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The combined effects of water and fluorine on the viscosity of silicic magmas

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Abstract—The Newtonian viscosity of water-plus-fluorine-bearing silicate melt of haplogranitic composition (HPG8) has been determined. Viscosities of HPG8 melt with addition of 3.11 and 4.25 wt.% of F and up to 3 wt.% H_2O have been obtained using a micropenetration technique in the interval $10^{9.74}$ to $10^{11.84}$ Pa · s and temperatures varying from 370 to 700°C, at ambient pressure. Determination of the temperature dependence of viscosity from this and previous studies permits the parameterization of the viscosity of melts containing water and fluorine, having similar composition, within a 0.3 log units standard error. The viscosity of water-bearing, F-rich haplogranitic samples is represented by a modified Vogel-Fulcher-Tammann (VFT) equation which provides a non-Arrhenian description of the temperature dependence of the viscosity. The results of this study indicate that, taken individually or together, both H_2O and F^- have a strong and similar effect on the viscosity of SiO_2-rich compositions. This similarity between F_2O_{-1} and H_2O greatly simplifies the task of predicting viscosity for volatile-rich, highly silicic magmas. The low viscosities of hydrous fluorine-bearing granitic melts favour efficient crystallization-fractionaction paths for these liquids, controlling degassing paths and consequently the eruptive behaviour. Numerical simulations of eruptive events normally do not take into account the contribution of fluorine; this may introduce a significant error in the description of the fluid-dynamic properties of magma and, therefore, in the accurate prediction of eruptive scenarios, as well as in hazard assessment studies. Fluorine, unlike water, remains dissolved in the melt at high concentrations and low confining pressures. The incorporation of fluorine data and the modelling of fluorine-bearing viscosity data are therefore of fundamental importance for simulations of magma dynamics and prediction of eruptive scenarios. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Dissolved volatiles are present in all terrestrial magmas and their presence affects all physical and chemical properties of igneous rocks. The volatile concentration governs the solidus temperature, the thermodynamic properties, the viscosity and the eruptive style of magmas. To understand how volatiles affect magma transport, we have investigated the volatile phases that are most frequently encountered in natural compositions and that are most effective at reducing the viscosity of silicate melts.

Fluorine is one of the most abundant volatiles in evolved volcanic suites and in late-stage granitic systems. The physical and chemical evolution of granitic and rhyolitic magmas are determined by liquid-crystal equilibria, volatile solubilities and transport properties. For instance, the recognition of fluorine-rich granites and rhyolites and their close spatial association with several varieties of mineral deposits has led to a discussion of the possible role of fluorine in the generation of such deposits (Dingwell, 1987a). Fluorine-rich silicate melts can be responsible for the existence of fluorine-rich eruptive rocks such as the topaz-bearing rhyolites from Spor Mountain (Burt et al., 1982), Honeycomb Hills, Utah (Congdon and Nash, 1991), the macusanites from Peru (Pichavant et al., 1987) and certain hypoabyssal and intrusive rocks with fluorine contents

up to 5 wt.% or higher (Bailey, 1977; Congdon and Nash, 1988; Kortemeier and Burt, 1988; Carroll and Webster, 1994). Moreover, fluorine contents up to 2 wt.% have been recognized even in basic igneous rocks (Aoki et al., 1981).

The presence of fluorine is mostly important for the petrogenesis and the phase relations in various F-rich differentiated felsic magmas (Pichavant et al., 1987; Kortemeier and Burt, 1988; Keppler and Wyllie, 1990; Keppler, 1993). Fluorine is known to increase the solubility of water in the melt (Holtz et al., 1993), to increase diffusivities (Dingwell, 1987a), to decrease density (Dingwell et al., 1993), to modify the glass transition behaviour of glasses (Dingwell and Webb, 1992) and to increase the rates of crystal-melt and melt-vapour interaction (crystal fractionation, melt zonation, magma degassing; see Lange, 1994, for a review). Despite this importance, very few studies have been performed to investigate the effect of fluorine on the viscosity of anhydrous and hydrous silicate melts. Most studies envisage that fluorine, like water, reduces the viscosity of both polymerized and depolymerized magmas by several orders of magnitude (Dingwell et al., 1985, 1993; Dingwell, 1987b; Dingwell, 1989; Baker and Bossanyi, 1994; Dingwell and Hess, 1998). In particular, high temperature viscosity determinations performed on water-free synthetic liquids, with compositions ranging from phonolitic to rhyolitic, showed that the viscosity-reducing power of fluorine increases with the SiO_2 content of the base melt (Dingwell et al., 1985).

On the other hand, Persikov (1991), in his model for the calculation of viscosity of magmatic liquids, predicts that the

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Table 1. Compositions (in wt% of the oxides) of the samples used here to calibrate Eqn. 3. Compositions for HPG8F3 and HPG8F5 were obtained by microprobe analysis (average of 13 and 12 data points, respectively,) by using the Cameca 50SX available at BRGM-CNRS Orléans.

Sample name	HPG8	HPG8F3	HPG8F5	AOQ	LCOAF3	RVDC1
SiO_2	78.60	77.22	76.67	76.12	74.39	76.17
Al_2O_3	12.50	11.84	11.13	13.53	14.72	12.48
Na_2O	4.60	4.77	4.69	4.65	3.9	4.1
K_2O	4.20	4.20	4.31	5.68	4.88	4.54
MgO	—	—	—	—	0.07	0.04
CaO	—	—	—	—	0.55	0.33
TiO_2	—	—	—	—	0.10	0.05
MnO	—	—	—	—	0.11	0.01
F	—	3.11	4.250	—	1.40	1.22
	Ref. 1		Ref. 2		Ref. 3	Ref. 4

Ref. 1 = Hess et al. (1995); Ref. 2 = Holtz et al. (1993); Ref. 3 = Schulze et al. (1996); Ref. 4 = Baker and Vaillancourt (1995).

addition of fluorine to a hydrous, granitic melt increases melt viscosity. Similarly, Luth (1988a, 1988b) investigated the effects of F on the liquidus phase relations of the CaO-CaF_2-SiO_2 and the $NaAlSiO_4$-$CaMgSi_2O_6$-SiO_2 systems, and inferred that fluorine, in substitution for oxygen in the melt, might increase depolymerized melt viscosities, due to the increase in SiO_2 activity.

