

The fluxing effect of fluorine at magmatic temperatures (600–800 °C): A scanning calorimetric study

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ABSTRACT

The effect of F on the glass transition behavior of albite, diopside, and four other silicate melts has been investigated using scanning calorimetry. The addition of F to all silicate melts investigated results in a strong, nonlinear decrease of the glass transition temperature (T_g , as recorded by the peak temperatures of heat capacity). The decreases observed extrapolate consistently to published fluoride glass transition temperatures. The largest T_g decrease is observed for albite- F_2O_{-1} melts ($\Delta T \cong 250$ °C at 6 wt% F). The effect of F is similar to that previously observed for H_2O (Taniguchi, 1981).

Physical properties of low-temperature silicate liquids are a valuable constraint on low-temperature petrogenetic processes in granite and pegmatite petrogenesis. Low-temperature viscosities can be estimated from the glass transition data. These data are combined with previously published high-temperature, concentric-cylinder viscosity data to obtain a much more complete description of the temperature dependence of viscosity for these melts.

The present data, obtained on supercooled liquids close to the glass transition, are of special significance because it is at the glass transition that silicate glass structures are frozen. A separate multinuclear NMR study of glasses quenched from these experiments has shown that the predominant coordination of F in albite glass is octahedral to Al. The coordination state of F does not appear to be concentration dependent, and thus the structural origin of the nonlinear T_g decrease does not arise from such a mechanism.

INTRODUCTION

The formation of igneous rocks involves processes that can only be fully understood through a complete description of the rheology of silicate melts. It has recently been suggested that silicate melts behave predominantly as relaxed liquid phases during such petrogenetic processes (Dingwell and Webb, 1989, 1990). Some exceptions do occur, and the extremely high rate of melt deformation during volcanic ash flow eruptions is an example of unrelaxed behavior of the melt (Webb and Dingwell, 1990a, 1990b). A second possible case is that of rapid crystal growth in extremely low-temperature melts such as pegmatitic systems. The viscosity of a silicate melt is a near-linear measure of the relaxation time, and it is at high viscosities and the corresponding high relaxation times that low-temperature processes of rhyolite, granite, and pegmatite petrogenesis occur.

Providing a complete description of the rheology and thermochemistry of silicate melts requires the study of undercooled liquids. An increasing number of studies of this nature are being performed as a result (Neuville and Richet, 1991; Taniguchi, 1989; Webb and Dingwell, 1990a, 1990b; Webb et al., 1992). Experiments on the behavior of supercooled liquids must avoid significant crystallization in order to observe the properties of the

silicate melt. Generally this is done in one of the two ways illustrated schematically in Figure 1. A time-temperature-transformation (TTT) curve is drawn for the crystallization of a single-phase system. Superimposed on the diagram is the time-temperature description of the glass transition and the liquidus. A favorable composition yields regions that, under experimental time scales, lie outside the TTT crystallization curve, both below the liquidus and above the glass transition. Experiments just below the liquidus temperature can take advantage of the finite time required for significant crystallization to provide data on the properties of supercooled liquids. Experiments just above the glass transition interval contribute to the undercooled-liquid data by avoiding significant crystallization from below.

This study is of the latter type. We have measured the heat capacity of F-bearing silicate melts at temperatures just above the glass transition but below the TTT envelope for our experimental time scale. The resulting calorimetric traces of the unrelaxed and relaxed silicate melts are also used to provide information on the low-temperature viscosity of these melts in a region that is difficult to access directly with viscosity measurements because of incipient crystallization during the longer excursion times above T_g that are required.

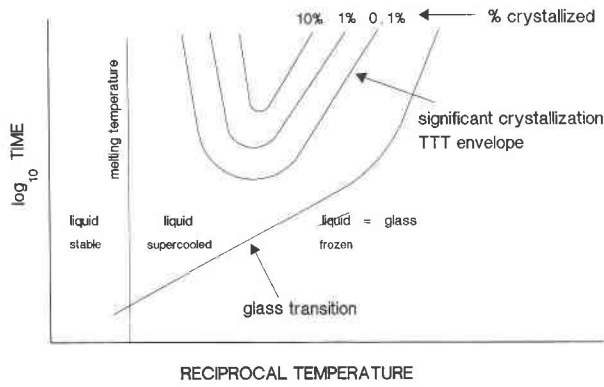


Fig. 1. Schematic representation of the time scales of structural relaxation, crystallization, and experiments on crystal-free supercooled liquids such as the present study.

