Anomalous Elasticity of Anhydrous and Hydrous Rhyolitic Glasses up to 3 GPa

Jesse Gu[1], Suyu Fu[1], James E. Gardner[1], Shigeru Yamashita[2], Takuo Okuchi[2], Jung-Fu Lin[1]

[1]Department of Geological Sciences, Jackson School of Geosciences, The University of Texas at Austin, Austin, TX 78712, USA

[2]Institute for Planetary Materials, Okayama University, Misasa, Tottori 682-0193, Japan

Abstract

Acoustic velocities of anhydrous and hydrous rhyolitic glasses containing up to 5.90 wt.% total water concentration (H_2O_t) have been determined using Brillouin Light Scattering (BLS) spectroscopy up to 3 GPa in a diamond anvil cell at ambient temperature. In addition, Fourier-transform infrared (FTIR) spectroscopy was used to measure the speciation of H_2O in the glasses as a function of pressure. With increasing pressure, some molecular water (H_2O_m) converts to hydroxyl groups (OH^-) ~~in hydrous rhyolitic glasses~~ in hydrous rhyolitic glasses. Most of this conversion occurs below ~1.5 GPa in glasses with >4 wt.% H_2O_t whereas most of this conversion occurs above ~1 GPa in glasses with <4 wt.% H_2O_t. Acoustic velocities in both anhydrous and hydrous glasses decrease with increasing pressure up to ~1-2 GPa before increasing with pressure. In this pressure range, the addition of H_2O_t decreases compressional and shear wave velocities (V_P, V_S), adiabatic bulk moduli (K_S), and shear moduli (G). This behavior is attributed to depolymerization of the silicate network due to incorporation of OH^-. Above ~1-2 GPa, however, acoustic velocities and elastic moduli in the hydrous glasses crossover and become larger than those in the dry glass counterpart. At these pressures, it is conceivable that H_2O_m in interstitial sites prevents the compression of hydrous glasses and makes

them elastically "stiffer". Our results indicate that H_2O_m and OH^- each play distinct roles in altering the elastic properties of rhyolitic glasses at high pressures. We have modeled a~~A~~coustic velocities in hydrous rhyolitic glasses for any given quantity of H_2O_t ~~can are predicted~~ up to 3 GPa at ambient temperature. Taking potential high-temperature effects into account, our results ~~can~~ could be combined with seismic data to predict melt fractions or volatile contents in rhyolitic melt reservoirs.

Keywords: hydrous glass, elasticity, velocity, water, rhyolite

Introduction

Igneous activity at Earth's surface significantly affects society and also shapes the physical and chemical properties of the crust (Carn et al. 2009). The role of "water" in igneous processes is a topic of great interest due to the widespread occurrence of H_2O in Earth's crust and mantle (Mysen and Richet 2005). H_2O is present in magmas and quenched silicate glasses as both molecular water (H_2O_m) and hydroxyl groups (OH^-), where OH^- depolymerizes the silicate network (Stolper 1982a, 1982b). Even at low concentrations, incorporation of these H_2O species has been shown to significantly alter the physical properties of glasses and melts, such as acoustic velocities and elastic moduli (Malfait et al. 2011; Whittington et al. 2012), melting temperature (Kushiro et al. 1968; Grove et al. 2012), density (Richet and Polian 1998; Ochs and Lange 1999; Richet et al. 2000), viscosity (Hess and Dingwell 1996; Richet et al. 1996; Whittington et al. 2000; Hui and Zhang 2007), chemical diffusivities (Behrens and Zhang 2001), and electrical conductivity (Ni et al. 2011; Guo et al. 2016). These effects are manifested in explosive volcanic eruptions, some of the largest of which involve felsic magmas. The intensity of volcanic eruptions is largely governed by the viscosity of constituent magmas and, correspondingly, the degree to which the magmas are polymerized. Paradoxically, H_2O

incorporated in silicate melts as OH^- depolymerizes the silicate network and decreases the viscosity of respective melts, but still plays an important role in explosive eruptions (Shaw 1963). H_2O solubility decreases during magma ascension and results in the exsolution of species into H_2O vapor, which expands rapidly at magmatic temperatures (Moore et al. 1995). This process, in combination with the inherently high viscosity of felsic magmas, causes the explosiveness of felsic, H_2O-rich magmas (Shaw 1972).

