Enstatite-Diopside Solvus and Geothermometry

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Abstract. The enstatite-diopside solvus presents certain interesting thermodynamic and crystal-structural problems. The solvus may be considered as parts of two solvi one with the ortho-structure and the other with clino-structure. By assuming the standard free energy change for the two reactions $(MgMgSi_2O_6)$opx $\rightleftharpoons (MgMgSi_2O_6)$cpx and $(CaMgSi_2O_6)$opx $\rightleftharpoons$ $(CaMgSi_2O_6)$cpx as 500 and 1000 to 3000 cal/mol respectively, it is possible to calculate the regular solution parameter W for orthopyroxene and clinopyroxene. These W's essentially refer to mixing on M2 sites. The expression for the equilibrium constant by assuming ideal mixing for Fe—Mg, Fe—Ca and non-ideal mixing for Ca—Mg on binary M1 and ternary M2 sites is given by

$$K_a = \frac{X_{\text{Mg-cpx}}^{\text{M1}} X_{\text{Mg-cpx}}^{\text{M2}} \exp\left[\dfrac{W_{\text{cpx}}}{RT}\{X_{\text{Ca-cpx}}^{\text{M2}}(X_{\text{Ca-cpx}}^{\text{M2}}+X_{\text{Fe-cpx}}^{\text{M2}})\}\right]}{X_{\text{Mg-opx}}^{\text{M2}} X_{\text{Mg-opx}}^{\text{M2}} \exp\left[\dfrac{W_{\text{opx}}}{RT}\{X_{\text{Ca-opx}}^{\text{M2}}(X_{\text{Ca-opx}}^{\text{M2}}+X_{\text{Fe-opx}}^{\text{M2}})\}\right]}$$

where X's are site occupancies, R is 1.987 and T is temperature in °K. Temperature of pyroxene crystallization may be estimated by substituting for T in the above equation until the equation $-RT \ln K_a = 500$ is satisfied. The shortcomings of this method are the incomplete standard free energy data on the end member components and the absence of site occupancy data in pyroxenes at high temperatures. The assumed free energy data do, however, show the possible extent of inaccuracy in temperature estimates resulting from the neglect of Mg—Ca non ideality.
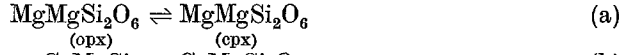
Introduction

Recently Nehru and Wyllie (1974) have determined the orthoenstatite-diopside solvus at 30 kbar. This solvus is based on the compositions of the coexisting phases determined by electron-probe technique. Similarly Warner and Luth (1974) have presented data on the solvus at other pressures. The solvus data on the coexisting phases can be used to advantage in petrogenesis. Petrologists would be inclined to use these data in constructing a geothermometer as proposed by Boyd (1973). The purpose of this paper is to outline the difficulties in the use of the solvus data in petrogenesis, and to present thermodynamic and crystal-structural aspects of the binary and ternary pyroxene crystalline solutions.

Binary Solutions

Diopside-enstatite solvus differs from the halite-sylvite (KCl-NaCl) solvus in one important way. The structure of the pyroxenes on the two limbs are significantly different. This necessitates the use of different standard states. The orthopyroxene end members are orthoenstatite $MgMgSi_2O_6$ and a hypothetical 'orthodiopside'

$CaMgSi_2O_6$. Similarly the clinopyroxenes are clinoenstatite and diopside. The equilibrium between the coexisting phases may be expressed as

$$MgMgSi_2O_6 \rightleftharpoons MgMgSi_2O_6 \qquad (a)$$
$$\text{(opx)} \qquad\qquad \text{(cpx)}$$

$$CaMgSi_2 \rightleftharpoons CaMgSi_2O_6 \qquad (b)$$
$$\text{(opx)} \qquad\quad \text{(cpx)}$$

The conditions of equilibrium at a given P and T are:

$$\mu_{\text{Mg-opx}} = \mu_{\text{Mg-cpx}} \qquad (1)$$

$$\mu_{\text{Ca-opx}} = \mu_{\text{Ca-cpx}} \qquad (2)$$

where the chemical potentials are

$$\mu_{\text{Mg-opx}} = \mu^0{}_{\text{Mg-opx}}(\text{orthoenstatite}) + RT \ln a_{\text{Mg-opx}} \qquad (3)$$

$$\mu_{\text{Mg-cpx}} = \mu^0{}_{\text{Mg-cpx}}(\text{clinoenstatite}) + RT \ln a_{\text{Mg-cpx}} \qquad (4)$$

$$\mu_{\text{ca-opx}} = \mu^0{}_{\text{Ca-opx}}(\text{'orthodiopside'}) + RT \ln a_{\text{Ca-opx}} \qquad (5)$$

$$\mu_{\text{Ca-cpx}} = \mu^0{}_{\text{Ca-cpx}}(\text{diopside}) + RT \ln a_{\text{Ca-cpx}}. \qquad (6)$$

