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Pressure - Temperature - Water Production Rate Paths in the Subduction Metamorphism

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Abstract

Metamorphic pressure and temperature paths were precisely inferred by chemical zonal structure of garnet from the core to the rim in pelitic systems using the differential thermodynamic method. We obtained P-T paths from the Sambagawa metamorphism such that the pressure and temperature increased gradually during the growth of garnet. The zonal structures of garnet show a continuous change of pressure and temperature but indicate wide variations in the garnet production rate. The molar production rates of garnet during prograde metamorphism, defined by dm/dP were precisely obtained, in which m is the molar production of garnet normalized by the grain volume. The rates commonly show two peaks near the early and late stages. The general trends of molar production rates show a gradual increase with increasing pressure, but there are several peaks and the rates suggest episodic water release from metamorphic rocks in the process of subduction.

Key words: metamorphism, dehydration, water release, subduction

1. Introduction

Recent studies of subduction dynamics are focused on the fluid flow in the wedge and subducting slab because dehydration and successive dewatering processes are quite essential for magmatism, metamorphism, and mechanical processes involving seismic activity in the slab and plate boundary (e.g., Tatsumi, 1989; Iwamori, 1999; Peacock, 1993; Mibe *et al.*, 1999). The role of water produced by the subducting slab is considered to be important for the generation of arc magma (Tatsumi, 1989) and the origin of the double seismic zone within the slab (Seno and Yamanaka, 1996), for the lock-unlock transition of the seismogenic zone of the plate boundary (Hyndman *et al.*, 1997; Fujie *et al.*, 2000).

Although dehydration reactions and related fluid flow are very important in metamorphism as petrologically and theoretically discussed by many authors (e.g., Ferry 1984; Lasaga and Rye, 1993), quantitative discussions of fluid production history associated with subduction metamorphism were not made until now. Recently, detailed investigations of synmetamorphic veins clarified regional distribution patterns of sealed cracks which had been filled by fluid during subduction metamorphism (Toriumi, 1990; Toriumi and Hara, 1995; Toriumi and Yamaguchi, 2000). In their papers, they showed that the density of sealed cracks increases drastically in the metamorphic grade zones of less than 400℃ but in higher grade zones plastic strains are very large, suggesting brittle - ductile transition in the natural system and sealed crack distribution patterns display strong clustering.

These results may strongly suggest that a large amount of fluid derived from subducting metamorphic rocks flowed in the overriding metamorphic rocks successively. Thus it is necessary to know the rate of water production accompanied with metamorphic dehydration reactions and flow rates of water through cracks together with grain boundaries as

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suggested by Toriumi and Yamaguchi (2000). Therefore, in this study we propose a new method that makes it possible to estimate fluid production and flow rates in the subduction metamorphism of the slab and accreted rocks, using the exact pressure - temperature paths inversion method proposed by Spear (1989) and applying this method to garnet bearing pelitic schists of the Sambagawa metamorphic belt in Japan.

2. Geological Outline of Sambagawa Metamorphic Belt

The Sambagawa metamorphic belt is a typical subduction related metamorphic belt in Southwest Japan that formed in the deep - seated accretion sediments sandwiched between slab and the wedge mantle. The metamorphic rocks distributed in the narrow zone extending from the Kanto Mountains to Kyushu and in Shikoku is widely exposed having a 50 km width. This metamorphic belt is sided with Izumi Cretaceous forearc sediments and the Ryoke low pressure and high temperature metamorphic belt along the Median Tectonic Line (transcurrent fault) in the north and along the Butsuzo Tectonic Line (thrust) in the south with the Shimanto Cretaceous accretionary complex. The belt is divided geologically into the Sambagawa zone, Mikabu zone, Chichibu zone and the Kurosegawa zone from north to the south. These boundaries are almost always north-dipping thrust formed at the accretion. There are several large recumbent folds, and large thrust and transcurrent faults in the Sambagawa metamorphic belt (Faure 1985, Hara *et al.* 1990, Wallis and Banno 1990). The recumbent folds have axial trends parallel to the length direction of the metamorphic belt and they are thought to be a sheath fold (Toriumi 1990, Wallis 1993). It suggests that the transport direction of the metamorphic belt should be east - westward (Faure, 1985, Toriumi 1982, 1985).

The age of metamorphism has been clarified using K-Ar and Ar-Ar radioisotopic methods to be in the range from 110 to 60 Ma (Isozaki and Itaya 1990, Takasu and Dallemayer 1990). Considering that the biotite and muscovite closure temperatures are about 350–400℃, the isotope ages of metamorphism has been identified as the age of retrograde metamorphism which points to the exhumation process of the subducted metamorphic complex.

