



## Effect of fluorine on the viscosity of diopside liquid

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### ABSTRACT

The effect of F on the shear viscosity of diopside liquid has been investigated at 1 atm and 1300 to 1500 °C using the concentric cylinder method. To obtain glass starting materials, 100-g batches of compositions along the  $\text{CaMgSi}_2\text{O}_6\text{-F}_2\text{O}_{-1}$  join— $\text{CaMgSi}_2\text{O}_6$ ,  $\text{CaMgSi}_2\text{O}_{5.875}\text{F}_{0.25}$ ,  $\text{CaMgSi}_2\text{O}_{5.75}\text{F}_{0.5}$ , and  $\text{CaMgSi}_2\text{O}_{5.5}\text{F}$  (denoted Di, DiF0.25, DiF0.5, and DiF1, respectively)—were melted in air. F volatilization was significant during batch melting but not during subsequent viscometry determinations. Electron-microprobe analyses of these glasses permit comparison of viscosities as a function of F content.

The exchange of F for oxygen in these liquids reduces viscosity over the range of compositions investigated in this study. The viscosity reduction as a function of  $F/(F + O)$  exhibits a positive curvature (i.e.,  $\partial^2(\log_{10}\eta)/\partial(F/(F + O))^2 > 0$ ), as is the case for albite melt (Dingwell, 1987a), but the viscosity-reducing effect of F on diopside melt is much less than that observed for albite melt (Dingwell et al., 1985).

Raman spectra of quenched melts (glasses) on the  $\text{CaMgSi}_2\text{O}_6\text{-F}_2\text{O}_{-1}$  join (Luth, 1988a) and liquidus phase equilibria in depolymerized systems (Foley et al., 1986; Luth, 1988b) have indicated that the addition of F (as  $\text{F}_2\text{O}_{-1}$ ) increases the activity of  $\text{SiO}_2$  in these liquids, and thus Luth (1988a, 1988b) has hypothesized that F (as  $\text{F}_2\text{O}_{-1}$ ) might increase depolymerized melt viscosities (due to the increase in  $\text{SiO}_2$  activity). Instead, the present study shows that the exchange of F for oxygen, the  $\text{F}_2\text{O}_{-1}$  component, reduces the melt viscosity of diopside melt.

The polymerization of diopside melt may be quantified using the NBO/T calculation (see Mysen, 1988) at 2.0, whereas anhydrous chemical analyses of the most basic, depolymerized, natural melts yield NBO/T values of 1.4 (Mysen, 1987). Thus the present study shows that the viscosity-reducing effect of F on silicate melts persists to compositions more depolymerized than any naturally occurring silicate melt. It is therefore proposed that F will reduce the viscosity of all low-pressure ( $\text{H}_2\text{O}$ -poor) silicate melts of geologic interest.

### INTRODUCTION

The viscosity-reducing effect of F in silicate melts has been known and utilized for centuries in glassmaking (Agricola, 1529). Indeed the element fluorine owes its name to this property. Fluorspar ( $\text{CaF}_2$ ) or “flow-stone” (from the Latin *fluere* meaning “flow” or “flux”) was the source of elemental fluorine that was first isolated in 1886.

Recently, the effect of F in reducing the viscosity of fully polymerized silicate melts has been determined (Dingwell et al., 1985; Dingwell, 1987a), and the significance of such viscosity reduction for the petrogenesis of various F-rich silicic igneous rocks has been recognized (e.g., Dingwell, 1985, 1987b; Christiansen et al., 1986; Clemens et al., 1986; Hannah and Stein, 1986; Stern et al., 1986; Pichavant et al., 1987; Kortemeier and Burt, 1988).

In addition, certain, very basic igneous rocks (e.g., melilitites, leucitites, minettes) also contain up to 2 wt% F (Aoki et al., 1981). The importance of F in influencing the petrogenesis of mantle-derived melts has been stressed

