The effect of F on the density of haplogranite melt

D. B. DINGWELL, R. KNOCHE, S. L. WEBB

Bayerisches Geoinstitut, Universität Bayreuth, Postfach 10 12 51, W8580 Bayreuth, Germany

ABSTRACT

The densities and thermal expansivities of F-bearing haplogranitic glasses and liquids have been investigated using a combination of scanning calorimetry and dilatometry. F_2O_{-1} reduces the density of haplogranitic liquids (at 750 °C) from 2.295 ± 0.006 g/cm^3 to 2.261 ± 0.005 g/cm^3 with the addition of 4.55 wt% F (0.33% per wt% of F added). The expansivities of the liquids increase with the addition of F_2O_{-1} from $29.9 \pm 3.0 \times 10^{-6}$/°C to $53.1 \pm 1.4 \times 10^{-6}$/°C (at 750 °C).

Densities have been converted into molar volumes based on the haplogranite and F_2O_{-1} components. The partial molar volume of F_2O_{-1} has been calculated at 750 °C to be 14.2 ± 1.3 cm^3/mol in these melts. This value is close to the molar volume per O for several components of silicate melts. F and O have similar ionic and covalent radii, and thus the substitution of two F for one O yields approximately the volume change expected, assuming no secondary consequences for the average coordination number of cations. This is despite evidence from quenched melts that [6]Al exists in these compositions.

F is significantly more effective (per wt% added) than B_2O_3 in reducing the density of haplogranitic melt. The effect of F on density reported here should complement the viscosity-reducing effect of F_2O_{-1} on granitic melts in significantly accelerating gravity-driven processes of crystal-melt fractionation in F-rich igneous systems.

INTRODUCTION

Volcanic systems containing F-rich eruptive rocks, such as the topaz-bearing rhyolites reported from Spor Mountain (Burt et al., 1982) and Honeycomb Hills, Utah (Congdon and Nash, 1991), and the macusanites from southeast Peru (Pichavant et al., 1987), demonstrate unequivocally that high F contents (up to a few weight percent) of certain hypabyssal rocks (Kovalenko, 1973; Kortemeier and Burt, 1988) and intrusive rocks (Bailey, 1977) can derive directly from the crystallization of F-rich silicate melts. At these levels of concentration F probably represents the most concentrated anionic substitution in igneous melts. Also evident from the geochemistry of these rocks is that high to extreme degrees of fractionation may be responsible for the high levels of incompatible elements concentrated in these igneous systems (Christiansen et al., 1983; Pichavant et al., 1987; Congdon and Nash, 1991). Several effects, both chemical and physical, of the solution of F in high-silica rhyolitic melts may influence these differentiation trends and facilitate the extreme enrichment of elements. Likely chemical effects are the enhancement of component solubilities by the formation of complexes (Be?) or indirect enhancement of solution sites for high field-strength cations (e.g., Zr, Ti; Keppler, 1991) and the large temperature reduction of melting relations with increasing fractionation (Manning, 1981; London et al., 1988, 1989). Physical effects include certainly the fluxing effect of F on the viscosity of silicate melts (Dingwell et al., 1985; Dingwell and Webb, 1992),

which must enhance the crystal-liquid fractionation rate and degree and probably is responsible for the eruption of pegmatitic magmas (Pichavant et al., 1987; Congdon and Nash, 1991). The effects of F on other physical properties of melts, such as density and surface tension, however, remain uninvestigated. In this study we are concerned with density.

At present, the estimation of granitic melt density is restricted to extrapolation from more basic compositions and from temperatures well above 1000 °C. Several of the components so important in granite and pegmatite genesis are not included in present models.

