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7 Linking high-pressure structure and density of albite liquid near the
8 glass transition
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1. Abstract

The pressure-induced densification of $\text{NaAlSi}_3\text{O}_8$ liquid is determined following annealing immediately above the glass transition and upon quenching from superliquidus temperatures. High-field ^{27}Al magic-angle-spinning NMR spectroscopy is used to investigate the corresponding changes in Al coordination environment that accompany the densification. We show that samples synthesized by quenching from superliquidus temperatures record lower fictive pressures (P_f) than annealed samples at the same nominal load and have lower recovered densities and average Al coordination number. Accounting for differences in P_f brings melt-quench and annealed samples into excellent agreement. The proportion of $^{[5]}\text{Al}$ increases from ~ 3 to 29% and $^{[6]}\text{Al}$ from 0 to 8% between 1.8 and 7.2 GPa. The production of high-coordinated Al ($^{[5]}\text{Al} + ^{[6]}\text{Al}$) with pressure is most dramatic above 3 GPa. Changes in network topology and structural disorder as revealed by the high-field ^{27}Al NMR spectra provide new insights into the structural mechanisms of densification of the albite liquid. We posit that it is an overall weakening of the network structure on compression that is largely responsible for the anomalous pressure dependence of the transport properties observed for this liquid below ~ 5 GPa.

2. INTRODUCTION

The properties of vitreous and molten $\text{NaAlSi}_3\text{O}_8$ (hereafter referred to as albite) have been studied extensively as an analogue for strongly polymerized (granitic) melts generated and differentiated in the Earth's crust. Most of what we know about these systems comes from one atmosphere experimental measurements, yet extrapolation to high pressure is often required to model magmatic processes. Accurate predictions of crystal – liquid density

relations, and rheological and kinetic properties at high pressure are intimately linked to the structural changes occurring when silicate liquids are compressed.

It is well-known that compression of silicate melts can drive an increase in cation and anion coordination permitting closer packing of structural units (e.g. Wolf et al., 1990; Yarger et al., 1995; Lee, 2004; Lee et al., 2006; Lee, 2010). The increase in the coordination number of network cations Si and Al from 4 to 5 and 6 commonly involves conversion of non-bridging oxygen to bridging oxygen (Yarger et al., 1995; Bryce et al., 1999; Lee et al., 2004; 2006; Allwardt et al., 2005a). Formation of 5 and 6 fold coordinated Si and Al can also occur in the absence of non-bridging oxygen by locally increasing the coordination number of oxygen associated with network cations (Wolf et al., 1990; Wolf and McMillan, 1995; Bryce et al., 1999; Poe et al., 2001). Relatively high pressures (≥ 5 GPa) are usually required to drive such coordination changes, yet appreciable densification of silicate melts is known to occur at lower pressures without significant changes in cation coordination. For network liquids, such as albite, several other structural changes can be active during compression and may be precursors to a collapse of the aluminosilicate tetrahedral network and accompany coordination changes. These include 1) reduction of Na-O bond distances (Lee et al., 2006, Gaudio et al., 2015); 2) reduction in inter-tetrahedral bond angles ($\angle \text{T-O-T}^\circ$; T = Si, Al) (Hochella and Brown Jr., 1985; Stebbins and Sykes, 1990; Sykes et al., 1993; Yamada et al., 2011); 3) increase in the distribution of T-O bond lengths (Stebbins and Sykes, 1990); and 4) reduction of average ring size in the tetrahedral network (Hochella and Brown Jr., 1984; 1985).

Much of our understanding of silicate melt structure at high pressure comes from spectroscopic studies of melts quenched from high T and P, most notably high-field ^{27}Al magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy (Lee et al., 2004; Allwardt et al., 2005a, Malfait et al., 2012). An implicit or explicit assumption made

in these studies is that the structure of the quenched melt (glass) reflects that of the liquid near the glass transition – a narrow temperature interval where the time for structural relaxation exceeds the observational time (Tool, 1946). The temperature at which the liquid structure is frozen into the glassy state is known as the fictive temperature (T_f); and by analogy, the pressure where this occurs is the fictive pressure (P_f). A challenge for studies of glasses recovered from high T and P is constraining T_f and P_f for any given synthesis route.

The goal of this study is to determine the nature of the links between the structure of albite glass, and the fictive temperature and pressure for its synthesis. This is achieved through extensive calibration of the multianvil apparatus used for glass synthesis by two methods; 1) annealing in the vicinity of the glass transition and 2) heating to superliquidus conditions, followed by quenching. Densities of glasses recovered from pressures as high as 7.2 GPa are related to Al bonding environment obtained by high-field ^{27}Al MAS NMR spectroscopy. These results provide insights into the structural changes that facilitate collapse of the open aluminosilicate network during compression and their consequences for the transport properties of strongly polymerized melts.