Very few studies investigated the effects of both water and fluorine on the viscosity of silicate melts. Dingwell and Mysen (1985) and Dingwell (1987b) argue that for albitic liquids water is slightly more effective than fluorine in reducing viscosity and that the effect of both combined volatiles in decreasing the melt viscosity is slightly larger compared to that of each individual volatile. On the other hand, Baker and Vaillancourt (1995) demonstrated that the effect of water and fluorine in reducing the viscosity of silicate melts is indeed very similar. Hess et al. (1995) emphasized that, if the fraction of H_2O inferred (on the basis of infrared spectroscopy) to be present as molecular water is subtracted, the effect of H_2O on melt viscosity is much larger than that of fluorine.

In this study, we chose to investigate the combined influence of fluorine and water on the viscosity of fluorine-rich and silica-rich magmas. Several water-bearing samples were synthesised from the HPG8F3 and HPG8F5 base-compositions (Dingwell et al., 1993). The composition used belongs to the system SiO_2-$NaAlSi_3O_8$-$KAlSi_3O_8$ chosen to be near that of the minimum liquidus temperature point at $P(H_2O) = 2$ kbar (Tuttle and Bowen, 1958; Dingwell, 1993).

2. METHODS

The experimental method used to determine the viscosity of the hydrous F-bearing melts is the same as that used by Hess et al. (1995) and Dingwell et al. (1996). The dry glasses (HPG8F3 and HPG8F5) were prepared by starting from powders of Na_2CO_3, K_2CO_3, Al_2O_3, SiO_2 and AlF_3. The fluorine-bearing compositions were fused directly for 2 hours at 1600°C in a platinum crucible in a $MoSi_2$ box furnace. To eliminate bubbles and promote a full reaction and homogenisation of the samples, the crucible was then transferred to a second $MoSi_2$ box furnace equipped with a rotational viscometer and stirred for ~24 hours using a $Pt_{80}Rh_{20}$ spindle. Additional details of the sample preparation can be found in Dingwell et al. (1993). Fluorine-rich water-bearing samples were synthesised from the HPG8F3 and HPG8F5 base composition already investigated by Dingwell et al. (1993) (Table 1).

One problem with trying to understand the effect of fluorine on physical-chemical properties of melts is isolating the effect of F^- from the other components in the system. When fluorine is added to the melt

as metal fluoride, separating the effect of the metal cation from the effect of F^- is virtually impossible. To investigate the effect of F^- separately from the effect of metal cation and at the same time to maintain constant the stoichiometry of HPG8 base composition, we decided to use starting compositions from Dingwell et al. (1993) where fluorine was added as AlF_3 and Al_2O_3 was removed from the HPG8 stoichiometry to keep a molar ratio of $Al_2O_3/(Na_2O + K_2O) = 1$. By this means two fluoride ions are exchanged for one oxygen ion and it is possible to isolate the effect of fluoride on the structure and viscosity of such a melt. Thus the peculiar F_2O_{-1} stoichiometric term used throughout this paper can be considered as a substitution coordinate.

Ten hydrothermal syntheses (5 for each sample) with water contents up to ~3.0 wt.% H_2O were prepared via use of a piston cylinder apparatus by rapidly quenching at 1 GPa from temperatures between 1400 and 1600°C. The quenched hydrous glasses were subsequently prepared for micropenetration viscometry and FTIR. The micropenetration technique involves determining the rate at which a spherically-tipped Ir indenter under a fixed load moves into the melt surface. These measurements were performed in a BAHR DIL 802 vertical push dilatometer. Details about the experimental procedure are reported in Dingwell et al. (1996) and Hess et al. (1995). The advantage of using a micropenetration technique is the small amount of material needed (10–30 mg) and the short time required to obtain reproducible measurements. After the heating stage, once the measurement temperature was reached (some tens of degrees above the glass transition temperature) a relaxation time before the measurement on the order of 15 to 20 min was typically adopted. For hydrous samples, measurement times from 1 to 10 min were sufficient to obtain the viscosity data. Viscosity determinations of water-bearing samples were obtained using 1-mm-thick samples. The accuracy of this technique (~0.06 log units) is determined by measurements performed on the NBS DGG-1 glass.

FTIR spectroscopy before and after the viscosity measurements, together with H_2O determinations by the Karl-Fisher titration (KFT) technique, were used to confirm homogeneity, stability and water content within the samples. Viscosities in the interval between $10^{9.74}$ and $10^{11.84}$ Pa · s were measured using the micropenetration technique described in Hess et al. (1995) and Dingwell et al. (1996). F was not analysed after viscosity measurements. However, optical microscopic examination of the samples after viscosity determination indicated neither devolatilization (e.g., foaming) nor crystallization. Additionally, the indenter displacement vs. time trace is extremely sensitive to small variations in composition (i.e., viscosity), and during the course of the measurements viscosity remained constant. Due to the relatively low temperatures of our measurements (a few tens of degrees above T_g), it is thus likely that only negligible amounts of F and H_2O are lost.

3. RESULTS AND DATA MODELLING

Viscosities of the hydrous HPG8F3 and the HPG8F5 liquids are presented vs. reciprocal temperature in Figure 1. The results of the viscosity determinations of the hydrated HPG8F3 and the
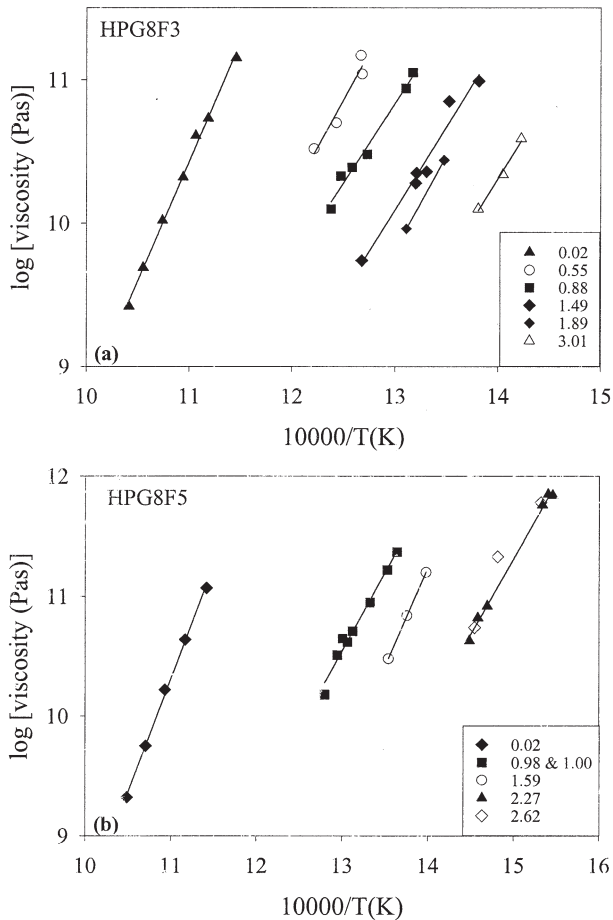
Fig. 1. Viscosities measured using micropenetration technique vs. reciprocal temperature for the investigated samples HPG8F3 (a) and HPG8F5 (b). The legend reports the dissolved water content values in wt.%. The data are fitted by an Arrhenian expression (lines in the figure).

