Chemical zoning of pegmatite garnets from the Ishikawa and Yamanoo areas, northeastern Japan

TAKANORI NAKANO and YUKIKO ISHIKAWA*

Institute of Geoscience, University of Tsukuba, Tennoudai 1-1-1, Tsukuba-shi, Ibaraki 305, Japan

(Received April 17, 1996; Accepted November 8, 1996)

Three coarse-grained garnets from granitic pegmatites in the Ishikawa and Yamanoo areas, northeastern Japan, were traversed by an electron probe microanalyser (EPMA). Garnets occur in the feldspar zone (Ishikawa) and in the muscovite-feldspar-quartz zone (Yamanoo). The three garnet grains display distinct chemical zonings one another. One garnet from Ishikawa is unzoned. In another garnet from Ishikawa and one garnet from Yamanoo, Fe and Mg contents increase from core to rim as Mn content decreases. In the two zoned garnets, Ca content either monotonously increases to the rim or increases then decreases. These patterns were modeled by assuming varying values for partition coefficients, associated solid-phase compositions, and final proportions of garnet crystallized from the melt. The Ca peak is reproduced if partition coefficients change during the garnet growth and crystallization of a Ca-mineral such as feldspar removes Ca from the melt. The different zoning patterns in garnets within a single pegmatite zone are largely attributable to the difference in the growth rates of garnet and co-crystallizing minerals.

INTRODUCTION

There are a number of studies done on the compositional growth zoning of metamorphic garnets (e.g., Hollister, 1966; Banno and Kurata, 1972; Tracy *et al.*, 1976; Dempster, 1985) since such zoning provides key constraints on the metamorphic processes. Likewise, the chemical zoning of garnet in granitic pegmatite may offer a great deal of information on the genesis of pegmatite and the evolution of granitic magma. Leake (1967) first described a decrease in Mn content with an antipathetic increase in Fe content from the core to rim in garnet from a granitic pegmatite in France. This finding suggests that the bell-shaped zoning of Mn in pegmatite garnet could be formed during the crystallization of pegmatitic magma, although similar patterns in metamorphic garnets have been explained in terms of an increase in temperature of metamorphism or Rayleigh fractionation under isothermal condition

during their growth.

In addition to Mn and Fe, the compositional zonings of Ca and Mg also occur in garnets in metamorphic and granitic rocks. Trace element zonings using ion probe have also been reported recently for metamorphic garnets (Hickmott *et al.*, 1987; Hickmott and Shimizu, 1990). Garnets in granitic pegmatites can contain some trace elements at concentration levels above the detection limit of EPMA (>50 ppm; Ramsden and French, 1990; Nakano *et al.*, 1991).

Modeling of pegmatite garnet zonings with respect to multiple elements may therefore provide further information on the crystallization history of pegmatites. However, such modeling has not yet been attempted probably due to the complexity of pegmatite-forming processes (i.e., changes in magma composition, partition of elements between garnet and granitic melt, growth rate of garnet, and compositions of associated minerals etc.) that may affect the compositional patterns of granitic

*Present address: Comfort Sugimura 302, Tanuma 4-2-26, Fujieda-shi, Shizuoka, Japan

garnet. Cygan and Lasaga (1982) presented a garnet growth model dependent on temperature and growth rate, and successfully applied their model to metamorphic garnets from Phillipston, Massachusetts. With modification, previous models are applicable to zoning in pegmatite garnet as well. In this paper, we describe the compositional patterns of garnets from granitic pegmatites in the Ishikawa and Yamanoo areas, northeastern Japan, and then analyze the patterns by a model incorporating the factors mentioned above.

DESCRIPTION OF PEGMATITES

Ishihara (1981) classified granitic rocks into two categories; that is, magnetite-series and ilmenite-series. Most granitic pegmatites in Japan including those in the Ishikawa and Yamanoo areas are associated with ilmenite-series granitoids and regarded as the final stage products of the fractionation of ilmenite-series granitic magma (Tsusue, 1976).

Pegmatite in the Ishikawa area

The Ishikawa area is located in the western part of the Abukuma Plateau, which is known for the wide distribution of metamorphic rocks and granitic plutons. Many granitic pegmatite deposits occur in the area (Sanbonsugi, 1953; Matsubara, 1956). Matsubara (1956) classified granitoids in the Ishikawa area into two groups based on cross-cutting relations: earlier hornblende-biotite granodiorite and later biotite granodiorite. Most pegmatites develop within the older granodiorite or along the boundary between the older and younger granitic rocks. The studied pegmatite at the Ishikawayama mine is located at the boundary between the two granitoids and is emplaced in the older granodiorite. The pegmatite has an elliptical form and is about 13 m by 4 m in size. It consists of graphic, feldspar, and quartz zones from the margin to the core. These zones are separated by sharp boundaries. The graphic zone is composed of graphic intergrowth of quartz and K-feldspar. Biotite megacryst occurs locally near the feldspar zone. Rare-earth element-bearing minerals such as

