

Thermodynamic Evaluation of Fe Effect on Alumina Solubility in Orthopyroxene coexisting with Garnet

Han Yeang Lee*

Korea Institute of Geosciences and Mineral Resources (KIGAM)
P.O. Box 111, Yusong 305-350, Daejeon

Abstract: In the FMAS system the effect of iron on alumina solubility in orthopyroxene has been determined by experiments with crystalline starting mixtures of garnet and orthopyroxene of known initial compositions at 20 kb, 975°C and 25 kb, 1,200°C. These data have been modeled to develop a thermodynamic method for the calculation of Al_2O_3 in orthopyroxene as a function of P, T and composition. The direct application of the alumina solubility data in the MAS system to natural assemblages could lead to significant overestimation of pressure, probably by about 5kb for the relatively common garnet-lherzolites with about 25 mol per cent $\text{Ca} + \text{Fe}^{2+}$ in garnet and about 1 wt. per cent Al_2O_3 in orthopyroxene since the effect of Fe is similar to that of Ca and Cr^{3+} in reducing the alumina solubility in orthopyroxene in equilibrium with garnet relative to that in the MAS system.

Keywords: Alumina solubility, Iron, Orthopyroxene, Garnet, FMAS system

Introduction

After Boyed and England (1964) suggested its potential of Al_2O_3 content of ortho pyroxene as a geobarometer, researches have been carried on intensively because natural orthopyroxene (Opx) may contain up to about 10 wt% Al_2O_3 , depending on pressure, temperature, and the compositions of the coexisting phases. Previous studies include MacGregor (1974), Wood and Banno (1973), Wood (1974), Obata (1976), Akella (1976), Howells and O'Hara (1978), Mori and Green (1978), Danckwerth and Newton (1978), Jekins and Newton (1979), Lane and Ganguly (1980), Perkins and Newton (1980), Perkins et al. (1981), Kawasaki and Mastsui (1983), Harley (1984), and Gasparik and Newton (1984).

However, most of the previous studies were done in the three component system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ (MAS). Only a few experiments in the $\text{CaO-FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CFMAS) system have been done (e.g., Wood, 1974; Harley, 1984; Bertrand et al., 1986), and those too on a very narrow range of

compositions which can not account for multi-component effects in natural system, with respect to X_{Ca} and X_{Fe} in orthopyroxene and garnet (Gt). Chatterjee and Terhart (1985) calculated the effect of Cr on the solubility of Al_2O_3 in orthopyroxene coexisting with garnet or spinel in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Cr}_2\text{O}_3$ system. Their calculations were based on experimental data obtained by Danckwerth and Newton (1978), Perkins et al. (1981), and Gasparik and Newton (1984). Chatterjee and Terhart (1985) showed that the solubility of Al_2O_3 in orthopyroxene in this system is sensitive to the Cr_2O_3 content of the coexisting garnet. Besides, most of the starting materials used in the experimental works were non-crystalline samples, in which case the determination of equilibrium Al_2O_3 was ambiguous.

Thus, more precise data on alumina solubility in $\text{FeO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (FMAS) system are necessary to constrain the effect of FeO on the Al_2O_3 solubility in orthopyroxene in equilibrium with garnet, which constitutes the most extensively used geobarometer for mantle derived rocks. The main goal of this study has been to obtain carefully reversed experimental data on the equilibrium alumina solubility in orthopyroxene in equilibrium with garnet in the simple FMAS system and then the

*E-mail: hanlee@kigam.re.kr

Tel: 82-42-868-3103

Fax: 82-42-861-9714

experimental data have been combined with the available thermodynamic data to have important implications for the evaluation of compositional effect on this geobarometer.

Experimental Method and Results

All experiments were conducted at 975, 1,200°C and 20-30 kb in a 3/4 or 1 inch diameter Piston-Cylinder apparatus with NaCl or CsCl pressure medium, using a mixture of PbO and PbF₂ as flux material to promote reactions. Details of flux material, pressure cells, and pressure and temperature measurements were described in Lee (1988).

Natural and synthetic garnet and orthopyroxene were used to prepare starting materials for this study. Natural samples with $X_{Fe} + X_{Mg} = 0.97$ were separated from various rocks and handpicked under binocular microscope. Two types of orthopyroxenes (aluminous and non-aluminous opx) were prepared from the natural and synthetic minerals for the determination of equilibrium alumina solubility in orthopyroxene in equilibrium with garnet such that the equilibrium Al₂O₃ content of the orthopyroxene could be approached from both higher and lower initial Al₂O₃ values during an experiment as in all classical reversal experiments. The starting orthopyroxene was mostly nonaluminous. Since it was difficult to synthesize a variety of aluminous orthopyroxenes of comparable composition with respect to X_{Fe} , limited experiments were performed to approach the equilibrium alumina solubility from a supersaturated composition, using a mixture of the synthetic aluminous enstatite and garnet. Description of the experimental procedure for synthetic starting minerals was given by Lee (1988). The compositions of starting materials are listed in Table 1.

