



# The effect of lithium on the viscosity of pegmatite forming liquids

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## ABSTRACT

Viscosity experiments were conducted to investigate the effect of Li<sub>2</sub>O on the viscosity of pegmatite forming melts and the possible difference to K<sub>2</sub>O. The individual effects of Li<sub>2</sub>O and K<sub>2</sub>O on melt viscosity were investigated by adding the same molar proportion of both components to a starting composition representing natural pegmatite forming melts. The viscosity experiments on hydrous melts (~1 to ~6 wt.% H<sub>2</sub>O) were carried out in the low temperature range at ambient pressure using the micropenetration technique and in the high temperature range at 200–300 MPa pressure using the falling sphere method.

The addition of Li<sub>2</sub>O and K<sub>2</sub>O results in a decrease of melt viscosity and, on a molar basis, the effect of Li<sub>2</sub>O is comparable to that of K<sub>2</sub>O. Viscosity-related properties such as activation energy of viscous flow, melt fragility and glass transition temperature are affected in a similar way by both alkali oxides. The observed effects of alkalis on the viscosity of melt are smaller when compared to an equal molar amount of OH<sup>-</sup> groups at low water content but become equal with increasing water content. Finally, it is shown that the low viscosity of pegmatite forming melts can only be explained by the combined effects of H<sub>2</sub>O, F and of non-charge balancing alkalis.

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## 1. Introduction

Lithium is a rare element in common magmatic systems and the crustal average for Li is only 20 ppm (Mason and Moore, 1982). In contrast, some highly fractionated pegmatitic systems are enriched in Li<sub>2</sub>O, reaching weight percent levels as indicated by the presence of lithium minerals such as spodumene (LiAlSi<sub>2</sub>O<sub>6</sub>) or petalite (LiAlSi<sub>4</sub>O<sub>10</sub>). In these high concentrations, lithium will become an important element governing crystallisation and melt properties (Maneta and Baker, 2014). For example in the systems Ab–Qz–H<sub>2</sub>O (NaAlSi<sub>3</sub>O<sub>8</sub>–SiO<sub>2</sub>–H<sub>2</sub>O) and Ab–Or–Qz–H<sub>2</sub>O (NaAlSi<sub>3</sub>O<sub>8</sub>–KAlSi<sub>3</sub>O<sub>8</sub>–SiO<sub>2</sub>–H<sub>2</sub>O), the addition of lithium (1–4 wt.% Li<sub>2</sub>O) depresses liquidus temperatures by approximately 80°–90 °C at 100–200 MPa, and shifts minimum melt compositions within Ab–Or–Qz projections towards the Ab–Or tie-line (e.g. Wyllie and Tuttle, 1964; Stewart, 1978; Martin, 1983; Martin and Henderson, 1984).

According to the model proposed by London (2008), fast crystallisation from undercooled aluminosilicate melts explains the typical textures observed in pegmatites. Thus, one of the most important properties controlling the crystallisation of a pegmatite body is the melt viscosity, which in turn controls diffusivity of cations. Pegmatites

are water-rich systems (e.g., Nabelek et al., 2010) and it is well known that melt viscosity is strongly affected by water. There are a large number of viscosity experiments in water-rich systems and several models can be used to predict accurately the effects of water on viscosity of felsic melts (e.g. Hui and Zhang, 2007; Giordano et al., 2008). Since pegmatite forming liquids are often highly enriched in elements like F, B, P or Li, the understanding of how these elements are influencing the rheology of melts is essential. In particular, the depolymerising effects of excess alkalis, fluorine and other fluxing elements are always lower in hydrous melts when compared to dry melts. Thus, the role of Li and other alkalis on viscosity of hydrous melts needs to be quantified to interpret the formation of pegmatites. Bartels et al. (2011) note that the viscosity of a hydrous synthetic melt, containing F, B, P and Li, can be more than 4 log units lower than that of a rhyolitic melt containing similar amounts of water. Additionally, Bartels et al. (2013) investigated the individual influences of H<sub>2</sub>O, F, B and P on the viscosity of pegmatite forming liquids. They conclude that besides water, fluorine is the main element influencing melt viscosity and that P and B do not play a major role on viscous flow in water-rich pegmatitic systems. However, according to their observations, the depolymerising effect of H<sub>2</sub>O and F is not sufficient to explain very low viscosities of complex pegmatite forming melts containing H<sub>2</sub>O, F, B, P and Li (Bartels et al., 2013). Thus, Li must play a crucial role in lowering the viscosity of natural highly evolved melts and combined effects between different constituents need to be taken into consideration.

