An experimental investigation of thermodynamic mixing properties and unit-cell parameters of forsterite–monticellite solid solutions

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Abstract

Olivines have been synthesized along the forsterite–monticellite join in the temperature range 1100 to 1490°C, and the pressure range 1 bar to 10 kbar. Previous X-ray determinative curves have been corrected. Unit-cell parameters, when plotted on an *a–b* diagram using the procedure of Lumpkin et al. (1983), indicate the possibility of a small degree of Ca–Mg disorder on M1 and M2, especially in forsterite-rich compositions. The apparent disorder appears to start at temperatures of about 1200°C; however, all the results are nearly within the stated error limits of complete order.

The two phase region of the forsterite–monticellite join was investigated at 5 and 10 kbar in the temperature range 1100 to 1490°C. Reversals of the solvi to within 1 mole% reveal the following features:

(1) The miscibility gap is asymmetric, with the monticellite limb exhibiting a greater degree of solution than the forsterite limb.

(2) Pressure has no measurable effect on either solvus limb in the pressure range investigated.

(3) A single-site asymmetric solution model adequately fits the two-phase miscibility data with $W_{G_{Fo}} = 43.1$ kJ/mole $- T(6.01$ J/deg-mole), and $W_{G_{Mo}} = 61.2$ kJ/mole $- T(15.2$ J/deg-mole).

Introduction

The usefulness of geothermometers and geobarometers based on exchange reactions between coexisting phases is limited by the necessity of having well-determined activity-composition data for the solid solutions involved. For example, the Fe^{2+}–Mg exchange between orthopyroxene (enstatite–ferrosilite solid solution) and ilmenite (ilmenite–geikielite solid solution) can produce temperature estimates nearly 900°C in error if the effects of the moderate non-ideality in ilmenite–geikielite solid solutions ($W_G = 6.79$ kJ/mole) are ignored (Bishop, 1980). As a result, the accuracy of some exchange geometers is not markedly better than that of geometers based on phase diagrams of simple analogue systems (Finnerty and Boyd, 1984). Significant progress in estimating intensive parameters of equilibration for petrologic samples depends on better activity-composition data becoming available.

It has recently been shown that Ca–Mg exchange between clinopyroxene and olivine has a significant ΔV, and can thus be used as a geobarometer in many systems of petrologic interest, including spinel peridotites (Adams and Bishop, 1982). In that study, experiments were carried out in the CaO–MgO–SiO_2 (CMS) system using crystalline starting materials synthesized along the forsterite–monticellite and diopside–enstatite joins. Activity-composition relationships for forsterite–monticellite solid solutions, used in modeling the results of the exchange

reactions, were obtained from the miscibility gap of Warner and Luth (1973). During the synthesis of olivines for use as starting material in the exchange experiments, a consistent discrepancy was noticed between unit-cell parameters at a given olivine composition determined for our olivines and unit-cell parameters reported by Warner and Luth (1973). Because they used an X-ray determinative curve to measure the compositions of coexisting phases along the monticellite–forsterite miscibility gap, we undertook a recalibration of this curve.

In addition, questions remain regarding whether equilibrium compositions along the forsterite–monticellite miscibility gap have been achieved, and whether or not the solvi display asymmetry. A symmetric miscibility gap at one atmosphere was reported by Ricker and Osborn (1954), while conflicting asymmetric miscibility gaps at one atmosphere were reported by Biggar and O'Hara (1969), and Yang (1973). Yang (1973), in a brief discussion of earlier results, concluded that the discrepancy is a result of nucleation and persistence of metastable phases or phase compositions, and of limited accuracy of X-ray diffraction methods used for the determination of phase compositions. Metastability is of particular concern because Ricker and Osborn (1954) used glasses and Biggar and O'Hara (1969) used gels for starting materials. To accelerate reaction rates and promote a closer approach to equilibrium, Yang's experiments, also using glass starting materials, were run at temperatures and compositions in which forsterite-rich solid solu-

tions (Fo_{ss}) and monticellite-rich solid solutions (Mo_{ss}) coexist with silicate liquids. This technique produced coarse-grained crystals of both Fo_{ss} and Mo_{ss} allowing analysis of the run products by electron microprobe. Yang obtained results very similar to Biggar and O'Hara for the Fo_{ss} solvus of the miscibility gap, but his Mo_{ss} solvus differed substantially in position and slope from those reported previously, yielding a markedly asymmetric miscibility gap. Because of the use of metastable starting materials in all of these studies, true reversals of the positions of the solvi could not be obtained.

Warner and Luth (1973), using crystalline starting materials, investigated the miscibility gap at hydrothermal pressures of 2, 5, and 10 kbar in the temperature range 800–1300°C. They produced a polythermal-polybaric equation of state for the forsterite–monticellite join based on compositions of coexisting phases determined by the previously mentioned X-ray curve. The miscibility gap generated in these experiments was nearly symmetric, although at 10 kbar an unusual decrease in miscibility relative to that for lower pressures for both solvus limbs occurred as temperature was increased above 1200°C. Warner and Luth, although believing the effect to be real, expressed dissatisfaction for all apparent explanations of the phenomenon. In addition, the positions of their solvus limbs disagree with all previous studies. They performed reversals at only two conditions, 900 and 1200°C at 2 kbar, but these were not in the range in which the miscibility decrease was observed. An additional question about this study has recently been raised. Lumpkin et al. (1983) have shown that the 131 diffraction line used by Warner and Luth to determine composition is affected by Mg–Ca order–disorder in the octahedral M1 and M2 sites. They suggest that the apparent miscibility decrease of the 10 kbar solvus at high temperatures is merely an artifact of progressive disorder as temperature increases.

