

High-pressure and high-temperature phase relations of an orthopyroxene granulite from McIntyre Island, Enderby Land, East Antarctica

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Abstract: High pressure experiments have been carried out from 9 to 20 kbar and 900 to 1300°C by the aid of a piston cylinder apparatus to simulate the equilibrium conditions of an orthopyroxene granulite from McIntyre Island, Enderby Land, East Antarctica. The following two assemblages have been obtained with increasing pressure at a constant temperature: orthopyroxene + quartz and garnet + orthopyroxene + quartz. The boundary curve between these two assemblages has been approximated as the following linear equation

$$P(\text{kbar}) = 0.0128T(^{\circ}\text{C}) - 0.27$$

Garnet is unstable and disappears at the low pressure side of this curve.

The Fe-Mg distribution coefficients between orthopyroxene and garnet, $K_D = (X_{\text{Fe}}^{\text{Grt}} X_{\text{Mg}}^{\text{Opx}}) / (X_{\text{Mg}}^{\text{Grt}} X_{\text{Fe}}^{\text{Opx}})$, were experimentally determined at these P - T conditions, showing that the logarithm of K_D can be approximately expressed by a linear function of the reciprocal of the absolute temperature

$$\ln K_D = -1.49 + 2815/T(\text{K})$$

Combining the petrographic data and the experimental data, we can infer this granulite experienced retrograde metamorphism at 11.2 kbar and 895°C and subsequently passed at a certain pressure between 10.9 kbar and 11.4 kbar at 873°C.

key words orthopyroxene-garnet equilibria, P - T estimation, geothermobarometer, ultra-high-temperature granulite, McIntyre Island, Napier Complex

1. Introduction

The Napier Complex (Fig. 1) is located in Enderby Land, East Antarctica, and covers a huge area (approximately 300 km EW \times 200 km NS in size). It is one of the oldest ultra-high-temperature metamorphic complexes in the world (Dallwitz, 1968, Sheraton *et al.*, 1980, 1987, Ellis *et al.*, 1980, Grew, 1980, Harley, 1985, 1987, Sandiford, 1985, Sandiford and Powell, 1986). McIntyre Island is situated close to the Fyfe Hills in Casey Bay (Fig. 2) and is underlain by granulites belonging to this complex. The basement rocks of McIntyre Island consist of a well-layered sequence of pelitic and basic rocks with subordi-

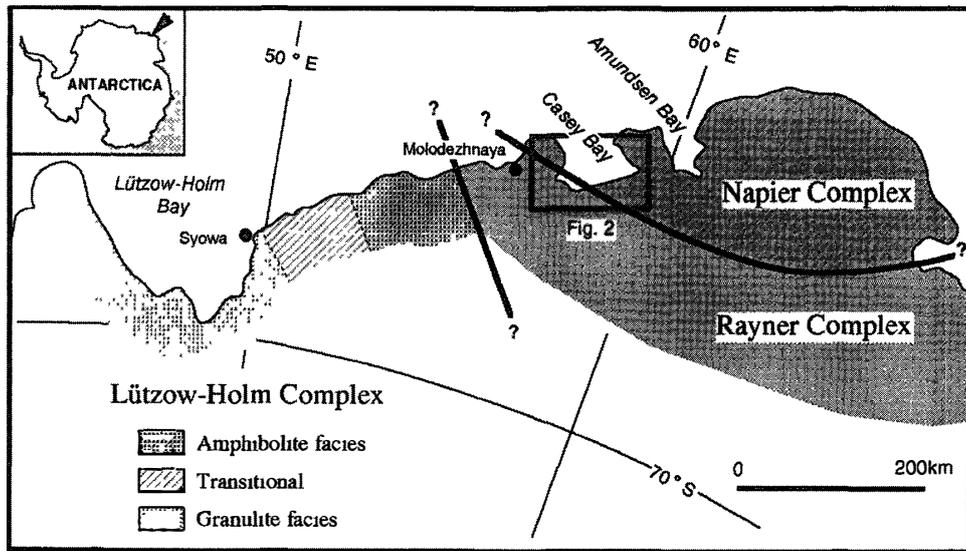


Fig 1 Geological outline of East Queen Maud Land and Western Enderby Land, East Antarctica

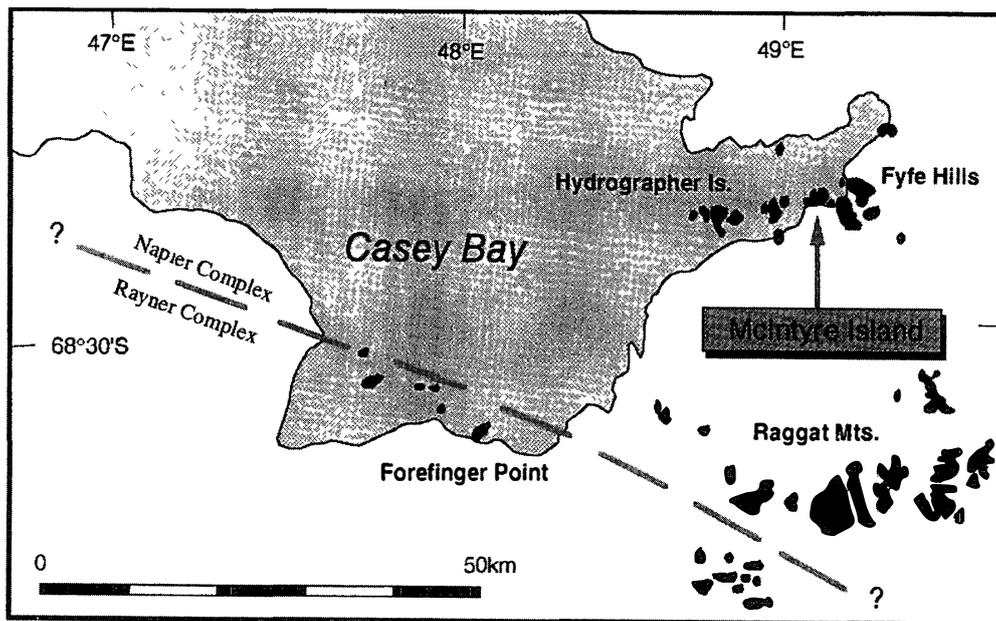


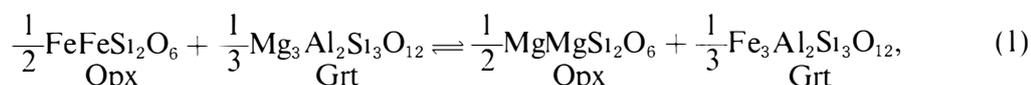
Fig 2 Locality of McIntyre Island. The boundary between the Napier and Rayner Complexes is after Sheraton et al (1987)

nate ultramafic rocks and discordant pegmatites. Grew and Manton (1979) reported 2500 Ma U-Pb ages for charnockitic pegmatites cutting the Napier complex. Compston and Williams (1982) reported 3800 Ma SHRIMP age for zircon in orthogneiss from the Fyfe Hills.

