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Effects of F on phase equilibria and liquid structure in the system $NaAlSiO_4$-$CaMgSi_2O_6$-SiO_2

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ABSTRACT

To delineate the effects of F on phase equilibrium in depolymerized, pyroxene-bearing silicate systems, liquidus phase relations along the join $CaMgSi_2O_6$-$NaAlSi_3O_8$-F_2O_{-1} have been determined at 1-bar pressure. The substitution of 1 wt% F for a corresponding molar amount of O reduces the temperature of the liquidus of pyroxene ~25 °C for a bulk composition of Di_{100} and ~50 °C for bulk compositions of $Di_{40}Ab_{60}$ (wt%), and $Di_{20}Ab_{80}$. Along this join, the liquid in equilibrium with diopside at 1250 °C has a composition (projected F-free) of $Di_{56}Ab_{44}$, compared to the $Di_{33}Ab_{67}$ liquid in equilibrium with diopside at 1250 °C in the F-free system. This systematic shift of the liquidus to more Di-rich compositions is consistent with a decrease in the activity coefficient of $CaMgSi_2O_6$ component (γ^l_{Di}) in these liquids accompanying the substitution of F for O.

To provide a comparison of the effects of F on phase equilibria with those of water, high-pressure experiments were undertaken to delineate the liquidus of $CaMgSi_2O_6$-F_2O_{-1} with 5.11 wt% F to 15-kbar pressure. Despite uncertainties concerning the amount that H_2O depresses the liquidus of diopside, it appears that equivalent amounts of F and water have similar effects on reducing the temperature of the liquidus.

Examination of quenched, crystal-free glasses with Raman spectroscopy reveals that the substitution of F for O increases the degree of polymerization of the silicate network, consistent with a solution mechanism where F complexes with Ca and Mg in the liquid rather than with Si. Removal of Ca or Mg from a network-modifying role results in the remaining silicate part of the liquid becoming more silica-rich and, thus, more polymerized.

Expressing the $CaMgSi_2O_6$-F_2O_{-1} system as a mixture of CaF_2, MgF_2, SiO_2, and $CaMgSi_2O_6$ allows comparison of the activity coefficient for $CaMgSi_2O_6$ component in the liquid (γ^l_{Di}) in the $CaMgSi_2O_6$-F_2O_{-1} system with the values of γ^l_{Di} in the $CaMgSi_2O_6$-SiO_2, $CaMgSi_2O_6$-CaF_2, and $CaMgSi_2O_6$-MgF_2 systems. The addition of SiO_2 increases γ^l_{Di}, whereas the addition of CaF_2 and MgF_2 decreases γ^l_{Di}. Consistent with the solution mechanism, the effect of the substitution of F for O in the $CaMgSi_2O_6$-F_2O_{-1} system on γ^l_{Di} is intermediate between that in the $CaMgSi_2O_6$-SiO_2 system and that in the $CaMgSi_2O_6$-CaF_2 and $CaMgSi_2O_6$-MgF_2 systems.

The increase in polymerization with substitution of F for O suggests that addition of F to depolymerized liquids may increase the viscosity of the liquid. Furthermore, the substantial shift in the liquidus boundaries with geologically reasonable quantities of F demonstrates that the effect of F in petrogenesis cannot be neglected.

INTRODUCTION

F is a significant component in certain magmas, such as alkali granites, topaz rhyolites, and ultrapotassic rocks. Some alkali granites and topaz rhyolites contain >1 wt% F (Bailey, 1977; Christiansen et al., 1983), and minettes, melilitites, and leucitites have up to 2 wt% F (Aoki et al., 1981). Precise values for the concentration of F in whole-rock samples are limited, as most workers do not analyze routinely for F, even in alkali granites and ultrapotassic rocks.

Previous work to experimentally calibrate the effects of F on phase equilibria in silicate systems has concentrated on the effect of HF, in addition to H_2O, on phase relations in the haplogranite ($NaAlSi_3O_8$-$KAlSi_3O_8$-SiO_2) system (Wyllie and Tuttle, 1961; Manning, 1981). These workers observed that the addition of HF decreased temperatures of liquidii in this system and increased the stability field of quartz at the expense of the feldspars. Even on the $NaAlSi_3O_8$-H_2O-HF join, a field of quartz + albite + liquid + vapor was stabilized (Wyllie, 1979), suggesting that the addition of HF increased the solubility of Na and Al in either the liquid or the vapor, resulting in a deviation of the composition of both the liquid and the vapor from

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this join. Other studies on the effects of F on phase equilibria include those of Lin and Burley (1969) on the system $CaMgSi_2O_6$-CaF_2 at 1 bar and Foley et al. (1986) on the system $KAlSiO_4$-Mg_2SiO_4-SiO_2-F_2O_{-1} at 28 kbar. To examine in detail the effects of F on the stability of pyroxene, the $NaAlSi_3O_8$-$CaMgSi_2O_6$-F_2O_{-1} join was studied at 1 bar, and additional experiments were conducted at high pressure on the $CaMgSi_2O_6$-F_2O_{-1} join.