Felsic eruptions can occur when differentiation of partially melted lower crustal materials produce melts with high silica contents (Borg and Clynne 1998). These melts have been reported to contain as much as ~6-8 wt.% H_2O_t at ~200-400 MPa and ~400-600°C (Lowenstern 1994; Wallace et al. 1999; Wallace 2005). Some of the largest felsic eruptions are supervolcanic eruptions that formed the Long Valley and Yellowstone calderas (Bailey et al. 1976; Crosweller et al. 2012). Others felsic eruptions occur along subduction zones, like in the Andes, Japan, and the Cascades (Wallace 2005; Kimura et al. 2015; Brandmeier and Wörner 2016). Although seismic observations can give insight into pre-eruptive processes, the detection and estimation of crustal melt volumes and volatile contents under extreme pressure-temperature (P-T) conditions remains challenging (Flinders and Shen 2017; Flinders et al. 2018). Understanding the acoustic velocities in glasses of relevant compositions and the role of different species of H_2O on altering these velocities with depth can aid in constraining and interpreting melt fractions and volatile contents of magmatic bodies observed from seismic studies. Furthermore, uncovering physical properties, such as density and compressibility, of rhyolitic melts at depth is essential to our interpretation of eruptive processes, such as melt buoyancy and melt migration.

Two previous studies have focused on the effect of H_2O on the elastic properties of quenched haplogranitic and rhyolitic glasses at ambient pressure (Malfait et al. 2011;

Whittington et al. 2012). Other experimental studies have explored the elastic properties of anhydrous silicate glasses of various compositions at high pressure (Meister et al. 1980; Suito et al. 1992; Zha et al. 1994; Sanchez-Valle and Bass 2010; Yokoyama et al. 2010; Liu and Lin 2014; Clark et al. 2016). These studies have shown that silicate glasses exhibit anomalous elastic properties with increasing pressure. In crystalline materials, acoustic velocities and elastic parameters increase approximately linearly with pressure. In silicate glasses, however, these properties decrease with pressure up to ~2-5 GPa, but then increase with pressure above a certain transition pressure at around ~2-5 GPa. This behavior has been attributed to the anomalous compression mechanisms in silicate glasses, whereby densification results from tightening and distortion of inter-tetrahedral bond angles rather than by decreasing bond lengths (Clark et al. 2014; Wang et al. 2014). The minima in velocities and compressibility correspond to pressures at which silicate glass reaches a packing limit. At higher pressures, densification occurs through shortening of bond lengths and increasing Al and Si coordination. The pressure dependence of the increasing coordination is dependent upon the composition and polymerization of the glass (Lee et al. 2004, 2011; Lee and Stebbins 2009). Glasses with different H_2O_t and different degrees of polymerization will have different transition pressures and behave differently in acoustic velocities and elasticity above their transition pressures. At pressures relevant to this study (<3 GPa), however, the majority (>98%) of Al and Si remains in fourfold coordination in their local configurations (Malfait et al. 2012). Therefore, Al and Si coordination are not expected to play a major role on the velocities reported here.

The polymerization of hydrous rhyolitic melts and glasses may also change if the proportion of OH^- to H_2O_m changes as a function of pressure and temperature. The relative proportion of H_2O_m and OH^- have been shown to change at high pressures above ~1.0 GPa and could alter the structures and physical properties of hydrous glasses and melts at higher pressures (Ihinger et al. 1999; Hui et al. 2008; Malfait et al. 2012; Ardia et al. 2014; Helwig et al. 2016). With increasing temperature, the ratio of OH^- to H_2O_m will increase, and OH^- will dominate at magmatic temperatures (Keppler and Bagdassarov 1993; Nowak and Behrens 1995; Shen and Keppler 1995). Because studying the properties of melts at high pressure and temperature conditions remains challenging, silicate glasses have commonly been used as analogues for silicate melts (Williams and Jeanloz 1998; Lee et al. 2008). Previous studies have shown that quenched glasses retain the structure of their corresponding liquids (Seifert et al. 1981; Malfait et al. 2014), which has been commonly used as justification for the analogue approach.

