Densification mechanisms of haplogranite glasses as a function of water content and pressure based on density and Raman data

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Abstract

This study investigates the effect of pressure (1 atm–2.5 GPa) and water (0.15, 2.7, 3.6 and 5.2 wt% H_2O) on the network structure of alkali-rich alumino-silicate glasses synthesized at 1000 °C. Density increases linearly with pressure in the water-poor composition, while in the water-rich glasses and above 1.5 GPa densification decreases with pressure. Raman data suggest that several structural changes follow one upon another with increasing pressure and water content. The almost dry glasses undergo large modifications of the network ring structure with pressure, namely a decrease in average T–O–T angle, change in ring size statistics and possibly an increasingly homogeneous distribution of Al- and Si-rich domains at high pressure. Water dissolution favors a homogenization of ring sizes at low pressures. Pressure essentially induces a decrease in the average intertetrahedral angle and, above 1.5 GPa, a possible redistribution of Al/Si-rich regions. Pressure induces an increase in O–H bonding but decreases the O–H bond strength. The observed structural modifications are consistent with the decreasing net effect of pressure on viscosity as temperature and water increase through variation of the activation volume of viscosity.

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1. INTRODUCTION

The structural evolution of alkali and silica rich melts and glasses with pressure and dissolved total water contents (H_2O_T) is crucial for understanding the physical–chemical properties of silicic (rhyolitic, phonolitic or trachytic) magmas at crustal depths and, eventually, for modelling intrusive and eruptive processes. Considerable effort has been devoted to interpreting changes of bulk properties such as density and viscosity in Si-rich alumino-silicate melts in terms of short- and medium-range structural variations (Mysen et al., 1980a; Mysen and Virgo, 1986; Matson et al., 1986; Lange and Carmichael, 1987, 1989; Okuno et al., 1996; Zotov and Keppler, 1998; Zotov, 2003; Allwardt et al., 2007). Pressure, temperature and dissolved water content play contrasting roles on liquid structural rearrangement and physico-chemical properties. Density decreases with increasing temperature and bulk water content due to thermal expansivity and to the large molar volume of "water" (sum of hydroxyl OH and molecular water H_2O Ochs and Lange, 1999; Richet et al., 2000). In haplogranite melts, water has a major effect on melt and glass properties and its solubility is a positive function of pressure, alkali ratio (Na/K) and, subordinately, of temperature (Holtz et al., 1992; Acosta-Vigil et al., 2005; Ardia et al., 2008). Conversely, compression results in network densification and a linear increase in bulk

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density (1 atm–2 GPa, Kushiro, 1978; 2.6–5.3 GPa, Suzuki et al., 2002). Similarly, the viscosity of silicic melts is drastically affected by temperature, water-content and pressure (Shaw, 1963; Hess and Dingwell, 1996; Dingwell et al., 1996; Ardia et al., 2008; Giordano et al., 2008a; del Gaudio and Behrens, 2009; Hui et al., 2009). At high temperature, both the first compression applied to haplogranite melts and the first dissolution of H_2O induces a stronger decrease in viscosity than subsequent increments (Kushiro, 1978; Schulze et al. 1996; Behrens and Schulze, 2003; Ardia et al., 2008). On the other hand, pressure increases the viscosity of hydrous rhyolites at low temperatures (Hui et al., 2009). Structural models designed to interpret the effect of pressure on the properties of alkali-bearing alumino-silicate melts must therefore explain the simultaneous linear density increase and the non-linear evolution of viscosity with increasing pressure at varying water content.

Kushiro (1978) interpreted the structural evolution of albitic and silica-rich melts with increasing pressure by analogy to the structural changes observed in crystals. In this model, a gradual change of Al-coordination from IV to VI is proposed at pressures below 1.0 GPa. Alternatively, Sharma et al. (1979) suggested that the observed decrease in melt viscosity with pressure relates to ordering or reorganization of the three-dimensional network. More specifically, Seifert et al. (1982) and Mysen et al. (1983) proposed that the decrease in average T–O–T angles with pressure determines the counterintuitive decrease in viscosity with increasing density. Hochella and Brown (1985) summarized the investigations on albitic to jadeitic compositions and only report minor changes in Raman spectra up to 4.0 GPa thus discarding the possibility that Al-coordination changes would be responsible for the observed melt densification and viscosity changes. This has been further confirmed by more recent Raman spectroscopy studies (Okuno et al., 1999; Reynard et al., 1999; Shimoda et al., 2004; Champagnon et al., 2008), which investigate the effect of pressure on water-poor natural obsidians and dry synthetic glass analogues (silica, anorthite and albite glass compositions) between 1 atm and 25 GPa. Spectral analysis suggests that the densification process operates through two main mechanisms, a decrease in the intertetrahedral angles (T–O–T), and a re-organization of the connected rings forming the alumino-silicate network.

