#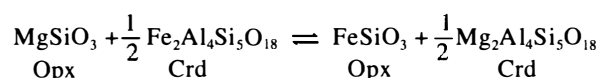 AN EXPERIMENTAL STUDY OF Fe–Mg PARTITIONINGS BETWEEN ORTHOPYROXENE AND CORDIERITE IN THE Mg-RICH PORTION OF THE $Mg_3Al_2Si_3O_{12}$–$Fe_3Al_2Si_3O_{12}$ SYSTEM AT ATMOSPHERIC PRESSURE: CALIBRATION OF ITS GEOTHERMOMETRY FOR HIGH-TEMPERATURE GRANULITES AND IGNEOUS ROCKS

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Abstract: Exchange reactions of Fe^{2+} and Mg^{2+} between orthopyroxene and cordierite (abbreviated to Opx and Crd, respectively):

$$MgSiO_3 + \frac{1}{2} Fe_2Al_4Si_5O_{18} \rightleftharpoons FeSiO_3 + \frac{1}{2}Mg_2Al_4Si_5O_{18}$$
$$\text{Opx} \qquad \text{Crd} \qquad\qquad \text{Opx} \qquad \text{Crd}$$

were experimentally investigated in the Mg-rich portion of the pyrope $(Mg_3Al_2Si_3O_{12})$– almandine $(Fe_3Al_2Si_3O_{12})$ system at temperatures from 1000°C to 1325°C under atmospheric pressure. Combining the volume data, the distribution coefficient of Fe–Mg partitionings between these phases, K_D $(= \dfrac{X_{Fe}^{Opx} \, X_{Mg}^{Crd}}{X_{Mg}^{Opx} \, X_{Fe}^{Crd}})$, was formulated as

$$\ln K_D = (1424 + 7.02P)/T - 0.619,$$

where P and T are in kbar and K. This reaction is temperature–dependent and would be a useful geothermometer.
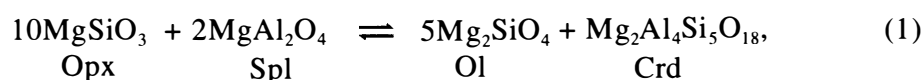
The applications of this orthopyroxene–cordierite thermometer to some Antarctic granulites yield equilibration temperatures of 100°C–200°C lower than the previous estimations. This suggests that the exchange reaction of Fe^{2+} and Mg^{2+} between orthopyroxene and cordierite continued down to closure temperatures of 500°C–600°C caused by subsequent cooling after the peak of metamorphism. Temperature estimations using the present orthopyroxene-cordierite thermometer for the igneous suites including S-type tonalite, rhyolite and granulitic xenoliths in andesite are in good agreement with those obtained from other thermometers.

key words: orthopyroxene, cordierite, Fe–Mg partitioning, geothermometer, granulite

1.   Introduction

In spite of the petrologic significance, we find ambiguities on the experimental constraints as to the phase relations and the Fe–Mg partitionings among olivine, orthopyroxene, cordierite, spinel and quartz which are the low-pressure assemblages of the pyrope $(Mg_3Al_2Si_3O_{12})$–almandine $(Fe_3Al_2Si_3O_{12})$ garnet system. Many experimental investigations have been carried out on the end member systems of garnets. Keesmann *et al.* (1971) studied the melting relations for the almandine $(Fe_3Al_2Si_3O_{12})$ composition at

pressures 10 to 26 kbar. Boyd and England (1959) carried out an experimental study on the phase relations for $Mg_3Al_2Si_3O_{12}$ (pyrope composition) in the $MgO-Al_2O_3-SiO_2$ system at pressure range of 15–47 kbar, and determined the stability field of pyrope garnet. Rankin and Merwin (1918), Schreyer and Schairer (1961) and Onuma and Arima (1975) studied the phase relations in the $MgO-Al_2O_3-SiO_2$ system at atmospheric pressure and reported that olivine+cordierite is the stable subsolidus assemblage. Chinner and Schairer (1962) reported that the assemblage of olivine+cordierite+spinel is stable above $1140°C$ for the $Mg_3Al_2Si_3O_{12}$ composition. Fawsett and Yoder (1966) and Seifert (1974) concluded that the phase boundary of the univariant reaction:

$$10MgSiO_3 + 2MgAl_2O_4 \rightleftharpoons 5Mg_2SiO_4 + Mg_2Al_4Si_5O_{18}, \qquad (1)$$
$$\text{Opx} \qquad\quad \text{Spl} \qquad\qquad \text{Ol} \qquad\qquad \text{Crd}$$

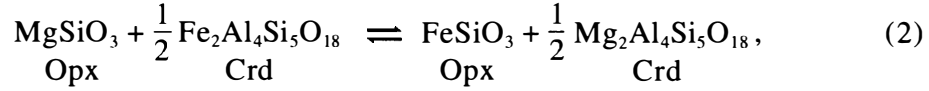has a negative slope $(dP/dT<0)$ and the assemblage of enstatite+spinel is stable on the high-temperature and high-pressure side. Hsu and Burnham (1969) concluded that the assemblage of olivine+cordierite+spinel+ fluid is stable on the low-temperature side and orthopyroxene+cordierite+spinel+fluid is the high-temperature assemblage from the hydrothermal experiments in the system $Mg_3Al_2Si_3O_{12}-Fe_3Al_2Si_3O_{12}-H_2O$.

