EMPIRICAL DERIVATION OF ACTIVITY COEFFICIENTS FOR THE MAGNESIUM-RICH PORTION OF THE OLIVINE SOLID SOLUTION

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ABSTRACT

Activity coefficients at 1100°C for Mg^{2+} and Fe^{2+} in the olivine solid solution, in the compositional range Fo 90–100, are derived empirically from the measured Mg–Fe distribution in a group of equilibrated iron meteorites that contain silicate phases. The solution exhibits a positive nonideality in this range and the results agree qualitatively with those of Nafziger and Muan (1967). Overall activity coefficients were calculated for the orthopyroxene solid solution (En 88–100) by derivation from recent Mössbauer data of Virgo and Hafner (1969). This solution exhibits a negative deviation from ideality. It is concluded that a petrologic thermometer based on the Mg–Fe distribution between olivine and coexisting orthopyroxene probably will not work with sufficient sensitivity for those Mg-rich rocks and meteorites which are more common and of greatest interest.

INTRODUCTION

A petrological thermometer based on the magnesium and iron distribution between coexisting olivine and Ca-poor pyroxene was first considered by Ramberg and Devore (1951) and later by others, principally Mueller (1964). The major problem with this thermometer has been its calibration (Olsen and Mueller, 1966). If calibrated it would provide an attractive thermometer for use with many ultramafic rocks, especially Ca-poor ones to which the Ca-rich—Ca-poor pyroxene thermometer (Kretz, 1963) [hereafter called the pyroxene-pyroxene thermometer] could not be applied. Calibration has been recently complicated by the report of a positive nonideality at 1150°C relative to Mg and Fe in the olivine solid solution (Nafziger and Muan, 1967). Similarly recent Mössbauer data of Virgo and Hafner (1969) show that Mg and Fe are fractionated between two different sites, $M1$ and $M2$, in Ca-poor orthopyroxenes

and the solid solution between Mg and Fe end-members must therefore be nonideal up through the same temperature range (up to 1250°C). Direct laboratory measurement of the distribution with temperature faces the usual problems of the demonstrable attainment of equilibrium. This is especially difficult at the highly magnesian end of the system, from Fo 90 to Fo 100, relative to olivine, where isothermal distribution curves crowd together; for any distribution, ideal or nonideal must, from theoretical considerations, intersect the composition point [Fo 100, En 100]. Most terrestrial rocks of interest and some non-terrestrial ones lie in this range. Less magnesian compositions are more amenable to the experimental determination of distribution shifts with temperature, however, field occurrences of rocks of these compositions are complicated by the presence of other ions, principally, Ca, Mn, and Ni (Simkin and Smith, 1970).

Recently Grover and Orville (1969) raised a question concerning the measured nonideality of the olivine solution. Applying the activity coefficients for the olivine solid solution (Nafziger and Muan, 1967) to the exchange reaction:

$$0.5Mg_2SiO_4 + FeSiO_3 = 0.5Fe_2SiO_4 + MgSiO_3 \qquad (a)$$

the calculated distribution curve departs considerably from the experimentally determined distribution points of Nafziger and Muan (Fig. 1). Grover and Orville suggested that the olivine solid solution requires additional investigation and that equilibrated olivine-pyroxene pairs from meteorites might provide further information concerning the olivine solid solution.