Plastic deformation of the Sambagawa metamorphic rocks has been studied in detail using spherical species of radiolaria in metacherts (Toriumi 1982, Toriumi and Noda 1986, Toriumi and Masui 1986). They have clarified three important facts: one is the gradual increase of strain magnitude with increasing metamorphic temperature in the metamorphic belt, the second is the strain geometries changing from oblate to prolate shape with increasing temperature, and the third is the orientation of principal strain axes indicating that the maximum elongation axis is nearly parallel to the length direction of the metamorphic belt. Judging from the mineral lineations of amphiboles and epidote and stretching lineations assigned by the pull-apart of crossite occupied by actinolite, Wintsch *et al.* (1999) concluded that the large amount of plastic deformation has taken place during the time of retrograde metamorphism, which is the exhumation period.

Metamorphic pressure and temperature paths of the Sambagawa metamorphic rocks have been studied by Inui (1999) and Okamoto and Toriumi (2001) by means of the differential thermodynamic method, although there are several papers on conventional pressure and temperature path estimations in this metamorphic belt (e.g., Enami, 1998). Recently, Wintsch *et al.* (1999) noticed that crossite - actinolite composite grains in the radiolaria bearing micaschists contain zoned hornblende in the core of pull-apart crossite, and concluded that the prograde P-T path indicates higher temperature conditions shown by actinolite to hornblende growth in the early stage of metamorphism than retrograde metamorphism represented by crossite to actinolite growth in the later stage. Further, retrograde metamorphism should have been the path running anticlockwise (Okamoto and Toriumi, 2001). Furthermore, in the pelitic schists there are abundant occurrence of biotite accompanied by the breakdown of garnet. These facts indicate that the retrograde metamorphism must occur in the process accompanied by a hydration reaction. Therefore, the important problems are concerned with the relationship among pressure and temperature paths, deformation, and water volume as related to dehydration and hydration reactions during metamorphism.

The studied locality is the Dozan-gawa area in central Shikoku, as shown in Fig. 1. The Sambagawa

