Thermodynamic formulations of $(\text{Ca,Fe,Mg})_2\text{SiO}_4$ olivine.

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Abstract

The multi-site regular solution model is applied to the intracrystalline exchange reaction of Fe^{2+} and Mg^{2+} between M1 and M2 sites of olivine. Effects of Ca on the Fe–Mg intracrystalline distribution coefficient $K_D [= (X_{\text{Mg}}^{\text{M2}} X_{\text{Fe}}^{\text{M1}}) / (X_{\text{Fe}}^{\text{M2}} X_{\text{Mg}}^{\text{M1}})]$ are derived from this solution model, which indicates that Fe preferentially orders onto the larger M2 site accompanying with increasing Ca. This reaction would be assumed to be temperature-independent. The difference between Fe–Mg mixing parameters of M1 and M2 sites is very small and temperature-independent, so that the fayalite–forsterite olivine would be approximated as a binary regular solution.

The miscibility gaps between high-Ca and low-Ca olivines are sufficiently described by the disordered multi-site regular solution model, which is very similar to a symmetric regular solution model. The present estimates for Margules parameters $W_{\text{MgCa}}^{\text{M2}}$ is consistent with Davidson and Mukhopadhyay's (1984) analysis of miscibility gap in Ca–Fe–Mg olivines, and is slightly less non-ideal than the Adams and Bishop's (1985) results estimated from the monticellite–forsterite solvus. The Ca–Fe mixing is more non-ideal than the previous estimates.

Introduction

We have accumulated fairly reliable data for the thermodynamic properties of the fayalite–forsterite olivine from studies of the Fe–Mg exchange equilibria (Nafziger and Muan, 1967; Kitayama and Katsura, 1968; Medaris, 1969; Matsui and Nishizawa, 1974; Kawasaki and Matsui, 1977, 1983; Kawasaki, 1979; O'Neill and Wood, 1979; Hackler and Wood, 1989; Engi, 1983; Schulien *et al.*, 1972; Bartholomew, 1989; Perkins and Vielzeuf, 1992; Kawasaki and Ito, 1992, 1994), and from the calorimetric measurements (Wood and Kleppa, 1981; Thierry *et al.*, 1981; Wiser and Wood, 1991; Kojitani and Akaogi, 1994). These data suggest that fayalite–forsterite olivine is essentially a symmetric regular solution with $W_G = 7\text{--}10$ kJ at temperatures from 700 to 1300°C, whereas Sack and Ghiorso's (1989) model is much more non-ideal than any of the others.

The monticellite (CaMgSiO_4)–forsterite (MgMgSiO_4) join (Biggar and O'Hara, 1969; Yang, 1973; Warner and Luth, 1973; Adams and Bishop, 1985) shows the asymmetric mis-

cibility gap at the subsolidus temperatures and the limited solubility of CaO in forsterite olivine. Adams and Bishop (1985) analyzed the two-phase miscibility data and evaluated the excess energy for mixing of Ca^{2+} and Mg^{2+} in olivine solid solution under the asymmetric regular solution model with W_{Fo} (kJ) = $43.1 - 6.01T$ and W_{Mo} (kJ) = $61.2 - 15.2T$. Mukhopadhyay and Lindsley (1983) studied the phase relations in the join fayalite (FeFeSiO_4)–kirschsteinite (CaFeSiO_4) and concluded that this miscibility gap is described by the symmetric Margules model with $W_{\text{CaFe}} = 21.866$ kJ. Brown (1980) suggested that the continuous solid solution exists along CaMgSiO_4 – CaFeSiO_4 join.

The overall regular solution model is unrealistic for the Ca–Fe–Mg olivine because the Ca_2SiO_4 end member does not crystallize with olivine structure under normal conditions (Smith, *et al.*, 1965) and the Ca–Fe–Mg olivine is plotted onto the quadrilateral bounded by four end members: forsterite (Mg_2SiO_4), fayalite (Fe_2SiO_4), kirschsteinite (CaFeSiO_4) and monticellite (CaMgSiO_4). Crystallographic studies show that Ca is very strongly partitioned into the M2 site (Brown, 1980; Lumpkin *et al.*, 1983). Davidson and Mukhopadhyay (1984) presented a solution model and analyzed the phase relations of the $(\text{Ca,Fe,Mg})_2\text{SiO}_4$ olivines. Their model was so incomplete that the fayalite–forsterite olivine was assumed to be ideal and the compositional dependence could not be explained adequately on the Fe–Mg intracrystalline exchange reaction.

This paper concerns the thermodynamic formulations for Ca–Fe–Mg olivines. Using the multi-site regular solution model presented here, thermodynamic analyses are carried out on the experimental data of the Fe–Mg intracrystalline exchange equilibria for the Ca-free olivine. The present multi-site model is more realistic than those of Davidson and Mukhopadhyay (1984) and Davidson and Lindsley (1989) because the compositional dependence of the Fe–Mg intracrystalline exchange equilibria and the Fe–Mg mixing property with a positive deviation from ideality are incorporated into this model. The formulation can be carried out by the analogy with the model presented by Kawasaki and Matsui (1983) for $(\text{Fe,Mg})^{\text{M2}}(\text{Fe,Mg,Al})^{\text{M1}}(\text{Si,Al})_2\text{O}_6$ orthopyroxene. Finally a new mixing model, namely, the disordered multi-site regular solution model, is applied to analyze the miscibility gaps between high-Ca and low-Ca olivines. This model is very similar to the overall regular solution model, and is framed under the constraints of chemical compositions that olivines are plotted onto the quadrilateral.