The Al₂O₃ contents of orthopyroxene were made to evolve from both undersaturated (low-aluminous orthopyroxene + garnet) and oversaturated (synthetic high-aluminous orthopyroxene + garnet) directions at 975°C, 20 Kb and 1,200°C, 25 Kb to investigate the

effect of FeO on alumina solubility in orthopyroxene in equilibrium with garnet. Although exact reversal of Al₂O₃ content of orthopyroxene was not attained, the overall pattern of a plot of Al₂O₃ content vs. X_{Fe}^{Opx} enables us to bracket the solubility range of Al₂O₃ in orthopyroxene in equilibrium with garnet. The resulting data have been plotted in Fig. 1 and summarized in Table 2. From these data it is clear that alumina solubility in orthopyroxene in equilibrium with garnet decreases significantly with increasing FeO content of orthopyroxene.

Thermodynamic Evaluation

An important step in the thermodynamic analysis of Al₂O₃ solubility in orthopyroxene concerns the formulation of an aluminous orthopyroxene component that leads to a relatively simple expression of garnet-orthopyroxene equilibrium. This problem has been addressed using these experimental data for the effect of FeO on Al₂O₃ solubility in orthopyroxene.

The Mg-tschermak molecule, MgAl₂SiO₆, is the most commonly used aluminous orthopyroxene component. Ganguly and Ghose (1979), on the other hand, showed that the solubility of Al₂O₃ in orthopyroxene is limited to 25 mole%, and for this reason suggested $Mg_3Al_2Si_3O_{12}(3MgSiO_3 \cdot Al_2O_3)$ component with orthopyroxene structure as the Al-orthopyroxene end-member component. This component has been called orthopyrope (opy) by Lane and Ganguly (1980), it has the stoichiometry of pyrope garnet, and has since been used in the literature by other workers. The experimental data on Al₂O₃ solubility in FMAS system have been analyzed by casting the composition of orthopyroxene solid solution in terms of the following sets of components:

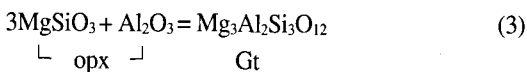
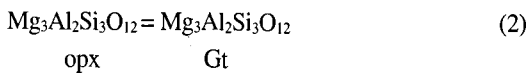
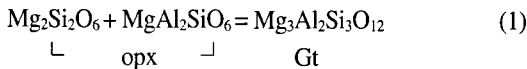
- (a) Mg₂Si₂O₆ - Fe₂Si₂O₆ - MgAl₂SiO₆
- (b) Mg₄Si₄O₁₂ - Fe₄Si₄O₁₂ - Mg₃Al₂Si₃O₁₂
- (c) MgSiO₃ - FeSiO₃ - Al₂O₃

Using these components, the equilibrium relations between orthopyroxene and garnet may be treated according to the following reactions.

Table 1. Chemical compositions of starting materials

	Orthopyroxenes				Garnet		
	Opx/1	Opx/2	Opx/3	Opx/4	Gt/1	Gt/2	Gt/3
FeO*	9.32	46.76	31.14	-	35.37	22.74	0.04
MgO	33.91	5.09	17.80	37.77	5.34	13.01	29.80
SiO ₂	56.30	47.57	51.79	56.62	38.48	39.18	44.95
Al ₂ O ₃	0.08	0.75	0.07	6.43	21.33	23.25	25.74
CaO	0.32	0.61	-	-	0.40	1.80	0.19
MnO	0.05	0.05	-	-	0.03	0.49	-
Cr ₂ O ₃	-	0.01	-	-	-	-	-
TiO ₂	-	0.02	-	-	0.02	-	-
Na ₂ O	-	0.03	-	-	0.05	0.02	-
NiO	0.05	-	-	-	-	-	-
K ₂ O	-	-	-	-	-	-	-
Total	99.94	100.90	100.70	100.82	101.09	100.40	100.72
Fe	0.545	3.260	1.999	-	2.322	1.424	0.002
Mg	3.529	0.635	2.037	3.734	0.624	1.452	2.960
Si	3.942	3.966	3.976	3.755	3.021	2.934	2.994
Al	0.006	0.074	0.006	0.502	1.973	2.051	2.020
Ca	0.023	0.054	-	-	0.040	0.144	0.013
Mn	0.003	0.003	-	-	0.001	0.031	-
Cr	-	-	-	-	-	-	-
Ti	-	-	-	-	0.001	-	-
Na	-	0.004	-	-	0.007	0.003	-
Ni	0.002	-	-	-	-	-	-
K	-	-	-	-	-	-	-
Cation Total 0:12	8.050	7.996	8.018	8.091	7.989	8.039	7.089
Fe/Mg	0.154	5.154	0.981	0.000	3.717	0.980	0.000
Fe/Fe+Mg	0.133	0.837	0.495	0.000	0.788	0.495	0.000