Under these circumstances we have started experimental investigations on the phase relations as well as the Fe–Mg partitionings among the low-pressure assemblages of the pyrope $(Mg_3Al_2Si_3O_{12})$–almandine $(Fe_3Al_2Si_3O_{12})$ garnet system. Sakai and Kawasaki (1997) determined the phase relations for $Mg_3Al_2Si_3O_{12}$ (pyrope composition) in the system $MgO-Al_2O_3-SiO_2$ at temperatures from $1000°C$ to $1550°C$ under atmospheric pressure, and found that enstatite+spinel is the low-temperature assemblage below $1000°C$, and the forsterite–cordierite join is stable above $1025°C$. These results do not agree with those obtained previously from hydrothermal experiments (Fawsett and Yoder, 1966; Seifert, 1974; Hsu and Burnham, 1969).

This paper concerns the exchange of Fe^{2+} and Mg^{2+} between orthopyroxene and cordierite. The experimental constraints indicated that this reaction would be a useful geothermometer (Hensen and Green, 1972; Holdaway, 1976; Bertrand et al., 1991; Carrington and Harley, 1995; Carrington, 1995). However, these experimental studies were carried out at low temperatures and also done in a narrow temperature range. Moreover, calibrations to evaluate equilibrium temperatures were less precise. There is an urgent need to perform a series of experiments in order to calibrate the temperature dependence on the exchange of Fe^{2+} and Mg^{2+} between orthopyroxene and cordierite with high precision from the experimental data. In this paper we present new data on the Fe–Mg partitioning between orthopyroxene and cordierite through a wide range of temperatures in order to determine the temperature dependence and to calibrate an orthopyroxene-cordierite geothermometer.

2.   Thermodynamic Background

For the exchange of Fe^{2+} and Mg^{2+} between orthopyroxene and cordierite (abbreviated Opx and Crd, respectively):

$$\underset{\text{Opx}}{\text{MgSiO}_3} + \frac{1}{2}\underset{\text{Crd}}{\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}} \; \rightleftharpoons \; \underset{\text{Opx}}{\text{FeSiO}_3} + \frac{1}{2}\underset{\text{Crd}}{\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}}, \qquad (2)$$

the free energy change of the reaction (2), ΔG^o, in the standard state referring to the pure phases at the pressures and temperatures of interest is given by

$$-\Delta G^o = - (\Delta H^o - T\Delta S^o + P\Delta V^o)$$

$$= RT \ln K_{\text{Fe}\cdot\text{Mg}}^{\text{Opx}\cdot\text{Crd}}$$

$$= RT \ln K_D - (1 - 2X_{\text{Mg}}^{\text{Opx}})W_{\text{Fe}\cdot\text{Mg}}^{\text{Opx}} + (1 - 2X_{\text{Mg}}^{\text{Crd}})W_{\text{Fe}\cdot\text{Mg}}^{\text{Crd}}, \qquad (3)$$

where both orthopyroxene and cordierite are assumed to be regular solutions (THOMPSON, 1967) as the first approximation. Margules parameters, $W_{\text{Fe}\cdot\text{Mg}}^{\text{Opx}}$ and $W_{\text{Fe}\cdot\text{Mg}}^{\text{Crd}}$, are the interaction energies between Fe^{2+} and Mg^{2+} in orthopyroxene and cordierite per one mole for one exchangeable cation, and are equivalent to W_G in the notation of THOMPSON (1967). Parameters $X_{\text{Mg}}^{\text{Opx}}$ and $X_{\text{Mg}}^{\text{Crd}}$ denote the cationic mole fractions of Mg^{2+} in orthopyroxene and cordierite solid solutions, respectively. Thermodynamic variables ΔH^o, ΔS^o and ΔV^o are the enthalpy, entropy and volume changes of the chemical reaction (2), respectively. These are assumed to be constant or independent of both temperature and pressure under the present experimental conditions.

