

## The effect of fluorine on viscosities in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ : implications for phonolites, trachytes and rhyolites

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### Abstract

The effect of fluorine on melt viscosities of five compositions in the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  has been investigated at one atmosphere and 1000–1600°C by concentric-cylinder viscometry. The compositions chosen were albite, jadeite and nepheline on the join  $\text{NaAlO}_2-\text{SiO}_2$  and two others off the join at 75 mole percent  $\text{SiO}_2$ , one peralkaline and one peraluminous. All melt viscosities were independent of shear rate over two orders of magnitude, indicating Newtonian behavior. All viscosity–temperature relationships were Arrhenian within error. Fluorine reduces the viscosities and activation energies of all melts investigated. The viscosity-reducing power of fluorine increases with the  $\text{SiO}_2$  content of melts on the join  $\text{NaAlO}_2-\text{SiO}_2$  and is a maximum at  $\text{Na}/\text{Al}$  (molar) = 1 for melts containing 75 mole percent  $\text{SiO}_2$ . Fluorine and water have similar effects on aluminosilicate melt viscosities, probably due to depolymerization of these melts by replacement of Si–O–(Si, Al) bridges with Si–OH and Si–F bonds, respectively. Evidence from slag systems shows that fluorine also reduces the viscosity of depolymerized silicate melts. The viscous flow of phonolites, trachytes and rhyolites will be strongly affected by fluorine. It appears that fluorine contents of igneous rocks may be combined with water in calculation schemes for determining the viscosity of natural melts.

### Introduction

It is well known in the glass and ceramics literature that the incorporation of fluorine into silicate melts has an important effect on their properties (Weyl, 1950; Eitel, 1965). More specifically, fluorine, as  $\text{CaF}_2$  has been used in ceramics for several hundred years as a flux to promote fining or bubble removal from glass melts and more recently as a flux to aid the kinetics of slag-iron separation in steelmaking. The ceramics and glass literature contains a large body of data on the effect of fluorine additions to various slag compositions (Schwerin, 1934; Owens-Illinois Glass Company, General Research Laboratory, 1944; Kozakevitch, 1954; Bills, 1963; Hirayama and Camp, 1969). In the geological literature it has been shown that fluorine plays an important role in melt structure and properties (Wyllie and Tuttle, 1961; Manning, 1981).

For these reasons we have investigated the effect of fluorine on the viscosity of melts in the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . Temperature–viscosity relationships of fluo-

rine-containing melts of albite, jadeite, nepheline, one peralkaline and one peraluminous composition have been measured between 1000–1600°C. The results were then compared with available data from fluorine-free melts in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system, with studies on fluorine-containing slags, and with data for hydrous rhyolites. From these comparisons we infer that (1) reductions in viscosity of polymerized melts occur by substitution of fluorine for bridging oxygens and (2) water and fluorine have similar effects on the viscosities of polymerized melts.

### Experimental method

The compositions studied were chosen to evaluate the influence of varying alkali/aluminum ratio and silica content on the viscosity of fluorine-containing melts. The five base compositions are albite, jadeite, nepheline and two others with 75 mole%  $\text{SiO}_2$ , one peralkaline and one peraluminous (Fig. 1). The system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  was chosen because viscosities in the base system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  have been studied by Riebling (1966) and the structure and physical properties of glasses and melts in this system have been investigated (Hunnold and Bruckner, 1979; Taylor and Brown, 1979; Navrotsky et al., 1982; Seifert et al., 1982). The normative compositions of many fluorine-rich igneous melts containing greater than 50 mole% feldspars + feldspathoids are well represented by this system.

Fluorine was included in the melt compositions by substituting

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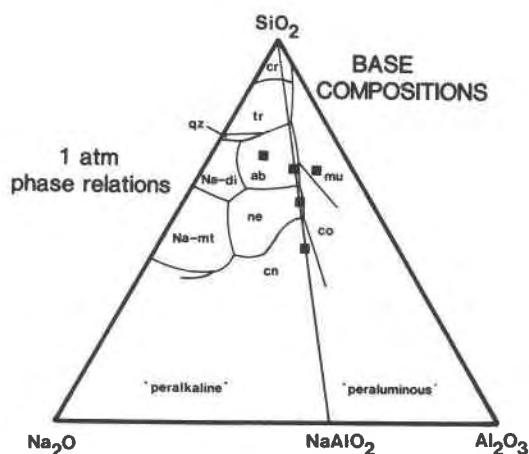


Fig. 1. Melt compositions projected into  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . One atm liquidus phase fields; cristobalite (cr), tridymite (tr), albite (ab), sodium disilicate (Na-di), sodium metasilicate (Na-mt), nepheline (ne), carnegieite (cn), corundum (co) and mullite (mu).

