An *in situ* high-pressure NMR study of sodium coordination environment compressibility in albite glass

Sarah J. Gaudio[1*], Trenton G. Edwards[2], Sabyasachi Sen[2]

[1]Department of Earth and Planetary Sciences, University of California, Davis, California 95616, USA

[2]Division of Materials Science and Engineering, University of California, Davis, California, 95616, USA

*Corresponding author (e-mail sjgaudio@ucdavis.edu)

REVISION 1

Abstract

The pressure dependent modification of the Na-O coordination environment in albite glass is studied *in situ* to 2 GPa using high-pressure solid-state ^{23}Na nuclear magnetic resonance spectroscopy. Compression of the glass at ambient temperature results in shortening of the Na-O bond distance. The concomitant decrease in volume of the local Na-O coordination environment alone can account for the bulk compressibility of albite glass at 300 K. These results provide the first direct experimental evidence of a collapse of the open aluminosilicate framework that helps explain previously reported densification of aluminosilicate glasses and liquids at relatively low pressures without accompanying change in the average coordination number of the network forming Al and Si cations. Such structural changes at relatively low pressures may have far reaching implications for the mechanistic understanding of compressibility and viscosity anomalies characteristic of open tetrahedral aluminosilicate network glasses and melts of geological importance.

Keywords: in situ, high pressure, NMR, glass structure, compressibility, albite, sodium aluminosilicate

Introduction

The physical properties of vitreous and molten $NaAlSi_3O_8$ (hereafter referred to as albite) have been studied extensively as an analog for strongly polymerized melts generated and differentiated in the Earth's crust. Although the thermal expansion, compressibility, and viscosity of albite glass/liquid at 1 atm conditions are relatively well constrained (e.g. Kress et al. 1988; Lange 1996; Sipp et al. 2001), one must extrapolate these physical properties to higher pressures to model the magmatic processes that occur within the Earth. Accurate predictions of

45 silicate melt properties at pressure depend on detailed understanding of the structural changes
46 accompanying their densification.

47 Albite, like silica, is a fully connected three-dimensional network of corner-shared
48 $[AlO_{4/2}]^{-1}$ and $[SiO_{4/2}]^{0}$ tetrahedra. Much like silica, but with (Na^{+} + Al^{3+}) substituted for 1/4 of
49 the Si^{4+}, albite glass at 1 atm maintains an open framework structure. Na^{+} cations occupy the
50 large holes within the aluminosilicate framework and charge-compensate for the negatively
51 charged $[AlO_{4/2}]^{-1}$ tetrahedra (Lee and Stebbins 1999, 2000). Both albite and silica glass are
52 highly compressible, and become more compressible with increasing pressure below ~ 2.5 GPa
53 (Bridgeman et al. 1925; Kuryaeva and Surkov 2010; Sonneville et al. 2013). This behavior is
54 considered to be anomalous as it is the opposite of what is expected and observed for crystals
55 with the same chemistry (Benusa et al. 2005).

56 While the changes in the density of albite and silica glass are large within the first few
57 GPa of compression, the concomitant structural changes of the coordination environments of the
58 network forming cations are found to be rather subtle. X-ray diffraction (XRD) studies of albite
59 glass structure recovered from pressures <2.0 GPa identify only minor distortions of the
60 tetrahedral network (Hochella and Brown Jr. 1985). On the other hand, samples synthesized at
61 relatively high pressures >6 GPa show shortening of both the Na-O (Lee et al., 2006) and T-O (T
62 = Si,Al) bond distances, reduction of the intertetrahedral bond angles <T-O-T°> (Stebbins and
63 Sykes 1990; Sykes et al. 1993) and the presence of some Al coordinated by >4 oxygens (Yarger
64 et al. 1995; Allwardt et al. 2005). The lack of major changes to glass structure at low pressure
65 forced these studies to speculate that the shortening of the Na-O bond distance must be the
66 dominant mechanism of densification, similar to what is observed in perovskites with organic
67 charge-balancing cations (e.g. Swainson et al. 2007), and indicative of a collapse of the open