The effect of the Tschermak substitution:

$$\text{Mg}^{2+} + \text{Si}^{4+} \; \rightleftharpoons \; \text{Al}^{3+} + \text{Al}^{3+}, \qquad (4)$$
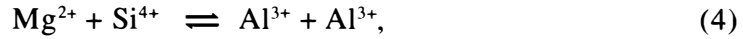
on the Fe–Mg exchange can be negligible. This effect is caused by non-ideal mixing of Mg–Al and Al–Fe in M1 sites of orthopyroxene. The quantity of this effect can be estimated from the following δ_{Al} term:

$$\delta_{\text{Al}} = -\frac{1}{2}X_{\text{Al}}^{\text{M1}}(W_{\text{Mg}\cdot\text{Al}}^{\text{M1}} - W_{\text{Al}\cdot\text{Fe}}^{\text{M1}}), \qquad (5)$$

which appeared in KAWASAKI and MATSUI's (1983) eq. (26). By adding this term to the righthand side of eq. (3), the free energy change of the reaction (2) would be modified. In the present experiments, however, δ_{Al} is small, ranging from 80 cal to 150 cal. Therefore, we can neglect the effect of the Tschermak substitution.

The distribution coefficient K_D is given by

$$K_D = \frac{X_{\text{Fe}}^{\text{Opx}}\, X_{\text{Mg}}^{\text{Crd}}}{X_{\text{Mg}}^{\text{Opx}}\, X_{\text{Fe}}^{\text{Crd}}}, \qquad (6)$$

and should be distinguished with the equilibrium constant $K_{\text{Fe}\cdot\text{Mg}}^{\text{Opx}\cdot\text{Crd}}$ defined by the ratio of activities a:

$$K_{\text{Fe}\cdot\text{Mg}}^{\text{Opx}\cdot\text{Crd}} = \frac{a_{\text{FeSiO}_3}^{\text{Opx}}\, (a_{\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}}^{\text{Crd}})^{1/2}}{a_{\text{MgSiO}_3}^{\text{Opx}}\, (a_{\text{Fe}_2\text{Al}_4\text{Si}_5\text{O}_{18}}^{\text{Crd}})^{1/2}}. \qquad (7)$$

We can evaluate the thermodynamic parameters, including ΔG°, $W_{Fe \cdot Mg}^{Opx}$ and $W_{Fe \cdot Mg}^{Crd}$, by the application of the least squares calculation for eq. (3) if we have a sufficient number of high quality data on the chemical compositions of coexisting orthopyroxene and cordierite at given physical conditions. This approach has been carried out successfully (Kawasaki and Ito, 1994).

3. Experimental Procedures

3.1. Starting materials

Oxide mixtures with garnet composition $(Mg_xFe_{1-x})_3Al_2Si_3O_{12}$, where x=0.6, 0.8 and 0.9, used in the present experiment as starting materials were prepared from regent-grade chemicals, namely, iron metal sponge, magnesium metal powder, aluminum metal powder and silica gel. In order to obtain chemically homogeneous oxide mixtures, weighted amounts of iron, magnesium and aluminum were dissolved in a dilute solution of nitric acid at about 80°C, and then silica gel was stirred into the solution. The mixtures were dried at 110°C for one day and were heated by a gas burner. In order to remove nitric acid completely, the mixture with x=0.8 was kept at 1000°C for 3 hours and others were kept at 500°C for about 12 hours. Dried materials were ground in an agate mortar under ethyl alcohol for one hour. Grain sizes of the oxide mixture were about 1–20 μm; about 30% of it was less than 5 μm after grinding.

3.2. Experimental technique

Powdered starting materials were hand-pressed to a pellet with about 3 mm thickness and 12.5 mm diameter in a die. The oxide mixture with garnet composition was reacted in a fine Pt-wire basket at high temperatures ranging from 1000°C to 1325°C using the electric furnace with oxygen controlling system at Ehime University. Oxygen fugacity equivalent to the iron–wüstite or wüstite–magnetite buffer was controlled by the mixed gas technique using CO_2–H_2 system for 16–388 hours. We employed the gas flow ratio as CO_2: H_2=0.7 l/min:0.3 l/min. We confirmed that wüstite was synthesized from hematite at 800°C and 1300°C under this gas flow ratio.

The temperatures at the top in the sample space and at the outer-side in contact with the reaction tube of the furnace were measured by the use of a $Pt/Pt_{87}Rh_{13}$ thermocouple. We found that the difference between the inner- and outer- temperatures of the furnace was within ±2°C for the run temperature range. In the present experiments we controlled the run temperatures by measurement of the outer-side temperature of the reaction tube. The run temperatures were kept constant within ±1°C of the nominal values. After being kept at a desired temperature for a certain duration, samples were quenched by dropping into distilled water in the bottom of the reaction tube.

