Viscosity of K$_2$TiSi$_4$O$_{11}$ melt at high pressure

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The viscosity of alkali titanosilicate melt with a composition of K$_2$TiSi$_4$O$_{11}$ (KTS4) was measured at pressures up to of 7.41 GPa and temperatures up to of 2133 K. The aim of this study is to determine the effect of pressure on the viscosity change and to estimate the relation between structural change and the viscosity change under high pressures. The viscosity decreased up to 3.30 GPa, whereas it increased from 3.30 to 7.41 GPa. The viscosity change above 3.30 GPa is likely caused by the dominance of six-fold coordinated titanium.

Keywords: Viscosity, Magma, Alkali titanosilicate melt, K$_2$TiSi$_4$O$_{11}$, X-ray radiography

INTRODUCTION

The viscosity of silicate melt controls many volcanic processes, including rates of melt extraction, ascent, and magma mixing. Therefore, the viscosities of various silicate melts have been extensively measured under high pressures (e.g., Suzuki et al., 2002; Sakamaki et al., 2013). However, previous studies were conducted on aluminosilicate melts in simple systems and terrestrial magmas. Remarkably little is known about the viscosity of titanosilicate melt under high pressure.

Ti is a minor component in terrestrial magmas, but a major component in lunar magmas with concentrations of up to 16.4 wt% (e.g., Delano, 1986). Therefore, there is a possibility that titanium plays an important role in the physical properties of lunar magmas. Ti$^{4+}$ in silicate melts occurs in four-, five-, and six-fold coordination, and the physical properties of Ti-bearing silicate melts can be complex functions of temperature, titanium concentration, and chemical composition (Mysen and Richet, 2018). Because the viscosity of silicate liquid depends on the degree of polymerization (Wang et al., 2014), changes in coordination of the network-forming cations under pressure may affect the changes in viscosity.

In this study, the viscosity of a Ti-bearing silicate melt with a composition of K$_2$TiSi$_4$O$_{11}$ (KTS4, i.e., K$_2$O·TiO$_2$·4SiO$_2$) was measured under high pressures and temperatures via the falling-sphere method using X-ray radiography. A simple system was adopted to determine the effect of pressure on the viscosity change and to estimate the relation between structural change and the viscosity change under high pressures.

EXPERIMENTAL METHODS

I performed in situ falling-sphere viscometry by using the MAX-III high pressure apparatus at the BL-14C2 and AR-NE7A at the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. This experimental procedure has been reported elsewhere (Suzuki et al., 2011; Suzuki, 2018, 2019). Glass with a KTS4 composition was synthesized from a mixture of dried powders of reagent-grade oxides (SiO$_2$ and TiO$_2$) and carbonate (K$_2$CO$_3$). This mixture was melted at 1473 K for 5 min after decarbonation for 12 h at 973 K. To ensure homogeneity, grounding and melting were repeated three times. A Kawai-type apparatus driven by the MAX-III press was used for all experiments. Eight tungsten carbide anvils with cubic edge lengths of 22 mm and 12 mm truncation were used as second-stage anvils. The design of the cell assembly and the experimental procedure have been reported in previous studies (Suzuki et al., 2002, 2005, 2011). A glass sample was loaded into the Mo container with a Pt sphere. Based on electron probe analysis of the recovered samples using JEOL JXA8800M, molybdenum contamination in the melts was not observed. X-ray diffraction of a pressure marker (MgO) was detected through the energy-dispersive method using a pure-Ge solid state detector soon after the observation of the sphere falling. The pressure under the experimental conditions was determined using the equation of state of...
MgO (Jamieson et al., 1982). Pressure was initially applied at room temperature. The temperature was gradually increased to 1273 K, and the pressure was measured to determine the target temperature. The temperature was increased at 100 K/min to about 50 K below the melting point, and the sample was then rapidly heated—within a few seconds—to the desired temperature. An X-ray radiography movie image was obtained using an X-ray charge-coupled-device camera with a YAG:Ce fluorescence screen. The settling velocity of the Pt sphere was measured in the recorded X-ray radiographic images. The density of the KTS4 composition melt was calculated using the partial molar volume data at ambient pressure (Lange and Carmichael, 1987) and compressibility (Kress and Carmichael, 1991). Pt was used as the sphere material, and its density under the experimental conditions was calculated using the equation of state proposed by Holmes et al. (1989). Stokes’ equation with Faxén’s correction was used to calculate the viscosity (e.g., Suzuki, 2018, 2019). The errors in the viscosity values were mainly derived from uncertainties in X-ray camera resolution, terminal velocities of the falling spheres, sphere diameter, calculated density, and the Faxén’s correction factor for the container wall.