Opx/1: Sample from Telmark, Norway (UCLA Mineral Museum). Opx/2: Sample No. XYZ, Tamberg an Devore (1951). Opx/3: Synthetic sample. Opx/4: Synthetic sample. Gt/1: Natural sample, Schneider Co. Gt/2: Natural sample No. 143895, Smithsonian collection. Gt/3: Synthetic pyrope. *All Iron assumed to be FeO.



At equilibrium, we then have

$$K_1(\text{P,T}) = \left[\frac{(X_{\text{Mg}}^{\text{Gt}})^3}{(X_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{Opx}}) \cdot (X_{\text{MgAl}_2\text{SiO}_6}^{\text{Opx}})} \right] = K_x(1) \cdot K_r(1) \quad (4)$$

$$K_2(\text{P,T}) = \left[\frac{(X_{\text{Mg}}^{\text{Gt}})^3}{(X_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^{\text{Opx}})} \right] \cdot K_r(2) = K_x(2) \cdot K_r(2) \quad (5)$$

$$K_3(\text{P,T}) = \left[\frac{(X_{\text{Mg}}^{\text{Gt}})^3}{(X_{\text{MgSiO}_3}^{\text{Opx}}) \cdot (X_{\text{Al}_2\text{O}_3}^{\text{Opx}})} \right] \cdot K_r(3) = K_x(3) \cdot K_r(3) \quad (6)$$

Where K_1 is the equilibrium constant for the reaction (1) and $K_r(1)$ collectively represents the activity coefficient terms in the expression of equilibrium constant; similarly for other reactions. For brevity, we call the terms within the square brackets of (1)

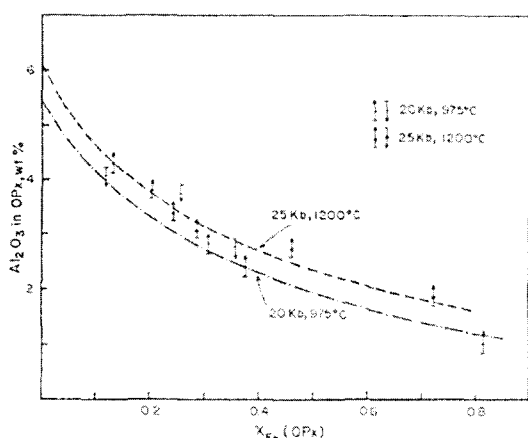


Fig. 1. Experimental data on the alumina solubility in equilibrium with garnet in the FMAS system at (a) 20 Kb, 975°C, and (b) 25 Kb, 1200°C. Upward and downward pointing arrows indicate direction of approach to equilibrium.

as $K_x(1)$, and so on. K_x is independent of composition when the corresponding K_r is constant. The latter condition will hold when both garnet and orthopyroxene behave as ideal solutions with respect to the specified choice of components, or there is a fortuitous cancellation among the nonideal properties of the solid solutions so that K_r remains independent of composition.

The $\ln K_x$ values for the three different formulations as functions of the compositions of orthopyroxenes at 20 Kb, 975°C and 25 Kb, 1,200°C were

illustrated in Fig. 2. In the FMAS system $K_x(1)$ and $K_x(2)$ depend strongly on compositions whereas $K_x(3)$ is insensitive to compositional changes, at least in the range of experimental conditions. It, therefore, seems that thermodynamic evaluation in terms of the reaction (3) will lead to relatively simple analytical formulation of Al_2O_3 solubility in orthopyroxene in equilibrium with garnet in multicomponent system. In particular, it may be possible to treat the system as nearly ideal. This approach should be tested for CMAS system.