HPG8F5 samples are tabulated in Table 2 together with the total water content determined by Karl Fisher titration (KFT) technique. Included in Table 2 are also viscosity data for dry HPG8F3 and HPG8F5 from Dingwell et al. (1993), dry as well as hydrous HPG8 at low temperature from Hess et al. (1995) and Dingwell et al. (1996), together with high temperature viscosity values from Schulze et al. (1996) on the AOQ haplogranite, a composition similar to HPG8, and the high temperature viscosity values from Baker and Vaillancourt (1995) pertaining the F-rich hydrous meta and peralouminous rhyolites.

Because of the similarity in composition between the samples (Tab. 1) the viscosity data on the hydrous HPG8 and AOQ haplogranites (Hess et al., 1995; Dingwell et al., 1996; Schulze et al., 1996) as well as those from Baker and Vaillancourt (1995) on the F-rich hydrous samples LCOAF3 (peraluminous) and RVDC1 (metaluminous), are fitted by the following equation:

$$\log \eta = A + \frac{B}{T - T_0}$$

where A, B, T_0 can be expressed as follows:

$$A = -4.31 - 0.038 \times (H_2O + F_2O_{-1})$$
$$B = [12820 - 599.5 \times \ln(1 + H_2O) - 24.37 \times \ln(1 + F_2O_{-1})]$$
$$T_0 = 307.2 - 137.6 \times \ln(1 + H_2O + F_2O_{-1}) \quad (1)$$

where η is the viscosity expressed in Pa · s, A (Pa · s), B (K), and T_0 (K) are constants, termed the preexponential factor, the pseudoactivation energy and the VFT-temperature, respectively, and T is the absolute temperature. H_2O and F_2O_{-1} are the concentrations expressed in mol.%, assuming the total water dissolved as molecular water. Eqn. 1 can be used in the complete magmatic-temperature interval (from $\sim$375 to 1400°C) and in a range of water contents from dry to 8.21 wt.% and fluorine F^- up to 4.25 wt.%. Eqn. 1 is capable of reproducing the measured data within a standard error of estimation of $\sim$0.3 log units. Even though the viscosities used for the parameterisation of Eqn. 1 have been obtained by using experimental techniques operating in a range of pressure from 1 MPa to 1 GPa, our parameterisation does not include the effect of pressure. However, variations in viscosity over the temperature and compositional ranges of our investigation are quite large with respect to those which we can expect as a function of pressure up to 1 GPa (Wolf and McMillan, 1995).

Attempts to reproduce the viscosity measurements of Table 2 with other forms of equations were performed. These equations were discarded as providing large absolute standard deviations. Based on our study, Eqn. 1 constitutes the most promising and accurate fitting able to approximate the viscosities of Table 2. Figure 2 shows a comparison of the measured viscosities with those calculated via Eqn. 1, and Table 2 reports the measured and the calculated values. It is worth mentioning that, in our modelling, we are able to explore the entire viscosity range, from high (our study) to low viscosity data (Baker and Vaillancourt, 1995; Schulze et al., 1996), keeping possible errors arising from extrapolation of data to a minimum.

To address separately the effect of fluorine on the viscosity of silicic melts, we compared Eqn. 1 with a second equation obtained by independently fitting the viscosity values of F-free, water-bearing samples (Hess et al., 1995; Dingwell et al., 1996; Schulze et al., 1996). The variation of the viscosity as a function of temperature and water content can be described by the following non-Arrhenian expression describing the hydrous viscosity data only:

$$\log \eta = -7.24 + 0.02192 \cdot \ln (1 + H_2O)$$
$$+ \frac{19,190.6 - 113.3 \cdot (H_2O)}{[T(K) - 106.98 + 192.30 \cdot \ln(1 + H_2O)]} \quad (2)$$

Such an equation permits the comparison between the isothermal viscosities of water-bearing liquids with those of water + fluorine–bearing liquids presented in this study. The standard deviation we obtain using Eqn. 2 is $\sim$0.2 log units.

Figures 3a and 3b show the isothermal viscosities as a function of water + fluorine content, here expressed on a molar basis of H_2O and F_2O_{-1} components. Figure 3a shows the difference between the Arrhenian extrapolations of the experimental data (symbols and linear fits in Fig. 1) and the values calculated from Eqn. 1, taken at $T = 800$ K (solid curves). This figure indicates that, at conditions close to those of our exper-

Table 2. Viscosities of the hydrous and dry melts investigated in this work (120 data). Water determinations from this work were performed using KFT. Data from literature are taken into account to evaluate the effect of H_2O and F_2O_{-1} on the viscosity of the haplogranitic compositions. Literature data are indicated in the table with "ref." The viscosity value indicated with the asterisk (*) refers to a measurement obtained by Dorfman et al. (1996).

