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Melt viscosities in the system $NaAlSi_3O_8$–H_2O–F_2O_{-1}

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Abstract—The viscosities of eight melt compositions in the system albite–H_2O–F_2O_{-1} have been determined at high pressure and temperature. Measurements were performed using the falling sphere method at 1000–1600°C and 2.5 to 22.5 kbar.

Fluorine and water strongly decrease the viscosity of albite melt at all pressures and temperatures investigated. The viscosity of a fluorine-bearing albitic melt decreases from 1 bar to 22.5 kbar, whereas there is a viscosity maximum near 7.5 kbar for a water–bearing albite melt. At constant pressure the effects of fluorine and water, compared on an equimolar basis of added F_2O_{-1} and H_2O (or F and OH), are broadly similar and both F_2O_{-1} and H_2O are less effective than Na_2O in reducing the viscosity of albite melt. Log viscosity exhibits a positive curvature as a function of mole fraction of added fluorine or water.

The effect of HF on albite melt viscosity is greater than that predicted from a linear interpolation of the effects of water and fluorine. This negative deviation from additivity may result in extremely low viscosities for granitic magmas enriched in both fluorine and water.

INTRODUCTION

THE MOST IMPORTANT melt structural parameter determining silicate melt viscosity is the degree of polymerization of the aluminosilicate tetrahedra which form the basic building blocks of silicate melts. Model granitic melts of the dry haplogranite system (SiO_2–$NaAlSi_3O_8$–$KAlSi_3O_8$) are fully polymerized liquids with all oxygens shared between two tetrahedral (T) cations (Si or Al) to form a three-dimensional network structure. This fully polymerized structure results in extremely high viscosities for melts of albite, orthoclase and SiO_2 and mixtures of these haplogranite components (HOFMAIER and URBAIN, 1968; RIEBLING, 1966; URBAIN *et al.*, 1982). Previous work on the viscosity of silicate melts has confirmed a decrease in melt viscosity accompanying the depolymerization of silicate melts due to the incorporation of water into the melt structure (BURNHAM, 1963; FRIEDMAN *et al.*, 1963; SHAW, 1963; BURNHAM, 1975; STOLPER, 1982).

Preliminary investigations of the effects of fluorine on melt structure have also illustrated a positive correlation between viscosity and polymerization in fluorine–bearing silicate melts (DINGWELL *et al.*, 1985; MYSEN and VIRGO, 1985). A direct comparison of the effects of fluorine and water on the viscosity of a simple silicate melt would be very useful for placing constraints on the relative importance of fluorine and water in determining the viscosities of granitic melts and on the relationship between structure and viscosity in silicate melts. Until now, such a comparison has not been possible because the limited viscosity data available for water– and fluorine–bearing melts have been obtained under differing conditions of temperature, pressure, bulk composition, and fluorine or water concentration. In order to provide a comparative data base for the effects of water and fluorine on the viscosity of a fully polymerized melt, DINGWELL and MYSEN (1985) initiated a study of the temperature–, pressure–, and composition–dependence of viscosity in the binary systems albite–H_2O and albite–F_2O_{-1}. The present study extends the investigation of melt viscosities in the system albite–H_2O–F_2O_{-1} with direct comparisons of the temperature–, pressure– and concentration-dependence of the effects of fluorine and water on albite melt viscosity. The additive effect of fluorine and water on albite melt viscosity has also been investigated.

Stoichiometry of fluorine and water substitutions

The additions of fluorine and water to albite melt are discussed below in terms of the anionic mol fraction, $X/(X + O)$ where X = F, OH. This parameter was calculated from the bulk stoichiometry of the melt composition assuming complete dissociation of water to form OH units. This computation is not intended to reflect the proportion of dissociation of water that occurs in albite melt under the conditions of these experiments but rather to provide a basis for comparison of water with fluorine in terms of the variable $X/(X + O)$. Thus the quantitative comparison of water and fluorine is based

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on a stoichiometry derived from the known added concentrations of fluorine and water.

The incorporation of fluorine into the albite glasses involves the exchange of two moles of fluorine for one mole of oxygen, denoted by the exchange operator F_2O_{-1} (molar). The substitutions are described by the following equations:

$$NaAlSi_3O_8 + yF_2O_{-1} = NaAlSi_3O_{8-y}F_{2y} \quad (1a)$$

$$NaAlSi_3O_8 + yH_2O = NaAlSi_3O_{8-y}OH_{2y}. \quad (1b)$$

The fluorine and water contents of this study correspond to $X/(X + O) = 0.1$, 0.2 and 0.3. The melts containing these quantities of F or OH are denoted AB1F, AB2F and AB3F; and AB1H, AB2H and AB3H, respectively. The one melt investigated that contains both water and fluorine has $X/(X + O) = 0.2$ and is denoted ABHF (Figure 1).

EXPERIMENTAL

The starting materials for viscometry experiments were water-bearing and fluorine-bearing albitic composition glasses. The water-bearing glasses were synthesized by high-pressure fusion of water + previously prepared albite glass as described by DINGWELL and MYSEN (1985). Small, known amounts of water were added to 200–250 mg of powdered albite glass, sealed in 5 mm diameter platinum capsules and fused in a solid-media high-pressure apparatus at 1400°C and 15 kbar for 1 hour. This method was also used for the preparation of the single hydrous, fluorine-bearing albite glass. The resulting, water-undersaturated, albite glasses were bubble-free and were used in the high-pressure viscosity experiments. The synthesis and analysis of the fluorine-bearing albite glass containing 5.8 weight percent fluorine has been previously described by DINGWELL *et al.* (1985). Attempts to synthesize albite glasses with higher fluorine contents at 1 bar were unsuccessful due to significant volatilization of Si and Na with F during fusion. Therefore, the fluorine-bearing albite glasses containing 11.7 and 18.3 weight percent (nominal) fluorine were synthesized at high pressure. Powder mixes of Al_2O_3, SiO_2, NaF, and AlF_3 were mixed under alcohol in an agate mortar for 2 hours and dried at 110°C. The samples were fired at 400°C for 1 minute immediately prior to sealing in platinum capsules. Then, the 200–250 mg batches of mix were sealed in platinum capsules and fused at 1400°C and 15 kbar for 1 hour. The quenched melts were used for the AB2F and AB3F viscometry runs.

