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Two-pyroxene geothermometer: a model with an approximate solution

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Abstract

Composition of coexisting ortho- and Ca-pyroxene or pigeonite may be used to estimate the temperature of crystallization at low to moderate pressures by solving the equation:

$$RT \ln X^{\mathrm{Cpx}}_{\mathrm{Mg}-M1}\, X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2}\, \gamma^{\mathrm{Cpx}}_{\mathrm{Mg}-M2} = RT \ln a_{\mathrm{Mg-Opx}} - 500 \qquad (16)$$

where R is gas constant, T temperature in °K to be estimated, $X^{\mathrm{Cpx}}_{\mathrm{Mg}-M1}$ the site of occupancy of Mg on the site $M1$ or $M2$ in clinopyroxene (Cpx), γ the $M2$ site activity coefficient and $a_{\mathrm{Mg-Opx}}$ the activity of Mg in orthopyroxene. A non-ideal model for the $M2$ site in both the pyroxenes is used to obtain the activity composition relations. The site occupancy data in orthopyroxene are available in the literature. The site occupancy data in clinopyroxene are obtained by using compositional data on three coexisting pyroxenes by using the condition that in such coexisting pyroxenes the intracrystalline equilibrium constants are simply related. Using the activity–composition data, equation (16) may be solved graphically or by using a computer to match the two sides of the equation at various assumed temperatures. The temperature estimates must be based on an accurate compositional analysis of several samples. It is expected that further work on the solution parameters and determination of site occupancies as a function of temperature and composition will be actively pursued to improve temperature estimates. The proposed geothermometer is recommended as a relative temperature scale to test models of chemical equilibrium and differentiation in metamorphic and igneous rocks.

Introduction

Compositional data on coexisting pyroxenes (Kretz, 1963) indicate that for pyroxene pairs with similar Ca content a distinct difference in the distribution of Fe and Mg must be attributed to a difference of temperature of crystallization. However, concentration of Ca in pyroxenes generally varies with temperature, and mixing of Ca with Fe and Mg is generally non-ideal, which changes the simple correlation between temperature and Fe–Mg distribution. Therefore it is necessary to synthesize the compositional data and recent theoretical results on solution models into a tentative model for geothermometry. Such a model would provide a relative (but at present not absolute) scale of temperature estimate. Its application to a variety of rocks would point to its weaknesses, which could be improved with new compositional, experimental, and theoretical data.

As noted later in the paper, the temperature scale will be relative because of the lack of information on some thermodynamic quantities for the crystalline solutions. For such quantities, numbers inferred on the basis of crystal–chemical information may be used and then improved by trial and error, in an attempt to obtain meaningful estimates of temperatures required by the temperature–composition relationship in a set of experimental or empirical data. However, once the framework of the model for the geothermometer is constructed, the temperature estimates for other rocks are relative to the standard of reference, which is the chosen temperature–composition relationship. In this paper, the compositional data of Ross and Huebner (1975) are used to arrive at the model. The thermodynamic solution parameters could be revised as and when new compositional data are available.

Construction of a model geothermometer requires the knowledge of activity–composition data on the pyroxenes. There are several papers in the literature which discuss solution properties of pyroxenes (more recently by Grover, 1974, and Blander, 1972). A solution model for orthopyroxene based on site occupancy (Fe^{2+} and Mg^{2+} distribution in non-equivalent $M1$ and $M2$ sites) data must take into account the non-ideality of solution on the sites discussed by Saxena and Ghose (1971). Similarly a solution model for Ca-pyroxene must be based on the intracrystalline Fe^{2+}, Mg^{2+}, and Ca^{2+} distribution data, take into account the influence of Ca^{2+} on $M2$ site occupancy, and explain the immiscibility in the Ca–Mg pyroxene. This is not possible without regarding the sites as non-ideal solutions. At present, our understanding of the crystal energetics and its relationship with the macroscopic thermodynamic properties is by no means perfect. However, instead of choosing a purely mathematical formulation of the geothermometer, a thermodynamic formulation based on the theory of regular solution or simple mixtures (Guggenheim, 1967) as applied to the solutions on crystal structural sites is preferred (Saxena, 1973).

By regarding the sites as subphases, the process of the ion-exchange reaction between sites becomes analogous to interphase ion-exchange. One of the problems with this method is of defining two different chemical potentials for one species (on two sites) in a single homogeneous phase (Mueller *et al.*, 1970). The site terms have, therefore, been regarded as 'partial' such as 'partial' activity or site activity as used in this paper. These sites are then two interpenetrating subsystems considered as more or less independent of each other with solutions on the sites. The total energy is divided as if it were an addition of 'partial' energies on the sites. This method is similar to the method of defining partial molal properties of constituents in solution. Thus a site energy property, say Mg–$M1$, is the total response of the crystalline system to the addition of an infinitesimal amount of Mg to $M1$ site when the process is carried out at constant T, P, and other site occupancies. Clearly thermodynamic equilibrium requires that any change, however small, in $M1$ site occupancy must result in redistribution of species. Sites, therefore, cannot be considered separately as macro-phases. The sites, however, may be considered separately for the purpose of assigning 'partial' properties as long as in the final application a site does not appear as an individual phase. Fortunately this is never necessary in petrologic work.

