Pressure-temperature conditions for the formation of peridotite inclusions.

—An application of a regular solution model to partitioning of Mg, Fe and Co between coexisting olivine and orthopyroxene—

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Abstract—The partitioning of Mg, Fe and Co between coexisting olivine and orthopyroxene found in peridotite inclusions is examined from the thermodynamic point of view, using a binary and a ternary regular solution models. The following two exchange reactions are considered:

and

The apparent partition coefficients are respectively:

$$RT \cdot \ln K'_{\text{Fe,Mg}} = -\Delta G_1 - (2X_{\text{Mg}}^{01} - 1)(W^{01}P + \alpha^{01}) + (2X_{\text{Mg}}^{\text{opx}} - 1)(W^{\text{opx}}P + \alpha^{\text{opx}}) \quad (3)$$

and

$$RT \cdot \ln K'_{\text{Co,Mg}} = -\Delta G_2 + (\Delta\alpha + \Delta WP)X_{\text{Fe}} \quad (4)$$

Using (3) and (4), we can estimate the P - T conditions at equilibrium of peridotite inclusions, if we know the numerical values of the apparent partition coefficients.

Examination of the equilibrium relations in a peridotite inclusion from a South African kimberlite and in an Ichinomegata lherzolite leads to the conclusion that the garnet peridotite is formed at higher pressure and lower temperature than the lherzolite.

INTRODUCTION

In their pioneering work, RAMBERG and DEVORE (1951) concluded that the partitioning of Mg and Fe between coexisting olivine and orthopyroxene is relatively insensitive to the variation in pressure, but may be sensitive to that in temperature. They suggested that this might be a useful geothermometer.

MUELLER (1962) has introduced the thermodynamics of the intra-crystalline partitioning between non-equivalent lattice sites of cummingtonite. He has shown that the thermodynamics can be approximated by a regular solution type formula.

MATSUI and BANNO (1965) and BANNO and MATSUI (1967) have studied the intra- and inter-crystalline partitioning of Mg and Fe between coexisting orthopyroxene and clinopyroxene, and interpreted the mechanism of the non-ideality of orthopyroxene. Recently, GROVER and ORVILLE (1969) presented a theory of partitioning between a single site and a multi-site phases in essentially the same manner as that by MATSUI and BANNO (1965).

THOMPSON (1967) has made theoretical considerations concerning the thermodynamic properties of solutions, which can be applied to the element partitioning between coexisting phases.

Along with the theoretical analyses of the partitioning, experimental investigations have also appeared. Among others, NAFZIGER and MUAN (1967), SPEIDEL and OSBORN (1967) and MEDARIS (1969) have made important contributions to the element partitioning between coexisting olivine and orthopyroxene.

By combining thermodynamic analyses, experimental studies and the petrographical data on olivine-orthopyroxene equilibrium, it is possible to estimate to some extent the physical conditions of peridotite inclusions in basalts and kimberlite.

THEORETICAL CONSIDERATIONS

It is possible in principle to determine both temperature and pressure by combining at least two of the independent exchange reactions (MATSUI and BANNO, 1967). In order to apply this principle to the P - T determination of peridotite inclusions, the partitioning of Mg, Fe and Co between coexisting olivine and orthopyroxene is taken up. Thus our consideration is concerned with the following two exchange reactions:

and

Partitioning of Mg and Fe

The partition coefficient of Mg and Fe between coexisting olivine and orthopyroxene, which is denoted by $K_{\text{Fe,Mg}}$ hereafter, is defined as:

$$K_{\text{Fe,Mg}} = (a_{\text{fa}}/a_{\text{fo}})(a_{\text{en}}/a_{\text{fe}}) = K'_{\text{Fe,Mg}}(\gamma_{\text{fa}}/\gamma_{\text{fo}})(\gamma_{\text{en}}/\gamma_{\text{fe}}), \quad (3)$$

wherein fa: fayalite, fo: forsterite, fe: ferrosilite, en: enstatite and a_i : activity of component i in olivine or in orthopyroxene. γ_i : activity coefficient of component i in olivine or in orthopyroxene and $K'_{\text{Fe,Mg}}$: apparent partition coefficient defined as $(X_{\text{Fe}}/X_{\text{Mg}})_{\text{ol}}(X_{\text{Mg}}/X_{\text{Fe}})_{\text{opx}}$, where X_i means the mole fraction of component i in olivine or in orthopyroxene.