$2\text{AlF}_3$  for some of the  $\text{Al}_2\text{O}_3$  of the base composition. Thus the substitution is essentially 2 moles of fluorine for one mole of oxygen, denoted by the exchange operator  $\text{F}_2\text{O}_{-1}$ . The starting compositions were synthesized from reagent grade sodium carbonate, alumina, aluminum fluoride and purified quartz sand. Carbonate + oxides + fluoride, equivalent to a decarbonated weight of 600 g, were mixed thoroughly for 12 hr and then fused in a 10.5 cm long by 5.5 cm diameter platinum crucible for 6 to 10 hr at  $1600^\circ\text{C}$  to ensure homogeneity and escape of air bubbles.

Viscosities were determined using a concentric cylinder viscometer which uses a  $\text{Pt}_{90}\text{Rh}_{10}$  inner cylinder 5 cm long and 1.2 cm in diameter with conical ends. The inner cylinder is rotated and the resultant torque is measured and converted into a millivolt signal. The apparatus was calibrated with NBS standard lead-silica glass SRM #711 for which the viscosity-temperature relationship is well known. The viscosities are accurate to  $\pm 5\%$  with a precision of  $\pm 1\%$  and temperatures have uncertainties of  $\pm 1^\circ\text{C}$ . Measurements were made at  $50^\circ\text{C}$  intervals over the temperature range  $1000-1600^\circ\text{C}$ . Viscosities were independent of shear rate for all compositions (e.g., Fig. 2) indicating Newtonian behavior.

Volatilization of fluorine was significant during melt synthesis but not during viscosity measurement. The viscosity measurements were obtained at successively lower temperatures for each composition and then the highest temperature measurement was repeated. Due to the powerful viscosity-reducing effect of fluorine in these melts, returning to the high temperature data point for each composition is an excellent check for significant fluorine volatilization during measurements. High temperature readings at the start and finish of each set of measurements were within error, indicating that fluorine volatilization during the measurements was insignificant. According to the glass compositions analyzed after viscometry, there was no significant sodium loss.

Na, Al and Si contents of quenched melts (glasses) were determined, after completion of the viscosity measurements, by energy dispersive analysis using an ARL-SEM-Q microprobe fitted with an EEDS-ORTEC energy dispersive system. Operating conditions were 15 kV, 4 nA sample current and 240 second

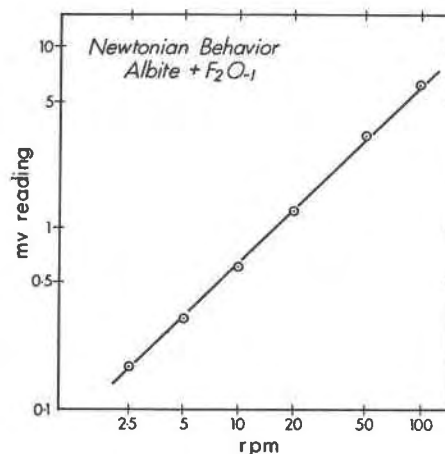


Fig. 2. Newtonian behavior of fluorine-containing albite (data at  $1500^\circ\text{C}$ ).

count times. The beam was rastered over a  $20 \times 20$  micrometer area, a technique which proved adequate for avoiding volatilization of Na or F during analysis. The homogeneity of glasses was confirmed for Na, Al and Si by analyzing six spots on each glass.

Fluorine contents were determined by neutron activation analysis. Twelve replicates of each glass were determined against a curve for reagent-grade  $\text{CaF}_2$ . The technique was verified with standard opal glass SRM#91 (5.72 wt.%F). Fluorine contents were combined with the raw spectra for Na, Al and Si as input for EDATA2 (Smith and Gold, 1979), allowing full ZAF reduction of the Na, Al and Si data (Table 1).