While making a thorough study of the mineral chemistry of the silicate phases in the group of meteorites called irons-with-silicate-inclusions (Bunch, Keil, and Olsen, 1970), coexisting Ca-poor and Ca-rich pyroxenes, and olivines were analyzed by electron microprobe. Fourteen meteorites of this group contain all three phases although not all of these will be used in this paper for reasons that will become apparent. In performing the analyses each mineral was checked for homogeneity. Within-grain and grain-to-grain compositional variabilities for any particular meteorite are small, usually less than 5 weight percent of the amounts present; a few show variabilities of major elements as high as 16 weight percent of the amounts present. Since these irons have extremely slow cooling histories (1.6 to 2.7°C per 10^6 years for three of the irons in this group that have been measured, Goldstein and Short, 1967), which are at least one or two orders of magnitude slower than in terrestrial crustal rocks, equilibrium should have obtained. The very small grain-to-grain variation in composition, lack of any zoning, and the constant distribu-
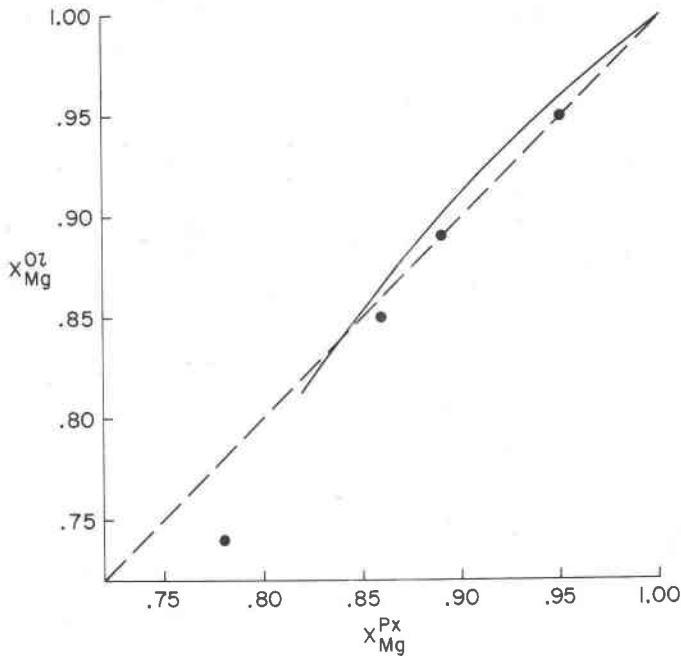
Fig. 1. Experimentally determined distribution points (solid circles) at 1200°C from Nafziger (1966). Solid line shows calculated distribution using activity coefficients for the olivine solution from Nafziger and Muan (1967), with the orthopyroxene solution treated as ideal. 45° line for reference (dashed).

tion coefficients of major and minor elements for any given sample clearly indicate this.

From the pyroxene-pyroxene thermometer one can establish temperatures of equilibration. In using this thermometer we have accepted the calibration of McCallum (1968). In the igneous temperature range this does not differ significantly from the original calibration of Kretz (1963), nor with the approximate recalibration of Grover and Orville (1969). These can be compared with the temperatures obtained using the Ca content of the Ca-poor pyroxene (Boyd and Schairer, 1964). The agreement is quite good. These data are detailed in Bunch, Keil, and Olsen (1970) and will not be repeated here. The temperatures so obtained ranged from 750°C to 1600°C. The bulk of them, however, lie between 900°C and 1200°C, and these average close to 1100°C (Table 1). In addition, an equilibration temperature of 1100°C was also determined from the δO^{18} measured on the feldspar in one of the irons of this group (Onuma, pers. comm.). Temperatures based on the Mg–Fe distribution

TABLE 1. COMPOSITIONS OF OLIVINE AND PYROXENE IN METEORITES

Meteorite	$X_{Mg}{}^{ol}$	$X_{Mg}{}^{px}$	$T°C$ from pyroxene-pyroxene thermometer
Odessa	0.965	0.934	1123
Campo del Cielo	.959	.939	1023
Linwood	.956	.927	988
Pitts	.956	.932	1096
Four Corners	.945	.936	1152
Woodbine	.936	.923	953
Pine River	.989	.964	1161
Persimmon Creek[a]	.938	.928	1638
Copiapo	.948	.928	1230
Udei Station[a]	.924	.917	761
Enon	.911	.893	974
Netschaëvo[a]	.858	.862	—
Kodaikanal[b]	.793	.834	1058
Mount Stirling	.969	.935	1067

[a] These data values not used in computations in this paper.

[b] These data used only in computation of distribution curve. Not used in any subsequent computations because they are more iron-rich than is our concern here.

between olivine and coexisting chromite (Jackson, 1969) give generally higher values, averaging around 1200°C. This method, however, is based on the ideality of both the olivine and chromite solutions. It is theoretically possible these solutions could have activity coefficients which cancel each other and the system could act essentially ideally. This, however, has never been tested.

