



# The effect of chlorine, fluorine and water on the viscosity of aluminosilicate melts



A. Baasner<sup>\*</sup>, B.C. Schmidt, S.L. Webb

Mineralogy Department, GZG, Georg-August-University Göttingen, 37077 Göttingen, Germany

## ARTICLE INFO

### Article history:

Received 14 May 2013

Received in revised form 7 August 2013

Accepted 13 August 2013

Available online 20 August 2013

Editor: D.B. Dingwell

### Keywords:

Fluorine

Chlorine

Hydrous

Aluminosilicate melt

Viscosity

Density

## ABSTRACT

The influence of 1.6 to 14.5 mol% water, 1.1 to 18.3 mol% fluorine (F) and 0.5 to 1.4 mol% chlorine (Cl) on the viscosity of peralkaline and peraluminous  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  melts as a model system for phonolites was studied with the micropenetration method within the range of  $10^9$  to  $10^{13}$  Pa s. Water and F alone and combined decrease viscosity non-linearly. With increasing F and water concentration the further addition of F and water becomes less effective in decreasing viscosity. Water decreases the viscosity of peraluminous melts more strongly than that of peralkaline melts. In the halogen-free peraluminous sample 5 mol% water decreases  $T_g^{1/2}$  (the temperature where the viscosity =  $10^{12}$  Pa s) by  $259 \pm 5$  K, while in the halogen-free peralkaline sample 5 mol% water decreases  $T_g^{1/2}$  by  $189 \pm 5$  K. Fluorine (on a mol% basis) decreases the viscosity of  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  melts less than water. In the peraluminous melts the addition of 5 mol% F decreases  $T_g^{1/2}$  by  $\sim 95$  K. In the peralkaline melt 5 mol% F decreases  $T_g^{1/2}$  by  $\sim 30$  K. However, a significant decrease in  $T_g^{1/2}$  was only observed up to a F concentration of 1.9 mol% F, another sample with 6.2 mol% F showed no further decrease of  $T_g^{1/2}$ . In all hydrous peraluminous and peralkaline samples that contain F alone or combined with Cl, the decrease of viscosity due to the addition of water is smaller than in the halogen-free samples. In a peraluminous melt with 18.3 mol% F the addition of 5 mol% water decreases  $T_g^{1/2}$  by about  $152 \pm 5$  K compared to the dry melt. In a peralkaline melt with 1.9 mol% F the addition of 5 mol% water decreases  $T_g^{1/2}$  by about  $146 \pm 5$  K compared to the dry melt. In both cases this is significantly less than for the halogen-free samples. In peralkaline melts Cl has no influence on the decrease in viscosity upon the addition of water. The effects of water and Cl on viscosity are independent of each other and add together. The effects of water and F on viscosity are not independent, which could be, in the case of the peralkaline samples related to changes in F speciation due to the presence of water.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

In nature felsic and intermediate magmas can contain several wt.% of volatiles like water ( $\text{H}_2\text{O}/\text{OH}$ ), fluorine (F) and chlorine (Cl) at magmatic pressures. The influence of volatiles on viscosity is a matter of interest, as viscosity is an important parameter for magma ascent, magma degassing, and magma fragmentation (e.g. Sparks et al., 1994; Scaillet et al., 1998; Papale, 1999; Gottsmann et al., 2009). Water is the most abundant volatile in felsic and intermediate magmas, in which melt inclusions reveal pre-eruptive  $\text{H}_2\text{O}$  contents up to 6–10 wt.% (e.g. Di Muro et al., 2006). Detailed research has investigated the influence of water on the viscosity of silicate melts across a wide range of compositions (e.g. Shaw, 1963; Dingwell et al., 1996; Romano et al., 2001; Whittington et al., 2001). In all investigated silicate melts water reduces the viscosity. This effect is stronger in polymerised melts like rhyolites than in depolymerised melts like basalts (e.g. Mysen