METHODS

The compositions investigated in this study represent the substitution of F_2O_{-1} into base compositions of diopside ($\text{CaMgSi}_2\text{O}_6$) and albite ($\text{NaAlSi}_3\text{O}_8$) as well as reconnaissance of four other compositions in the system Na-Al-Si-O-F. The glasses used in the study originate from the viscosity investigations of Dingwell et al. (1985) and Dingwell (1989). Additionally, $\text{NaAlSi}_3\text{O}_8$ glasses containing 1.6 and 3.4% F were produced by mixing powders of the requisite proportions of albitic and albite + 5.8% F glasses and fusing at 1200 °C for 2 h in a Pt crucible.

The scanning calorimetry was performed using commercial instruments (Setaram DSC111 and HTC). The calibration of both instruments was carried out with Al_2O_3 . The heat capacity data are accurate to 2.5% (DSC instrument) and 5% (HTC instrument), and the glass transition peak temperatures are reproducible to ± 3 °C.

RESULTS

The scanning calorimetric traces of the diopside F_2O_{-1} glasses are presented in Figure 2. The effect of this extent of F substitution on the liquid and glassy heat capacities is within the precision of these data (Fig. 2). The general appearance of the transition is unchanged except for the shift to lower temperatures with F addition. The ratios of peak height to liquid heat capacity and of glass to liquid heat capacity are not measurably influenced by the F contents.

The effect of F content on the glass transition of diopside and albite melts is parameterized in Figure 3 and Table 1 in the form of peak temperature vs. F content. The peak temperature is a strongly nonlinear function of F content for both the diopside and albite melts.

DISCUSSION

In Figure 3 the composition dependence of the peak temperature for F-bearing albite and diopside are compared. The decrease of T_g observed is consistent with existing information placing the glass transition temper-

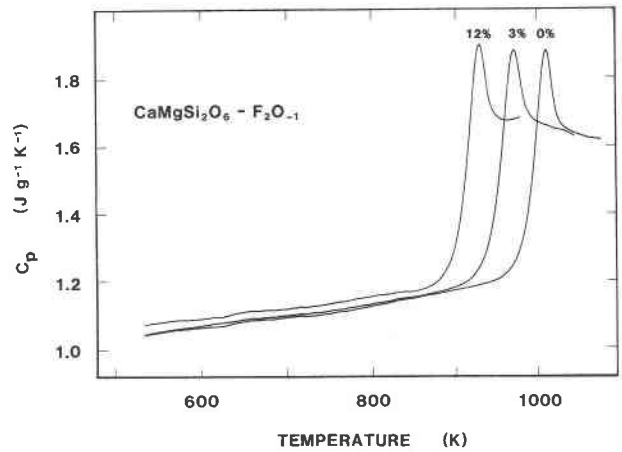


Fig. 2. Scanning calorimetric traces of the heat capacity of glassy and liquid melts on the join diopside- F_2O_{-1} cooled and subsequently reheated at 5 K/min.

ature of fluoride glasses at ≈ 600 K (Gan and Zhang, 1990; Koide et al., 1990). The trends of peak temperatures extrapolate consistently to the values obtained for pure fluoride melts.

