American Mineralogist, Volume 76, pages 512–529, 1991

Garnet-clinopyroxene geobarometry: The problems, a prospect, and an approximate solution with some applications

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ABSTRACT

No calibrated geobarometer is presently available for estimating P of equilibration of the garnet + clinopyroxene two-phase assemblage. Because of the high thermodynamic variance of this assemblage, experimental calibration of a geobarometer for garnet + clinopyroxene is virtually impossible unless composition of one of the phases is internally buffered. This is theoretically simulated by rigorous analytical formulation of a garnet + clinopyroxene two-phase equilibrium in the simple CaO-MgO-Al_2O_3-SiO_2 system and by theoretically constructing P-sensitive X_{CaTs} isopleths of clinopyroxenes in equilibrium with a garnet of fixed composition in two experimentally equilibrated garnet + clinopyroxene assemblages. However, a calibration based entirely on measured and derived thermodynamic quantities such as enthalpies, entropies, heat capacities, and volumes of the end-members and those resulting from the mixing of the end-member components is possible for the continuous reaction

$$\tfrac{2}{3}Ca_3Al_2Si_3O_{12} + \tfrac{1}{3}Mg_3Al_2Si_3O_{12} = CaMgSi_2O_6 + CaAlAlSiO_6.$$

The resulting geobarometric equation is

$$P\text{ (bars)} = \Delta V_r^{-1}[-28201.1 + 37.35T(\text{K}) + 8.314T(\text{K})\ln K_X$$
$$+ 8.314T(\text{K})\ln K\gamma]$$

where $K_X = (X_{CaTs}\cdot X_{Di})/[(X_{Gr})^{2/3}\cdot(X_{Py})^{1/3}]$; $K_\gamma = [(\gamma_{CaTs}\cdot\gamma_{Di})/[(\gamma_{Gr})^{2/3}\cdot(\gamma_{Py})^{1/3}]$ and ΔV_r is the partial molar volume change of the reaction. Formulations for K_X, K_γ, and ΔV_r are given. Although analysis of available volume data along binary joins of the Ca-Mg-Fe garnets and across the Di-En-CaTs ternary clinopyroxenes yields a very comprehensive model for calculating the partial molar volumes of the various components in complex systems, the compositional variance cannot be reduced by attributing all nonidealities to the P-V terms. Thus, the nonidealities are dealt with in terms of variations in P-T-X(composition). In that event, the geobarometric equation reproduces the P of equilibration of the experimentally determined compositions of coexisting garnet and clinopyroxene at a given temperature within the reasonable uncertainty limit (a few kilobars) of the experimental values of P in the simple system CaO-MgO-Al_2O_3-SiO_2 as well as in more complex multicomponent systems.

A literature survey and an analysis of published chemical data on assemblages containing coexisting garnet + clinopyroxene show that the clinopyroxenes in these two-phase assemblages that (1) occur as xenoliths in nonkimberlitic continental volcanics, (2) formed as crystallization products from a melt at high pressure, and (3) occur in granulite-facies metamorphic environments, are not truly omphacitic clinopyroxenes. Thus, these assemblages should not be referred to as eclogites, sensu stricto. Because the clinopyroxenes in these assemblages are enriched in quadrilateral and Tschermak components, the garnet-clinopyroxene geobarometer can be applied with much more confidence to these classes of garnet clinopyroxenite rocks. A unique P-T condition is obtained by simultaneous solution of the Ellis-Green geothermometric equation and the geobarometric equation presented above. Such applications indicate that the pressure of formation of the garnet clinopyroxenite xenoliths from Delegate breccia pipe range from 16–25 kbar (1000–1200 °C), from Israel (Mt. Carmel volcano) range from 15–21 kbar (940–1270 °C), and from Camp Creek latite range from 8–18 kbar (740–900 °C). The garnet clinopyroxenites of the Bohemian massif equilibrated in the range of 20–30 kbar and 1000–1200 °C. These calculations are consistent with the geological interpretations of the respective suite of samples.

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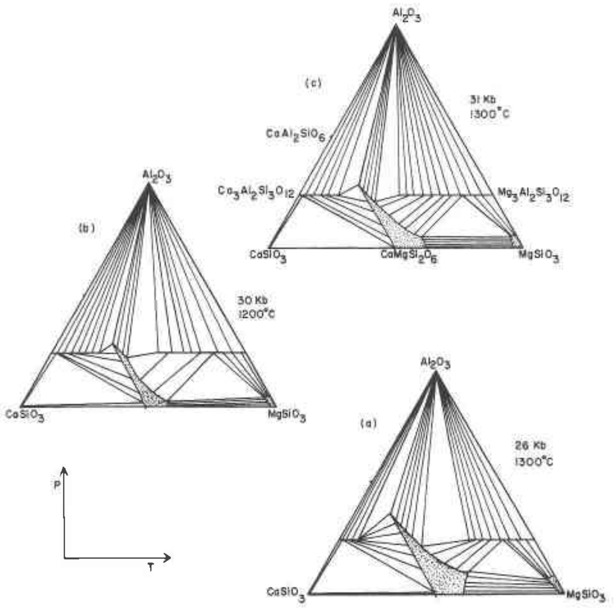

Fig. 1. Subsolidus phase relations on the join Al_2O_3-$CaSiO_3$-$MgSiO_3$ at three different P-T conditions, inferred from various experimental observations (see text).

INTRODUCTION

Garnet-clinopyroxene rocks, or eclogites, sensu lato, are an important part of the earth's upper mantle and lower crust. Quantitative estimation of pressure (P) of equilibration of the eclogitic mineral assemblages is a key problem in petrology. Various workers have attempted to quantify the temperature (T) of equilibration of garnet + clinopyroxene assemblages (e.g., Banno, 1970; Ganguly, 1979; Ellis and Green, 1979). The garnet-clinopyroxene geothermometer is based on Fe-Mg exchange between coexisting garnet and clinopyroxene. The intrinsic problem with any geothermometer based on an ion-exchange equilibrium is that independent estimation of P is required. However, no calibration is presently available by which P of equilibration of garnet + clinopyroxene assemblages can be quantified. Therefore, a method to estimate P of equilibration of garnet + clinopyroxene assemblages would be of fundamental value to the petrogenesis of eclogites and other garnet-clinopyroxene rocks.

Newton (1986) proposed a geobarometer for group B and group C eclogites (cf. Coleman et al., 1965) that requires the presence of a third phase, quartz. However, the eclogite and garnet clinopyroxenite xenoliths found in kimberlites and alkalic basalts are most commonly bimineralic. Many workers (e.g., Koons, 1984; Newton, 1986) have acknowledged that estimation of P of formation of bimineralic eclogite (and garnet clinopyroxenite) is notoriously difficult.

In this paper, the problems inherent in the geobarometry of eclogitic mineral assemblages are discussed quantitatively and an approximate solution to the determination of P based on Al_2O_3 content of clinopyroxene and Ca-Mg ratio of the coexisting garnet is presented.

THE *P*-DEPENDENT COMPOSITIONAL PARAMETER OF THE GARNET + CLINOPYROXENE ASSEMBLAGE IN THE CaO-MgO-Al_2O_3-SiO_2 (CMAS) SYSTEM

The model system CMAS encompasses all the major phases found in high-P assemblages of basaltic and peridotitic bulk compositions. The major solid solution series for these phases, except those involving Fe, are also present in this system. Since the Fe-Mg exchange between coexisting garnet and clinopyroxene is mainly a function of T, the P dependence of any compositional parameter between coexisting garnet and clinopyroxene should be addressed in the CMAS system.

Plagioclase- and quartz-free garnet pyroxenites can be adequately modeled by phase relations on the Al_2O_3-$CaSiO_3$-$MgSiO_3$ plane of the CMAS composition space. On this plane, pyroxenes are ternary solutions with $CaMgSi_2O_6$ (Di), $MgMgSi_2O_6$ (En), and $CaAlAlSiO_6$ (CaTs) as the end-member components, and garnets are binary solutions between $Ca_3Al_2Si_3O_{12}$ (Gr) and $Mg_3Al_2Si_3O_{12}$ (Py). Subsolidus phase relations of garnet pyroxenites in this subsystem are truly ternary at any P and T.

The stability of the garnet + clinopyroxene two-phase assemblage in the CMAS system was experimentally determined by Boyd (1970) at 30 kbar and 1200 °C. A schematic facies variation diagram can be constructed at three different P-T conditions (Fig. 1). In Figure 1 the 30 kbar, 1200 °C phase diagram is a reproduction of Boyd's diagram (note, however, that mole percent is plotted here instead of weight percent), while the other two diagrams are inferred from pieces of experimental data given by Gasparik (1984a), Akella (1976), and Lindsley and Dixon (1976). Thompson (1979) presented detailed theoretical arguments to predict qualitatively the topologic and compositional changes of the phase relations on this plane as a function of P and T. With a set of additive components and exchange vectors, he argued that in the three-phase assemblage garnet + clinopyroxene + orthopyroxene (garnet websterite), clinopyroxene and garnet become more enriched in tschermakite and grossularite components, respectively, with increasing temperature (at constant P), whereas with increasing P (at constant T) clinopyroxene becomes more diopsidic and garnet becomes more pyropic. Increase in T (at constant P) also increases mutual solubility of the two ternary pyroxenes, but an increase in P has the reverse effect. In the three-phase assemblage garnet + clinopyroxene + corundum (corundum eclogites), clinopyroxene becomes more tschermakitic and garnet more pyropic with increasing T, and increasing P will cause clinopyroxene to become more diopsidic and garnet more grossularitic. The behavior of these two three-phase regions completely defines the behavior of the two-phase region garnet + clinopyroxene.

From the above considerations, it appears that the Al_2O_3 content of clinopyroxene depends on pressure, whereas

TABLE 1. Notations and definitions

R = universal gas constant.
P = pressure.
T = temperature.
T^0 = standard state temperature at 1 bar pressure.
Q_i^0 = standard state molar thermochemical property, Q, of an end-member component i; in particular, S_i^0 and V_i^0 refer to molar entropy and volume, respectively.
Q^j = molar thermochemical property, Q, of the phase j which is a solid solution.
Q_i^j = partial molar thermochemical property of component i in the phase j, a solid solution; in particular, S_i^j, V_i^j, X_i^j, and μ_i^j refer to partial molar entropy, volume, thermodynamic mole fraction, and chemical potential, respectively, of component i in the solid solution phase j.
$\bar{G}^j$ = molar Gibbs energy of phase j, a solid solution.
$\Delta Q^0 = \sum_{i=1}^{n} \alpha_i Q_i^0$, where α_i is the stoichiometric coefficient of i in a balanced chemical reaction.
$(\Delta Q^0)_T^P$ = ΔQ^0 at pressure P and temperature T (when the superscript P is dropped, e.g., $\Delta Q^0_{T^0}$, then it signifies ΔQ^0 at 1 bar pressure and standard state temperature T^0).
a_i^j = activity of component i in phase j.
γ_i^j = activity coefficient of component i in phase j (superscript j is dropped after first use).
$W^Q_{m\text{-}n}$ = symmetric margules parameter for molar quantity Q due to mixing of components (or atoms) m and n (in Eqs. 44 and 45 the hyphen in the subscript is dropped for simplicity).
W^Q_m = asymmetric margules parameter for component m. W^Q_{mn} and W^Q_{nm} are used to distinguish W_m in m-n and m-p binaries in the m-n-p ternary system.

the Ca-Mg distribution between coexisting garnet and clinopyroxene mainly varies according to the temperature. These aspects can be quantified by using the following relationships.

The Al_2O_3 content of clinopyroxenes in equilibrium with garnet in the simple system is governed by the following equilibrium condition:

$$\tfrac{2}{3}Ca_3Al_2Si_3O_{12} + \tfrac{1}{3}Mg_3Al_2Si_3O_{12} = CaMgSi_2O_6 + CaAl_2SiO_6. \quad (1)$$

At equilibrium P and T, the standard free energy change, $(\Delta G^0)_T^P$, is given by

$$(\Delta G^0)_T^P = -RT \ln K \quad (2)$$

where K is the equilibrium constant for Reaction 1.

The thermochemical data used in this study are taken from Berman (1988) and the modified versions of the polynomial functions representing the heat capacities given by Berman and Brown (1985) are used. From these data, the molar volume change of the reaction, ΔV^0_{298}, is found to be 0.843 J/bar. The thermochemical data listed by Berman (1988) are found to be very internally consistent since they reproduce many experimentally determined equilibria within reasonable limits of uncertainty.