In this study, we investigate the effect of pressure on the structure of water-poor (H_2O_T: 0.15 wt%) and water-rich (H_2O_T: 2.7–5.2 wt%) haplogranite glasses ($Qz_{36}Ab_{37}Or_{27}$) combining density measurements and Raman spectroscopy on isobarically quenched glasses from 1000 °C at five different pressures (0.5, 1.0, 1.5, 2.0 and 2.5 GPa). High pressure glasses are compared to a reference water-poor glass relaxed at 1 atm. Because of similarities in composition, our vibrational data are interpreted by comparison with the extensively investigated $(Na,K)AlO_2$–SiO_2 system (Mysen et al., 1980a; Seifert et al., 1983) with special reference to silica (Champagnon et al., 1996; Okuno et al., 1999; Champagnon et al., 2008) and albite composition glasses (Kushiro, 1978; Romano et al., 2001; Suzuki et al., 2002; Behrens and Schulze, 2003; Poe et al., 2006)

whose structure and physical properties are known over a broad range of pressures and temperatures.

Quenching is presumed to freeze the densest configuration attained at high pressure and the water-speciation (OH/H_2O_m ratio) (Hui et al., 2008) at the glass transition (T_g), while the purely elastic part of the deformation is eventually released during decompression. In glasses, it has been proposed that water speciation does not depend on pressure (Richet et al., 2000). This conclusion has been recently questioned for rhyolites by Hui et al. (2008), who observed a variation of water speciation with quench pressure and employed the speciation to calculate viscosities at various pressures (Hui et al., 2009). As we will show, our data suggest that densification involves a set of mechanisms, which change with increasing pressure and water content and affect the molar volume of H_2O, at least at pressures above 1.5 GPa.

2. GLASS SYNTHESIS AND QUENCH CONDITIONS

2.1. Synthesis

HGG haplogranite glasses ($Na_{0.56}K_{0.38}Al_{0.95}Si_{5.19}O_{12.2}$) are silica-rich (Si/(Si + Al) = 0.85) and slightly peralkaline ((Na + K)/Al = 1.04; Na/K = 1.5). The starting glasses with different water contents were synthesized in a hot isostatic press (HIP) and one of those was dehydrated using a concentric cylinder technique (Ardia et al., 2008). The resulting four compositions are from the same batches used for viscosity measurements at high pressure and temperature (Ardia et al., 2008), for elasticity measurements using Brillouin spectroscopy and for ^{27}Al NMR studies (Malfait et al., 2011, 2012). Samples HGG0, HGG3, HGG4 and HGG5 correspond to haplogranite glasses with total dissolved water contents of 0.15, 2.7, 3.6 and 5.2 wt%, respectively. Water contents of the bulk glasses were determined by Karl–Fischer titration at ETH Zurich (KFT, Behrens and Stuke, 2003). Glass homogeneity was confirmed by micro-FTIR and micro-Raman analyses in Paris (Di Muro et al., 2006a) for water content, and with electron microprobe (JEOL JXA 8200) analyses of bulk compositions at ETH Zurich (Ardia et al., 2008). The glass samples for spectroscopic investigation were prepared in an end-loaded piston cylinder by melting the starting glasses from a previous synthesis (Ardia et al., 2008) in Pt capsules at various pressures (0.5–2.5 GPa) and a constant temperature of 1000 °C. Complete homogenization and relaxation were assured by keeping the melts at run condition for 12 h for water-rich samples (HGG3, 4, 5) and for 2 h for the nearly anhydrous synthesis HGG0, because the synthesis using concentric cylinder already ensures homogenization (Ardia et al., 2008). Samples were isobarically quenched by manually maintaining pressure. Although small pressure drops cannot be excluded, they cannot be precisely evaluated and are assumed to be similar for each run. The cooling rate of the end-loaded piston cylinder is 150–200 °C/s and is assumed to be constant for each experiment. Recovered glasses were optically examined and minor quench crystallization was identified at the rims of some water-rich glasses close to the glass–capsule interface. Thin glass chips