

## Diopside-tridymite liquidus boundary line in the system $\text{Mg}_2\text{SiO}_4\text{-CaMgSi}_2\text{O}_6\text{-SiO}_2$ at atmospheric pressure\*

TEH-CHING LIU, DEAN C. PRESNALL

Geosciences Program, The University of Texas at Dallas, P.O. Box 830688, Richardson, Texas 75083-0688, U.S.A.

### ABSTRACT

The presence or absence of a temperature maximum and minimum on the diopside-tridymite liquidus boundary line in the system  $\text{Mg}_2\text{SiO}_4\text{-CaMgSi}_2\text{O}_6\text{-SiO}_2$  at atmospheric pressure has been a matter of dispute. To resolve this controversy, we have determined the temperature profile and compositions of coexisting diopside and liquid along the diopside-tridymite liquidus boundary line from the invariant point tridymite-diopside-pigeonite (1376 °C) to a point on the opposite side of the join  $\text{CaMgSi}_2\text{O}_6\text{-SiO}_2$  from the invariant point. The temperature profile along the diopside-tridymite liquidus boundary is constrained by (1) close brackets of the first appearance of diopside for starting compositions in the tridymite primary phase field and (2) determination of the compositions of glasses along this boundary line at known temperatures. Because the temperature gradient is extremely small and near the limit of experimental resolution, our data do not definitively resolve the issue. However, the data are most consistent with continuously decreasing temperatures along the diopside-tridymite boundary from the tridymite-diopside-pigeonite invariant point. Also, three-phase triangles of glass + diopside + tridymite, determined for a range of liquid compositions along the boundary line, show the same orientation over the entire length of the diopside-tridymite boundary line and are consistent with a continuously decreasing temperature profile.

### INTRODUCTION

The system  $\text{Mg}_2\text{SiO}_4\text{-CaMgSi}_2\text{O}_6\text{-SiO}_2$ , a classic ternary system used to discuss the petrogenesis of basaltic magmas, was first investigated at atmospheric pressure by Bowen (1914). In his original diagram, temperatures along the boundary line between the pyroxene and silica primary phase fields were shown continuously decreasing from the  $\text{Mg}_2\text{SiO}_4\text{-SiO}_2$  side to the  $\text{CaMgSi}_2\text{O}_6\text{-SiO}_2$  side. Schairer and Yoder (1962) recognized a boundary line separating the fields of diopside and protoenstatite and showed a temperature minimum on the diopside-tridymite boundary line. Schairer and Kushiro (1964) subsequently found that the join  $\text{CaMgSi}_2\text{O}_6\text{-SiO}_2$  is not binary and therefore cannot be a thermal barrier. In their diagram, they omitted the temperature minimum and showed the temperature continuously decreasing from the tridymite-protoenstatite-diopside invariant point to the join  $\text{CaMgSi}_2\text{O}_6\text{-SiO}_2$ . Kushiro (1972) recognized a third pyroxene, pigeonite, at the liquidus, and redetermined the location of the diopside-tridymite boundary line using electron-microprobe analyses. He again showed the temperature profile along the diopside-tridymite boundary line to be continuously decreasing from the tridymite-pigeonite-diopside invariant point (previously thought to be the tridymite-protoenstatite-diopside invariant point)

to the join  $\text{CaMgSi}_2\text{O}_6\text{-SiO}_2$ . Longhi and Boudreau (1980) located an orthoenstatite liquidus field but did not study the diopside-tridymite boundary line. In their diagram, they took the diopside-tridymite boundary from the work of Kushiro (1972).