McIntyre granulites are characterized by high-temperature mineral assemblages¹ including orthopyroxene+sillimanite, sapphirine+quartz, and by exsolution lamellae of

¹Abbreviations of minerals are after Kretz (1983)

garnet in orthopyroxene porphyroblasts (Motoyoshi, 1995) Harley (1998) estimated the equilibrium conditions of the McIntyre granulites from application of the Fe-Mg partitioning between orthopyroxene and garnet (Harley and Green 1982, Harley, 1984, Ganguly *et al* , 1996, Aranovich and Berman, 1997)



and concluded that these granulites equilibrated at temperatures 728°C to 1045°C assuming that the equilibration pressure was 11 kbar

In this paper we present new experimental data on the phase relations of the McIntyre granulite with exsolution lamellae of garnet in orthopyroxene, and the Fe-Mg partitioning between orthopyroxene and garnet at 9–20 kbar and 900–1300°C. New experimental and petrographic data provide important constraints on the nature and the *P-T* history of the Archaean granulite

2. McIntyre granulite used in the present experiments

2.1. Petrographic descriptions

The McIntyre granulite (Sample no SP93022004A) used in the present experiments was collected by Yoichi Motoyoshi at the end of the wintering operation of the 33rd Japanese Antarctic Research Expedition (JARE-33). This granulite consists of orthopyroxene (more than 80 modal %), garnet, quartz, a small quantity of sillimanite (less than 1 modal %), very rare rutile, phlogopite and zircon. Garnets are found as small euhedral blebs, exsolution lamellae (about 5–30 μm in the width and 10 μm in average) in orthopyroxene and thin films (about 100 μm in the width) wrapping orthopyroxene, euhedral sillimanite, rutile and phlogopite (Fig 3). Extinction positions of orthopyroxene porphyroblasts framed by thin films of garnet differ. This indicates that thin films of garnet developed on the original grain boundaries of orthopyroxenes. Some lamellae are continuous with the garnet rims around orthopyroxene. Similar textures of garnet, occurring as exsolution lamellae and as thin continuous rims, have been reported from Hydrographer Island, Field Island, Tonagh Island and Mt. Hollingsworth (Harley, 1985). Small euhedral orthopyroxenes, with grain sizes of about 20–50 μm, are occasionally included in rather thick (200–300 μm) films of garnet. Sillimanites are always enclosed by thin films of garnet and are not in direct contact with orthopyroxene and quartz. Quartz is enclosed in orthopyroxene, and is elongated in the same direction as the exsolution lamella of garnet. It also occurs as roundish bleb in orthopyroxene. Quartz is never in contact with garnet. Rutiles occur as needle-shaped and granular crystals. Granular rutiles are moated by garnet or are in contact with garnet blebs in orthopyroxene. Needle-shaped rutiles are not surrounded by garnet, and occur in orthopyroxene with the same directions as the garnet lamellae. Rare phlogopite inclusions are also encircled by thin films of garnet.

2.2. Bulk chemistry

The bulk composition of the granulite is given in Table 1. It was obtained by an

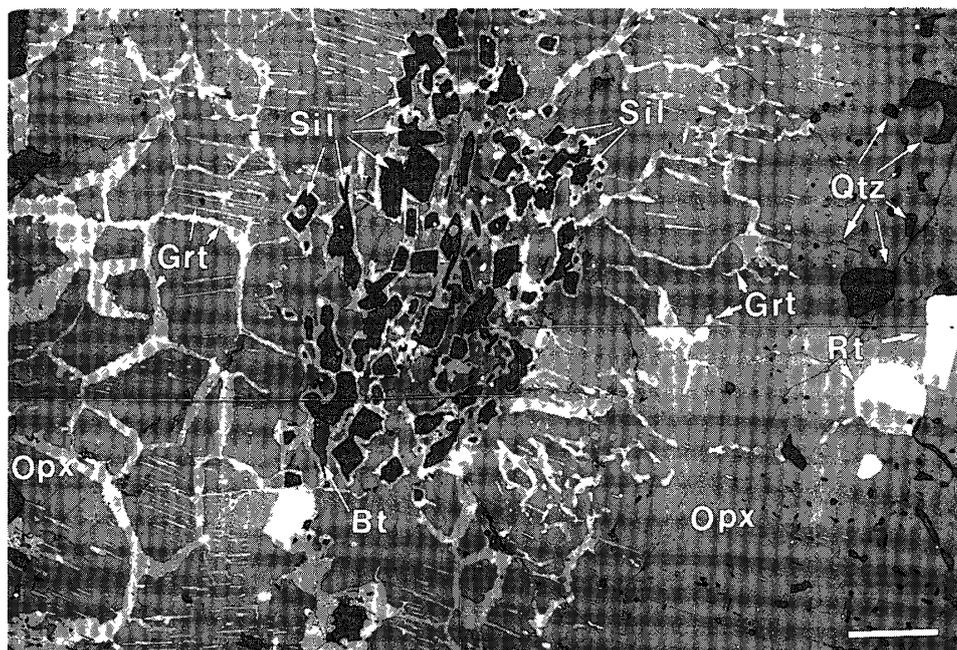


Fig 3 Back scattered electron image (BSEI) of McIntyre granulite (SP93022004A) Garnet (Grt) crystallized as exsolution lamellae within orthopyroxene (Opx) Thin films of garnet surrounded the orthopyroxene porphyroblasts, euhedral sillimanite (Sil), phlogopite (Phl) and rutile (Rt) Quartz (Qtz) is not surrounded by garnet, but is included in orthopyroxene as roundish or needle grains Bar, 500 μm

Table 1 Bulk, CIPW norm and primary compositions of McIntyre orthopyroxene granulite (SP93022004A).

| | Bulk* | CIPW Norm | | Primary** | |
|--------------------------------|-----------|-----------|-------|--------------------------------|-------|
| SiO ₂ | 54.08(4) | Q | 9.08 | Qtz | 9.57 |
| TiO ₂ | 0.19(1) | C | 8.12 | Opx | 88.50 |
| Al ₂ O ₃ | 8.38(2) | F | 1.00 | SiO ₂ | 44.51 |
| Cr ₂ O ₃ | 0.04(1) | or | 0.18 | Al ₂ O ₃ | 8.38 |
| FeO*** | 13.10(2) | ab | 0.42 | FeO | 13.10 |
| MnO | 0.04(1) | an | 0.40 | MgO | 22.51 |
| MgO | 22.51(2) | Hy | 79.92 | | |
| NiO | 0.04(1) | en | 56.07 | | |
| CaO | 0.08(1) | fs | 23.85 | | |
| Na ₂ O | 0.05(5) | il | 0.36 | | |
| K ₂ O | 0.03(1) | cm | 0.06 | | |
| ZnO | 0.05(1) | | | | |
| Total | 98.53 | Sum | 98.54 | Sum | 98.07 |
| X _{Mg} | 0.7539(2) | | | | |

*Mean values of 29 glasses by defocused electron microprobe analyses. Standard errors are in parentheses and refer to the last decimal point.