Theory of a Multi-site Solution for $(\text{Ca, Fe, Mg})_2\text{SiO}_4$ Olivine

Let us consider the complex solid solution of $(\text{Ca,Fe,Mg})_2\text{SiO}_4$ olivine. Chemical formulae are generally written as $(\text{Ca,Fe,Mg})^{\text{M2}}(\text{Fe,Mg})^{\text{M1}}\text{SiO}_4$, where the superscripts M1 and M2 refer to the distinct types of octahedral site in the olivine. The following assumptions are employed: (a) Ca^{2+} ions are restricted to M2 sites; (b) Fe and Mg atoms are disordered in M1 sites; (c) there is the Ca–Fe–Mg disorder in M2 sites; and: (d) the configuration of the cations on the M1 and M2 sites occurs independently of each other. The hypothetical components such

as Fe^{M2}Mg^{M1}SiO₄ and Mg^{M2}Fe^{M1}SiO₄ are derived to analyze the Fe–Mg intracrystalline exchange reaction between M1 and M2 sites of olivine by analogy with the solution model presented by Kawasaki and Matsui (1983) for (Fe,Mg)^{M2}(Fe,Mg,Al)^{M1}(Si, Al)₂O₆ orthopyroxenes. Olivine, therefore, has six possible components: CaFeSiO₄, CaMgSiO₄, FeFeSiO₄, FeMgSiO₄, MgFeSiO₄ and MgMgSiO₄. Here the superscripts M2 and M1 are omitted, and the first and second atoms occupy the M2 and M1 sites, respectively.

The Gibbs' free energy of Ca–Fe–Mg olivine, G , is given by the summation of the products of the number of moles and the chemical potential of component ABSiO₄, which can be expressed by the chemical potential of the pure phase at the standard state (μ°), entropy of mixing (S^{mix}) and the excess free energy of mixing (G^{ex}):

$$G = \sum n_{\text{ABSiO}_4} \mu_{\text{ABSiO}_4} = \sum n_{\text{ABSiO}_4} \mu_{\text{ABSiO}_4}^\circ - TS^{\text{mix}} + G^{\text{ex}}, \quad (1)$$

where n_{ABSiO_4} is the number of moles of component ABSiO₄. Under the assumption that the ions of Fe²⁺ and Mg²⁺ are randomly mixing at M1 sites and the Ca–Fe–Mg disorder occurs at M2 sites of olivine, the entropy of mixing (S^{mix}) is given by

$$S^{\text{mix}} = -Rn(X_{\text{Fe}}^{\text{M2}} \ln X_{\text{Fe}}^{\text{M2}} + X_{\text{Mg}}^{\text{M2}} \ln X_{\text{Mg}}^{\text{M2}} + X_{\text{Ca}}^{\text{M2}} \ln X_{\text{Ca}}^{\text{M2}} + X_{\text{Fe}}^{\text{M1}} \ln X_{\text{Fe}}^{\text{M1}} + X_{\text{Mg}}^{\text{M1}} \ln X_{\text{Mg}}^{\text{M1}}), \quad (2)$$

where R is the gas constant.

The formulation of the excess energy term (G^{ex}) in eq. (1) depends on the thermodynamic model of olivine as is discussed in the latter sections. Differentiating the eq. (1) by the number of moles of the component ABSiO₄, we can obtain the chemical potential of the component (μ_{ABSiO_4}) as follows:

$$\mu_{\text{ABSiO}_4} = \frac{\partial G}{\partial n_{\text{ABSiO}_4}} = \sum_{\alpha} \frac{\partial G}{\partial n_{\alpha}^{\text{M2}}} \frac{\partial n_{\alpha}^{\text{M2}}}{\partial n_{\text{ABSiO}_4}} + \sum_{\beta} \frac{\partial G}{\partial n_{\beta}^{\text{M1}}} \frac{\partial n_{\beta}^{\text{M1}}}{\partial n_{\text{ABSiO}_4}} = \frac{\partial G}{\partial n_{\text{A}}^{\text{M2}}} + \frac{\partial G}{\partial n_{\text{B}}^{\text{M1}}}. \quad (3)$$

This is a general equation of the chemical potential for the multi-site solution. In the latter sections, the chemical potentials of components of olivine are given in the exact equations.

From eq. (1), the condition for the intracrystalline exchange is given by

$$dG = \sum \mu_{\text{ABSiO}_4} dn_{\text{ABSiO}_4} = 0, \quad (4)$$

where the Gibbs-Duhem relation ($\sum n_{\text{ABSiO}_4} d\mu_{\text{ABSiO}_4} = 0$) is satisfied at the constant temperature and pressure. The condition of the internal equilibrium is rewritten in the terms of chemical potentials:

$$\mu_{\text{FeFeSiO}_4} + \mu_{\text{MgMgSiO}_4} = 2\mu_{\text{MgFeSiO}_4}, \quad (5)$$

$$\mu_{\text{FeMgSiO}_4} = \mu_{\text{MgFeSiO}_4}, \quad (6)$$

and

$$2\mu_{\text{CaMgSiO}_4} + \mu_{\text{FeFeSiO}_4} = 2\mu_{\text{CaFeSiO}_4} + \mu_{\text{MgMgSiO}_4}. \quad (7)$$

Eq. (7) is also derived from the macroscopic phase relations between olivine and Ca-bearing phase such as clinopyroxene. These equations (5), (6) and (7) are physically equivalent to one another.

FIG. 1. Fe–Mg intracrystalline exchange between M1 and M2 sites of olivine. A slight preference for Fe in M1 site is shown. Curves are the calculated occupancies of Fe at 300°C and 1000°C based on eq. (18). These results indicate the intracrystalline exchange is temperature-independent. Data plotted are the results of the X-ray diffraction analyses of a single crystal of olivine at high temperatures (Finger, 1970; Brown and Prewitt, 1973; Smyth and Hazen, 1973; Will and Nover, 1979; Nover and Will, 1981; Aikawa *et al.*, 1985; Motoyama and Matsumoto, 1989; Ottonello *et al.*, 1990).

Ca-free Olivine

The X-ray diffraction analyses of a single crystal of olivine at high temperatures (Finger, 1970; Brown and Prewitt, 1973; Smyth and Hazen, 1973; Will and Nover, 1979; Nover and Will, 1981; Aikawa *et al.*, 1985; Motoyama and Matsumoto, 1989; Ottonello *et al.*, 1990) showed a slight preference for Fe in M1 site (Fig. 1). The values of the Fe–Mg intracrystalline distribution coefficient K_D :

$$K_D = \frac{X_{\text{Mg}}^{\text{M2}} X_{\text{Fe}}^{\text{M1}}}{X_{\text{Fe}}^{\text{M2}} X_{\text{Mg}}^{\text{M1}}} \quad (8)$$

range from 1.02 to 1.56 at temperatures 300 to 1000°C, and slightly increase with temperature and the values of X_{Fe} . Akamatsu *et al.* (1993) showed K_D is insensitive to the equilibration pressure.