## Results

Fifty viscosity measurements were made on five compositions. The results are presented in Table 2 and in Figure 3. All five compositions show a log-linear dependence of viscosity on reciprocal temperature. Such behavior is described mathematically by the following Arrhenius equation

$$\log_{10}\eta = \log_{10}\eta_0 + E\eta/2.3026RT \quad (1)$$

where  $\eta$  is the viscosity at temperature  $T$  (in K),  $\eta_0$  is a constant,  $R$  is the gas constant and  $E\eta$  is termed the

Table 1. Analyzed melt compositions\*

	Na	Al	Si	F	O	Total
albite	8.31	9.15	31.54	5.8	44.5	99.30
jadeite	11.17	12.75	26.72	6.3	43.0	99.94
nepheline	15.97	17.57	19.40	5.2	41.1	99.24
peralkaline	10.88	5.42	34.09	3.7	45.9	99.99
peraluminous	6.14	10.87	31.58	5.4	45.5	99.49

\*Na, Al and Si determined by electron microprobe; F determined by neutron activation analysis; O by stoichiometry. Errors for microprobe data expressed as percent of the amount present at 3 standard deviations: Na (4.3%), Al (2.0%), Si (1.0%). Errors in fluorine determinations are  $\pm 0.1\text{wt}\%$  F at 1 standard deviation.

Table 2. Viscosity results and computed Arrhenian parameters

Temperature (degrees C)	Log <sub>10</sub> Viscosity (poise)				
	albite	jadeite	nepheline	peralkaline	peraluminous
1600	2.76	2.45	-	-	3.12
1550	2.93	2.68	1.87	2.04	3.33
1500	3.10	2.88	2.10	2.19	3.58
1450	3.28	3.08	2.31	2.32	3.82
1400	3.46	3.29	2.53	2.44	4.09
1350	3.65	3.51	2.76	2.59	4.38
1300	3.84	3.73	3.00	2.77	4.68
1250	4.05	3.97	3.26	2.97	4.96
1200	4.25	4.21	-	3.16	5.28
1150	4.50	4.62*	-	3.37	-
1100	4.73	-	-	3.60	-
1050	4.96	-	-	3.86	-
1000	-	-	-	4.14	-
Arrhenian parameters					
E <sub>n</sub> **	45.5	55.0	58.0	40.3	68.7
log <sub>10</sub> τ <sub>0</sub>	-2.50	-3.92	-5.05	-2.81	-4.89

\* at 1137 degrees C  
 \*\* (in kcal/mole)

activation energy of viscous flow. The method of least squares was used to fit the data to straight lines (Fig. 3) from which the Arrhenian parameters were determined. Above 1400°C, viscosities of the fluorine-containing melts decrease in the order peraluminous > albite > jadeite > peralkaline > nepheline. Activation energies of viscous flow of fluorine-containing melts decrease with increasing SiO<sub>2</sub> along the join NaAlO<sub>2</sub>-SiO<sub>2</sub> from nepheline (58.0 kcal/mole) to albite (45.5 kcal/mole), and increase from the peralkaline melt (40.3 kcal/mole) to the peraluminous melt (68.7 kcal/mole) at 75 mol% SiO<sub>2</sub>. Different activation energies for the various melts result in two viscosity-temperature curve crossovers within the range of experimental measurements (Fig. 3). As a result, below 1350°C fluorine-containing jadeite melt is more viscous than fluorine-containing albite melt, and below 1400°C fluorine-containing nepheline melt is more viscous than fluorine-containing peralkaline melt (Fig. 3).

## Discussion

### Comparison with previous work

Discussion of these data is facilitated by comparison with viscosities of equivalent fluorine-free melts in Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. In Figure 3 we have included data from Riebling (1966) for the five base compositions and the data of Rau et al. (1977) for vitreous silica and fluorine-containing silica. Figure 3 shows that the addition of fluorine strongly reduces the viscosity and the activation energy of all melts studied. These reductions (denoted  $d\eta$  and  $dE\eta$ , respectively) are different in magnitude for each