We found, using a scanning electron microscope, a metastable phase, including silica mineral surrounded by orthopyroxene moat in the first synthesis (see Fig. 1A). We carried out two or three additional recrystallizing cycles with grinding between each cycle in order to obtain well crystallized and homogeneous orthopyroxene and cordierite without unreacted metastable materials (see Fig. 1B).
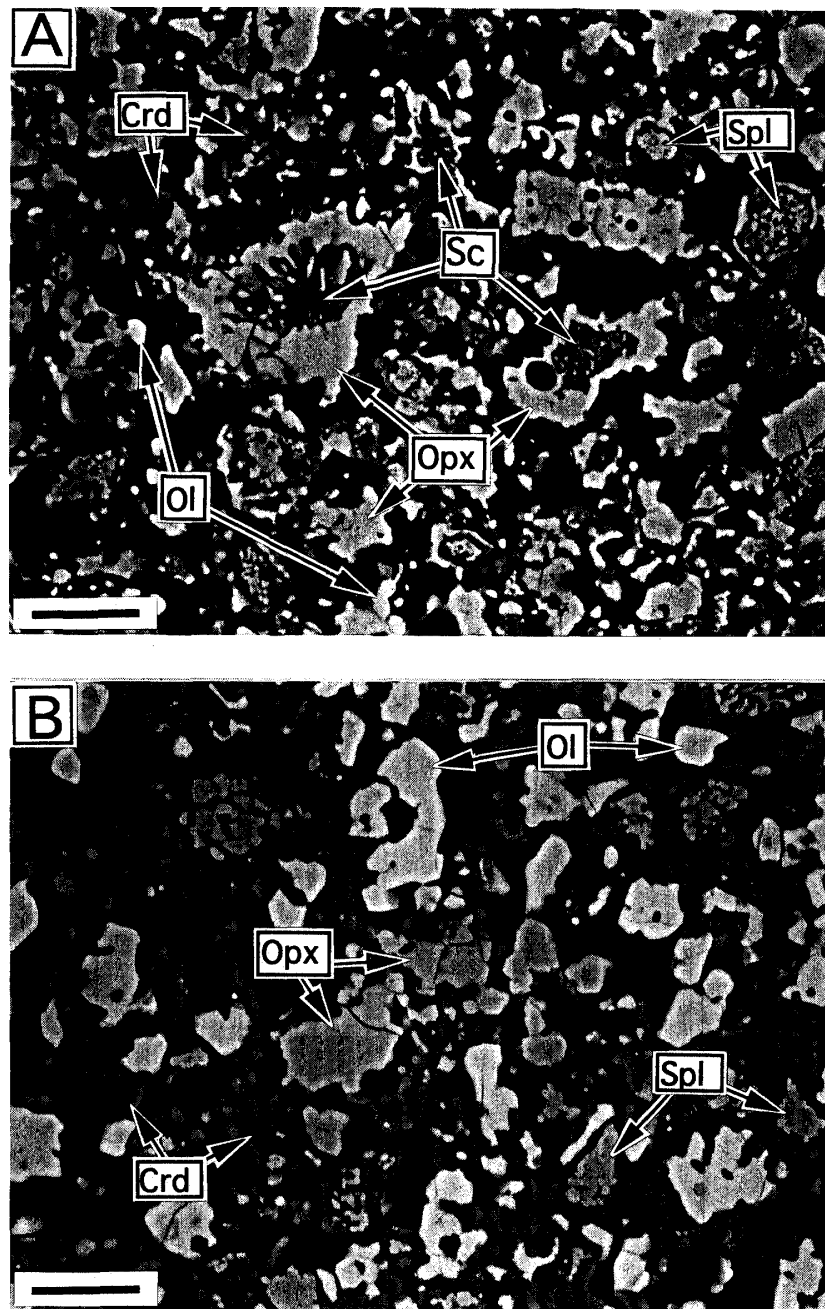
Fig. 1.A. Back scattered electron image (BSEI) of the run products sintered from oxide gel mixtures at 1200°C and atmospheric pressure under controlling oxygen fugacity (IW buffer) for 45 hours (Run No. 941227A). The Mg-value in bulk of this run is X_{Mg}=0.8. Unreacted silica minerals (tridymite?) persisted and were surrounded by orthopyroxene. Cordierites crystallized as fine grains contacted with olivines or as rather large crystals containing very fine spinel inclusions. Ol: olivine, Opx: orthopyroxene, Crd: cordierite, Spl: spinel, Sc: silica mineral (tridymite?).

