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:

\[ \frac{1}{2}\text{Fe}_2\text{SiO}_4 + \text{CaMgSi}_2\text{O}_6 = \frac{1}{2}\text{Mg}_2\text{SiO}_4 + \text{CaFeSi}_2\text{O}_6 \]  

(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 \([W'_{FAMe}] = 1540\) cal: Kawasaki and Matsui, 1983 and the unit-cell volume data of olivine \([W'_{VAMe}] = 2.22\) cal/kbar: Akimoto and Fujisawa, 1968 and clinopyroxene \([W'_{VAMe}] = -5.14\) cal/kbar: Perkins and Vielzeuf, 1992, the free energy change \((\Delta G^0)\) of Reaction 1 and the Fe-Mg mixing parameter of clinopyroxene \((W'_{FAMe})\) are evaluated by the application of a nonlinear least-squares technique and found to be \(\Delta G^0\) (cal) = \((4960 \pm 230) - (2.66 \pm 0.15)T\) (K) + \(7.17P\) (kbar) and \(W'_{FAMe}\) (cal) = \((800 \pm 380) + (0.54 \pm 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 \(W'_{FAMe}/RT)\) 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 \(W'_{FAMe} = 1.6\) kcal. From Fe-Mg partition experiments between olivine and clinopyroxene, Kawasaki and Ito (1992) found \(W'_{FAMe}\) 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)$_2$SiO$_4$ 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), spinel (Engi, 1983), and chloride solution (Schulien et al., 1972;
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 \( W_{\text{FeMg}} = 1.7 - 2.6 \) kcal at temperatures 700–1300 °C. This enables us to determine the mixing properties of Ca(Fe,Mg)\(_2\)Si\(_2\)O\(_7\) 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 CaFeSi\(_2\)O\(_6\)-CaMgSi\(_2\)O\(_6\)-CaAl\(_2\)SiO\(_4\) 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 Fe\(^{2+}\) and Mg\(^{2+}\) between olivine and clinopyroxene (abbreviated to ol and cpx, respectively) on the join of hedenbergite and diopside can be expressed by

\[
\frac{1}{2}\text{Fe}\text{SiO}_4 + \text{CaMgSi}_2\text{O}_6 = \frac{1}{2}\text{Mg}\text{SiO}_4 + \text{CaFeSi}_2\text{O}_6. \tag{1}
\]

At equilibrium, we have Equation 2:

\[
\Delta G = \frac{1}{2} \mu_{\text{MgSiO}_3}^{\text{ol}} + \mu_{\text{CaFeSi}_2\text{O}_6}^{\text{ol}} - \frac{1}{2} \mu_{\text{FeSiO}_4}^{\text{cpx}} - \mu_{\text{CaMgSi}_2\text{O}_6}^{\text{cpx}} = 0 \tag{2}
\]

where \( \mu^i \) 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 (\( \mu^s \)), chemical potentials in Equation 2 are algebraically defined as

\[
\mu_{\text{MgSiO}_3}^{\text{ol}} = \mu_{\text{MgSiO}_3}^{\text{ol}_0} + RT \ln a_{\text{MgSiO}_3}^{\text{ol}}
= \mu_{\text{MgSiO}_3}^{\text{ol}_0} + 2RT \ln X_{\text{Mg}}^{\text{ol}} + RT \ln \gamma_{\text{MgSiO}_3}^{\text{ol}} \tag{3a}
\]

\[
\mu_{\text{FeSiO}_4}^{\text{cpx}} = \mu_{\text{FeSiO}_4}^{\text{cpx}_0} + RT \ln a_{\text{FeSiO}_4}^{\text{cpx}}
= \mu_{\text{FeSiO}_4}^{\text{cpx}_0} + 2RT \ln X_{\text{Fe}}^{\text{cpx}} + RT \ln \gamma_{\text{FeSiO}_4}^{\text{cpx}} \tag{3b}
\]

\[
\mu_{\text{CaMgSi}_2\text{O}_6}^{\text{ol}} = \mu_{\text{CaMgSi}_2\text{O}_6}^{\text{ol}_0} + RT \ln a_{\text{CaMgSi}_2\text{O}_6}^{\text{ol}}
= \mu_{\text{CaMgSi}_2\text{O}_6}^{\text{ol}_0} + RT \ln X_{\text{CaMgSi}_2\text{O}_6}^{\text{ol}} + RT \ln \gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{ol}} \tag{3c}
\]

and

\[
\mu_{\text{CaFeSi}_2\text{O}_6}^{\text{ol}} = \mu_{\text{CaFeSi}_2\text{O}_6}^{\text{ol}_0} + RT \ln a_{\text{CaFeSi}_2\text{O}_6}^{\text{ol}}
= \mu_{\text{CaFeSi}_2\text{O}_6}^{\text{ol}_0} + RT \ln X_{\text{Fe}}^{\text{ol}} + RT \ln \gamma_{\text{CaFeSi}_2\text{O}_6}^{\text{ol}} \tag{3d}
\]

where \( X \) and \( \gamma \) 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, \( \Delta G^o \), for pure phases at the pressures and temperatures of interest:

\[
-\Delta G^o = -(\Delta H^o - T\Delta S^o + P\Delta V^o)
= -(\frac{1}{2} \mu_{\text{MgSiO}_3}^{\text{ol}_0} + \mu_{\text{CaFeSi}_2\text{O}_6}^{\text{ol}_0} - \frac{1}{2} \mu_{\text{FeSiO}_4}^{\text{cpx}_0} - \mu_{\text{CaMgSi}_2\text{O}_6}^{\text{ol}_0})
= RT \ln K
= RT \ln K_D + RT \ln K_T
= RT \ln K_D + \frac{RT}{2} RT \ln \frac{\gamma_{\text{MgSiO}_3}^{\text{ol}}}{\gamma_{\text{FeSiO}_4}^{\text{cpx}}} + RT \ln \frac{\gamma_{\text{CaFeSi}_2\text{O}_6}^{\text{ol}}}{\gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{ol}}} \tag{4}
\]

where the equilibrium constant \( K_D \), the distribution coefficient \( K_T \), and the quotient of activity coefficients \( K_D \), are defined as

\[
K_D = \frac{\left( \frac{\gamma_{\text{MgSiO}_3}^{\text{ol}}}{\gamma_{\text{FeSiO}_4}^{\text{cpx}}} \right)^{\frac{a_{\text{FeSiO}_4}^{\text{cpx}}}{a_{\text{FeSiO}_4}^{\text{cpx}}}}}{\frac{\gamma_{\text{CaFeSi}_2\text{O}_6}^{\text{ol}}}{\gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{ol}}}} \tag{5a}
\]

\[
K_T = \frac{X_{\text{Fe}}^{\text{ol}}}{X_{\text{Mg}}^{\text{cpx}}} \tag{5b}
\]

\[
K_D = \frac{\left( \frac{\gamma_{\text{MgSiO}_3}^{\text{ol}}}{\gamma_{\text{FeSiO}_4}^{\text{cpx}}} \right)^{\frac{a_{\text{FeSiO}_4}^{\text{cpx}}}{a_{\text{FeSiO}_4}^{\text{cpx}}}}}{\frac{\gamma_{\text{CaFeSi}_2\text{O}_6}^{\text{ol}}}{\gamma_{\text{CaMgSi}_2\text{O}_6}^{\text{ol}}}} \tag{5c}
\]

There are many thermodynamic models that describe the mixing properties of olivine and clinopyroxene. Hirschmann (1991) adopted the double-sited model for the (Ca,Mg,Fe)\(_2\)SiO\(_4\) ternary olivine and evaluated the nonidealities of calcium-magnesium and calcium-iron olivines. The effect of Ca\(^{2+}\) in olivine on the \( \Delta G^o \) 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 (Fe,Mg)\(_2\)SiO\(_4\) 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

\[
RT \ln \gamma_{\text{MgSiO}_3}^{\text{ol}} = 2\left( X_{\text{Mg}}^{\text{ol}} \right)^2 \left( W_{\text{FeMg}}^{o} \right) \tag{6a}
\]
where $W_{\text{FeMg}}^{\text{ol}}$ 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)SiO$_3$ 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

$$\ln \gamma_{\text{FeMg}}^{\text{ps}} = 2(W_{\text{FeMg}}^{\text{ps}})^2$$

and

$$\ln \gamma_{\text{CaMgSiO}_3}^{\text{ps}} = (X_{\text{Fe}})W_{\text{FeMg}}^{\text{ps}}$$

where $W_{\text{FeMg}}^{\text{ps}}$ is equivalent to $\alpha$, $W_{\text{ps}}$, and $w$ in the notations of Prigogine and Defay (1954), Thompson (1967), and Guggenheim (1977), respectively. We can interpret $W_{\text{FeMg}}^{\text{ps}}$ as the Fe-Mg interaction parameter at the M1 site of clinopyroxene. This parameter is equivalent to $W_{\text{ps}}^\text{mol}$ in Equation A7, following the notation of Davidson and Lindsley (1989).

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

$$W = W_{\text{ps}} - TW_{\text{s}} + PW_{\text{v}}$$

where $W_{\text{ps}}$, $W_{\text{s}}$, and $W_{\text{v}}$ are the nonideal parameters for enthalpy, entropy, and volume. For the Fe-Mg binary solution of phase A, the $(W_{\text{FeMg}}^{\text{ps}})^{\text{FeMg}}$ is defined as follows (e.g., O'Neill and Wood, 1979):

$$V_{\text{A}} - V_{\text{FeMg}}^{\text{ps}} = V_{\text{FeMg}}^{\text{ps}} - V_{\text{FeMg}}^{\text{ps}} = X_{\text{Fe}} X_{\text{Mg}} (W_{\text{FeMg}}^{\text{ps}})$$

where $V_{\text{FeMg}}^{\text{ps}}$ is the molar volume of the pure i of the phase A and the excess volume $V_{\text{FeMg}}^{\text{ps}}$ 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 $2(W_{\text{FeMg}}^{\text{ps}})^{\text{FeMg}}$ and $(W_{\text{FeMg}}^{\text{ps}})^{\text{FeMg}}$ 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$_2$SiO$_4$-Mg$_2$SiO$_4$ olivine solid solution (Fig. 1A). The deviation from the linearity is calculated to be $0.186 \pm 0.049$ cm$^3$/mol in the term of $2(W_{\text{FeMg}}^{\text{ps}})^{\text{FeMg}}$ 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 $2(W_{\text{FeMg}}^{\text{ps}})^{\text{FeMg}}$ are estimated to be $0.322 \pm 0.021$ cm$^3$/mol from the data of Fisher and Medaris (1969) and $0.335 \pm 0.052$ cm$^3$/mol from Perkins and Vielzeuf's data (1992).