**Primary assemblage is assumed as orthopyroxene + quartz, and the FeO-MgO-Al₂O₃-SiO₂ ratios are those of the bulk.

***Total Fe as FeO.

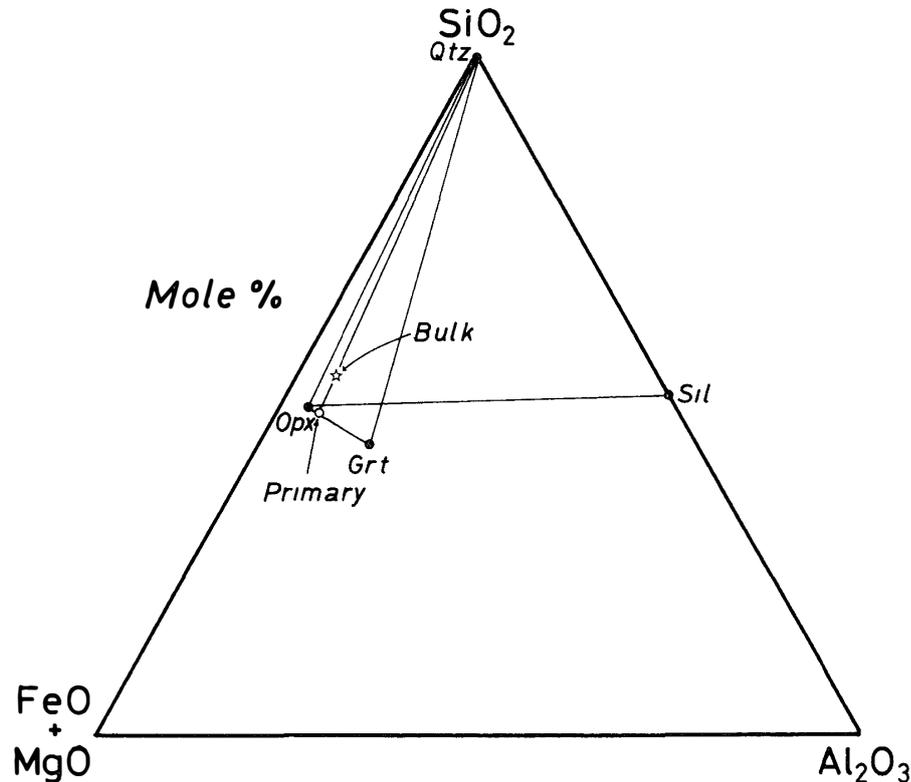


Fig 4 Bulk composition of the McIntyre granulite, the mean compositions of orthopyroxene and garnet, and primary composition of orthopyroxene on the $(\text{FeO} + \text{MgO})\text{-Al}_2\text{O}_3\text{-SiO}_2$ plane. Bulk (\star) is plotted very near the Opx-Qtz join and near Opx. Primary orthopyroxene (\circ) is plotted as an intersection of $(\text{Fe}, \text{Mg})\text{SiO}_3$ pyroxene- Al_2O_3 join and the extension line of the bulk-Qtz join. The $\text{Fe}/(\text{Fe} + \text{Mg})$ of primary orthopyroxene is assumed to be preserved as same as the bulk.

electron microprobe analyzer averaging 29 spot analyses of glass using a defocused beam ($5 \mu\text{m}$ in diameter). Chemically homogeneous glass was prepared by fusing the powdered rock at 10 kbar and more than 1600°C for 5 min in a graphite capsule (run no 971128). We found neither metal iron droplets nor refractory minerals such as orthopyroxene and quartz in the glass. The bulk chemistry of this granulite approximates the $\text{FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system and plots near the aluminous orthopyroxene-quartz join (Fig 4). The projected composition of the bulk onto the $\text{FeSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ plane from SiO_2 is called the *primary* composition of orthopyroxene, which is also given in Table 1, in the sense that it represents the approximate composition of orthopyroxene before garnet crystallized as exsolution lamellae, films and blebs. This approximation is reasonable because sillimanite and phlogopite are very rare, and can be neglected for the estimation of the *primary* composition of orthopyroxene.

2.3 Chemical compositions of orthopyroxene and garnet

Orthopyroxene and garnet are relatively homogeneous. The CaO contents of these phases are extremely low, 0.01 and 0.30 wt% for orthopyroxene and garnet, respectively (Table 2). Mean chemical compositions of orthopyroxene and garnet are given in Table 2. Compositions of garnets in the different textures are given in the histograms

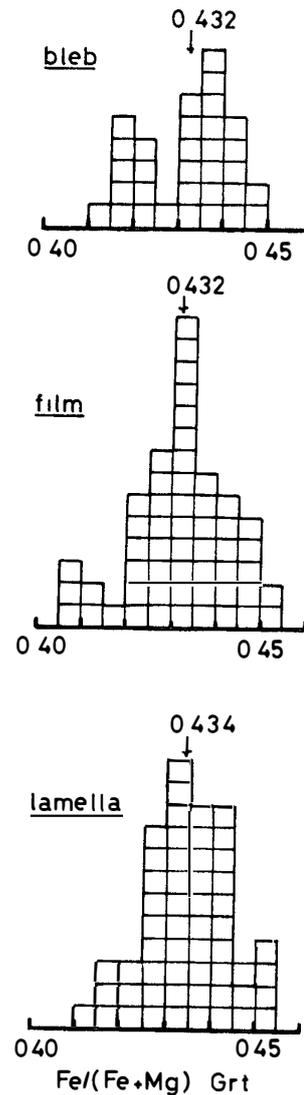


Fig 5 Histograms of the $Fe/(Fe+Mg)$ value of garnet. Mean Fe-values of the bleb, film and lamella of garnets are 0.432, 0.432 and 0.434, respectively

(Fig. 5) Mean values of $Fe/(Fe+Mg)$ are 0.432, 0.432 and 0.434 for blebs, films and lamellae, respectively. The chemical compositions of orthopyroxene are plotted in the Al_2O_3 - $Fe/(Fe+Mg)$ variation diagram (Fig. 6). These data were obtained from analyses of orthopyroxenes very close to the exsolution lamellae, films and blebs of garnets, and inclusions in garnets. Values of $Mg/(Fe+Mg)$ in orthopyroxene range from 0.770 to 0.792, with a mean value of 0.783. The content of Al_2O_3 in orthopyroxene ranges from about 6.53 wt% to 8.00 wt%. The mean Al_2O_3 content is 7.08 wt% (Table 2). As is seen in Fig. 6, Al_2O_3 decreases with increase of the Mg-value of orthopyroxene. This cannot be explained by the Fe-Mg-Al partition between orthopyroxene and garnet in a constant pressure-temperature condition because the Al_2O_3 content increases monotonically with increase of the Mg-value of orthopyroxene in equilibrium with garnet at constant pressure and temperature (Kawasaki and Matsui, 1983). This trend may be due to the nucleation mechanism of garnet from aluminous orthopyroxene and/or a change in the pressure-temperature condition.

To assess the possibility of the nucleation mechanism occurring, we examine two

extreme cases, namely *fractional* and *equilibrium* crystallizations of garnet from *primary* orthopyroxene (Fig 6). In the *fractional* crystallization model, we assume that an infinitesimal quantity of garnet (10^{-5} times the amount of *primary* orthopyroxene) crystallizes, and orthopyroxene varies its composition by subtraction of an infinitesimal amount of the newly crystallizing garnet under a constant Fe-Mg distribution coefficient

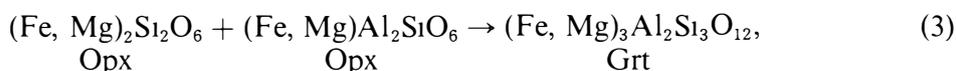
$$K_D = \frac{X_{\text{Mg}}^{\text{Opx}} X_{\text{Fe}}^{\text{Grt}}}{X_{\text{Fe}}^{\text{Opx}} X_{\text{Mg}}^{\text{Grt}}} \quad (2)$$

As a result, orthopyroxene becomes MgO-rich and Al₂O₃-poor with increase in the amount of garnet, and at the same time garnet changes its composition from Fe-rich to Mg-rich as the crystallization proceeds. The chemical trends of orthopyroxene for $K_D=2.0$, 2.5 and 3.0 are illustrated in Fig 6. This figure indicates that the *fractional* crystallization trend is insensitive to the variation of K_D .

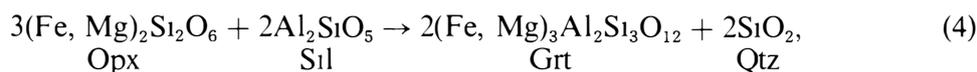
In the strict sense of equilibrium, the chemical compositions of coexisting garnet and orthopyroxene, as well as the amount ratio of these phases, can be uniquely determined for the given pressure-temperature-composition condition. In this argument, we assume that K_D is always constant, and the compositions of orthopyroxene and garnet change to keep the bulk chemistry constant with increasing fraction of garnet (Fig 6). Orthopyroxene becomes MgO-rich and Al₂O₃-poor, and garnet changes from Fe-rich to Mg-rich with increasing fraction of garnet, as in the case of *fractional* crystallization. As is seen in this figure, the *equilibrium* crystallization trend changes significantly with K_D as compared with the *fractional* crystallization. Most orthopyroxene analyses plot within a field delimited by the *equilibrium* crystallization trend of $K_D=2.0$ and the *fractional* crystallization trend of $K_D=3.0$. These two models indicate that, at an early stage of garnet crystallization, orthopyroxene is Fe-rich and Al-rich and garnet is also Fe-rich, and, at a later stage, Mg-values of orthopyroxene and garnet increase and simultaneously orthopyroxene becomes Al₂O₃-poor as the amount of garnet increases.

