

High-pressure and high-temperature experiments on the phase relations in the system of Mg-rich garnet composition (Prp₇₅Alm₂₅): Implication for the Fe-Mg partitioning between garnet and orthopyroxene

Kei Sato and Toshisuke Kawasaki

*Division of Earth Sciences, Department of Biosphere-Geosphere Sciences, Faculty of Science, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-8577
(ksato@sci.ehime-u.ac.jp)*

Abstract: The phase relations in the system of Mg-rich garnet composition (Prp₇₅Alm₂₅) were investigated using a piston cylinder apparatus at 11–23 kbar and 1000–1300°C. The following mineral assemblages were obtained with decreasing pressure at 1200°C: garnet, garnet+orthopyroxene+sapphirine+quartz, orthopyroxene+sapphirine+quartz. At 11 kbar, the assemblage of orthopyroxene+sapphirine+quartz changed to that of orthopyroxene+sapphirine+quartz+sillimanite at a certain temperature between 1000 and 1100°C.

The Fe-Mg distribution coefficients of coexisting garnet and orthopyroxene

$$K_D = (X_{Mg}/X_{Fe})^{Opx} (X_{Fe}/X_{Mg})^{Grt}$$

was experimentally determined. The new garnet-orthopyroxene geothermometer has been obtained as

$$T (^{\circ}\text{C}) = (2387 \pm 146) / [\ln K_D + (1.20 \pm 0.10)] - 273$$

We estimated the retrograde metamorphic temperatures of UHT metamorphic rocks from Enderby Land, East Antarctica as 812–1010°C. Our estimations matched with previous estimations based on Fe-Mg exchange and were about 200–300°C lower than those of previous estimations based on feldspar thermometry.

key words *P-T* diagram of the Mg-rich garnet system, Fe-Mg partitioning, geothermometer, ultrahigh-temperature metamorphism

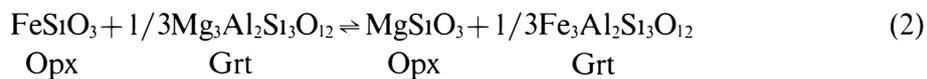
1. Introduction

It is important to determine the phase relations of Mg-rich garnet and its low-pressure phases in the pyrope (Mg₃Al₂Si₃O₁₂)-almandine (Fe₃Al₂Si₃O₁₂) system. Phase relations of end member garnets have been determined for pyrope (Boyd and England, 1959), and for almandine (Schaerer and Yagi, 1952, Hsu, 1968, Keesman *et al.*, 1971) systems, respectively. Boyd and England's experiments in the pressure range 15–47 kbar showed that pyrope garnet decomposed directly to orthopyroxene+sapphirine+sillimanite through the univariant reaction



Keesman *et al* (1971) investigated the melting relation of almandine garnet in the pressure range of 10–26 kbar and estimated the locations of the invariant points using the experimental data obtained by Schairer and Yagi (1952) at 1 atm, and by Hsu (1968) at pressures up to 2 kbar. In their experiments, almandine garnet decomposed directly into fayalite + hercynite solid solution + quartz or fayalite + hercynite solid solution + ferrocordierite. Hsu and Burnham (1969) carried out experiments on the $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - H_2O system at 2 kbar, and reported the stability phases (orthopyroxene + cordierite + spinel + liquid in high- T side, olivine + cordierite + spinel + liquid in low- T side) at low-pressure. Although these two end members were experimentally investigated, the high-pressure and high-temperature phase relations of the intermediate composition have never been clarified.

The Fe-Mg exchange reaction between garnet and orthopyroxene



has been investigated by many authors (*e.g.* Kawasaki and Matsui, 1983, Harley, 1984). Harley (1984) carried out experiments in the FeO-MgO- Al_2O_3 - SiO_2 and CaO-FeO-MgO- Al_2O_3 - SiO_2 systems, and the geothermometer was proposed. Harley used glasses of $X_{\text{Mg}} < 0.7$ in bulk as starting materials, moreover, iron capsules were used in some experiments. So the bulk compositions shifted to the Fe-rich side by the addition of Fe from a capsule in Harley's experiment. As Kawasaki and Matsui (1983) pointed out, the distribution coefficient decreases with Fe/(Fe+Mg) of the system. The decrease in the distribution coefficient with Fe/(Fe+Mg) was not incorporated in Harley's Fe-Mg geothermometry (Kawasaki and Motoyoshi, 2000). Kawasaki and Motoyoshi (2000) carried out experiments using glasses of $X_{\text{Mg}} = 0.75$ in bulk as starting materials. Graphite capsules were used in Kawasaki and Motoyoshi's experiments. They proposed a new garnet-orthopyroxene geothermometer. Kawasaki and Motoyoshi adapted the new geothermometer to the natural sample from an orthopyroxene granulite from McIntyre Island, Napier Complex, East Antarctica. On the other hand, an experimental study in the synthetic system and $X_{\text{Mg}} = 0.75$ in bulk composition has never been carried out.

In this paper, we present new data on the high-pressure and high-temperature phase relations for composition of $\text{Prp}_{75}\text{Alm}_{25}$ and on the Fe-Mg distribution between garnet and orthopyroxene. Abbreviations of minerals are after Kretz (1983).

2. Experimental procedures

2.1. Starting materials

High-pressure and high-temperature phase relations were investigated in the FeO-MgO- Al_2O_3 - SiO_2 system. In the present experiment, we mainly used a glass as the starting material, the bulk of it is $\text{Prp}_{75}\text{Alm}_{25}$ (Table 1). The following starting materials were prepared: (1) glass with $\text{Prp}_{75}\text{Alm}_{25}$ composition, (2) 90 wt% glass with $\text{Prp}_{75}\text{Alm}_{25}$ composition plus 10 wt% seed mineral aggregation of garnet, orthopyroxene, spinel, olivine, cordierite and quartz, and (3) 95 wt% glass with $\text{Prp}_{75}\text{Alm}_{25}$ composition plus 5 wt%