An alternative formulation of activity–composition relation is possible by considering Mg–$M1$ as a distinct species from Mg–$M2$, as discussed by Mueller *et al.* (1970) and Saxena (1973). Orthopyroxene, therefore, may be considered as a solution of four species Mg–$M1$, Mg–$M2$, Fe–$M1$, and Fe–$M2$. The intracrystalline ion-exchange is expressed as a reaction among species as follows:

$$\text{Mg-}M2 + \text{Fe-}M1 \rightleftarrows \text{Mg-}M1 + \text{Fe-}M2$$

If the quaternary solution is a regular solution, the activity coefficient for each species such as Fe–$M1$ may be given by

$$\begin{aligned} RT \ln \gamma_1 = {} & W_{12}X_2^2 + W_{13}X_3^2 + W_{14}X_4^2 \\ & + (W_{12} - W_{23} + W_{13})X_2X_3 \\ & + (W_{13} - W_{34} + W_{14})X_3X_4 \\ & + (W_{12} - W_{24} + W_{14})X_2X_4 \end{aligned}$$

where subscripts 1, 2, 3, and 4 represent the species Fe–$M1$, Mg–$M1$, Fe–$M2$, and Mg–$M2$ respectively, W's the interaction energy, and X's the site occupancies. The number of W's in such a solution is six (disregarding the three possible ternary and one quaternary interaction parameters). A similar treatment of clinopyroxene results in at least nine binary W's. There is no doubt that such constants can be determined if there are extensive site occupancy data on equilibrated pyroxenes. In the present paper the first alternative is used. In some years it is likely that the second alternative could be tested.

The following symbols are adopted

Opx = orthopyroxene, Cpx = clinopyroxene (general symbol for both augite and pigeonite), Pig = Pigeonite, Ca-px = Ca-rich clinopyroxene, X^{α}_{i-M1} = site occupancy of i in site $M1$ in phase α; similarly for $M2$.

$X_{i-\alpha}$ = mole fraction of i in the phase

Thermodynamics

Composition of the pyroxenes may be expressed in terms of the following real or hypothetical end members:

Ca ($M2$) Mg($M1$) Si_2O_6
diopside, 'ortho'diopside, 'ortho'pigeonite

Mg ($M2$) Mg($M1$) Si_2O_6
enstatite, clinoenstatite

Ca ($M2$) Fe($M1$) Si_2O_6
hedenbergite, 'ortho'hedenbergite

Fe ($M2$) Fe($M1$) Si_2O_6
ferrosilite, clinoferrosilite

Chemical equilibrium in coexisting pyroxenes may be discussed in terms of any of the species. Let us consider the following relations:

$$\underset{\text{Opx}}{\mathrm{Mg(MgSi_2O_6)}} \rightleftharpoons \underset{\text{Cpx}}{\mathrm{Mg(MgSi_2O_6)}} \tag{a}$$

$$\underset{\text{Opx}}{\mathrm{Ca(MgSi_2O_6)}} \rightleftharpoons \underset{\text{Cpx}}{\mathrm{Ca(MgSi_2O_6)}} \tag{b}$$

The conditions of equilibrium at a given P and T are

$$\mu_{\mathrm{Mg-Opx}} = \mu_{\mathrm{Mg-Cpx}} \tag{1}$$

$$\mu_{\mathrm{Ca-Opx}} = \mu_{\mathrm{Ca-Cpx}} \tag{2}$$

where the chemical potentials are

$$\mu_{\mathrm{Mg-Opx}} = \overset{0}{\mu}_{\mathrm{Mg-Opx}} \quad \text{(orthoenstatite)} + RT \ln a_{\mathrm{Mg-Opx}} \tag{3}$$

$$\mu_{\mathrm{Mg-Cpx}} = \overset{0}{\mu}_{\mathrm{Mg-Cpx}} \quad \text{(clinoenstatite)} + RT \ln a_{\mathrm{Mg-Cpx}} \tag{4}$$

$$\mu_{\mathrm{Ca-Opx}} = \overset{0}{\mu}_{\mathrm{Ca-Opx}} \quad \text{(orthodiopside)} + RT \ln a_{\mathrm{Ca-Opx}} \tag{5}$$

$$\mu_{\mathrm{Ca-Cpx}} = \overset{0}{\mu}_{\mathrm{Ca-Cpx}} \quad \text{(diopside)} + RT \ln a_{\mathrm{Ca-Cpx}} \tag{6}$$

where a represents activity. Note that although there is some structural difference between diopside and pigeonite, we have to ignore it in the following discussion. We are, however, going to consider the structural difference between clinoenstatite (isostructural with diopside) and enstatite as explained by Saxena and Nehru (1975). Assuming that the two *binary* (Mg–Ca) pyroxenes are simple mixtures (Guggenheim, 1967), by substituting appropriate terms for chemical potentials in (1), we arrive at the equation:

$$RT \ln \frac{X_{\mathrm{Mg-Opx}}}{X_{\mathrm{Mg-Cpx}}} + (1 - X_{\mathrm{Mg-Opx}})^2 W^{\mathrm{Opx}}_{\mathrm{Mg-Ca}} - (1 - X_{\mathrm{Mg-Cpx}})^2 W^{\mathrm{Cpx}}_{\mathrm{Mg-Ca}} = \overset{0}{\mu}_{\mathrm{Mg-Cpx}} - \overset{0}{\mu}_{\mathrm{Mg-Opx}} = \Delta\overset{0}{\mu}_{\mathrm{Mg}} \tag{7}$$

Saxena and Nehru (1975) assumed $\Delta\mu_{\mathrm{Mg}}{}^0$ to be 500 cal/mol and arrived at $W^{\mathrm{Opx}}_{\mathrm{Mg-Ca}} = 7184$ and $W^{\mathrm{Cpx}}_{\mathrm{Mg-Ca}} = 6531$ cal/mol by the analysis of Nehru and Wyllie's (1974) data on the enstatite–diopside solvus.