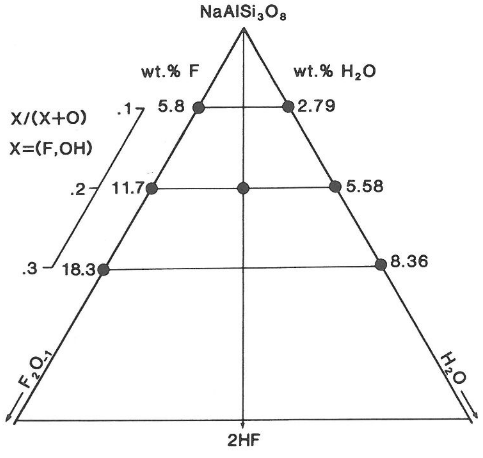

FIG. 1. The starting compositions used in this study, plotted in the system $NaAlSi_3O_8$–H_2O–F_2O_{-1} (molar). The weight percent additions of fluorine and water listed are equivalent in terms of the molar variable $X/(X + O)$ as defined in the text.

The anhydrous fluorine-free and fluorine-bearing albite glasses were analysed by electron microprobe with wavelength dispersive analysis. Microprobe analyses of the anhydrous fluorine-free and fluorine-bearing glasses are presented in Table 1 along with the operating conditions and standard compositions.

Platinum capsules for viscosity experiments were tightly packed with powdered glass and spheres of platinum were placed near the top of the charge. A small amount of the fine (<1 μm) platinum powder was placed at this level to mark the starting location of the spheres and a thin layer of powdered glass was placed above this level to prevent the spheres from sticking to the capsule.

The viscometry experiments at 2.5 kbar were conducted in an internally-heated pressure vessel using Argon as the pressure medium. The capsules were pressurized to 2.2 kbar and then heated to run temperature at a rate of 35–40°C/min for the final 400°C. The pressure climbed during heating to final run pressure. The viscometry experiments at 7.5, 15 and 22.5 kbar were conducted in a solid-media high-pressure apparatus using the technique described by DINGWELL and MYSEN (1985). Sealed platinum capsules were placed within ¾″-diameter talc-pyrex furnace assemblies with tapered graphite heaters to reduce temperature gradients along the length of the capsule to <10°C (KUSHIRO, 1976). The temperatures were measured with a Pt-$Pt_{90}Rh_{10}$ thermocouple with no correction for the effect of pressure on e.m.f. The experimental charges were raised to final pressure plus 15–20% (except for 7.5 kbar experiments which were overpressured to 15 kbar during initial heating) and then heated to 400°C below the final temperature and held there for 1 minute while the pressure was trimmed to the final value. The pressure correction for this procedure is −3%, as calibrated with the quartz-coesite transition. The final temperature was approached at 400°C/min using an automatic controller.

The experiments ranged in duration from 8 to 200 minutes and were quenched by turning off the power to the furnace. The quench rate for the solid-media apparatus is greater than 250°C/sec whereas that for the internally-heated argon vessel is 350°C/min for the first minute.

After an experiment, the capsule was sawn lengthwise on opposite sides to remove part of the platinum capsule walls. The resulting plate of glass was taped to the X-ray film holder of a flat-plate camera, and the film was exposed to Mo white radiation (35 kV, 12 mA) for 10 seconds (HAZEN and SHARPE, 1983). The sphere positions were measured from the developed film with a microscope.

The results of time series experiments by DINGWELL and MYSEN (1985) indicated that the time versus distance relationship for this type of experiment is a straight line passing through the origin. In this study, a time series of two experiments has been performed for each viscosity determination and the relationship reported above has been confirmed.

Table 1. Analyses of starting glasses.

Element	Albite	AB1F	AB2F	AB3F	Stoichiometric Ab
Na	8.79	8.31	9.19	8.03	8.74
Al	10.36	9.15	9.98	9.39	10.29
Si	31.95	31.54	28.90	28.55	32.12
O	48.76	44.5	39.78	35.71	48.84
F	—	5.8	12.4	18.9	—
Total	99.86	99.30	100.25	100.58	100.00

Analysis of Albite is from DINGWELL and MYSEN (1985); analysis of AB1F is from DINGWELL *et al.* (1985). Analyses of AB2F and AB3F by wavelength dispersive analysis using a JEOL JSM-35 instrument and Krisel control system. Operating conditions were 15 kV accelerating voltage, 150 nA beam current on carbon, and 200 sec maximum count times using a 10 × 10 micron raster and moving the sample under the beam continuously. Standards were a synthetic diopside-jadeite glass for Na, Al and Si and AB1F for F. Oxygen by stoichiometry. Microprobe uncertainties quoted at 3σ are: ±3% relative for Na, Al and Si and ±7% relative for F.

The experiments yield sphere position data relative to the platinum powder datum. Settling velocity data (accuracy = ±5%) derived from the sphere positions versus time were related to the viscosity of the silicate melt by Stokes law for the settling of a sphere in a less dense media:

$$\eta = 2r^2 g\Delta\rho/9v \qquad (2)$$

where η is the viscosity, v is settling velocity, $\Delta\rho$ is density contrast, g is acceleration due to gravity and r is the sphere radius (all in cgs units). The density contrast, $\Delta\rho$, between platinum metal and silicate melt in this system is so large ($\Delta\rho = 19.1 \pm 0.1$ g/cm^3 at 1 bar and 20°C) (DINGWELL and MYSEN, 1985) that corrections to this term due to the different compressibilities and thermal expansion coefficients of metal and melt yield insignificant changes (<1%) in the value of $\Delta\rho$ in equation (2). Therefore, $\Delta\rho$ was assigned a value of 19.1 for the calculation of viscosities with Equation (2). The final measured quantity in Equation (2) is the sphere radius, r, which was measured with a microscope to an accuracy of ±0.0005 cm, corresponding to a maximum of ±5% uncertainty for the range of sphere sizes used in this study (0.0100 to 0.0200 cm radii).