For the MAS system, the expression for the equilibrium constant for the reaction (3) reduces to

$$K_3(P,T) = \left[\frac{1}{(X_{\text{MgSiO}_3}^{\text{Opx}}) \cdot (X_{\text{Al}_2\text{O}_3}^{\text{Opx}})} \right] \cdot K_r^{\text{MAS}}(3) = K_x(3) \cdot K_r(3) \quad (7)$$

Equating (6) and (7), and rearranging terms, we get

$$(X_{\text{Al}_2\text{O}_3}^{\text{Opx}}) = \left[\frac{X_{\text{Mg}}^{\text{Gt}}}{X_{\text{Mg}}^{\text{Opx}}} \right] \left[\frac{1}{K_x^{\text{MAS}}} \right] \left[\frac{K(3)}{K_r^{\text{MAS}}(3)} \right] \quad (8)$$

Note that $K_r(3)$ and $K_r^{\text{MAS}}(3)$ refer to the activity coefficient terms in a general multicomponent system and in the MAS system, respectively, and

Table 2. Summary of selected run data

Nominal*		Time hrs	Starting mixture	Flux/sample	Initial		Results*	
T°C	P, Kb			wt ratio	Al_2O_3 wt% in Opx	$X_{\text{Fe}}^{\text{Gt}}$	$X_{\text{Fe}}^{\text{Opx}}$	Al_2O_3 wt% in Opx
978±5	20±0.5	168	Opx/4, Gt/2	0.80	6.4	0.44	0.26	3.75
			Opx/1, Gt/2	0.80	0.08	0.49	0.31	2.85
			Opx/1, Gt/1	0.80	0.08	0.56	0.37	2.55
			Opx/4, Gt/1	0.80	6.43	0.58	0.38	2.18
			Opx/2, Gt/1	0.80	0.75	0.91	0.83	1.44
1,200±5	26±1	120	Opx/4, Gt/2	0.10	6.43	0.22	0.13	3.90
			Opx/1, Gt/2	0.10	0.08	0.44	0.30	2.91
			Opx/1, Gt/2	0.10	0.08	0.40	0.25	3.18
			Opx/3, Gt/3	0.10	0.07	0.34	0.22	3.64
			Opx/3, Gt/3	0.10	0.07	0.24	0.15	4.23
1,200±10	25.5±0.5	55	Opx/1, Gt/2	0.05	0.08	0.64	0.47	2.61
1,200±10	32.5±1.5	48	Opx/2, Gt/1	0.05	0.75	0.84	0.74	1.46

*The temperatures should be revised upward, as follow, to correct for the pressure effect on the e.m.f. of W-Re thermocouple: 975 to 979, 1200 to 1206. *Average of at least 20 spot analyses.

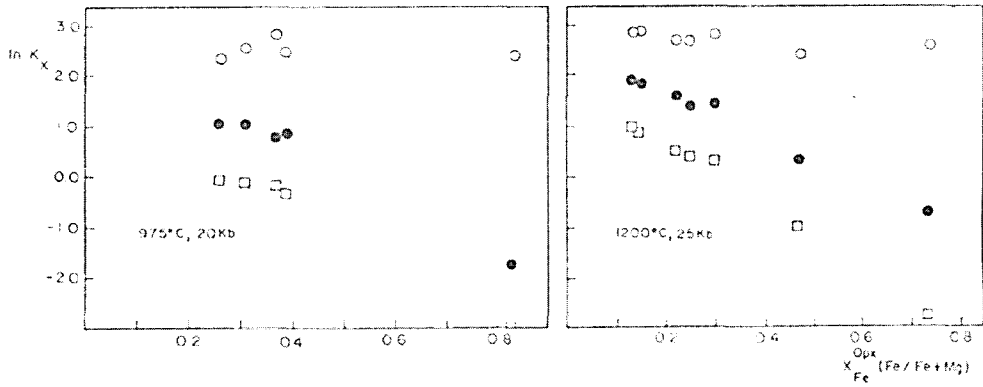


Fig. 2. $\ln K_X$ vs. X_{Fe}^{Opx} . Showing non-ideality of alumina solubility in orthopyroxene coexisting with garnet. Open, solid circles, and open squares represent reactions 3), (1), and (2) respectively in text.

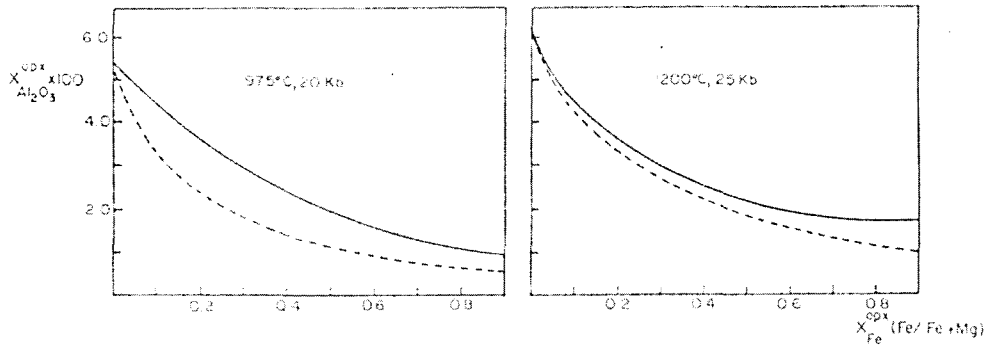


Fig. 3. $X_{Al_2O_3}^{Opx}$ vs. X_{Fe}^{Opx} plot showing the effect of Fe on alumina solubility. Solid line represents the best visual fit to the experimental data while the dashed line represents $X_{Al_2O_3}^{Opx}$ vs. X_{Fe}^{Opx} calculated on the assumption of ideal mixing (see text).