In order to explain the compositional dependence of K_D , the Fe–Mg interactions are assumed to be proportional to the number of the Fe–Mg pair in M1 and M2 sites of olivine. Then the excess energy of Fe–Mg olivine is written as

$$G_{\text{FeMg}}^{\text{ex}} = n(X_{\text{Fe}}^{\text{M1}} X_{\text{Mg}}^{\text{M1}} W_{\text{FeMg}}^{\text{M1}} + X_{\text{Fe}}^{\text{M2}} X_{\text{Mg}}^{\text{M2}} W_{\text{FeMg}}^{\text{M2}}). \quad (9)$$

As is written by eq. (6), the condition of the internal equilibrium of olivine in the Ca-free system is

$$\begin{aligned} \mu_{\text{FeMgSiO}_4}^\circ - \mu_{\text{MgFeSiO}_4}^\circ &= RT \ln K_D - (1 - 2X_{\text{Fe}}^{\text{M2}}) W_{\text{FeMg}}^{\text{M2}} + (1 - 2X_{\text{Fe}}^{\text{M1}}) W_{\text{FeMg}}^{\text{M1}} \\ &\quad - (X_{\text{Fe}}^{\text{M1}} - X_{\text{Fe}}^{\text{M2}})(\delta_1 + \delta_2), \end{aligned} \quad (10)$$

where the chemical potentials of the components MgFeSiO₄ and FeMgSiO₄ are obtained from eqs. (1), (2), (3) and (9). Here the excess interaction energies δ_1 and δ_2 are defined as

$$\delta_1 = \mu_{\text{FeFeSiO}_4}^\circ + \mu_{\text{CaMgSiO}_4}^\circ - \mu_{\text{FeMgSiO}_4}^\circ - \mu_{\text{CaFeSiO}_4}^\circ \quad (11)$$

and

$$\delta_2 = \mu_{\text{MgMgSiO}_4}^\circ + \mu_{\text{CaFeSiO}_4}^\circ - \mu_{\text{MgFeSiO}_4}^\circ - \mu_{\text{CaMgSiO}_4}^\circ. \quad (12)$$

These excess interaction energies δ_1 and δ_2 are concerned with the exchange of Fe²⁺ and Mg²⁺ between M1 and M2 sites of olivine, and denote the interactions between iron and magnesium ions on the different type of the sites. Summation of δ_1 and δ_2 :

$$\delta_1 + \delta_2 = \mu_{\text{FeFeSiO}_4}^\circ + \mu_{\text{MgMgSiO}_4}^\circ - \mu_{\text{FeMgSiO}_4}^\circ - \mu_{\text{MgFeSiO}_4}^\circ \quad (13)$$

is equivalent to $-\Delta\bar{G}_*^\circ$ term of Grover (1974) and Davidson and Mukhopadhyay (1984). This term is interpreted as the mean of the interactions between Fe²⁺ in M2 sites and Mg²⁺ in M1 sites and between Mg²⁺ in M2 sites and Fe²⁺ in M1 sites.

As is clear in the eq. (10), it is impossible to evaluate the magnitudes of the individual parameters such as $\mu_{\text{FeMgSiO}_4}^\circ - \mu_{\text{MgFeSiO}_4}^\circ$, $W_{\text{FeMg}}^{\text{M1}}$, $W_{\text{FeMg}}^{\text{M2}}$ and $\delta_1 + \delta_2$, because we can not separate these parameters with respect to the variables $X_{\text{Fe}}^{\text{M2}}$ and $X_{\text{Fe}}^{\text{M1}}$. So eq. (10) is rewritten as

$$\begin{aligned} \Delta G_{\text{FeMg}}^* &= \mu_{\text{FeMgSiO}_4}^\circ - \mu_{\text{MgFeSiO}_4}^\circ - W_{\text{FeMg}}^{\text{M1}} + W_{\text{FeMg}}^{\text{M2}} \\ &= RT \ln K_D + 2(W_{\text{FeMg}}^{\text{M2}} + \frac{\delta_1 + \delta_2}{2})X_{\text{Fe}}^{\text{M2}} - 2(W_{\text{FeMg}}^{\text{M1}} + \frac{\delta_1 + \delta_2}{2})X_{\text{Fe}}^{\text{M1}}. \end{aligned} \quad (14)$$

This equation has a same form as an empirical equation eq. (36) of Kawasaki and Matsui (1983) for the Fe–Mg site preference of orthopyroxene. Using the Fe–Mg site preference data of olivine from the heating experiments, the temperature dependence of the thermodynamic parameters in eq. (14) are evaluated by the application of the non-linear least-squares technique:

$$\left. \begin{aligned} \Delta G_{\text{FeMg}}^* &= \mu_{\text{FeMgSiO}_4}^{\circ} - \mu_{\text{MgFeSiO}_4}^{\circ} - W_{\text{FeMg}}^{\text{M1}} + W_{\text{FeMg}}^{\text{M2}} = -0.087 + 0.448 \times 10^{-3}T, \\ W_{\text{FeMg}}^{\text{M1}} + \frac{\delta_1 + \delta_2}{2} &= 0.090 + 15.585 \times 10^{-3}T, \\ W_{\text{FeMg}}^{\text{M2}} + \frac{\delta_1 + \delta_2}{2} &= 0.039 + 15.830 \times 10^{-3}T, \\ W_{\text{FeMg}}^{\text{M1}} - W_{\text{FeMg}}^{\text{M2}} &= 0.051 - 0.245 \times 10^{-3}T, \end{aligned} \right\} \quad (15)$$

where the units of energy and temperature are in kJ/mol and K, respectively.

