The effect of F and Cl on the interdiffusion of peralkaline intermediate and silicic melts

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Abstract

Interdiffusion experiments between peralkaline fluoridated melts of rhyolitic and dacitic composition (with ~1.3 wt% F) at 1200–1600 °C, 1.0 GPa, have yielded effective binary diffusion coefficients for Si. Similar interdiffusion experiments between a natural peralkaline pantelleritic glass with 0.89 wt% Cl and a trachytic glass, with virtually no Cl, give effective binary diffusion coefficients for Si in the presence of Cl at 1.0 GPa. As previously observed in other studies, all nonalkalis (Al, Ti, Fe, Mg, and Ca) appear to diffuse only as rapidly as Si, whereas alkali transport is much more rapid. The effective binary diffusion coefficient for Si is, at most, weakly dependent on silica concentration in the compositional range investigated, approximately 61–73 wt% SiO_2. Arrhenius equations have been fitted to the measured diffusivities; at the center of the diffusion profiles (where the highest quality data are acquired) the Arrhenius equations for Si diffusion are

With F: $D = 5.41 \times 10^{-7} \exp(192.8 \pm 7.1/RT)$ at 70 wt% SiO_2

With Cl: $D = 1.86 \times 10^{-5} \exp(236.9 \pm 8.7/RT)$ at 66 wt% SiO_2

where D is in squared meters per second, and the activation energies are in kilojoules per mole. At concentrations studied, the effects of F and Cl on diffusion are minor, typically within experimental error of diffusivities in volatile-free equivalent compositions. It does appear, however, that the addition of F decreases activation energies for diffusion and the addition of Cl increases the same activation energies. Differences in activation energies between volatile-free and fluorinated melts are proposed to be due to depolymerization through formation of Al that is octahedrally coordinated by F; highly coordinated Al previously has been observed spectroscopically in F-bearing aluminosilicate glasses (Kohn et al., 1991; Schaller et al., 1992). Increasing activation energies with the addition of Cl are proposed to be caused by increasing polymerization of the melt through conversion of an Al-bearing Q^3 species into a Q^4 species as the result of alkali complexing with Cl.

A relation exists between either activation energies or preexponential factors and the ratio of the volatile anion or radical (F, $OH^- = X$) to the sum of the anions (F or OH^- + the O in the volatile-free melt = X + O) in the system

$$E_a = -1636[X/(X + O)] + 214.44$$

$$D_o = 1.152 \times 10^{-6} \exp\{-50.1934[X/(X + O)]\}.$$

These equations reproduce measured activation energies for Si diffusion to within 10% (relative), and preexponential factors within a factor of 10. Using these relations, diffusion in halogen-bearing intermediate to silicic melts can be calculated to within an order of magnitude, and the significance of diffusion-controlled processes in the petrogenesis of hydrous or fluorinated magmas evaluated.

Introduction

The presence of the halogens, F and Cl, in natural silicic magmas has been the subject of much study in the past 20 years. F is typically abundant in many peraluminous pegmatitic granites (Christiansen and Lee, 1986) and in some subvolcanic and eruptive magmas of similar composition (e.g., Kovalenko et al., 1971; Pichavant et al., 1987; Gavigan et al., 1989; Congdon and Nash, 1991). The Honeycomb Hills of Utah (Gavigan et al., 1989; Congdon and Nash, 1991) perhaps have the highest concentrations of F in any fresh samples: vitrophyres contain up to 2.3 wt% F, and melt inclusions in quartz pheno-

crysts from the same area reach concentrations of 3.5 wt%. Cl contents in natural extrusive rocks can attain levels approaching 1 wt%, as exemplified by pantelleritic glasses from the island of Pantelleria (Zies, 1960; Civetta et al., 1984).

These moderately high concentrations of halogens have stimulated the study of the effects of halogens, particularly F, on the phase equilibria (Koster van Groos and Wyllie, 1968, 1969; Manning, 1981; Webster et al., 1987) and viscosity (Hirayama and Camp, 1969; Dingwell et al., 1985; Dingwell, 1987) of silicate melts. These studies have demonstrated significant effects of halogens on both equilibrium and kinetic properties. To date, there have been no comprehensive studies on the effects of halogens on diffusional behavior in silicic melts, although Dingwell and Scarfe (1984, 1985) studied the diffusion of F in simple $Na_2O-Al_2O_3-SiO_2$ melts. The purpose of this study is to measure the effective binary diffusion coefficient of Si during interdiffusion of intermediate and silicic melts containing F and Cl concentrations similar to those in nature. These new data are then compared with previously measured diffusivities on similar, or identical, composition melts under anhydrous and hydrous conditions.

