American Mineralogist, Volume 90, pages 1453–1457, 2005

LETTER

The effect of fictive temperature on Al coordination in high-pressure (10 GPa) sodium aluminosilicate glasses

JEFFREY R. ALLWARDT,[1,*] BRENT T. POE,[2] AND JONATHAN F. STEBBINS[1]

[1]Department of Geological and Environmental Sciences, Stanford University, Building 320, Stanford, California 94305-2115, U.S.A.
[2]Istituto Nazionale di Geofisica e Vulcanologia, Rome

ABSTRACT

Typical liquidus temperatures can be over 1000 °C greater than the glass transition temperatures for high-pressure aluminosilicate melts so the effect of temperature must be determined if glass data is to be used to approximate the structural speciation present in geologic melts. This study has investigated the effect of fictive temperature (T_f, taken as the temperature where the melt structure is the same as that of the glass) on the percentage of $^{[5]}$Al and $^{[6]}$Al species in two high-pressure (10 GPa) Na-aluminosilicate glasses ($Na_3AlSi_7O_{17}$ and $NaAlSi_3O_8$) where one glass of each composition was quenched from the high-pressure melt while the other was annealed near the glass transition temperature. The ^{27}Al MAS NMR spectra of the $Na_3AlSi_7O_{17}$ samples show that the higher T_f (quenched) glass contains more high-coordinated Al than the lower T_f (annealed, 475 °C) glass. However, the ^{27}Al spectra of the $NaAlSi_3O_8$ samples show the opposite temperature dependency, which in addition to the lack of NBO in this glass, may suggest differing mechanisms for the generation of high-coordinated Al.

INTRODUCTION

Conventional models of ambient pressure aluminosilicate melt and glass structure assume that all aluminum is tetrahedrally coordinated ($^{[4]}$Al) when the composition is metaluminous (e.g., mole fractions of Na_2O and Al_2O_3 are equal) or peralkaline (e.g., mole fractions of Na_2O are greater than Al_2O_3) (Mysen 1988, 2003). A few previous theoretical and experimental studies have shown that small amounts of high-coordinated Al ($^{[5]}$Al and $^{[6]}$Al) exist in some peralkaline (Stebbins and Farnan 1992; Poe et al. 1994; Allwardt et al. 2003) and metaluminous glasses (McMillan and Kirkpatrick 1992; Stebbins et al. 2000; Toplis et al. 2000; Neuville et al. 2004). These structural species have been suggested to be an energetically favorable transition complex for viscous flow in aluminosilicate melts, similar to $^{[5]}$Si in silicate melts (Stebbins 1995a; Toplis et al. 2000).

Spectroscopic studies of glasses have shown that the coordination numbers of network formers (e.g., Si, Al, B) gradually increases with increasing pressure (Xue et al. 1991; Yarger et al. 1995; Du et al. 2005). Mineral phase analysis, molecular dynamics, and nuclear magnetic resonance (NMR) investigations have all shown that Al is more susceptible to increasing coordination with pressure than Si in aluminosilicates (Waff 1975; Yarger et al. 1995). This increase in the average Al coordination is one manner in which the melt can accommodate increasing densification with pressure. These structural changes are likely responsible for the anomalous pressure dependence of physical properties such as ionic diffusion and viscosity, which correlate to $^{[5]}$Al concentrations measured in quenched melts (Poe and Rubie 2000).

Most of the previous work on the structure of high-pressure aluminosilicate glasses has concentrated on charge-balanced glasses, such as $NaAlSi_3O_8$, due to the relatively good glass-forming ability and low melting temperature relative to other aluminosilicates (Mysen et al. 1980, 1983; McMillan and Graham 1981; Hochella and Brown 1985). However, none of this early work detected a coordination change of Al in high-pressure glasses, even at pressures to 4 GPa. A slightly more recent aluminum-27 magic-angle spinning (^{27}Al MAS) NMR study (9.8 and 11.4 T) observed a tetrahedral Al peak that possibly contained two small discontinuities in the "tail" at approximately 25 and 0 ppm and used this to suggest the presence of $^{[5]}$Al and $^{[6]}$Al species, respectively, in $NaAlSi_3O_8$ glasses quenched from a liquid at 8 and 10 GPa (Stebbins and Sykes 1990). A recent ^{27}Al triple-quantum (3Q) MAS study (7.1 T) has confirmed the presence of $^{[5]}$Al in glasses synthesized at 8 GPa, but did not detect $^{[6]}$Al (Lee 2004). Additionally, Al *K*-edge XANES spectra have been used to suggest that the average Al-coordination is greater than four in several high-pressure (4.4 GPa) glasses along the $NaAlSi_3O_8$-$NaAlSi_2O_6$ join (Li et al. 1996).