Note that in reaction (a) the exchange may be regarded as taking place at the $M2$ site. The quantities W's and $\Delta\overset{0}{\mu}_{\mathrm{Mg}}$, therefore, principally reflect the energetic nature of the $M2$ site. A general ternary relation for reaction (a), involving Ca, Mg, and Fe, is as follows:

$$RT \ln \frac{a_{\mathrm{Mg-Cpx}}}{a_{\mathrm{Mg-Opx}}} = -\Delta G^0_a = -500 \tag{8}$$

Writing activities in terms of site occupancies (X's) and site-activity coefficients (γ's) (partial activity-coefficients of Saxena and Ghose, 1971), we have

$$a_{\mathrm{Mg-Cpx}} = a^{\mathrm{Cpx}}_{\mathrm{Mg-}M1} a^{\mathrm{Cpx}}_{\mathrm{Mg-}M2} = X^{\mathrm{Cpx}}_{\mathrm{Mg-}M1} \gamma^{\mathrm{Cpx}}_{\mathrm{Mg-}M1} X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2} \gamma^{\mathrm{Cpx}}_{\mathrm{Mg-}M2} \tag{9}$$

A similar expansion may be made for $a_{\mathrm{Mg-Opx}}$. In the absence of any other information on the solution of species on $M1$ site in clinopyroxene, we use the simplest approximation of ideal solution for the site. By substituting

$$X^{\mathrm{Cpx}}_{\mathrm{Mg-}M1} = (2X_{\mathrm{Mg-Cpx}} - X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}) \tag{10}$$

in equation (9), we have

$$a_{\mathrm{Mg-Cpx}} = (2X_{\mathrm{Mg-Cpx}} - X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}) \cdot (X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}) \gamma^{\mathrm{Cpx}}_{\mathrm{Mg-}M2} \tag{11}$$

Note that $X_{\mathrm{Mg-Cpx}}$ is the mole fraction

$$\frac{\mathrm{Mg}}{\mathrm{Mg + Fe + Ca}}$$

in the mineral, while $X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}$ is the site occupancy on $M2$ site. Thus

$$2X_{\mathrm{Mg-Cpx}} = X^{\mathrm{Cpx}}_{\mathrm{Mg-}M1} + X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}$$

For the site-activity coefficient $\gamma^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}$ we have

$$\gamma^{\mathrm{Cpx}}_{\mathrm{Mg-}M2} = \exp\left[\frac{W^{M2}_{\mathrm{Mg-Fe}}}{RT}(1 - X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}) X^{\mathrm{Cpx}}_{\mathrm{Fe-}M2} + \frac{W^{M2}_{\mathrm{Mg-Ca}}}{RT}(1 - X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}) X^{\mathrm{Cpx}}_{\mathrm{Ca-}M2} - \frac{W_{\mathrm{Fe-Ca}}}{RT} \cdot (1 - X^{\mathrm{Cpx}}_{\mathrm{Ca-}M2} - X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}) X^{\mathrm{Cpx}}_{\mathrm{Ca-}M2}\right] \tag{12}$$

The ternary solution expression has been obtained by combining the three binary solution expressions for simple mixtures as discussed by King (1969) or Saxena (1973).

Substituting in (12) $X^{\mathrm{Cpx}}_{\mathrm{Fe-}M2} = (1 - 2X_{\mathrm{Ca-Cpx}} - X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2})$ and $X^{\mathrm{Cpx}}_{\mathrm{Ca-}M2} = 2X_{\mathrm{Ca-Cpx}}$ (since virtually all Ca is on $M2$ site), we have:

$$\gamma^{\mathrm{Cpx}}_{\mathrm{Mg-}M2} = \exp\left[\frac{W^{M2}_{\mathrm{Mg-Fe}}}{RT}(1 - X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}) \cdot (1 - 2X_{\mathrm{Ca-Cpx}} - X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}) + \frac{2W^{M2}_{\mathrm{Mg-Ca}}}{RT} \cdot (1 - X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}) X_{\mathrm{Ca-Cpx}} - \frac{2W^{M2}_{\mathrm{Fe-Ca}}}{RT} \cdot (1 - 2X_{\mathrm{Ca-Cpx}} - X^{\mathrm{Cpx}}_{\mathrm{Mg-}M2}) X_{\mathrm{Ca-Cpx}}\right] \tag{13}$$