3. METHODS

3.1. Glass synthesis

The starting material is $\text{NaAlSi}_3\text{O}_8$ glass synthesized at Corning Inc. in a five-kilogram batch from stoichiometric proportions of Puratronic® grade Na_2CO_3 , Al_2O_3 , and SiO_2 . The batch was decarbonated by heating overnight at 873 K and subsequently melted in a platinum crucible at 1873 K for 3 hours. Melt is quenched to glass by removing the crucible from the furnace and cooling in air. To ensure chemical homogeneity, the recovered

glass was crushed and re-melted under identical conditions. The as-made glass is finely vesicular. The least vesiculated portion was used for the present experiments. Electron probe microanalysis, following the methods described in Morgan and London (1996), confirmed chemical homogeneity of the starting glass composition that contains near stoichiometric proportions of Na₂O (11.83±0.23 mol %), Al₂O₃ (12.62±0.22 mol %), and SiO₂ (75.57±0.81 mol%) for NaAlSi₃O₈ (Table 1).

3.2. High-Pressure experiments

High-pressure annealing and melt-quench experiments were performed in a 6-8 Walker-style multianvil apparatus using 10 mm truncated edge length (TEL) castable MgO octahedra (Walker et al., 1990; Walker et al. 1991). The cell assembly consists of a graphite capsule (containing a 2 mm O.D. x 2.5 mm long glass cylinder), surrounded by an electrically insulating sleeve of boron nitride and end plugs of semi-sintered MgO and fired Al₂O₃ thermocouple tubing. These components are placed into a cylindrical stepped-graphite heater within the MgO octahedron (Fig. 1). Temperature is monitored and controlled by a W5%Re-W26%Re (Type C) thermocouple inserted along the longitudinal axis of the assembly with the thermocouple junction positioned 2.2 mm above the center of the sample capsule. Pressure is constrained using both the calibration of the 10 mm TEL assembly during the heating and cooling by the UC Davis group over the last decade using the T25 6-8 multianvil device on beam line 13-ID-D at GSECARS (Advanced Photon Source, Argonne National Laboratory), and fixed-point phase transitions in standard materials. Pressure is determined *in situ* from the lattice parameters of polycrystalline periclase (MgO) derived by energy dispersive x-ray diffraction in conjunction with the equation of state of Matsui et al. (2000). These methods are described in Leshner et al. (2003), Tinker (2004), and Tinker et al. (2004).

Assemblies for the annealing and melt-quench experiments were compressed to the target pressure at room temperature and heated at 150 K/minute to 938 – 1037 K (for annealing) and to 1773 - 2073 K (for melt-quenching). Annealing temperatures were selected just above the glass transition temperature (T_g) at pressure, assuming T_g at 1 atm is 1088 K (Hummel and Arndt, 1985) and a pressure dependence of -9.4 to -50 K/GPa constrained by electrical conductivity, viscosity and calorimetry measurements (Bagdassarov et al., 2004, Behrens and Schulze, 2003; Rosenhauer et al., 1979; Wondraczek et al., 2009). Samples were held at peak temperatures for 5-10 minutes before thermal quenching by cutting power to the graphite resistance furnace. A detailed discussion of quench rates is provided below. Following thermal quenching, samples were decompressed at 4.5 ton/s by metered release of the hydraulic oil from the main ram and extracted for characterization. No crystals were observed by visual and microscopic inspection of the samples recovered after annealing or quenching from superliquidus conditions.

3.3. Density and ^{27}Al MAS NMR measurements

Densities of recovered glasses were determined by Archimedes method using a Berman density balance. The mass of each sample (13-20 mg) and the quartz standard were measured in air and toluene 6-19 times with an uncertainty of ± 0.01 mg.

^{27}Al MAS NMR spectra of recovered glasses were collected using a JNM-ECA 930 (JEOL) spectrometer at the NIMS facility in Tsukuba, Japan, operating at ^{27}Al Larmor frequency of 241.85 MHz (21.8 T) and a 3.2 mm, Al-background free JEOL MQ/MAS probe. Crushed samples were taken in zirconia rotors and spun at 22 kHz. Single-pulse spectra were collected using a solid 10° pulse corresponding to a pulse length of ~ 0.67 μs and a recycle delay of 0.3 s. For each spectrum, 2500 transients were averaged and Fourier transformed with 100 Hz line broadening. Spectra were externally referenced to 0.1 M

aqueous AlCl_3 .

4. RESULTS

4.1. Estimation of fictive temperature and pressure

In order to properly interpret the results obtained on glasses synthesized at high pressure, it is necessary to constrain the T-P conditions for samples as they pass through the glass transition during thermal quenching. The details of the time-temperature-pressure path during heating and cooling in the multianvil apparatus depend on the configuration of the resistance heater, surrounding pressure medium, containment system, as well as peak temperature, pressure and run duration, among others factors. Empirical calibrations are essential. For our experimental setup, we consider three major factors governing the glass synthesis conditions. The first is the pressure at the peak run temperature (P_T) for each experiment. In annealing experiments, P_T is at the temperature of annealing, i.e. near the glass transition temperature (T_g), while P_T for melt-quench experiments is at temperatures more than 700 K above T_g . The second is the cooling rate for the sample as it approaches and crosses the glass transition. Significant differences in cooling rate conceivably can impart significant differences in the fictive temperature, T_f , of annealed and melt-quench samples. Finally, thermal quenching may result in a significant pressure drop before the sample passes through the glass transition such that the resulting fictive pressure, P_f , of sample can be substantially below P_T .