Although the general properties of the forsterite–monticellite miscibility gap are known, it is apparent from the above discussion that sufficient uncertainties exist in the available data that they are inadequate to calculate an activity model with the confidence required for use in the Ca–Mg exchange reaction between olivine and clinopyroxene. For these reasons we have redetermined the unit-cell parameters for forsterite–monticellite solid solutions, and have reinvestigated the forsterite–monticellite miscibility gap. We have paid particular attention to reversing the experiments fixing the positions of the solvi, and to addressing the possibility of Ca–Mg disorder on M1 and M2.

Experimental methods

Single-phase starting materials were synthesized with both forsterite-rich and monticellite-rich compositions. Stoichiometric mixes of MgO (prepared from reagent-grade basic magnesium carbonate by decomposition in air at 1300°C), $CaCO_3$ (dried at 400°C in a CO_2 atmosphere), and SiO_2 glass were pressed into pellets with a butyl acetate binder. The pellets were sintered at either 1300°C or 1425°C for three days. All products were checked for homogeneity by optical and X-ray techniques, and those that showed incomplete reaction were reground, pelletized, and sintered for additional three-day cycles. No more than three cycles were required for any given composition. Single phases with compositions from Fo_{100} to Fo_{84}, and Fo_{18} to Fo_6 were successfully synthesized at these conditions, as well as a two-phase assemblage of $Fo_{3.5}$ and 1–2% merwinite. As reported by other investigators (e.g., Ferguson and Merwin, 1919; Davidson and Mukhopadhyay, 1984), pure monticellite could not be made at one atmosphere pressure. The results of the single-phase syntheses are given in Table 1. Fine grain size of the run products (< 2 μm) prevented microprobe corroboration of the compositions.

Unit-cell dimensions of each product were determined by X-ray powder diffractometry using synthetic spinel ($a = 8.0847$Å) as an internal standard. Up to ten diffraction lines were included in unit-cell refinements determined by the least-squares procedure of Burnham (1962). Results of these calculations, as well as selected d-spacings, are given in Table 1.

In the two-phase region of the binary system, rigorous demonstration of equilibrium requires that the equilibrium composition for each phase be approached from both higher and lower degrees of solid solution. For runs in which the coexisting phases approached each other in composition, starting materials were a mechanical mixture of pure forsterite (Fo_{100}) and the $Fo_{3.5}$ with trace merwinite. For runs in which the phase compositions moved away from each other, starting materials were usually a mixture of Fo_{84} and Fo_{18}. The one exception was run 109 in which the run product from 107 ($Fo_{81.2}$ and $Fo_{23.8}$) was used as starting material. A small quantity of water or oxalic acid was commonly added to enhance reaction rates (Table 2). Starting mixes were sealed in platinum capsules and run in a piston-cylinder apparatus at temperatures in the range 1100–1490°C, and at uncorrected pressures of 5 and 10 kbar (Table 2). At 1400°C and above, the experiments were run without a flux to prevent excessive melting.

Two-phase run products were analyzed by X-ray diffraction and electron microprobe. Unit-cell parameters for both Fo_{ss} and Mo_{ss} were determined by procedures similar to those described for single-phase syntheses. Phase compositions were determined by comparison with X-ray determinative curves based on volume, d_{130}, d_{131}, and d_{112}. The validity of using these curves in light of the effects of possible disorder (Lumpkin et al., 1983) is discussed in detail below. Run products of sufficient grain size were also analyzed by an ARL-EMX electron microprobe. A 1 μA beam current, 15 kV accelerating potential, and 10 second counting time were used for all elements except Ca. Ca was counted for 90 seconds, which is sufficient to obtain ± 5% precision in Fo_{ss}. ZAF corrections were applied to all analyses. Acceptable analyses satisfy all of the following criteria: at least four separate analyses, each within 1σ of the mean; stoichiometry within 0.98–1.02 Si/4 oxygen atoms; and total wt.% of 98–102. Results of the microprobe and X-ray analyses are given in Table 2.

Results

Single-phase experiments

Results of single-phase sintering experiments presented in Figures 1 and 2 indicate that monticellite-rich solid solutions have little or no excess volume of mixing whereas forsterite-rich solid solutions exhibit a small negative excess volume of mixing. Results in the monticellite-rich part of the join (Fig. 1) agree well with those of Warner and Luth (1973); however, results in the forsterite-rich part of the join have a smaller negative excess volume of mixing