2.4. Scenario of garnet formation

The petrographic and petrochemical features of the McIntyre granulite suggest that garnet was directly formed from aluminous orthopyroxene by the reaction



rather than by consumption of orthopyroxene+sillimanite by the reaction



because quartz is found only within orthopyroxene and does not coexist together with garnet surrounding sillimanite. This indicates that sillimanite did not take part in the reaction of the formation of garnet from orthopyroxene. Sillimanite, therefore, was coated by garnet and survived as a relict during recrystallization. The textures suggest that at first aluminous orthopyroxene coexisted with quartz and sillimanite. Subsequently, garnet formed as lamellae, blebs and thin films in and around orthopyroxene. The origin

Table 2 Chemical compositions of orthopyroxenes and garnets

| | Most Mg-rich | | Most Fe-rich | | Initial | Mean | |
|---------------------------------|--------------|-------|--------------|--------|-------------------|----------|----------|
| | Opx | Grt | Opx | Grt | Opx* | Opx** | Grt*** |
| SiO ₂ | 52.46 | 40.42 | 50.86 | 40.56 | 50.29 | 51.34 | 40.39 |
| TiO ₂ | 0.09 | 0.16 | 0.05 | 0.08 | — | 0.08 | 0.10 |
| Al ₂ O ₃ | 6.53 | 22.87 | 8.00 | 22.89 | 9.47 | 7.08 | 22.87 |
| Cr ₂ O ₃ | — | 0.08 | — | 0.07 | — | 0.03 | 0.06 |
| FeO [†] | 13.19 | 19.43 | 14.14 | 21.54 | 14.80 | 13.49 | 20.79 |
| MnO | — | 0.18 | — | 0.25 | — | 0.05 | 0.19 |
| MgO | 28.24 | 15.83 | 26.58 | 14.74 | 25.44 | 27.29 | 15.25 |
| CaO | 0.01 | 0.30 | 0.04 | 0.32 | — | 0.01 | 0.30 |
| Total | 100.52 | 99.27 | 99.67 | 100.44 | 100.00 | 99.35 | 99.95 |
| Number of Cations for N Oxygens | | | | | | | |
| | N=6 | N=12 | N=6 | N=12 | N=6 | N=6 | N=12 |
| Si | 1.854 | 2.995 | 1.823 | 2.998 | 1.800 | 1.840 | 2.991 |
| Ti | 0.002 | 0.009 | 0.001 | 0.004 | — | 0.002 | 0.006 |
| Al | 0.272 | 1.997 | 0.338 | 1.995 | 0.399 | 0.299 | 1.996 |
| Cr | — | 0.005 | — | 0.004 | — | 0.001 | 0.004 |
| Fe | 0.390 | 1.204 | 0.424 | 1.331 | 0.443 | 0.404 | 1.288 |
| Mn | — | 0.011 | — | 0.015 | — | 0.001 | 0.012 |
| Mg | 1.488 | 1.749 | 1.420 | 1.624 | 1.357 | 1.458 | 1.684 |
| Ca | — | 0.024 | 0.002 | 0.025 | — | — | 0.024 |
| Total | 4.006 | 7.995 | 4.007 | 7.998 | 4.000 | 4.006 | 8.003 |
| Mg/(Fe+Mg) | 0.792 | 0.592 | 0.770 | 0.549 | 0.754 | 0.783(2) | 0.567(7) |
| K _D | 2.63 | | 2.75 | | 2.51 [‡] | 2.76 | |

*Recalculated to 100.00 from the *primary* orthopyroxene in Table 1

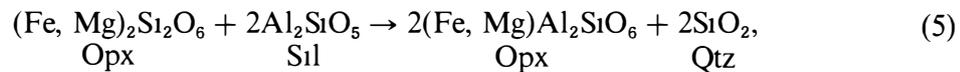
**Mean of 106 orthopyroxenes

***Mean of 142 garnets

[†]Total Fe as FeO

[‡]K_D is calculated from *initial* orthopyroxene and the most Fe-rich garnet

of the formation of elongated quartz in orthopyroxene may be due to the reaction



during prograde conditions

As has been mentioned in the previous section, garnet, which started to nucleate *fractionally* or in *equilibrium* from the primary orthopyroxene, was iron-rich. The more Fe-rich garnet nucleated at an earlier stage. We believe the most Fe-rich garnet represents the *initial* composition. The Mg-value of such Fe-rich garnet is 0.549 (Table 2). The K_D between the *initial* orthopyroxene and garnet is evaluated to be 2.51. If the reaction between garnet and orthopyroxene proceeds and the amount of garnet increases, orthopyroxene would become MgO-rich and Al₂O₃-poor, and garnet enriched in MgO. This indicates that the MgO-rich and Al₂O₃-poor orthopyroxene and MgO-rich garnet represent later-stage compositions caused by the Napier metamorphism. Therefore, the final K_D is estimated as 2.63 from the most magnesian pair of orthopyroxene and garnet given in

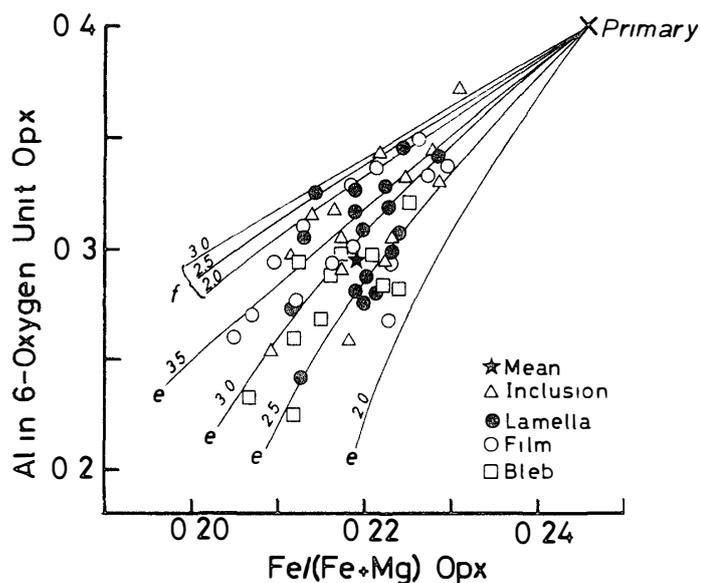


Fig 6 Compositions of orthopyroxene of the McIntyre granulite. A star (★) denotes the mean composition. Analyses of orthopyroxene were made very near lamellae (●), films (○) and blebs (□) of garnets. Inclusions (△) within the garnet were also analyzed. Content of Al decreases with decreasing the Fe/(Fe+Mg) value of orthopyroxene. Compositional trends of orthopyroxene were calculated with models of the fractional (f) crystallization of garnet for $K_D=2.0, 2.5$ and 3.0 , and equilibrium (e) crystallization for $K_D=2.0, 2.5, 3.0$ and 3.5 from primary orthopyroxene (see text).

Table 2 Thus, the Fe-Mg distribution coefficient increases from 2.51 to 2.63, and the Al_2O_3 content of orthopyroxene decreases from 0.399 to 0.272 in 6-oxygen unit. This indicates that garnet was formed during a decrease in the equilibration temperature (retrograde metamorphism). Some increase in the pressure cannot be ruled out but the Fe-Mg partitioning is mostly temperature-sensitive.

