Toriumi, in press). We will discuss the validity of the *P–T* path and the proposed forward model.

THE FORWARD MODEL

Outline of the model

Formation of Mg–Fe–Mn garnet from chlorite was modeled in the $MnO–FeO–MgO–Al_2O_3–SiO–H_2O$ system. If bulk chemical composition is fixed, the thermodynamic variance of the system is two, as specified by Duhem's theorem. Given the *P–T* condition, the mole amounts of all minerals and their chemical compositions are uniquely determined. The formation of garnet can be reconstructed by giving serial *P–T* conditions.

Chemical diffusion is assumed to be none in garnet and very fast in chlorite, thus chlorite is kept homogeneous. New garnet with new chemical composition forms consuming chlorite, covering the old crystal. With no diffusion, crystallized garnet is isolated from the bulk rock chemistry. To reproduce this process, serial bulk rock chemistries are given as well as *P–T* conditions. The new bulk rock chemistry is determined from the amount and composition of garnet formed in the previous step.

The thermodynamic properties of mineral end-members were taken from the internally consistent data set of Holland & Powell (1998). Non-ideal mixing properties were taken from Holland & Powell (1998), their web site (http://www.esc.cam.ac.uk/astaff/holland/ds5/HP98_index.html), and Ganguly *et al.* (1996). Details are described in the section below. Quartz and water were assumed as excess phases, since the formation reaction involves those phases. Fugacity of water was taken from Holland & Powell (1990). No Fe^{3+} was considered, and the content of Ca end-member in garnet was fixed in this study.

Basic equations

The unit formula of garnet is written as $(Mg, Fe, Mn, Ca)_3^{M1}Al_2^{M2}Si_3^{T}O_{12}$. M1 and M2 are the octahedral sites, T is the tetrahedral site. Garnet is expressed as a solid solution of four end-members: pyrope (Mg end-member), almandine (Fe), spessartine (Mn), and grossular (Ca). The unit formula and abbreviation of each end-member are listed in Table 1. The mole fraction of each end-member is defined as follows:

$$X^{Grt}_{Prp} = Mg^{M1} = (Mg/(Mg + Fe + Mn + Ca)),$$
$$X^{Grt}_{Alm} = Fe^{M1} = (Fe/(Mg + Fe + Mn + Ca)),$$
$$X^{Grt}_{Sps} = Mn^{M1} = (Mn/(Mg + Fe + Mn + Ca)),$$
$$X^{Grt}_{Grs} = Ca^{M1} = (Ca/(Mg + Fe + Mn + Ca)),$$

where X^{A}_{b} represents the mole fraction of end-member b in phase A, C^{M1} represents the fraction of cation C in M1 site, and C represents the number of cation C per unit formula.

Table 1 Chemical formulae and abbreviations of the mineral end-members used in the forward model.

Mineral	End-member	Formula unit
Garnet (Grt)	Pyrope (Prp)	$Mg_3Al_2Si_3O_{12}$
	Almandine (Alm)	$Fe_3Al_2Si_3O_{12}$
	Spessartine (Sps)	$Mn_3Al_2Si_3O_{12}$
	Grossular (Grs)	$Ca_3Al_2Si_3O_{12}$
Chlorite (Chl)	Clinochlore (Cln)	$Mg_5Al_2Si_3O_{10}(OH)_8$
	Amesite (Ame)	$Mg_4Al_4Si_2O_{10}(OH)_8$
	Daphnite (Dph)	$Fe_5Al_2Si_3O_{10}(OH)_8$
	Mn-chlorite (Mnc)	$Mn_5Al_2Si_3O_{10}(OH)_8$
Quartz (Qtz)		SiO_2
Water		H_2O

Chlorite is assumed as the reactant. Chlorite unit formula can be written as $(Mg, Fe, Mn)_4^{M1}(Mg, Fe, Mn, Al)^{M2}(Al)^{M3}(Al, Si)_2^{T1}Si_2^{T2}O_{10}(OH)_8$. M1, M2, and M3 are the octahedral sites; T1 and T2 are the tetrahedral sites. Different description of unit formula may be necessary if amount of Al cation varies extremely, but it is sufficient for normally observed metamorphic chlorite. Chlorite is treated as a solid solution of four end-members: clinochlore (Mg end-member), amesite (Mg end-member plus Tschermak's substitution), daphnite (Fe), Mn-chlorite (Mn). Tschermak's substitution (MgSi–AlAl) is represented by Mg end-members. Unit formulae are listed in Table 1. Mole fractions of end-members are defined as follows:

$$X^{Chl}_{Ame} = Al^{M2} = Al - (4 - Si) - 1,$$
$$X^{Chl}_{Cln} = Mg^{M2} = 1 - X_{Ame} - X_{Dph} - X_{Mnc},$$
$$X^{Chl}_{Dph} = Fe^{M2} = (Fe/(Mg + Fe + Mn))(5 - X^{Chl}_{Ame})/5,$$
$$X^{Chl}_{Mnc} = Mn^{M2} = (Mn/(Mg + Fe + Mn))(5 - X^{Chl}_{Ame})/5.$$