of the base compositions. The lowering of viscosities and activation energies of melts on the join NaAlO<sub>2</sub>-SiO<sub>2</sub> is a positive function of SiO<sub>2</sub> content. For example, at 1400°C the viscosity reduction with the addition of 1 wt.% fluorine (by substitution of fluorine for oxygen) to SiO<sub>2</sub> is 0.45 log<sub>10</sub> units. Under equivalent conditions, the viscosities of albite, jadeite and nepheline melts decrease 0.26, 0.19 and 0.16 log<sub>10</sub> units/wt.% F, respectively. All activation energies for fluorine-containing melts are reduced from the values for their fluorine-free counterparts: albite (85.3 kcal/mole), jadeite (86.8 kcal/mole) and nepheline (74.2 kcal/mole) (Riebling, 1966). Interestingly, the decrease in activation energy of these three melts upon addition of fluorine is a linear function of mole fraction of SiO<sub>2</sub> over the range of 0.5 to 0.75 (Fig. 4). This results in decreasing activation energies with increasing SiO<sub>2</sub> content from fluorine-containing nepheline to fluorine-containing albite. Extrapolation of the line in Figure 4 to X(SiO<sub>2</sub>) = 1 is not possible due to the large uncertainty in the activation energy of silica (see Hofmaier and Urbain, 1968) and the possibility that 1 and 6 wt.% additions of fluorine may not have an equivalent effect on the activation energy of SiO<sub>2</sub>. However, the activation energy decrease is larger for the addition of fluorine to silica than for the addition of fluorine to any Al-bearing melts.

The three melts studied at 75 mole% SiO<sub>2</sub> are: peralka-

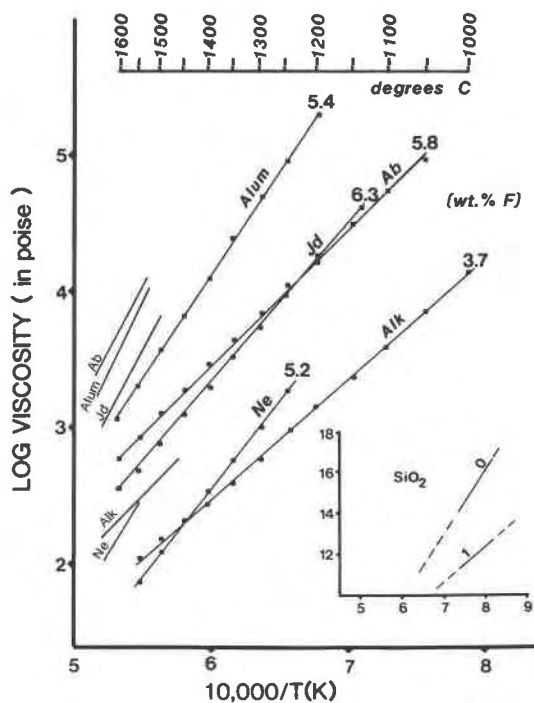


Fig. 3. Measured viscosities of fluorine-containing melts (this study) and base melts (Riebling, 1966). Numbers on curves refer to the wt.% of fluorine. Inset: Viscosities of vitreous and fluorine-containing SiO<sub>2</sub> (Rau et al., 1977).

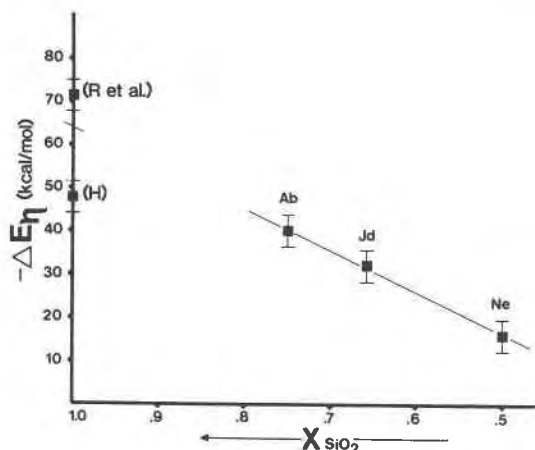


Fig. 4. Decreases in activation energy of viscous flow ( $dE\eta$ ) as a function of mole fraction of  $\text{SiO}_2$  (R et al. = Rau et al., 1977; H = Hofmaier and Urbain, 1968).

line, albite and peraluminous. At  $1400^\circ\text{C}$ , the albite melt undergoes the largest decrease in viscosity ( $0.26 \log_{10}$  units/wt.%F), whereas the peralkaline and peraluminous melts show smaller decreases of 0.16 and 0.14  $\log_{10}$  units/wt.%F, respectively. These three melts all experience decreases in activation energy with fluorine addition, but the peralkaline and peraluminous melts drop only 5 and 16 kcal/mole, respectively, compared to a 40 kcal/mole drop for albite. As a result the viscosities and activation energies increase in the order peraluminous > albite > peralkaline.