Figure 2 shows the distribution points plotted for those eleven meteorites which exhibit pyroxene-pyroxene temperatures within one standard deviation of 1100°C. A least squares quadratic curve was fitted to them. For the least squares calculation the point [Fo 100, En 100] was weighted at 10 times to insure intersection at that point. The plot clearly behaves similarly to the calculated curve in Figure 1 showing, however, a more marked deviation from ideality. By utilizing the recent Mössbauer data of Virgo and Hafner (1969) for the orthopyroxene solid solution it is possible to assess the character of the olivine solution by assuming these meteorite distribution data represent an equilibrium distribution close to 1100°C.

THE ORTHOPYROXENE SOLID SOLUTION

The overall nonideality of the orthopyroxene solution is due to the nonequivalence of the $M1$ and $M2$ octahedral sites in the structure. This
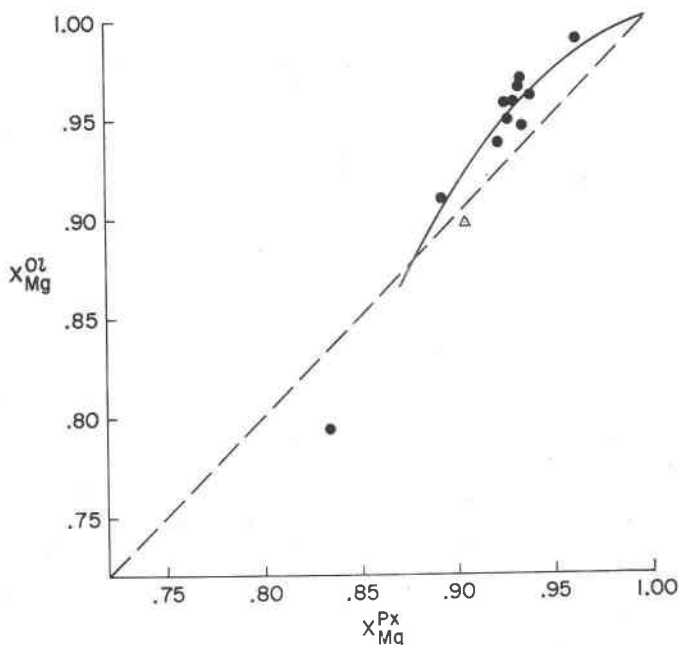
Fig. 2. Observed distribution of eleven coexisting olivine-pyroxene pairs in iron meteorites (*cf.* Table 1). Solid line is calculated, least squares fit to observed points. The point "△" represents a pair from Himmelberg and Coleman (1968) for 800°C in a terrestrial assemblage. 45° line for reference (dashed).

was first demonstrated by Ghose (1965) using X-ray methods, and more recently by the extensive Mössbauer spectroscopy of Virgo and Hafner (1969). These data clearly indicate that Mg and Fe are distributed ideally over the $M1$ and $M2$ sublattices (Mueller, 1961, 1962, 1967) from (mole fraction) $X^{px}_{Mg} = 1.00$ to about 0.30, which more than covers the range of interest in this paper, namely 1.00 to 0.90. To convert these data into overall activity coefficients for the pyroxene solution use is made of the equations suggested by Mueller (1962):

$$\alpha^{px}_{Mg} = (X^{I}_{Mg} X^{II}_{Mg})^{\frac{1}{2}} \qquad (1)$$

$$\alpha^{px}_{Fe} = (X^{I}_{Fe} X^{II}_{Fe})^{\frac{1}{2}} \qquad (2)$$

where the α's are the activities, X^{I}_{Mg} and X^{II}_{Mg}, and X^{I}_{Fe} and X^{II}_{Fe} are the site occupancy numbers of, respectively, Mg and Fe on the $M1$ and $M2$ sublattices.