EXPERIMENTAL METHODS

F may be added to a system either as HF or by exchanging F for O. In practice, adding HF to a system also requires adding H_2O. Consequently, it is difficult to separate the effects of the F from those of the water or from those of the hydrogen in the HF. To focus on the effects of F, F was added as the F_2O_{-1} exchange operator, by substituting an amount of a fluoride, such as CaF_2, for a corresponding amount of the analogous oxide, CaO, during synthesis of the glass starting materials. In this technique, only F is added to the system, and the effects of F may be studied without interference from those of water or H. In addition, direct comparisons with the effect of H_2O may be made by recasting part of the $CaMgSi_2O_6$-H_2O system as $CaMgSi_2O_6$-$CaMgSi_2(OH)_{12}$ and comparing with the $CaMgSi_2O_6$-$CaMgSi_2F_{12}$ system.

Starting materials for this study were glasses, synthesized in two steps. Spectroscopically pure Na_2CO_3, $CaCO_3$, MgO, Al_2O_3, and SiO_2 were weighed in appropriate proportions, ground in an agate mortar under ethanol for ~1.5 h, decarbonated at 800–1000 °C for 3–4 h, and fused at 1400–1450 °C for 3–4 h. The sample was quenched, ground, and remelted, typically two to three times. After grinding and drying, an appropriate amount of F, either as AlF_3 or as CaF_2, was added to the glass and the mixture was ground under ethanol for ~1.5 h. The F-free glass was deficient in either Ca or Al when originally synthesized to compensate for this addition. Approximately 75 mg of this mixture was dried, sealed into a 5-mm-diameter Pt capsule and run in a vertical-tube, quench furnace at 1450 °C for 3–4 h, and quenched in H_2O. The capsule was weighed before and after the run to determine if the capsule had leaked and possibly lost F. The resultant glass was analyzed with the electron microprobe to confirm that the glass was homogeneous and had the assumed composition.

Glasses synthesized in this fashion were the starting materials for both the 1-bar and the high-pressure experiments. For the 1-bar experiments, approximately 5–10 mg of the appropriate starting material was loaded into a 3-mm-diameter Pt capsule, dried at ~400 °C, and welded shut. The capsule was suspended in a vertical-tube, Pt-wound quench furnace next to a Pt-$Pt_{90}Rh_{10}$ thermocouple encased in 99.98% pure alumina ceramic. The calibration of the thermocouple was periodically checked against the melting point of Au; the uncertainty in temperature was ±3 °C. At the end of the experiment, the charge was quenched in water.

The high-pressure experiments were carried out in a solid-media, high-pressure apparatus (Boyd and England, 1960). A double-capsule technique was employed for these experiments. The inner capsule was identical to that used for the 1-bar experiments, and the outer capsule contained the inner capsule and hematite, which minimized the f_{H_2} imposed on the sample. The double capsule was run vertically in a 19-mm-diameter furnace assembly (Kushiro, 1976), with the temperature monitored by a Pt-$Pt_{90}Rh_{10}$ thermocouple in contact with the top of the capsule. The piston-out technique, with a −7% friction correction, was used.

After the experiments, the sample capsules were weighed to check for loss of F and opened. Comparison of the weight of the capsule before and after the 1-bar experiments, as well as analysis of the glass with the electron microprobe, confirmed that single capsules were adequate to contain the F-bearing samples without loss of F. The experimental charges were examined in immersion oils with a petrographic microscope, and selected charges were analyzed with the electron microprobe. In the 1-bar experiments, quenched liquid was present as glass. In contrast, in slightly superliquidus experiments at high pressure, the liquid commonly quenched to dendritic crystals of pyroxene that were easily distinguishable from the euhedral prisms of pyroxene stable at subliquidus conditions.

The samples for Raman spectroscopic studies were chips of glass taken from the 1-bar, sealed-capsule syntheses. Raman spectra of these glasses were obtained with the automated Raman system described by Mysen et al. (1982) and Seifert et al. (1982). Small, 2–10-mm^3 chips of the glasses were excited by the 488-nm line of a Coherent CR-18 Ar^+ laser operating at 1.5 to 2.5 W. Other details of the data acquisition and storage, the corrections of instrumental background and of temperature- and frequency-dependent scattering are described by Mysen et al. (1982).