Table 1 Chemical compositions of starting material

	Ideal value	Glass**	Glass 95 + Sil 5**
SiO ₂	42.24	42.81	42.52
Al ₂ O ₃	23.89	23.87	25.83
FeO*	12.62	11.79	11.20
MgO	21.25	20.80	19.76
Total	100.00	99.27	99.31
Number of cations for N oxygens			
	N = 12	N = 12	N = 12
Si	3.000	3.045	2.891
Al	2.000	2.001	2.070
Fe	0.750	0.702	0.637
Mg	2.250	2.206	2.003
Total	8.000	7.954	7.601
X _{Mg}	0.750	0.759	0.759

* Total Fe as FeO

** Analyzed by defocused electron beam

sillimanite

The glass with Prp₇₅Alm₂₅ composition was prepared as follows. First, MgO gel, magnetite (Fe₃O₄), Al₂O₃ gel and SiO₂ gel were weighted to meet Prp₇₅Alm₂₅ composition, pulverized for one hour under ethyl alcohol in an agate mortar and pressed into a tablet in a die. This tablet was put into the Pt wire basket, hung in the electric furnace and heated under controlled oxygen fugacity by the mixing gas technique (CO₂/H₂=0.8/0.2 [ml/min]). This gas flow ratio realized the iron-wustite buffer at 1150°C. It was made to react for 25 hours. The run product was orthopyroxene + spinel + olivine + cordierite + quartz (run no 990728). Quartz persisted as a metastable phase. Therefore, after grinding and mixing this assemblage, repeated experiments were carried out at 1150°C under atmospheric pressure for 75 hours in the electric furnace (run no 990809). As a result, a

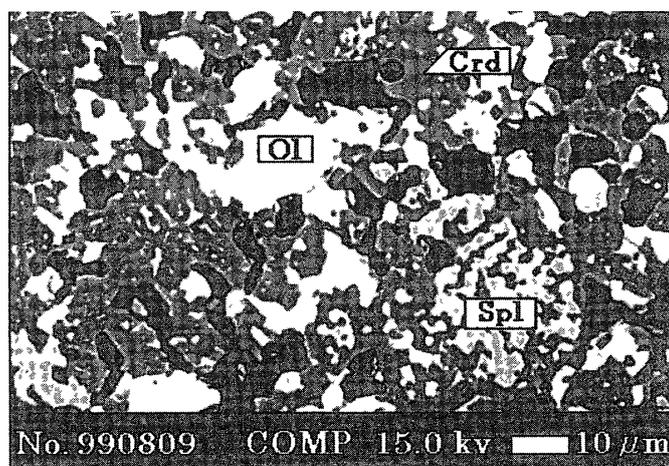


Fig 1 Photomicrograph of back-scattered electron image (BSEI) of run products under atmospheric pressure at 1150°C for 75 hours (run no 990809). The spinel + olivine + cordierite assemblage was synthesized in a Pt wire basket from the recycled run using an electric furnace. The black area is a cavern. Bar, 10 μm.

spinel+olivine+cordierite assemblage was obtained (Fig 1) In this run, cordierite is found around olivine and spinel The mineral mixture of spinel, olivine and cordierite was ground again in an agate mortar to pulverize to 10–20 μm The powdered sample was put into a graphite capsule The glass was obtained by quenching after a melting experiment at 10 kbar and 1600°C for 2 minutes using a piston cylinder apparatus X-ray microprobe analyses showed that the glass was chemically homogeneous The glass was slightly SiO₂-rich, FeO-poor, MgO-poor and enriched in X_{Mg} compared with the relevant composition of what (see Table 1)

The crystalline mixture of garnet, orthopyroxene, spinel, olivine, cordierite and quartz was prepared as a seed mineral mixture Chemical compositions of seed minerals are given in Table 2 The powdered spinel, olivine and cordierite, synthesized at 1150°C under atmospheric pressure (run no 990809), was reacted in a graphite capsule at 25 kbar and 1300°C for 3 hours to produce the assemblage of garnet+orthopyroxene+quartz+

Table 2 Average compositions of seed minerals

	Grt*	Opx**	Spl**	Ol**	Crd**
SiO ₂	40.42	45.07	0.27	37.75	50.23
Al ₂ O ₃	23.96	10.57	67.01	0.36	33.79
FeO	10.87	15.64	15.06	22.80	5.10
MgO	19.81	27.83	17.10	38.05	9.72
Total	95.06	99.11	99.44	98.96	98.84
X_{Mg}	0.765	0.760	0.669	0.748	0.772

* Garnet was obtained at 25 kbar and 1300 °C for 3 hours (run no 990917) In this run, small amounts of orthopyroxene, quartz and liquid were found (Fig 2A)

** A mineral assemblage of orthopyroxene, spinel, olivine and cordierite was obtained at 25 kbar and 1200 °C for 24 hours (run no 991026) These minerals were metastably crystallized Olivine never contacts cordierite, being coated by orthopyroxene and spinel (Fig 2B)

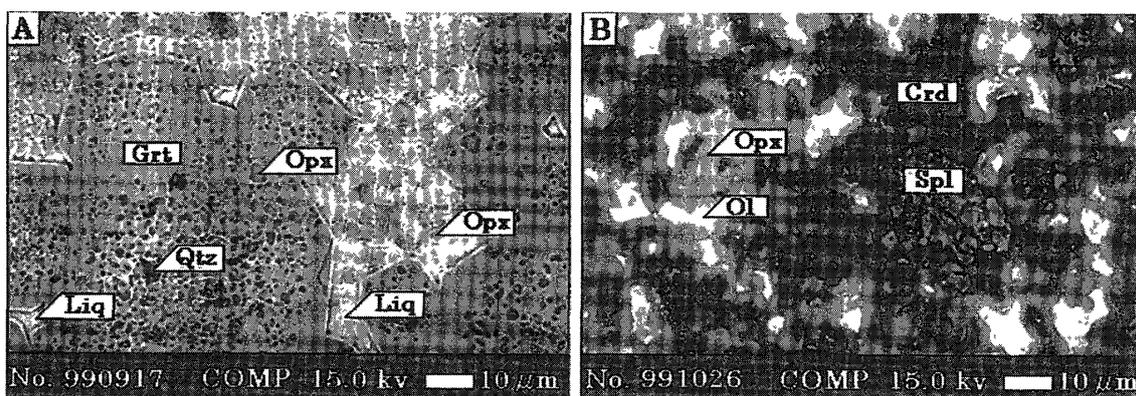


Fig 2 Photomicrograph of BSEI of seed minerals

A Run no 990917 The assemblage of garnet, orthopyroxene, quartz and liquid was metastably synthesized in a graphite capsule at 25 kbar and 1300°C for 3 hours from a mixture of spinel, olivine and cordierite This photograph shows a liquid-rich domain Bar, 10 μm Liq, liquid phase

B Run no 991026 The orthopyroxene+spinel+olivine+cordierite assemblage was metastably synthesized in a graphite capsule at 25 kbar and 1200°C for 24 hours from a mineral mixture of spinel, olivine and cordierite

liquid (run no 990917). A photomicrograph of the run products is shown in Fig 2A. In this run, orthopyroxene, quartz and liquid were included within the garnet. Moreover, orthopyroxene and liquid were found around the garnet. This garnet accompanied by orthopyroxene+quartz+liquid is available to use as the seed mineral for the high-pressure assemblage.