Non-bridging oxygen (NBO) atoms are bonded to only one tetrahedrally coordinated network former (e.g., $^{[4]}$Si-O^-) where the rest of the valence charge of the oxygen is associated with "softer" network modifier-oxygen bonds (e.g., Na^+-O). NBO have been shown to be important in the generation of high-coordinated species in aluminosilicate glasses (Yarger et al. 1995; Lee 2004) as well as in Al-free silicate glasses (Xue et al. 1991; Wolf et al. 1990; Allwardt et al. 2004). A previous ^{27}Al MAS NMR study showed that Al-coordination gradually increases with

* E-mail: allwardt@pangea.stanford.edu

0003-004X/05/0809–1453$05.00/DOI: 10.2138/am.2005.1736

increasing pressure in high-pressure peralkaline ($Na_3AlSi_7O_{17}$) glasses (Yarger et al. 1995), as was previously suggested based on the variation of bond angles in glasses and melts relative to crystalline material (Waff 1975; Stolper and Ahrens 1987). However, the previous ^{27}Al NMR spectra were collected at 9.8 T, which increases the quadrupolar peak broadening relative to spectra gathered at higher fields (e.g., 14.1 or 18.8 T), making quantification dependent on accurately representing the unconstrained, overlapping peaks and their low-field tails for the different Al-coordinations ($^{[4]}$Al, $^{[5]}$Al, and $^{[6]}$Al). More recent technological advances in high-field NMR spectroscopy have drastically increased the available external magnetic fields and sample spinning rates, which allow a more reliable approach to quantifying the NMR spectra as the peaks are more Gaussian in shape and contain a significantly smaller "tail" than is observed in spectra from lower fields (Stebbins et al. 2000).

The present study utilizes high-field ^{27}Al MAS NMR (18.8 T) to investigate the following compositions that have been previously studied at lower magnetic fields in order to more directly assess the distribution of Al coordinations in these high-pressure glasses: $Na_3AlSi_7O_{17}$ (Yarger et al. 1995) and $NaAlSi_3O_8$ (Ohtani et al. 1985; Stebbins and Sykes 1990). Glass is commonly used as a structural analog for geologic melts because the structure is that of the corresponding liquid at the fictive temperature (T_f), so any structural differences between glasses with different T_f values represent the configurational dependence of the structure with temperature (Richet and Neuville 1992). For this reason, we also collected spectra from glasses with different thermal histories to represent melts with different fictive temperatures. The comparison of these spectra can be used to investigate the effect of increasing temperature on melt structure, which is a first step to qualitatively extrapolating structural data from high-pressure glasses to the actual structure of high-pressure melts.

Experimental procedures

Ambient pressure $Na_3AlSi_7O_{17}$ and $NaAlSi_3O_8$ glasses were used as starting materials for the high-pressure samples. The ambient pressure $Na_3AlSi_7O_{17}$ glass was made by melting appropriate amounts of Na_2CO_3, Al_2O_3, and SiO_2 with about 0.2 wt% cobalt oxide to speed spin-lattice relaxation. Synthetic and natural starting materials were used to make the $NaAlSi_3O_8$ glass. One was remelted from a glass (Ab-1) previously described by Taylor and Brown (1979) while the other was a high purity natural albite crystal from Cazadero, California (George and Stebbins 1995) that was melted and quenched to a glass (Ab-2). All ambient pressure glasses were made by melting the appropriate starting materials in a Pt crucible and dipping the bottom of the crucible into a dish of water to quench the liquid into a glass (approximately 1000 K/s; Dingwell 1995). The high-pressure experiments were done at Bayerisches Geoinstitut in the 1000 ton multi-anvil press using an 18/11 type assembly. High-pressure glasses were synthesized from dried glass wrapped in Re-foil to form a 2 mm (diameter) by 3.5 mm (length) cylindrical capsule. Two or more samples were made for each composition, two of which had different fictive temperatures (T_f). The higher T_f samples were isobarically quenched from 2200 °C at 10 GPa by turning off the power to the $LaCrO_3$ furnace, yielding a quench rate of approximately 200-400 K/s. The lower T_f glasses were annealed at 10 GPa and near T_g, which was approximated from ambient pressure T_g data and $T_g(P)$ trends for $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$ compositions (Bagdassarov et al. 2004). The two $NaAlSi_3O_8$ glass samples were annealed at somewhat different temperatures to test for effects of uncertainties in estimating the high-pressure T_g. Ab-1 was used as the starting material for the quenched sample and the 715 °C annealing experiment (Ab-715) while Ab-2 was used for the 630 °C annealing (Ab-630) experiment. All high-pressure glasses were decompressed at a rate of about 2-3 GPa/hour and all compositions were verified using an electron microprobe with a large beam size of 30 μm to minimize Na migration. A small amount of an unknown crystalline impurity was detected in the Ab-715 sample using X-ray diffraction (XRD) and ^{27}Al MAS NMR. XRD was also used to verify that the Ab-630 sample was free of crystalline material. The lack of crystallinity in the Ab-630 glass shows that the unexpected ^{27}Al MAS results (see next section) for both annealed Ab samples are not due to crystallization, but reflect the actual structure of the $NaAlSi_3O_8$ glass.