xenotime, monazite, samarskite, and zircon accompany biotite. Plagioclase and muscovite are rarely observed in grain boundaries between the quartz and K-feldspar. The feldspar zone mainly consists of microcline. Fine-grained plagioclase (10–100 μm) and coarse-grained muscovite (1–10 cm) are locally concentrated. Small amounts of garnet also occur in this zone. The quartz zone is composed exclusively of quartz. Its color grades inward from colorless through white to orange. In the western part of this zone, tourmaline crystals from a few cm to several cm in length occur along the boundary with the feldspar zone. A representative composition of the younger biotite granodiorite, which is likely related to the pegmatization, is given in Table 1.

Pegmatite in the Yamanoo area

Takahashi (1982) divided granitic rocks of the Tsukuba district, Ibaraki Prefecture, Japan, into seven bodies based on the mode of occurrence. K-Ar ages of these granitic rocks are 53–63 m.y.

Table 1. Representative chemical compositions of granitic rocks in the Ishikawa and Yamanoo areas, determined by XRF

	Ishikawa	Yamanoo
SiO ₂ (wt.%)	74.19	70.28
TiO ₂	0.14	0.31
Al ₂ O ₃	13.36	15.19
FeO*	1.94	3.02
MgO	0.38	0.70
MnO	0.10	0.10
CaO	1.52	1.92
Na ₂ O	3.84	3.33
K ₂ O	2.99	4.39
P ₂ O ₅	0.09	0.12
Total	98.54	99.36
Ba (ppm)	367	836
Rb	85	162
Sr	206	276
Y	15	30
Zn	43	51
Zr	115	127

FeO*: Total Fe as FeO.

(Kawano and Ueda, 1966; Shiba *et al.*, 1979). The Yamanoo fine-grained granite is one of those and is composed of plagioclase, quartz, K-feldspar, and biotite with zircon, apatite, allanite, titanite, and ilmenite as accessory minerals. The Yamanoo granitic pegmatites were emplaced in the Yamanoo granite. It is elliptical, 30 m in length and 5 m in thickness, and displays a similar arrangement of mineral zones to the Ishikawa pegmatite with a succession of graphitic, muscovite-feldspar-quartz, feldspar, and quartz zones from the margin inwards. Garnets occur in the muscovite-feldspar-quartz zone, intimately associated with muscovite. A representative composition of the Yamanoo granitic rock is given in Table 1.

SAMPLE DESCRIPTION AND CHEMICAL COMPOSITION OF GARNET

Garnet samples

Garnets from the Ishikawayama mine are brown to black, and those from the Yamanoo area are red-brown in color, respectively. Both of them range from a few mm to 2–3 cm in diameter. All of these garnets possess a well-developed dodecahedral crystal form, which can be simulated as a sphere without serious problems. The grain size of garnets a and b from the feldspar zone of the Ishikawayama mine (termed hereafter as I-a and I-b) are 7 mm and 12 mm, respectively, while that from the muscovite-feldspar-quartz zone of

Fig. 1. Comparison of rim to rim compositional profile of garnet I-a (left) with calculated profile (right).

the Yamono garnet (Y-a) is 10 mm. All garnet crystals are optically isotropic and have some internal cracks. The Ishikawayama garnets contain no mineral inclusions, whereas the Yamono garnet contains muscovite in its core. In order to determine the elemental distribution patterns in these garnet crystals, we carefully prepared polished thin sections which intersect through each crystal center.

Analytical method

Quantitative spot analyses of garnets were performed using a JEOL JXA-8621 EPMA, at the Chemical Analysis Center of the University of Tsukuba. Analytical conditions of EPMA were 15

kV accelerating voltage and 1×10^{-8} A probe current for elements Si, Al, Ti, Cr, Ni, Fe, Mn, Mg, Ca, Na, and K, and 25 kV accelerating voltage and 1×10^{-7} A probe current for Y. The diameter of the electron beam was set to be 20 μm on ZrO_2 . Corrections were made using ZAF correction program provided by JEOL.

Compositional mapping was carried out for elements (Fe, Mn, Mg, Ca, Y, Al, and Ti) under the following conditions; 25 kV accelerating voltage, 5×10^{-7} A probe current, 1 second measuring time, 20 μm beam diameter, and 60 μm step interval. Of the analyzed elements, the concentrations of Al and Ti are homogeneous within individual grains, whereas other elements, Fe, Mn, Ca,

Fig. 2. Comparison of rim to rim compositional profile of garnet I-b (left) with calculated profile (right).

Mg, and Y, show concentric patterns around the crystal center; no compositional heterogeneity due to the crystal plane was observed. Therefore, the quantitative compositional features within each garnet grain are represented by the spot analyses along the rim to rim traverse passing through the crystal center. Analytical errors of the spot analyses are within 5% for Fe and Mn, 10% for Ca and Mg, and 20% for Y.