B. Back scattered electron image (BSEI) of the run products sintered from crystalline mixtures at 1200°C and atmospheric pressure after 61 hours (Run No. 941230A). The starting material of this run was prepared by grinding run products of No. 941227A. Olivines and orthopyroxenes grew up to euhedral to subhedral crystals. Cordierites are anhedral crystals and often contain spinel inclusions. Silica minerals were not observed in this run. The bulk composition of this run contains as X_{Mg}=0.8.

3.3. Chemical analysis

The run products were mounted in epoxy resin and carefully polished for examination with the scanning electron microscope and microprobe analysis. Chemical compositions of all run products were determined with electron microprobe analyzers JEOL model JSM–5400 with a Link ISIS energy-dispersive system and JEOL model JXA–8800 with ZAF correction method. The instrumental conditions were as follows: the accelerating voltage 15 kV; Faraday cup current 4×10^{-10}A for JSM–5400 and 5×10^{-9}A for JXA–8800. Electron beam diameter was 1–2 μm, estimated from the size of contamination spots formed by excitation during analysis.

The accuracy of the chemical analyses was checked using test substances such as olivine, clinopyroxene and garnet from a garnet lherzolite. All relevant elements were measured simultaneously and at least 10–20 analyses were performed on both orthopyroxene and cordierite phases in every run. Acceptable analyses of the run products satisfied all the following criteria: agreement with the ideal stoichiometry within ±2% relative; total oxide weight per cent in the range 98–102%. We did chemical analyses in limited areas near the grain boundary of orthopyroxene and cordierite. If the analyses for a phase within one charge indicated heterogeneity in compositions, of which the mean standard error of X_{Mg} ($\sigma_{X_{Mg}}$) exceeded ±0.03, the run product was considered to be in non-equilibrium and all data of that run were discarded. Representative analyses of the synthesized orthopyroxenes and cordierites are given in Table 1.

Table 1.   Representative analyses of orthopyroxenes and cordierites synthesized at 1200°C (Run No. 941230A) and 1300°C (Run No. 960603).

Run No.	941230A		960603	
T	1200°C		1300°C	
Duration	61 hours		42 hours	
X_{Mg}^{bulk}	0.8		0.9	
Phase	Crd	Opx	Crd	Opx
Anal. No.	4	10	3	10
SiO₂	50.40	53.59	51.30	55.39
Al₂O₃	33.31	3.58	33.62	5.62
FeO	3.99	15.17	1.62	6.94
MgO	11.68	27.26	13.14	33.02
Totals	99.38	99.60	99.68	100.97
Number of Cations for N Oxygens				
$N=$	18	6	18	6
Si	5.028	1.927	5.046	1.891
Al	3.916	.152	3.898	.226
Fe	.333	.456	.133	.198
Mg	1.737	1.462	1.927	1.681
Totals	11.014	3.997	11.005	3.996
X_{Mg}	0.839	0.762	0.935	0.895

4. Experimental Results

Chemical compositions of coexisting orthopyroxenes and cordierites are summarized in Table 2. All the present experiments were carried out under subsolidus conditions, and we could not find any glass phase in the run products. The scanning electron microscope revealed that the run products consisted of an aggregation of olivine, orthopyroxene, cordierite and spinel with almost homogeneous granular texture, suggesting that the products were at or near chemical equilibrium. The grain sizes of the assemblages were 2–15 μm depending on temperature and run duration. Run products were large enough to determine the compositions of individual phases by the electron microprobe analysis, avoiding chemical contamination from surrounding minerals.

In all runs listed in Table 2, we found olivines and spinels coexisting with orthopyroxenes and cordierites. The ratio in the modal amounts of olivine and orthopyroxene increases with increasing temperature. This indicates that the reaction (1) would progress to right-hand side with elevating temperature, showing that olivine+cordierite is a high-temperature assemblage and orthopyroxene-spinel join is stable on the low-temperature side, as has been pointed out by SAKAI and KAWASAKI (1997). Details of the phase relations of the pyrope $(Mg_3Al_2Si_3O_{12})$–almandine $(Fe_3Al_2Si_3O_{12})$ system will be described elsewhere.

In order to estimate the reliabilities of each synthetic experiment, mean standard errors $\sigma_{X_{Mg}^{Opx}}$ and $\sigma_{X_{Mg}^{Crd}}$ were calculated from all analytical data in the compositions of orthopyroxenes and cordierites. These standard errors are also given in Table 2. The inverse squares of these standard errors are assumed to be proportional to the weights of data sets ($1/\sigma^2 \propto$ weight: DEMING, 1943). These parameters were used in the least squares fittings.

Table 2. Experimental data for chemical compositions of orthopyroxene and cordierite coexisting with olivine and spinel.