The metastable assemblage of orthopyroxene+spinel+olivine+cordierite was obtained in a graphite capsule at 25 kbar and 1200°C for 24 hours (run no 991026). A photomicrograph of back-scattered electron image (BSEI) of this run product is shown in Fig 2B. Olivine never contacts cordierite directly, as it is coated by orthopyroxene and spinel. Spinel is found between orthopyroxene and cordierite. This indicates that at least the olivine-cordierite join is unstable. The assemblage of orthopyroxene, spinel, olivine and cordierite is unstable at 25 kbar and 1200°C, where garnet is a stable phase as is discussed in the latter section. This indicates that the garnet formation reaction is very sluggish. Therefore we didn't use the crystalline mixture for a starting material. The metastable assemblage of orthopyroxene, spinel, olivine and cordierite was used as a low-pressure seed. The high- and low-pressure seeds were mixed in equal weights, and added to glass. The weight ratio of glass and seeds is 90/10.

Sillimanite from Rundvågshetta, Lutzow-Holm Bay, East Antarctica (RVH18-SIL, Kawasaki *et al.*, 1993) was also used for the seed mineral. Sillimanite was ground in an agate mortar, and then added into the glass. Addition of 5 wt% sillimanite to glass slightly changes the bulk (see Table 1).

2.2 Experimental techniques

High-pressure and high-temperature experiments were carried out using a 160 mm piston cylinder apparatus at Ehime University. Graphite was used as a heater. Temperature was controlled using PtRh or WRe thermocouples. Pressure was monitored by reading an oil pressure gauge. During each experiment, the fluctuations of temperature and pressure were less than $\pm 1\%$. Room temperature was kept at 25°C. Starting materials were ground using an agate mortar (grain size, 10–20 μm), then the powdered

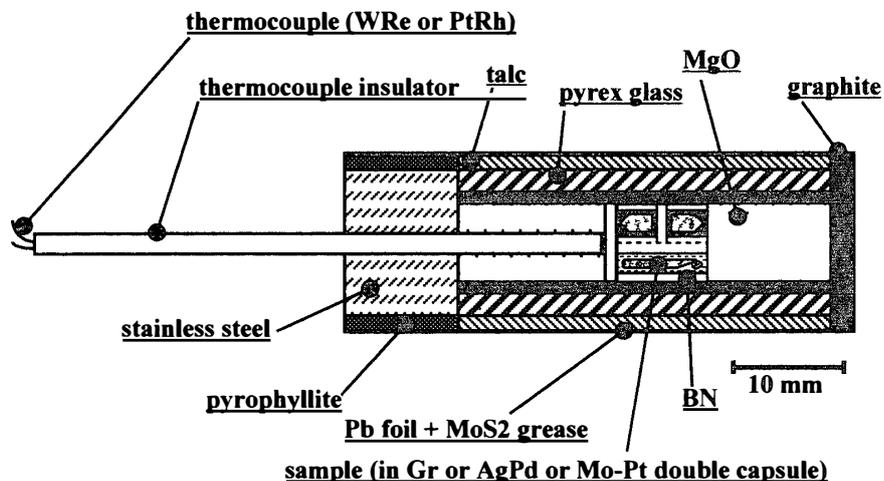


Fig 3 The cell assembly used in the present experiment

sample was put into a graphite, AgPd or Mo-Pt capsule. The sectional view of a cell is shown in Fig. 3.

The experiments were conducted under the anhydrous condition at 11–23 kbar and 900–1300°C. The run time depended on the run temperature: 1300°C, 7–48 hours; 1200°C, 96–261 hours; 1100°C, 330–506 hours; 1050°C, 507 hours; 1000°C, 455–767 hours; 900°C, 1005 hours. After maintaining the pressure and temperature for the desired duration, the electric power supply was turned off, and a sample was quenched.

All products were mounted in the epoxy resin and polished for the X-ray microprobe examination. Chemical analyses of all run products were carried out using an electron microprobe analyzer JEOL model JXA-8800 Superprobe with the ZAF correction method at Ehime University. The instrumental conditions were as follows: Accelerating voltage was 15 kV. Electron beam current was 5×10^{-9} A. Beam diameter was 1–2 μm , estimated from the size of contamination spots formed by chemical analysis.

3. Run products

The present high-pressure and high-temperature experiments revealed that mineral assemblages changed as pressure decreased at 1200°C as follows: garnet, garnet + orthopyroxene + quartz \pm sapphirine, garnet + orthopyroxene + sapphirine + quartz, orthopyroxene + sapphirine + quartz. At 11 kbar, the assemblage of orthopyroxene + sapphirine + quartz changed to orthopyroxene + sapphirine + quartz + sillimanite at 1000°C. The run

