**On the solubility of alumina in orthopyroxene
coexisting with olivine and spinel
in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$**

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ABSTRACT

The solubility of alumina in orthopyroxene coexisting with spinel and forsterite has been discussed using a simple mixing model of orthopyroxene and it was revealed that the recent experimental results in $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system (MacGregor, 1974) do not agree with the model. Reexamination of the system gave the results which are in good agreement with thermodynamically calculated alumina solubility in orthopyroxene and indicated that, in the spinel-stability field, it is not sensitive to pressure.

Introduction

Estimation of the temperature and pressure of equilibration for the materials originated from the upper mantle is very important to the understanding of the thermal condition in the earth's interior. Phase equilibria in the system enstatite-pyroxene and the enstatite-diopside have been applied to estimate the equilibration temperature and pressure of the ultramafic xenolith in the kimberlite of South Africa and it has been revealed that the method is very useful. As most ultramafic rocks of upper mantle origin, as far as we can obtain, contain spinel instead of garnet as aluminous phase, we must develop a geobarometer useful for the spinel bearing ultramafic rocks. Recently, it was suggested that the Al_2O_3 content of the orthopyroxene

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coexisting with spinel and olivine is a good indicator of equilibration pressure (MacGregor, 1974). In this report we will discuss the ability of such a geobarometer.

Thermodynamic formulation

The solubility of Al_2O_3 in orthopyroxene (opx) coexisting with olivine (oliv) and spinel (sp) is expressed by the chemical equation;

Taking the standard state of each component to be the pure phase at the pressure and the temperature of consideration, we can get the equation;

$$(\Delta G^\circ)_{P,T} = -RT \ln \left(\frac{a_{\text{Mg-Tsh}}^{\text{Opx}} \cdot a_{\text{Fo}}^{\text{Oliv}}}{a_{\text{En}}^{\text{Opx}} \cdot a_{\text{Sp}}^{\text{Sp}}} \right), \quad (2)$$

where a_i^j is the activity of component i in the phase j .

According to Wood and Banno (1973), the activities of the components of the pyroxene can be expressed as a function of mole fractions on the basis of the two site model as follows.

$$\begin{aligned} a_{\text{MgAl}_2\text{SiO}_6}^{\text{Opx}} &= (X_{\text{Mg}}^{\text{M2}})(X_{\text{Al}}^{\text{M1}}) \cdot \gamma_{\text{MgAl}_2\text{SiO}_6}, \\ a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{Opx}} &= (X_{\text{Mg}}^{\text{M2}})(X_{\text{Mg}}^{\text{M1}}) \cdot \gamma_{\text{Mg}_2\text{Si}_2\text{O}_6}, \end{aligned} \quad (3)$$

where γ_n refers to the activity coefficient of component n in orthopyroxene and X_i^j refers to the mole fraction of cation i in the site j of orthopyroxene. Both activity coefficients were assumed to be 1.0 at 1 atm, values at higher pressures being obtained from partial molar volumes of components in the orthopyroxene solid solution (Wood and Banno, 1973). In a simple system;

$$a_{\text{Mg}_2\text{SiO}_4}^{\text{Oliv}} = a_{\text{MgAl}_2\text{O}_4}^{\text{Sp}} = 1. \quad (4)$$

Substitution of the activity expressions (3) and (4) into equation (2) gives

$$\begin{aligned}
(\Delta G^\circ)_{1,T} + \int_1^P (V_{\text{MgAl}_2\text{SiO}_6}^\circ + V_{\text{MgSiO}_4}^\circ - V_{\text{Mg}_2\text{Si}_2\text{O}_6}^\circ - V_{\text{MgAl}_2\text{O}_4}^\circ) dP \\
= -RT \cdot \ln \left(\frac{X_{\text{Al}}^{\text{M}_1}}{X_{\text{Mg}}^{\text{M}_1}} \right)_{\text{Opx}} - RT \int_1^P \left\{ \frac{\partial \ln(\gamma_{\text{MgAl}_2\text{SiO}_6})}{\partial P} \right\}_{T,X} dP \\
+ RT \int_1^P \left\{ \frac{\partial \ln(\gamma_{\text{Mg}_2\text{Si}_2\text{O}_6})}{\partial P} \right\}_{T,X} dP. \quad (5)
\end{aligned}$$

At constant $X_{\text{Al}}^{\text{M}_1}$ and $X_{\text{Mg}}^{\text{M}_1}$, the following relation exists;

$$\left(\frac{\partial \ln \gamma_i}{\partial P} \right)_{T,X} = \frac{\bar{V}_i - V_i^\circ}{RT},$$

where $\bar{V}_i$ is the partial molar volume of component i . Thus equation (5) can be rearranged to give

$$\begin{aligned}
\Delta H^\circ - T\Delta S^\circ + \int_1^P (V_{\text{Mg}_2\text{Si}_2\text{O}_6}^\circ + \bar{V}_{\text{MgAl}_2\text{SiO}_6} - V_{\text{MgAl}_2\text{O}_4}^\circ - \bar{V}_{\text{Mg}_2\text{Si}_2\text{O}_6}) dP \\
= -RT \ln \left(\frac{X_{\text{Al}}^{\text{M}_1}}{X_{\text{Mg}}^{\text{M}_1}} \right)_{\text{Opx}}. \quad (6)
\end{aligned}$$

Using the result by Wood and Banno (1973), molar volume of enstatite-Mg-tschermakite solid solution can be written as

$$V_{\text{ss}} = 62.65 X_{\text{Mg}}^{\text{M}_1} + 58.37 X_{\text{Al}}^{\text{M}_1} + 3.76 (X_{\text{Al}}^{\text{M}_1})^2.$$

Thus equation (6) can be reduced to

$$\begin{aligned}
\Delta H^\circ - T\Delta S^\circ + 24 \times 10^{-3} (P-1) (7.52 X_{\text{Al}}^{\text{M}_1} - 0.31) \\
= -RT \ln \left(\frac{X_{\text{Al}}^{\text{M}_1}}{X_{\text{Mg}}^{\text{M}_1}} \right)_{\text{Opx}}, \quad (7)
\end{aligned}$$

where the values for the molar volume of forsterite and spinel were taken from Robie and Waldbaum (1968).