The Faxen correction for extra drag exerted on the settling sphere by capsule walls (SHAW, 1963; KUSHIRO, 1976) was applied to the results of Equation (2) with the term:

$$1 - 2.104(r/\mathrm{R}) + 2.09(r/R)^3 - 0.95(r/R)^5 \qquad (3)$$

where r is the sphere radius and R is the capsule radius. In practice, this correction term results in a 15% reduction in calculated viscosities for the sphere and capsule dimensions of this study. Table 2 lists the measured sphere radii and calculated settling velocities and viscosities obtained in this study along with the preliminary data of DINGWELL and MYSEN (1985) in this system.

RESULTS

The temperature dependence of viscosity has been expressed as a log–linear, Arrhenius function of reciprocal absolute temperature using an equation of the form;

$$\log_{10}\eta = A + B/2.303RT, \qquad (4)$$

where R is the gas constant, $\log_{10}\eta$ is the logarithm of viscosity at temperature, T (in K) and A and B are termed the pre-exponential or frequency factor and the activation energy of viscous flow, respectively. There is ample experimental evidence that the viscosity-temperature relationships of most silicate melts are non–linear over larger temperature ranges (>500°C), exhibiting, instead, a positive curvature ($\partial^2(\log\eta)/\partial(1/T)^2 > 0$) versus reciprocal absolute temperature (RICHET, 1984). The data in this study, however, are not extensive enough to permit the calculaton of non–linear functions for the temperature dependence of viscosity and the linear approximations to the temperature-viscosity relationships provide extrapolations to lower temperature which must be viewed as lower limits for the low temperature viscosities of these melts.

The pressure dependence of melt viscosity has been studied for two melt compositions, AB1H and AB1F. The data for AB1F have been obtained at 1200 and 1400°C and pressures of 7.5, 15 and 22.5 kbar. These data are presented in Figure 2 along with the data of KUSHIRO (1978) for albite melt at high pressure and the 1 bar data of DINGWELL *et al.* (1985) for AB1F.

The viscosity of AB1F melt decreases with increasing pressure from 1 bar to 22.5 kbar. The viscosity decrease is not linear but describes instead a positive curvature with respect to pressure (Figure 2). Comparison of the 1400°C curves of Figure 2 for albite and AB1F reveals that the effect of F_2O_{-1} on the viscosity of albite melt is largest in the pressure range of 6–8 kbar. The Arrhenian activation energy of viscous flow for AB1F is constant within the uncertainties of the data from 1 atm to 22.5 kbar (Figure 2).

The pressure dependence of viscosity of AB1H is complex compared with that of AB1F (Figures 2,3). The 1200°C data exhibit an increasing viscosity from 2.5 to 7.5 kbar and a decreasing viscosity

Table 2. Viscosity data for the system Albite–H_2O–F_2O_{-1}

Composition	Temperature (°C)	Pressure (kbar)	Radius ($\times 10^{-2}$ cm)	Speed ($\times 10^{-4}$ cm/sec)	$\log_{10}\eta$ (poise)
Ab	1600	7.5	1.0	0.789	3.65
AB1F	1200	7.5	—	—	3.70
	1400	7.5	—	—	3.11
	1200	15.0	—	—	3.46
	1400	15.0	—	—	2.91
	1200	22.5	—	—	3.20
	1400	22.5	—	—	2.63
AB2F	1200	7.5	1.00	1.75	3.30
	1400	7.5	1.00	9.85	2.55
AB3F	1200	7.5	1.33	8.43	2.85
AB1H	1100	2.5	1.67	0.253	4.55
	1200	2.5	1.67	1.27	3.85
	1200	7.5	1.33	0.474	4.10
	1400	7.5	—	—	2.81
	1200	15.0	1.55	1.57	3.70
	1400	15.0	—	—	2.57
	1400	22.5	—	—	2.60
AB2H	1000	7.5	1.33	1.06	3.75
	1200	7.5	1.00	6.18	2.76
AB3H	1000	7.5	1.00	1.25	3.45
	1200	7.5	1.00	15.7	2.35
ABHF	1000	7.5	1.33	2.38	3.40
	1200	7.5	1.00	8.00	2.64

Uncertainties are as follows: *T*, ±10°C; *P*, ±0.5 kbar; radii, ±.0005 cm; velocity, ±5%; viscosity, ±15%.

from 7.5 to 15 kbar, resulting, therefore, in a viscosity maximum for AB1H at 1200°C and a pressure of 7.5 kbar. The 1400°C data indicate a decreasing viscosity with increasing pressure from 7.5 to 15 kbar and a constant viscosity with further pressure increase to 22.5 kbar. The activation energy for AB1H from 2.5 to 15 kbar is constant.

The composition dependence of viscosity along the binary joins albite–H_2O and albite–F_2O_{-1} has been investigated at 7.5 kbar pressure in the range of 1000 to 1600°C (Figure 4). The viscosity of albite melt at 1600°C and 7.5 kbar was measured to determine the temperature dependence of albite melt at 7.5 kbar in combination with interpolated data from Kushiro (1978) at 1400°C. The data for AB1H, AB2H and AB3H illustrate that the isothermal decrease of melt viscosity with addition of H_2O to albite melt is a strongly nonlinear, positively curved function (see below). The activation energy of viscous flow decreases from 89.6 kcal/mol for albite melt to 72.7 kcal/mol for AB1H, whereas the values for AB2H and AB3H are constant within error at 42.5kcal/mol and 47.2 kcal/mol, respectively. Similarly, the isothermal dependence of viscosity on F_2O_{-1} content for melts on the join albite–F_2O_{-1} exhibits a very strong positive curvature.