O'Neill and Wood (1979) evaluated $W_{\text{FeMg}}^{\text{ps}}$ 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 $W_{\text{FeMg}}^{\text{ps}}$ 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 $W_{\text{FeMg}}^{\text{ps}}$ 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, $W_{\text{FeMg}}^{\text{ps}}$, 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)SiO$_3$ clinopyroxene solid solution. The values of $(W_{\text{FeMg}}^{\text{ps}})^{\text{FeMg}}$ are also given in Table 1, derived from the data of the molar volumes of the CaFeSi$_2$O$_6$-CaMgSi$_2$O$_6$ 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 $(W_{\text{FeMg}}^{\text{ps}})^{\text{FeMg}}$ is calculated to be $0.924 \pm 0.125$ cm$^3$/mol.

We find $(W_{\text{FeMg}}^{\text{ps}})^{\text{FeMg}}$ to be $0.036 \pm 0.074$ from the data of Rutin and Yund (1969) and $-0.034 \pm 0.072$ cm$^3$/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 $-0.215 \pm 0.081$ cm$^3$/mol for $(W_{\text{FeMg}}^{\text{ps}})^{\text{FeMg}}$. We can examine these values of $(W_{\text{FeMg}}^{\text{ps}})^{\text{FeMg}}$, as far as $K_0$
is concerned, by comparing the magnitude of $W_{\text{Fe-Mg}}^{\text{excess}}$ 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 $W_{\text{Fe-Mg}}^{\text{excess}}$ at 10.5 kbar and 1000 °C using ($W_{\text{Fe-Mg}}^{\text{excess1}}$) 1540 cal (Kawasaki and Matsui, 1983) and ($W_{\text{Fe-Mg}}^{\text{excess2}}$) 2.22 cal/kbar (Akimoto and Fujisawa, 1968). The least-squares fitting yielded $W_{\text{Fe-Mg}}^{\text{excess}}$ at 10.5 kbar and 1000 °C of 1390 cal. The addition of the excess volume term to this result gives $W_{\text{Fe-Mg}}^{\text{excess}}$ 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 $W_{\text{Fe-Mg}}^{\text{excess}}$ of 1060 cal. From this good agreement between the latter value and that obtained from Perkins and Vielzeuf's experiments, within ±1σ, 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 ($\Delta G^o$):

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

$$= RT \ln K_D - (1 - 2X_{\text{Fe}}^{\text{excess}}) W_{\text{Fe-Mg}}^{\text{excess}}$$

$$(1 - 2X_{\text{Fe}}^{\text{excess}}) W_{\text{Fe-Mg}}^{\text{excess}}$$

where

$$W_{\text{Fe-Mg}}^{\text{excess}} = (W_{\text{Fe-Mg}}^{\text{excess1}}) + P(W_{\text{Fe-Mg}}^{\text{excess2}})$$

and

$$W_{\text{Fe-Mg}}^{\text{excess}} = (W_{\text{Fe-Mg}}^{\text{excess1}}) - T(W_{\text{Fe-Mg}}^{\text{excess2}}) + P(W_{\text{Fe-Mg}}^{\text{excess2}})$$

We can evaluate the thermodynamic parameters, including $\Delta G^o$ and $W_{\text{Fe-Mg}}^{\text{excess}}$ 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)$_2$SiO$_4$ and clinopyroxenes Ca(Fe,Mg)Si$_2$O$_6$ 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 CaFeSiO₃-CaMgSiO₃ 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 Fe/Mg equivalent to the quartz + magnetite + fayalite buffer were controlled by the mixed gas technique using the CO₂-H₂ system for 10-30 h. The temperature was raised linearly according to the increase in the CaMgSiO₃ 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 single-phase material. Chemical homogeneity was obtained by using a scanning electron microscope, a single-phase material. Chemical homogeneity was obtained by using a scanning electron microscope, a single-phase material. Chemical homogeneity was obtained by using a scanning electron microscope, a single-phase material. Chemical homogeneity was obtained by using a scanning electron microscope, a single-phase material.

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 using an electron microprobe analyzer, JEOL model-T330A, with a Link Systems Model AN10000/SQ-200J energy-dispersive system. The ranges of variations in XFe 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% Cr₂O₃ to reduce the thermal conductivity. A lanthanum chromite (LaCrO₃) 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

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<th>Expt.</th>
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<td>0.4200</td>
<td>75 kbar/1100 °C</td>
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<td>0.4200</td>
<td>75 kbar/1100 °C</td>
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<td>0.4403</td>
<td></td>
</tr>
</tbody>
</table>

- Standard errors are in parentheses and refer to the last decimal place.
- Coexisting with γ spinel (Xγ < 0.01).
- Au capsule was used, and metallic Fe was not observed in these experiments. Others were graphite capsules, and metallic Fe was observed.