In summary, in order to account for the role of fluorine in melts in the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  any model must explain the following general features: (1) the decrease of all viscosities and activation energies; (2) the positive dependence of  $dE\eta$  and  $d\eta$  (see above) on  $\text{SiO}_2$  content for melts on the join  $\text{NaAlO}_2-\text{SiO}_2$  and the resulting negative dependence of  $E\eta$  on  $\text{SiO}_2$  for fluorine-containing melts on this join; and (3) the positive dependence of  $E\eta$  and  $\eta$  on  $\text{Al}/\text{Na}$  at constant  $\text{SiO}_2$  that contrasts with the presence of viscosity maxima at or near  $\text{Al}/\text{Na}$  (molar) = 1 for fluorine-free melts (Riebling, 1966).

There have been several studies conducted on the effects of fluorine on viscosities of Al-poor slags (Schwerin, 1934; Owens-Illinois Glass Company, General Research Laboratory, 1944; Kozakevitch, 1954; Bills, 1963; Hirayama and Camp, 1969). The compositions of slags vary widely, especially in silica content (25 to 75 wt.%) but, due to insufficient aluminum, none of the melts represent highly polymerized liquids such as those of the join  $\text{NaAlO}_2-\text{SiO}_2$ . Representative compositions and results from these studies are presented in Figure 5 with the results of the present study, thus providing a comparison of the effect of fluorine on polymerized and depolymerized melt viscosities. It is clear from Figure 5 that fluorine decreases the viscosities of all melts studied. However,

the decreases in activation energy with fluorine addition are smaller for the depolymerized slags than for the polymerized melts in  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ .

### Structural implications

The three-dimensional structure of melts on the join  $\text{NaAlO}_2-\text{SiO}_2$  has been discussed by several investigators (Riebling, 1966; Hunnold and Bruckner, 1979; Taylor and Brown, 1979; Navrotsky et al., 1982; Seifert et al., 1982). A continuous three-dimensional network of  $(\text{Al},\text{Si})\text{O}_4$  tetrahedra is stabilized by the inclusion of one network modifying Na atom per tetrahedrally coordinated Al atom. In such a structure all oxygen is bonded to two tetrahedrally-coordinated, network-forming cations to form oxygen bridges. In contrast, melts in  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  whose compositions lie off the join  $\text{NaAlO}_2-\text{SiO}_2$ , whether they are peralkaline or peraluminous, cannot maintain the structure of an uninterrupted three-dimensional network. These melts probably contain a discontinuous three-dimensional network perturbed by the presence of excess Na or Al atoms, coordinated by nonbridging oxygens (NBO) (Mysen et al., 1980). The degree of polymerization of aluminosilicate melts may be represented by the ratio of NBO/T (where T represents a tetrahedrally-coordinated cation; Mysen et al. 1982). Analyses of the melts along the join  $\text{NaAlO}_2-\text{SiO}_2$  yield base compositions (projected from  $\text{F}_2\text{O}_{-1}$  (molar)) with NBO/T values close to zero (albite = 0.013; jadeite = 0.008; nepheline = 0.032). The peralkaline base composition yields NBO/T = 0.193. The peraluminous composi-

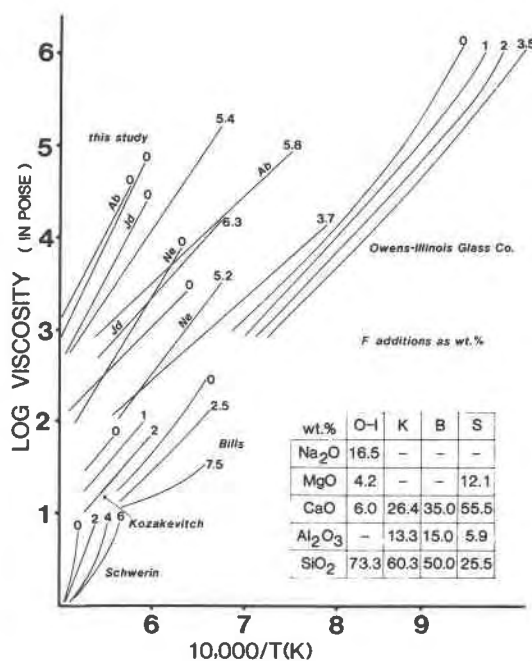


Fig. 5. Effect of fluorine on melt viscosity for several slag compositions. See text for references.

tion is difficult to deal with using the calculation procedure of Mysen et al. (1982) because of the uncertainty in assigning some or all of the aluminum to the value of  $T$ . If we assume as a limiting case that each tetrahedrally coordinated Al atom requires a Na atom for stabilization, then the maximum NBO/T for the peraluminous composition is 0.292. Viscosities in  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (Riebling, 1966) appear to reflect the structural characteristics of these melts quite well. The presence of viscosity maxima at or near  $\text{Na}/\text{Al}$  (molar) = 1 along joins of constant silica content in  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (Riebling, 1966) imply that at the 1:1 composition melts are completely polymerized (i.e., all Al is in tetrahedral coordination; Hunnold and Bruckner, 1979).