Garnet composition

Compositional mapping over individual grains shows that the zoning patterns are spherically symmetrical. Figures 1, 2, and 3 represent the rim to rim compositional profiles for garnet grains I-

a, I-b, and Y-a, respectively. In these figures, the numbers on the vertical axis denote the concentration of each cation on the basis of 12 total oxygens. Of the cations, Mn and Fe are dominant whereas Ca, Mg, and Y are minor. As the Al contents are virtually constant and are around 2.00 (1.99–2.02), the andradite component is likely to be negligible.

Individual garnets have different compositional patterns and absolute concentration for each cation (Figs. 1–3). Garnet I-b does not display distinct compositional zoning, whereas the other garnets show systematic compositional trends from the core to the rim. Garnets I-a and Y-a have a tendency to increase in Fe content with a decrease in

Fig. 3. Comparison of rim to rim compositional profile of garnet Y-a (left) with calculated profile (right).

Mn content from the core to the rim: this depletion pattern in Mn is consistent with previous studies of metamorphic garnets. It is also conspicuous that these compositionally zoned garnets have a tendency to increase monotonically in Mg from the core to the rim. The most characteristic feature of the chemical zoning in garnet is the compositional pattern of Ca: the Ca content of garnet I-a increases from the core toward the margin and then decreases again at the rim. Such a compositional pattern of Ca has also been noted for some metamorphic garnets (Banno and Kurata, 1972) and pegmatite garnets (Leake, 1967), which indicates that the pattern is not uncommon.

Y contents were determined only for garnets in the Ishikawa rare-element pegmatites (Fig. 4). Garnet I-a contains Y up to 0.95 wt.%. The bell-shaped zoning profile of Y in the garnet I-a is similar to that described for metamorphic garnets using ion microprobe (Hickmott *et al.*, 1987; Hickmott and Shimizu, 1990). It is notable in Figs. 1 and 2 that the two Ishikawa garnets have the same contents of Fe, Mn, Mg, and Ca in their cores, whereas have different values in their rims. However, the compositional zoning of Y is different from these elements, and it will be described in a later section. Although EPMA is inferior in the detection of trace elements to ion microprobe, it has a great advantage for the matrix correction over a wide compositional variety of geological

materials. The present example demonstrates the utility of EPMA for the determination of trace Y content in solid materials.

MODEL FOR GARNET CRYSTALLIZATION

It is still controversial whether the garnets in pegmatites crystallized from a granitic melt or an aqueous fluid exsolved from the melt. London *et al.* (1990) have recently suggested that pegmatites form from fractional crystallization of volatile-rich melts. Here we tentatively adopt his idea and assume that the garnets in the Ishikawa and Yamanoo pegmatites were formed from a pegmatitic melt.

Hollister (1966) proposed a model of compositional variation in metamorphic garnets by modifying Rayleigh fractionation. He assumed that the formation of metamorphic garnets progresses with the decomposition of biotite or chlorite. He also assumed that (1) surface equilibrium of Mn between the garnet and chlorite is attained, (2) Mn is partitioned to a greater extent into garnet than biotite or chlorite, (3) diffusion of Mn in biotite or chlorite is fast enough to preserve a homogeneous Mn content throughout the matrix during reaction, and (4) the diffusion rate of Mn in garnet is slow even at peak metamorphism to preserve Mn zoning in garnet. The compositional zoning pattern of Mn in garnet from the Kowiek in Canada was simulated very well by assigning a partition coefficient of 23 for Mn from biotite or chlorite to garnet.

In order to apply Hollister's model to the pegmatite garnet, some modifications to the model are necessary. Hollister (1966) treated Mn as a trace element. However, because the studied garnets contain a high spessartine component, Mn must be treated as a major element and can not be simulated easily by a simple Rayleigh model (e.g., Banno and Chii, 1976; Cygan and Lasaga, 1982). The model should also explain a systematic compositional pattern with respect to other elements besides Mn. Although the Hollister's model is directly applicable to isothermal conditions, garnet-melt partition coefficients should be a

Fig. 4. Compositional pattern of Y content (wt.%) in garnets (I-a and I-b) from the Ishikawayama mine.

function of temperature in a cooling granitic pegmatite. The model by Cygan and Lasaga (1982) incorporates temperature dependence of partition coefficients. In addition to the variation of partition coefficients, variation of melt composition due to co-crystallizing phases may also have played an important role in the pegmatitic system. However, any model has not been applied to the pegmatite system and the Ca peak in garnet I-a does not seem to be well reproduced even by previous models. Here we present a model incorporating these effects to reproduce the observed compositional patterns in pegmatite garnets.