are not necessarily equal. For an arbitrarily specified composition of orthopyroxene, the ratio $(K_{Mg}^{Gt}/X_{Mg}^{Opx})$ can be derived from the Gt-Opx geothermometric expression of K_D (Lee, 1988) as a function of P and T . Using the definition of K_D , the expression (8) can be rewritten as

$$X_{Al_2O_3}^{Opx} = \left[\frac{1}{1 + X_{Fe}^{Opx}(K_D - 1)} \right]^3 \left[\frac{1}{K_X^{MAS}} \right] \phi \quad (9)$$

Where ϕ stands for the ratios of K_r in eqn. (8). At fixed P - T condition, K_X^{MAS} is a constant.

Thus, since $K_D > 1$ (Lee, 1988), $X_{Al_2O_3}^{Opx}$ is expected to decrease exponentially with X_{Fe}^{Opx} . The special case for $\phi = 1$ is illustrated in Fig. 3 for P - T conditions of 20 Kb, 975°C and 25 Kb, 1,200°C. K_X^{MAS} values are taken from the data of Perkins et

al. (1981). The calculated alumina solubility in orthopyroxene agrees with the experimentally determined relation within 1 wt. percent. For 25 kb, 1200°C, the ideal approximation underestimates alumina solubility in orthopyroxene by less than 0.5 wt. percent. This difference implies that with decreasing temperature ϕ value in eqn. (9) becomes greater than unity.

It is evident from eqn. (9) that this ratio, which we denote by ϕ , is given by

$$\phi = \left[\frac{K_{FMAS}^{(3)}}{K_X^{MAS}(3)} \right] = \left[\frac{(X_{Al_2O_3}^{Opx})_{expt}}{(X_{Al_2O_3}^{Opx})_{cal}} \right]_{FMAS} \quad (10)$$

Where $(X_{Al_2O_3}^{Opx})_{expt}$ and $(X_{Al_2O_3}^{Opx})_{cal}$ refer $X_{Al_2O_3}^{Opx}$ values from experimental data and calculation from

Table 3. Values of ϕ and χ for alumina solubility in orthopyroxene

In ϕ	χ	Opx		X_{Mg}^{Gt}	P,T
		X_{MgSiO_3}	$X_{Al_2O_3}$		
0.494	-0.042	0.6606	0.0310	0.4924	20 Kb, 975°C
0.587	-0.048	0.6104	0.0279	0.4258	
0.505	-0.054	0.6022	0.0242	0.4121	
0.609	-0.081	0.1699	0.0103	0.0846	
0.000	-0.043	0.8320	0.040	0.760	20Kb, 1200°C
0.026	-0.037	0.8137	0.043	0.758	
0.156	-0.046	0.7493	0.038	0.639	
0.217	-0.056	0.7125	0.033	0.573	
0.078	-0.059	0.6760	0.031	0.556	
0.355	-0.086	0.2575	0.017	0.159	

eqn. (9) on the assumption of $\phi=1$ respectively. Table 3 shows values of ϕ calculated from the experimental data at 975°C and 1200°C. At constant P-T condition, it may be expressed as a function of composition by expanding the K terms according to a specific solution model. A simple form of the compositional dependence of ϕ , which can be developed from the simple mixture model and some simplifying assumptions (appendix), is as follows

$$\ln \phi = \frac{3W_{MgAl}^{Opx}}{RT} \cdot \chi \quad (11)$$

with defined as

$$\chi = (X_1^2 - X_2^2) + (1 - X_1)^2 - (1 - X_2)^2 \quad (12)$$

where $X_1 = X_{Al_2O_3}^{Opx}$ in MAS and $X_2 = X_{Al_2O_3}^{Opx}$ in FMAS system. W_{MgAl}^{Opx} is the simple mixture interaction parameter between the $MgSiO_3$ and $AlAlO_3$ components in orthopyroxene, and is assumed to be approximately equal to the interaction parameter between $FeSiO_3$ and $AlAlO_3$ components. It is also assumed, based on the Fe-Mg fractionation between garnet and orthopyroxene (Lee, 1988), that $W_{FeMg}^{Opx} / RT = W_{MgAl}^{Opx} / RT = 0$ at $T > 975^\circ\text{C}$.