Using the orthopyroxene-garnet geothermobarometry proposed by Kawasaki and Matsui (1983), *ie* the Fe-Mg exchange reaction between orthopyroxene and garnet given by reaction (1), and the solubility of Al_2O_3 in orthopyroxene



and



the estimation of the equilibrium condition was failed. The purpose of Kawasaki and Matsui's (1983) study was to constrain the thermodynamic model of orthopyroxene as the Fe-Mg multisite solution, and experiments were carried out at 50 kbar pressure equivalent to the depth of the middle part of the upper mantle. Low Al_2O_3 orthopyroxenes are stable under these conditions. It is erroneous to apply this geothermobarometry directly to

metamorphic rocks such as granulites occurring in the lower parts of the Earth's crust. In the present study we also intend to propose a new geothermobarometry and to estimate the physical conditions of the granulite facies metamorphic rocks to high accuracy.

3. Experimental procedures

3.1. Experimental technique

High pressure experiments were carried out using a 160 mm piston cylinder apparatus at Ehime University. The furnace assembly used in the present experiments is illustrated in Fig. 7. We used a pressure medium of talc and Pyrex glass. The starting material was packed into a 3.5-mm-long graphite capsule having an outside diameter of 2.0 mm and an inside diameter of 1.0 mm. The capsule was covered by a 0.5-mm-thick graphite lid with a diameter of 1.0 mm. Two or three graphite capsules were inserted into holes drilled in a boron nitride disk (70 mm in diameter and 3.5 mm in thickness). The lids of the graphite capsules in a boron nitride disk faced those in another disk with a thin boron nitride sheet (70 mm in diameter and 0.4 mm in thickness) between two disks. In a graphite heater within a talc+Pyrex glass assembly, 12.8-mm-long MgO rods with a diameter of 7.0 mm were placed on the upper and lower sides of two boron nitride disks in which two or three sample containers were inserted. The top MgO rod was bored with a hole of 1.6 mm in diameter to insert a thermocouple insulator. The bottom MgO rod was molded from fine powder and sintered overnight at 1000°C.

The hot piston-in technique was applied for all runs. At about 1 kbar the charge was heated above the softening point of Pyrex glass (about 750°C), which was used as the pressure transmitting medium, and then was compressed to the desired pressure. Finally, the sample was heated to the desired temperature. The generated pressures were measured against the oil pressure of the press. Pressures were calibrated on the basis of NH_4F I-II (3.63 kbar), II-III (10.8 kbar), and Bi I-II (25.5 kbar) transitions at room temperature (Hall, 1971). The quartz-coesite transformation (Bohlen and Boettcher, 1982) at 1000°C (29.7 kbar) was also used for calibration. In the present experiments, a negative correction of 12.4% to the nominal pressure value was adopted as internal friction. Run pressures in Table 3 are given as corrected values.

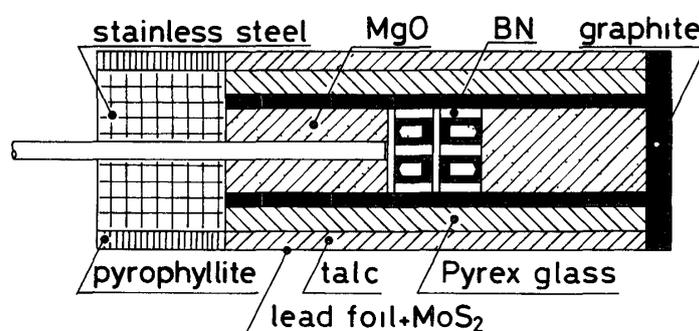


Fig. 7. Furnace assembly used in the present experiments. Two or three capsules were inserted into a single boron nitride disk facing each other. In this cross section, four sample containers are illustrated, whereas one or two capsules are hidden in another cross section.

Temperatures were monitored with Pt/Pt₈₇Rh₁₃ (0.3 mm in diameter) or W₉₅Re₅/W₇₄Re₂₆ (0.2 mm in diameter) thermocouple without correction for the pressure effect on emf. The temperatures at the top, center and bottom in the sample space were directly measured by the use of three-junction thermocouples. It was found that the temperature gradient was about 1–2°C/mm along the axial direction within the sample space at 10.6 kbar and 1400°C (Kawasaki *et al.*, 1993). During each experiment the temperature and pressure were kept constant within $\pm 1^\circ\text{C}$ and ± 0.1 kbar of the nominal values. The relative fluctuations of the electric power during heating were less than $\pm 1\%$. Samples were quenched by cutting off the electric supply. The thermocouple reading dropped below 50°C in a few seconds and to the ambient temperature in one minute. The pressure was then released to atmospheric pressure in about 5 min, and the run product was recovered.

3.2 Starting materials

The McIntyre granulite was cut into thin slabs (about 1 mm thickness), and was ground in an agate mortar under ethyl alcohol for 1 hour. Grain sizes of mineral fragments in the powdered rock were 10–100 μm . It is not possible to obtain the equilibrium assemblage of minerals from the experiments using the powdered rock as a starting material. The recrystallization experiments of run nos 990927AC and 990918B were carried out at 12 kbar and 1000°C for 400 hours and 30 min and at 12 kbar and 1100°C for 129 hours, respectively. In the charges of these runs we found angular mineral fragments of orthopyroxene, garnet, quartz and rutile without recrystallization (see Fig. 8A). Garnets persisted and survived during experiments. We found, however, no garnets and obtained well-crystallized orthopyroxene and quartz in the simultaneous experiments, run nos 990927B and 990918F, where glass was used as a starting material under the same experimental conditions. Thus the reaction was very sluggish if the rock powder was used as a starting material.

For the present experiments we prepared the following starting materials: (1) glass, (2) glass plus 10 wt% of powdered rock, and (3) glass + orthopyroxene + quartz \pm garnet. Glass was obtained by fusing powdered rock at 10 kbar and more than 1600°C for 5 min in a graphite capsule. Rock powder was added to glass to provide seeds of garnet, orthopyroxene and quartz to overcome nucleation problems. We also prepared the mixture of orthopyroxene, quartz and very rare garnet as a seed aggregate. This mineral mixture was obtained from the glass plus powdered rock at 15 kbar and 1200°C for 136 hours (run no 991116). We found only 5 crystals of garnet (about 3–10 μm in grain size) in a polished section of this run product. The mode of garnet is less than 0.02% estimated from the area ratio between garnet and other minerals identified from the back scattered electron image of the run product. About 5 wt% of this mineral assemblage of orthopyroxene, quartz and very rare garnet was added to the glass as seed minerals.

3.3 Run products

Starting material was put into the graphite capsule, and kept at the desired pressure and temperature for 2 days to 4 weeks depending on temperature. After the end of the run, electric power was cut off. The sample was quenched to room temperature and recovered. The charge was polished for electron microprobe analysis and subjected to