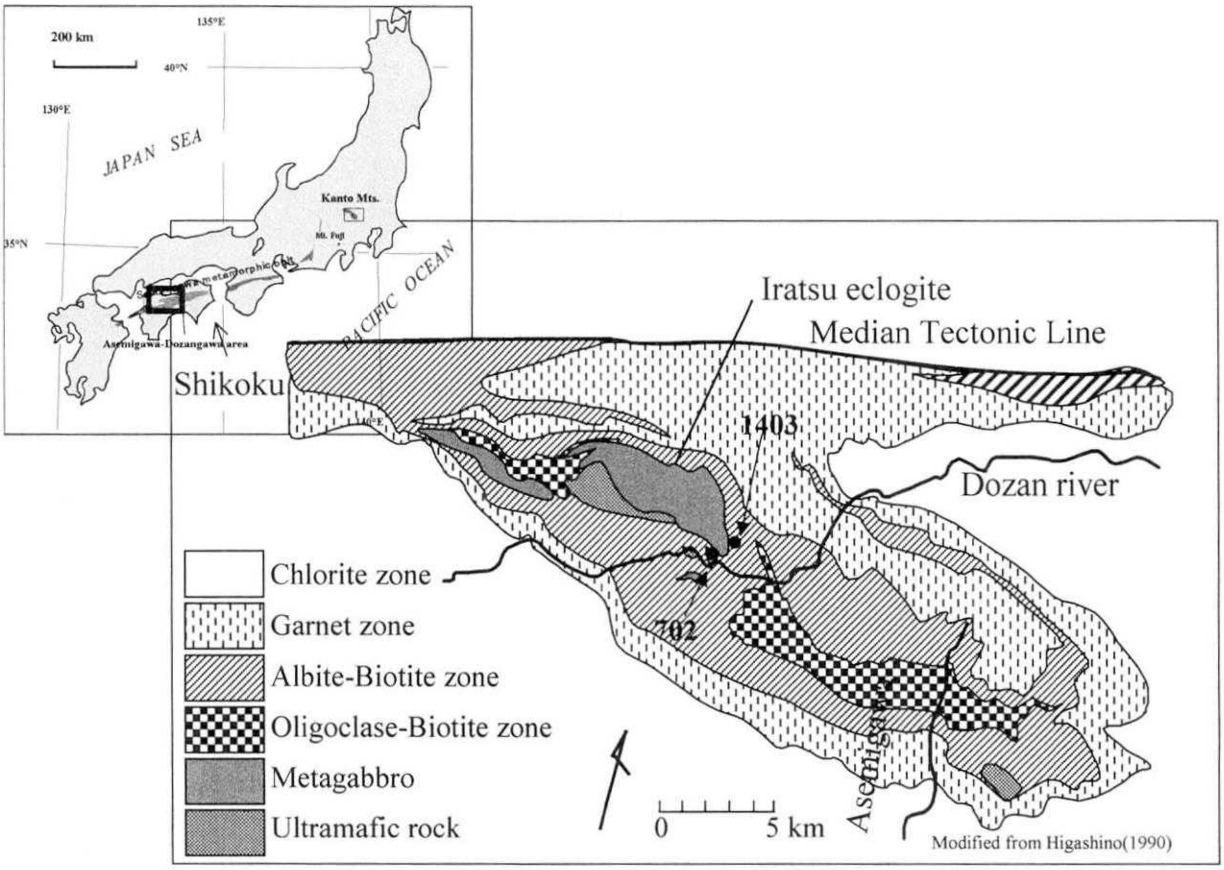

Fig. 1. Metamorphic map of the central Shikoku area in the Sambagawa metamorphic belt showing the localities of the studied samples.

metamorphic belt in central Shikoku is widely exposed and is composed of the chlorite zone, garnet zone, albite - biotite zone and the oligoclase biotite zone in the ascending order of metamorphic grades (Higashino, 1990). The studied pelitic schists contain abundant garnet, but a small amount of biotite and they belong to the albite - biotite zone and the petrography of these rocks are described in detail in Inui (1999).

3. Petrography and Pressure - Temperature Paths of Metamorphic Rocks

Pelitic schists in the region of the Dozan river contain commonly muscovite, albite, chlorite, epidote, garnet, quartz, biotite, rutile, and graphite. The garnet in these rocks show an euhedral outline and the grain size ranges from 0.1 to several mm. The size distribution of garnet in pelitic schists are commonly unimodal and show the pattern of the Ostwald ripening process with a long term tail (Miyazaki, 1991; Toriumi and Nomizo, 2001). The number density of garnet grains in pelitic schists are commonly 10^6 cc^{-1} (Miyazaki, 1991, Toriumi, 1986). Garnet contains commonly fine - grained mineral inclusions of rutile, quartz, albite, epidote and muscovite. Rare pelitic schists have large garnet grains showing abundant quartz inclusions, but the studied pelitic schists have no inclusion rich garnet grains. Platy grains of muscovite, paragonite and chlorite form a schistosity and their sizes range from 10 to 100 microns in thickness. In the muscovite and chlorite rich thin layers, fine grains of sphene were commonly found.

Biotite occurs very sporadically around the grains of garnet, suggesting a formation by the hydration reaction of garnet. Mn - content in the rim of garnet accompanied with biotite is slightly higher than that without biotite, suggesting the resorption reaction of garnet mentioned above. Epiodte occurs as tabular grains both in the matrix and in the garnet grains. It appears rounded and displays a resorption texture.

The mineral assemblages of the studied pelitic schists are as follows;

1. garnet - chlorite - muscovite - paragonite - albite - epidote - quartz
2. garnet - chlorite - biotite - muscovite - paragonite - albite - epidote - quartz

As shown by Inui (1999), garnet grew in equilibrium with chlorite, muscovite, paragonite, epidote, albite and quartz, but not with biotite, judging from occurrences of mineral inclusions in garnet porpyroblasts, and from the relationships of chemical compositions between garnet and mineral inclusions and clear concentric growth zoning of garnet in contrast to sector zoning in disequilibrium tiny garnet grains (Inui, 1999) as stated later.

The studied pelitic rocks have major components of Si-Al-Mg-Fe-Ca-Na-K-H-O, and then the mineral assemblage of 1, and 2 are divariant and univariant systems, respectively assuming the existence of water. As noted previously, biotite should be excluded in the equilibrium system, the system should be divariant.

Inui (1999) indicated that there are two types of garnet zoning in studied pelitic schists: one is coarse - grained garnet displaying normal zoning, and the other is fine - grained garnet showing sector zoning. Obviously sector - zoned garnet was not in equilibrium with matrix minerals and neighboring normally zoned garnet (Inui, 1999). On the other hand, all coarse - grained garnet displays the same zoning pattern from the core to the rim even if the grain size changes greatly. Sakai, *et al.* (1985) indicated a similar zoning pattern of garnet with a wide range of grain sizes. According to chemical zoning corresponding to the P-T path of rocks, the self-similar zoning pattern should be considered to be the growth rate depending upon the grain size.

Pressure and temperature paths were determined from chemical zonings of garnet in the studied pelitic schists by Inui (1999) in detail by means of the precise differential thermodynamic method (Spear, 1989) using the data set of Holland and Powell (1998) for the garnet assemblages described above. The evaluation of this inversion method was done very well by comparison to calculated chemical changes and the observed zoning of chlorite, epidote and muscovite and their inclusions in garnet as shown by Inui (1999).