On the join  $\text{CaMgSi}_2\text{O}_6\text{-MgSiO}_3$ , Kushiro and Schairer (1963) found a temperature maximum on the diopside liquidus that lies slightly toward  $\text{MgSiO}_3$  from  $\text{CaMgSi}_2\text{O}_6$ . Kushiro (1972) redetermined the location of this maximum and placed it slightly toward the  $\text{Mg}_2\text{SiO}_4$  apex from the join  $\text{CaMgSi}_2\text{O}_6\text{-MgSiO}_3$ . On the basis of the existence of this maximum, Morse (1980, p. 203–206) argued that there must exist a special diopside-silica tie-line corresponding to a point of maximum thermal stability (point  $M'$  in Fig. 1) on the diopside-tridymite boundary line. Because temperatures must decrease slightly along this boundary line as it extends from the tridymite-pigeonite-diopside invariant point, Morse correctly argued that his postulated temperature maximum would also require a temperature minimum (point  $m$  in Fig. 1). Longhi (1987, p. 304, 313) stated that Tucker, working in Longhi's laboratory, has confirmed the existence of the maximum  $M'$  and the minimum  $m$  (Fig. 1), but that the results are inconclusive.

In the absence of diopside solid solution, the argument of Morse would hold. However, because (1) diopside solid solution occurs on both sides of the liquidus maximum and (2) temperatures along the diopside-tridymite boundary line are lower than the diopside liquidus maximum,

\* Contribution no. 587, Geosciences Program, The University of Texas at Dallas.

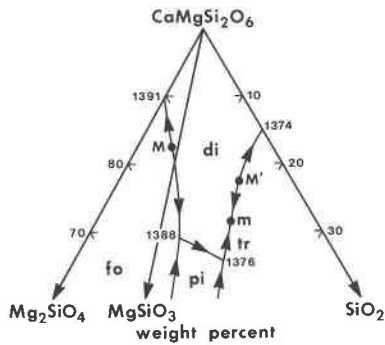


Fig. 1. Liquidus surface of the system  $\text{Mg}_2\text{SiO}_4$ - $\text{CaMgSi}_2\text{O}_6$ - $\text{SiO}_2$  at atmospheric pressure (redrafted after Morse, 1980). Point  $M$  is a temperature maximum on the forsterite-diopside boundary line. Points  $M'$  and  $m$  are a temperature maximum and a temperature minimum, respectively, on the diopside-tridymite boundary line proposed by Morse (1980).

the diopside apex of diopside-tridymite-liquid three-phase triangles is not constrained to lie at the diopside liquidus maximum. Stated another way, the diopside liquidus maximum would fix the composition of diopside in equilibrium with tridymite and liquid only at the temperature of the diopside liquidus maximum. However, this maximum occurs at a temperature above which all diopside-tridymite tie-lines have vanished. Thus, no topological requirement exists for a temperature maximum along the diopside-tridymite boundary line. In this case, a temperature minimum also would not occur, and temperatures along the boundary line would decrease continuously from the pigeonite-diopside-tridymite invariant point toward the join  $\text{CaMgSi}_2\text{O}_6$ - $\text{SiO}_2$ .

The controversy could normally be resolved experimentally with little difficulty. However, temperature gradients along the diopside-tridymite boundary line are extremely small, and the increase in temperature caused by the temperature maximum, if it exists, would be near the limit of temperature reproducibility ( $\pm 1^\circ\text{C}$ ). Nevertheless, we have carried out a careful experimental study designed to resolve the controversy. Two approaches have been used. First, we have determined the temperature profile along the diopside-tridymite boundary line. Second, we have analyzed the compositions of coexisting glass and diopside in experiments that consist of glass, tridymite, and diopside. These analyses define a series of three-phase triangles along the diopside-tridymite boundary line. The liquid apices of these three-phase triangles must always point toward lower temperatures along the boundary line and would reveal the existence of a temperature maximum or minimum.

