



## The effect of fluorine, boron and phosphorus on the viscosity of pegmatite forming melts

Alexander Bartels<sup>a,\*</sup>, Harald Behrens<sup>a</sup>, Francois Holtz<sup>a</sup>, Burkhard C. Schmidt<sup>b</sup>, Michael Fechtelkord<sup>c</sup>, Jaayke Knipping<sup>a</sup>, Lars Crede<sup>a</sup>, Amrei Baasner<sup>b</sup>, Nina Pukallus<sup>b</sup>

<sup>a</sup> Institut für Mineralogie, Leibniz Universität Hannover, Callinstr. 3, D-30167 Hannover, Germany

<sup>b</sup> Institut für Mineralogie, Geowissenschaftliches Zentrum der Universität Göttingen, Goldschmidtstraße 1, D-37077 Göttingen, Germany

<sup>c</sup> Institut für Geologie, Mineralogie und Geophysik der Ruhr-Universität Bochum, Universitätsstr. 150, D-44780 Bochum, Germany

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### ABSTRACT

The individual influences of F, B and P on viscosity of hydrous pegmatite forming melts have been determined experimentally. A starting glass composition (68.01 wt.% SiO<sub>2</sub>, 20.14 wt.% Al<sub>2</sub>O<sub>3</sub>, 7.73 wt.% Na<sub>2</sub>O and 4.26 wt.% K<sub>2</sub>O, Al/(Na + K) = 1.16) was doped with different amounts of F (up to 4.81 wt.%), B<sub>2</sub>O<sub>3</sub> (0.93 wt.%) and P<sub>2</sub>O<sub>5</sub> (up to 2.98 wt.%). The viscosity of melts containing 0.08 to 6.15 wt.% H<sub>2</sub>O was determined in the high and low viscosity range using the micropenetration technique and the falling sphere method, respectively. Falling sphere experiments were carried out at 200 to 650 MPa and 1173 to 1530 K. Micropenetration measurements were performed in the temperature range of 586 to 1124 K at ambient pressure.

For all compositions a large decrease of viscosity upon hydration was observed, consistent with previous findings. The results also confirm that the viscosity decreases with the addition of F at all investigated temperatures. This decrease is more pronounced at low temperature and at low water content. According to our data, P and B do not play a major role on viscous flow in water-rich systems. However, the depolymerizing effect of H<sub>2</sub>O and F is not sufficient to explain very low viscosities of complex highly fractionated melts containing H<sub>2</sub>O, F, B, P and Li (Bartels et al., 2011). Thus, although we confirm that F is clearly a fluxing agent, Li must play a crucial role in lowering the viscosity of natural pegmatite forming melts and combined effects between different constituents need to be taken under consideration.

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### 1. Introduction

According to London (2008), a pegmatite is an essentially igneous rock, commonly of granitic composition that is distinguished from other igneous rocks by its extremely coarse but variable grain size, or by an abundance of crystals with skeletal, graphic, or other strongly directional growth-habits. Pegmatites occur as sharply bounded homogeneous to zoned bodies within igneous or metamorphic host-rocks. Although there is no general model to explain all features observed in pegmatites, most of the recent studies agree on the hypothesis that pegmatites derive from the crystallization of a residual melt which is highly enriched in fluxes, volatiles and rare elements (e.g., London, 1987; London, 2008; Simmons and Webber, 2008; Nabelek et al., 2010).

In contrast to common silicate melts the residual liquids from which pegmatites crystallize, are characterized by elevated concentrations of

additional volatile constituents, including mainly H<sub>2</sub>O, F and B. In addition, elements such as P and Li can also be present in high concentrations. Bartels et al. (2011) showed that the viscosity of melts which are enriched in these elements is much lower than predicted by available viscosity models (Hui and Zhang, 2007; Giordano et al., 2008) and concluded that these volatiles play an important role on the behavior of pegmatite forming melts. Furthermore, as detailed below, it has been shown by different authors that these elements individually play a crucial role in lowering melt viscosities at least in anhydrous systems.

It is well known that the addition of water results in a strong decrease of the melt viscosity (e.g., Shaw, 1963; Hess and Dingwell, 1996; Richet et al., 1996; Scaillet et al., 1996; Schulze et al., 1996; Whittington et al., 2000, 2001; Romano et al., 2001, 2003; Liebske et al., 2003; Zhang et al., 2003; Giordano et al., 2004). Viscosity measurements on anhydrous haplogranitic melt compositions with different amounts of F, B and P (Dingwell et al., 1993) allow us to estimate the individual effect of these elements. Dingwell et al. (1993) concluded that the effect of phosphorus on haplogranitic melt viscosity is much lower than that of boron or fluorine, and that phosphorus will not significantly influence melt viscosity at least at the investigated experimental conditions. On the other hand, boron must be considered as a fluxing agent in B-rich granitic and pegmatitic systems (Dingwell et al., 1992).