and Richet, 2005). The general abundance of F in intermediate and felsic magmas is very variable depending on the geological setting. Tin-granites and topaz-rhyolites can contain up to 7 wt.% F (e.g. Aiuppa et al., 2009). There are several studies, which show that F decreases the viscosity of silicate melts (Dingwell et al., 1985; Dingwell, 1989; Dingwell et al., 1993a; Dingwell and Hess, 1998; Zimova and Webb, 2007; Baasner et al., 2013; Bartels et al., 2013). Evolved peralkaline magmas can contain up to  $\sim 1$  wt.% Cl like for example phonolites (Cioni et al., 1998; Aiuppa et al., 2009) and pantellerites (Lowenstern, 1994), while other felsic and intermediate magmas usually contain lower concentrations (Aiuppa et al., 2009). There are just a few studies investigating the influence of Cl alone (Dingwell and Hess, 1998; Zimova and Webb, 2006) and combined with F (Zimova and Webb, 2007; Baasner et al., 2013) on the viscosity of silicate melts. A comparison of these studies shows that the influence of Cl, whether it decreases or increases viscosity, depends on the melt composition and temperature. Baasner et al. (2013) found in  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  melts that Cl decreases viscosity in peraluminous melts ( $\text{Al}_2\text{O}_3 > [\text{Na}_2\text{O} + \text{CaO}]$ ) and increases viscosity in peralkaline melts ( $\text{Al}_2\text{O}_3 < [\text{Na}_2\text{O} + \text{CaO}]$ ). F decreases the viscosity in both types of melts. The effects of F and Cl on viscosity are independent of each other, i.e. the single effects are additive if both halogens are present in the

<sup>\*</sup> Corresponding author at: Mineralogy Department, GZG, Goldschmidtstraße 1, 37077 Göttingen, Germany. Fax: +49 551 393863. Present address: Pétrologie expérimentale, LMV, Université Blaise Pascal, 63000 Clermont-Ferrand, France.

E-mail address: [amrei.baasner@geo.uni-goettingen.de](mailto:amrei.baasner@geo.uni-goettingen.de) (A. Baasner).

melt. Up to now there have been only three studies about the combined influence of F and water on the viscosity of silicate melts (Baker and Vaillancourt, 1995; Giordano et al., 2004; Bartels et al., 2013) and none on the combined effect of Cl, F and water on viscosity. Giordano et al., (2004) found that at volatile contents of more than 10 mol% ( $H_2O + F_2O_{-1}$ ) the combined effect of water and F on the viscosity of haplogranitic melts is undistinguishable. Bartels et al. (2013) found that in pegmatite forming melts the addition of water and fluorine decreases the viscosity less than the addition of the same amount of pure water, but with increasing water and F content the differences become less.

In this study we have investigated with the micropenetration technique within the range of  $10^9$  to  $10^{13}$  Pa s the combined effect of Cl (0.5–1.4 mol%/0.2–0.8 wt.%), F (1.1–18.3 mol%/0.1–6 wt.%) and water (1.6–14.5 mol%/0.1–4.5 wt.%) on the viscosity–temperature behaviour of peraluminous and peralkaline  $Na_2O$ – $CaO$ – $Al_2O_3$ – $SiO_2$  melts as a simple approach to natural evolved magmas like phonolites. We also look at the effect of these volatiles on density. With this study we want to answer the question, whether the effects of Cl, F and water on viscosity of  $Na_2O$ – $CaO$ – $Al_2O_3$ – $SiO_2$  melts are independent of each other or not.