Fig. 4 illustrates the variation of $\ln \phi$ as a function of χ at 975°C and 1200°C. A statistical fit of the data using the constraint that $\ln \phi = 0$ at $\chi = 0$ yields.

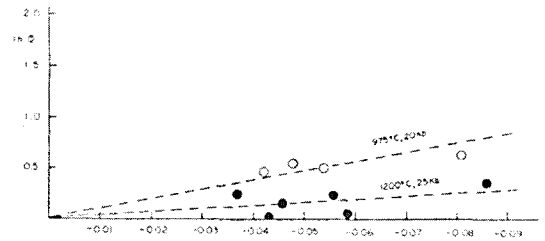


Fig. 4. A plot of $\ln \phi$ vs. χ , showing the effect of composition and temperature on alumina solubility. Open and solid circles indicate 975°C and 1200°C runs respectively.

$$W_{MgAl}^{Opx} (20\text{Kb, } 975^\circ\text{C}) = -7.997 \text{ Kcal}$$

$$W_{MgAl}^{Opx} (25\text{Kb, } 1200^\circ\text{C}) = -3.594 \text{ Kcal}$$

As a first approximation, one may assume that W varies as a linear function of T around 975-1200°C to yield.

$$W = -31883 + 19.14T^\circ\text{K} \quad (13)$$

The eqn. (13) can be combined with (9) and (11) to calculate $X_{Al_2O_3}^{Opx}$ as a function of temperature and composition in the FMAS system at pressures around 25 Kb, and temperatures around 975-1200°C. In principle, W is a function of pressure, but there are no data at present to evaluate the pressure effect on W . Calculated alumina solubilities in orthopyroxene using the above relations at 20 Kb, 975°C and 25 Kb, 1200°C agree well with visual fits derived from experimental data in this study in Fig. 1.

Discussion

The equilibrium pressures of garnet-Iherzolite xenoliths are often estimated on the basis of data on alumina solubility in orthopyroxene in MAS system without correction for the effects of additional components (e.g., Finnerty and Body, 1984; Ganguly and Bhattacharya, 1987). Although there are still inadequate experimental and thermodynamic data to make appropriate corrections for the compositional effects and that in natural assemblages, the Al_2O_3 in orthopyroxene in equilibrium with garnet could be significantly lower than that in MAS system at the same P-T condition.

The effect of Al_2O_3 content in orthopyroxene on K_D will be manifested through that on $(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Opx}}$ (Lee, 1988; eqn. 1). The importance of this effect may be illustrated by assuming orthopyroxene as a ternary 'Simple Mixture' (Ganguly and Saxena, 1987) of FeSiO_3 , MgSiO_3 and Al_2O_3 components in FMAS system. We can then write, following Ganguly and Kennedy (1974),

$$RT \ln \left(\frac{\gamma_{\text{Fe}}}{\gamma_{\text{Mg}}} \right)^{\text{Opx}} = W_{\text{FeMg}}^{\text{Opx}} - (X_{\text{Mg}} - X_{\text{Fe}})^{\text{Opx}} + (\Delta W X_{\text{Al}_2\text{O}_3})^{\text{Opx}} \quad (9)$$

Where W_{ij}^{Opx} is a 'Simple Mixture' interaction parameter, and $\Delta W = W_{\text{FeAl}} - W_{\text{MgAl}}$. Since orthopyroxene behaves very nearly ideally at $T > 700^\circ\text{C}$ (Chatillon-Colinet et al., 1983b), the first term in eqn. 9 after equality should be negligible. Also, for the same reason, the ΔW term should be very small. In this study, the Al_2O_3 content of orthopyroxene varied approximately between 1 and 4 mol per cent (Table 2). Consequently, even allowing for a magnitude of 1 Kcal for the ΔW term at 1000°C , 4 mol per cent Al_2O_3 leads to a change of in $(\gamma_{\text{Fe}}/\gamma_{\text{Mg}})^{\text{Opx}}$ of 0.016, which corresponds to a change of K_D by a factor of 1.016. Thus, it can be concluded that the variation of Al_2O_3 solubility in orthopyroxene is of no practical significance in the determination of equilibrium K_D values in the

FMAS system.

Acknowledgments

The helpful review by Dr. Jonglk Lee at Korea Ocean Research and Development Institute is appreciated and thanks Sunyoung Kim and Minsub Song for typing and arranging data and complicated thermodynamic formulations.

