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An experimental determination of the exchange reaction of Fe^{2+} and Mg^{2+} between olivine and Ca-rich clinopyroxene

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Abstract

High-pressure experiments were carried out to determine the Fe-Mg mixing properties of Ca-rich clinopyroxene and the temperature and pressure dependence of Fe-Mg partitioning with olivine over a temperature range 1100–1500 °C at 75 kbar, and at 900 and 1100 °C at 30 kbar. Combining new and previously published data (Kawasaki and Ito, 1992; Perkins and Vielzeuf, 1992), thermodynamic analyses were carried out on the following chemical reaction:

$$\underset{\text{olivine}}{\tfrac{1}{2}Fe_2SiO_4} + \underset{\text{clinopyroxene}}{CaMgSi_2O_6} = \underset{\text{olivine}}{\tfrac{1}{2}Mg_2SiO_4} + \underset{\text{clinopyroxene}}{CaFeSi_2O_6}. \qquad (1)$$

Symmetric regular solution models for both olivine and clinopyroxene are sufficient to describe the mixing properties. Using the Fe-Mg mixing parameter of olivine solid solution [$(W^{ol}_{H})_{FeMg}$ = 1540 cal: Kawasaki and Matsui, 1983] and the unit-cell volume data of olivine [$(W^{ol}_{V})_{FeMg}$ = 2.22 cal/kbar: Akimoto and Fujisawa, 1968] and clinopyroxene [$(W^{cpx}_{V})_{FeMg}$ = −5.14 cal/kbar: Perkins and Vielzeuf, 1992], the free energy change (ΔG^0) of Reaction 1 and the Fe-Mg mixing parameter of clinopyroxene (W^{cpx}_{FeMg}) are evaluated by the application of a nonlinear least-squares technique and found to be ΔG^0 (cal) = (4960 ± 230) − (2.66 ± 0.15)T (K) + 7.17P (kbar) and W^{cpx}_{FeMg} (cal) = (800 ± 380) + (0.54 ± 0.26)T (K) − 5.14P (kbar). The exchange reaction of Fe^{2+} and Mg^{2+} between olivine and clinopyroxene is temperature dependent, but insensitive to pressure. This reaction would be a geothermometer.

Introduction

At the present stage of mineralogical thermodynamics little is known about the Fe-Mg mixing properties of clinopyroxene. Many authors have accepted that diopside-enstatite solid solution can be described as a regular solution (Newton et al., 1979; Holland et al., 1979; Lindsley and Davidson, 1980; Lindsley et al., 1981; Davidson et al., 1988; Gasparik, 1990). The qualitative mixing properties of clinopyroxene have been illustrated by the Fe-Mg partitionings with orthopyroxene in granulites (Saxena, 1971; Froese and Gordon, 1974; Kawasaki and Matsui, 1978) and with garnet in peridotites (Oka and Matsumoto, 1974). However, absolute values of the Margules parameters for mixing of Fe^{2+} and Mg^{2+} in the clinopyroxene solid solution cannot be derived directly, and only the ratios of thermodynamic parameters to the temperature ($\Delta G^0/RT$ and W^{cpx}_{FeMg}/RT) would be evaluated from these analyses using the natural data because the equilibration temperature remains unknown.

Hydrothermal experiments on the exchange of Fe^{2+} and Mg^{2+} between chloride solution and clinopyroxene by Iiyama (1982) suggested that clinopyroxene would behave as an asymmetric regular solution, which is only slightly asymmetric and is virtually equivalent to a symmetric regular solution with W^{cpx}_{FeMg} = 1.6 kcal. From Fe-Mg partition experiments between olivine and clinopyroxene, Kawasaki and Ito (1992) found W^{cpx}_{FeMg} to be 920 ± 210 cal at 75 bar ad 1300 °C, whereas Perkins and Vielzeuf (1992) obtained 950 ± 100 cal at 10.5 kbar and 1000 °C. These two values are consistent within ±1 σ.

These experimental results suggest that the hedenbergite-diopside solid solution would be nonideal with a positive deviation from the Raoult's law. However, we are still far from a quantitative understanding of the mixing properties of clinopyroxene, including the temperature- and pressure-dependence of the excess energy for mixing. The best way to reveal the Fe-Mg mixing properties of clinopyroxene is to analyze the experimental data of the Fe-Mg partitioning with olivine. We have accumulated fairly reliable data for the thermodynamic properties of $(Fe,Mg)_2SiO_4$ olivine from studies of the Fe-Mg exchange equilibrium with orthopyroxene (Nafziger and Muan, 1967; Kitayama and Katsura, 1968; Medaris, 1969; Matsui and Nishizawa, 1974), garnet (Kawasaki and Matsui, 1977; Kawasaki, 1979; O'Neill and Wood, 1979; Kawasaki and Matsui, 1983; Hackler and Wood, 1989), spinel (Engi, 1983), and chloride solution (Schulien et al., 1972;

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Bartholomew, 1989). We also have data from calorimetric measurements (Wood and Kleppa, 1981; Thierry et al., 1981; Wiser and Wood, 1991; Kojitani and Akaogi, 1993). These data suggest that olivine is essentially a symmetric regular solution with $W^{\mathrm{ol}}_{\mathrm{FeMg}} = 1.7\text{–}2.6$ kcal at temperatures 700–1300 °C. This enables us to determine the mixing properties of $\mathrm{Ca(Fe,Mg)Si_2O_6}$ clinopyroxene with high precision from the Fe-Mg partitioning data.

The Fe-Mg partitioning in an olivine + clinopyroxene pair has received little attention. Experimental calibrations have been made in only two studies (Kawasaki and Ito, 1992; Perkins and Vielzeuf, 1992). This chemical equilibrium has been proposed as an empirical geothermometer (Mori and Banno, 1973; Obata et al., 1974). Powell and Powell (1974) discussed the olivine-clinopyroxene geothermometer with no experimental evidence. As has been pointed out by Wood (1976), the Powells' geothermometer is, however, erroneous because the derived values of mixing parameters imply a large miscibility gap in $\mathrm{CaFeSi_2O_6}$-$\mathrm{CaMgSi_2O_6}$-$\mathrm{CaAl_2SiO_6}$ clinopyroxene at high temperatures.

In this study we present new data on the Fe-Mg partitioning between olivine and clinopyroxene at a wide range of temperatures and pressures in order to determine its temperature-, pressure-, and composition-dependence and to calibrate an olivine-clinopyroxene geothermometer.

THERMODYNAMIC BACKGROUND

The exchange of $\mathrm{Fe^{2+}}$ and $\mathrm{Mg^{2+}}$ between olivine and clinopyroxene (abbreviated to ol and cpx, respectively) on the join of hedenbergite and diopside can be expressed by

$$\underset{\mathrm{ol}}{\tfrac{1}{2}\mathrm{Fe_2SiO_4}} + \underset{\mathrm{cpx}}{\mathrm{CaMgSi_2O_6}} = \underset{\mathrm{ol}}{\tfrac{1}{2}\mathrm{Mg_2SiO_4}} + \underset{\mathrm{cpx}}{\mathrm{CaFeSi_2O_6}}. \quad (1)$$

At equilibrium, we have Equation 2:

$$\Delta G = \tfrac{1}{2}\mu^{\mathrm{ol}}_{\mathrm{Mg_2SiO_4}} + \mu^{\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}} - \tfrac{1}{2}\mu^{\mathrm{ol}}_{\mathrm{Fe_2SiO_4}} - \mu^{\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}} = 0 \quad (2)$$

where μ^{A}_{i} refers to the chemical potential of the component i in the phase A at the pressure and temperature of interest.

Using the activity and the standard-state chemical potential (μ^0), chemical potentials in Equation 2 are algebraically defined as

$$\mu^{\mathrm{ol}}_{\mathrm{Mg_2SiO_4}} = \mu^{0,\mathrm{ol}}_{\mathrm{Mg_2SiO_4}} + \mathrm{R}T\ln a^{\mathrm{ol}}_{\mathrm{Mg_2SiO_4}}$$

$$= \mu^{0,\mathrm{ol}}_{\mathrm{Mg_2SiO_4}} + 2\mathrm{R}T\ln X^{\mathrm{ol}}_{\mathrm{Mg}} + \mathrm{R}T\ln \gamma^{\mathrm{ol}}_{\mathrm{Mg_2SiO_4}} \quad (3a)$$

$$\mu^{\mathrm{ol}}_{\mathrm{Fe_2SiO_4}} = \mu^{0,\mathrm{ol}}_{\mathrm{Fe_2SiO_4}} + \mathrm{R}T\ln a^{\mathrm{ol}}_{\mathrm{Fe_2SiO_4}}$$

$$= \mu^{0,\mathrm{ol}}_{\mathrm{Fe_2SiO_4}} + 2\mathrm{R}T\ln X^{\mathrm{ol}}_{\mathrm{Fe}} + \mathrm{R}T\ln \gamma^{\mathrm{ol}}_{\mathrm{Fe_2SiO_4}} \quad (3b)$$

$$\mu^{\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}} = \mu^{0,\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}} + \mathrm{R}T\ln a^{\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}}$$

$$= \mu^{0,\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}} + \mathrm{R}T\ln X^{\mathrm{cpx}}_{\mathrm{Mg}} + \mathrm{R}T\ln \gamma^{\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}} \quad (3c)$$

and

$$\mu^{\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}} = \mu^{0,\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}} + \mathrm{R}T\ln a^{\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}}$$

$$= \mu^{0,\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}} + \mathrm{R}T\ln X^{\mathrm{cpx}}_{\mathrm{Fe}} + \mathrm{R}T\ln \gamma^{\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}} \quad (3d)$$

where X and γ are the cationic mole fraction and activity coefficient, respectively. In Equations 3a and 3b, the factor 2 is the number of sites of olivine formula unit on which mixing takes place. By the substitution of Equation 3 into Equation 2, the condition of Equilibrium 2 is rewritten using the free energy change of Reaction 1, ΔG^0, for pure phases at the pressures and temperatures of interest:

$$-\Delta G^0 = -(\Delta H^0 - T\Delta S^0 + P\Delta V^0)$$

$$= -(\tfrac{1}{2}\mu^{0,\mathrm{ol}}_{\mathrm{Mg_2SiO_4}} + \mu^{0,\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}} - \tfrac{1}{2}\mu^{0,\mathrm{ol}}_{\mathrm{Fe_2SiO_4}} - \mu^{0,\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}})$$

$$= \mathrm{R}T\ln K$$

$$= \mathrm{R}T\ln K_{\mathrm{D}} + \mathrm{R}T\ln K_{\gamma}$$

$$= \mathrm{R}T\ln K_{\mathrm{D}} + \tfrac{1}{2}\mathrm{R}T\ln\frac{\gamma^{\mathrm{ol}}_{\mathrm{Mg_2SiO_4}}}{\gamma^{\mathrm{ol}}_{\mathrm{Fe_2SiO_4}}} + \mathrm{R}T\ln\frac{\gamma^{\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}}}{\gamma^{\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}}} \quad (4)$$

where the equilibrium constant K, the distribution coefficient K_{D}, and the quotient of activity coefficients K_{γ} are defined as

$$K = \frac{(a^{\mathrm{ol}}_{\mathrm{Mg_2SiO_4}})^{1/2} a^{\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}}}{(a^{\mathrm{ol}}_{\mathrm{Fe_2SiO_4}})^{1/2} a^{\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}}} \quad (5a)$$

$$K_{\mathrm{D}} = \frac{X^{\mathrm{ol}}_{\mathrm{Mg}} X^{\mathrm{cpx}}_{\mathrm{Fe}}}{X^{\mathrm{ol}}_{\mathrm{Fe}} X^{\mathrm{cpx}}_{\mathrm{Mg}}} \quad (5b)$$

$$K_{\gamma} = \frac{(\gamma^{\mathrm{ol}}_{\mathrm{Mg_2SiO_4}})^{1/2} \gamma^{\mathrm{cpx}}_{\mathrm{CaFeSi_2O_6}}}{(\gamma^{\mathrm{ol}}_{\mathrm{Fe_2SiO_4}})^{1/2} \gamma^{\mathrm{cpx}}_{\mathrm{CaMgSi_2O_6}}}. \quad (5c)$$

There are many thermodynamic models that describe the mixing properties of olivine and clinopyroxene. Hirschmann (1991) adopted the double-sited model for the $\mathrm{(Ca,Mg,Fe)_2SiO_4}$ ternary olivine and evaluated the nonidealities of calcium-magnesium and calcium-iron olivines. The effect of $\mathrm{Ca^{2+}}$ in olivine on the ΔG^0 in Equation 4 is negligible for the present experiment because the content of Ca in olivine is very small (Appendix 1).

