

## The solubility of $\text{Al}_2\text{O}_3$ in orthopyroxenes in spinel and plagioclase peridotites and spinel pyroxenite

MASAAKI OBATA

*Department of Earth and Planetary Sciences  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139*

### Abstract

The solubility of  $\text{Al}_2\text{O}_3$  in orthopyroxene coexisting with olivine and spinel in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  was calculated. The model used is based on the theoretical treatments by Wood and Banno (1973) and Wood (1974) for garnet–orthopyroxene equilibria and on the experimental data of MacGregor (1964) for the reaction orthopyroxene + spinel = forsterite + pyrope. The reaction curve was extrapolated outside the experimental range using a simple solution model for orthopyroxene proposed by Wood and Banno (1973). The solubility of  $\text{Al}_2\text{O}_3$  in orthopyroxene is calculated to be much less sensitive to pressure than suggested by MacGregor (1974), and is essentially a function of temperature alone below  $1000^\circ\text{C}$ . Based on the results in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , the univariant curves for the reactions forsterite + anorthite = clinopyroxene + orthopyroxene + spinel and clinopyroxene + orthopyroxene + spinel = forsterite + garnet in the four-component system  $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , and the solubilities of  $\text{Al}_2\text{O}_3$  in orthopyroxene in plagioclase peridotite and in spinel pyroxenite, were also calculated. Because of the compositional changes of pyroxenes which are involved in the reactions, the univariant lines curve significantly, and simple linear extrapolations of high-temperature experimental data to low temperatures are not valid. A method for applying the calculated results to natural rocks is proposed.

### Introduction

Among chemical parameters of minerals, the solubility of  $\text{Al}_2\text{O}_3$  in pyroxenes is one of the most sensitive indicators of physical conditions, and is especially applicable to peridotites. Quantitative estimates of equilibration pressure have become possible since the experimental work on the join  $\text{MgSiO}_3-\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  by Boyd and England (1964) and that in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  by MacGregor (1974). These experimental data have recently been applied to garnet peridotite xenoliths in kimberlites (Boyd, 1973; Boyd and Nixon, 1975) and to spinel peridotite xenoliths in basalts and peridotite intrusions (MacGregor, 1974; Mercier and Carter, 1975). Some apparent discrepancies in the experimental data for garnet peridotite between simple and complex systems were discussed through a theoretical treatment of orthopyroxene–garnet equilibria by Wood and Banno (1973) and Wood (1974). From more extensive experimental data by Akella and Boyd (1972, 1973, and 1974) and Akella (1976), we

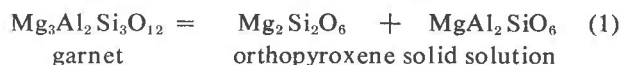
can now estimate equilibration pressure of garnet peridotites with some confidence, provided equilibration temperatures are known by independent methods. On the other hand, there are still some contradictions about the  $\text{Al}_2\text{O}_3$  solubility in orthopyroxene in spinel peridotite among different authors: MacGregor's experiments (1974) suggest that the  $\text{Al}_2\text{O}_3$  isopleths for orthopyroxene have definite positive slopes in the spinel peridotite field as well as in the garnet peridotite field, and that the  $\text{Al}_2\text{O}_3$  content decreases with increasing pressure. This contradicts O'Hara's (1967) inference that the  $\text{Al}_2\text{O}_3$  isopleths for clinopyroxene, and also by implication for orthopyroxene, have negative slopes, and that the solubility increases with increasing pressure. Moreover, there are notable discrepancies between MacGregor's experiments (1974) and the low-pressure experiments by Anastasiou and Seifert (1972) on the  $\text{Al}_2\text{O}_3$  solubility in orthopyroxene, as noted by MacGregor (1974). Obviously more careful experiments and theoretical examination of this parameter are necessary before geologic applications can be made with

confidence. Theoretically the solubilities of  $Al_2O_3$  for garnet peridotite and for spinel peridotite are not independent, and there is some way to examine internal consistencies of the experimental data.

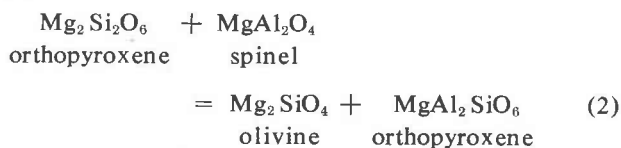
The purpose of this paper is to demonstrate that the  $Al_2O_3$  solubilities in orthopyroxene in spinel peridotite, plagioclase peridotite, and spinel pyroxenite may be uniquely derived by simple thermodynamic calculations from the published experimental data for garnet peridotite and from positions of boundaries between garnet-spinel and spinel-plagioclase peridotite facies.

### Thermodynamic considerations

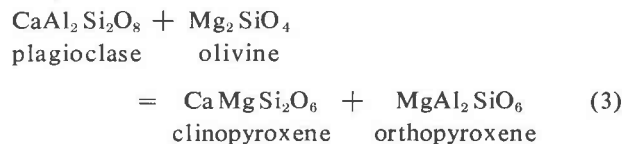
In order to calculate the  $Al_2O_3$  solubility in orthopyroxene in various mineral assemblages, it is convenient to first write appropriate stoichiometric expressions of the aluminous pyroxene component,  $MgAl_2SiO_6$ ,<sup>1</sup> in terms of sets of components in the phases present. For example, the equation



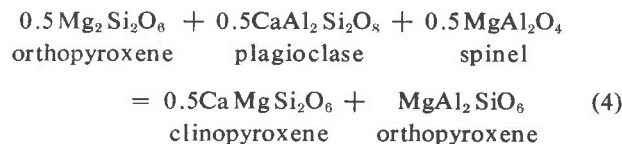
has been used by Wood and Banno (1973) to analyze orthopyroxene-garnet equilibria. Similarly, the equation



may be used for an olivine-spinel-orthopyroxene assemblage,



for a plagioclase-olivine-clinopyroxene-orthopyroxene assemblage,



for a spinel-plagioclase-clinopyroxene-orthopyroxene

assemblage, *etc.* Regarding these mathematical expressions as chemical reactions, the equilibrium condition for the reaction is:

$$-RT \ln K(i) = \Delta G^0(i) \quad (5)$$

where  $K(i)$  and  $\Delta G^0(i)$  are, respectively, equilibrium constant and free energy change of reaction (*i*) at the pressure and temperature of interest. The equilibrium constants for each reaction are:

$$K(1) = \frac{a_{MgAl_2SiO_6}^{opx} \cdot a_{Mg_2Si_2O_6}^{opx}}{a_{Mg_3Al_2Si_3O_{12}}^{grt}} \quad (6)$$

$$K(2) = \frac{a_{MgAl_2SiO_6}^{opx} \cdot a_{Mg_2SiO_4}^{ol}}{a_{Mg_2Si_2O_6}^{opx} \cdot a_{MgAl_2O_4}^{sp}} \quad (7)$$

$$K(3) = \frac{a_{MgAl_2SiO_6}^{opx} \cdot a_{CaMgSi_2O_6}^{cpx}}{a_{Mg_2SiO_4}^{ol} \cdot a_{CaAl_2Si_2O_8}^{pl}} \quad (8)$$

$$K(4) = \frac{a_{MgAl_2SiO_6}^{opx} \cdot (a_{CaMgSi_2O_6}^{cpx})^{1/2}}{(a_{Mg_2Si_2O_6}^{opx})^{1/2} \cdot (a_{CaAl_2Si_2O_8}^{pl})^{1/2}} \quad (9)$$

where  $a_j^\alpha$  is the activity of component *j* in phase  $\alpha$ .<sup>2</sup>

If the free energy change  $\Delta G^0$  and the activity-composition relationships are known, the  $Al_2O_3$  solubility in orthopyroxene for each mineral assemblage can be calculated as a function of pressure and temperature. Wood and Banno (1973) proposed a simple mixing model for orthopyroxene solid solution, and calculated  $\Delta G^0(1)$  using Boyd and England's (1964) experimental data on the  $Al_2O_3$  solubility in orthopyroxene coexisting with pyrope. In spite of simplifying assumptions, the model satisfied available experimental data in simple and complex systems within the limits of experimental precision.

In this paper, the Wood-Banno model for the  $Mg_2Si_2O_6$ - $MgAl_2SiO_6$  orthopyroxene solid solution is adopted, that is:

- (1) Octahedral Al atoms occupy only the smaller of the two octahedral positions, *M1*.
- (2) Tetrahedral Al atoms are completely coupled to the octahedral Al atoms to maintain local charge balance.
- (3) An ideal random mixing of Al and Mg atoms was assumed in *M1* sites, so that considering assumption (2) entropy of mixing of the solution is calculated

<sup>1</sup> Although Ganguly and Ghose (1975) suggested that  $Mg_3Al_2Si_3O_{12}$  is preferable to  $MgAl_2SiO_6$  as an aluminous pyroxene component, the choice of a different component will not cause differences in the result.

<sup>2</sup> The names of phases are abbreviated as follows: cpx = clinopyroxene; opx = orthopyroxene; sp = spinel; ol = olivine; fo = forsterite; gar = garnet; py = pyrope; pl = plagioclase; an = anorthite.

from the proportion of Mg and Al atoms in the  $M1$  site only.

(4) The solid solution is ideal at 1 bar and the non-ideality is introduced by the excess partial molar volume at high pressures.