Figure 2a shows pressure as a function of temperature during the initial heating of the multianvil assembly subject to loading by the hydraulic ram to forces of 80 to 330 tons. Data for a given force (load) are fit using a 2nd-order polynomial function (see Table 2 for fit parameters). At 80 tons, pressure increases slightly on heating to ~ 1273 K but drops on

further heating. In contrast, at 120 tons pressure remains essentially constant over the entire temperature range, while at higher loads pressure first drops and then builds above 1273 K. Overall, the pressure increase with temperature is more pronounced for higher loads. Similar behavior has been reported for other multianvil assemblies (Leinenweber et al., 2012) and is commonly attributed to the tradeoffs between the effects of thermal expansion driving up pressure during heating, and assembly softening and gasket extrusion causing pressure to drop. Thermal pressure effects tend to dominate at higher loads where the gaskets are better supported by the carbide anvils. Figure 2b shows that relationship between sample pressure and hydraulic ram force (load) based on the results presented in Figure 2a. These calibration curves are used to estimate sample pressure immediately prior to quenching. We refer to this as the peak pressure (P_T). A single calibration of pressure versus load is applicable to our annealing experiments performed at 938 - 1037 K, while separate calibrations are required for experiments at temperatures of 1773, 1823 and 2073 K (Fig. 2b). We estimate a pressure uncertainty of ± 0.6 GPa (2σ) for these calibrations, except at 2073 K, where the uncertainty is estimated to be ± 1.2 GPa based on modest extrapolation of the data in Figure 2a.

Data on cooling rates for the 10 mm TEL assembly are summarized in Figure 3, based on more than a decade of experiments by the UC Davis group for which temperature – time data were collected during the quench. In all cases power to the furnace was cut instantaneously. The entire dataset is included within the shaded envelopes for temperature and cooling rate versus the time following the cut in power to the furnace, for peak temperatures of 1070 K to 2200 K and run times from minutes to hours. The solid, dashed and dotted curves are the thermal trajectories for specific experiments quenched from 1070 K, 1773 K and 2200 K, respectively. The reason for considering such a wide range in run conditions is to place upper and lower limits on the cooling rates in the vicinity of the glass transition for our experimental assembly. Based on these results we predict initial cooling

rates q of ~ 400 K/sec for annealing experiments, while for melt-quench experiments q initially can be as high as 800 K/sec. In both cases q decreases to ~ 200 K/sec when temperatures reach ~ 800 K.

To determine the cooling rates in the vicinity of the glass transition requires knowledge of T_g over the range of pressure investigated. Since $T_g(P)$ is poorly constrained at high pressure, at best we can place upper and lower bounds given $T_g = 1088$ K at 1 atm (Hummel and Arndt, 1985) and 826 K at 7.2 GPa, assuming an average linear pressure dependence of -36.4 K/GPa (Rosenhauer et al., 1979; Behrens and Schulze, 2003; Wondraczek et al., 2009). We do not include the electrical impedance measurements of albite by Bagdassarov et al., 2004 that show a substantially weaker pressure dependence for T_g . Based on these limits and the calibrations shown in Figure 3, q is between 200 K/s and 450 K/s in the vicinity of the glass transition – annealed samples being subject to higher cooling rates than melt-quench samples for the same P_f .

While there is a slight difference in the cooling rates crossing the glass transition, the values are uniformly high, implying relaxation times of much less than 1 s and thus comparatively low viscosities and high fictive temperatures for the glass transition. Using the empirical relation $\log \eta(T_f) = 11.5 - \log q$ (K/s) from Toplis et al. (2001), where $\eta(T_f)$ is the viscosity at the limiting fictive temperature (the temperature at which the enthalpy of the glass and fully relaxed liquid are equal). We estimate viscosities in the range of $10^{9.2}$ to $10^{8.9}$ Pa s for samples encountering the glass transition at cooling rates of 200 - 450 K/s. These are small differences in viscosity implying small differences in T_f for samples encountering glass transition at the same P_f (Moynihan et al., 1976). We contend, based on these calibrations that samples determined to have similar P_f should also have similar T_f . The T_f calculated for albite glass quenched at 200-450 K/s and 1 atm $\eta(T)$ constraints from Hummel and Arndt (1985) is 134-156 K above the temperature at which viscosity = 10^{12} Pa s. Unfortunately, our

work cannot quantitatively constrain the absolute magnitude of $T_f(P)$ for any given synthesis route. However, if we assume that the fragility of albite liquid does not change appreciably over the pressures of interest, then a reasonable approximation for $T_f(P)$ is: $T_f(P) = T_g(P) + 145 \pm 11$ K.