The viscous flow of pure silica involves an activation energy similar to the Si-O bond strength of Si-O-Si bridging bonds and thus viscous flow in  $\text{SiO}_2$  is thought to proceed by the breakage of such bridging bonds (Bockris and Reddy, 1970). Melts along the join  $\text{NaAlO}_2-\text{SiO}_2$  also require the breakage of bridging oxygen bonds but the average T-O-T bond strength is lowered from that of pure  $\text{SiO}_2$ . Peralcaline and peraluminous melts in  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  probably owe their lower viscosities to the smaller average size of flow units. Their lower activation energies may be due to a decrease in the number of bond breakages required for viscous flow.

Fluorine substitutes for oxygen in silicate melts (Rabinovich, 1983). If oxygen occurs in melts on the join  $\text{NaAlO}_2-\text{SiO}_2$  entirely as Si-O-(Si,Al) bridges, then fluorine must break oxygen bridges. It is clear from the viscosity data for fluorine-containing silica (Rau et al., 1977) that the exchange of Si-O-Si bridges for Si-F bonds occurs with a drastic change of melt viscosity (Fig. 3, inset). However, for melts along the join  $\text{NaAlO}_2-\text{SiO}_2$  the question is whether Al-O or Si-O bonds, or both, are the primary target for fluorine substitution. Fluorine-free melts have decreasing viscosities in the order albite > jadeite > nepheline, but similar activation energies (Riebling, 1966). The magnitude of the effect of fluorine on both activation energies and viscosities of melts on the join  $\text{NaAlO}_2-\text{SiO}_2$  is a positive function of  $\text{SiO}_2$  content. Figure 4 therefore supports the proposal that the decreasing efficiency of activation energy reduction with decreasing  $\text{SiO}_2$  content is a result of the decrease in the proportion of Si-O-Si bridges in these melts.

The three melts at 75 mole%  $\text{SiO}_2$  vary in Al/Na and their viscosities and activation energies increase with Al/Na. Apparently the addition of fluorine to melts along this join eliminates the viscosity maximum at or near  $\text{Al}/\text{Na} = 1$  for fluorine-free melts. Fluorine in the peralcaline and peraluminous melts may be replacing non-bridging or bridging oxygens.

Breakage of Si-O-Si bridges can also explain the effect of fluorine on the viscosities of depolymerized melts such as those included in Figure 5. Melts shown in Figure 5 have NBO/T ranging to 4.7 and thus are more depolymerized than the melts we have investigated. Despite their

calculated values of NBO/T, the  $\text{SiO}_2$ -poor melts probably contain some bridging oxygens (Gotz et al., 1976; Smart and Glasser, 1978). Reduction of viscosities by fluorine addition to these melts may result from substitution of fluorine for bridging or nonbridging oxygens.

### Comparison with water

Water has a strong influence on the viscosity of silicate melts (Shaw, 1963; Friedman et al., 1963; Burnham, 1964; Scarfe, 1973). The similar size and charge of  $\text{F}^-$  and  $\text{OH}^-$  ions encourage comparison of their effects. We would prefer to compare the influences of water and fluorine on identical melt compositions; however, the data do not exist. In Figure 6 we present viscosity-temperature curves for dry and wet rhyolites (Shaw, 1963; Friedman et al., 1963; Carron, 1969), a wet pegmatite (Burnham, 1964), albite (Riebling, 1966) and fluorine-containing albite (this study). Activation energies decrease similarly with addition of fluorine to albite and addition of water to rhyolite. This implies similar roles for fluorine and water in the depolymerization and resulting reduction of viscosity in these polymerized melts (Fig. 6). The magnitude of viscosity reduction is a much more difficult comparison. If we select a dry rhyolite curve to coincide with the albite curve then the reduction of viscosity (normalized on a weight percent or mole percent basis of added water or fluorine) is slightly greater for the addition of water to rhyolite than for the addition of fluorine to albite. However, recalling the positive relationship between  $\text{SiO}_2$  content and the viscosity-reducing power of fluorine, it is likely that comparison of two rhyolites rather than albite and rhyolite would remove this discrepancy (note that

