

# Experimental Study of Fe–Mg Exchange Reaction Between Orthopyroxene and Sapphirine and its Calibration as a Geothermometer

Toshisuke Kawasaki and Kei Sato

Division of Earth Sciences, Department of Biosphere-Geosphere Sciences, Faculty of Science, Ehime University,  
Bunkyo-cho 2-5, Matsuyama 790-8577, Japan

(Manuscript received July 25, 2001; accepted April 8, 2002)



## Abstract

The exchange of Fe<sup>2+</sup> and Mg<sup>2+</sup> between orthopyroxene and sapphirine has been investigated at pressures 7–16 kbar and temperatures 850–1300°C using a piston cylinder apparatus for the synthetic and natural systems. This reaction is temperature-dependent and would be a good geothermometer. The equilibration temperature *T* is approximately expressed by the distribution coefficient  $K_D (= \frac{X_{Fe}^{Opx} X_{Mg}^{Spr}}{X_{Mg}^{Opx} X_{Fe}^{Spr}})$  as follows:

$$T(^{\circ}\text{C}) = 1515 / (\ln K_D + 0.943) - 273.$$

This empirical equation was applied to some Antarctic granulites and associated rocks. The new orthopyroxene-sapphirine geothermometer gives consistent results with those estimated from the Fe–Mg orthopyroxene-garnet geothermometer.

**Key words:** Fe–Mg partition, Opx-Spr geothermometer, ultrahigh-temperature granulite, Napier complex, Lützow-Holm Complex.

## Introduction

The ultrahigh-temperature granulites often contain sapphirine coexisting with combinations of quartz, orthopyroxene, sillimanite, spinel, cordierite, osumilite and garnet (e.g., Dallwitz, 1968; Ellis et al., 1980; Grew, 1980; Harley, 1998a). Experimental study indicated that sapphirine+quartz is stable only at temperatures above 1050°C (Hensen and Green, 1973; Bertrand et al., 1991). We have no experimental constraints on the Fe–Mg partitioning between sapphirine and other phases apart from the data of Bertrand et al. (1991).

Many experimental investigations have been carried out as to the orthopyroxene-garnet geothermobarometry (Harley and Green, 1982; Kawasaki and Matsui, 1983; Harley, 1984; Ganguly et al., 1996; Aranovich and Berman, 1997; Kawasaki and Motoyoshi, 2000). It is widely accepted that this geothermometer is available to estimate the *P–T* conditions of the Antarctic granulites (e.g., Harley, 1998b). However, there is still some ambiguity as the results are obtained only from the single

thermometer. In order to estimate more precise *P–T* conditions of ultrahigh-temperature granulites and/or to reduce uncertainties in the obtained results, another thermometer should be established in addition to the orthopyroxene-garnet pair. Checking the derived results, we can assess the reliability of the thermometer.

Sakai and Kawasaki (1997) postulated the orthopyroxene-cordierite geothermometer. This thermometer is very useful for igneous suites, in which it yields results consistent with those obtained from other thermometers. However, it is unsuitable to apply this thermometer to the Antarctic granulites because the calculated temperatures are 100–200°C lower than those estimated by orthopyroxene-garnet geothermometry and because the primary state of correlate is questionable. Sakai and Kawasaki (1997) concluded that the Fe–Mg partition reaction between orthopyroxene and cordierite would be quenched in the igneous conditions. In the case of the ultrahigh-temperature metamorphism, this reaction continued down to the closure temperature of 500–600°C caused by subsequently slow cooling after the peak

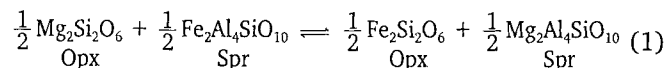
metamorphism, and cordierite is, moreover, very rare as a peak mineral in the Napier Complex.

Harley and Motoyoshi (2000) estimated the peak temperature of Mt. Riiser-Larsen granulites as 1120°C from thermodynamic considerations on the  $\text{Al}_2\text{O}_3$  solubility of orthopyroxene coexisting with sapphirine and quartz. The thermodynamic calculations were carried out based on the experimental and thermodynamic data, particularly on implications of the entropy of sapphirine (Hensen and Essene, 1971; Anastasiou and Seifert, 1972; Chatterjee and Schreyer, 1972; Hensen and Green, 1973; Arima and Onuma, 1977; Waters, 1986; Holland and Powell, 1990; Bertrand et al., 1991; Viellard, 1992; Aranovich and Berman, 1996; Lal, 1997). These temperature evaluations have been made using the experimental results in  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  system and have not as yet been experimentally constrained on the sapphirine-orthopyroxene-quartz equilibria in the natural granulite system and in the  $\text{FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  system.

In this paper, we present new experimental data on the exchange of  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  between orthopyroxene and sapphirine at pressures 7–16 kbar and temperatures 850–1300°C in the synthetic and natural systems to determine the temperature dependence and to develop an orthopyroxene-sapphirine geothermometer.