Partition coefficient between garnet and granitic melt

Cygan and Lasaga (1982) stressed an importance of an exchange reaction to represent partitioning of major elements between garnet and other phases. Considering the garnet mineral chemistry that the 8-coordinated site is entirely occupied by divalent cations Fe, Mn, Mg, and Ca, the exchange reactions are expressed:

These relations are given by:

$$(\text{Mn/Fe})_{\text{garnet}} = K_{(\text{Mn-Fe})} \times (\text{Mn/Fe})_{\text{melt}}, \quad (1)$$

$$(\text{Mg/Fe})_{\text{garnet}} = K_{(\text{Mg-Fe})} \times (\text{Mg/Fe})_{\text{melt}}, \quad (2)$$

$$(\text{Ca/Fe})_{\text{garnet}} = K_{(\text{Ca-Fe})} \times (\text{Ca/Fe})_{\text{melt}}, \quad (3)$$

where $K_{(\text{Mn-Fe})}$, $K_{(\text{Mg-Fe})}$, and $K_{(\text{Ca-Fe})}$ are partition coefficients between the garnet and melt, which are primarily dependent on temperature. Y is not treated in the calculation partly owing to the

trivalent cation and low contents. Although there are no data on the values of $K_{(\text{Mn-Fe})}$, $K_{(\text{Mg-Fe})}$, and $K_{(\text{Ca-Fe})}$ in the granitic system, it is possible from these equations to calculate the proportion of Fe, Mn, Mg, and Ca in the garnet which was in equilibrium with granitic melt of a given composition. It is assumed in the calculation that the concentrations of cations Fe, Mn, Mg, and Ca in the melt phase were homogeneous throughout garnet crystallization, whereas the diffusion rate of those cations in garnet was slow enough to preserve the growth record of garnet. It is assumed that the partition coefficients of elements are constant under constant temperature; however, the partition coefficients will be variable if the garnets grew with a decrease in temperature.

Initial melt composition

The composition of pegmatitic melt from which the garnet crystallized is difficult to determine. The bulk composition of granitic pegmatite melt may be represented by that of granitic pegmatite, which is also difficult to determine due to its strong zonation of coarse-grained minerals. Černý (1982), however, reported that the bulk composition of a granitic pegmatite magma was similar to that of the associated granitic rocks. Hence, it is assumed in this study that the composition of garnet-forming pegmatite melt is approximated by its associated granitic rocks (young biotite granodiorite for the Ishikawa garnet and the Yamanoo granodiorite for the Yamanoo garnet).

Proportion of garnet crystallized from pegmatitic magma

The Ishikawa and Yamanoo garnets crystallized locally from the pegmatitic melt responsible for the formation of the feldspar zone and that of the muscovite-feldspar-quartz zone, respectively. Because the composition of garnet is likely to vary depending on the amount of the pegmatitic melt from which the garnet crystallized, the proportion of crystallizing garnet to the initial pegmatitic mass was considered as an independent factor in the calculation.

Fig. 5. Calculated rim to rim compositional profile of Fe, Mn, Mg, and Ca of garnet with variable conditions of factors which affect the garnet composition. Refer to text for the details.

Composition of minerals accompanying garnet

Formation of other phases during garnet growth may also affect the composition of garnet. The major associated minerals with the garnet are K-feldspar, quartz, and muscovite. These minerals contain only trace amounts of Fe, Mn, and Mg. Therefore, pyrope, spessartine, and almandine components are unlikely to have been affected by the growth of those minerals. In contrast, as plagioclase (An_{1-6}) and K-feldspar contain minor contents of Ca, it is likely that the feldspar growth affected the grossular content of the garnets. Trace minerals with high Fe, Mn, Mg, and Ca contents which would have some effect on the garnet zoning are not observed in the garnet bearing zone.

Calculation procedures

In order to evaluate how the individual factors affect the compositional profile of garnet, calculation was made using a personal computer. As far as the partition coefficient deviates from unity, each element tends to concentrate into or deplete from the garnet with the advance of crystallization. As the first step, the garnet compositions were calculated from Eqs. (1) to (3) by assuming the initial melt composition and values of partition coefficients. It is assumed that feldspar crystallizes with garnet. However, the amount of feldspar removed from the melt can arbitrarily be specified, because the Ca contents of K-feldspar and plagioclase are variable from 200 to 2000 ppm and from 1000 to 6000 ppm, respectively. The total amount of elements removed from the melt is calculated from the composition of garnet and feldspar and the proportion of both minerals crystallized from the melt. In the second step, the chemical composition of garnet is computed using the magma composition modified after the removal of both minerals. The same computation is iterated until the given amount of garnet is formed.

We assumed that the growth rate of garnet is constant in volume and is independent of temperature, and the partition coefficient is a linear function of temperature. Although values of $K_{(Mn-Fe)}$, $K_{(Mg-Fe)}$, and $K_{(Ca-Fe)}$ are not known, they are estimated by trial and error, taking into account

the partitioning data on metamorphic garnets. Partition coefficients are changed if garnet forms in accordance with the change of temperature.