tetrahedral framework in the region of anomalous compressibility, as mentioned above. However, this hypothesis lacks direct experimental confirmation because such pressure-induced topological changes are either partially or fully reversible on decompression making the evaluation of their true nature and extent impossible for *ex situ* structural studies. Observation of nearest-neighbor structural changes associated with elastic deformation requires application of an element-specific spectroscopic technique such as nuclear magnetic resonance (NMR) spectroscopy. The application of solid-state NMR spectroscopy *in situ* at high pressure is limited owing to the technological challenges associated with designing a high-pressure probe head (1) having suitable non-magnetic materials that can operate up to a few GPa, and (2) provides sufficient sensitivity and sample volume. Recently, we developed a high-pressure NMR probe in our laboratory capable of maintaining hydrostatic pressures up to 2.5 GPa. Here, we report the results of an *in situ* high-pressure (HP) static ^{23}Na NMR spectroscopic study of compression on the Na-O nearest-neighbor coordination environment in albite glass to 2 GPa. We exploit the well-established trends relating the ^{23}Na NMR peak position with the average Na-O distance and coordination number that are reported for sodium aluminosilicate minerals and glasses (Xue and Stebbins 1993; George and Stebbins 1995; Lee and Stebbins 2003) to demonstrate the nature of the pressure-induced elastic deformation of the Na-O coordination environment. This has important implications for understanding the pressure dependence of Na^+ mobility, viscosity, Na partitioning behavior, and the pressure and temperature dependence of bulk albite glass and liquid density.

Methods

The albite glass was prepared at Corning, Inc. in a 5 kg batch from stoichiometric proportions of Puratronic® grade Na_2CO_3, Al_2O_3, and SiO_2 powders. The powder mixture was decarbonated by heating overnight in a box furnace at 873 K and then melted in a platinum crucible at 1873 K for 3 hours. Molten albite was quenched to glass by removing the crucible from the furnace and cooling in air. The recovered glass was crushed and re-melted twice under identical conditions to ensure chemical homogeneity. Electron probe micro-analysis confirmed the homogeneity and near stoichiometric proportions of Na_2O, Al_2O_3, and SiO_2 of the starting glass (Gaudio et al., *In Review*).

The *in situ* high-pressure NMR experiments were performed using a custom-built NMR probe where a core-drilled rod of the albite glass (~ 1 mm diameter by 3 mm length) was pressurized using a cylindrical high-pressure cell (*EasyCell 30*, Almax-Easylab) that was configured for NMR measurements (Wang et al. 2011). A simple cross-sectional schematic of the cell configuration is shown in Figure 1. The cell sleeve has an outer and an inner shell made of non-magnetic Cu-Be alloy and MP35N superalloy, respectively (Walker 1999). An NMR coil was wrapped directly onto the sample and the leads were epoxied into a pressure cell feed-through. The sample/coil is fitted inside a Teflon® cylindrical cup filled with Daphne 7373 paraffin industrial oil as a pressure transmitting fluid and is held in the pressure sleeve using a locking nut (Otero-Leal et al. 2009). Pressure is applied to the Teflon cup using a hydraulic ram traveling through a hollow locking nut and subsequently advancing a sapphire piston (8mm diameter x 25mm length) from the opposite end of the cell. The piston-side locking nut secures the advancing piston, allowing for the cell to remain pressurized when separated from the hydraulic press. The compression of the Teflon cap and fluid allow for the application of hydrostatic pressure on the sample. Cell pressure was determined from the applied hydraulic

pressure that was calibrated in separate runs using the known relationship between pressure and the electrical resistance of a manganin wire (Nomura et al. 1979). The loaded pressure cell is placed in the NMR probe and positioned such that the coil is perpendicular to the applied external magnetic field (additional experimental details are given in Edwards et al. 2014).

The ^{23}Na static NMR spectra were collected in a horizontal bore (inner bore diameter of 180 mm) 7T Bruker imaging magnet equipped with a BrukerBioSpec spectrometer system operating at a ^{23}Na Larmor frequency of 79 MHz. Single-pulse ^{23}Na NMR spectra were collected at 0.5 GPa intervals in pressure, ranging between ambient (~ 0 GPa) and 2 GPa, using a $\pi/8$ solid pulse (1.5μs) with a recycle delay of 0.5 s. Approximately 1000 to 2000 free induction decays were averaged and Fourier transformed to obtain each spectrum. Phasing methods and parameters were kept constant for processing of all spectra. Due to the large quadrupolar broadening of the static ^{23}Na line shapes, only relative changes in the spectral peak position as a function of pressure are of interest. Therefore, all ^{23}Na NMR spectra are referenced to the peak maximum of the unpressurized albite glass sample in the pressure cell.