Note that although the chemical formula contains two cations, $(MgMgSi_2O_6)$ one in each M1 and M2 sites, the expression for the chemical potential is written on one cation basis ($RT \ln a$ and not $2 RT \ln a$). This is equivalent to considering the mixing of cations only on M2 site with the end members expressed as $Mg(MgSi_2O_6)$—$Ca(MgSi_2O_6)$.

Even in the two isostructural binary solutions, we must expect large miscibility gaps as shown schematically in Fig. 1. In the two component—two phase system, free energy of mixing (G_M) is minimum at a temperature T_1 with two coexisting structurally different pyroxenes. The curves for G_M at T_1 have been superimposed on the solvus to show the two other possible isostructural solvi. The points a and b show the compositions of the coexisting phases.

Let us assume that the two pyroxenes are Guggenheim's 'simple mixtures' (Saxena, 1973) with the expression for activity coefficient (γ) as:

$$\ln\gamma_i = \frac{W}{RT}(1 - X_i)^2 \qquad (7)$$

where W is an energy parameter and X the mole fraction. For activity we have

$$RT\ln a_i = RT\ln X_i + W(1-X_i)^2. \qquad (8)$$

Substituting for activity in (3) and (4) and the result in (1), we obtain:

$$RT\ln \frac{X_{\text{Mg-opx}}}{X_{\text{Mg-cpx}}} + (1 - X_{\text{Mg-opx}})^2 W_{-\text{opx}} - (1 - X_{\text{Mg-cpx}})^2 W_{-\text{cpx}} = \mu^0{}_{\text{Mg-cpx}} - \mu^0{}_{\text{Mg-opx}}. \qquad (9)$$

Similarly we have

$$RT\ln \frac{X_{\text{Ca-opx}}}{X_{\text{Ca-cpx}}} + (1 - X_{\text{Ca-opx}})^2 W_{-\text{opx}} - (1 - X_{\text{Ca-cpx}})^2 W_{-\text{cpx}}$$

$$= \mu^0{}_{\text{Ca-cpx}} - \mu^0{}_{\text{Ca-opx}}. \qquad (10)$$

Note that we should expect some asymmetry in the two isostructural solvi, which means that a two constant expression for the activity coefficient, such as

the one with Margule's parameters, would be more appropriate. However, we have already too many unknowns for a meaningful solution. The unknowns are the two energy constants W's and the two potential differences on the right hand side of the equations. It would be highly inappropriate to neglect W's and assume the Mg—Ca pyroxenes to be ideal in the present situation. To demonstrate this point, we may calculate W's by assuming certain probable values of the pure potentials (μ^0's) in (9) and (10).

Let us consider the composition of the coexisting phases at 1300°C. At this high temperature the difference between the standard free energy of formation of clino- and ortho-enstatite may not be much and let us assume it to be 500 cal/mol. Unfortunately we cannot be sure about the potential difference between the hypothetical 'orthodiopside' and diopside. The former would be undoubtedly extrinsically very unstable. As an example let this difference vary between 1000 and 3000 cal/mol. Nehru and Wyllie's data at 1300°C and 30 kbar are

$$X_{\text{Ca-opx}} = 0.0612 \qquad X_{\text{Ca-cpx}} = 0.7867$$

$$X_{\text{Mg-opx}} = 0.9388 \qquad X_{\text{Mg-cpx}} = 0.2133.$$

Substituting these values and the assumed potential differences in (9) and (10) and solving for $W_{-\text{opx}}$ and $W_{-\text{cpx}}$, we obtained the values at 1300°C, shown in Table 1. The W's at other temperatures were similarly calculated using Nehru and Wyllie's data.

It may be noted that there is little use of these W's or the activity-composition relations, if we are only interested in using the experimental results on mole-fractions for a direct comparision with the composition of coexisting pyroxenes in natural assemblages. However, natural pyroxenes are rarely binary solutions and the effect of additional components needs to be evaluated. In such evaluations, it is essential that we take into account the non-ideality in the binary system. The estimation of temperature, otherwise, may be merely a mathematical exercise.