The variables in this system are the amount of minerals, mole fractions of mineral end-members, and the temperature and pressure. As described above, mole amounts of quartz and water are not constrained, and X^{Grt}_{Grs} is fixed. There are eleven variables in total: *T* (temperature), *P* (pressure), M_{Grt} (mole amount of garnet), M_{Chl} (mole amount of chlorite), $X^{\mathrm{Grt}}_{\mathrm{Prp}}$, $X^{\mathrm{Grt}}_{\mathrm{Alm}}$, $X^{\mathrm{Grt}}_{\mathrm{Sps}}$, $X^{\mathrm{Chl}}_{\mathrm{Cln}}$, $X^{\mathrm{Chl}}_{\mathrm{Ame}}$, $X^{\mathrm{Chl}}_{\mathrm{Dph}}$, and $X^{\mathrm{Chl}}_{\mathrm{Mnc}}$.

Constraints on the system are devided into three categories: constraints of stoichiometry, constraints of mass balance, and constraints of equilibrium. Constraints of stoichiometry are the simple rules as follows:

$$X^{\mathrm{Grt}}_{\mathrm{Prp}}+X^{\mathrm{Grt}}_{\mathrm{Alm}}+X^{\mathrm{Grt}}_{\mathrm{Sps}}=\text{constant}, \tag{1}$$

$$X^{\mathrm{Chl}}_{\mathrm{Cln}}+X^{\mathrm{Chl}}_{\mathrm{Ame}}+X^{\mathrm{Chl}}_{\mathrm{Dph}}+X^{\mathrm{Chl}}_{\mathrm{Mnc}}=1. \tag{2}$$

The constant in the equation (1) is not 1 because of $X^{\mathrm{Grt}}_{\mathrm{Grs}}$. $X^{\mathrm{Grt}}_{\mathrm{Grs}}$ is fixed to 0.2 in this study.

Constraints of mass balance are the expression of constant bulk rock chemical composition. As the amounts of quartz (SiO_2) and water (H_2O) are excess, there are four constraints of mass balance:

$$\mathrm{TotalMg}=3M_{\mathrm{Grt}}X^{\mathrm{Grt}}_{\mathrm{Prp}}+5M_{\mathrm{Chl}}X^{\mathrm{Chl}}_{\mathrm{Cln}} +4M_{\mathrm{Chl}}X^{\mathrm{Chl}}_{\mathrm{Ame}}, \tag{3}$$

$$\mathrm{TotalFe}=3M_{\mathrm{Grt}}X^{\mathrm{Grt}}_{\mathrm{Alm}}+5M_{\mathrm{Chl}}X^{\mathrm{Chl}}_{\mathrm{Dph}}, \tag{4}$$

$$\mathrm{TotalMn}=3M_{\mathrm{Grt}}X^{\mathrm{Grt}}_{\mathrm{Sps}}+5M_{\mathrm{Chl}}X^{\mathrm{Chl}}_{\mathrm{Mnc}}, \tag{5}$$

$$\mathrm{TotalAl}=2M_{\mathrm{Grt}}(X^{\mathrm{Grt}}_{\mathrm{Prp}}+X^{\mathrm{Grt}}_{\mathrm{Alm}}+X^{\mathrm{Grt}}_{\mathrm{Sps}}) +2M_{\mathrm{Chl}}(X^{\mathrm{Chl}}_{\mathrm{Cln}}+X^{\mathrm{Chl}}_{\mathrm{Dph}}+X^{\mathrm{Chl}}_{\mathrm{Mnc}}) +4M_{\mathrm{Chl}}X^{\mathrm{Chl}}_{\mathrm{Ame}}. \tag{6}$$

TotalC is the total molar amount of the C cation.

Three independent reactions are found in this system, that make three non-linear constraints of chemical equilibrium. Pyrope forming reaction consuming chlorite is written as follows:

$$\underset{\text{Clinochlore}}{Mg_5Al_2Si_3O_{10}(OH)_8}+\underset{\text{Amesite}}{Mg_4Al_4Si_2O_{10}(OH)_8} + \underset{\text{Quartz}}{4SiO_2} =\underset{\text{Pyrope}}{3Mg_3Al_2Si_3O_{12}}+\underset{\text{Water}}{8H_2O}. \tag{7}$$

Following exchange reactions express the behavior of Fe and Mn end-members:

$$5Fe_3Al_2Si_3O_{12}+3Mg_5Al_2Si_3O_{10}(OH)_8 =5Mg_3Al_2Si_3O_{12}+3Fe_5Al_2Si_3O_{10}(OH)_8, \tag{8}$$

$$5Mn_3Al_2Si_3O_{12}+3Fe_5Al_2Si_3O_{10}(OH)_8 =5Fe_3Al_2Si_3O_{12}+3Mn_5Al_2Si_3O_{10}(OH)_8. \tag{9}$$