Despite previous efforts, the effects of H_2O_m and OH^- on the elasticity of anhydrous and hydrous rhyolitic glasses at pressures above a few hundred megapascals have been poorly studied. At these pressures, elasticity depends not only on H_2O_t, but also on how the different species of H_2O alter the polymerization and structure of the glass. Due to the anomalous behavior of silicate glasses and melts at depth, and the lack of literature data on the elastic behavior of hydrous rhyolitic glasses and melts, it is essential to constrain these parameters at high pressures. Here, we report acoustic velocities, elastic moduli, and H_2O speciation in both anhydrous and hydrous rhyolitic glasses containing up to 5.90 wt.% H_2O_t, measured using Brillouin Light Scattering (BLS) spectroscopy and FTIR spectroscopy in a diamond anvil cell (DAC) up to 3 GPa. These observations are applied to correlate how the different species of H_2O contribute to the observed changes in velocities of hydrous rhyolitic glasses at high pressures. We also discuss how high temperatures relevant to conditions in magmatic reservoirs may alter our results and interpretations by estimating potential high temperature effects on acoustic velocities. Finally, we apply these results to help understand the seismic signatures of hydrous rhyolitic melts in natural magma bodies at depth.

Experimental Methods

Rhyolitic glass samples were cored from a natural obsidian, which consisted of high-silica rhyolitic glass and less than 1 vol.% microlites of Fe-Ti oxides (Gardner and Ketcham 2011). Two cores were placed in Au capsules, along with enough deionized water to ensure H_2O-saturation at run conditions. The capsules were welded shut and then heated and weighed to ensure that no leaks existed. The samples were then run in externally heated pressure vessels at high P-T conditions for approximately 7 days in the Petrology Laboratory of the University of Texas at Austin (Table 1). A third core was placed inside a Pt capsule, which was left open, and was placed inside an externally heated pressure vessel and run at 0.5 MPa and 1150°C in Ar gas. All samples were quenched rapidly, and the two runs at elevated pressures were weighed to check for leaks. After quenching, sample compositions and homogeneity were evaluated by the JEOL JXA-8200 Electron Microprobe in the Department of Geological Sciences at The University of Texas at Austin (Table 2).

In total, three samples were synthesized: one anhydrous glass (AHRG), one glass with 3.28 wt.% H_2O_t (HRG-3), and one glass with 5.90 wt.% H_2O_t (HRG-6) (Table 1). FTIR analyses of double-polished samples at ambient conditions were carried out on all glass samples in the Department of Geological Sciences at The University of Texas at Austin to determine H_2O_t using a Thermo Electron Nicolet 6700 spectrometer and Continuum IR microscope. Absorbances in the near-infrared region at ~4500 cm^{-1} and ~5200 cm^{-1} were used to calculate H_2O_t at ambient conditions following the procedures of Gardner and Ketcham (2011). Furthermore, ambient pressure densities (ρ_0) for the glasses were determined from the partial molar volumes of oxide components and H_2O at 300 K (Richet et al. 2000; Lin and Liu 2006). Archimedes' method with toluene as the immersion liquid was used to confirm that the density of HRG-6 matched the calculated density. The other two glass samples, AHRG and HRG-3, were not checked with this method because of insufficient materials.

Two runs of micro-FTIR measurements were carried out on all glass samples in DACs at the Institute for Planetary Materials, Okayama University in Misasa, Japan. Micro-FTIR measurements were taken using a Jasco FTIR-6200 Fourier-transform spectrometer fitted with a Jasco IRT-7000 microscope with Cassegrain optics (Chertkova and Yamashita 2015). Transmitted light was received by a LN_2-cooled HgCdTe detector for both mid-infrared (MIR) and near-infrared (NIR) measurements. Analytical procedures were similar to those described in Chertkova and Yamashita (2015) except a CaF_2/Si beamsplitter was used for NIR measurements while a KBr/Ge beamsplitter was used for MIR measurements. Glass sample platelets were prepared by polishing both sides using 1-0.3 μm 3M diamond films. In the first run, a DAC with a pair of 600 μm anvils was equipped with a 250 μm thick Re gasket with a 300 μm hole in the center. One piece of AHRG that was 23 ± 3 μm thick and one piece of HRG-6 that was 28 ± 3 μm thick were simultaneously loaded into the DAC along with Ne and a ruby sphere as pressure medium and pressure calibrant, respectively (Mao et al. 1986; Chijioke et al. 2005; Silvera et al. 2007). The MIR region from 1400-4000 cm^{-1} was used in this run to measure H_2O_t and H_2O_m in the glasses (Figure 1). OH^- contents were then calculated based on the difference between H_2O_t and H_2O_m. In the second run, a DAC with a pair of 750 μm anvils was equipped with a 500 μm thick Re gasket with a 650 μm hole in the center. A 333 ± 3 μm thick piece of HRG-3 was loaded into the DAC along with Ne and a ruby sphere. Due to the thickness of the sample, the NIR region from 4000-6000 cm^{-1} was used to measure H_2O speciation (Figure 1).

