Effects of Pressure and Ca^{2+} on the Fe-Mg Partitioning between Olivine and Clinopyroxene

Toshisuke KAWASAKI

Division of Earth Sciences, Department of Biosphere and Geosphere Sciences, Faculty of Science, Ehime University, Bunkyo-cho 2-5, Matsuyama 790-77, Japan

The exchange reaction of Fe^{2+} and Mg^{2+} between olivine and clinopyroxene has been experimentally determined at 1150°C, and at pressures 1 and 1.5 GPa in the Ca-poor and Ca-enriched systems, the bulk ratio $\text{Fe}/(\text{Fe}+\text{Mg})$ which was fixed as about 0.5. The CaO contents of olivine and clinopyroxene seriously affect on the Fe-Mg partition coefficient K_D [$= (X_{\text{Mg}}^{\text{Cpx}} X_{\text{Fe}}^{\text{Ol}})/(X_{\text{Fe}}^{\text{Cpx}} X_{\text{Mg}}^{\text{Ol}})$], which increases with increasing $X_{\text{Ca}}^{\text{Ol}}$. The K_D was found as 1.50 at 1 GPa for the assemblage of olivine ($X_{\text{Ca}}^{\text{Ol}} = 0.006$) and subcalcic clinopyroxene ($X_{\text{Ca}}^{\text{Cpx}} = 0.2898$); 2.90 at 1.5 GPa for the assemblage of diopside-hedenbergite clinopyroxene and olivine ($X_{\text{Ca}}^{\text{Ol}} = 0.1048$), in contrast to 3.00 at 1 GPa for the assemblage of diopside-hedenbergite clinopyroxene, olivine with $X_{\text{Ca}}^{\text{Ol}} = 0.1464$ and ferroan monticellite. On the other hand, the distribution coefficient K_D was found to be insensitive to pressure comparing with the previous data. The olivine-ferroan monticellite solvus becomes narrow with increasing pressure, but this pressure effect on the solvus is very small.

[olivine, clinopyroxene, ferroan monticellite, Fe-Mg partitioning, solution properties]

1. Introduction

The experimental constraints on the exchange of Fe^{2+} and Mg^{2+} between olivine and Ca-rich clinopyroxene (near the join of hedenbergite and diopside):

indicated that the $\text{Ca}(\text{Fe,Mg})\text{Si}_2\text{O}_6$ clinopyroxene would be a regular solution as the first approximation [1,2]. The distribution coefficient K_D is found to be highly temperature-dependent. This chemical reaction would be a good geothermometer [2].

The Ca contents of coexisting olivine and clinopyroxene seriously affect the Fe-Mg partitioning between these phases [3], especially in the Ca-enriched system [4]. It is essential to frame the thermodynamic constraints of the distribution of Ca^{2+} between these phases when we use the Fe-Mg partitioning in an olivine+clinopyroxene pair as a geothermometer to estimate the equilibration temperatures of the natural lherzolites.

The fayalite (FeFeSiO_4)-forsterite (MgMgSiO_4) olivine is essentially a symmetric regular solution with $W_{\text{FeMg}}^{\text{Ol}} = 7-10$ kJ/mol at temperatures from 700°C to 1300°C [2,5,6,7]. The forsterite (MgMgSiO_4)-monticellite (CaMgSiO_4) [8] and fayalite (FeFeSiO_4)-kirschsteinite (CaFeSiO_4) [9] miscibility gaps can be described by the symmetric Margules model with $W_{\text{MgCa}}^{\text{Ol,M2}} = 32-37$ kJ/mol and $W_{\text{CaFe}}^{\text{Ol,M2}} = 21-22$ kJ/mol [8,9,10,11], respectively. Davidson and Mukhopadhyay [10] analyzed the phase relations of the $(\text{Ca,Fe,Mg})_2\text{SiO}_4$ olivines employing the symmetric multi-site regular solution model.