recently by Foley et al. (1986), who noted that the effect of F on liquidus phase relations in the  $\text{KAlSiO}_4\text{-Mg}_2\text{SiO}_4\text{-SiO}_2$  system can be explained in terms of an increase in the activity of  $\text{SiO}_2$  in liquids in this system. Similarly, Luth (1988b) has studied the effect of F on the liquidus phase relations in the  $\text{NaAlSiO}_4\text{-CaMgSi}_2\text{O}_6\text{-SiO}_2$  system, concluding that the substitution of F for oxygen (via the  $\text{F}_2\text{O}_{-1}$  exchange operator) results in an increase in the activity of  $\text{SiO}_2$  in these liquids. Additionally, Luth (1988a) presented Raman spectra of quenched melts (glasses) in the  $\text{CaO-CaF}_2\text{-SiO}_2$  system in support of F complexation with Ca and concomitant increase in the activity of  $\text{SiO}_2$  in these glasses. If one defines the polymerization of the melt simply as a measure of the concentration of bridging oxygens, rather than a ratio of nonbridging oxygens to tetrahedrally coordinated cations (as is done for the calculation of NBO/T), then one can describe the effect of F substitution for oxygen (resulting in an increase in the activity of  $\text{SiO}_2$ ) as a polymerization of the melt. This was done by Luth (1988a, 1988b) and Foley et al. (1986) and resulted in the hypothesis of Luth (1988a) that the

“polymerizing” effect of  $F_2O_{-1}$  on depolymerized melts might result in an increase in melt viscosity.

This last point highlights two different uses of the term “polymerization” that must be distinguished. The structure and properties of melts along binary metal oxide-silica joins due to the presence of different metal cations are often discussed in terms of differences in “polymerization” at a constant mole fraction of  $SiO_2$  (e.g., Hess, 1980). This usage of the term “polymerization” derives from the literature dealing with polymer theory applied to basic silicate melts (e.g., Masson, 1972). The term “polymerization” in this sense deals with the fact that the bridging-oxygen content, and, therefore, the  $SiO_2$  activity (Hess, 1977), varies with the identity of the metal cation in melts with equal molar content of  $SiO_2$ . A melt with a higher concentration of bridging oxygens is said to be more polymerized.

The second use of the term “polymerization” is to describe the stoichiometrically constrained ratio of non-bridging oxygens to tetrahedrally coordinated cations or NBO/T (e.g., Mysen et al., 1985). The concept of NBO/T as a structural parameter of silicate melts is derived from the glass-science concept of a stoichiometrically defined “oxygen-bridge density” (e.g., Carron, 1969). It is useful for illustrating the stoichiometric constraint of the number of nonbridging oxygens present in the structure, [assuming that the concentration of (free) oxygens unbridged to tetrahedrally coordinated cations is minimal]. It is not yet clear which use of the term “polymerization” is best suited to structural modeling of the process of viscous flow in liquid silicates.

Many previous studies of the effect of fluorides on depolymerized melts already exist (e.g., Schwerin, 1934; Hellbrügge and Endell, 1941; Owens-Illinois Glass Company, 1944; Kozakevitch, 1954; Bills, 1963; Hirayama and Camp, 1969) and invariably indicate that the addition of fluorides to basic, depolymerized slags reduces liquid viscosity (see Fig. 5, Dingwell et al., 1985). The complication arising from the simultaneous additions of F and an alkali or alkaline earth (as a fluoride) however, precludes the isolation of the effect of  $F_2O_{-1}$  on the liquid viscosity from these previous studies. I am aware of no previous study where the effect of  $F_2O_{-1}$  on the viscosity of depolymerized, Al-free silicate melts has been investigated. Accordingly, the present study was performed to test the hypothesis of Luth (1988a) that  $F_2O_{-1}$  might increase the viscosity of a depolymerized melt.

Diopside was chosen for the present investigation because (1) the phase diagram for  $CaMgSi_2O_6-F_2O_{-1}$  has been investigated by Luth (1988b), (2) the Raman spectra of quenched melts on this join are consistent with increasing  $SiO_2$  activity with increasing F content, (3) the 1-atm stability of F in Ca-bearing silicate liquids is substantially higher than in alkali-silicate liquids, and (4) the viscosity of diopside is well known at 1 atm (Licko and Danek, 1986; Scarfe et al., 1983) and liquid viscosities in the CaO-MgO- $SiO_2$  system are well investigated (Machin et al., 1952; Machin and Yee, 1954).