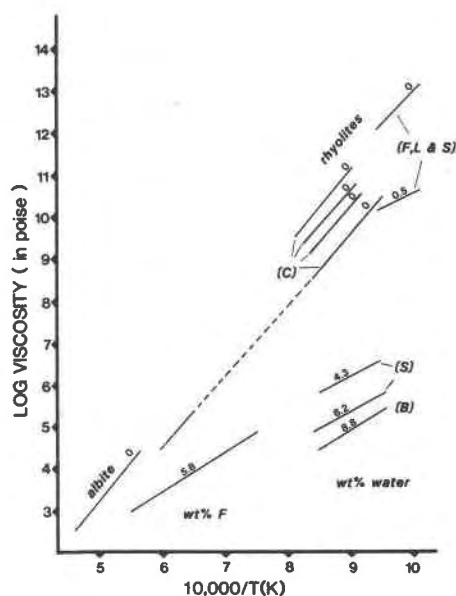


Fig. 6. Comparison of the effects of water and fluorine on polymerized melt viscosities. Numbers on curves refer to wt.% of fluorine or water. See text for data sources.

converting from weight to mole percent does not significantly alter comparisons between fluorine and water as their molecular weights are 19.0 and 18.0 grams/mole, respectively). Therefore, our conclusion from comparison of water and fluorine is that one mole of fluorine is structurally analogous to one mole of water in depolymerizing highly polymerized melts. The equivalence of the viscosity reductions strongly implies that  $H_2O$  and  $F$  disrupt an equivalent number of oxygen bridges when incorporated in highly polymerized melts. We cannot discuss the effect of fluorine on hydrous melt viscosities because, with the exception of the Harding pegmatite (0.33 wt.%  $F$ , 8.8 wt.%  $H_2O$ ), there are no data on the viscosities of fluorine-containing hydrous melts.

### Geological applications

Many volcanic rocks have anhydrous chemical compositions very close to the compositional plane  $KAlSiO_4-NaAlSiO_4-SiO_2$ . In particular, "average" compositions of phonolites, trachytes and rhyolites (Cox et al., 1979, p.401) have values of  $K_2O+Na_2O+Al_2O_3+SiO_2$  near 90 wt.%. Thus the bulk physical properties of melts in the system  $K_2O-Na_2O-Al_2O_3-SiO_2$  closely resemble the properties of these natural melts. Also, the molar effects of  $K_2O$  and  $Na_2O$  on melt viscosities are similar and  $K_2O + Na_2O$  (molar) is a single parameter in Shaw's (1972) scheme for calculation of natural melt viscosities. The molar equivalence of  $Na_2O$  and  $K_2O$  means that the system  $K_2O-Na_2O-Al_2O_3-SiO_2$  may be effectively reduced to the simpler system  $Na_2O-Al_2O_3-SiO_2$  that is used as a basis for this investigation. These arguments allow us to apply our results to natural melts. In our previous discussion we stressed the importance of  $SiO_2$  content in determining the ability of fluorine to reduce viscosities. The observation that the magnitude of the reduction in viscosity is positively correlated with  $SiO_2$  is illustrated in Figure 7, where  $\log_{10}$  viscosity is plotted versus mole fraction  $SiO_2$  for several compositions. Rather than plot a mixture of experimental and calculated viscosities in Figure 7, we have calculated all viscosities using the method of Shaw (1972). Figure 7 contains melt compositions expressed in terms of their mole fraction of  $SiO_2$ . All natural and synthetic melts were cast into desilicated norms (composed of  $SiO_2$ ,  $NaAlO_2$ ,  $CaAl_2O_4$ ,  $FeO$ ,  $MgO$ , etc.) from which mole fractions of  $SiO_2$  ( $SiO_2/(SiO_2 + NaAlO_2 + KAlO_2 + CaAl_2O_4, \text{ etc.})$ ) were obtained. The synthetic phonolite, trachyte and rhyolite are anhydrous projections of the 1 kbar thermal minima in the system  $KAlSiO_4-NaAlSiO_4-SiO_2-H_2O$  (Tuttle and Bowen, 1958; Hamilton and MacKenzie, 1965) and the three natural compositions are "averages" from Cox et al., (1979). The lines labelled 1, 2, 3, 4 and 5 represent viscosity decreases with weight percent additions of fluorine that are derived from linear interpolation of our data. At an eruption temperature of  $1000^\circ C$  the viscosities of phonolites, trachytes and rhyolites containing 1 wt.%