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, \(1 \times 10^{-9} \) 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 within +2% relative and contained a total oxide weight percent of +0.3%. 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 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 \((\text{Fe},_2\text{Mg},_0.3)\text{SiO}_4\) olivine and \(\text{Ca}(_{0.4}\text{Fe},_0.6)\text{Si}_2\text{O}_5\) clinopyroxene. Final compositions of olivine and clinopyroxene in this experiment showed \(X_{\text{Fe}} = 0.300\) and \(X_{\text{Fe}}^{\text{cpx}} = 0.254\) (Fig. 2). In contrast, in experiment no. MSA920520A with a starting mix of olivine with \(X_{\text{Fe}} = 0.4\) and clinopyroxene with \(X_{\text{Fe}} = 0.1\), olivine became more magnesian, and clinopyroxene became enriched in \(\text{Fe}^{2+}\). The final compositions were \(X_{\text{Fe}} = 0.292\) and \(X_{\text{Fe}}^{\text{cpx}} = 0.242\) (Fig. 2).

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

\[
\text{Fe}_2\text{Si}_3\text{O}_6 = \text{Fe}_0 + \text{FeSiO}_3 + \frac{1}{2}\text{O}_2, \tag{12}
\]

From this chemical reaction, the clinopyroxenes became slightly Ca-poor relative to the initial compositions on the hedenbergite-diopside join. This depletion of the \(\text{CaSiO}_3\) component in clinopyroxene would also arise partly from the small amount of substitution of \(\text{Ca}^{2+}\) for \(\text{Mg}^{2+}\) and \(\text{Fe}^{2+}\) in olivine solid solution:

\[
\text{Ca}_2\text{MgSi}_2\text{O}_6 + \frac{1}{2}\text{Mg}_2\text{Si}_2\text{O}_5 = \frac{1}{2}\text{Mg}_2\text{Si}_2\text{O}_5 + \frac{1}{2}\text{Ca}_2\text{Si}_2\text{O}_5, \tag{13}
\]
Reversal experiments on the solubility of Ca\textsuperscript{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\textsuperscript{2+} and Mg\textsuperscript{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 $W_{FeMg}^{ol}$ and $W_{FeMg}^{cpx}$ terms. We believe such calculations have no meaning in themselves. The free energy change of reaction, $\Delta G^0$, in Equation 9 is rewritten by

$$-\Delta G^0 = RT \ln K_D - (1 - 2X_{Fe})\Delta W + 2X_{Fe} W_{FeMg}^{cpx}$$

(15a)

where

$$\Delta W = W_{FeMg}^{ol} - W_{FeMg}^{cpx}$$

(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.

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

The terms $W_{Fe}^{ol}$ and $W_{Fe}^{cpx}$ are poorly determined in the present regression because the $\Delta X_{Fe}$ term does not vary much as a function of composition. The reliable results will only be obtainable for the difference in the mixing parameters, $\Delta W$. This indicates that the exchange reaction is insensitive to the absolute magnitudes of $W_{Fe}^{ol}$ and $W_{Fe}^{cpx}$ 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 $\Delta G^0$ and $\Delta W$, and with large uncertainty for $W_{Fe}^{ol}$ and $W_{Fe}^{cpx}$. Fortunately, we have other evidence to limit the Fe-Mg mixing properties of olivine. The magnitude of the nonideality, $W_{Fe}^{cpx}$, 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 $(W_{Fe}^{ol})^{cpx}$ (on the basis of 1540 cal for one exchangeable cation), and Akimoto and Fujisawa’s (1968) excess volume term $(W_{Fe}^{ol})^{cpx}$ (2.22 cal/kbar, see Table 1). Nonlinear least-squares fittings were then carried out to evaluate the $\Delta G^0$ and $W_{Fe}^{cpx}$, assuming that $W_{Fe}^{ol} = 1540 + 2.22P$. 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.

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 $W_{Fe}^{cpx}$ and $\Delta G^0$ 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, $\Delta W$, are also given in Table 3.

**The nonideality of Ca(Fe,Mg)Si$_2$O$_6$ clinopyroxene**

The calculated values of $W_{Fe}^{cpx}$ 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

<table>
<thead>
<tr>
<th>P (kbar)</th>
<th>T (°C)</th>
<th>ΔG° (cal)</th>
<th>W_{FeMg}° (cal)</th>
<th>ΔW (cal)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>1500</td>
<td>770(40)**</td>
<td>1440(100)</td>
<td>270(40)</td>
</tr>
<tr>
<td>75</td>
<td>1300</td>
<td>1300(70)</td>
<td>920(190)</td>
<td>790(250)</td>
</tr>
<tr>
<td>75</td>
<td>1100</td>
<td>1950(210)</td>
<td>1060(400)</td>
<td>640(350)</td>
</tr>
<tr>
<td>10.5†</td>
<td>1100</td>
<td>1400(130)</td>
<td>1460(310)</td>
<td>140(160)</td>
</tr>
<tr>
<td>10.5†</td>
<td>1100</td>
<td>1730(40)</td>
<td>950(100)</td>
<td>130</td>
</tr>
<tr>
<td>10.5†</td>
<td>1100</td>
<td>1930(40)</td>
<td>900(100)</td>
<td>130</td>
</tr>
<tr>
<td>10.5†</td>
<td>1100</td>
<td>1930(40)</td>
<td>900(100)</td>
<td>130</td>
</tr>
<tr>
<td>10.5†</td>
<td>1100</td>
<td>1730(40)</td>
<td>950(100)</td>
<td>130</td>
</tr>
<tr>
<td>75</td>
<td>900</td>
<td>1920(60)</td>
<td>1410(140)</td>
<td>150(140)</td>
</tr>
</tbody>
</table>

Note: W_{FeMg}° (cal) = -1540 + 2.22P (kbar) is assumed.