Kojitani and Akaogi (1993) reported the experimental results of the calorimetric measurements that the $\mathrm{(Fe,Mg)_2SiO_4}$ binary olivine solid solutions have a positive excess enthalpy of mixing deviated symmetrically from ideality. Hackler and Wood (1989) also confirmed that olivine is essentially a symmetric solution. In the present analysis we assume that olivines in equilibrium with Ca-rich clinopyroxenes would behave as the Fe-Mg symmetric regular solution for the first approximation. Therefore, the activity coefficients of olivine are given by

$$\mathrm{R}T\ln \gamma^{\mathrm{ol}}_{\mathrm{Mg_2SiO_4}} = 2(X^{\mathrm{ol}}_{\mathrm{Fe}})^2 W^{\mathrm{ol}}_{\mathrm{FeMg}} \quad (6a)$$

and

$$RT \ln \gamma^{ol}_{Fe_2SiO_4} = 2(X^{ol}_{Mg})^2 W^{ol}_{FeMg} \qquad (6b)$$

where W^{ol}_{FeMg} is the Margules parameter and denotes the interaction energy between Fe^{2+} and Mg^{2+} in olivine per mole for one exchangeable cation.

Although the double-sited solution model was proposed for the quadrilateral clinopyroxene (e.g., Davidson, 1985; Davidson and Lindsley, 1985, 1989), we prefer to treat clinopyroxene as the $Ca(Fe,Mg)Si_2O_6$ binary regular solution with symmetric excess energy for mixing (see Appendix 2). As has been discussed by Perkins and Vielzeuf (1992), this model adequately describes our experimental results because the clinopyroxenes are nearly saturated in Ca and close to the hedenbergite-diopside join for all experiments.

Therefore, activity coefficients of hedenbergite and diopside components of clinopyroxene solid solution are

$$RT \ln \gamma^{cpx}_{CaMgSi_2O_6} = (X^{cpx}_{Fe})^2 W^{cpx}_{FeMg} \qquad (6c)$$

and

$$RT \ln \gamma^{cpx}_{CaFeSi_2O_6} = (X^{cpx}_{Mg})^2 W^{cpx}_{FeMg} \qquad (6d)$$

where W^{cpx}_{FeMg} is equivalent to α, W_G, and w in the notations of Prigogine and Defay (1954), Thompson (1967), and Guggenheim (1977), respectively. We can interpret W^{cpx}_{FeMg} as the Fe-Mg interaction parameter at the M1 site of clinopyroxene. This parameter is equivalent to W^{M1} in Equation A7, following the notation of Davidson and Lindsley (1989).

The Fe-Mg mixing parameter is generally expressed by the following equation:

$$W = W_H - TW_S + PW_V \qquad (7)$$

where W_H, W_S, and W_V are the nonideal parameters for enthalpy, entropy, and volume. For the Fe-Mg binary solution of phase A, the $(W^A_V)_{FeMg}$ is defined as follows (e.g., O'Neill and Wood, 1979):

$$V^A - V^{0,A}_{Mg} X^A_{Mg} - V^{0,A}_{Fe} X^A_{Fe} = V^{A,ex}_{FeMg} = X^A_{Fe} X^A_{Mg} (W^A_V)_{FeMg} \qquad (8)$$

where $V^{0,A}_i$ is the molar volume of the pure i of the phase A and the excess volume $V^{A,ex}_{FeMg}$ is assumed to be expressed by a symmetric function with respect to composition because we adopt the symmetric solution models for both olivine and clinopyroxene. The values of $2(W^{ol}_V)_{FeMg}$ and $(W^{cpx}_V)_{FeMg}$ are given in Table 1. Relations between excess volume and composition for olivine and clinopyroxene are illustrated in Figure 1A and 1B, respectively.

Akimoto and Fujisawa (1968) found the slightly positive excess volumes of mixing for the Fe_2SiO_4-Mg_2SiO_4 olivine solid solution (Fig. 1A). The deviation from the linearity is calculated to be 0.186 ± 0.049 cm³/mol in the term of $2(W^{ol}_V)_{FeMg}$ on the basis of Equation 8. As is seen Figure 1A, there are, however, some discrepancies between the results of volume data of Akimoto and Fujisawa (1968) and other authors (Fisher and Medaris, 1969; Perkins and Vielzeuf, 1992). Values of $2(W^{ol}_V)_{FeMg}$ are estimated to be 0.322 ± 0.021 cm³/mol from the data of Fisher and Medaris (1969) and 0.335 ± 0.052 cm³/mol from Perkins and Vielzeuf's data (1992).

TABLE 1. Volume data (cm³/mol)

$V^{0,ol}_{Fe_2SiO_4}$	$V^{0,ol}_{Mg_2SiO_4}$	$2(W^{ol}_V)_{FeMg}$	Ref.
46.28(2)	43.68(2)	0.186(49)	1
46.26(4)	43.62(2)	0.322(21)	2
46.30(3)	43.65(2)	0.335(52)	3
$V^{0,cpx}_{CaFeSi_2O_6}$	$V^{0,cpx}_{CaMgSi_2O_6}$	$(W^{cpx}_V)_{FeMg}$	
67.82(4)	66.25(4)	0.036(74)	4
68.08(3)	—	0.924(125)	5
67.90(5)	66.20(3)	−0.034(72)	6
67.91(5)	66.31(3)	−0.215(81)	3

Note: 1 = Akimoto and Fujisawa (1968); 2 = Fisher and Medaris (1969); 3 = Perkins and Vielzeuf (1992); 4 = Rutstein and Yund (1969); 5 = Matsui et al. (1972); 6 = Turnock et al. (1973).

O'Neill and Wood (1979) evaluated W^{ol}_{FeMg} to be 1051 cal at 50 kbar and 1100 °C from the Fe-Mg partition experiments between olivine and garnet by Kawasaki and Matsui (1977) and found it in good agreement with their own value of 990 cal at 30 kbar and 1100 °C. By the addition of the excess volume term to their 30-kbar result, they found W^{ol}_{FeMg} of 1050 cal at 50 kbar and 1100 °C if they used Akimoto and Fujisawa's (1968) volume data. O'Neill and Wood (1979), therefore, concluded that the mixing parameter W^{ol}_{FeMg} is independent of temperature, and they adopted the excess volume term calculated from Akimoto and Fujisawa's data of unit-cell parameters of olivine solid solution. We follow the recommendation of O'Neill and Wood (1979) and adopt the excess volume evaluated from the data of Akimoto and Fujisawa (1968). We, therefore, assume that the nonideality of olivine, W^{ol}_{FeMg}, is found to increase systematically with increasing pressure and to be temperature independent.

This assumption for the mixing property cannot be extended to the $Ca(Fe,Mg)Si_2O_6$ clinopyroxene solid solution. The values of $(W^{cpx}_V)_{FeMg}$ are also given in Table 1, derived from the data of the molar volumes of the $CaFeSi_2O_6$-$CaMgSi_2O_6$ clinopyroxene reported by Rutin and Yund (1969), Matsui et al. (1972), Turnock et al. (1973), and Perkins and Vielzeuf (1992). There are some disparities among these data (Fig. 1B). Matsui et al. (1972) found an appreciably positive excess volume on the hedenbergite-diopside join, and $(W^{cpx}_V)_{FeMg}$ is calculated to be 0.924 ± 0.125 cm³/mol.

We find $(W^{cpx}_V)_{FeMg}$ to be 0.036 ± 0.074 from the data of Rutstein and Yund (1969) and −0.034 ± 0.072 cm³/mol from the data of Turnock et al. (1973). These two findings indicate that this parameter would be practically zero in view of the small values and its relatively large uncertainties. Perkins and Vielzeuf (1992) found that the molar volume of the intermediate clinopyroxene was considerably smaller than the molar sum of the end-member volumes, and we interpret the volume to indicate a value of −0.215 ± 0.081 cm³/mol for $(W^{cpx}_V)_{FeMg}$. We can examine these values of $(W^{cpx}_V)_{FeMg}$, as far as K_D

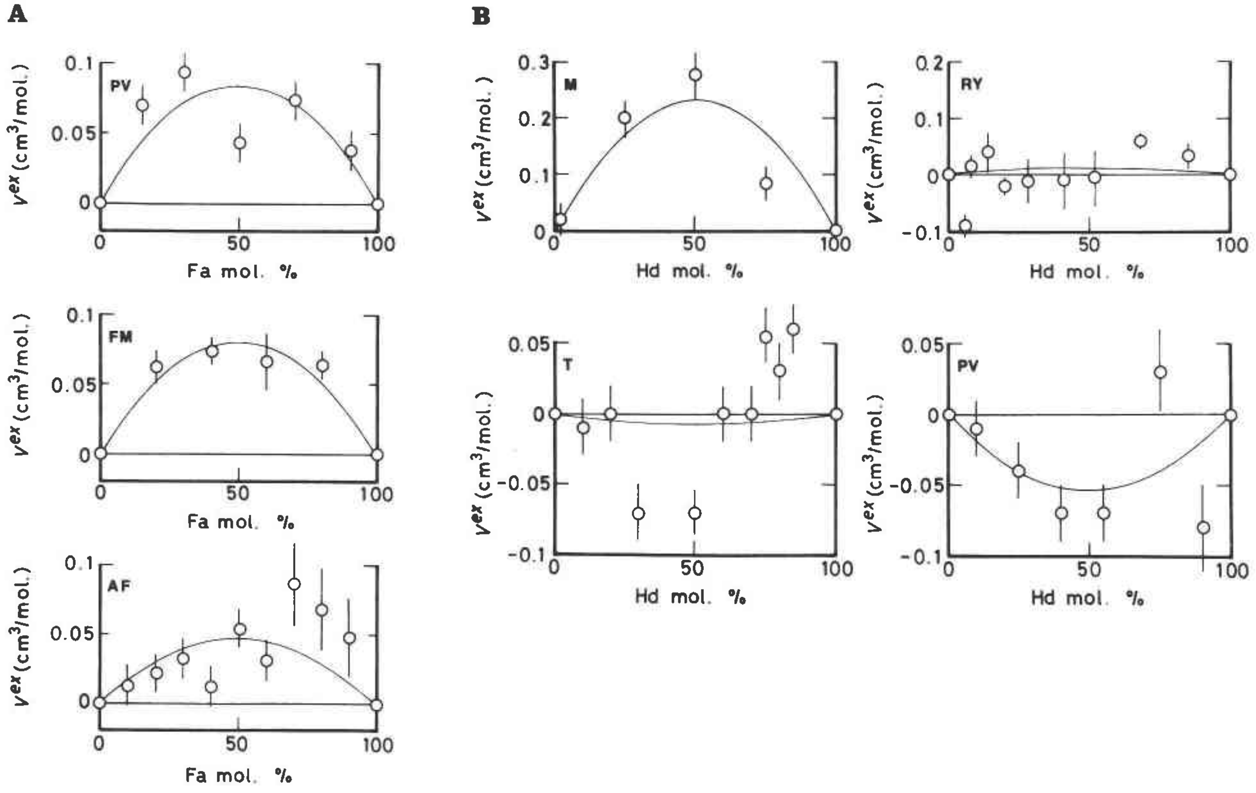

Fig. 1. (**A**) Relation between excess volume of $(Fe,Mg)_2SiO_4$ and composition. PV = Perkins and Vielzeuf (1992); FM = Fisher and Medaris (1969); AF = Akimoto and Fujisawa (1968). Vertical bars = $\pm 1\sigma$. (**B**) Relation between excess volume of $Ca(Fe,Mg)Si_2O_6$ and composition. M = Matsui et al. (1972); T = Turnock et al. (1973); RY = Rutstein and Yund (1969); PV = Perkins and Vielzeuf (1992).

is concerned, by comparing the magnitude of W^{cpx}_{FeMg} estimated from the Fe-Mg partition data in a wide range of pressures. Fortunately, we can use the experimental data of Perkins and Vielzeuf (1992) at 10.5 kbar and 1000 °C for this purpose.

We fitted Perkins and Vielzeuf's data to estimate W^{cpx}_{FeMg} at 10.5 kbar and 1000 °C using $(W^{ol}_{H})_{FeMg}$ of 1540 cal (Kawasaki and Matsui, 1983) and $(W^{ol}_{V})_{FeMg}$ of 2.22 cal/kbar (Akimoto and Fujisawa, 1968). The least-squares fitting yielded W^{cpx}_{FeMg} at 10.5 kbar and 1000 °C of 1390 cal. The addition of the excess volume term to this result gives W^{cpx}_{FeMg} at 75 kbar and 1000 °C of 1058 cal if we use Perkins and Vielzeuf's volume data. Our data at 75 kbar and 1100 °C resulted in a W^{cpx}_{FeMg} of 1060 cal. From this good agreement between the latter value and that obtained from Perkins and Vielzeuf's experiments, within $\pm 1\sigma$, we adopt the volume data of the clinopyroxene reported by Perkins and Vielzeuf (1992).