The ^{27}Al MAS NMR spectra were collected with both a Varian Unity/Inova 600 spectrometer (14.1 T) and a Varian 18.8 T spectrometer operated by the Stanford Magnetic Resonance Laboratory. At both fields, Varian/Chemagnetics 'T3' probes with 3.2 mm zirconia rotors were used. The ^{27}Al frequencies are reported relative to aqueous $Al(NO_3)_3$. The ^{27}Al MAS experiments consisted of a single pulse acquisition with pulse widths (about 1 μs) corresponding to approximately 30° radiofrequency tip angles (solid); delays of 0.2 seconds were used between pulses to optimize the signal to noise ratio. No differential relaxation was observed in spectra with longer delay times. Samples were spun at 20 kHz at both magnetic fields, which resulted in slight peak overlap of the first spinning sideband of the $^{[4]}$Al peak with the low-frequency edge of the central transition of the $^{[6]}$Al in spectra collected at 18.8 T. Intensity from the spinning sidebands were subtracted from the $^{[6]}$Al region by fitting the corresponding sideband (approx. 150 ppm) and using this to obtain the relevant peak height, location, and widths. The MAS spectra were also background subtracted to remove a small signal due to substitution of $^{[6]}$Al into the zirconia rotors. The resulting background subtracted MAS spectra were fit with 2 Gaussian peaks for each of the Al coordinations (4, 5, and 6) to account for the slight non-Gaussian peak shapes, which are apparent even at 18.8 T.

Results and discussion

The effect of increasing external magnetic field on the peak widths is illustrated in the comparison of the spectra collected at 14.1 and 18.8 T (Fig. 1). These spectra have greater peak resolution, but are consistent with the previous ^{27}Al MAS NMR work collected at 9.4 T for this composition ($NaAlSi_3O_8$) and pressure (10 GPa) by Stebbins and Sykes (1990) and likely supports their suggestion that there are $^{[5]}$Al and $^{[6]}$Al species in glasses quenched from pressures as low as 8 GPa. The reduced peak overlap for different Al-coordinations ($^{[4]}$Al, $^{[5]}$Al, and $^{[6]}$Al) and the more Gaussian peak shapes in the spectrum collected at 18.8 T allow us to more robustly quantify these data relative to

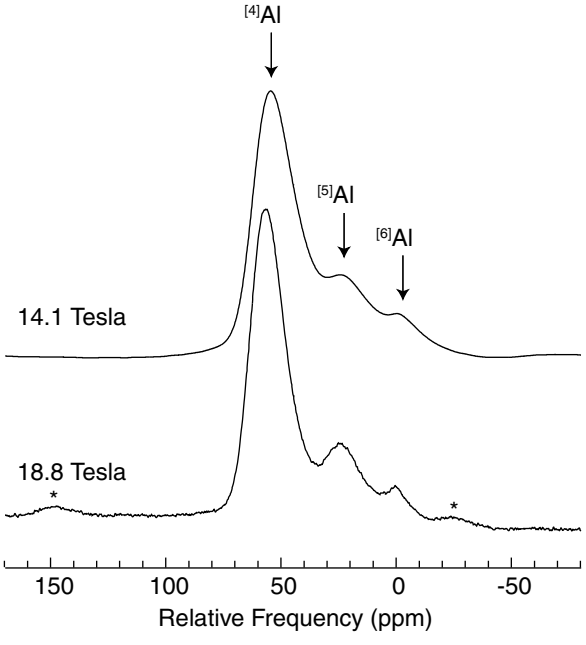

Figure 1. ^{27}Al MAS NMR spectra showing the effect of the external magnetic field (14.1 T vs. 18.8 T) on the spectrum for the $NaAlSi_3O_8$ (Ab) glass quenched from a liquid at 10 GPa. * denotes a spinning sideband.

those obtained at lower magnetic fields.