## Thermodynamic Background

For the exchange of  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  between orthopyroxene and sapphirine (abbreviated\* to Opx and Spr, respectively):



the free energy change  $\Delta G^\circ$  of reaction (1) at the standard state referring to the pure phases at the pressures and temperatures of interest is given by

$$\begin{aligned} -\Delta G^\circ &= -(\Delta H^\circ - T\Delta S^\circ + P\Delta V^\circ) \\ &= RT \ln K \\ &= RT \ln K_D + RT \ln K_\gamma \end{aligned} \quad (2)$$

where we assume  $\Delta C_p = 0$ ,  $(\partial\Delta V/\partial P)_T = 0$  and  $(\partial\Delta V/\partial T)_P = 0$ . The equilibrium constant  $K$  is defined by the quotient of activities  $a$ :

$$K = \left( \frac{a_{\text{Opx}}^{\text{Opx}} a_{\text{Spr}}^{\text{Spr}}}{a_{\text{Opx}}^{\text{Mg}_2\text{Si}_2\text{O}_6} a_{\text{Spr}}^{\text{Fe}_2\text{Al}_4\text{SiO}_{10}}} \right)^{1/2} \quad (3)$$

This parameter should be distinguished from the distribution coefficient  $K_D$  defined by the quotient of the cationic mole fractions  $X$ :

$$K_D = \frac{X_{\text{Fe}}^{\text{Opx}} X_{\text{Mg}}^{\text{Spr}}}{X_{\text{Mg}}^{\text{Opx}} X_{\text{Fe}}^{\text{Spr}}} \quad (4)$$

The  $K_\gamma$  in Eq. (2) is the quotient of the activity coefficients. Thermodynamic variables  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta V^\circ$  in the Eq. (2) are the enthalpy, entropy and volume changes of the chemical reaction (1), respectively. These are assumed to be constant or independent of both temperature and pressure under the present experimental conditions.

Kawasaki and Matsui (1983) formulated the strict solution of activity-composition relations of  $\text{FeSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$  orthopyroxene. The effects of the excess energy terms, arising from non-ideal Mg-Al, Al-Fe, Fe-Mg mixings, are important but are not assessed independently. These non-ideal effects can be negligible or can be regarded as constant in the present data because  $K_D \approx 1$  and bulk  $\text{Fe}/(\text{Fe}+\text{Mg})$  ranges from 0.2 to 0.5 (Tables 1 and 2). Similar treatments were carried out to develop the empirical thermometers from the Fe–Mg partition data with narrow compositional range or constant bulk composition by Sakai and Kawasaki (1997) and Kawasaki

Table 1. Representative compositions of coexisting orthopyroxenes and sapphirines at 11 kbar.

Run No.	MA000828E	MA000918A		
Temperature	1200°C	1100°C		
Duration	237 hrs	342 hrs		
Capsule	Gr	AgPd		
Coexisting phase	Qtz	Sil, Qtz		
	Opx	Spr	Opx	Spr
SiO <sub>2</sub>	48.52	16.11	49.22	16.22
TiO <sub>2</sub>	0.22	—	0.16	0.29
Al <sub>2</sub> O <sub>3</sub>	12.54	56.89	11.20	57.25
Cr <sub>2</sub> O <sub>3</sub>	—	—	0.02	0.07
FeO	11.74	7.36	12.75	7.46
MnO	0.10	0.10	0.02	—
MgO	26.78	18.66	26.19	18.78
NiO	—	0.10	0.05	0.08
CaO	0.02	0.03	0.05	0.03
Na <sub>2</sub> O	0.03	0.01	0.02	—
Total	99.96	99.26	99.72	100.15
Number of Cations for n Oxygens				
	n=6	n=10	n=6	n=10
Si	1.718	0.965	1.754	0.963
Ti	0.006	—	0.004	0.013
Al	0.523	4.016	0.470	4.005
Cr	—	—	0.001	0.003
Fe	0.348	0.369	0.380	0.370
Mn	0.003	0.005	0.002	—
Mg	1.414	1.666	1.392	1.662
Ni	—	0.005	0.001	0.004
Ca	0.001	0.002	0.002	0.002
Na	0.002	0.001	0.001	—
Total	4.015	7.028	4.007	7.020
Mg/(Fe+Mg)	0.803	0.819	0.784	0.818
$K_D$	1.11		1.22	

Note: The distribution coefficient  $K_D$  is defined as

$$K_D = \frac{X_{\text{Fe}}^{\text{Opx}} X_{\text{Mg}}^{\text{Spr}}}{X_{\text{Mg}}^{\text{Opx}} X_{\text{Fe}}^{\text{Spr}}} \quad (\text{see text}).$$

\*Kretz (1983).

Table 2. Run details and the Fe–Mg distribution coefficient between orthopyroxene and sapphirine.