It is interesting to note that change in the value ($\mu^0_{\text{Ca-cpx}} - \mu^0_{\text{Ca-opx}}$) does not significantly change the parameter W_{cpx}. The value of W_{opx}, however, does change. Note that since the orthoenstatites or other natural orthopyroxenes contain only little Ca, the uncertainty in W_{opx} is not a serious problem. If it is assumed that $\Delta\mu^0_{\text{Mg}}$ is $+500$ and $\Delta\mu^0_{\text{Ca}} - 2000$, W_{Cpx} and W_{opx} are 6719 and 7131 cal/mol respectively. Let us consider how we may estimate the approximate temperature of crystallization of coexisting pyroxenes. The purpose of the calculations is mainly to demonstrate the effect of non-ideality of Mg—Ca pyroxenes on temperature estimates.

Nehru and Wyllie (1975) following Wood and Banno (1973) arrived at the following equation on the basis of their newly determined solvus:

$$\ln \frac{X_{\text{Mg-cpx}}}{X_{\text{Mg-opx}}} = -\frac{5006}{T} + 1.72 \quad (30 \text{ kbar}) \tag{11}$$

where T is in °K. For non-ideal solutions a comparable equation may be written a

$$RT \ln \frac{X_{\text{Mg-cpx}}}{X_{\text{Mg-opx}}} + (1 - X_{\text{Mg-cpx}})^2 \, W_{\text{cpx}} - (1 - X_{\text{Mg-opx}})^2 \, W_{\text{opx}} = -500 \tag{12}$$

which is applicable over a range of temperature and pressure where G_a^0 does not vary significantly. W_{cpx} and W_{opx} may be determined at each temperature using olvus data as shown for 1 100 to 1 300°C in Table 1. Eq. (12) is the same as

$$+500 = +\Delta G_a^0 = -RT\ln\frac{a_{\text{Mg-cpx}}}{a_{\text{Mg-opx}}}. \tag{13}$$

For strictly binary solutions, it is immaterial which of the two equations is used but Eq. (12) may also be used for ternary solutions as discussed below.

Ternary Solutions

If we do not concern ourselves with orthopyroxenes richer in ferrosilite by more than 50%, we may choose the three components as $Mg(MgSi_2O_6)$, $Fe(MgSi_2O_6)$ and $Ca(MgSi_2O_6)$ with mixing taking place only on M2 site. The standard states would be these end members occurring in clino- and 'ortho'-structures. In order to estimate temperature of crystallization using composition of coexisting pyroxenes, the following information is needed:

1) Activity-composition relations of the three binary systems in ortho- and clino-pyroxenes; or

2) Data on distribution of Fe^{2+}, Mg^{2+}, and Ca^{2+} between the non-equivalent M1 and M2 sites as a function of temperature and

3) 'Partial' activity-composition relations on the two sites in ortho- and clino-structures.

Note that activity of an ion in a pyroxene solution may be expressed as

$$a_{i-\text{px}} = X_{i-\text{M1}} \, X_{i-\text{M2}}.$$

This expression signifies a negative deviation from ideal solution. While at high temperature this is a good approximation for Fe and Mg (Saxena and Ghose, 1971), it is incorrect for Mg and Ca as considered in the previous section.

Some information on points (2) and (3) is available. Virgo and Hafner (1969) found that the distribution of Fe^{2+} and Mg between M1 and M2 in orthopyroxene may be nearly ideal at 1 000°C. This distribution, however, is non-ideal below 1 000°C (Saxena and Ghose, 1971). Saxena, Ghose and Turnock (1973) found that in calcic pyroxenes, the preference of Fe^{2+} in M2 site increases with increasing concentration of Ca. At higher temperatures above 1 000°C, no information is available on the solution of Mg, Fe and Ca on M2 site except what we have discussed about Mg and Ca in the previous section.

At present it may be best to consider an approximate model of the pyroxene solutions. This would not only demonstrate clearly the problems we encounter in pyroxene thermometry, but would encourage the collection of the required additional theoratical and experimental data. In this model in both pyroxenes Fe and Mg mix ideally on M1 sites. M2 is a ternary solution with Ca, Mg and Fe. The mixing of Ca and Mg is non-ideal with W's as 7 184 and 6 531 cal/mol approximately for ortho- and clino-pyroxene respectively. The mixing of Ca and Fe may be assumed as ideal at temperatures above 1 000°C. The following example will demonstrate the use of this model for estimation of temperature.