The left-hand side of Equation 2 is given by

$$(\Delta G^0)_T^P = \Delta H^0_{T^0} + \int_{T^0}^{T} \Delta C_P \, dT - T\left(\Delta S^0_{T^0} + \int_{T^0}^{T} \Delta C_P/T \, dT\right) + (P-1)\Delta V^0 \quad (3)$$

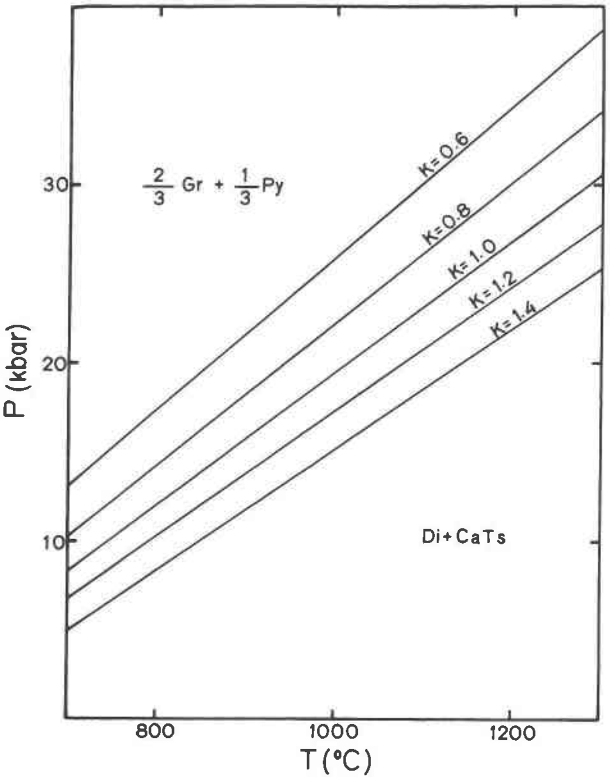

Fig. 2. Equilibrium P-T conditions of Reaction 1 for various values of the equilibrium constant, K. Note the P-dependent character of the reaction.

where the enthalpy, H^0; entropy, S^0; heat capacity, C_P; and the molar volume, V^0 are the molar thermochemical properties of the pure phases at 1 bar and reference temperature, T^0 (see Table 1 for notations). For solid solutions, K can assume various values depending on the mole fractions and activity coefficients of the components. If the molar volume does not change appreciably with P and T, the equilibrium pressure at a given T can be calculated from the equation

$$P = 1 - \{[(\Delta G^0)^1_T + RT \ln K]/\Delta V^0\}. \quad (4)$$

P-T curves for Equilibrium 1, generated for some arbitrary values of K, are shown in Figure 2. It is evident from this figure that Equilibrium 1 is sufficiently P sensitive to be used as a geobarometer. For a multicomponent system, evaluation of K is a problem which will be discussed in detail later.

The Ca-Mg exchange between coexisting garnet and clinopyroxene solid solution can be expressed by the following equilibrium condition:

$$\tfrac{1}{3}Mg_3Al_2Si_3O_{12} + CaMgSi_2O_6 = \tfrac{1}{3}Ca_3Al_2Si_3O_{12} + MgMgSi_2O_6. \quad (5)$$

It was pointed out earlier that Ca-Mg exchange between coexisting garnet and clinopyroxene is mainly a function of T and thus possibly cannot be of much value to the

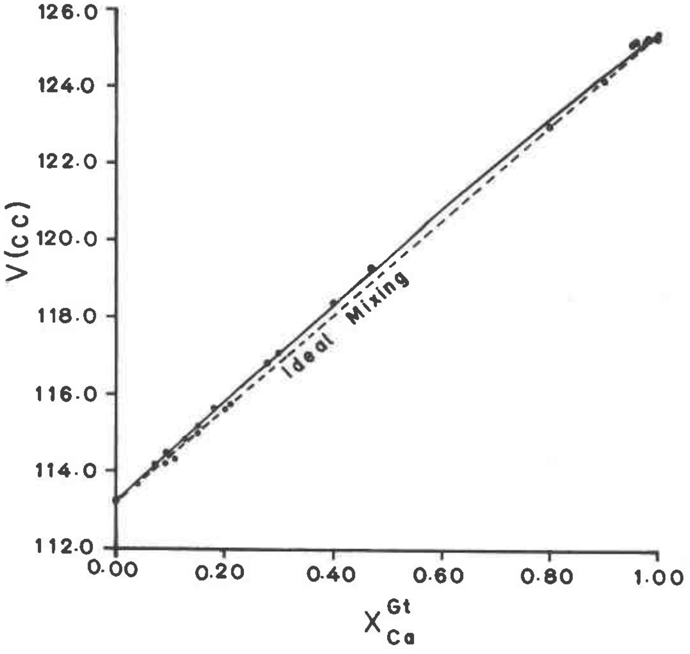

Fig. 3. Molar volumes along the Py-Gr garnet join. The data are from various sources as given by Wood (1988). Notice the scatter in the experimental observations. The solid line is the third-degree polynomial (see text) fitted through all the data points, and the dashed line indicates ideal mixing behavior.

geobarometry of garnet + clinopyroxene assemblages. As discussed earlier, X_{Ca} in garnet in eclogitic assemblages varies with P. The Ca-Mg ratio in garnet alone is, however, controlled by Reaction 1.

PROBLEM OF GARNET-CLINOPYROXENE THERMOBAROMETRY

The problem of thermobarometry of garnet + clinopyroxene assemblages is rooted in their high thermodynamic variance. Even in the simple system Al_2O_3-$CaSiO_3$-$MgSiO_3$, the assemblage garnet + clinopyroxene is trivariant. The assemblage garnet + clinopyroxene + orthopyroxene in this system is divariant. For this reason Al_2O_3 isopleths of clinopyroxene in equilibrium with both garnet and orthopyroxene can be constructed in P-T space from experimental data (see Fig. 7 of Herzberg, 1978; Fig. 7 of Wood and Holloway, 1984; and Fig. 6 of Gasparik, 1984b). Construction of Al_2O_3 isopleths of clinopyroxene in equilibrium with only garnet suffers from the problem that another compositional variable can also vary independently in addition to P and T. However, it follows from Duhem's theorem (Prigogine and Defay, 1954; Ganguly and Saxena, 1987) that for a particular bulk composition, the Al_2O_3 isopleths of clinopyroxene in equilibrium with garnet can be uniquely defined in P-T space.

The fundamental proposition of the Gibbs phase rule is that the state of chemical equilibrium of an assemblage of phases can be precisely defined by a set of equations, as long as the difference between the number of unknowns involved in the equations and the number of equations equals the thermodynamic variance of the assemblage. Rumble (1974) and Spear et al. (1982) gave an account of the formulations describing the state of chemical equilibrium among phases in a system with a fixed number of components. Following their approach, we arrive at the following equations describing the two-phase assemblage garnet + clinopyroxene in the model system Al_2O_3-$CaSiO_3$-$MgSiO_3$. For each phase to be in homogeneous equilibrium, we have two Gibbs-Duhem equations, one for garnet (Gt) and another for clinopyroxene (Cpx), respectively (for notation of symbols, see Table 1):

$$S^{Gt}\,dT - V^{Gt}\,dP + X_{Py}^{Gt}\,d\mu_{Py}^{Gt} + X_{Gr}^{Gt}\,d\mu_{Gr}^{Gt} = 0 \quad (6)$$

$$S^{Cpx}\,dT - V^{Cpx}\,dP + X_{CaTs}^{Cpx}\,d\mu_{CaTs}^{Cpx} + X_{Di}^{Cpx}\,d\mu_{Di}^{Cpx} + X_{En}^{Cpx}\,d\mu_{En}^{Cpx} = 0. \quad (7)$$

The conditions of heterogeneous equilibria are expressed as follows. For Ca-Mg exchange between coexisting garnet and clinopyroxene we can write the energy balance reaction corresponding to Equation 5 as follows:

$$\tfrac{1}{3}\,d\mu_{Gr}^{Gt} + d\mu_{En}^{Cpx} - \tfrac{1}{3}\,d\mu_{Py}^{Gt} - d\mu_{Di}^{Cpx} = 0. \quad (8)$$

Similarly, the energy-balance equation that corresponds to the mass balance Equation 1 is

$$d\mu_{Di}^{Cpx} + d\mu_{CaTs}^{Cpx} - \tfrac{2}{3}\,d\mu_{Gr}^{Gt} - \tfrac{1}{3}\,d\mu_{Py}^{Gt} = 0. \quad (9)$$

For stability of the binary garnet solid solution we obtain

$$d(\mu_{Gr}^{Gt} - \mu_{Py}^{Gt}) = -(S_{Gr}^{Gt} - S_{Py}^{Gt})\,dT + (V_{Gr}^{Gt} - V_{Py}^{Gt})\,dP + \left(\frac{\partial^2 \bar{G}^{Gt}}{\partial (X_{Gr}^{Gt})^2}\right) dX_{Gr}^{Gt}. \quad (10)$$

For stability of the clinopyroxene solid solution, which is ternary in this system, we obtain

$$\begin{aligned} d(\mu_{CaTs}^{Cpx} - \mu_{Di}^{Cpx}) = {} & -(S_{CaTs}^{Cpx} - S_{Di}^{Cpx})\,dT \\ & + (V_{CaTs}^{Cpx} - V_{Di}^{Cpx})\,dP \\ & + \left(\frac{\partial^2 \bar{G}^{Cpx}}{\partial (X_{CaTs}^{Cpx})^2}\right) dX_{CaTs}^{Cpx} \\ & + \left(\frac{\partial^2 \bar{G}^{Cpx}}{\partial X_{CaTs}^{Cpx} \cdot \partial X_{En}^{Cpx}}\right) dX_{En}^{Cpx} \quad (11) \end{aligned}$$

and

$$\begin{aligned} d(\mu_{En}^{Cpx} - \mu_{Di}^{Cpx}) = {} & -(S_{En}^{Cpx} - S_{Di}^{Cpx})\,dT + (V_{En}^{Cpx} - V_{Di}^{Cpx})\,dP \\ & + \left(\frac{\partial^2 \bar{G}^{Cpx}}{\partial X_{CaTs}^{Cpx} \cdot \partial X_{En}^{Cpx}}\right) dX_{CaTs}^{Cpx} \\ & + \left(\frac{\partial^2 \bar{G}^{Cpx}}{\partial (X_{CaTs}^{Cpx})^2}\right) dX_{En}^{Cpx}. \quad (12) \end{aligned}$$

We thus obtain seven equations with ten unknowns. The unknowns are dP, dT, differential chemical potentials of each of the phase components in each of the phases, $\partial X_{\mathrm{Gr}}^{\mathrm{Gt}}$, $\partial X_{\mathrm{CaTs}}^{\mathrm{Cpx}}$, and $\partial X_{\mathrm{En}}^{\mathrm{Cpx}}$. To calculate the P-T isopleths for $\mathrm{Al_2O_3}$ content of clinopyroxene in equilibrium with garnet, we can solve the system for $(\partial P/\partial T)_{X_{\mathrm{CaTs}}^{\mathrm{Cpx}}}$. Since the garnet + clinopyroxene assemblage is trivariant in this system, it is necessary to hold two independent compositional variables constant for the calculation of any dP/dT slope. The choices are $\partial X_{\mathrm{CaTs}}^{\mathrm{Cpx}}$ and either $\partial X_{\mathrm{En}}^{\mathrm{Cpx}}$ or $\partial X_{\mathrm{Gr}}^{\mathrm{Gt}}$. In this way we obtain a system of seven nonhomogeneous equations with seven unknowns to solve for the variable $(\partial P/\partial T)_{X_{\mathrm{CaTs}}^{\mathrm{Cpx}},X_{\mathrm{En}}^{\mathrm{Cpx}}}$. Analytical solution to this system yields

$$\begin{aligned}(\partial P/\partial T)_{X_{\mathrm{CaTs}}^{\mathrm{Cpx}},X_{\mathrm{En}}^{\mathrm{Cpx}}} = {} & [-(S_{\mathrm{En}}^{\mathrm{Cpx}} - S_{\mathrm{Di}}^{\mathrm{Cpx}})(2 - 2X_{\mathrm{En}}^{\mathrm{Cpx}} - 3X_{\mathrm{Gr}}^{\mathrm{Gt}}) \\ & + (S_{\mathrm{CaTs}}^{\mathrm{Cpx}} - S_{\mathrm{Di}}^{\mathrm{Cpx}})(1 - 2X_{\mathrm{CaTs}}^{\mathrm{Cpx}}) \\ & + S^{\mathrm{Gt}} - 2S^{\mathrm{Cpx}}]/ \\ & [-(V_{\mathrm{En}}^{\mathrm{Cpx}} - V_{\mathrm{Di}}^{\mathrm{Cpx}})(2 - 2X_{\mathrm{En}}^{\mathrm{Cpx}} - 3X_{\mathrm{Gr}}^{\mathrm{Gt}}) \\ & + (V_{\mathrm{CaTs}}^{\mathrm{Cpx}} - V_{\mathrm{Di}}^{\mathrm{Cpx}})(1 - 2X_{\mathrm{CaTs}}^{\mathrm{Cpx}}) \\ & + V^{\mathrm{Gt}} - 2V^{\mathrm{Cpx}}]. \end{aligned} \tag{13}$$