EXPERIMENTAL TECHNIQUES

Starting compositions

The compositions of the diffusion couples used for the measurement of the effect of F on Si interdiffusion were base glasses of AT150 and LCO compositions (Baker, 1990) to which reagent-grade NaF was added, creating glasses AT150F and LCOF (Table 1). After each base glass and NaF were ground together, the new compositions were remelted multiple times. LCOF was melted three times at 1400 °C, with grinding between each fusion, and then twice at 1575 °C; AT150F was fused once at 1375 °C and once at 1500 °C. This technique results in a mean F content of 1.3 wt% and 2.6 wt% more Na_2O in the fluoridated glasses than in the original compositions. The F content is less than initially added because of the volatilization during the fusions necessary for homogenization. The F content of these glasses is similar to that of the Spor Mountain rhyolite of Webster et al. (1987), 1.2 wt%, and the macusanite glass of London et al. (1989), 1.3 wt%, but is slightly above the maximum Congdon and Nash (1991) observed in the felsites, 0.85 wt%, and is approximately one half of that in vitrophyres, 2.3 wt%, from the Honeycomb Hills, Utah (Congdon and Nash, 1991).

Compositions used for diffusion couples to investigate the effect of Cl on Si interdiffusion are glasses P7 and P231 of pantelleritic and trachytic composition (Table 1) from the island of Pantelleria (donated by G.A. Mahood). The pantellerite, P7, contains 0.89 wt% Cl, near the maximum content of any extrusive igneous rock, whereas P231 contains 0.02 wt% Cl. Thus, experiments with these compositions mimic the natural case for diffusion between two such melts.

TABLE 1. Electron microprobe analyses of starting glasses

	AT150F	LCOF	P231	P7
SiO_2	61.47	73.61	64.03	68.73
TiO_2	0.53	0.11	0.71	0.53
Al_2O_3	17.02	12.65	15.92	8.61
FeO*	4.64	0.67	6.53	9.52
MnO	0.00	0.08	0.29	0.31
MgO	1.64	0.06	0.45	0.11
CaO	5.05	0.52	1.36	0.43
Na_2O	7.31	6.87	5.94	6.19
K_2O	1.71	4.54	4.50	4.34
P_2O_5	0.00	0.00	0.13	0.00
F	1.23	1.45	0.00	0.00
Cl	0.00	0.00	0.02	0.89
TOTAL	100.60	100.56	99.88	99.66
$-O$ = halogen	0.52	0.61	0.02	0.83
TOTAL	100.08	99.95	99.86	98.83

* All Fe as FeO.

Interdiffusion between F- and Cl-free, peraluminous base glasses (AT150A and LCOA), metaluminous base glasses (AT150 and LCO), and peralkaline base glasses (P231D and P7D), have been measured (Baker, 1990) at 1.0 GPa and serve as references for this study.

Experimental procedures

Experimental procedures followed those used previously (Baker, 1990) for the study of diffusion in the volatile-free systems. For each experiment, equal amounts of glass powders were packed into cylindrical cavities in graphite plugs. The denser, less silicic glass was always placed in the lower portion of the cavity for gravitational stability. Powders were tamped into the cavities with a rod machined to fit snugly inside the cavity with an end polished to a 1-μm finish. After cavities were filled, graphite lids were placed on top, graphite plugs inserted into pyrophyllite cups, and experiments performed using a 1.91-cm NaCl-pyrex assembly (Jurewicz and Watson, 1984) at 1.0 GPa in a piston-cylinder apparatus. Pressure and temperature of the experiments were controlled to within 50 MPa and 3 °C of the desired conditions. Experiments were quenched by turning off the power, which resulted in quench rates of 2000 °C/min to below-solidus temperatures.

Analytical techniques

After each experiment, samples were mounted in epoxy, ground longitudinally to expose the diffusion couples, and polished for electron microprobe analysis. Analyses were made parallel to the diffusion path using a 15-KeV accelerating voltage and either 8- or 4-nA beam currents; standards were natural and synthetic minerals and glasses. Diffusivities were calculated from the diffusion profiles (e.g., Fig. 1) using Boltzmann-Matano analysis (Crank, 1975), after fitting diffusion profiles with two second- or third-order polynomial functions that intersected near, but not at, the center of the diffusion profile and the Matano interface. Using Boltzmann-Matano analysis, the effect of silica content on the effective binary diffusion coefficient (EBDC) of Si was measured. Based
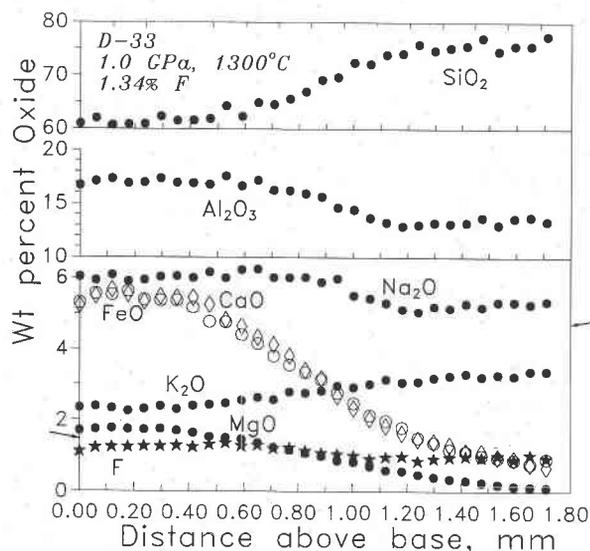
Fig. 1. Interdiffusion profiles for a typical F-bearing experiment. Note that the lengths of all nonalkali profiles are the same as the length of the SiO_2 profile. Diamonds are CaO and open circles are FeO analyses. Arrows point to original K_2O concentrations at ends of diffusion profiles that have been modified by rapid diffusion of K.