Chemical composition of coexisting pyroxenes in Netschaevo meteorite, has been determined by Bunch, Keil and Olsen (1970). Clinopyroxene is

Table 1. The interaction energy parameter W

	W_{opx}			W_{cpx}		
$\Delta\mu^0_{Mg}$		$+500$			$+500$	
$\Delta\mu^0_{Ca}$	-1000	-2000	-3000	-1000	-2000	-3000
$1100°$ C	8339.8	7262.32	6185.39	6423.05	6421.22	6420.98
$1200°$ C	8264.03	7159.57	6055.11	6444.23	6453.62	6462.52
$1300°$ C	8266.3	7131.2	5997.03	6726.03	6719.2	6712.3
Average	8289	7184	6079	6531	6531	6531

$(Fe_{0.114}Mg_{0.980}Ca_{0.906})$ Si_2O_6 and orthopyroxene $(Fe_{0.284}Mg_{1.688}Ca_{0.028})Si_2O_6$. We have the following intracrystalline distribution:

$$X^{M1}_{Mg\text{-cpx}}0.896 \qquad X^{M1}_{Mg\text{-opx}}0.856$$

$$X^{M1}_{Fe\text{-cpx}}0.104 \qquad X^{M1}_{Fe\text{-opx}}0.144$$

$$X^{M2}_{Mg\text{-cpx}}0.084 \qquad X^{M2}_{Mg\text{-opx}}0.832$$

$$X^{M2}_{Fe\text{-cpx}}0.010 \qquad X^{M2}_{Fe\text{-opx}}0.140$$

$$X^{M2}_{Ca\text{-cpx}}0.906 \qquad X^{M2}_{Ca\text{-opx}}0.028.$$

The distribution has been made according to the following scheme. All Ca is allotted to M2 site. The remaining of the M2 sites are filled with Fe and Mg in the proportion they occur in the mineral. M1 sites recieve the remaining cations. For activity of Mg in orthopyroxene we have

$$a_{Mg\text{-opx}} = a^{M1}_{Mg\text{-opx}} \, a^{M2}_{Mg\text{-opx}} \qquad (14)$$

$$= X^{M1}_{Mg\text{-opx}} \, X^{M2}_{Mg\text{-opx}} \, \gamma^{M2}_{Mg\text{-opx}} \qquad (15)$$

where, as mentioned before, M1 is a binary ideal solution and M2 ternary non-ideal. The activity coefficient γ is given by

$$RT\ln\gamma^{M2}_{Mg\text{-opx}} = W^{M2}_{Mg\text{-Ca-opx}} X^{M2}_{Ca\text{-opx}}(X^{M2}_{Ca\text{-opx}} + X^{M2}_{Fe\text{-opx}}). \qquad (16)$$

The above expression is obtained by substituting $W_{Mg-Fe\text{-opx}}$ and $W_{Fe-Ca\text{-opx}}$ as zero in the expression for activity coefficient in a ternary solution (see Saxena, 1973). A similar expression may be written for M2 site in clinopyroxene:

$$RT\ln\gamma^{M2}_{Mg\text{-cpx}} = W^{M2}_{Mg-Ca\text{-cpx}} X^{M2}_{Ca\text{-cpx}}(X^{M2}_{Ca\text{-cpx}} + X^{M2}_{Fe\text{-cpx}}). \qquad (17)$$

Finally combining (13), (16) and (17) we may write for the equilibrium condition in reaction (a):

$$+ RT\ln\frac{X^{M1}_{Mg\text{-cpx}} X^{M2}_{Mg\text{-cpx}} \exp\dfrac{W^{M2}_{cpx}}{RT} X^{M2}_{Ca\text{-cpx}}(X^{M2}_{Ca\text{-cpx}} + X^{M2}_{Fe\text{-cpx}})}{X^{M1}_{Mg\text{-opx}} X^{M2}_{Mg\text{-opx}} \exp\dfrac{W^{M2}_{opx}}{RT} X^{M2}_{Ca\text{-opx}}(X^{M2}_{Ca\text{-opx}} + X^{M2}_{Fe\text{-opx}})} = -\Delta G^0_a = -500$$

$$(18)$$

where (Mg—Ca) has been dropped from the subscript for W. For estimation of temperature, we have to use the iteration procedure and continue substituting different values of T, until Eq. (18) is satisfied. For each substitution, we must first obtain the appropriate W's from Table 1 or by calculating from the solvus data using Eqs. (9) and (10). For the present discussion, we may use average values of W's for the temperature range between 1000 to 1400°C (see Table 1). The estimation of temperature is simplified because it is possible to solve for Eq. (18) graphically as done in the following section.

