

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

DONALD B. DINGWELL,¹ CHRISTOPHER M. SCARFE AND DAVID J. CRONIN²

*Experimental Petrology Laboratory
Department of Geology, University of Alberta
Edmonton, Alberta T6G 2E3, Canada*

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 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 SiO_2 content of melts on the join $\text{NaAlO}_2-\text{SiO}_2$ and is a maximum at Na/Al (molar) = 1 for melts containing 75 mole percent 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 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% 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

¹Present address: Geophysical Laboratory, 2801 Upton St., N.W., Washington, D.C. 20008.

²Present address: Center for Materials Science, National Bureau of Standards, Washington, D.C. 20234.

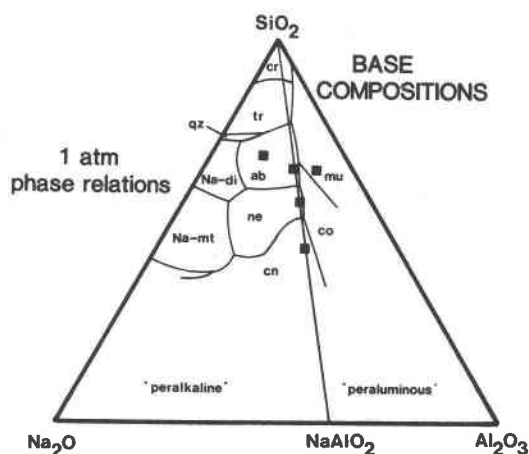


Fig. 1. Melt compositions projected into $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$. One atm liquidus phase fields; cristobalite (cr), tridymite (tr), albite (ab), sodium disilicate (Na-di), sodium metasilicate (Na-mt), nepheline (ne), carnegieite (cn), corundum (co) and mullite (mu).

2AlF_3 for some of the Al_2O_3 of the base composition. Thus the substitution is essentially 2 moles of fluorine for one mole of oxygen, denoted by the exchange operator F_2O_{-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°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°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

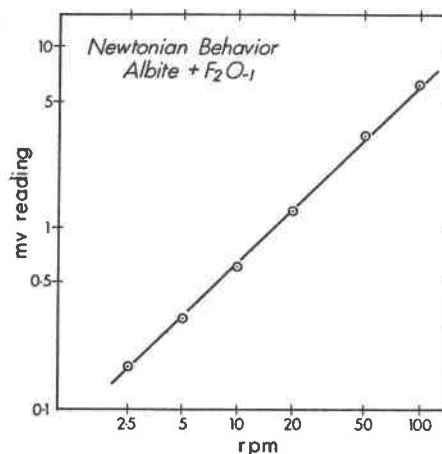


Fig. 2. Newtonian behavior of fluorine-containing albite (data at 1500°C).

count times. The beam was rastered over a 20×20 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 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 η is the viscosity at temperature T (in K), η_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 ₁₀ 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 _n **	45.5	55.0	58.0	40.3	68.7
log ₁₀ τ ₀	-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 SiO₂ along the join NaAlO₂-SiO₂ 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% SiO₂. 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 Na₂O-Al₂O₃-SiO₂. 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 NaAlO₂-SiO₂ is a positive function of SiO₂ content. For example, at 1400°C the viscosity reduction with the addition of 1 wt.% fluorine (by substitution of fluorine for oxygen) to SiO₂ is 0.45 log₁₀ units. Under equivalent conditions, the viscosities of albite, jadeite and nepheline melts decrease 0.26, 0.19 and 0.16 log₁₀ 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 SiO₂ over the range of 0.5 to 0.75 (Fig. 4). This results in decreasing activation energies with increasing SiO₂ content from fluorine-containing nepheline to fluorine-containing albite. Extrapolation of the line in Figure 4 to X(SiO₂) = 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 SiO₂. 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% SiO₂ are: peralka-