RESULTS

The results of the 1-bar experiments are shown in Figures 1 and 2, and the run conditions of critical experiments are summarized in Table 1. For comparison, Figure 1 also shows the results of Schairer and Yoder (1960) for the F-free $CaMgSi_2O_6$-$NaAlSi_3O_8$ join. The addition of 1 wt% F depresses the temperature of the liquidus along the $CaMgSi_2O_6$-$NaAlSi_3O_8$-F_2O_{-1} join by >25 °C. Alternatively, the presence of F shifts the composition of the liquid coexisting with pyroxene at 1250 °C from $Di_{33}Ab_{67}$ to $Di_{56}Ab_{44}$ (projected from F_2O_{-1}). No F-containing phase was observed at near-liquidus temperatures. Figure 2 illustrates the effect of increasing the amount of F in the system on the phase relations of $CaMgSi_2O_6$-F_2O_{-1} at 1-bar pressure. Addition of 5.11 wt% F depresses the temperature of the liquidus to ~1275 °C.

Figure 3 shows the results of the high-pressure phase-equilibria experiments on the DiF_5 bulk composition, which contains 5.11 wt% (= 5 mol%) F. Critical run data are summarized in Table 2. The substitution of F for O depresses the temperature of the liquidus by ~60 °C at 10 and 15 kbar, approximately half the size of the depression found at 1 bar (Fig. 2).

The background-corrected Raman spectra of Di and DiF_5 are shown in Figure 4. In the high-frequency region (800–1200 cm^{-1}), the most intense band has shifted from ~1000 cm^{-1} in the Raman spectrum of Di to ~1050 cm^{-1} in the spectrum of DiF_5. In addition, the frequency of the band at ~650 cm^{-1} decreases from ~650 cm^{-1} in the Raman spectrum of Di to ~635 cm^{-1} in the Raman spectrum of DiF_5. For comparison, the Raman spectrum of $Di_{91.1}Qz_{8.9}$ (wt%) glass is also shown in Figure 4. The similarity between the spectra of DiF_5 and $Di_{91.1}Qz_{8.9}$ is not coincidental and will be discussed below.

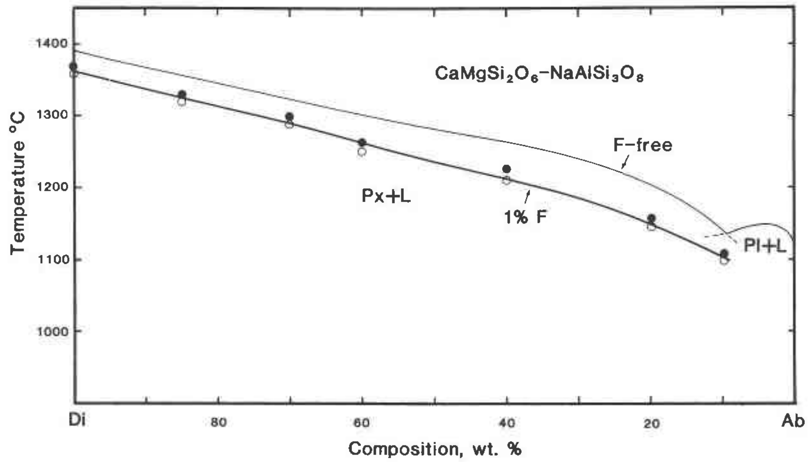

Fig. 1. Temperature-composition projection of liquidus phase equilibria for the join $CaMgSi_2O_6$-$NaAlSi_3O_8$ with 1 wt% F added. F-free phase equilibria from Schairer and Yoder (1960).

DISCUSSION

The 1-bar results on the $CaMgSi_2O_6$-$NaAlSi_3O_8$-F_2O_{-1} join demonstrated that the substitution of F for O decreases the temperature of the liquidus of clinopyroxene. Furthermore, even a relatively small depression of the temperature of the liquidus may lead to large differences in the composition of the liquid coexisting with clinopyroxene at a given temperature, because of the shallow slope of the liquidus in *T*-*X* space. The influence of F on the phase relations suggests that the relative effects of water and F on the stability of diopside would be useful to compare. The reactions for the dissolution of H_2O and F_2O_{-1} may be written formally as

$$CaMgSi_2O_6 + xH_2O \rightleftharpoons CaMgSi_2O_{6-x}(OH)_{2x}, \quad (1)$$

and

$$CaMgSi_2O_6 + xF_2O_{-1} \rightleftharpoons CaMgSi_2O_{6-x}(F)_{2x}. \quad (2)$$