The spacings between isopleths are given by the following derivative, which is obtained in a similar fashion:

$$\begin{aligned}(\partial P/\partial X_{\mathrm{CaTs}}^{\mathrm{Cpx}})_{T,X_{\mathrm{En}}^{\mathrm{Cpx}}} = {} & (\mathrm{A} + 2\mathrm{B} - 2X_{\mathrm{En}}^{\mathrm{Cpx}} \\ & \cdot\mathrm{B} - 2X_{\mathrm{CaTs}}^{\mathrm{Cpx}}\cdot\mathrm{A} - X_{\mathrm{Gr}}^{\mathrm{Gt}}\cdot\mathrm{B})/ \\ & [-(V_{\mathrm{En}}^{\mathrm{Cpx}} - V_{\mathrm{Di}}^{\mathrm{Cpx}})(2 - 2X_{\mathrm{En}}^{\mathrm{Cpx}} - 3X_{\mathrm{Gr}}^{\mathrm{Gt}}) \\ & + (V_{\mathrm{CaTs}}^{\mathrm{Cpx}} - V_{\mathrm{Di}}^{\mathrm{Cpx}})(1 - 2X_{\mathrm{CaTs}}^{\mathrm{Cpx}}) \\ & + V^{\mathrm{Gt}} - 2V^{\mathrm{Cpx}}] \end{aligned} \tag{14}$$

where

$$\mathrm{A} = [\partial^2\bar{G}^{\mathrm{Cpx}}/\partial(X_{\mathrm{CaTs}}^{\mathrm{Cpx}})^2]_{P,T,X_{\mathrm{En}}^{\mathrm{Cpx}}}; \quad \text{and}$$
$$\mathrm{B} = [\partial^2\bar{G}^{\mathrm{Cpx}}/\partial X_{\mathrm{CaTs}}^{\mathrm{Cpx}}\cdot\partial X_{\mathrm{En}}^{\mathrm{Cpx}}]_{P,T}.$$

Equation 13 yields the instantaneous dP/dT slope of an equilibrium representing the assemblage garnet + clinopyroxene that crystallized from a fixed bulk composition. Because the slope is given in differential form, it can be evaluated at a reference P-T condition. Boyd (1970) gave the compositions of coexisting garnet and clinopyroxene that crystallized from a particular bulk composition at 1200 °C and 30 kbar (experiment 9 of Boyd). His data can be used to evaluate the dP/dT slope of the X_{CaTs} isopleth of clinopyroxenes that coexist with the garnet under these conditions, using the following procedures.

The molar entropy of a garnet solid solution is given by

$$\begin{aligned} S^{\mathrm{Gt}} = {} & S_{\mathrm{Py}}^{0}X_{\mathrm{Py}}^{\mathrm{Gt}} + S_{\mathrm{Gr}}^{0}X_{\mathrm{Gr}}^{\mathrm{Gt}} \\ & - 3\mathrm{R}(X_{\mathrm{Py}}^{\mathrm{Gt}}\ln X_{\mathrm{Py}}^{\mathrm{Gt}} + X_{\mathrm{Gr}}^{\mathrm{Gt}}\ln X_{\mathrm{Gr}}^{\mathrm{Gt}}) + S^{XS} \end{aligned} \tag{15}$$

where $S^{XS} = X_{\mathrm{Ca}}X_{\mathrm{Mg}}(X_{\mathrm{Ca}}W_S{}^{\mathrm{CaMg}} + X_{\mathrm{Mg}}W_S{}^{\mathrm{MgCa}})$ and $W_S{}^{\mathrm{CaMg}} = 2.1$ J/mol·K and $W_S{}^{\mathrm{MgCa}} = 39$ J/mol·K (Wood, 1988). Since

$$\bar{Q}_i^j = Q^j + (1 - X_i)\frac{\partial Q^j}{\partial X_i} \tag{16}$$

the partial molar entropies are calculated from Equation 15 according to Equation 16 as

$$\bar{S}_{\mathrm{Py}}^{\mathrm{Gt}} = S_{\mathrm{Py}}^{0} - 3\mathrm{R}\ln X_{\mathrm{Py}}^{\mathrm{Gt}} - 3\mathrm{R}T\frac{\partial \ln \gamma_{\mathrm{Py}}}{\partial T}$$

and

$$\bar{S}_{\mathrm{Gr}}^{\mathrm{Gt}} = S_{\mathrm{Gr}}^{0} - 3\mathrm{R}\ln X_{\mathrm{Gr}}^{\mathrm{Gt}} - 3\mathrm{R}T\frac{\partial \ln \gamma_{\mathrm{Gr}}}{\partial T}. \tag{17}$$

The partial derivatives, $\partial \ln \gamma_i/\partial T$, are evaluated from the formulations of γ_i given later. Molar volume (in cc) of the Ca-Mg binary garnet solid solution was given by Haselton and Newton (1980) as

$$\begin{aligned} V^{\mathrm{Gt}} = {} & 125.24 - 11.205X_{\mathrm{Py}}^{\mathrm{Gt}} - 0.512(X_{\mathrm{Py}}^{\mathrm{Gt}})^2 \\ & - e^{-[(X_{\mathrm{Py}}^{\mathrm{Gt}}-0.94)/0.11738]^2}. \end{aligned} \tag{18}$$

However, Wood (1988) argued that the volume along the Ca-Mg binary garnet solid solution can be adequately described as nearly ideal. Figure 3 shows the volume data listed by Wood (1988) along the Ca-Mg binary garnet from his own measurements and from earlier sources. It is evident from this plot that the scatter in the experimental data can indeed be treated by a linear fit. However, such a linear fit implies ideal mixing for pyrope-rich compositions, but there still appear to be slight positive deviations from ideality near the grossular-rich compositions. Berman (1990) adopted a symmetric model (i.e., a quadratic fit in Fig. 3), but this may again overestimate the positive deviation near the pyrope-rich compositions (and completely ignores the negative deviation shown by some data points of Haselton and Newton without providing arguments that Wood's data are better than those of Haselton and Newton). The best fit through the scattered data points in Figure 3 is obtained by a third-degree (i.e., slightly asymmetric) polynomial (Fig. 3) given by (in cc)

$$\begin{aligned} V^{\mathrm{Gt}} = {} & 113.175 + 12.866X_{\mathrm{Gr}}^{\mathrm{Gt}} + 0.1168(X_{\mathrm{Gr}}^{\mathrm{Gt}})^2 \\ & + 0.7453(X_{\mathrm{Gr}}^{\mathrm{Gt}})^3. \end{aligned} \tag{19}$$

The partial molar volumes are computed from the above expression according to Equation 16. Note that the equation given by Wood (1988) for expressing the volume of the Ca-Mg garnet solid solution [i.e., $V^{\mathrm{Gt}} = V_{\mathrm{Gr}}^{0}X_{\mathrm{Gr}}^{\mathrm{Gt}} + V_{\mathrm{Py}}^{0}X_{\mathrm{Py}}^{\mathrm{Gt}} + 0.14X_{\mathrm{Gr}}^{\mathrm{Gt}}(X_{\mathrm{Py}}^{\mathrm{Gt}})^2 + 2.61X_{\mathrm{Pyr}}^{\mathrm{Gt}}(X_{\mathrm{Gr}}^{\mathrm{Gt}})^2$] and Equation 19 are essentially equivalent.

Similarly, the molar entropy of the clinopyroxene solid solution is obtained by assuming ideal ionic mixing and is given by

$$\begin{aligned} S^{\mathrm{Cpx}} = {} & S_{\mathrm{Di}}^{0}X_{\mathrm{Di}}^{\mathrm{Cpx}} + S_{\mathrm{CaTs}}^{0}X_{\mathrm{CaTs}}^{\mathrm{Cpx}} + S_{\mathrm{En}}^{0}X_{\mathrm{En}}^{\mathrm{Cpx}} - \mathrm{R} \\ & \cdot(X_{\mathrm{Di}}^{\mathrm{Cpx}}\ln X_{\mathrm{Di}}^{\mathrm{Cpx}} + X_{\mathrm{CaTs}}^{\mathrm{Cpx}}\ln X_{\mathrm{CaTs}}^{\mathrm{Cpx}} + X_{\mathrm{En}}^{\mathrm{Cpx}}\ln X_{\mathrm{En}}^{\mathrm{Cpx}}). \end{aligned} \tag{20}$$

From this we obtain

$$\bar{S}_{\mathrm{Di}}^{\mathrm{Cpx}} = S_{\mathrm{Di}}^{0} - \mathrm{R}\ln X_{\mathrm{Di}}^{\mathrm{Cpx}} \tag{21}$$

and similar expressions for $\bar{S}_{\mathrm{CaTs}}^{\mathrm{Cpx}}$ and $\bar{S}_{\mathrm{En}}^{\mathrm{Cpx}}$.

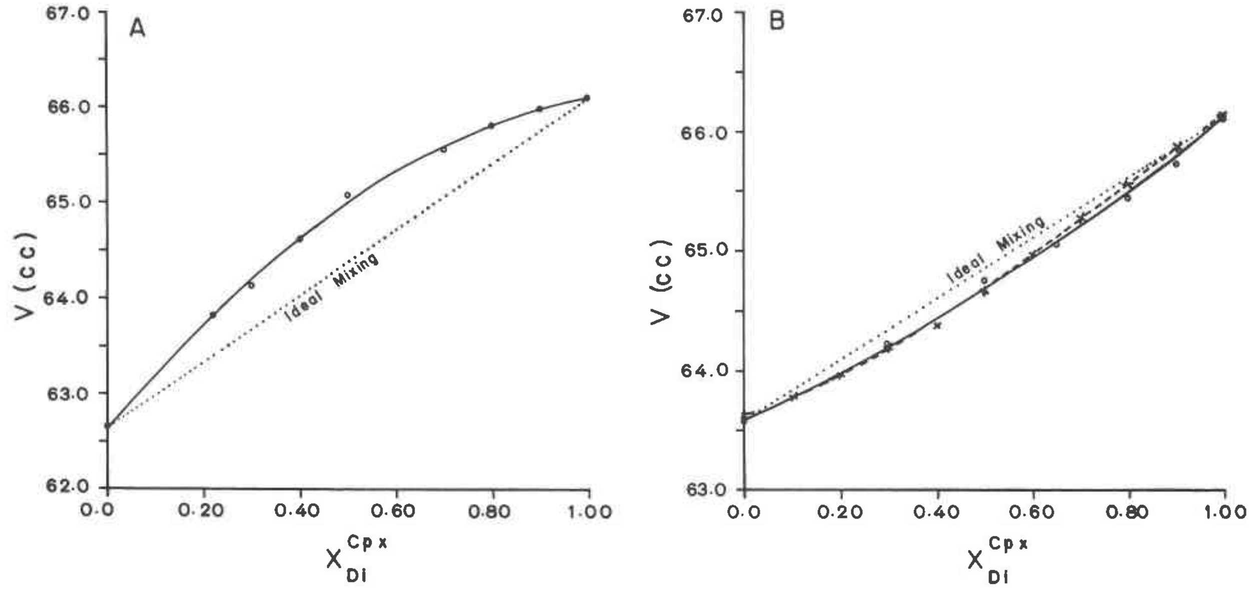

Fig. 4. Variation of molar volumes with compositions along the two binary joins of clinopyroxene compositions. (**A**) Di-En binary (data are from Newton et al., 1979). (**B**) Di-CaTs binary (crosses = data are from Gasparik, 1986; open circles = data are from Newton et al., 1977). Solid lines represent the polynomial fitted through the data points. The dashed line in the Di-CaTs join is the third-degree polynomial fitted through Gasparik's data only. In each case, the ideal mixing behavior is indicated by the dotted line.