As has been pointed out by Hirschmann (1991), these results show that the difference between $W_{\text{FeMg}}^{\text{M1}}$ and $W_{\text{FeMg}}^{\text{M2}}$ is very small and temperature-independent. This indicates that the magnitude of the Fe–Mg interactions in the M1 and M2 sites are practically equivalent to each other ($W_{\text{FeMg}}^{\text{M1}} = W_{\text{FeMg}}^{\text{M2}}$). The similar assumption was postulated by Sack (1980), Davidson and Mukhopadhyay (1984), Davidson and Lindsley (1989) and Sack and Ghiorso (1989). Davidson and Mukhopadhyay (1984) and Davidson and Lindsley (1989) neglected these Fe–Mg interactions. We have no positive evidence that $W_{\text{FeMg}}^{\text{M1}} = W_{\text{FeMg}}^{\text{M2}} = 0$. Therefore, it is natural to assume the Fe–Mg interaction terms as $W_{\text{FeMg}}^{\text{M1}} = W_{\text{FeMg}}^{\text{M2}} = W_{\text{FeMg}} \neq 0$. By the use of the interaction parameter for the symmetric solution W_{FeMg} , the excess energy of mixing of Fe^{2+} and Mg^{2+} in M1 and M2 sites of olivine would be modified as

$$G_{\text{FeMg}}^{\text{ex}} = n(X_{\text{Fe}}^{\text{M1}} X_{\text{Mg}}^{\text{M1}} W_{\text{FeMg}}^{\text{M1}} + X_{\text{Fe}}^{\text{M2}} X_{\text{Mg}}^{\text{M2}} W_{\text{FeMg}}^{\text{M2}}) = n(X_{\text{Fe}}^{\text{M1}} X_{\text{Mg}}^{\text{M1}} + X_{\text{Fe}}^{\text{M2}} X_{\text{Mg}}^{\text{M2}}) W_{\text{FeMg}}. \quad (16)$$

The olivine solid solution would be assumed to have the mixing property described by this empirical relation, whereas such relation is not always satisfied for all Fe–Mg silicates. Kawasaki and Matsui (1983) found $W_{\text{FeMg}}^{\text{Opx,M1}} \neq W_{\text{FeMg}}^{\text{Opx,M2}}$ for (Fe,Mg)SiO₃ orthopyroxene solid solution. Kawasaki and Ito (1994) employed the following value for the mixing parameter W_{FeMg} :

$$W_{\text{FeMg}} \text{ (kJ/mol)} = 6.44 + 0.09P \text{ (GPa)}. \quad (17)$$

These recommended values are adopted for the Fe–Mg mixing parameter of olivine in this paper.

By the relation of eq. (16), eq. (10) is modified as

$$\mu_{\text{FeMgSiO}_4}^{\circ} - \mu_{\text{MgFeSiO}_4}^{\circ} = RT \ln K_D - 2(X_{\text{Fe}}^{\text{M1}} - X_{\text{Fe}}^{\text{M2}})(W_{\text{FeMg}} + \frac{\delta_1 + \delta_2}{2}). \quad (18)$$

Using the Fe–Mg occupancy data of olivine, the parameters in eq. (18) are reevaluated (units in kJ/mol and K):

$$\begin{aligned} \mu_{\text{FeMgSiO}_4}^{\circ} - \mu_{\text{MgFeSiO}_4}^{\circ} &= -0.125 + 0.418 \times 10^{-3}T \\ W_{\text{FeMg}} + \frac{\delta_1 + \delta_2}{2} &= 0.661 + 14.447 \times 10^{-3}T. \end{aligned} \quad (19)$$

The results of the least-squares are illustrated in Fig. 1. As is clear from this figure, the Fe–Mg intracrystalline exchange of olivine is practically temperature-independent. Thus, the experiments by X-ray diffraction analyses of heated olivines show a slight preference of Fe in the smaller M1 octahedral site. On the other hand, the single-crystal neutron diffraction experiment (Artioli *et al.*, 1995), which appears to contradict with the most experimental

evidence, indicated that K_D decreases from 1.26 to 0.52 with elevating temperatures from 880°C to 1060°C. The decrease in K_D with temperature would constrain that the positive value of the nonideal parameter of entropy $(W_{\text{FeMg}})_S$ of olivine solid solution (Kojitani and Akaogi, 1994), resulting that $(W_{\text{FeMg}})_G$ decreases with increasing temperature. The discrepancy between the results of X-ray and neutron diffraction experiments might be due to the differences in the experimental conditions such as the heating durations and/or the oxygen fugacities of experiments. In the present discussion, the empirical formulation given by eq. (18) is used for the Fe–Mg partitioning between M1 and M2 sites of olivine.

Ca–Fe–Mg Olivine

The thermodynamic formulation for the Ca–Mg olivines was developed by Davidson and Mukhopadhyay (1984). The model was superseded by the asymmetry of the experimentally determined monticellite–forsterite solvus (Adams and Bishop, 1985). Davidson and Lindsley (1989) adopted the asymmetric model. The Ca–Mg interaction term of the excess energy of olivine is written as

$$G_{\text{MgCa}}^{\text{ex}} = n(X_{\text{Mg}}^{\text{M2}} W_{\text{Mo}} + X_{\text{Ca}}^{\text{M2}} W_{\text{Fo}}) X_{\text{Mg}}^{\text{M2}} X_{\text{Ca}}^{\text{M2}}. \quad (20)$$

Using the Adams and Bishop's (1985) data, the Margules parameters W_{Mo} and W_{Fo} are reevaluated as

$$\begin{aligned} W_{\text{Mo}}(\text{kJ/mol}) &= 58.2 - 12.53 \times 10^{-3} T(\text{K}) - 1.41 P(\text{GPa}) \\ W_{\text{Fo}}(\text{kJ/mol}) &= 38.6 - 2.707 \times 10^{-3} T(\text{K}) - 0.82 P(\text{GPa}). \end{aligned} \quad (21)$$

Fig. 2 shows the results of least-squares for the experimental data for the monticellite–forsterite solvus of Adams and Bishop (1985).

Experiments on the determination of the miscibility gap of the CaFeSiO_4 – FeFeSiO_4 join by Mukhopadhyay and Lindsley (1983) showed the fayalite–kirschsteinite series behaves as the symmetric regular solution (Fig. 3). The excess energy is written as

$$G_{\text{CaFe}}^{\text{ex}} = n X_{\text{Ca}}^{\text{M2}} X_{\text{Fe}}^{\text{M2}} W_{\text{CaFe}}^{\text{M2}}. \quad (22)$$

The mixing parameter of the fayalite–kirschsteinite solution is evaluated to be

FIG. 2. Results of the least squares for the miscibility gaps at 0.5 GPa (upper) and 1 GPa (lower) in the monticellite (CaMgSiO_4)–forsterite (Mg_2SiO_4) system (Adams and Bishop, 1985). The curve is drawn by the asymmetric regular solution model discussed in the text.