The viscosity of ABHF has been determined at 1000 and 1200°C and 7.5 kbar (Figure 5). The viscosity of ABHF is lower than that of AB2H. The viscosity of ABHF is lower than that of either AB2F or AB2H at 1000°C and lower than the viscosity of AB2F but equal to the viscosity of AB2H at 1200°C.

DISCUSSION

As noted above the equivalence of the stoichiometry of F– and OH–bearing melts of this study, in terms of the molar variable $X/(X + O)$, permits a comparison of the effects of F_2O_{-1} and H_2O on the viscosity of albite on an equimolar basis. Qualitatively, several aspects of the viscosities of albite melts with equimolar additions of F_2O_{-1} and H_2O are similar. The activation energy and viscosity of albite melt decrease strongly with the addition of F_2O_{-1} or H_2O and secondly, and the rates of decrease of activation energy and viscosity diminish as a function of added F_2O_{-1} or H_2O. On closer inspection, however, it is clear that the viscosities

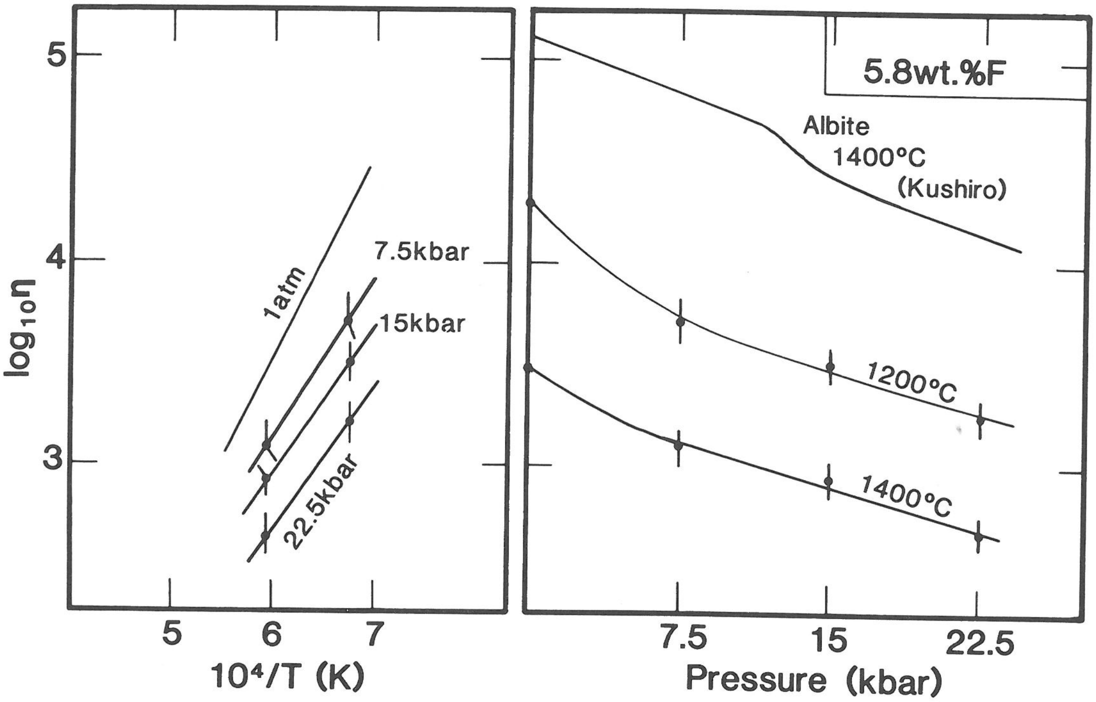

FIG. 2. The viscosity of AB1F melt at 1200–1400°C and 1 bar to 22.5 kbar: (a) viscosity data for AB1F melt at 1 bar, 7.5, 15 and 22.5 kbar plotted versus reciprocal absolute temperature; (b) the pressure dependence of AB1F melt viscosity at 1200 and 1400°C. (1 bar AB1F data from DINGWELL *et al.*, 1985; Ab viscosity data at 1400°C from KUSHIRO, 1978).

of AB1F and AB1H, AB2F and AB2H, and AB3F and AB3H are not equivalent. The relationship between viscosity and composition for the albite–H_2O and albite–F_2O_{-1} systems is demonstrated in Figure 6 where log η is plotted vs. $X/(X + O)$ for experiments at 1200°C. Also included in Figure 6 are data for the system albite–Na_2O that were interpolated from the systems $Na_2Si_2O_5$–$Na_4Al_2O_5$ (DINGWELL, 1986) and $Na_2Si_4O_9$–$Na_6Al_4O_9$ (DINGWELL *et al.*, in prep.) which intersect the join albite–Na_2O at 0.67 and 0.50 mol fraction Na_2O, respectively. There is evidence from studies of peralkaline melts in the system Na_2O–Al_2O_3–SiO_2 that the effect of adding excess Na_2O to albite melt results in depolymerization due to coordination of non-bridging oxygens (NBOs) by Na atoms. Such a solution mechanism involves no change in the number of tetrahedral (T) cations (*i.e.*, there is no evidence for non-tetrahedral coordination of Al in these melts). Therefore $X/(X + O)$ is linearly proportional to NBO/T or bulk polymerization for this join. Figure 6 illustrates therefore that in the system albite–Na_2O, log η is not a linear function of bulk polymerization. This observation is consistent with the more general observation that log η varies greatly in binary systems of constant bulk polymerization (RIEBLING, 1966; DINGWELL, 1986).