RESULTS AND DISCUSSION

The experimental conditions and results are shown in Table 1. The experiments were carried out at pressures of 1.27–7.41 GPa and temperatures of 1583–2133 K. The viscosity of the KTS4 melt at ambient pressure was calculated using data from Bouhifd et al. (1999). To calculate the viscosity using Stokes’ equation, the density of the KTS4 melt at the experimental conditions was necessary. However, to my knowledge, there are no reliable data on KTS4 melt density at high pressures and temperatures. In this study, the density of the KTS4 melt under the experimental conditions (ρh in Table 1) was calculated using the partial molar volume and its temperature dependence at ambient pressure (Lange and Carmichael, 1987) and compressibility (Kress and Carmichael, 1991). Because only the compressibility of the partial molar volume was used in the calculation, the density (ρh) was overestimated. In this study, ρh was adopted as the upper density limit. Because pressure was applied, the density at the experimental conditions was higher than that at ambient pressure. The KTS4 melt density at ambient pressure (ρ0 in Table 1) using the partial molar volume (Lange and Carmichael, 1987) was assumed to be the lower density limit. The KTS4 melt density (ρm, shown in Table 1 and used for the calculation of viscosity) was expected to be between ρh and ρ0.

The viscosities of the KTS4 melt are plotted with the viscosities of the K2Si4O9 (KS4) melt (Dickinson et al., 1990) in Figure 1. Suzuki et al. (2011) measured the viscosity of melt with jadeite composition and observed no significant changes in the activation energy for viscosity under pressure. Therefore, in Figure 1, the isothermal lines are drawn assuming that the activation energy on compressibility (Kress and Carmichael, 1991). Because only the compressibility of the partial molar volume was used in the calculation, the density (ρh) was overestimated. In this study, ρh was adopted as the upper density limit. Because pressure was applied, the density at the experimental conditions was higher than that at ambient pressure. The KTS4 melt density at ambient pressure (ρ0 in Table 1) using the partial molar volume (Lange and Carmichael, 1987) was assumed to be the lower density limit. The KTS4 melt density (ρm, shown in Table 1 and used for the calculation of viscosity) was expected to be between ρh and ρ0.

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viscosity at high pressures is the same as that at ambient pressure (Suzuki et al., 2011; Suzuki, 2019). This study showed that the viscosity of the KTS4 melt decreased with increasing pressure and reached a minimum at around 3.3 GPa. Viscosity increased above 3.3 GPa.

Neutron diffraction studies of K$_2$TiSi$_6$O$_{18}$ (KTS2, K$_2$O·TiO$_2$·2SiO$_2$) glass and melt at ambient pressure have indicated that Ti$^{4+}$ is predominantly in a five-fold coordination (Yarker et al., 1986; Cormier et al., 2001). These studies further indicated that TiO$_3$ consists of one short and four long Ti–O bonds. Larsen et al. (2007) investigated the structure of KTS2 glass using $^{17}$O nuclear magnetic resonance (NMR) spectra and revealed the absence of Ti–O–Ti linkage. The authors suggested that TiO$_3$ links with SiO$_4$ in the KTS2 glass at ambient pressure. However, little is known about the structure of KTS4 melt under pressure. Structural studies of high-pressure silicate liquids and glasses are crucial for understanding the viscosity under pressure. In particular, it is important to know how the networks in melt change with compression.

Paris et al. (1994) carried out an X-ray absorption near edge structure study of KTS4 glasses quenched at pressures of 0.5–3.0 GPa. The average coordination number of titanium was 4.8 in glass quenched at ambient pressures of 0.5 GPa. The coordination number increased to 5.8 at 3.0 GPa. The average coordination number of titanium further increased to 5.8 at 3.0 GPa. Therefore, six-fold coordinated titanium became dominant at pressures above 3.0 GPa. A minimum viscosity at high pressures has also been identified in a Ca$_3$Al$_2$Si$_6$O$_{18}$ melt (Allwardt et al., 2007). Allwardt et al. (2007) also performed a $^{27}$Al magic angle spinning NMR study of glasses quenched from melts at high pressures and suggested that the minimum viscosity was related to the formation of high-coordinated Al. In the present study, the minimum viscosity of the KTS4 melt occurred around at 3.3 GPa. This behavior suggests that the network is shredded by the coordination change of titanium under high pressure.

Dickinson et al. (1990) carried out viscosity measurements of KS4 composition melts at pressures of up to 2.4 GPa at 1200 °C. The authors showed that the viscosity decreases linearly with increasing pressure. The structures of KS4 glasses quenched at high pressures were investigated using $^{29}$Si NMR spectra (Stebbins and McMillan, 1989; Allwardt et al., 2004; Stebbins and Bista, 2019). Stebbins and McMillan (1989) reported that the amounts of five- and six-fold coordinated silicon in the KS4 composition glass quenched at 1.9 GPa were 0.4 and 0.2%, respectively. NMR spectra of KS4 glass quenched at 5.7 GPa indicated that 5% of five- and 5% of six-fold coor-

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