Large substitutions of F into silicate melts are required to optimize the quality of density and derived partial molar volume data for components, whether they be minor or major in abundance in natural liquids. For volatile elements, such high degrees of substitution are difficult to attain and almost impossible to stabilize under the 1-atm and high-temperature experimental conditions that allow well-tested, highly precise density determinations. Preliminary attempts in our lab to directly measure the densities of F-rich melts at the high temperatures and low viscosities required for the double-bob Archimedean technique were unsuccessful because of F volatilization. New insights into the nature of metastable liquid properties at temperatures just above the glass transition (Dingwell and Webb, 1989, 1990) have, however, opened up some possibilities for density determinations in silicate melts at much lower temperatures (Webb et al., 1992), under which volatility is not a problem during property

TABLE 1. Glass compositions (wt%)

Compo-sition	Na_2O	K_2O	Al_2O_3	SiO_2	F	Total
HPG8	4.53	4.17	11.89	77.90	—	98.49
	(0.06)	(0.05)	(0.08)	(0.21)		
HPG8F5	4.57	4.02	11.73	77.05	2.86	100.23
	(0.05)	(0.08)	(0.07)	(0.29)		
HPG8F10	4.50	4.08	11.08	76.96	4.55	101.17
	(0.05)	(0.06)	(0.06)	(0.19)		

Note: Na, K, Si, and Al analyses are averages of 20 by electron microprobe. F is by specific ion electrode (CNRS-CRPG, Nancy). Cameca Camebax in wavelength-dispersive mode using defocused beam (10 μm) and 20-s count times (15 kV, 15 nA on brass). Standards were albite (Na, Al, Si) and orthoclase (K). Totals are corrected for $2F - O$.

measurement. Such measurements have the powerful advantage of access to a wide range of volatile components under stable conditions.

Specifically, we have developed a method for the direct determination of densities and expansivities in highly viscous, low-temperature silicate liquids (Webb et al., 1992). We are using this method both to investigate the fundamentals of silicate expansivity-temperature relationships and to derive a haplogranite-based density model for granite and pegmatite petrogenesis. The method, described below, uses calorimetric and dilatometric data for heat capacity and expansivity. We have now applied this method, in combination with high-temperature liquid-density data, to a large number of silicate melts (Knoche et al., 1992a, 1992b), with the general result that temperature-dependent expansivities of silicate liquids are evident. The method has also been used to stabilize the contents of volatile elements during density determination by using low temperatures, for example for B_2O_3-bearing haplogranitic melts (Knoche et al., 1992c). Here we apply the method to F-rich melts whose densities at high temperature are difficult to obtain because of F volatility.

METHODS

Starting materials for the preparation of F-bearing samples were Na_2CO_3, K_2CO_3, Al_2O_3, SiO_2, and AlF_3. The powders of the starting reagents were dried at 120 °C overnight prior to weighing. The AlF_3 was weighed immediately after opening the airtight seal on the original packing. Decarbonated, dehydrated powders were weighed into plastic bottles in 100-g batches and mixed by agitation for 5–10 minutes. The starting compositions were chosen to represent 5 and 10 wt% additions of F to haplogranite HPG8 composition, near the 1-kbar pH_2O ternary minimum composition in the system SiO_2-NaAlSi_3O_8-KAlSi_3O_8-H_2O. The HPG8 composition is taken from Holtz et al. (1992). The F-bearing haplogranitic compositions were fused directly for 2 h at 1600 °C in 75-cm³ thin-walled Pt crucibles in a $MoSi_2$ box furnace. The products of these fusions were partially unreacted and bubble-rich. To eliminate the bubbles and to promote full reaction and homogenization of the samples,

the crucibles were transferred to a second $MoSi_2$ box furnace equipped with a concentric cylinder viscometer. The samples were heated to 1600 °C and stirred for ~24 h using a $Pt_{80}Rh_{20}$ spindle. The melt was inspected periodically by removing the spindle and checking the adhered glass. The crystal- and bubble-free products of this process were cooled slowly in the viscometry furnace to less than 400 °C and then removed to cool to room temperature. Cylinders (6.5 mm in diameter) of the glasses were cored from the thin-walled crucibles. A number of cylinders were prepared with parallel polished ends. The polished cylinders were stored in a desiccator until use in the dilatometry and calorimetry experiments.