#### EXPERIMENTAL METHOD

Starting mixtures (Table 1 and Fig. 2) were prepared according to procedures described by Presnall (1966) and Presnall et al. (1972). Ten grams of each bulk composition (Table 1) were taken through two cycles of firing in a Pt crucible for 2 h at about  $1550^\circ\text{C}$ , quenching to a

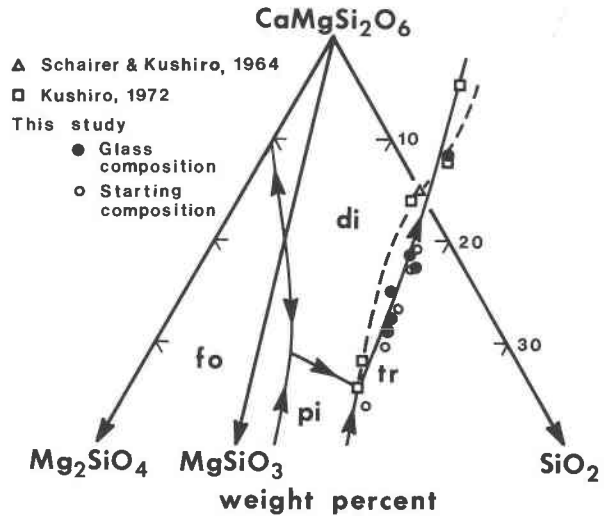


Fig. 2. The  $\text{CaMgSi}_2\text{O}_6$ -rich portion of the system  $\text{Mg}_2\text{SiO}_4$ - $\text{CaMgSi}_2\text{O}_6$ - $\text{SiO}_2$  at atmospheric pressure. Compositions of liquids along the diopside-tridymite boundary line determined in this study are shown as solid dots. Starting mixtures used in this study are shown as open circles. The dashed line is the diopside-tridymite boundary line determined by Kushiro (1972). The position of the uppermost open square is based on the composition listed in Table 1 of Kushiro (1972) and is slightly displaced from the plotted position of this point in Figure 1 of the same paper. The diopside-tridymite boundary line determined in the present study is shown as a solid line.

glass, and crushing to a powder. The glass powders were loaded into Pt envelopes, suspended in a 1-atm vertical-quenching furnace, and subsequently quenched by dropping them directly from the hot zone of the furnace into water. All temperatures were measured with a Pt-Pt<sub>90</sub>Rh<sub>10</sub> thermocouple calibrated by comparison against a standard Pt-Pt<sub>90</sub>Rh<sub>10</sub> thermocouple, which was in turn standardized by the National Bureau of Standards (NBS). All temperatures, including those of previous investigators, were corrected to conform to the International Practical Temperature Scale of 1968 (Anonymous, 1969). The liquidus temperature of diopside ( $\text{CaMgSi}_2\text{O}_6$ ) on this scale is  $1394.3^\circ\text{C}$  ( $1391.5^\circ\text{C}$  on the Geophysical Laboratory scale). Precision of the temperature measurements is estimated to be  $\pm 1^\circ\text{C}$ , and the calibration of the standard thermocouple is stated by NBS to be accurate to  $\pm 2^\circ\text{C}$ . The close agreement of the temperatures of our quenching experiments with those of previous investigations

TABLE 1. Compositions of starting mixtures (wt%)

Mixture	A	B	X	Y	Z
$\text{SiO}_2$	63.00	63.00	63.00	63.00	63.00
MgO	19.00	17.00	20.50	18.00	16.50
CaO	18.00	20.00	16.50	19.00	20.50
$\text{Mg}_2\text{SiO}_4$	10.6	4.5	15.0	7.5	3.0
$\text{CaMgSi}_2\text{O}_6$	69.6	77.3	63.8	73.4	79.2
$\text{SiO}_2$	19.9	18.1	21.2	19.0	17.7