## 2. Methods

### 2.1. Starting materials

The anhydrous peraluminous (ANCS) and peralkaline (NACS)  $Na_2O$ – $CaO$ – $Al_2O_3$ – $SiO_2$  starting glasses from Baasner et al. (2013) and Baasner et al. (in review), were melted in a 1 atm furnace at 1523 and 1923 K for 1–7 h from oxide and carbonate compounds, which were decarbonated at 1173 K for 12 h. The halogen-bearing peralkaline glasses were produced by adding  $NH_4Cl$  and  $NH_4F$  to the halogen-free base glass, while the halogen-bearing peraluminous melts were produced from mixtures of  $NaCl$ ,  $NaF$ ,  $CaCl_2$ ,  $CaF_2$  with oxide and carbonate compounds in the correct proportion to maintain a

constant base composition. The peraluminous glasses required melting temperatures above 1873 K, due to their high liquidus temperatures, while the peralkaline melts were already molten around 1473 K, but were produced at temperatures above 1523 K to reduce the amount of bubbles. Tables 1a–1b show the composition of the glasses in mol% and at.%. The composition of the glasses with a  $SiO_2$  concentration of ~66 mol% was chosen as a model system for phonolites. The composition was analysed on 8–14 spots per sample with a JEOL JXA-8900RL electron microprobe using a 15 kV, 15 nA beam defocused to 30  $\mu m$  (effective 21  $\mu m$ ). The composition of NACS 6.2F was measured before and after the viscosity measurements with minimum repolishing, however, no significant difference in composition was found. We also provide in Table 1a the ratio  $\gamma = (Na_2O + CaO) / (Na_2O + CaO + Al_2O_3)$  in mole fraction, which is an indicator for the degree of polymerisation of the melt. This ratio takes into account the number of Na and Ca atoms that could either charge-balance Al or create non-bridging oxygens (NBO) in the melt (e.g. Toplis et al., 1997; Webb et al., 2007). Peraluminous melts, where not enough cations are available to charge-balance all Al tetrahedra (Al tetrahedrally coordinated by 4 oxygen) and most O exist as bridging oxygens (BO) (e.g. Thompson and Stebbins, 2011), have a  $\gamma$  ratio <0.5. Peralkaline melts, which contain enough cations (Na, Ca) to charge balance all of the Al tetrahedra and to create non-bridging oxygens (NBO), have a  $\gamma$  ratio >0.5. For the present peraluminous melts  $\gamma$  is  $0.41 \pm 0.03$  and for the present peralkaline melts  $\gamma$  is  $0.65 \pm 0.01$ . Another indicator for the degree of polymerisation is the number of non-bridging oxygens per tetrahedron (NBO/T), which is zero for fully polymerised and four for fully depolymerised melts (Mysen, 1987). The calculated NBO/T ratio can become negative, if there is more Al than charge-balancing cations. The dry halogen-free peraluminous melt have a  $NBO/T = -0.08$  and the dry halogen-free peralkaline melt has a  $NBO/T = 0.24$  (Baasner et al., 2013).

Hydrous samples were produced from the nominally dry glasses under pressure. For the hydrous peralkaline samples 200–300 mg glass powder of the dry starting glasses together with 0.5, 1.0, 2.5 and

**Table 1a**

Electron microprobe (EMP) analysis as oxide components of the glass samples with the 2 $\sigma$  standard deviation normalised to 100 mol%.<sup>a</sup>