The denominator in equation (8) for activity of Mg in Opx is given by

$$\begin{aligned} a_{\mathrm{Mg-Opx}} &= a^{\mathrm{Opx}}_{\mathrm{Mg}-M1} a^{\mathrm{Opx}}_{\mathrm{Mg}-M2} \\ &= X^{\mathrm{Opx}}_{\mathrm{Mg}-M1}\gamma^{\mathrm{Opx}}_{\mathrm{Mg}-M1} X^{\mathrm{Opx}}_{\mathrm{Mg}-M2}\gamma^{\mathrm{Opx}}_{\mathrm{Mg}-M2} \qquad (14) \end{aligned}$$

where $M1$ and $M2$ are binary and ternary solutions respectively. Using appropriate expressions for γ's for binary and ternary simple mixtures on sites (Saxena, 1973, p. 12 and 24) and equalities of mole fractions and site occupancies are explained above, we have

$$\begin{aligned} a_{\mathrm{Mg-Opx}} = \Big[&(1 - X^{\mathrm{Opx}}_{\mathrm{Fe}-M1}) \exp \left\{\frac{A^{M1}_{\mathrm{Mg-Fe}}}{RT} (X^{\mathrm{Opx}}_{\mathrm{Fe}-M1})^2\right\} \\ &\cdot\{(1 - 2X_{\mathrm{Ca-Opx}} - 2X_{\mathrm{Fe-Opx}} + X^{\mathrm{Opx}}_{\mathrm{Fe}-M1})\} \\ &\cdot \exp \Big\{\frac{A^{M2}_{\mathrm{Fe-Mg}}}{RT} (2X_{\mathrm{Fe-Opx}} - X^{\mathrm{Opx}}_{\mathrm{Fe}-M1}) \\ &\cdot(2X_{\mathrm{Fe-Opx}} - X^{\mathrm{Opx}}_{\mathrm{Fe}-M1} + 2X_{\mathrm{Ca-Opx}}) + \frac{2A^{M2}_{\mathrm{Mg-Ca}}}{RT} \\ &\cdot X_{\mathrm{Ca-Opx}}(2X_{\mathrm{Fe-Opx}} - X^{\mathrm{Opx}}_{\mathrm{Fe}-M1} + 2X_{\mathrm{Ca-Opx}}) \\ &- \frac{2A^{M2}_{\mathrm{Fe-Ca}}}{RT} X_{\mathrm{Ca-Opx}}(2X_{\mathrm{Fe-Opx}} - X^{\mathrm{Opx}}_{\mathrm{Fe}-M1})\Big\}\Big] \qquad (15) \end{aligned}$$

where A's represent the regular solution or simple mixture parameter W for the sites in orthopyroxene.

If all the parameters, W's and A's, and the site occupancies are known as a function of temperature, and the compositions of coexisting phases are known, it is possible to estimate temperature from equation (8) by using any iterative technique. At assumed temperatures, a test for equality of the two sides in the following equation may be made:

$$\begin{aligned} RT \ln X^{\mathrm{Cpx}}_{\mathrm{Mg}-M1} X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2} \gamma^{\mathrm{Cpx}}_{\mathrm{Mg}-M2} \\ = RT \ln a_{\mathrm{Mg-Opx}} - 500 \qquad (16) \end{aligned}$$

where $\gamma^{\mathrm{Cpx}}_{\mathrm{Mg}-M2}$ and $a_{\mathrm{Mg-Opx}}$ are given by equations (13) and (15) respectively. While some information is available on W's, A's and site occupancies in orthopyroxene, the data on site occupancy in calcic pyroxenes are meagre (Hafner *et al.*, 1971; Saxena *et al.*, 1974). We have to approach this problem in another way.

Thermodynamics of three coexisting phases and the site-occupancy in clinopyroxene

Ross and Huebner (1975) presented data on the chemical composition of coexisting ortho- and Ca-pyroxene and pigeonite. These data are in part experimental and in part based on the composition of coexisting phases in nature. The $M2$ site in pigeonite and Ca-pyroxene may be referred energetically to the same standard state ($M2$ in diopside). At equilibrium among the three pyroxenes we have

$$\mu_{\mathrm{Mg-Opx}} = \mu_{\mathrm{Mg-Capx}} = \mu_{\mathrm{Mg-Pig}}$$

representing the reactions

$$\underset{\mathrm{Opx}}{\mathrm{Mg(MgSi_2O_6)}} \rightleftharpoons \underset{\mathrm{Ca\text{-}px}}{\mathrm{Mg(MgSi_2O_6)}} \qquad \text{(a)}$$

$$\underset{\mathrm{Opx}}{\mathrm{Mg(MgSi_2O_6)}} \rightleftharpoons \underset{\mathrm{Pig}}{\mathrm{Mg(MgSi_2O_6)}} \qquad \text{(c)}$$

Next, consider the intracrystalline ion-exchange in clinopyroxene (Ca–px or Pig) as follows:

$$\mathrm{Fe}\text{-}M2 + \mathrm{Mg}\text{-}M1 \rightleftharpoons \mathrm{Mg}\text{-}M2 + \mathrm{Fe}\text{-}M1 \qquad \text{(d)}$$

where $M1$ is assumed as binary ideal solution and $M2$ ternary non-ideal. The equilibrium constant for reaction (d) is given by

$$\begin{aligned} RT \ln K_d = RT& \\ &\cdot \ln \left[\frac{(1-2X_{\mathrm{Mg-Cpx}} + X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2}) X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2}}{(2X_{\mathrm{Mg-Cpx}} - X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2})(1-2X_{\mathrm{Ca-Cpx}} - X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2})}\right] \\ &+ 2X_{\mathrm{Ca-Cpx}}(W^{M2}_{\mathrm{Mg-Ca}} - W^{M2}_{\mathrm{Fe-Ca}}) + [W_{\mathrm{Mg-Fe}} \\ &\cdot(1 - 2X_{\mathrm{Ca-Cpx}} - X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2})(1 - X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2})] \\ &- W_{\mathrm{Mg-Fe}}[X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2}(2X_{\mathrm{Ca-Cpx}} + X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2})] \qquad (17) \end{aligned}$$