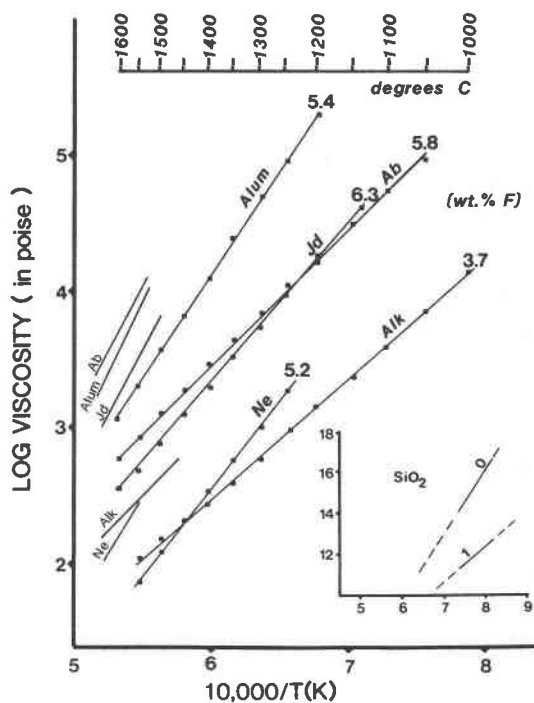


Fig. 3. Measured viscosities of fluorine-containing melts (this study) and base melts (Riebling, 1966). Numbers on curves refer to the wt.% of fluorine. Inset: Viscosities of vitreous and fluorine-containing SiO₂ (Rau et al., 1977).

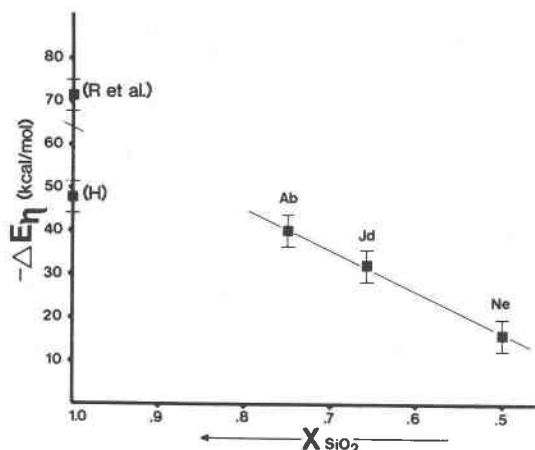


Fig. 4. Decreases in activation energy of viscous flow ($dE\eta$) as a function of mole fraction of SiO_2 (R et al. = Rau et al., 1977; H = Hofmaier and Urbain, 1968).

line, albite and peraluminous. At 1400°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 SiO_2 content for melts on the join $\text{NaAlO}_2-\text{SiO}_2$ and the resulting negative dependence of $E\eta$ on SiO_2 for fluorine-containing melts on this join; and (3) the positive dependence of $E\eta$ and η on Al/Na at constant SiO_2 that contrasts with the presence of viscosity maxima at or near Al/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 F_2O_{-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-

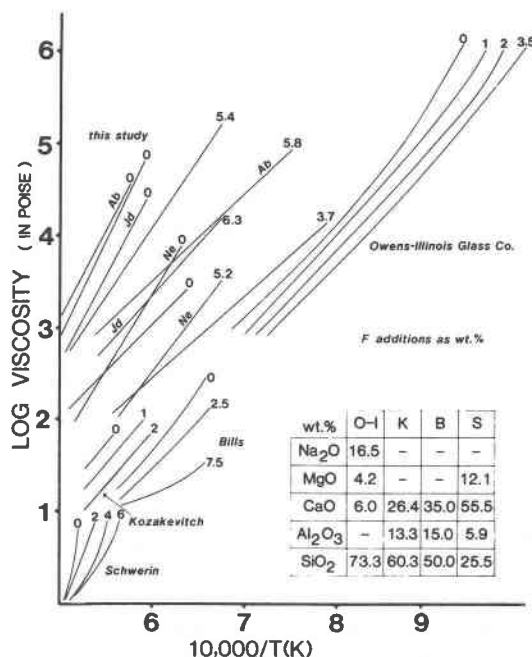


Fig. 5. Effect of fluorine on melt viscosity for several slag compositions. See text for references.