Samples of the glasses were analyzed by electron microprobe (Na, K, Si, Al) and specific ion electrode (F) methods. The results of the analyses are presented in Table 1. The samples lost significant quantities of the added F_2O_{-1} during the fusions, but the base compositions remained within error of the binary [(HPG8) $-$ (F_2O_{-1})] haplogranite system, and the analyzed F_2O_{-1} contents are the basis for discussion of the results.

A combination of dilatometry and calorimetry measurements is used to determine the thermal expansivity and volume of the supercooled liquids at temperatures just above the glass transition. The dilatometric and calorimetric measurements were performed on glass cylinders (6.5 mm in diameter, 10 mm long) using the same methods as those described by Webb et al. (1992). The calorimetry was performed in continuous scanning mode using a Setaram DSC 111 instrument. The heat flow was measured for a heating rate of 5 °C/min on glasses that had been previously cooled from above the glass transition temperature at rates of 1, 2, 5, and 10 °C/min. The calorimeter is calibrated regularly against a geometrically identical cylinder of sapphire, using the heat capacity data of Robie et al. (1979). The glass and melt heat capacities are estimated to have a precision of ±1% at 1σ, based on the four experiments performed on each composition. The dilatometry was performed using a Netzsch TMA 402 quartz-rod dilatometer. This instrument has been calibrated against sapphire (NBS sheet 732), and the molar expansivities have an accuracy of ±3% at 1σ, based on repeated measurements for each composition. The glass cylinders used in the dilatometry are those that were used in the calorimetry measurements. The thermal history of the glasses and the scanning rates of the dilatometry measurements are identical to those of the calorimetry measurements. Room-temperature densities of crystal- and bubble-free glasses were determined by the Archimedean method in toluene. These densities are accurate to ±0.2%. The temperature ranges of dilatometric and calorimetric measurements are given in Table 2.

THEORY

The derivation of liquid expansivity and volume data from calorimetric and dilatometric data is based on the principles of structural relaxation in silicate melts (Narayanaswamy, 1971; Moynihan et al., 1976; Scherer,

TABLE 2. Measured C_P and dV/dT data for glasses and liquids

T (°C)	HPG8F5		HPG8F10	
	C_P J/g °C	dV/dT 10^{-4} cm³/mol °C	C_P J/g °C	dV/dT 10^{-4} cm³/mol °C
120	0.9134	5.6870	0.9152	5.0917
130	0.9235	5.2123	0.9262	4.9488
140	0.9333	4.8808	0.9363	5.1146
150	0.9427	5.0509	0.9464	5.0741
160	0.9519	5.1689	0.9561	5.1339
170	0.9604	4.9871	0.9653	5.0165
180	0.9696	4.6293	0.9752	5.3302
190	0.9785	4.8060	0.9846	5.3250
200	0.9863	5.3151	0.9932	5.1132
210	0.9931	5.3550	1.0005	5.2557
220	1.0006	5.1210	1.0079	5.2210
230	1.0067	4.8999	1.0148	4.9854
240	1.0120	4.9527	1.0209	4.9743
250	1.0173	5.3579	1.0270	5.1878
260	1.0225	4.7715	1.0334	5.0466
270	1.0272	4.6285	1.0391	5.0945
280	1.0319	4.8423	1.0458	5.0125
290	1.0373	4.9692	1.0524	5.0487
300	1.0431	4.9263	1.0584	4.9784
310	1.0506	4.6962	1.0658	5.0501
320	1.0571	4.7360	1.0720	5.0508
330	1.0621	4.4623	1.0734	5.1107
340	1.0648	4.1755	1.0708	5.0641
350	1.0681	4.7770	1.0743	4.9109
360	1.0711	5.0650	1.0767	4.9234
370	1.0742	4.7587	1.0805	5.2497
380	1.0784	5.2515	1.0860	4.8952
390	1.0822	4.9952	1.0909	5.0379
400	1.0861	4.9174	1.0945	4.9913
410	1.0889	5.0554	1.0974	5.1815
420	1.0934	5.3176	1.1022	4.9868
430	1.0966	4.9783	1.1070	5.1771
440	1.1009	5.0576	1.1121	5.2312
450	1.1043	5.2545	1.1171	5.4512
460	1.1076	5.2159	1.1222	5.6298
470	1.1121	5.3738	1.1282	5.9152
480	1.1157	5.5316	1.1346	5.8450
490	1.1187	6.5534	1.1411	6.2017
500	1.1219	6.0177	1.1511	6.7723
510	1.1279	6.1344	1.1647	7.5921
520	1.1342	7.5192	1.1841	8.3987
530	1.1427	7.8547	1.1976	9.5796
540	1.1542	8.4307	1.2087	10.8921
550	1.1693	9.8631	1.2237	12.5520
560	1.1874	11.3600	1.2495	14.8730
570	1.2106	14.0450	1.2767	16.5449
580	1.2358	15.5389	1.2988	17.0611
590	1.2582	17.3363	1.3098	15.9703
600	1.2750	17.8497	1.3078	14.3980
610	1.2813	17.8639	1.2982	12.7245
620	1.2782	15.5658	1.2911	9.4315
630	1.2694	14.0536	1.2873	
640	1.2589	13.1403	1.2866	
650	1.2505	11.4808		
660	1.2458	9.8769		
670	1.2426	4.9206		
680	1.2400			
690	1.2381			