Pressure - temperature paths of Sambagawa metamorphism deduced by this method were different from previous paths inferred from conventional methods (e.g., Banno amd Wallis, 1995). Previous conventional methods concluded that the pressure and temperature conditions in the early stage of the Sambagawa metamorphism are of high pressure metamorphism. On the other hand, the studied pressure - temperature paths indicated that the mean dT/dP of the paths ranges from 3℃/kb to 10℃/kb which is about three times the adiabatic compression of the pelitic rocks at most, being similar to Enami *et al.* (1994) by sodic pyroxenes and albite assemblages in metacherts. In this situation, the prograde metamorphism recorded in garnet interiors ranges from 500 to 600℃ and from 5 kb to 10 kb. The core of garnet grew in conditions of about 500℃ and 5 kb. This seems to be supported by the fact that Wintsch *et al.* (1999) found the zoned hornblende core in the crossite composite grains in central Shikoku.

4. Production Rate of Garnet and Pressure - Temperature Paths

Chemical zonings of garnet which display a gradual increase of Mg and Fe, but a decrease of Mn from the core to the rim indicate the pressure and temperature tracks during growth for garnet grew under the conditions of surface equilibrium with matrix minerals. These tracks are indicated by the relationship between pressure and distance from the center of the garnet grains as shown in Fig. 2. The production of garnet can be simply measured as dV/dP where dV is the change in volume of garnet associated with the small pressure change. As shown in Fig. 3, the volume change of garnet normalized by the grain volume as pressure increased was calculated using the following relation;

$$dx = dV/L^3 = 4\pi r^2\,dr \qquad (1)$$

in which x is the volume change normalized by the studied garnet volume, V is the volume of the studied garnet, and r is the distance normalized by L (grain size of a studied garnet grain) from the center of garnet. Here we assume the volume of garnet as a sphere.