In this paper, new data are presented for the assemblages of clinopyroxene+olivine and clinopyroxene+olivine+ferroan

monticellite at pressures 1 and 1.5 GPa and 1150°C, and thermodynamic analyses are carried out on the equilibria between olivine and clinopyroxene in the system CaO-FeO-MgO-SiO_2 using the disordered multi-site solution model for olivine [4] and regular solution for clinopyroxene [1,2].

2. Thermodynamic Background for the Fe-Mg Exchange Reaction between $(\text{Ca,Fe,Mg})_2\text{SiO}_4$ Olivine and $\text{Ca}(\text{Fe,Mg})\text{Si}_2\text{O}_6$ Clinopyroxene

In the present argument, it is assumed that Ca-Fe-Mg olivine behaves as the disordered multi-site regular solution, and $\text{Ca}(\text{Fe,Mg})\text{Si}_2\text{O}_6$ clinopyroxene is to be the symmetric regular solution. The free energy change of reaction (1) at the standard state is given by

$$\begin{aligned} -\Delta G_1^\circ = RT \ln & \frac{X_{\text{Mg}}^{\text{Cpx}} X_{\text{Fe}}^{\text{Ol}}}{X_{\text{Fe}}^{\text{Cpx}} X_{\text{Mg}}^{\text{Ol}}} + 2(X_{\text{Mg}}^{\text{Ol}} - X_{\text{Fe}}^{\text{Ol}})W_{\text{FeMg}}^{\text{Ol}} \\ & - 2X_{\text{Ca}}^{\text{Ol}}(W_{\text{MgCa}}^{\text{Ol,M2}} - W_{\text{CaFe}}^{\text{Ol,M2}}) - (1 - 2X_{\text{Fe}}^{\text{Cpx}})W_{\text{FeMg}}^{\text{Cpx}}, \end{aligned} \quad (2)$$

where X and W are the cationic mole fraction and the Margules parameter, respectively. Eq. (2) is very similar to the equation derived from the overall Ca-Fe-Mg ternary regular solution model for olivine [4]. Eq. (2) indicates that, if $W_{\text{MgCa}}^{\text{Ol,M2}} - W_{\text{CaFe}}^{\text{Ol,M2}}$ is positive, the Fe-Mg partition coefficient K_D would increase as increasing $X_{\text{Ca}}^{\text{Ol}}$. The case of $W_{\text{MgCa}}^{\text{Ol,M2}} > W_{\text{CaFe}}^{\text{Ol,M2}}$ 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.

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

$$\mu_i^{\text{Ol}}|_{\text{olivine}} = \mu_i^{\text{Ol}}|_{\text{ferroan monticellite}} \quad (3)$$

Eq. (3) satisfies for six components. The number of the independent equations is 3 because the relations among components are given by the following Fe-Mg intracrystalline

exchange reaction:

and

Eqs. (2) and (3) are applied to the evaluation of the Margules parameters $W_{\text{MgCa}}^{\text{Ol,M2}}$ and $W_{\text{CaFe}}^{\text{Ol,M2}}$ using previous data [2] on the Fe–Mg mixing data of olivine and clinopyroxene, and the free energy change of reaction (1).

3. Experimental Details and Results

Synthesized olivine (Fo₅₀) and clinopyroxene (Di₅₀) were used as starting materials [2,4]. The wollastonite CaSiO₃ component was prepared from reagent-grade chemical, namely, calcium silicate gel, and added to the mixture of olivine and clinopyroxene to control the Ca/(Ca+Fe+Mg) ratio of the bulk. Dried materials were ground in an agate mortar under ethyl alcohol for one hour. Grain sizes of the mineral mixture were about 1–20 μm and about 30 % of it was less than 5 μm after grinding.