Equations (1) and (2) were suggested by Mueller with the constraint that the sublattice mixing be ideal, which is the case here over the range in which we are interested. Since the Virgo and Hafner data do not cover

compositions more magnesian than $X^{px}{}_{Mg} = 0.822$ it is necessary to extrapolate their data by some means to more highly magnesian compositions. Because the sublattice mixing is ideal, site occupancy fractions can be read directly from figure five of Virgo and Hafner (1970, p. 75), with the values for 1000°C sufficing for 1100°C since the Mössbauer data indicate that the sublattice distribution does not change appreciably with temperature in the range 1000°–1200°C. These values may be related to the overall mole fractions of Mg and Fe by

$$X^{px}{}_{Mg} = \frac{X^{I}{}_{Mg} + X^{II}{}_{Mg}}{2} \tag{3}$$

$$X^{px}{}_{Fe} = \frac{X^{I}{}_{Fe} + X^{II}{}_{Fe}}{2}, \tag{4}$$

and from equations (1) and (2) we obtain the required activity coefficients (Table 2). It is possible to do this all analytically by using equations (1) through (4) and the relationship

$$\frac{X^{I}{}_{Fe}X^{II}{}_{Mg}}{X^{II}{}_{Fe}X^{I}{}_{Mg}} = k, \tag{5}$$

where k is the sublattice distribution constant, and since this distribution is ideal, it is the sublattice equilibrium constant.

From equations (1) through (5) two equations could be solved to obtain the activities, $a^{px}{}_{Mg}$ and $a^{px}{}_{Fe}$ as direct functions of the mole fractions, $X^{px}{}_{Mg}$ and $X^{px}{}_{Fe}$ and k. Such functions were determined, however, they turned out to be clumsy and did not improve upon the direct graphical method.

The derived activity coefficients in Table 2 are based on the real solid solution. It was also thought worthwhile, at this juncture, to ex-

TABLE 2. ACTIVITY COEFFICIENTS FOR THE PYROXENE SOLID SOLUTION

Distribution Coefficient $X_{Mg}{}^{px}$	Equation 2 $\gamma_{Mg}{}^{px}$	Equation 3 $\gamma_{Fe}{}^{px}$	Regular Solution Model	
			$\gamma_{Mg}{}^{px}$	$\gamma_{Fe}{}^{px}$
1.00	1.000	0.670	1.000	0.807
0.98	1.000	.690	1.000	.814
.96	1.000	.738	1.000	.820
.94	1.000	.758	1.000	.827
.92	1.000	.792	0.999	.834
.90	1.000	.797	.998	.840
.88	1.000	.808	.997	.847

amine how well the pyroxene solid solution might be approximated by the regular solution model (Lewis and Randall, 1961, pp. 82–86). If adequate it would have the advantage of providing relatively simple relationships between activity coefficients and mole fractions that would not involve graphical steps. A plot of the α-function (Darken and Gurry, 1953, pp. 264–66) for isothermal values of all experimental mole fractions determined by Virgo and Hafner shows considerable scatter, however, it is possible to use an average α-value which is constant and independent of composition. When $Mg_2Si_2O_6$ and $Fe_2Si_2O_6$ are used as end-members equations (1) and (2) can be used to derive the equation which was derived by Grover and Orville (1969) by other means,

$$\Delta H_{\mathrm{mix}} = \frac{X^{\mathrm{II}}{}_{\mathrm{Mg}} - X^{\mathrm{I}}{}_{\mathrm{Mg}}}{2} \Delta G_{\mathrm{E}}{}^{\circ} \tag{6}$$

where ΔH_{mix} is the enthalpy of mixing of the overall pyroxene solution and $\Delta G^{\circ}{}_{\mathrm{E}}$ is the standard Gibbs function for the sublattice exchange reaction:

$$Fe^{\mathrm{II}}SiO_3 + Mg^{\mathrm{I}}SiO_3 = Fe^{\mathrm{I}}SiO_3 + Mg^{\mathrm{II}}SiO_3 \tag{b}$$

For the regular solution at the composition point $X^{\mathrm{px}}{}_{\mathrm{Fe}} = 0.5$, then $\alpha^{\mathrm{px}}{}_{\mathrm{Mg}}/\alpha^{\mathrm{px}}{}_{\mathrm{Fe}} = 1.00$. This is equivalent to the condition that at $X^{\mathrm{px}}{}_{\mathrm{Fe}} = 0.5$, $X^{\mathrm{I}}{}_{\mathrm{Mg}} + X^{\mathrm{II}}{}_{\mathrm{Mg}} = 1$, and $X^{\mathrm{I}}{}_{\mathrm{Fe}} + X^{\mathrm{II}}{}_{\mathrm{Fe}} = 1$. For points quite near to $X^{\mathrm{px}}{}_{\mathrm{Fe}} = 0.5$ in the Virgo and Hafner data this is close to being true. Some values for these sums are 1.064, 0.936, 1.149.