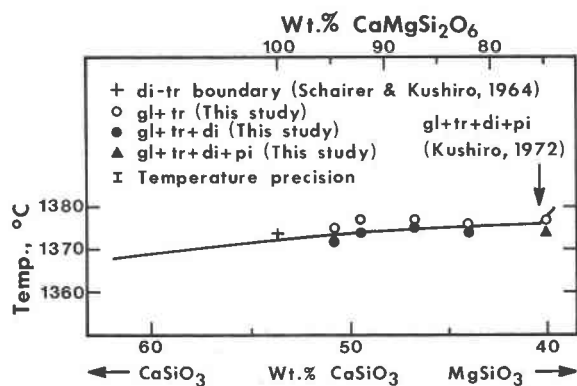


Fig. 3. Projection from  $\text{SiO}_2$  of the  $\text{CaMgSi}_2\text{O}_6$ -rich portion of the pyroxene-tridymite boundary line onto the join  $\text{CaSiO}_3$ - $\text{MgSiO}_3$ . The plus symbol is the position of the diopside-tridymite boundary at the join  $\text{CaMgSi}_2\text{O}_6$ - $\text{SiO}_2$  determined by Schairer and Kushiro (1964). The location of the tridymite-pigeonite-diopside invariant point is from Kushiro (1972). The curve is identical to that in Fig. 4 and is based on the combined data in Figs. 3 and 4 (see text).

suggests that the NBS accuracy limits are very conservative. Durations of experiments ranged from 72 to 93 h.

Phases were identified in polished sections by reflected-light microscopy. Compositions of glasses and diopsides coexisting with tridymite were analyzed with a JEOL JXA-733 electron microprobe at Southern Methodist University. All data were collected by wavelength-dispersive methods and reduced by the Bence-Albee procedure with the alpha factors of Albee and Ray (1970). Operating conditions were an accelerating potential of 15 kV, a beam current of 20 nA, and a beam diameter of 1  $\mu\text{m}$ . A glass chip of mixture B (Table 1) was used as a standard for analyses of both glasses and diopsides.

All crystals and pools of glass used for analysis have a diameter larger than 30  $\mu\text{m}$  except for some glasses and diopsides in experiment A-4, which have a diameter of about 10 to 25  $\mu\text{m}$ . Analyses of diopsides were accepted if (1) the sums of element oxides were between 99 and 101 wt% and (2) the structural formulae showed between

TABLE 2. Reversal experiments

Expt. no.	Initial condition		Final condition		Phases*
	Temp. (°C)	Duration (h)	Temp. (°C)	Duration (h)	
<b>Mixture B</b>					
B-46	1367	73	1380	58	gl + tr
B-47	1380	58	1365	73	gl + tr + di
<b>Mixture X</b>					
X-35	1373	72	1379	72	gl + tr
X-33	1379	72	1373	72	gl + tr + di + pi
<b>Mixture Z</b>					
Z-38	1361	73	1379	73	gl + tr
Z-39	1378	72	1363	72	gl + tr + di

\* gl = glass, tr = tridymite, di = diopside, pi = pigeonite.

3.98 and 4.02 cations and between 1.98 and 2.02 Si atoms per six oxygen atoms (Turnock and Lindsley, 1981).

### REVERSAL EXPERIMENTS

The diopside-tridymite boundary line has been reversed for mixtures B, X, and Z (Table 2). All of these mixtures lie in the tridymite primary phase field toward the silica apex from the diopside-tridymite boundary (Fig. 2). On cooling, they initially crystallize tridymite and then diopside. Reversals were accomplished by the method of Presnall et al. (1978). By this procedure, the first appearance of diopside was bracketed by two experiments of a specific duration, for example, 72 h. To obtain a reversal, one experiment was made in which the sample was first held above the diopside-appearance temperature for 72 h. Then, without taking the sample out of the furnace, the temperature was changed to a temperature lower than the diopside-appearance temperature and held for another 72 h. A second experiment was made in which the sample was first held at a temperature below the diopside-appearance temperature for 72 h and then raised to a higher temperature for another 72 h. Successful reversal experiments showed the phase assemblage presumed to be stable at the temperature of the second half of the experiment. This type of reversal has the advantage of being independent of the nature of the starting material. The shortest reversal time attempted was 58 h (Table 2); all experiments were held for at least 72 h.