The viscosities were determined at 1-atm pressure using the concentric-cylinder method. Although 1-atm viscometry has the drawback of possible F volatilization, in practice such volatilization can be ruled out during viscometry because no drift in viscosity is recorded during a closed cycle of viscosity-temperature determinations. The alternative method of high-pressure synthesis and measurement of viscosity using the falling-sphere method (e.g., Dingwell, 1987a) was ruled out because the errors associated with this technique, at high pressure, are much larger than for concentric-cylinder viscometry at 1 atm, and the effect of F on depolymerized melt viscosity was anticipated to be smaller than that observed for the more polymerized melts studied by Dingwell et al. (1985).

## EXPERIMENTAL METHOD

### Starting materials

The compositions of this investigation were chosen to lie on the compositional join  $CaMgSi_2O_6-F_2O_{-1}$ . Four compositions, corresponding to progressive substitution of F for oxygen in this system, were chosen at molar values of 0, 0.25, 0.5, and 1.0 mol of F per four-cation-basis diopside (i.e.,  $CaMgSi_2O_6$ ,  $CaMgSi_2O_{5.875}F_{0.25}$ ,  $CaMgSi_2O_{5.75}F_{0.5}$ , and  $CaMgSi_2O_{5.5}F$ , denoted Di, DiF0.25, DiF0.5, and DiF1, respectively). The starting glasses for the viscometry experiments were synthesized from  $CaCO_3$  (ultrapure precipitate—Merck),  $MgO$  (99.5% pure, -325 mesh—Ventron),  $SiO_2$  (99.9% pure, -325 mesh—Ventron), and  $CaF_2$  (gefällt rein—Merck).  $CaCO_3$ ,  $CaF_2$ , and  $MgO$  powders were dried at 120 °C for at least 24 h,  $SiO_2$  was fired at 1250 °C for 1–2 h, and all were stored at 120 °C prior to use. The powders were weighed in stoichiometric proportions into 100-g (decarbonated weight) batches in a 250-mL plastic beaker, transferred to a plastic bottle, and mixed by agitation for ~15 min. The powder mixes were fused directly at 1500 °C by stepwise addition of powder mixes to a 50-cm<sup>3</sup> thin-walled Pt crucible. The melts were held at 1500 °C for 1 h in a  $MoSi_2$  box furnace. The fused samples thus obtained were poured onto a stainless-steel plate for cooling.

### Glass analysis

Chips of these starting glasses were analyzed by microprobe for Ca, Mg, Si, and F, and the results of these analyses are presented in Table 1. The instrument was a JEOL JSM-35 with Krisel control system. The standards were synthetic diopside-jadeite glass for Ca, Mg, and Si and synthetic F-bearing albite glass for F. Precautions were taken to avoid F volatilization during analysis. Further details of microprobe analyses are given in Table 1. All batches probably lost F by volatilization, and the loss is noticeable in DiF1, which is low in F. The Ca, Mg, and Si contents of the glasses are within microprobe errors of the nominal composition, although the Mg values are slightly low, perhaps owing to F loss as  $MgF_2$  (cf. Dingwell and Scarfe, 1985).

TABLE 1. Glass analyses

Sample	CaMg-Si <sub>2</sub> O <sub>6</sub>	Di (nominal)	wt% oxides*		
			DiF0.25	DiF0.5	DiF1
CaO	25.90	26.61	26.39	25.42	26.01
MgO	18.61	19.29	17.75	17.55	17.75
SiO <sub>2</sub>	55.49	54.11	55.96	57.03	56.24
F	—	—	2.39	4.65	12.65
Total		98.21	97.42	99.11	98.55
<b>Four-cation molar basis</b>					
Ca	1.000	1.024	1.019	0.986	1.008
Mg	1.000	1.033	0.957	0.948	0.958
Si	2.000	1.944	2.024	2.066	2.034
O	6.000	5.944	5.883	5.792	5.230
F <sup>-</sup>	—	—	0.284	0.548	1.549
F/(F + O)	—	—	0.0461	0.0864	0.2285

Note: Glass analyses were performed by wavelength-dispersive analysis using a JEOL JSM-35 instrument and Krisel control system. Operating conditions were 15-kV accelerating voltage, 100-nA beam current on C, 30-s maximum count times using a  $10 \times 10 \mu\text{m}$  raster and moving the sample continuously under the beam. Standards were a synthetic diopside-jadeite glass for Ca, Mg, and Si and AB1F glass (see Dingwell et al., 1985) for F. Analyses of F-bearing glasses are the means of five analysis points.