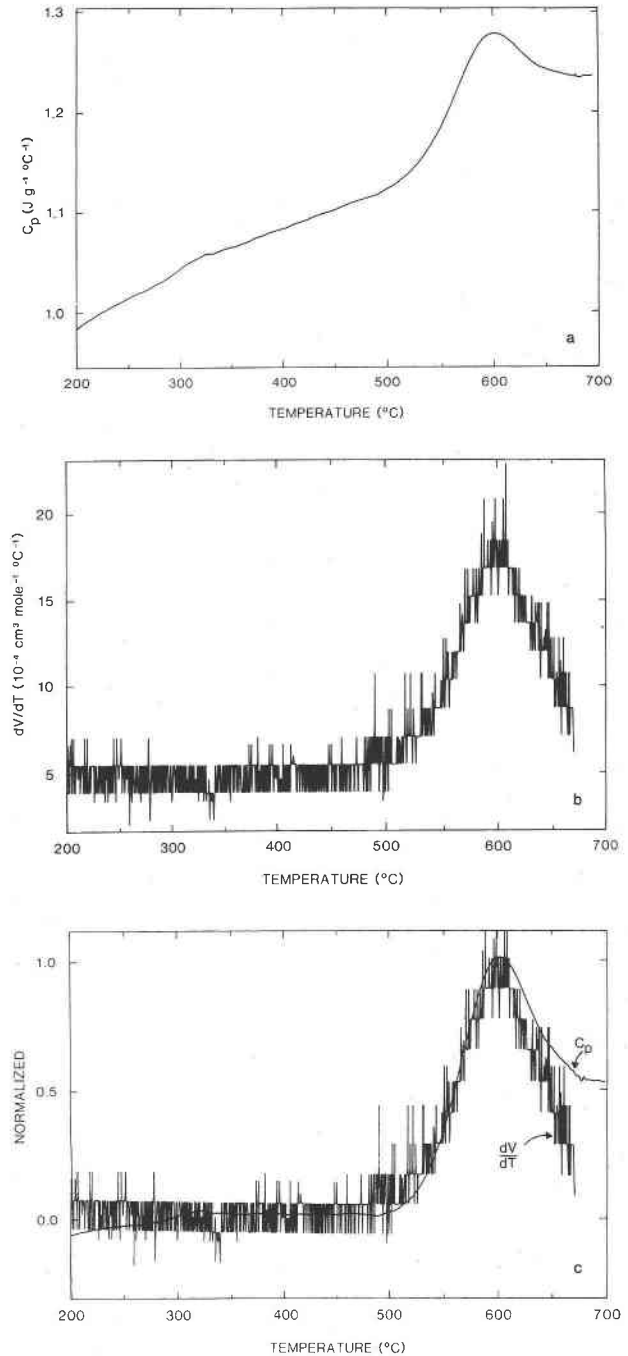*Note:* Cooling rate 1 °C/min; heating rate 5 °C/min.