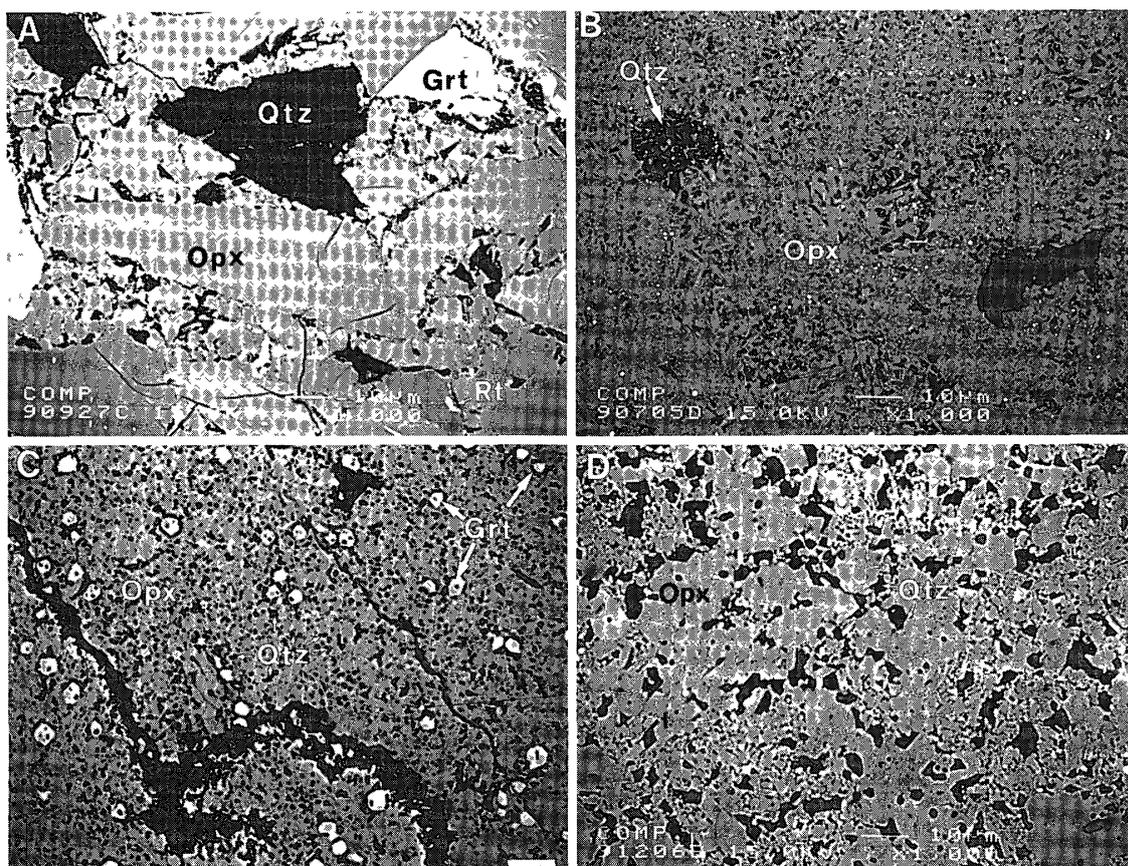


Fig 8 Back scattered electron image (BSEI) of the run products A Run no 990927AC sintered at 12 kbar and 1000°C for 400 hours and 30 min using rock powder as a starting material Orthopyroxene, garnet, quartz and rutile persisted without re-equilibration and recrystallization remaining the angular-shaped grains at the time of crushing and pulverizing B Run no 990705D Orthopyroxene and quartz crystallized from glass at 10 kbar and 1100°C for 237 hours Quartz crystal grew among the grain boundaries of orthopyroxene Rather big quartz includes very fine orthopyroxene Euhedral orthopyroxenes are found Small drops of metal iron precipitated from reduction C Garnet, orthopyroxene and quartz crystallized from glass at 15 kbar and 1100°C for 270 hours (run no 971205D3) Quartz occurs among grain boundaries of orthopyroxenes and garnets and/or is included within euhedral garnets Euhedral orthopyroxenes are also observed D Run products of run no 991206B at 16 kbar and 1300°C for 46 hours from mixture of powdered glass and rock Rather big crystals of orthopyroxene include round quartz Fine euhedral crystals of orthopyroxene are bounded by fine quartz Droplets of metal iron are observed Bar, 10 µm Opx, orthopyroxene Grt, garnet Qtz, quartz Rt, rutile

X-ray powder diffraction experiments

Figure 8B shows the back scattered electron image (BSEI) of the mineral assemblage synthesized from glass at 10 kbar and 1100°C for 237 hours (run no 990705D) Rather fine-grained orthopyroxene and quartz were the only phases present Quartz crystallized at the grain boundaries of orthopyroxenes Small amounts of metal iron droplets were precipitated by reduction, because a graphite capsule was used Although the bulk composition of the silicate phases shifted slightly to SiO₂-rich and FeO-poor sides by

3.4. Chemical analysis

The run products were mounted in the epoxy resin and carefully polished for examination by microprobe analysis. Chemical compositions of all run products were determined with the electron microprobe analyzer JEOL model JXA-8800 Superprobe with the ZAF correction method at Ehime University. The instrumental conditions were as follows: the accelerating voltage, 15 KV, electron beam current, 5×10^{-9} A, electron beam diameter, 1–2 μm estimated from the size of contamination spots formed by excitation during analysis. The accuracy of the chemical analyses was checked by test substances such as orthopyroxene and garnet from a garnet lherzolite. Acceptable analyses of the run products satisfied all the following criteria: agreement with the ideal stoichiometry to be within $\pm 0.5\%$ relative, the total oxide weight per cent in the range 99–101%. Chemical analyses were made near the grain boundaries of coexisting phases.

4. Experimental results

4.1. Stability field of garnet

Runs nos 000107A and 000107B were carried out at 14 kbar and 1200°C for 96 hours. We found that only 11 crystals of garnet persisted in run no 000107A, the starting material of which was a mixture of glass and rock powder. The grain size of garnet was about 1–10 μm . We could not find garnet in the run product of no 000107B in which a mixture of glass and the aggregate of orthopyroxene and quartz including rare garnet (run no 991116) was used as the starting material. The stable phases in this condition are presumably orthopyroxene and quartz.

The experimental details are compiled in Table 3. Figure 9 shows the phase boundary between two assemblages of orthopyroxene+quartz and garnet+orthopyroxene+quartz. This phase boundary is approximated as:

$$P \text{ (kbar)} = 0.0128 T \text{ (}^\circ\text{C)} - 0.27 \quad (9)$$

The garnet in/out curve is seriously affected by $X_{\text{Mg}}^{\text{bulk}}$, *ie* in the MgO-rich system, the position of the boundary curve is located at the higher pressure side with a rather flat slope compared with that in the FeO-rich system (Berman and Aranovich, 1996, Aranovich and Berman, 1996, 1997).

As has been mentioned before, sillimanite is found in this granulite. This implies that the maximum pressure, which this granulite experienced during ultra high-temperature metamorphism, was below the sillimanite \rightleftharpoons kyanite phase boundary (Holdaway, 1971). The minimum pressure of the formation of garnet is bounded by the curve given by eq (9). This curve intersects with the sillimanite-kyanite phase boundary at about 10 kbar and 800°C. This indicates garnet exsolved from aluminous orthopyroxene in the narrow *P-T* field between these two curves at pressures more than 10 kbar and temperatures more than 800°C.

4.2. Fe-Mg partitioning between orthopyroxene and garnet

Reversal experiments on the Fe-Mg partitioning were not successful in the strict sense of the word. The compositions of orthopyroxene and garnet obtained from high pressure experiments at 15 kbar and 1100°C (run no 971205D3) are illustrated in Fig 10 as an

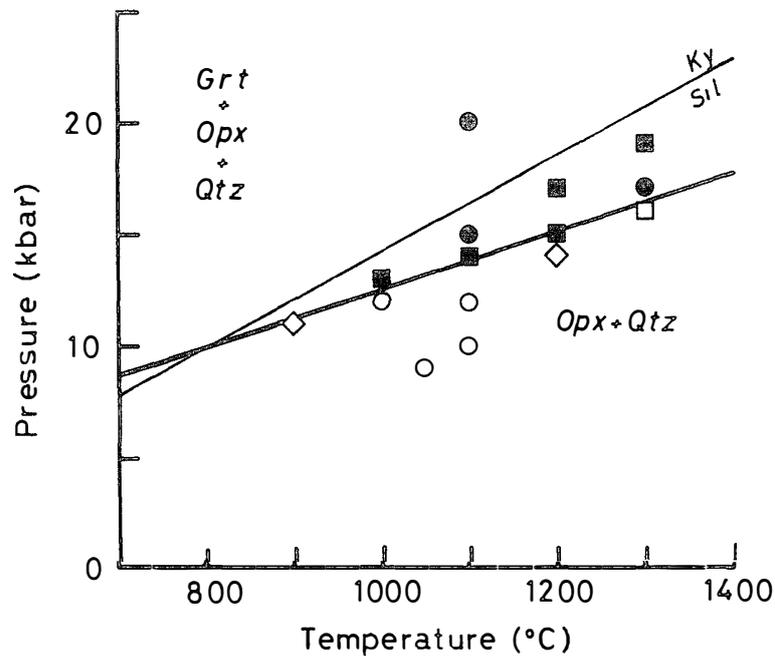


Fig 9 Experimental results of the phase boundary between assemblages of garnet+orthopyroxene+quartz and orthopyroxene+quartz. Filled and open symbols denote the assemblages of garnet+orthopyroxene+quartz and orthopyroxene+quartz, respectively. Circles and squares denote the starting materials of glass and glass+rock, respectively. Diamonds denote the runs using two types of starting materials of glass+rock and glass+orthopyroxene+quartz (\pm garnet). Garnet is stable at higher pressures than those of the curve P (kbar) = $0.0128T$ ($^{\circ}$ C) - 0.27. This curve intersects with the phase boundary between kyanite and sillimanite (Holdaway, 1971) at about 10 kbar and 800° C. The McIntyre granulite equilibrated in the narrow P - T field between these curves; the upper limit of the pressure is bounded by the kyanite-sillimanite phase boundary and the lower by the garnet-appearance curve, and the lower limit of temperature is about 800° C.