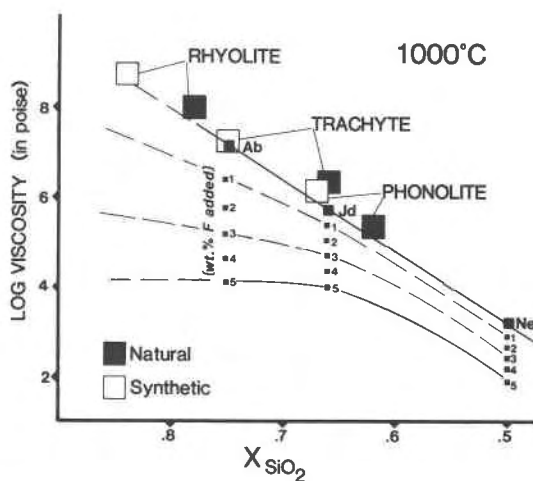


Fig. 7. Application of experimental results to synthetic and natural melts. The effect of fluorine content on melt viscosity for rhyolites, trachytes and phonolites at eruption temperatures near  $1000^\circ C$ . See text for explanation.

fluorine will be approximately 0.25, 0.5 and 1 orders of magnitude lower than the viscosities of equivalent fluorine-free melts. In comparison, strongly peraluminous or peralkaline melts will experience a smaller influence of fluorine on their viscosities.

The most dramatic effects of fluorine addition will be felt in relatively dry, fluorine-rich, high-silica rhyolites. Pre-eruption water contents of many silicic magmas may be lost during degassing immediately prior to eruption (Sparks, 1978). Due to a high melt/fluid partition coefficient (Hards, 1978), fluorine will be retained in the melt. Fluorine remaining in erupted lavas will maintain low viscosities. In certain cases fluorine may significantly influence eruptive style enhancing fluid flow and strongly reducing the pyroclastic component of a given eruption. Fluorine-rich topaz rhyolites exhibit just such features (Christiansen et al., 1983).

Fluorine-rich intrusive rocks occur in a wide variety of settings. The rates of crystal settling and bubble ascent in such intrusions will be enhanced by high fluorine contents. The relatively dry magmas which form fluorine-rich alkalic intrusives will experience reduced viscosities as outlined above. The water-saturated emplacement of fluorine-rich melts such as  $Li-F$  leucogranites and associated pegmatites (Bailey, 1977; Manning, 1981) may be significantly more fluid due to an additive effect of fluorine and water on the viscosities of such melts. At the greater depths and lower temperatures associated with water-saturated emplacement of leucogranitic melts the distinction between low viscosity fluorine-rich, water-saturated melts and coexisting fluids may be diminished. This distinction is the subject of considerable controversy regarding the magmatic or hydrothermal origin of certain late-stage fluorine- and water-rich cupolas and dykes (e.g., Kovalenko, 1973; Eadington and Nashar, 1978).



### Summary and conclusions

We have shown that the addition of fluorine to melts in the system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  strongly reduces viscosities and activation energies. Viscosities of fluorine-containing aluminosilicate melts are Arrhenian functions of temperature. The viscosity-lowering effect of fluorine increases with increasing  $\text{SiO}_2$  content along the join  $\text{NaAlO}_2-\text{SiO}_2$  and is a maximum at or near  $\text{Na}/\text{Al}$  (molar) = 1 for melts containing 75 mole%  $\text{SiO}_2$ . The most probable explanation for viscosity decrease is depolymerization of melts by replacement of  $\text{Si}-\text{O}-(\text{Si},\text{Al})$  bridges with  $\text{Si}-\text{F}$  bonds. When the effects of water and fluorine are compared, similar reductions in viscosities and activation energies suggest similar mechanisms of melt depolymerization. The most important implications of this work concern relatively dry, crystal-poor, magmas of phonolite, trachyte and rhyolite composition and their intrusive equivalents, both wet and dry. Due to the activation energy decreases, the viscosity-lowering effect of fluorine will be greater at the lower temperatures associated with water-saturated emplacement of igneous melts at depth. We also speculate that the effects of fluorine and water might be additive, resulting in extremely large viscosity reductions for certain melts.

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