* The ΔW = W_{FeMg}° - W_{FeMg}°
** Standard errors are in parentheses and refer to the last decimal place.
† Results of Perkins and Vielzeuf (1992), who assumed W_{FeMg}° = 1080 cal. Note that ΔW = 130 cal.
‡ Recalculated from Perkins and Vielzeuf’s (1992) data, assuming W_{FeMg}° = 1080 cal. Note that ΔW = 170 cal.
§ Recalculated from Perkins and Vielzeuf’s (1992) data, assuming W_{FeMg}° (cal) = 1540 + 2.22P (kbar). Note that ΔW = 170 cal.

The (W_{FeMg}°)_{FeMg} is pressure and temperature dependent. Using the values of (W_{FeMg}°)_{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

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

The (W_{FeMg}°)_{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 $\partial W^{\text{mix}}_{\text{FeMg}}/\partial P$ of −6.17 in Equation 16 within ±1σ. Therefore, we adopt the volume data of clinopyroxene reported by Perkins and Vielzeuf (1992). Using (W_{FeMg}°)_{FeMg} of −5.14 cal/kbar estimated from Perkins and Vielzeuf’s (1992) volume data, we evaluated again the temperature dependence of $W^{\text{mix}}_{\text{FeMg}}$. The result was as follows:

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

The first term of this Equation is in very good agreement with $W^{\text{mix}}$ of 790 cal derived by Davidson and Lindsay (1989) for clinopyroxene from the thermodynamic analysis of pyroxene + olivine + quartz equilibria in the system CaO-FeO-MgO-SiO₂. 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 Fe²⁺ and Mg²⁺ 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 $\partial G^{\text{mix}}/\partial T > 0$ 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 $K_i = (X_A^2X_M^1)/(X_B^2X_M^1)$ would approach unity with increasing temperature, and $K_i = 1$ at the completely disordered state. The excess energy $G^{\text{mix}} = W^{\text{mix}}_{\text{M1}}X_A^2X_M^1 + W^{\text{mix}}_{\text{M2}}X_B^2X_M^1$ would increase 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, $W^{\text{mix}}_{\text{FeMg}}$, decreases as pressure increases, but it increases as temperature increases.
As has been discussed in the previous section, the Fe-Mg partition reaction is insensitive to the absolute magnitudes of $W^0_{FeMg}$ and $W^0_{MgMg}$ but strongly dependent on the difference between these two parameters. We obtained the following result:

$$\Delta W = W^0_{FeMg} - W^0_{MgMg} = 170 \pm 100 \text{ cal.} \quad (19)$$

Perkins and Vielzeuf (1992) obtained $\Delta W$ of 130 cal at 10.5 kbar and 1000 °C. A slight discrepancy between the present and Perkins and Vielzeuf's results in the $\Delta W$ 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 ±1σ.

**Pressure and temperature dependence of $\Delta G^0$**

The effect of pressure on $\Delta G^0$ of Reaction 1 at constant temperature is calculated from the volume data of (Fe,Mg),SiO$_4$ olivine (Akimoto and Fujisawa, 1968) and Ca(Fe,Mg)Si$_2$O$_6$ clinopyroxene (Perkins and Vielzeuf, 1992):

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

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

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

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

The $\Delta V^0$ 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 ($X_{Fe} \approx 0$). Equation 9 becomes

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

$$= RT \ln K_0 - (1 - 2X_{Fe}^0)[(W^0_H)^{FeMg} + P(W^0_S)^{FeMg}] + (1 - 2X_{Fe}^0)[(W^0_H)^{MgMg} - T(W^0_S)^{MgMg}] + P(W^0_S)^{MgMg}$$

$$+ RT \ln K_0 - (\Delta W_H - T\Delta W_S + P\Delta W_T) \quad (22a)$$

where

$$\Delta W_H = (W^0_H)^{FeMg} - (W^0_H)^{MgMg} = 1540 - 800 = 740 \text{ cal} \quad (22b)$$

$$\Delta W_S = (W^0_S)^{FeMg} - (W^0_S)^{MgMg} = 0 - (-0.54) = 0.54 \text{ cal/K} \quad (22c)$$
the Fe-Mg partitioning is sensitive to the variation of effective volume change $A I^* / AV_o$ instead of $AV_o$. In such an temperature in the Fe-rich system (Fig. 8). Although AS* of 2.12 callK is smaller than AS0, this indicates that the Fe-Mg partition between extremely high-Mg system, the value of AV* is extremely unity, Equation 23, definitions of the effective enthalpy, and volume changes (Al1*, AS*, and AZ*), are rearranged Equation 22, we find:

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

where thermodynamic parameters $\Delta G^*$, $\Delta H^*$, $\Delta S^*$, and $\Delta V^*$ are the effective free energy, enthalpy, entropy, and volume changes of Reaction 1, respectively, and defined as (see Matsui and Nishizawa, 1974)

$$\Delta H^* = \Delta H^0 - \Delta W_H = 4960 - (1540 - 800) = 4220 \text{ cal}$$

$$(23b)$$

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

and

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

The dependence of $K_o$ on pressure is derived from the effective volume change $\Delta V^*$ instead of $\Delta V^0$. In such an extremely high-Mg system, the value of $\Delta V^*$ 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 $K_o$ originates in the magnitude of the effective entropy, $\Delta S^*$, 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 $X_o$ of the system would be close to unity, Equation 23, definitions of the effective enthalpy, entropy, and volume changes ($\Delta H^*$, $\Delta S^*$, and $\Delta V^*$), are rewritten as

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

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

and

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

In the Fe-rich system, effective volume change, $\Delta V^*$, 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 $\Delta S^*$ of 2.12 cal/K is smaller than $\Delta S^0$, the Fe-Mg partitioning is sensitive to the variation of temperature in the Fe-rich system (Fig. 8).