Only one peak with a maximum at 58 ppm is observed in the background-subtracted ^{27}Al MAS NMR spectrum (18.8 T) for the ambient pressure $NaAlSi_3O_8$ (Ab-1atm) glass (Fig. 2), which coincides with the region of the spectrum that is commonly assigned to fully polymerized (Q^4) tetrahedral Al ($^{[4]}$Al) in aluminosilicates (chemical shifts of approximately 56 to 64 ppm, Stebbins 1995b). Chemical shifts for 5 or 6-coordinated Al are in the ranges of 30 to 45 ppm and 0 to 16 ppm, respectively, yielding expected locations of peak maxima a few parts per million lower at the fields used here (Du and Stebbins 2005). Previous studies have shown that metaluminous Ca- and Mg-aluminosilicate glasses contain one to eight percent of the total aluminum present as $^{[5]}$Al (Stebbins et al. 2000; Toplis et al. 2000; Neuville et al. 2004). These differences between the metaluminous Na-, Ca-, and Mg-aluminosilicate glasses are completely consistent with a recent ^{27}Al MAS NMR study of depolymerized aluminosilicate glasses, which also shows that alkaline-earth aluminosilicate glasses contain more high-coordinated Al than alkali aluminosilicate glasses at ambient pressure and up to 10 GPa (Allwardt et al. 2005). Additionally, the lack of $^{[5]}$Al and $^{[6]}$Al present in the ambient pressure Ab glass may further support the conclusion of Toplis et al. (1997), which suggests that the presence of triclusters (oxygen bonded to three instead of two tetrahedral network formers) rather than $^{[5]}$Al or $^{[6]}$Al is responsible for a shift of viscosity maxima away from the charge balanced join in Na-aluminosilicate glasses ($NaAlO_2$-SiO_2). This structural observation may suggest that triclusters exist in these glasses, but are not necessarily present in Ca- or Mg-aluminosilicates, which may also explain why the viscosity trends for the alkaline earth and alkali systems are different (Toplis and Dingwell 2004). However, there has yet to be direct spectroscopic evidence to support the presence of triclusters in aluminosilicate glasses.

Quantification of the ^{27}Al MAS NMR spectrum of the ambient pressure $Na_3AlSi_7O_{17}$ (NTS-Ab-1atm) glass (Fig. 2) shows that about 1% of the Al in the sample is present as $^{[5]}$Al. The previous ^{27}Al MAS study (9.4 T) did not detect the presence of high-coordinated Al (Yarger et al. 1995), presumably due to the severe overlap of the $^{[4]}$Al peak in the region of the $^{[5]}$Al peak, especially since the $^{[5]}$Al peak is near the minimum detection limit in the spectrum measured at 14.1 T (not shown). We did not detect a peak attributable to $^{[6]}$Al, suggesting that a small peak in this region reported for a glass of similar composition at 9.4 T could be due to a minor crystalline impurity (Stebbins and Farnan 1992). Small amounts of $^{[5]}$Al have also been detected in ^{27}Al MAS NMR spectra (18.8 T) from $Na_3AlSi_3O_9$, $K_3AlSi_3O_9$, $Ca_3Al_2Si_6O_{18}$, and $Mg_3Al_2Si_6O_{18}$ glass at ambient pressure (Allwardt et al. 2003, 2005).

Two high-pressure $Na_3AlSi_7O_{17}$ glasses were synthesized at 10 GPa to investigate the temperature dependence of the percentage of high-coordinated Al in high-pressure glasses where one glass was quenched from a liquid (NTS-Ab-quench) and the other was annealed near T_g (NTS-Ab-475). The annealed glass represents the structure of the liquid at T_g (about 475 °C at 10 GPa), while the quenched glass probably represents a temperature slightly higher than T_g because of the 200 to 400 K/s quench rate. The peaks in the ^{27}Al MAS NMR spectrum (Fig. 3) for NTS-Ab-quench glass are narrower and more Gaussian than that previously reported (Yarger et al. 1995) due to the increased external magnetic field, but appear to agree with the previous results. By comparing the spectra from the 10 GPa NTS-Ab glasses (Fig. 3), it is clear that there is less high-coordinated Al in the annealed glass with lower T_f than in the quenched glass (Table 1). This suggests that for $Na_3AlSi_7O_{17}$ glasses, the amount of