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 Na/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 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 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 SiO_2 content. Figure 4 therefore supports the proposal that the decreasing efficiency of activation energy reduction with decreasing 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% 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 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 F^- and 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 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

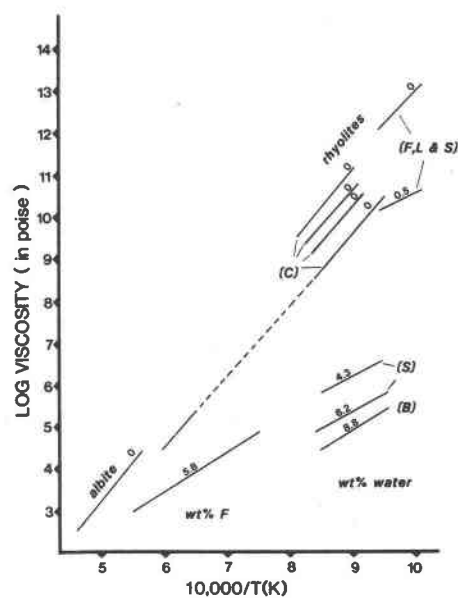


Fig. 6. Comparison of the effects of water and fluorine on polymerized melt viscosities. Numbers on curves refer to wt.% of fluorine or water. See text for data sources.

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.%

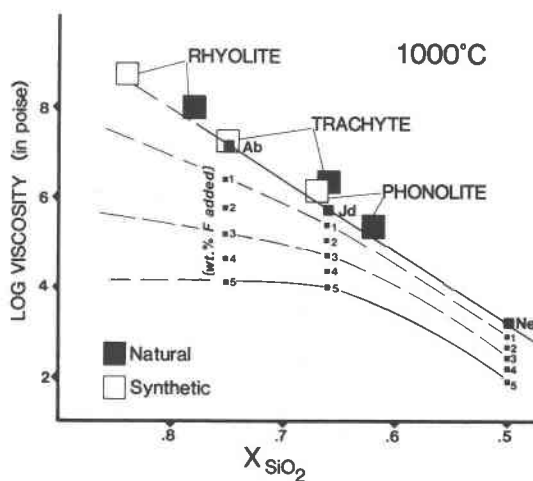


Fig. 7. Application of experimental results to synthetic and natural melts. The effect of fluorine content on melt viscosity for rhyolites, trachytes and phonolites at eruption temperatures near $1000^\circ C$. See text for explanation.

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 SiO_2 content along the join $\text{NaAlO}_2-\text{SiO}_2$ and is a maximum at or near Na/Al (molar) = 1 for melts containing 75 mole% 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.

Acknowledgments

These experiments were conducted at the National Bureau of Standards, Washington, D.C. D. Kauffman (NBS) assisted with viscometry and melt preparation and J. Duke (SLOWPOKE Reactor Center, U. of A.) performed fluorine analyses. S. Launsbach assisted with microprobe operation and data reduction and F. Dimitrov helped with drafting. Scarfe was supported as a visiting scientist at NBS and by funds from Canadian NSERC operating grant A 8394. Dingwell acknowledges support from a 1967 NSERC Science scholarship and the use of facilities at NBS. The microprobe facilities at U. of A. are operated with funds from NSERC Grant A 4254 awarded to D. G. W. Smith. We wish to thank M. Brearley and T. Dunn for their comments on an early version of this paper. A. Navrotsky and F. Spera provided helpful reviews. Experimental Petrology Laboratory contribution #81.