Finally, the pressure drop on thermal quenching is constrained as follows. Figure 4a shows a calibration experiment performed at the Advanced Photon Source synchrotron heated to 1800 K at 225 tons, followed by quenching in a manner similar to our annealing and melt-quench experiments. In this experiment, in-situ study of the periclase standard indicates a ~60% drop in pressure upon cooling from 1800 to 300 K. Likewise, we estimate a 40% pressure drop on cooling from 1800 K to the temperature range of our annealing experiments, i.e. 938 – 1037 K. Several such data sets are combined in Figure 4b by normalizing the measured pressure at a given load to the pressures at 1273 K and at room temperature (300 K) post-quench, such that $P/P_{1273} = 1$ and $P/P_{300} = 0$. The results for heating and cooling are nearly identical above 1273 K, but differ markedly below 1273 K. The average pressure drop from 1273 K to room T (post-quench) is 2.4 GPa for the calibration experiments presented in Table 3. The significance of these calibrations is that for annealing experiments operating very close to the glass transition, P_f will be very close to, if not equivalent to P_T . On the other hand, melt-quench samples will experience a large pressure drop on cooling by more than 700 K before locking in P_f at T_f . Thus, we expect $P_f < P_T$ for our melt-quench experiments. Furthermore, for $T_f(P) < 1273$ K, melt-quench samples will record lower P_f compared to the annealed samples for experiments performed at the same load. The difference in P-T pathways between annealed and melt-quench experiments, as determined by the comprehensive calibrations performed in the present study, are illustrated in Figure 5.

4.2. Density and ^{27}Al MAS NMR Spectroscopy

The recovered density ρ_r as a function of pressure is shown in Figure 6a. Both datasets show a positive and near-linear dependence on P_T , with ρ_r increasing by $\sim 17\%$ from 0 to 7.2 GPa (Fig. 6a). There is also a clear offset of melt-quench glasses to lower densities at comparable P_T – not surprisingly, given our pressure and cooling rate calibrations. The vertical downward-directed arrows point to the values of P_f estimated for our melt-quench samples based on the calibration shown in Figure 4b and the abovementioned approximation $T_f(P) = T_g(P) + 145 \text{ K}$ (Table 4). Accounting for the pressure drop during quenching brings glass densities for both synthesis routes into better agreement supporting a robust calibration of ρ_r versus P_f as shown in Figure 6b. In light of the excellent first-order agreement of the two data-sets, we subsequently used the relationship between ρ_r and P_f for annealed samples to estimate P_f for our melt-quench samples.

Figure 7a presents the ^{27}Al MAS NMR spectra of the annealed and melt-quenched glasses. The dominant peak is centered at $\sim 56 \text{ ppm}$ corresponding to Al bonded to four oxygen atoms ($^{[4]}\text{Al}$). There is a clear emergence of peaks centered at $\sim 25 \text{ ppm}$ and $\sim 1 \text{ ppm}$, corresponding to $^{[5]}\text{Al}$, and $^{[6]}\text{Al}$, respectively, with increasing P_f . To quantify the relative fractions of $^{[4]}\text{Al}$, $^{[5]}\text{Al}$, and $^{[6]}\text{Al}$, we have simulated the quadrupolar line shapes for each Al site with the Czjzek distribution of quadrupolar coupling constants (C_q) using the DmFit software package (Massoit et al., 2002) (Fig. 7b). The NMR simulation parameters and the associated error bars for each peak in each spectrum, including the isotropic chemical shift (δ_{iso}), the average C_q , relative proportions of $^{[4]}\text{Al}$, $^{[5]}\text{Al}$, and $^{[6]}\text{Al}$, and average Al coordination number are given in Table 4.

The average Al coordination number and average C_q for $^{[4]}\text{Al}$ are plotted against ρ_r in Figures 8a and 8b. In the pressure range of 0-7.2 GPa, ρ_r increases by over 17% (Fig. 6b)

while the average Al coordination number increases from 4.0 to 4.45 (Fig. 8a) and the average C_q for $^{[4]}\text{Al}$ increases from 4.8 to 9.5 MHz (Fig. 8b). Interestingly, the production of high-coordinated Al follows the distortion of the $^{[4]}\text{Al}$ coordination environment as reflected by its average C_q (Ghose and Tsang, 1973; Kirkpatrick and Phillips, 1993). It should be noted that while the abundance of high coordinated Al is small (<3%) below ~3 GPa and essentially all of it is $^{[5]}\text{Al}$, $^{[6]}\text{Al}$ begins to appear with the onset of the rapid increase in $^{[5]}\text{Al}$ above 3 GPa (Table 4). Overall, $^{[5]}\text{Al}$ increases from ~2.5 to 29% and $^{[6]}\text{Al}$ from 0 to 8% between 1.8-7.2 GPa.

Table 4 presents peak pressures (P_T), fictive pressures (P_f), recovered densities (ρ_r) and NMR results for albite glasses synthesized by the annealing and high temperature melt-quenching routes.