For the Netschaevo meteorite, temperature is now estimated using the ideal and non-ideal model and for the latter by using the three W_{opx} values due to changing μ_{Ca}^0.

Ideal Solution. The mole fraction in the crystal as a whole is the activity of the component. For the ternary solutions in terms of the components $Mg_2Si_2O_6$, $CaMgSi_2O_6$ and $FeMgSi_2O_6$ we have

$$\ln \frac{X_{\mathrm{Mg\text{-}cpx}}}{X_{\mathrm{Mg\text{-}opx}}} = \ln \frac{0.084}{0.832}. \tag{19}$$

Using Nehru and Wyllie's results (see Eq. 11), the temperature is estimated to be 974°C.

Negative Non-Ideal Solution. If the activity is defined as the product of site occupancies, we have

$$\ln \frac{X_{\mathrm{Mg\text{-}cpx}}^{\mathrm{M1}} X_{\mathrm{Mg\text{-}cpx}}^{\mathrm{M2}}}{X_{\mathrm{Mg\text{-}opx}}^{\mathrm{M1}} X_{\mathrm{Mg\text{-}opx}}^{\mathrm{M2}}} = \ln \frac{0.896 \times 0.084}{0.856 \times 0.832}. \tag{20}$$

Using Eq. (11) again, the temperature is 988 °C.

Positive Deviation on Sites. In Fig. 2, the straight line is for Eq. (13) ($-RT\ln K_a = 500$). We may now calculate K_a using the expression in the bracket in Eq. (18). W_{cpx} is 6531 cal/mol, while W_{opx} varies between 8289 to 6079 cal/mol depending on the $\Delta\mu_{\mathrm{Ca}}^0$. Therefore we have

$$\ln K = \frac{0.896 \times 0.084 \exp \dfrac{6531}{1.987 \times T} \, 0.906 (0.906 + 0.010)}{0.856 \times 0.832 \exp \dfrac{W_{\mathrm{opx}}}{1.987 \times T} \, 0.028 (0.028 + 0.140)}. \tag{21}$$

Using W_{opx} as 8289, 7184 and 6079 cal/mol at 1273 and 1373°K, $\ln K$ values were calculated and plotted in Fig. 2. The intersection of these lines with the $\ln K_a$ vs $1/T$ line yields the temperature of crystallization. The line for $W_{\mathrm{opx}} = 8289$ has been shown in Fig. 2. The intersection of the lines is at 1317°K or 1044°C. It is also noted that the change in W_{opx} does not affect the estimation by more than a few degrees.

Discussion

The temperatures mentioned here are only for demonstrating the possible effect of non-ideality in Mg—Ca pyroxene. These are obviously not precise, the first two because of the neglect of important non-ideality effects and the last because of the several points discussed below.
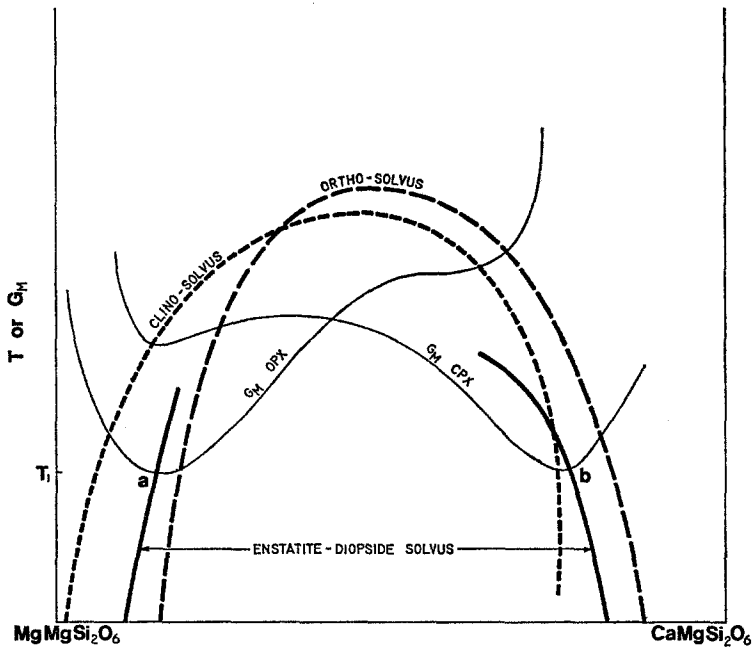
Fig. 1. Isostructural solutions of ortho- and clino-pyroxene with immiscibility gaps. The light curves show the free energy of mixing. See text for discussion
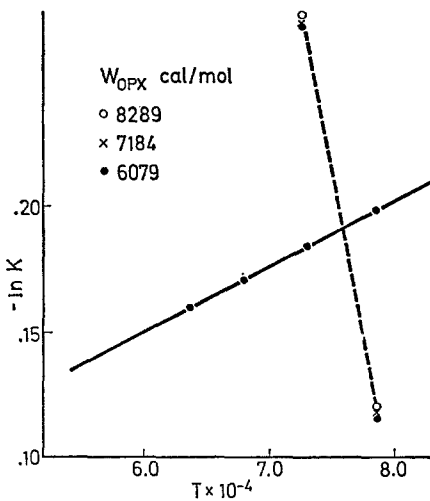