Table 1. Unit cell dimensions and d-spacings for synthetic olivines

100 X_{Fo}	T(°C)	a(Å)	b(Å)	c(Å)	V(Å³)	d_{130}	d_{131}	d_{112}
6.0	1425	4.8220(7)	11.0597(9)	6.3586(8)	339.10(5)	2.9287	2.6601	2.5810
9.0	1425	4.8206(14)	11.0300(9)	6.3416(7)	337.19(8)	2.9234	2.6549	2.5759
13.5	1425	4.8179(4)	10.9867(5)	6.3228(3)	334.68(3)	2.9155	2.6476	2.5698
18.0	1425	4.8153(14)	10.9469(8)	6.3045(7)	332.32(8)	2.9083	2.6408	2.5640
84.0	1300	4.7702(2)	10.3265(10)	6.0380(3)	297.34(2)	2.7908	2.5333	2.4765
84.0	1300	4.7698(3)	10.3235(6)	6.0387(4)	297.43(3)	2.7912	2.5337	2.4767
84.0	1425	4.7709(7)	10.3289(10)	6.0394(9)	297.61(4)	2.7919	2.5342	2.4771
88.0	1300	4.7662(8)	10.2976(12)	6.0262(5)	295.77(5)	2.7854	2.5284	2.4724
88.0	1425	4.7659(12)	10.2968(14)	6.0248(7)	295.66(7)	2.7852	2.5281	2.4719
93.0	1300	4.7624(6)	10.2521(7)	6.0090(5)	293.50(3)	2.7765	2.5202	2.4654
93.0	1425	4.7624(7)	10.2541(9)	6.0072(5)	293.36(4)	2.7769	2.5206	2.4660
97.0	1300	4.7592(5)	10.2275(6)	5.9960(3)	291.85(3)	2.7715	2.5157	2.4621
97.0	1425	4.7590(5)	10.2290(8)	5.9953(5)	291.85(4)	2.7717	2.5158	2.4619
98.0	1300	4.7590(5)	10.2181(5)	5.9918(3)	291.37(3)	2.7698	2.5141	2.4607
100.0	1300	4.7551(5)	10.1984(8)	5.9822(5)	290.10(3)	2.7654	2.5102	2.4573
100.0	1300	4.7563(2)	10.2005(4)	5.9823(3)	290.24(2)	2.7661	2.5107	2.4575

(Fig. 2). This discrepancy is not believed to be a systematic error resulting from different X-ray techniques because unit-cell parameters for end-member forsterite and for monticellite-rich solid solutions are totally consistent between the two studies.

Warner and Luth (1973) reported 1–2% unreacted periclase or other phases in most of the syntheses they used in their determinative curve. Residual periclase would produce olivine slightly richer in Ca than the bulk composition of the mix, and therefore the olivine should display larger apparent unit-cell parameters, rather than smaller. This effect was tested in one synthesis by sintering a loose mixture of reagents at 1425°C. The product contained 1–2% periclase and the olivine, nominally Fo₈₈, has a cell

Table 2. Run conditions and compositions from two-phase experiments

Run#*	T(°C)	P(kb)	Run Time (hours)	Flux wt%	Flux Comp.	Additional phases**	Composition Mo$_{ss}$*** micro-probe	d_{130}	d_{131}	d_{112}	V	Composition Fo$_{ss}$*** micro-probe	d_{130}	d_{131}	d_{112}	V
54U	1100	5	72.5	5	oxalic	ak,cc	–	7.4	7.2	7.3	7.3	95.6	95.5	95.2	95.4	95.8
69S	1100	5	25.0	5	H₂O	ak,di	6.6			6.4		96.3	97.0		97.3	97.0
71U	1100	5	24.0	5	H₂O		–	7.2	6.8	7.3	6.8	–	97.0	96.4	96.3	96.2
72S	1100	10	24.0	5	H₂O		5.4			6.6		96.1	96.8	96.6	96.6	96.8
72U	1100	10	24.0	5	H₂O		5.9	6.9	6.3	6.9	6.4	95.6	96.0	96.4	96.0	95.9
52S	1200	5	13.0	5	oxalic		–	8.6	8.0	8.2	8.2	94.4	94.9	94.5	95.2	95.1
52U	1200	5	13.0	5	oxalic		9.0	10.6	9.5	10.1	9.8	93.7	93.9	93.4	93.5	93.6
63U	1200	5	10.1	5	oxalic	ak,cc	–	8.6	8.7	8.8	8.5	94.1	93.3	93.6	93.0	93.4
64S	1200	5	21.4	5	oxalic	ak,cc	9.1	9.8	10.2	9.7	9.7	94.0	93.6	93.8	94.1	93.9
64U	1200	5	21.4	5	oxalic	ak,cc	9.0	9.6	9.5	9.3	9.2	94.0	93.6	93.1	93.2	93.3
58U	1200	10	47.2	5	oxalic	ak,cc	8.6	9.4	8.9	9.4	9.3	94.8	94.1	94.3	94.3	94.3
111S	1200	10	38.0	–	–		8.7	9.4	9.2	9.1	9.0	93.8	93.3	92.9	93.5	93.4
56S	1300	5	8.7	5	oxalic		–	11.6	11.2	11.6	11.2	92.2	91.2	91.3	91.3	91.1
56U	1300	5	8.7	5	oxalic		–	11.4	11.7	11.4	11.2	91.7	91.3	91.2	90.8	91.1
68S	1300	5	5.2	1	H₂O		12.8	12.5	12.2	12.5	12.2	–	90.3	91.0	90.2	90.7
57S	1300	10	11.8	5	oxalic	ak	10.1	11.0	10.7	11.0	10.5	92.7	92.6	92.5	92.4	92.5
67S	1300	10	7.0	–	–	me	–	10.8	10.9	10.8	10.6	–	91.8	91.5	91.9	91.7
84S	1400	5	3.5	–	–		–	15.3	15.4	15.3	15.0	–	88.1	88.4	87.8	88.0
87U	1400	5	5.0	–	–		17.0	16.6	16.9	16.6	16.5	86.5	86.8	86.8	87.0	87.0
106S	1460	5	4.0	–	–		–	17.9	19.1	18.8	18.4	–	84.5	84.7	84.2	84.6
109U	1460	5	3.0	–	–		22.9	21.4	22.1	21.9	21.5	84.5	82.7	82.3	82.4	82.3
107S	1490	5	4.0	–	–		26.6	23.9	24.4	23.8	23.8	81.8	81.6	80.9	81.0	81.2