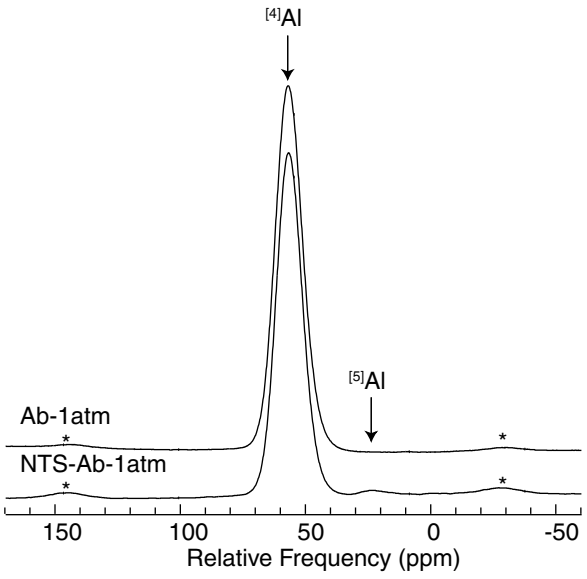

FIGURE 2. ^{27}Al MAS NMR spectra (18.8 T) of the ambient pressure Ab and $Na_3AlSi_7O_{17}$ (NTS-Ab) glasses.

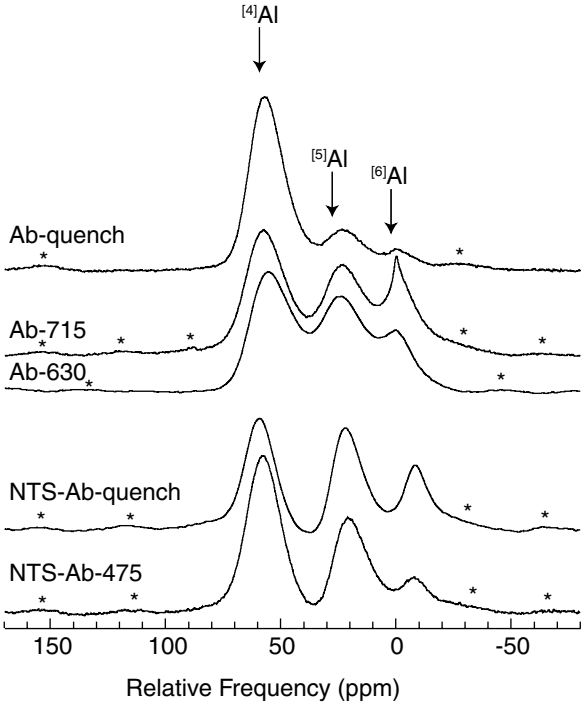

FIGURE 3. ^{27}Al MAS NMR spectra (18.8 T) of the 10 GPa high-pressure glasses. The sharp peak in the Ab-715 spectrum is due to $^{[6]}$Al in the crystalline impurity phase.

TABLE 1. Aluminum speciation of high-pressure glasses

	NTS-Ab 10 GPa		Ab 10 GPa	
	quenched	annealed (475 °C)	quenched	annealed (630 °C)
$^{[4]}$Al	38%	57%	79%	45%
$^{[5]}$Al	39%	29%	15%	36%
$^{[6]}$Al	23%	14%	6%	19%

high-coordinated Al likely increases with increasing temperature, suggesting that the percentages measured in a glass represent the minimum present in the melt structure at that pressure. These results agree with previous NMR and theoretical studies (Stebbins and Farnan 1992; Poe et al. 1993; Massiot et al. 1995) of ambient pressure NBO-containing aluminates and aluminosilicates. One explanation for this observation is that there is a lengthening of the Al-O bond with increasing temperature, which allows some of the tetrahedral Al in the sample to increase coordination to five (Stebbins and Farnan 1992).

Annealed and quenched glasses were also synthesized at 10 GPa for the $NaAlSi_3O_8$ composition to investigate how the amount of high-coordinated Al in a metaluminous glass depends on temperature. The peaks in the ^{27}Al MAS spectra (Fig. 3) were fit to obtain the percentage of high-coordinated Al of the Ab samples and reveals that, in contrast to the more depolymerized $Na_3AlSi_7O_{17}$ glasses, there is a drastic decrease in the percentage of high-coordinated Al with increasing fictive temperature. Additionally, the ^{27}Al MAS spectrum of the Ab-715 glass reveals a small amount of crystalline material (Fig. 3). Another glass annealed at 10 GPa, but at a lower temperature (630 °C) confirms that the crystalline impurity cannot be responsible for the large difference between the spectra of the quenched and annealed samples. The ^{27}Al MAS spectra of the two annealed glasses are identical, verifying that the thermal history dependence for the Ab glasses is fundamentally different from that observed for the NTS-Ab glasses.