	$SiO_2$	2 $\sigma$	$Al_2O_3$	2 $\sigma$	CaO	2 $\sigma$	$Na_2O$	2 $\sigma$	F	2 $\sigma$	Cl	2 $\sigma$	$\gamma^c$
	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	[mol%]	
<i>Peralkaline</i>													
NACS <sup>d</sup>	66.62	0.52	11.28	0.34	5.23	0.12	16.87	0.22	–	–	–	–	0.66
NACS 0.7F 0.6Cl <sup>d</sup>	64.06	1.44	12.28	1.12	5.39	0.96	16.98	0.50	0.71	0.26	0.57	0.14	0.65
NACS 1.1F 1.1Cl <sup>d</sup>	64.75	0.64	11.83	0.26	5.34	0.26	15.89	0.38	1.06	0.26	1.13	0.16	0.64
NACS 2.6F 1.4Cl <sup>d</sup>	64.50	0.50	11.60	0.14	5.33	0.20	14.61	0.16	2.58	0.44	1.38	0.10	0.63
NACS 1.1Cl <sup>d</sup>	65.96	0.40	11.73	0.20	5.61	0.18	15.57	0.26	–	–	1.13	0.02	0.64
NACS 1.9F <sup>d</sup>	64.73	0.28	11.41	0.14	5.50	0.16	16.50	0.18	1.86	0.18	–	–	0.66
NACS 6.2F <sup>b,e</sup>	63.30	0.68	11.22	0.16	5.36	0.12	13.92	0.21	6.20	0.71	–	–	0.63
NACS 6.2F <sup>b,f</sup>	63.49	0.52	11.18	0.10	5.48	0.13	13.73	0.22	6.13	0.60	–	–	0.63
<i>Peraluminous</i>													
ANCS <sup>d</sup>	65.94	1.62	19.2	1.08	4.19	0.38	10.67	0.24	–	–	–	–	0.44
ANCS 0.5F 0.5Cl <sup>d</sup>	66.40	1.64	19.06	1.20	3.81	0.40	9.82	0.14	0.46	0.24	0.45	0.14	0.42
ANCS 1.2F 1.1Cl <sup>d</sup>	64.56	1.84	20.58	1.22	3.85	0.14	8.69	0.28	1.21	0.22	1.10	0.16	0.38
ANCS 2.3F 0.9Cl <sup>d</sup>	62.84	1.36	21.25	1.14	4.06	0.26	8.58	0.12	2.34	0.24	0.92	0.08	0.37
ANCS 0.6Cl <sup>d</sup>	65.89	0.54	20.32	0.30	3.73	0.12	9.43	0.50	–	–	0.63	0.04	0.39
ANCS 1.1F <sup>b,e</sup>	64.38	0.22	19.36	0.20	3.65	0.10	11.52	0.13	1.09	0.24	–	–	0.44
ANCS 3.5F <sup>b,e</sup>	63.51	1.36	18.43	0.76	3.53	0.25	11.05	0.67	3.48	0.26	–	–	0.44
ANCS 9.7F <sup>b,e</sup>	59.14	0.71	18.00	0.34	3.65	0.08	9.48	0.91	9.73	0.48	–	–	0.42
ANCS 18.3F <sup>d</sup>	53.12	0.54	16.26	0.18	3.11	0.18	9.27	0.14	18.25	0.42	–	–	0.43

<sup>a</sup> Standards were: Wollastonite = Si, Ca; Anorthite = Al; Albite = Na, Topaz = F; Halite = Cl; Sanidine = K, Cobalt oxide = Co. In all samples contaminations of  $K_2O$  (<0.1 mol%) from the  $SiO_2$  and  $Al_2O_3$  chemicals were observed.

<sup>b</sup> Doped with <0.12 mol%  $CoO$ , because samples were used also for NMR spectroscopy.

<sup>c</sup>  $\gamma = (Na_2O + CaO) / (Na_2O + CaO + Al_2O_3)$  in mole fraction is an indicator for the degree of polymerisation of the melt by taking into account the number of sodium and calcium that is either used for charge-balancing aluminium or creating non-bridging oxygens in the melt (e.g. Toplis et al., 1997; Webb et al., 2007). If  $\gamma > 0.5$  the glass is peralkaline and if  $\gamma < 0.5$  the glass is peraluminous.

<sup>d</sup> Published in Baasner et al. (2013).

<sup>e</sup> Published in Baasner et al. (in review).

<sup>f</sup> Control analysis after viscosity measurements. Analysis was not used for further evaluation.

Download English Version:

<https://daneshyari.com/en/article/6436872>

Download Persian Version:

<https://daneshyari.com/article/6436872>

[Daneshyari.com](https://daneshyari.com)