References

- Bailey, J. C. (1977) Fluorine in granitic rocks and melts: a review. *Chemical Geology*, 19, 1-42.
- Bills, P. M. (1963) Viscosities in silicate slag systems. *Journal of the Iron and Steel Institute*, 201, 133-140.
- Bockris, J. O'M. and Reddy, A. K. N. (1970) *Modern Electrochemistry* Vol. 1. Plenum Press, New York.
- Burnham, C. W. (1964) Viscosity of a water-rich pegmatite. (abstr.) *Geological Society of America Special Paper* 76, 26.
- Carron, J.-P. (1969) Vue ensemble sur la rhéologie des magmas silicatés naturels. *Bulletin de la Société Française de Minéralogie et de Cristallographie*, 92, 435-446.
- Christiansen, E. H., Burt, D. M., Sheridan, M. F. and Wilson, R. T. (1983) The petrogenesis of topaz rhyolites from the western United States. *Contributions to Mineralogy and Petrology*, 83, 16-30.
- Cox, K. G., Bell, J. D. and Pankhurst, R. J. (1979) The Interpretation of Igneous Rocks. Allen and Unwin, London.
- Eadington, P. J. and Nashar, B. (1978) Evidence for the magmatic origin of quartz topaz rocks from the New England batholith. *Contributions to Mineralogy and Petrology*, 67, 433-438.
- Eitel, W. (1965) *Silicate Science II, Glasses, enamels and slags*. Academic Press, New York.
- Friedman, I., Long, W. and Smith, R. L. (1963) Viscosity and water content of rhyolite glass. *Journal of Geophysical Research*, 68, 6523-6535.
- Gotz, J., Hoebbel, D. and Wieker, W. (1976) Silicate groupings in glassy and crystalline $2\text{PbO}-\text{SiO}_2$. *Journal of Non-Crystalline Solids*, 20, 413-425.
- Hamilton, D. L. and MacKenzie, W. S. (1965) Phase equilibrium studies in the system $\text{NaAlSiO}_4-\text{KAlSiO}_4-\text{SiO}_2-\text{H}_2\text{O}$. *Mineralogical Magazine*, 34, 214-231.
- Hards, N. (1978) Distribution of elements between the fluid phase and silicate melt phase of granites and nepheline syenites. *NERC Progress in Experimental Petrology IV*, 88-90.
- Hirayama, C. and Camp, F. E. (1969) The effect of fluorine and chlorine substitution on the viscosity and fining of soda-lime and potassium-barium silicate glass. *Glass Technology*, 10, 123-127.
- Hofmaier, G. and Urbain, G. (1968) The viscosity of pure silica. *Science of Ceramics*, 4, 25-32.
- Hunnold, V. K. and Bruckner, R. (1979) *Physikalische Eigenschaften und struktureller Feinbau von Natrium-Aluminosilikatglasern und -schmelzen*. *Glastechnische Berichte*, 53, 149-161.
- Kovalenko, V. I. (1973) Distribution of fluorine in a quartz keratophyre dyke (ongonite) and solubility of fluorine in granitic melts. *Geokhimiya*, 57-66 (transl. *Geochemistry International*, 10, 41-49, 1967).
- Kozakevitch, P. (1954) Sur la viscosité des laitiers de hauts fourneaux. *Revue de Metallurgie*, 8, 569-584.
- Manning, D. A. C. (1981) The effect of fluorine on liquidus phase relationships in the system $\text{Qz}-\text{Ab}-\text{Or}$ with excess water. *Contributions to Mineralogy and Petrology*, 76, 206-215.
- Mysen, B. O., Virgo, D. and Scarfe, C.M. (1980) Relations between the anionic structure and viscosity of silicate melts.—a Raman spectroscopic study. *American Mineralogist*, 65, 690-710.
- Mysen, B. O., Virgo, D. and Seifert, F. A. (1982) The structure of silicate melts: implications for chemical and physical properties of natural magma. *Reviews of Geophysics and Space Physics*, 20, 353-383.
- Navrotsky, A., Peraudeau, G., McMillan, P. and Coutures, J.-P. (1982) A thermochemical study of glasses and crystals along the joins silica-calcium aluminate and silica-sodium aluminate. *Geochimica et Cosmochimica Acta*, 46, 2039-2047.
- Owens-Illinois Glass Company, General Research Laboratory (1944) Effect of fluorine and phosphorus pentoxide on properties of soda-dolomite lime-silica glass. *Journal of the American Ceramic Society*, 27, 369-372.
- Rabinovich, E. M. (1983) On the structural role of fluorine in glass. *Physics and Chemistry of Glasses*, 24, 54-56.
- Rau, K., Muhlisch, A. and Treber, N. (1977) Progress in silica fibers with fluorine dopant. (abstr.) *Topical Meeting on Optical Fiber Transmission II, Williamsburg—conference proceedings, TuC1-TuC4*.
- Riebling, E. F. (1966) Structure of sodium aluminosilicate melts containing at least 50 mole% SiO_2 at 1500°C . *Journal of Physical Chemistry*, 44, 2857-2865.