\* Corresponding author. Tel.: +49 511 762 5517.

E-mail addresses: [a.bartels@mineralogie.uni-hannover.de](mailto:a.bartels@mineralogie.uni-hannover.de) (A. Bartels),

[h.behrens@mineralogie.uni-hannover.de](mailto:h.behrens@mineralogie.uni-hannover.de) (H. Behrens),

[f.holtz@mineralogie.uni-hannover.de](mailto:f.holtz@mineralogie.uni-hannover.de) (F. Holtz),

[burkhard.schmidt@geo.uni-goettingen.de](mailto:burkhard.schmidt@geo.uni-goettingen.de) (B.C. Schmidt),

[Michael.Fechteltkord@ruhr-uni-bochum.de](mailto:Michael.Fechteltkord@ruhr-uni-bochum.de) (M. Fechteltkord).

So far only a few studies are available to understand the combined effect of water and elements like F, B, P and Li and to verify whether the effects of these elements on dry silicate melt viscosity are also transferable to hydrous systems. The combined effect of H<sub>2</sub>O and F on granitic melts was studied by Baker and Vaillancourt (1995) and Giordano et al. (2004). For the investigated conditions Baker and Vaillancourt (1995) concluded that, on a molar basis, fluorine has the same effect as water. Giordano et al. (2004) confirmed that water and fluorine can have additive effects on viscosity within a hydrous system, but at low combined concentrations, the effect of F compared to water is smaller. However, the individual influences of B and P in hydrous melts are not quantitatively determined yet. In this study we present the results of an experimental study on melt viscosity that allows us to discuss the individual influences of F, B and P in hydrous highly fractionated melts in the low and high temperature range.

## 2. Experimental methods

### 2.1. Starting materials

The composition of the starting glass (PEG3-base) was chosen to be representative of a highly fractionated melt, from which a pegmatite would crystallize. The molar concentrations of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and K<sub>2</sub>O (~75.50 mol%, 13.17 mol%, 8.32 mol% and 3.01 mol%) were comparable to a composition previously investigated by Bartels et al. (2011) (composition PEG2). The PEG3-base glass composition was synthesized from a mixture of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> powder. This mixture was homogenized in an agate ball mill and fused for three hours at 1873 K in a platinum crucible placed in a 1 atm chamber furnace. To ensure homogeneity, the resulting glass was crushed and melted again for 4 h at 1873 K.

Different amounts of F, B and P were added to the PEG3-base composition. For the fluorine-bearing starting glasses, a composition with a lower Al<sub>2</sub>O<sub>3</sub> concentration than the PEG3-base composition was synthesized (two times melting at 1873 K, see above). In a second step, AlF<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> were added to the glass powder in different proportions. Thus, two glasses with similar molar proportions of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and K<sub>2</sub>O but different F contents of 1.68 wt.% (PEG3-F2) and 4.81 wt.% (PEG3-F5) were synthesized. The nominal F-contents of the glasses were ~2.00 and ~6.00 wt.%. Although fusion time was reduced to two hours the batches lost 0.32 and 1.19 wt.% F, respectively.

For the boron- and phosphorus-bearing glasses, PEG3-B, PEG3-P2 and PEG3-P3, the PEG3-base composition was doped with either H<sub>3</sub>BO<sub>3</sub> or NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and homogenized in an agate ball mill. Afterwards the doped glass powders were fused twice at 1873 K for 3 h in the case of the boron-bearing melt and for 2 h in the case of the phosphorus-bearing melts.

The glass compositions were analyzed by electron microprobe (at least 15 analyses on two or three glass pieces). The compositions

of PEG3-base, PEG3-F2, PEG3-F5, PEG3-B, PEG3-P2 and PEG3-P3 together with the PEG2 composition from Bartels et al. (2011) are given in Table 1. All glasses were found to be homogeneous (see standard deviations in Table 1). The aluminum saturation index (A.S.I.: molar ratio Al/(Na + K)) varies between 1.11 and 1.19. The PEG2 composition has an A.S.I. of 1.23. However, when Li is taken into account, the composition PEG2 is peralkaline (Al/(Na + K + Li) = 0.92).