HPG8F3	H_2O (wt%)	H_2O (mol%)	F_2O_{-1} (mol%)	T (°C)	log[η(Pas)] measured	log[η(Pas)] calculated	HPG8F5	H_2O (wt%)	H_2O (mol%)	F_2O_{-1} (mol%)	T (°C)	log[η(Pas)] measured	log[η(Pas)] calculated
823	0.55	1.77	4.67	545.60	10.52	10.89	868	2.62	7.95	5.96	414.55	10.74	10.39
823	0.55	1.77	4.67	515.70	11.04	11.50	868	2.62	7.95	5.96	379.90	11.78	11.13
823	0.55	1.77	4.67	531.50	10.70	11.17	868	2.62	7.95	5.96	402.20	11.33	10.65
823	0.55	1.77	4.67	516.35	11.17	11.49	860	2.27	7.01	6.02	376.30	11.85	11.53
818	0.88	2.81	4.62	521.70	10.39	10.74	860	2.27	7.01	6.02	374.00	11.84	11.58
818	0.88	2.81	4.62	528.60	10.33	10.60	860	2.27	7.01	6.02	379.13	11.76	11.46
818	0.88	2.81	4.62	512.60	10.48	10.92	860	2.27	7.01	6.02	412.80	10.82	10.72
818	0.88	2.81	4.62	486.20	11.05	11.47	860	2.27	7.01	6.02	407.70	10.92	10.83
818	0.88	2.81	4.62	490.15	10.94	11.38	860	2.27	7.01	6.02	417.50	10.63	10.63
818	0.88	2.81	4.62	534.75	10.10	10.49	861	1.59	4.98	6.15	454.05	10.84	10.59
824	1.49	4.67	4.53	451.00	10.99	11.28	861	1.59	4.98	6.15	465.60	10.48	10.36
824	1.49	4.67	4.53	466.40	10.85	10.95	861	1.59	4.98	6.15	442.55	11.20	10.80
824	1.49	4.67	4.53	478.60	10.36	10.70	862	1.00	3.18	6.27	492.45	10.62	10.58
824	1.49	4.67	4.53	484.15	10.35	10.59	862	1.00	3.18	6.27	495.80	10.65	10.52
824	1.49	4.67	4.53	484.55	10.28	10.58	862	1.00	3.18	6.27	499.40	10.51	10.45
824	1.49	4.67	4.53	515.75	9.74	9.99	862	1.00	3.18	6.27	466.37	11.22	11.11
867	1.89	5.91	4.48	469.10	10.44	10.39	862	1.00	3.18	6.27	489.00	10.71	10.65
867	1.89	5.91	4.48	489.75	9.96	10.00	869	0.98	3.11	6.27	477.40	10.95	10.91
866	3.01	9.19	4.32	429.95	10.59	10.08	869	0.98	3.11	6.27	508.25	10.18	10.31
866	3.01	9.19	4.32	438.80	10.34	9.91	869	0.98	3.11	6.27	460.30	11.37	11.27
866	3.01	9.19	4.32	451.25	10.10	9.68	869	0.98	3.11	6.27	489.00	10.71	10.68
Ref. 1	0.02	0.07	4.75	599.9	11.15	11.27	Ref. 1	0.02	0.06	6.47	602.8	11.07	10.48
Ref. 1	0.02	0.07	4.75	621.1	10.73	10.87	Ref. 1	0.02	0.06	6.47	622.5	10.64	10.14
Ref. 1	0.02	0.07	4.75	630.9	10.61	10.69	Ref. 1	0.02	0.06	6.47	641.8	10.22	9.82
Ref. 1	0.02	0.07	4.75	641.0	10.32	10.51	Ref. 1	0.02	0.06	6.47	661.0	9.75	9.51
Ref. 1	0.02	0.07	4.75	658.1	10.02	10.21	Ref. 1	0.02	0.06	6.47	630.4	9.32	9.22
Ref. 1	0.02	0.07	4.75	674.6	9.69	9.94							
Ref. 1	0.02	0.07	4.75	687.2	9.42	9.73							

HPG8	H_2O (wt%)	H_2O (mol%)	F_2O_{-1} (mol%)	T (°C)	log[η(Pas)] measured	log[η(Pas)] calculated	AOQ	H_2O (wt%)	H_2O (mol%)	F_2O_{-1} (mol%)	T (°C)	log[η(Pas)] measured	log[η(Pas)] calculated
Ref. 2	0.02	0.07	0.00	831.7	11.02	10.60	Ref. 4	0.02	0.07	0.00	1400	4.91	4.93
Ref. 2	0.02	0.07	0.00	905.0	10.63	10.21	Ref. 4	1.05	3.70	0.00	1200	4.21	4.17
Ref. 2	0.02	0.07	0.00	925.7	10.28	9.87	Ref. 4	1.05	3.70	0.00	1300	3.77	3.59
Ref. 2	0.02	0.07	0.00	938.8	10.16	9.67	Ref. 4	1.55	5.39	0.00	1200	3.85	3.72
Ref. 1	0.02	0.07	0.00	844.2	11.50	11.28	Ref. 4	1.55	5.39	0.00	1300	3.45	3.18
Ref. 1	0.02	0.07	0.00	903.3	10.90	10.23	Ref. 4	1.55	5.39	0.00	1400	2.98	2.71
Ref. 1	0.02	0.07	0.00	969.2	9.77	9.22	Ref. 4	2.09	7.17	0.00	1200	3.61	3.36
Ref. *	0.02	0.07	0.00	1179.9	6.79	6.75	Ref. 4	2.09	7.17	0.00	1300	3.20	2.85
Ref. 1	0.02	0.07	0.00	1396.3	4.90	5.01	Ref. 4	2.58	8.74	0.00	1300	3.07	2.61
Ref. 1	0.02	0.07	0.00	1445.1	4.53	4.69	Ref. 4	3.22	10.74	0.00	1200	3.27	2.82
Ref. 1	0.02	0.07	0.00	1496.8	4.15	4.37	Ref. 4	3.22	10.74	0.00	1300	2.88	2.35
Ref. 1	0.02	0.07	0.00	1545.0	3.81	4.09	Ref. 4	3.75	12.35	0.00	1300	2.54	2.16
Ref. 1	0.02	0.07	0.00	1592.5	3.58	3.84	Ref. 4	5.00	15.99	0.00	1150	2.75	2.47
Ref. 1	0.02	0.07	0.00	1642.6	3.24	3.59	Ref. 4	5.00	15.99	0.00	1000	3.37	3.28
Ref. 3	0.42	1.49	0.00	687.61	11.40	11.39	Ref. 4	5.00	15.99	0.00	900	3.95	3.94
Ref. 3	0.42	1.49	0.00	703.56	10.76	11.07	Ref. 4	5.90	18.48	0.00	800	4.26	4.38
Ref. 3	0.42	1.49	0.00	649.00	11.80	12.21	Ref. 4	5.90	18.48	0.00	900	3.69	3.65
Ref. 3	0.99	3.46	0.00	649.51	9.68	10.08	Ref. 4	5.90	18.48	0.00	1000	3.18	3.02
Ref. 3	0.99	3.46	0.00	611.17	10.48	10.79	Ref. 4	7.03	21.47	0.00	900	3.46	3.34
Ref. 3	0.99	3.46	0.00	593.55	10.98	11.14	Ref. 4	7.03	21.47	0.00	800	4.03	4.04
Ref. 3	0.99	3.46	0.00	611.17	10.45	10.79	Ref. 4	8.21	24.44	0.00	900	3.12	3.05
Ref. 3	0.99	3.46	0.00	666.85	9.42	9.78	Ref. 4	8.21	24.44	0.00	800	3.68	3.74