upon replicate experiments and measurements of different, parallel microprobe traverses in the same experiment, errors in measured diffusivities using this technique are estimated at no more than a factor of 3 (Table 2) and usually less than a factor of 2 (cf. Baker, 1989, 1990, 1991), except near the ends of the profiles where errors increase to higher levels (Crank, 1975). The standard deviation about the mean of the two diffusivity measurements for 1200 °C, 70 wt% SiO_2 (Table 2) is 7.5% (relative), and the standard deviation about the mean of the two diffusivities measured for 1400 °C, 70 wt% SiO_2 is 70% (relative). The average standard deviation is therefore calculated as 38% (relative) of the measured value. This average standard deviation can then be used to cal-

culate the expected standard deviation of the single diffusion measurements at other temperatures (p. 2–10, Natrella, 1963). This expected standard deviation for other experiments is 75% (relative).

These two sets of experiments at 1200 °C, 26 and 60 h, and 1400 °C, 2.02 and 7.5 h, also demonstrate that measured diffusivities at the centers of the profile are independent of time, to within the maximum estimated error of a factor of 3 (Fig. 2). This independence with respect to time substantiates the premise that diffusion is the only transport mechanism occurring in these experiments.

Following Harrison and Watson (1983), Arrhenius lines were calculated from diffusivities using equations of York (1969). The 1σ standard errors, calculated using average errors of 1% (relative) in temperature and 40% (relative) in diffusivity, are given for activation energies and preexponential factors. Because previous diffusivity measurements were fitted using a different procedure (Baker 1990, 1991), Arrhenius lines for all earlier experiments were recalculated by the York (1969) technique, using the same errors, for more accurate comparison with the results of this study.

RESULTS

As previously observed for anhydrous (Watson, 1982; Koyaguchi, 1989; Baker, 1990) and hydrous (Baker, 1991) interdiffusion experiments, profiles in both the fluoridated and chlorinated experiments for all nonalkalis (Al_2O_3, TiO_2, FeO, MgO, and CaO) are the same length as the SiO_2 profile (Fig. 1). Alkalis, however, diffuse much more rapidly. In fact, K diffusion is so rapid that the AT150F end of the diffusion couple (Fig. 1) increased in K_2O from 1.71 wt% to approximately 2.3 wt% and the LCOF end was correspondingly depleted from 4.54 wt% to approximately 3.5 wt%. This coupled behavior between the diffusion profiles of other elements and the SiO_2 profile, denoted "transient partitioning" by Watson (1982), is the result of local equilibrium along the diffusion profiles. The major control on this local equilibrium is the re-

TABLE 2. Experimental conditions and measured diffusivities

|			AT150F-LCOF		
Expt.	T (°C)	Duration (s)	D^*_{64}	D^*_{70}	D^*_{72}
D-37	1200	214 380	2.47×10^{-13}	6.79×10^{-14}	5.32×10^{-14}
D-45	1200	92 040	9.37×10^{-14}	6.11×10^{-14}	4.49×10^{-14}
D-33	1300	79 200	6.54×10^{-13}	3.53×10^{-13}	3.19×10^{-13}
D-35	1400	27 180	3.94×10^{-13}	2.71×10^{-13}	2.52×10^{-13}
D-59	1400	7260	1.14×10^{-12}	8.03×10^{-13}	5.83×10^{-13}
D-40	1500	14 400	2.60×10^{-12}	1.73×10^{-12}	2.11×10^{-12}
D-57	1600	7260	2.52×10^{-12}	1.56×10^{-12}	1.66×10^{-12}
			P231-P7		
Expt.	T (°C)	Duration (s)	D^*_{64}	D^*_{66}	D^*_{68}
D-27	1200	48 888	7.74×10^{-14}	8.31×10^{-14}	9.77×10^{-14}
D-25	1300	69 900	1.94×10^{-13}	2.38×10^{-13}	2.40×10^{-13}
D-31	1400	18 000	6.40×10^{-13}	6.50×10^{-13}	1.72×10^{-12}
D-61	1600	7200	2.39×10^{-12}	4.99×10^{-12}	4.37×10^{-12}