A previous discussion of the compositional dependence of log viscosity in the system granite–water by STOLPER (1982) suggested that the curvature of log viscosity as a function of added water was due to the increasing proportion of water dissolved in the form of undissociated, molecular water as total water content increased. As discussed by DINGWELL and MYSEN (1985) the coincidence of dissociation and log viscosity curves illustrated in Figure 14 of STOLPER (1982) implies that the functional form of log viscosity corrected to the anionic proportion of OH units (and therefore NBO/T by the solution mechanism of Stolper (1982)) would be linear whereas the data of Figure 6 indicate that the system albite–Na_2O exhibits a slightly curved relationship between log viscosity and $X/(X + O)$.

The system albite–F_2O_{-1} also exhibits a strongly curved log η–$X/(X + O)$ relationship. It is unlikely that this viscosity behavior can be explained in a manner analogous to that of STOLPER (1982) for the granite–H_2O system simply because there is no evidence for molecular fluorine in these melts (MYSEN and VIRGO, 1985). What alternative explana-

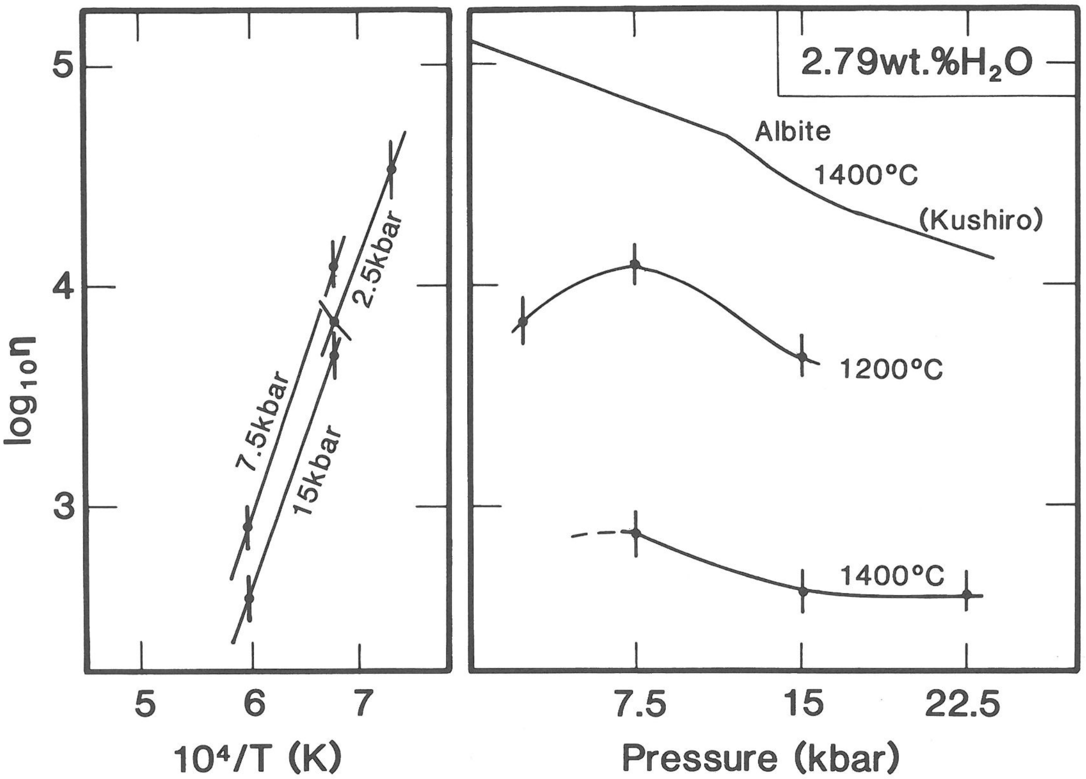

FIG. 3. The viscosity of AB1H melt at 1100–1400°C and 2.5 to 22.5 kbar: (a) viscosity data for AB1H melt at 2.5, 7.5 and 15 kbar plotted versus reciprocal absolute temperature; (b) the pressure dependence of AB1H melt viscosity at 1200 and 1400°C. (albite viscosity data at 1400°C from KUSHIRO, 1978).

tions exist to explain the extreme curvature in log viscosity versus $X/(X + O)$? Two possibilities are (1) the expulsion of tetrahedral cations during fluorine solution such that $X/(X + O)$ is no longer linearly related to bulk polymerization expressed as NBO/T and (2) variation in the types of cations coordinating fluorine as a function of fluorine concentration such that the rate of depolymerization per mole of fluorine is not constant. Both of these concepts have been put forth by MYSEN and VIRGO (1985) in their interpretation of Raman spectra in the system albite–F_2O_{-1}.

There is evidence to suggest that the configurational entropy theory of viscous flow (ADAM and GIBBS, 1965) provides a self-consistent and independently verifiable framework for interpreting the temperature and composition dependence of the viscosity of silicate melts (RICHET, 1984; HUMMEL and ARNDT, 1985; BREARLEY *et al.*, 1986; RICHET *et al.*, 1986; TAUBER and ARNDT, 1986). This theory states that the viscosity of a silicate melt is related to the temperature and configurational entropy of the melt by the following relationship:

$$\log_{10}\eta = Ae + Be/TS_{\mathrm{conf}}, \tag{5}$$

where Ae and Be are constants for a given melt composition and S_{conf} (configurational entropy) varies with temperature in a manner that may be computed where sufficient thermodynamic data exist (specifically, C_p data for liquid, crystal and glass; the configurational entropy of the crystal and the fusion temperature and entropy of fusion of the crystal). Thus, the composition-dependence of viscosity of a silicate melt at temperature, T is determined by three independent parameters, Ae, Be and S_{conf}. The slope parameter, Be, is interpreted as a potential energy barrier to cooperative rearrangements of melt units that must occur during viscous flow. If this energy barrier is an expression of the average bond strength of silicate melts then the value of Be should be positively correlated with melt polymerization. It follows from Equation (5) that it is the temperature dependence of S_{conf} which produces the non-linear or non-Arrhenian behavior of melt viscosity as a function of reciprocal absolute temperature.