### TEMPERATURE PROFILE ALONG THE DIOPSIDE-TRIDYMITE BOUNDARY LINE

Two methods were used to determine temperatures along the diopside-tridymite liquidus boundary. In one method, temperatures were determined by closely bracketing the first appearance of diopside for five starting compositions located near the boundary line but within

TABLE 3. Quenching experiments

Expt. no.	Temperature (°C)	Duration (h)	Phases*
A-26	1376	74	gl + tr
A-4	1374	72	gl + tr + di
A-15	1370	74	tr + di
B-27	1377	72	gl + tr
B-7	1374	73	gl + tr + di
B-16	1370	73	gl + tr + di
B-6	1361	93	tr + di
X-25	1377	72	gl + tr
X-17	1374	72	gl + tr + di + pi
Y-37	1377	72	gl + tr
Y-31	1375	72	gl + tr + di
Y-23	1373	72	gl + tr + di
Y-21	1369	72	gl + tr + di
Z-48	1375	72	gl + tr
Z-24	1372	72	gl + tr + di
Z-22	1370	72	gl + tr + di
Z-30	1369	72	gl + tr + di

\* Abbreviations same as in Table 2.

the tridymite primary phase field (Fig. 2). The results of the quenching experiments are in Table 3. Figure 3 shows the data of Table 3 projected from  $\text{SiO}_2$  onto the join  $\text{CaSiO}_3$ - $\text{MgSiO}_3$ . As shown in Figure 3, our results agree with the results of Schairer and Kushiro (1964) for the temperature of the diopside-tridymite boundary where it crosses the join  $\text{CaMgSi}_2\text{O}_6$ - $\text{SiO}_2$ . Bowen's (1914) result, however, is 10 °C lower than that of Schairer and Kushiro (1964). Other liquidus temperatures determined by Bowen (1914) in this region of the phase diagram are also slightly lower than modern determinations.

In the second method, the temperature profile along the diopside-tridymite boundary line was determined from electron-microprobe analyses of glasses coexisting with diopside and tridymite (Table 4). In Figure 4, the glass compositions in Table 4 are projected from the silica apex onto the join  $\text{CaSiO}_3$ - $\text{MgSiO}_3$ , as in Figure 3.

There is a suggestion of a temperature maximum in Figure 3 between 45 and 50%  $\text{CaSiO}_3$ , but the temperature uncertainty is large enough that a continuously decreasing temperature along the boundary line is also consistent with the data. Conversely, at the same location along the boundary line in Figure 4 (45–50%  $\text{CaSiO}_3$ ), there is a suggestion of a temperature minimum. Again, the data are also consistent with a continuously decreasing temperature profile toward  $\text{CaSiO}_3$ . The temperature profile drawn in Figure 3 is the same as that shown in Figure 4. It is a compromise between the two sets of data and is drawn to be consistent with both.

#### LOCATION OF THE DIOPSIDE-TRIDYMITE BOUNDARY LINE

Figure 2 shows the diopside-rich region of the system  $\text{Mg}_2\text{SiO}_4$ - $\text{CaMgSi}_2\text{O}_6$ - $\text{SiO}_2$  with our redetermined location for the diopside-tridymite boundary line. Our data consist of electron-microprobe analyses of the glass in six experiments (Table 4) that contain the coexisting phases diopside, tridymite, and liquid. The new determination of the position for the boundary line removes the serpentine shape of the boundary drawn by Kushiro (1972) but is still essentially in agreement with his data points and

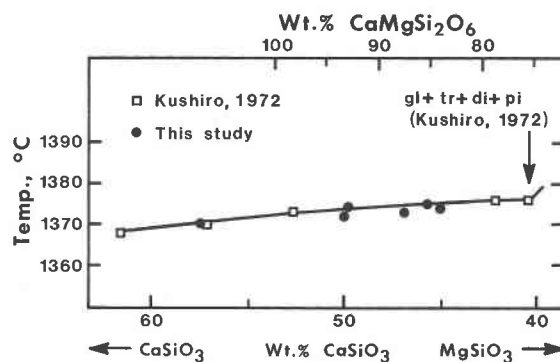


Fig. 4. Compositions of glasses coexisting with diopside and tridymite projected from the silica apex onto the join  $\text{CaSiO}_3$ - $\text{MgSiO}_3$ . See also caption to Fig. 3.

the one data point of Schairer and Kushiro (1964) on the join  $\text{CaMgSi}_2\text{O}_6$ - $\text{SiO}_2$ .