The olivine-spinel-orthopyroxene equilibria in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  are first discussed; and based on the result, the assemblages plagioclase-olivine-clinopyroxene-orthopyroxene and spinel-plagioclase-clinopyroxene-orthopyroxene in the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  will be treated. A method is then described whereby the results of calculations in simple systems can be used as indicators of equilibrium conditions in natural rocks.

*Solubility of  $\text{Al}_2\text{O}_3$  in orthopyroxene coexisting with forsterite and spinel in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$*

In the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ ,  $a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{ol}}$  and  $a_{\text{MgAl}_2\text{SiO}_6}^{\text{sp}}$  in a spinel peridotite are unity, and

$$a_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{opx}} = X_{\text{Mg}}^{M1} \cdot \gamma_{\text{Mg}_2\text{Si}_2\text{O}_6} \quad (10)$$

$$a_{\text{MgAl}_2\text{SiO}_6}^{\text{opx}} = X_{\text{Al}}^{M1} \cdot \gamma_{\text{MgAl}_2\text{SiO}_6} \quad (11)$$

$$X_{\text{Mg}}^{M1} + X_{\text{Al}}^{M1} = 1$$

where  $X_{\text{Mg}}^{M1}$  and  $X_{\text{Al}}^{M1}$  are the concentrations of Mg and Al atoms in the  $M1$  site, and  $\gamma$ 's are activity coefficients in orthopyroxenes. By introducing a parameter,  $K'(2) \equiv X_{\text{Al}}^{M1}/X_{\text{Mg}}^{M1}$ , which is called the apparent equilibrium constant, we may write for reaction (2):

$$-RT \ln K'(2) = \Delta G^0(2) + \Delta G^{\text{ex}}(2) \quad (12)$$

where  $G^{\text{ex}}(2)$  is an excess Gibbs free energy change of reaction (2) and

$$\Delta G^{\text{ex}}(2) = -RT \ln \left( \frac{\gamma_{\text{MgAl}_2\text{SiO}_6}}{\gamma_{\text{Mg}_2\text{Si}_2\text{O}_6}} \right) \quad (13)$$

$$\Delta G^{\text{ex}}(2) = \Delta H^{\text{ex}}(2) - T\Delta S^{\text{ex}}(2) \quad (14)$$

where the suffix "ex" denotes the excess term for reference to the ideal system (Thompson, 1967).  $\Delta S^{\text{ex}}(2)$  equals zero for the ideal random mixing model of orthopyroxene used here, so relation (14) becomes:

$$\Delta G^{\text{ex}}(2) = \Delta H^{\text{ex}}(2) \quad (15)$$

Since

$$\left( \frac{\partial \Delta H}{\partial P} \right)_{S,T} = \Delta V \quad (16)$$

and

$$\left( \frac{\partial \Delta H^{\text{ex}}}{\partial P} \right)_{S,T} = \Delta V^{\text{ex}} \quad (17)$$

equation (12) becomes:

$$-RT \ln K'(2) = \Delta H_{1,T}^0(2) + (P-1) \Delta V^0(2) + (P-1) \Delta V^{\text{ex}}(2) - T\Delta S^0(2)$$

or

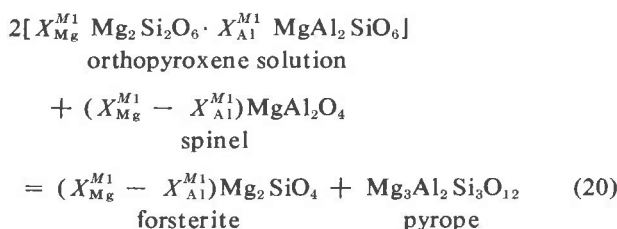
$$-RT \ln K'(2) = \Delta H_{1,T}^0(2) + (P-1) \Delta V(2) - T\Delta S^0(2) \quad (18)$$

where  $\Delta H_{1,T}^0(2)$  and  $\Delta S^0(2)$  are an enthalpy change at 1 bar, and entropy change of reaction (2), respectively.  $\Delta V(2)$  is a molar volume change of reaction (2):

$$\Delta V(2) = V_{\text{Mg}_2\text{Si}_2\text{O}_6}^0 + \bar{V}_{\text{MgAl}_2\text{SiO}_6} - \bar{V}_{\text{Mg}_2\text{Si}_2\text{O}_6} - V_{\text{MgAl}_2\text{O}_4}^0 \quad (19)$$

where  $V_j^0$  and  $\bar{V}_j$  are the molar volume of the pure phase and the partial molar volume of component  $j$ , respectively. The values of  $\Delta H_{1,T}^0(2)$  and  $\Delta S^0(2)$  are not known, but as described below, may be indirectly derived using values of  $H_{1,T}^0(1)$  and  $\Delta S^0(1)$  determined by Wood and Banno (1973) and Wood (1974), and the position of the univariant curve of the reaction orthopyroxene + spinel = forsterite + pyrope in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  (MacGregor, 1964).

An expression for the univariant reaction,  $\text{opx} + \text{sp} = \text{fo} + \text{py}$  may be written:



which is simply a linear combination of equations (1) and (2):

$$(20) = (X_{\text{Mg}}^{M1} - X_{\text{Al}}^{M1}) \cdot (2) - (1) \quad (21)$$

Similar relations can therefore be written for molar enthalpy and molar entropy changes of reactions (1), (2), and (20):<sup>3</sup>

$$\Delta H(20) = (X_{\text{Mg}}^{M1} - X_{\text{Al}}^{M1}) \cdot \Delta H(2) - \Delta H(1) \quad (22)$$

$$\Delta S(20) = (X_{\text{Mg}}^{M1} - X_{\text{Al}}^{M1}) \cdot \Delta S(2) - \Delta S(1) \quad (23)$$

The composition of pyroxene may be calculated using equation (13) of Wood and Banno (1973). The Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta S(20)}{\Delta V(20)} \quad (24)$$

<sup>3</sup> It should be noted that these changes are on partial molar quantities of the components, and not on those of pure phases.

expresses  $\Delta S(20)$  in terms of  $\Delta V(20)$  and the slope of the univariant curve in  $P$ - $T$  space. The slope can be read directly from MacGregor's (1964) phase diagram, and  $\Delta V(20)$  can be calculated from published data<sup>4</sup> for spinel, forsterite, aluminous enstatite, and pyrope. A value for  $\Delta S(20)$  is thus obtained.  $\Delta H(20)$  is immediately known, because

$$\Delta H(20) = T\Delta S(20) \quad (25)$$

on the univariant curve. We also have relationships:

$$\Delta H(1) = \Delta H_{1,T}^0(1) + (P - 1) \Delta V(1) \quad (26)$$

$$\Delta S(1) = \Delta S^0(1) - R \ln (X_{Al}^{M1} \cdot X_{Mg}^{M1}) \quad (27)$$

<sup>4</sup> Sources of data for molar volumes and entropies of minerals used in this paper are given in Appendix 1.

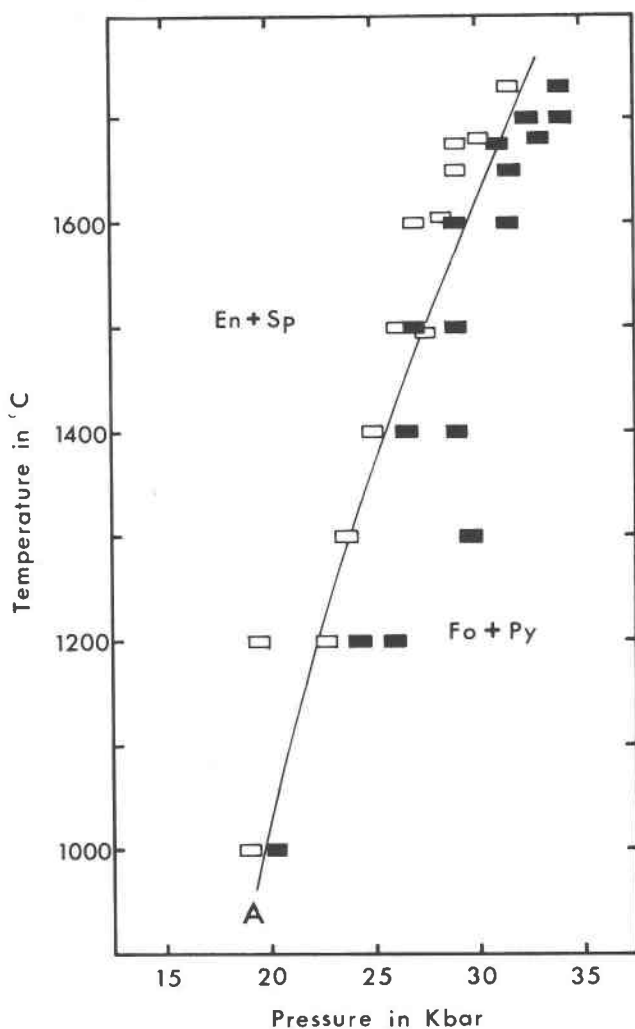


FIG. 1. Calculated univariant line (curve A) of the reaction  $opx + sp = fo + py$  in the system  $MgO-Al_2O_3-SiO_2$  compared with the experimental data of MacGregor (1964): open rectangles =  $opx + sp$ ; filled rectangles =  $fo + py$ .