The difference in free energies of the reaction (1) is given by the following equation:

$$\Delta G_1 = -RT \ln K_{\text{Fe,Mg}}. \quad (4)$$

Combining (3) and (4), we have

$$\Delta G_1 = -RT \{ \ln K'_{\text{Fe,Mg}} + \ln(\gamma_{\text{fa}}/\gamma_{\text{fo}})(\gamma_{\text{en}}/\gamma_{\text{fe}}) \}. \quad (5)$$

In general, the partial derivatives of the activity coefficient of component *i* with respect to temperature and pressure are given by the following relations:

$$(\partial \ln \gamma_i / \partial T)_P = -(\bar{H}_i - H_i^0) / RT^2 \quad (6)$$

and

$$(\partial \ln \gamma_i / \partial P)_T = (\bar{V}_i - V_i^0) / RT, \quad (7)$$

wherein the superscript zero indicates the molal quantity of pure substance and the bar indicates the partial molal quantity of component *i*.

NAFZIGER and MUAN (1967) have experimentally determined the partitioning of Mg and Fe between coexisting olivine and orthopyroxene at 1,200°C, suggesting that the thermodynamics of olivine and orthopyroxene is approximated by a regular solution model.

In the binary regular solution comprising components *i* and *j*, the characteristic parameter measuring the deviation from the ideal solution is separable into two terms: one is measuring the mixing heat, which is represented by α (cal/mole), and the other mixing volume, which is represented by W (cm³/mole). For these parameters, the following relations hold:

$$\bar{H}_i - H_i^0 = X_j^2 \alpha \quad (8)$$

and

$$\bar{V}_i - V_i^0 = X_j^2 W. \quad (9)$$

Combining (6), (7), (8) and (9), we have the following relation for the binary regular solution:

$$\ln \gamma_i = \frac{1}{RT} (\alpha + WP) X_j^2, \quad (10)$$

wherein the standard state is defined as zero pressure. Therefore, the following relation is obtained:

$$\ln \left(\frac{\gamma_{\text{fa}}}{\gamma_{\text{fo}}} \frac{\gamma_{\text{en}}}{\gamma_{\text{fe}}} \right) = \frac{1}{RT} \{ (2X_{\text{Mg}}^{\text{ol}} - 1)(W^{\text{ol}}P + \alpha^{\text{ol}}) + (2X_{\text{Mg}}^{\text{opx}} - 1)(W^{\text{opx}}P + \alpha^{\text{opx}}) \} \quad (11)$$

Combining (3), (4) and (11), we have:

$$RT \ln K'_{\text{Fe,Mg}} = -\Delta G_1 - (2X_{\text{Mg}}^{\text{ol}} - 1)(W^{\text{ol}}P + \alpha^{\text{ol}}) + (2X_{\text{Mg}}^{\text{opx}} - 1)(W^{\text{opx}}P + \alpha^{\text{opx}}) \quad (12)$$

This is the expression of the apparent partition coefficient between the Mg-Fe olivine and orthopyroxene, both of which are binary regular.

ΔG_1 can be estimated by combining the following two reactions

According to KELLEY (1968), the free energy of reaction (13), which is denoted by ΔG_{13} is given as follows:

$$\Delta G_{13} \text{ (cal/mole)} = -1,725 + 0.92T.$$

By determining the reaction boundary curve at high temperatures and high

pressures, AKIMOTO *et al.* (1965) gave the free energy of reaction (14), which is denoted by ΔG_{14} as follows:

$$\Delta G_{14}(\text{cal/mole}) = -36 + 0.45T.$$

Accordingly, we have

$$\Delta G_1(\text{cal/mole}) = -1,689 + 0.47T.$$

Using the cell dimension data of ferrosilite given by AKIMOTO *et al.* (1965) and those of forsterite and enstatite by MATSUI and SYONO (1968) and MATSUI *et al.* (1968), we can estimate the value of ΔV_1 as