Results and Discussion

Static ^{23}Na NMR spectra of albite glass collected *in situ* at pressures from 0 to 2 GPa show a single broad peak with a full width at half maximum of ~ 110 ppm, that does not change significantly with pressure (Fig. 2). Over 2.0 GPa, the frequency of the peak maximum increases by 4.6 ppm relative to the peak maximum position in the non-compressed sample (Fig. 3-top). The relative shift in the ^{23}Na NMR peak position is completely reversible upon decompression, indicating that cold (room temperature) compression on albite glass structure to 2.0 GPa is fully elastic (Fig. 2 and Table 1).

Previous work indicates that the Na-O bond distance is inversely proportional to the ^{23}Na isotropic chemical shift (δ_{iso}) for Na sites in crystalline albite (Xue and Stebbins 1993; George and Stebbins 1995). For sodium aluminosilicate glasses and liquids at 1 atm and for those recovered from high pressures, the ^{23}Na NMR spectrum displays a single broad peak (e.g. Oestrike et al. 1988; Maekawa et al. 1997; Lee and Stebbins, 2003; Lee et al. 2006) whose position can be related to the average Na-O bond distance. Systematic studies of aluminosilicate crystals and glass compositions established a relationship of between −0.0155 to −0.0119 Å/ppm (Xue and Stebbins 1993; Angeli et al. 2000; Lee and Stebbins 2003) between the ^{23}Na NMR peak position and the Na-O bond distance. This relationship, in combination with the average Na-O bond distance of 2.71 Å for albite glass prepared at 1 atm (Hochella and Brown Jr. 1985), enables the calculation of the average Na-O bond distance using pressure-dependent relative frequency shift of the ^{23}Na NMR peak maximum obtained in the present study. Substitution of the relative frequency shift of the ^{23}Na NMR peak maximum for the corresponding shift in δ_{iso} is supported by the lack of any significant change in the quadrupolar coupling constant of ^{23}Na nuclides in albite and Na-Ca aluminosilicate glass samples recovered from pressures up to 8 GPa (Lee et al. 2006; Lee 2011). The average Na-O bond distance as a function of pressure is shown in Figure 3(top). The average Na-O distance displays a monotonic decrease with pressure by 0.063±0.009Å or ~2.3% at 2.0 GPa (Fig. 3-top and Table 1). We calculate the decrease in the average volume of the Na-O coordination environment with pressure by assuming the environment is spherical after Wu et al. (2009) using the Na-O bond distance as the sphere's radius (Table 1). Over 2 GPa, the Na-O coordination sphere volume decreases by 6.9±0.9% (Fig. 3-bottom). The changes in volume of the Na-O environment alone and that of bulk albite

158 glass upon compression at ambient temperature (Kuryaeva and Surkov 2010) show remarkable
159 agreement over the same pressure range (Fig. 3-bottom).

160 When taken together, these results directly demonstrate that the majority of the
161 compressibility of the local Na environment accounts for the bulk compressibility of albite glass.
162 It is consistent with the structural scenario for aluminosilicate glasses where the modifier cations
163 occupy the highly compressible "voids" in the open tetrahedral framework. Furthermore, the
164 nearest-neighbor coordination environments of these cations act as a passive indicator of
165 tetrahedral network collapse upon compression at relatively low pressures. In the absence of a
166 significant change in the coordination of the network-forming cations Si^{4+} and Al^{3+} (Gaudio et al.
167 In Review), such network collapse is also likely related to the anomalous compressibility in this
168 low pressure regime that is characteristic of albite and silica glasses with fully polymerized
169 tetrahedral networks (Bridgeman et al. 1925; Kuryaeva and Surkov 2010; Sonneville et al. 2013)
170

171 **Implications**

172 The pressure dependence of the ^{23}Na NMR spectra indicates that monotonic reduction of
173 the average Na-O bond length and the corresponding volume reduction of the Na-O nearest
174 neighbor coordination shell accounts for the bulk densification of albite glass to 2 GPa. These
175 results provide confirmation of a long-speculated mechanism of low pressure densification via
176 the collapse of the open tetrahedral aluminosilicate framework, and may have important
177 implications for our mechanistic understanding of the nature of elastic deformation, pressure
178 dependence of element partitioning and viscosity of fully polymerized aluminosilicate magmatic
179 liquids. In particular, volume reduction within the oxygen "cage" for Na^+ should effectively
180 increase its ionic field strength (Angell et al. 1982; Kelsey et al. 2009), a condition that favors