By the substitution of Equations 6 and 7 into Equation 4, we can obtain the expression of the free energy change of reaction at the standard state (ΔG^0):

$$\begin{aligned} -\Delta G^0 &= -(\Delta H^0 - T\Delta S^0 + P\Delta V^0) \\ &= RT \ln K_D - (1 - 2X^{ol}_{Fe})W^{ol}_{FeMg} \\ &\quad + (1 - 2X^{cpx}_{Fe})W^{cpx}_{FeMg} \end{aligned} \tag{9}$$

where

$$W^{ol}_{FeMg} = (W^{ol}_{H})_{FeMg} + P(W^{ol}_{V})_{FeMg} \tag{10}$$

and

$$W^{cpx}_{FeMg} = (W^{cpx}_{H})_{FeMg} - T(W^{cpx}_{S})_{FeMg} + P(W^{cpx}_{V})_{FeMg}. \tag{11}$$

We can evaluate the thermodynamic parameters, including ΔG^0 and W^{cpx}_{FeMg}, by an application of the least-squares calculation for Equation 9 if we have a sufficient amount of high-quality data on the chemical compositions of coexisting olivine and clinopyroxene at given physical conditions. The approach of this kind has been carried out with fair success (Kawasaki and Matsui, 1977, 1978, 1983; Seifert and O'Neill, 1987; Kawasaki and Ito, 1992). The procedures of the systematic calculation of least-squares fitting are given in Appendix 3.

EXPERIMENTAL PROCEDURES

Starting materials

Mineral mixtures of microcrystalline olivines $(Fe,Mg)_2SiO_4$ and clinopyroxenes $Ca(Fe,Mg)Si_2O_6$ were used as the starting materials in all the high-pressure experiments to constrain the equilibrium (or near-equilibrium) compositions of coexisting phases. The initial values of K_D were essentially lower or higher than those at equilibrium or near equilibrium. Final compositions of olivine and clinopyroxene were easily determined by means of electron microprobe analysis.

Olivine solid solutions were synthesized using the same method described by Ito et al. (1984). The clinopyroxene solid solutions on the join $CaFeSi_2O_6$-$CaMgSi_2O_6$ were prepared from reagent-grade chemicals, namely, Fe sponge, Mg powder, calcium carbonate, and silica gel. In order to obtain the chemically homogeneous clinopyroxene, weighed amounts of Fe, Mg, and calcium carbonate were dissolved in a dilute solution of nitric acid at about 80 °C, and then silica gel was stirred into the solution. After the mixture was dried at 110 °C for 1 d, it was heated by a gas burner and then kept at 600 °C for >2 d to remove nitric acid completely. Dried materials were ground in an agate mortar under ethyl alcohol for 1 h.

The hedenbergite-diopside-clinopyroxene solid solutions with the desired composition were heated in fine Pt-wire basket at high temperatures ranging from 900 to 1300 °C. Values of f_{O_2} equivalent to the quartz + magnetite + fayalite buffer were controlled by the mixed gas technique using the CO_2-H_2 system for 10–30 h. The temperature was raised linearly according to the increase in the $CaMgSi_2O_6$ component. End-member hedenbergite was crystallized at 900 °C, lower than the temperature of transition to pyroxenoid (Lindsley and Munoz, 1969; Turnock et al., 1973), and diopside was crystallized at 1300 °C. As has been mentioned by Perkins and Vielzeuf (1992), it is difficult to obtain homogeneous clinopyroxene. We found, using a scanning electron microscope, a metastable mixture of quartz, wollastonite, and olivine in the first synthesis. We carried out four or five additional recrystallizing cycles with grinding between each cycle in order to get well-crystallized and homogeneous clinopyroxene without unreacted metastable materials.

Each olivine and clinopyroxene sample used in starting materials was examined by powder X-ray diffraction, revealing single-phase material. Chemical homogeneity was checked by the use of an electron microprobe analyzer, JEOL model-T330A, with a Link Systems Model AN10000S/QX-200J energy-dispersive system. The ranges of variations in X_{Fe} for olivines and clinopyroxenes were found to be within ±1–2 mol% of their nominal values. Initial compositions are given in Table 2.

Mixtures of olivine and clinopyroxene (about 1:1 to 1:5 in weight) were used for the starting materials and were ground in an agate mortar under ethyl alcohol for about 1 h. Grain sizes of the mineral mixture were about 1–8 μm, and about 30% of it was <5 μm after grinding.

Experimental technique

Experiments at pressures of 30 kbar were carried out using a 16.0-mm piston-cylinder device at Kochi University. We used a pressure medium of talc and Pyrex glass. The temperatures at the top, center, and bottom of the sample space were directly measured by the use of three-junction thermocouples. We found a temperature gradient of about 2 °C/mm within the sample space at 30 kbar and 1400 °C (Osanai et al., 1992). The sample containers of graphite or Au were placed in a boron nitride medium within the talc Pyrex glass system.

In the present study, we used a multicapsule technique for the simultaneous recrystallization of many kinds of starting materials in the graphite or Au containers at 30 kbar and 900 °C. Five Au capsules, filled with starting mixtures of 3–10 mg of olivine and clinopyroxene, were put into the holes pierced in a boron nitride rod. Graphite capsules were inserted into the four- and five-chambered boron nitride rods. In a preliminary experiment, mixtures were directly put into seven holes in a graphite disk. In some experiments, samples contaminated each other through the cracks of the graphite disk, and so this technique was abandoned. Identification of the charges was easily made by noting differences in the lengths of Au capsules or in the outside diameters of graphite containers.

The generated pressures were measured against the oil pressure of the press. Pressures in the piston-cylinder apparatus were calibrated by the phase transformation of Bi I-II at room temperature (Hall, 1971) and by the quartz-coesite transition at 1000 °C (Bohlen and Boettcher, 1982). In the present experiments, we adopted a negative correction of 12% to the pressure value as an internal friction.

Experiments at 75 kbar were performed using a uniaxial split sphere apparatus at the Institute for Study of the Earth's Interior, Okayama University. The inner cubic assemblies of eight tungsten carbide anvils are compressed with an aid of a 1000-t hydraulic press. We used the same heating assemblages as that reported by Kawasaki and Ito (1992). A combination of anvils with an 11-mm edge and a magnesia octahedron with an 18-mm edge was adopted for all experiments at 75 kbar. The pressure medium of a semisintered magnesia octahedron contained 5% Cr_2O_3 to reduce the thermal conductivity. A lanthanum chromite ($LaCrO_3$) sleeve was used as a thermal insulator for the cylindrical graphite heater to keep high temperatures stable for the duration. Powdered starting materials were put into a sample container of graphite, 3 mm long, 1.5-mm o.d., and 0.3-mm wall thickness. Graphite capsules were inserted in the boron nitride or alumina sleeves placed symmetrically against a junction of thermocouples.

Electric power was supplied to the graphite heater through graphite disks 1 mm thick, which contacted with the faces of a pair of tungsten carbide anvils. Temperatures were monitored with a thermocouple [Pt + (Pt + 13% Rh)] 0.2 mm in diameter without any corrections for the pressure effect on emf. The junction of the thermocouple was sandwiched within thin boron nitride disks (<0.1 mm thick) to keep it from contact with the sample container. Powdered boron nitride was packed in the space between the two disks. The thermocouple was insulated from its surroundings by magnesia tubes of 0.6 mm o.d. Thermocouple leads were directly brought out to the thermometer through the gasket between the anvils.

Pressure calibrations were made for the split-sphere apparatus at room temperature on the basis of the NBS

TABLE 2. Experimental and calculated compositions of coexisting olivines and clinopyroxenes

Expt.	Initial Fa Hd (mol%)	t (h)	Olivine			Clinopyroxene			K_D	
			Fe/(Fe + Mg)		Ca/(Ca + Fe + Mg)	Fe/(Fe + Mg)		Ca/(Ca + Fe + Mg)		
			Obs	Calc		Obs	Calc		Obs	Calc
75 kbar/1500 °C										
MSA910522A	10 0	2	0.021(6)*	0.021	0.0041(9)	0.019(6)	0.018	0.483(13)	0.89(38)	0.86
MSA910522B	0 10	2	0.026(2)	0.025	0.0042(14)	0.020(4)	0.022	0.469(16)	0.77(17)	0.86
MSA920718A	20 0	1	0.101(16)	0.105	0.0065(26)	0.091(8)	0.090	0.489(17)	0.89(18)	0.84
MSA920620B	0 20	1	0.128(16)	0.129	0.0041(10)	0.112(19)	0.110	0.466(11)	0.86(21)	0.84
MSA920621B	10 20	1.23	0.146(8)	0.146	0.0050(15)	0.126(19)	0.125	0.450(12)	0.85(16)	0.83
MSA920622A	20 10	2	0.165(16)	0.165	0.0051(13)	0.141(13)	0.141	0.403(22)	0.83(14)	0.83
MSA920718B	20 30	1	0.252(5)	0.254	0.0052(13)	0.219(7)	0.216	0.438(11)	0.83(4)	0.83
MSA920620A	30 20	1	0.268(15)	0.270	0.0050(13)	0.230(6)	0.230	0.431(18)	0.81(7)	0.81
MSA920520A	40 10	1	0.292(10)	0.289	0.0068(37)	0.242(13)	0.246	0.463(13)	0.77(7)	0.80
MSA920518B	20 40	1	0.300(7)	0.299	0.0067(14)	0.254(7)	0.254	0.458(29)	0.79(4)	0.80
MSA920518A	30 30	1	0.338(11)	0.336	0.0068(14)	0.282(14)	0.286	0.410(8)	0.77(7)	0.79
MSA920719A	50 30	1	0.432(8)	0.432	0.0064(13)	0.371(9)	0.370	0.437(17)	0.78(4)	0.77
MSA920622B	30 50	2	0.442(12)	0.443	0.0061(6)	0.380(9)	0.380	0.434(15)	0.77(5)	0.77
MSA920719B	40 50	1	0.461(15)	0.465	0.0065(9)	0.407(18)	0.400	0.464(11)	0.80(8)	0.77
MSA920621A	50 40	1.23	0.489(8)	0.483	0.0071(21)	0.413(6)	0.417	0.443(13)	0.73(3)	0.76
MSA920520B	50 50	1	0.532(9)	0.537	0.0065(12)	0.467(3)	0.467	0.456(9)	0.77(3)	0.76
75 kbar/1300 °C										
MSA900926B	10 0	4	0.051(3)	0.050	0.0032(7)	0.032(7)	0.040	0.481(10)	0.62(15)	0.79
MSA9005242	20 20	3	0.227(4)	0.226	0.0044(12)	0.164(13)	0.175	0.453(10)	0.67(6)	0.72
MSA9005231	30 20	2	0.281(5)	0.284	0.0056(22)	0.226(8)	0.217	0.450(32)	0.75(4)	0.70
MSA9005243	30 30	3	0.329(4)	0.329	0.0059(20)	0.251(11)	0.250	0.470(13)	0.68(4)	0.68
MSA920720A	40 20	4	0.360(6)	0.361	0.0060(15)	0.275(9)	0.273	0.446(25)	0.67(4)	0.66
MSA9006204	50 10	3	0.402(19)	0.384	0.0065(12)	0.285(8)	0.290	0.441(17)	0.59(5)	0.65
MSA900809A	40 40	1.67	0.446(19)	0.447	0.0064(16)	0.337(12)	0.336	0.446(12)	0.63(6)	0.63
MSA9005235	50 50	2	0.571(6)	0.569	0.0090(11)	0.430(9)	0.434	0.477(9)	0.57(3)	0.58
MSA9006206	50 60	3	0.599(10)	0.604	0.0075(10)	0.477(16)	0.465	0.450(17)	0.61(5)	0.57
MSA901023A	70 70	6	0.739(6)	0.738	0.0073(24)	0.598(13)	0.601	0.479(15)	0.53(3)	0.53
75 kbar/1100 °C										
MSA900815A	10 10	13	0.138(6)	0.138	0.0016(8)	0.076(8)	0.077	0.475(17)	0.52(6)	0.52
MSA900815B	20 20	13	0.293(5)	0.296	0.0031(17)	0.185(12)	0.161	0.459(20)	0.55(5)	0.46
MSA910521A	30 30	11	0.386(6)	0.385	0.0067(14)	0.207(20)	0.213	0.476(11)	0.42(9)	0.43
MSA910521B	40 40	11	0.442(13)	0.441	0.0059(14)	0.242(20)	0.247	0.479(14)	0.41(7)	0.42
MSA910519A	60 20	12	0.543(21)	0.537	0.0063(11)	0.307(25)	0.319	0.471(6)	0.37(5)	0.40
MSA921021A	50 50	12	0.605(21)	0.609	0.0092(16)	0.382(26)	0.375	0.492(5)	0.40(6)	0.39
MSA921021B**	60 60	12	0.667(13)	0.667	0.0057(15)	0.428(27)	0.428	0.445(8)	0.37(5)	0.37
30 kbar/1100 °C										
KCH920708	30 0	150	0.197(3)	0.198	0.0048(27)	0.138(12)	0.128	0.468(25)	0.65(7)	0.60
KCH900706	30 30	9	0.363(3)	0.362	0.0054(11)	0.225(12)	0.235	0.473(12)	0.51(3)	0.54
KCH900803	40 40	21.23	0.446(6)	0.442	0.0136(15)	0.282(8)	0.291	0.495(5)	0.49(2)	0.52
KCH920606	50 50	120	0.569(9)	0.572	0.0110(27)	0.401(13)	0.394	0.483(6)	0.51(3)	0.49
KCH920611	60 60	120	0.657(6)	0.658	0.0212(22)	0.484(18)	0.476	0.490(4)	0.49(4)	0.47
30 kbar/900 °C										
KCH9009128	20 20	100	0.328(11)	0.319	0.0033(11)	0.141(6)	0.147	0.484(8)	0.34(2)	0.37
KCH9009127	40 10	100	0.358(5)	0.358	0.0049(27)	0.165(9)	0.166	0.475(10)	0.36(3)	0.36
KCH9009122	30 30	100	0.424(9)	0.430	0.0032(22)	0.214(9)	0.203	0.471(13)	0.37(2)	0.34
KCH9009124	40 40	100	0.484(15)	0.483	0.0151(23)	0.232(16)	0.233	0.499(10)	0.32(3)	0.33
KCH9009126	60 20	100	0.547(8)	0.549	0.0116(23)	0.281(10)	0.276	0.497(3)	0.32(2)	0.31
KCH9009121	55 55	100	0.676(9)	0.687	0.0103(50)	0.413(12)	0.396	0.486(7)	0.34(2)	0.30
KCH9009125	60 60	100	0.702(11)	0.697	0.0073(37)	0.394(20)	0.408	0.479(11)	0.28(3)	0.30
KCH900912B	80 30	100	0.721(8)	0.712	0.0106(43)	0.386(18)	0.425	0.496(6)	0.24(2)	0.30
KCH9009123	80 40	100	0.741(18)	0.738	0.0081(47)	0.458(14)	0.459	0.479(12)	0.29(3)	0.30
KCH910807C†	70 70	220	0.757(14)	0.764	0.0077(13)	0.500(13)	0.495	0.470(19)	0.32(3)	0.30
KCH910807B†	80 80	220	0.849(10)	0.842	0.0082(13)	0.625(13)	0.631	0.469(12)	0.30(3)	0.32
KCH910807D†	100 70	220	0.906(6)	0.906	0.0089(10)	0.771(12)	0.771	0.458(14)	0.35(4)	0.35
KCH910807A†	90 90	220	0.926(9)	0.929	0.0088(12)	0.827(11)	0.825	0.445(10)	0.38(6)	0.36