A preliminary comparison of the effect of F and H_2O on the glass transition and low-temperature viscosity of silicic melts can be made using the data of Taniguchi (1981) on wet rhyolites. The effects of H_2O and F are compared in Figure 4 on the basis of equivalent F and $\text{H}_2\text{O}/2$. The comparison indicates similar effects of F and H_2O on T_g . The slope of the decrease in T_g with H_2O

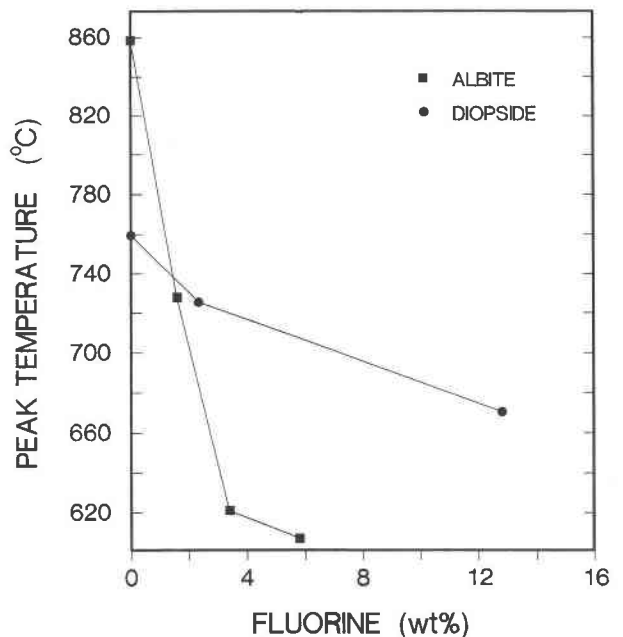


Fig. 3. The effect of F on the glass transition of diopside and albite melts as indicated by the peak temperature of glasses cooled and subsequently reheated at 5 K/min.

TABLE 1. Peak temperatures from scanning calorimetry

Composition	Peak temperature (K)
DI	1014
DIF0.25	978
DIF1	933
AB	1131
ABF1.6	1000
ABF3.4	893
ABF6	880
JDF	812
NEF	833
AKF	823
ALUMF	870

added is within error of that for F. This comparison indicates that H₂O and F are equally effective in reducing relaxation times in low-temperature silicic melts. The inset of Figure 4 is a comparison of the effects of F and H₂O on the viscosity of albite melt (Dingwell, 1987). Similar trends are shown for the effects of F and H₂O in melt viscosity at 1200 °C, consistent with the calorimetric data from 600 to 800 °C.

The low-temperature viscosities of silicic melts containing F are of direct relevance to rock-forming processes in granitic and pegmatitic environments. The effects of F are likely to be much increased at petrogenetic temperatures compared with the superliquidus regime, where data are available. Attempts to extrapolate high-temperature viscosity data to lower temperatures relevant to granite and pegmatite petrogenesis are difficult because the high-temperature data are too restricted to account for any potential non-Arrhenian behavior of the temperature dependence of viscosity. Low-temperature data are required.

Viscosities of undercooled F-bearing melts are however difficult to measure using dilatometric means because of the mineralizing action of F in these melts. Attempts to obtain such data using the fiber elongation method indicated that the strength of such fibers is strongly reduced with addition of F (Dingwell and Webb, unpublished

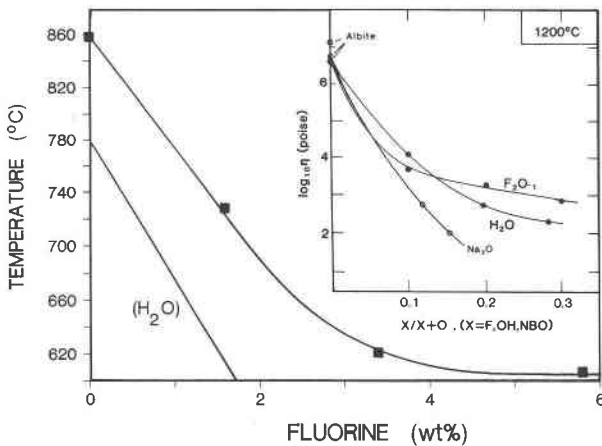


Fig. 4. Comparison of the effects of H₂O and F on the glass transition in rhyolite (marked H₂O) and albite melts, respectively.