Fig. 3. Results of the least squares for the miscibility gaps in the fayalite (Fe_2SiO_4)–kirschsteinite (CaFeSiO_4) system (Mukhopadhyay and Lindsley, 1983). The curve is drawn by the symmetric regular solution model discussed in the text.

$$W_{\text{CaFe}}^{\text{M2}} (\text{kJ/mol}) = 23.78 - 1.94 \times 10^{-3} T (\text{K}) + 0.022 P (\text{GPa}). \quad (23)$$

From eqs. (16), (20) and (22), the excess energy term of olivine given by the following equation:

$$\begin{aligned} G^{\text{ex}} = & n(X_{\text{Fe}}^{\text{M1}} X_{\text{Mg}}^{\text{M1}} + X_{\text{Fe}}^{\text{M2}} X_{\text{Mg}}^{\text{M2}}) W_{\text{FeMg}} \\ & + n X_{\text{Mg}}^{\text{M2}} X_{\text{Ca}}^{\text{M2}} (X_{\text{Mg}}^{\text{M2}} W_{\text{Mo}} + X_{\text{Ca}}^{\text{M2}} W_{\text{Fo}}) \\ & + \frac{1}{2} n (W_{\text{Mo}} + W_{\text{Fo}}) X_{\text{Fe}}^{\text{M2}} X_{\text{Mg}}^{\text{M2}} X_{\text{Ca}}^{\text{M2}} \\ & + n X_{\text{Ca}}^{\text{M2}} X_{\text{Fe}}^{\text{M2}} W_{\text{CaFe}}^{\text{M2}}. \end{aligned} \quad (24)$$

The third term of this equation arises from preserving the coherence between the asymmetric and symmetric Ca–Fe–Mg ternary expressions, assuming that the third-degree coefficient ' W_{123} ' term (Andersen and Lindsley, 1981) would be equal to zero in any binary system. Substituting the eq. (24) into eq. (1), the Gibbs' energy of olivine is

expressed in the complete form.

We can obtain the chemical potentials of the component of olivine differentiating the Gibbs' energy by the number of moles of component in the same procedure described in eq. (3). Substituting the chemical potentials of olivine into the condition of internal equilibrium eq. (5), (6) or (7), we can obtain the expression of the intracrystalline exchange of Fe^{2+} and Mg^{2+} between M1 and M2 sites of olivine in the system CaO–FeO–MgO–SiO_2 :

$$\begin{aligned} & -(\mu_{\text{MgFeSiO}_4}^{\circ} - \mu_{\text{FeMgSiO}_4}^{\circ}) \\ & = RT \ln K_D + (1 - 2X_{\text{Fe}}^{\text{M1}} - X_{\text{Mg}}^{\text{M2}} + X_{\text{Fe}}^{\text{M2}}) W_{\text{FeMg}} + 2X_{\text{Mg}}^{\text{M2}} X_{\text{Ca}}^{\text{M2}} W_{\text{Mo}} + (X_{\text{Ca}}^{\text{M2}})^2 W_{\text{Fo}} \\ & \quad + \frac{1}{2} (W_{\text{Mo}} + W_{\text{Fo}}) X_{\text{Ca}}^{\text{M2}} (X_{\text{Fe}}^{\text{M2}} - X_{\text{Mg}}^{\text{M2}}) - X_{\text{Ca}}^{\text{M2}} W_{\text{CaFe}}^{\text{M2}} - (X_{\text{Fe}}^{\text{M1}} - X_{\text{Fe}}^{\text{M2}}) \delta_1 + (X_{\text{Mg}}^{\text{M1}} - X_{\text{Mg}}^{\text{M2}}) \delta_2. \end{aligned} \quad (25)$$

Eq. (25) is the general equation for the Fe–Mg intracrystalline equilibria of olivine in the system CaO–FeO–MgO–SiO_2 , whether or not olivine coexists with some other phases or none at all. As is seen in this equation, the Fe–Mg interaction parameter W_{FeMg} does not disappear even if we assume $W_{\text{FeMg}}^{\text{M1}} = W_{\text{FeMg}}^{\text{M2}} = W_{\text{FeMg}}$.

We can estimate the Ca-effect on the K_D qualitatively from modifying eq. (25) to eq. (26):

$$\begin{aligned} & -(\mu_{\text{MgFeSiO}_4}^{\circ} - \mu_{\text{FeMgSiO}_4}^{\circ}) = RT \ln K_D - (X_{\text{Fe}}^{\text{M1}} - X_{\text{Fe}}^{\text{M2}}) (W_{\text{FeMg}} + \delta_1) \\ & \quad + (X_{\text{Mg}}^{\text{M1}} - X_{\text{Mg}}^{\text{M2}}) (W_{\text{FeMg}} + \delta_2) + X_{\text{Ca}}^{\text{M2}} (W_{\text{MgCa}}^{\text{M2}} - W_{\text{CaFe}}^{\text{M2}}), \end{aligned} \quad (26)$$

where the symmetric model is employed for the monticellite-forsterite solid solution ($W_{\text{Fo}} = W_{\text{Mo}} = W_{\text{MgCa}}^{\text{M2}}$). This equation indicates that, if $W_{\text{MgCa}}^{\text{M2}} - W_{\text{CaFe}}^{\text{M2}}$ is positive, K_D decreases as

TABLE 1. Comparison of the mixing parameters of (Ca,Fe,Mg)₂SiO₄ olivines (units in kJ).