example. Glass was used as the starting material in this experiment. Garnet nucleated and grew at the expense of glass from the bulk equivalent to aluminous orthopyroxene plus quartz. Then the composition of glass shifted to the Al_2O_3 -poor and MgO-rich sides. As the crystallization progressed, garnet became more magnesian. This is supported by Harley's (1984) experiments using glass as the starting material, which showed that garnet displays the usual zoning to Mg-richer rim. As a result, orthopyroxene crystallizing from the residual glass after crystallization of garnet became Al_2O_3 -poor and MgO-rich. Consequently, the equilibrium or near equilibrium compositions of garnet and orthopyroxene are those indicated by arrows in Fig 10. The chemical compositions of orthopyroxene and garnet are compiled in Table 4. Standard errors of the mean compositions are also given in this table to assess the reliability and weight of the experimental data.

The relation between the Fe-Mg distribution coefficient and temperature is illustrated in Fig 11. As is seen in this figure, $\ln K_D$ is approximated by the linear inverse of the temperature ($1/T$). Kawasaki and Matsui (1983) formulated the strict solution of K_D from the multisite regular solution model for the FeSiO_3 - MgSiO_3 - Al_2O_3 ternary orthopyroxene (their eq. (26)). For a system in which the bulk chemistry is constant, the K_D is approxi-

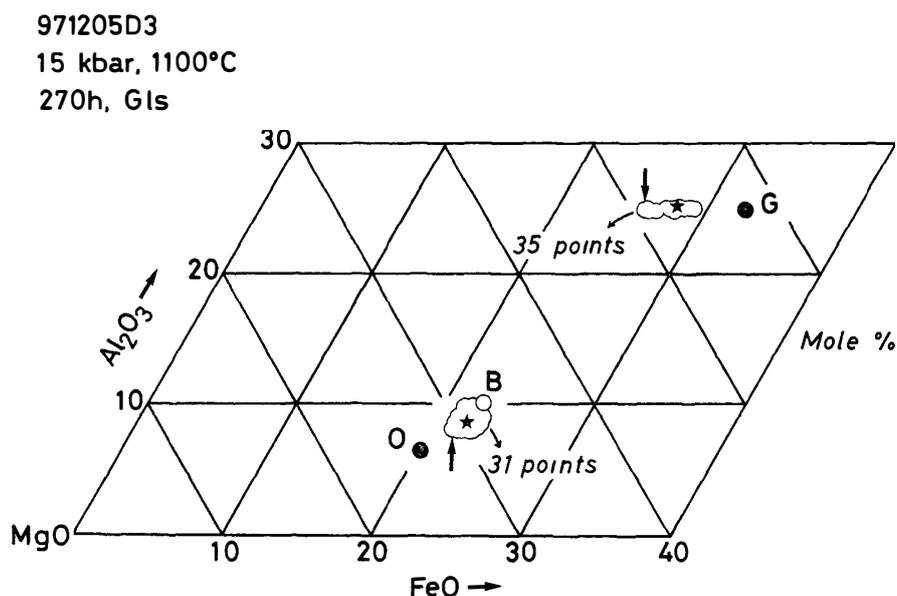


Fig 10 Microprobe analyses of orthopyroxene and garnet at 15 kbar and 1100°C (run no 971205D3) Mean compositions of orthopyroxene and garnet of run products are denoted by stars (★) Bulk composition is labeled by B Mean compositions of orthopyroxene and garnet of the McIntyre granulite are indicated by letters O and G, respectively Glass was used as the starting material in this experiment The Fe-rich garnet nucleated from the glass As the reaction proceeded, garnet became Mg-rich and at the same time orthopyroxene changed its composition to Mg-rich and Al-poor sides Arrows indicate the final compositions of orthopyroxene and garnet of the run products

Table 4 Chemical compositions of coexisting orthopyroxene and garnet

| Run No | P kbar | T °C | Orthopyroxene | | Garnet | |
|----------|-----------|---------|---------------|---------------------|------------|----------|
| | | | Fe/(Fe+Mg) | Al in 6-oxygen unit | Fe/(Fe+Mg) | K_D |
| 991208A | 13 | 1000 | 0.2302(18)* | 0.3016(80) | 0.3776(8) | 2.03(2) |
| 991124A | 14 | 1100 | 0.2396(4) | 0.3352(44) | 0.3466(21) | 1.68(1) |
| 971205D3 | 15 | 1100 | 0.2274(1) | 0.3212(4) | 0.3335(17) | 1.70(1) |
| 990426D | 20 | 1100 | 0.2306(3) | 0.3260(13) | 0.3440(2) | 1.75(1) |
| 000107A | 14 | 1200 | 0.2451(4) | 0.4196(84) | 0.3348(23) | 1.55(7) |
| 991116 | 15 | 1200 | 0.2382(9) | 0.4132(60) | 0.3164(42) | 1.48(4) |
| 991102A | 17 | 1200 | 0.2302(2) | 0.3788(15) | 0.3125(1) | 1.52(1) |
| 991122A | 19 | 1300 | 0.2300(69) | 0.3664(98) | 0.2936(31) | 1.39(10) |

*Standard errors are in parentheses and refer to the last decimal place

mated as

$$\Delta H^* - T\Delta S^* + P\Delta V^* = -RT \ln K_D, \quad (10)$$

where ΔH^* , ΔS^* and ΔV^* denote the effective enthalpy, entropy and volume changes, respectively The present Fe-Mg exchange experiments were carried out at pressures from 13 kbar to 20 kbar The contribution of the $P\Delta V^*$ term as pressure varies to ΔG^* ($=\Delta H^* - T\Delta S^* + P\Delta V^*$) is estimated as of order ± 100 cal in the present experiments This means that the variation in K_D ranges within 3–5% relative at 1000°C Thus the

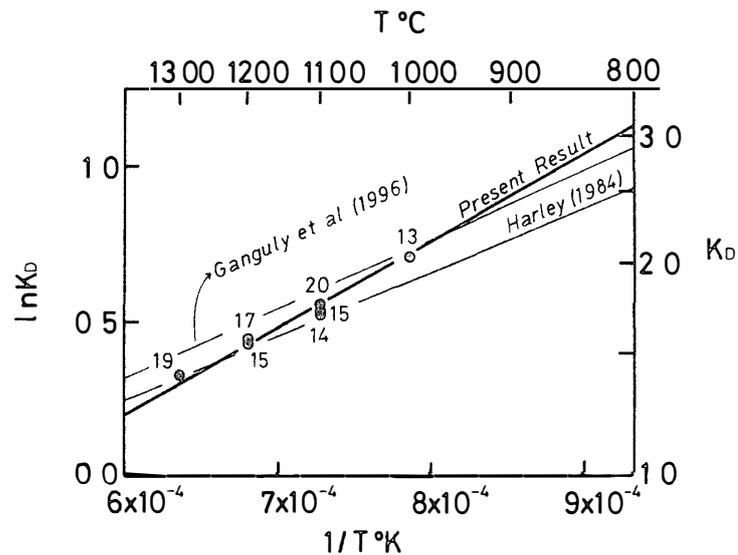


Fig 11 Relation between the Fe-Mg distribution coefficient and temperature. Run pressures are given in this figure. The Fe-Mg distribution coefficient is approximated by $\ln K_D = -1.49 + 2815/T(K)$. Estimations of temperature by the Fe-Mg geothermometries of Harley (1984) and Ganguly *et al* (1996) are about 100°C and 20°C lower, respectively, than those by the present thermometry for the 900°C data, and about 40°C lower and 50°C higher, respectively, for 1100°C data. Using the initial and final K_D of the McIntyre granulite, the equilibration temperatures are estimated as 895°C and 873°C , respectively. Standard errors of $\ln K_D$ are hidden behind the plotted data (●).