	H_2O (wt%)	H_2O (mol%)	F_2O_{-1} (mol%)	T (°C)	log[η(Pas)] measured	log[η(Pas)] calculated	LCOAF3	H_2O (wt.%)	H_2O (mol.%)	F_2O_{-1} (mol.%)	T (°C)	log[η(Pas)] measured	log[η(Pas)] calculated
Ref. 3	1.33	4.60	0.00	567.34	10.58	10.82	Ref. 5	6.0	17.32	1.86	1000	2.47	2.97
Ref. 3	1.33	4.60	0.00	549.37	10.96	11.18	Ref. 5	6.0	17.32	1.86	950	2.68	3.27
Ref. 3	1.33	4.60	0.00	583.16	10.38	10.51	Ref. 5	6.0	17.32	1.86	950	2.59	3.27
Ref. 3	1.33	4.60	0.00	602.66	9.88	10.15	Ref. 5	6.0	17.32	1.86	900	3.42	3.60
Ref. 3	1.33	4.60	0.00	621.45	9.60	9.81	Ref. 5	6.0	17.32	1.86	900	3.44	3.60
Ref. 3	1.33	4.60	0.00	612.74	9.83	9.97	Ref. 5	6.0	17.32	1.86	800	4.12	4.33
Ref. 3	1.85	6.32	0.00	546.67	10.10	10.23							
Ref. 3	1.85	6.32	0.00	508.25	11.30	10.99							

	H_2O (wt%)	H_2O (mol%)	F_2O_{-1} (mol%)	T (°C)	log[η(Pas)] measured	log[η(Pas)] calculated	RVDC1	H_2O (wt.%)	H_2O (mol.%)	F_2O_{-1} (mol.%)	T (°C)	log[η(Pas)] measured	log[η(Pas)] calculated
Ref. 3	1.85	6.32	0.00	576.62	9.69	9.69							
Ref. 3	2.27	7.68	0.00	545.33	9.62	9.65	Ref. 5	6.0	17.38	1.59	1000	2.43	2.99
Ref. 3	2.27	7.68	0.00	502.19	10.49	10.45	Ref. 5	6.0	17.38	1.59	900	3.16	3.61
Ref. 3	3.00	9.97	0.00	515.02	9.93	9.36	Ref. 5	6.0	17.38	1.59	800	4.07	4.35
Ref. 3	3.00	9.97	0.00	548.69	9.12	8.80							

Ref. 1 = Dingwell et al. (1993); ref. 2 = Hess et al. (1995); ref. 3 = Dingwell et al. (1996); ref. 4 = Schulze et al. (1996); ref. 5 = Baker and Vaillancourt (1995).
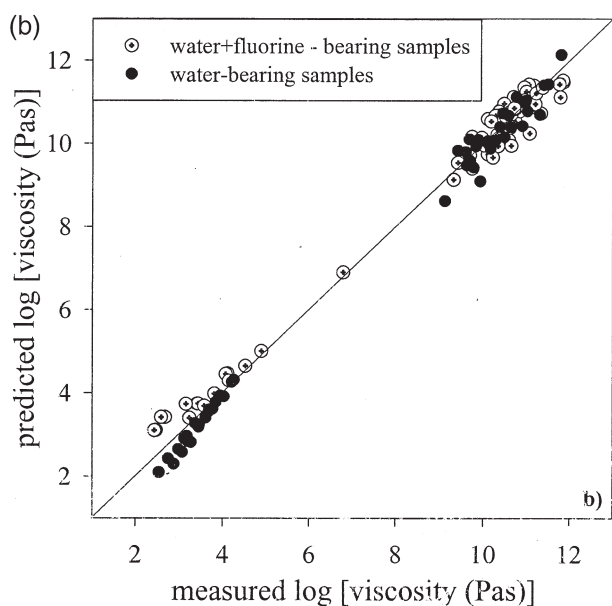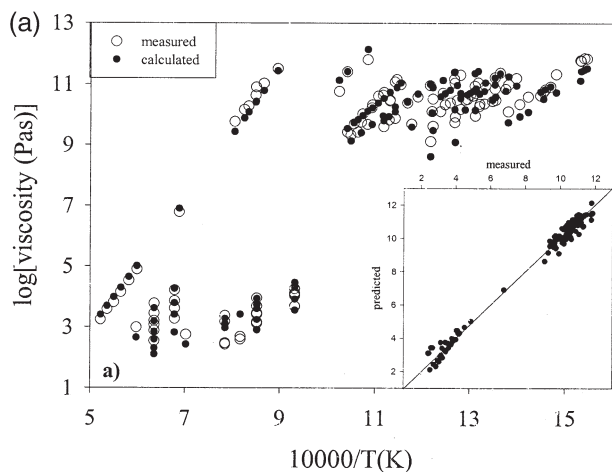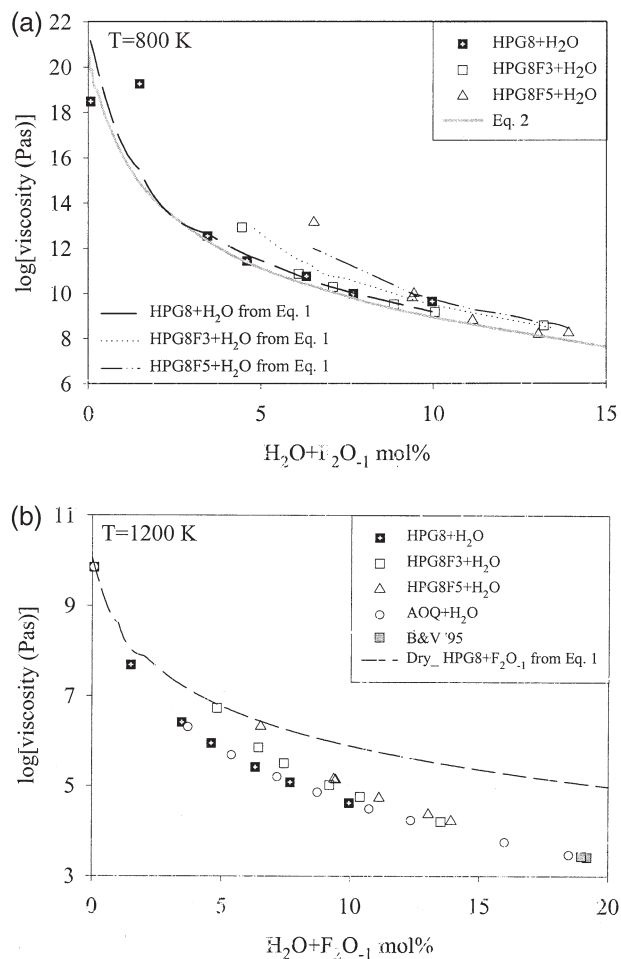
Fig. 3. (a) Isotherm at 800 K ($10^4 / T$ [K] = 12.75). This diagram compares the viscosities at $T = 800$ K obtained by linear (Arrhenian) fitting of the high viscosity for each water content (symbols) with those calculated (curves) by using Eqn. 1. Water and fluorine are expressed as molar basis of $H_2O + F_2O_{-1}$. The viscosity curve calculated with Eqn. 2, that independently fits the viscosity of water-bearing (fluorine-free) samples, is also reported for comparison (solid gray curve). (b) Calculated viscosities at $T = 1200$ K vs. the dissolved volatile content. The viscosity of all the samples is reported at temperatures close to eruptive conditions showing that the viscosity of fluorine-bearing liquids strongly diverges from that of water and/or "water plus fluorine"–bearing liquids. This is only slightly distinguishable when water-bearing samples are compared with "water plus fluorine"–bearing liquids. The dashed curve shows the effect of fluorine on the calculated viscosity of dry HPG8 composition. "B&V '95" represents the viscosity values calculated from Eqn. 1 at the water and fluorine content considered by Baker and Vaillancourt (1995).