$$\Delta H(2) = \Delta H_{1,T}^0(2) + (P - 1) \Delta V(2) \quad (28)$$

$$\Delta S(2) = \Delta S^0(2) - R \ln (X_{Al}^{M1} / X_{Mg}^{M1}) \quad (29)$$

Substituting the values of  $\Delta H(20)$  and  $\Delta S(20)$  which were obtained previously and  $\Delta H$  and  $\Delta S$  of equations (26), (27), (28), (29) into equations (22) and (23), we finally arrive at values of  $\Delta H_{1,T}^0(2)$  and  $\Delta S^0(2)$ .  $\Delta S^0(2)$  is also, by definition,

$$\Delta S^0(2) = S_{Mg_2SiO_6}^0 + S_{MgAl_2SiO_6}^0 - S_{Mg_2Si_2O_6}^0 - S_{MgAl_2O_4}^0 \quad (30)$$

where  $S_j^0$  is an entropy of formation of component  $j$  in a pure phase at standard state (1 bar, 298°K). Temperature dependence of  $\Delta S^0$  was neglected, since heat capacity changes of the reactions are very small. Using published entropy data at standard state for forsterite, enstatite, and spinel, the entropy of  $MgAl_2SiO_6$  pyroxene, as yet unknown, may be obtained. The entropy of pyrope may also be obtained using the relationship,

$$\Delta S^0(1) = S_{Mg_2Si_2O_6}^0 + S_{MgAl_2SiO_6}^0 - S_{Mg_3Al_2Si_3O_{12}}^0 \quad (31)$$

Reading of the slope of the univariant curve has to be varied continuously with temperature to hold a value of  $\Delta S^0(2)$  constant. In the actual calculation, the best value of  $\Delta S^0(2)$  was sought such that the computed curve, which can be drawn by changing pressure and temperature in a stepwise manner starting from an arbitrary point of pressure and temperature using the Clapeyron equation (24), satisfies the experimental points. One of the calculated curves which best fits the experimental data of MacGregor (1964) is shown in Figure 1. The parameters of the curve are  $\Delta S^0(2) = 4.05$  cal/deg/mol and  $\Delta H_{1,T}^0(20) = 10.4$  kcal/mole. Entropies of  $MgAl_2SiO_6$  pyroxene and pyrope at standard state were calculated to be 33.0 cal/deg/mole and 61.6 cal/deg/mole, respectively.

A -10 percent friction correction was applied to all the pressure values of the runs as proposed by MacGregor (1974, p. 117). The values  $\Delta H_{1,T}^0(1)$  and  $\Delta S^0(1)$  of 7012 cal/mole and 3.89 cal/deg/mole calculated by Wood (1974) were used instead of those calculated by Wood and Banno (1973) for reasons mentioned by Wood (1974, p. 3). Substituting the obtained values of  $\Delta H_{1,T}^0(2)$  and  $\Delta S^0(2)$  into equation (18), the  $MgO-Al_2O_3-SiO_2$  phase diagram was constructed in pressure-temperature-composition space

(Fig. 2). This figure shows that, although the univariant curve of the reaction  $\text{opx} + \text{sp} = \text{fo} + \text{py}$  is nearly a straight line in the experimentally investigated area of pressure and temperature, the slope becomes steeper as temperature decreases and is almost vertical below 800°C. Slopes of  $\text{Al}_2\text{O}_3$  isopleths for spinel peridotite are very shallow and almost horizontal below 1000°C. Anastasiou and Seifert (1972) determined the  $\text{Al}_2\text{O}_3$  solubility in orthopyroxene on the reaction curve  $\text{opx} + \text{sp} = \text{fo} + \text{cordierite}$ , using a hydrothermal apparatus. Their data, 7.2 mole percent  $\text{MgAl}_2\text{SiO}_6$  at 900°C–3 kbar, 13 mole percent  $\text{MgAl}_2\text{SiO}_6$  at 1000°C–2.8 kbar, and 17.2 mole percent  $\text{MgAl}_2\text{SiO}_6$  at 1100°C–2.6 kbar agree well with the calculated values of 8, 11, and 15 mole percent  $\text{MgAl}_2\text{SiO}_6$  at the same conditions within the limits of experimental uncertainty. These, however, are in marked contrast to MacGregor's (1974) values of approximately 15, 21, and 24 mole percent  $\text{MgAl}_2\text{SiO}_6$  respectively, at the same conditions. The reasons for large discrepancies between the values calculated here or those of Anastasiou and Seifert and MacGregor's data are not well understood.<sup>5</sup> MacGregor (1974) considered a possibility that the  $\text{Al}_2\text{O}_3$  isopleths flatten as pressure decreases to match his experiments to those of Anastasiou and Seifert. The change of the slope may be caused through the changes of molar volume and/or molar entropy changes of reaction (2) with temperature and/or pressure at constant composition of pyroxenes. It is very difficult to expect the appearance of curvature of the isopleths only in the spinel peridotite field while the isopleths in the garnet peridotite field are well approximated by straight lines. The only possible way to have local rapid changes of the slopes of the isopleths is by having some kind of polymorphic transformation of aluminous enstatite. Examination of this possibility must await detailed X-ray crystallographic studies on aluminous enstatite at high pressure and temperature.

If the shallow slopes are correct, it is practically impossible to use the  $\text{Al}_2\text{O}_3$  solubility in orthopyroxene in spinel peridotite as a geobarometer except at very high temperatures where the slopes are steeper.

<sup>5</sup> The thermodynamic treatment and the conclusions in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  are almost identical to those of Wood (1975), whose manuscript became available to the author after the 1975 International Conference of Geothermometry and Geobarometry at Pennsylvania State University. Wood discussed several possibilities for the discrepancies between the calculated and the experimental results and reached the conclusion that MacGregor's (1974) experiments are in error.

Nevertheless, this model for spinel peridotite enables us to calculate the solubilities of  $\text{Al}_2\text{O}_3$  in orthopyroxene in plagioclase peridotite and in spinel pyroxenite as is shown in the following section.

*Phase equilibria in the system of  $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  and the solubility of  $\text{Al}_2\text{O}_3$  in orthopyroxene in plagioclase peridotite and in spinel pyroxenite*

The apparent equilibrium constant of reaction (2) remains essentially constant even after the fourth component CaO is introduced into the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , because the amounts of CaO entering orthopyroxene, spinel, and olivine are not great enough to cause significant changes of  $\Delta V(2)$  in equation (18). Therefore, the calculated result for spinel peridotite in the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  is a "bridge" between the  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  and  $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  systems.

Kushiro and Yoder (1966) experimentally investigated the reactions  $\text{an} + \text{fo} = \text{cpx} + \text{opx} + \text{sp}$ , and  $\text{cpx} + \text{opx} + \text{sp} = \text{gar} + \text{fo}$ . It is possible to calculate these reactions using the model of the  $\text{Al}_2\text{O}_3$  solubility

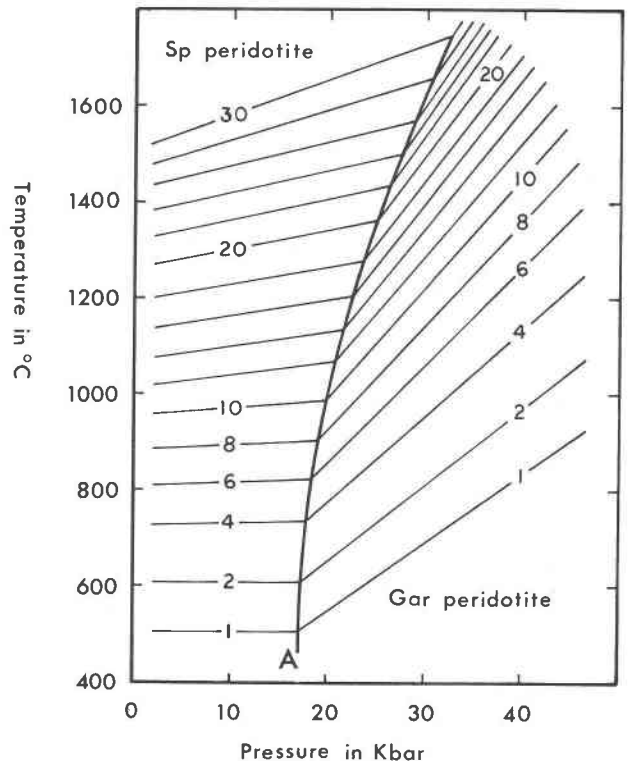


FIG. 2. Calculated phase diagram for the system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  in temperature–pressure–composition space. Curve A is the same as in Fig. 1. Isoleths refer to percentages of the M1 site in orthopyroxene occupied by aluminum atoms. The garnet peridotite portion is taken from Wood (1974).