The degree of homogeneity of the glasses is indicated by the standard error of the mean shown for each value in Table 4. Most of the values shown are the mean of 4 to 6 individual spot analyses, but the homogeneity of experiment Y-23 was examined in greater detail (22 spots analyzed). The standard deviations for the oxides in this glass (not given in Table 4) are similar to those of the other glasses analyzed, but the listed standard error of the mean, as expected, is considerably smaller because of the larger number of spots analyzed. Except for experiment A-4, the listed values for the standard error of the mean are within the range expected from counting statistics, so with this one exception, compositional heterogeneity of the glasses was not detected. The larger uncertainties in the analyses of glasses in A-4 may be caused by the small areas (about 20  $\mu\text{m}$  in diameter) available for microprobe analysis.

#### THREE-PHASE TRIANGLES ALONG THE DIOPSIDE-TRIDYMITE BOUNDARY LINE

Electron-microprobe analyses of diopside coexisting with glass and tridymite are in Table 5. On the basis of

TABLE 4. Compositions of glasses (wt%) in equilibrium with diopside and tridymite

Expt. no.:	A-4	B-7	B-16	Y-23	Y-31	Z-24
No. of spots:	4	6	7	22	5	5
$\text{SiO}_2$	61.73(0.20)	62.92(0.09)	62.62(0.12)	62.23(0.07)	63.01(0.10)	62.46(0.13)
$\text{MgO}$	18.40(0.21)	16.70(0.09)	14.03(0.05)	18.20(0.03)	18.53(0.08)	16.87(0.05)
$\text{CaO}$	18.07(0.43)	19.92(0.08)	22.75(0.06)	19.32(0.02)	18.75(0.04)	20.25(0.05)
Total	98.20	99.54	99.41	99.74	100.28	99.58
$\text{Mg}_2\text{SiO}_4$	9.6	4.1	—*	7.5	8.7	4.0
$\text{CaMgSi}_2\text{O}_6$	71.1	77.4	—*	74.9	72.3	78.6
$\text{SiO}_2$	19.3	18.5	—*	17.6	19.0	17.4
$\text{MgSiO}_3$	16.2**	7.2	—†	12.6	14.8	6.9
$\text{CaMgSi}_2\text{O}_6$	83.8**	92.8	—†	87.4	85.2	93.1

Note: Standard error of the mean in parentheses.

\* Composition lies outside the system  $\text{Mg}_2\text{SiO}_4$ - $\text{CaMgSi}_2\text{O}_6$ - $\text{SiO}_2$ .

\*\* Composition as projected from silica apex onto the join  $\text{MgSiO}_3$ - $\text{CaMgSi}_2\text{O}_6$ .

† Composition as projected from silica apex lies outside the join  $\text{MgSiO}_3$ - $\text{CaMgSi}_2\text{O}_6$ .

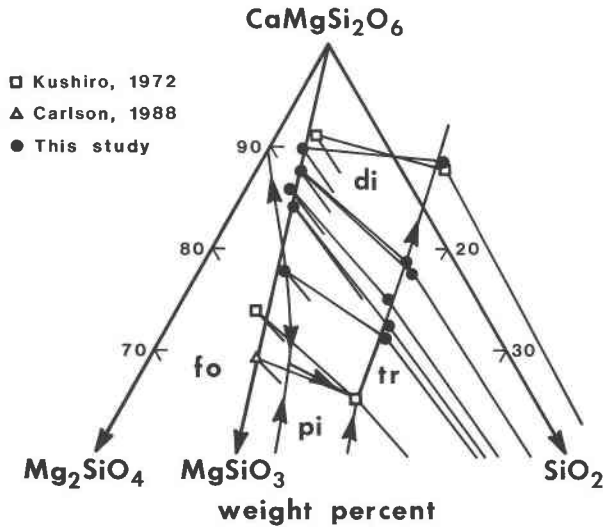


Fig. 5. Unsmoothed three-phase triangles showing the coexistence of diopside, tridymite, and glass along the diopside-tridymite boundary line. The data point of Carlson (1988) is for the equilibrium assemblage forsterite-pigeonite-diopside. It is used here on the assumption that the compositions of forsterite-saturated and tridymite-saturated diopsides in equilibrium with pigeonite are the same. Exclusion of this point would not change any of the conclusions.