**ACKNOWLEDGMENTS**

We express our hearty thanks to Dexter Perkins and an anonymous reviewer for their critical discussions. Donald H. Lindsley kindly gave T.K. the computer program QUIIF. Some of the expenses of this study were defrayed by the Grant in Aid for Scientific Research from the Ministry of Education, Science, and Culture of the Japanese Government to T.K. (no. 04460740).

**REFERENCES CITED**


Bartholomew, P.R. (1989) Interpretation of the solution properties of Fe-Mg olivines and aqueous Fe-Mg chlorides from ion-exchange experiments. American Mineralogist, 74, 37–49.


APPENDIX 1. MIXING OF (Ca,Fe,Mg)2SiO4 OLIVINE

The solubility of Ca2+ 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 Xca at pressures of 30 and 75 kbar and temperatures 900-1500 °C. Perkins and Vielzeuf (1992) reported Xca = 0.003-0.049 in olivines at 10.5 kbar and 1000 °C. We present the Ca effects on AG0 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:

\[ \frac{\gamma_{\text{MgSiO}_4}^{\text{FeSiO}_4}}{\gamma_{\text{FeSiO}_4}^{\text{MgSiO}_4}} = \frac{1}{2RT} \ln \frac{W_{\text{FeSiO}_4}^{\text{MgSiO}_4}}{W_{\text{MgSiO}_4}^{\text{FeSiO}_4}} = -\frac{1}{2}(1 - 2X_{\text{MCa}})W_{\text{FeCa}}^{\text{MgCa}} + \frac{1}{2}X_{\text{MCa}}(W_{\text{MgCa}}^{\text{FeCa}} - W_{\text{FeCa}}^{\text{MgCa}}) \]

\[ + \frac{1}{2}(1 - X_{\text{FeCa}}^2)X_{\text{MgCa}} - \frac{1}{2}(1 - X_{\text{FeCa}}^2)X_{\text{MgCa}} \]

where \( W \) is the Margules parameter, and the excess interaction energies \( \delta_1 \) and \( \delta_2 \) are defined as

\[ \delta_1 = \mu_{\text{FeSiO}_4}^{\text{MgSiO}_4} + \mu_{\text{CaMgSiO}_4}^{\text{MgSiO}_4} - \mu_{\text{FeMgSiO}_4}^{\text{MgSiO}_4} - \mu_{\text{CaFeSiO}_4}^{\text{MgSiO}_4} \]

\[ (A2) \]

and

\[ \delta_2 = \mu_{\text{MgSiO}_4}^{\text{FeSiO}_4} + \mu_{\text{CaFeSiO}_4}^{\text{FeSiO}_4} - \mu_{\text{FeMgSiO}_4}^{\text{FeSiO}_4} - \mu_{\text{CaMgSiO}_4}^{\text{FeSiO}_4} \]

\[ (A3) \]

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):

\[ W_{\text{MCa}}^{\text{FeMg}} = 8246 + 83.65P \text{ and } W_{\text{CaFe}}^{\text{MgCa}} = 5234. \]

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)2SiO4 olivine. Equation A1 is rewritten by

\[ \frac{1}{2RT} \ln \frac{\gamma_{\text{MgSiO}_4}^{\text{FeSiO}_4}}{\gamma_{\text{FeSiO}_4}^{\text{MgSiO}_4}} = -\frac{X_{\text{Ca}}^2}{2}W_{\text{FeCa}}^{\text{MgCa}} + \frac{X_{\text{Ca}}}{2}(W_{\text{MgCa}}^{\text{FeCa}} - W_{\text{FeCa}}^{\text{MgCa}}) \]

Equation A5 implies that the effects of Ca ions are negligible if olivines have extremely low Ca2+ contents:

\[ \frac{1}{2RT} \ln \frac{\gamma_{\text{MgSiO}_4}^{\text{FeSiO}_4}}{\gamma_{\text{FeSiO}_4}^{\text{MgSiO}_4}} = \frac{X_{\text{Ca}}}{2}(2X_{\text{Ca}} - 1) \quad \text{if } X_{\text{Ca}} < 1. \]

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)SiO4 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

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

\[ = -\frac{1}{2}(\mu_{\text{FeCa}}^{\text{MgSiO}_4} + \mu_{\text{CaFeSiO}_4}^{\text{MgSiO}_4} - \mu_{\text{FeMgSiO}_4}^{\text{MgSiO}_4} - \mu_{\text{CaSiO}_4}^{\text{MgSiO}_4}) \]

\[ = \frac{1}{2RT} \ln \frac{a_{\text{FeCa}}^{\text{MgSiO}_4}}{a_{\text{CaFeSiO}_4}^{\text{MgSiO}_4}} + \frac{1}{RT} \ln \frac{a_{\text{FeMgSiO}_4}^{\text{MgSiO}_4}}{a_{\text{CaSiO}_4}^{\text{MgSiO}_4}} \]

\[ + (F^0 + \Delta G^0)(1 - X_{\text{Mg}}^2) \]