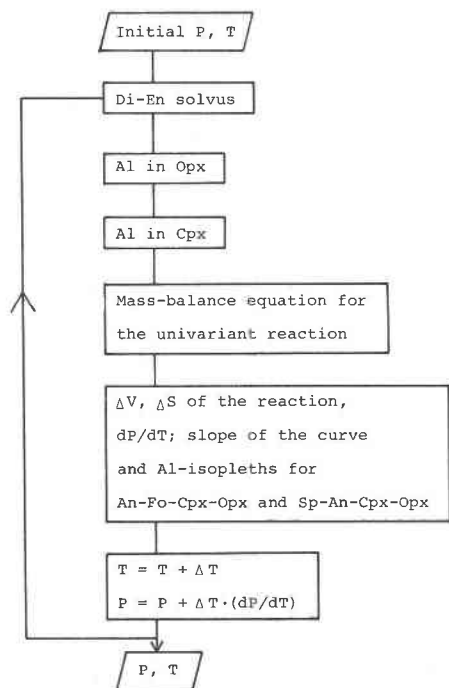


FIG. 3. Calculation scheme for the reaction  $\text{an} + \text{fo} = \text{cpx} + \text{opx} + \text{sp}$  in the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ .

in orthopyroxene and experimental data on the diopside-enstatite solvus. Calculation for the reaction  $\text{an} + \text{fo} = \text{cpx} + \text{opx} + \text{sp}$  was performed as schematically illustrated in Figure 3. The data of Mori and Green (1975) were used to calculate the  $\text{Ca}/(\text{Ca} + \text{Mg})$  ratio of coexisting ortho- and clinopyroxene. It was assumed that these numbers are independent of the  $\text{Al}_2\text{O}_3$  content of the pyroxenes, judging from Boyd's (1970) data on the pyroxene solvus in the system  $\text{Al}_2\text{O}_3\text{-CaSiO}_3\text{-MgSiO}_3$ .<sup>6</sup> The procedure by which  $\text{Al}_2\text{O}_3$  content in clinopyroxene was calculated from that in orthopyroxene is described in Appendix 2. If the compositions of pyroxenes are known, we may write a mass-balance equation for the reaction  $\text{an} + \text{fo} = \text{cpx} + \text{opx} + \text{sp}$ , and calculate the

<sup>6</sup> Some experiments indicate that  $\text{Al}_2\text{O}_3$  appreciably reduces enstatite solubility in clinopyroxene (O'Hara and Schairer, 1963; Herzberg and Chapman, 1976). The effect of the reduction was also examined in the calculation and was found to be no more than 1 kbar reduction of the position of the boundary around  $1000^\circ\text{C}$ , fixing the point at 8.5 kbar,  $1200^\circ\text{C}$ , yet the slope at lower temperatures (below  $800^\circ\text{C}$ ) stays the same, and the general shape of the boundary remains unchanged regardless of the model used.

volume and entropy changes<sup>7</sup> of the reaction and finally the slope of the curve from the Clapeyron equation.

The calculation was started from 8.5 kbar,  $1200^\circ\text{C}$ , which is a well-bracketed experimental point. The agreement with the experimental runs is satisfactory as is seen in Figure 4. The ratio of the amount of  $\text{Al}_2\text{O}_3$  in orthopyroxene to that in clinopyroxene changes regularly along the univariant curve from 1.2 at  $1300^\circ\text{C}$  to 0.9 at  $500^\circ\text{C}$ .

The same approach was taken to compute another univariant line for the reaction  $\text{cpx} + \text{opx} + \text{sp} = \text{gar} + \text{fo}$ . The method of each step of the calculation is the same as that for the reaction  $\text{an} + \text{fo} = \text{cpx} + \text{opx} + \text{sp}$ , except that the  $\text{CaO}$  content in garnet is also considered, as described in Appendix 2. The calculation was started from 18.5 kbar,  $1300^\circ\text{C}$ , with the ratio  $\text{Ca}/(\text{Mg} + \text{Ca})$  of garnet varying from 0.13 at  $1500^\circ\text{C}$  to 0.16 at  $500^\circ\text{C}$ . The agreement with the

<sup>7</sup> The calculation procedure of entropies of complex pyroxenes is described in Appendix 3.

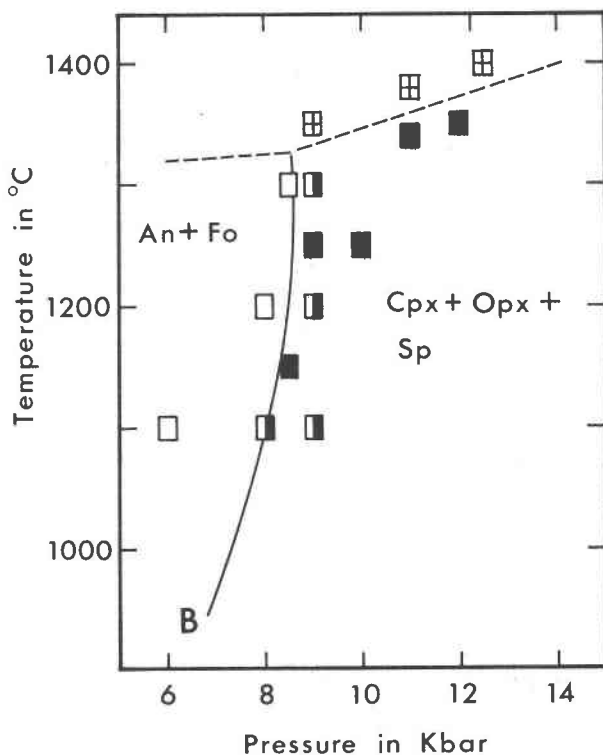


FIG. 4. Calculated univariant line (curve *B*) for the reaction  $\text{an} + \text{fo} = \text{cpx} + \text{opx} + \text{sp}$  in the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ , compared with the experimental data of Kushiro and Yoder (1966): open rectangles =  $\text{an} + \text{fo}$ ; filled rectangles =  $\text{cpx} + \text{opx} + \text{sp}$ ; half-filled rectangles = indeterminate; crossed rectangles = above solidus.

experimental data is excellent, as is shown in Figure 5.

Slopes of the  $\text{Al}_2\text{O}_3$  isopleths for orthopyroxene coexisting with plagioclase + olivine + clinopyroxene and also with spinel + clinopyroxene + plagioclase were calculated along the univariant curve of the reaction  $\text{an} + \text{fo} = \text{cpx} + \text{opx} + \text{sp}$  using the Clapeyron equation for constant composition of orthopyroxene:

$$\left(\frac{\partial P}{\partial T}\right)_{X_{\text{Al}}^{\text{M}_1}} = \frac{\Delta S}{\Delta V} \quad (32)$$

where  $\Delta S$  and  $\Delta V$  are respectively molar entropy and molar volume changes of the reactions (3) or (4). Similarly, the slopes of the  $\text{Al}_2\text{O}_3$  isopleths for garnet-clinopyroxene-orthopyroxene were calculated along the curve for the reaction  $\text{cpx} + \text{opx} + \text{sp} = \text{gar} + \text{fo}$ . In contrast to the three-component system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , the isopleths are not straight in the system  $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  since the  $\text{Ca}/(\text{Ca} + \text{Mg})$  ratio of pyroxenes and the  $\text{Al}_2\text{O}_3$  content in

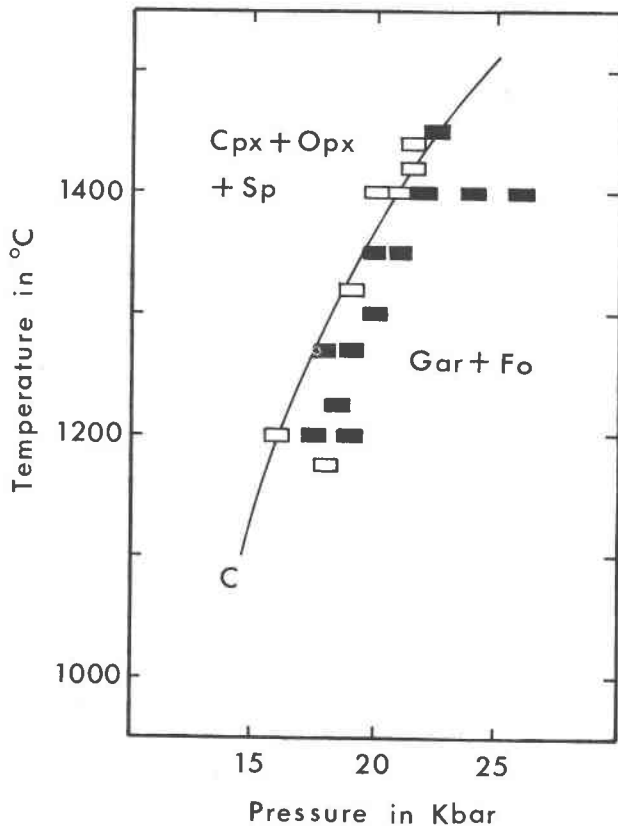


FIG. 5. Calculated univariant line (curve C) for the reaction  $\text{cpx} + \text{opx} + \text{sp} = \text{gar} + \text{fo}$  in the system  $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , compared with the experimental data of Kushiro and Yoder (1966): open rectangles =  $\text{opx} + \text{cpx} + \text{sp}$ ; filled rectangles =  $\text{gar} + \text{fo}$ .