In this study, melt viscosity data are presented, allowing us to discuss the influence of lithium in hydrous pegmatite forming melts in

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the low and high temperature ranges. Additionally, the difference between the effects of Li and K on melt viscosity in such systems is discussed.

## 2. Experimental methods

### 2.1. Starting material

The synthetic melt composition PEG3-base from Bartels et al. (2013), which is free of Li and other fluxing elements, was chosen as a reference material for the experiments presented here. The 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 in that composition are ~75.50 mol%, 13.17 mol%, 8.32 mol% and 3.01 mol%, respectively (Table 1). The lower proportion of SiO<sub>2</sub> when compared to normal granitic systems, takes into account that the increased amount of fluxing elements in highly evolved systems will shift the haplogranitic minimum composition towards the albite–orthoclase tie-line (Manning, 1981; Pichavant, 1981; London et al., 1993).

The starting compositions (PEG3-K and PEG3-Li, Table 1) were synthesised to determine to which extent the excess of individual alkalis affects the viscosity of the melt. For both compositions, the same molar proportion of either K<sub>2</sub>O or Li<sub>2</sub>O was added to the PEG3-base composition. To be able to compare the results of this study with the data for the synthetic pegmatite-forming melt composition PEG2 (Table 1) investigated by Bartels et al. (2011), the aluminium saturation index (A.S.I.<sub>Li</sub> = Al/(Na + K + Li)) after the addition of alkalis was chosen to be identical in all compositions (A.S.I.<sub>Li</sub> ~ 0.9). The glasses were synthesised from a mixture of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and/or Li<sub>2</sub>CO<sub>3</sub> powders. These mixtures were homogenised in an agate ball mill or a swing mill and fused for 2 h at 1873 K in a platinum crucible, placed in a 1 atm. chamber furnace. To ensure homogeneity, the resulting glasses were crushed and melted again under same conditions.

The final glass compositions (Table 1) were analysed by an electron microprobe (Cameca SX-100; at least 15 analyses on two or three glass pieces) and the bulk Li content was determined by Actlabs/Canada using sodium peroxide fusion ICP-MS.

All glasses were found to be homogeneous (see standard deviations in Table 1). The molar Al/(Na + K + Li) ratios are 0.90 and 0.88 for PEG3-K and PEG3-Li, respectively which is comparable to the A.S.I.<sub>Li</sub> of 0.91 for the PEG2 composition (Bartels et al., 2011). The small differences in A.S.I.<sub>Li</sub> in the three peralkaline compositions are probably caused by the loss of small amount of Li and K during fusion of the glasses.

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

Oxides	PEG2 [wt.%]		PEG3-base [wt.%]		PEG3-K [wt.%]		PEG3-Li [wt.%]
SiO <sub>2</sub>	59.73	(0.13)	68.01	(0.72)	64.39	(0.62)	66.92 (0.47)
Al <sub>2</sub> O <sub>3</sub>	19.75	(0.13)	20.14	(0.25)	19.31	(0.29)	19.67 (0.28)
Na <sub>2</sub> O	7.25	(0.1)	7.73	(0.20)	7.89	(0.27)	7.95 (0.15)
K <sub>2</sub> O	3.82	(0.02)	4.26	(0.05)	7.93	(0.15)	4.20 (0.07)
F	5.46	(0.01)	n.d.		n.d.		n.d.
P <sub>2</sub> O <sub>5</sub>	2.46	(0.21)	n.d.		n.d.		n.d.
Li <sub>2</sub> O	1.68	(0.01)	n.d.		n.d.		1.36 (0.01)
B <sub>2</sub> O <sub>3</sub>	2.75	(0.01)	n.d.		n.d.		n.d.
2 F = O	-2.3						
total	100.6		100.14		99.52		100.1
A.S.I. <sub>Li</sub>	0.91		1.16		0.90		0.88

Values are mean of at least 15 electron microprobe analyses; n.d.: not determined.