Run No.	P kbar	T °C	Duration	Capslue	Starting Material	$K_D$		$\sigma^*$	Coexisting phases
						Mg-rich	Fe-rich		
$(\text{Fe}_{0.25}\text{Mg}_{0.75})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ System									
MA001201D	11	1000	573h	AgPd	Gls	1.15	1.27	0.03	Qtz,Sil
MA000918B	11	1100	342h	AgPd	Gls+Sil	1.08	1.20	0.02	Qtz,Sil
MA000828A	11	1200	237h	Gr	Gls+Sil	1.03	0.92	0.02	Qtz
MA000515	12	1200	96h	Gr	Gls	1.17	1.15	0.01	Qtz, Gls(?)
MA000107D	14	1200	96h	Gr	Gls+Sil	1.19	1.11	0.01	Grt,Qtz
MA991206C	16	1300	46h	Gr	Gls+CM <sup>†</sup>	1.09	0.95	0.05	Grt,Qtz,Gls(?)
$(\text{Fe}_{0.2}\text{Mg}_{0.8})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ System									
UNSW960624GT20	7	1100	266h	AuPd	Gls	1.22	0.95	0.01	Spl,Qtz
$2(\text{Fe}_{0.5}\text{Mg}_{0.5})_2\text{SiO}_4 + \text{Al}_2\text{O}_3$ System									
MA971205U2	15	1100	270h	Gr	Ol+Opx+ Spl+Crd	1.02	1.15	0.03	Grt,Spl,Crn
$4(\text{Fe}_{0.5}\text{Mg}_{0.5})\text{SiO}_3 + \text{Al}_2\text{SiO}_5$ System									
MA971205U2-3	15	1100	270h	Gr	Ol+Opx+ Spl+Crd	1.13	1.27	0.05	Grt,Spl,Sil
McIntyre Granulite + Sillimanite System									
MA000918A	11	1100	342h	AuPd	Gls	1.05	1.30	0.02	Sil,Qtz
MA000828E	11	1200	237h	Gr	Gls	0.98	1.38	0.02	Qtz
Rundvågshetta Granulite System									
MS930722	7	850	240h	AgPd	RC <sup>‡</sup>	1.41	1.61	0.08	Bt,Rt,Crd,Pl
MS930917	9	950	110h	AgPd	RC	1.18	1.81	0.20	Bt,Rt,Spl,Gls
KC931001	10	1000	70h	AgPd	RC	1.24	1.26	0.02	Bt,Rt,Crd,Spl,Zr,Gls (Grt)
MS930819	7	1050	96h	AgPd	RC	1.20	1.37	0.19	Bt,Rt,Spl,Gls,V
KC940120	9	1050	100h	AgPd	RC	1.23	1.34	0.02	Bt,Rt,Spl,Gls
UNSW960624RV	7	1100	266h	AuPd	RC	1.17	1.39	0.05	Bt,Rt,Spl,Gls,V
MA950721	9	1100	64h	AgPd	RC	1.29	1.05	0.08	Bt,Rt,Spl,Gls,V
MA980617	15	1100	266h	AuPd	RC	1.03	1.28	0.01	Bt,Rt,Grt,Gls

Note: Abbreviations of minerals are after Kretz (1983). Crn–corundum, Bt–biotite, Crd–cordierite, Gls–glass, Gr–graphite, Grt–garnet, Opx–orthopyroxene, Ol–olivine, Qtz–quartz, Rt–rutile, Sil–sillimanite, Spl–spinel, V–vapor, Zr–zircon. \*Standard errors of  $K_D$ . <sup>†</sup>Added 10 wt. % of crystalline mixture Grt+Ol+Opx+Spl+Crd+Qtz to glass. <sup>‡</sup>Powdered rock.

and Motoyoshi (2000). So we can incorporate the excess energy terms into the  $\Delta G^\circ$  term. We rewrite the Eq. (2) as  $-\Delta G^\circ = -\Delta H^\circ + T\Delta S^\circ - P\Delta V^\circ = RT \ln K_D$ , (5) where we call  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta V^\circ$  as the effective Gibbs' free energy, enthalpy, entropy and volume changes. The  $-P\Delta V^\circ$  term is also negligible or nearly constant. In the present study, the experimental pressures are ranged from 7 kbar to 16 kbar. The contribution of the  $P\Delta V^\circ$  term as pressure varies to  $\Delta G^\circ$  is estimated as of order  $\pm 100$  cal in the present experiments. This is equivalent to the variation of 3–5% relative in  $K_D$  at 1000°C. As a consequence the logarithm of the distribution coefficient  $K_D$  can be approximated by the following equation:

$$-\Delta H^\circ + T\Delta S^\circ \approx RT \ln K_D. \quad (6)$$

This approximation is experimentally supported as is seen in figure 1. By the least-squares or graphical evaluation of the empirical thermodynamic parameters  $\Delta H^\circ / R$  and  $T\Delta S^\circ / R$  from the experimental data, we can calibrate this equation as a thermometer. An approach of this kind has been carried out with fair success (Sakai and Kawasaki, 1997; Kawasaki and Motoyoshi, 2000).

## Experimental Procedures

We prepared 4 types of starting materials with different bulk compositions in the synthetic FeO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system and 2 types in the natural rock system. Oxide mixtures with bulk compositions of  $(\text{Fe}_{0.25}\text{Mg}_{0.75})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ,  $(\text{Fe}_{0.2}\text{Mg}_{0.8})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ,  $4(\text{Fe}_{0.5}\text{Mg}_{0.5})\text{SiO}_3 + \text{Al}_2\text{SiO}_5$  and  $2(\text{Fe}_{0.5}\text{Mg}_{0.5})_2\text{SiO}_4 + \text{Al}_2\text{O}_3$  were prepared from reagent-grade chemicals, namely, iron metal sponge, magnesium metal powder, aluminum metal ribbon and silica gel. Weighed metals were dissolved in a dilute solution of nitric acid at about 80°C, and then stirred silica gel into a solution. After drying at 110°C for a day, the mixture was heated by a gas burner and then kept at about 600°C for more than 2 hours to remove nitric acid completely.