Fig. 1. (a) A calorimetric trace of heat capacity for HPG8F5 previously cooled at 1 °C/min and subsequently heated at 5 °C/min. (b) A dilatometric trace of expansivity for HPG8F5 previously cooled at 1 °C/min and subsequently heated at 5 °C/min. (c) The normalized comparison of a dilatometric and a calorimetric trace of the glass transition region.

1984). The more general aspects of structural relaxation in silicate melts and their influence on diffusion, viscosity, and density have been discussed previously (Dingwell, 1990; Dingwell and Webb, 1989, 1990). The theory of our procedure for obtaining relaxed-liquid molar expansivity data from a combination of scanning calorimetry and dilatometry has been presented in full by Webb et al. (1992). This method of determining the volume and thermal expansivity of relaxed supercooled melts has been successfully tested against the volume and thermal expansivity extrapolated from high-temperature double-bob

TABLE 3. Volume and coefficient of thermal expansion data for haplogranite-F_2O_{-1} melts

	HPG8	HPG8F5	HPG8F10
Wt% F	—	2.89	4.55
Mol. wt. (g/mol)	64.35	62.39	61.12
Mol. fraction F_2O_{-1}	—	0.0490	0.0727
Density (g/cm³) (15.4 °C)	2.316 ± 0.005	2.302 ± 0.005	2.300 ± 0.005
Density (g/cm³) (750 °C)	2.295 ± 0.006	2.271 ± 0.005	2.261 ± 0.005
Mol. vol. (cm³/mol) (750 °C)	28.039 ± 0.076	27.482 ± 0.054	27.030 ± 0.053
$dV/(Vd T)$ $(10^{-6}/°C)$			
In glass	14.6 ± 1.0	19.3 ± 1.0	19.3 ± 0.2
	730 °C	470 °C	460 °C
In liquid	29.9 ± 3.0	43.2 ± 2.9	53.1 ± 1.4
	920 °C	720 °C	660 °C

Archimedean density measurements in a silicate melt (Webb et al., 1992).

The physical properties of a silicate melt depend upon the ambient temperature, T, and the configuration or structure of the melt. Silicate glasses quenched from liquids preserve a configuration that is thought to approximate the equilibrium structure of the liquid at some fictive temperature, T_f. The temperature derivatives of melt properties (e.g., heat capacity and molar thermal expansivity) can be used to describe the temperature derivative of the fictive temperature. To do this, the temperature derivative $(d\Phi/dT)$ of any property (Φ) in the glass transition interval is normalized with respect to the temperature derivative of the liquid and glassy properties. This normalized temperature derivative, which is equal to dT_f/dT, must equal zero for the glass (T_f is constant) and one for the liquid (T_f equals T).

In the present study, enthalpy and volume take the place of the general property Φ. With the assumption of the equivalence of volume and enthalpy relaxation behavior (Webb, 1992), the behavior of heat capacity and thermal expansion in the glass transition interval can be related by the temperature derivative of T_f (Webb et al., 1992)

$$\frac{C_P(T') - C_{Pg}(T')}{C_{Pe}(T_f) - C_{Pg}(T_f)} = \frac{dT_f}{dT}\bigg|_{T'}$$

$$= \frac{\dfrac{dV(T)}{dT} - \dfrac{dV_g(T)}{dT}\bigg|_{T'}}{\dfrac{dV_e(T)}{dT} - \dfrac{dV_g(T)}{dT}\bigg|_{T_f}} \quad (1)$$

where the subscripts "e" and "g" are for liquid (equilibrium) and the glassy values of the property. In the above equation relating C_P and thermal expansivity dV/dT, the unknown parameter is the thermal expansivity of the relaxed liquid at temperature T' in the glass transition interval.