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

** Coexisting with γ spinel (X_{Fe} = 0.891).

† Au capsule was used, and metallic Fe was not observed in these experiments. Others were graphite capsules, and metallic Fe was observed.

pressure scale (Hall, 1971): Bi I-II: 25.5 kbar; Bi III-V: 75 kbar. We also corrected the pressures at 1000 and 1300 °C using the polymorphic phase transformations of olivine to spinel in Fe_2SiO_4 (Yagi et al., 1987), olivine-modified spinel to spinel in Co_2SiO_4 (Akimoto and Sato, 1968), and coesite to stishovite in SiO_2 (Yagi and Akimoto, 1976).

Experiment durations were 1–13 h for the 75-kbar experiments and 9–220 h for the 30-kbar experiments. During the 75-kbar experiments the experiment temperatures and pressures were kept constant within ±10 °C and ±0.5 kbar. For long experiments at 30 kbar, temperatures were kept constant within ±5 °C, and fluctuations of the electric power for heating were <±1% (relative). After being kept at the desired pressure and temperature for the desired duration, samples were quenched by cutting off the electric power supply. Thermocouple reading dropped to below 50 °C in a few seconds and to the ambient temperature in 2 min. The pressure was then released slowly, at about 10 kbar/h for the 75-kbar experiments, and the experiment products were recovered. We reduced experiment pressures in the piston cylinder to an atmospheric pressure for 15 min.

Chemical analysis

The experimental products were mounted in epoxy resin and carefully polished for examination with the scanning electron microscope and microprobe analysis. Chemical compositions of all experimental products were determined with an electron microprobe analyzer. Analyses were corrected using a ZAF-FLS program. The instrumental conditions were as follows: the accelerating voltage, 15 kV; Faraday cup current, 1×10^{-9} A. The 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 by test substances such as olivine and clinopyroxene from spinel lherzolite. All relevant elements were measured simultaneously, and at least 10–20 analyses were made on both olivine and clinopyroxene phases in every experiment. Acceptable analyses for each phase in the experimental products agreed with ideal stoichiometry to within ±2% relative and contained a total oxide weight percent in the range 98–102%. We made the chemical analyses near the grain boundary of olivine and clinopyroxene. If the analyses for a phase within one charge indicated heterogeneity in compositions whose mean standard error of $X_{\mathrm{Fe}}(\sigma_{X_{\mathrm{Fe}}})$ exceeded ± 0.03, the experimental product was considered to be in nonequilibrium, and all data from that experiment were discarded.

EXPERIMENTAL RESULTS

Final and initial compositions of olivines and clinopyroxenes are summarized in Table 2. The scanning electron microscope revealed that the experimental products consisted of the aggregation of olivine and clinopyroxene with almost homogeneous equigranular texture, suggesting that the products were at or near chemical equilibrium. The grain size of the assemblages were 10–50 μm depending on temperature, pressure, and experiment duration. Experiment products were large enough to determine the compositions of individual phases without contamination from surrounding minerals.

Reversal experiments, in the strict sense of the word, were not successful. It is impossible to prepare starting materials with the same bulk composition for the reversal experiments on the Fe-Mg partitioning. We can only carry out the experiments using the mixture of Fe-rich olivine and Mg-rich clinopyroxene. For example, we consider that the equilibrium compositions are approximately represented by those of the most Fe-rich olivine and the most Mg-rich clinopyroxene in the case of a recrystallization experiment at 75 kbar and 1500 °C for 1 h (experiment no. MSA920518B), the starting material for which was a mixture of $(\mathrm{Fe}_{0.2}\mathrm{Mg}_{0.8})_2\mathrm{SiO}_4$ olivine and $\mathrm{Ca}(\mathrm{Fe}_{0.4}\mathrm{Mg}_{0.6})\mathrm{Si}_2\mathrm{O}_6$ clinopyroxene. Final compositions of olivine and clinopyroxene in this experiment showed $X_{\mathrm{Fe}}^{\mathrm{ol}} = 0.300$ and $X_{\mathrm{Fe}}^{\mathrm{cpx}} = 0.254$ (Fig. 2). In contrast, in experiment no. MSA920520A with a starting mix of olivine with $X_{\mathrm{Fe}} = 0.4$ and clinopyroxene with $X_{\mathrm{Fe}} = 0.1$, olivine became more magnesian, and clinopyroxene became enriched in Fe^{2+}. The final compositions were $X_{\mathrm{Fe}}^{\mathrm{ol}} = 0.292$ and $X_{\mathrm{Fe}}^{\mathrm{cpx}} = 0.242$ (Fig. 2).

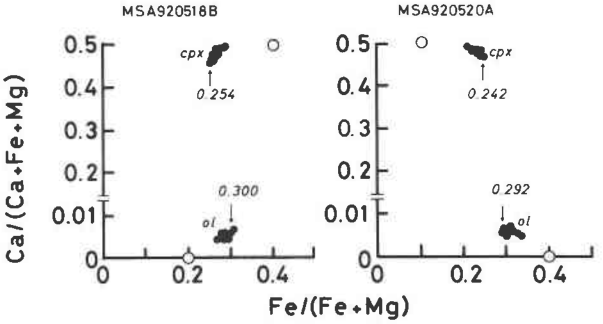

Fig. 2. Microprobe analyses of olivines and clinopyroxenes at 75 kbar and 1500 °C for the experiments of MSA920518B and MSA920520A. The starting materials (open circles) are the mechanical mixtures of Fa_{20} olivines and Hd_{40} clinopyroxenes (expt. no. MSA920518B) and of Fa_{40} + Hd_{10} (expt. no. MSA-920520A). Final compositions are the mean values of three of the most Mg-rich olivines, Fe-rich clinopyroxenes (MSA920520A), Fe-rich olivines, and Mg-rich clinopyroxenes (MSA920518B), shown with arrows.

Thus we easily determined the final compositions of coexisting phases. In order to estimate the reliabilities of each synthetic experiment, mean standard errors were calculated from all analytical data in the compositions of olivine and clinopyroxene. These standard errors are given in Table 2. The inverse squares of these standard errors are assumed to be proportional to the weights of data sets (Deming, 1943). These parameters were used in the least-squares fittings (Appendix 3).

About 2–3 modal% of anhedral metallic Fe, which precipitated from silicate phases, was observed within the graphite capsules. The appearance of the metallic Fe can be described by

$$\underset{\mathrm{ol}}{\mathrm{Fe}_2\mathrm{SiO}_4} = \underset{\mathrm{metal}}{\mathrm{Fe}} + \underset{\mathrm{cpx}}{\mathrm{FeSiO}_3} + \underset{\mathrm{gas}}{\tfrac{1}{2}\mathrm{O}_2}. \qquad (12)$$

From this chemical reaction, the clinopyroxenes became slightly Ca-poor relative to the initial compositions on the hedenbergite-diopside join. This depletion of the CaSiO_3 component in clinopyroxene would also arise partly from the small amount of substitution of Ca^{2+} for Mg^{2+} and Fe^{2+} in olivine solid solution:

$$\underset{\mathrm{cpx}}{\mathrm{CaMgSi}_2\mathrm{O}_6} + \underset{\mathrm{ol}}{\tfrac{1}{2}\mathrm{Mg}_2\mathrm{SiO}_4} = \underset{\mathrm{cpx}}{\tfrac{1}{2}\mathrm{Mg}_2\mathrm{Si}_2\mathrm{O}_6} + \underset{\mathrm{ol}}{\tfrac{1}{2}\mathrm{Ca}_2\mathrm{SiO}_4} \qquad (13)$$

and

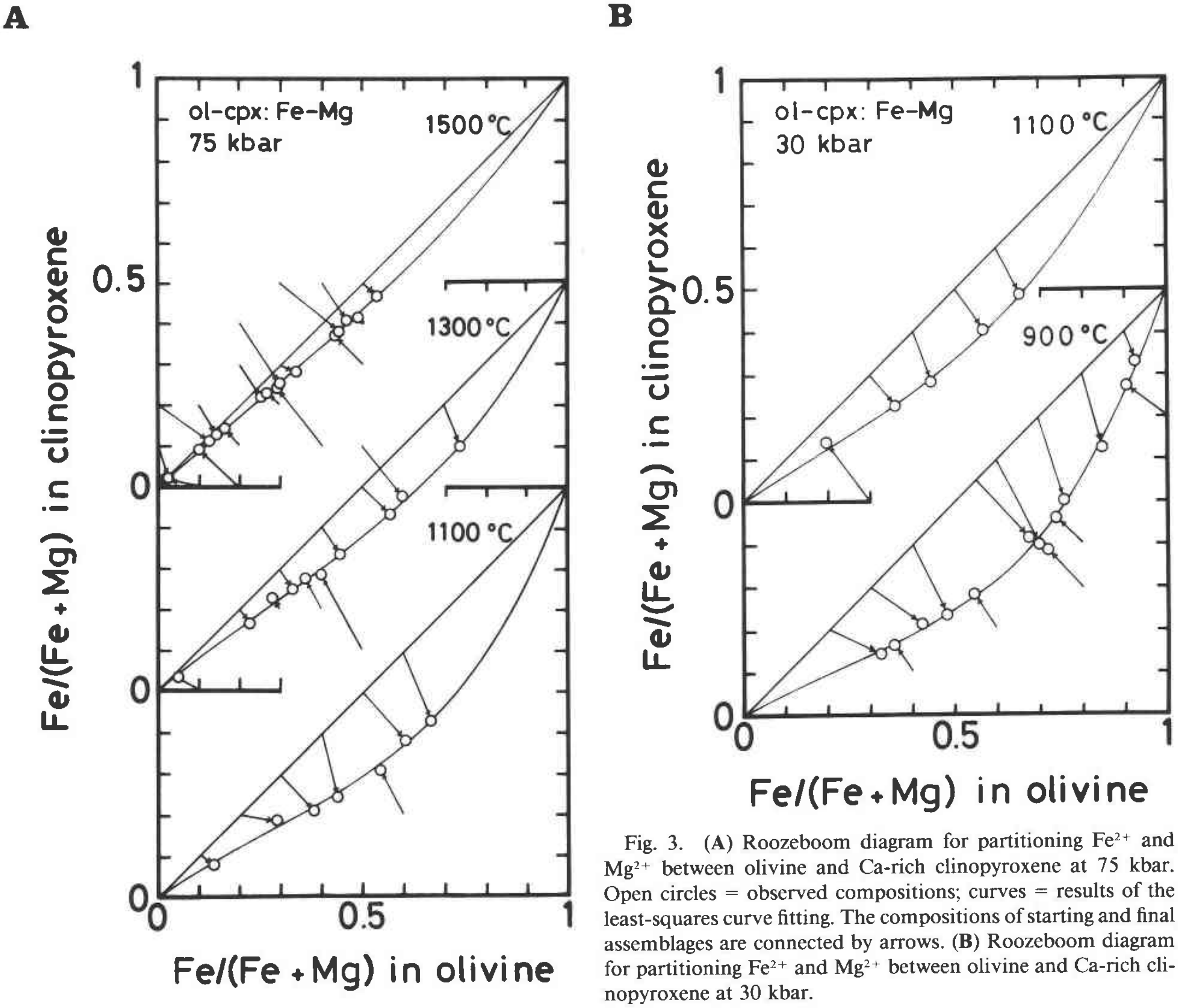

Fig. 3. (**A**) Roozeboom diagram for partitioning Fe^{2+} and Mg^{2+} between olivine and Ca-rich clinopyroxene at 75 kbar. Open circles = observed compositions; curves = results of the least-squares curve fitting. The compositions of starting and final assemblages are connected by arrows. (**B**) Roozeboom diagram for partitioning Fe^{2+} and Mg^{2+} between olivine and Ca-rich clinopyroxene at 30 kbar.