Table 3 Run details

Run No	<i>P</i> (kbar)	<i>T</i> (°C)	Time (hours)	Capsule	Starting Material	Run Product
000526A	23	1200	96	Gr	Gls	Grt
000821D	19	1200	167	Gr	Gls + Sil	Grt
010713D	20	1100	330	AgPd	Gls	Grt
991122C	19	1300	48	Gr	Gls + CM	Grt + Opx + Qtz \pm Spr?
000907A	17	1200	261	Gr	Gls + Sil	Grt + Opx + Qtz \pm Spr? (+Sil)
001030C	16	1000	767	AgPd	Gls + Sil	Grt + Opx + Qtz \pm Spr? (+Sil)
010803C	16	1300	40	Mo-Pt*	Gls	Grt + Opx + Spr + Qtz
000107D	14	1200	96	Gr	Gls + CM	Grt + Opx + Spr + Qtz
011203C	12	1100	506	AgPd	Gls	Grt + Opx + Spr + Qtz
010628C	13	1100	362	AgPd	Gls	Grt + Opx + Spr + Qtz
011001C	12	1050	507	AgPd	Gls	Grt + Opx + Spr + Qtz
991208B	13	1000	455	Gr	Gls + CM	N I (Grt appear)
000109D	12	900	1005	AgPd	Gls	N I (Grt appear)
010928C	13	1300	7	Mo-Pt*	Gls	Opx + Spr + Qtz \pm Glc
000515A	12	1200	96	Gr	Gls	Opx + Spr + Qtz
000828A	11	1200	237	Gr	Gls + Sil	Opx + Spr + Qtz
000918B	11	1100	341	AgPd	Gls + Sil	Opx + Spr + Qtz (+Sil)
001201D	11	1000	573	AgPd	Gls	Opx + Spr + Qtz + Sil

N I We cannot identify the phases because the obtained crystals were too small to analyze with the electron microprobe analyzer. But garnet was clearly recognized from its shape and high back scattered image.

* An inner sample container of molybdenum foil was put into the outer capsule of the Pt tube.

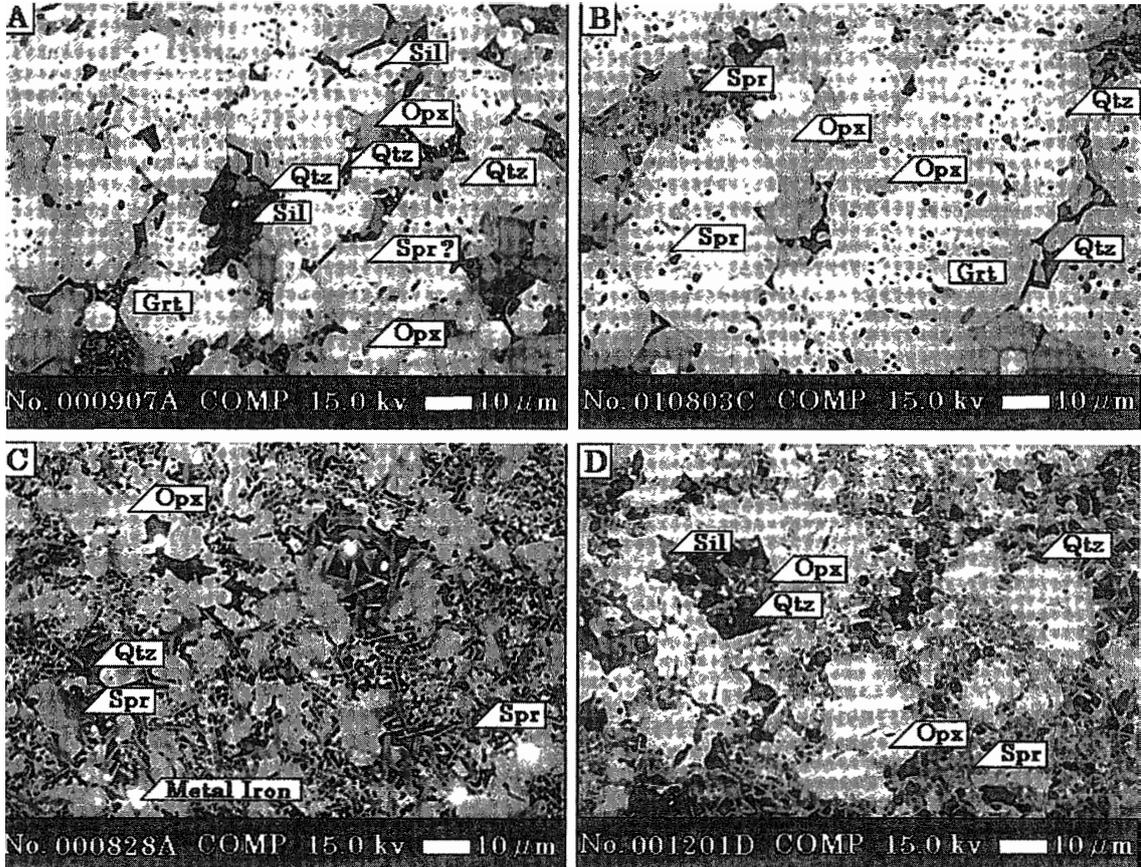


Fig 4 Photomicrograph of BSEI of run products

A This run (no 000907A) was carried out in a graphite capsule at 17 kbar and 1200°C for 261 hours using a mixture of 95 wt% glass plus 5 wt% sillimanite as starting materials. Sillimanite persisted. Reverse zoning as to Fe and Mg is observed in garnet. Bar, 10 μm

B The run product of no 010803C was derived from glass in the Mo-Pt double capsule at 16 kbar and 1300°C for 40 hours. Reverse zoning is observed in garnet and orthopyroxene.

C Run no 000828A. Orthopyroxene, sapphirine and quartz crystallized in a graphite capsule at 11 kbar and 1200°C for 237 hours from the mixture of 95 wt% glass plus 5 wt% sillimanite. Iron droplets are observed. Seed sillimanites disappear.

D Run no 001201D. Orthopyroxene, sapphirine, quartz and sillimanite crystallized in a AgPd capsule at 11 kbar and 1000°C for 573 hours from glass. In this run, sillimanite appears.

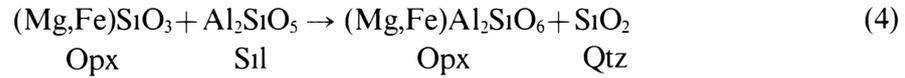
details are given in Table 3. Figure 4 shows photomicrographs of the run products. Descriptions of run products are given below.