Before simulating the chemical zoning of studied garnets, we evaluated the effect of the factors mentioned above on the garnet zoning. We considered four cases using a standard granitic rock of JG1 from Geological Survey of Japan (Ando *et al.*, 1987) as the initial pegmatite melt; this rock contains 15411 ppm of Fe, 488 ppm of Mn, 4462 ppm of Mg, and 12121 ppm of Ca. Other initial conditions for the calculation are (1) partition coefficients $K_{(Mn-Fe)}$, $K_{(Mg-Fe)}$, and $K_{(Ca-Fe)}$ are 10, 0.07, and 0.03, respectively; (2) mass proportion of crystallized garnet is 0.1%; (3) the Ca content of associated solid phases is 1000 ppm. Considering that the garnets have well-developed 24 faced euhedral forms, the calculation results were represented as rim to rim compositional profiles for each element by simplifying the garnet as a sphere (Fig. 5).

RESULTS AND DISCUSSION

Influence of partition coefficient and melt composition

The ratios of elements Fe, Mn, Mg, and Ca in the garnet depend largely on partition coefficients. It is evident from Eqs. (1) to (3) that the values of the partition coefficients are intimately related with the melt composition for a given garnet composition. For example, if the Fe and Ca contents in the melt are both 10,000 ppm, the studied garnets can not be formed unless the value of $K_{(Ca-Fe)}$ is below 1. The value of $K_{(Ca-Fe)}$ must be above 1 if the Ca content in the melt is as low as several hundred ppm, which is unlikely from the Ca content in granitoids (Table 1).

Although the chemical composition of granitic rocks is variable within a single zoned pluton (e.g., Bateman and Chappell, 1979; Shimizu, 1986) and between granitic-rock types (e.g., Chappell and White, 1974; Whalen *et al.*, 1987), it generally varies in the order $Fe \geq Ca > Mg > Mn$. This is consistent with that of studied granitic rocks (Table 1). Since the Fe and Ca contents in the pegmatite

melt are assumed to be similar to those of the granitic melt (Černý, 1982), the value of $K_{(Ca-Fe)}$ is certainly below 1. Similarly, the value of $K_{(Mn-Fe)}$ cannot be below 1, since the pegmatite melt is assumed to contain more Fe than Mn. In other words, the concentration profiles of pegmatite garnets are not significantly altered by the melt composition. This is supported by calculation using pegmatite (Fehn, 1986) as the melt composition, which indicates that almandine-spessartine garnet can occur irrespective of such melt composition as long as the value of $K_{(Mn-Fe)}$ is around 10.

The calculated results show that the compositional profiles of minor elements (Ca and Mg in garnets) are affected by the value of partition coefficients of major elements (Fe and Mn); however, the opposite is unlikely to occur. This is shown in Figs. 5(A) and (B); three cases are shown for each. In Fig. 5(A), the partition coefficient of $K_{(Mn-Fe)}$ varies from 10 in the initial crystallization of core garnet to 10, 25 and 40 (case 1, 2, and 3, respectively) in the final crystallization of rim garnet, while other factors are preserved. The contents of four elements change successively as the garnet crystallizes. In Fig. 5(B), only the partition coefficient of $K_{(Ca-Fe)}$ varies from 0.1 in the initial garnet crystallization to 0.1, 0.2, and 0.3 (case 1, 2, and 3, respectively) in the final garnet. The concentration of Ca changes with the progress of crystallization, while other elements do not display any significant variation in their concentration. The most important point, which is described later in detail, is that the compositional profile of Ca with a maximum between the core and rim (as in garnet I-a) could not be formed under the constant partition coefficient, even if other factors were changed.

Influence of proportion of garnet crystallized from melt

The compositional variation of garnet becomes larger as the proportion of the garnet crystallized from the melt (termed R) increases. This is illustrated in Fig. 5(C), where only the value of R increases from 0.3 through 0.6 to 0.9% (case 1, 2,

and 3, respectively). It is notable that the compositional variation in the rim becomes larger for all elements with an increase in the value.

Influence of elements removed by minerals associated with garnet

The concentrations and concentration patterns of elements in the garnets are affected by the proportions and elemental concentrations of the associated minerals, if the elements in question are contained in the associated minerals. The amount of Ca removed mainly by feldspars from the pegmatite melt, although it is low, may be sufficient to affect the Ca content of coexisting garnet. The Ca content in the feldspar with which the garnet crystallized is difficult to estimate due to the heterogeneous occurrence of garnet and plagioclase in the feldspar zone. If removal of Ca from the pegmatite melt into the feldspar increases, the rim to rim profile of Ca content in the garnet becomes significant in accordance with the rapid decrease of the Ca content in the associated melt. Figure 5(D) shows the rim to rim concentration profiles of four elements in garnet when the Ca content in feldspar is 11000, 8000, and 5000 ppm (case 1, 2, and 3, respectively). It is evident from this figure that the garnet decreases in Ca content in the rim with an increase in Ca of feldspar, while the rim to rim profiles of other elements do not vary significantly, as noted above. The results of the calculation further demonstrate that the Ca peak, as illustrated in the Ishikawa garnet I-a, cannot be formed unless two conditions are satisfied; the partition coefficient of $K_{(Ca-Fe)}$ varies during garnet growth and an adequate amount of Ca is removed from the melt into the feldspar.