References

- Akella, J., 1976, Garnet-pyroxene equilibria in the system $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ and in a natural mineral mixture. *American Mineralogist*, 61, 589-598.
- Bertrand, P., Sotin, C., Mercier, J.C.C., and Takahashi, E., 1986. From the simplest chemical system to the natural one: garnet peridotite barometry. *Contributions to Mineralogy and Petrology*, 93, 168-178.
- Boyd, F.R. and England, J.L., 1964, The system of enstatite-pyroxene. *Carnegie Institute of Washington, Yearbook*, 63, 157-161.
- Chatillon-Colinet, C., Newton, R.C., Perkins, D., and Kleppa, O.J., 1983b. Thermochemistry of $(\text{Fe}^{2+}, \text{Mg})\text{SiO}_3$ orthopyroxene. *Geochim. Cosmochim. Acta*, 47, 1597-1603.
- Chatterjee, N.D. and Terhart, L., 1985, Thermodynamic calculation of peridotite phase relations in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Cr}_2\text{O}_3$, with some geological applications. *Contributions to Mineralogy and Petrology*, 89, 273-284.
- Danckwerth, P.A. and Newton, R.C., 1978, Experimental determination of the spinel peridotite to garnet peridotite reaction in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ in the range $900\text{-}1100^\circ\text{C}$ and Al_2O_3 isopleths of enstatite in the spinel field. *Contributions to Mineralogy and Petrology*, 66, 189-201.
- Finnerty, A.A. and Boyd, F.R., 1984, Evaluation of thermobarometer for garnet peridotites. *Geochim. Cosmochim. Acta*, 48, 15-27.
- Ganguly, J. and Kennedy, C.C., 1974, The energetics of natural garnet solid solution I. Mixing of the aluminosilicate end members. *Contributions to Mineralogy and Petrology*, 48, 137-148.
- Ganguly, J. and Ghose, S., 1979, Aluminous orthopyroxene: order-disorder, thermodynamic properties, and petrologic implications. *Contributions to Mineralogy and Petrology*, 69, 375-385.
- Ganguly, J. and Saxena, S.K., 1987, Mixtures and mineral reactions. New York, Berlin, Heidelberg: Springer-Ver-

- lag.
- Ganguly, J. and Bhattacharya, P.K., 1987, Xenolith in Proterozoic Kimverites from southern India: Petrology and geophysical implications. In: Nixon, P. H. (Ed.) *Mantle Xenoliths*. New York: John Wiley and sons, 249-265.
- Gasparik, T. and Newton, R.C., 1984, The reversed alumina contents of orthopyroxene in equilibrium with spinel and forsterite in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$. *Contributions to Mineralogy and Petrology*, 86, 186-196.
- Harley, S.L., 1984, An experimental study of the partitioning of Fe and Mg between garnet and orthopyroxene. *Contributions to Mineralogy and Petrology*, 86, 359-373.
- Howells, S. and O'Hara, J.J., 1978, Low solubility of alumina in enstatite and uncertainties in estimated paleogeotherms. *Philosophy of Transactions of Royal Society of London*, A-288, 471-486.
- Jenkins, D.M. and Newton, R.C., 1979, Experimental determination to the spinel peridotite to garnet peridotite inversion at 900°C and 1000°C in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$, and at 900°C with natural garnet and olivine. *Contributions to Mineralogy and Petrology*, 68, 407-419.
- Kawasaki, T. and Matsui, Y., 1983, Thermodynamic analysis of equilibria involving olivine, orthopyroxene and garnet. *Geochim. cosmochim. Acta*, 47, 1661-1679.
- Lane, D.L. and Ganguly, J., 1980, Al_2O_3 solubility in orthopyroxene in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_3$: A reevaluation, and mantle geotherm. *Journal of Geophysical Research*, 86, 6963-6972.
- Lee, H.Y., 1988, Garnet-orthopyroxene geothermometer and geological applications. *Journal of Korean Institute of Mining Geology*, 21, 29-44.
- MacGregor, I.D., 1974, The system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_3$: Solubility of Al_2O_3 in enstatite for spinel and garnet peridotite compositions. *American Mineralogist*, 59, 110-119.
- Mori, T. and Green, D.H., 1978, Laboratory duplication of phase equilibria observed in natural garnet-lherzolite. *Journal of Geology*, 86, 83-97.
- Obata, M., 1976, The solubility of Al_2O_3 in orthopyroxenes in spinel and plagioclase peridotites and spinel pyroxene. *American Mineralogist*, 61, 804-816.
- Perkins, D. and Newton, R.C., 1980, The compositions of coexisting pyroxenes and garnet in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ at 900-1100°C and high pressures. *Contributions to Mineralogy and Petrology*, 75, 291-300.
- Perkins, D., Holland, T.J.B., and Newton, T.C., 1981, Al_2O_3 contents of enstatite in equilibrium with garnet in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ at 15-49 kb and 900-1600°C. *Contributions to Mineralogy and Petrology*, 78, 99-109.
- Wood, B.J. and Banno, S., 1973, Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems. *Contributions to Mineralogy and Petrology*, 42, 109-124.
- Wood, B.J., 1974, The solubility of alumina in orthopyroxene coexisting with garnet. *Contributions to Mineralogy and Petrology*, 46, 1-15.