For the species $M^{\mathrm{I}}{}_{\frac{1}{2}} M^{\mathrm{II}}{}_{\frac{1}{2}} SiO_3$ Virgo and Hafner calculate $\Delta G^{\circ}{}_{\mathrm{E}} = 1825$ cal., which we will use at the temperature 1100°C. Arbitrarily choosing the site occupancy numbers for the Virgo and Hafner specimen 37218-E1, for which $X^{\mathrm{px}}{}_{\mathrm{Fe}} = 0.531$ (which is close to 0.5), we obtain $\Delta H_{\mathrm{mix}} = -330$ cal. from equation (6). For the regular solution,

$$\Delta H_{\mathrm{mix}} = (X^{\mathrm{px}}{}_{\mathrm{Mg}} X^{\mathrm{px}}{}_{\mathrm{Fe}}) \left(\Omega - T \frac{\partial \Omega}{\partial T} \right) \tag{7}$$

$$\Delta S^{\mathrm{xs}}{}_{\mathrm{mix}} = - X^{\mathrm{px}}{}_{\mathrm{Mg}} X^{\mathrm{px}}{}_{\mathrm{Fe}} \frac{\partial \Omega}{\partial T} \tag{8}$$

where Ω is the so-called interaction parameter of the regular solution model, and $\Delta S^{\mathrm{xs}}{}_{\mathrm{mix}}$ is an excess entropy of mixing term. This latter term can be evaluated by setting it equal to the configurational entropy for the sublattice distribution of this specimen, 37218-E1, in going from the completely disordered to the completely ordered sublattice at $X^{\mathrm{px}}{}_{\mathrm{Fe}}$ $= 0.531$, and assuming that non-configurational entropy contributions are zero. For $M^{\mathrm{I}}{}_{\frac{1}{2}} M^{\mathrm{II}}{}_{\frac{1}{2}} SiO_3$ then

$$\Delta S^{xs}_{mix} = -\frac{R}{2}\left[X^{I}_{Mg}\ln X^{I}_{Mg} + X^{I}_{Fe}\ln X^{I}_{Fe} + X^{II}_{Mg}\ln X^{II}_{Mg}\right.$$

$$\left. + X^{II}_{Fe}\ln X^{II}_{Fe} - 2X^{px}_{Mg}\ln X^{px}_{Mg} - 2X^{px}_{Fe}\ln X^{px}_{Fe}\right]$$

$$= -0.134 \text{ (for this specimen).} \qquad (9)$$

Using this value we can evaluate the derivative in equation (8) as 0.538 cal/deg. for $X^{px}_{Fe}=0.531$. Then from equation (7) we obtain $\Omega = -586$ cal. at 1100°C. Activity coefficients are then computed from

$$\ln \gamma^{px}_{Mg} = \Omega/RT(X^{px}_{Fe})^2 \qquad (10)$$

$$\ln \gamma^{px}_{Fe} = \Omega/RT(X^{px}_{Mg})^2 \qquad (11)$$

Computed values over the range $X^{px}_{Mg}=1.00$ to 0.88 are given in Table 2. They differ significantly from the values obtained by the direct graphical method. Thus, unfortunately, the pyroxene solid solution is not well-approximated by a regular solution model, and the real values for activity coefficients, obtained by graphical methods, will be used in subsequent calculations. It should be noted that the experimental results of Nafziger and Muan (1967) indicated no significant deviation from ideality for this solution at 1150°C. The sublattice ordering, however, requires that some deviation exist. It is clearly not large and lies essentially at the limit of their experimental uncertainties.