where W's are the same quantities as in equation (13). The equation above uses the following relation between mole fraction $X_{i-\mathrm{Cpx}}$ and site occupancy X^{Cpx}_{i-M2}

$$2X_{i-\mathrm{Cpx}} = X^{\mathrm{Cpx}}_{i-M2} + X^{\mathrm{Cpx}}_{i-M1}$$

At a given temperature the equilibrium constant K_{d} should be the same for pigeonite and Ca-pyroxene. K_{d} calculated by using equation (17) is only a function of temperature. If W's and A's are known, equations (13), (15), (16), and (17) may be used to calculate by iteration X^{M2}_{Mg} in pigeonite and X^{M2}_{Mg} in augite, which will result in the same value of K_{d}, and at the same time the X^{M2}_{Mg} will also satisfy equation (16) at the calculated temperature.

The solution parameters

As mentioned before little information is available on W's for the $M2$ site in clinopyroxene. Unless these data are available no estimate of any temperature error can be made. Some probable values of W's may be chosen and tested empirically. The values which are used here and finally adopted are (all values in cal/mol, T in °K):

$$W^{M2}_{\mathrm{Mg-Ca}} = 6531$$

(for details see Saxena and Nehru, 1975)

$$W^{M2}_{\mathrm{Fe-Ca}} = 5200$$

(obtained by trial and error in fitting the equations to the data of Ross and Huebner, 1975).

$$W^{M2}_{\mathrm{Mg-Fe}} = 5218 - 16807\left(\frac{10^3}{T}\right) + 14280\left(\frac{10^3}{T}\right)^2$$

(as above, but it was found necessary to vary it with temperature).

$$A^{M2}_{\mathrm{Fe-Mg}} = \frac{2458 \times 10^3}{T} - 1261 \text{ (Saxena, 1973)}$$

$$A^{M2}_{\mathrm{Mg-Ca}} = 7184 \text{ (Saxena and Nehru, 1975)}$$

$$A^{M2}_{\mathrm{Fe-Ca}} = 5000$$

(assumed, since concentration of Ca is small in orthopyroxene, the effect of this parameter is insignificant)

$$A^{M1}_{\mathrm{Mg-Fe}} = \frac{3525 \times 10^3}{T} - 1667 \text{ (Saxena, 1973)}$$

All the solution parameters listed here should be the subject of future experimental and theoretical study. For the present they can be considered as physically meaningful (*i.e.* with the right sign and order of magnitude), and as long as these are maintained, the relative temperature would be the same.

Ross and Huebner's data are listed in Table 1. A computer program was used to execute the following steps. 1) For a given temperature (900–1250°C) the site occupancy in orthopyroxene was determined by using the expression (Saxena, 1973):

$$\begin{aligned} -4479 + \frac{1948 \times 10^3}{T} &= RT \\ &\cdot \ln\left[\frac{X^{M1}_{\mathrm{Fe-Opx}}(1 - 2X_{\mathrm{Fe-Opx}} + X^{M1}_{\mathrm{Fe-Opx}})}{(2X_{\mathrm{Fe-Opx}} - X^{M1}_{\mathrm{Fe-Opx}})(1 - X^{M1}_{\mathrm{Fe-Opx}})}\right] \\ &+ A^{M1}_{\mathrm{Mg-Fe}}(1 - 2X^{M1}_{\mathrm{Fe-Opx}}) \\ &- A^{M2}_{\mathrm{Mg-Fe}}(1 - 2(2X_{\mathrm{Fe-Opx}} - X^{M1}_{\mathrm{Fe-Opx}}) \end{aligned} \tag{18}$$

2) The right hand side of equation (16) was determined using equation (15) and site occupancy from (18). Note that in equation (16) $M2$ is treated as ternary whereas in equation (18) it is binary. This introduces little error, as concentration of Ca expressed as wollastonite is less than 4 percent.

3) Assuming $W^{M2}_{\mathrm{Fe-Ca}}$ in the range of 4000 to 6000 and $W^{M2}_{\mathrm{Mg-Fe}}$ in the range of 0 to 1000 cal/mol, an attempt was made to find $X^{M2}_{\mathrm{Mg-Ca-px}}$ and $X^{M2}_{\mathrm{Mg-Pig}}$ which would yield the same value of K_d and at the same time satisfy equation (16) with the right hand side value found in step (2).

Results of the computations are presented in Table 2, which shows the combination of the solution parameters and K_d which yields the closest fit to the maximum number of data. The W's and A's presented before and the K_d calculated using the equation:

$$RT \ln K_d = -28456 + 65596\left(\frac{10^3}{T}\right) - 54737\left(\frac{10^3}{T}\right)^2 + 15259\left(\frac{10^3}{T}\right)^3 \tag{19}$$

TABLE 1. Composition of three coexisting pyroxenes for use as a standard

S. No.	T°C	Orthopyroxene			Pigeonite			Ca-pyroxene		
		X_{Ca}	X_{Mg}	X_{Fe}	X_{Ca}	X_{Mg}	X_{Fe}	X_{Ca}	X_{Mg}	X_{Fe}
1	900	No solution								
2	950	.033	.200	.767	.080	.180	.745	.345	.160	.495
3	1000	.035	.305	.660	.085	.280	.637	.345	.245	.410
4	1050	.040	.415	.545	.085	.385	.530	.345	.330	.325
5	1100	.040	.525	.435	.085	.505 (.483)	.430	.350	.405	.245
6	1150	.040	.640	.320	.090	.627 (.590	.320	.350	.470	.180
7	1200	.040	.745	.210	No solution			.350	.530	.110
8	1250	.045	.855	.100	No solution			.350	.585	.065

Composition of the coexisting phases used to obtain approximate solution parameters W's and $-RT \ln K_d$ for determining site occupancy in clinopyroxene (pigeonite and Ca-pyroxene). The data are same as of Ross and Huebner's data except for some pigeonite compositions. The pigeonite composition of Ross and Huebner is shown in brackets for such samples. "No solution" means that no solution could be obtained for compositions close to Ross and Huebner's data.