If the system is in equilibrium, the Gibbs' energy change of each of the above reaction is zero. The general equation of chemical equilibrium at the T and P of interest is as follows:

$$\begin{aligned}0&=\Delta \mathrm{G_r}\\ &=\Delta \mathrm{H_r}+\int_{297}^{T}\mathrm{C_p}dT-T\left(\Delta \mathrm{S_r}+\int_{297}^{T}(\mathrm{C_p}/T)dT\right)\\ &\quad+\Delta \mathrm{V_r}(P-1)+\mathrm{R}T\ln K,\end{aligned}$$

where G is the Gibbs' free energy (J), H is the enthalpy (J), S is the entropy (J/K), $\mathrm{C_p}$ is the heat capacity (J/K), V is the volume (J/bar), R is the gas constant, and $\Delta \mathrm{A_r}$ represents the change of A due to the reaction. $\Delta \mathrm{V_r}$ only concerns with solid phases. The contribution of water is involved in the fugacity term mentioned below. T and P are the temperature (K) and pressure (bar) of interest, respectively. H, S, $\mathrm{C_p}$, and V for each mineral end-members were taken from the internally consistent thermodynamic data set of Holland & Powell (1998). Bar unit is used according to the data set. Correction terms for Gibbs' free energy are included in the above equation since the data are standardized to 25°C, 1 bar. Dependence of V on pressure is ignored. K is the equilibrium constant and this is where mineral compositions are involved in the equations:

$$K=\Pi a^{v}$$

where a is the activity, and v is the stoichiometric coefficient. Activity of water is usually expressed by water fugacity, f_{H_2O}, i.e., the term for the reaction (7) is written as follows:

$$\mathrm{R}T\ln K=\mathrm{R}T\ln\{(a_{\mathrm{Prp}})^3/(a_{\mathrm{Cln}})(a_{\mathrm{Ame}})\}+8\mathrm{R}T\ln f_{H_2O}.$$

The ideal parts of the activities of garnet are:

$$a^{\mathrm{ideal}}_{\mathrm{Prp}}=(X^{\mathrm{Grt}}_{\mathrm{Prp}})^3 \text{ etc.}$$

The non-ideal mixing between the Fe and Mg end-members of garnet was modeled as regular solution, with the Margules parameter ($\mathrm{W_{Prp\text{-}Alm}}=0.8$ kJ/mol) as required in Holland & Powell (1998). The non-ideal mixing properties of other binary joins in garnet were described using the asymmetric mixing parameter of Ganguly *et al.* (1996). The ideal parts of the activities of chlorite end-members are formulated with ideal mixing on site model (Holland *et al.*, 1998). To reduce the number of variables, the activity-composition relationships are expressed with mole fraction of end-members in this study:

$$\begin{aligned}a^{\mathrm{ideal}}_{\mathrm{Ame}}&=(\mathrm{Mg^{M1}})^4(\mathrm{Al^{M2}})(\mathrm{Al^{T1}})^2\\ &=1/4\times\{(5X^{\mathrm{Chl}}_{\mathrm{Cln}}+4X^{\mathrm{Chl}}_{\mathrm{Ame}})/(5-X^{\mathrm{Chl}}_{\mathrm{Ame}})\}^4\\ &\quad X^{\mathrm{Chl}}_{\mathrm{Ame}}(1+X^{\mathrm{Chl}}_{\mathrm{Ame}})^2,\\ a^{\mathrm{ideal}}_{\mathrm{Cln}}&=4(\mathrm{Mg^{M1}})^4(\mathrm{Mg^{M2}})(\mathrm{Al^{T1}})(\mathrm{Si^{T1}})\\ &=\{(5X^{\mathrm{Chl}}_{\mathrm{Cln}}+4X^{\mathrm{Chl}}_{\mathrm{Ame}})/(5-X^{\mathrm{Chl}}_{\mathrm{Ame}})\}^5\\ &\quad(1-X^{\mathrm{Chl}}_{\mathrm{Ame}})^2(1+X^{\mathrm{Chl}}_{\mathrm{Ame}}),\\ a^{\mathrm{ideal}}_{\mathrm{Dph}}&=4(\mathrm{Fe^{M1}})^4(\mathrm{Fe^{M2}})(\mathrm{Al^{T1}})(\mathrm{Si^{T1}})\\ &=\{5X^{\mathrm{Chl}}_{\mathrm{Dph}}/(5-X^{\mathrm{Chl}}_{\mathrm{Ame}})\}^5\\ &\quad(1-X^{\mathrm{Chl}}_{\mathrm{Ame}})^2(1+X^{\mathrm{Chl}}_{\mathrm{Ame}}),\\ a^{\mathrm{ideal}}_{\mathrm{Mnc}}&=4(\mathrm{Mn^{M1}})^4(\mathrm{Mn^{M2}})(\mathrm{Al^{T1}})(\mathrm{Si^{T1}})\\ &=\{5X^{\mathrm{Chl}}_{\mathrm{Mnc}}/(5-X^{\mathrm{Chl}}_{\mathrm{Ame}})\}^5\\ &\quad(1-X^{\mathrm{Chl}}_{\mathrm{Ame}})^2(1+X^{\mathrm{Chl}}_{\mathrm{Ame}}).\end{aligned}$$

Non-ideal parts of chlorite activities are modeled as regular solution using Margules parameters taken from Holland and Powell (1998, http://www.esc.cam.ac.uk/astaff/holland/ds5/HP98_index.html): $\mathrm{W_{Cln\text{-}Ame}}=18$, $\mathrm{W_{Cln\text{-}Dph}}=2.5$, $\mathrm{W_{Ame\text{-}Dph}}=13.5$ kJ/mol. Ideal mixing is assumed between Mn-chlorite and other end-members, as is required for the data set (Holland & Powell, 1998).