CALCULATION OF OLIVINE ACTIVITY COEFFICIENTS

It is first necessary to obtain a value for the equilibrium constant for equation (a). Using the experimentally determined distributions of Nafziger (1966) for 1200°C we obtain values that range from 1.2 to 1.5, with an average of 1.3. From the experimental work of Larimer (1968) he obtained close to 1.30 for all temperatures from 1100°–1300°C. For our purposes in this paper the adoption of either of these data introduces a certain circularity to subsequent calculations in that each set of experimental data required the use of Nafziger and Muan's activity coefficients for olivine in order to obtain the equilibrium constants. Also, in each case the coexisting pyroxene solution was taken to be ideal. Nafziger (1966), however, further estimated that $\Delta G°$ for reaction (a) at 1200°C is about -600 cal., which yields an equilibrium constant of $K_e = 1.23$. Olsen and Fuchs (1967) estimated thermodynamic data for ferrosilite from the experimental data of Lindsley, MacGregor, and Davis (1965). Use of these data yields calculated values of K_e of 1.4 for 1200°C and 1.3 for 1100°C. It would appear that for this temperature range the true value must be close to 1.3. All following calculations were repeated, however, using a lower extreme value of 1.1.

From the least squares fit to the observed meteorite distributions we obtained values for the distribution "constant", K_D, at each 0.02 of X^{ol}_{Mg} from 1.00 to 0.90 (where $X^{ol}_{Mg} = Mg/(Mg+Fe)$ for olivine). Since,

$$K_e = 1.3 = K_D K_\gamma \tag{12}$$

where $K_\gamma = \gamma^{px}_{Mg}\gamma^{ol}_{Fe}/\gamma^{px}_{Fe}\gamma^{ol}_{Mg}$, and where the γ's are the respective activity coefficients, we can obtain values for K_γ. Using the activity coefficients for the pyroxene we obtain values for the ratio

$$\gamma^{ol}_{Mg}/\gamma^{ol}_{Fe} = (1/K_\gamma)(\gamma^{px}_{Mg}/\gamma^{px}_{Fe}). \tag{13}$$

We next obtained a least squares fit of the logarithms of these calculated ratios,

$$\ln (\gamma^{ol}_{Mg}/\gamma^{ol}_{Fe}) = -0.84 + 10.94(X^{ol}_{Fe}) - 38.81(X^{ol}_{Fe})^2. \tag{14}$$

By a corollary of the Gibbs-Duhem equation

$$d \ln \gamma^{ol}_{Fe} = -(X^{ol}_{Mg}/X^{ol}_{Fe})d \ln \gamma^{ol}_{Mg} \text{ must also be satisfied.} \tag{15}$$

Equation (14) was then differentiated, solved similtaneously with equation (15) and integrated from $X^{ol}_{Fe}=0$ to $N^{ol}_{Fe}\leq 0.10$, where the N has the same meaning as X.

$$\ln \gamma^{ol}_{Mg} = 5.47(N^{ol}_{Fe})^2 - 25.87(N^{ol}_{Fe})^3 \tag{16}$$

$$\ln \gamma^{ol}_{Fe} = 0.84 - 10.94(N^{ol}_{Fe}) + 44.28(N^{ol}_{Fe})^2 - 25.87(N^{ol}_{Fe})^3 \tag{17}$$