Fig. 2. (a) Comparison in a "viscosity–reciprocal temperature space" of the measured viscosity (empty circles) from this and previous studies (see text) with those calculated (full circles) using Eqn. 1. The insert shows the same comparison in the calculated viscosity vs. measured viscosity space. (b) Larger relative discrepancies between the measured and the calculated viscosity values are observed in the high-T region for melt with low water concentrations and at low T for the "water plus fluorine"–bearing samples (see Table 2).

iments, only a slight deviation from Arrhenian rheological behaviour occurs. Figure 3b reports the calculated viscosity using Eqn. 1 at 1200 K. Viscosity of hydrous samples calculated by using Eqn. 2 are also reported in Figures 3a and 3b. Figure 3b also shows a calculated trend of the viscosity of dry, fluorine-rich samples (dashed curve). These figures show that, if only fluorine is added to the anhydrous sample, the decrease in viscosity is slightly smaller compared to that observed if water is added to the melt. For fluorine contents > ~7 mol.%, the calculated curve for fluorine rich melts tends to level off sharply (dashed curve in Fig. 3b) whereas the decrease in viscosity is still observed if a equal amount of water is added to

the melt. At high volatile concentrations, this leads to a remarkable difference in viscosity between the fluorine-rich melts and the water-bearing melts. This difference is further enhanced if the temperature is decreased.

Comparing the viscosities of hydrous melts with those of water plus fluorine-rich melts leads to different results. In fact, as soon as water is introduced in the fluorine-rich melt, the viscosities tend to converge to those of the fluorine-free hydrous melts. In other words, the viscosity of hydrous rhyolitic samples can be considered insensitive to whether only water or fluorine plus water is added to the samples. Both fluorine and
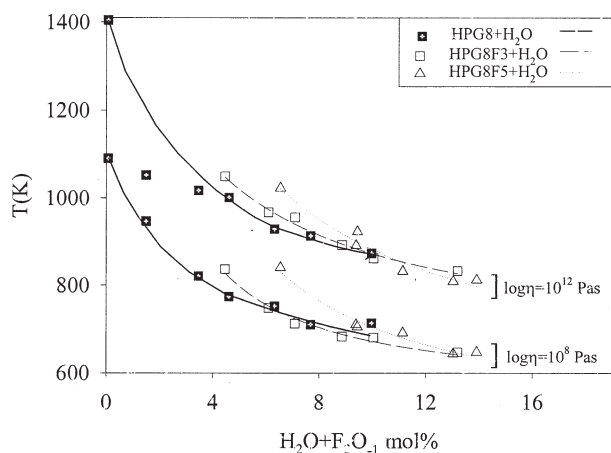
Fig. 4. Isokom temperatures corresponding to 10^8 and 10^{12} Pa · s as a function of volatile content for the HPG8, HPG8F3 and HPG8F5 samples. At volatile content > ~10 mol.% the curves tend to merge.

water-bearing samples show sharp viscosity decreases with the first addition of volatiles that tends to level off as further volatiles are added to the original composition. Baker and Vaillancourt (1995) who measured the viscosities of a haplogranitic melt with 1.5 wt.% F and 6% H_2O and compared them with those measured for the same composition to which 7.5 wt.% H_2O was added, reached a similar conclusion.

Figure 4 shows a comparison between curves calculated at fixed viscosity values (isokoms) for different starting compositions. This type of representation allows a comparison between interpolated values minimizing possible errors due to the fitting procedure. In particular, the 10^8 and the 10^{12} Pa · s isokoms are compared. The figure shows a similar decrease of isokom temperatures with increasing volatile concentrations independent of whether water or water + fluorine are added to the rhyolitic composition. Below ~2 mol.% dissolved volatiles, the decrease of isokom temperature is more evident at high than at low viscosity, whereas for dissolved $H_2O+F_2O_{-1}$ concentrations > 2 mol.% the temperature decrease flattens and the trends at low and high viscosity are parallel.

4. DISCUSSION AND STRUCTURAL IMPLICATIONS

The results in Figures 1 to 4 show the following:

1. The viscosity of both water-bearing and F-rich water bearing samples can be parameterized by the use of a single modified VFT equation.
2. The effect that dissolved volatiles have on the viscosity of rhyolitic composition is very important. An addition of 2 mol.% volatiles produces a viscosity decrease of up to ~4 orders of magnitude even at 1200 K; increasing the volatile concentration to values above 5 mol.% causes little additional lowering of the viscosity.
3. The effect of fluorine in the dry melts is smaller than the effect of water in a fluorine-free melt. The difference in the effect on viscosity tends to increase at high volatile concentrations.

4. With the addition of water in a fluorine-rich melt, viscosities tend to converge to those of the hydrous ryholites and only a single curve can be discerned.
5. The combination of water and fluorine does not appear to influence the viscosity of highly silicic melts significantly more than the addition of water alone.