NBO have been shown to be an important component in the generation of five- and six-coordinated Al (Yarger et al. 1995; Lee et al. 2003). However the Ab glass contains little or no NBO (Mysen 1988; Lee and Stebbins 2000), which would require that a different mechanism is responsible for generating high-coordinated Al in high-pressure metaluminous glasses than that recently observed in depolymerized glasses. One possibility is to form triclusters (and thereby creating NBO) by the mechanism proposed by Toplis et al. (1997), and then consume these NBO to form $^{[5]}$Al and $^{[6]}$Al. Another possibility is to form $^{[5]}$Al and $^{[6]}$Al by forcing a bridging oxygen atom (e.g., Si-O-Al or Si-O-Si) into the coordination sphere of an AlO_4 species, resulting in $^{[5]}$Al bonded to a three-coordinated oxygen atom (Daniel et al. 1996). Whatever the mechanism for Al coordination increases in Ab glasses, it appears to be less favorable at higher temperature.

A very recent study has indicated that some high-coordinated species may be lost during decompression after the isobaric quench (Allwardt et al. 2004). This, combined with the temperature effects observed for the depolymerized $Na_3AlSi_7O_{17}$ glass in the present study, suggest that the average Al-coordination measured in glasses should be considered a minimum value of the high-pressure melt. With this in mind, it still seems reasonable to believe that the maximum in oxygen diffusivity and the corresponding minimum in viscosity at 8 GPa is due to a maximum in the percentage of $^{[5]}$Al in the melt (Poe et al. 1997; Poe and Rubie 2000); however, neither the absolute percentage of $^{[5]}$Al measured in the glass nor the pressure at which the maximum is observed needs to be the same as it is in the melt structure.

Here we have attributed the observed effects of thermal history on glass structure to variations in T_g and thus to variations in melt structure with temperature. There remains the possibility that a portion of this phenomenon could instead be related to poorly known transient pressure drops in the multi-anvil apparatus during the quench from higher temperature, which is the result of thermal contraction of the sample and the surrounding media. This would suggest that the quenched samples would represent a slightly lower pressure; however, the exact value is dependent on the thermal expansivities of the materials involved. Such an effect is not likely to be responsible for the greater amounts of high-coordinated Al observed in the annealed $NaAlSi_3O_8$ glasses as we would expect a similar temperature dependence for the $Na_3AlSi_7O_{17}$ glasses. In fact, $Na_3AlSi_7O_{17}$ has a greater thermal expansivity (Lange and Carmichael 1987), at least at ambient pressure, and a greater pressure drop on quench than would be expected, yet more $^{[5]}$Al and $^{[6]}$Al are observed in the quenched glass.

ACKNOWLEDGMENTS

The authors thank B. Schmidt and A. Vailionis for collection of XRD data and R. Jones for assistance with operating the electron microprobe. Additionally, the authors thank N. Bagdassarov for unpublished data on $T_g(P)$ for albite glasses and J. Puglisi for access to the 18.8 T NMR at the Stanford Magnetic Resonance Laboratory. This work was supported by the National Sciences Foundation [EAR-0104926 (J.R.A. and J.F.S.)]. We would also like to thank the visitor's program at the Bayerisches Geoinstitut for additional funding for J.R.A. B.T.P. acknowledges partial support from EU "IHP-Access to Research Infrastructures" Programme (HPRI-1999-CT-00004 to D.C. Rubie of the Bayerisches Geoinstitut).

REFERENCES CITED

Allwardt, J.R., Stebbins, J.F., Frost, D.J., and Schmidt, B.C. (2003) The effect of modifier cations on the amount of five- and six-coordinated aluminum present in high-pressure aluminosilicate glasses. Bayerisches Forschunsintitut für Experimentelle Geochemie und Geophysik, Universität Bayreuth, Annual Report, 3.7i.

Allwardt, J.R., Schmidt, B.C., and Stebbins, J.F. (2004) Structural mechanisms of compression and decompression in high-pressure $K_2Si_4O_9$ glasses: An investigation utilizing Raman and NMR spectroscopy of high-pressure glasses and crystals. Chemical Geology, 213, 137–151.

Allwardt, J.R., Stebbins, J.F., Schmidt, B.C., Frost, D.J., Withers, A.C., Hirschmann, M.M. (2005) Aluminium coordination and density of high-pressure aluminosilicate glasses. American Mineralogist, in press.

Bagdassarov, N.S., Maumus, J., Poe, B., Slutskiy, A-B., Bulatov, V.K. (2004) Press dependence of Tg, in silicate glasses from electrical impedance measurements. Physics and Chemistry of Glasses, 45, 197–214.

Daniel, I., McMillan, P.F., Gillet, P., and Poe, B.T. (1996) Raman spectroscopic study of structural changes in calcium aluminate ($CaAl_2O_4$) glass at high pressure and high temperature. Chemical Geology, 128, 5–15.