Three separate runs of BLS measurements were carried out up to 3 GPa in DACs (Figure 2). Each DAC with a pair of 600 μm culets was equipped with a 250 μm thick Re gasket with a 300 μm hole in the center. Glass samples with diameters of ~100 μm were double-polished down to <70 μm thick using 1-0.3 μm 3M diamond films and placed in a sample chamber with either Ne or 4:1 methanol:ethanol as the pressure medium (Figure 2). It has been proposed that the use of noble gases pressure media could alter the compressibilities and measured velocities in silicate glasses (Shen et al. 2011; Weigel et al. 2012; Clark et al. 2014; Coasne et al. 2014), so 4:1 methanol:ethanol was used as the pressure medium in a separate run to check for these effects. In two of the three runs, two samples were placed in the sample chamber simultaneously, whereas only one sample was placed in the chamber in the third run. In all runs, a ruby sphere was used as the pressure calibrant (Mao et al. 1986; Chijioke et al. 2005; Silvera et al. 2007).

BLS measurements were taken at the Mineral Physics Laboratory of The University of Texas at Austin. The Brillouin system is equipped with a 532 nm Coherent Verdi V2 laser and a JRS six-pass tandem Fabry-Perot interferometer (Lu et al. 2013; Yang et al. 2014; Fu et al. 2017). The focused beam size at the sample position was ~30 μm. Spectra were collected at a forward scattering geometry with an external angle of 48.1°. The system is calibrated monthly using standard distilled water and silica glass (Lu et al. 2013). Acoustic velocities were calculated from the measured frequency shift from:

$$V_{P,S} = \frac{\Delta \upsilon_B \lambda_0}{2sin(\theta/2)}$$

where $V_{P,S}$ is the measured compressional (V_P) or shear (V_S) velocity, $\Delta\upsilon_B$ is the measured Brillouin shift, λ_0 is the laser wavelength (532 nm), and θ is the external scattering angle (48.1°). Representative Brillouin spectra of rhyolitic glasses at high pressure are shown in Figure 2.

Data Analysis and Modelling

Measured FTIR spectra were used to calculate H_2O speciation of the samples as a function of pressure via the Beer-Lambert law, which relates absorbance and thickness of a material to the concentration of the absorbing species within it (Newman et al. 1986; Ihinger et al. 1999; McIntosh et al. 2017), according to:

$$C_{H_2O_{t,m},OH} = \frac{M * A}{\rho * t * \varepsilon}$$

where $C_{H_2O_{t,m},OH}$ is the concentration of either H_2O_t, H_2O_m, or H_2O dissolved as OH^-, M is the molar mass of the species of interest, A is the absorbance, ρ is density of the glass, t is thickness of the glass, and ε is the molar absorption coefficient of the FTIR band of interest (Figure 3). Density of glass samples as a function of pressure were determined from equation of state (EoS) fitting, which is discussed later. Because glass is elastically isotropic, the thickness of a sample at high pressure is determined from:

$$t = t_0\sqrt[3]{\frac{\rho_0}{\rho}}$$

where t_0 is the sample thickness in μm at ambient pressure that was measured using an optical microscope (Amin et al. 2012). The MIR region was used to determine the H_2O speciation HRG-6. The area under the peaks at ~1600 cm^{-1} and ~3500 cm^{-1} were determined after a linear baseline was subtracted from the raw spectra (Newman et al. 1986). The species-dependent method of determining H_2O_t from the band at ~3500 cm^{-1} was used along with molar absorption coefficients from Newman et al. (1986) and McIntosh et al. (2017). Because of the thickness of HRG-3, the bands in the MIR region were oversaturated. The ~4500 cm^{-1} and ~5200 cm^{-1} peaks in the NIR region were therefore used instead to determine H_2O speciation. However, the sample was bridged and crushed by the diamond anvils at ~1.5 GPa, so no spectra were recorded above this pressure. Using published values for the molar absorption coefficients, the speciation of H_2O_m and OH^- were determined from the area under the peaks at ~4500 cm^{-1} and ~5200 cm^{-1} after a flexicurve baseline was subtracted from the raw spectra (Figure 3) (Withers and Behrens 1999). Throughout the pressure range in this study, no significant change was observed in the structure or shape of any of the absorbance bands corresponding to H_2O in silicate glasses (Figure 3).