Parameter		Reference
$W_{\text{MgCa}}^{\text{M2}}$	33.922 ± 0.116	Mukhopadhyay and Lindsley (1983)
	32.9	Davidson and Mukhopadhyay (1984)
	38.7*	Adams and BISHOP (1985)
	32.58*	Davidson and Lindsley (1989)
	32.12 ± 0.37	Present Study**
$W_{\text{CaFe}}^{\text{M2}}$	21.866 ± 0.143	Mukhopadhyay and Lindsley (1983)
	21.4	Davidson and Mukhopadhyay (1984)
	21.56	Davidson and Lindsley (1989)
	26.76 ± 0.90	Present Study**

* Converted to the symmetric model at 1000°C and atmospheric pressure.

** Reevaluated from the data of Davidson and Mukhopadhyay (1984).

increasing X_{Ca} of olivine; i.e., Fe would become to preferentially order onto M2 site accompanying with a strong partitioning of Ca onto the larger M2 site. The case of $W_{\text{MgCa}}^{\text{M2}} > W_{\text{CaFe}}^{\text{M2}}$ is plausible because of the qualitative considerations that the degree of the non-ideality would become higher with increase in the difference of the size of the substituting ions in a solid solution.

Fe–Mg Random Mixing Model for Ca–Fe–Mg Olivine

In the crude treatment we can regard that the distribution coefficient K_D of the Fe–Mg intracrystalline exchange between M1 and M2 sites of olivine in eq. (8) would be nearly equal to the unity (see Fig. 1). The Fe–Mg random mixing assumption is fulfilled in the following case:

$$\left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}}\right)^{\text{M1}} = \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}}\right)^{\text{M2}} = \left(\frac{\text{Fe}}{\text{Fe}+\text{Mg}}\right)^{\text{Ol}}. \quad (27)$$

In this case for the Ca-free olivine, eq. (16) is modified as

$$G_{\text{FeMg}}^{\text{ex}} = 2nX_{\text{Fe}}X_{\text{Mg}}W_{\text{FeMg}}, \quad (28)$$

where X_{Fe} and X_{Mg} are the mole fractions of Fe^{2+} and Mg^{2+} in olivine solid solution $2X_{\text{Fe}} = X_{\text{Fe}}^{\text{M1}} + X_{\text{Fe}}^{\text{M2}}$ and $2X_{\text{Mg}} = X_{\text{Mg}}^{\text{M1}} + X_{\text{Mg}}^{\text{M2}}$. The assumption for the Fe–Mg random mixing is also examined by comparing the magnitude of the excess energy functions of olivine, $G_{\text{FeMg}}^{\text{ex}}$, given by eqs. (16) and (28), the values of which are calculated as 3.19 and 3.22 kJ/mole, respectively, at 1 atm and 1000°C for $X_{\text{Fe}}^{\text{Ol}}=0.5$. This indicates that the non-idealities of olivine derived from these models are energetically consistent each other, and olivine could be treated as a disordered solution for the Fe–Mg mixing. The assumption of the symmetric regular solution for the Fe–Mg olivines is supported by the calorimetric measurements by Kojitani and Akaogi (1994).

Substituting the relations (27) into eq. (25), we can derive the conditions of complete

disorder for the Fe–Mg intracrystalline equilibria:

$$\begin{aligned} \mu_{\text{FeMgSiO}_4}^{\circ} &= \mu_{\text{MgFeSiO}_4}^{\circ}, W_{\text{Fo}} = W_{\text{Mo}} = W_{\text{MgCa}}^{\text{M2}}, \delta_1 = -W_{\text{FeMg}} + W_{\text{MgCa}}^{\text{M2}} - W_{\text{CaFe}}^{\text{M2}}, \\ \text{and } \delta_2 &= -W_{\text{FeMg}} - W_{\text{MgCa}}^{\text{M2}} + W_{\text{CaFe}}^{\text{M2}}. \end{aligned} \quad (29)$$

It is worth to notice that the complete disordered state would lead to the condition of the symmetric solution.

At the complete disordered state as to the Fe–Mg substitution, chemical potentials of components eqs. (3) are given by

$$\begin{aligned} \mu_{\text{CaFeSiO}_4}^{\circ} &= \mu_{\text{CaFeSiO}_4}^{\circ} + RT \ln X_{\text{Ca}}^{\text{M2}} X_{\text{Fe}}^{\text{M1}} + 2(1-2X_{\text{Fe}})X_{\text{Mg}}W_{\text{FeMg}} \\ &+ 2X_{\text{Mg}}(1-2X_{\text{Ca}})W_{\text{MgCa}}^{\text{M2}} - (1-2X_{\text{Ca}})(1-2X_{\text{Fe}})W_{\text{CaFe}}^{\text{M2}}, \end{aligned} \quad (30)$$

$$\begin{aligned} \mu_{\text{CaMgSiO}_4}^{\circ} &= \mu_{\text{CaMgSiO}_4}^{\circ} + RT \ln X_{\text{Ca}}^{\text{M2}} X_{\text{Mg}}^{\text{M1}} + 2X_{\text{Fe}}(1-2X_{\text{Mg}})W_{\text{FeMg}} \\ &- (1-2X_{\text{Mg}})(1-2X_{\text{Ca}})W_{\text{MgCa}}^{\text{M2}} + 2(1-2X_{\text{Ca}})X_{\text{Fe}}W_{\text{CaFe}}^{\text{M2}}, \end{aligned} \quad (31)$$

$$\begin{aligned} \mu_{\text{FeFeSiO}_4}^{\circ} &= \mu_{\text{FeFeSiO}_4}^{\circ} + RT \ln X_{\text{Fe}}^{\text{M2}} X_{\text{Fe}}^{\text{M1}} + 4(1-X_{\text{Fe}})X_{\text{Mg}}W_{\text{FeMg}} \\ &- 4X_{\text{Mg}}X_{\text{Ca}}W_{\text{MgCa}}^{\text{M2}} + 4X_{\text{Ca}}(1-X_{\text{Fe}})W_{\text{CaFe}}^{\text{M2}}, \end{aligned} \quad (32)$$