\[ - \Delta G(\frac{X_{\text{Fe}}}{2} - \frac{X_{\text{Mg}}}{2} + \frac{W_{\text{FeCa}}^{\text{MgCa}}}{2}) = (A7) \]

where \( W_{\text{Mg}}^{\text{FeMg}} \) is the Fe-Mg interaction parameter on the M1
site, and $X^A_i$ is the cation mole fraction of $i$ ions of the A site in the clinopyroxene solid solution. Here energy parameters $F^0$, $\Delta G^0$, and $\Delta G^2$ are given by (Davidson, 1985)

$$F^0 = 2(\mu_{M_2SiO_3} - \mu_{FeSiO_3}) - (\mu_{M_1SiO_3} - \mu_{FeSiO_3})$$

$$\Delta G^0 = \mu_{FeM_2SiO_3} - \mu_{FeSiO_3}$$

and

$$\Delta G^2 = \mu_{M_2FeSiO_3} - \mu_{M_1SiO_3} - \mu_{FeSiO_3}$$

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

$$\Delta G^0 = \frac{1}{2}RT \ln \frac{a_{FeSiO_3}^{X_{Fe}}}{a_{M_2SiO_3}^{X_{M2}}} + RT \ln \frac{X_{Fe}^{X_{Fe}}}{X_{M2}^{X_{M2}}}$$

where we assume that $X_{Fe}^{X_{Fe}} = X_{M2}^{X_{M2}}$ and $W^{Fe} = W^{M2}$ because the clinopyroxenes are nearly saturated in Ca ($X^{Ca^+}_i = 1$). Equation A9 is equivalent to Equation 9, which is derived from the binary regular solution model for Ca(Fe,Mg)Si$_2$O$_6$ 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 $W^{Fe}_{FeSiO_3} = 1540 + 2.22P$ (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 $\Delta G^0$, $W^{Fe}_{FeSiO_3}$, and $W^{X_{Fe}}_{FeSiO_3}$ 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

$$S = \sum (\text{weight} \cdot \text{residual})^2$$

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

$$v_i = X_i - x_i$$

and

$$v_i = Y_i - y_i$$

where $X$ and $Y$ are the observed $X^{Fe}_i$ and $X^{M2}_i$, respectively, and $x$ and $y$ are the calculated $X^{Fe}_i$ and $X^{M2}_i$, respectively. We assume that the observed compositions $X$ and $Y$ have the standard errors $\sigma_x$ and $\sigma_y$, or weights $w_x (= 1/\sigma^2_x)$ and $w_y (= 1/\sigma^2_y)$, respectively. We shall write the sum $S$ as follows:

$$S = \sum (w_xv_x^2 + w_yv_y^2).$$

Then the requirement of the least squares is rewritten:

$$\frac{1}{2} \delta S = \sum w_x v_x \delta x_i + \sum w_y v_y \delta y_i = 0.$$  

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

$$F_i = -A - \ln \left(\frac{1 - X_i}{X_i(1 - Y_i)}\right) + B(1 - 2X_i) - C(1 - 2Y_i)$$

where $A = \Delta G^0/RT$, $B = W^{Fe}_{FeSiO_3}/RT$, $C = W^{X_{Fe}}_{FeSiO_3}/RT$. 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

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

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 $C$:

$$F_i(X_i, \text{I}; A, B, C) = -A - \ln \left(\frac{1 - X_i}{X_i(1 - Y_i)}\right) + B(1 - 2X_i) - C(1 - 2Y_i)$$

$$\neq 0.$$  

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:

$$F_i(X_i, Y_i; A, B, C) = F_i^a v_x + F_i^b v_y + F_i^c A_0 + F_i^d B_0 + F_i^e C_0$$

where $A_0$, $B_0$, and $C_0$ are

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

Here $F_i^a$, $F_i^b$, $F_i^c$, $F_i^d$, and $F_i^e$ denote the derivatives:
By the differentiation of the Equation A17, we find the following equation:

$$F'_x = \frac{\partial F}{\partial x} = \frac{1}{X(1 - X)} - 2B$$ (A19a)

$$F'_y = \frac{\partial F}{\partial y} = \frac{1}{Y(1 - Y)} + 2C$$ (A19b)

$$F'_a = \frac{\partial F}{\partial a} = -1$$ (A19c)

$$F'_b = \frac{\partial F}{\partial b} = 1 - 2X_i$$ (A19d)

and

$$F'_c = \frac{\partial F}{\partial c} = -1 + 2Y_i.$$ (A19e)

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

$$\delta F_i = F'_i \delta v_{x_i} + F'_i \delta v_{y_i} + F'_i \delta A_0 + F'_i \delta B_0 + F'_i \delta C_0 = 0.$$ (A20)

Multiplying Equation A20 through Lagrange multipliers \((\lambda_i)\), we get

$$- \sum_i \lambda_i F'_i \delta v_{x_i} - \sum_i \lambda_i F'_i \delta v_{y_i} - \sum_i \lambda_i F'_i \delta A_0$$

$$- \sum_i \lambda_i F'_i \delta B_0 - \sum_i \lambda_i F'_i \delta C_0 = 0.$$ (A21)

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

$$\sum_i (w_{x_i} v_{x_i} - \lambda_i F'_x) \delta v_{x_i} + \sum_i (w_{y_i} v_{y_i} - \lambda_i F'_y) \delta v_{y_i}$$

$$- \sum_i \lambda_i F'_i \delta A_0 - \sum_i \lambda_i F'_i \delta B_0 - \sum_i \lambda_i F'_i \delta C_0 = 0.$$ (A22)