Dried material was ground in an agate mortar under ethyl alcohol for one hour. The oxide mixture with desired composition was hand-pressed to several pieces of pellet in a die. The size of each pellet was about 5 mm in thickness and 12.5 mm in diameter. The mixture was reacted in a fine Pt-wire basket at 1150°C using an electric

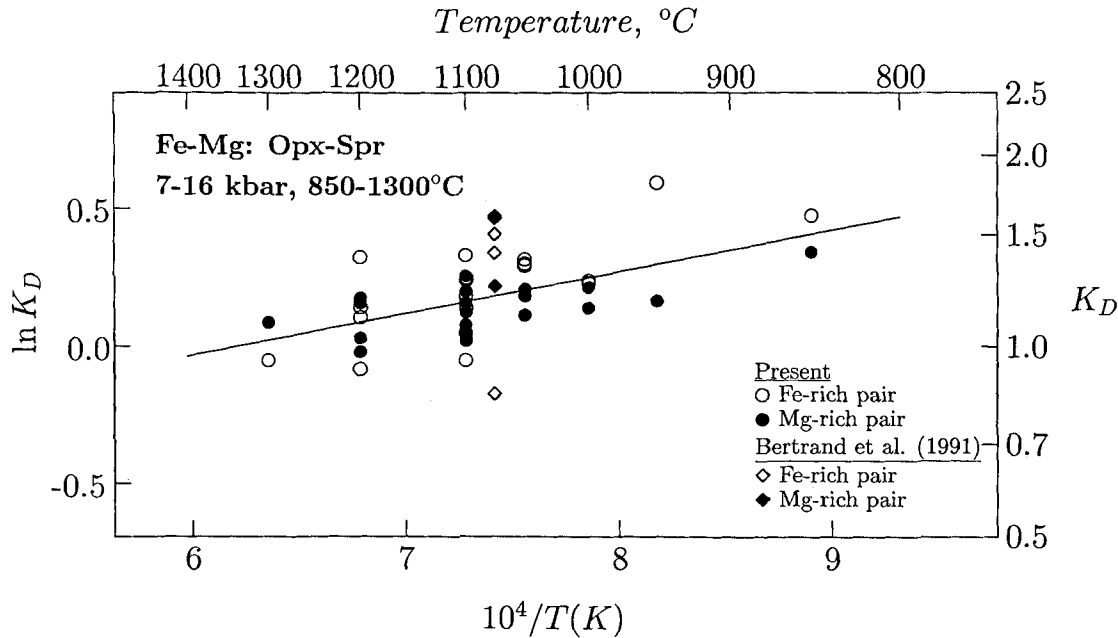


Fig. 1. Relation between the Fe–Mg distribution coefficient  $K_D$  and temperature  $T$ . Run pressures are 7 to 16 kbar. The distribution coefficients obtained from the Mg-rich pair are plotted by filled symbols, and those from the Fe-rich pair by open symbols. Circles=present study. Diamonds = Bertrand et al.'s (1991) data. The Fe–Mg distribution coefficient is approximated by  $\ln K_D = -0.943 + 1515/T(^{\circ}\text{K})$ .

furnace with the oxygen controlling system equipped at Ehime University. Oxygen fugacity was controlled to attain to the iron-wüstite buffer by the mixed gas technique using  $\text{CO}_2$  and  $\text{H}_2$ . The gas flow ratio was adopted as  $\text{CO}_2:\text{H}_2 = 0.8 \text{ l/min}:0.2 \text{ l/min}$ . Hematite converted to wüstite completely at  $1150^{\circ}\text{C}$  under this gas flow ratio (Kawasaki, 2001).

The mineral mixture of olivine, orthopyroxene, spinel and cordierite was obtained after sintering. The mineral assemblage is called as the 1-atm product. This 1-atm product was metastably converted to the assemblage of garnet, orthopyroxene, spinel and quartz at 25 kbar and  $1300^{\circ}\text{C}$  for 3 hours in a graphite capsule. We call this as the 25-kbar product. The 1-atm product was fused at 10 kbar and  $1600^{\circ}\text{C}$  for 2 minutes in a graphite capsule using a piston cylinder apparatus. Glass was used in the additional experiments. The mixture of the 1-atm and 25-kbar products was used as low- and high-pressure seed assemblage. About 10 wt.% of seed mixture was added to the glass to provide seeds to overcome nucleation problems. In the experiments for the  $(\text{Fe}_{0.25}\text{Mg}_{0.75})_3\text{Al}_2\text{Si}_3\text{O}_{12}$  composition, we added 5 wt.% of powdered sillimanite collected from Rundvågshetta, East Antarctica (Sample No. RVH18SIL) to the glass. The experimental details for the  $(\text{Fe}_{0.25}\text{Mg}_{0.75})_3\text{Al}_2\text{Si}_3\text{O}_{12}$  system are given by Sato and Kawasaki (2002).