\* Weight percent analyses have been normalized on the basis of CaO + MgO + SiO<sub>2</sub> = 100% to facilitate comparison with nominal diopside.

### Viscometry

The viscosities were determined with the concentric-cylinder method using a modified version of the apparatus described by Dingwell (1986). Improvements in the design of the present viscometer include a precise positioning system for the immersion depth and the *x-y* centering of the spindle, using micropositioning stage components precise to  $\pm 50 \mu\text{m}$ , and a computer-based time-averaging of the output signal. The viscometer has been standardized with National Bureau of Standards Standard Reference material SRM 711, lead-silica glass. The torque was recorded over a range of spindle speeds at a series of temperatures for SRM 711. Plots of the millivolt signal (from the rotary variable displacement transducer) versus viscosity (from the SRM 711 certificate of viscosity values) were constructed for each speed and used as calibration curves for viscosity determinations. The precision of this apparatus, determined by replicate measurements of viscosity is  $\pm 2.5\%$  at  $2\sigma$ . The accuracy of the method is taken as the sum of the precision of standard and sample determinations at  $\pm 5\%$ . The spindle used in this study is the same as described by Dingwell and Virgo (1987). Each viscosity determination was made at three different rotation speeds (20, 50, and 100 rpm). The calculated viscosity was independent of shear rate; i.e., Newtonian behavior was observed for all compositions. The melts were sampled by dipping a Pt wire loop into the sample crucible after each viscosity determination to ensure that the sample was a single-phase silicate liquid. No liquation, crystallization, or vesiculation was observed. The viscometry runs were begun at the highest temperature and then at successively lower temperatures constrained by the phase diagram of the CaMgSi<sub>2</sub>O<sub>6</sub>-F<sub>2</sub>O<sub>-1</sub> system (Luth, 1988b) to lie above the liquidus (where known). The final determination of the run was a reoc-

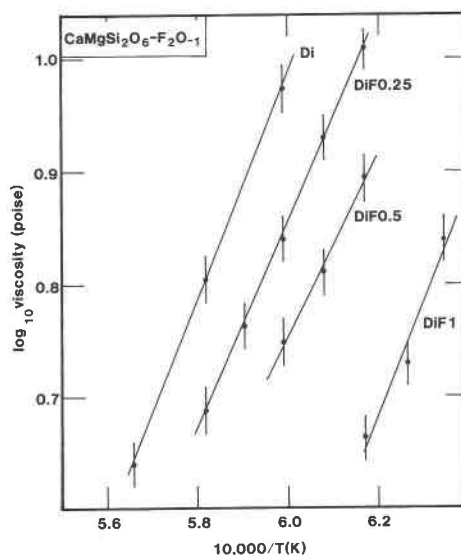


Fig. 1. The viscosity-temperature relationships of four melts on the join CaMgSi<sub>2</sub>O<sub>6</sub>-F<sub>2</sub>O<sub>-1</sub>. Error bars represent  $2\sigma$ . See Table 1 for compositions.

cupation of the highest-temperature determination. No difference was observed between initial and final determinations at the high-temperature point, indicating that no instrumental or compositional drift took place during the viscometry experiments.

### RESULTS AND DISCUSSION

The results of the viscosity determinations on Di, DiF0.25, DiF0.5, and DiF1 are presented in Table 2 and illustrated in Figure 1. The viscosities decrease with increasing F content at all temperatures. The temperature dependence of the viscosities are Arrhenian within error and are fit to equations of the form

$$\log_{10}\eta = \log_{10}\eta_0 + E_a/2.303RT, \quad (1)$$

where  $\eta$  is the viscosity at temperature  $T$ ,  $R$  is the gas constant, and  $E_a$  and  $\eta_0$  are termed the activation energy and pre-exponential factor, respectively.

In order to quantify the effect of F<sub>2</sub>O<sub>-1</sub> on the viscosity of CaO-MgO-SiO<sub>2</sub> melts, we have plotted the viscosity of these melts on the CaMgSi<sub>2</sub>O<sub>6</sub>-F<sub>2</sub>O<sub>-1</sub> join as a function of the anionic mole fraction of F, F/(F + O), in Figure 2. The dependence of viscosity on composition exhibits a smooth function with positive curvature when plotted against F/(F + O).