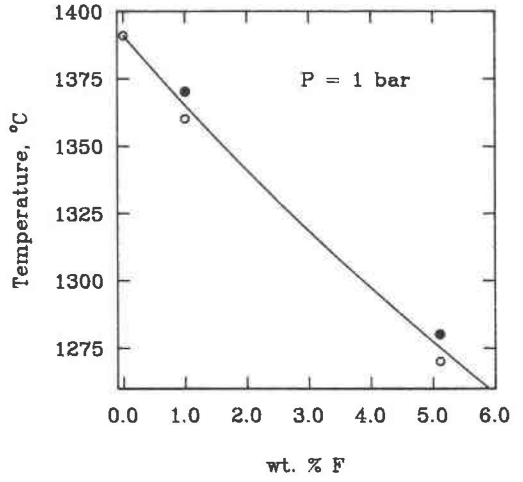

Fig. 2. Temperature-composition section for the system $CaMgSi_2O_6$-F_2O_{-1} at 1-bar pressure, illustrating the effect of addition of F on the liquidus of diopside.

TABLE 1. Results for selected experiments at 1 bar along the $CaMgSi_2O_6$-$NaAlSi_3O_8$-F_2O_{-1} join with 1 wt% added

Composition	Run	Temperature (°C)	Duration (h)	Results*
Ab_0Di_{100}	222	1330	15	px + L
	226	1340	3	px + L
	227	1350	4	px + L
	228	1360	3.3	px + L
	229	1370	3.5	L
	220	1380	3	L
$Ab_{15}Di_{85}$	233	1310	20	px + L
	234	1320	5.7	px + L
	232	1330	3	L
	221	1350	14.5	L
	223	1360	3	L
$Ab_{30}Di_{70}$	156	1280	70.3	px + L
	160	1290	70.75	px + L
	174	1290	70.0	px + L
	149	1300	49	L
$Ab_{40}Di_{60}$	102	1240	48.3	px + L
	148	1240	73.3	px + L
	104	1250	73.5	px + L
	159	1250	71.5	px + L
	106	1255	69.75	px + L
	100	1260	50	L
	155	1260	69.75	L
	99	1280	42	L
	98	1300	43	L
$Ab_{60}Di_{40}$	200	1000	936	px + pl + L
	180	1200	70	px + L
	186	1216	190	px + L
	187	1214	190	px + L
	188	1226	147	L
	179	1240	94.5	L
$Ab_{80}Di_{20}$	355	1120	48	px + L
	358	1140	48	px + L
	359	1150	72	px + L
	356	1160	120	L
$Ab_{90}Di_{10}$	171	1060	92.5	pl + px + L
	170	1100	93	L + px + pl
	185	1108	70	L
	184	1120	90.5	L
	176	1140	70	L

* Abbreviations: L = liquid, px = pyroxene, pl = plagioclase. Phases listed in order of estimated abundance in experimental charge.

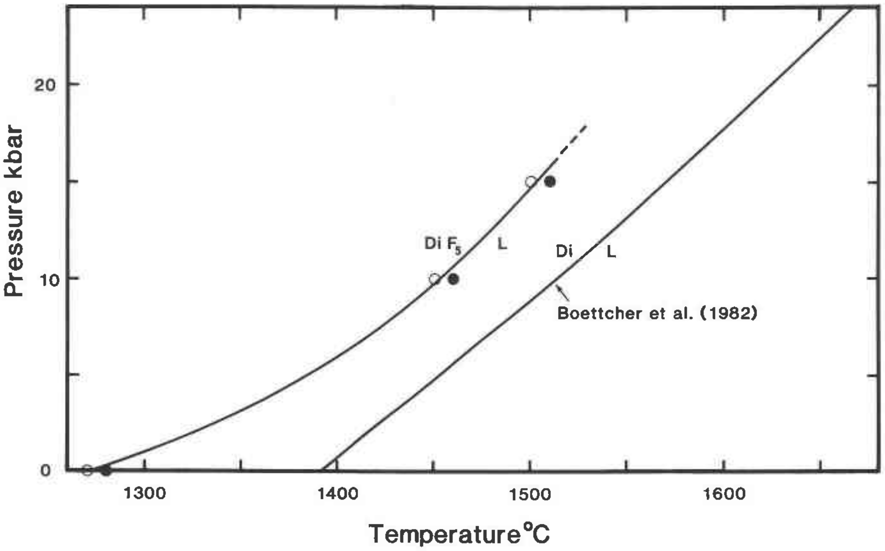

Fig. 3. Pressure-temperature projection of liquidus phase relations for the composition $0.95CaMgSi_2O_6$-$0.05CaMgSi_2F_{12}$ (DiF_5). For comparison, the liquidus of diopside in the absence of volatiles is shown as well from Boettcher et al. (1982).