181 the formation of stable high-coordinated Al (Stebbins et al. 2013 and citations therein), which
182 contributes to a decreasing viscosity and increasing density with pressure.
183
184 **Acknowledgements**
185 This work was supported by a grant from the National Science Foundation (NSF-DMR
186 1104869) to SS.
187

188

Table 1: Pressure, Relative shift of ^{23}Na peak maximum, calculated average Na-O bond distance, Na-O coordination shell volume, and volume change with pressure

Pressure (GPa)	relative shift of peak maximum (ppm)	average Na-O distance** Å	Na-O coordination shell volume Å^3	Relative *volume* change %
0.0	0	2.710	83.4	0.0
0.5	1.6	2.689±0.003	81.2±0.2	-2.3±0.3
1.0	3.5	2.662±0.006	78.6±0.6	-5.2±0.7
1.5	3.9	2.656±0.007	78.1±0.6	-5.9±0.8
2.0	4.6	2.647±0.009	77.2±0.7	-6.9±0.9
0.0*	0	2.710	83.4	0.0

* Following decompression

**Data from Xue and Stebbins (1993), George and Stebbins (1995), Angeli et al., 2000 and Lee and Stebbins (2003) were used to relate the relative shift of the ^{23}Na peak maximum to the average Na-O distance (d<Na-O>) assuming 8 nearest neighbor oxygens. There is some dispersion in the average Na-O versus ^{23}Na chemical shift relationships reported in Lee and Stebbins (2003) and Angeli et al. (2000). Therefore, we report the average of the d<Na-O> bond distance calculated for each relationship, while the uncertainty in this value represents the difference between the average value and the maximum or minimum calculated value. The average$_{Max}$ Na-O bond distance is calculated using the Na-O versus ^{23}Na chemical shift relationship given in Lee and Stebbins (2003) where d<Na-O> =–0.0155*(relative shift in peak position) + 2.71 Å. The average$_{Min}$ Na-O bond distance is calculated using the Na-O versus ^{23}Na chemical shift relationship given in Angeli et al. (2000) were d<Na-O>=–0.0119*(relative shift in peak position) +2.71 Å. 2.71 Å is the average Na-O bond distance in albite glass reported in Hochella and Brown Jr. (1985) and in Xue and Stebbins (1993).

189

References Cited

Allwardt, J.R., Poe, B.T., and Stebbins, J.F. (2005) The effect of fictive temperature on Al coordination in high-pressure (10 GPa) sodium aluminosilicate glasses. American Mineralogist 90, 1453-1457.

Angeli F., Delaye J.M., Charpentier T., Petit J.C., Ghaleb D. , Faucon P.(2000) Influence of glass chemical composition on the Na-O bond distance: A Na-23 3Q-MAS NMR and molecular dynamics study, Journal of Non-Crystalline Solids, 276, 132–144

Angell, C. A., Cheeseman, P. A., and Tamaddon, S. (1982) Pressure enhancement of ion mobilities in liquid silicates from computer simulation studies to 800 kilobars. Science 218, 885-887.

Benusa, M. D., Angel, R. J., Ross, N. L. (2005) Compression of albite, NaAlSi3O8. American Mineralogist 90, 1115-1120.

Bridgman, P. W. (1925) Compressibility of glasses. American Journal of Science 58, 359-367.

Edwards, T., Endo, T., Walton, J. H., Sen, S. (2014) Observation of the transition state for pressure-induced $BO_3 \rightarrow BO_4$ conversion in glass. Science 345, 1027-1029.

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

Hochella, M.F., and Brown, G.E. (1985) The structures of albite and jadeite composition glasses quenched from high pressure. Geochimica et Cosmochimica Acta 49, 1137-1142.

Kress, V. C., Williams, Q., and Carmichael, I. S. (1988) Ultrasonic investigation of melts in the system Na_2O-Al_2O_3-SiO_2. Geochimica et Cosmochimica Acta 52, 283-293.

Kelsey, K.E., Stebbins, J.F., Mosenfelder, J.L., and Asimow, P.D. (2009) Simultaneous aluminum, silicon, and sodium coordination changes in 6 GPa sodium aluminosilicate glasses. American Mineralogist 94, 1205-1215.