Previous studies have shown that the molar volume of a clinopyroxene solid solution behaves nonideally. Molar volumes of Di-En binary solid solutions are given by Newton et al. (1979). A second-degree polynomial (i.e., a symmetric model) given by

$$V^{Cpx} = 62.624 + 5.972X_{Di}^{Cpx} - 2.498(X_{Di}^{Cpx})^2 \quad (22)$$

can be fitted through these data points (Fig. 4A). On the other hand, the molar volumes of the Di-CaTs binary solid solutions given by Gasparik (1986) can be best approximated by a third-degree polynomial (asymmetric model) as shown in Figure 4B. However, when the data of Newton et al. (1977) along this join are considered (Fig. 4B), an asymmetric model results only from a bias toward Gasparik's (1986) data. I have no way to judge which set of data is better. Thus, as a compromise, I have combined both sets of data and fitted a quadratic polynomial (symmetric model) given by

$$V^{Cpx} = 63.58 + 1.868X_{Di}^{Cpx} + 0.666(X_{Di}^{Cpx})^2 \quad (23)$$

and shown in Figure 4B. No volume data are available along the En-CaTs binary join. However, from the symmetric nature of the Di-CaTs and En-Di binaries, if it is assumed that molar volumes in the Di-CaTs-En ternary clinopyroxenes should be modeled as strictly regular solutions, then the molar volume of the clinopyroxene solid solution will be given as

$$V^{Cpx} = V^{IM} + V^{XS} \quad (24)$$

where

$$V^{IM} = X_{Di}^{Cpx}V_{Di}^{0} + X_{CaTs}^{Cpx}V_{CaTs}^{0} + X_{En}^{Cpx}V_{En}^{0} \quad (25)$$

and (neglecting the ternary term)

$$V^{XS} = X_{Di}^{Cpx}X_{CaTs}^{Cpx}W_{Di\text{-}CaTs}^{V} + X_{CaTs}^{Cpx}X_{En}^{Cpx}W_{CaTs\text{-}En}^{V} + X_{En}^{Cpx}X_{Di}^{Cpx}W_{En\text{-}Di}^{V}. \quad (26)$$

Benna et al. (1981) provided a very important data set, giving the experimentally determined values of molar volumes of 33 diopside-rich Di-CaTs-En ternary clinopyroxenes. Their ternary data along with the binary data of Gasparik (1986) and Newton et al. (1977, 1979) were statistically regressed to fit Equation 24 (Eqs. 25 and 26 combined). The following six parameters (in J/bar) were obtained (with a correlation coefficient of 0.998):

$$V_{Di}^{0} = 6.6166 \pm 0.0017$$
$$V_{CaTs}^{0} = 6.3566 \pm 0.0027$$
$$V_{En}^{0} = 6.2619 \pm 0.0032$$
$$W_{Di\text{-}CaTs}^{V} = -0.0696 \pm 0.0099$$
$$W_{CaTs\text{-}En}^{V} = 0.2240 \pm 0.0382$$
$$W_{En\text{-}Di}^{V} = 0.2350 \pm 0.0063.$$

These values were used in conjunction with Equations 24, 25, and 26. Partial molar volumes of Di and CaTs in a clinopyroxene solid solution were then computed from these equations.

So far no attention has been paid to the variation of entropies and volumes as functions of P and T. Standard-

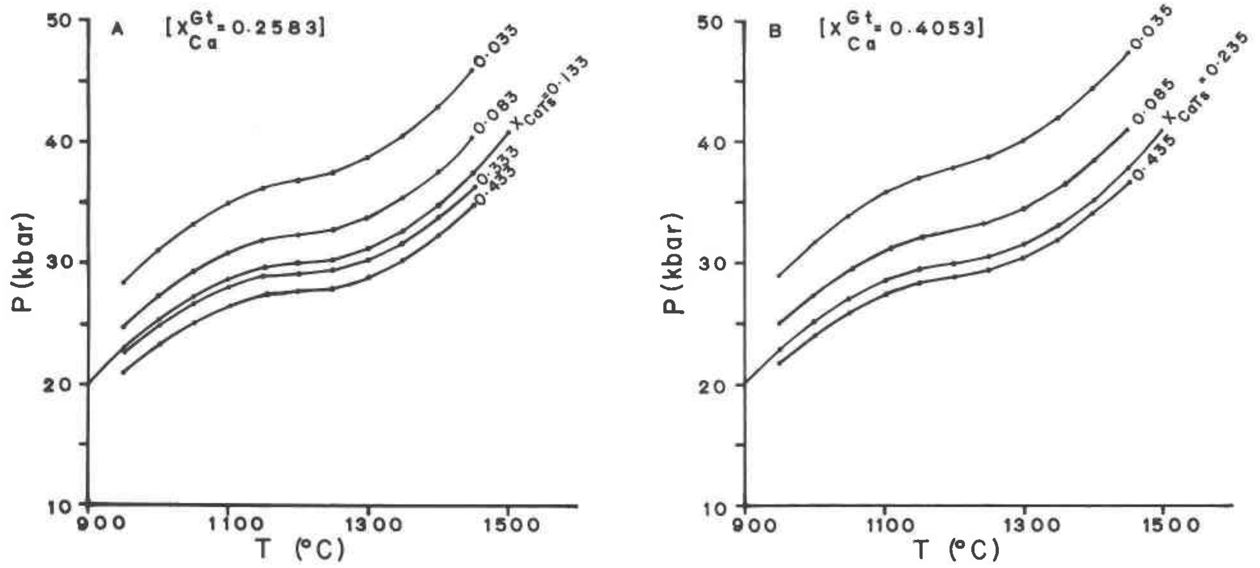

Fig. 5. X_{CaTs}^{Cpx} isopleths for two experimentally determined assemblages bearing garnet + clinopyroxene (for details see text). (**A**) For the bulk composition of experiment 9. (**B**) For the bulk composition of experiment 11. (Data are from Boyd, 1970.)

state entropies of the end-members are computed at the reference *T* from the heat capacity data, and for the sake of simplicity, molar volumes are assumed to be unchanged with *P* and *T*.

Equation 13 can now be solved at finite incremental steps, and the resulting isopleth through 1200°C and 30 kbar is shown in Figure 5A. The isothermal pressure dependence of the X_{CaTs} isopleths are computed from Equation 14 using $\bar{G}^{Cpx}$ given by

$$\bar{G}^{Cpx} = G^{IM} + G^{XS}$$

where $G^{IM} = -TS^{Cpx}$ (see Eq. 20 and Wood and Holloway, 1984; with the parameters discussed later in this paper)

$$G^{XS} = X_{Ca}^{M2} \cdot X_{Mg}^{M2} \cdot W_{Ca\text{-}Mg}^{GM2} + X_{Al}^{M1} \cdot X_{Mg}^{M1} \cdot W_{Al\text{-}Mg}^{GM1} + X_{Al}^{M1} \cdot X_{Mg}^{M2} \cdot \Delta G_2^0. \qquad (27)$$

The resulting *P-T* contours shown in Figure 5A are valid only for the bulk composition used by Boyd (1970) for his experiment 9. Boyd (1970) also gave data (experiment 11) for coexisting garnet and clinopyroxene that crystallized from another bulk composition. The *P-T* contours resulting from this data set constructed in the same way described above are shown in Figure 5B.

In all of the above formulations, the molecular fractions of the clinopyroxene components are calculated as follows:

$$X_{En}^{Cpx} = X_{Mg}^{M2} = 1 - \mathrm{Ca}; \qquad X_{CaTs}^{Cpx} = X_{Al}^{M1} = 0.5\mathrm{Al}_{tot}$$

(for the CMAS system this $\approx \mathrm{Al}_{tot} - 2 + \mathrm{Si}$)

and

$$X_{Mg}^{M1} = \mathrm{Mg}_{tot} - X_{Mg}^{M2}; \qquad X_{Di}^{Cpx} = \mathrm{Mg}_{tot} - 2X_{En}^{Cpx}. \quad (28)$$

From the above considerations the following points become evident. (1) Each of the curves in Figures 5A and 5B represents the *P-T* trajectory along which a garnet and a clinopyroxene of fixed compositions are in equilibrium. (2) The isopleths represent changing X_{CaTs}, whereas the other independent compositional parameters remain unchanged. This condition is virtually impossible to attain experimentally and is the probable reason why Brey et al. (1986) were unsuccessful in experimentally calibrating Reaction 1. The only way this problem can be circumvented in experiments is by equilibrating clinopyroxene to an overwhelming proportion of garnet so that the composition of garnet is internally buffered (although this would not allow one to observe the compositional variation of garnet with changing *P* and *T*). To provide an analogy, the reader can recall the garnet-biotite two-phase equilibrium experiments of Ferry and Spear (1978). These authors equilibrated garnet + biotite in mixtures with very high garnet/biotite ratios so that the initial composition of garnet (Py_{10}) did not change. If additional phases are present, such as plagioclase or orthopyroxene, then additional chemical potentials are fixed, but the system no longer remains trivariant. (3) X_{CaTs} of clinopyroxene, in equilibrium with garnet, is a function of pressure. The isopleths shown in Figures 5A and 5B are valid only for two particular bulk compositions. This compositional effect can only be modeled in terms of the equilibrium constant of Reaction 1. Due to this compositional dependence, Reaction 1 is less amenable to direct experimental calibration. The standard Gibbs energy for Reaction 1 is difficult to deduce directly and accurately from phase equilibrium data because the reaction is neither univariant nor divariant. It should be noted that the experimental calibration of the garnet-clinopyroxene geothermometer is an empirical one (Ellis and Green, 1979) where the compositional effect was monitored by expressing the Fe-Mg K_d between garnet and clinopyroxene as a function of P, T, and X_{Ca} in garnet.

THERMODYNAMIC CALIBRATION OF THE GARNET-CLINOPYROXENE GEOBAROMETER

For the reasons stated above, the equilibrium condition describing Al_2O_3 solubility in clinopyroxenes and the Ca-Mg ratio in the coexisting garnet should be calibrated almost entirely from measured and derived thermochemical parameters. It is important to calibrate the geobarometer in the compositionally simple system CMAS to judge how the compositional variance can be reduced. Once such a calibration becomes successful, attempts can be made to apply it to complex natural systems.

Application to the CMAS system

In general, the equilibrium constant K for Equation 1 is given by

$$\mathrm{K} = \frac{a_{\mathrm{Di}}^{\mathrm{Cpx}} \cdot a_{\mathrm{CaTs}}^{\mathrm{Cpx}}}{[a_{\mathrm{Gr}}^{\mathrm{Gt}}]^{2/3} \cdot [a_{\mathrm{Py}}^{\mathrm{Gt}}]^{1/3}} \tag{29}$$

$$= \frac{(X_{\mathrm{Di}}^{\mathrm{Cpx}} \cdot X_{\mathrm{CaTs}}^{\mathrm{Cpx}})}{[(X_{\mathrm{Gr}}^{\mathrm{Gt}})^{2/3} \cdot (X_{\mathrm{Py}}^{\mathrm{Gt}})^{1/3}]} \cdot \frac{\gamma_{\mathrm{Di}}^{\mathrm{Cpx}} \cdot \gamma_{\mathrm{CaTs}}^{\mathrm{Cpx}}}{[(\gamma_{\mathrm{Gr}}^{\mathrm{Gt}})^{2/3} \cdot (\gamma_{\mathrm{Py}}^{\mathrm{Gt}})]^{1/3}} = \mathrm{K}_X \cdot \mathrm{K}_\gamma \tag{30}$$

where K_X is the distribution coefficient involving the products and ratios of thermodynamic mole fractions, and K_γ involves similar products and ratios of corresponding activity coefficients.

For CMAS garnets, mixing in tetrahedral and octahedral sites can be ignored and Ca-Mg mixing in the dodecahedral sites results in

$$X_{\mathrm{Gr}} = (X_{\mathrm{Ca}})^3, \qquad X_{\mathrm{Py}} = (X_{\mathrm{Mg}})^3. \tag{31}$$

For CMAS clinopyroxenes, the site fractions of the cations are calculated according to Equation 28.

Thermodynamic mole fractions are then calculated by assuming a two-site model (Wood and Banno, 1973; Herzberg, 1978; Perkins and Newton, 1980; Gasparik and Newton, 1984; Brey et al., 1986):

$$X_{\mathrm{Di}}^{\mathrm{Cpx}} = X_{\mathrm{Ca}}^{\mathrm{M2}} \cdot X_{\mathrm{Mg}}^{\mathrm{M1}}; \qquad X_{\mathrm{CaTs}}^{\mathrm{Cpx}} = X_{\mathrm{Ca}}^{\mathrm{M2}} \cdot X_{\mathrm{Al}}^{\mathrm{M1}}. \tag{32}$$

The next step in applying Equation 4 is to make the simplest assumption that both garnet and clinopyroxene solid solutions behave ideally. Banno (1974) used such an assumption to use Reaction 1 as a geobarometer and argued that such an assumption is applicable to Boyd's (1970) data. In that context,

$$\mathrm{K} = \mathrm{K}_X. \tag{33}$$

If this assumption is made, equilibrium pressure at a given temperature can be obtained by substituting K_X for K in Equation 4. The validity of this model can be tested by attempting to reproduce $P = 30$ kbar at a temperature of 1200 °C for the compositions of coexisting garnet and clinopyroxene in the two experiments reported by Boyd (1970) and discussed above. These two values are given in Table 2. It is evident that the ideal solution approximation cannot reproduce the experimental observation within reasonable limits of uncertainty.