Measured acoustic velocities from BLS were used to derive other elastic parameters, including bulk sound velocity (V_ϕ), density (ρ), adiabatic bulk modulus (K_S), and shear modulus (G) (Sanchez-Valle and Bass 2010; Liu and Lin 2014). To derive elastic moduli, it is first necessary to determine the density of the glasses as a function of pressure. Assuming the glass samples behave elastically under compression, the density of the glasses at high pressures can be derived from:

$$\rho - \rho_0 = \int_{P_0}^{P} \frac{1}{(V_p^2 - \frac{4}{3}V_s{}^2)} dP$$

where ρ is the density of the glass at high pressure, ρ_0 is the density of the glass at ambient pressure (0.1 MPa), and P is the pressure (Sanchez-Valle and Bass 2010; Liu and Lin 2014; Sakamaki et al. 2014). Once acoustic velocities and densities at corresponding pressures were determined, the elastic moduli, K_s and G, were determined from:

$$K_S = \rho(V_p^2 - \frac{4}{3}V_s^2)$$

$$G = \rho V_s^2$$

The derived elastic moduli were then fit with the fourth-order Eulerian finite-strain EoS (Birch 1978). The fourth-order EoS was used rather than the commonly used third-order EoS because of the anomalous compressibility and non-linear change in K_S and G in silicate glasses with increasing pressure (Clark et al. 2014; Liu and Lin 2014). Fitted elastic moduli could then be used to fit measured acoustic velocities as a function of pressure up to 3 GPa. Once the fitted velocities were obtained, the effect of H_2O on velocities at any given pressure could be determined. To do so, modeled velocities were fit at fixed pressures as a function of H_2O_t at 0.15 GPa increments up to 3 GPa with second-order polynomials. These polynomial fits allowed V_P and V_S for any given concentration of H_2O_t to be determined as a function of pressure (Figure 9).

Results

The pressure dependence of H_2O speciation was determined by fitting the measured species abundances to a second-order polynomial to minimize the residual sum of squares. With increasing pressure, H_2O_m in HRG-6 appears to be converted into OH^-; HRG-6 contains 4.23 ± 0.17, 3.61 ± 0.34, and 3.55 ± 0.34 wt.% H_2O_m and 1.58 ± 0.06, 2.12 ± 0.25, and 2.56 ± 0.44 wt.% H_2O as OH^- at ambient pressure, 1 GPa, and 2.84 GPa, respectively (Figure 4). However, this conversion may be superficial due to the large errors in our calculated species abundances. If present, this conversion mostly occurs below 1.5 GPa in HRG-6. In glasses with low H_2O_t (<4 wt.%), the conversion from H_2O_m to OH^- has only been observed above 1 GPa in previous studies (Ihinger et al. 1999; Hui et al. 2008). This also appears to be the case for HRG-3 based on the fitted polynomial; HRG-3 contains and 1.70 ± 0.07, 1.73 ± 0.07, and 1.80 ± 0.07 wt.% H_2O_m and 1.58 ± 0.06, 1.55 ± 0.06, and 1.48 ± 0.06 wt.% H_2O as OH^- at ambient pressure, 0.69 GPa, and 1.44 GPa, respectively (Figure 4). Therefore, the pressure dependence of H_2O speciation varies with the H_2O_t in the glasses. With increasing H_2O_t, the conversion of H_2O_m to OH^- occurs at lower pressures. It should be noted that although such a conversion occurs in both hydrous glasses, OH^- and H_2O_m contents in HRG-3 remain nearly equal, whereas H_2O_m consistently dominates in HRG-6 up to 3 GPa.

The addition of H_2O into rhyolitic glasses slows all V_P and V_S in hydrous glasses at ambient pressure, consistent with previous studies (Figure 5) (Malfait et al. 2011; Whittington et al. 2012). Compared to AHRG at ambient pressure, V_P (V_S) in HRG-3 and HRG-6 are reduced by ~4.8% (~6.7%) and ~5.1% (~8.6%), respectively. The differences in velocities between HRG-6 and HRG-3 are much smaller than the differences between HRG-3 and AHRG. Therefore, the effect of adding H_2O on V_P and V_S is reduced at higher H_2O_t. These results show a non-linear relationship between H_2O_t and V_P or V_S, in contrast with previous studies that have observed linear relationships between V_P or V_S and H_2O_t (Malfait et al. 2011; Whittington et al. 2012).