3.1 $Grt + Opx + Qtz \pm Spr$

Figure 4A shows BSEI of the mineral assemblage synthesized from 95 wt% glass plus 5 wt% sillimanite at 17 kbar and 1200°C for 261 hours (run no 000907A). Garnet has inclusions of orthopyroxene, quartz and sillimanite. Sizes of these inclusions are 1–5 μm. The original size of the seed sillimanite was about 20 μm. This indicates that sillimanite has been consumed to produce garnet and quartz as the reaction



Sillimanite is also surrounded by quartz and orthopyroxene in the space between garnets. This reaction texture indicates the following reaction



Although sapphirine was not found in this run product, it is considered that sapphirine exists from the bulk composition. It is good to check by XRD. We considered that sillimanite is unstable and the stable phase assemblage was garnet+orthopyroxene+quartz±sapphirine at 17 kbar and 1200°C.

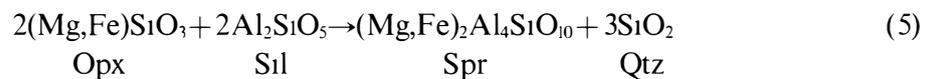
As is seen in Fig 4A, reverse zoning was observed to form the Fe-rich core and Mg-rich rim. In this run, we used the graphite capsule. The reduction of ferrous to metal iron in the charge would form reverse zoning. Nucleation kinetics was discussed by Kawasaki and Motoyoshi (2000): garnet precipitates first from glass, then the bulk composition excluding garnet composition shifts toward the Mg-rich side, and so the later garnet should become magnesian. Harley (1984) also reported reverse zoning in run products.

3.2 *Grt + Opx + Spr + Qtz*

Figure 4B indicates the run product of no. 010803C synthesized from glass in a Mo-Pt double capsule at 16 kbar and 1300°C for 40 hours. We confirm the stable assemblage is garnet+orthopyroxene+sapphirine+quartz. Inclusions in garnet are orthopyroxene, quartz and needle sapphirine. Orthopyroxene, sapphirine and quartz are found at the grain boundary. Reverse zoning is also found in both garnet and orthopyroxene.

3.3 *Opx + Spr + Qtz*

In run no. 000828A, a mixture of 95 wt% glass plus 5 wt% sillimanite was used as the starting material. Assemblage of orthopyroxene+sapphirine+quartz was generated at 11 kbar and 1200°C for 237 hours (Fig. 4C). Sillimanite disappeared completely as explained by the following reaction



Needle sapphirine and anhedral quartz crystallized around orthopyroxene. Metal irons are found as spots, due to reduction by using a graphite capsule.

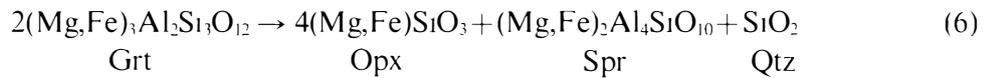
3.4 *Opx + Spr + Qtz + Sil*

In the run product of no. 001201D, orthopyroxene, sapphirine, quartz and sillimanite crystallized from glass at 11 kbar and 1000°C for 573 hours (Fig. 4D). Although sillimanite was not added to the starting material, sillimanite crystallized in this run. Therefore, the stable mineral assemblage at this pressure-temperature condition is orthopyroxene+sapphirine+quartz+sillimanite. Although the exact boundary can not be determined, we confirm the high-temperature assemblage of orthopyroxene+sapphirine+quartz converted to a low-temperature one of orthopyroxene+sapphirine+quartz+sillimanite at a certain temperature between 1000°C and 1100°C. Slightly reverse zoning was found in large orthopyroxene.

4. Experimental results

4.1 *P-T* diagram of the Mg-rich garnet system

Run details are given in Table 3. The experimental *P-T* diagram is shown in Fig. 5. We find that garnet does not convert directly to its low-pressure assemblage. The intermediate stability field of garnet + orthopyroxene + sapphirine + quartz is confirmed between the fields of garnet and orthopyroxene + sapphirine + quartz. The amounts of garnet decrease with decreasing pressure in the field of garnet + orthopyroxene + sapphirine + quartz. Garnet was consumed completely at a certain pressure between 12 kbar and 14 kbar at 1200°C by the following reaction



We find the assemblage of orthopyroxene + sapphirine + quartz + sillimanite at 11 kbar and 1000°C, converting from orthopyroxene + sapphirine + quartz assemblage by the following reaction



The exact boundary between the field of orthopyroxene + sapphirine + quartz and ortho-

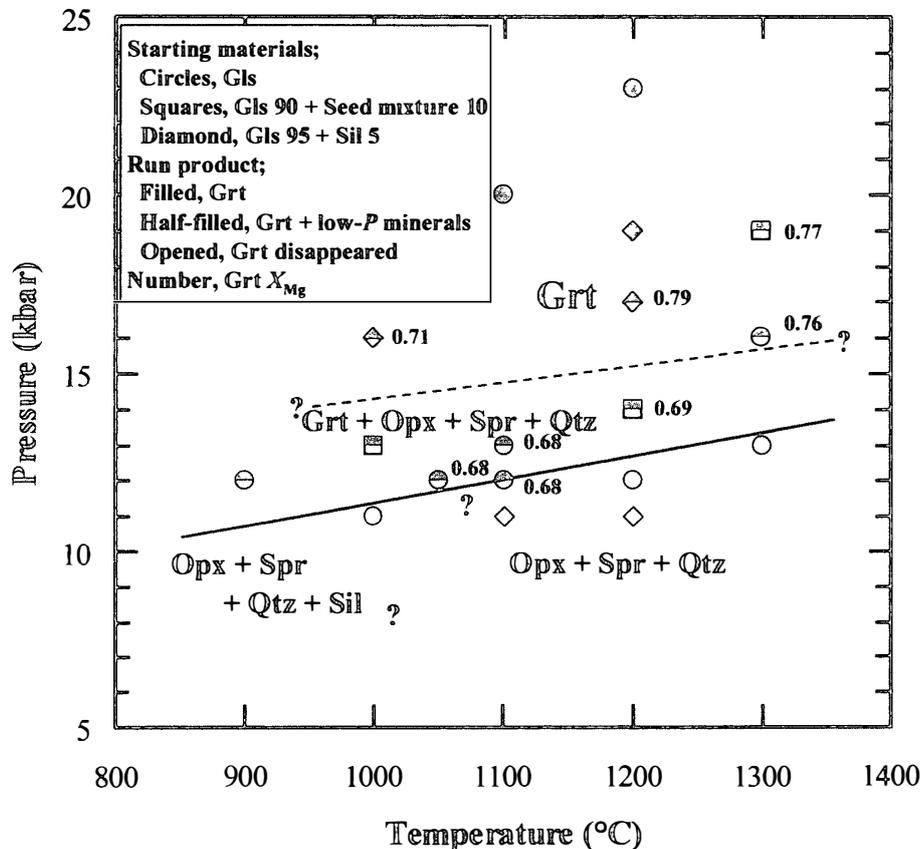


Fig. 5. Experimental *P-T* diagram for the system of Mg-rich garnet composition ($\text{Prp}_{75}\text{Alm}_{25}$).