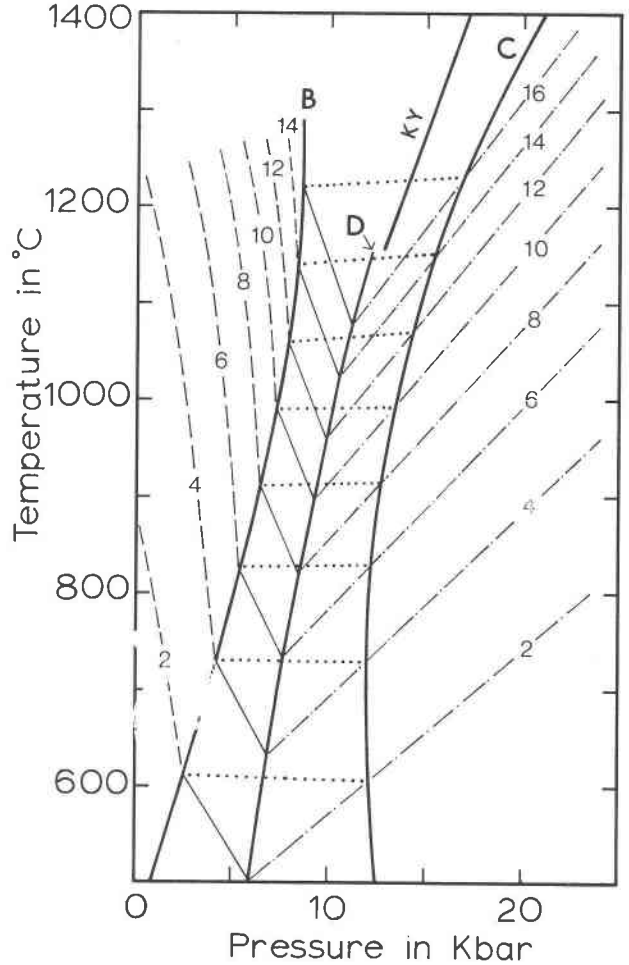


FIG. 6. Calculated Al isopleths for orthopyroxene in plagioclase-peridotite (dashed lines), spinel-peridotite (dotted lines), and garnet-websterite or garnet-peridotite (dash-dot lines) in the system  $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . Thick solid lines B and C are the same as in Fig. 4 and Fig. 5, respectively. Curve D is another univariant line for the reaction  $\text{cpx} + \text{opx} + \text{sp} + \text{an} = \text{gar}$ , which was graphically derived. KY is Kushiro and Yoder's (1966) experimentally-determined line for the same reaction in the four-component system.

clinopyroxene change with temperature, resulting in the gradual changes of molar entropy changes of the reactions. Isopleths for the plagioclase-peridotite were drawn by calculating the slope from the Clapeyron equation (32) in a stepwise manner, starting from the points on the univariant line of the reaction  $\text{an} + \text{fo} = \text{cpx} + \text{opx} + \text{sp}$ , as was done in drawing the univariant lines, and the results are shown in Figure 6. They become less steep at high temperatures with constant values of  $X_{\text{Al}}^{\text{M}_1}$ . Those for spinel-peridotite and for garnet-peridotite, on the other hand, may be safely approximated by straight lines, since extrapolations are not far enough to cause significant errors. Those for garnet-peridotite will become steeper as

temperature increases with constant values of  $X_{Al}^{M1}$ , but here they are approximated by straight lines. Error by this simplification will be as much as one kilobar overestimate in pressure.

The curve *D*, which appeared by connecting intersection points of the isopleths for garnet-clinopyroxene-orthopyroxene with those for spinel-plagioclase-clinopyroxene-orthopyroxene, is another univariant line of a reaction  $cpx+opx+sp+an = gar$ . This reaction has been investigated by Kushiro and Yoder (1966), and the curve graphically drawn here is also consistent with their experimental curve (KY in Fig. 6).

### Discussion

The calculated results in the four-component system  $CaO-MgO-Al_2O_3-SiO_2$  are illustrated over a wide temperature range in Figure 6. The curve for the reaction  $cpx+opx+sp = gar+fo$  (curve *C*) retains the same character as that in the  $MgO-Al_2O_3-SiO_2$  system (curve *A* in Fig. 2), *i.e.* it curves significantly and is nearly vertical below  $800^\circ C$ . The pressure is reduced by some 5-7 kbar from curve *A* by introducing  $CaO$  in the system, and the minimum value of the pressure of curve *C* is 12 kbar. The present theoretical calculation supports O'Hara *et al.*'s (1971) conclusion, based on their experiments, that simple linear extrapolation of the univariant line out of the experimentally investigated *P-T* range to uninvestigated lower temperatures is not valid, and that garnet peridotite is not stable in normal continental crust. The line for the reaction  $an+fo = cpx+opx+sp$  curves in the opposite direction, *i.e.*, the slope becomes less steep as temperature decreases, and this curve intersects the temperature axis above  $400^\circ C$ . This may imply high-temperature origins of plagioclase peridotites, either as direct crystallization products from magma or as recrystallized products of hot spinel or garnet peridotites of high-pressure origin. Curves *B* and *C* do not intersect each other, and there is no condition where plagioclase peridotite directly converts to garnet peridotite, in contrast to the prediction by Kushiro and Yoder (1966).

The  $Al_2O_3$  solubility in orthopyroxene sensitively increases with pressure but is not so sensitive to temperature in plagioclase peridotite. In spinel pyroxene it increases with both pressure and temperature. Since the solubility is insensitive to pressure in spinel peridotite, this parameter may be used as a geothermometer, and in fact is a better one than the frequently used  $Ca/(Ca+Mg)$  ratio in coexisting pyrox-

enes, which is insensitive to temperature below  $1000^\circ C$ .

### Geothermometry and geobarometry

Although the bulk chemical composition of most mafic and ultramafic rocks are well expressed in the system  $CaO-MgO-Al_2O_3-SiO_2$ , the presence of other components, such as  $FeO$ ,  $Na_2O$ ,  $Cr_2O_3$ ,  $Fe_2O_3$ , is not negligible in some cases. The effects of these minor components are removed by the use of the "apparent equilibrium constants" which are defined as

$$K'(1) = \frac{(X_{Mg}^{M2,opx} \cdot X_{Al}^{M1,opx})(X_{Mg}^{M2,opx} \cdot X_{Mg}^{M1,opx})}{a_{Mg_3Al_2Si_3O_{12}}^{gr}} \quad (33)$$

$$K'(2) = \frac{(X_{Mg}^{M2,opx} \cdot X_{Al}^{M1,opx})a_{Mg_2SiO_4}^{ol}}{(X_{Mg}^{M2,opx} \cdot X_{Mg}^{M1,opx})a_{MgAl_2O_4}^{sp}} \quad (34)$$

$$K'(3) = \frac{(X_{Mg}^{M2,opx} \cdot X_{Al}^{M1,opx})a_{CaMgSi_2O_6}^{cpx}}{(a_{Mg_2SiO_4}^{ol})(a_{CaAl_2Si_2O_6}^{pl})} \quad (35)$$

$$K'(4) = \frac{(X_{Mg}^{M2,opx} \cdot X_{Al}^{M1,opx})(a_{CaMgSi_2O_6}^{cpx})^{1/2}}{(X_{Mg}^{M2,opx} \cdot X_{Mg}^{M1,opx})^{1/2}(a_{CaAl_2Si_2O_6}^{pl})^{1/2}(a_{MgAl_2O_4}^{sp})^{1/2}} \quad (36)$$

corresponding to the equations (1), (2), (3), and (4), respectively. The simplest model, which is the ideal solution model, may be applied to crystallographic sites of the minerals as long as they are chemically close to the system  $CaO-MgO-Al_2O_3-SiO_2$ , and the activities are:

$$\begin{aligned} a_{Mg_3Al_2Si_3O_{12}}^{gr} &= (X_{Mg})^3(X_{Al})^2 \\ a_{Mg_2SiO_4}^{ol} &= (X_{Mg}^{M2})(X_{Mg}^{M1}) \\ a_{CaMgSi_2O_6}^{cpx} &= (X_{Ca}^{M2})(X_{Mg}^{M1}) \\ a_{CaAl_2Si_2O_6}^{pl} &= X_{CaAl_2Si_2O_6} \\ a_{MgAl_2O_4}^{sp} &= (X_{Mg}^{Tet})(X_{Al}^{Oct})^2 \end{aligned} \quad (37)$$

where  $X_{Mg}^{Tet}$  and  $X_{Al}^{Oct}$  are the concentrations of Mg and Al atoms in tetrahedral and octahedral sites in spinel, respectively. Rigorously, all of these sites in the solid solutions are expected to show positive non-ideal behavior (Saxena and Ghose, 1971), but since those excess terms will tend to cancel each other in calculation of  $K'$  in equations (33) to (36), it would be more consistent at the moment to adopt an ideal solution model for all the individual crystallographic sites of the participating phases, rather than applying more sophisticated models to some of the phases whose thermodynamic properties are better understood than others. This simplification may cause serious errors, if the chemical composition of the



phases are far from the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{MgO}-\text{SiO}_2$  especially at low temperature, and in this case nonideality has to be taken into account.

As demonstrated for  $K'(2)$  in equations (12) to (18), the equilibrium condition (5) may generally be rewritten as follows:

$$-RT \ln K'(i) = \Delta H_{1,T}^0(i) + (P-1) \Delta V(i) - T \Delta S^0(i) \quad (38)$$

$\Delta H_{1,T}^0(i)$  and  $\Delta S^0(i)$  are independent of composition by definition, and  $\Delta V(i)$  only depends on the amount of  $\text{Al}_2\text{O}_3$  in orthopyroxene. If we neglect small changes of  $\Delta V(i)$  which will be caused by a small shift of the amount of  $\text{Al}_2\text{O}_3$  after the correction described below, it follows that the values of  $K'(i)$  will not change by the introduction of components other than  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ . The values of  $K'(2)$ ,  $K'(3)$ , and  $K'(4)$ , which are apparent equilibrium constants for, respectively, spinel peridotite, plagioclase peridotite, and spinel pyroxenite, have also been calculated along the univariant line of the reaction  $\text{an} + \text{fo} = \text{cpx} + \text{opx} + \text{sp}$ , and they are tabulated with the values of  $X_{\text{Al}}^{M1}$  in Table 1.