Measured V_P and V_S, along with calculated V_ϕ, show non-linear and negative changes with pressure below ~1-2 GPa (Figure 6). Above ~1-2 GPa, both V_P and V_ϕ increase with pressure. This “anomalous” change in velocities is consistent with previous studies (Suito et al. 1992; Sanchez-Valle and Bass 2010; Clark et al. 2014; Liu and Lin 2014). As H_2O_t content increases, velocity profiles become “flatter” below ~1-2 GPa. In other words, the reductions in velocities at the velocity minima with respect to those at ambient pressure decreases. The pressure at which acoustic velocities reach their velocity minima is termed the “transition” pressure (Liu and Lin 2014). In hydrous glasses, this “transition” occurs at ~1.5 GPa whereas it occurs at ~2.5 GPa in AHRG. This “transition” pressure decreases with increasing H_2O_t and appears to be closely related to the polymerization of the glasses; both hydrous glasses have similar amounts of OH^-, and therefore, similar degrees of polymerization. The decrease in transition pressure with increasing H_2O_t causes velocities to begin increasing at lower pressures in hydrous glasses. This results in a velocity crossover above the transition pressure where the velocities in hydrous glasses become higher than those in the dry glass. Within the pressure range in this study, V_P in HRG-6 becomes higher than both V_P in AHRG and in HRG-3. Based on the modeled velocities, the crossover in V_P between AHRG and HRG-3 occurs above 3 GPa. Similar crossovers occur in both V_ϕ and V_S, but at different pressures with respect to the crossovers in V_P. In V_S, these crossovers likely occur above 3 GPa based on the modeled velocities, whereas they occur at lower pressures (~0.5-1.5 GPa) in V_ϕ.

The derived densities of hydrous rhyolitic glasses are consistent with the patterns observed in hydrous haplogranitic glasses; the addition of H_2O decreases the density of rhyolitic glasses (Figure 7) (Ardia et al. 2014). At ambient pressure, the densities of AHRG, HRG-3, and HRG-6 are 2.353 ± 0.010 g/cm^3, 2.318 ± 0.010 g/cm^3, and 2.270 ± 0.010 g/cm^3, respectively. The modelled elastic moduli of the glasses also show anomalous behavior at high pressure due to hydration (Figure 8). The addition of H_2O decreases elastic moduli non-linearly below ~1.5 GPa. At ambient pressure, measured K_S (G) are 39.54 ± 0.30 (31.25 ± 0.21), 37.19 ± 0.42 (26.73 ± 0.22), and 36.57 ± 0.38 (25.01 ± 0.18) in AHRG, HRG-3, and HRG-6, respectively. Above ~1.5 GPa, bulk moduli in hydrous glasses exceed those in AHRG. This crossover also appears to occur in shear moduli at higher pressures above 3 GPa. Similar to the transitions in acoustic velocities, the transition pressure in elastic moduli decrease with increasing H_2O_t. Under pressure, the density differences between AHRG and hydrous glasses fluctuates in response to the elastic moduli (Figure 7). At ~ 1 GPa, the bulk moduli in the hydrous glasses begin to increase while the bulk moduli in AHRG is still decreasing with pressure, resulting in increasing density differences. Above ~2 GPa, however, the increase in the bulk moduli in AHRG results in the eventual decrease in the density differences.

Previous studies have reported that the use of noble gases (He or Ne) as pressure media can significantly alter the observed elastic properties in silicate glasses (Shen et al. 2011; Weigel et al. 2012; Clark et al. 2014; Coasne et al. 2014). These effects have been attributed to the adsorption of noble gas molecules into interstitial sites in silicate glasses, which “stiffens” the glass network, making it more incompressible. The divergence in our results are, however, much smaller compared to those observed in silica glass with Ne as the pressure medium at similar pressures (Figure 6) (Coasne et al. 2014). The glass compositions used, in addition to the structure of the SiO_2 and basaltic glasses used in those respective studies may have played a role in the observed changes in elasticity of glasses (Shen et al. 2011; Weigel et al. 2012; Coasne et al. 2014; Clark et al. 2016). According to our velocity results using Ne and 4:1 methanol:ethanol, respectively, we observed little change in velocities below ~2.5 GPa. Above ~2.5 GPa, velocities from the run with Ne as the pressure medium begin to diverge from the velocities from the run where 4:1 methanol:ethanol was used as the pressure medium. We note that using Ne as the pressure medium may alter the elasticity of glasses at higher pressures in DAC studies, but does not display any noticeable effects on rhyolitic glasses in the pressure range investigated here.