pressure effect on K_D is negligible for the narrow pressure range in the present experiments and the K_D is approximated by eq (10) in this McIntyre granulite system

5. Discussion and conclusion

From Fig 11, the Fe-Mg distribution coefficient K_D is approximated by the following equation

$$\ln K_D = -1.49 + 2815/T(K) \quad (11)$$

Illustrated for comparison are the previous investigations on the temperature dependence of the Fe-Mg exchange between orthopyroxene and garnet by Harley (1984) and Ganguly *et al* (1996) in Fig 11 assuming the pressure to be 16.5 kbar, which is a mean of the present run pressures. As is seen in this figure, Harley's (1984) Fe-Mg orthopyroxene-garnet geothermometry is in very good agreement with the present results except for the 1000°C experiments. Harley's geothermometry gives about 80°C lower than the present thermometry in the estimation of temperature for the 1000°C data. The discrepancy between the present and Harley's results becomes larger at low temperature. Estimation using the thermometry of Ganguly *et al* (1996) leads to about 20°C lower for the 900°C data, about 50°C higher for the 1100°C data and about 80°C higher for the 1200°C data than the present thermometry.

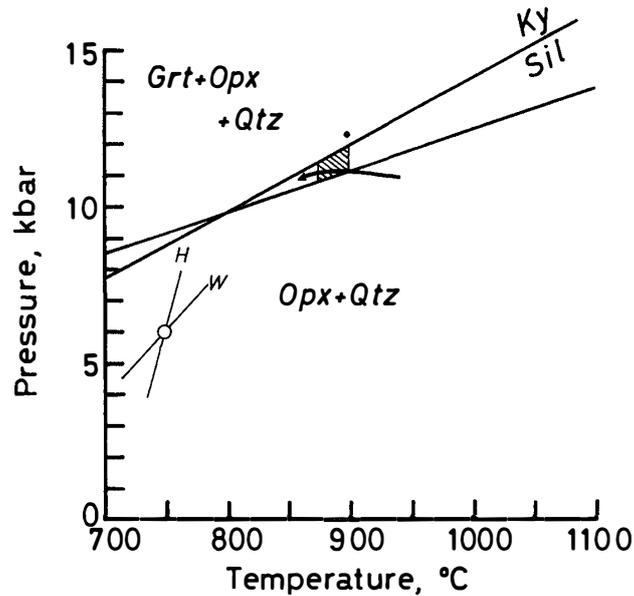


Fig 12 Estimated P - T condition of the McIntyre granulite. Garnet exsolved from orthopyroxene at 11.2 kbar and 895°C. Then the granulite experienced retrograde metamorphism and passed through a certain pressure between 10.9 kbar and 11.4 kbar and 873°C. The intersection of the two P - T relations, obtained from the previous geobarometry (W. Wood, 1974) and geothermometry (H. Harley, 1984) for the initial compositions of orthopyroxene and garnet of the McIntyre granulite, is less than about 5.4 kbar and about 150°C below the present estimate. Wood's (1974) geobarometry yields $P = 12.4$ kbar at the equilibration temperature of 895°C for the initial orthopyroxene and garnet (●).

As has been mentioned in the previous section, the Fe-Mg distribution coefficient K_D of the McIntyre granulite changed from 2.51 for *initial* compositions of orthopyroxene and garnet to 2.63 for the *final* compositions. The metamorphic temperatures are estimated from eq. (11), showing that garnet began to nucleate and grow from aluminous orthopyroxene at 895°C and then the metamorphic temperature decreased to 873°C as recorded in the *final* compositions. Framing the P - T field by this temperature range, we can specify the physical conditions of metamorphism that the McIntyre granulite experienced in the narrow region as illustrated in Fig. 12, that is, the metamorphic pressures are constrained by two reaction boundaries of orthopyroxene + quartz \rightleftharpoons garnet + orthopyroxene + quartz given by eq. (9) and sillimanite \rightleftharpoons kyanite (Holdaway, 1971), yielding the minimum and maximum pressures as 11.2 and 12.0 kbar, respectively, at 895°C, and 11.0 and 11.4 kbar, respectively, at 873°C.

If we simply take the data set of the most Al_2O_3 -rich orthopyroxene and the most magnesian garnet, the lowest K_D is obtained as 2.31 and leads to $T = 937^\circ\text{C}$ from eq. (11), and $P = 11.7$ kbar from eq. (9). This condition may represent probably the highest metamorphic temperature (thermal peak). The pair of the most Mg-rich orthopyroxene and the most Fe-rich garnet records the highest K_D of 3.13, yielding $T = 797^\circ\text{C}$ and $P = 9.9$ kbar. This is extremely close to the intersection between the sillimanite \rightleftharpoons kyanite phase boundary and the garnet in/out curve, but in the kyanite stability field and 0.5 kbar higher than the sillimanite \rightleftharpoons kyanite phase boundary (Holdaway, 1971). This condition might

indicate the lowest closure temperature as to the Fe-Mg partitioning during the retrograde metamorphism

Using the geobarometry of the Al_2O_3 solubility in orthopyroxene (Wood, 1974) and the geothermometry of the Fe-Mg partition (Harley, 1984), the P - T relations for the *initial* compositions of orthopyroxene and garnet of McIntyre granulite (Table 2) are obtained and are illustrated in Fig 12 for comparison with the present result. The intersection of these two curves denotes the pressure and temperature to be 6 kbar and 750°C, about 5.4 kbar and 150°C below the present estimates, and is plotted in the stability field of orthopyroxene+quartz, not in the stability field of garnet. The pressure of 12.4 kbar is obtained at the equilibration temperature of 895°C for the *initial* orthopyroxene-garnet pair using Wood's (1974) geobarometry. This estimated condition of 12.4 kbar/895°C plots in the stability field of kyanite, and is 1 kbar higher than the sillimanite \rightleftharpoons kyanite phase boundary (Holdaway, 1971). Harley (1984) carried out the Fe-Mg partitioning experiments in the more Fe-rich system than in the present system, *i.e.* rather Fe-rich glasses ($X_{\text{Mg}}^{\text{bulk}} < 0.7$) were employed as starting materials, and, moreover, iron capsules were used as sample containers in some experiments. So the bulk shifted to the Fe-rich side by the addition of Fe from the iron capsule in Harley's experiments. As has been pointed out by Kawasaki and Matsui (1983), the distribution coefficient K_D decreases with Fe/(Fe+Mg) of the system. The decrease in K_D with Fe/(Fe+Mg) was not incorporated in Harley's (1984) Fe-Mg geothermometry. This decrease in K_D cannot be neglected at low temperatures. As a result, Harley's (1984) geothermometry yields a temperature estimate about 150°C lower than the present result.

We conclude that the McIntyre granulite precipitated garnet from pre-existing aluminous orthopyroxene as exsolution lamellae and continuous films around orthopyroxene grains at 11.2 kbar and 895°C, and then experienced subsequent retrograde metamorphism at a certain pressure between 10.9 kbar and 11.4 kbar and 873°C.

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