* The letter in each run number indicates the type of run: S is a solution run, in which the phase compositions approach each other, U is an unmixing run, in which the phase compositions diverge.
** Abbreviations are ak = akermanite, cc = calcite, di = diopside, me = merwinite.
*** Compositions are given as 100 X_{Fo} where X_{Fo} is the mole fraction of forsterite component.
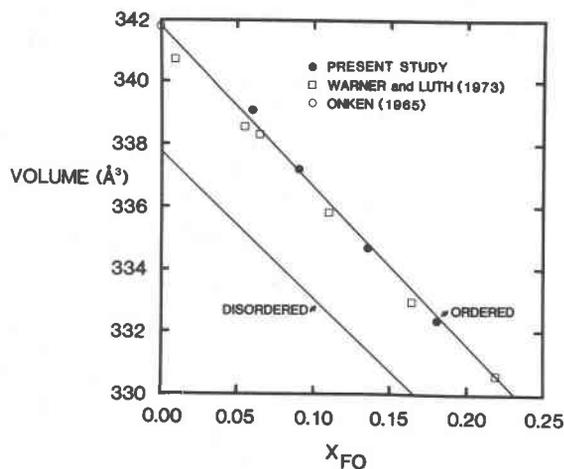
Fig. 1. Unit-cell volumes vs. X_{Fo} for monticellite-rich solid solutions. Solid circles are data from the present work synthesized at 1425°C, squares are from Warner and Luth (1973) synthesized at temperatures ranging from 890–1450°C, and open circle is from Onken (1965). Upper line connects monticellite and forsterite end-member volumes, and is equivalent to Lumpkin and Ribbe's (1983) ordered curve. Lower line connects forsterite with γ-Ca_2SiO_4, and is equivalent to Lumpkin and Ribbe's (1983) disordered curve. Estimated standard deviations are smaller than symbol size.

volume greater than that predicted from either curve (Fig. 2). Correcting Warner and Luth's curve for residual periclase increases the discrepancy between the two curves. Residual silica glass was reported in some of their syntheses, and if this were also present in their other runs and was
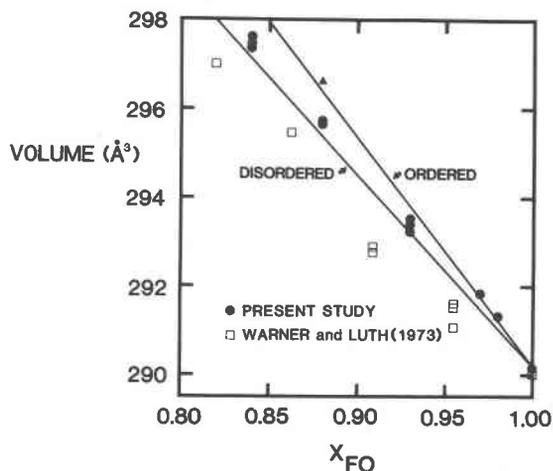
Fig. 2. Unit-cell volumes vs. X_{Fo} for forsterite-rich solid solutions. Solid circles are present syntheses at 1300°C and 1425°C. Solid triangle is Fo_{88} sintered from loose powder as described in text. Open squares are Warner and Luth (1973) synthesized at a variety of temperatures. Estimated standard deviations are smaller than symbol size. Upper line connects monticellite and forsterite end-member volumes and lower line connects forsterite and γ-Ca_2SiO_4.
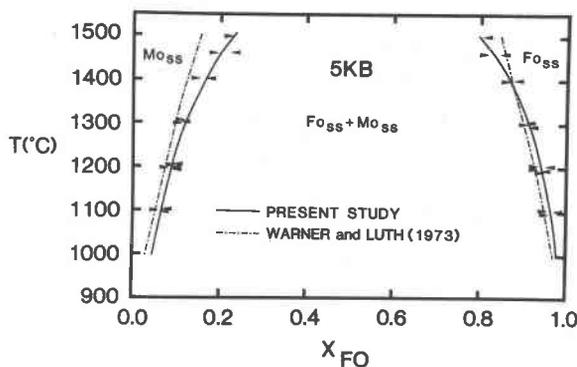

Fig. 3. Miscibility gap at 5 kbar in the forsterite–monticellite system. Arrows give the direction of composition changes in experiments. Solid curve is the model discussed in the text. Dashed curve is the model of Warner and Luth (1973).

richer in Ca than the coexisting olivine, it could account for the difference.