Compositional pattern of the Ishikawa and Yamanoo garnet

Calculations were made for the Ishikawa and Yamanoo garnets by considering the effect of the factors mentioned above. The results of the simulations are illustrated on the right hand sides of Figs. 1 to 3, compared with the measured compositional data. The calculation results simulate well the compositional pattern of pegmatite garnets.

Table 2. Initial and boundary conditions used to calculate the compositional profiles of the Ishikawa and Yamanoo pegmatitic garnets

Garnet		I-a	I-b	Y-a
Mass ratio of crystallized garnet	<i>R</i>	0.10%	0.03%	0.10%
Melt composition (ppm)	Fe	15049	15049	23435
	Mn	787	787	757
	Mg	2333	2333	4265
	Ca	10882	10882	13753
Partition coefficient	Mn/Fe	12 → 8	12 → 11	30 → 18
	Mg/Fe	0.07 → 0.10	0.07 → 0.08	0.01 → 0.07
	Ca/Fe	0.03 → 0.07	0.03 → 0.03	0.006 → 0.03
Ca concentration of other minerals (ppm)		7500	2000	5000

Calculation was made by simplifying garnet as a sphere.

Partition coefficients vary linearly with the growth of garnet from the initial value at which the garnet begins to crystallize to the final value at which the garnet is completely crystallized.

Table 2 summarizes values of factors used for the calculation.

Although four factors were considered in the calculation, the Ishikawa younger granodiorite is used as the initial melt composition for both of the Ishikawa garnets. The other factors were different in the calculation for each garnet. It is assumed that the Ca content in the solid phases co-crystallizing with garnet is different between the two garnet grains; 7500 ppm for grain I-a and 2000 ppm for grain I-b, respectively. This assumption, however, may be acceptable by taking into account the local variation of Ca in the pegmatite zone. Other important factors to simulate the different compositional patterns in the Ishikawa garnets are *R* values and the variation of the partition coefficients. The variation of partition coefficients is larger in the I-a zoned garnet than in the I-b unzoned garnet. As the partition coefficients are strongly affected by temperature, a large variation in the partition coefficients seems to imply that temperature changed during the garnet growth, most likely a decrease in temperature. In the case of grain I-b, an apparent small change in the partition coefficients indicated by its compositional homogeneity suggests that this garnet was formed under an approximately constant temperature

condition. This indicates that the garnet I-b grew more rapidly than the garnet I-a, considering that the garnet I-b is larger in size than grain I-a. A smaller value of *R* for garnet I-b than for garnet I-a suggests that garnet I-b was enclosed in the feldspar zone more rapidly than garnet I-a. It is likely that the growth rate varied locally in the coarse-grained pegmatite minerals. The *R* value corresponds to the mass ratio of the garnet in the feldspar zone. This value is a measurable parameter, although it is not determined at present due to the localized distribution of garnet and field conditions. However, values of *R* from 0.03 to 0.1% seem qualitatively reasonable.

Hickmott and Shimizu (1990) showed that several trace elements in metamorphic garnets exhibit a hump in the rim to rim traverse, and considered such a hump as evidence of disequilibrium partitioning of the element during the garnet growth. However, the present calculation demonstrates that the Ca hump in garnet I-a can be reproduced in terms of the cation exchange equilibrium between the growing garnet surface and ambient pegmatite melt, if a sufficient amount of Ca is removed from the melt by feldspars. Heterogeneous compositional zoning in metamorphic garnets could be analyzed quantitatively in

terms of the rim equilibrium, by taking into account the effect of the dissolution and growth of surrounding minerals.

The conditions and values of factors for forming the Yamanoo garnet are slightly different from those for the Ishikawa garnets, except for the R value and the concentration of Ca removed by minerals accompanying the garnet. One of the major differences is the initial composition of the granitic melt, especially in the Fe and Mg concentrations. The different initial melt composition may lead to a difference in the value of the partition coefficients. The temperatures may also have differed between the two pegmatites. Thus, there are some inconsistencies in the simulation, and a more accurate simulation may be possible. However, the factors adopted here seem prerequisite for the formation of pegmatite garnet.