Discussion

Effects of H_2O at Ambient Pressure

At ambient pressure, the incorporation of H_2O species decreases acoustic velocities and elastic moduli because dissolved H_2O is much more compressible than the surrounding silicate network (Figure 5, 8) (Richet and Polian 1998). The reduction in velocities and elastic moduli as a function of H_2O_t correlates well with the quantity of OH^- in hydrous glasses. Both hydrous glasses contain similar quantities of OH^- and have velocities and elastic moduli that are closer to each other than those between AHRG and HRG-3. While OH^- dominates H_2O speciation in glasses with <4 wt.% H_2O_t, H_2O_m becomes the major species of H_2O in glasses with >4 wt.% H_2O_t (Stolper 1982a; Ihinger et al. 1999). This complex variation in H_2O speciation as a function of H_2O_t can partially explain the non-linear decrease in acoustic velocities (Malfait et al. 2011; Whittington et al. 2012). The presence of large Ca and Fe cations may also contribute to the differences between our results and those in haplogranitic glasses from Malfait et al. (2011). In basaltic glasses, the incorporation of large Ca and Fe cations have been shown to reduce acoustic velocities, most likely as a result of the disorder in local structure (Stebbins et al. 1997; Liu and Lin 2014). Whereas our results are relatively consistent with previous results when H_2O_t is below ~5 mol%, acoustic velocities diverge from and become lower than the results in hydrous haplogranitic glasses from Malfait et al. (2011) with increasing H_2O_t (Figure 5). Large cation-water interactions may cause these observed differences (Oglesby et al. 2002). We note that the hydrous glasses in this study and in previous studies have similar concentrations of Ca and Fe (Table 2). The divergence in velocities are thus attributed to the presence of the cations at high concentrations of H_2O_t. Therefore, the largest differences in acoustic velocities between the rhyolitic glasses and haplogranitic glasses are observed when H_2O_t is high.

Effects of H_2O at High Pressures

The anomalous pressure-dependence of sound velocities in silicate glasses has been attributed to compression mechanisms. Rather than reducing bond lengths, glasses are compressed by collapse of interstitial void spaces and tightening of bond angles between bridging tetrahedra (Weigel et al. 2012; Clark et al. 2014; Wang et al. 2014). The transition at which acoustic velocities change from decreasing with pressure to increasing with pressure has been associated with a tetrahedral packing limit, above which the compression mechanism changes in silicate glasses (Wang et al. 2014). The hydrous glasses in this study have different transition pressures compared to that of AHRG; the transition pressure appears to decrease with increasing H_2O_t (Figure 6). Both hydrous glasses have similar amounts of OH^-, and therefore, similar degrees of polymerization, which can explain the similarity in the transition pressures. Furthermore, the presence of H_2O_m in interstitial sites, and, to a lesser degree, some OH^- bonded to cations, may contribute to this shift in transition pressure with increasing H_2O_t (Xue and Kanzaki 2008; Xue 2009). The packing limit of hydrous glasses is reached at a lower pressure because H_2O_m in interstitial sites prevents compression of the surrounding silicate network. As the silicate network is compressed, some interstitial H_2O_m converts to OH^-. Even though the quantity of H_2O_m is reduced in HRG-6 with pressure, the quantity of H_2O_m in HRG-6 is still significantly higher than that in HRG-3 (Figure 4). As a result of the lower transition pressure and the presence of interstitial H_2O_m, the acoustic velocities and the elastic moduli in the hydrous glasses exceed those of AHRG at high pressure above ~1.5 GPa (Figure 6, 8). This crossover in velocities and elastic moduli can be attributed to the presence of H_2O_m which causes hydrous glasses to be more incompressible (Figure 8). The fact that a similar crossover in velocities is observed in SiO_2 glass containing ~1 wt.% H_2O_t by Murakami (2018) indicates that glasses become less compressible at high pressures, even with small quantities of H_2O_m.

The polymerization of the glasses also changes the pressure-dependence of velocities in silicate glasses (Sakamaki et al. 2014). With increasing pressure, relatively depolymerized glasses, such as diopside and enstatite glass, show “flat” velocity profiles with almost no decrease in V_P, V_S, or V_ϕ (Sanchez-Valle and Bass 2010; Liu and Lin 2014; Sakamaki et al.

2014). This contrasts with polymerized silicate glasses that display a decrease in velocities with pressure up to a transition after which velocities increase with pressure (Zha et al. 1994; Clark et al. 2014). In the rhyolitic glasses in this study, the reduction in velocities at the velocity minima decreases with increasing H_2O_t (Figure 6). In other words, the hydrous glasses, which have higher OH^- contents and are less polymerized, show "flatter" pressure-dependent velocity profiles.