We are able to obtain the change in the mole

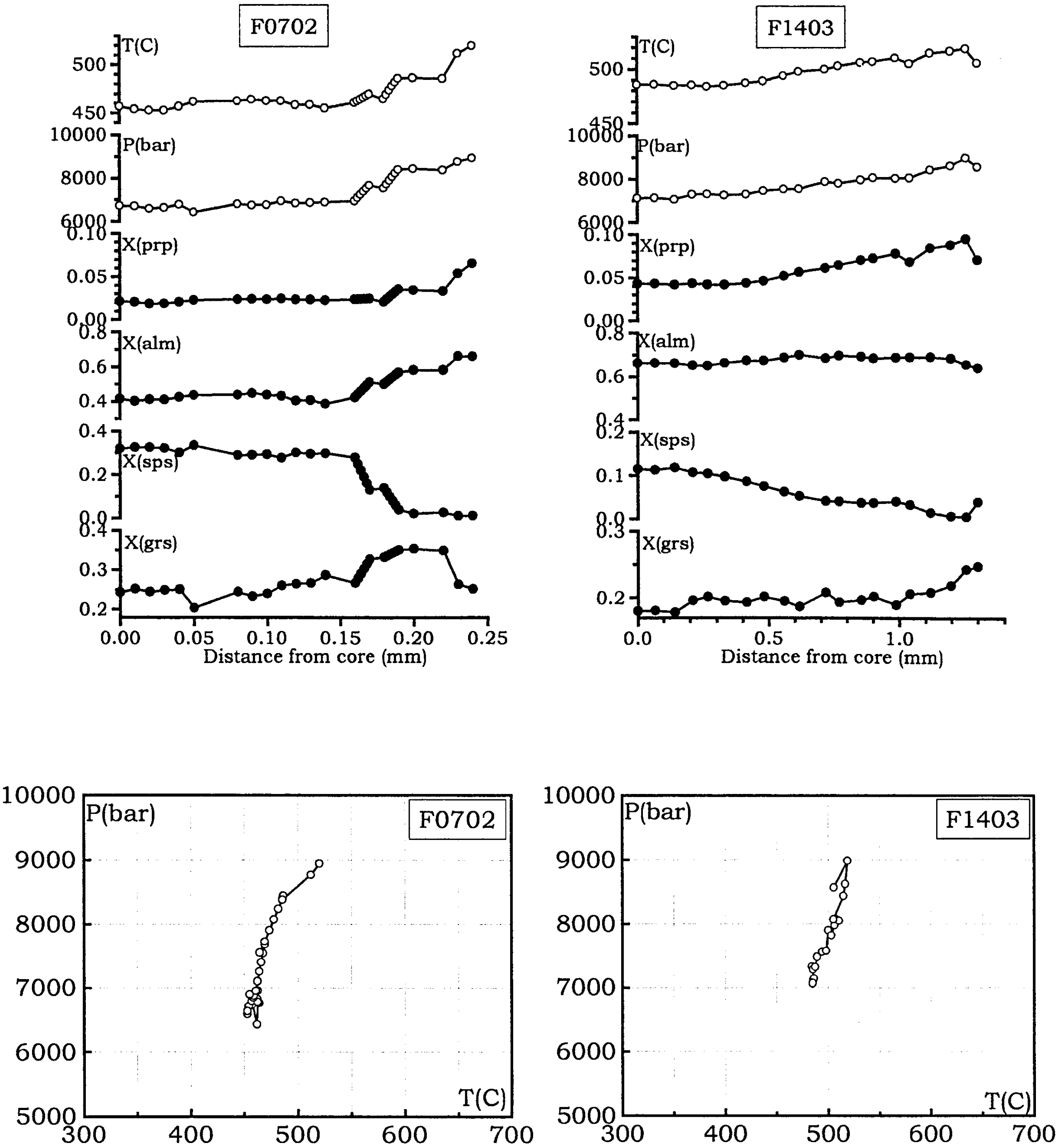

Fig. 2. Representative pressure and temperature tracks and observed chemical zonings of garnet from the core to the rim (top) and P-T paths (bottom).

number of garnet normalized by the grain volume, dm, and the change in pressure for a small distance of dr at the distance r from the core for a grain of studied garnet of pelitic schists as shown in Fig. 2. Then, the garnet production rate defined by dm/dP can be obtained as,

$$dm/dP = dx/v_g\, dr/dP/dr, \qquad (2)$$

where v_g is the molar volume of growing garnet. Garnet in this study is approximated to be $\text{almandine}_{70}\text{grossular}_{10}\text{spessartine}_{15}\text{pyrope}_{5}$ and thus the molar volume can be assumed as 110 cc/mol. In Fig. 4, the relationship between the production rate of garnet, dm/dP and the pressure are shown, indicating a wide range of their variations.

In order to see the general trend of garnet production rate during prograde metamorphism, large values 100 times over the initial production rate were deleted from the data sets, and then the data was

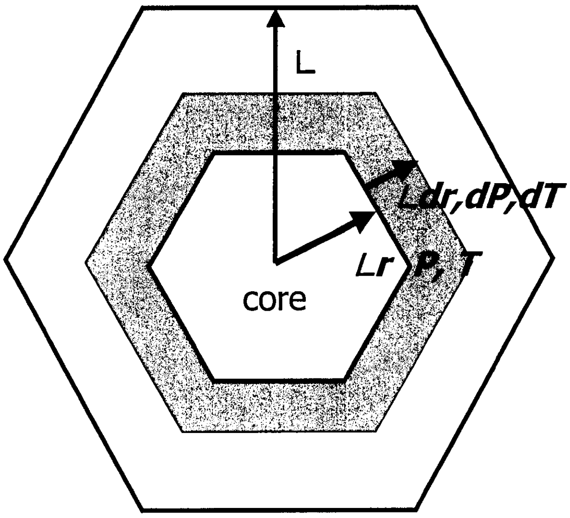

Fig. 3. Illustration of changes in pressure and temperature with the change of distance Ldr of garnet at (Lr, P, T) where L is the grain size of the studied garnet.

plotted in the diagrams of P vs dm/dP as shown in Fig. 5. It indicates that the production rates of garnet increase gradually with increasing pressure.

On the other hand, two peaks of the production rates dm/dP appear around 7.0 and 8.5 kb and their intensities exceed the two order of magnitude against the surrounding production rates. The pressure conditions at the peaks of the garnet production rate are listed in Table 1. It shows that all rocks studied here have two peaks at the same pressure conditions, suggesting that the studied production rate is regional, but not local.

5. Garnet Production Rate and Water Release during Prograde Metamorphism

As stated in the previous sections, garnet grew mainly in the process of pressure and temperature - increase of prograde metamorphism. This implies that garnet production during continuous subduction of metamorphic rocks is associated with slab subduction. Production of garnet is derived from the dehydration reactions including chlorite, epidote, paragonite, albite, muscovite, biotite and quartz, and thus it is accompanied by water flow in the metamorphic rocks.