The next simplest method that can be formulated is one in which all nonideality is attributed to the pressure-volume term (Wood and Banno, 1973). This step is important for two reasons. First, among all nonideal parameters (enthalpy, entropy, and volume), adequate data on the excess volumes of the solid solutions are available (discussed above and below) and the volume data can be taken with much more confidence than the measured enthalpy or entropy data (for which the experimental uncertainties are often very large). Second, for geobarometric calculations, molar volumes play an important role. Thus, if the nonidealities can be handled only by considering the P-V terms, then the task becomes easier. Nonetheless, this means,

$$(\Delta G^0)_T^1 + \int_1^P \Delta V^0 \, \mathrm{d}P = -\mathrm{R}T \ln \mathrm{K}_X - \mathrm{R}T \cdot \int_1^P \frac{\partial \ln}{\partial P} \left[\frac{\gamma_{\mathrm{Di}} \cdot \gamma_{\mathrm{CaTs}}}{\gamma_{\mathrm{Gr}}^{2/3} \cdot \gamma_{\mathrm{Py}}^{1/3}} \right] \mathrm{d}P \tag{34}$$

where the pressure coefficients of the activity coefficients can be calculated from the equation

$$\left(\frac{\partial \ln \gamma_i}{\partial P} \right)_{T,X_j} = \frac{V_i^j - V_i^0}{\mathrm{R}T}. \tag{35}$$

On simplification, Equation 34 yields

$$(\Delta G^0)_T^1 + \int_1^P \Delta V_r \, \mathrm{d}P = -\mathrm{R}T \ln \mathrm{K}_X \tag{36}$$

where

$$\Delta V_{\mathrm{r}} = V_{\mathrm{Di}}^{\mathrm{Cpx}} + V_{\mathrm{CaTs}}^{\mathrm{Cpx}} - \tfrac{2}{3} V_{\mathrm{Gr}}^{\mathrm{Gt}} - \tfrac{1}{3} V_{\mathrm{Py}}^{\mathrm{Gt}}. \tag{37}$$

Thus, the partial molar volumes of Di and CaTs in the clinopyroxene solid solution and those of pyrope and grossular in the garnet solid solution need to be evaluated. For CMAS garnets, V_{Gr} and V_{Py} are calculated from Equation 19. Partial molar volume of diopside and CaTs were calculated from Equation 24 and using the W^V parameters derived in this study (above).

The results of P estimation using partial molar volume change for experiments 9 and 11 of Boyd are shown in Table 2. It is evident that while correction for partial molar volumes had a substantial effect on the ideal solution assumption, the reproduction of P was still not satisfactory. This convincingly demonstrates that the K_X of Equilibrium 1 is a function of composition and that correction for compositional dependence of K_X is neces-

TABLE 2. Comparison of pressures calculated from assemblages equilibrated at 1200 °C and 30 kbar

Experiment 9	Experiment 11
Ideal Solution Model	
$K_X = 1.864$	$K_X = 1.66$
$P = 18$	$P = 19$
Nonideality is attributed to *P-V* terms	
$\Delta V_r = 0.56$	$\Delta V_r = 0.45$
$P = 27$	$P = 37$
$\gamma_i = f(P, T, X)$	
(1) Ca-Mg binary garnet is modeled according to Wood (1988)*	
$P = 29$	$P = 32$
(2) Ca-Mg binary garnet is modeled according to Haselton and Newton (1980)/Ganguly and Saxena (1984)**	
$P = 27$	$P = 33$

* In this calculation the Ca-Mg and Mg-Al interaction parameters for clinopyroxene were taken as 26.58 and 12.5 kJ per mole, respectively.

** In this calculation the above interaction parameters were taken as 23.0 and 2.0 kJ per mole, respectively.

sary. Wood and Banno (1973) were quite successful in calibrating the garnet-orthopyroxene geobarometer by attributing all nonidealities to the *P-V* terms, but such simplification cannot be extended to garnet-clinopyroxene equilibria.

In general, $\gamma_i = f(T, P, X)$. The *P* coefficients are given by Equation 35. The *T* and compositional dependence of γ_{Py} and γ_{Gr} are given by assuming the Ca-Mg binary join as an asymmetric regular solution:

$$3RT \ln \gamma_{Py} = (X^{Gt}_{Gr})^2[W^H_{Py} + 2(W^H_{Gr} - W^H_{Py})X^{Gt}_{Py} - TW^S]$$

and

$$3RT \ln \gamma_{Gr} = (X^{Gt}_{Py})^2[W^H_{Gr} + 2(W^H_{Py} - W^H_{Gr})X^{Gt}_{Gr} - TW^S]. \tag{38}$$

The values of W^H_{Gr}, W^H_{Py}, and W^S are variously given by different authors (Table 3). The values derived by Wood (1988) are preferred for the reasons discussed in the next section.

Gasparik (1984b) noted in the CMAS system that the X_{En} in Cpx, i.e., Mg/(Ca + Mg) ratio in the M2 site is nearly independent of the Al content in the M1 site. Thus, the ternary clinopyroxene can be treated as a two-site reciprocal solution (Wood and Nicholls, 1978) and each of the sites can be assumed to behave as a strictly regular binary (Ca-Mg mixing in M2, Mg-Al mixing in M1, and no enthalpy or entropy contribution due to mixing in the tetrahedral site) solution. This model yields

$$RT \ln \gamma_{Di} = (X^{M2}_{Mg})^2 W^G_{Ca\text{-}Mg} + (X^{M1}_{Al})^2 W^G_{Mg\text{-}Al} + X^{M2}_{Mg} \cdot X^{M1}_{Al} \cdot \Delta G^0_2$$

and

$$RT \ln \gamma_{CaTs} = (X^{M2}_{Mg})^2 W^G_{Ca\text{-}Mg} + (X^{M1}_{Mg})^2 W^G_{Mg\text{-}Al} - X^{M2}_{Mg} \cdot X^{M1}_{Mg} \cdot \Delta G^0_2 \tag{39}$$

where ΔG^0_2 is the standard free energy change of the reciprocal Equilibrium A2 given in Appendix 1 and $W^G_{Ca\text{-}Mg}$ and $W^G_{Mg\text{-}Al}$ are the Ca-Mg and Mg-Al interaction parameters in the M2 and M1 sites, respectively. The values of these two interaction parameters, used in the following calculations, are discussed below.

Using the relationship

$$RT \ln K = RT \ln K_X + RT \ln K_\gamma$$

and transferring the pressure coefficients to the left-hand side of Equation 4, the equilibrium pressure at a given *T* is calculated according to

$$P = \Delta V^0/\Delta V_r - \{[(\Delta G^0)^1_T + RT \ln K_X + RT \ln(K_\gamma)]/\Delta V_r\}. \tag{40}$$

The pressures calculated for both experiments 9 and 11 at 1200 °C by use of Equation 40 are shown in Table 2. As can be seen from Table 2, the calculated values of

TABLE 3. Binary interaction parameters for (Ca,Mg,Fe) garnets, given by different authors

		Ganguly and Saxena (1984)	Wood (1987)	Wood (1988)	Newton et al.* (1986)	Hackler and Wood (1989)	Berman (1990)	Koziol (1990)
Ca-Mg	W^H_{12}	50790.00	46900.0	56520.0	50793.76	—	69200.00	—
binary	W^H_{21}	12552.00	13400.0	15000.0	12552.00	—	21560.00	—
	W_S	18.83	0.0	**	46.82(Mg-Ca)	—	18.79	—
Mg-Fe	W^H_{23}	31380.00	12550.0		36149.76	6350.00	3720.00	—
binary	W^H_{32}	2508.00	2500.00		−15773.68	2080.00	230.00	—
	W_S	0	0		0	0	0	—
Fe-Ca	W^H_{31}	57990.00	12550.00		13681.68	—	20320.00	7770.00
binary	W^H_{13}	−7908.00	4200.00		−9079.28	—	2620.00	−3270.00
	W_S	18.83	0		0	—	5.08	0.0

Note: W_H = J/mol; W_S = J/mol·K; all parameters are on the basis of three cations. In this table Ca = 1, Mg = 2, and Fe = 3.

* In Newton et al. (1986) the Ca-Mg binary data are from Haselton and Newton (1980); Mg-Fe and Fe-Ca binary data are from Geiger et al. (1987) (R.C. Newton, written communication).

** Asymmetric entropy parameters: $W_{S12} = 2.1$ and $W_{S21} = 39.0$.

P are strongly dependent on the solution model of both the Ca-Mg binary garnet and Ca-Mg-Al ternary clinopyroxene solid solutions. Holland et al. (1979) calibrated the value of $W^G_{\text{Ca-Mg}}$ as 24.47 kJ without giving any error limit to this value. However, Lindsley and Davidson (1980) statistically analyzed the same set of data Holland et al. (1979) analyzed and refined its value as 25.197 ± 1.387 kJ. The value of $W^G_{\text{Mg-Al}}$ was empirically calibrated as 7.53 kJ/mol by Wood and Holloway (1984). Since uncertainties exist in the solution models of garnet, it is difficult to calibrate these values without fixing the model for garnet. Thus, the solution model of garnet was first fixed according to that of Wood (1988). This procedure required the value of $W^G_{\text{Ca-Mg}}$ to be near the upper limit of the error bar stated above and the value of $W^G_{\text{Mg-Al}}$ to be 12.5 kJ for a better fit of the calculated P to that of the experiments. If, on the other hand, the garnet model is fixed according to the model of Haselton and Newton (1980) or Ganguly and Saxena (1984), the value of $W^G_{\text{Ca-Mg}}$ is required to be near the lower limit of the above mentioned error bar, and the value of $W^G_{\text{Mg-Al}}$ is required to be as low as 2.0 kJ/mol. Although experiments 9 and 11 of Boyd (1970) encompass compositionally very contrasting assemblages (in the former pyrope-rich garnet coexisting with diopside-rich clinopyroxene and in the latter grossular-rich garnet coexisting with CaTs-rich clinopyroxene) these two data points may not be sufficient for such calibration. However, the first approach is preferred over the second because: (1) the garnet model of Wood (1988) is a better model than that of Haselton and Newton (1980) because the large asymmetry in the W^H parameters for Gr and Py is also indicated by Berman (1990) and because of reasons discussed later; (2) a larger value of $W^G_{\text{Ca-Mg}}$ is preferred because larger values of this parameter were also suggested by Newton et al. (1979) from solution calorimetry (28 ± 4 kJ), by Saxena and Nehru (1975) from analysis of phase-equilibrium data (27.33 kJ), and also by Nickel and Brey (1984) from experimental calibration; (3) a larger value of $W^G_{\text{Mg-Al}}$ means a smaller stability field of CaTs-rich clinopyroxene. This is supported by experimental observations of Gasparik (1984a). A larger value for the Mg-Al interaction was also suggested by Cohen (1986).

However, for natural systems (discussed below), such adjustments to $W^G_{\text{Ca-Mg}}$ and $W^G_{\text{Mg-Al}}$ were marginally necessary because it was found that a value of 24.5–25.0 kJ for $W^G_{\text{Ca-Mg}}$ and a value of 7.0–9.0 kJ for $W^G_{\text{Mg-Al}}$ yield satisfactory P values.

Nevertheless, the calculated P in each case is within reasonable limits of all uncertainties involved in experimental observations (apart from P-T values, the greatest experimental uncertainties lie in the assumption of equilibrium and the accuracy of electron microprobe analyses, particularly for the earlier usage of microprobe data for the experiments) and the nonideal solution properties of the phases, and this exercise demonstrates the potential applicability of the geobarometer.

Application to natural systems

For a multicomponent garnet solid solution

$$X_{\text{Gr}} = {}^{[8]}(X_{\text{Ca}})^3 \cdot {}^{[6]}(X_{\text{Al}})^2 \cdot {}^{[4]}(X_{\text{Si}})^3$$

where the atomic proportions are given by

$$X_{\text{Ca}} = {}^{[8]}[\text{Ca}/(\text{Ca} + \text{Mg} + \text{Fe}^{2+} + \text{Mn})]$$
$$X_{\text{Al}} = {}^{[6]}[\text{Al}/(\text{Al} + \text{Cr}^{3+} + \text{Fe}^{3+})]$$
$$X_{\text{Si}} = {}^{[4]}[\text{Si}/(\text{Si} + \text{Al} + \text{Fe}^{3+})]$$

a similar expression for X_{Py} will result. However, mixing in the tetrahedral site can be disregarded because it is almost entirely occupied by Si.

The structural formula of a clinopyroxene in which Fe-Mg random mixing occurs between M1 and M2 sites can be expressed as

$$(\text{Na,Ca,Mn,Mg,Fe}^{2+})^{\text{M2}}(\text{Mg,Fe}^{2+},$$
$$\text{Al,Cr,Fe}^{3+},\text{Ti})^{\text{M1}\,[4]}(\text{Fe}^{3+},\text{Al,Si})_2\text{O}_6.$$

For such a clinopyroxene where random mixing occurs on all the three sites, we obtain (Powell, 1977)

$$X_{\text{Di}} = (X_{\text{Ca}})^{\text{M2}} \cdot (X_{\text{Mg}})^{\text{M1}} \cdot {}^{[4]}(X_{\text{Si}})^2$$

and

$$X_{\text{CaTs}} = 4(X_{\text{Ca}})^{\text{M2}} \cdot (X_{\text{Al}})^{\text{M1}} \cdot {}^{[4]}(X_{\text{Al}}) \cdot {}^{[4]}(X_{\text{Si}}).$$

A two-site clinopyroxene model (i.e., where random mixing occurs over the M1 and M2 sites) is the most popular one (Wood and Banno, 1973) as it has been satisfactorily used in various thermobarometric calculations (e.g., Perkins and Newton, 1980). However, corrections must be made for the effects of other cations in a complex natural clinopyroxene. The following method is adopted in calculating the thermodynamic mole fractions of diopside and Ca-Tschermak components.