$$\underset{\text{cpx}}{CaFeSi_2O_6} + \underset{\text{ol}}{{}^1\!/\!_2Fe_2SiO_4} = \underset{\text{cpx}}{{}^1\!/\!_2Fe_2Si_2O_6} + \underset{\text{ol}}{{}^1\!/\!_2Ca_2SiO_4}. \tag{14}$$

Reversal experiments on the solubility of Ca^{2+} in olivine were not successful. We investigated only the Ca gain by olivine and Ca loss by clinopyroxene. We have found that the Ca content of olivine systematically increased as the Fe content in the system increased. The value of X_{Ca} in olivine increased from 0.0016 to 0.0212 at pressures of 30 and 75 kbar and temperatures of 900–1500 °C. These values for Ca concentration were not very accurate because of the large uncertainties introduced by the counting statistics.

In the experimental products of no. MSA921021B, a very small amount (<0.1 modal%) of euhedral prismatic shaped γ spinel crystallized as inclusions in the olivine crystals at 75 kbar and 1100 °C. The values of X_{Fe} of these spinels and olivines were determined to be 0.891 and 0.667, respectively. This is consistent with the results of the Fe-Mg partition experiments between olivine and spinel by Nishizawa and Akimoto (1973) and those of the thermochemical calculations by Akaogi et al. (1989).

DISCUSSION

Least-squares fitting

Experimental data for the exchange of Fe^{2+} and Mg^{2+} at pressures of 30 and 75 kbar and temperatures of 900–1500 °C are compiled in Table 2. Attempts at three-variable least-squares regression using Equation 9 were not successful; stable solutions were not obtained. We found the results yielded large standard errors for both W^{ol}_{FeMg} and W^{cpx}_{FeMg} terms. We believe such calculations have no meaning in themselves. The free energy change of reaction, ΔG^0, in Equation 9 is rewritten by

$$-\Delta G^0 = RT \ln K_D - (1 - 2X^{ol}_{Fe})\Delta W + 2\Delta X_{Fe} W^{cpx}_{FeMg} \tag{15a}$$

where

$$\Delta W = W^{ol}_{FeMg} - W^{cpx}_{FeMg} \tag{15b}$$

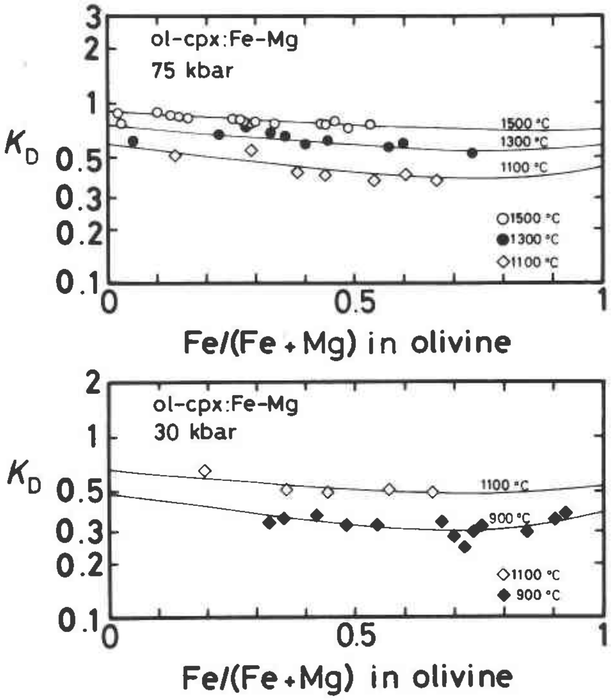

Fig. 4. Relations between the distribution coefficient (K_D) and composition of olivine at pressures 75 kbar (**upper**) and 30 kbar (**lower**). Curves: results of nonlinear least-squares calculations.

and

$$\Delta X_{Fe} = X_{Fe}^{ol} - X_{Fe}^{cpx}. \tag{15c}$$

The terms W_{FeMg}^{ol} and W_{FeMg}^{cpx} are poorly determined in the present regression because the ΔX_{Fe} term does not vary much as a function of composition. The reliable results will only be obtainable for the difference in the mixing parameters, ΔW. This indicates that the exchange reaction is insensitive to the absolute magnitudes of W_{FeMg}^{ol} and W_{FeMg}^{cpx} but strongly dependent on the difference between two nonideal parameters (Matsui and Nishizawa, 1974; O'Neill and Wood, 1979). Therefore, the least-squares calculation yields results with high precision for ΔG^0 and ΔW, and with large uncertainty for W_{FeMg}^{ol} and W_{FeMg}^{cpx}. Fortunately, we have other evidence to limit the Fe-Mg mixing properties of olivine. The magnitude of the nonideality, W_{FeMg}^{ol}, is about 1–2 kcal (e.g., O'Neill and Wood, 1979; Wood and Kleppa, 1981; Kawasaki and Matsui, 1983; Hackler and Wood, 1989). In order to reduce the number of unknown parameters in our regression, we used Kawasaki and Matsui's (1983) value of $(W_H^{ol})_{FeMg}$ (on the basis of 1540 cal for one exchangeable cation), and Akimoto and Fujisawa's (1968) excess volume term $(W_V^{ol})_{FeMg}$ (2.22 cal/kbar, see Table 1). Nonlinear least-squares fittings were then carried out to evaluate the ΔG^0 and W_{FeMg}^{cpx}, assuming that $W_{FeMg}^{ol} = 1540 + 2.22P$. The calculated compositions of phases (see Appendix 3) are also compiled in Table 2.

Results of the curve fitting are shown in Figure 3 in the form of a Roozeboom diagram. The initial and final compositions are connected by arrows, which show the direction of approach to equilibrium, and the observed and calculated values are also illustrated in these figures. The relations between the distribution coefficient (K_D) and the composition of olivine are given in Figure 4. The dependence of K_D on composition in Figure 4 indicates that both olivine and clinopyroxene are nonideal solutions. As is seen in Figure 4, it is clear that the Fe-Mg partitioning between olivine and clinopyroxene is temperature dependent. In Figure 5, we show that the Fe-Mg partitioning is pressure dependent in the form of a Roozeboom diagram at 1100 °C and pressures of 30 and 75 kbar, but this pressure effect is very small. As is discussed below, the Fe-Mg partitioning between olivine and clinopyroxene is insensitive to pressure. From this figure we can read values of K_D at 30 and 75 kbar in the intermediate composition to be 0.52 and 0.42, respectively. The value of dK_D/dP is roughly estimated to be -2×10^{-3}/kbar at the intermediate composition.

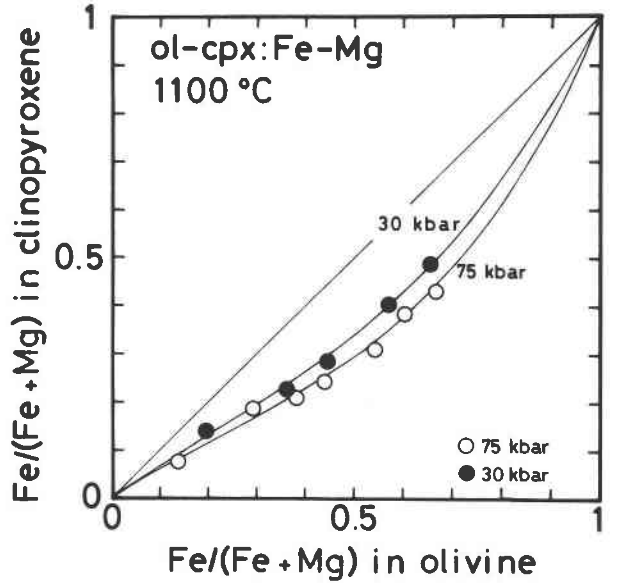

Fig. 5. Exchange of Fe^{2+} and Mg^{2+} between olivine and clinopyroxene at 1100 °C and at pressures 75 and 30 kbar.

The curve fits are quite satisfactory, as seen in Figures 3, 4, and 5. The good fit implies that the exchange reaction of Fe^{2+} and Mg^{2+} between olivine and Ca-rich clinopyroxene can be described with reasonable precision by Equation 9 under the present experimental conditions. The results of the present least-squares analyses are given in the terms of W_{FeMg}^{cpx} and ΔG^0 in Table 3 and illustrated in Figures 6 and 7. Included for comparison are the results of curve fittings of Perkins and Vielzeuf's (1992) data. Differences in nonideality between olivine and clinopyroxene, ΔW, are also given in Table 3.

The nonideality of $Ca(Fe,Mg)Si_2O_6$ clinopyroxene

The calculated values of W_{FeMg}^{cpx} are plotted for the variation of temperature in Figure 6. As is clear from this figure, the Fe-Mg mixing parameter of clinopyroxene,

TABLE 3. Results of nonlinear least-squares calculation of the thermodynamic parameters in Equation 7

P (kbar)	T (°C)	ΔG^0 (cal)	W^{cpx}_{FeMg} (cal)	ΔW (cal)*
75	1500	770(40)**	1440(100)	270(40)
75	1300	1340(70)	920(190)	790(250)
75	1100	1960(210)	1060(400)	640(350)
30	1100	1420(130)	1460(310)	140(160)
10.5†	1000	1720(40)	950(100)	130
10.5‡	1000	1930(40)	900(100)	170(100)
10.5§	1000	1730(40)	1390(100)	170(100)
30	900	1920(60)	1410(140)	190(140)

Note: W^{ol}_{FeMg} (cal) = 1540 + 2.22P (kbar) is assumed.

* The $\Delta W = W^{ol}_{FeMg} - W^{cpx}_{FeMg}$.

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

† Results of Perkins and Vielzeuf (1992), who assumed W^{ol}_{FeMg} = 1080 cal. Note that ΔW = 130 cal.

‡ Recalculated from Perkins and Vielzeuf's (1992) data, assuming W^{ol}_{FeMg} = 1080 cal. Note that ΔW = 170 cal.

§ Recalculated from Perkins and Vielzeuf's (1992) data, assuming W^{ol}_{FeMg} (cal) = 1540 + 2.22P (kbar). Note that ΔW = 170 cal.