These calculated activity coefficients, shown graphically in Figure 3, exhibit a positive deviation from ideality. The deviation is more extreme than that obtained experimentally by Nafziger and Muan. Many assumptions and averaging processes were involved in the translation of these observational data from the meteorites into the derived activity coefficients over this compositional range, and it is not possible to assess the accuracy of these results relative to those of Nafziger and Muan. These calculations were repeated using an equilibrium constant of 1.1. The effect on γ^{ol}_{Mg} was negligible. The values, curve B', lie essentially on those of curve B (Fig. 3). The effect on γ^{ol}_{Fe} was more pronounced, yielding a lower set of coefficients. It is clear, however, that to obtain the kind of distribution observed some nonideality of the olivine solution is required in addition to the clear nonideality of the pyroxene solution. These two solutions work in opposite directions in reaction (a). If the pyroxene solution exhibited a more pronounced deviation from ideality then a smaller deviation would be required of the olivine solution. It is also possible that equations (1) and (2) do not establish the correct relationship between ideal sublattice distribution and overall nonideality. There is no clear-cut relationship dictated by thermodynamic theory.
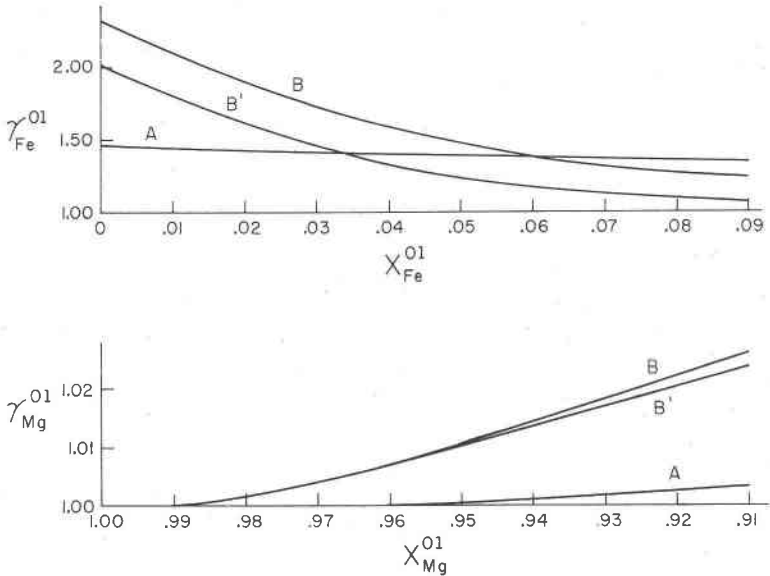
Fig. 3. Curves B show olivine activity coefficients for Mg and Fe from Fo 91–100 calculated from empirical meteorite distribution data for an equilibrium constant of 1.3 for 1100°C. Curves B′ are calculated for an equilibrium constant of 1.1 at the same temperature. Curves A are values determined experimentally by Nafziger and Muan (1967).

Indeed, Mueller (1962) states, "Whether or not such an expression [as equation (1) or (2) of this paper] works then becomes a matter of experience". In addition, sublattice ordering is not the only cause for deviations of a solid solution from ideality. So it is possible that the pyroxene solution may exhibit a larger nonideality from that used in this paper due to other factors.

DISCUSSION

The data on coexisting olivine and pyroxene compositions compiled by Ramberg and Devore (1951), Mueller (1964), and Grover and Orville (1969) clearly indicate points at the magnesian end which are on the opposite side of the 45° line from the distributions observed in these meteorites (Fig. 2). Only two meteorites of this whole group show distribution points on the side below the 45° line and those are more iron-rich, plotting below the point [Fo 88, En 88] (cf. Table 1). The distribution indicates the same kind of cross-over of the distribution curve as in Figure 1. Mueller (personal commun.) believes that all these meteorite points above the 45° line at the magnesian end could represent disequilibrium. If true it is difficult to account for the very small grain-to-

grain variation in composition and the lack of any zoning. The disequilibrated chondrite meteorites exhibit enormous grain-to-grain variation (*e.g.*, *cf.* Keil, *et al.* 1964) as well as zoning. In addition, one would expect that among the fourteen meteorites measured some, at the Mg-rich end, would show distribution points randomly scattered below the 45° line if disequilibrated. It seems clear that these meteorite pairs represent an unequivocal close approach to equilibrium and that the cross-over below [Fo 88, En 88] is a real feature of the distribution. The points from Ramberg and Devore, Mueller, and Grover and Orville below the 45° line and above [Fo 88, En 88] must represent the approach to equilibrium distributions at other, probably lower, temperatures.

To examine this we have taken the recent microprobe data of Himmelberg and Coleman (1968) for a terrestrial assemblage containing co-existing olivine, Ca-rich pyroxene, and Ca-poor pyroxene. From the pyroxene-pyroxene thermometer we obtain a temperature of 800°C. The point is plotted in Figure 2. Its position suggests that with falling temperature the activity coefficients of the two solutions shift in a manner that moves the cross-over point of the distribution curve upwards towards the magnesian end. It is possible that more Fe-rich compositions may show little distributional shift with falling temperature, as indicated by the data of Larimer (1968). The recent experimentally determined distribution data of Medaris (1969) at 900°C bear this out as an overall pattern, however, at the very magnesian end, Fo 85–100, these experimental distribution points scatter. For eight pairs in this range four plot below the 45° line, three plot well above it, and one plots on it. We discussed earlier the problem of attainment of perfect experimental equilibrium distribution at the very magnesian end, close to the 45° line. At this end small errors in the measurement of compositions can scatter points to both sides of the line. This is an additional reason for believing the meteorite pairs are compositionally accurate. At more Fe-rich compositions Medaris' data plot as expected, and support the work of Larimer.