Run No.	T (°C)	Duration	X_{Mg}^{bulk}	X_{Mg}^{Opx}	X_{Mg}^{Crd}	K_D
960605	1325	22h	0.9	0.913(4)[1]	0.927(2)	1.21(7)
960603	1300	42h	0.9	0.905(10)	0.928(6)	1.35(20)
941230A	1200	61h	0.8	0.763(3)	0.837(5)	1.60(6)
950517A	1100	147h	0.8	0.758(9)	0.830(7)	1.56(11)
950717	1050	199h	0.8	0.765(8)	0.839(3)	1.60(8)
951127A	1000	388h	0.8	0.762(3)	0.841(10)	1.65(13)
950809	1100	43h	0.6	0.589(7)	0.681(24)	1.49(17)
951127B	1000	310h	0.6	0.602(10)	0.700(7)	1.54(8)

[1]Standard errors are in parentheses and refer to the last decimal place.

5. Discussion

5.1. Least squares fitting

In Fig. 2A, compositions of coexisting orthopyroxene and cordierite are plotted in the form of the distribution coefficient K_D as a function of the inverse of temperature $1/T$. This figure indicates that the exchange of Fe^{2+} and Mg^{2+} between orthopyroxene cordierite is highly temperature-dependent. Attempts at four-variable (ΔH°, ΔS°, $W_{Fe \cdot Mg}^{Opx}$ and $W_{Fe \cdot Mg}^{Crd}$) least squares regression using eq. (3) were not successful, and stable solutions were not obtained. We found that the results yielded large standard errors for both $W_{Fe \cdot Mg}^{Opx}$ and $W_{Fe \cdot Mg}^{Crd}$ terms. We believe that such calculations have no meaning in themselves. The terms $W_{Fe \cdot Mg}^{Opx}$ and $W_{Fe \cdot Mg}^{Crd}$ are poorly constrained in the present regression because the present experiments were carried out for the Mg-rich portions in the system $Fe_3Al_2Si_3O_{12}$–$Mg_3Al_2Si_3O_{12}$, showing that coefficients of these terms do not depend on composition. Therefore, the free energy change of reaction ΔG° in eq. (3) is rewritten as

$$-\Delta G^\circ = -(\Delta H^\circ - T\Delta S^\circ + P\Delta V^\circ)$$

$$\simeq RT \ln K_D + W_{Fe \cdot Mg}^{Opx} - W_{Fe \cdot Mg}^{Crd} . \qquad (8)$$

This equation is equivalent to the Fe–Mg partitioning between ideal solutions (KAWASAKI and ITO, 1994):

$$-\Delta H^* + T\Delta S^\circ - P\Delta V^\circ = RT \ln K_D , \qquad (9)$$

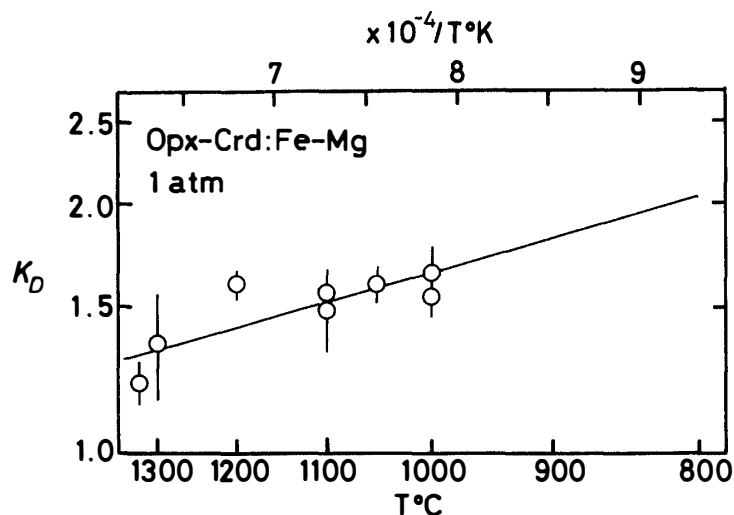where the effective enthalpy change of reaction (2), ΔH^*, is given by

Fig. 2A.   Least squares result of the distribution coefficient K_D against $1/T$ for the exchange of Fe^{2+} and Mg^{2+} between orthopyroxene and cordierite at atmospheric pressure. Open circles and vertical bars are the experimental data of the distribution coefficient K_D. Line is the calculated K_D at atmospheric pressure: $\ln K_D = 1424/T(K) - 0.619$. The distribution coefficient K_D increases with decreasing temperature.

$$\Delta H^* = \Delta H^\circ + W_{Fe\cdot Mg}^{Opx} - W_{Fe\cdot Mg}^{Crd}. \tag{10}$$

We can evaluate the temperature dependence of the Fe–Mg partitioning between orthopyroxene and cordierite using this equation.