These equations are valid for $0 \leq x \leq 6$, $x = 6$ corresponding to the compositions of the end members $CaMgSi_2(OH)_{12}$ and $CaMgSi_2F_{12}$, which contain 33.3 wt% H_2O and 65.4 wt% F, respectively. The most F-rich composition, DiF_5, contains 5.11 wt% F, or 5 mol% $CaMgSi_2F_{12}$, well below the maximum value. In the H_2O-bearing analogue system, 5 mol% of $CaMgSi_2(OH)_{12}$ translates to 2.43 wt% H_2O. Figure 5 shows the projection of the liquidus surfaces for diopside, DiF_5, and Di + 2.43 wt% H_2O in pressure-temperature space. The liquidus for Di + 2.43 wt% H_2O was calculated from the thermodynamic models of Eggler and Burnham (1984) and of Silver and Stolper (1985). The liquidus for DiF_5 falls between the liquidii of Di + 2.43 wt% H_2O calculated with the two different models. It must be stressed that $CaMgSi_2F_{12}$ and $CaMgSi_2(OH)_{12}$ are used here as thermodynamic components and not as species; neither $CaMgSi_2F_{12}$ nor $CaMgSi_2(OH)_{12}$ are likely to be found as discrete entities in the liquid. Although the depression of the temperature of the liquidus is of similar magnitude for equivalent amounts of water and F, more work is required on the H_2O-bearing system for more precise comparisons. The lack of appropriate experimental data is reflected in the ~50 °C discrepancy between the liquidii calculated with the two thermodynamic models.

TABLE 2. Results for experiments on the DiF_5 composition

Run	Pressure (kbar)	Temperature (°C)	Duration (h)	Results*
252	0.001	1260	4	px + L
255	0.001	1270	4	px + L
254	0.001	1280	4	L
246	0.001	1300	4	L
245	0.001	1340	4	L
285	10	1420	0.50	px + L
288	10	1440	0.50	px + L
295	10	1450	0.50	L + px
272	10	1460	0.50	L + qpx
289	10	1460	0.50	qpx + L
294	10	1480	0.50	L
259	15	1490	0.50	L + px
270	15	1500	0.50	L + px
284	15	1510	0.50	L
283	15	1520	0.50	L
271	15	1540	0.50	L

* Abbreviations: L = liquid, px = pyroxene, qpx = quench pyroxene. Phases listed in order of estimated abundance in experimental charge.

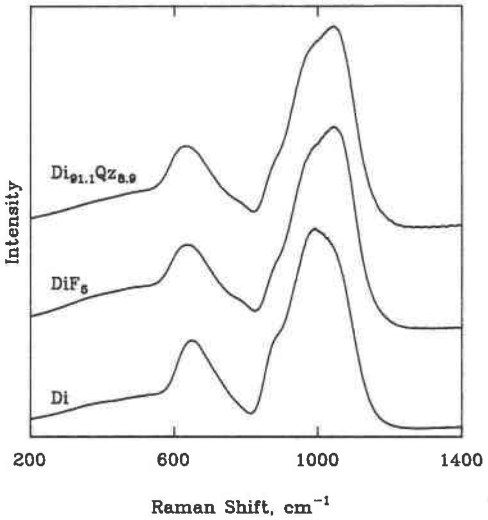

Fig. 4. Unpolarized Raman spectra for Di, DiF_5, and $Di_{91.1}Qz_{8.9}$. All spectra corrected for instrumental background and temperature- and frequency-dependent scattering (Mysen et al., 1982).

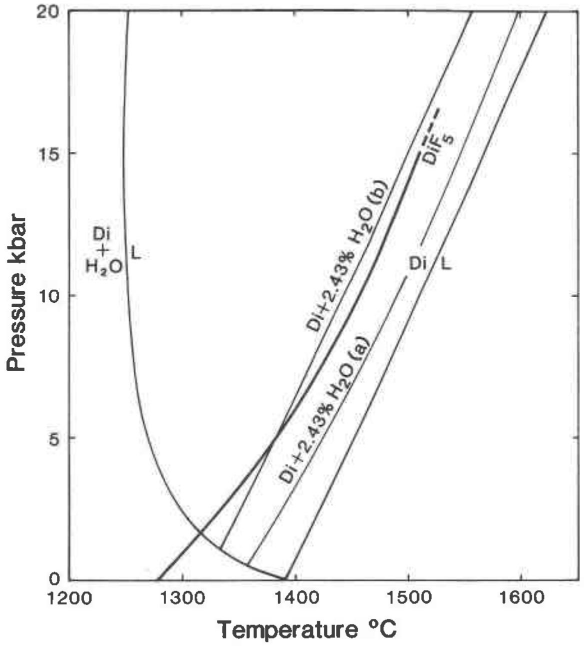

Fig. 5. Pressure-temperature projection showing the liquidus curves for diopside, DiF_5, Di + 2.43 wt% H_2O, and the solidus for Di + excess H_2O. The liquidus for diopside is from Boettcher et al. (1982) and the liquidus for DiF_5 is from Figure 3. The liquidii for Di + 2.43 wt% H_2O are calculated with (a) the model of Eggler and Burnham (1984) and (b) the model of Silver and Stolper (1985). The solidus for Di + H_2O was taken from the data of Eggler and Rosenhauer (1978).