Lumpkin and Ribbe (1983) have shown that disordering on M1 and M2 can affect the size of the olivine unit-cell parameters at a given composition. Although the a and b cell dimensions are the most sensitive to disordering, there is a small volume effect to assess. At Fo_{90}, for example, the difference in unit-cell volume between a completely ordered and a completely disordered olivine is 0.77Å^3. As can be seen from Figure 2, this quantity is insufficient to account for the discrepancy between the two sets of results. In fact, Warner and Luth's results fall below the completely disordered curve. Disordering is even more unlikely as a cause of the discrepancy given the similar degrees and small total amounts of disordering that occur in these two studies, as shown below.

Two-phase experiments

Compositions of coexisting phases from the two-phase experiments are listed in Table 2, and are plotted on isobaric phase diagrams at 5 and 10 kbar in Figures 3 and 4.
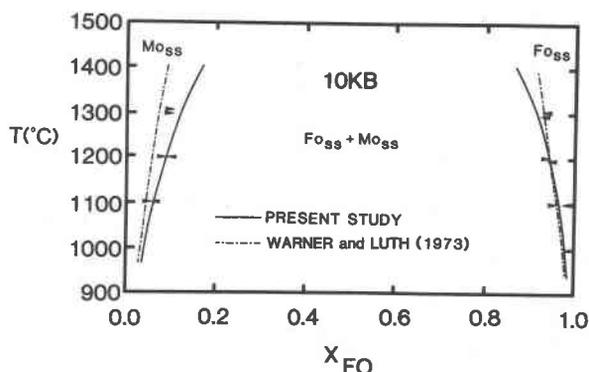

Fig. 4. Miscibility gap at 10 kbar in the forsterite–monticellite system. Arrows give the direction of composition change during experiments. Solid line is the model discussed in the text. Dashed curve is model of Warner and Luth (1973).

Reversals that generally are within 1 mole% of each other indicate that equilibrium has been approached closely throughout the series of experiments. In some runs, minor amounts of additional phases such as akermanite and merwinite were detected both by X-ray and microprobe. The presence or absence of these phases apparently has no measurable effect on the compositions of coexisting Fo_{ss} and Mo_{ss}, as indicated by the lack of any inflections in the curves of Figures 3 and 4, and by the tight reversals for runs containing different phase assemblages (e.g., 69s and 71u).

Akermanite commonly occurs in runs to which oxalic acid was added. In several runs akermanite was accompanied by magnesian calcite which allowed crystallization of the more SiO_2-rich phase. Merwinite occurs with Mo_{ss} and Fo_{ss} in one run (67s) at 1300°C and 10 kbar, and with only Fo_{ss} at 1400°C and 10 kbar (83s). This latter assemblage is apparently due to the breakdown reaction reported by Yoder (1968):

$$Mo_{ss} = Merwinite + Fo_{ss} \qquad (1)$$

At a pressure of 10 kbar, 1300°C is close to the univariant boundary curve, and 1400°C is within the merwinite field. The presence of residual Mo_{ss} at 1300°C may be kinetically controlled, but the agreement in Mo_{ss} composition between 67s and 57s (10 kbar, 1300°C, no merwinite) indicates that the Mo_{ss} composition is in equilibrium with Fo_{ss} in 67s. Because of reaction (1), 1300°C represents the upper temperature limit for two-phase experiments at 10 kbar.

In one run containing an H_2O flux, the run product consisted of a mixture of forsterite and diopside, with minor akermanite and monticellite. No silica-deficient phase was found in this run to maintain the bulk composition on the forsterite–monticellite join. Also, according to the phase relations summarized by Warner and Luth (1973), forsterite, diopside, akermanite and monticellite are not mutually compatible under any conditions. The reason for the appearance of diopside is not known.

Cation disordering on M1 and M2

In general, Ca, with an ionic radius of 1.00Å (Shannon, 1976), is strongly partitioned into the larger M2 site, whereas Mg (0.72Å) is partitioned into the M1 site. The degree of disordering in olivine can be determined from the a–b diagram of Lumpkin et al. (1983) because disordering requires Ca to go into M1, stretching the olivine structure in the a-direction. In order to assess the impact of disordering on our X-ray data, the unit-cell parameters of our single-phase and two-phase run products were used to calculate octahedral site occupancies using the a–b diagram (Figures 5 and 6). The single-phase syntheses of Warner and Luth (1973) have also been plotted in these diagrams.

Ideally, the a–b diagram is based on observed cell data for end-member forsterite, γ-Ca_2SiO_4, and monticellite. The end-member data used by Lumpkin et al. (1983) for γ-Ca_2SiO_4 and monticellite have been incorporated in Figures 5 and 6, but a small correction has been made in the
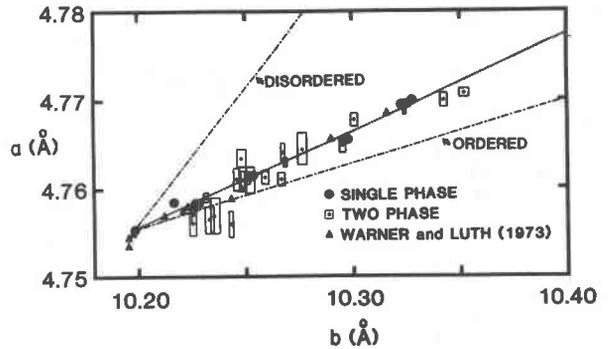