Considering pelitic schists containing garnet, chlorite, muscovite, epidote, paragonite, albite, and quartz, the observed garnet production should be governed by the following chemical reactions using the end components of these minerals;

1. 6 paragonite + 4 clinochlore = 6 albite + 5 amesite + water
2. 4 grossular + 5 paragonite + 6 quartz = 6 clinozoisite + 5albite + 2 water
3. amesite + clinochlore + 4 quartz = 3 pyrope + 8 water
4. 2 paragonite + 3 daphnite + 6 quartz = 5 almandine + 2 albite + 14 water
5. 5 spessartine + 3 daphnite = 5 almandine + 3 Mn-chlorite
6. 5 almandine + 3 clinochlore = 5 pyrope + 3 daphnite
7. almandine + 3 celadonite = pyrope + 3 ferroceladonite
8. celadonite + amesite = muscovite + clinochlore

In these equations, end components of garnet, chlorite, mica and epidote are almandine ($Fe_3Al_2Si_3O_{12}$), pyrope ($Mg_3Al_2Si_3O_{12}$)), spessartine ($Mn_3Al_2Si_3O_{12}$)), and grossular ($Ca_3Al_2Si_3O_{12}$)) for garnet, clinochlore ($Mg_5Al_2Si_3O_{10}(OH)_8$), amesite ($Mg_4Al_4Si_2O_{10}(OH)_8$), daphnite ($Fe_5Al_4Si_3O_{10}(OH)_8$) and Mn-chlorite ($Mn_5Al_2Si_3O_{10}(OH)_8$) for chlorite, muscovite ($KAl_3Si_3O_{10}(OH)_2$), and celadonite ($KMgAlSi_4O_{10}(OH)_2$ for mica, and clinozoisite ($Ca_2Al_3Si_3O_{12}(OH)$) for epidote, respectively.

Here, we can rule out the reaction of garnet - formation from consumption of biotite because there was no biotite during the prograde stage. These reactions are used in the calculation of pressure and temperature paths using the differential thermodynamic method (Inui, 1999). Following these reactions, garnet production is mainly controlled by net transfer reactions 2, 3 and 4. Namely pyrope components in garnet are produced by reaction 3, almandine components by reaction 3 and grossular componets by reaction 2. Thus, considering the compositional zoning of garnet grains from $Pyr_5Alm_{30}Sps_{50}Grs_5$ to $Pyr_{10}Alm_{70}Sps_{10}Grs_{10}$, total water produced by a unit mol of garnet formation becomes from 2.348 to 2.456 mol. Then we can assume this factor to be 2.4 in this study. Therefore, we can estimate the water production rate associated with pressure change defined by dm_w/dP corresponding to the garnet production rate as follows;

$$dm_w/dP = 2.4\,dm/dP \qquad (3)$$

in which dm_w is water production in mole normalized by the grain volume accompanied with the studied

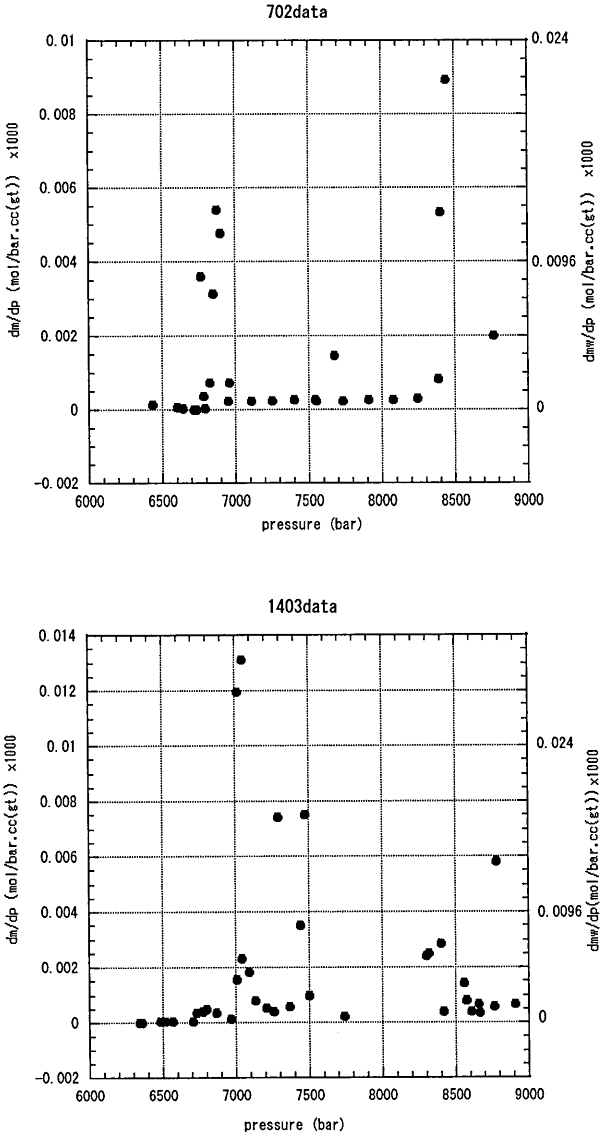

Fig. 4. Diagrams of garnet production rate dm/dP (left measure) and water production rate dm_w/dP (right measure) with increasing pressure showing two peaks. top; 702, bottom; 1403.

garnet formation.