Raman spectra and solution mechanisms

The results of the Raman spectroscopic studies (Fig. 4) corroborate those for the CaO-CaF_2-SiO_2 system (Luth, 1988), which were the basis for proposing that F dissolved in the liquid by forming complexes with network-modifying cations rather than with network-forming cations, resulting in polymerization of the liquid. The substitution of F for O in $CaMgSi_2O_6$ liquid increases the intensity of the band in the Raman spectrum of the glass (Figure 4) at ~1050 cm^{-1} and decreases the intensity of the shoulder at ~900 cm^{-1} relative to the intensity of the band at ~1000 cm^{-1}, as well as decreasing the frequency of the band at ~650 cm^{-1}. The same changes in the Raman spectrum are observed when SiO_2 is added to $CaMgSi_2O_6$ liquid ($Di_{91.1}Qz_{8.9}$ glass, Fig. 4). The bands at 900, 1000, and 1050 cm^{-1} in the spectrum of the $Di_{91.1}Qz_{8.9}$ glass are attributed to symmetric-stretching Si–O vibrations involving units with nonbridging oxygens per tetrahedrally coordinated cation (NBO/T) of three, two, and one, respectively (Mysen et al., 1980; Furukawa et al., 1981; McMillan, 1984). The changes accompanying addition of SiO_2 to $CaMgSi_2O_6$ liquid are consistent with increasing proportions of units with NBO/T = 1 at the expense of less-polymerized units with NBO/T = 2 and 3, as would be anticipated for this increase in silica content. It is suggested on the basis of the similarity of the spectra of the DiF_5 glass and the $Di_{91.1}Qz_{8.9}$ glass that the same increase in polymerized units occurs when F substitutes for O. These changes are explicable if F forms complexes with network-modifying Ca and Mg cations rather than with network-forming Si cations. This solution mechanism may be illustrated schematically by the reaction

$$x\mathrm{CaMgSi_2O_6} + y\mathrm{F_2O_{-1}} \rightleftharpoons (x - \tfrac{1}{2}y)\mathrm{CaMgSi_2O_6} + \tfrac{1}{2}y\mathrm{CaF_2} + \tfrac{1}{2}y\mathrm{MgF_2} + y\mathrm{SiO_2} \qquad (3)$$

The generation of SiO_2 by this reaction polymerizes the liquid, as inferred from the Raman spectra.

The composition of the $Di_{91.1}Qz_{8.9}$ glass (Fig. 4) corresponds to the F-free part of DiF_5, if all F formed complexes with Ca and Mg. The spectrum of this glass is identical to that of DiF_5, as predicted by the solution mechanism if there are no observable peaks in the Raman spectrum from F-containing species. Because of the highly ionic nature of Ca-F or Mg-F complexes, vibrations involving these complexes would be very weak in the Raman spectrum. Therefore, the absence of such bands in the spectra cannot be taken as evidence that such complexes are not present in the glass. By the same token, Si-F complexes may be present to some extent, despite the absence of new bands at ~945 cm^{-1} from vibrations involving SiO_3F tetrahedra (Dumas et al., 1982; Mysen and Virgo, 1985a, 1985b), for example. The polymerization of the liquid attendant upon the substitution of F for O, however, rules out the possibility that Si-F complexes are the dominant F-bearing complex.

Thermodynamic implications of F solubility

The activity of $CaMgSi_2O_6$ in liquids (a^l_{Di}) coexisting with clinopyroxene may be calculated by combining the phase-equilibrium data for the $CaMgSi_2O_6$-F_2O_{-1} join (Figs. 2, 3) with data for the enthalpy of fusion for diopside (Ghiorso and Carmichael, 1980). The standard state is taken as pure diopside liquid at the pressure and temperature of interest. Table 3 shows the calculated activities for DiF_1 (1 wt% F) and DiF_5 (5.11 wt% F) liquids at 1-bar pressure and for DiF_5 liquid at high pressure. Note, however, that all of these activities are at different temperatures. Rigorous comparison of these activities requires that they be corrected to a common temperature, which in turn requires an assumption be made concerning the dependence of the activity coefficient on temperature. If it is assumed that the excess enthalpy is independent of temperature (Ryerson, 1985), the equation