Potential High-Temperature Effects

High-temperature behavior of glasses and melts remains poorly understood despite efforts to determine the acoustic velocities of silicate melts at magmatic temperatures (Vo-Thanh et al. 1996; Polian et al. 2002; Hushur et al. 2013). Hushur et al. (2013) reported acoustic velocities of haplogranitic glasses and melts with varying sodium and potassium contents as a function of temperature up to ~800°C. Those measurements indicate that, in general, acoustic velocities in haplogranites decrease with temperature, although the change is small (<5%). This minor temperature dependence is consistent with the pattern of temperature dependence in silicate glasses and melts as a function of composition (Vo-Thanh et al. 1996; Polian et al. 2002; Schilling et al. 2003; Hushur et al. 2013). Previous Brillouin measurements on acoustic velocities in SiO_2 glasses and melts show positive temperature dependencies whereas acoustic velocities in basaltic glasses and melts show negative temperature dependencies (Polian et al. 2002; Schilling et al. 2003; Yokoyama et al. 2010). Therefore, we expect that the acoustic velocities in felsic glasses and melts to show little dependence on temperature.

In addition to the direct effect of temperature on acoustic velocities in dry glasses, it should be noted that H_2O speciation in hydrous glasses is also impacted by temperature. At magmatic temperatures (~650-800°C), the ratio of OH^- to H_2O_m will increase dramatically compared to that at ambient temperatures (Keppler and Bagdassarov 1993; Nowak and Behrens 1995; Shen and Keppler 1995). That is, OH^- will dominate, with very little H_2O_m present in the melt. As a result, melts at high temperatures will be much more compressible with lower bulk moduli because of the greater abundance of OH^- depolymerizing the silicate network and with little H_2O_m present in interstitial sites. Overall, therefore, hydrous melts at high temperatures and ambient pressure are thus expected to show enhanced velocity reductions compared to their respective anhydrous melts at 300 K.

Implications

By modeling acoustic velocities at different H_2O_t as a function of pressure, we can infer how acoustic velocities of hydrous rhyolitic glasses will be altered for a given amount of H_2O_t at high pressure and 300 K (Figure 9). On the other hand, reductions in V_P at ambient pressure magmatic temperatures (~800 °C) can be estimated by taking into account the direct effect of temperature on velocities and by assuming the incorporation of OH^- dominates the velocity reductions at high temperatures for a given speciation of H_2O in haplogranitic melts (Nowak and Behrens 1995; Hushur et al. 2013; Evans et al. 2016). The elastic behavior of felsic glasses at simultaneous high P-T conditions remains unclear. Yokoyama et al. 2010 have explored the behavior of SiO_2 glass at high P-T conditions up to 6 GPa and 800 K (~527 °C). Their results indicate that the effects of temperature on acoustic velocities are enhanced at high pressures, yet, their results conflict with ambient pressure and high-temperature measurements (Polian et al. 2002). Additionally, the effects likely are not large at pressures relevant to rhyolitic magmas (~0.5 GPa). Due to the lack of dependable data, we disregard the effects of temperature at high pressures. Our results therefore serve as lower bounds on the velocity reductions in rhyolitic melts.

Combining the pressure and temperature effects determined above, ~~we can~~one could estimate V_P reductions at high pressures and temperatures with respect to average continental crust (Christensen and Mooney 1995). At a depth of ~15 km (0.5 GPa) and at temperatures of ~800 °C we expect anhydrous melts, melts containing 3.28 wt.% H_2O_t, and melts containing 5.90 wt.% H_2O_t to show at least ~11.9%, ~22.6%, and ~28.8% reductions in V_P, respectively. These velocity reductions are in the range of maximum V_P reductions (8-30%) recorded with teleseismic studies of rhyolitic magmatic reservoirs beneath Long Valley caldera and Yellowstone at depths of 7-20 km (Dawson et al. 1990; Weiland et al. 1995; Huang et al. 2015; Flinders et al. 2018). Increasing melt fractions and volatile contents will both increase velocity reductions in magma chambers. Therefore, our results allow constraints to be placed on volatile contents only if regions where maximum reductions in V_P are observed correspond to melt-dominated regions. On the other hand, if previous constraints on volatile contents exist, then our results could be applied to constrain melt fractions.

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