$$\begin{aligned} \mu_{\text{FeMgSiO}_4}^{\circ} &= \mu_{\text{MgFeSiO}_4}^{\circ} = \mu_{\text{FeMgSiO}_4}^{\circ} (\text{or } \mu_{\text{MgFeSiO}_4}^{\circ}) + RT \ln X_{\text{Fe}}^{\text{M2}} X_{\text{Mg}}^{\text{M1}} \\ &- (1-2X_{\text{Fe}})(1-2X_{\text{Mg}})W_{\text{FeMg}} + 2(1-2X_{\text{Mg}})X_{\text{Ca}}W_{\text{MgCa}}^{\text{M2}} + 2X_{\text{Ca}}(1-2X_{\text{Fe}})W_{\text{CaFe}}^{\text{M2}}, \end{aligned} \quad (33)$$

and

$$\begin{aligned} \mu_{\text{MgMgSiO}_4}^{\circ} &= \mu_{\text{MgMgSiO}_4}^{\circ} + RT \ln X_{\text{Mg}}^{\text{M2}} X_{\text{Mg}}^{\text{M1}} + 4X_{\text{Fe}}(1-X_{\text{Mg}})W_{\text{FeMg}} \\ &+ 4(1-X_{\text{Mg}})X_{\text{Ca}}W_{\text{MgCa}}^{\text{M2}} - 4X_{\text{Ca}}X_{\text{Fe}}W_{\text{CaFe}}^{\text{M2}}, \end{aligned} \quad (34)$$

where FeMgSiO_4 and MgFeSiO_4 are the hypothetical components, and denote the complete ordered and anti-ordered components, respectively (Spear, 1993). The cationic mole fractions of Fe^{2+} , Mg^{2+} and Ca^{2+} in M1 and M2 sites are calculated from the compositional relations eq. (27):

$$\left. \begin{aligned} X_{\text{Fe}}^{\text{M2}} &= \frac{(1-2X_{\text{Ca}})X_{\text{Fe}}}{1-X_{\text{Ca}}}, \quad X_{\text{Mg}}^{\text{M2}} = \frac{(1-2X_{\text{Ca}})X_{\text{Mg}}}{1-X_{\text{Ca}}}, \\ X_{\text{Ca}}^{\text{M2}} &= 2X_{\text{Ca}}, \quad X_{\text{Fe}}^{\text{M1}} = \frac{X_{\text{Fe}}}{1-X_{\text{Ca}}}, \quad \text{and } X_{\text{Mg}}^{\text{M1}} = \frac{X_{\text{Mg}}}{1-X_{\text{Ca}}}. \end{aligned} \right\} \quad (35)$$

Eqs. (30) to (34) for the expressions of chemical potentials of quadrilateral end member components are very similar to those derived from the overall Ca–Fe–Mg ternary regular solution model for olivine (see Appendix). The essential difference between these models is found in the variable range of X_{Ca} . The value of X_{Ca} is restricted within 0–0.5 for the disordered multi-site olivine as is clear from eqs. (35), and $0 \leq X_{\text{Ca}} \leq 1$ for the Ca–Fe–Mg ternary regular solution model. The overall regular solution model does not show any compositional constraints that olivines are plotted within the Ca–Fe–Mg olivine quadrilateral bounded by MgMgSiO_4 , FeFeSiO_4 , CaFeSiO_4 and CaMgSiO_4 (Davidson and Mukhopadhyay, 1984). This compositional constraint can not be explained by the ternary regular solution model.

The necessary and sufficient conditions for equilibria between high-Ca and low-Ca olivines are given by

$$\mu_i|_{\text{high-Ca olivine}} = \mu_i|_{\text{low-Ca olivine}} \quad (36)$$

Eq. (36) satisfies for six components, CaFeSiO₄, CaMgSiO₄, FeFeSiO₄, MgMgSiO₄, FeMgSiO₄ and MgFeSiO₄, whereas the number of the independent equations is 3 because the relations among components given by the Fe–Mg intracrystalline exchange reaction are (5), (6) and (7). The choice of the independent equations (36) is made for the components FeFeSiO₄, MgMgSiO₄ and CaMgSiO₄.

Non-ideality of (Ca,Fe,Mg)₂SiO₄ Olivine

The Margules parameters $W_{\text{MgCa}}^{\text{M2}}$ and $W_{\text{CaFe}}^{\text{M2}}$ have been estimated by Mukhopadhyay and Lindsley (1983), Davidson and Mukhopadhyay (1984), Adams and Bishop (1985), and Davidson and Lindsley (1989). The results of these estimations are given in Table 1 for comparison. Mukhopadhyay and Lindsley (1983) studied the phase relations in the join fayalite (FeFeSiO₄)–kirschsteinite (CaFeSiO₄) and concluded that this miscibility gap is described by the symmetric Margules model with $W_{\text{CaFe}}^{\text{M2}} = 21.866 \pm 0.143$ kJ/mol. Using the 2 kbar data on the monticellite–forsterite join by Warner and Luth (1973), Mukhopadhyay and Lindsley (1983) also evaluated $W_{\text{MgCa}}^{\text{M2}}$ as 33.922 ± 0.116 kJ/mol. Davidson and Mukhopadhyay (1984) analyzed the phase relations of the (Ca, Fe, Mg)₂SiO₄ olivines employing the symmetric multi-site regular solution model, resulting that $W_{\text{MgCa}}^{\text{M2}} = 32.9$ kJ/mol and $W_{\text{CaFe}}^{\text{M2}} = 21.4$ kJ/mol. Using the Fe–Mg mixing data of olivine in eq. (17), the experimental data of the miscibility gap between high-Ca and low-Ca olivines by Davidson and Mukhopadhyay (1984) are thermodynamically analyzed under eqs. (36):

$$W_{\text{MgCa}} = 32.12 \pm 0.37 \text{ kJ/mol, and } W_{\text{CaFe}} = 26.76 \pm 0.90 \text{ kJ/mol.} \quad (37)$$

Adams and Bishop (1985) experimentally determined monticellite–forsterite solvus with the asymmetric excess energy given by eq. (20). The Margules parameters can be approximated as $W_{\text{MgCa}}^{\text{M2}} = 38.7$ kJ/mol at 1000°C and atmospheric pressure in the symmetric solution model. The Adams and Bishop's (1985) estimation gave slightly more non-ideal than the present and the other models. Davidson and Lindsley (1989) estimated the solution parameters of Mg–Ca and Ca–Fe olivines using the two-olivine data of Davidson and Mukhopadhyay (1984) and Adams and Bishop (1985) to be $W_{\text{Fa}} = W_{\text{Kir}} (= W_{\text{CaFe}}^{\text{M2}}) = 21.56$ kJ/mol, $W_{\text{Mo}} = 34.25$ kJ/mol and $W_{\text{Fo}} = 30.90$ kJ/mol for atmospheric pressure. These results of the asymmetric Mg–Ca mixing parameters obtained by Davidson and Lindsley (1989) can be converted to $W_{\text{MgCa}}^{\text{M2}} = 32.58$ kJ/mol for the symmetric solution at atmospheric pressure.