* D_n = diffusivities at n wt% silica in m²/s.
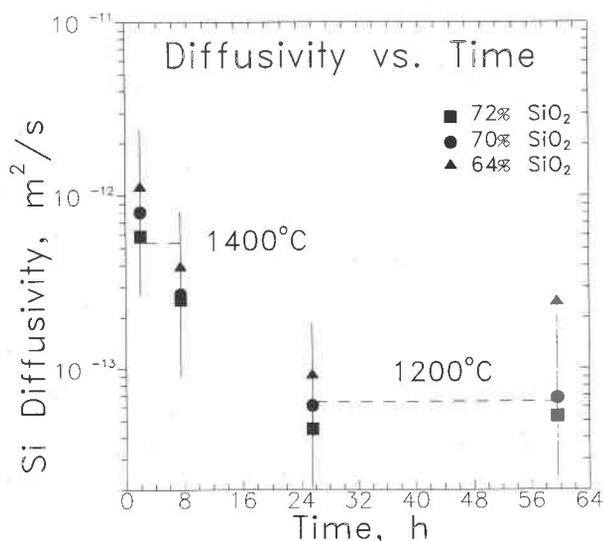
Fig. 2. Diffusivities at 64, 70, and 72 wt% SiO₂ measured in two sets of interdiffusion experiments between AT150F and LCOF. These data demonstrate the independence of diffusivity from experimental duration. Maximum error bars (see text) are shown for 70 wt% SiO₂ diffusivities only. Dashed lines are at the mean diffusivities for each temperature at 70 wt% SiO₂.
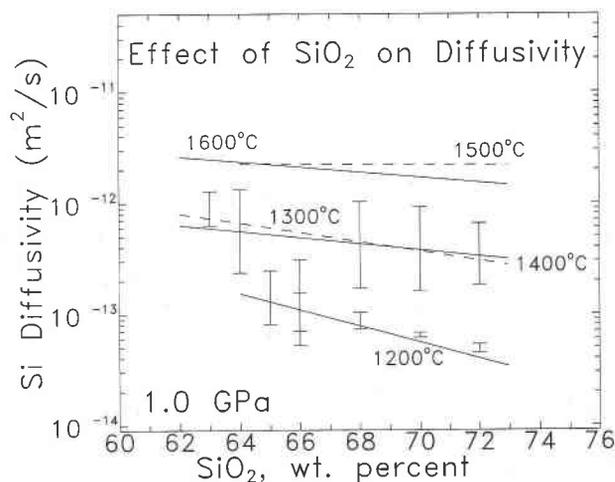

Fig. 3. The minor effect of SiO₂ content on Si EBDC for AT150F-LCOF experiments. The 1σ error bars for diffusivities at 1200 and 1400 °C are shown. Errors at other temperatures are expected to be similar.

quirement of local charge balance, which is controlled dominantly by the ratio of the two interdiffusing network formers, Si and Al (Watson, 1982; Baker, 1990, 1991; Watson and Baker, 1991). The much greater diffusivity of alkalis is most probably the result of the relative ease of charge balancing +1 cations, as opposed to cations with higher valence states (Baker, 1991).

At any given temperature the effect of silica concentration on the measured Si EBDC in the fluorinated melts is very small (Table 2, Fig. 3), almost always within error of the measurements. Most experiments may demonstrate small decreases in diffusivity with increasing silica concentration. There is some suggestion in the measurements that with decreasing temperature the effect of SiO₂ content on Si diffusivities increases, but even at 1200 °C the effect is still small and within error (Fig. 3). Experimental scatter results in the similar 1300 and 1400 °C, and 1500 and 1600 °C diffusivities. For the chlorinated system, no discernible effect of silica concentration on diffusivities was found, except for possibly in the experiment at 1400 °C (Table 2, Fig. 4).

Measured EBDC for Si in AT150F-LCOF at 65, 70, and 74 wt% SiO₂ and in P231-P7 at 64 and 66 wt% SiO₂ are plotted on Arrhenius diagrams (Fig. 4), together with previously measured diffusivities in the halogen-free systems (Baker, 1990, 1991). These measurements demonstrate that halogens, at the concentration levels studied, have little effect on the EBDC of Si when compared with the halogen-free systems. The activation energy for diffusion at 70 wt% SiO₂ decreases from 237.1 ± 5.6 kJ/mol in the volatile-free metaluminous system, AT150-LCO (Baker, 1990), to 192.8 ± 7.1 kJ/mol (Table 3, Fig.

5) with 1.3 wt% F (Table 2). This reduction in activation energy is much less than the effect of 3 wt% H_2O in the metaluminous system, which reduces the activation energy to 126.0 ± 7.3 kJ/mol (Baker, 1991).

Comparison of activation energies of the metaluminous halogen-free AT150-LCO and the peralkaline halogen-bearing AT150F-LCOF systems is complicated because Baker (1990) demonstrated that alkalinity of volatile-free melts has a small effect on the EBDC of Si. Measured activation energies for the EBDC of Si in peralkaline chlorine-free P231D-P7D diffusion couples (Baker, 1990) are 204.2 ± 12.4 kJ/mol at 64 wt% silica and 176.6 ± 12.6 kJ/mol at 68 wt% silica (calculated from experiments in Baker, 1990; at 1300 °C, $D = 2.80 \times 10^{-13}$; at 1400 °C, $D = 2.30 \times 10^{-12}$; and at 1600 °C, $D = 3.20 \times 10^{-12}$ m²/s). The activation energy at 70 wt% SiO₂ is not significantly different from that measured in the fluoridated AT150F-LCOF system (Fig. 5). With the addition of F the activation energy for interdiffusion at 65 wt% SiO₂ decreases from the measured value in volatile-free P231D-P7D (Fig. 5).