Because of the lack of relaxed thermal expansivity data, we recover the liquid molar thermal expansivity from the dilatometric trace by normalizing both the scanning calorimetric and dilatometric data:

$$\Phi'(T) = \frac{\Phi(T) - \Phi_g(T)}{\Phi_p - \Phi_g(T)} \quad (2)$$

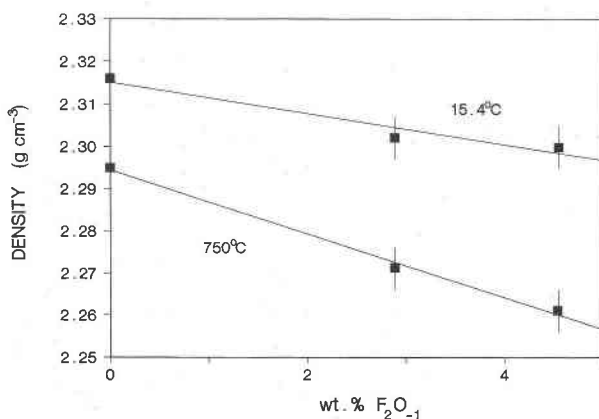where the subscripts "p" and "g" refer to peak and glassy

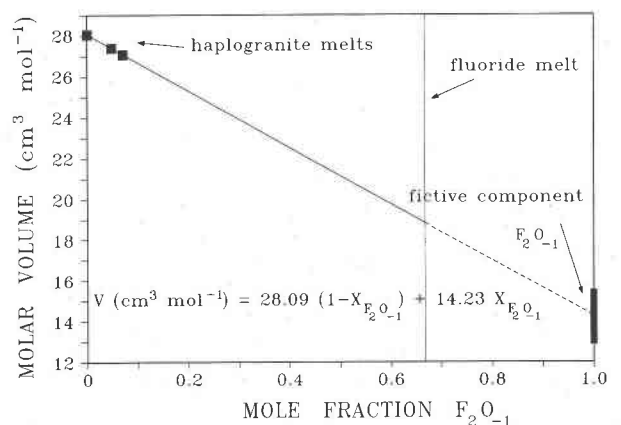Fig. 2. The effect of F on the density of haplogranitic melt at room temperature and 750 °C.

Fig. 3. Volume-composition relationship along the haplogranite-F_2O_{-1} join at 750 °C.

TABLE 4. Partial molar volumes at 750 °C

$V_{haplogranite}$	$V_{F_2O_{-1}}$
28.09(7)	14.2(1.3)

Note: Values are in cm³/mol.

values of the property. The relaxed value of thermal expansivity can now be generated from the peak and extrapolated glassy values of thermal expansivity; the volume and coefficient of volume thermal expansion α_v [$1/V \cdot (dV/dT)$] of the melt can also be calculated. We wish to stress that the above method can only be applied to calorimetric and dilatometric data obtained on the same sample using identical thermal histories. It is only this internal consistency that permits the use of the assumption of the equivalence of the enthalpy and volume relaxation behavior. Small changes in composition or fictive temperature of the melt can strongly influence relaxation behavior.

RESULTS AND DISCUSSION

Examples of the heat capacity and expansivity data are illustrated in Figure 1a and 1b and tabulated in Table 2. The density and expansivity data for the HPG8, HPG8F5, and HPG8F10 melts are tabulated in Table 3. The effect of F_2O_{-1} on the density of HPG8 glass (15.4 °C) and melt (750 °C) is illustrated in Figure 2. The molar volumes in Table 3 are calculated from the densities based upon the haplogranite and F_2O_{-1} components. F_2O_{-1} reduces the density of haplogranitic glasses obtained upon quenching from the liquid at 5 °C/min from 2.316 ± 0.005 g/cm³ to 2.300 ± 0.005 g/cm³ at room temperature, with the addition of 4.55 wt% F_2O_{-1} or approximately 0.1%/wt% of F_2O_{-1}. The expansivities of the glasses measured up to the glass transition increase with the addition of F_2O_{-1} from $14.6 \pm 1.0 \times 10^{-6}$/°C to $19.3 \pm 0.2 \times 10^{-6}$/°C. The liquid expansivities for the HPG8F5 and HPG8F10 have been derived using the normalization procedure outlined above. The liquid expansivity of HPG8 is from Knoche et al. (1992c). Expansivity of the liquids increases from $29.9 \pm 3.0 \times 10^{-6}$/°C to $53.1 \pm 1.4 \times 10^{-6}$/°C with the addition of 4.55 wt% F.