The method to find an  $\text{Al}_2\text{O}_3$  isopleth for a given natural rock is as follows:

(1) Calculate activities of components  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ,  $\text{Mg}_2\text{SiO}_4$ ,  $\text{CaMgSi}_2\text{O}_6$ ,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ,  $\text{MgAl}_2\text{O}_4$  in garnet, olivine, clinopyroxene, plagioclase, and spinel, respectively, by equations (37), and calculate  $K'(i)$  by one of the equations (33) to (36), depending on the mineralogy of the rock. The method of Wood and Banno (1973, p. 118) may be followed to assign cations over  $M1$  and  $M2$  sites in ortho- and clinopyroxenes.

(2) Read a temperature which corresponds to the calculated value of  $K'$  for the mineral assemblage of the rock from Table 1.

(3) Using the diagram in Figure 6 and starting from the temperature point on the univariant line, draw a line parallel to the nearest isopleth for the particular mineral assemblage. The equilibrium condition for the rock lies somewhere on the line. Equilibration temperature and pressure may be uniquely obtained by combining another thermometer or barometer, such as the diopside-*enstatite* solvus or the partitioning of Fe and Mg between ferromagnesian minerals. For garnet peridotite and garnet pyroxenite, equation (2) in Wood (1974), which is a more direct reduction from the experimental data than the present model calculation, is to be used.

Evaluation of overall uncertainties in the calcu-

lated results is a difficult task, with direct experimental points being absent in plagioclase peridotite and spinel pyroxenite fields. Uncertainties in the calculated values of  $\Delta S^0(2)$  and  $\Delta H^0(2)$  are estimated to be  $\pm 0.5$  cal/deg/mole and  $\pm 0.5$  kcal/mole, respectively, without considering errors in the original experimental data. These result in the uncertainties in the positions of isopleths for spinel peridotite being approximately  $\pm 20^\circ\text{C}$  around  $1000^\circ\text{C}$  and  $\pm 50^\circ\text{C}$  around  $800^\circ\text{C}$ . The slope, however, will not be appreciably changed, since the values of volume change of the reaction (2) are very small compared with the large values of entropy change. The uncertainties in the spinel peridotite field are directly propagated into those in the position of the isopleths for plagioclase peridotite and for spinel pyroxenite; an uncertainty of  $\pm 50^\circ\text{C}$  in an isopleth for spinel peridotite at  $800^\circ\text{C}$ , for example, will cause uncertainties of approximately  $\pm 1$  kbar for plagioclase peridotite and of  $\pm 2$  kbar or  $\pm 50^\circ\text{C}$  for spinel peridotite. Other sources of uncertainties, especially the use of random mixing model of Al and Mg atoms in  $M1$  site and the use of the ideal solution model for  $\text{MgSiO}_3-\text{MgAl}_2\text{SiO}_6$  pyroxenes at one atmosphere, have not been considered, but they may become serious at low temperatures or for highly aluminous pyroxenes. The ordering of Al atoms in  $\text{SiB}$  site of orthopyroxene (Takeda, 1972; Ganguly and Ghose, 1975) may also cause some ordering of Al atoms in  $M1$  site, but the effect has not been evaluated.

It is obvious now that more experimental work,<sup>8</sup> both to locate the positions of the facies boundaries and to determine the compositions of pyroxenes, is highly desirable to evaluate the thermodynamic model adopted here and to improve the accuracy of the diagram in Figure 6 for its practical use in geothermometry and geobarometry.

### Conclusions

The solubility of  $\text{Al}_2\text{O}_3$  in orthopyroxene is uniquely derived as a function of pressure and temperature in spinel and plagioclase peridotites and spinel pyroxenite, using published experimental data on pyroxene compositions in garnet peridotite and

<sup>8</sup>Recently three experimental studies relevant to the problem have appeared; Herzberg and Chapman (1976) on the  $\text{Al}_2\text{O}_3$  solubility in clinopyroxene in spinel peridotite, and Presnall (1976) and Fujii and Takahashi (1976) on the  $\text{Al}_2\text{O}_3$  solubility in orthopyroxene in spinel peridotite. All the results agree well with the present calculated results, confirming the minimal pressure dependence of the parameter in spinel peridotite, except that of Presnall, which suggests a negative slope for the 8.5 weight percent  $\text{Al}_2\text{O}_3$  isopleth.

TABLE 1. Apparent equilibrium constants:  $K$ 's and concentrations of Al atoms in the M1 site of orthopyroxene:  $X_{Al}^{M1}$  on the univariant line of the reaction: an + fo = cpx + opx + sp.

Temp. (°C)	$K'(2) \times 100$	$K'(3) \times 100$	$K'(4) \times 100$	$X_{Al}^{M1} \times 100$
1300	21.9	9.18	15.2	18.0
1250	20.2	9.43	14.6	16.8
1200	18.4	9.39	13.8	15.6
1150	16.7	9.14	12.9	14.3
1100	14.9	8.75	11.9	13.0
1050	13.2	8.22	10.8	11.7
1000	11.5	7.59	9.62	10.3
950	9.91	6.88	8.46	9.02
900	8.39	6.11	7.31	7.74
850	6.98	5.30	6.20	6.53
800	5.69	4.50	5.14	5.39
750	4.54	3.71	4.16	4.34
700	3.52	2.97	3.27	3.40
650	2.65	3.30	2.49	2.58
600	1.93	1.71	1.83	1.89
550	1.35	1.22	1.29	1.33
500	0.89	0.82	0.86	0.89

$K'(2)$ : for spinel peridotites (sp+ol+cpx+opx)

$K'(3)$ : for plagioclase peridotites (pl+ol+cpx+opx)

$K'(4)$ : for spinel pyroxenites (sp+pl+cpx+opx)

the locations of facies boundaries for garnet and spinel peridotites. The main conclusions are:

(1) The facies boundary between garnet and spinel peridotites and that between spinel and plagioclase peridotites curve significantly due to the compositional changes of pyroxenes with pressure and temperature. The former becomes vertical below 800°C and 12 kbar, and the latter curves in the opposite direction and becomes less steep as temperature decreases. This further constrains the geological occurrences of garnet and plagioclase peridotites in the earth's crust.

(2) The solubility of  $Al_2O_3$  in orthopyroxene in spinel peridotite is insensitive to pressure, but may be used as a geothermometer. On the other hand, the parameter for plagioclase peridotite is very sensitive to pressure, and that for spinel pyroxenite is sensitive to both pressure and temperature. Practically, these parameters may be used as geothermometers and geobarometers, if the effects of components other than CaO, MgO,  $Al_2O_3$ , and  $SiO_2$  are considered properly.

### Appendix 1

Molar volumes and entropies at 1 bar and 298°K of forsterite, anorthite, spinel, diopside, and grossular and entropy of  $CaAl_2SiO_6$  pyroxene are from Robie and Waldbaum (1968).

The entropy of clinoenstatite given by Robie and Waldbaum (1968) was used for orthoenstatite, since the difference between the two is very small (R. C. Newton, personal communication, 1975).

Molar volumes of pyrope and orthoenstatite are from Skinner (1956) and Turnock *et al.* (1973), respectively.

Partial molar volumes of  $CaAl_2SiO_6$  and  $Mg_2Si_2O_6$  in diopside solid solution are constant between diopside and diopside(50)-enstatite(50) and are 63.22 and 64.05  $cm^3/gfw$ , respectively.

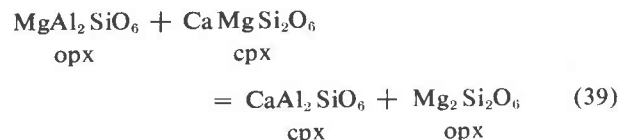
The partial molar volume of  $CaMgSi_2O_6$  in orthopyroxene near  $MgSiO_3$  was calculated to be 69.8  $cm^3/gfw$  from the pressure dependence of the diopside-enstatite solvus (Mori and Green, 1975).

Partial molar volumes of  $Mg_2Si_2O_6$  and  $MgAl_2SiO_6$  components in orthopyroxene were calculated by equation (12) in Wood and Banno (1973), which is based on Skinner and Boyd (1964) and Chatterjee and Schreyer (1972).