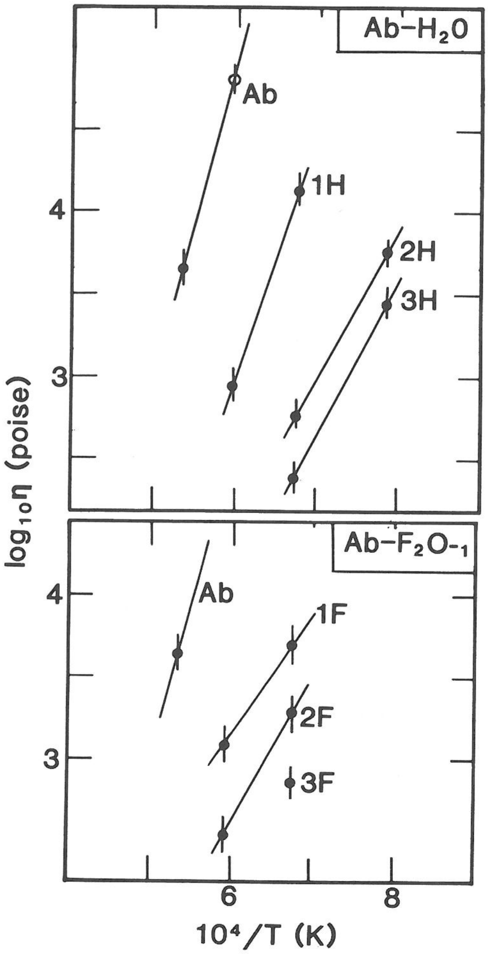

FIG. 4. The composition dependence of melt viscosity in the systems $NaAlSi_3O_8$-H_2O and $NaAlSi_3O_8$-F_2O_{-1} at 7.5 kbar. (albite data at 1400°C from KUSHIRO, 1978).

The composition–dependence of viscosity along some binary silicate joins that exhibit diminishing negative deviations of viscosity from linear interpolation are explained for systems of constant polymerization such as albite–anorthite and $K_2Si_3O_7$–$Na_2Si_3O_7$ by the increase in configurational entropy in these systems due to the entropy of mixing term (HUMMEL and ARNDT, 1985; RICHET, 1984).

Figure 7 illustrates the viscosity temperature relationships for the binary join AB2F–AB2H. This join represents the exchange of F_2O_{-1} for H_2O (or F for OH) under conditions of constant $X/(X + O)$. Clearly, the presence of up to 0.1 anionic mol fraction of F or OH does not diminish the viscosity-reducing effect of a further addition of either OH or F, respectively, when compared with the viscosity of AB2H or AB2F.

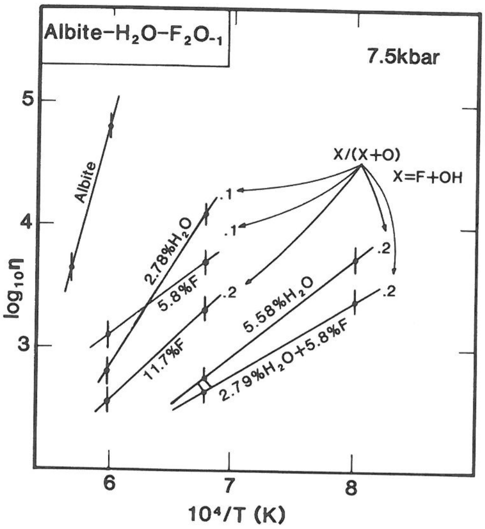

FIG. 5. Viscosities of melts in the system $NaAlSi_3O_8$–H_2O–F_2O_{-1} with $X/(X + O) = 0.1$ and 0.2 plotted versus reciprocal absolute temperature.

The negative deviation of the viscosity of ABHF from the weighted mean of the viscosities of AB2F and AB2H (the straight lines in Figure 7) increases with decreasing temperature such that the exchange

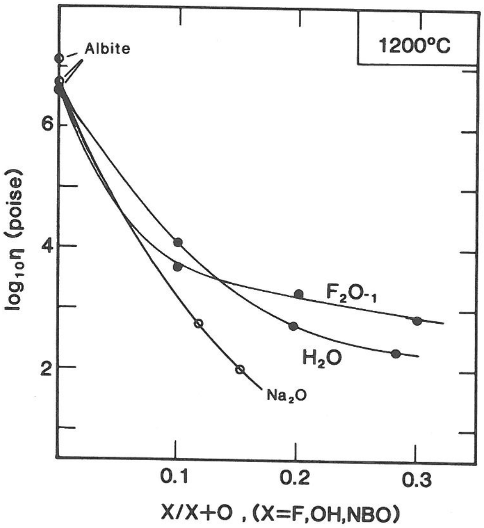

FIG. 6. The relative effects of three depolymerizing components, F_2O_{-1}, H_2O and Na_2O on the viscosity of albite melt compared on the equimolar basis of $X/(X + O)$ where $X =$ F, OH, NBO ($P = 7.5$ kbar). (albite–Na_2O data (1 bar) from DINGWELL, 1986 and DINGWELL *et al.*, in prep.; albite data (1 bar) from RIEBLING, 1966; SCARFE and CRONIN, 1986; URBAIN *et al.*, 1982). NBO—nonbridging oxygen. In the system $NaAlSi_3O_8$–Na_2O, one nonbridging oxygen is formed per Na added to the system.