$$\ln a^l_{Di,T_2} = (T_1/T_2)\ln a^l_{Di,T_1} \qquad (4)$$

describes the relationship between the activities at two temperatures. The correction to the high-pressure activities is zero if the excess volume is independent of pressure, as is reasonable given the negligible excess volumes found for silicate liquids to date (e.g., Nelson and Carmichael, 1979; Mo et al., 1982). With these assumptions, the activities are corrected to 1650 K and 1 bar (Table 3). The value of a^l_{Di} in the liquid decreases from DiF_1 to DiF_5, consistent with the increasing F concentration in the liquid and the decreasing temperature of the liquidus.

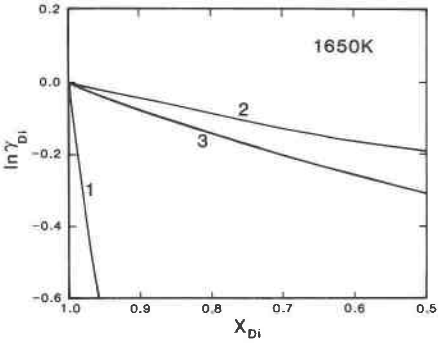

Fig. 6. Relation between the activity coefficient and the mole fraction of diopside at 1 bar; (1) refers to components $CaMgSi_2O_6$-$CaMgSi_2F_{12}$, (2) refers to $CaMgSi_2O_6$-SiO_2-CaF_2-MgF_2, and (3) refers to $Ca_{1.33}Mg_{1.33}Si_{2.67}O_8$-$Si_4O_8$-$CaF_2$-$MgF_2$. All activity coefficients have been normalized to 1650 K with Equation 3.

Increasing pressure increases the value of a^l_{Di} in liquids of DiF_5 composition between 1 bar and 10 kbar, whereupon the activity remains constant, within error, to 15 kbar.

To translate these calculated activities into activity coefficients (γ^l_{Di}), the mole fraction of diopside in the liquid must be known. To convert the composition of the liquid from weight percent to mole percent, a set of components with which to express the composition of the liquid must be selected. Activity coefficients have been calculated for three different sets of components: $CaMgSi_2O_6$-$CaMgSi_2F_{12}$, $CaMgSi_2O_6$-SiO_2-CaF_2-MgF_2, and $Ca_{1.33}Mg_{1.33}Si_{2.67}O_8$-$Si_4O_8$-$CaF_2$-$MgF_2$. The first of these is consistent with the attempt earlier in this report to describe this system in this fashion, the second is the simplest way to describe the products of the complex-forming reactions of the proposed solution mechanism, and the third recasts the silicate portion in accord with the model of Burnham (1979, 1981). The results are shown in Figure 6 in terms of the dependence of $\ln \gamma^l_{Di}$ on the mole fraction of diopside (X_{Di}). An ideal solution would have $\ln \gamma^l_{Di} = 0.00$ for all values of X_{Di}. The trends of the curves in Figure 6 are the same, independent of the set of components selected. The activity coefficients for the latter two sets of components, however, are considerably closer to unity than are those for the $CaMgSi_2O_6$-$CaMgSi_2Fi_{12}$ set. Finally, recasting the silicates on the basis of eight oxygens made the solution less ideal.

The activity coefficients for $CaMgSi_2O_6$ derived for the $CaMgSi_2O_6$-F_2O_{-1} join, with the composition of the liquid expressed by the $CaMgSi_2O_6$-SiO_2-CaF_2-MgF_2 set of components, can be compared with activity coefficients derived for the bounding binary joins, $CaMgSi_2O_6$-SiO_2, $CaMgSi_2O_6$-CaF_2, and $CaMgSi_2O_6$-MgF_2. The data used were the liquidus phase equilibria of Bowen (1914) for the $CaMgSi_2O_6$-SiO_2 join, the data of Lin and Burley (1969) for the $CaMgSi_2O_6$-CaF_2 join, and my unpublished data for the $CaMgSi_2O_6$-MgF_2 join. The value of γ^l_{Di} of $CaMgSi_2O_6$ in $CaMgSi_2O_6$-SiO_2 liquids is greater than one (Fig. 7), and it increases with increasing $x^l_{SiO_2}$, consistent with the presence of a miscibility gap at higher $X^l_{SiO_2}$ (Bowen, 1914). In contrast, the value of γ^l_{Di} in $CaMgSi_2O_6$-CaF_2 and $CaMgSi_2O_6$-MgF_2 liquids is less than one (Fig. 7), indicating negative deviations from ideality. Furthermore, the value of γ^l_{Di} decreases with increasing $X^l_{CaF_2}$ or $X^l_{MgF_2}$. As anticipated, the curve for $\ln \gamma^l_{Di}$ for the $CaMgSi_2O_6$-SiO_2-CaF_2-MgF_2 liquids lies between those for the $CaMgSi_2O_6$-SiO_2 and the $CaMgSi_2O_6$-CaF_2 and $CaMgSi_2O_6$-MgF_2 liquids. Furthermore, the near-linearity of the curves in the $\ln \gamma^l_{Di}$ versus X_{Di} plot (Fig. 7) demonstrates that the regular-solution model, which predicts a linear relation between $\ln \gamma^l_{Di}$ and X^2_{Di}, not between $\ln \gamma^l_{Di}$ and X_{Di}, is inadequate to describe the relationship between γ^l_{Di} and X_{Di}.