### 2.2. Falling sphere method

The melt viscosity at high pressure and temperature was measured with the falling sphere method (e.g. Shaw, 1963; Schulze et al., 1996; Holtz et al., 1999; Vetere et al., 2006) using the procedure described by Bartels et al. (2011). For each composition, glass cylinders with water contents ranging from 1 to 6 wt.% were synthesized in an internally heated pressure vessel (IHPV) at 1373 K, 300 MPa and run durations from 17 to 22 h, except for PEG3-P2 with only one cylinder containing ~6 wt.% water. All glasses were optically homogeneous and microscopically free of crystals and bubbles except for PEG3-base-1 and PEG3-base-3 in which some crystals were observed. These crystals were too small for microprobe analyses and were most likely aluminosilicates because of the excess of aluminum in the PEG3-base composition. In any case, the amount of crystals was so low (<3 vol.%) that it should not have affected the viscosity determination.

The falling sphere setup is composed by a large glass cylinder with a Pt-horizon as immobile marker on bottom and one or two noble metal spheres on top. The distance of the sphere(s) with respect to the marker is measured before and after the viscosity experiment to determine the settling distance for given heating time. Pt spheres with radii ranging from 83.5 to 150 μm and Pd spheres with radii ranging from 188 to 194 μm were used (Table A.1 (appendix)). In samples PEG3-F5-1 and PEG3-B-6 two spheres were placed on top of the cylinder in distance of approx. 2 mm. This allows determining two viscosity values in a single experiment. The falling sphere experiments were performed in an IHPV in the temperature range of 1173 to 1530 K at pressures between 200 and 650 MPa. The heating rate was always 80 K/min. The experimental duration varied from 96 h (PEG3-F5-1c) to 15 min (PEG3-base-6c and PEG3-F5-6b, uncorrected values) (Table A.1). Except for experiment PEG3-B-6d, the variation of temperature along the samples was less than 10 K. The measured variation in T within an experiment (Table 2a) was included in the error calculation of the viscosity. In the case of sample PEG3-B-6d a temperature variation of approximately 20 K was observed, leading to a very high relative error for viscosity calculation of around 21%.

### 2.3. Micropenetration technique

The melt viscosity at low temperatures was measured using the micropenetration technique. Water-bearing samples were synthesized

**Table 1**  
Composition of the starting glasses.

Oxides	PEG2 [wt.%]	PEG3-base [wt.%]	PEG3-F2 [wt.%]	PEG3-F5 [wt.%]	PEG3-P2 [wt.%]	PEG3-P3 [wt.%]	PEG3-B [wt.%]
SiO <sub>2</sub>	59.73 (0.13)	68.01 (0.72)	66.02 (0.42)	64.79 (0.51)	66.57 (0.90)	65.55 (1.00)	67.42 (0.43)
Al <sub>2</sub> O <sub>3</sub>	19.75 (0.13)	20.14 (0.25)	20.01 (0.38)	19.45 (0.22)	19.38 (0.25)	19.51 (0.35)	19.66 (0.30)
Na <sub>2</sub> O	7.25 (0.1)	7.73 (0.20)	8.11 (0.24)	7.93 (0.14)	7.35 (0.37)	7.37 (0.42)	7.47 (0.48)
K <sub>2</sub> O	3.82 (0.02)	4.26 (0.05)	4.16 (0.07)	4.11 (0.08)	4.10 (0.07)	4.00 (0.07)	4.11 (0.06)
F	5.46 (0.01)		1.68 (0.25)	4.81 (0.28)			
P <sub>2</sub> O <sub>5</sub>	2.46 (0.21)				2.20 (0.32)	2.98 (0.11)	
Li <sub>2</sub> O	1.68 (0.01)						
B <sub>2</sub> O <sub>3</sub>	2.75 (0.01)						0.93 (0.05)
2F=O	-2.3		-0.71	-2.03			
total	100.6	100.14	99.27	99.06	99.60	99.41	99.59
A.S.I.	1.23	1.16	1.12	1.11	1.17	1.19	1.17
A.S.I. <sub>Li</sub>	0.91						

Notes: Values are mean of at least 15 electron microprobe analyses. 1σ standard deviation is given in parentheses. A.S.I. molar ratio of Al/(Na + K); A.S.I.<sub>Li</sub> molar ratio of Al/(Na + K + Li). Additionally PEG2 from Bartels et al. (2011) is shown.

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