These last two very interesting observations are in agreement with the high temperature results of Baker and Vaillancourt (1995). The similarity in the behaviour of water and fluorine with respect to the rheology of silicic magmas is quite puzzling if one considers the different interactions of these two volatiles with the silicate network. As far as fluorine is concerned, debate still exists as to whether fluorine is present within the silicate framework in substitution of oxygen, or isolated from the network in the form of complexes with other cations. Studies have shown that in silica glass fluorine substitutes for oxygen forming Si-F bonds (Rau et al., 1977; Rabinovich, 1983; Yamamoto et al., 1983; Duncan et al., 1986). In this simple scheme one bridging bond is broken and replaced by two non bridging fluoride ions. In aluminosilicate glasses, the presence of aluminum and of cations in both network-modifying and charge-balancing roles complicates the structural role played by fluorine. Various mechanisms of depolymerization can be considered. The first is replacement of Si-O-(Si,Al) bridging bonds to form Si-F bonds, (Mysen and Virgo, 1985a). Other proposed fluoride complexes were combinations of either $Na^+ + F^-$ or $Al^{3+} + F^-$, increasing in concentration as a function of increasing amounts of NaF or AlF_3 in the starting glasses (Mysen and Virgo, 1985a). Different solution mechanisms have also been proposed. Mysen and Virgo (1985b) suggested, on the basis of their Raman spectroscopic data of an albitic melt, that fluorine can remove an unequal proportion of Al or Na from their charge-balancing roles in the silicate network to form complexes with either of these two cations. The remaining cation in excess is expelled from tetrahedral coordination and would become a network modifier coordinated by non-bridging oxygens. According to Mysen and Virgo (1985b), F^- shows more affinity to Na and Al with respect to Si, and it has been proposed that fluorine forms charge-balanced complexes with Na and Al outside the silicate network. By doing so, fluorine disrupts the structure leading to depolymerization of the "residual" aluminosilicate or oxide proportion of the melt (formation of Q^3-O^- and $Q^2[O^-]_2$ in addition to residual Q^4 units) leading to lower viscosities and higher diffusivities. Similar conclusions were reached by Manning et al. (1980), Kohn et al. (1991), Schaller et al. (1992), and Liu and Nekvasil (2001). In a recent NMR study of fluoride sites in aluminosilicate glasses, Zeng and Stebbins (2000) confirmed the presence of fluoride complexes with Al and Na or Ca, but they also suggest the existence of silicon-fluoride groups. Mysen et al. (in press) in their Raman and NMR study of fluorine in peralkaline and metaluminous silicate glasses, identified four different fluoride complexes in the glasses: (1) Na-F complexes (NF), (2) Na-Al-F complexes with [4]Al (NAF), (3) Na-Al-F complexes with [6]Al, and (4) Al-F complexes with both [4]Al and [6]Al. According to their study, the three latter complexes could, at least in part, be linked to the aluminosilicate network via Al-O-Si bridges.

Most of these studies have been performed on highly poly-

merized compositions, similar to those investigated in this study, and reached the conclusion that the effect of fluorine is one of depolymerizing the melt or of an overall weakening of the melt structure. In both cases, the overall effect of decreasing viscosity is easily explained. From NMR and Raman studies it is not possible to determine the type of complexes generated (i.e., Q^0 [AlF_4^-], Q^1 [e.g., $AlF_3O_{br}^-$], Q^2 [e.g., $AlF_2(O_{br})_2^-$] or Q^3 [e.g., $AlF(O_{br})_3^-$]) upon the addition of F to alkali aluminosilicate glass, or the extent of Si-F groups formed by direct O-F substitution. Therefore the extent of depolymerization induced by the addition of F in any of the mechanisms proposed above remains an unsolved question.

The structural role of water is also quite complex and still strongly debated. While it is now accepted that water depolymerizes the network of alkali silicate glasses debate still exists on the mechanism of dissolution of water in aluminosilicate glasses (Sykes and Kubicki, 1994; Kohn et al., 1998; Zeng et al., 1999; Robert et al., 2001). The common argument is that water depolymerizes the structure (rupturing the network) via reaction with bridging oxygens in the melt (Stolper, 1982; Zotov and Keppler, 1998; Zeng et al., 1999; Robert et al., 2001; Nowak and Behrens, 2001). This mode of depolymerization, according to the Adam-Gibbs theory of configurational entropy of viscous flow, would decrease the average size of the flow unit, leading to a lower viscosity.

Another interesting theory on water interaction with silicate melts was proposed by Kohn et al. (1989, 1992, 1998). According to these studies, water decreases the average strength of the T-O-T bond by exchange reaction of Na^+ for H^+ as charge balancing cations for AlO_4 tetrahedra (protonated BO), and formation of NaOH complexes. Other studies seem to indicate that both dissolution mechanisms can be viable in different water concentration and compositional (Al/Si) ranges (Sykes and Kubicki, 1993; Zeng et al., 1999; Schmidt et al., 2000).

From a rheological point of view, as viscous flow results from the breaking of T-O-T (T = Si,Al) bonds (at least for the case of highly polymerized melts) a decrease of average T-O-T bond strength (given by the protonation with H) would also result in a lower viscosity of the melt. Given these very different interactions of water and fluoride with the aluminosilicate network, one can question if the similarity of the effect on viscosity is purely coincidental. Three interesting observations have been made from the analysis of Figures 3a, 3b, and 4:

1. The effect on viscosity of fluorine in a dry-HPG8 melt is less than that of water in a fluorine-free HPG8 melt.
2. Upon addition of small amounts of water, the two curves tend to converge into one single master curve of viscosity vs. total volatile content (Figs. 3a and 3b). At total volatile content > ~10 mol.% (see in particular Fig. 3a), the effect of water and fluorine on the viscosity of aluminosilicate melts is almost indistiguishable.
3. Our choice of parameterization is supported by the fact that the above mentioned relationship is maintained if we consider the measured data obtained by examining the isokome temperature curves for both water and water + fluorine samples.

Although there are suggestions that the Al-bearing fluoride complexes could be linked to the silicate network via bridging oxygens (Liu and Tossell, in press; Mysen et al., in press), most spectroscopic studies have demonstrated that fluorine forms complexes mainly with Al (Al-F or Na-Al-F complexes) in a non-network position. By doing so, it liberates an equivalent amount of alkalies from a charge balancing role and depolymerizes the structure. It is not possible to estimate the extent of such depolymerization as the type of complexes and their relative abundances are not quantifiable through conventional NMR techniques. However, assuming that all fluorine dissolved into the melt would participate in such complexes, forming for example AlF_6^{3-} and AlF_5^{2-} species, then the amount of NBOs created by this process would be in a ratio of 1:6 (one NBO for every six fluorine atoms) or 1:5, due to the liberation of a single Na^+ ion from its charge-balancing role. The extent of depolymerization would be much less than that induced by the introduction of water (assuming a dissociation reaction like $H_2O + O^{2-} = 2OH^-$) thus explaining the smaller effect of fluorine compared to that of water on the viscosity of HPG8 melts. Upon introduction of water into the fluorine-rich melts, however, the viscosity relationships change and the viscosity data converge into one single curve. The effect of fluorine and water on the viscosity appears to become similar if not identical. It can be suggested that, by introducing water, an interaction between the two volatiles occurs such that the overall effect on the silicate structure become similar, or at least similar is their effect on rheological properties.