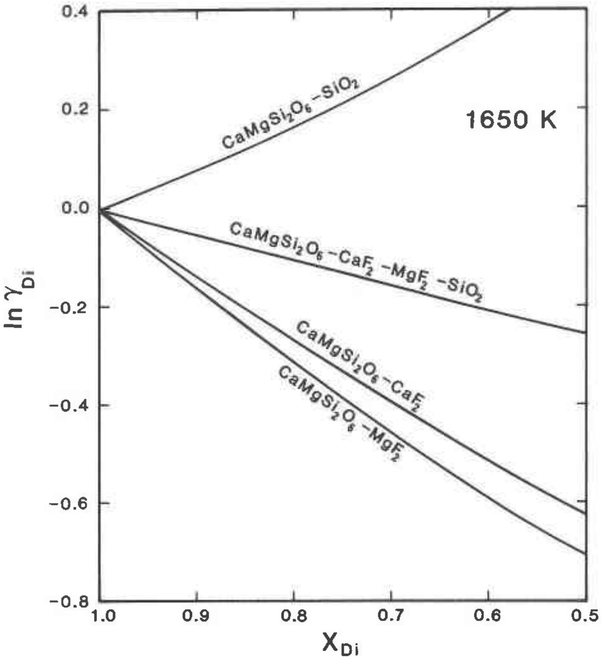

Fig. 7. Relationship between the mole fraction and the activity coefficient of $CaMgSi_2O_6$ in the $CaMgSi_2O_6$-SiO_2, the $CaMgSi_2O_6$-CaF_2, the $CaMgSi_2O_6$-MgF_2, and the $CaMgSi_2O_6$-SiO_2-CaF_2-MgF_2 systems. Data used were the thermodynamic data set of Ghiorso and Carmichael (1980) and the data on the liquidus phase equilibria from Bowen (1914), Lin and Burley (1969), and this report. All activity coefficients have been normalized to 1650 K with Equation 3.

Implications for physical properties

The polymerization accompanying the substitution of F for O in these depolymerized liquids may be reflected in higher viscosity for F-containing liquids, if the con-

TABLE 3. Activity of diopside component in $CaMgSi_2O_6$-F_2O_{-1} liquids

Composition	Pressure (kbar)	Temperature (°C)	a_{Di}	a_{Di} (1650 K)
DiF_1	0.001	1365 ± 5	0.847 ± 0.027	0.848
DiF_5	0.001	1275 ± 5	0.468 ± 0.016	0.491
	10	1455 ± 5	0.632 ± 0.019	0.618
	15	1505 ± 5	0.620 ± 0.019	0.597

trolling factor for viscous flow is the bulk polymerization of the liquid. There are no data, at present, with which to test this hypothesis. If the presence of fluoride complexes, as well as the polymerization, affects the viscosity of the liquid, then it may be that F will still decrease the viscosity of the liquid, but to a lesser degree than occurs in a polymerized liquid. The effect of F on viscosity will then be dependent on the interplay of these two factors.

CONCLUSIONS

F substantially shifts the liquidus of clinopyroxene at 1 atm in the system $CaMgSi_2O_6$-$NaAlSi_3O_8$, changing the liquid in equilibrium with clinopyroxene to more pyroxene-rich compositions. Furthermore, studies at high pressure establish that F has approximately the same effect on the temperature of the liquidus of $CaMgSi_2O_6$. Interpretation of Raman spectroscopic data on quenched glasses indicates that the F-bearing liquids are more polymerized than are the corresponding F-free liquids, consistent with a solution mechanism whereby F forms complexes with Ca and Mg rather than with Si. This polymerization accompanying the substitution of F for O leads to the suggestion that this substitution would cause an increase in viscosity of these liquids. More work is required to establish the effects of F on physical properties and phase equilibria in these systems.

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