Figure 4 shows a series of purely speculative drawings illustrating how the distribution may shift with falling temperature. These figures take into account the distribution points shown in Grover and Orville which lie below the 45° line at the magnesian end. These curves show perhaps more shift for intermediate compositions (in the En 50 range) than may actually be the case. In this intermediate range the experimental data of Larimer and Medaris indicate that rapidly changing activity coefficients for the two solutions dampen distribution effects with falling temperature. It would be interesting to see how natural lower temperature pairs, richer in iron than these meteorites, bear this out, provided
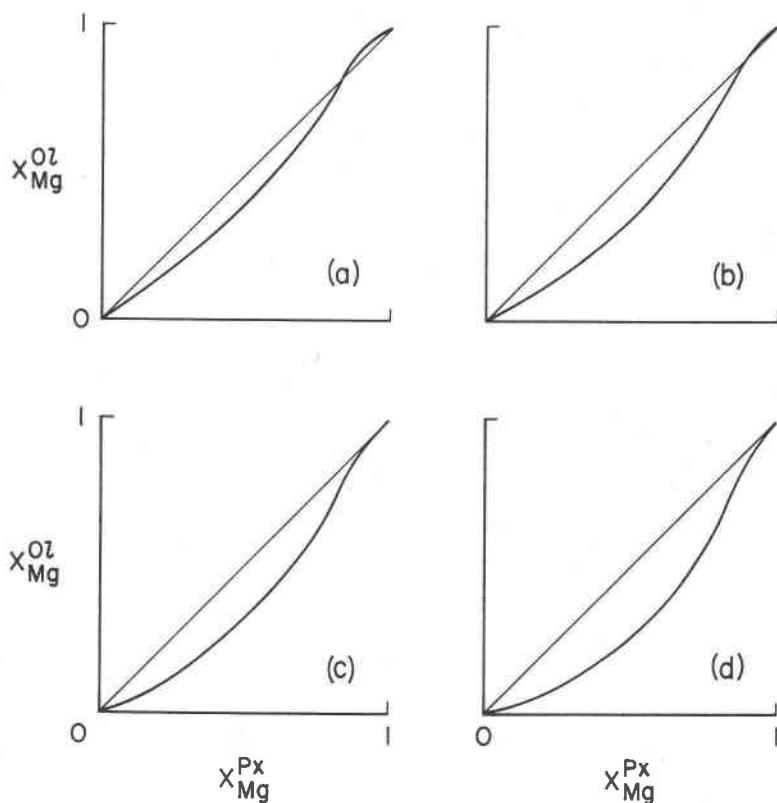
FIG. 4. Proposed estimated configurations for olivine-pyroxene distribution curves with falling temperature. (a) represents approximately 1100–1200°C; (d) represents approximately 600–700°C.

pairs can be found that are at equilibrium and free of compositional complications from Mn, Ca, etc.

It is concluded that the nature of these two solutions and the shapes of the distribution curves with changing temperature are too uncertain in the compositional range of most interest, highly magnesian, to be used at all as a petrological thermometer. In addition, we have confirmed, at least qualitatively, the overall nonideality of the olivine solid solution. What may be the cause of this is unknown. The differences between the two sublattice octahedral sites in olivine are small, compared to pyroxenes, leading one intuitively to think that sublattice ordering should not be large, though it is not precluded. It may be that the fundamental differences in the bonding characteristics of Mg^{2+} and Fe^{2+} in silicates are

sufficient to create higher lattice energies when lattice sites are similar than when they are sufficiently different and can accommodate lower symmetry bonding and lower overall lattice energy. In a relatively non-distorted structure such as olivine any Fe must occupy a site with symmetry almost as high as that of Mg. In pyroxenes any Fe has available lower symmetry $M2$ sites. This would possibly account for the apparent smaller gross deviation from ideality of the pyroxene solution relative to olivine.

If this speculative kind of argument has any validity it leads one to the hope that distribution-thermometers may operate in more complex silicates, such as amphiboles and micas. Indeed, Mueller (1961) indicates that the deviation of cummingtonite from ideality is relatively small.

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