In the chlorine-bearing P231-P7 diffusion couples, the activation energy for diffusion at 66 wt% SiO₂, 236.9 ± 8.7 kJ/mol (Table 3, Fig. 5), is greater than the activation energy for Si diffusion at 65 wt% SiO₂ in volatile-free melts, 204.2 ± 12.4 kJ/mol (Baker, 1990). However, activation energies calculated from diffusivities measured at the low-silica ends of diffusion profiles in this study at 64 wt% SiO₂, 200.0 ± 8.8 kJ/mol, are within error of measurements in the dry system (Fig. 5). At 68% SiO₂, activation energies in the volatile-free melts are below those of Cl-bearing melts: 176.6 ± 12.6 kJ/mol volatile free and 227.4 ± 8.7 kJ/mol with the addition of Cl (Table 3).

It is important to stress that the effects of halogens on diffusion are small at the concentration levels studied.
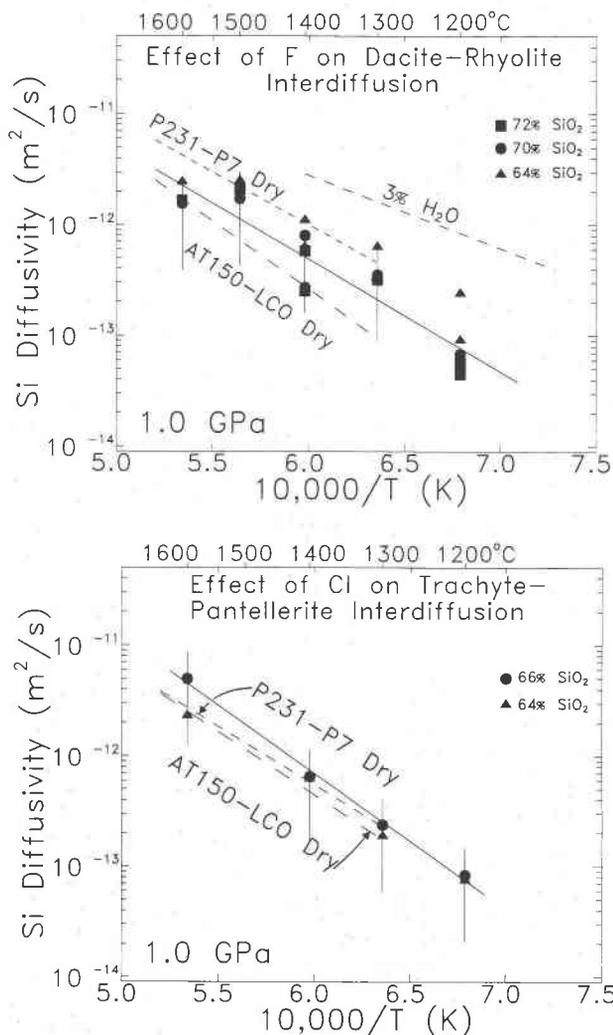
Fig. 4. Arrhenius diagrams for Si EBDC measured in the AT150F-LCOF system and in the P231-P7 system. Calculated 1σ errors at 70 wt% SiO_2 are shown for 1200 °C (hidden by data points) and 1400 °C diffusivities; error bars for other temperatures are estimated 1σ errors (see text). The solid line is the Arrhenius fit to the diffusivities measured at 70% SiO_2, and dashed lines are Arrhenius fits for diffusion in the dry metaluminous, AT150-LCO, volatile-free peralkaline, P231D-P7D (Baker, 1990), and hydrous metaluminous, AT150-LCO (Baker, 1991) diffusion couples at 68–70 wt% SiO_2. All error bars for the effect of Cl are estimated from 1σ errors calculated for diffusion measurements on AT150F-LCOF at 1200 and 1400 °C. The solid line is fit to diffusivities measured at 66 wt% SiO_2 for P231-P7, and the two dashed lines show Arrhenius fits to Si diffusivities measured in volatile-free P231D-P7D and volatile-free AT150-LCO at 65 wt% SiO_2 (Baker, 1990).