In Na-bearing clinopyroxenes, estimation of Fe^{3+} is critically important since Na in the M2 site can be balanced by either Fe^{3+} or Al^{M1}, or by both. In all the calculations, where Fe^{3+} was not given by wet chemical analyses, Fe^{3+} was first calculated from the microprobe data after the method described by Rayburn et al. (1976), and site occupancies of various cations were calculated according to the procedure given by Wood and Banno (1973) and Wood (1979). Thus, the following hypothetical or real end-members were calculated: $\text{NaAlSi}_2\text{O}_6$, $(\text{NaK})(\text{Fe}^{3+}\text{Cr})\text{Si}_2\text{O}_6$, $\text{Ca}(\text{Fe}^{3+}\text{Cr})_2\text{SiO}_6$, $\text{CaTiAl}_2\text{O}_6$, $\text{CaMgSi}_2\text{O}_6$, $\text{CaAl}_2\text{SiO}_6$, $\text{Fe}_2\text{Si}_2\text{O}_6$, and $\text{Mg}_2\text{Si}_2\text{O}_6$.

If $\text{Na} + \text{K} < \text{Fe}^{3+} + \text{Cr}$, then

$$X_{\text{CaTs}} = \frac{\text{Al}_{\text{tot}} - 2\text{Ti}}{2}; \qquad X_{\text{Jadeite}} = 0.0.$$

Otherwise,

$$X_{\text{CaTs}} = \frac{\text{Al}_{\text{tot}} - 2\text{Ti} - (\text{Na} + \text{K} - \text{Fe}^{3+} - \text{Cr})}{2};$$

$$X_{\text{Jadeite}} = \text{Na} + \text{K} - \text{Fe}^{3+} - \text{Cr}.$$

However, if Na + K > Σ R^{3+}, or if X_{CaTs} in the above formulation is negative, then the method presented here will not work. However, for all the natural samples tested here (see below), such a case was not found and the method was applied safely. It should also be noted that, in some cases, Fe^{3+} estimation from microprobe analyses may be risky. In such cases also, the above procedure can be applied safely; in those cases, (1) the chance of formation of jadeite component increases, (2) a T estimate from the Ellis-Green geothermometer is high, and (3) for the preceding two reasons, the P estimate becomes higher (see Table 4, discussed later). Nevertheless, in the above approach, the effect of $CaFe^{3+}$-Tschermak component (formed only if Na + K < Fe^{3+} + Cr) and CaTi-Tschermak component should be considered in calculating the site occupancy of Ca in the M2 site. Thus, $X_{Ca}^{M2} = Ca_{tot} - (Fe^{3+} + Cr - Na - K) - Ti$; $X_{Al}^{M1} = X_{Jadeite} + X_{CaTs}$. Finally, thermodynamic mole fractions were calculated according to Equation 32.

Garnet solid solutions can be adequately modeled as a single site $(Ca,Mg,Fe)_3Al_2Si_3O_{12}$ solution (since Mn is a negligible component in the natural garnet clinopyroxenite assemblages). Recent advances in the thermochemistry of the garnet solid solution strongly indicate that Ca-Mg-Fe garnet should be modeled as a subregular solution. The interaction parameters along the three binary joins, given by various authors, are noted in Table 3.

Helffrich and Wood (1989) claimed to present the correct generalization for deriving the activity coefficients from binary and ternary interaction parameters for an n-component subregular solution. They also argued that all other formulations are incorrect. For a ternary subregular garnet solid solution, their formulation yields

$$\begin{aligned}
&3RT \ln \gamma_1 \\
&= 0.5W_{12}X_2[1 - X_1 + X_2 + 2X_1(X_1 - X_2 - 1)] \\
&\quad + 0.5W_{21}X_2[1 - X_1 - X_2 - 2X_1(X_1 - X_2 - 1)] \\
&\quad + 0.5W_{13}X_3[1 - X_1 + X_3 + 2X_1(X_1 - X_3 - 1)] \\
&\quad + 0.5W_{31}X_3[1 - X_1 - X_3 - 2X_1(X_1 - X_3 - 1)] \\
&\quad + W_{23}X_2X_3(X_2 - X_3 - 0.5) \\
&\quad + W_{32}X_3X_2(X_3 - X_2 - 0.5) \\
&\quad + W_{123}X_2X_3(1 - 2X_1) \qquad (41)
\end{aligned}$$

$$\begin{aligned}
&3RT \ln \gamma_2 \\
&= 0.5W_{21}X_1[1 - X_2 + X_1 + 2X_2(X_2 - X_1 - 1)] \\
&\quad + 0.5W_{12}X_1[1 - X_2 - X_1 - 2X_2(X_2 - X_1 - 1)] \\
&\quad + 0.5W_{23}X_3[1 - X_2 + X_3 + 2X_2(X_2 - X_3 - 1)] \\
&\quad + 0.5W_{32}X_3[1 - X_2 - X_3 - 2X_2(X_2 - X_3 - 1)] \\
&\quad + W_{13}X_1X_3(X_1 - X_3 - 0.5) \\
&\quad + W_{31}X_3X_1(X_3 - X_1 - 0.5) \\
&\quad + W_{123}X_1X_3(1 - 2X_2) \qquad (42)
\end{aligned}$$

where the subscripts 1 = Gr(Ca), 2 = Py(Mg), and 3 = Alm(Fe), and W_{123} refers to a ternary interaction parameter. The binary interaction parameter, W_{ij}, is obtained from the relationship: $W_{ij} = W_{ij}^H - TW_{ij}^S$. Although Berman (1990) presented a compact set of binary interaction parameters that seem to be internally consistent, those parameters may not be used with the above formulations since Berman (1990) used a different set of mixing equations (which are not equivalent to those presented by Helffrich and Wood, 1989) to extract the binary parameters. With this difficulty in mind, it seems reasonable to use those binary interaction parameters that were derived by some independent means for using in higher order formulations (e.g., those derived by Haselton and Newton, 1980; Koziol, 1990) but are also internally consistent. Thus, the following choices were made for the reasons given below and seemed to produce meaningful results:

1. Ca-Mg binary: the model of Wood (1988) was used. The asymmetric enthalpy parameters, derived from reversed and displaced phase equilibrium measurements, are in quite good agreement with those derived from solution calorimetry (Newton et al., 1977) and the derived asymmetric entropy parameters are based on measurements of entropy (Haselton and Westrum, 1980) and the excess-volume vs. excess-entropy relationship.

2. Fe-Mg binary: the model of Hackler and Wood (1989) was applied. The asymmetric enthalpy parameters (assuming $W^S = 0$) of Ganguly and Saxena (1984) and Geiger et al. (1987) do not fit experimental data on Fe-Mg partitioning between garnet and orthopyroxene as well as between garnet and olivine. Hackler and Wood's data were obtained by reversed Fe-Mg partitioning values (with olivine) over a wide range of Mg-Fe ratios, and this factor alone should be a sound basis for selecting their parameters.

3. Fe-Ca binary: the model of Koziol (1990) was used. The asymmetric enthalpy parameters, based on reversed and displaced phase-equilibrium measurements, are in good agreement with solution calorimetric data (Geiger et al., 1987).

Although Ganguly and Saxena (1984, 1987) presented the following equation for estimating the ternary interaction parameter, W_{123}

$$\begin{aligned}
W_{123} = [(W_{MgCa} - W_{CaMg}) + (W_{CaFe} - W_{FeCa}) \\
+ (W_{FeMg} - W_{MgFe})]/2
\end{aligned}$$

Helffrich and Wood (1989) showed mathematically that this equation is completely ad hoc and does not provide an unequivocal means for estimating the magnitude of this parameter. In the absence of any other constraint for estimating W_{123}, it was set to zero. Moreover, as pointed out by Helffrich and Wood (1989), an added advantage of their activity formalisms is that these give considerable latitude for setting the ternary interaction parameter to zero. Berman's (1990) formulations, even if they are correct, lead to highly interdependent binary and ternary parameters, and hence they do not allow one to set the ternary interaction parameter to be zero.

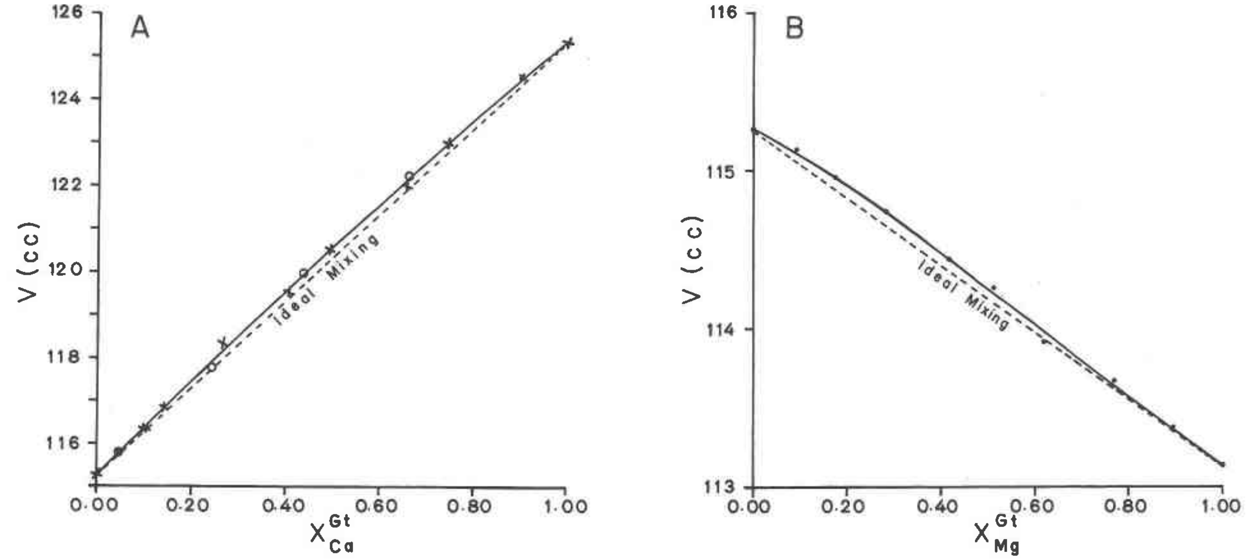

Fig. 6. Variation of molar volumes with compositions along the two binary garnet joins. (A) Alm-Gr binary (crosses = data are from Geiger et al., 1987; open circles = data are from Koziol, 1990). (B) Py-Alm join (data are from Geiger et al., 1987). Solid lines represent the polynomial fitted through the data points.

Multicomponent clinopyroxenes can be modeled as reciprocal two-site solutions as discussed before (i.e., mixing in the tetrahedral site does not contribute to the free energy of mixing either as entropy or as enthalpy). The M2 site, however, becomes a quaternary regular solution of Mg-Fe-Ca-Na and the M1 site becomes a ternary regular solution of Al-Mg-Fe. However, if we disregard all interactions with Na in the M2 site then,

$$\begin{aligned}\mathrm{R}T \ln \gamma_{\mathrm{Di}} = {} & (X_{\mathrm{Fe}}^{\mathrm{M2}})^2 W_{\mathrm{CaFe}} + (X_{\mathrm{Mg}}^{\mathrm{M2}})^2 W_{\mathrm{CaMg}} \\ & + (W_{\mathrm{CaFe}} + W_{\mathrm{CaMg}} - W_{\mathrm{MgFeM2}}) X_{\mathrm{Mg}}^{\mathrm{M2}} X_{\mathrm{Fe}}^{\mathrm{M2}} \\ & + (X_{\mathrm{Fe}}^{\mathrm{M1}})^2 W_{\mathrm{MgFeM1}} + (X_{\mathrm{Al}}^{\mathrm{M1}})^2 W_{\mathrm{MgAl}} \\ & + (W_{\mathrm{MgFeM1}} + W_{\mathrm{MgAl}} - W_{\mathrm{AlFe}}) \\ & \cdot X_{\mathrm{Al}}^{\mathrm{M1}} X_{\mathrm{Fe}}^{\mathrm{M1}} + G_r^0 \qquad (44)\end{aligned}$$

$$\begin{aligned}\mathrm{R}T \ln \gamma_{\mathrm{CaTs}} = {} & (X_{\mathrm{Fe}}^{\mathrm{M2}})^2 W_{\mathrm{CaFe}} + (X_{\mathrm{Mg}}^{\mathrm{M2}})^2 W_{\mathrm{CaMg}} \\ & + (W_{\mathrm{CaFe}} + W_{\mathrm{CaMg}} - W_{\mathrm{MgFeM2}}) X_{\mathrm{Mg}}^{\mathrm{M2}} X_{\mathrm{Fe}}^{\mathrm{M2}} \\ & + (X_{\mathrm{Mg}}^{\mathrm{M1}})^2 W_{\mathrm{MgAl}} + (X_{\mathrm{Fe}}^{\mathrm{M1}})^2 W_{\mathrm{FeAl}} \\ & + (W_{\mathrm{FeAl}} + W_{\mathrm{MgAl}} - W_{\mathrm{MgFeM1}}) \\ & \cdot X_{\mathrm{Mg}}^{\mathrm{M1}} X_{\mathrm{Fe}}^{\mathrm{M1}} + G_r^0 \qquad (45)\end{aligned}$$

where G_r^0 represents the standard free energy change of the reciprocal equilibria for a two-site solution (Wood and Nicholls, 1978). All the interaction parameters for the reciprocal equilibria and the reciprocal terms that are added to the above site-terms are derived and given in Appendix 1. The binary interaction parameters for both the M2 and M1 sites are adapted from Wood (1987).