Fig. 5. Unit-cell a dimension vs. b dimension for forsterite-rich solid solutions. Solid circles are single-phase syntheses from the present work. Rectangles are forsteritic members of two-phase experiments run at 1100 to 1500°C, 5 and 10 kbar, with the size of the rectangle corresponding to the estimated standard deviation of the unit-cell determination. Solid triangles are data of Warner and Luth (1973). Dashed lines are calculated from Lumpkin et al. (1983); the lower line connects calculated monticellite and forsterite end-members, and the upper connects forsterite and γ-Ca_2SiO_4 end-members. Dotted line is least-squares fit through single-phase data from present work, and corresponds to 11% of the Ca on M1.

forsterite parameters based on recent syntheses of pure forsterite (Table 3). Unfortunately, the Crestmore, California monticellite used in the diagram contains 3.98 wt.% FeO (Moehlman and Gonyer, 1934). Also, the degree of order has not been directly determined (Onken, 1965). Because pure, ordered monticellite cannot be synthesized, there is presently some uncertainty as to where the monticellite point should lie in Figures 5 and 6. Given this uncertainty, we estimate that the site-occupancy calculations near the monticellite end-point have errors as high as ±0.05%. Be-
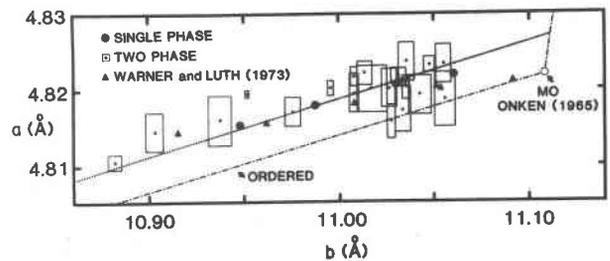

Fig. 6. Unit-cell a dimension vs. b dimension for monticellite-rich solid solutions. Solid circles are single-phase syntheses from the present work. Rectangles are monticellite-rich members of two-phase experiments, with the size of the rectangle corresponding to the estimated standard deviation of the unit-cell determination. Solid triangles are data from Warner and Luth (1973). Open circle is monticellite from Onken (1965). Dashed lines are calculated from Lumpkin et al. (1983); the lower line connects monticellite and forsterite end-members, and the near-vertical line connects monticellite and γ-Ca_2SiO_4 end-members. Dotted line corresponds to 2% of the Ca on M1.

Table 3. Unit-cell dimensions for end-member forsterite

$a(\text{Å})$	$b(\text{Å})$	Reference
4.759	10.210	Calculated: Lumpkin et al. (1983)
4.7551(5)	10.1984(8)	Present study
4.7563(2)	10.2005(4)	
4.7537(6)	10.1980(11)	Warner and Luth (1973)
4.7555(6)	10.1996(10)	
4.7549(3)	10.1976(11)	
4.7553(6)	10.1977(14)	Nishizawa and Matsui (1972)
4.752(3)	10.193(8)	Hazen (1976)
4.755(1)	10.198(1)	Brousse et al. (1984)
4.754(2)	10.195(4)	

cause of the usefulness of the a–b diagram for determining site occupancies and subsequent thermodynamic parameters, it is especially important that it be well calibrated. Further work on this system, particularly with a sensitive site-occupancy determinant such as CHEXE (Smyth and Taftø, 1982), is desirable.

Single-phase run products from Warner and Luth (1973) display similar degrees of disorder to single-phase products from this study. A maximum of about 11% of the total Ca is on M1 at the forsterite-rich end and about 2% of total Ca is on M1 at the monticellite-rich end. These results are consistent with the fact that the size difference between M1 and M2 is smaller for Fo_{ss} than Mo_{ss}. Warner and Luth (1973) do not report refinements of their two-phase data so that it is impossible to determine the degree of disorder in these run products. The maximum degree of disorder in two-phase olivines from the present study is similar to those of the single-phase results.

A small temperature effect on disordering may be indicated by the two-phase data plotted in Figure 5. All but one of the 1100°C runs and one 1200°C run actually plot slightly below the ordered curve in the figure. The rest of the 1200°C runs and all of the higher-temperature data fall close to the curve of 11% total Ca on M1. This may indicate that the degree of disorder is temperature dependent, with discernible disorder beginning at about 1200°C. The results are unsystematic, however, since higher temperatures do not lead to progressively more disorder. This may be due to an inability to quench higher degrees of disorder in forsteritic olivines. All of the single-phase olivines were synthesized above 1200°C (1300–1425°C), and these also fall near 11% total Ca on M1. Warner and Luth's single-phase olivines were synthesized in the temperature range 890–1450°C. The limited amount of disorder in the single-phase Fo_{ss} syntheses is consistent with our small negative excess mixing volumes plotted in Figure 2.