The water production rates deduced from a single garnet zoning are shown in Fig. 4. In Fig. 4, it seems that the water production rates in the process of prograde metamorphism have two peaks at the early and late stages. On the other hand, in the figure lacking very large water production rates at the two peaks defined by 100 times the initial value, the pattern of water production rates with an increasing pressure condition displays a gradual increase from the early to the late stage.

6. Discussions

Water Production during Subduction of Metamorphic Rocks

The water production associated with growth of a single garnet grain during the process of pressure - increase. The increase in pressure, however, means subduction of metamorphic rocks derived from slab subduction. If the subduction speed of the slab is constant, the subduction of the metamorphic rocks may be also constant in the absence of slip between the slab and the metamorphic rocks. Another possible situation may be that the intermittent slip occurred between the slab and the metamorphic rocks. Even in this case, the water production rate dm_w/dt associated with growth of a single grain of garnet holds, using the increasing rate of pressure dP/dt as,

$$dm_w/dt = (dP/dt)((dm_w/dP) \qquad (5)$$

in which P is in kbar, t is in year and m_w is in mol per unit volume. In the case of negative dP from the observed pressure - temperature - distance paths, dP/dt should be negative and this means a slight obduction of metamorphic rocks. As a result, dm_w/dt becomes positive according to the advance of the dehydration reaction forming garnet.

Let us consider the constant slab subduction and its drag to metamorphic rocks. Then, we may take dP/dt as a system parameter related to the subduction velocity and angle as follows;

$$dP/dt = \rho g\ V_p \sin\theta \qquad (6)$$

where ρ, θ and V_p are the average densities of rocks, subduction angle, and subduction velocity of metamorphic rocks, respectively, and g is the gravitational accerlation. We may assume $\rho = 3.0$ g/cc, $V_p = 5$ cm/year, and $\theta = 45°$ and thus we obtain $dP/dt = 0.007$ bar/year. In this case, the water volume associated with the growth of a single grain of garnet can be estimated as,

$$dv_w/dt = k_w\ dm_w/dt \qquad (7)$$

where k_w is the molar volume of water and here it is assumed to be 18 cc. Furthermore, we infer the total water volume from the unit rock volume using the grain size distribution function of garnet in the studied metamorphic rocks. As described in the earlier section, the grain size distribution of garnet is simply the LSW type having long - term tail (Toriumi 1975; Miyazaki, 1991; Toriumi and Nomizo, 2001). Therefore, we obtain the water voume rate per unit rock volume, dV_{total}/dt as follows;

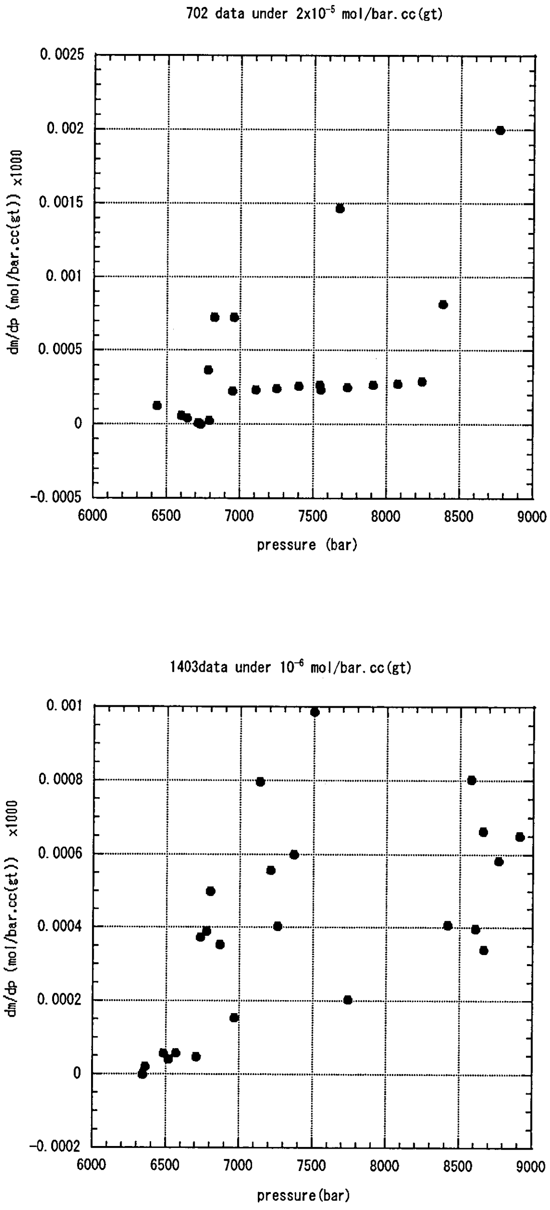

Fig. 5. Diagrams of general trends of garnet production rates with increasing pressure showing gradual increase. top; 702, bottom; 1403.