TABLE 2. Results of the analytical work on Ross and Huebner's data

$T^{o}C$	$-\underline{RT}$ ln $\underline{K}$(Pig)	$-\underline{RT}$ ln $\underline{K}$(Ca-px)	$\underline{X}^{M2}_{Mg-Pig}$	$\underline{X}^{M2}_{Mg-Capx}$	$\underline{T}$(Px-Pig)	$\underline{T}$)Opx-Capx)
900	No solution					
950	3085	3016	.063	.021	955	940
1000	3205	3229	.116	.039	980	985
1050	3616	3616	.188	.063	1060	1060
1100	3955	3914	.252	.091	1120	1115
1150	4107*	4051	.314	.127	1150	1140
1200	4275*	4330	.350	.171	1180	1190
1250	No solution	4583	--	.223	--	1235

*The composition of pigeonites are somewhat different as indicated in Table 1.

yielded results for the maximum number of triplets (950, 1000, 1050°) and for nearly all the pairs of orthopyroxene and Ca-pyroxene. For those cases where an estimate for the orthopyroxene–pigeonite pairs could not be obtained from Ross and Huebner's data, pigeonite compositions which will satisfy our relations have been presented. Such compositions at 1100° and 1150°C are shown in Figure 1 (see also Table 2).

Application of the results

Two-pyroxene geothermometer

The steps in the calculations are as follows: (1) Assume a temperature of crystallization. (2) Calculate $X^{M1}_{\mathrm{Fe-Opx}}$ and other site occupancies using equation (18) (trial and error or an iteration technique is needed). (3) Calculate $a_{\mathrm{Mg-Opx}}$ using equation (15) and obtain right hand side of equation (16). (4) Calculate $X^{\mathrm{Cpx}}_{\mathrm{Mg}-M2}$ from equation (17) using K_{d} from equation (19), $\gamma^{\mathrm{Cpx}}_{\mathrm{Mg}-M2}$ from equation (12) and $a_{\mathrm{Mg-Cpx}}$ and substitute on the left hand side of equation (16). (5) If equation (16) is not satisfied, choose another temperature and continue until the two sides are as close to each other as desired (in the present paper a difference of 10 cal or less was accepted).

Calculation of errors

The *W*'s and *A*'s as used here are crude. However, if these quantities are accepted, a rigid framework is established, controlled by the various relationships, and the results can be used as a model of reference against which theories of equilibrium crystallization and magmatic differentiation can be tested and compared. The only error in the temperature estimate would be due to uncertainty in chemical composition. No definite error limits can be assigned. A change in $X_{\mathrm{Mg-Cpx}}$ by .005 leads to a change of 30°C (Table 3). The magnitude of the error is discouraging. However, as the application of the method to natural assem-

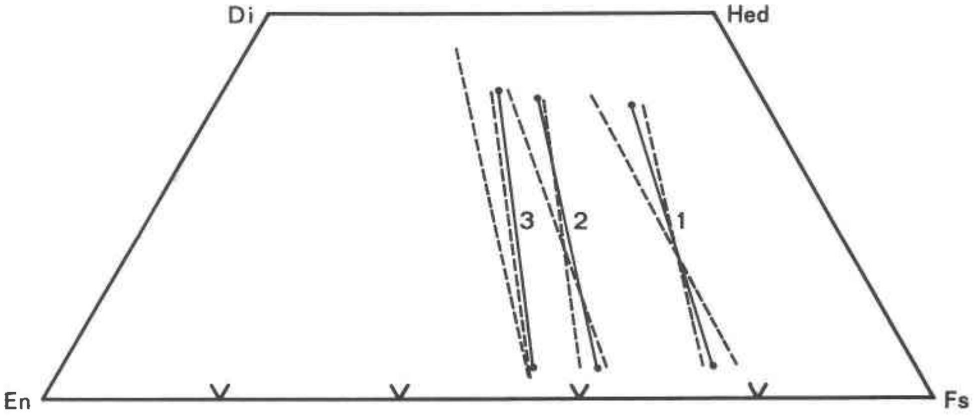

FIG. 1. Tie lines for coexisting pyroxenes between 800° to 825°C. The dashed lines enclose the area in which Lindsley *et al.* (1974) tie lines at 810°C may lie.

TABLE 3. Estimate of errors

S. No.	X_{Ca-Opx}	X_{Fe-Opx}	X_{Ca-Cpx}	X_{Mg-Cpx}	Estimated T°C
7	.040	.210	.350	.520	1130
				.530	1190
				.540	1260
6	.040	.320	.350	.470	1140
				.475	1170

blages in the following section shows, the method is a highly sensitive probe to test chemical equilibrium and crystallization temperature on a relative scale.