The degree of disorder that can be quenched into Ca-Mg olivines apparently has little effect on the X-ray determinative curves used in this study. Lumpkin et al. (1983) show that d_{130} and d_{131} are both strongly dependent on the degree of order and that d_{112} is nearly independent of the degree of order. X-ray determinative curves for all of these d-spacings, as well as for unit-cell volume, have been calculated from our single-phase results. Apparent compositions of the two-phase olivines have been calculated from these

four curves and listed in Table 2. The agreement among the apparent compositions from these four curves is excellent, averaging 0.3% for Fo_{ss} and 0.5% for Mo_{ss}. In addition, when run products were of sufficient size, compositions were ascertained by electron microprobe (Table 2). The agreement between the microprobe compositions and the mean X-ray value averaged 0.6% for Fo_{ss} and 0.8% for Mo_{ss}. The four X-ray determinative curves, based on the present single-phase syntheses, are:

$$100 \, X_{Fo} = 4447.38 - 2513.20(d_{130}) + 340.38(d_{130})^2 \quad (2)$$

$$r^2 = 0.99987$$

$$100 \, X_{Fo} = 4683.86 - 2957.30(d_{131}) + 450.70(d_{131})^2 \quad (3)$$

$$r^2 = 0.99990$$

$$100 \, X_{Fo} = 6435.89 - 4305.24(d_{112}) + 702.81(d_{112})^2 \quad (4)$$

$$r^2 = 0.99990$$

$$100 \, X_{Fo} = 1308.35 - 6.0809(V) + 6.6087 \times 10^{-3}(V)^2 \quad (5)$$

$$r^2 = 0.99991$$

As Lumpkin et al. (1983) point out, it is preferable to use d_{112} to calculate olivine compositions if the degree of disorder is unknown. The equation they give for d_{112} was based on the syntheses of Warner and Luth (1973) and should be replaced by equation (4) given here.

It has been suggested that the widening in the 10 kbar miscibility gap reported by Warner and Luth may be an artifact of using d_{131} as the composition determinant, because increasing disorder as temperature increases would cause the apparent compositions to shift (Lumpkin et al., 1983). The results of the present study suggest that the degree of disorder that can be quenched into experimental Ca–Mg olivines, particularly Mo_{ss}, is insufficient for a significant composition effect to be noticed. Other evidence supports this conclusion. If disorder were sufficient to be observed at 1300°C and 10 kbar, it would probably also be observed at 1300°C and 5 kbar. The 5 kbar data of Warner and Luth show a steady increase in miscibility from 800 to 1300°C. Also, as noted by Lumpkin et al. (1983), increasing disorder in Mo_{ss} would cause an apparent composition, based on d_{131}, to shift toward Mo. However, concomitant increasing disorder in Fo_{ss} would also cause the apparent composition to shift toward Mo. As a result, instead of a symmetric widening of the miscibility gap, both solvus limbs would curve in the same direction.

None of the partially disordered Fo_{ss} reported in this study has Ca in M1 greater than 0.03. Thus, even the olivines with apparent disorder of 11% of total Ca in M1 are nearly within the stated error limits of being completely ordered. Although the amount of disordering indicated in Figures 5 and 6 is slight, it is important in several respects. Besides the possible effect on apparent bulk compositions from X-ray curves, it also has an effect on the thermodynamic properties of the minerals involved. In particular, the entropy increase associated with disordering may have an effect on the Ca–Mg exchange reaction between olivine

and clinopyroxene. All modeling of the experimental results on that exchange reaction to date have assumed a one-site exchange reaction to be occurring (Adams and Bishop, 1982).

Discussion

There is considerable disagreement between compositions of coexisting Fo_{ss} and Mo_{ss} determined in this study and those determined by Warner and Luth (1973). These lead to different conclusions concerning the amount of asymmetry in the solvus limbs (Figs. 3 and 4), presence of high-temperature widening of the miscibility gap at 10 kbar (Fig. 4), and the effect of pressure (Fig. 7). Because the degree of disorder is minor and probably similar in the two studies, the discrepancies must be due to other factors. Most of the differences can be ascribed to failure to reach equilibrium in the experiments of Warner and Luth. This is most easily seen in the Mo_{ss} data at 5 and 10 kbar (Figs. 3 and 4). The compositions between the two sets of experiments can be compared directly because there is no disagreement between the X-ray determinative curves in this composition range. It is apparent from the reversed data in this study that the Mo-rich compositions of Warner and Luth, which started from higher Mo concentrations, did not completely come to equilibrium, particularly at high temperature.

Comparison of the Fo_{ss} data is complicated by differences in the X-ray determinative curves. It appears from Figures 3 and 4 that some of the experiments of Warner and Luth have acquired higher Mo contents than those of the present study. However, the X-ray determinative curve they used causes the Mo component to be overestimated by about 3 mole% $CaMgSiO_4$ in the composition range of interest. When this correction is applied to their results, it once again becomes apparent that equilibrium was not achieved, especially at high temperatures.
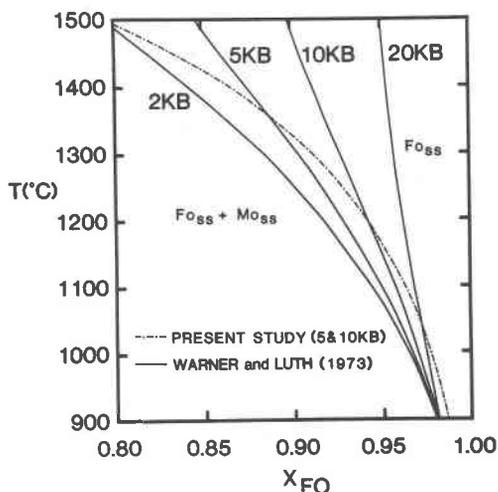
Because one of the X-ray determinative curves used by Warner and Luth (1973) is incorrect, the apparent symmetry that they report for the Fo_{ss} and Mo_{ss} solvus limbs does not exist (Figs. 3 and 4). This is in contrast to the nearly symmetric miscibility gap for kirschsteinite-fayalite (Mukhopadhyay and Lindsley, 1983), but similar to the asymmetric miscibility gap between enstatite and diopside in which the Ca-rich component displays greater solid solution (e.g., Lindsley et al., 1981).