Dingwell, D.B. (1995) Relaxation in silicate melts: Some applications. In J.F. Stebbins, P.F. McMillan, and D.B. Dingwell, Eds., Structure, Dynamics and properties of silicate melts. Reviews in Mineralogy, 32, 21–66. Mineralogical Society of America, Washington, D.C.

Du, L.-S. and Stebbins, J.F. (2005) Site connectivities in sodium aluminoborate glasses: Multinuclear and multiple quantum NMR results. Solid State NMR, 27, 37–49.

Du, L.-S., Allwardt, J.R., Schmidt, B.C., and Stebbins, J.F. (2004) Pressure-induced structural changes in a borosilicate glass-forming liquid: boron coordination, non-bridging Oxygens, and network ordering. Journal of Non-Crystalline Solids, 337, 196–200.

George, A.M. and Stebbins, J.F. (1995) High-temperature Na-23 MAS NMR data for albite: comparison to chemical shift models. American Mineralogist, 80, 878–884.

Hochella, M.F., Jr. and Brown, G.E., Jr. (1985) The structures of albiteand jadeite

composition glasses quenched from high pressure. Geochimica et Cosmochimica Acta, 49, 1137–1142.
Lange, R.L. and Carmichael, I.S.E. (1987) Thermodynamic properties of silicate liquids with emphasis on density, thermal expansion, and compressibility. In J. Nicholls and J.K. Russell, Eds., Modern Methods of Igneous Petrology: Understanding Magmatic Processes. Reviews in Mineralogy, 24, 25–64. Mineralogical Society of America, Washington, D.C.
Lee, S.K. (2004) Structure of silicate glasses and melts at high pressure: Quantum chemical calculations and solid-state NMR. Journal of Physical Chemistry B, 108, 5889–5900.
Lee, S.K and Stebbins, J.F. (2000) Al-O-Al and Si-O-Si sites in framework aluminosilicate glasses with Si/Al=1: quantification of framework disorder. Journal of Non-Crystalline Solids, 270, 260–264.
Lee, S.K., Fei, Y., Cody, G., and Mysen, B.O. (2003) Disorder in silicate glasses and melts at 10 GPa. Geophysical Research Letters, 30, 1845.
Li, D., Secco, R.A., Bancroft, G.M., and Fleet, M.E. (1996) Pressure induced coordination change of Al in silicate melts from Al K edge XANES of high pressure $NaAlSi_2O_6$-$NaAlSi_3O_8$ glasses. Geophysical Research Letters, 22, 3111–3114.
Massiot, D., Trumeau, D., Touzo, B., Farnan, I., Rifflet, J.-C., Douy, A., and Coutres, J.-P. (1995) Structure and dynamics of $CaAl_2O_4$ from liquid to glass: A high-temperature ^{27}Al NMR time-resolved study. Journal of Physical Chemistry, 99, 16455–16459.
McMillan, P.F. and Graham, C.M. (1981) The Raman spectra of quenched albite and orthoclase glasses from 1 atm to 40 kb. In C.E. Ford, Ed., Progress in experimental petrology, p. 112–115. National Environmental Research Council, London.
McMillan, P.F. and Kirkpatrick, R.J. (1992) Al coordination in magnesium aluminosilicate glasses. American Mineralogist, 77, 898–900.
Mysen, B.O. (1988) Structure and Properties of Silicate Melts. Elsevier, Amsterdam.
——— (2003) Physics and chemistry of silicate glasses and melts. European Journal of Mineralogy, 15, 781–802.
Mysen, B.O., Virgo, D., and Scarfe, C.M. (1980) Relations between the anionic structure and viscosity of silicate melts—a Raman spectroscopic study. American Mineralogist, 65, 690–710.
Mysen, B.O., Virgo, D., Danckwerth, P., Seifert, F.A., and Kushiro, I. (1983) Influence of pressure on the structure of melts on the joins $NaAlO_2$-SiO_2, $CaAl_2O_4$-SiO_2, and $MgAl_2O_4$-SiO_2. Neues Jahrbuch Für Mineralogie-Abhandlungen, 147, 281–303.
Neuville, D., Cormier, L., and Massiot, D. (2004) Al environment in tectosilicate and peraluminous glasses: A ^{27}Al MQ-MAS NMR, Raman, and XANES investigations. Geochimica et Cosmochimica Acta, 68, 5071–5079.
Ohtani, E., Taulle, F., and Angell, C.A. (1985) Al^{3+} coordination changes in liquid aluminosilicates under pressure. Nature, 314, 78–81.