pyroxene+sapphirine+quartz+sillimanite is unclear, but is at a temperature between 1000°C and 1100°C at 11 kbar

Boyd and England (1959) reported the breakdown reaction of the pyrope garnet by the univariant reaction (1). Here, the pyrope garnet directly decomposed to the low-pressure phase assemblage of orthopyroxene+sapphirine+sillimanite. The present study indicates the possibility of the direct breakdown of pyrope to orthopyroxene, sapphirine and quartz as eq (6). Taylor (1973) reported the coexistence of aluminous enstatite, sapphirine and quartz at 15 kbar and 1400°C in the MgO-Al₂O₃-SiO₂ system indicating the univariant reaction (6).

Almandine garnet decomposes directly into a low-pressure phase assemblage of olivine, spinel and quartz or olivine, cordierite and spinel (Schairer and Yagi, 1952, Hsu, 1968, Keesman *et al*, 1971). The present study shows that the Mg-rich garnet (Prp₇₅Alm₂₅) converts to the assemblages of garnet+orthopyroxene+sapphirine+quartz at high temperatures, the assemblage of which changes to orthopyroxene+sapphirine+quartz+sillimanite at lower temperatures. This suggests that the appearance of sillimanite would be limited to below 1000°C with orthopyroxene, sapphirine and quartz.

4.2. Fe-Mg partitioning between garnet and orthopyroxene

As has been mentioned, reverse zoning was found in both garnet and orthopyroxene. Mg-rich garnet and orthopyroxene indicate the last stage products and represent equilibrium compositions of those phases. Figure 6 shows an example (run no 991122C) of chemical analyses of run products. The mean of 19 Mg-rich garnet analyses of rim and mean of 26 orthopyroxene analyses are given in Table 4.

The Fe-Mg distribution coefficient between garnet and orthopyroxene

$$K_D = (X_{Mg}/X_{Fe})^{Opx} (X_{Fe}/X_{Mg})^{Grt}, \quad (8)$$

is also given in Table 4. Kawasaki and Motoyoshi's (2000) distribution coefficient data were combined to the present results. The logarithms of Fe-Mg distribution coefficients are plotted versus $1/T$ in Fig 7. As is seen in this figure, the Fe-Mg partitioning depends on the experimental temperature. The pressure dependence is negligible because the pressure effect is small in the present pressure range of 11–23 kbar; the difference in K_D is 0.15 at 1200°C. The relation between distribution coefficient and temperature was approx-

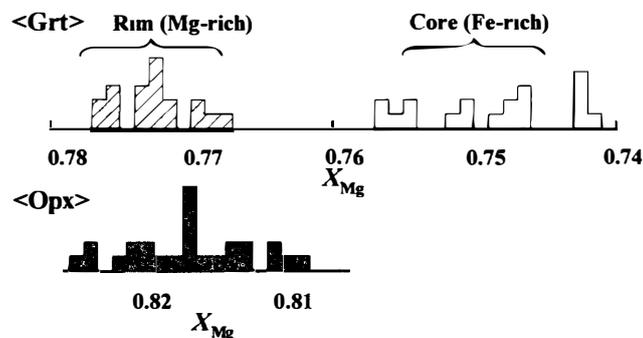


Fig 6 Histograms of X_{Mg} of garnet and orthopyroxene synthesized at 19 kbar and 1300°C for 48 hours (run no 991122C). In this run, reverse zoning is observed in garnet, but not in orthopyroxene.

Table 4 X_{Mg} and the distribution coefficients of coexisting garnet and orthopyroxene

Run No	P (kbar)	T (°C)	X_{Mg}		K_D^*
			Mg-rich Grt	Mg-rich Opx	
001030C	16	1000	0.714	0.836	2.04
011001C	12	1050	0.683	0.787	1.71
011203C	12	1100	0.682	0.783	1.69
010628C	13	1100	0.679	0.780	1.67
000107D	14	1200	0.693	0.777	1.55
000907A	17	1200	0.785	0.848	1.53
010803C	16	1300	0.762	0.816	1.39
991122C	19	1300	0.773	0.818	1.32

* The distribution coefficient is defined as

$$K_D = (X_{Mg}/X_{Fe})^{Opx} (X_{Fe}/X_{Mg})^{Grt}$$

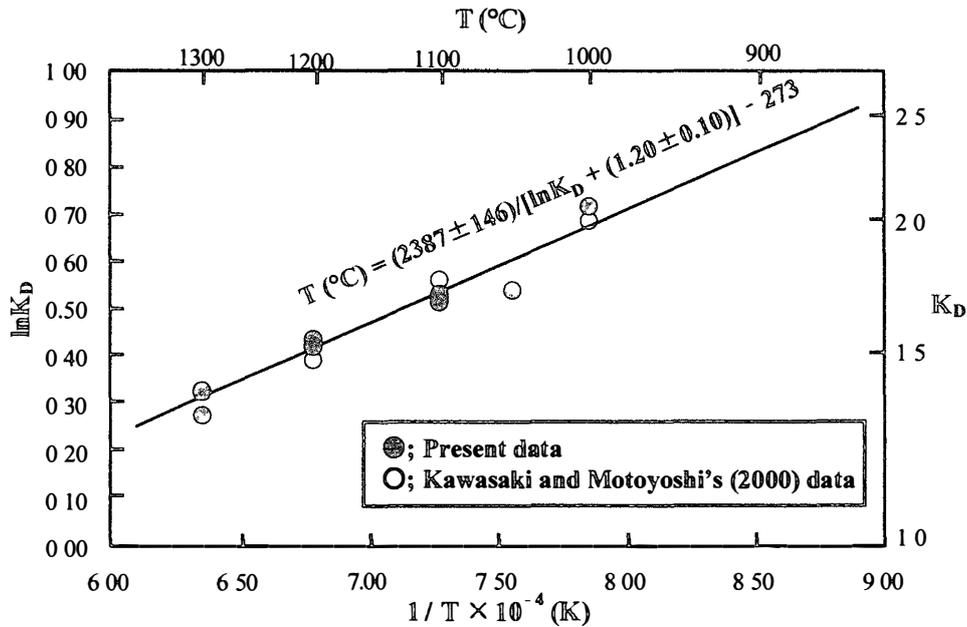


Fig 7 Relation between the Fe-Mg distribution coefficient (K_D) and temperature (T). The present and Kawasaki and Motoyoshi's (2000) distribution coefficient data were combined. Present run pressures are 12–19 kbar. Kawasaki and Motoyoshi's run pressures are 9–20 kbar. The Fe-Mg distribution coefficient