Compositional pattern of Y in garnet

Similarly to the major elements, the compositional pattern of Y in the garnet I-a is zoned and that in the garnet I-b is homogeneous (Fig. 4). The Y content of the garnet I-a is high and constant in the core, and decreases linearly toward the rim. However, its depletion pattern toward the rim is different from other elements (Figs. 1 and 2). Furthermore, the Y content of the two garnets is different in the core and in the rim. Thus, the concentration pattern of Y in the garnets is different from that of Mn, Fe, Mg, and Ca, suggesting an involvement of some additional factors. The concentration of Y in the core should have been the same between the two garnets, if the garnets began to crystallize simultaneously in a single pegmatitic melt as suggested from other element data. The lack of attainment of this expectancy suggests that the distribution of Y content in the melt was heterogeneous during the garnet growth. A majority of Y in the Ishikawa pegmatite is contained in the rare-earth containing minerals such as xenotime, monazite, and samarskite. These minerals are distributed heterogeneously and locally concentrated in the pegmatite zone. The local crystallization of these rare-earth containing minerals may have produced the heterogeneous dis-

tribution of Y content in the Ishikawa pegmatitic melt, and in turn various distribution patterns of Y content in the garnet. This will, however, be examined in a future study.

CONCLUSIONS

Two coarse-grained spessartine-almandine garnets, having a 24-faced euhedral crystal form, in the Ishikawa pegmatite show different compositional variations along the rim through center to rim traverses. Analysis of the compositional patterns in the pegmatite garnet in terms of an extended Hollister's model (Hollister, 1966) demonstrates that (1) the bell-shaped Mn zoning in garnet forms following a change of the garnet-melt partition coefficients of Mn and Fe, (2) coprecipitation of a Ca-containing mineral (feldspar) is necessary to form the zoned garnet with a Ca hump between the core and rim, (3) the unzoned garnet develops when small amounts of garnets crystallize from the melt at relatively constant garnet-melt partition coefficients, and (4) the distribution of Y content in garnet may have been affected by the local distribution of rare-earth containing minerals within a single pegmatite melt. The Yamanoo garnet having a compositional zoning different from the Ishikawa garnet can be reproduced by changing the initial melt composition and partition coefficients. As the garnet-melt partition coefficient is largely dependent on temperature, the compositionally-zoned garnet presumably formed with decreasing temperature, and the difference in the garnet zoning between the Ishikawa and Yamanoo pegmatites is ascribed to the difference in temperature conditions. The model calculation further implies a local heterogeneity of melt composition within a single pegmatite zone and different growth rates of grains. This view is consistent with London *et al.* (1990), who state that chemical equilibrium is approached between crystal rims and melt but is not attained within a total pegmatite system.

Geochemical data on the magmatic-hydrothermal transition in the granite-pegmatite system provides crucial information on the genesis of

magmatic-hydrothermal deposits. The chemical composition of magmatic aqueous fluid separated from a crystallizing granitic magma cannot be determined independently from the solidified granitoids and pegmatites owing to difficulty in estimating the amount of elements escaped from granitic and pegmatitic melt, and therefore has been estimated by assuming various factors and using melt-fluid partition coefficients of elements (Candela, 1989; Nakano and Urabe, 1989). Extension of the present method would make it possible to calculate the concentration of elements Fe, Mn, Mg, and Ca in the pegmatitic melt removed by garnets or other pegmatite minerals. Therefore, this method can be used as an additional tool to trace the geochemical evolution of the final stage of granitic magma.

Acknowledgments—The authors express their thanks to late Emeritus Professor Takashi Fujii for his encouragement throughout this study. They also thank Dr. Masaharu Kamitani, Geological Survey of Japan (presently at Sumiko Consultant Co., Ltd.) and Mr. Yoshimasa Yabe, Ishikawayama mine, for help in the field survey, to Dr. Jeff Hedenquist, Geological Survey of Japan, who critically read an early version of the manuscript, and to two Geochemical Journal referees for their careful and constructive review comments. This work was supported in part by a Grant-in-Aid for Special Research Project (Evolution of hydrothermal systems and relation to mineralization potential) from the Agency of Industrial Science and Technology.