In total, there are nine constraints for eleven variables. Seven of the constraints are non-linear (equations (3) to (9)). Given the pressure and temperature, the mole amounts of all garnet and chlorite, and their chemical compositions are uniquely determined.

Calculation

Simultaneous non-linear equations are solved by iterative calculation. The model was coded using Microsoft Visual Basic for Applications. The algorithm is shown in the flow chart (Fig. 1). Constraints (1) and (2) are linear equations. Constraints (3) to (6) involve multiplications of two of the variables. These six simultaneous equations could be solved by substitution method. Thus, values of three variables are assumed at first place. Equations (1) to (6) are solved to find the six other variables. Equations (7) to (9) are calculated using the derived values. If the equa-

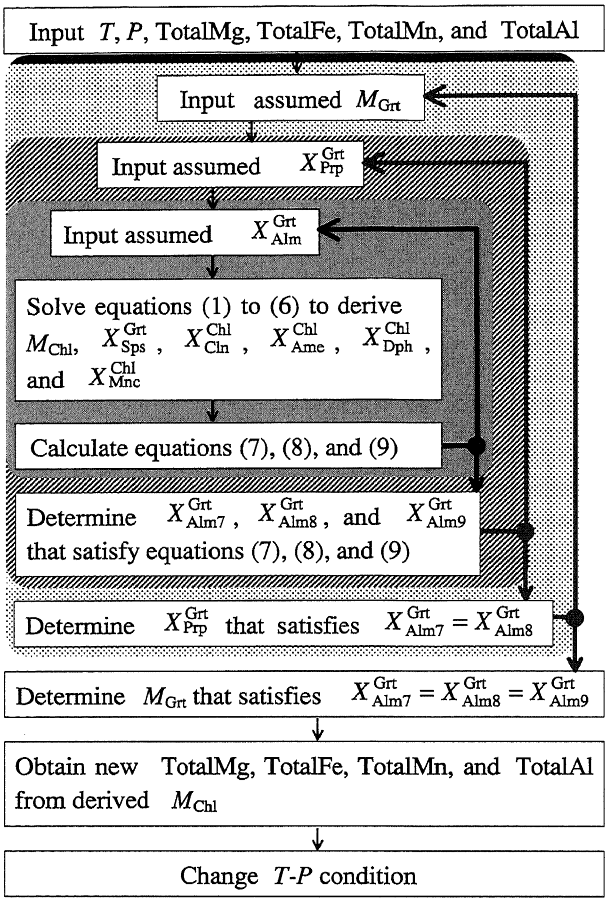

Fig. 1. Flow chart showing the algorithm to solve the highly non-linear simultaneous equations. Three independent variables are systematically varied and iterative calculation is performed to seek the set of values where all three of the non-linear equations are satisfied. The algorithm consists of three nested calculation loops shown in different hatches.

tions are not satisfied, the first assumption for the three variables are reconsidered. Calculations are iterated until all of the equations (7) to (9) are satisfied. The calculation of chemical composition is done to the fourth decimal place. Theoretically, it is not tested whether the simultaneous equations (1) to (9) have a solution or not, but the fact that the derived set of value does satisfy all of the equations justifies the result.

To start the calculation, temperature, pressure, and the bulk rock chemical compositions (totalMg, totalFe, totalMn, totalAl) must be given. Bulk rock chemical compositions should be determined from the typical chlorite composition. Starting P–T condition must be identified by preliminary calculation, because calculation is possible only in the condition where both garnet and chlorite are stable. This is known by the calculated amount of garnet, M_{Grt}, that satisfies the nine constraints. Positive M_{Grt} value means garnet is stable, whereas negative M_{Grt} value indicates garnet does not exist in equilibrium with chlorite under the given P–T condition. Changing the P–T condition systematically, an isopleth is found where M_{Grt} changes from negative to positive. The reasonable starting P–T condition is the point where M_{Grt} just turns positive. The starting condition depends on the initial bulk chemical composition.

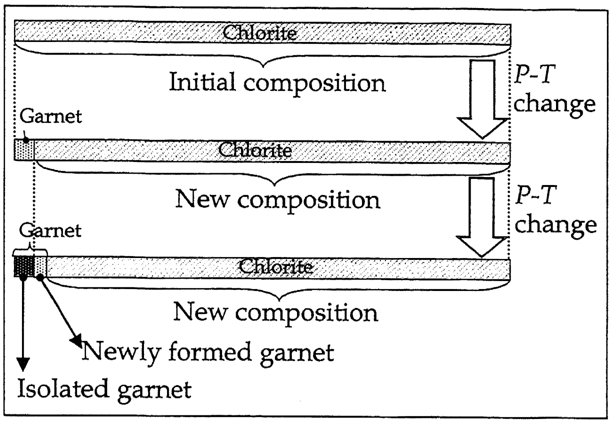

Fig. 2. General idea of the proposed forward model. Volume and mineral compositions of equilibrium garnet and chlorite are uniquely determined under certain P–T condition. Chlorite is always homogeneous due to very fast diffusion. On the other hand, crystallized garnet is isolated from the bulk chemical composition in the next step.