- Scarfe, C. M. (1973) Viscosity of basic magmas at varying pressure. *Nature*, 241, 101–102.
- Schwerin, L. (1934) The effect of fluorspar on the viscosity of basic slags. *Metals and Alloys*, 5, 117–123.
- Seifert, F., Mysen, B. O. and Virgo, D. (1982) Three-dimensional network structure of quenched melts (glass) in the systems $\text{SiO}_2\text{-NaAlO}_2$, $\text{SiO}_2\text{-CaAl}_2\text{O}_4$ and $\text{SiO}_2\text{-MgAl}_2\text{O}_4$. *American Mineralogist*, 67, 696–717.
- Shaw, H. R. (1963) Obsidian- H_2O viscosities at 1000 and 2000 bars in the temperature range 700°C to 900°C. *Journal of Geophysical Research*, 68, 6337–6343.
- Shaw, H. R. (1972) Viscosities of magmatic silicate liquids: an empirical method of prediction. *American Journal of Science*, 272, 870–893.
- Smart, R. M. and Glasser, F. P. (1978) Silicate anion constitution of lead silicate glasses and crystals. *Physics and Chemistry of Glasses*, 19, 95–102.
- Smith, D. G. W. and Gold, C. M. (1979) EDATA2: a FORTRAN IV computer program for processing wavelength- and/or energy-dispersive electron microprobe analyses. In D. Newbury, Ed., *Microbeam Analysis Society Proceedings*, p. 273–278. 14th Annual Conference, San Antonio.
- Sparks, R. S. J. (1978) The dynamics of bubble formation and growth in magmas: A review and analysis. *Journal of Volcanology and Geothermal Research*, 3, 1–37.
- Taylor, M. and Brown, G. E. (1979) Structure of mineral glasses. I. The feldspar glasses $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 , $\text{CaAl}_2\text{Si}_2\text{O}_8$. *Geochimica et Cosmochimica Acta*, 43, 61–77.
- Tuttle, O. F. and Bowen, N. L. (1958) Origin of granite in the light of experimental studies in the system $\text{NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$. *Geological Society of America Memoir* 74.
- Weyl, W. A. (1950) Fluorine compounds in glass technology and ceramics. In J. H. Simmons, Ed., *Fluorine Chemistry*, p. 553–574. Academic Press, New York.
- Wyllie, P. J. and Tuttle, O. F. (1961) Experimental investigation of silicate systems containing two volatile components. Part II. The effects of NH_3 and HF in addition to water on the melting temperatures of granite and albite. *American Journal of Science*, 259, 128–143.

*Manuscript received, February 24, 1984;
accepted for publication, August 6, 1984.*