5. DISCUSSION

When taken together, the evolution of the density and the average Al coordination number with P_f yield a robust structural model of pressure-induced densification of albite liquid. Average Al coordination number determined for albite glass samples in the present study are in good agreement with previous experiments performed using annealing methods (Allwardt et al., 2005b), forming a nearly linear trend with pressure above 2.6 GPa (Fig. 8). However, melt-quench experiments presented by Allwardt et al. (2005b) and Lee et al. (2004) fall below the average Al coordination number trends for annealed samples by 4.4 GPa and 4.3 GPa, respectively (Fig. 8). While the specific calibrations developed in this study cannot be used to correct for the pressure drops during quenching in other multianvil devices using different pressure cells, it is noteworthy that Allwardt et al. (2005b) found that samples annealed at or slightly above T_g had significantly more high coordinated Al and

higher density than those quenched from superliquidus conditions at even higher peak pressures. They attributed these differences to differences in T_f ; however, based on the present work, specifically the relationships shown in Figure 6, we believe that it is more likely that the differences reported by Allwardt et al. reflect differences in P_f - melt-quench samples recording greater pressure loss on nearing the glass transition during quenching than annealed samples. This underscores the importance of constraining the P-T trajectory of quenching when comparing the properties of glasses synthesized in large volume, solid medium pressure devices.

To the extent that the recovered glasses preserve structural features of the melt at high pressure, it is instructive to consider the role of Al coordination change in densification. Again, we find that $^{[4]}Al$ is the dominant coordination state for aluminum in albite glass up to 7.2 GPa and distortion of the tetrahedral Al environment increases continuously and monotonically with P_f and density (Table 4 and Fig. 8b). For pressures of up to 2.6 GPa, high-coordinated Al is present only as $^{[5]}Al$ and is in very low abundance (<3%), while the recovered density increases by over 7%. The initial lack of high-coordinated Al with densification demonstrates the importance of other structural mechanisms of densification in albite glass in response to the initial increase in pressure. Previous structural studies suggest that at pressures below ~ 3 GPa, the primary mechanism for densification is the collapse of the tetrahedral aluminosilicate network around the Na-O coordination polyhedra, resulting in a decreasing average Na-O bond distance (Stein and Spera, 1993; Lee and Stebbins, 2003; Lee et al., 2006; Tenner et al., 2007; Kuryaeva and Surkov, 2010; Gaudio et al., 2015). Furthermore, examination of the effect of pressure on open framework glass structures from the Si perspective suggest a general decrease in $\langle T-O-T^\circ \rangle$ (Hochella and Brown Jr., 1985; Stebbins and Sykes, 1990; Sykes et al., 1993; Lee et al. 2003, 2006; Yamada et al., 2011) with densification. All of these mechanisms are consistent with the reduction in ring size

proposed by Hochella and Brown Jr. (1985) and support the conclusion of Kelsey et al. (2009) that Al coordination change, is one of many densification mechanisms activated during compression of aluminosilicate glasses and melts (Stebbins et al., 2013 and citations there in).

A P_f of ~ 2.6 GPa marks the onset of the formation of stable $^{[6]}\text{Al}$. The proportion of both $^{[5]}\text{Al}$ and $^{[6]}\text{Al}$ increases with pressure from ~ 3 to 29% and from 0 to $\sim 8\%$, respectively, between 2.6 and 7.2 GPa and average aluminum coordination number increases from 4.03 to 4.45 over the same range in pressure (Fig. 8a and Table 4). Samples recovered from 7.2 GPa are nearly 17% denser than the non-compressed glass, while a third of the Al cations are highly coordinated by oxygen (Table 4). High-coordinated Si is absent in recovered albite glasses up to 10 GPa (Stebbins and Sykes, 1990), which means that $\sim 8\%$ of the total network-forming cations are highly coordinated (coordination number > 4). Partially polymerized glass compositions, such as $\text{Na}_3\text{AlSi}_3\text{O}_9$, NS3 ($\text{Na}_2\text{Al}_2\text{O}_4\text{-Na}_2\text{Si}_3\text{O}_7$), and NS4 ($\text{Na}_2\text{Al}_2\text{O}_4\text{-Na}_2\text{Si}_4\text{O}_9$), show far greater proportions of high-coordinated Al with less densification than are found in the present study for albite (Allwardt et al., 2005b; Kelsey et al., 2009), which provides support for the notion that it is difficult to form high-coordinated Al in the absence of NBO (Wolf et al., 1990; Yarger et al., 1995). Additionally, several multi-nuclear NMR studies also show the ease with which Al coordination increases on compression and heating compared to Si (Waff et al., 1975; Stebbins and Sykes, 1990; Allwardt et al., 2005b; Kelsey et al., 2009). For these partially polymerized systems it is proposed that the formation of high-coordinated Al occurs by the consumption of non-bridging oxygen (Lee et al., 2004; Lee et al., 2006). This pathway is limited for highly polymerized liquids such as albite where very few, if any, NBO exist at low pressure (Mysen and Toplis, 2007). The formation of high-coordinated Al in albite on compression then has to be accompanied by the formation O coordinated by three network-forming cations (Bryce

et al., 1999; Poe et al., 2001). The results presented in the present work provide no direct experimental evidence in favor of this hypothesis. However, this mechanism of simultaneous Al and O coordination change cannot be avoided in a fully polymerized tetrahedral network and is expected to be more effective in densification of the melt structure compared to the scenario where the neighboring NBO atoms get consumed by the AlO_4 tetrahedra during the coordination change.