When starting condition is obtained, forward calculation can be performed giving a sequence of P–T conditions. The calculation proceeds as follows (Fig. 2):

(1) Input initial temperature, pressure, and composition of chlorite (= bulk rock chemical composition) to solve the simultaneous non-linear equations. Derive all variables.

(2) Subtract the molar amount of each cation newly incorporated into garnet from the previous bulk rock chemical composition.

(3) Input the next temperature, pressure, and bulk rock chemical composition to solve the simultaneous non-linear equations. Derive all variables.

(4) Iterate steps (2) and (3).

CASE STUDY

The Sambagawa metamorphic belt

The Sambagawa metamorphic belt is a high-pressure intermediate type metamorphic belt, which extends for around 800 km in the southwestern part of the Japanese islands (Fig. 3) (Wallis & Banno, 1990). It originates mainly from Mesozoic trench sediments and other ocean floor volcanics accreted to the eastern margin of the Eurasian continent. The Sambagawa metamorphism is known as subduction related. The prograde pressure-temperature path (P–T path during temperature increase) will constrain the thermal structure of the subduction zone, which will be important information to unravel the mechanism of plate subduction.

The Sambagawa sequence was subject to regional

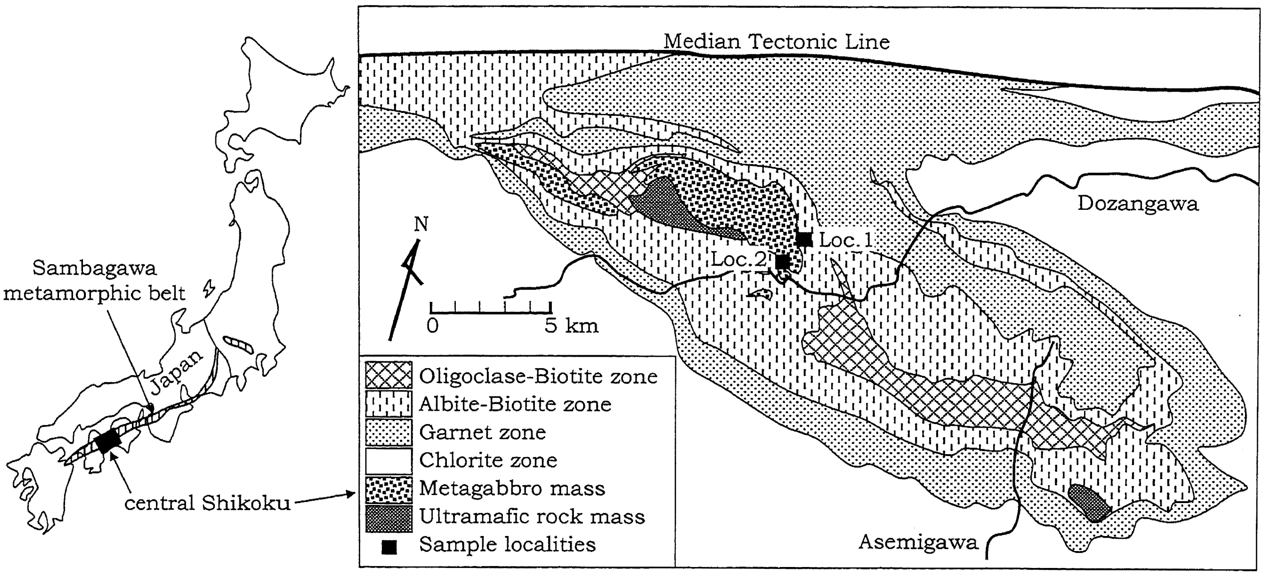

Fig. 3. Metamorphic zonal map of the Sambagawa metamorphic belt in central Shikoku. Samples were collected from the albite-biotite zone. Modified from Higashino (1990).

metamorphism up to the epidote-amphibolite facies, probably during the Late Cretaceous (116 ± 10 Ma), followed by exhumation and cooling during the interval 110–50 Ma (Isozaki & Itaya, 1990). North of the Sambagawa metamorphic belt lies the roughly contemporaneous Ryoke high-temperature metamorphic belt, the boundary being a major fault zone called the Median Tectonic Line. The southern boundary of the Sambagawa metamorphic belt in contact with the northern Chichibu belt is generally conformable (Dallmeyer *et al.*, 1995).

The largest extent of the Sambagawa metamorphic belt is exposed in the central Shikoku. It consists mainly of pelitic schists accompanied by smaller amount of mafic and quartz schists. Four metamorphic zones are defined using mineral assemblages in pelitic rocks: the chlorite zone, the garnet zone, the albite-biotite zone, and the oligoclase-biotite zone, in the order of increasing metamorphic grade, as shown in Fig. 3 (Higashino, 1990). Estimated peak metamorphic conditions are 520 ± 25°C at 0.8–0.95 GPa, and 610 ± 25°C at around 0.9–1.1 GPa for the albite-biotite zone and the oligoclase-biotite zone, respectively (Enami, 1983; Enami *et al.*, 1994).