Fig. 2. Estimation of temperature of crystallization of pyroxenes, using the relations— $RT \ln K_a = 500$ and Eq. (18)

First, there is the problem of the lack of free energy data on the standard state end members. From thermodynamic and crystal-chemical considerations ΔG_a^0 may be of the order of 500 cal/mol. Boyd and Schairer (1964) did find clinoenstatite in their experiments, although Warner and Luth (1974) did not. The differ-

ence in free energy between clino-diopside and 'ortho'-diopside is uncertain. The latter, if possible, must be a high energy form and may be highly unstable in the range of temperature and pressure of interest. Fortunately, however, if the free energy difference is of the order of a few thousand cal/mol, the calculation of activity-composition may not be seriously jeopardized particularly if we have only a few mole percent of $CaMgSi_2O_6$ in orthopyroxene. Although we can have an approximate method of temperature estimate, more exact determinations must await the solution to the problem of standard free energies which have to be obtained through theoretical crystal energetic calculations and calorimetric measurements on stable and metastable pyroxene structures.

Second, even if we have more information on standard free energies of various pyroxenes, we can calculate the free energy of mixing only with one solution parameter W, which means the pyroxene solvi have to be symmetric. This would contribute further uncertainty to activity values. A solution to this problem would lie in the determination of 'partial' activities on the M2 sites from the data on the distribution of cations between M1 and M2 as suggested by Saxena (1973).

Third, although it appears from Lindsley and Munoz's (1969) work that the solvus for the hedenbergite-ferrosilite lies below $1000°C$, the assumption that Ca and Fe mix ideally on M2 site above $1000°C$ may not be true.

Fourth, for any precision in temperature estimate, it is essential that we have data on the site occupancies in pyroxenes at various temperatures. For an approximate determination, the scheme of cation partitioning as used here may be justified because of the small changes in the site occupancies above $800°C$. The distribution isotherms are very closely spaced towards the equal distribution line [compare Saxena and Ghose's (1971) results upto $800°C$ with Virgo and Hafner's (1969) curve at $1000°C$].

Finally, it may be mentioned that the substitution of Mg^{2+}, Fe^{2+} and Ca^{2+} by Al^{3+}, Ti^{4+} and Mn^{2+} in pyroxenes would further present problems in energy calculations. However, if the problems of the ternary pyroxenes can be solved, the problem of the minor elements would not be very difficult to tackle. In fact some progress has already been made by MacGregor (1974). In the meantime, it is recommended that temperature estimates for pyroxenes close to ternary solutions may be made by calculating K_a as below

$$K_a = \frac{X^{M1}_{Mg\text{-}cpx} X^{M2}_{Mg\text{-}cpx} \exp \dfrac{6531}{RT} X^{M2}_{Ca\text{-}cpx}(X^{M2}_{Ca\text{-}cpx} + X^{M2}_{Fe\text{-}cpx})}{X^{M1}_{Mg\text{-}opx} X^{M2}_{Mg\text{-}opx} \exp \dfrac{7184}{RT} X^{M2}_{Ca\text{-}opx}(X^{M2}_{Ca\text{-}opx} + X^{M2}_{Fe\text{-}opx})} \qquad (22)$$

and solving graphically as shown in Fig. 2. The cations between M1 and M2 sites are distributed according to the scheme discussed before.

The effect of pressure, although small, on the binary solvus is not yet well defined. This effect when better known could be included in the calculation of W's and the ΔG^0_a.

In conclusion, we hope that Eq. (22) will be used only with the knowledge of all the assumptions involved and the approximate nature of the results obtained. More crystal-chemical calculations and experiments on stable and metastable pyroxenes would be necessary for a final solution of the problem.

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