Compared with volatile-free melts, activation energies for halogen-bearing melts are only affected approximately 10% (relative) (Fig. 5). However, near 65 wt% SiO_2 the addition of F appears to decrease activation energies, whereas the addition of Cl may increase activation energies for diffusion (Fig. 5). At 70 wt% SiO_2, the addition

TABLE 3. Activation energies and preexponential factors

	$D = D_o\exp(-E_a/RT)$	
	D_o	E_a
AT150F-LCOF		
64% SiO_2	1.29×10^{-7} $\begin{matrix}+8.52 \times 10^{-8}\\-5.13 \times 10^{-8}\end{matrix}$	165.6 ± 6.9
70% SiO_2	5.41×10^{-7} $\begin{matrix}+3.67 \times 10^{-7}\\-2.19 \times 10^{-7}\end{matrix}$	192.8 ± 7.1
72% SiO_2	2.45×10^{-6} $\begin{matrix}+1.67 \times 10^{-6}\\-9.91 \times 10^{-7}\end{matrix}$	214.7 ± 7.1
P231-P7		
64% SiO_2	9.56×10^{-7} $\begin{matrix}+8.69 \times 10^{-7}\\-4.55 \times 10^{-7}\end{matrix}$	200.0 ± 8.8
66% SiO_2	1.86×10^{-5} $\begin{matrix}+1.65 \times 10^{-5}\\-8.73 \times 10^{-6}\end{matrix}$	236.9 ± 8.7
68% SiO_2	1.20×10^{-5} $\begin{matrix}+1.06 \times 10^{-5}\\-5.63 \times 10^{-6}\end{matrix}$	227.4 ± 8.7

Note: D and D_o in m²/s, E_a in kJ/mol, R = 8.314 J/mol K, T in K.

of Cl increases activation energies, and F may have a similar effect (Fig. 5). The possibility that the addition of F increases activation energies for diffusion is unlikely because viscosity studies on similar multicomponent melts (Dingwell et al., 1985) demonstrate that the addition of F decreases activation energies for viscous transport and therefore should have the same effect on activation energies for diffusion (Watson and Baker, 1991).

DISCUSSION

Activation energies for Si diffusion in volatile-free (Baker, 1990), hydrous (Baker, 1991), and halogenated melts (this study) have been plotted (Fig. 6) as a function of the molar ratio of volatiles to the sum of volatiles + O in the anhydrous melt, following Mysen and Virgo (1986). The concentration of OH^- in the melt has been estimated from measurements of OH^- and H_2O in quenched rhyolitic melts by Silver et al. (1990). The straight line on this diagram is fitted to only the volatile-free and H_2O-bearing data at 1.0 GPa (Baker, 1990, 1991). However, activation energies for the fluoridated system plot near this line.

The apparent linear relation between the activation energy for diffusion and the ratio of F or OH^- to the sum of all anionic species suggests that a common mechanism decreases activation energies for diffusion in fluorinated and hydrated melts. This mechanism is probably a change in melt structure, particularly a change in the bonding between network-forming, tetrahedrally coordinated cations, Si or Al, and O due to the addition of F or OH^- (as previously discussed for OH by many authors, e.g., Stolper, 1982; Harrison and Watson, 1983; Baker, 1991). Such a change in melt structure should be detectable by spectroscopic techniques.
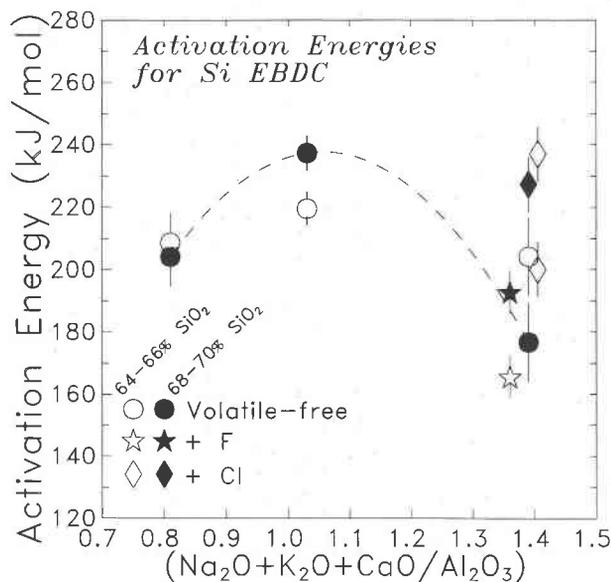
Fig. 5. Activation energy for Si EBDC vs. alkalinity (molar) of the melt. For each type of melt, measurements were made in the range of 64–66 wt% and 68–70 wt% SiO₂. For Cl-bearing melts, both activation energies, measured at 64 and 66 wt% SiO₂, are plotted. Activation energies for halogen-free melts have been recalculated from data of Baker (1990) using equations of York (1969). Error bars represent 1 standard error. The dashed line connects activation energies for interdiffusion in volatile-free melts at 68–70 wt% SiO₂ and demonstrates that activation energies reach a maximum near $(Na_2O + K_2O + CaO/Al_2O_3) = 1$ (cf. Baker, 1990).
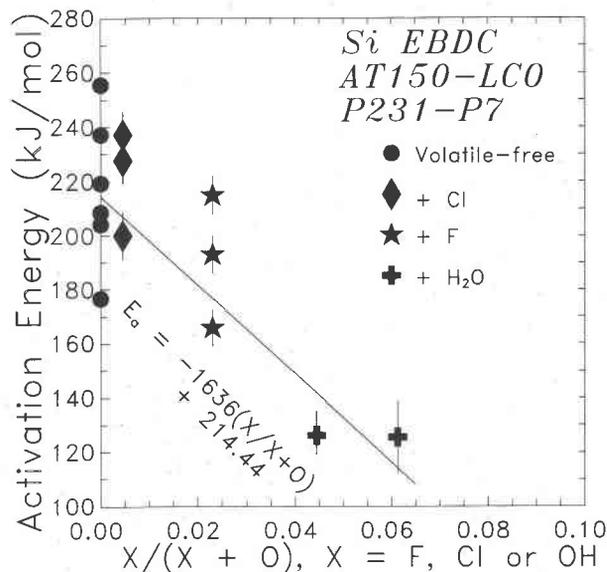
Fig. 6. Activation energy for Si EBDC vs. the individual ratios of F, Cl, and OH⁻ to total anions in the melt for silica contents between approximately 65 and 75 wt% SiO₂. The line is fit only to activation energy measurements from volatile-free and hydrous experiments. F and Cl concentrations are the mean values for diffusion couples investigated. Concentrations of OH⁻ were estimated from H_2O_{tot} content in experiments by Baker (1991) and measured concentrations of OH⁻ in melts of similar anhydrous composition and H_2O_{tot} content (Silver et al., 1990). Error bars represent 1 standard error. Although errors bars for volatile-free melts are not plotted, they are typically the same as for F-bearing samples and always less than the error bars on the sample at the highest H_2O content.