We also prepared the following Antarctic granulites: (1) pulverized sillimanite-cordierite-sapphirine bearing granulite (Sample No. RVH92011102A) collected at Rundvågshetta region, Lützow-Holm Bay, East Antarctica

(Kawasaki et al., 1993) and: (2) powdered mixture of 85 wt.% McIntyre granulite (Sample No. SP93022004A; Kawasaki and Motoyoshi, 2000) and 15 wt.% sillimanite (RVH18SIL). The Rundvågshetta granulite is characterized by high MgO content (MgO, 18.74 wt.%), high Mg/(Fe+Mg) value ( $X_{\text{Mg}}^{\text{bulk}} = 0.764$ ), low CaO content (0.4 wt.%) and relatively high  $\text{TiO}_2$  (1.86 wt.%) and alkali ( $\text{Na}_2\text{O}$ , 1.36 wt.%;  $\text{K}_2\text{O}$ , 3.34 wt.%) contents in the bulk composition (Kawasaki et al., 2002). The petrographic descriptions of the Rundvågshetta granulite were given by Kawasaki et al. (1993). The bulk composition of the McIntyre granulite is well approximated by the Qtz-Crn- $\text{En}_{75}$  system with extremely low  $\text{TiO}_2$  (0.19 wt.%), CaO (0.08 wt.%),  $\text{Na}_2\text{O}$  (0.05 wt.%) and  $\text{K}_2\text{O}$  (0.03 wt.%) contents. The petrographic feature was given by Kawasaki and Motoyoshi (2000). The experimental details and preparation of these starting materials are reported (Rundvågshetta granulite system: Kawasaki and Motoyoshi, 2002; McIntyre granulite-sillimanite system: Kawasaki et al., 2002) and are omitted in this paper.

High-pressure experiments were carried out using a 16.0 mm piston cylinder apparatus at Ehime University and Kochi University. We also used 3/4-inch piston cylinders at the Institute of the Study of Earth's Interior and the University of New South Wales. Run conditions were at 7–16 kbar and  $850\text{--}1300^{\circ}\text{C}$ . Run durations were 46–573 hours depending on temperature. Starting materials were encapsulated in the sample containers of graphite,  $\text{Ag}_{70}\text{Pd}_{30}$  or  $\text{Au}_{75}\text{Pd}_{25}$  alloys.

## Experimental Results

Representative compositions of orthopyroxene and sapphirine are given in table 1. We find some sapphirines are saturated in silica compared with those occurring in ultrahigh-temperature granulites (e.g., Kawasaki et al., 1993; Motoyoshi and Ishikawa, 1997; Harley and Motoyoshi, 2000; Motoyoshi and Hensen, 2001). Although the origin of silica-saturated sapphirine is unclear, it would be caused partly from pressure effect on the  $\text{Al}_2\text{O}_3$  solubility of sapphirine; i.e.,  $\text{Al}_2\text{O}_3$  content decreases with pressure due to the Tschermak substitution  $\text{AlAl} \rightarrow \text{MgSi}$  as is commonly found in aluminous orthopyroxene. Das et al. (2001) reported the highly silica-saturated sapphirines synthesized at 8.5 kbar/1000°C and 8 kbar/1050°C.

Reversal experiments on the Fe–Mg partitioning were not carried out. Orthopyroxene and sapphirine, more or less, showed reverse zoning. We found the Mg-rich rims of orthopyroxene and sapphirine in some runs. The formation of the Mg-rich rims would be caused by (1) reduction of charge to precipitate small amounts of metal iron droplets with the result that the bulk composition of the silicate phase shifts to Mg-rich side; (2) iron loss dissolving to metal capsule; and: (3) kinetics of nucleation and growth of minerals.

The reverse zoning due to the nucleation and growth kinetics can be explained as follows. The bulk compositions of the starting materials in the  $(\text{Fe}_{0.25}\text{Mg}_{0.75})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ,  $(\text{Fe}_{0.2}\text{Mg}_{0.8})_3\text{Al}_2\text{Si}_3\text{O}_{12}$  and McIntyre granulite-sillimanite systems, using the glass or glass plus seed minerals, were approximated to aluminous pyroxene. Under such bulk chemistry, sapphirine and the additional phases such as garnet and spinel, nucleated and grew at the expense of glass from the bulk equivalent to aluminous orthopyroxene. Then the glass shifted to the  $\text{Al}_2\text{O}_3$ -poor and MgO-rich sides in composition. Additional phases of garnet and spinel would become more magnesian in the progress of crystallization. As a result, orthopyroxene and sapphirine, which newly crystallized from the residual glass after the crystallization of garnet and spinel, are enriched in MgO. This kinematic model is supported by the Harley's (1984) experiments using glass as the starting material that orthopyroxene displayed the usual zoning to Mg-rich rim. The Mg-rich orthopyroxene and sapphirine indicates the latest stage compositions in the crystallization. Contrarily, the Fe-rich pair represents the early stage. The difference between the chemical compositions of Fe-rich core and Mg-rich rim ranges from 0.02 to 0.03 in  $X_{\text{Mg}}$ . This leads to the discrepancy of less than 0.1 in the relative  $K_D$ . The distribution coefficients  $K_D$  obtained from the Mg-rich and Fe-rich pairs are given

in table 2. These tables indicate that the distribution coefficient  $K_D$  is very close to unity.