$$K_D = (X_{Mg}/X_{Fe})^{Opx} (X_{Fe}/X_{Mg})^{Grt}$$

is approximated by

$$T(^{\circ}C) = (2387 \pm 146) / [\ln K_D + (1.20 \pm 0.10)] - 273$$

imated with the following equation

$$T(^{\circ}C) = (2387 \pm 146) / [\ln K_D + (1.20 \pm 0.10)] - 273 \quad (9)$$

This equation was approximately a straight line. So non-ideality of the solid solution is negligible as stated by Kawasaki and Motoyoshi (2000).

A comparison of the present experiment and previous geothermometers (Harley, 1984,

Ganguly *et al.*, 1996) is given in Fig 8. The difference of temperature between Harley's geothermometer and present experimental temperature was not so large at 1050–1200°C. However, the difference will become large at 1000 or lower temperatures, and 1300 or higher temperatures. Although temperatures by Ganguly *et al.*'s thermometer were higher than present experimental temperatures, they will match experimental temperatures at low temperature. Metamorphic temperatures of granulites from the Napier Complex and Lutzow-Holm Complex, East Antarctica, are estimated using garnet-orthopyroxene geothermometers. A comparison of present and previous estimations is given in Table 5.

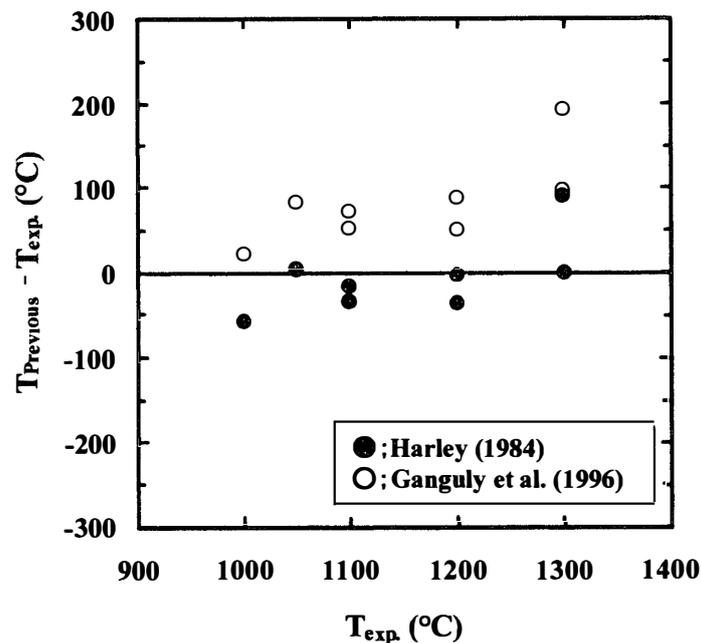


Fig 8 The comparison of the present experiment and previous geothermometers

Table 5 Comparison of estimated temperatures of ultra-high temperature granulites

Area (Sample No.)	K_D	T_H^* (°C)	T_G^* (°C)	T_{KM}^* (°C)	T_{new}^{**} (°C)	Source of data of K_D
<Tonagh Island>						
A98012902D	2.46	797	856	906	864	Hokada <i>et al.</i> (1999)
A98021106A	2.71	750	799	859	812	Hokada <i>et al.</i> (1999)
<Mt Riser-Larsen>						
3423	2.38	810	875	921	880	Harley (1998)
<McIntyre Island>						
4518	2.26	850	907	948	909	Harley (1998)
49607	2.20	865	927	963	926	Harley (1998)
<Rundvågshetta>						
92011102I	2.35	828	887	928	891	Kawasaki <i>et al.</i> (1993)
93010601X	1.93	962	1023	1038	1010	Motoyoshi and Ishikawa (1997)
<Forefinger Point>						
2220	1.95	953	1015	1031	1003	Harley (1998)
4652	2.01	933	992	1014	983	Harley <i>et al.</i> (1990)

* T_H , Harley (1984), T_G , Ganguly *et al.* (1996), T_{KM} , Kawasaki and Motoyoshi (2000)

** T_{New} , New thermometer (this study) T (°C) = $(2387 \pm 146) / [\ln K_D + (1.20 \pm 0.10)] - 273$

5. Discussion and conclusions

The present experiment shows that the system of Mg-rich garnet composition changes to the assemblage of garnet+orthopyroxene+sapphirine+quartz, and finally garnet decomposes to form orthopyroxene+sapphirine+quartz at high temperatures as the pressure decreases. At low pressure and low temperature, the assemblage is orthopyroxene+sapphirine+quartz+sillimanite. Although Boyd and England (1959) reported orthopyroxene+sapphirine+sillimanite, Taylor (1973) reported orthopyroxene+sapphirine+quartz as the low-pressure phase in the MgO-Al₂O₃-SiO₂ system. The present result is in agreement with Taylor's report.