The partial molar volume change is computed as follows. The partial molar volumes of grossular and pyrope along the pyrope-grossular join are computed from Equation 19. Geiger et al. (1987) and Koziol (1990) provided volume data across the Alm-Gr join. Their data (Fig. 6A) can be fitted by a symmetric model (contrary to the proposition of Berman, 1990). The quadratic function, expressing volume along this join, is given by

$$V^{\mathrm{Gt}} = 115.282 + 10.96 X_{\mathrm{Gr}}^{\mathrm{Gt}} + 0.89 (X_{\mathrm{Gr}}^{\mathrm{Gt}})^2. \qquad (46)$$

Partial molar volume of grossular along the Gr-Alm join is calculated from Equation 46 and a proportional average of V_{Gr} along the Gr-Py and Gr-Alm joins is taken to represent V_{Gr} in the ternary (Ca,Mg,Fe)-garnet solid solution. The volume data of Geiger et al. (1987, Fig. 6B) along the Py-Alm join can be approximated by a third-degree polynomial given by

$$\begin{aligned}V^{\mathrm{Gt}} = {} & 115.26 + 1.5416 X_{\mathrm{Py}}^{\mathrm{Gt}} - 1.3315 (X_{\mathrm{Py}}^{\mathrm{Gt}})^2 \\ & + 0.7549 (X_{\mathrm{Py}}^{\mathrm{Gt}})^3. \qquad (47)\end{aligned}$$

Partial molar volume of Py along the Py-Alm join is obtained from Equation 47 and a proportional average of the partial molar volumes across the Py-Gr and Py-Alm joins was used to represent V_{Py} in the ternary (Ca,Mg,Fe)-garnet solid solution. The partial molar volumes of Di and CaTs were computed from Equations 23, 24, and 25 after calculating the molecular fraction of diopside, enstatite, and CaTs components in the way described above and after normalizing those components to 1.

Wood (1976) equilibrated multicomponent garnet and clinopyroxene in the range of 1100–1400 °C and 20–45 kbar, and he determined the compositions of the coex-

TABLE 4. Results of *P-T* estimations

Sample no.	*T* (°C)	*P* (kbar)	Notes
Delegate xenoliths, southeast Australia			
R392	1038	16	Wet chemical analysis; Fe^{3+} determined
392	1002	16	Fe^{3+} determined
113	1249	30	Fe^{3+} determined
117	1087	18	Fe^{3+} determined
396	1063	18	Fe^{3+} determined
11	1117	17	Fe^{3+} determined
829	1314	24	Microprobe analysis; $Fe^{2+} = Fe_{tot}$
	(669)	(8)	If Fe^{3+} is estimated from stoichiometry
834	1229	19	Microprobe analysis; $Fe^{2+} = Fe_{tot}$
	(775)	(10)	If Fe^{3+} is estimated from stoichiometry
Mt. Carmel xenoliths, Israel			
UNC-12	940	15	Microprobe analysis; $Fe^{2+} = Fe_{tot}$
UNC-21	1057	19	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(1417)	(35)	If $Fe^{2+} = Fe_{tot}$
UNC-48	905	13	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(1270)	(29)	If $Fe^{2+} = Fe_{tot}$
UNC-54	909	12	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(1206)	(27)	If $Fe^{2+} = Fe_{tot}$
MC-373	1139	21	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(1357)	(30)	If $Fe^{2+} = Fe_{tot}$
UNC-60	1016	19	Microprobe analysis; $Fe^{2+} = Fe_{tot}$
Camp Creek xenoliths, Arizona			
7501	873	9	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(979)	(11)	If $Fe^{2+} = Fe_{tot}$
7502	950	23	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(972)	(25)	If $Fe^{2+} = Fe_{tot}$
7503	733	12	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(1007)	(30)	If $Fe^{2+} = Fe_{tot}$
7541	886	18	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(1021)	(30)	If $Fe^{2+} = Fe_{tot}$
7552	659	10	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(955)	(40)	If $Fe^{2+} = Fe_{tot}$
7514	817	18	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(889)	(30)	If $Fe^{2+} = Fe_{tot}$
7556	747	19	Microprobe analysis; Fe^{3+} estimated from stoichiometry
7520	776	15	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(943)	(34)	If $Fe^{2+} = Fe_{tot}$
7549	649	9	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(988)	(34)	If $Fe^{2+} = Fe_{tot}$
Garnet clinopyroxenite xenolith from the minette diatreme, Colorado Plateau			
	858	13	$Fe^{2+} = Fe_{tot}$
Garnet clinopyroxenites of Bohemian massif, Austria			
1847	1097	29	Microprobe analysis; $Fe^{3+} = Fe_{tot}$
851(Core garnet)	1023	20	Microprobe analysis; $Fe^{3+} = Fe_{tot}$
851(Rim garnet)	864	10	Rim of the garnent is retrogressed (see reference)
852	1174	29	Microprobe analysis; $Fe^{3+} = Fe_{tot}$
853(Core garnet)	1106	24	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(1208)	(26)	If $Fe^{2+} = Fe_{tot}$
853(Rim garnet)	861	14	Rim is retrogressed (see reference)
ME	817	12	This also possibly represents retrogressed sample
	(896)	(14)	If $Fe^{2+} = Fe_{tot}$
MI	1044	21	Microprobe analysis; Fe^{3+} estimated from stoichiometry
	(1247)	(29)	If $Fe^{2+} = Fe_{tot}$
Sittampundi garnet clinopyroxenite			
	787	6	Wet chemical analysis; Fe^{3+} determined
South Harris garnet clinopyroxenite			
	860	8	Wet chemical analysis; Fe^{3+} determined

isting garnet and clinopyroxene in each of the experiments (note that in spite of the availability of the experimental data on the garnet + clinopyroxene two-phase assemblages, no other raw data on the compositions are available in the literature). Wood's data are used to test the validity of the model presented above. Figure 7 shows the *P-T* curve for each of the experiments, calculated according to the method presented here. In this figure, the experimental *P-T* conditions, reported by Wood (1976), are also shown. It can be seen from Figure 7 that the present method yields *P-T* conditions from the compositional data within reasonable limits (±3 kbar) of the experimental values. Given the uncertainties in the determination of the *P-T* and, most importantly, the compositional characteristics of the phases, and the uncertainties in attainment of equilibrium in subsolidus

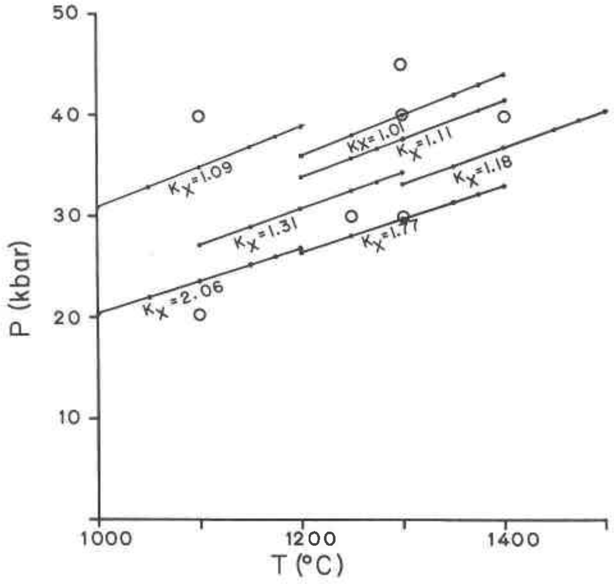

Fig. 7. *P-T* diagram for the garnet + clinopyroxene assemblages, calculated from the compositional data given by Wood (1976). For each experiment, *P* was calculated at six different temperatures around the value of the experimental *T*. The experimental values of *P* and *T* are shown by open circles. For each experiment, the value of K_X is given.

experiments, it can be argued that the present theoretical calculation is quite successful in reproducing the experimental observation.

Summary

The numerical geobarometric expression, based on a linear regression analysis of Equation 40, is

$$P = \Delta V_r^{-1} \cdot (-28201.122 + 37.35T + \mathrm{R}T \ln \mathrm{K}_X + \mathrm{R}T \ln \mathrm{K}_\gamma) \quad (48)$$

where P is in bars, T is in K, and R = 8.3147J. The ΔV_r (Eq. 48) should be calculated in J/bar according to the procedure described above. Procedures for formulations of K_X and K_γ are given above. The solution, however, is still approximate since compositional variations in all directions were not considered. Moreover, the models of major compositional variations that are considered here may yet be modified with more refined data on the mixing behavior of the solid solutions. The above formulation gives the flexibility of incorporating any such modifications.

APPLICATION TO NATURAL GARNET CLINOPYROXENITE ASSEMBLAGES

The geobarometric method described above is applicable to low-Na clinopyroxenes since, in the above formulations, some octahedral alumina should be available for the formation of the CaTs component. Eclogitic clinopyroxenes, on the other hand, are high-Na clinopyroxenes. However, an important class of garnet clinopyroxenites, which are often misrepresented as eclogites, contain low-Na clinopyroxenes. The geobarometric method outlined above is applied to this class of garnet clinopyroxenites in order to decipher their *P-T* conditions of equilibration.

Eclogite xenoliths in kimberlites have been the subject of numerous investigations. Similar xenoliths containing garnet + clinopyroxene have also been reported from continental, nonkimberlitic volcanic hosts by various authors in recent years. A general consensus, however, has not yet emerged regarding the nomenclature and genesis of these latter varieties of xenoliths. Some eclogite xenoliths found in kimberlitic hosts resemble metamorphic eclogites (e.g., see Helmstaedt and Doig, 1975) exposed on the surface (group B and group C). However, most of the kimberlite-hosted eclogite xenoliths are clearly group A eclogites, as they were originally classified by Coleman et al. (1965). Interestingly, xenoliths containing garnet + clinopyroxene (± orthopyroxene ± plagioclase ± amphibole) that are commonly found in continental volcanics resemble none of group A, B, or C eclogites. Rather, they resemble both a granulite-facies eclogitic assemblage, as well as a high-pressure magmatic eclogitic assemblage. This point is illustrated below.

Classification of garnet + clinopyroxenite assemblages

Various authors have termed the xenoliths containing garnet + clinopyroxene as either garnet clinopyroxenites or eclogites without suggesting a clear distinction between these two terms. Several authors have also described the occurrence of both garnet clinopyroxenites and eclogites from the same host without making any quantitative distinction of phase compositions between the two types (e.g., Schulze and Helmstaedt, 1979; Esperanca and Holloway, 1984; Dodge et al., 1988). Attempts have also been made to classify those xenoliths containing garnet + clinopyroxene as group A, B, or C eclogites based on the garnet compositions. However, it should be remembered that eclogites were originally defined as rocks having omphacitic clinopyroxene and garnet. Coleman et al. (1965) classified such eclogites into three groups on the basis of garnet composition. Thus, the distinction between eclogites and garnet clinopyroxenites should be made on the basis of clinopyroxene composition. When the compositions of clinopyroxenes alone are taken into account, the differentiation between garnet clinopyroxenites and eclogites becomes unambiguous. Further subdivision of eclogites into group A, B, and C on the basis of garnet composition then becomes meaningful.

It is difficult to map complex pyroxene compositions from a multidimensional composition space onto a two-dimensional projection to show the distinctions firmly. Two diagrams, one proposed by Morimoto et al. (1988) and the other proposed by Aoki and Shiba (1973), serve our purpose.