Estimated *P–T* path

Prograde *P–T* path of the Sambagawa metamorphism has been estimated based on the chemical zoning of garnet by Inui & Toriumi (in press). Their samples were pelitic schists from the albite-biotite zone, with the prograde mineral assemblage of garnet + muscovite + chlorite + epidote + paragonite + albite + quartz (+ biotite). The representative chemical trend in garnet is shown in Fig. 4. The *P–T* condition at the garnet rim determined by geothermobarometry was around 515 ± 30°C and 0.8–1.0 GPa. Differential thermodynamic method was then applied to calculate the *P–T* change from the core to the rim

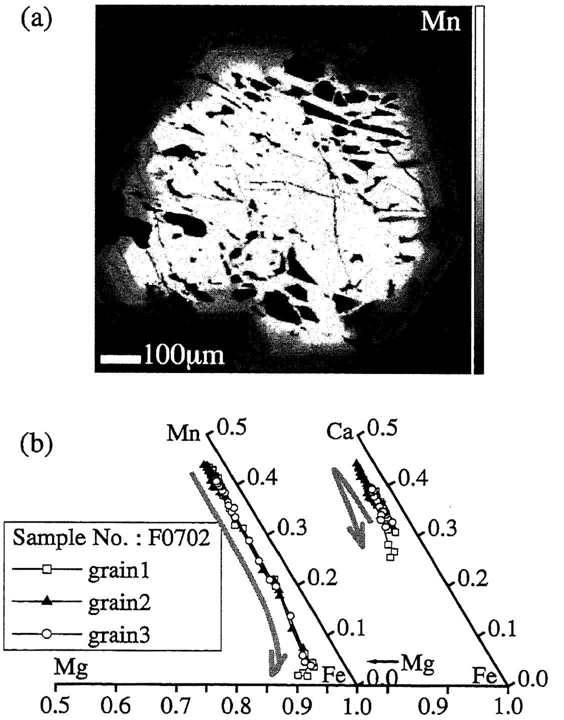

Fig. 4. Representative chemical composition trends of garnet in the pelitic schists of the Sambagawa metamorphic belt (sample F0702, Loc. 2). (a) Chemical mapping analysis of Mn. (b) Trends shown in Mg–Fe–Mn and Mg–Fe–Ca ternary diagrams. Arrows indicate the trends from the core to the rim. Mn is extremely enriched in the core and decrease toward the rim. Mg/Fe ratio increases from the core to the rim. In this sample, Ca content has a maximum in the midst from the core to the rim.

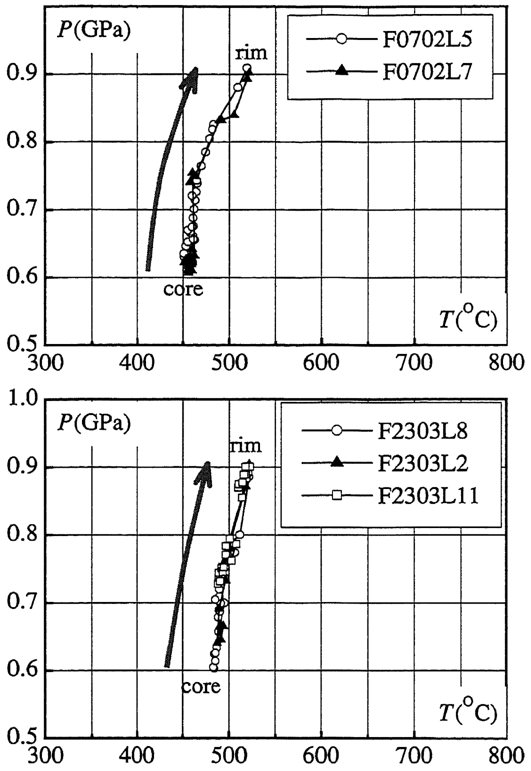

Fig. 5. Representative P–T trajectories deduced from garnet normal zoning. Arrows on the P–T diagrams indicate growth trends from the core to the rim. Sample F0702 is taken from Loc. 2, sample F2303 is from Loc. 1, in Fig. 3.

of garnet. Differential thermodynamic method has been established and described in detail by Spear & Selverstone (1983), and Spear (1989, 1993). The method reduces the problem into a set of simultaneous linear equations, using "changes" of chemical conditions recorded in zoned minerals. The bulk rock chemistry was not constrained. Calculation programs were coded using VBA (Visual Basic for Applications).

The deduced P–T paths are shown in Fig. 5. Garnet with normal zoning indicated heating with compression throughout garnet growth. Overall increase in pressure during the formation of garnet was around 0.3 GPa in response to heating of 50–70°C. Average dP/dT was around 0.4–0.5 GPa/100°C. The average P–T condition at the garnet core was around 460°C and 0.6 GPa.

Predicted zoning by forward model

The garnet growth was calculated by the forward model proposed in this study, under the estimated P–T evolution of the Sambagawa metamorphism. The starting chemical composition of chlorite was taken from that of chlorite zone (Table 2) (Higashino, 1975). Chlorite zone is the only grade zone in the Sambagawa metamorphic belt, where garnet does not occur. The chlorite in the chlorite zone may represent the chlorite chemistry before the formation of garnet.