Summary

Formulations of the multi-site regular solution for the Ca–Fe–Mg olivine have been carried out in order to describe the Fe–Mg intracrystalline exchange reaction of olivine. From this model the effect of Ca on the Fe–Mg partitioning would be derived. The distribution coeffi-

cient K_D decreases with increasing Ca. This indicates that Fe would become to partition preferably into the larger M2 sites accompanying with increase in X_{Ca} of olivine. The K_D would increase slightly with increasing temperature. This increase is so small that the Fe–Mg intersite exchange reaction would be assumed to be temperature-independent. The Fe–Mg mixing parameters in M1 and M2 sites of olivine would be assumed to have a similar magnitude to each other ($W_{FeMg}^{M1} = W_{FeMg}^{M2} = W_{FeMg}$). The disordered multi-site regular solution can be derived from these assumptions in order to explain the miscibility gaps between high-Ca and low-Ca olivines. This model is very similar to the overall Ca–Fe–Mg regular solution model. The present model is consistent with previous models for Mg–Ca olivine except for the estimation of Adams and Bishop (1985), and slightly more non-ideal for the Ca–Fe olivine. But the discrepancy in the non-ideality for Ca–Fe olivine is within the experimental uncertainties.

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Appendix. Ternary Regular Solution of (Ca, Fe, Mg)₂SiO₄ Olivine

From the theory of ternary regular solution (*e.g.* Prigogine and Defay 1954) assuming that Ca, Fe and Mg atoms are disordered in the olivine solid solution, the following excess energy is defined as:

$$G^{ex} = 2n(X_{Fe}X_{Mg}W_{FeMg} + X_{Mg}X_{Ca}W_{MgCa} + X_{Ca}X_{Fe}W_{CaFe}). \quad (A1)$$

Here it is worth to note that the compositional range of X_{Ca} is from 0 to 1. The chemical potentials of end member components of olivines, FeFeSiO₄, MgMgSiO₄ and CaCaSiO₄, are given by

$$\begin{aligned} \mu_{CaCaSiO_4} = & \mu_{CaCaSiO_4}^{\circ} + 2RT \ln X_{Ca} - 2X_{Fe}X_{Mg}W_{FeMg} + 2X_{Mg}(1-X_{Ca})W_{MgCa} \\ & + 2(1-X_{Ca})X_{Fe}W_{CaFe}, \end{aligned} \quad (A2)$$

$$\begin{aligned} \mu_{FeFeSiO_4} = & \mu_{FeFeSiO_4}^{\circ} + 2RT \ln X_{Fe} + 2(1-X_{Fe})X_{Mg}W_{FeMg} - 2X_{Mg}X_{Ca}W_{MgCa} \\ & + 2X_{Ca}(1-X_{Fe})W_{CaFe} \end{aligned} \quad (A3)$$

and

$$\begin{aligned} \mu_{MgMgSiO_4} = & \mu_{MgMgSiO_4}^{\circ} + 2RT \ln X_{Mg} + 2X_{Fe}(1-X_{Mg})W_{FeMg} \\ & + 2(1-X_{Mg})X_{Ca}W_{MgCa} - 2X_{Ca}X_{Fe}W_{CaFe}, \end{aligned} \quad (A4)$$

where CaCaSiO₄ is the hypothetical component with an olivine structure. From eqs. (A2) to (A4), we can define the chemical potentials of other components such as CaFeSiO₄, CaMgSiO₄ and MgFeSiO₄ (or FeMgSiO₄):

$$\begin{aligned} \mu_{CaFeSiO_4} = & \frac{1}{2} (\mu_{CaCaSiO_4} + \mu_{FeFeSiO_4}) \\ = & \frac{1}{2} (\mu_{CaCaSiO_4}^{\circ} + \mu_{FeFeSiO_4}^{\circ}) + RT \ln X_{Ca}X_{Fe} + (1-2X_{Fe})X_{Mg}W_{FeMg} \\ & + X_{Mg}(1-2X_{Ca})W_{MgCa} + (X_{Ca} + X_{Fe} - 2X_{Ca}X_{Fe})W_{CaFe} \end{aligned} \quad (A5)$$

$$\begin{aligned} \mu_{CaMgSiO_4} = & \frac{1}{2} (\mu_{CaCaSiO_4} + \mu_{MgMgSiO_4}) \\ = & \frac{1}{2} (\mu_{CaCaSiO_4}^{\circ} + \mu_{MgMgSiO_4}^{\circ}) + RT \ln X_{Ca}X_{Mg} + X_{Fe}(1-2X_{Mg})W_{FeMg} \\ & + (X_{Mg} + X_{Ca} - 2X_{Mg}X_{Ca})W_{MgCa} + (1-2X_{Ca})W_{CaFe} \end{aligned} \quad (A6)$$

and

$$\begin{aligned} \mu_{FeMgSiO_4} = & \mu_{MgFeSiO_4} = \frac{1}{2} (\mu_{FeFeSiO_4} + \mu_{MgMgSiO_4}) \\ = & \frac{1}{2} (\mu_{FeFeSiO_4}^{\circ} + \mu_{MgMgSiO_4}^{\circ}) + RT \ln X_{Fe}X_{Mg} + (X_{Fe} + X_{Mg} - 2X_{Fe}X_{Mg})W_{FeMg} \\ & + (1-2X_{Mg})X_{Ca}W_{MgCa} + X_{Ca}(1-2X_{Fe})W_{CaFe}, \end{aligned} \quad (A7)$$

where these components are not independent with one another. Eqs. (A3) to (A7) are similar to eqs. (30) to (34) which are derived from the present multi-site regular solution model except for the factor 2.