Finally, the evidence presented here for changes in local bonding environment for Al with pressure indicate both an increasing distortion of the Al coordination environment coupled at higher pressure with an increase in coordination number that is expected to lead to longer, weaker T-O bonds within the network (Scamehorn and Angell, 1991). Such weakening of the network structure may be responsible for the anomalous decrease in viscosity and increase in diffusivities for network atoms and electrical conductivity in polymerized aluminosilicate liquids at pressures below 5-10 GPa (Poe et al., 1997; Poe and Rubie, 2000, Suzuki et al. 2002). Importantly, albite liquid possesses these anomalous properties at pressures where silicic magmas are generated and differentiated in the lithosphere. The present work provides an atomistic understanding of the pressure-induced densification mechanisms in albite liquid that can contribute to a better understanding of silicic magmas important in a wide range of geologic settings.

6. CONCLUSIONS

In this study, we demonstrate that after careful calibration of the multianvil device used to synthesize albite glasses at high pressure, clear correlations emerge between the density of the recovered glasses, the fictive pressure for glass formation, and the structural changes in the tetrahedral network. We show for the first time that annealing and melt-

quench synthesis routes give consistent results once one accounts for differences in the fictive pressure at the glass transition. We present evidence for increasing Al coordination and structural disorder as density and P_f increase. Between 0 and 7.2 GPa, density increases by ~17% and by 7.2 GPa 33% of the Al is in 5- or 6-fold coordination. Significant changes in the network topology precede and then accompany the formation of high-coordinated Al, reflecting increasing distortion of the aluminosilicate network with increasing pressure. We posit that these structural changes lead to an overall weakening of the tetrahedral aluminosilicate network on compression that is largely responsible for the anomalous pressure dependence of viscosity and network component diffusivities observed for albite liquid below ~5 GPa.

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FIGURE CAPTIONS

Figure 1. Schematic of 10 mm truncation edge length (TEL) multianvil assembly showing the location of the sample contained within a graphite capsule surrounded by semi-sintered MgO, all within the sectioned graphite resistance heater. The MgO octahedral is cast with fins from “old style” Ceramacast 584 ceramic. Temperature is controlled via a C-type thermocouples entering from the top with the junction located at the top of the graphite capsule.

Figure 2. a) Pressure - temperature - load calibrations of the 10 mm TEL assembly based on lattice parameters of a MgO standard determined by energy dispersive X-ray diffraction at GSECAR-APS and the EOS of Matsui et al. (2000). Lines through the data points are second-order polynomial fits for constant loads as given in Table 2. The corresponding load for each dataset is given alongside the curves in units of Ton. b) Pressure versus load calibrations for temperatures relevant to the present study. Open circles indicate the peak T-P conditions for melt-quench experiments, while the solid circles show these conditions for the annealed experiments.

Figure 3. Cooling rate ($q = \partial T / \partial t$) calibration is shown for the castable MgO 10 mm TEL assembly. Temperature versus time measurements were collected during rapid cooling of high-pressure experiments with a 1-2 sec sampling rate for a range of peak run temperatures (~1070-2200 K). Black lines represent temperature-time data recorded for experiments at 1070 K (solid black line), 1773 K (dashed black line) and 2200 K (dotted black line). The dark grey shaded region illustrates the range of temperature-time data collected for experiments in the 10 mm TEL. Cooling rate q versus time is shown on the secondary axis as grey lines. Grey lines represent temperature-time data recorded for experiments 1070 K (solid grey line), 1773 K (dashed grey line) and 2200 K (dotted grey line). The light grey shaded region illustrates the range of $\partial T / \partial t$ calculated for the range of temperature-time data collected for experiments in the 10 mm TEL.

Figure 4. a) P-T pathway during heating (solid circles and line) and cooling (open circles dashed line) for a single experiment measured *in situ* at 225 tons. b) Summary of multiple P-T pathways for heating (solid circles) and cooling (open circles), where pressure is normalized such that $P/P_{1273} = 1$ and $P/P_{300} = 0$ (see text for details). The data used for this

calibration are given in Table 3. The dashed line is used to estimate the pressure loss during thermal quenching below 1273 K at any load, where $P_{\text{normalized}} = 9.26 \times 10^{-4}T - 0.303$, assuming an average pressure drop from P_{1273} to $P_{300} = 2.4$ GPa. P_{1273} is calculated for a given load from the calibration shown in Figure 2b since this point is approximately the same pressure on heating and cooling.