Q-J diagram. Figure 8 is a geometrical representation of clinopyroxene composition for several varieties of eclogites and garnet clinopyroxenites after the method of Morimoto et al. (1988). Q is a measure of the quadrilateral components in clinopyroxene and J is a measure of the nonquadrilateral components. Plotted points include representative clinopyroxene compositions from Franciscan eclogites (Coleman et al., 1965; Essene and Fyfe, 1967; Brown and Bradshaw, 1979), Norwegian eclogites (Krogh, 1982; Jamtveit, 1987), and Roberts Victor eclogite xenoliths (Kushiro and Aoki, 1968; Hatton and Gurney, 1977; Bishop et al., 1978). These three are typical examples of group C (blueschist-facies), group B (amphibolite-facies), and group A (xenoliths in kimberlites) eclogites, respectively. Clinopyroxene compositions from nonkimberlite-hosted xenoliths of garnet clinopyroxenite include those from Mt. Carmel, Israel (Esperanca and Garfunkel, 1986; Mittelfehldt, 1986); Delegate breccia pipe, southeast Australia (Lovering and White, 1969); Chino Valley, Arizona (Arculus and Smith, 1979; Schulze and Helmstaedt, 1979); Camp Creek, Arizona (Esperanca and Holloway, 1984); and minette diatreme of Navajo volcanic field, Colorado Plateau (Ehrenberg and Griffin, 1979). To show the distinction in composition between clinopyroxenes of garnet clinopyroxenites found in nonkimberlitic hosts and those of eclogites in kimberlitic hosts, data from some kimberlite-borne eclogitic xenoliths from the Colorado Plateau (Alter et al., 1984; Helmstaedt and Schulze, 1979) are also plotted on this diagram. Two other types of clinopyroxene compositions, designated as granulite-facies garnet clinopyroxenites and high pressure experiments, are also plotted. The garnet clinopyroxenites from the granulite facies include: one garnet clinopyroxenite of the Sittampundi igneous complex of south India (Chappel and White, 1970); one assemblage from South Harris, Scotland (Livingstone, 1967); and six assemblages from the Bohemian massif of Austria (Scharbert and Carswell, 1983). No other data on garnet clinopyroxenite from granulite-facies terrains were found in the literature. The high-pressure experiments include data on clinopyroxenes coprecipitated with garnet from a melt (Bultitude and Green, 1971).

$^{[4]}$Al-$^{[6]}$Al diagram. The same set of compositional data for clinopyroxene is plotted in Figure 9 on a diagram of $^{[4]}$Al (a measure of Ca-Tschermak component) vs. $^{[6]}$Al (a measure of jadeite component) in the clinopyroxenes.

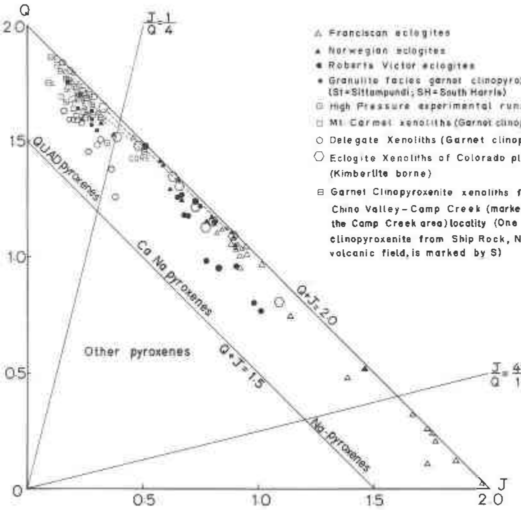

Fig. 8. Q (= Ca + Mn + Mg + Fe^{2+}) − J (= 2Na) diagram for clinopyroxenes in various assemblages containing garnet + clinopyroxene (for sources see text). The core and rim compositions joined by a dashed line represent core and rim of a clinopyroxene in a garnet clinopyroxenite xenolith from Chino Valley (Schulze and Helmstaedt, 1979). Two Colorado Plateau eclogite xenoliths, joined by a dashed line (with an arrow) represent a garnet clinopyroxenite–eclogite transitional xenolith (Helmstaedt and Schulze, 1979) from Moses Rock kimberlite diatreme.

From these pyroxene composition diagrams, the following points emerge. (1) Xenolithic clinopyroxenes, which are truly eclogitic by their omphacitic composition, are not discriminated from clinopyroxenes of undoubted metamorphic eclogites (group B and C). Thus, all eclogitic clinopyroxenes lie in the Ca-Na and Na pyroxene fields. The garnet clinopyroxenite xenoliths, many of which were formerly described as eclogites, and most of which are found in nonkimberlitic hosts, are characterized by enrichment in quadrilateral and Tschermak components. The pyroxene in garnet clinopyroxenites is thus clearly discriminated from eclogitic clinopyroxene in the Q-J and $^{[4]}$Al-$^{[6]}$Al diagrams. (2) The xenoliths containing garnet + clinopyroxene in kimberlites are truly eclogites in having sodic clinopyroxene, but the xenoliths containing garnet + clinopyroxene in nonkimberlitic hosts should be properly called garnet clinopyroxenites. The clinopyroxene in garnet pyroxenites shows similarity to that from the granulite-facies garnet clinopyroxenites and high-pressure magmatic garnet clinopyroxenites (Figs. 8 and 9). (3) Attempts to classify the garnet clinopyroxenite xenoliths into true eclogites and garnet clinopyroxenites on the basis of garnet compositions are therefore unsatisfactory. Compositions of garnet may or may not fall into any one of the fields of group A, B, or C eclogites (not shown here).

As pointed out at the beginning, several authors have described the occurrence of both garnet clinopyroxenite and eclogite xenoliths from the same host volcanic without making sharp distinctions between the two on the basis of mineral chemistry. Examples include those described by Dodge et al. (1988) from Big Creek, Esperanca and Holloway (1984) from Camp Creek, and Schulze and Helmstaedt (1979) from Chino Valley (Arculus and Smith, 1979, however, described all xenoliths containing garnet + clinopyroxene from Chino Valley as eclogites). Considering Figures 8 and 9, it appears appropriate to refer to all these xenoliths as garnet clinopyroxenites. Mukhopadhyay (1989), using similar arguments, showed that

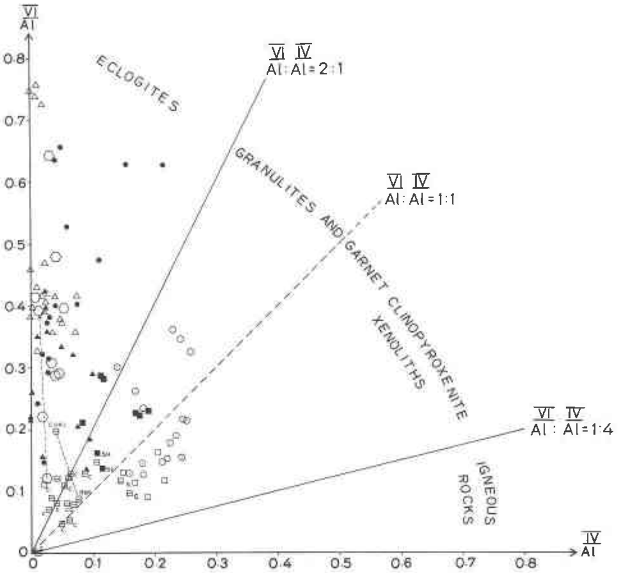

Fig. 9. $^{[4]}$Al (= 2 − Si) vs. $^{[6]}$Al (= Al_{tot} − $^{[4]}$Al) of the clinopyroxenes shown in Figure 8. The various fields are marked after Aoki and Shiba (1973). The symbols are the same as in Figure 8.

none of the xenoliths containing garnet + clinopyroxene from Big Creek are truly eclogitic.

Application of garnet-clinopyroxene geobarometry

Garnet + clinopyroxenite assemblages that (1) occur as xenoliths in nonkimberlitic volcanics, (2) formed as high-pressure cumulates from a melt, or (3) occur in granulite-facies environments contain quadrilateral component-rich Tschermakitic clinopyroxene. The garnet-clinopyroxene geobarometer presented above is applied to some of the cases of the above-mentioned occurrences, i.e., specifically excluding eclogitic assemblages (sensu stricto). This was done to avoid the nonideality which must result from Na in the M2 site. A computer program (available from the author upon request) was used to calculate T of these assemblages using the Ellis-Green geothermometric equation at selected pressures, and then the computed temperatures were used to calculate P according to Equation 49. The point of intersection of the two equations in P-T space gives the unique P-T condition of equilibration of a single garnet + clinopyroxene assemblage. The results are shown in Table 4. The effect of Fe^{3+} estimation is also shown in Table 4 for most of the data obtained by microprobe analysis. Note that by either method, the variation of the calculated P values within a single suite of samples (except one or two exotic values due to some other reason) is very minor. Moreover, such calculations, for each of the suites, are consistent with the geological interpretations of the respective suite of rocks by the respective authors. For example, Scharbert and Carswell (1983) interpreted the garnet clinopyroxenites of the Bohemian massif as crystallization products of mafic melts at high pressure (in the upper mantle condition) later retrogressed to the granulite facies condition. The Delegate xenoliths were interpreted by Lovering and White (1969) as subsolidus recrystallization products of basalts in the range of 7–15 kbar and 700–1200 °C. The Mt. Carmel xenoliths were interpreted by Mittlefehldt (1986) as magmatic crystallization products in the range of 20–30 kbar and 1160–1190 °C, while the Camp Creek xenoliths were interpretated by Esperanca and Holloway (1984) to represent lower crustal materials. In any event, the geobarometer presented here provides, for the first time, a quantitative estimation of the wide range of pressure under which the garnet clinopyroxenite xenoliths equilibrated.

ACKNOWLEDGMENTS

This work emerged from a doctoral dissertation presented by the author to The University of Texas at Dallas and was supported by National Science Foundation Grant EAR-841865 (to D.C. Presnall). The final version of the work was completed at the Southern Methodist University and was supported by NSF Grant EAR-8904777 (to M.J. Holdaway). These two grants are gratefully acknowledged. R.G. Berman, J. Ganguly, T. Gasparik, J. Goodge, T. Hoisch, M.J. Holdaway, and D.C. Presnall reviewed the various versions of the manuscript and provided helpful comments and criticisms that resulted in the present version. Detailed discussions with J. Ganguly and a preliminary discussion with B.J. Wood were very helpful. The author is deeply indebted to all of them.

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Manuscript received January 9, 1990
Manuscript accepted January 11, 1991

Appendix 1. Reciprocal equilibria in clinopyroxene solid solution

If interaction of Na in M2 site is neglected (or assumed to be ideal) then activity coefficients of diopside and Ca-Tschermak can be modeled by assuming clinopyroxene as a two-site reciprocal solution of type $(Ca,Mg,Fe)^{M2}(Mg,Fe,Al)^{M1}\,{}^{[4]}(Al,Si)_2O_6$. With this formulation of a two-site model, we can choose to describe the chemical composition of the clinopyroxene in terms of the components, $CaMgSi_2O_6$, $CaFeSi_2O_6$, $CaAlAlSiO_6$, $MgMgSi_2O_6$, and $FeMgSi_2O_6$. In that event, we have the following four reciprocal equilibria involving those five components and the four other possible components, $MgFeSi_2O_6$, $MgAlAlSiO_6$, $FeFeSi_2O_6$, and $FeAlAlSiO_6$ (see Wood and Nicholls, 1978 for such selections).

$$\begin{aligned} &CaAlAlSiO_6 + FeMgSi_2O_6 \\ &\quad = FeAlAlSiO_6 + CaMgSi_2O_6 \qquad \text{(A1)} \end{aligned}$$

$$\begin{aligned} &CaAlAlSiO_6 + MgMgSi_2O_6 \\ &\quad = MgAlAlSiO_6 + CaMgSi_2O_6 \qquad \text{(A2)} \end{aligned}$$

$$\begin{aligned} &CaFeSi_2O_6 + FeMgSi_2O_6 \\ &\quad = FeFeSi_2O_6 + CaMgSi_2O_6 \qquad \text{(A3)} \end{aligned}$$

$$\begin{aligned} &CaFeSi_2O_6 + MgMgSi_2O_6 \\ &\quad = MgFeSi_2O_6 + CaMgSi_2O_6. \qquad \text{(A3)} \end{aligned}$$

The standard free energy change of each of the equilibria can be computed from the standard state data of the components given by Wood (1987) and the following additional relations:

$$\mu^0_{FeAl_2SiO_6} = \mu^0_{FeAl_2O_4} + \mu^0_{SiO_2} \quad \text{and} \quad \mu^0_{FeMgSi_2O_6} = \mu^0_{FeSiO_3} + \mu^0_{MgSiO_3}.$$

Thus, $\Delta G^0_1 = -21$ kJ; $\Delta G^0_2 = -0.31$ kJ; $\Delta G^0_3 = -4.68$ kJ; $\Delta G^0_4 = -5.01$ kJ. The reciprocal terms that are additive to the site terms, given in Equations 44 and 45, are (see Wood and Nicholls, 1978, for such derivations):

$$\begin{aligned} RT \ln \gamma_{CaTs} &= (1 - X^{M1}_{Al})(X^{M2}_{Fe}\Delta G^0_1 + X^{M2}_{Mg}\Delta G^0_2) \\ &\quad - X^{M1}_{Fe}(X^{M2}_{Fe}\Delta G^0_3 + X^{M2}_{Mg}\Delta G^0_4) \\ RT \ln \gamma_{Di} &= -X^{M1}_{Al}(X^{M2}_{Fe}\Delta G^0_1 + X^{M2}_{Mg}\Delta G^0_2) \\ &\quad - X^{M1}_{Fe}(X^{M2}_{Fe}\Delta G^0_3 + X^{M2}_{Mg}\Delta G^0_4). \end{aligned}$$