High pressure experiments were carried out using a 16.0 mm piston cylinder device at Ehime University. The run pressures were 1 and 1.5 GPa and the temperature was fixed at 1150°C. Experiments were conducted in the graphite capsules (about 7 mm long and 3.5 mm in outside diameter) for durations from 60 to 312 hours. The sample container of graphite was placed in a boron nitride sleeve within a talc + Pyrex glass assembly [2]. The hot piston-in technique was applied for all runs. At about 0.1 GPa the charge was heated above the softening point of Pyrex glass (about 750°C) of a pressure transmitting medium and was compressed to the desired pressure. Finally the sample was held at the desired temperature and pressure during the run. The generated pressures were measured against the oil pressure of the press. Pressures were calibrated on the basis of NH₄F I–II (0.363 GPa), II–III (1.08 GPa), and Bi I–II (2.55 GPa) transitions at room temperature [12]. The quartz–coesite transformation [13] at 1000°C (2.97 GPa) was also used for calibration. In the present experiments, a negative correction of 12.4 % was adopted to the nominal pressure value as an internal friction.

Temperatures were monitored with a Pt/Pt13%Rh thermocouple of 0.3 mm in diameter without correction for the pressure effect on emf. The junction of the thermocouple was protected by a thin platinum foil to avoid contact with the sample container. The temperatures at the top, center and bottom in the sample space were directly measured by the use of three-junction thermocouples. I found a temperature gradient of about 2°C/mm along the axial direction within the sample space at 1.06 GPa and 1400°C [14]. During each experiment the temperatures and pressures were kept constant within $\pm 1^\circ\text{C}$ and ± 0.01 GPa of the nominal values. The fluctuations of the electric power for heating were less than $\pm 1\%$ relative.

After being kept at a desired pressure and temperature for a certain duration, samples were quenched by cutting

off the electric supply. Thermocouple reading dropped below 50°C in a few seconds and to a surrounding temperature in one minute. The pressure was then released to an atmospheric pressure in about 5 minutes, and the run product was recovered.

Fig. 1. Relation between the distribution coefficient K_D and $X_{\text{Ca}}^{\text{Ol}}$ at 1150°C. The curve is calculated using the mean Fe/(Fe+Mg) of 0.62 for olivines. Data plotted by circles were obtained at 1 atm and 1150°C [4]; diamonds, at 1 GPa; squares, at 1.5 GPa. Open symbols and "P" are K_D between Ca-poor olivine and clinopyroxene; open symbols and "S", Ca-poor olivine-subcalcic clinopyroxene; solid symbols and "R", Ca-rich olivine (ferroan monticellite)-clinopyroxene. Standard errors of K_D are shown by the vertical bars. The Fe–Mg partitioning between olivine and clinopyroxene is insensitive to the variation of pressure. The olivine–ferroan monticellite solvus at 1 GPa becomes narrow comparing with data at 1 atm.

All run products were mounted in epoxy resin, cut into thin sections, and polished for identification of the phases by means of an optical microscope, and for the examination with an electron probe micro analyzers JEOL JXA-8800 at Ehime University. The instrumental conditions were as follows: the accelerating voltage, 15 KV; electron beam current, 5×10^{-9} A; electron beam diameter, 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 a garnet lherzolite. The elements of Ca, Fe and Mg were measured simultaneously and at least 30–50 analyses were made on both olivine and clinopyroxene phases in every run. Acceptable analyses of the run products satisfied all the following criteria: agreement with the ideal stoichiometry to be within $\pm 2\%$ relative; the total oxide weight per cent in the range 98–102 %. Chemical analyses were made at the limited areas near the grain boundaries of olivine and clinopyroxene avoiding the effect of secondary X-ray fluorescence [15]. If

the analyses for a phase within one charge indicated heterogeneity in compositions in which the mean standard error of X_{Fe} exceeded ± 0.03 , the run product was considered to be in non-equilibrium and all data of such run were discarded.