Table 2 Initial chlorite composition used in the case study. It is the average composition of the four chlorite chemistry data shown in Higashino (1975). See text for the calculation of end-member fractions.

	wt%		cation no.
			(O = 14)
MgO	10.8	Mg	1.7
SiO_2	26.6	Si	2.8
Al_2O_3	20.7	Al	2.6
TiO_2	0.05	Ti	0.004
MnO	0.85	Mn	0.077
FeO	29.2	Fe	2.6

End-member	Molar fraction
X_{Cln}	0.003
X_{Ame}	0.44
X_{Dph}	0.54
X_{Mnc}	0.016

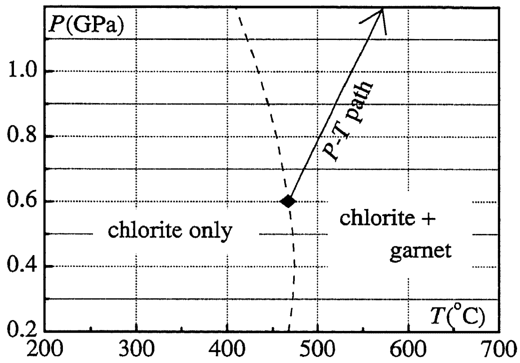

Fig. 6. The broken line is the isopleth of garnet formation derived for the case study. Garnet and chlorite do not coexist in the lower temperature side of the isopleth, whereas garnet and chlorite can exist in equilibrium in the higher temperature side. Calculation is possible on the higher temperature side. The solid line shows the input P–T path for the case study, which is similar to the estimated P–T paths shown in Fig. 5. ◆ marks the starting P–T condition.

The starting P–T condition was sought for the adopted chlorite composition. Applying the constant pressure of 0.6 GPa, the molar amount of garnet (M_{Grt}), which can exist in equilibrium with chlorite, was calculated changing the temperature with the increment of 1°C. M_{Grt} turned positive at 467°C. 467°C and 0.6 GPa were adopted as the starting conditions of garnet formation, which is very close to the estimation described in the previous section. The isopleth for the beginning of garnet formation was obtained by applying the same method to pressures 0.2 to 1.2 GPa (Fig. 6).

To model the estimated P–T trajectory, uniform P–T increase was given toward the estimated peak P–T condition, 520°C and 0.9 GPa (Fig. 6). The increments of tem-

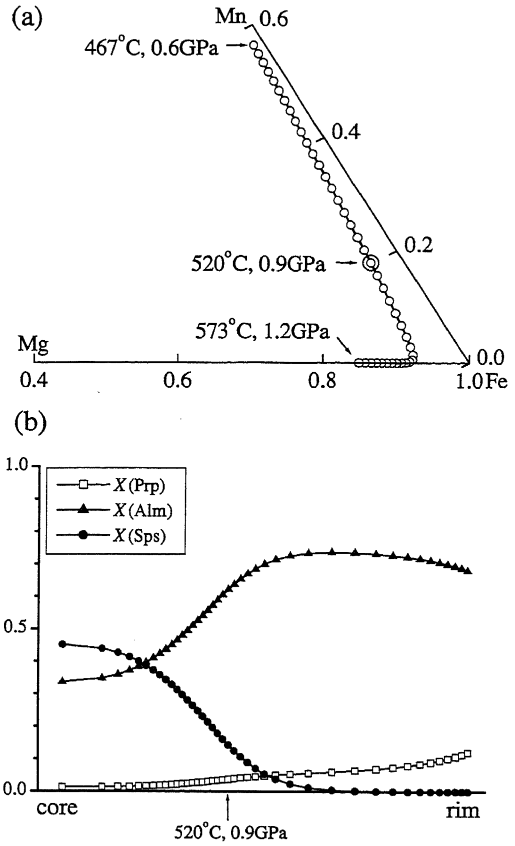

Fig. 7. Chemical zoning in garnet predicted by the forward model. (a) Predicted chemical trend in the Mg–Fe–Mn system. (b) Predicted composition change from the core to the rim. The horizontal axis is the standardized radius (garnet volume raised to the 1/3 power).

perature and pressure increase were set to 2.65°C and 0.015 GPa. The calculation was continued through the estimated peak condition until 573°C and 1.2 GPa.

The predicted garnet zoning is shown in Fig. 7. The calculated garnet composition at the estimated peak *P–T* condition, 520°C and 0.9 GPa, is different from the observed chemical composition. However, when calculation is continued, the overall shape of the chemical zoning in the Mg–Fe–Mn system is the same as the natural zoning. It is also seen that the commonly observed bell-shaped profile of Mn is reproduced.

The forward model also predicts the amount of garnet formed at each increment (Fig. 8). It is seen that the garnet formation is small in volume at the earlier stages. The volume increases rapidly at the middle stage and then decreases.

DISCUSSION

Figure 6 shows that the starting *P–T* condition of garnet formation deduced by the proposed forward model is similar to the values estimated from natural rocks. It seems that the model reasonably reproduces the crystallization mechanism.