Recent nuclear magnetic resonance spectroscopy (NMR) studies on quenched glasses (presumed to be structurally equivalent to melts) of aluminosilicate composition (Kohn et al., 1991; Schaller et al., 1992) indicate that the addition of F results in the transformation of a small amount of Al, 2–6.5% (relative) from a tetrahedrally coordinated, network-forming role into a fivefold- or sixfold-coordinated network-modifying role complexed with F, depolymerizing the melt (Kohn et al., 1991; note that Schaller et al., 1992, question the validity of the quantitative calculations of Kohn et al.). Importantly, neither study found evidence of Si-F complexes in these aluminosilicate glasses, which corroborates previous Raman spectroscopic results (Mysen and Virgo, 1985). Conversion of Al from its network-forming role to a network-modifying role is most probably responsible for the decrease in activation energy for diffusion observed for F-bearing melts. This conversion can also explain decreases in viscosity of F-bearing multicomponent melts compared with F-free equivalents (Dingwell et al., 1985; Dingwell and Webb, 1992; Schaller et al., 1992).

Because of the similar effects of OH and F on activation energies for diffusion (Fig. 6), one would expect to see evidence of the same transition of Al from a fourfold-coordinated network former to a fivefold- or sixfold-coordinated network modifier in H_2O-bearing melts. Raman spectroscopic data (Mysen and Virgo, 1986) have

been used to support the presence of an Al-OH network-modifying species in hydrous aluminosilicate melts, although in that study the Al did not appear to be in a higher than normal coordination state. Recent NMR studies of the effect of H_2O on the structure of albite glass (Kohn et al., 1989) are inconsistent with the Raman studies of Mysen and Virgo (1986), however, because they provide evidence of NaOH, not AlOH, complexes.

The effects of F and OH⁻ on diffusion observed in this study support similar interaction mechanisms between these species and the silicate melt. The lack of observed complexing between OH⁻ and Al by Kohn et al. (1989) is inconsistent with this hypothesis. If the amount of Al-OH⁻ complexing necessary to affect activation energies for diffusion is smaller than the amount detectable by NMR spectroscopy, then the inconsistency may be eliminated. However, this speculation must await further study on the effects of H_2O on Al coordination in silicate melts before it can be proven.

The activation energies for diffusion in the chlorinated melts also plot near the line in Figure 6. However, the results plotted in Figure 5 indicate that activation energy for diffusion increases with the addition of Cl. Therefore, the correlation may be coincidental. Although relatively little research on the role of Cl in silicate melts has been
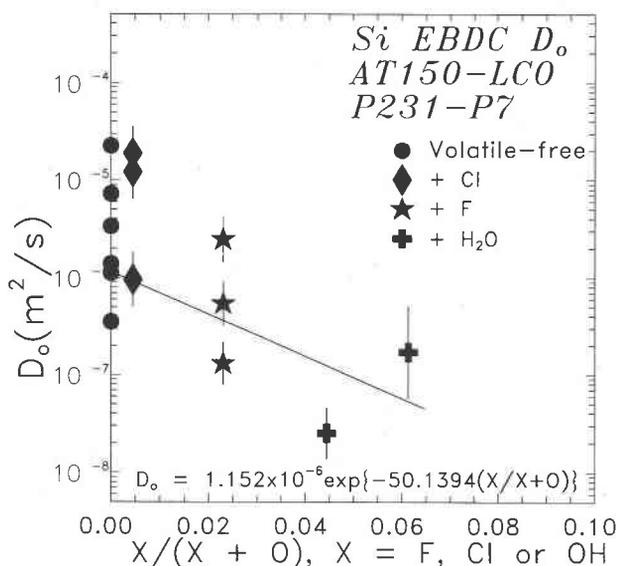
Fig. 7. Preexponential values for Si EBDC vs. individual ratios of F, Cl, and OH$^-$ to total anions in the melt for silica contents between approximately 65 and 75 wt% SiO$_2$. As in Fig. 6, the line is fit only to preexponential values measured in volatile-free and hydrous experiments.