The scanning electron microscope revealed that the run products consisted of the aggregation of olivine and clinopyroxene with almost homogeneous granular texture, suggesting that the products were at or near chemical equilibrium. The grain sizes of the assemblages were 30–50 μm depending on run duration. Run products were large enough to determine the compositions of individual phases by the electron microprobe analysis avoiding the chemical contamination from surrounding minerals.

Reversal experiments were not carried out. Experiments were carried out using initially Ca-free olivine+clinopyroxene+wollastonite gel with initial $K_D=1$. Final compositions of olivine and clinopyroxene were easily determined. I consider that the equilibrium compositions are approximately represented by those of Fe-rich and Ca-rich olivines, (Fe-rich and Ca-poor monticellite), and Mg-rich clinopyroxenes. The experimental results are given in Fig. 1 in the form of the relation between the Fe-Mg partition coefficient K_D and the mole fraction of Ca^{2+} of olivine X_{Ca}^{Ol} .

Fig. 2. Calculated solvus of the $(\text{Ca,Fe,Mg})_2\text{SiO}_4$ olivine. High-Ca and low-Ca olivines are connected by the tie lines. Open circles (○) are the previous results at 1 atm and 1150°C [4]; diamonds (◇), present results at 1 GPa and 1150°C. These results at 1150°C show that the olivine-ferroan monticellite solvus becomes narrow slightly with increasing pressure. The previous data [10] at 800°C (▲), 1000°C (●) and 1100°C (■) are also plotted. Fo, forsterite (MgMgSiO_4); Fa, fayalite (FeFeSiO_4); Mo, monticellite (CaMgSiO_4); Kir, kirschsteinite (Ca FeSiO_4).

4. Discussion and Conclusion

The least-squares calculation of the experimental data including the previous data at 1 atm [4] yields the following results:

$$W_{\text{MgCa}}^{\text{Ol,M2}} = 30.8 \pm 0.5 \text{ kJ/mol} \quad (7)$$

$$W_{\text{CaFe}}^{\text{Ol,M2}} = 22.8 \pm 0.7 \text{ kJ/mol}$$

The curve fitting are shown in Fig. 1 in the form of the relation between the Fe-Mg partition coefficient K_D and the mole fraction of Ca^{2+} of olivine X_{Ca}^{Ol} . The curve in

Fig. 1 was calculated from 1 atm data [4] and the present experimental data assuming that the $\text{Fe}/(\text{Fe}+\text{Mg})$ is to be 0.62 which was the mean value of olivine obtained in the present experiments.

As seen in Fig. 1, it is clear that the Fe-Mg partitioning between olivine and clinopyroxene is highly composition-dependent and is insensitive to the variation of pressure. Comparing the present results at 1 GPa and 1150°C with the previous ones at 1 atm and 1150°C, we can read that the olivine-ferroan monticellite solvus becomes narrow slightly with increasing pressure (Fig. 2). This indicates that the excess volume for the quadrilateral olivine (MgMgSiO_4 , CaMgSiO_4 , CaFeSiO_4 and FeFeSiO_4) would have a negative value. The unit-cell data suggested the negative excess volume for the mixing of the forsterite-monticellite series [8] whereas the fayalite-kirschsteinite series showed the positive deviation from ideal mixing [9]. As seen in Fig. 1, the curve fitting is quite satisfactory. The good fitting implies that the Ca-effect on the exchange of Fe^{2+} and Mg^{2+} between olivine and clinopyroxene can be satisfactorily described by Eq. (2), and the mixing properties of the Ca-Fe-Mg olivine are sufficiently explained by the present solution model.

The present results are consistent with previous estimates [8,9,10,11] within the experimental uncertainties. Under Eqs. (3) the compositions of coexisting high-Ca and low-Ca olivines are calculated using the present results (Fig. 2). Included for comparison are the previous experimental data [10] in this figure. As is shown in Fig. 2, the present results are consistent with those of the previous data except for the Mg-rich data.

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