## Discussion and Conclusion

The relation between the Fe–Mg distribution coefficient  $K_D$  and temperature  $T$  is illustrated in figure 1. The Bertrand et al.'s (1991) data are also plotted in this figure. Filled and open symbols indicate the data from Mg-rich and Fe-rich pairs, respectively. This figure indicates that the  $\ln K_D$  is approximated to be linear to the inverse of the temperature ( $1/T$ ). This relation is derived from the theoretical considerations and expressed by Eq. (6). The parameters  $\Delta H^\ominus$  and  $\Delta S^\ominus$  in Eq. (6) are estimated by the least squares method (Deming, 1943) using the experimental data of  $K_D$  given in table 2:

$$\begin{aligned}\Delta H^\ominus (\text{cal}) &= -3010 \pm 660 \\ \Delta S^\ominus (\text{cal/K}) &= -1.874 \pm 0.482.\end{aligned}\quad (7)$$

From these data, the Fe–Mg distribution coefficient  $K_D$  is approximated by the following equation:

$$\ln K_D = -(0.943 \pm 0.242) + (1515 \pm 332)/T(^{\circ}\text{K}), \quad (8)$$

which is drawn by a straight line in figure 1. Kawasaki and Motoyoshi (2000) inferred that the  $K_D$  is given by this type of equation as far as the bulk chemistry is constant within the narrow pressure range. In the case of the Fe–Mg partition between orthopyroxene and sapphirine,  $K_D$  is almost unity as is seen in figure 1. This indicates that we can neglect the compositional dependence on  $K_D$  (see previous section). As is clear in figure 1, the Fe–Mg partitioning between orthopyroxene and sapphirine is slightly temperature-dependent.

The temperature conditions of Antarctic and associated granulites can be assessed through the Fe–Mg orthopyroxene-sapphirine geothermometry. Results of calculations of the equilibration temperatures of Antarctic and associated granulites from Mather Peninsular, Rauer Group (Harley, 1998c), Forefinger Point (Harley et al., 1990; Motoyoshi et al., 1994), Mt. Riiser-Larsen (Harley and Motoyoshi, 2000; Motoyoshi and Hensen, 2001), Rundvågshetta (Kawasaki et al., 1993; Motoyoshi and Ishikawa, 1997) and Labwor Hills (Sandiford et al., 1987) are summarized in table 3. Comparison of the estimated temperatures from the orthopyroxene-garnet (Harley, 1984; Kawasaki and Motoyoshi, 2000), orthopyroxene-cordierite (Sakai and Kawasaki, 1997) and the present orthopyroxene-sapphirine thermometers are also given in table 3. The exchange thermometry of Fe–Mg between orthopyroxene and sapphirine gives us consistent results compared with the previous estimates by Fe–Mg garnet-orthopyroxene geothermometry.

As has been pointed out by Sakai and Kawasaki (1997), the Fe–Mg orthopyroxene-cordierite geothermometry

Table 3. Comparison of the garnet-orthopyroxene thermometers and the present orthopyroxene-sapphirine thermometer.

	Grt-Opx: Fe-Mg			Opx-Spr: Fe-Mg		Opx-Crd: Fe-Mg	Source of data
	$K_D$	$T_{HA84}$	$T_{KM00}$	$K_D$	$T^{Opx-Spr}$	$T_{SK97}$	
Mather Peninsular, Rauer Group							
88-218	1.93	975	1039	1.29	990(90)	—	Harley (1998c)
91-73	2.07	923	996	1.32	970(80)	—	Harley (1998c)
Forefinger Point							
4652	2.01	933	1013	1.19	1080(110)	729	Harley et al. (1990)
2203	2.58	784	881	1.48	860(50)	600	Motoyoshi et al. (1994)
2223	3.26	675	780	1.40	910(70)	690	Motoyoshi et al. (1994)
Mt. Riiser-Larsen							
49377	—	—	—	1.18	1090(110)*	—	Harley and Motoyoshi (2000)
2344B	—	—	—	1.48	860(50)	680	Motoyoshi and Hensen (2001)
5072	2.38	805	922	1.38	920(70)	—	Motoyoshi and Hensen (2001)
Rundvågshetta							
9201102A	2.36	851	925	1.55	820(40)	612	Kawasaki et al. (1993)
93010601X	1.93	983	1039	1.27	1010(100)	521	Motoyoshi and Ishikawa (1997)
Labwor Hills							
4800	1.98	923	1017	1.30	980(90)	650	Sandiford et al. (1987)

Note: Uncertainties of the calculated temperatures from the orthopyroxene-sapphirine thermometer are given in parentheses.  $T_{HA84}$ , Harley (1984);  $T_{KM00}$ , Kawasaki and Motoyoshi (2000);  $T_{SK97}$ , Sakai and Kawasaki (1997).  $T^{Opx-Spr}$ , orthopyroxene-sapphirine thermometer:  $T(^{\circ}\text{C}) = 1515 / (\ln K_D + 0.943) - 273$ . \*Harley and Motoyoshi (2000) estimated the peak temperature as 1120°C.

gives us the minimum temperatures compared with those calculated from the other geothermometry. This indicates that the exchange reaction of  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  between orthopyroxene and cordierite would continue to operate during retrograde metamorphism caused after peak metamorphism.

We conclude that the orthopyroxene-sapphirine geothermometer is useful to evaluate the temperature conditions of Antarctic and associated granulites and this thermometer gives results consistent with those from the orthopyroxene-garnet geothermometer.