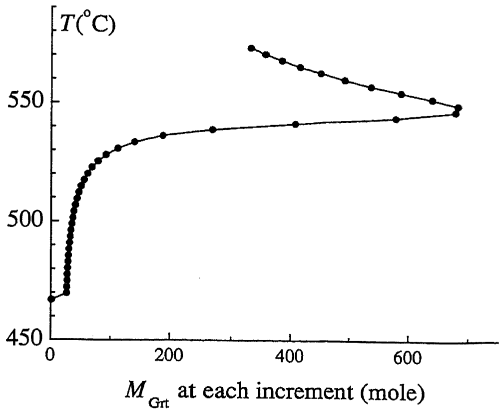

Fig. 8. Garnet formation per each increment (dM_{Grt}/2.65°C) plotted against temperature. The molar amount is calculated assuming the initial chlorite molar amount as 10000 mol.

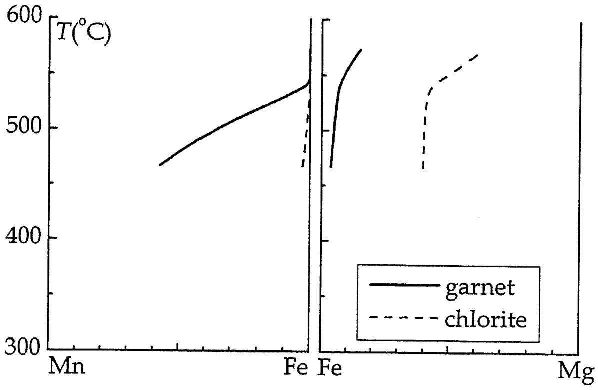

Fig. 9. Pseudobinary *T–X* diagrams, showing predicted garnet and chlorite composition changes in response to temperature. Mg–Fe–Mn ternary system is decomposed into two pseudobinary systems. The shift from Fe–Mn binary system to Mg–Fe system seems to occur at around 550 °C.

It is observed that the reaction isopleth of garnet formation from chlorite has high dP/dT. It suggests that the beginning of garnet formation largely depends on temperature. It is not likely that the difference in pressure during garnet growth is distinct in the zoning of Mg–Fe–Mn garnet. This is consistent with the commonly accepted view.

The predicted change of molar amount of garnet (dM/dT, dM/dP) rapidly increased at certain condition, and decreased thereafter. The phenomenon is explained by decomposing the ternary behavior into two pseudobinary behaviors (Fig. 9). The pseudobinary loop of Fe–Mn system is located at the lower temperature condition compared to that of Mg–Fe system. Therefore, garnet is mainly produced by the Fe–Mn system during the lower temperature, and the system shifts into the Mg–Fe system at higher temperature. Since Mn is basically a trace element, the molar amount of garnet produced remains small when the Fe–Mn system is effective. The production rate increases rapidly when Mg–garnet begins to form. Mn in the reactant is depleted by then. Within the Mg–Fe system, the production rate gently decreases following the pseudobinary loop.

Although the overall shape of the chemical zoning is reproduced, the predicted garnet composition at the estimated peak metamorphic condition (520°C, 0.9 GPa) is different from those of natural grains. There are several possible causes for this discrepancy. First, there are uncertainties in the published thermodynamic data set, or the activity-composition relationships. It is still not easy to reproduce the equilibrium state of minerals by means of experiments, since the duration time might be very long. Especially the behaviors of Mn-phases are not yet well explored, where empirical correction is applied instead based on natural samples. The large discrepancy observed in this study is also due to the behavior of Mn. The future improvement in the thermodynamic data may improve the prediction by this model. In this study, the problem is minimized by using the latest available data set at present. The thermodynamic properties and the activity-composition relationships of minerals should be revised to always reflect the latest experimental result. Fortunately, the proposed forward model is ready for revision, because the calculation algorithm is straightforward iteration and does not depend on the form of equations. Secondly, some of the assumed variables are uncertain: e.g., initial chlorite composition, mole fraction of Ca end-member in garnet, or H_2O fugacity. It is known that the amount of Mn significantly widens the stability field of garnet (Mahar et al., 1997). Parameter study should be performed to explore the influence of the Mn content in chlorite. To solve the problem of Ca end-member and/or H_2O fugacity, it is essential to extend the forward model to involve other phases in the metamorphic rocks. Due to the straightforwardness of the model again, it will be possible to consider all the relevant phases in the future. The proposed model here will serve as a prototype of the general model. Thirdly, the kinetics is not considered in this model. If diffusion is not perfect in chlorite, the effective bulk rock chemical composition may become substantially different. Overstepping in the crystallization of garnet may also influence the results. It is not yet suitable to discuss the non-equilibrium state, with the equilibrium state not perfectly understood, but some parameter studies will be desirable to explore the magnitude of possible influence.

CONCLUSION

Forward model was proposed to reconstruct the formation of normal chemical zoning in garnet, based on available thermodynamic data set of minerals. Volume increase and chemical composition change of garnet was calculated quantitatively, through straightforward iterative algorithm. Dependence of enthalpy on T, and non-ideal mixing property were also considered. Estimated P–T path in the pelitic schists of the Sambagawa metamorphic belt, central Shikoku, Japan, was used for the case study. Though the predicted composition did not coincide well with natural samples, the overall shape and trend of chemical zoning of garnet were reproduced. The mechanism of volume change in ternary garnet was explained by the relationship of two pseudobinary loops.

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