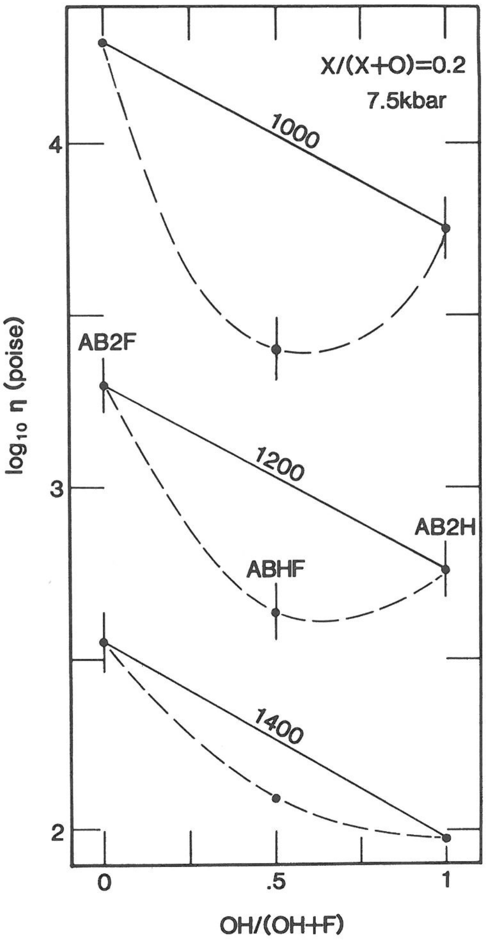

FIG. 7. The variation of melt viscosity with composition along the join AB2F–AB2H. The lower activation energy of ABHF in the temperature range investigated results in a negative deviation of viscosity from additivity, which increases with diminishing temperature. (Points without error bars are extrapolated.)

of F for OH results in a decrease in melt viscosity at temperatures below 1400°C.

As noted above, a negative deviation of viscosity from additivity that increases with decreasing temperature is the behavior predicted from the configurational entropy concept of viscous flow (ADAM and GIBBS, 1965; RICHET, 1984). According to this concept, the mixing of AB2F and AB2H melts to form ABHF could result in an additional contribution to the total configurational entropy of the mixture due to a configurational entropy of mixing term arising from F–OH mixing on melt structural sites.

The general behavior exhibited in Figure 7 will result in extremely large negative deviations from additivity and correspondingly low viscosities for F + OH–bearing albite melts at the lower temperatures relevant to the petrogenesis of F– and OH–rich granitic magmas. The data of Figure 7 are the first clear indication the fluorine and water in combination will be even more effective in reducing melt viscosities than previous data on fluorine–bearing and water–bearing melt viscosities have indicated (BURNHAM, 1963; SHAW, 1963; DINGWELL *et al.*, 1985; DINGWELL and MYSEN, 1985).

The data available on the pressure dependence of silicate melt viscosity includes examples of several types of behavior. Both $\delta(\log \eta)/\delta P$ and $\delta^2(\log \eta)/\delta P^2$ may be positive, negative or equal to zero depending on melt composition. Only two studies provide data on the pressure dependence of melt viscosity as a systematic function of melt composition; one by KUSHIRO (1981) in a system of constant polymerization and one by BREARLEY *et al.* (1986) in a system of varying polymerization. KUSHIRO (1981) investigated the pressure dependence of the viscosities of melts on the join SiO_2–$CaAl_2O_4$ observing a linear pressure dependence of melt viscosity that changed from a negative value ($\partial(\log \eta)/\partial P < 0$) at mol fraction $CaAl_2O_4 = 0.15$ and 0.2, through pressure invariance ($\partial(\log \eta)/\partial P = 0$) at $CaAl_2O_4 = 0.33$ to a positive pressure dependence of viscosity ($\partial(\log \eta)/\partial P > 0$) at mol fraction $CaAl_2O_4 = 0.4$.

BREARLEY *et al.* (1986) have investigated the pressure dependence of viscosity of melts on the join albite-diopside. The transition from negative to positive pressure dependence of viscosity occurs at 10–15 kbar in the intermediate composition $Di_{75}Ab_{25}$ which exhibits a viscosity minimum in this pressure range. Thus, the transition from negative to positive pressure–dependence of melt viscosity may occur in a different manner along this join of variable polymerization than that which is observed for joins of constant polymerization. Probably the non–linearity of the pressure–dependence of viscosity of many relatively depolymerized silicate melts is a response to variations of the proportions of various polyanionic units in these melts (SCARFE *et al.*, 1979).

Although it is premature to reach conclusions on the structural significance of the pressure–dependence of the viscosities of silicate melts; the contrasting pressure dependence of the viscosities of AB1F and AB1H indicates that some structural parameter is significantly different for these two melts. One possible explanation of the positive pressure dependence of viscosity of AB1H at low pressure is that the speciation of dissolved water in this melt may be pressure–dependent. If the speciation of water in albite melt is quenchable (STOLPER *et al.*, 1983; MCMILLAN *et al.*, 1983) then the pressure dependence of water speciation in this undersaturated melt may require further investigation.

SUMMARY

Investigation of the pressure–, temperature– and composition–dependence of melt viscosity in the system albite–H_2O–F_2O_{-1} has provided an experimental framework for further evaluation of structural models of melt viscosity and has provided a model system for the estimation of viscosities of fluorine– and water–rich granitic magmas.

The viscosity–composition relationships observed in the system albite–Na_2O, albite–H_2O and albite–F_2O_{-1} are qualitatively similar. If the diminishing effectiveness of H_2O in reducing melt viscosity is attributed to the increasing proportion of H_2O dissolved as the molecular species then alternative, more and less effective mechanisms must be provided to explain the viscosity reductions due to F_2O_{-1} and Na_2O, respectively. If current models for the structure of peralkaline melts in the system Na_2O–Al_2O_3–SiO_2 are correct, then the variation of log viscosity with melt polymerization shows a positive curvature. Thus attempts to rationalize melt structure to obtain a linear relationship between log viscosity and polymerization may lead to erroneous conclusions.