$$dV_{total}/dt = V_{gt}\, dv_w/dt = 0.3024\, V_{gt}\, dm/dP \qquad (8)$$

Here, V_{gt} means total volume of garnet in the unit volume of studied rocks. This can be allowed because the growth zoning of the peak size grain is very similar to that of other grains having different grain sizes as indicated by Sakai *et al.*, 1985; Inui, 1999; Toriumi and Nomizo, 2001). Further, we can take into consideration that the grain density of garnet did not change during prograde metamorphism because garnet grains display similar zonal structure from the core to the rim (Sakai *et al.*, 1985, Toriumi and Nomizo 2001). Considering the grain density of garnet about $10^6 cc^{-1}$, the geometric constant S is approximated to be this value. Then, it is inferred that the peak of water release reaches about $1-2\times10^{-2}$ cc/year. On the other hand, the low water production rate is inferred to be 1×10^{-4} cc/year. This large difference should be explained by the very slow subduction velocity of metamorphic rocks or by the large garnet production rates in rocks under the constant subduction velocity of rocks.

The episodic garnet growth during subduction of metamorphic rocks may be apparent but not actual, because dm/dt becomes very small if dP/dt is very small in eqn (2). This may be suggested by the temperature change during the subduction of metamorphic rocks. Considering that the dP/dt is neary zero, the temperature of metamorphic rocks may change greatly compared to a case of constant dP/dt subduction of metamorphic rocks. In figure 1, the temperature changes in the growth of garnet are also indicated, but there is no clear difference in the temperature changes between the stages of very large dm/dP and small dm/dP. Thus we may consider that the episodic large dm/dP is derived from episodic large production rates of garnet.

As stated in the previous works (Inui, 1999, Toriumi and Nomizo, 2001), garnet grew in surface equilibrium with matrix minerals (chlorite muscovite, paragonite, epidote and others) judging from the similar zoning structures of different grains. Then, the variations in the growth velocity of garnet should be responsible for the difference in the diffusional flux in chlorite and other matrix minerals (Hollister, 1966; Kretz, 1973; Banno and Chii, 1978; Cashman and Ferry, 1988; Carlson, 1989; Miyazaki, 1991; Toriumi and Nomizo, 2001). The small growth velocities of garnet are probably due to very slow diffusivity of Si and Al in chlorite and other matrix minerals, but rapid growth velocities can be derived from fast effective diffusivity of Si and Al of the matrix. Even in this case, we can apply surface equilibrium conditions in the formation of garnet if we consider the very fast diffusion of Mg, Fe and Mn in chlorite. The reason why the fast effective mobility of Al and Si in the matrix at the episodic stages of large dm/dP may be due to deformation - induced

Table 1. Pressures of the peak production rates of garnet in studied pelitic schists.

sample number	first peak(kb)	second peak(kb)
201	6.8	8.2
702	6.9	8.4
801	7.6	8.4 - 8.9
1401	7.0	8.8
1403		8.1
2205	7.3	
2302	7.0	8.0 - 8.5
2303	7.2	8.0 - 8.7
2503		8.0 - 8.6
3201	7.8	

grain reduction of matrix chlorite. Effective diffusivity of Al and Si in the matrix chlorite should be related to the grain size if their diffusion is controlled by interface diffusion as suggested by Carlson (1989). As the grain size of chlorite changes largely from several microns in mylonitic rocks to 1mm in the coarse grained schists in the matrix (Inui, 1999), the grain size ratio may possibly change in the one to three order of magnitude, giving a large effective diffusivity contrast. Thus, it may be possible that the garnet production rates vary possibly in a very wide range reaching a two to three order of magnitude as observed in this study.

7. Conclusions

The history of the garnet production rate against change of pressure defined by dm/dP was obtained by using data sets of precise pressure, temperature, and normalized distance from the center of the grain of garnet during the prograde metamorphism. Then, the pressure - temperature - water production rate paths were deduced based on garnet - forming reactions in the process of continuous subduction of the metamorphic rocks.

The observed chemical zonings of garnet in the pelitic schists which contain garnet, muscovite, chlorite, paragonite, ablite, epidote and quartz indicate that the pressure - temperature - water production rate paths are as follows;

1. water production rate gradually increased with increasing pressure and temperature.
2. there are two peaks in the water production rate of the studied samples.
3. the ratios of peak water production in small productions reach about 100.

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