Effect of pressure

There is a small but significant pressure effect on the solvus between low pressure (2 to 10 kbar) and high pressure (~30 kbar) (Nehru, 1975). With increasing pressure at a given temperature Ca/(Ca + Mg) decreases slightly. In the pressure range of 1 to 15 kbar, the effect may be disregarded for the present.

Effect of other components

Application of the results of the ternary system to natural assemblages requires a consideration of the effect of components other than Ca^{2+}, Fe^{2+}, and Mg^{2+}. Al^{3+} in particular may be incorporated to significant concentration in pyroxenes at high pressures. The present results apply to systems as close to the ternary system as possible.

Augite and hypersthene at 810°C

Lindsley *et al.* (1974) synthesized coexisting pyroxenes in equilibrium at 810°C and 15 kbar. Figure 1 shows three tie lines for coexisting ortho- and Ca-pyroxene in the temperature range of 800° to 825°C. Lindsley *et al.* plotted five tie lines in their figure (Fig. 2, p. 135) considered to be the best fit. Two of their samples showed a wide range of probable compositions and were not considered here. Two of the tie lines in Figure 1 match very well with their best fit lines. The third tie line is displaced slightly to the right but lies close to their range of possible compositions.

Pyroxene equilibration in chondrites

Bunch and Olsen (1974) recently presented chemical compositions of coexisting pyroxenes in H6, L6, and LL6 chondrites. Estimated temperatures, using Kretz's (1963) and McCallum's (1968) method of Fe/Mg distribution coefficient, were found to be dif-

TABLE 4. Temperature estimate for H6, L6 and LL6 pyroxenes
(Data from Bunch and Olsen, 1974)

	Orthopyroxene			Clinopyroxene		Estimated T°C	
	X_{Ca}	X_{Fe}		X_{Ca}	X_{Fe}		
			H6				
Oakley	.012	.172		.452	.453	990	
Estacado	.010	.163		.465	.477	825	
Guarena	.013	.168		.463	.476	840	
Cedar (Kansas)	.011	.168		.469	.470	785	Average (875)
Cape Girardeau	.012	.170		.450	.482	910	
Seoni	.012	.160		.447	.490	935	
Kernouve	.010	.161		.456	.481	845	
			L6				
Mocs	.015	.209		.457	.466	840	
Colby	.013	.204		.463	.462	825	
Langhalsen	.011	.213		.447	.473	930	
Kyushu	.014	.214		.441	.474	950	
Kyle	.016	.210		.434	.477	970	Average
Bath Furnace	.014	.215		.442	.467	970	(904)
Bruderheim	.013	.202		.449	.467	890	
Modoc	.012	.209		.453	.460	860	
			LL6				
Lake Labyrinth	.021	.248		.443	.455	920	
Dhurmsala	.017	.229		.443	.464	930	
Nas	.015	.255		.449	.447	880	Average
Ottawa	.018	.250		.431	.463	975	(920)
Manbhoom	.015	.253		.445	.447	885	
Ensisheim	.013	.242		.435	.459	935	

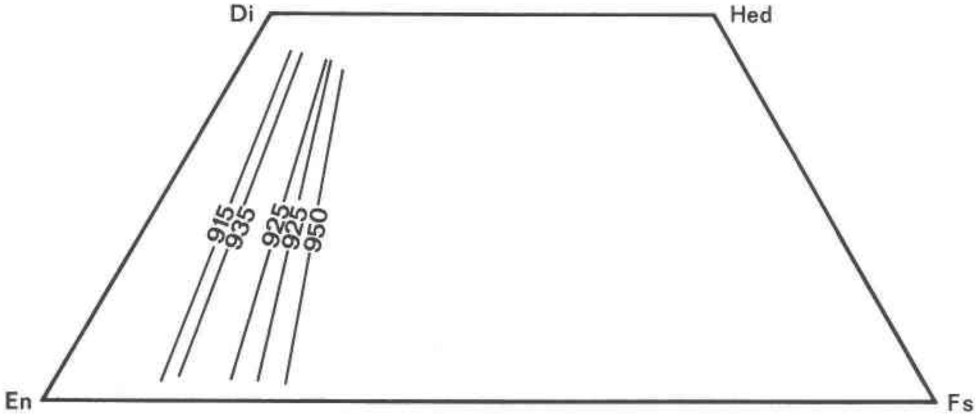

FIG. 2. Estimated temperature of crystallization for Bushveld pyroxenes (data from Atkins, 1969).

ferent for the different groups. In view of the variation in Ca (see Table 4) among the three groups, the differences in K_D could not be unambiguously assigned to differences in temperature of crystallization.

The temperature estimates in Table 4 indicate that the pyroxenes in the different groups equilibrated at somewhat different temperatures. Although Bunch and Olsen (1974) indicate that the chemical analyses are of high accuracy, and we are considering averages over several samples, the temperature differences may not be significant.

Pyroxenes from Bushveld intrusion

Figure 2 shows tie lines with temperature estimates for coexisting pyroxenes in the Bushveld intrusion. These pyroxenes appear to have crystallized in the range of 900° to 950°C (Table 5), which is probably somewhat low. It may be that the intercrystalline ion-exchange continued even after most of the rock solidified under 1000°C, and the pyroxenes represent the temperature of final equilibration. Considering the probable errors in these estimates due to chemical analytical errors in determining compositions, the results in Figure 2 are consistent with a narrow range of crystallization under plutonic conditions.