The additive effect of fluorine and water on the viscosity of silicate melts is greater than that predicted from a linear interpolation from the albite–H_2O and albite–F_2O_{-1} systems. This negative deviation from additivity results in the estimation of extremely low viscosities for granitic magmas enriched in both water and fluorine.

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REFERENCES

ADAM G. and GIBBS J. H. (1965) On the temperature dependence of cooperative relaxation properties in glass forming liquids. *J. Phys. Chem.* **43**, 139–146.

BOTTINGA Y. and WEILL D. F. (1972) The viscosity of magmatic liquids: a model for calculation. *Amer. J.Sci.* **272**, 438–475.

BREARLEY M., DICKINSON J. and SCARFE C. M. (1986) Pressure dependence of melt viscosity on the join albite-diopside: implications for melt structure. *Geochim. Cosmochim. Acta* (In press).

BURNHAM C. WAYNE (1963) Viscosity of a water–rich pegmatite. (abstr.) *Geol. Soc. Am. Special Pap.* **76**, 26.

BURNHAM C. WAYNE (1975) Water and magmas: a mixing model. *Geochim. Cosmochim. Acta* **39**, 1077–1084.

DINGWELL D. B. (1986) Viscosity–temperature relationships in the system $Na_2Si_2O_5$–$Na_4Al_2O_5$. *Geochim. Cosmochim. Acta* **50**, 1261–1265.

DINGWELL D. B. and MYSEN B. O. (1985) Effects of fluorine and water on the viscosity of albite melt at high pressure: a preliminary investigation. *Earth Planet. Sci. Lett.* **74**, 266–274.

DINGWELL D. B., SCARFE C. M. and CRONIN D. J. (1985) The effect of fluorine on viscosities in the system Na_2O–Al_2O_3–SiO_2: implications for phonolites, trachytes and rhyolites. *Amer. Mineral.* **70**, 80–87.

FRIEDMAN I., LONG W. and SMITH R. L. (1963) Viscosity and water content of rhyolite glass. *J. Geophys. Res.* **68**, 6523–6535.

HAZEN R. M. and SHARPE M. R. (1983) Radiographic determination of the positions of platinum spheres in density–viscosity studies of silicate melts. *Carnegie Inst. Wash. Yearb.* **82**, 428–430.

HOFMAIER G. and URBAIN G. (1968) The viscosity of pure silica. *Sci. Ceram.* **4**, 25–32.

HUMMEL W. and ARNDT J. (1985) Variation of viscosity with temperature and composition in the plagioclase system. *Contrib. Mineral. Petrol.* **90**, 83–92.

KUSHIRO I. (1976) Changes in viscosity and structure of melt of $NaAlSi_2O_6$ composition at high pressures. *J. Geophys. Res.* **81**, 6347–6350.

KUSHIRO I. (1978) Viscosity and structural changes of albite ($NaAlSi_3O_8$) melt at high pressures. *Earth Planet. Sci. Lett.* **41**, 87–90.

KUSHIRO I. (1981) Change in viscosity with pressure of melts in the system SiO_2–$CaAl_2O_4$. *Carnegie Inst. Wash. Yearb.* **80**, 339–341.

MCMILLAN P. F., JAKOBSSON S., HOLLOWAY J. R. and SILVER L. A. (1983) A note on the Raman spectra of water-bearing albite glasses. *Geochim. Cosmochim. Acta* **47**, 1937–1943.

MYSEN B. O. and VIRGO D. (1985) Structure and properties of fluorine–bearing aluminosilicate melts: the system Na_2O–Al_2O_3–SiO_2–F at 1 atm. *Contrib. Mineral. Petrol.* **91**, 205–220.

RICHET P. (1984) Viscosity and configurational entropy of silicate melts. *Geochim. Cosmochim. Acta* **48**, 471–483.

RICHET P., ROBIE R. A. and HEMINGWAY B. S. (1986) Low-temperature heat capacity of glassy diopside ($CaMgSi_2O_6$): A calorimetric test of the configurational–entropy theory applied to the viscosity of liquid silicates. *Geochim. Cosmochim. Acta* **50**, 1521–1533.

RIEBLING E. F. (1966) Structure of sodium aluminosilicate melts containing at least 50 mole% SiO_2 at 1500°C. *J. Phys. Chem.* **44**, 2857–2865.

SCARFE C. M. and CRONIN D. J. (1986) Viscosity–temperature relationships of melts at 1-atm in the system albite-diopside. *Amer. Mineral.* **71**, 767–771.

SCARFE C. M., MYSEN B. O. and VIRGO D. (1979) Changes in viscosity and density of melts of sodium disilicate, sodium metasilicate and diopside composition with pressure. *Carnegie Inst. Wash. Yearb.* **78**, 547–551.

SHAW H. R. (1963) Obsidian-H_2O viscosities at 1000 and 2000 bars in the temperature range 700° to 900°C. *J. Geophys. Res.* **68**, 6337–6343.

STOLPER E. (1982) Water in silicate glasses: an infrared spectroscopic study. *Contrib. Mineral. Petrol.* **81**, 1–17.

STOLPER E., SILVER L. A. and AINES R. (1983) The effects of quenching rate and temperature on the speciation of water in silicate glasses. (abstr.) *EOS* **64**, 339.

TAUBER P. and ARNDT J. (1986) Viscosity-temperature relationship of liquid diopside. *Phys. Chem. Earth Plan. Inter.* **43**, 97–103.

URBAIN G., BOTTINGA Y. and RICHET P. (1982) Viscosity of liquid silica, silicates and aluminosilicates. *Geochim. Cosmochim. Acta* **46**, 1061–1072.