$$\Delta V_1 = -0.33\text{cm}^3/\text{mole}.$$

Thus ΔG_1 is given in terms of temperature and pressure (atm) as follows:

$$\Delta G_1(\text{cal/mole}) = -1,689 + 0.47T - 8 \times 10^{-3}P. \quad (15)$$

NAFZIGER and MUAN (1967) have derived activity-composition relations for the silicate solid solutions within the system $\text{MgO-FeO-Si}_{0.5}\text{O}$, having concluded that Mg-Fe orthopyroxene is well approximated by a regular solution, in which the characteristic parameter α^{opx} has a value between -76cal/mole and $+579\text{cal/mole}$ at $1,250^\circ\text{C}$.

Fig.1. Composition-free energy relation of the Mg-Fe olivines. The broken line indicates a symmetric curve assuming a regular solution model defined by $\alpha^{\text{ol}}=1,160\text{cal/mole}$.

Using the activity-composition relations at 1,200°C given by them, the excess free energy in Mg-Fe olivine solid solution is calculated to be $\alpha^{\text{ol}} = 1,160 \text{ cal/mole}$. Fig. 1 shows that the observed values are well fitted by the calculated ones.

MATSUI and SYONO (1968) and MATSUI *et al.* (1968) determined the unit cell dimensions of olivine group solid solutions and of orthopyroxene group solid solutions, from which we can obtain molal volumes and hence mixing volumes of these solid solutions. The Mg-rich portions of the Mg-Fe olivine and orthopyroxene solid solutions are excellently approximated by regular solutions. Their characteristic parameters W^{ol} and W^{opx} are $+0.12 \text{ cm}^3/\text{mole}$ and $-0.21 \text{ cm}^3/\text{mole}$, respectively (Fig. 2 and 3).

Partitioning of Mg and Co

According to the cell dimension data of Co-Mg olivine and orthopyroxene solid solutions reported by MATSUI and SYONO (1968) and MATSUI *et al.* (1968), $W_{\text{Co,Mg}}^{\text{ol}}$ and $W_{\text{Co,Mg}}^{\text{opx}}$ are practically zero.

Although the cell dimension data of Co-Fe olivine and orthopyroxene are not available at present, it may be assumed that these solid solutions have little excess volume on mixing, as the difference in effective ionic size between Co (0.745 Å) and Fe (0.780 Å) is smaller than that between Mg (0.720 Å) and Fe. Then, we assume that

Fig. 2. Mixing volume-composition relation (chain line) for the Mg-Fe olivines. The broken line indicates the symmetric curve assuming a regular solution model defined by $W^{\text{ol}} = +0.12 \text{ cm}^3/\text{mole}$.

Fig.3. Mixing volume-composition relation (chain line) for the Mg-Fe orthopyroxenes. The broken line indicates the symmetric curve assuming a regular solution model defined by $W^{\text{opx}} = -0.21 \text{ cm}^3/\text{mole}$.

Mg-Co and Co-Fe olivine and orthopyroxene solid solutions are ideal in a tentative approximation.

In olivines and orthopyroxenes found in peridotite inclusions, the effects of Mg and Fe fractions upon the activities of such components as Co-olivine and Co-orthopyroxene can not be neglected because of the high fractions of Mg and Fe.

Thus the activity coefficients $\gamma_{\text{Co-ol}}$ and $\gamma_{\text{Co-opx}}$ can be approximated on the basis of a ternary regular solution model. In a ternary regular solution comprising the components 1, 2 and 3, excess free energy per mole denoted by $\bar{G}_{\text{ex}}$ is given as follows (THOMPSON, 1967):

$$\bar{G}_{\text{ex}} = X_1 X_2 \alpha_{12} + X_2 X_3 \alpha_{23} + X_3 X_1 \alpha_{13},$$

in which α_{12} etc. represent characteristic parameters.