## Acknowledgments

One of the authors (K.T.) got an idea about this study through the discussions with his esteemed friend, Motoyoshi Yoichi, just on the outcrop of the sillimanite-cordierite-sapphirine bearing granulite at Rundvågshetta, East Antarctica on January 11, 1992 (JARE-33). Takahashi Eiichi gave him technical advice on the research program of 1993 for a ten-month sabbatical at the Institute for the Study of the Earth's Interior, Okayama University. Bas Hensen gave a chance of the research program of 1996 for a half-year sabbatical at the University of New South Wales. During this sabbatical time some experiments were carried out. At the various stage of this study, we had invaluable discussions with and suggestions from Hiroi Yoshikuni, Arima Makoto, Ishizuka Hideo, Osanai Yasuhito and Shiraishi Kazuyuki. We are also thankful to Simon Harley who critically read this manuscript and gave us constructive comments toward its improvement. This study is financially supported by the Grant-in-Aid for

Scientific Research from the Ministry of Education, Science and Culture of the Japanese Government (No. 11640481 and 14654093).

## References

- Anastasiou, P. and Seifert, F. (1972) Solid solubility of  $\text{Al}_2\text{O}_3$  in enstatite at high temperatures and 1–5 kbar water pressure. *Contrib. Mineral. Petrol.*, v. 34, pp. 272–287.
- Aranovich, L.Y. and Berman, R.G. (1996) Optimized standard state and solution properties of minerals. II. Comparisons, predictions, and applications. *Contrib. Mineral. Petrol.*, v. 126, pp. 25–37.
- Aranovich, L.Y. and Berman, R.G. (1997) A new garnet-orthopyroxene thermometer based on reversed  $\text{Al}_2\text{O}_3$  solubility in  $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$  orthopyroxene. *Amer. Mineral.*, v. 82, pp. 345–353.
- Arima, M. and Onuma, K. (1977) The solubility of alumina in enstatite and the phase equilibria in the join  $\text{MgSiO}_3\text{-MgAl}_2\text{SiO}_6$  at 10–25 kbar. *Contrib. Mineral. Petrol.*, v. 61, pp. 251–265.
- Bertrand, P., Ellis, D.J. and Green, D.H. (1991) The stability of sapphirine-quartz and hypersthene-sillimanite-quartz assemblages: an experimental investigation in the system  $\text{FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  under  $\text{H}_2\text{O}$  and  $\text{CO}_2$  conditions. *Contrib. Mineral. Petrol.*, v. 108, pp. 55–71.
- Chatterjee, N.D. and Schreyer, W. (1972) The reaction  $\text{enstatite}_{ss} + \text{sillimanite} \rightleftharpoons \text{sapphirine}_{ss} + \text{quartz}$  in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ . *Contrib. Mineral. Petrol.*, v. 36, pp. 49–62.
- Dallwitz, W.B. (1968) Coexisting sapphirine and quartz in granulites from Enderby Land, Antarctica. *Nature*, v. 219, pp. 476–477.
- Das, K., Dasgupta, S. and Miura, H. (2001) Stability of osumilite coexisting with spinel solid solution in metapelitic granulites at high oxygen fugacity. *Amer. Mineral.*, v. 86, pp. 1423–1434.