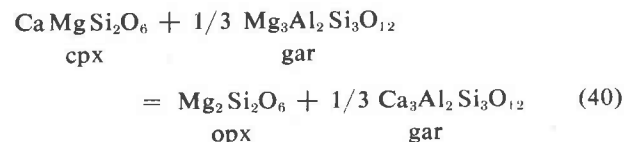
### Appendix 2

*Method to calculate the amounts of  $Al_2O_3$  in clinopyroxene and that of CaO in garnet from the composition of orthopyroxene*

The aluminous pyroxene component  $CaAl_2SiO_6$  in clinopyroxene may be related to the component  $MgAl_2SiO_6$  by:



The calcium garnet component  $Ca_3Al_2Si_3O_{12}$  may be expressed as:



The equilibrium condition for these reactions may be written in the same form as equation (18):

$$-RT \ln K'(i) = \Delta H_{1,T}^0(i) + (P-1)\Delta V(i) - T\Delta S^0(i) \quad (41)$$

where  $K'(i)$  are defined as:

$$K'(39) = \frac{(X_{Mg}^{M2,opx} \cdot X_{Mg}^{M1,opx})(X_{Ca}^{M2,cpx} \cdot X_{Al}^{M1,cpx})}{(X_{Ca}^{M2,cpx} \cdot X_{Mg}^{M1,cpx})(X_{Mg}^{M2,opx} \cdot X_{Al}^{M1,opx})} \quad (42)$$

$$K'(40) = \frac{(X_{Mg}^{M2,opx} \cdot X_{Mg}^{M1,opx})X_{Ca}^{gar}}{(X_{Ca}^{M2,cpx} \cdot X_{Mg}^{M1,cpx})X_{Mg}^{gar}} \quad (43)$$

The values of  $K'$  may be calculated using the above equations from Boyd's (1970) microprobe analyses of synthetic garnet, clino- and orthopyroxene which

were equilibrated at 1200°C and 30 kbar in the system  $\text{Al}_2\text{O}_3\text{-CaSiO}_3\text{-MgSiO}_3$ . The compositions of the phases are:

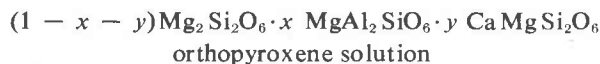
$$\begin{aligned} X_{\text{Al}}^{M1, \text{opx}} &= 0.080, X_{\text{Mg}}^{M1, \text{opx}} = 0.920, X_{\text{Mg}}^{M2, \text{opx}} = 0.953, \\ X_{\text{Al}}^{M1, \text{cpx}} &= 0.062, X_{\text{Mg}}^{M1, \text{cpx}} = 0.938, X_{\text{Ca}}^{M2, \text{cpx}} = 0.836, \\ &\text{and } X_{\text{Ca}}^{\text{gar}} = 0.15. \end{aligned}$$

$\Delta H_{1,T}^0(39)$  and  $\Delta H_{1,T}^0(40)$  were then calculated to be  $-168$  cal/mole and  $433$  cal/mole, respectively, substituting the previously derived values of  $S_{\text{MgAl}_2\text{SiO}_6}^0$  and  $S_{\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}}^0$ , and volume data into equation (41). In the calculation of  $\Delta V(i)$ , clinopyroxene and garnet solid solutions were assumed to be ideal in terms of volume-composition relationships, based upon the unit cell data of clinopyroxenes on the joins  $\text{CaMgSi}_2\text{O}_6\text{-CaAl}_2\text{SiO}_6$  and  $\text{CaMgSi}_2\text{O}_6\text{-Mg}_2\text{Si}_2\text{O}_6$  (Clark *et al.*, 1962), and those of garnets on the join  $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}\text{-Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  (Chinner *et al.*, 1960).  $K'$  (39) and  $K'$  (40) can now be calculated at any pressure and temperature by substituting the calculated values of  $\Delta H_{1,T}^0(39)$  and  $\Delta H_{1,T}^0(40)$  in equation (41).  $X_{\text{Al}}^{M1, \text{cpx}}$  and  $X_{\text{Ca}}^{\text{gar}}$  may be calculated using equations (42) and (43), if the other quantities in these equations are known.

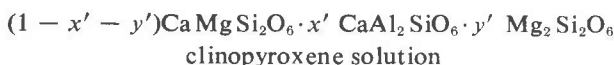
### Appendix 3

#### Entropies of complex pyroxenes

Compositions of ortho- and clinopyroxenes in the three-component system  $\text{Al}_2\text{O}_3\text{-MgSiO}_3\text{-CaSiO}_3$  may be generally expressed as



and



Assigning Al and Ca atoms into  $M1$  and  $M2$  sites, respectively, atomic concentrations in the individual sites of orthopyroxene are:

$$\begin{aligned} X_{\text{Mg}}^{M1} &= 1 - x, \quad X_{\text{Al}}^{M1} = x, \quad X_{\text{Mg}}^{M2} = 1 - y, \\ &\text{and } X_{\text{Ca}}^{M2} = y. \end{aligned}$$

Similarly those of clinopyroxene are:

$$\begin{aligned} X_{\text{Mg}}^{M1} &= 1 - x', \quad X_{\text{Al}}^{M1} = x', \quad X_{\text{Mg}}^{M2} = y', \\ &\text{and } X_{\text{Ca}}^{M2} = 1 - y'. \end{aligned}$$

The Wood-Banno model for pyroxenes assumes random mixing of atoms in  $M1$  and  $M2$  sites and no

interaction between the two sites. If we can neglect excess mixing entropy due to thermal vibration of atoms,<sup>9</sup> partial molar entropies of these pyroxene components are:

$$\begin{aligned} \bar{S}_{\text{Mg}_2\text{Si}_2\text{O}_6} &= S_{\text{Mg}_2\text{Si}_2\text{O}_6}^0 - R \ln (X_{\text{Mg}}^{M1} \cdot X_{\text{Mg}}^{M2}) \\ \bar{S}_{\text{MgAl}_2\text{SiO}_6} &= S_{\text{MgAl}_2\text{SiO}_6}^0 - R \ln (X_{\text{Al}}^{M1} \cdot X_{\text{Mg}}^{M2}) \\ \bar{S}_{\text{CaMgSi}_2\text{O}_6} &= S_{\text{CaMgSi}_2\text{O}_6}^0 - R \ln (X_{\text{Mg}}^{M1} \cdot X_{\text{Ca}}^{M2}) \\ \bar{S}_{\text{CaAl}_2\text{SiO}_6} &= S_{\text{CaAl}_2\text{SiO}_6}^0 - R \ln (X_{\text{Al}}^{M1} \cdot X_{\text{Ca}}^{M2}) \end{aligned} \quad (44)$$

The molar entropies of complex ortho- and clinopyroxenes:  $S^{\text{opx}}$  and  $S^{\text{cpx}}$  are by definition:

$$\begin{aligned} S^{\text{opx}} &= (1 - x - y)\bar{S}_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{opx}} \\ &\quad + x\bar{S}_{\text{MgAl}_2\text{SiO}_6}^{\text{opx}} + y\bar{S}_{\text{CaMgSi}_2\text{O}_6}^{\text{opx}} \end{aligned} \quad (45)$$

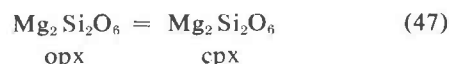
$$\begin{aligned} S^{\text{cpx}} &= (1 - x' - y')\bar{S}_{\text{CaMgSi}_2\text{O}_6}^{\text{cpx}} \\ &\quad + x'\bar{S}_{\text{CaAl}_2\text{SiO}_6}^{\text{cpx}} + y'\bar{S}_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{cpx}} \end{aligned}$$

The entropy of pure  $\text{CaMgSi}_2\text{O}_6$  pyroxene in the orthopyroxene phase and that of pure  $\text{Mg}_2\text{Si}_2\text{O}_6$  pyroxene in the clinopyroxene phase are not known, but may be estimated empirically from experimental data for the enstatite-diopside solvus as described below.

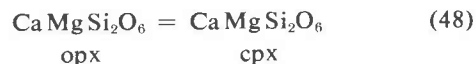
The conditions of the two-pyroxene equilibrium may be written in the same form as equation (12):

$$-RT \ln K'(i) = \Delta G^0(i) + \Delta G^{\text{ex}}(i) \quad (46)$$

where  $\Delta G^0(i)$  is the free energy change of reaction (i):



and



$K'(47)$  and  $K'(48)$  are defined to be  $X_{\text{Mg}}^{M2, \text{cpx}}/X_{\text{Mg}}^{M2, \text{opx}}$  and  $X_{\text{Ca}}^{M2, \text{cpx}}/X_{\text{Ca}}^{M2, \text{opx}}$  respectively. The suffix "ex" denotes the excess term for reference to the ideal system. Differentiation of equation (46) with temperature gives:

$$\left( \frac{\partial [-RT \ln K'(i)]}{\partial T} \right)_P = -\Delta S^0(i) - \Delta S^{\text{ex}}(i) \quad (49)$$

For reaction (47),

$$\begin{aligned} \Delta S^0(47) + \Delta S^{\text{ex}}(47) &= S_{\text{Mg}_2\text{Si}_2\text{O}_6}^{0, \text{cpx}} \\ &\quad - S_{\text{Mg}_2\text{Si}_2\text{O}_6}^{0, \text{opx}} + S_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{ex, cpx}} - S_{\text{Mg}_2\text{Si}_2\text{O}_6}^{\text{ex, opx}} \end{aligned} \quad (47')$$

<sup>9</sup> This approximation may be too crude for the  $\text{Mg}_2\text{Si}_2\text{O}_6\text{-CaMgSi}_2\text{O}_6$  pyroxenes, but the treatment will be improved by considering the excess terms later.