Each of the partial molal excess free energies of components 1, 2 and 3 is given as partial derivative of the excess free energy of the solution with respect to the mole number of each component, respectively. Therefore, we have the relations as follows:

$$RT \ln \gamma_1 = X_2^2 \alpha_{12} + X_3^2 \alpha_{13} + X_2 X_3 (\alpha_{12} - \alpha_{23} + \alpha_{13})$$

$$RT \ln \gamma_2 = X_3^2 \alpha_{23} + X_1^2 \alpha_{12} + X_1 X_3 (\alpha_{23} - \alpha_{13} + \alpha_{12})$$

$$RT \ln \gamma_3 = X_1^2 \alpha_{13} + X_2^2 \alpha_{23} + X_1 X_2 (\alpha_{13} - \alpha_{12} + \alpha_{23}).$$

Accordingly, on the basis of a ternary regular solution model, the activity coefficients $\gamma_{\text{Co-ol}}$ and $\gamma_{\text{Co-opx}}$ are represented by the relations as follows:

$$RT \ln \gamma_{\text{Co-ol}} = X_{\text{Fe}}^{\text{ol}} X_{\text{Mg}}^{\text{ol}} (\alpha^{\text{ol}} + W^{\text{ol}} P) \quad (16)$$

and

$$RT \ln \gamma_{\text{Co-opx}} = -X_{\text{Fe}}^{\text{opx}} X_{\text{Mg}}^{\text{opx}} (\alpha^{\text{opx}} + W^{\text{opx}} P). \quad (17)$$

$K'_{\text{Co,Mg}}$ has the form analogous to that of $K'_{\text{Fe,Mg}}$:

$$\ln K'_{\text{Co,Mg}} = -\Delta G_2 / RT - \ln (\gamma_{\text{Co-ol}} / \gamma_{\text{fo}}) (\gamma_{\text{en}} / \gamma_{\text{Co-opx}}). \quad (18)$$

Combining (6), (7), (16), (17) and (18), and from the fact that $X_{\text{Mg}}^{\text{ol}} X_{\text{Fe}}^{\text{ol}} \div X_{\text{Mg}}^{\text{opx}} X_{\text{Fe}}^{\text{opx}}$ in usual peridotite inclusions, we have

$$RT \ln K'_{\text{Co,Mg}} = -\Delta G_2 + (\Delta \alpha + \Delta W P) X_{\text{Fe}}. \quad (19)$$

In this equation, $\Delta \alpha = \alpha^{\text{ol}} - \alpha^{\text{opx}}$ and $\Delta W = W^{\text{ol}} - W^{\text{opx}}$.

ΔG_2 can be determined by combining the following two reactions

and

By determining the reaction boundary curve at high temperatures and high pressures, AKIMOTO *et al.* (1965) determined the free energy of reaction (21), which is denoted by ΔG_{21} , as follows:

$$\Delta G_{21} (\text{cal/mole}) = 600 + 0.35T.$$

Therefore, we have $\Delta G_2 (\text{cal/mole}) = -2,325 + 0.57T$.

From the cell dimension data given by MATSUI and SYONO (1968) and MATSUI *et al.* (1968), we obtain the value of volume change in the reaction (2) as follows:

$$\Delta V = -0.24 \text{ cm}^3/\text{mole}.$$

Hence, we have:

$$\Delta G_2 = -2,325 + 0.57T - 5.82 \times 10^{-3} P.$$

Now thus, if we can determine the apparent partition coefficients of Mg, Fe and Co between coexisting olivine and orthopyroxene found in a peridotite inclusion, it is possible to estimate the temperature and the pressure of equilibrium of this mineral pair by combining (12) and (19).

PHYSICAL CONDITIONS OF SOME PERIDOTITE INCLUSIONS

In order to demonstrate the effectiveness of the regular solution model, equilibrium relations in a lherzolite occurring as an ejected block at the Ichinomegata maar, Oga Peninsula, Japan and a garnet peridotite inclusion found in a South African kimberlite have been examined.

The analyses of the olivine and orthopyroxene from these rocks, which were provided by MATSUI (unpublished), are presented in Table 1, together with the values of $K'_{\text{Fe,Mg}}$ and $K'_{\text{Co,Mg}}$.