backscattered-electron images and the uniform compositions of the various spots analyzed, no compositional zoning was observed in the diopsides listed in Table 5. The raw data for compositions of diopsides in equilibrium with liquids along the diopside-tridymite boundary line are plotted in Figure 5. The large variation in the orientations of the tie-lines is probably caused by the extremely small temperature gradient (see Fig. 3) along the boundary line. Small temperature fluctuations of only  $\pm 1$  °C during an experiment would cause significant movement of the liquid composition along the boundary line.

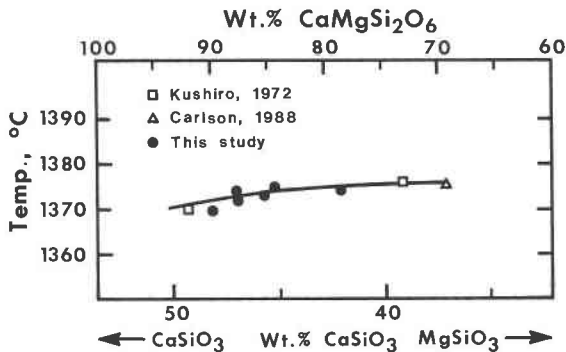


Fig. 6. Compositions of diopsides coexisting with glass and tridymite projected from the silica apex onto the join  $\text{CaSiO}_3$ - $\text{MgSiO}_3$ . The open triangle and the right-hand open square show two different determinations of the composition of diopside at the tridymite-pigeonite-diopside invariant point. See caption to Fig. 5 for statement regarding the datum of Carlson (1988).

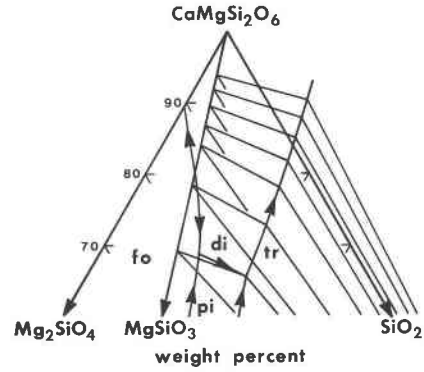


Fig. 7. Smoothed three-phase triangles at 1 °C intervals from 1376 to 1370 °C along the diopside-tridymite boundary line. Smoothed compositions of diopsides are from Fig. 6. Smoothed compositions of glasses are intersections of the diopside-tridymite boundary line with lines of projection between the silica apex and the projected glass compositions in Figs. 3 and 4. The three-phase triangle at the tridymite-pigeonite-diopside invariant point at 1376 °C (Kushiro, 1972) is constructed with the composition of diopside at this invariant point determined by Carlson (1988).

The tridymite-diopside-glass tie-lines define a series of three-phase triangles along the boundary line whose apices all point down-temperature away from the tridymite-pigeonite-diopside invariant point toward increasingly Ca-rich compositions.

Figure 6 shows the compositions of diopsides in equilibrium with glass and tridymite projected from the silica-apex onto the join  $\text{CaSiO}_3$ - $\text{MgSiO}_3$ . Figure 7 shows smoothed three-phase triangles along the diopside-tridymite boundary line at 1 °C intervals from 1376 °C at the tridymite-diopside-pigeonite invariant point to 1370 °C. The triangles are constructed by reading the smoothed compositions of glass and diopside from Figures 4 and 6, respectively, at each temperature.