REFERENCES

- Ando, A., Mita, N. and Terashima, S. (1987) 1986 values of fifteen GSJ rock reference samples, "Igneous Rock Series". *Geostandard Newsletter* **11**, 159–166.
- Banno, S. and Chii, S. (1976) Genesis of oscillatory-zoned garnet, in "Progress in Research on Rock Forming Minerals". *J. Jap. Assoc. Min. Petr. Econ. Geol.* (special paper) **1**, 283–299 (in Japanese).
- Banno, S. and Kurata, H. (1972) Distribution of Ca in zoned garnet of low-grade pelitic schists. *J. Geol. Soc. Jpn.* **78**, 507–512.
- Bateman, P. C. and Chappell, B. W. (1979) Crystallization, fractionation, and solidification of the Tuolumne intrusive series, Yosemite National Park, California. *Geol. Soc. Am. Bull.* **90**, 465–482.
- Candela, P. A. (1989) Magmatic ore-forming fluids: thermodynamic and mass-transfer calculations of metal concentrations. In ore deposition associated with magmas. *Rev. Econ. Geol.* **4**, 203–221.
- Černý, P. (1982) Petrogenesis of granitic pegmatites. In granitic pegmatites in science and industry. *Mineral. Assoc. Canada Short Course* **8**, 405–462.
- Chappell, B. W. and White, A. J. R. (1974) Two contrasting granite types. *Pacific Geol.* **8**, 173–174.
- Cygan, R. T. and Lasaga, A. (1982) Crystal growth and the formation of chemical zoning in garnets. *Contr. Mineral. Petrol.* **79**, 187–200.
- Dempster, T. J. (1985) Garnet zoning and metamorphism of the Barrovian type area, Scotland. *Contr. Mineral. Petrol.* **89**, 30–38.
- Fehn, P. M. (1986) On the origin of graphic granite. *Am. Mineral.* **71**, 325–330.
- Hickmott, D. D. and Shimizu, N. (1990) Trace element zoning in garnet from the Kwoiek area, British Columbia: disequilibrium partitioning during garnet growth? *Contr. Mineral. Petrol.* **104**, 619–630.
- Hickmott, D. D., Shimizu, N., Spear, F. S. and Selverstone, J. (1987) Trace-element zoning in metamorphic garnet. *Geology* **15**, 573–576.
- Hollister, L. S. (1966) Garnet zoning: An interpretation based on the Rayleigh fractionation model. *Science* **154**, 1147–1151.
- Ishihara, S. (1981) The granitoid series and mineralization. *Econ. Geol.* 75th. Anniv. Vol. 458–484.
- Kawano, T. and Ueda, Y. (1966) K-Ar dating on the igneous rocks in Japan (IV)—Granitic rocks of Backone range in northeastern Japan and its western district. *Sci. Rep. Tohoku Univ. Ser. III*, 525–539.
- Leake, B. E. (1967) Zoned garnets from the Galway granite and its aplites. *Earth Planet. Sci. Lett.* **3**, 311–316.
- London, D., Morgan, G. B., VI. and Hervig, R. H. (1990) Vapor-undersaturated experiments with Macusani glass + H₂O at 200 MPa, and the internal differentiation of granitic pegmatites. *Contr. Mineral. Petrol.* **102**, 1–17.
- Matsubara, H. (1956) Reports on the pegmatites in Ishikawa district, Fukushima prefecture—One of the fundamental studies on uranium-thorium resources in Japan. *Jap. Geol. Surv. Bull.* **7**, 335–348 (in Japanese with English abstract).
- Nakano, T. and Urabe, T. (1989) Calculated compositions of fluids released from a crystallizing granitic melt: Importance of pressure on the genesis of ore forming fluid. *Geochem. J.* **23**, 307–319.
- Nakano, T., Yoshino, T. and Nishida, N. (1991) Rapid analytical method for trace Zn contents in some mafic minerals using the electron microprobe: Potential utility as a metallogenetic and petrogenetic indica-

- tor. *Chem. Geol.* **89**, 379–389.
- Ramsden, A. R. and French, D. H. (1990) Routine trace-element capabilities of electron-microprobe analysis in mineralogical investigations: an empirical evaluation of performance using spectrochemical standard glasses. *Can. Mineral.* **28**, 171–180.
- Sanbonsugi, M. (1953) On the granite-pegmatite deposits, occurring in western-margin of the Abukuma mountains, and its relation to the geologic structure. *Sci. Rep. Fukushima Univ.* **3**, 1–26 (in Japanese with English abstract).
- Shiba, M., Ueda, Y. and Onuki, H. (1979) K-Ar ages of metamorphic rocks from the Tsukuba district, Ibaraki Prefecture. *J. Jap. Assoc. Min. Petr. Econ. Geol.* **74**, 122–125 (in Japanese with English abstract).
- Shimizu, M. (1986) The Tokuwa batholith, central Japan—An example of occurrence of ilmenite-series and magnetite-series granitoids in a batholith. *Univ Museum Univ. Tokyo Bull.* **28**, 146 pp.
- Takahashi, Y. (1982) Geology of the granitic rocks in the Tsukuba area. *J. Geol. Soc. Jpn.* **88**, 177–184 (in Japanese with English abstract).
- Tracy, R. J., Robinson, P. and Thompson, A. B. (1976) Garnet composition and zoning in the determination of temperature and pressure of metamorphism, Central Massachusetts. *Am. Mineral.* **61**, 762–775.
- Tsutsue, A. (1976) Granitic magmas and ore deposits, (1) especially those of southwest Japan. *Mining Geol.* (special issue) **7**, 13–24.
- Whalen, J. B., Currie, K. L. and Chappell, B. W. (1987) A-type granites: geochemical characteristics, discrimination and petrogenesis. *Contr. Mineral. Petrol.* **95**, 407–419.