As stated in the previous sections, the temperature and the pressure of the

Table 1. Chemical data on the olivines and orthopyroxenes in the garnet peridotite and in the lherzolite (Y. MATSUI, unpublished)

South African kimberlite	MgO, %	FeO, %	Co, ppm	Ni, ppm	$K'_{\text{Fe.Mg}}$	$K'_{\text{Co.Mg}}$	$K'_{\text{Ni.Mg}}$
BKM-Opx	36.36*	3.96*	59	765	1.10	1.64	3.17
BKM-Ol	51.8	6.28	137	3450			
Ichinomegata lherzolite							
MI1X1502-Opx	34.0	6.63	86	855	1.05	1.39	2.69
MI1X1502-Ol	48.5	9.95	170	3270			

* BANNO, *et al.*, 1963.

Note: These analyses have been made in order to construct a partition pattern diagram (MATSUI and BANNO, 1970). The data are all tentative, and the accuracies are expected not to be very high. However, the resulting difference in apparent partition coefficients is considered to be significant. (Y. MATSUI, Oral communication).

formation of these rocks are estimated by combining (12) and (19), and the data given in Table 1. The simultaneous solution of equations (12) and (19), however, is not unique because of the ambiguity of the value of α^{Opx} and hence that of $\Delta\alpha$.

In Figs.4 and 5 showing temperature, pressure and $\Delta\alpha$ relations diagrammatically, each of parallel lines represents Eq (12) defined by a definite value of $\Delta\alpha$, whereas the

Fig.4. $\Delta\alpha$ -pressure-temperature diagram projected onto the basal plane defined by pressure and temperature for the Ichinomegata lherzolite.

Fig.5. $\Delta\alpha$ -pressure-temperature diagram projected onto the basal plane defined by pressure and temperature for the South African kimberlite.

line A-B represents Eq (19) practically independent of $\Delta\alpha$.

Then, for a definite value of $\Delta\alpha$, the intersection of the corresponding line and the line A-B gives the temperature and the pressure of equilibrium.

By comparing Figs.4 and 5, it is certain that the pressure for the garnet peridotite is about 40×10^3 atm higher than that for the Ichinomegata lherzolite. If the pressure of equilibrium represents that of the formation of these rocks, it is concluded that the former is formed at a pressure about 40×10^3 atm higher than the latter. As pointed out in the previous section, the minimum value of $\Delta\alpha$ is 582 cal/mole and therefore the pressure for the garnet peridotite can not be higher than 60×10^3 atm, whereas that for the lherzolite can not be higher than about 20×10^3 atm.

Inspection of Fig.4 indicates that the pressure for the lherzolite is zero for about 640 cal/mole contour line, and in this case the pressure for the garnet peridotite is 38×10^3 atm. Hence, it is concluded that the garnet peridotite is formed at a pressure between 38×10^3 atm and 60×10^3 atm.

It is not likely, however, that the Ichinomegata lherzolite can be formed at zero pressure, since its mineral assemblage suggests its origin at a depth of the uppermost mantle at least, as pointed out by KUNO (1967). If, then, we assume tentatively that the pressure of formation of the Ichinomegata lherzolite is 15×10^3 atm and consequently assume 600 cal/mole as the value of $\Delta\alpha$, we have 57×10^3 atm as the pressure of the formation of the garnet peridotite.

Then, as the equilibrium temperatures, we obtain 1,500°C for the garnet peridotite and 1,700°C for the lherzolite, respectively. The present result for the garnet peridotite

is rather in agreement with the experimental one given by ITO *et al.* (1968). The equilibrium temperature for the lherzolite, however, is clearly too high, since the determination of the solidus of the lherzolite carried out by KONO *et al.* (1969) gives 1,470°C at 15×10^3 atm.

In spite of disagreement in the temperature estimation of the Ichinomegata lherzolite, it may be possible that the garnet peridotite is formed at a higher pressure and at a lower temperature than the lherzolite.

The results obtained above indicate the importance of pressure effect on the activity of solid solutions and the effectiveness of regular solution approximation for olivine and orthopyroxene solid solutions. With the further refined thermodynamic data on silicate solid solutions the analysis of minor element partitioning may serve as a useful indicator for physical conditions of the formation of rocks, and hence the minor element geochemistry will play an important role in petrogenetical considerations.

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