One possible hypothesis is that the presence of water inhibits the formation of complexes and favours a mechanism similar to that for water dissociation:

$$F_2O_{-1} + O^{2-} \Leftrightarrow 2F^- \tag{3}$$
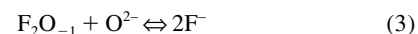
where O^{2-} represents a bridging oxygen between two tetrahedral network-former cations.

According to this reaction, fluorine substitutes for oxygen in the structure, directly depolymerizing the silicate network. One mole of F_2O_{-1} substitutes for one mole of oxygen, breaking an equivalent mole of T-O-T linkages. Fluorine would then bond directly to Si in the network, as Si-F bonds, or possibly to tetrahedrally coordinated Al. This mechanism of incorpororation of F in the melt would lead to a much stronger decrease in viscosity compared to the formation of complexes as discussed above.

This reaction is virtually identical to the water speciation reaction

$$H_2O + O^{2-} \Leftrightarrow 2OH^- \tag{4}$$

which also leads to the formation of two NBOs for each H_2O introduced into the melt.

According to these reactions, both volatiles would interact with the same number of equivalent oxygens in the melt, producing non bridging species, with different bonding characteristics but identical degree of depolymerization of the silicate framework and therefore similar effect on the viscosity. An interaction between fluorine and water is supported by the increase in solubility of water as a function of fluorine content in the melt, as previously documented (Holtz et al., 1993). Our hypothesis is supported by the density data from Dingwell et al. (1993). These authors, in their study of the effect of fluorine on the density of a haplogranitic melt, calculated the partial molar volume of F_2O_{-1} to be 14.3 cm^3 mol^{-1} at 750°C. According to

these authors the substitution of two F for one O yields approximately the volume change expected without assuming changes in the average coordination number of cations, and therefore without the need of assuming the presence of complexes with Al in octahedral coordination, contrary to the results of some NMR studies. As reported previously, NMR studies are not conclusive in defining the local configuration of F in anhydrous and hydrous melts. Several authors (Zeng and Stebbins, 2000; Liu and Tossell, in press; Mysen et al., in press), however, suggest that, together with the presence of AlF_x complexes in a non-network position, there could exist Si-F or Al-F sites which are likely to be linked to the main framework. The formation of these sites would help explain the nearly indistinguishable viscosities of H_2O-bearing and fluorine plus H_2O-bearing melts. Based on the similar roles of fluoride and water in affecting the viscosity of silicate melts, we suggest that, in the presence of water, fluoride preferentially reacts with the silicate framework by substituting for oxygen in the silicate framework and creating non bridging fluoride in the melt, rather than forming fluoride complexes with aluminium. Interestingly, the viscosity data point of Baker and Vaillancourt (1995), on a haplogranitic composition with 1.5 wt.% F and 6 wt.% H_2O, included in Figure 3b falls perfectly in line with our data. This provides corroboration of the similar role of the volatiles in affecting the rheology of high silicic magmas. Dingwell (1987b) observed that the effect of fluorine and water on the viscosity of an albite melt is greater than that predicted from a linear interpolation. In his work Dingwell suggests that an additional contribution to the total configurational entropy of viscous flow given by a configurational entropy of mixing term arising from F-OH mixing on melt structural sites could explain such an additive effect. In our case we do not observe such an effect.

The effect of temperature on the F speciation in the melt should also be taken into account when discussing the implications of melt structure for the rheology of these melts. Mysen et al. (in press), in their Raman and NMR study of the structural role of fluorine in aluminosilicate melts, showed Raman spectra recorded at temperatures from 25 to 1400°C. Based on the similarity of the high temperature spectra to their equivalent 25°C glasses, they suggested that the structure of their glasses, similar in composition to those here investigated, is not affected by temperature and that no major changes in the structural configuration occur as the materials transform from a glass to a liquid.

Regardless of the interaction mechanism between water and fluorine, the implications of our results are quite important. The existence of a single master curve of viscosity can greatly simplify the task of predicting the viscosities of volatile rich rhyolitic melts. The low viscosity of water + fluoride rhyolitic melts will significantly affect the transport properties of magmas, thereby enhancing crystallization, affecting degassing paths and controlling eruptive dynamics in volcanic systems (e.g., Villemant and Boudon, 1999; Melnik and Sparks, 1999). Models of melt segregation, transport, magma chamber convection, crystal settling and bubble ascent will have to consider the combined effects of these volatiles. The evolution of degassing crystallization-related paths observed during the succession from dome-forming to plinian activity (Villemant and Boudon, 1999) and the characterization of the transition from

explosive to effusive eruptive style (e.g., Melnik and Sparks, 1999), have been performed considering exclusively the effect of water on the crystallization path and on the rheology of such magmas. F is known to have a $D < 1$ and it is therefore expected to remain in the silicic melt and not contribute significantly to the eruptive degassing process (Villemant and Boudon, 1999).

In our study we demonstrated that the effect of fluorine is very important for determining the rheological behaviour of eruptive magmas. Most interestingly, the effect of fluorine is markedly different if a water-bearing or anhydrous melt is considered. As water degasses, the melt viscosity will increase non linearly and the path will depend on the fluorine/water content at any time. This behaviour gives rise to multiple possible paths of degassing and crystallization and can lead to drastically different eruptive styles. The viscous flow timescale and the volatile dissolution timescale (Villemant and Boudon, 1999) are intimately related and control the crystallization and degassing paths (Melnik and Sparks, 1999). We therefore believe that a characterization of the degassing processes due to the contemporaneous presence of multiple volatile components from a rheological point of view is very important to accurately determine the eruptive style and it is a critical consideration in different numerical simulation environments. From Figure 3b it can be observed that the loss of dissolved water from a fluorine-bearing rhyolitic melt will reduce the viscosity orders of magnitude less than what is expected in the case of a fluorine-free liquid. As a consequence, we expect that the different degassing behaviours of a fluorine-bearing melt will strongly change the viscosity-temperature-time paths of a evolving magma. Finally it is important to stress that the solution mechanism of fluorine may strongly depend on composition (Mysen et al., in press) and that the fluorine effect on rheological properties can also be composition-dependent. Future studies aimed at investigating the effect of different composition on the rheological behaviour of such melts are therefore recommended.

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