W^{cpx}_{FeMg}, is pressure and temperature dependent. Using the values of W^{cpx}_{FeMg} tabulated in Table 3, we carried out the linear regression to evaluate the P-T dependence of the Fe-Mg mixing parameter of clinopyroxene. We found

$$W^{cpx}_{FeMg}\ (\text{cal}) = 690 - 6.17P + 0.64T. \tag{16}$$

The $(W^{cpx}_V)_{FeMg}$ term calculated from the volume data of Perkins and Vielzeuf (1992) in Table 1 is converted to -5.14 ± 1.94 cal/kbar. This value is consistent with $\partial W^{cpx}_{FeMg}/\partial P$ of -6.17 in Equation 16 within $\pm 1\sigma$. Therefore, we adopt the volume data of clinopyroxene reported by Perkins and Vielzeuf (1992). Using $(W^{cpx}_V)_{FeMg}$ of -5.14 cal/kbar estimated from Perkins and Vielzeuf's (1992) volume data, we evaluated again the temperature dependence of W^{cpx}_{FeMg}. The result was as follows:

$$W^{cpx}_{FeMg}\ (\text{cal}) = (800 \pm 390) - 5.14P\ (\text{kbar}) + (0.54 \pm 0.26)T\ (\text{K}). \tag{18}$$

The first term of this Equation is in very good agreement with W^{M1} of 790 cal derived by Davidson and Lindsley (1989) for clinopyroxene from the thermodynamic analysis of pyroxene + olivine + quartz equilibria in the system CaO-FeO-MgO-SiO$_2$. Equation 18 implies that the magnitude of the nonideality of clinopyroxene increases as temperature increases. This may partly originate in the effect of the intracrystalline exchange of Fe^{2+} and Mg^{2+} between the M1 and M2 sites of clinopyroxene because clinopyroxenes in the present experiments were slightly less calcic than the hedenbergite-diopside join. Thus the unusual phenomenon of $\partial G^{ex}/\partial T > 0$ is occasionally observed for the double-sited solutions, including iron-magnesium orthopyroxene (Kawasaki and Matsui, 1983), nickel-magnesium olivine (Ottonello et al., 1989), and iron-magnesium olivine (Ottonello et al., 1990; Akamatsu et al., 1993). The macroscopic increase in the nonideality for the double-sited solution with increasing temperature is briefly explained as follows. As is generally accepted, the intracrystalline distribution factor $K_i = (X^{M2}_A X^{M1}_B)/(X^{M2}_B X^{M1}_A)$ would approach unity with increasing temperature, and $K_i = 1$ at the completely disordered state. The excess energy $G^{ex} = W^{M1}X^{M1}_A X^{M1}_B + W^{M2}X^{M2}_A X^{M2}_B$ would increase as $K_i \rightarrow 1$ and attain the maximum $G^{ex} = (W^{M1} + W^{M2})X^{M1}_A X^{M1}_B$ at $K_i = 1$, where $X^{M1}_A = X^{M2}_A = X^{crystal}_A$ and $X^{M1}_B = X^{M2}_B = X^{crystal}_B$.

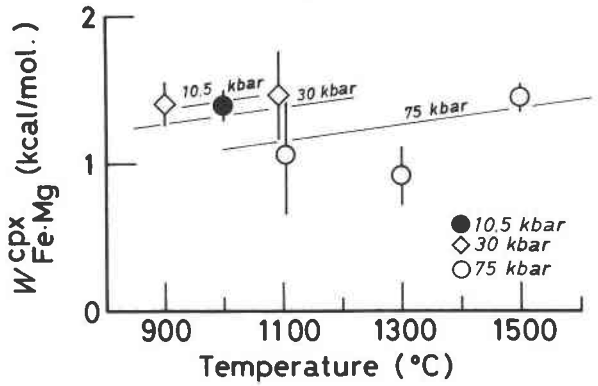

Fig. 6. Fe-Mg mixing parameter of Ca-rich clinopyroxene plotted against temperature. Estimated standard errors are indicated by vertical bars on respective points. Experimental pressures are shown in the figure. Curves are the calculated W^{cpx}_{FeMg} at given pressures: $W^{cpx}_{FeMg} = 800 + 0.54T - 5.14P$. The nonideality, W^{cpx}_{FeMg}, decreases as pressure increases, but it increases as temperature increases.

It is important to note that the deviation from ideality in olivine is greater than that in clinopyroxene (see Table 3). The nonideality of the hedenbergite-diopside solid solution is small compared with that of the enstatite-diopside solid solution. Gasparik (1990) concluded that the (Ca,Mg)MgSi$_2$O$_6$ clinopyroxene was really an asymmetric solution, but it could be described as a symmetric solution with $W^{cpx,M2}_{CaMg}$ = 6.3 kcal. Saxena (1971) derived W^{cpx}_{FeMg} = 1.0 kcal from studying six granulites, assuming the equilibration temperature to be 680 °C. Oka and Matsumoto (1974) estimated the W^{cpx}_{FeMg} to be 2.4 kcal from the Fe-Mg partition data of clinopyroxene and garnet pair of Mount Higasi-Akaisi mass (Mori and Banno, 1973).

Iiyama (1982) concluded that the clinopyroxene would behave as an asymmetric regular solution based on the Fe-Mg partition experiments of the chloride solution and clinopyroxene pair at 1 kbar and 600 °C, assuming that the chloride solution would be an ideal solution. The excess free energy of clinopyroxene calculated by Iiyama is equivalent to a symmetric regular solution with W^{cpx}_{FeMg} = 1.5 kcal. This value, however, is actually the difference between the nonidealities of clinopyroxene and chloride solution, $W^{cpx}_{FeMg} - W^{sol}_{FeMg}$ (Matsui and Nishizawa, 1974; Kawasaki and Matsui, 1977).

Perkins and Vielzeuf (1992) evaluated the W^{cpx}_{FeMg} as 950 ± 100 cal at 10.5 kbar and 1000 °C, assuming W^{ol}_{FeMg} = 1080 cal from Fe-Mg partition experiments. We recalculated Perkins and Vielzeuf's data and found that $W^{cpx}_{FeMg} = 1390 \pm 100$ cal, assuming $W^{ol}_{FeMg} = 1540 + 2.22P$ (see Table 3). This discrepancy is not statistically signif-

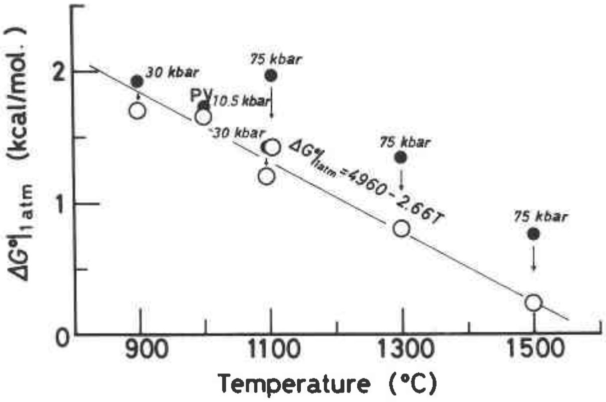

Fig. 7. Free energy change at 1 atm ($\Delta G^0|_{1\,\mathrm{atm}}$) plotted against temperature. Pressure corrections are shown by arrows. Experiment pressures are indicated in the figure. PV = results derived from the data of Perkins and Vielzeuf (1992).

icant. As has been discussed in the previous section, the Fe-Mg partition reaction is insensitive to the absolute magnitudes of $W^{\mathrm{ol}}_{\mathrm{FeMg}}$ and $W^{\mathrm{cpx}}_{\mathrm{FeMg}}$ but strongly dependent on the difference between these two parameters. We obtained the following result:

$$\Delta W = W^{\mathrm{ol}}_{\mathrm{FeMg}} - W^{\mathrm{cpx}}_{\mathrm{FeMg}} = 170 \pm 100 \text{ cal.} \qquad (19)$$

Perkins and Vielzeuf (1992) obtained ΔW of 130 cal at 10.5 kbar and 1000 °C. A slight discrepancy between the present and Perkins and Vielzeuf's results in the ΔW term at 10.5 kbar and 1000 °C is caused by the difference in the method of estimation of the thermodynamic parameters. These values are consistent with each other within $\pm 1\sigma$.

Pressure and temperature dependence of ΔG^0

The effect of pressure on ΔG^0 of Reaction 1 at constant temperature is calculated from the volume data of $(\mathrm{Fe,Mg})_2\mathrm{SiO}_4$ olivine (Akimoto and Fujisawa, 1968) and $\mathrm{Ca(Fe,Mg)Si_2O_6}$ clinopyroxene (Perkins and Vielzeuf, 1992):

$$\left(\frac{\partial \Delta G^0}{\partial P}\right)_T = \Delta V^0 = 7.17 \text{ cal/kbar.} \qquad (20)$$

With $\Delta V^0 = 7.17$ cal/kbar, the linear regression of the values of ΔG^0 given in Table 3 leads to the following result:

$$\Delta G^0 \text{ (cal)} = (4960 \pm 230) - (2.66 \pm 0.15)T \text{ (K)} + 7.17P \text{ (kbar)}. \qquad (21)$$

The relation between $\Delta G^0|_{1\,\mathrm{atm}}$ and temperature is illustrated in Figure 7. As is clear in Figure 7, a good fit implies that the temperature and pressure dependence of ΔG^0 is given by Equation 21.

The ΔV^0 term given by Equation 20 has a small value. This indicates that the Fe-Mg partitioning is not sensitive to the variation of the pressure, especially in the Mg-rich system (Fig. 8). High Mg to Fe ratios are always observed in ultramafic rock systems. In an extreme case, the value of Fe/(Fe + Mg) would be insignificantly small ($X_{\mathrm{Fe}} \doteqdot 0$). Equation 9 becomes

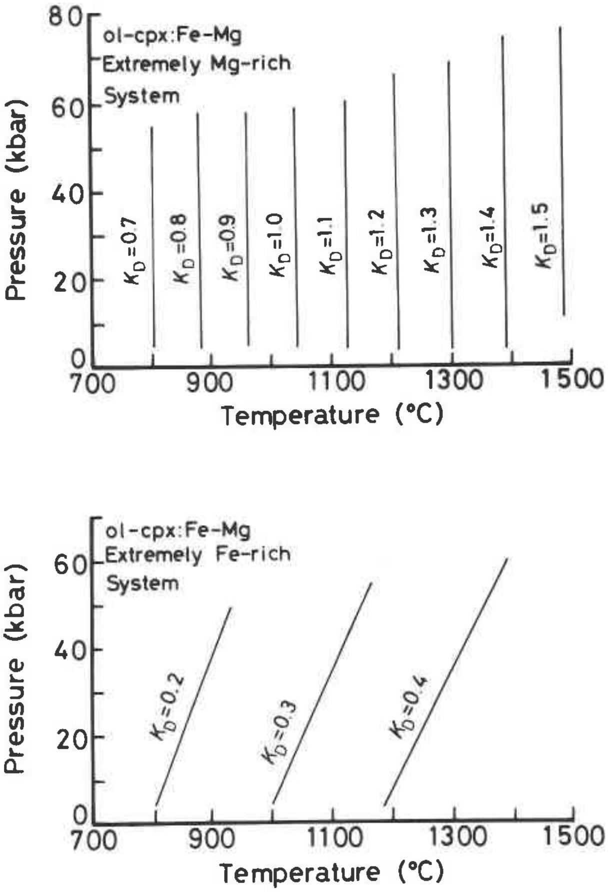

Fig. 8. Calculated distribution coefficient, K_D, in the extremely Mg-rich (upper) and Fe-rich (lower) systems. The Fe-Mg partitioning between olivine and clinopyroxene is insensitive to pressure but sensitive to temperature in the Mg-rich system. The K_{D} is dependent on both pressure and temperature in the Fe-rich system.

$$\begin{aligned}
-\Delta G^0 &= -(\Delta H^0 - T\Delta S^0 + P\Delta V^0) \\
&= \mathrm{R}T \ln K_{\mathrm{D}} - (1 - 2X^{\mathrm{ol}}_{\mathrm{Fe}})[(W^{\mathrm{ol}}_{H})_{\mathrm{FeMg}} + P(W^{\mathrm{ol}}_{V})_{\mathrm{FeMg}}] \\
&\quad + (1 - 2X^{\mathrm{cpx}}_{\mathrm{Fe}})[(W^{\mathrm{cpx}}_{H})_{\mathrm{FeMg}} - T(W^{\mathrm{cpx}}_{S})_{\mathrm{FeMg}} \\
&\qquad + P(W^{\mathrm{cpx}}_{V})_{\mathrm{FeMg}}] \\
&\doteqdot \mathrm{R}T \ln K_{\mathrm{D}} - (\Delta W_H - T\Delta W_S + P\Delta W_V) \qquad (22\mathrm{a})
\end{aligned}$$

where

$$\begin{aligned}
\Delta W_H &= (W^{\mathrm{ol}}_{H})_{\mathrm{FeMg}} - (W^{\mathrm{cpx}}_{H})_{\mathrm{FeMg}} \\
&= 1540 - 800 = 740 \text{ cal} \qquad (22\mathrm{b})
\end{aligned}$$

$$\begin{aligned}
\Delta W_S &= (W^{\mathrm{ol}}_{S})_{\mathrm{FeMg}} - (W^{\mathrm{cpx}}_{S})_{\mathrm{FeMg}} \\
&= 0 - (-0.54) = 0.54 \text{ cal/K} \qquad (22\mathrm{c})
\end{aligned}$$

and

$$\begin{aligned}\Delta W_V &= (W_V^{\text{ol}})_{\text{FeMg}} - (W_V^{\text{cpx}})_{\text{FeMg}} \\ &= 2.22 - (-5.14) = 7.36 \text{ cal/kbar.} \quad (22d)\end{aligned}$$

Rearranging Equation 22, we find:

$$-\Delta G^* = -(\Delta H^* - T\Delta S^* + P\Delta V^*) = RT \ln K_D \quad (23a)$$

where thermodynamic parameters ΔG^*, ΔH^*, ΔS^*, and ΔV^* are the effective free energy, enthalpy, entropy, and volume changes of Reaction 1, respectively, and defined as (see Matsui and Nishizawa, 1974)

$$\begin{aligned}\Delta H^* &= \Delta H^0 - \Delta W_H \\ &= 4960 - (1540 - 800) = 4220 \text{ cal} \quad (23b)\end{aligned}$$

$$\begin{aligned}\Delta S^* &= \Delta S^0 - \Delta W_S \\ &= 2.66 - (0 - 0.54) = 3.20 \text{ cal/K} \quad (23c)\end{aligned}$$

and

$$\begin{aligned}\Delta V^* &= \Delta V^0 - \Delta W_V \\ &= 7.17 - [2.22 - (-5.14)] = -0.19 \text{ cal/kbar.} \quad (23d)\end{aligned}$$

The dependence of K_D on pressure is derived from the effective volume change ΔV^* instead of ΔV^0. In such an extremely high-Mg system, the value of ΔV^* is extremely small. This indicates that the Fe-Mg partition between olivine and clinopyroxene in the Mg-rich system is insensitive to the variation of pressure (Fig. 8). The temperature dependence of K_D originates in the magnitude of the effective entropy, ΔS^*, which has a fairly large value in the Mg-rich system. This indicates that the exchange of Fe^{2+} and Mg^{2+} between olivine and clinopyroxene is sensitive to temperature in the Mg-rich system (Fig. 8).