and for reaction (48),

$$\Delta S^0(48) + \Delta S^{ex}(48) = S_{CaMgSi_2O_6}^{0,OPX} - S_{CaMgSi_2O_6}^{0,OPX} + S_{CaMgSi_2O_6}^{ex,OPX} - S_{CaMgSi_2O_6}^{ex,OPX} \quad (48')$$

where  $S_j^{0,\alpha}$  and  $S_j^{ex,\alpha}$  are the molar entropy of component  $j$  in pure phase  $\alpha$  and the excess partial molar entropy of component  $j$  in phase  $\alpha$ , respectively. For an orthopyroxene close to pure  $Mg_2Si_2O_6$ , the value of  $S_{Mg_2Si_2O_6}^{0,OPX}$  will be very small and may be safely neglected, but  $S_{Mg_2Si_2O_6}^{ex,OPX}$  which may be a complex function of pressure, temperature, and composition, may not be negligible, since the composition of the co-existing clinopyroxene is far from pure  $Mg_2Si_2O_6$ .  $S_{CaMgSi_2O_6}^{ex,OPX}$  is negligible, but  $S_{CaMgSi_2O_6}^{ex,OPX}$  is not, by the same argument for equation (48'). The values of  $S_{Mg_2Si_2O_6}^{0,OPX} + S_{Mg_2Si_2O_6}^{ex,OPX}$  and those of  $S_{CaMgSi_2O_6}^{0,OPX} + S_{CaMgSi_2O_6}^{ex,OPX}$  may be calculated by obtaining the temperature dependences of  $-RT \ln K'(i)$  determined from the experimental data of Mori and Green (1975), and by substituting Robie and Waldbaum's (1968) data for  $S_{Mg_2Si_2O_6}^{0,OPX}$  and  $S_{CaMgSi_2O_6}^{0,OPX}$  into equations (47') and (48'). Substitution of the resulting values of  $S_{Mg_2Si_2O_6}^{0,OPX} + S_{Mg_2Si_2O_6}^{ex,OPX}$  and  $S_{CaMgSi_2O_6}^{0,OPX} + S_{CaMgSi_2O_6}^{ex,OPX}$  for  $S_{Mg_2Si_2O_6}^{0,OPX}$  and  $S_{CaMgSi_2O_6}^{0,OPX}$ , respectively, in equation (44) will reduce the error which may have been introduced by neglecting the excess term of mixing entropy for  $Mg_2Si_2O_6$ - $CaMgSi_2O_6$  pyroxenes.

### Acknowledgments

The author thanks J. S. Dickey, Jr., A. J. Irving, and E. B. Watson for discussions and critical reading of the manuscript. Discussions with T. Mori, S. Banno, and A. B. Thompson at various stages of the work were very stimulating and are gratefully acknowledged. The paper has benefitted from the advice and criticisms of the reviewers; B. W. Evans, J. Ganguly, I. D. MacGregor, and B. J. Wood are thanked for their efforts. This work was supported by the Earth Science Section, National Science Foundation, NSF Grant DES 73-00264 to J. S. Dickey, Jr.

### References

- AKELLA, J. (1976) Garnet pyroxene equilibria in the system  $CaSiO_3$ - $MgSiO_3$ - $Al_2O_3$  and in a natural mineral mixture. *Am. Mineral.* **61**, 589-598.
- AND F. R. BOYD (1972) Partitioning of Ti and Al between pyroxenes, garnets, and oxides. *Carnegie Inst. Wash. Year Book*, **71**, 378-384.
- AND — (1973) Effect of pressure on the composition of co-existing pyroxenes and garnet in the system  $CaSiO_3$ - $MgSiO_3$ - $FeSiO_3$ - $CaAlTi_2O_6$ . *Carnegie Inst. Wash. Year Book*, **72**, 523-526.
- AND — (1974) Petrogenetic grid for garnet peridotites. *Carnegie Inst. Wash. Year Book*, **73**, 269-273.
- ANASTASIOU, P. AND F. SEIFERT (1972) Solid solubility of  $Al_2O_3$  in enstatite at high temperatures and 1-5 kb water pressure. *Contrib. Mineral. Petrol.* **34**, 272-287.
- BOYD, F. R. (1970) Garnet peridotites and the system  $CaSiO_3$ - $MgSiO_3$ - $Al_2O_3$ . *Mineral. Soc. Am. Spec. Pap.* **3**, 63-75.
- (1973) A pyroxene geotherm. *Geochim. Cosmochim. Acta*, **37**, 2533-2546.
- AND J. L. ENGLAND (1964) The system enstatite-pyroxene. *Carnegie Inst. Wash. Year Book*, **63**, 157-161.
- AND P. H. NIXON (1975) Origins of the ultramafic nodules from some kimberlites of northern Lesotho and the Monastery Mine, South Africa. *Phys. Chem. Earth*, **9**, 431-454.
- CHATTERJEE, N. D. AND W. SCHREYER (1972) The reaction enstatite<sub>80</sub> + sillimanite = sapphirine<sub>80</sub> + quartz. *Contrib. Mineral. Petrol.* **36**, 49-62.
- CHINNER, G. A., F. R. BOYD AND J. L. ENGLAND (1960) Physical properties of garnet solid solutions. *Carnegie Inst. Wash. Year Book*, **59**, 76-78.
- CLARK, S. P., J. F. SCHAIRER AND J. DE NEUFVILLE (1962) Phase relations in the system  $CaMgSi_2O_6$ - $CaAl_2SiO_6$ - $SiO_2$  at low and high pressure. *Carnegie Inst. Wash. Year Book*, **61**, 59-68.
- FUJII, T. AND E. TAKAHASHI (1976) On the solubility of alumina in orthopyroxene coexisting with olivine and spinel in the system  $MgO$ - $Al_2O_3$ - $SiO_2$ . *Mineral. J. (Japan)*, **8**, No. 2, in press.
- GANGULY, J. AND S. GHOSE (1975) Intracrystalline cation distributions in aluminous orthopyroxene, and its implications. *Extended Abstracts, International Conference on Geothermometry and Geobarometry*, Pennsylvania State University.
- HERZBERG, C. T. AND N. A. CHAPMAN (1976) Clinopyroxene geothermometry of spinel-lherzolites. *Am. Mineral.* **61**, 626-637.
- KUSHIRO, I. AND H. S. YODER, JR. (1966) Anorthite-forsterite and anorthite-enstatite reactions and their bearing on the basalt-eclogite transformation. *J. Petrol.* **7**, 337-362.
- MACGREGOR, I. D. (1964) The reaction 4 enstatite + spinel = forsterite + pyroxene. *Carnegie Inst. Wash. Year Book*, **63**, 157.
- (1974) The system  $MgO$ - $Al_2O_3$ - $SiO_2$ : solubility of  $Al_2O_3$  in enstatite for spinel and garnet peridotite compositions. *Am. Mineral.* **59**, 110-119.
- MERCIER, J.-C. C. AND N. L. CARTER (1975) Pyroxene geotherms. *J. Geophys. Res.* **80**, 3349-3362.
- MORI, T. AND D. H. GREEN (1975) Pyroxenes in the system  $Mg_2Si_2O_6$ - $CaMgSi_2O_6$  at high pressure. *Earth Planet. Sci. Lett.* **26**, 277-286.
- O'HARA, M. J. (1967) Mineral paragenesis in ultrabasic rocks. In: P. J. Wyllie, Ed., *Ultramafic and Related Rocks*. John Wiley and Sons, Inc., New York, pp. 393-401.
- AND J. F. SCHAIRER (1963) The join diopside-pyroxene at atmospheric pressure. *Carnegie Inst. Wash. Year Book*, **62**, 107-115.
- , S. W. RICHARDSON AND G. WILSON (1971) Garnet peridotite stability and occurrence in crust and mantle. *Contrib. Mineral. Petrol.* **32**, 48-68.
- PRESNALL, D. C. (1976) Alumina content of enstatite as a geobarometer for plagioclase and spinel lherzolites. *Am. Mineral.*, **61**, 582-588.
- ROBIE, R. A. AND D. R. WALDBAUM (1968) Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure and at high temperatures. *U.S. Geol. Surv. Bull.* **1259**.
- SAXENA, S. K. AND S. GHOSE (1971)  $Mg^{2+}$ - $Fe^{2+}$  order-disorder and thermodynamics of the orthopyroxene crystalline solution. *Am. Mineral.* **56**, 532-559.
- SKINNER, B. J. (1956) Physical properties of endmembers of the garnet group. *Am. Mineral.* **41**, 428-436.

- AND F. R. BOYD (1964) Aluminous enstatites. *Carnegie Inst. Wash. Year Book*, **63**, 163-165.
- TAKEDA, H. (1972) Crystallographic studies of coexisting aluminan orthopyroxene and augite of high pressure origin. *J. Geophys. Res.* **77**, 5798-5811.
- THOMPSON, J. B., JR., (1967) Thermodynamic properties of simple solutions. In, P. H. Abelson, Ed., *Researches in Geochemistry*. Vol. 2, John Wiley and Sons, Inc. p. 341-375.
- TURNOCK, A. C., D. H. LINDSLEY AND J. E. GROVER (1973) Synthesis and unit cell parameters of Ca-Mg-Fe pyroxenes. *Am. Mineral.* **58**, 50-59.
- WOOD, J. B. (1974) The solubility of alumina in orthopyroxene coexisting with garnet. *Contrib. Mineral. Petrol.* **46**, 1-15.
- (1975) The application of thermodynamics to some sub-solidus equilibria involving solid solutions. *Fortschr. Mineral.* **52**, 21-45.
- AND S. BANNO (1973) Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems. *Contrib. Mineral. Petrol.* **42**, 109-124.