Figure 5. Schematic plot of the P-T pathway for samples produced by annealing ($P_T = P_{f(a)}$) and melt-quench ($P_f \ll P_{T(m)}$) type experiments both compressed initially at 300 K to 6.1 GPa (267 tons). The P-T pathways for high-pressure glass synthesis experiments (black lines with arrows indicating direction along P-T path) are superimposed over a composite phase diagram for albite (grey line-Labeled T_M) using data from both Tenner et al. (2007) to 3 GPa and Boyd and England (1963) from 3 to 5 GPa. Above 5 GPa the melting curve is extrapolated and inferred from the albite viscosity experiments of Suzuki et al (2002). The average negative pressure dependence of T_g (thin grey line) is ~ -36.4 K/GPa (Average value from Rosenhauer et al., 1979; Behrens and Schulze, 2003; and Wondraczek et al., 2009) and estimate of fictive temperatures $T_f(P) = T_g(P) + 145 \pm 11$ K (thick grey line) are illustrated (see 4.1 in the results section for explanation of $T_f(P)$ estimate). The shape of P-T pathway on cooling is taken from Figure 4a.

Figure 6. a) Pressure versus recovered density for albite glass. The pressure at peak run temperature for melt-quench (open grey diamonds and open black diamonds) experiments is corrected for thermal pressure loss using estimates from the calibration presented in Figure 4a and 4b and Table 3 (open black diamonds). Arrows indicate the shift in position of melt-quench experiments when pressure is plotted as estimated P_f (open black symbols) rather than P_T (open grey symbols). Solid black diamonds indicate annealing experiments. b) P_f versus recovered density for albite glass. P_f for melt-quench experiments (open symbols) are calculated from the ρ_r versus P_f trend of the annealed experiments (solid diamonds), where $P_f = 8.5759(\rho_r)^2 - 26.878(\rho_r) + 15.478$. Density of vesicle-free albite glass at 1 atm is from Wondraczek et al., (2009).

Figure 7. a) ^{27}Al MAS NMR spectra of albite glasses recovered from high pressure and temperature are shown as normalized intensity versus relative frequency. P_f for each sample is labeled to the left of each spectrum. Peak assignments are labeled on figure and side bands

are indicated with asterisks. b) Example of Czjzek fits to ^{27}Al MAS NMR spectra of albite glasses recovered from high pressure and temperature are shown as normalized intensity versus relative frequency in ppm. Components of the Czjzek simulation are labeled within the figure and side bands are indicated with an asterisk.

Figure 8. a) Average Al coordination number as a function of recovered density (black symbols). Symbols same as figure 6a. b) C_q for $^{[4]}\text{Al}$ as a function of recovered density. Symbols same as figure 6a. C_q at 1 atm from Lee (2004) and the density of vesicle-free albite glass at 1 atm is from Wondraczek et al., 2009.

Figure 9. Average Al. coordination # versus P_f from the present study (diamonds), Lee et al. (2004) (square), and Allwardt et al. (2005b) (triangles). Samples produced by the melt-quench method are shown as open symbols. ΔP indicated with an arrow, shows the deviation in pressure of the melt-quench samples of Lee et al. (2004) and Allwardt et al. (2005b) from the trend established with annealed samples for their reported fraction of high coordinated Al.

Table 1: Composition of glass starting material and run products normalized to 100 mol %.

	Mol %		
	Na ₂ O	Al ₂ O ₃	SiO ₂
Ave. Uncertainty in mol % from counting statistics	±0.23 %	±0.22 %	±0.81 %
^a Experiment Information			
<i>Stoichiometric Albite</i>	(12.50)	(12.50)	(75.00)
Starting glass (non-compressed/heat treated)	11.78	12.70	76.03
Annealed at 1042 K and 137 tons	11.94	12.68	75.77
Annealed at 956 K and 367 tons	11.86	12.69	75.89
Melt-quench from 1773 K and 137 tons	11.81	12.66	75.53

^aGlass compositions were determined by electron microprobe. Na, Al, Si, were simultaneously collected for 10 s, with a beam current of 7 nAmp and spot size of 15 μm.

Table 2: Calibration of pressure-temperature at constant load*

Load (Tons) [symbol]	A (10 ⁻⁶)	B(10 ⁻³)	C
80 [○]	-0.8375	2.3190	-0.102
120 [▲]	0.0885	-0.0991	2.249
150 [◇]	0.2164	-0.1948	3.000
180±10 [□]	1.0400	-2.3300	4.680
225 [●]	1.4980	-3.2640	6.038
250 [◆]	1.5230	-3.1700	6.715
270 [△]	1.5210	-3.0300	6.845
330±5 [■]	1.4640	-2.8780	7.594

*Pressure is calculated from temperature-load information using the following equation $P=A\cdot T^2+B\cdot T+C$, where T is temperature at constant load

Table 3: P measurements during during cooling to room T of 10 mm TEL assembly

Expt. #	Load	P_{Tmax}^a	$P_{1273\text{ K}}$	$P_{room\text{ T}}^b$	ΔP^c
	(Tons)	measured			
		(GPa)			
T0335	225	5.4 _{1773K}	4.4	2.2	2.2
T0336	180	3.4 _{1773K}	3.4	0.9	2.5
T0357	225	6.1 _{2023K}	4.4	2.2	2.2
T0698	170	4.1 _{1873K}	3.7	0.7	3.0
T0805	150	3.8 _{1925K}	3.0	0.7	2.3
T1020	150	3.5 _{1773K}	2.8	0.4	2.4
T0544 ^d	120	2.3 _{1673K}	2.2	0.3	1.8
T0362 ^e	335	7.6 _{1923K}	6.2	n/a	

^a P measured at maximum experimental run temperature

^b P measured at room T. Post-quench room T is ~330 K.