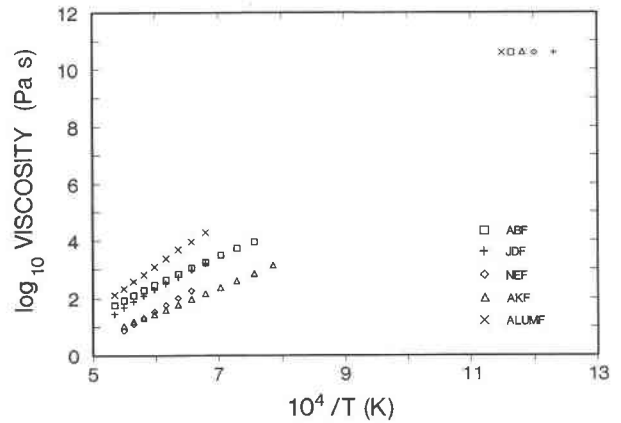


Fig. 5. Comparison of high-temperature, concentric-cylinder viscosity data of Dingwell et al. (1985) and Dingwell (1989) with low-temperature viscosity data derived from the peak temperatures of scanning calorimetric experiments (this study).

data). The cause of such a reduction is probably imperfections caused by crystallization.

The time scales of shear and enthalpy relaxation in silicate melts are closely related (Dingwell and Webb, 1989, 1990). Recent comparisons of shear viscosities and calorimetric glass transition temperatures (Knoche et al., 1992; Webb et al., 1992) have confirmed that peak temperatures from enthalpy relaxation represent isokoms (i.e., constant viscosities) for silicate melts (e.g., Richet, 1984). Thus the peak temperatures of this study yield low-temperature viscosity data for the investigated compositions. Calibration of the peak temperatures of melts along the diopside-anorthite join by Knoche et al. (1992) confirms the common assumption of constant viscosity at a consistently defined glass transition temperature for glasses with the same thermal history. Knoche et al. (1992) established that glasses cooled at 5 K/min and subsequently reheated at 5 K/min yielded calorimetric peak temperatures at a viscosity of $11.0 \pm 0.3 \log_{10}$ Pa s.

Low-temperature viscosities derived from the scanning calorimetry are plotted together with the high-temperature data of Dingwell et al. (1985) and Dingwell (1989) in Figure 5. The low-temperature viscosities obtained for the alkali aluminosilicate melts indicate an even stronger viscosity decrease with the addition of F at low temperature than is the case at superliquidus temperatures. The peralkaline melt is strongly non-Arrhenian, and the peraluminous melt is Arrhenian. The albite, jadeite, and nepheline F-bearing melts exhibit only slightly non-Arrhenian temperature dependences with the result that the strong lowering of activation energy observed at high temperatures (Dingwell et al., 1985) continues to lower temperatures. The effect of F in low-temperature silicic melts is indeed much greater than that observed at higher temperatures.

The F-bearing diopsidic melts exhibit viscosity temperature relations that are subparallel to that of diopside itself. The activation energy of viscous flow is not strong-

ly affected by the addition of F to diopside at high or at low temperatures. The effect of F on melt viscosity does however increase with decreasing temperature.

The frozen structures of the samples investigated in this study have been investigated by a variety of nuclear magnetic resonance methods (Schaller et al., 1992). Those results indicate that the predominant speciation of F is to octahedral Al atoms (Manning et al., 1980) for the F-bearing albite samples of this study. The ^{27}Al , ^{29}Si , and ^{19}F spectra of albite + 1.6, 3.4, and 5.8% F indicate no concentration dependence of F speciation. Thus the strongly nonlinear nature of the effects of F on the glass transition temperature (this study) and on viscosity (Dingwell, 1987) do not appear to result from varying proportions of different fluoride species.

CONCLUSION

The effects of F on the glass transition of silicate melts is characterized by a strong, nonlinear decrease of peak temperature in scanning calorimetric measurements of heat capacity. Low-temperature viscosity data estimated from the peak temperatures provide a more complete description of the temperature dependence of viscosity in these melts. The observed effects of F and H_2O on the glass transition temperature are similar. The effects on albite and diopside are qualitatively similar but quantitatively different. The much larger decrease in the activation energy of viscous flow in the albite melts compared with diopside melts may result from the contrasting solution mechanisms of F in these melts, inferred from NMR measurements on the quenched glasses.

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