Our normalization technique allows extrapolation beyond the peak found in the dilatometric trace across the glass transition (Fig. 1c). We can use such a trace to integrate the volume change of the sample up to a temperature just above the glass transition. The integrated expansivity data and the room-temperature molar volume data yield the high-temperature molar volumes of the relaxed liquids at temperatures just above the glass transition for each composition, as indicated in Table 3. The comparison of these high-temperature molar volumes and densities at a single temperature requires a correction using the liquid expansivities and the relaxed molar volumes obtained by integration. This has been calculated for a temperature of 750 °C. The calculated molar vol-

umes and densities of the three melts at 750 °C are presented in Table 3.

These molar volumes are plotted in Figure 3 as a function of the mole fraction of F_2O_{-1}. The molar volume data have been regressed to the mole fractions of the haplogranite and F_2O_{-1} components, resulting in a partial molar volume of 14.2 ± 1.3 cm³/mol for F_2O_{-1} (Table 4). Note that in Figure 3 the fully fluorinated end-member of the join lies at 66.7 mol% F_2O_{-1} because the molar formula of the haplogranite is taken on the basis of two O atoms per mole.

Data for F-bearing silicate melt densities are rare (Kogarko and Krigman, 1981; Grjotheim et al., 1990). Fluorides are stably soluble in extremely alkalic silicate melts, such as the binary alkali silicates at relatively low temperatures (1000 °C), and Kogarko and Krigman (1981) have determined the density of melts along several binary joins between alkali silicates and alkali fluorides at 1250 °C using a single-bob method. Similarly, Grjotheim et al. (1990) have investigated the density of cryolite melts with feldspar additions. Cryolite incidentally has a molar volume per fluoride of 16.6 cm³/mol at 1000 °C and an expansivity of 6.8×10^{-3} cm³/mol °C). Both studies indicate deviations from linear volumes of mixing, and thus extrapolations in composition are difficult. Nevertheless, we have taken the data of Kogarko and Krigman (1981) for the $Na_2Si_4O_9$-NaF, $Na_2Si_2O_5$-NaF, $Na_2Si_{1.5}O_4$, and Na_2SiO_3-NaF joins and recast their compositions into Na_2O-SiO_2-F_2O_{-1}. The results of a multilinear regression to the molar volumes yield a partial molar volume of 22.9 ± 0.8 cm³/mol for F_2O_{-1} at 1250 °C. The linear extrapolation of our liquid volumes to 1250 °C yields a partial molar volume of 19.0 cm³/mol. Any temperature dependence of the thermal expansivity of the F-bearing haplogranitic liquids is likely to reduce the calculated partial molar volume of F_2O_{-1} at 1250 °C (Knoche et al., 1992a), and thus the lower value obtained from the present study appears to be inconsistent with that of Kogarko and Krigman (1981). Recent studies of the structure of F-bearing haplogranitic and analogue compositions indicate, however, the presence of [6]Al (Kohn et al., 1991; Schaller et al., 1992). The generation of octahedral aluminum fluoride complexes could well be responsible for the lower partial molar volume of F_2O_{-1} observed in the present Al-bearing system relative to that for the alkali silicate melts. This possibility emphasizes the importance of the present determination of the volume effects of F in compositions and at temperatures of direct geological interest.

Any reduction in melt density will increase the density contrast between leucogranitic and pegmatitic melts and most of their equilibrium crystalline products. In this way the decrease in melt density due to the addition of F_2O_{-1} will accelerate gravity-driven crystal-melt fractionation processes. The effect of F_2O_{-1} on haplogranitic liquid density thus complements the strong reduction in viscosity accompanying F_2O_{-1} substitution in silicic melts (Dingwell et al., 1985).

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