In order to satisfy Equation A22 for all observations, the coefficients of the variations \(\delta v_{x_i}, \delta v_{y_i}, \delta A_0, \delta B_0,\) and \(\delta C_0\) are exactly equal to zero:

$$w_{x_i} v_{x_i} - \lambda_i F'_x = 0$$ (A23a)

$$w_{y_i} v_{y_i} - \lambda_i F'_y = 0$$ (A23b)

$$\sum_i \lambda_i F'_x = 0$$ (A23c)

$$\sum_i \lambda_i F'_y = 0$$ (A23d)

and

$$\sum_i \lambda_i F'_i = 0.$$ (A23e)

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

$$v_{x_i} = X_i - x_i = \frac{\lambda_i F'_x}{w_{x_i}}$$ (A24a)

and

$$v_{y_i} = Y_i - y_i = \frac{\lambda_i F'_y}{w_{y_i}}.$$ (A24b)

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

$$S = \sum_i \lambda_i L_i$$ (A25)

where \(L\) coefficients are defined as

$$L_i = \frac{(F_{x_i})^2}{w_{x_i}} + \frac{(F_{y_i})^2}{w_{y_i}}.$$ (A26)

By the substitution of Equations A24a, A24b, and A26 into Equation A17, we rewrite the conditional function \(F:\)

$$F_i = \lambda_i L_i + F'_x A_0 + F'_y B_0 + F'_C C_0.$$ (A27)

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

$$L_i = \sigma_{x_i},$$

$$= (F_{x_i} \sigma_{x_i})^2 + (F_{y_i} \sigma_{y_i})^2$$

$$= \left[ \frac{1}{X_i(1 - X_i)} - 2B \right] \sigma_{x_i}^2 + \left[ \frac{1}{Y_i(1 - Y_i)} - 2C \right] \sigma_{y_i}^2.$$ (A28)

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

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

$$\frac{1}{Y_i(1 - Y_i)} - 2C = 0.$$ (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 \(\lambda_i\) are obtained from Equation A27:

$$\lambda_i = (F_{x_i} - F_{x_i} A_0 - F_{y_i} B_0 - F_{C_i} C_0)/L_i.$$ (A30)

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

$$S = \sum_i \lambda_i L_i$$

and

$$S = \sum_i \lambda_i F_{x_i}$$

$$= \sum_i \frac{F_{x_i} F_{x_i}}{L_i} - \sum_i \frac{F_{x_i} F_{y_i}}{L_i} A_0 - \sum_i \frac{F_{x_i} F_{b}}{L_i} B_0 - \sum_i \frac{F_{x_i} F_{c}}{L_i} C_0.$$ (A31)
By the substitution of \( \lambda \) from Equation A30 in Equations A23c, A23d, and A23e, the normal equations are derived as

\[
\begin{align*}
\left[ \frac{F_a F_a}{L} \right] A_0 + \left[ \frac{F_a F_b}{L} \right] B_0 + \left[ \frac{F_a F_c}{L} \right] C_0 &= \left[ \frac{F F_a}{L} \right] \\
\left[ \frac{F_b F_a}{L} \right] A_0 + \left[ \frac{F_b F_b}{L} \right] B_0 + \left[ \frac{F_b F_c}{L} \right] C_0 &= \left[ \frac{F F_b}{L} \right] \\
\left[ \frac{F_c F_a}{L} \right] A_0 + \left[ \frac{F_c F_b}{L} \right] B_0 + \left[ \frac{F_c F_c}{L} \right] C_0 &= \left[ \frac{F F_c}{L} \right]
\end{align*}
\]  
(A32a)

(A32b)

(A32c)

where the Gauss bracket \([\text{ ]}\) 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

\[
a = A - A_0, \quad b = B - B_0, \quad c = C - C_0.
\]  
(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:

\[
\lambda_i = \frac{w_i (X_i - x_i)}{F_i} = \frac{w_i (Y_i - y_i)}{F_i}.
\]  
(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

Slope of the line segment

\[
= -\frac{w_i}{w_i} \cdot \frac{1}{\text{Slope of the curve}}.
\]  
(A35)

If \( w_i = w_i \) at the observed point, the line joining observed and calculated points is perpendicular to the curve.

Here we define the matrix \( \Delta \), factors of which are given by the coefficients of \( A_0, B_0, \) and \( C_0 \) in Equation A32:

\[
\Delta = \begin{pmatrix}
\frac{F_a F_a}{L} & \frac{F_a F_b}{L} & \frac{F_a F_c}{L} \\
\frac{F_b F_a}{L} & \frac{F_b F_b}{L} & \frac{F_b F_c}{L} \\
\frac{F_c F_a}{L} & \frac{F_c F_b}{L} & \frac{F_c F_c}{L}
\end{pmatrix}
\]  
(A36)

If the reciprocal matrix \( \Delta^{-1} \) to \( \Delta \) is defined as

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

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

\[
\sigma_a^2 = C_{11} \frac{S}{n - k},
\]

(A38a)

\[
\sigma_b^2 = C_{22} \frac{S}{n - k},
\]

(A38b)

and

\[
\sigma_c^2 = C_{33} \frac{S}{n - k},
\]

(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.