Coexisting pyroxenes from a pigeonite andesite

Nakamura and Kushiro's (1970) composition of coexisting pyroxenes from Weiselberg andesite and the estimated temperatures are shown in Figure 3. There is a close correspondence in temperature estimate for the hypersthene–augite pair (950°C) and the hypersthene–pigeonite pair (945°C) in Sample 2 (Nakamura and Kushiro's no. 12), indicating an equilibrium crystallization of the three pyroxenes. Sample 4 (original no. 74) contains hypersthene–augite crystallized at similar temperature (940°C). Sample 3 (original no. 69) consists of a disequilibrium assemblage and similarly as would be expected there is no equilibrium between pigeonite rim and hypersthene in sample 1 (original no. 4).

Pyroxenes in charnockites and charnockitic gneisses

The geothermometer was applied to the pyroxene compositions in charnockites from India (Howie, 1955, Leelanandam, 1967) and Varberg, Sweden (Saxena, 1968) and in charnockitic rocks from Uusimaa, Finland (Saxena, 1969). The results are presented in Table 6. The rocks are basic to intermediate in com-

TABLE 5. Estimated temperature of crystallization of pyroxenes in the Bushveld intrusion

S. No.	$\underline{X}_{Ca\text{-}Opx}$	$\underline{X}_{Fe\text{-}Opx}$	$\underline{X}_{Mg\text{-}Cpx}$	$\underline{X}_{Ca\text{-}Cpx}$	Estimated $\underline{T}^{o}C$	Reference
1.	.028	.122	.496	.454	915	Atkins (1969)
2.	.031	.136	.492	.446	935	"
3.	.023	.195	.461	.440	925	"
4.	.028	.195	.469	.439	925	"
5.	.022	.258	.453	.430	950	"

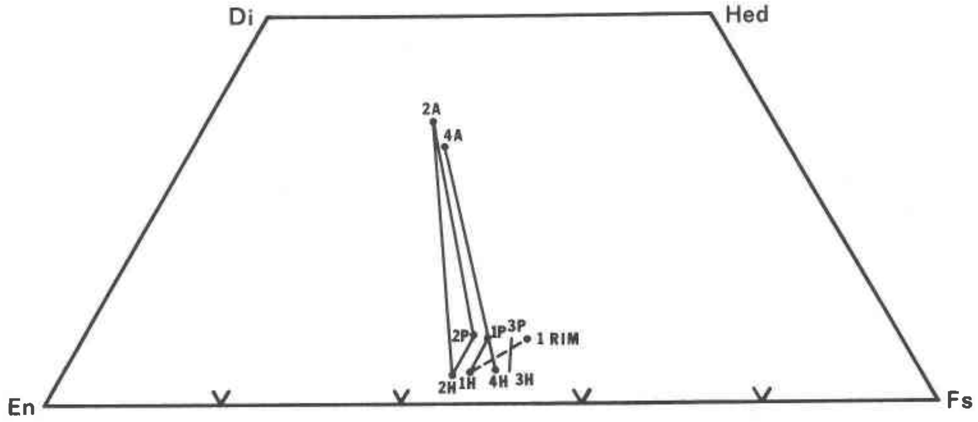

FIG. 3. The pyroxenes in a pigeonite andesite (Nakamura and Kushiro, 1970). The temperatures are 945°–950°C for the triplet (Sample 2) and 940°C for Sample 4. See text for discussion.

position and are commonly associated with migmatite activity. Therefore, the temperatures of crystallization around 800°C are appropriate for these pyroxenes. The charnockite pyroxenes will be reconsidered along with metamorphic pyroxenes at a later date.

Discussion and conclusions

The application of the geothermometer to natural assemblages as discussed in the preceding section leads to temperature estimates which are consistent with the petrologic information. The compositions of coexisting minerals considered cover a broad range of pyroxene compositions but do not cover the very Fe^{2+}-rich part of the pyroxene quadrilateral. The various solution parameters used here are approximate and will be subject to constant revision as more crystal energetic information is made available. In the meantime, the geothermometer proposed here is useful as a relative temperature scale. It is necessary to use accurate compositional data on a number of samples from a small area. The results are most reliable for pyroxenes with a minimum concentration of components other than Ca, Fe, and Mg. Pyroxenes from rocks which formed under very different pressures such as 5 kbar and 30 kbar should not be compared. Study of pyroxenes from various metamorphic and igneous rocks using the geothermometer is under way.

TABLE 6. Temperature of crystallization of pyroxenes in charnockites.

S.No.	$X_{Ca\text{-}Opx}$	$X_{Fe\text{-}Opx}$	$X_{Mg\text{-}Cpx}$	$X_{Ca\text{-}Cpx}$	Estimated T °C	Reference
1.	.020	.590	.260	.420	725	Saxena (1968)
2.	.015	.710	.185	.425	No solution	"
3.	.017	.445	.361	.453	790	" (1969)
4.	.020	.545	.310	.451	770	"
5.	.022	.537	.313	.474	No solution	"
6.	.020	.603	.287	.447	815	"
7.	.021	.570	.268	.454	700	"
8.	.000	.330	.421	.464	800	" (1968)
9.	.021	.608	.287	.438	870	"
10.	.021	.613	.275	.440	810	"
11.	.016	.740	.195	.448	No solution	"
12.	.010	.362	.408	.457	825	Leelanandam (1967)
13.	.012	.423	.377	.462	760	"
14.	.021	.438	.370	.442	865	"
15.	.016	.448	.369	.443	870	"
16.	.013	.490	.351	.453	820	"

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