performed, it has been known since the 1960s that Cl and F have different, sometimes opposing, effects in silicate melts, just as observed in this study. Wyllie and Tuttle (1961, 1964) demonstrated differences in the effects of F and Cl by comparing the melting temperatures of albite and granite in the presence of H$_2$O, H$_2$O + 5% HCl, and H$_2$O + 5% HF. Although both halogens lowered the melting point of albite, the change in temperature with respect to the H$_2$O-saturated melting temperature was approximately 200 °C for HF, compared with 100 °C for HCl. More interestingly, for the granite composition the addition of HCl increased the melting temperature by 18 °C, whereas HF decreased it by 62 °C. Viscosity studies by Hirayama and Camp (1969) on anhydrous silicate melts demonstrated decreasing viscosity with the addition of F and increasing viscosity with the addition of Cl, consistent with the higher measured activation energies for chlorinated melts in this study. Recent studies of Cl solubility and partitioning between hydrous granitic melts and fluids (Metrich and Rutherford, 1992; Webster, 1992) suggest that Cl complexes with network-modifying alkalis, Na and K, in peralkaline melts rather than network-forming Al as observed for F (Kohn et al., 1991; Schaller et al., 1992).

The increases in viscosity and activation energies for diffusion in chlorinated melts can be interpreted as an increase in the polymerization of the melt due to the addition of Cl, in contrast to F, which depolymerizes the melt. If alkalis are complexing with Cl, then a possible polymerizing reaction might be between Al in a Q^3 species (three bridging O atoms, one nonbridging O atom)

with two associated alkali cations (for charge balance) and Cl to form an alkali chloride complex and a Q^4 species (four bridging O atoms) with one alkali, e.g.,

$$Na_2Q^3_{Al} + Cl = NaCl + NaQ^4_{Al}.$$
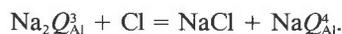
Such a reaction could account for increasing diffusion activation energies and viscosities with the addition of Cl (this study; Hirayama and Camp, 1969) and possibly even the increase in melting temperatures of granite found by Wyllie and Tuttle (1961, 1964). However, such a reaction must remain speculative until Cl-bearing aluminosilicate glasses are investigated spectroscopically.

CALCULATION OF DIFFUSIVITIES IN HALOGEN-BEARING SILICIC MELTS

The activation energies for diffusion in fluoridated and chlorinated melts can be directly applied to natural melts for the prediction of diffusion-controlled phenomena such as diffusive contamination and diffusion-controlled crystal growth, but only if the melt compositions are close to those used in this study. However, the relationship between the activation energy for Si EBDC and the ratio of F and OH$^-$ to the sum of all anions in the melt (Fig. 6) is a simple linear one, within the resolution of experimental data. Furthermore, the preexponential factor, D_o, in the Arrhenius relation also appears to be a simple function of the ratio of volatile anions to the sum of all anions (Fig. 7), although the scatter is greater than that observed for the activation energy.

Because the activation energies for diffusion in all volatile-free intermediate to silicic systems studied (Baker, 1990, 1991) are relatively independent of silica concentration between approximately 65 and 75 wt% SiO$_2$ (Fig. 5), the diagrams in Figures 6 and 7 can be used to calculate E_a and D_o for melts containing either F or H$_2$O with approximately 65 to 75 wt% silica. Additionally, the small effects of volatile-free composition on diffusion suggest that these diffusion measurements in peralkaline melts can be applied to metaluminous and peraluminous melts with silica concentrations between 65 and 75 wt% (Figs. 5–7). Using these correlations, the expected error for the activation energy is approximately 10%, and for D_o it is a factor of 10. These errors are similar to the actual errors of the measurements. Furthermore, these simple relationships suggest that for melts containing two or more volatiles (the most frequent case in nature) the effects of the individual volatiles are additive. This assumption is currently being tested for melts containing F and H$_2$O (Baker and Bossànyi, in preparation).

The error in the calculation of diffusivities in volatile-bearing intermediate to silicic melts is estimated to be approximately a factor of 10 or less; much of this error is due to the preexponential factor. Although this error may seem large, it should be remembered that the scale over which diffusion occurs can be estimated by the simple relationship: $x = (Dt)^{1/2}$, where x is the distance, D the diffusivity, and t the time. Because the dependence of x

is on the square root of D, an error of 10 in D only results in an error of 3.3 in x. Thus, with this technique for the estimation of diffusivities in melts, the importance of diffusion-controlled processes in the petrogenesis of intermediate to silicic magmas can be constrained, provided the duration of diffusion can be estimated.

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