^c Difference in pressure calculated between $P_{1273\text{ K}}$ and $P_{room\text{ T}}$. The average difference in pressure is 2.4 GPa.

^d P_{Tmax} is calculated from pressure calibrations in Fig. 2a

^e P reported as P_{1273K} was measured at 1473 K.

Table 4: Experimental run parameters, density, and simulation parameters for Al coordination environments from ²⁷Al MAS NMR spectra using the Czjzek EFG approximation (d=5)

Experiment #	Load (Tons)	T (K)	P _r ^a (GPa)	P _f ^b (GPa)	ρ _r ^c (g/cm ³)	q ^d (K/s)	Peak Max (ppm)	δ _{iso} ^e (ppm)	FWHM (ppm)			C _q ^e (MHz)			Area ^e (~1 %)		Ave. Al ^e #
									¹⁴ Al	¹⁵ Al	¹⁶ Al	¹⁴ Al	¹⁵ Al	¹⁶ Al	¹⁴ Al	¹⁵ Al	¹⁶ Al
<i>Annealed</i>																	
137(A)-PB0726	137	1037	2.6	2.6	2.543 (7)	450	57.7 26.7 -	61.8 28.5 -	11.5 21.0 -	6.4 3.0 -	97.5 2.5 0.0	4.03					
267(A)-PB0746	267	976	5.3	5.3	2.699 (11)	450	56.6 25.1 1.5	62.5 29.2 2.6	12.2 16.5 14.0	8.1 6.7 3.4	80.3 16.5 3.3	4.23					
368(A)-PB0772	368	938	7.2	7.2	2.785 (9)	450	56.1 25.3 1.9	63.4 30.6 2.5	13.0 14.8 13.3	9.5 8.7 4.0	63.1 29.2 7.7	4.45					
<i>Melt-Quench</i>																	
132(M-Q)-PB0767	132	1823	2.8	1.8 (1.9)	2.495 (8)	300	- - -	- - -	- - -	- - -	- - -	-					
137(M-Q)-PB0738	137	1823	2.9	1.8 (2.0)	2.494 (5)	300	57.5 - -	61.6 33 -	11.1 21 -	6.0 3.2 -	97.3 2.8 -	4.03					
153(M-Q)-PB0791	153	1773	3.2	1.9 (2.3)	2.502 (6)	300	- - -	- - -	- - -	- - -	- - -	-					
267(M-Q)-PB0739	267	2073	6.8	4.3 (4.5)	2.643 (11)	300	57.2 27 -0.6	62.1 29.0 1.0	11.7 18.5 12.0	7.0 4.7 3.4	87.3 9.7 3.0	4.16					

^aPressure calculated from the calibration curves presented in Figure 1 at the peak run temperature reported in the adjacent column. The 2σ uncertainty in pressure for annealed samples is 0.6 GPa up to 1823 K. The pressure-load calibration at 2073 K is an extrapolation of pressure-load-temperature data collected up to 1947 K and for this 2σ uncertainty is ±1.2 GPa.

^bP_r for melt-quench samples is calculated from the measured ρ_r versus P curve for the annealed samples in the present study. The pressure reported in parenthesis is estimated using the calibration presented in Figure 4b and Table 3 as well as estimates of T_r(P) = T_g(P) +145±11 K as discussed within text.

^cNumber of density measurements given in parentheses.

^dq calculated at T_g. The uncertainty in q is ±150 K/s, which results from the uncertainty in T_g at P and measurement of temperature with time. All cooling rates calculated for T_g = 826–1088 K fall between 150–450 K/s for peak run temperatures from 1050–2200 K.

^eWe determined the uncertainty in NMR parameters from repeated minimization of the residual for the model fit to each spectrum. Uncertainty for ¹⁴Al isotropic chemical shift (CS) is ±0.2 ppm and quadrupolar coupling constant (C_q) for ¹⁴Al is ±0.5 MHz. Uncertainties in CS and C_q for ¹⁵Al and ¹⁶Al are higher than those for ¹⁴Al, at ±1 ppm and 1 MHz, respectively. The uncertainty in the relative fractions of different Al species are small: <1.0% for ¹⁴Al and ¹⁵Al and ~ 1% for ¹⁶Al. After propagation, the uncertainty in the average coordination number is <1.73%.

Figure 1

Figure 2a,b

Figure 3

Figure 4a,b

Figure 5

Figure 6a,b

Figure 7

Figure 8a,b

Figure 9