The widening of the 10 kbar miscibility gap relative to that for lower pressures as temperature is increased above 1200°C was not observed in the present study. One possible explanation for the widening is that those experiments were even further from equilibrium than the experiments at lower temperature. The run times reported by Warner and Luth decrease as temperature increases. Although this may account for the progressive increase in disequilibrium in their data, it is difficult to reconcile with the fact that their run times are comparable to those reported here. The degree of widening, 1.0% in Fo_{ss} and 2.1% in Mo_{ss}, is of the same order as their stated precision of 1.5%. For example, their two 1100°C and 10 kbar runs of the same duration have Fo_{ss} compositions which differ by 1.6%. This is less precise than results in the present investigation because Warner and Luth (1973) used only the d_{131} diffraction line to determine compositions of coexisting phases in their two-phase experiments.

Another significant difference between our results and those of Warner and Luth is the effect of pressure on the position and shape of the solvi (Figure 7). Warner and Luth's data require a negative volume of mixing at temperatures below 890°C, and a positive volume of mixing at temperatures above 890°C. This is, in fact, the opposite trend one would expect if disorder were increasing at higher temperatures (cf., Figs. 1 and 2). Our data predict no measurable pressure effect (Fig. 7), consistent with the small excess volumes measured at 25°C and 1 bar.

Thermodynamic excess functions for forsterite–monticellite solid solutions were calculated from the two-phase composition data by a Margules-type expansion following the method of Thompson and Waldbaum (1969) and using the notation of Thompson (1967). The data were fitted to a single-site model, which assumes that all Ca–Mg mixing takes place on M2. The success of the model in reproducing the experimental data (Figs. 3 and 4) justifies this approach as a first approximation. Further experiments on the amount of disordering in these phases are needed before a two-site model can be constructed. The X-ray analysis from each run exhibiting the greatest re-equilibration was entered into the calculation. The resulting values for the excess functions are:

$$W_{G_{Fo}} = 43.1 \text{ kJ/mole} - T(6.01 \text{ J/deg-mole}) \qquad (6)$$

$$W_{G_{Mo}} = 61.2 \text{ kJ/mole} - T(15.2 \text{ J/deg-mole}) \qquad (7)$$

The large value of W_S in equation (7) may reflect the entropy associated with partial disorder in Fo_{ss}. Equations (6) and (7) were used to generate the smoothed solvi shown in

Fig. 7. Effect of pressure on the forsterite-rich end of the forsterite–monticellite miscibility gap. Solid curves are from Warner and Luth (1973), dashed curve from the present study.
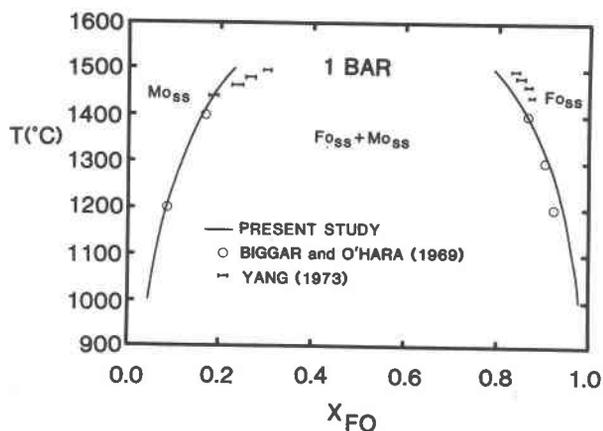
Fig. 8. Miscibility gap at one bar calculated from the present data. The data of Yang (1973) (plotted as error bars), and Biggar and O'Hara (1969) (circles) are shown for comparison.

Figures 3, 4 and 7 by the method of Scatchard (Luth and Fenn, 1973).

The results of previous work at one atmosphere (Biggar and O'Hara, 1969; Yang, 1973) and 2 kbar (Warner and Luth, 1973) may also be compared to the present experiments by calculating the appropriate miscibility gaps from the derived Margules parameters (Equations (6) and (7)). The 2 kbar miscibility gap of Warner and Luth contains two points which are reversed: 900°C and 1200°C. The agreement with our calculated solvi is 0.3 mole% for Fo_{ss} and 1.4 mole% for Mo_{ss}, within their stated error. The calculated one-atmosphere miscibility gap from our data is presented in Figure 8 along with the experimental data from Biggar and O'Hara (1969) and Yang (1973). Our model shows some discrepancy with the results of Yang (1973), but is very close to the results of Biggar and O'Hara (1969), indicating that they apparently achieved equilibrium despite the problems inherent in the use of metastable starting materials.

Acknowledgments

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