1σ standard deviation is given in parentheses.

Analytical conditions: 15 keV acceleration voltages, 4 nA beam current, beam diameter 20 μm. Counting time 4 to 10 s.

A.S.I.<sub>Li</sub> molar ratio of Al/(Na + K + Li).

PEG2 from Bartels et al. (2011) and PEG3-base from Bartels et al. (2013) are given for comparison.

### 2.2. Sample preparation for the 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). The experiments were performed in the temperature range of 1223 to 1531 K at pressures between 200 and 300 MPa (Table 2) using an internally heated pressure vessel (IHPV) at the Institute for Mineralogy, Leibniz University of Hannover, Germany. The exact procedure of the falling sphere method is described by Bartels et al. (2013). Hence, only the main principles of this method are described in the following.

The falling sphere method involves the synthesis of a water-bearing glass cylinder of approximately 30 mm in length and 6 mm in diameter containing a Pt-horizon as immobile marker and noble metal spheres as probes. This setup is brought to experimental conditions, and the effective settling distance of the spheres relative to the Pt-horizon is measured before and after the experiment. In this study, three cylinders with water contents of approximately 1, 3 and 6 wt.% H<sub>2</sub>O were synthesised for the PEG3-K and PEG3-Li compositions. For the falling sphere experiments, Pt spheres with radii ranging from 84 to 144 μm were used (Table A.1). In the cases of samples PEG3-K-6 and PEG3-Li-3, two spheres were placed within one cylinder. This allows determining two viscosity values within a single experiment.

### 2.3. Sample preparation for the micropenetration technique

The melt viscosity at low temperatures was measured using the micropenetration technique. Water-bearing samples were synthesised in an IHPV from the GZG (Geowissenschaftliches Zentrum der Universität Göttingen) in a temperature range of 1473 to 1523 K and pressures between 100 and 204 MPa. Heating was accomplished within 30 to 60 min and the experimental duration varied from 70 to 90 h. The water contents ranged from almost dry to ~4 wt.%. After synthesis, the samples were cut in 1 mm thick slices and polished on both sides. The micropenetration technique involves determining the rate of a moving sapphire sphere (diameter: 1 mm) under a fixed load into the sample surface (e.g. Webb et al., 2004). These measurements are conducted in a vertical dilatometer (Netzsch TMA 402) at the GZG. The sample is placed in a ceramic holder. The sapphire sphere is being held in the middle of the sample by a ceramic rod which is connected to a weight pan. The metal connection of the ceramic rod and the weight pan acts as the core of a calibrated linear voltage displacement transducer (LVDT). After the whole setup is inserted into a tube furnace and brought to experimental temperature, a weight is placed onto the weight pan and the movement of the sphere into the sample is recorded by the LVDT. The temperature is measured by Pt/Pt<sub>90</sub>Rh<sub>10</sub> thermocouples, which are calibrated against the melting temperatures of bismuth, zinc, aluminium and silver.

## 3. Determination of water contents in glasses

### 3.1. Karl–Fischer–Titration

The water contents of all synthesised hydrous glasses for micropenetration and falling sphere experiments and the falling sphere samples after the final viscosity experiments were determined by pyrolysis and the subsequent Karl–Fischer–Titration (KFT) (Behrens et al., 1996). An increment of 0.10 wt.% was added to the measured values to account for an incomplete dehydration of the samples during the analysis (Leschik et al., 2004). To check for homogeneous distribution of H<sub>2</sub>O, especially within the water-poor samples (samples with ~1 wt.% H<sub>2</sub>O), analyses from both ends of these cylinders were performed. The resulting values do not significantly differ from each other and mean values of both measurements are given in Table 2 for pre-experimental water content.

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