Results of the curve fitting are shown in Fig. 2A as the relation between the distribution coefficient K_D and the run temperature. The results of the present least squares analyses are given by

$$\left. \begin{aligned} \Delta H^* \ (cal) &= -2830 \pm 530 \\ \Delta S^\circ \ (cal/K) &= -1.230 \pm 0.430 \end{aligned} \right\}. \tag{11}$$

The curve fits are quite satisfactory, as seen in Fig. 2A. The good fit implies that the exchange reaction of Fe^{2+} and Mg^{2+} between orthopyroxene and cordierite can be described with reasonable precision by eq. (9) under the present experimental conditions.

5.2. Pressure- and temperature-dependence of the Fe–Mg partitioning between orthopyroxene and cordierite

The effect of pressure on the free energy change of reaction (2) ΔG° at constant temperature is predicted by the ΔV° term in eq. (9), based on the anhydrous molar volume data of orthopyroxene (WEAST et al., 1989) and cordierite (PERCHUK et al., 1979). Using ΔV° of -13.95 cal/kbar in Table 3, the linear regression of the values of K_D leads to the following result:

$$\ln K_D = (1424 + 7.02P)/T - 0.619. \tag{12}$$

In Fig. 2B, we present the pressure effect on the Fe–Mg partitioning calculated from the volume data in Table 3. This pressure effect is very small. From Fig. 2B we can read values of K_D at 10 kbar and 1000°K to be 2.40. The value of dK_D/dP is roughly estimated to be 0.02/kbar. The ΔV° term given in Table 3 has a small value. This indicates that the Fe–Mg partitioning is not sensitive to the pressure variation, especially in the Mg-rich system.

The temperature dependence of K_D originates from the magnitude of the entropy change ΔS°, which has a fairly large value in the Mg-rich system given in eq. (11), with

Table 3. Volume data.

End member	V (cal/kbar/mol)	Reference
$Mg_2Al_4Si_5O_{18}$	558.23	PERCHUK et al. (1979)
$Fe_2Al_4Si_5O_{18}$	568.48	PERCHUK et al. (1979)
$MgSiO_3$	75.14(12)	WEAST et al. (1989)
$FeSiO_3$	78.87(8)	WEAST et al. (1989)

$$MgSiO_3 + \tfrac{1}{2}Fe_2Al_4Si_5O_{18} \rightleftharpoons FeSiO_3 + \tfrac{1}{2}Mg_2Al_4Si_5O_{18}$$

Opx   Crd   Opx   Crd
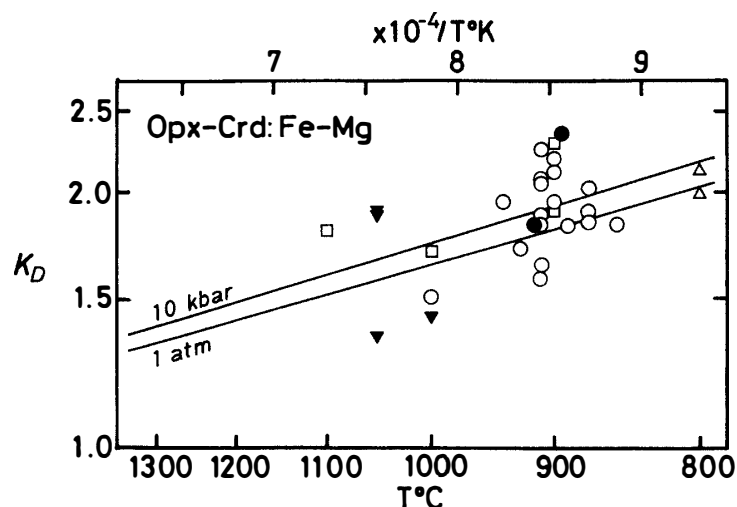
$$\Delta V^\circ = -13.95 \ cal/kbar$$

Fig. 2B. Comparison of the present least squares result and previous data for the relation between
distribution coefficient K_D and temperature. Line at 1 atm (lower) is the result of the present
least squares. Line at 10 kbar (upper) is calculated from eq. (12) assuming the reference
pressure is to be 10 kbar. Plotted data are obtained from previous experiments [□: Hensen
and Green (1972); △: Holdaway (1976); ○: Carrington and Harley (1995); ●: Carrington
(1995); ▼: Bertrand et al. (1991)]. Present result obtained from the high-temperature
experiments is consistent with the previous data at low temperatures.

the result that the Fe–Mg partitioning in the orthopyroxene–cordierite pair is sensitive to
temperature in the Mg-rich system (see Fig. 2A). The results of previous experiments
(Hensen and Green, 1972; Holdaway, 1976; Carrington and Harley, 1995; Carrington,
1995; Bertrand et al., 1991) are given in Fig. 2B for comparison. As is seen in Fig. 2B,
the present result is in agreement with these previous experiments within the experimen-
tal uncertainties.