### Comparison with polymerized melts

The results of the determination of diopside viscosity are within error of those of Licko and Danek (1986) using oscillation viscometry and those of Scarfe et al. (1983) using concentric-cylinder viscometry. This agreement il-

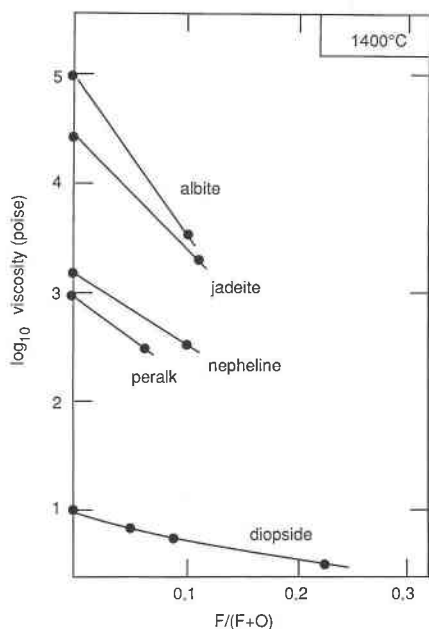


Fig. 2. Comparison of the effect on melt viscosity of substituting F for oxygen in several silicate melts at 1400 °C. Data from Riebling (1966), Dingwell et al. (1985), and this study. "Peralk" is a peralkaline composition with 75 mol% silica.

illustrates that the results of these two methods on melts in this viscosity range give consistent results.

The positive curvature in the viscosity vs. F content  $[F/(F + O)]$  plot of Figure 2 is similar to that obtained by Dingwell (1987a) for the  $\text{NaAlSi}_3\text{O}_8\text{-F}_2\text{O}_{-1}$  system at 7.5 kbar. Figure 2 compares the effects of F on reducing the viscosity of albite, jadeite, nepheline, and diopside melts at 1 atm. The viscosity-reducing effect of F on fully polymerized melts has already been shown to be a strong positive function of  $\text{SiO}_2$  content [or the  $\text{Si}/(\text{Al} + \text{Si})$  value]. Similarly, Figure 2 illustrates that at constant mole fraction  $\text{SiO}_2$  (equal to 0.50 for jadeite and diopside melts), the viscosity of the fully polymerized jadeite melt is lowered much more strongly than the viscosity of depolymerized diopside melt. This observation is consistent with the previous comparison (at 75 mol%  $\text{SiO}_2$ ; Dingwell et al., 1985) showing that F has a larger effect on the viscosity of fully polymerized albite melt than on peralkaline and peraluminous melts that are depolymerized by excesses of Na and Al, respectively.

### Melt structure

In the past few years there have been a series of papers in the geological literature outlining the possible solution mechanisms of F in silicate liquids; largely in the context of glass spectroscopy and experimental liquidus phase relations (e.g., Manning et al., 1980; Mysen and Virgo, 1985a, 1985b; Foley et al., 1986; Luth, 1988a, 1988b). In fully polymerized silicate melts such as albite and jadeite, it has been recognized that F substitution for oxygen

TABLE 2. Melt-viscosity data

	Log <sub>10</sub> viscosity (poise)			
	DI	DI F0.25	DI F0.5	DI F1
1495.0 °C	0.640	—	—	—
1445.8 °C	0.805	0.688	—	—
1421.2 °C	—	0.763	—	—
1396.6 °C	0.974	0.840	0.749	—
1372.0 °C	—	0.930	0.811	—
1347.5 °C	—	1.01	0.895	0.664
1322.9 °C	—	—	—	0.728
1303.2 °C	—	—	—	0.839
log η <sub>0</sub>	-5.024	-4.662	-4.078	-5.496
E <sub>a</sub> (kcal/mol)	45.83	42.07	36.85	45.61

must depolymerize the melt structure, as oxygens involved in bridging bonds to two adjacent tetrahedral cations are stoichiometrically replaced by F. The simplest scheme for F substitution might involve the formation of Si-F bonds to replace the bridging oxygens by what could be termed "nonbridging" F atoms. Spectroscopic evidence for this substitution mechanism in highly polymerized glasses is equivocal (Mysen and Virgo, 1985b; Hayashi et al., 1987).