Poe, B.T. and Rubie, D.C. (2000) Transport properties of silicate melts at high pressure. In H. Aoki, Y. Syono, R.J. Hemley, Eds., Physics Meets Mineralogy, p. 340–353. Cambridge University Press, Cambridge.
Poe, B.T., McMillan, P.F., Coté, B., Massiot, D., and Coutures, J.P. (1993) Magnesium and calcium aluminate liquids: In situ high-temperature ^{27}Al NMR spectroscopy. Science, 259, 786–788.
——— (1994) Structure and dynamics in calcium aluminate liquids: high-temperature ^{27}Al NMR and Raman spectroscopy. Journal of the American Ceramic Society, 77, 1832–1838.
Poe, B.T., McMillan, P.F., Rubie, D.C., Chakraborty, S., Yarger, J., and Diefenbacher, J. (1997) Silicon and oxygen self-diffusivities in silicate liquids measured to 15 gigapascals and 2800 Kelvin. Science, 276, 1245–1248.
Richet, P. and Neuville, D.R. (1992) Thermodynamics of silicate melts: Configurational properties. In S. Saxena, Ed., Advances in Physical Geochemistry, 11, 132–160. Springer-Verlag, Heidelberg.
Stebbins, J.F. (1995a) Dynamics and structure of silicate and oxide melts: Nuclear magnetic resonance studies. In J.F. Stebbins, P.F. McMillan, and D.B. Dingwell, Eds., Structure, Dynamics and properties of silicate melts. Reviews in Mineralogy, 32, 191–246. Mineralogical Society of America, Washington, D.C.
——— (1995b) Nuclear magnetic resonance spectroscopy of silicates and oxides in geochemistry and geophysics. In T.J. Ahrens, Ed., Handbook of Physical Constants, p. 303–332. American Geophysical Union, Washington D.C.
Stebbins, J.F. and Farnan, I. (1992) Effects of high-temperature on silicate liquid structure: A multinuclear NMR study. Science, 255, 586–589.
Stebbins, J.F. and Sykes, D. (1990) The structure of $NaAlSi_3O_8$ liquid at high pressure: new constraints from NMR spectroscopy. American Mineralogist, 75, 943–946.
Stebbins, J.F., Kroeker, S., Lee, S.K., and Kiczenski, T.J. (2000) Quantification of five-and six-coordinated aluminum in aluminosilicate and fluoride-containing glasses by high field, high resolution ^{27}Al-NMR. Journal of Non-Crystalline Solids, 275, 1–6.
Stolper, E.M. and Ahrens, T.J. (1987) On the nature of pressure-induced coordination changes in silicate melts and glasses. Geophysical Research Letters, 14, 1231–1233.
Toplis, M.J. and Dingwell, D.B. (2004) Shear viscosities of CaO-Al_2O_3-SiO_2 and MgO-Al_2O_3-SiO_2 liquids: Implications for the structural role of aluminum and the degree of polymerization of aluminosilicate melts. Geochimica et Cosmochimica Acta, 68, 5169–5188.
Toplis, M.J., Dingwell, D.B., and Lenci, T. (1997) Peraluminous viscosity maxima in Na_2O-Al_2O_3-SiO_2 liquids: The role of triclusters in tectosilicate melts. Geochimica et Cosmochimica Acta, 61, 2605–2612.
Toplis, M.J., Kohn, S.C., Smith, M.E., and Poplett, I.J.F. (2000) Fivefold-coordinated aluminum in tectosilicate glasses observed by triple quantum MAS NMR. American Mineralogist, 85, 1556–1560.
Waff, H.S. (1975) Pressure-induced coordination changes in magmatic liquids. Geophysical Research Letters, 2, 193–196.
Wolf, G.H., Durben, D.J., and McMillan, P.F. (1990) High-pressure spectroscopic study of sodium tetrasilicate ($Na_2Si_4O_9$) glass. Journal of Chemical Physics, 93, 2280–2288.
Xue, X., Stebbins, J.F., Kanzaki, M., McMillan, P.F., and Poe, B. (1991) Pressure induced silicon coordination and tetrahedral structural changes in alkali oxide-silica melts up to 12 GPa: NMR, Raman, and infrared spectroscopy. American Mineralogist, 76, 8–26.
Yarger, J.L., Smith, K.H., Nieman, J., Diefenbacher, J., Wolf, G.H., Poe, B.T., and McMillan, P.F. (1995) Al coordination changes in high-pressure aluminosilicate liquids. Science, 270, 1964–1967.

MANUSCRIPT RECEIVED JUNE 2, 2004
MANUSCRIPT ACCEPTED FEBRUARY 11, 2005
MANUSCRIPT HANDLED BY MICHAEL TOPLIS