The Fe-Mg partitioning between garnet and orthopyroxene is a good thermometer as reported by Harley (1984), Ganguly *et al* (1996) and Kawasaki and Motoyoshi (2000). Using the new thermometer, we estimated the metamorphic temperatures of granulites from the Napier Complex and Lutzow-Holm Complex, East Antarctica. Temperature estimation of Mt Riser-Larsen granulite shows 880°C, and of Tonagh Island granulites 864°C and 812°C. Harley and Motoyoshi (2000) reported the first definitive recording of metamorphic temperature in excess of 1120°C in Mt Riser-Larsen. Moreover, Hokada (2001) estimated temperatures in the Napier Complex, Mt Riser-Larsen, 1106°C and Tonagh Island, 1096°C, using Fuhrman and Lindsley's (1988) feldspar geothermometer. The present results are 230–300°C lower than those estimated by Harley and Motoyoshi (2000), and Hokada (2001). As Frost and Chako (1989), Fitzsimons and Harley (1994), and Pattison and Bégin (1994) have pointed out, the estimation by the orthopyroxene-garnet geothermometer would suggest the closure temperatures of Fe-Mg exchange reaction during retrograde metamorphism. As a result, the present garnet-orthopyroxene Fe-Mg geothermometer indicated the closure temperatures, granulites from Napier Complex record 812–926°C, and the Rundvågshetta granulites 891–1010°C. Our estimations of temperatures are higher than those of Harley (1984), lower than those of Kawasaki and Motoyoshi (2000), and consistent with those of Ganguly *et al* (1996) based on Fe-Mg exchange.

Acknowledgments

We received invaluable discussions and suggestions from Prof H Ishizuka, Drs T Hokada, A Kamei, T Miyamoto, Y Osanaï, T Tsunogae and Y Yoshimura. Constructive criticisms of Prof B J Hensen and an anonymous referee are much appreciated. This study was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of the Japanese Government to Toshisuke Kawasaki (no 14654093).

References

- Boyd F R and England J L (1959) *Pyrope* Carnegie Inst Wash Year Book **58** 83–87
Fitzsimons, I C W and Harley, S L (1994) The influence of retrograde cation exchange on granulite *P-T* estimates and a convergence technique for the recovery of peak metamorphic conditions. *J Petrol* **35** 543–576

- Frost, B R and Chako, T (1989) The granulite uncertainly principle Limitations on thermobarometry in granulites *J Geol*, **97**, 435-450
- Fuhrman, M L and Lindsley, D H (1988) Ternary-feldspar modeling and thermometry *Am Mineral*, **73**, 201-215
- Ganguly, J, Cheng, W and Tirone, M (1996) Thermodynamics of aluminosilicate garnet solid solution new experimental data, an optimized model, and thermodynamic applications *Contrib Mineral Petrol*, **126**, 137-151
- Harley, S L (1984) An experimental study of the partitioning of the Fe and Mg between garnet and orthopyroxene *Contrib Mineral Petrol*, **86**, 359-373
- Harley, S L, Hensen, B J and Sheraton, J W (1990) Two-stage decompression in orthopyroxene-sillimanite granulites from Forefinger Point, Enderby Land, Antarctica Implications for the evolution of the Archaean Napier Complex *J Metamorph Geol*, **8**, 591-613
- Harley, S L (1998) An appraisal of peak temperatures and thermal histories in ultrahigh-temperature (UHT) crustal metamorphism The significance of aluminous orthopyroxene *Mem Natl Inst Polar Res, Spec Issue*, **53**, 49-73
- Harley, S L and Motoyoshi, Y (2000) Al zoning in orthopyroxene in a sapphirine quartzite Evidence for $> 1120^{\circ}\text{C}$ UHT metamorphism in the Napier Complex, Antarctica, and implications for the entropy of sapphirine *Contrib Mineral Petrol*, **138**, 293-307
- Hokada, T, Osanai, Y, Toyoshima, T, Owada, M, Tsunogae, T and Crowe, W A (1999) Petrology and metamorphism of sapphirine-bearing aluminous gneisses from Tonagh Island in the Napier Complex, East Antarctica *Polar Geosci*, **12**, 49-70
- Hokada, T (2001) Feldspar thermometry in ultrahigh-temperature metamorphic rock Evidence of crustal metamorphism attaining $\sim 1100^{\circ}\text{C}$ in the Archaean Napier Complex, East Antarctica *Am Mineral*, **86**, 932-938
- Hsu, L C (1968) Selected phase relationships in the system Al-Mn-Fe-Si-O-H A model for garnet equilibria, *J Petrol*, **9**, 40-83
- Hsu, L C and Burnham, C W (1969) Phase relationships in the system $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - H_2O at 20 kilobars *Geol Soc Am Bull*, **80**, 2393-2408
- Kawasaki, T and Matsui, Y (1983) Thermodynamic analyses of equilibria involving olivine, orthopyroxene and garnet *Geochim Cosmochim Acta*, **47**, 1661-1679
- Kawasaki, T and Motoyoshi, Y (2000) High-pressure and high-temperature phase relations of an orthopyroxene granulite from McIntyre Island, Enderby Land, East Antarctica *Polar Geosci*, **13**, 114-134
- Kawasaki, T, Ishikawa, M and Motoyoshi, Y (1993) A preliminary report on cordierite-bearing assemblages from Rundvågshetta, Lutzow-Holm Bay, East Antarctica Evidence for a decompressional *P-T* path? *Proc NIPR Symp Antarct Geosci*, **6**, 47-56
- Keesman, I, Matthes, S, Schreyer, W and Seifert, F (1971) Stability of almandine in the system FeO - (Fe_2O_3) - Al_2O_3 - SiO_2 - (H_2O) at elevated pressures *Contrib Mineral Petrol*, **31**, 132-144
- Kretz, R (1983) Symbols for rock-forming minerals *Am Mineral*, **68**, 277-279
- Motoyoshi, Y and Ishikawa, M (1997) Metamorphic and structural evolution of granulites from Rundvågshetta, Lutzow-Holm Bay, East Antarctica *The Antarctic Region Geological Evolution and Processes*, ed by C A Ricci Siena, Terra Antarct Publ, 65-72
- Pattison, D R M and Begin, N J (1994) Zoning patterns in orthopyroxene and garnet in granulites Implications for geothermometry *J metamorph Geol*, **12**, 387-410
- Schairer, J F and Yagi, K (1952) The system FeO - Al_2O_3 - SiO_2 *Am J Sci*, Bowen Vol, 471-512
- Taylor, H C J (1973) Melting relations in the system MgO - Al_2O_3 - SiO_2 at 15 kb *Geol Soc Am Bul*, **84**, 1335-1348

(Received February 18, 2002, Revised manuscript accepted June 12, 2002)