Mysen and Virgo (1985b) realized that the effect of F on the properties of fully polymerized melts could be explained by an alternative solution mechanism for F where an unequal number of Na and Al atoms are withdrawn from their network-stabilizing and network-forming roles, respectively, to form charge-balanced fluoride complexes no longer directly participating in the aluminosilicate melt structure. Such a mechanism would depolymerize the "residual" aluminosilicate or oxide proportion of the melt because the unequal remaining Na and Al contents of the oxide portion would require a network-modifying role for the Na (or Al) in excess of that required to charge balance the Al (or Na). Mysen and Virgo (1985b) went on to propose that, to a first approximation, the viscosity vs. temperature relationships of the F-bearing melts of Dingwell et al. (1985) could be modeled in terms of the bulk composition of the "residual" aluminosilicate oxide portion of those melts. The proportions of Na and Al coordinated as fluoride complexes were estimated from Raman spectra, and the "residual" melt composition was calculated. The data of Riebling (1966) was then used as a "template" for estimating the bulk F-bearing melt viscosities. Central to this approach was the idea that the presence of neutral fluoride complexes has a negligible direct effect on the viscosity of F-bearing silicate melts.

In depolymerized melts, such as diopside, the solution of F might proceed by the formation of Si-F bonds in replacement of bridging or nonbridging oxygens or by the formation of calcium and magnesium fluoride complexes resulting, in this Al-free composition, in an increase in the proportion of oxygen that forms bridging bonds. Raman spectroscopic observations of glasses and liquidus phase equilibria favor the latter interpretation as both are consistent with an increase in the activity of  $\text{SiO}_2$  in the liquid (Foley et al., 1986; Luth, 1988a, 1988b). Using the

same reasoning as outlined by Mysen and Virgo (1985b), Luth (1988b) hypothesized that F might increase the viscosity of diopside melt owing to such an increase in the activity of  $\text{SiO}_2$ , which presumably reflects an increase in the proportion of oxygen bridging bonds. If the contribution of neutral fluoride complexes can be neglected, then this structural parameter, the activity of  $\text{SiO}_2$ , should dominate the effect of F addition on melt viscosity.

The present study shows that the effect of F is to significantly reduce the viscosity of diopside melt. Thus we conclude that if, as is likely, the F in diopside- $\text{F}_2\text{O}_{-1}$  melts is present as neutral fluoride complexes, then the presence of such fluoride complexes is the dominant control on melt viscosity. This conclusion leads to the generalization that it is not appropriate to model (quantitatively or qualitatively) viscous flow in mixed fluoride-oxide (silicate) melts entirely in terms of the oxide (silicate or aluminosilicate) proportion of the melt structure, to the exclusion of the consideration of fluoride complexes.

### Geological implications

The recognition that many depolymerized, silica-poor, mantle-derived magmas contain significant concentrations of F (Aoki et al., 1981) has led to interest in the possible effects of F on physical and chemical properties of depolymerized silicate melts (e.g., Foley et al., 1986). In this context, diopside is a useful model compound for discussing basaltic and more basic melts, just as albite is often used as a model for granitic melts. On the basis of a qualitative comparison of the effect of F on polymerized and depolymerized silicate melts, I conclude that F will be less effective in reducing the viscosities of more basic melts than is likely the case for granitic and other felsic melts. Several factors combine to reduce the predicted effect of F on more basic melts. First, the viscosity-reducing effect is smaller per wt% of F (Fig. 2). Second, the liquidus temperatures of more basic melts are much higher and thus the divergence of viscosity-temperature relationships that results from decreasing activation energy with F addition cannot be exploited to expand the effect of F on viscosity in basic systems as is possible in felsic systems.

### SUMMARY

The viscosity of diopside melt is significantly reduced by the substitution of F for oxygen (via the exchange operator  $\text{F}_2\text{O}_{-1}$ ) at least up to  $F/(F + O) = 0.23$ . The effect of F on melt viscosity is much less than that observed for polymerized melts such as albite and jadeite.

The substitution of F into diopside melt has been proposed to be accompanied by an increase in the activity of  $\text{SiO}_2$ . The present study shows that, if previous structural conclusions regarding the substitution of F into diopside melt are correct, then predictive models for the viscosity of mixed fluoride-oxide (silicate) melts must consider the effect of the presence of neutral fluoride complexes on the viscous flow process.

If diopside is a model for naturally occurring basic melts,

then F is predicted to decrease the viscosity of all such low-pressure, relatively dry, basic melts.

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