5.3. Thermometry of high-temperature granulites and igneous rocks

The temperature conditions of equilibration of granulites and igneous rocks can be
assessed through the orthopyroxene–cordierite thermometry. Results of calculations of
temperature for Antarctic granulites from Spot Height 945 (Ellis, 1980), Forefinger Point
(Harley et al., 1990; Motoyoshi et al., 1995), Rundvågshetta (Kawasaki et al., 1993)
and Austkampane in the Sør Rondane Mountains (Ishizuka et al., 1995), and related
granulites from the Sipiwesk Lake area of Pikwitonei granulite terrain, Manitoba, Canada
(Arima and Barnett, 1984), Namaqualand, South Africa (Waters, 1986) and Araku,
Eastern Ghats, India (Sengupta et al., 1991) are summarized in Table 4. The exchange
thermometry of Fe^{2+} and Mg^{2+} between orthopyroxene and cordierite gives us the mini-
mum temperatures in these granulites, compared with the previous estimates. These dis-
crepancies in the estimated temperatures could be caused partly by an exchange reaction
of Fe^{2+} and Mg^{2+} between orthopyroxene and cordierite that continues down to the clo-
sure temperatures through the retrograde metamorphism occurring after the peak of
metamorphism.

The orthopyroxene–cordierite thermometry for the volcanic rock suite including

Table 4. Thermometry of high-temperature granulites and igneous rocks.

Locality	$T°C*$	P kbar/$T°C$	Reference
<Antarctic Granulites>			
Spot Height 945	515–593	8–10/900–980	Ellis (1980)
Forefinger Point, Peak	645,729	10/900	Motoyoshi et al. (1995)
Forefinger Point, Retrograde	599–662	5/750	Harley et al. (1990)
Rundvågshetta	577,612	7–8/760–830	Kawasaki et al. (1993)
		8.5/920	Motoyoshi et al. (1993)
Sør Rondane	647	4/820–870	Ishizuka et al. (1995)
<Other Granulites>			
Sipiwesk Lake, Canada	581–615	3–11.2/860–890	Arima and Barnett (1984)
Namaqualand, South Africa	568–709	5/750–800	Waters (1986)
Eastern Ghats, India	612	8.5/960	Sengupta et al. (1991)
<Igneous Rock Suite>			
Xenoliths in Kuromori-yama andesite	807–855	3–5/800–850**	Komatsu et al. (1995)
Violet Town rhyolite	869	4/850	Clemens and Wall (1984)
Hidaka tonalite	721[a]	6/750–760	Shimura et al. (1992)
	563[b]	6/700	Shimura et al. (1992)

*Estimated from eq. (12), assuming the reference pressure is to be 10 kbar.
**From personal communications with Prof. Komatsu.
[a]Temperature was estimated from chemical data of orthopyroxene rim and cordierite core.
[b]Estimated from chemical compositions of rims of orthopyroxene and cordierite.

Violet Town rhyolite in central Victoria, Australia (Clemens and Wall, 1984) and xenoliths of the garnet–biotite-sillimanite gneiss in the Ishizuchi andesite from Kuromori-yama, southern Matsuyama, Japan (Komatsu et al., 1996) gives temperatures consistent with previous estimations. This implies that orthopyroxene–cordierite thermometry yields precisely the temperature quenched by volcanic eruptions.

As has been mentioned above, we must pay careful attention to apply the orthopyroxene–cordierite thermometry to the slowly cooled rocks such as high-temperature granulites. In the case of S-type tonalite of the Hidaka metamorphic belt, northern Japan (Shimura et al., 1992), we find a good example indicating the highest (peak) and lowest (closure) temperatures for the orthopyroxene–cordierite equilibrium (Table 4). Simura et al. (1992) estimated that crystallization of this tonalite took place at about 6 kbar and 900°C–700°C, and determined the crystallization sequence from the textural and compositional evidences: (1) crystallization of orthopyroxene from magma began at 860°C and finished at 760°C; and: (2) cordierite appeared at 750°C in the magma. Using chemical data of the orthopyroxene rim and cordierite core, the highest temperature in equilibrium between orthopyroxene and cordierite was estimated to be 721°C. The lowest (closure?) temperature was calculated to be 563°C from the compositions of rims of both orthopyroxene and cordierite. As in this case, we can evaluate the highest temperature of orthopyroxene–cordierite equilibrium from careful use of the chemical data.

6. Conclusion

The Fe–Mg partition between orthopyroxene and cordierite is very sensitive to the variations of temperature, but insensitive to pressure. This indicates that the exchange reaction would be a useful geothermometer.

Acknowledgments

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