In the case where X_{Fe} of the system would be close to unity, Equation 23, definitions of the effective enthalpy, entropy, and volume changes (ΔH^*, ΔS^*, and ΔV^*), are rewritten as

$$\begin{aligned}\Delta H^* &= \Delta H^0 + \Delta W_H = 4960 + (1540 - 800) \\ &= 5700 \text{ cal} \quad (24a)\end{aligned}$$

$$\begin{aligned}\Delta S^* &= \Delta S^0 + \Delta W_S = 2.66 + (0 - 0.54) \\ &= 2.12 \text{ cal/K} \quad (24b)\end{aligned}$$

and

$$\begin{aligned}\Delta V^* &= \Delta V^0 + \Delta W_V = 7.17 + [2.22 - (-5.14)] \\ &= 14.53 \text{ cal/kbar.} \quad (24c)\end{aligned}$$

In the Fe-rich system, effective volume change, ΔV^*, has a large value of 14.53 cal/kbar, with the result that the Fe-Mg partitioning would be highly pressure-dependent (Fig. 8). Although ΔS^* of 2.12 cal/K is smaller than ΔS^0, the Fe-Mg partitioning is sensitive to the variation of temperature in the Fe-rich system (Fig. 8).

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APPENDIX 1. MIXING OF $(Ca,Fe,Mg)_2SiO_4$ OLIVINE

The solubility of Ca^{2+} in olivine coexisting with clinopyroxene increases with increasing temperature and decreasing pressure, but the Ca contents of olivine are extremely low (Finnerty and Boyd, 1978; Adams and Bishop, 1982, 1986). In the present experiments, we have found that the Ca solubility of olivine ranged from 0.0016 to 0.0212 in the values of X_{Ca} at pressures of 30 and 75 kbar and temperatures 900–1500 °C. Perkins and Vielzeuf (1992) reported $X_{ca} = 0.003$–0.049 in olivines at 10.5 kbar and 1000 °C. We present the Ca effects on ΔG^0 in Equation 4 under two thermodynamic models: (1) the double-sited regular solution model and (2) the Ca-Fe-Mg ternary regular solution model.

Using the double-sited regular solution model (Grover, 1974), we can write the ratio of the activity coefficients of olivine in the second term of the right side of Equation 4:

$$\begin{aligned} \tfrac{1}{2}RT \ln\frac{\gamma^{ol}_{Mg_2SiO_4}}{\gamma^{ol}_{Fe_2SiO_4}} = {} & -\tfrac{1}{2}(1 - 2X^{M1}_{Fe})W^{M1}_{FeMg} \\ & - \tfrac{1}{2}(X^{M2}_{Mg} - X^{M2}_{Fe})W^{M2}_{FeMg} \\ & + \tfrac{1}{2}X^{M2}_{Ca}(W^{M2}_{MgCa} - W^{M2}_{CaFe}) \\ & + \tfrac{1}{2}(1 - X^{M1}_{Fe} - X^{M2}_{Fe})\delta_1 \\ & - \tfrac{1}{2}(1 - X^{M1}_{Mg} - X^{M2}_{Mg})\delta_2 \qquad \text{(A1)} \end{aligned}$$

where W is the Margules parameter, and the excess interaction energies δ_1 amd δ_2 are defined as

$$\delta_1 = \mu^0_{Fe_2SiO_4} + \mu^0_{CaMgSiO_4} - \mu^0_{FeMgSiO_4} - \mu^0_{CaFeSiO_4} \qquad \text{(A2)}$$

and

$$\delta_2 = \mu^0_{Mg_2SiO_4} + \mu^0_{CaFeSiO_4} - \mu^0_{MgFeSiO_4} - \mu^0_{CaMgSiO_4}. \qquad \text{(A3)}$$

Hirschmann (1991) evaluated the mixing parameters for the Ca-bearing olivines from the experimental data of the miscibility gaps (Mukhopadhyay and Lindsley, 1983; Davidson and Mukhopadhyay, 1984; Adams and Bishop, 1985) and from the olivine-pyroxene partition data (Adams and Bishop, 1986; Davidson and Lindsley, 1989). The results are as follows (in units of calories per atom and kilobars):

$$W^{M2}_{MgCa} = 8246 + 83.65P \text{ and } W^{M2}_{CaFe} = 5234. \qquad \text{(A4)}$$

By the substitution of these values into the third term of the right side in Equation A1, we can estimate the effect of Ca in olivine on the Fe-Mg partitioning. This term in Equation A1 is not significant for olivines because they have low CaO contents. This term has a value of 20—200 cal/mol for most of the experimental compositions. This implies that the effect of Ca in olivine on the free energy change of Reaction 1 is negligible, and olivine would be treated as an Fe-Mg binary solution for the Fe-Mg partition with clinopyroxene.

A similar point is made in the case of the ternary regular solution model (see Prigogine and Defay, 1954) for the $(Ca,Fe,Mg)_2SiO_4$ olivine. Equation A1 is rewritten by

$$\begin{aligned} \tfrac{1}{2}RT \ln\frac{\gamma^{ol}_{Mg_2SiO_4}}{\gamma^{ol}_{Fe_2SiO_4}} = {} & W^{ol}_{FeMg}(X^{ol}_{Fe} - X^{ol}_{Mg}) \\ & + (W^{ol}_{MgCa} - W^{ol}_{CaFe})X^{ol}_{Ca}. \qquad \text{(A5)} \end{aligned}$$

Equation A5 implies that the effects of Ca ions are negligible if olivines have extremely low Ca^{2+} contents:

$$\tfrac{1}{2}RT \ln\frac{\gamma^{ol}_{Mg_2SiO_4}}{\gamma^{ol}_{Fe_2SiO_4}} \doteqdot W^{ol}_{FeMg}(2X^{ol}_{Fe} - 1) \quad (\text{if } X^{ol}_{Ca} \ll 1). \qquad \text{(A6)}$$

We confirm that the quotient of activity coefficients of olivine is shown in Equation A6, and we can assume that olivine is the $(Fe,Mg)_2SiO_4$ regular solution.

APPENDIX 2. Ca-Fe-Mg MIXING IN CLINOPYROXENE

Using the double-sited asymmetric regular solution model for clinopyroxene (Davidson, 1985; Davidson and Lindsley, 1989), the free energy change of Reaction 1 is rewritten as

$$\begin{aligned} -\Delta G^0 & = -(\Delta H^0 - T\Delta S^0 + P\Delta V^0) \\ & = -(\tfrac{1}{2}\mu^{0,ol}_{Mg_2SiO_4} + \mu^{0,cpx}_{CaFeSi_2O_6} - \tfrac{1}{2}\mu^{0,ol}_{Fe_2SiO_4} - \mu^{0,cpx}_{CaMgSi_2O_6}) \\ & = \tfrac{1}{2}RT \ln\frac{a^{ol}_{Mg_2SiO_4}}{a^{ol}_{Fe_2SiO_4}} + RT \ln\frac{a^{cpx}_{CaFeSi_2O_6}}{a^{cpx}_{CaMgSi_2O_6}} \\ & = \tfrac{1}{2}RT \ln\frac{a^{ol}_{Mg_2SiO_4}}{a^{ol}_{Fe_2SiO_4}} + RT \ln\frac{X^{M1}_{Fe}}{X^{M1}_{Mg}} \\ & \quad + (F^0 + \Delta G^0_E)(1 - X^{M2}_{Ca}) \\ & \quad - \Delta G^0_*(X^{M2}_{Fe} - X^{M2}_{Mg}) + W^{M1}(1 - 2X^{M1}_{Fe}) \qquad \text{(A7)} \end{aligned}$$

where W^{M1} is the Fe-Mg interaction parameter on the M1 site, and X_i^{A} is the cationic mole fraction of i ions of the A site in the clinopyroxene solid solution. Here energy parameters F^0, ΔG_E^0, and ΔG_*^0 are given by (Davidson, 1985)

$$F^0 = 2(\mu^0_{\mathrm{CaMgSi_2O_6}} - \mu^0_{\mathrm{CaFeSi_2O_6}}) - (\mu^0_{\mathrm{Mg_2Si_2O_6}} - \mu^0_{\mathrm{Fe_2Si_2O_6}}) \quad \text{(A8a)}$$

$$\Delta G_E^0 = \mu^0_{\mathrm{Mg(M2)Fe(M1)Si_2O_6}} - \mu^0_{\mathrm{Fe(M2)Mg(M1)Si_2O_6}} \quad \text{(A8b)}$$

and

$$\Delta G_*^0 = \mu^0_{\mathrm{Fe(M2)Mg(M1)Si_2O_6}} + \mu^0_{\mathrm{Mg(M2)Fe(M1)Si_2O_6}} - \mu^0_{\mathrm{Mg_2Si_2O_6}} - \mu^0_{\mathrm{Fe_2Si_2O_6}}. \quad \text{(A8c)}$$

If the clinopyroxenes are close to the hedenbergite-diopside join ($X_{\mathrm{Ca}}^{\mathrm{M2}} \div 1$), the third and fourth terms of Equation A7 are approximately equal to zero, and Equation A7 is, therefore, rewritten by

$$-\Delta G^0 = \tfrac{1}{2}\mathrm{R}T \ln \frac{a^{\mathrm{ol}}_{\mathrm{Mg_2SiO_4}}}{a^{\mathrm{ol}}_{\mathrm{Fe_2SiO_4}}} + \mathrm{R}T \ln \frac{X^{\mathrm{cpx}}_{\mathrm{Fe}}}{X^{\mathrm{cpx}}_{\mathrm{Mg}}} + W^{\mathrm{cpx}}_{\mathrm{FeMg}}(1 - 2X^{\mathrm{cpx}}_{\mathrm{Fe}}) \quad \text{(A9)}$$

where we assume that $X_{\mathrm{Fe}}^{\mathrm{M1}} \div X_{\mathrm{Fe}}^{\mathrm{cpx}}$ ($X_{\mathrm{Mg}}^{\mathrm{M1}} \div X_{\mathrm{Mg}}^{\mathrm{cpx}}$) and $W^{\mathrm{M1}} \div W^{\mathrm{cpx}}_{\mathrm{FeMg}}$, because the clinopyroxenes are nearly saturated in Ca ($X_{\mathrm{Ca}}^{\mathrm{M2}} \div 1$). Equation A9 is equivalent to Equation 9, which is derived from the binary regular solution model for Ca(Fe,Mg)$\mathrm{Si_2O_6}$ clinopyroxene.

APPENDIX 3. LEAST-SQUARES REGRESSION OF THE PARTITION DATA

Least-squares methods usually have been applied to evaluate thermodynamic parameters of minerals on the assumption that the element partition reaction would be expressed by a linear-function (e.g., Perkins and Vielzeuf, 1992). As has been pointed out by Kawasaki and Matsui (1977, 1978), element partitioning is described essentially by a nonlinear equation with respect to chemical compositions of coexisting phases. Although we actually carried out a two-variable regression assuming $W^{\mathrm{ol}}_{\mathrm{FeMg}} = 1540 + 2.22P$ (units are calories per atom and kilobars), we present here, in a general form, the procedures of the systematic calculation of the thermodynamic parameters, including ΔG^0, $W^{\mathrm{ol}}_{\mathrm{FeMg}}$, and $W^{\mathrm{cpx}}_{\mathrm{FeMg}}$ from the element partition data.