The unsmoothed data on the three-phase triangles (Fig. 5) show clearly that temperatures along the diopside-tridymite boundary line near the  $\text{CaMgSi}_2\text{O}_6$ - $\text{SiO}_2$  join and also near the diopside-tridymite-pigeonite invariant point decrease away from the diopside-tridymite-pigeonite invariant point. These data are also consistent with the data of Kushiro (1972) and Carlson (1988). Therefore, only two possibilities exist. Either (1) temperatures decrease continuously from the diopside-tridymite-pigeonite invariant point or (2) a temperature minimum and maximum both occur, as suggested by Morse (1980). A single temperature minimum or maximum is not possible.

The diopside-liquid tie-lines at intermediate temperatures along the tridymite-diopside boundary line (Fig. 5) show an apparently consistent clockwise rotation relative to tie-lines at both higher and lower temperatures. This rotation is in the direction expected if a temperature minimum and maximum existed along the boundary line. However, the magnitude of the rotation is not sufficient

TABLE 5. Compositions of diopsides (wt%) in equilibrium with glass and tridymite

Expt. no.: No. of spots:	A-4 7	B-7 3	B-16 5	Y-23 12	Y-31 4	Z-24 5
SiO <sub>2</sub>	57.23(0.12)	56.34(0.04)	56.34(0.09)	56.20(0.09)	56.74(0.15)	56.25(0.05)
MgO	23.10(0.08)	21.30(0.10)	20.96(0.12)	22.08(0.11)	22.06(0.18)	21.33(0.09)
CaO	20.24(0.11)	22.73(0.20)	23.43(0.12)	22.32(0.11)	21.90(0.12)	22.73(0.11)
Total	100.57	100.37	100.70	100.60	100.69	100.31
<b>Cations per six oxygens</b>						
Si	2.013	2.002	1.999	1.992	2.004	2.000
Mg	1.210	1.128	1.109	1.166	1.161	1.310
Ca	0.762	0.865	0.890	0.847	0.828	0.865
Total	3.985	3.994	3.998	4.005	3.993	3.996
MgSiO <sub>3</sub> *	21.4	12.3	10.2	14.8	15.7	12.4
CaMgSi <sub>2</sub> O <sub>6</sub> *	78.6	87.7	89.8	85.2	84.3	87.6

Note: Standard error of the mean in parentheses.

\* Projection of pyroxene compositions from silica apex onto the join MgSiO<sub>3</sub>-CaMgSi<sub>2</sub>O<sub>6</sub>.

to cause a reversal in the orientation of any of the unsmoothed three-phase triangles (see Fig. 5), as would be required if a temperature minimum or maximum occurred. Some of the three-phase triangles are very narrow, and the composition and temperature uncertainties are such that the existence of a temperature minimum and maximum cannot be positively eliminated. However, because none of the unsmoothed three-phase triangles show a reversal, we argue that the data are fit best by a continuously decreasing temperature along the boundary line.

### PETROLOGICAL APPLICATIONS

Morse (1980, p. 212) suggested that the absence of a temperature minimum along the diopside-tridymite boundary line would lead to CaSiO<sub>3</sub> enrichment in fractionating liquids. He pointed out that igneous assemblages containing wollastonite are rare in nature, which is consistent with the presence of a temperature minimum. However, the lack of wollastonite-bearing assemblages, even in the absence of a temperature minimum, is easily explained when other components are added that make the ternary system Mg<sub>2</sub>SiO<sub>4</sub>-CaMgSi<sub>2</sub>O<sub>6</sub>-SiO<sub>2</sub> more directly applicable to natural compositions. For example, Presnall et al. (1979) showed that fractional crystallization in the CaMgSi<sub>2</sub>O<sub>6</sub>-Mg<sub>2</sub>SiO<sub>4</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>-SiO<sub>2</sub> tetrahedron yields a final residual liquid at the enstatite-quartz-anorthite-diopside quaternary eutectic point (see also Longhi, 1987). This result is independent of the presence or absence of a minimum on the diopside-tridymite boundary line. Therefore, the system Mg<sub>2</sub>SiO<sub>4</sub>-CaMgSi<sub>2</sub>O<sub>6</sub>-SiO<sub>2</sub> is not adequate to constrain this aspect of the fractional crystallization of natural liquids, and the absence of a temperature minimum is of no petrological concern.

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