LETTER

Densified glasses as structural proxies for high-pressure melts: Configurational compressibility of silicate melts retained in quenched and decompressed glasses

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ABSTRACT

The structures of high-pressure magmatic liquids have often been inferred from spectroscopic studies on quenched and decompressed glasses. However, it has not been completely verified whether the structures of quenched and decompressed glasses are representative of the structure of their corresponding liquids at the glass transition temperature and synthesis pressure. Here, we provide quantitative evidence for the retention of pressure-induced configurational changes upon isobaric quench and isothermal decompression for synthesis pressures up to 3.5 GPa. We use the degree of densification and elastic compressibility of permanently densified glasses, together with thermo-elastic data from the literature, to calculate the density of the melt at the glass transition temperature and synthesis pressure. The derived densities agree with those derived directly from the thermal equations of state of the melts. This observation indicates that, at least up to 3.5 GPa, the densified structure of the melt is preserved in the glass upon quenching and decompression; this validates past and future structural studies of high-pressure melts based on studies of quenched and decompressed glasses.

Keywords: Compressibility, silicate melts, relaxation, rhyolite, phonolite, basalt

INTRODUCTION

The structure of high-pressure magmatic liquids has often been inferred from spectroscopic and diffraction studies on quenched and decompressed glasses (Allwardt et al. 2005a, 2005b, 2007; Davoli et al. 1999; Du et al. 2004; Fleet et al. 1984; Fuss et al. 2006; Gaudio et al. 2008; Hochella and Brown 1985; Kelsey et al. 2009a, 2009b; Lee 2004, 2010, 2011; Lee et al. 2004, 2012; Li et al. 1995; Malfait et al. 2012; O’Neill et al. 2006; Paris et al. 1994; Stebbins and McMillan 1989; Stebbins and Poe 1999; Stebbins and Sykes 1990; Sykes et al. 1993; Velde and Kushiro 1978; Xue et al. 1989, 1991, 1994; Yamada et al. 2010; Yarger et al. 1995). The main advantage of using quenched glasses is that more numerous and more informative structural probes are available at ambient conditions than at in situ high pressure and temperature conditions. However, pressure-induced structural changes are not necessarily retained upon decompression, and studies on quenched and decompressed glasses may underestimate the effect of pressure on melt structure (Farber and Williams 1996; Shim and Catalli 2009). Until now, it has not been fully tested how representative the structures of quenched and decompressed glasses are of the structures of the corresponding melts.

Glasses differ fundamentally from melts. Liquids and glasses are commonly described in terms of equilibrium (relaxed) and non-equilibrium (unrelaxed) states, respectively (Dingwell and Webb 1990). The short lifetimes of the Si-O bonds allow for rapid re-equilibration in liquid silicates, but are too long for re-equilibration in the glassy state (Farman and Stebbins 1990, 1994; Malfait and Halter 2008). The glass transition temperature, \( T_g \), the boundary between the liquid and glassy states, defines the temperature at which the structure is frozen in because the material is no longer able to re-equilibrate to the change in temperature during cooling. This transition typically occurs over a few tens of degrees. The temperature for which the frozen structure corresponds to the equilibrium state is called the fictive temperature, \( T_f \) (Tool 1946). Experimental studies on quenched glasses, combined with in situ studies of the corresponding liquids, have confirmed that the structure of the glass is indeed representative of the melt at the fictive temperature, at least with respect to the Al coordination number (Stebbins et al. 2008), water speciation (Behrens and Nowak 2003), and silica speciation (Brandriss and Stebbins 1988; Malfait et al. 2008).

Liquids and glasses also show notable differences in the compression mechanisms, with both elastic and configurational compression in liquids, but only elastic compression in glasses (Dingwell and Webb 1990). As a result, liquids are more compressible than their analog glasses. Richet and Neuville (1992) reported that the greater compressibility of liquids reflects configurational contributions. In other words, liquids are more compressible because a large number of densified configurational states are available through pressure-induced structural changes. For a frozen structure, the effects of pressure are elastic only and mostly related to variations in the interatomic bond lengths (Richet and Neuville 1992). The relative importance of the vibrational and configurational contributions to the compressibility depends strongly on melt composition and structure (Askarpour et al. 1993). When a glass that was isobarically quenched from the liquid is decompressed to ambient pressure, the elastic contribution to the compressibility is released, but the configurational contribution is at least partially retained (Maurer 1957). However, the degree to which the configurational compression is retained upon decompression has not been quantified. Thus, it is not clear in how far the structure of quenched and decompressed glasses is representative of that of...