- Deming, W.E. (1943) Statistical adjustment of data. John Wiley Sons, New York, p. 261.
- Ellis, D.J., Sheraton, J.W., England, R.N. and Dallwitz, W.B. (1980) Osumilite-sapphirine-quartz granulites from Enderby Land, Antarctica – mineral assemblages and reactions. *Contrib. Mineral. Petrol.*, v. 72, pp. 123-143.
- 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.*, v. 126, pp. 137-151.
- Grew, E.S. (1980) Sapphirine+quartz association from Archaean rocks in Enderby Land, Antarctica. *Amer. Mineral.*, v. 65, pp. 821-836.
- Harley, S. (1998a) On the occurrence and characterization of ultrahigh-temperature crustal metamorphism. In: Treloar, P.J. and O'Brien, P.J. (Eds.), "What drives metamorphism and metamorphic reaction?" *Geol. Soc. London, Spl. Publ.*, v. 138, pp. 81-107.
- Harley, S. (1998b) An appraisal of peak temperatures and thermal histories in ultrahigh-temperature (UHT) crustal metamorphism: the significance of aluminous orthopyroxene. *Natl. Inst. Polar Res., Spl. Issue, Mem.* v. 53, pp. 49-73.
- Harley, S. (1998c) Ultrahigh temperature granulite metamorphism (1050°C, 12 kbar) and decompression in garnet (Mg<sub>70</sub>)-orthopyroxene-sillimanite gneisses from the Rauer Group, East Antarctica. *J. Metam. Geol.*, v. 16, pp. 541-562.
- Harley, S. and Green, D.H. (1982) Garnet-orthopyroxene barometry for granulites and peridotites. *Nature*, v. 300, pp. 697-701.
- Harley, S. and Motoyoshi, Y. (2000) Al zoning in orthopyroxene in a sapphirine quartzite: evidence for >1120°C UHT metamorphism in the Napier Complex, Antarctica, and implications for the entropy of sapphirine. *Contrib. Mineral. Petrol.*, v. 138, pp. 293-307.
- Harley, S.L. (1984) An experimental study of the partitioning of Fe and Mg between garnet and orthopyroxene. *Contrib. Mineral. Petrol.*, v. 86, pp. 359-373.
- Harley, S.L., Hensen, B.J. and Sheraton, J.W. (1990) Two-stage decompression in Antarctica: orthopyroxene-sillimanite granulites from Forefinger Point, Enderby Land, implications for the evolution of the Archaean Napier Complex. *J. Metam. Geol.*, v. 8, pp. 591-613.
- Hensen, B.J. and Essene, E.J. (1971) Stability of pyrope-quartz in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. *Contrib. Mineral. Petrol.*, v. 30, pp. 72-83.
- Hensen, B.J. and Green, D.H. (1973) Experimental study of the stability of cordierite and garnet in pelitic compositions at high pressures and temperatures. III. Synthesis of experimental data and geological applications. *Contrib. Mineral. Petrol.*, v. 38, pp. 151-166.
- Holland, T.J.B. and Powell, R. (1990) An internally consistent thermodynamic data set for phases of petrological interest. *J. Metam. Geol.*, v. 16, pp. 309-343.
- Kawasaki, T. (2001) Experimental investigation of mixing properties of (Ca,Fe,Mg)<sub>2</sub>SiO<sub>4</sub> olivine: Fe-Mg exchange with Ca-rich clinopyroxene and phase relations in olivine quadrilateral. *J. Mineral. Petrol. Sci.*, v. 96, pp. 217-242.
- Kawasaki, T. and Matsui, Y. (1983) Thermodynamic analyses of equilibria involving olivine, orthopyroxene and garnet. *Geochim. Cosmochim. Acta*, v. 47, pp. 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.*, v. 13, pp. 114-133.
- Kawasaki, T. and Motoyoshi, Y. (2002) Silicic melts derived from a sapphirine-cordierite granulite of Rundvågshetta, East Antarctica under lower crustal conditions, (in preparation).
- Kawasaki, T., Ishikawa, M. and Motoyoshi, Y. (1993) A preliminary report on cordierite-bearing assemblages Rundvågshetta, Lützow-Holm bay, East Antarctica: evidence for a decompressional P-T path? *Proc. NIPR Symp. Antarct. Geosci.*, v. 6, pp. 47-56.
- Kawasaki, T., Sato, K. and Motoyoshi, Y. (2002) Experimental constraints on the thermal peak of a granulite from McIntyre Island, Enderby Land, East Antarctica. *Gondwana Res.*, v. 5, pp. 749-756.
- Kretz, R. (1983) Symbols for rock-forming minerals. *Amer. Mineral.*, v. 68, pp. 277-279.
- Lal, R.K. (1997) Internally-consistent calibrations for geothermobarometry of high-grade Mg-Al rich rocks in the system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and their application to sapphirine-spinel granulites of Eastern Ghats, India and Enderby Land, Antarctica. *Proc. Indian Acad. Sci. (Earth Planet. Sci.)*, v. 106, pp. 91-113.
- Motoyoshi, Y. and Hensen, B.J. (2001) F-rich phlogopite stability in ultrahigh-temperature metapelites from the Napier Complex, East Antarctica. *Amer. Mineral.*, v. 86, pp. 1404-1413.
- Motoyoshi, Y. and Ishikawa, M. (1997) Metamorphic and structural evolution of granulites from Rundvågshetta, Lützow-Holm Bay, East Antarctica. In: Ricci, C.A. (Ed.), *The Antarctic region: geological evolution and processes*. Siena, Terra Antarctica Publications, pp. 65-72.
- Motoyoshi, Y., Ishikawa, M. and Fraser, G.L. (1994) Reaction textures in granulites from Forefinger Point, Enderby Land, East Antarctica: an alternative interpretation of the metamorphic evolution of the Rayner Complex. *Proc. NIPR Symp. Antarct. Geosci.*, v. 7, pp. 101-114.
- Sakai, S. and Kawasaki, T. (1997) An experimental study of Fe-Mg partitionings between orthopyroxene and cordierite in the Mg-rich portion of the Mg<sub>2</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>-Fe<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> system at atmospheric pressure: its calibration of geothermometry for high-temperature granulites and igneous rocks. *Proc. NIPR Symp. Antarct. Geosci.*, v. 10, pp. 150-159.
- Sandiford, M., Neall, F.B. and Powell, R. (1987) Metamorphic evolution of aluminous granulites from Labwor Hills, Uganda. *Contrib. Mineral. Petrol.*, v. 95, pp. 217-225.
- Sato, K. and Kawasaki, T. (2002) High-pressure and high-temperature experiments on the phase relations in the system of Mg-rich garnet composition, (Fe<sub>0.25</sub>Mg<sub>0.75</sub>)<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>, and on the Fe-Mg partitioning between garnet and orthopyroxene. *Polar Geosci.*, v. 15 (in press).
- Viellard, P.H. (1992) Prediction of enthalpy of formation based on refined crystal structures of multisite compounds. Part 2: Application to minerals belonging to the system Li<sub>2</sub>O-Na<sub>2</sub>O-K<sub>2</sub>O-BeO-MgO-CaO-MnO-FeO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. Results and discussion. *Geochim. Cosmochim. Acta*, v. 58, pp. 4065-4108.
- Waters, D.J. (1986) Metamorphic history of sapphirine-bearing and related magnesian gneisses from Namaqualand, South Africa. *J. Petrol.*, v. 27, pp. 541-565.