Manuscript received, December 20, 2003

Revised manuscript received, January 30, 2004

Manuscript accepted, January 30, 2004

Appendix

Derivation of ϕ as a Simple Function of T and X

$$(X_{\text{Al}_2\text{O}_3}^{\text{Opx}}) = \left[\frac{X_{\text{Mg}}^{\text{Gt}}}{X_{\text{Mg}}^{\text{Opx}}} \right]_{\text{FMAS}} \cdot \left[\frac{1}{(K_x)_{\text{MAS}}} \right] \cdot \phi$$

where $\phi = K_r(\text{FMAS}) / K_r(\text{MAS})$

$$K_r = \frac{(\gamma_{\text{Mg}}^{\text{Gt}})^3}{(\gamma_{\text{MgSiO}_3}^{\text{Opx}})^3 \cdot (\gamma_{\text{Al}_2\text{O}_3}^{\text{Opx}})}$$

For MAS system, $\gamma_{\text{Mg}} = 1$

$$\ln \gamma_{\text{MgSiO}_3}^{\text{Opx}} = \frac{W_{\text{MgAl}}^{\text{Opx}}}{RT} \cdot (X_{\text{Al}_2\text{O}_3})^2$$

$$\ln \gamma_{\text{Al}_2\text{O}_3}^{\text{Opx}} = \frac{W_{\text{MgAl}}^{\text{Opx}}}{RT} \cdot (1 - X_{\text{Al}_2\text{O}_3})^2$$

For FMAS system

$$RT \ln \gamma_{\text{Mg}}^{\text{Gt}} = W_{\text{FeMg}}^{\text{Gt}} (X_{\text{Fe}}^{\text{Gt}})^2$$

$$RT \ln \gamma_{\text{MgSiO}_3}^{\text{Gt}} = W_{\text{MgAl}} \cdot X_{\text{Al}_2\text{O}_3}^2 + W_{\text{MgFe}} X_{\text{FeSiO}_3}^2 + (W_{\text{MgAl}} + W_{\text{MgFe}} - W_{\text{FeAl}}) X_{\text{Al}_2\text{O}_3} X_{\text{MgSiO}_3}$$

$$RT \ln \gamma_{\text{Al}_2\text{O}_3}^{\text{Gt}} = W_{\text{MgAl}} \cdot X_{\text{Mg}} + W_{\text{MgFe}} \cdot X_{\text{Fe}} + (W_{\text{MgAl}} + W_{\text{FeAl}} - W_{\text{FeMg}}) \cdot X_{\text{Mg}} X_{\text{Fe}}$$

Where $W_{\text{MgAl}} = W_{\text{FeAl}}$ and $W_{\text{FeMg}} = 0$ according to Fe-Mg partitioning data (Lee, 1988)

$$RT \ln \gamma_{\text{MgSiO}_3}^{\text{Gt}} = W_{\text{MgAl}} \cdot X_{\text{Al}_2\text{O}_3}^2$$

$$RT \ln \gamma_{\text{Al}_2\text{O}_3}^{\text{Gt}} = W_{\text{MgAl}} (X_{\text{Mg}} + X_{\text{Fe}})^2$$

$$RT \ln K\gamma(\text{MAS}) = -3W_{\text{MgAl}} (X_1^2 + (X_{\text{Mg}}^{\text{Opx}})_{\text{FMAS}}^2)$$

$$RT \ln K\gamma(\text{FMAS}) = -3W_{\text{MgAl}} (X_2^2 + (X_{\text{Mg}}^{\text{Opx}} + X_{\text{Fe}}^{\text{Opx}})_{\text{FMAS}}^2)$$

Where $X_1 = X_{\text{Al}_2\text{O}_3}^{\text{Opx}}(\text{MAS})$ and $X_2 = X_{\text{Al}_2\text{O}_3}^{\text{Opx}}(\text{FMAS})$

$$RT \ln \phi = RT(\ln K\gamma(\text{FMAS}) - \ln K\gamma(\text{MAS})) = 3W_{\text{MgAl}} (X_1^2 - X_2^2 + (1 - X_1)^2 - (1 - X_2)^2) = 3W_{\text{MgAl}} \cdot \chi$$

$$\text{where } \chi = X_1^2 - X_2^2 + (1 - X_1)^2 - (1 - X_2)^2$$

$$\text{thus, } \ln \phi = \frac{3W_{\text{MgAl}}}{RT} \cdot \chi$$