We applied the least-squares technique (e.g., Deming, 1943) to estimate the thermodynamic parameters minimizing the sum of weighted squares of the residuals, which are defined as the difference between the directly observed and calculated compositions. This sum is given by

$$S = \Sigma(\text{weight}\cdot\text{residual}^2) \quad \text{(A10)}$$

where the summation is carried out for all observations. In the present least-squares fitting, the residuals are defined as

$$v_{x_i} = X_i - x_i \quad \text{(A11a)}$$

and

$$v_{y_i} = Y_i - y_i \quad \text{(A11b)}$$

where X and Y are the observed $X^{\mathrm{ol}}_{\mathrm{Fe}}$ and $X^{\mathrm{cpx}}_{\mathrm{Fe}}$, respectively, and x and y are the calculated $X^{\mathrm{ol}}_{\mathrm{Fe}}$ and $X^{\mathrm{cpx}}_{\mathrm{Fe}}$, respectively. We assume that the observed compositions X and Y have the standard errors σ_x and σ_y, or weights w_x (= $1/\sigma_x^2$) and w_y (= $1/\sigma_y^2$), respectively. We shall write the sum S as follows:

$$S = \sum_i (w_{x_i} v_{x_i}^2 + w_{y_i} v_{y_i}^2). \quad \text{(A12)}$$

Then the requirement of the least squares is rewritten:

$$\tfrac{1}{2}\delta S = \sum_i w_{x_i} v_{x_i} \delta v_{x_i} + \sum_i w_{y_i} v_{y_i} \delta v_{y_i} = 0. \quad \text{(A13)}$$

In order to perform the least-squares calculation systematically, we define the conditional function, which is derived from Equation 9:

$$F_i = -A - \ln \frac{(1 - X_i)Y_i}{X_i(1 - Y_i)} + B(1 - 2X_i) - C(1 - 2Y_i) \quad \text{(A14)}$$

where $A = \Delta G^0/\mathrm{R}T$, $B = W^{\mathrm{ol}}_{\mathrm{FeMg}}/\mathrm{R}T$, $C = W^{\mathrm{cpx}}_{\mathrm{FeMg}}/\mathrm{R}T$. It is obvious that the conditional function F is nonlinear with respect to the compositions (X and Y) of coexisting phases.

For the calculated compositions x_i and y_i and the true values of the thermodynamic parameters a, b, and c, we find

$$F_i(x_i, y_i; a, b, c) = -a - \ln \frac{(1 - x_i)y_i}{x_i(1 - y_i)} + b(1 - 2x_i) - c(1 - 2y_i) = 0. \quad \text{(A15)}$$

On the other hand, the conditional function F_i is generally not equal to zero for the observed compositions X_i and Y_i and the approximate parameters A, B, and C:

$$F_i(X_i, Y_i; A, B, C) = -A - \ln \frac{(1 - X_i)Y_i}{X_i(1 - Y_i)} + B(1 - 2X_i) - C(1 - 2Y_i) \neq 0. \quad \text{(A16)}$$

The $F_i(X_i, Y_i; A, B, C)$ has a small value. By the expansion of Equation A16 by Taylor's series and by retaining the first powers of residuals, we can obtain the following reduced conditions:

$$F_i(X_i, Y_i; A, B, C) = F_x^i v_{x_i} + F_y^i v_{y_i} + F_a^i A_0 + F_b^i B_0 + F_c^i C_0 \quad \text{(A17)}$$

where A_0, B_0, and C_0 are

$$A_0 = A - a, \quad B_0 = B - b, \quad \text{and} \quad C_0 = C - c. \quad \text{(A18)}$$

Here F_x^i, F_y^i, F_a^i, F_b^i, and F_c^i denote the derivatives:

$$F_x^i = \frac{\partial F_i}{\partial x_i} = \frac{1}{X_i(1 - X_i)} - 2B \qquad \text{(A19a)}$$

$$F_y^i = \frac{\partial F_i}{\partial y_i} = -\frac{1}{Y_i(1 - Y_i)} + 2C \qquad \text{(A19b)}$$

$$F_a^i = \frac{\partial F_i}{\partial a} = -1 \qquad \text{(A19c)}$$

$$F_b^i = \frac{\partial F_i}{\partial b} = 1 - 2X_i \qquad \text{(A19d)}$$

and

$$F_c^i = \frac{\partial F_i}{\partial c} = -1 + 2Y_i. \qquad \text{(A19e)}$$

By the differentiation of the Equation A17, we find the following equation:

$$\delta F_i = F_x^i \delta v_{x_i} + F_y^i \delta v_{y_i} + F_a^i \delta A_0 + F_b^i \delta B_0 + F_c^i \delta C_0 = 0. \qquad \text{(A20)}$$

Multiplying Equation A20 through Lagrange multipliers $(-\lambda)$, we get

$$-\sum_i \lambda_i F_x^i \delta v_{x_i} - \sum_i \lambda_i F_y^i \delta v_{y_i} - \sum_i \lambda_i F_a^i \delta A_0 - \sum_i \lambda_i F_b^i \delta B_0 - \sum_i \lambda_i F_c^i \delta C_0 = 0. \qquad \text{(A21)}$$

Adding Equations A13 and A21, we get the following equation:

$$\sum_i (w_{x_i} v_{x_i} - \lambda_i F_x^i) \delta v_{x_i} + \sum_i (w_{y_i} v_{y_i} - \lambda_i F_y^i) \delta v_{y_i} - \sum_i \lambda_i F_a^i \delta A_0 - \sum_i \lambda_i F_b^i \delta B_0 - \sum_i \lambda_i F_c^i \delta C_0 = 0. \qquad \text{(A22)}$$

In order to satisfy Equation A22 for all observations, the coefficients of the variations δv_{x_i}, δv_{y_i}, δA_0, δB_0, and δC_0 are exactly equal to zero:

$$w_{x_i} v_{x_i} - \lambda_i F_x^i = 0 \qquad \text{(A23a)}$$

$$w_{y_i} v_{y_i} - \lambda_i F_y^i = 0 \qquad \text{(A23b)}$$

$$\sum_i \lambda_i F_a^i = 0 \qquad \text{(A23c)}$$

$$\sum_i \lambda_i F_b^i = 0 \qquad \text{(A23d)}$$

and

$$\sum_i \lambda_i F_c^i = 0. \qquad \text{(A23e)}$$

From Equations A23a and A23b, differences between the observed and calculated compositions are given by the following equations:

$$v_{x_i} = X_i - x_i = \frac{\lambda_i F_x^i}{w_{x_i}} \qquad \text{(A24a)}$$

and

$$v_{y_i} = Y_i - y_i = \frac{\lambda_i F_y^i}{w_{y_i}}. \qquad \text{(A24b)}$$

Substituting Equation A24 into Equation A12, we obtain the new expression of S:

$$S = \sum_i \lambda_i^2 L_i \qquad \text{(A25)}$$

where L coefficients are defined as

$$L_i = \frac{(F_x^i)^2}{w_{x_i}} + \frac{(F_y^i)^2}{w_{y_i}}. \qquad \text{(A26)}$$

By the substitution of Equations A24a, A24b, and A26 into Equation A17, we rewrite the conditonal function F:

$$F_i = \lambda_i L_i + F_a^i A_0 + F_b^i B_0 + F_c^i C_0. \qquad \text{(A27)}$$

The L coefficients in Equation A26 are rewritten as Equation A28, using standard errors σ_{x_i} and σ_{y_i} of observed quantities X_i and Y_i:

$$\begin{aligned} L_i &= \sigma_{F_i}^2 \\ &= (F_x^i \sigma_{x_i})^2 + (F_y^i \sigma_{y_i})^2 \\ &= \left[\frac{1}{X_i(1 - X_i)} - 2B\right]^2 \sigma_{x_i}^2 + \left[\frac{1}{Y_i(1 - Y_i)} - 2C\right]^2 \sigma_{y_i}^2. \end{aligned} \qquad \text{(A28)}$$

As is clear in Equation A28, the uncertainty of the conditional function results from the propagations of errors σ_{x_i} and σ_{y_i}.

It is interesting to note that the least-squares calculation is impossible when the quantity of the L coefficient is equal to zero. This singular point coincides with the condition of spinodal unmixing for both phases:

$$\frac{1}{X_i(1 - X_i)} - 2B = 0,$$

and

$$\frac{1}{Y_i(1 - Y_i)} - 2C = 0. \qquad \text{(A29)}$$

It is obvious from Equation A28 that the L coefficient has an infinite value if $X = 0$ or $X = 1$ (or $Y = 0$ or $Y = 1$), and the uncertainty of F becomes larger for the near end-member composition than for the intermediate compositions. This indicates that the weights ($= 1/L_i$) of the conditional function F for the intermediate composition are essentially greater than those for the end compositions.

The Lagrange multipliers λ_i are obtained from Equation A27:

$$\lambda_i = (F_i - F_a^i A_0 - F_a^i B_0 - F_c^i C_0)/L_i. \qquad \text{(A30)}$$

If Equations A24 and A30 are substituted into Equation A25, S is given by

$$\begin{aligned} S &= \sum_i \lambda_i^2 L_i \\ &= \sum_i \lambda_i F_i \\ &= \sum_i \frac{F_i F_i}{L_i} - \sum_i \frac{F_i F_a^i}{L_i} A_0 - \sum_i \frac{F_i F_b^i}{L_i} B_0 - \sum_i \frac{F_i F_c^i}{L_i} C_0. \end{aligned} \qquad \text{(A31)}$$

By the substitution of λ_i from Equation A30 in Equations A23c, A23d, and A23e, the normal equations are derived as

$$\left[\frac{F_aF_a}{L}\right]A_0 + \left[\frac{F_aF_b}{L}\right]B_0 + \left[\frac{F_aF_c}{L}\right]C_0 = \left[\frac{FF_a}{L}\right] \quad \text{(A32a)}$$

$$\left[\frac{F_bF_a}{L}\right]A_0 + \left[\frac{F_bF_b}{L}\right]B_0 + \left[\frac{F_bF_c}{L}\right]C_0 = \left[\frac{FF_b}{L}\right] \quad \text{(A32b)}$$

$$\left[\frac{F_cF_a}{L}\right]A_0 + \left[\frac{F_cF_b}{L}\right]B_0 + \left[\frac{F_cF_c}{L}\right]C_0 = \left[\frac{FF_c}{L}\right] \quad \text{(A32c)}$$

where the Gauss bracket [ ] means the summation of the data.

Once we obtain the parameter residuals A_0, B_0, and C_0 from Equation A32, the calculated values a, b, and c are given by

$$a = A - A_0,\ b = B - B_0,\ \text{and}\ c = C - C_0. \quad \text{(A33)}$$

By iterate calculations, the values of a, b, and c in Equations A33 are substituted into Equation A16 as the approximated values of A, B, and C, respectively. Then we can carry out the least-squares fitting under the requirement of minimization of S in Equation A12. These procedures are repeated until the parameter residuals A_0, B_0, and C_0 have infinitesimal values.

From Equations A24a and A24b, we find the relation between calculated and observed values:

$$\lambda_i = \frac{w_{x_i}(X_i - x_i)}{F_x^i} = \frac{w_{y_i}(Y_i - y_i)}{F_y^i}. \quad \text{(A34)}$$

This equation expresses the geometric relation between the slope of the line segment joining the observed and calculated points. The slope of the curve is given by

$$\text{Slope of the line segment} = -\frac{w_{x_i}}{w_{y_i}} \cdot \frac{1}{\text{Slope of the curve}}. \quad \text{(A35)}$$

If $w_{x_i} = w_{y_i}$ at the observed point, the line joining observed and calculated points is perpendicular to the curve.

Here we defince the matrix Δ, factors of which are given by the coefficients of A_0, B_0, and C_0 in Equation A32:

$$\Delta = \begin{pmatrix} \left[\frac{F_aF_a}{L}\right] & \left[\frac{F_aF_b}{L}\right] & \left[\frac{F_aF_c}{L}\right] \\ \left[\frac{F_bF_a}{L}\right] & \left[\frac{F_bF_b}{L}\right] & \left[\frac{F_bF_c}{L}\right] \\ \left[\frac{F_cF_a}{L}\right] & \left[\frac{F_cF_b}{L}\right] & \left[\frac{F_cF_c}{L}\right] \end{pmatrix}. \quad \text{(A36)}$$

If the reciprocal matrix Δ^{-1} to Δ is defined as

$$\Delta^{-1} = \begin{pmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{pmatrix} \quad \text{(A37)}$$

the estimated errors of parameters a, b, and c are given by

$$\sigma_a^2 = C_{11}\frac{S}{n-k} \quad \text{(A38a)}$$

$$\sigma_b^2 = C_{22}\frac{S}{n-k} \quad \text{(A38b)}$$

and

$$\sigma_c^2 = C_{33}\frac{S}{n-k} \quad \text{(A38c)}$$

where k and n are the number of parameters determined in the regression (now $k = 3$) and the number of the observed data, respectively.