Similar treatment is possible for the solubility of alumina in orthopyroxene coexisting with garnet as developed by Wood and Banno (1973) and the result is

$$\begin{aligned}
\Delta H^\circ - T\Delta S^\circ + 24 \times 10^{-3} (P-1) (7.8 + 7.52 X_{\text{Al}}^{\text{M}_1} \cdot X_{\text{Mg}}^{\text{M}_1}) \\
= -RT \ln \left(\frac{1}{X_{\text{Al}}^{\text{M}_1} \cdot X_{\text{Mg}}^{\text{M}_1}} \right). \quad (8)
\end{aligned}$$

We can calculate enthalpies and entropies in these equations by least square fit of the equations to the Al_2O_3 solubility in orthopyroxene coexisting with spinel and forsterite, determined experimentally by MacGregor (1974). The results are given in Table 1. In Fig. 1, the isopleths of Al_2O_3 calculated using the enthalpies and entropies of Table 1 are drawn.

Table 1. Least square fit of equation (8), using the experimental data by MacGregor (1974).

	ΔH°	ΔS°
Spinel-stability field	8972	3.5
Garnet-stability field	-7613	-4.4

Fig. 1. Calculated isopleths of Al_2O_3 in orthopyroxene, using equations (7), (8) and values in Table 1 to garnet-stability field and spinel-stability field respectively. Dotted data are quoted from MacGregor (1974). Numbers are atomic percent of Al in octahedral site M1 of orthopyroxene.

The isopleths in garnet-stability field agree well with the experimental results dotted in the figure, whereas those in spinel-stability field do not. Furthermore, the large misfit of the isopleth is observed at the boundary between spinel-stability field and garnet-stability field.

These may indicate that MacGregor's results in spinel-stability field are not correct.

In order to examine if our conclusion is correct, we have determined the solubility of alumina in orthopyroxene coexisting with spinel and forsterite over the pressure range 10-20 kb at 1400°C.

Experimental procedure

Homogeneous glass of the composition $\text{Fo}_{31}\text{En}_{38}\text{Sp}_{31}$ (mol %) was prepared as starting material from pure chemicals of SiO_2 , Al_2O_3 and $\text{Mg}(\text{OH})_2$. Weighed mixtures of the reagents were melted by carbon arc and quenched. The glass was ground under alcohol in agate mortar down to average grain size of $5\text{ }\mu\text{m}$. Some pieces of glass were examined by optical microscope and X-ray powder photography, and revealed that the starting chemicals are consumed up.

High pressure experiments were carried out in 1/2 inch piston-cylinder apparatus and a pressure correction of -10% of nominal load pressure, using piston-in technique, was applied. This correction is based on the calibration of the Bi at room temperature (Shimomura, unpublished data). Samples were encased in graphite capsule, and temperature measurement was made by Pt/Pt-13%Rh thermocouple without correcting for pressure effect on thermocouple emf.

Chemical analyses of the run products were made with an electron microprobe JXA-5. Analytical procedures are similar to Nakamura and Kushiro (1970).

Results and discussion

The analysed compositions of aluminous enstatite in equilibrium with forsterite and spinel are shown in Table 2. The Al_2O_3 content in enstatite does not vary with pressure. Therefore, solubility of Al_2O_3 in enstatite is not sensitive to pressure.

Table 2. Analyses of synthesized orthopyroxene.

(pressure) (run time)	10 kb 240 min	15 kb 240 min	20 kb 240 min
SiO ₂	53.6	53.3	54.2
Al ₂ O ₃	11.1	10.5	10.3
MgO	36.0	35.9	35.0
Total	100.7	99.7	99.5
Si	1.783	1.818	1.788
Al	0.434	0.408	0.417
Mg	1.782	1.752	1.797

Atomic ratio is calculated on 6 oxygen basis.

The results of our experiments are different from those of MacGregor (1974). The slope of isopleths is not so steep as indicated by him.

Using MacGregor's result in garnet-stability field, we can calculate the Al₂O₃ content in orthopyroxene coexisting with spinel, olivine and garnet on the univariant line. Fitting the Al₂O₃ content in

Fig. 2. Calculated isopleths of Al₂O₃ in orthopyroxene using data of garnet-stability field (MacGregor, 1974) only. Large circles and numbers are our experimental results.

orthopyroxene on the univariant line to equation (7), we can calculate the isopleths in spinel stability field and the results are shown in Fig. 2.

The results of our experiments are also plotted in Fig. 2. They are in good agreement with the calculated isopleth. This probably means that the solubility of alumina in orthopyroxene depends little on pressure but strongly on temperature. Therefore, it is doubtful whether the Al_2O_3 content in orthopyroxene coexisting with spinel and olivine can be used as a geobarometer.

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