Kuryaeva, R. G., and Surkov, N. V. (2010) Behavior of the refractive index and compressibility of albite glass at pressures up to 6.0 GPa. Geochemistry International 48, 835-841.

Lange, R. A. (1996) Temperature independent thermal expansivities of sodium aluminosilicate melts between 713 and 1835 K. Geochimica et Cosmochimica Acta 60, 4989-4996.

Lee, S. K. (2011) Simplicity in melt densification in multicomponent magmatic reservoirs in Earth's interior revealed by multinuclear magnetic resonance. Proceedings of the National Academy of Sciences 108, 6847-6852.

Lee, S. K., and Stebbins, J. F. (1999) The degree of aluminum avoidance in aluminosilicate glasses. American Mineralogist 84, 937-945.

Lee, S. K., and Stebbins, J. F. (2000) The structure of aluminosilicate glasses: high-resolution ^{17}O and ^{27}Al MAS and 3Q MAS NMR study. The Journal of Physical Chemistry B 104, 4091-4100.

Lee, S.K., and Stebbins, J.F. (2003) The distribution of sodium ions in aluminosilicate glasses: A high-field Na-23 MAS and 3Q MAS NMR study. Geochimica et Cosmochimica Acta 67, 1699-1709.

Lee, S.K., Cody, G.D., Fei, Y., and Mysen, B.O. (2006) The effect of Na/Si on the structure of sodium silicate and aluminosilicate glasses quenched from melts at high pressure: A multi-nuclear (Al-27, Na-23, O-17) 1D and 2D solid-state NMR study. Chemical Geology 229, 162-172.

Maekawa, H., Nakao, T., Shimokawa, S., and Yokokawa, T. (1997) Coordination of sodium ions in $NaAlO_2$–SiO_2 melts: a high temperature ^{23}Na NMR study. Physics and chemistry of Minerals 24, 53-65.

Nomura, M., Yamamoto, Y., Ochiai, Y., & Fujiwara, H. (1979) The measurement of the resistance of manganin wire with the cubic-anvil type pressure apparatus. Japanese Journal of Applied Physics 18, 363-366.

Oestrike, R., Yang, W. H., Kirkpatrick, R. J., Hervig, R. L., Navrotsky, A., and Montez, B. (1987) High-resolution ^{23}Na, ^{27}Al and, ^{29}Si NMR spectroscopy of framework Aluminosilicate glasses. Geochimica et Cosmochimica Acta 51, 2199-2209.

Otero-Leal, M., Rivadulla, F., Saxena, S. S., Ahilan, K., & Rivas, J. (2009) Nature of the high-pressure tricritical point in MnSi. Physical Review B 79, 060401.

Sipp, A., Bottinga, Y., and Richet, P. (2001) New high viscosity data for 3D network liquids and new correlations between old parameters. Journal of non-crystalline solids 288,166-174.

Sonneville, C., De Ligny, D., Mermet, A., Champagnon, B., Martinet, C., Henderson, G. H., Deschamps, T., Margueritat, J., and Barthel, E. (2013) In situ Brillouin study of sodium alumino silicate glasses under pressure. The Journal of Chemical Physics 139, 074501.

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., Wu, J., and Thompson, L. M. (2013) Interactions between network cation coordination and non-bridging oxygen abundance in oxide glasses and melts: Insights from NMR spectroscopy. Chemical Geology 346, 34-46.

Swainson, I. P., Tucker, M. G., Wilson, D. J., Winkler, B., & Milman, V. (2007). Pressure response of an organic-inorganic perovskite: Methylammonium lead bromide. Chemistry of materials 19, 2401-2405.

Walker, I. R. (1999) Nonmagnetic piston–cylinder pressure cell for use at 35 kbar and above. Review of scientific instruments 70, 3402-3412.

Wang, X. F., Liu, R. H., Gui, Z., Xie, Y. L., Yan, Y. J., Ying, J. J., Luo, X.G. and Chen, X. H. (2011). Superconductivity at 5 K in alkali-metal-doped phenanthrene. Nature communications 2, 507.

Wu, J., Deubener, J., Stebbins, J.F., Grygarova, L., Behrens, H., Wondraczek, L., and Yue, Y., (2009) Structural response of a highly viscous aluminoborosilicate melt to isotropic and anisotropic compression. Journal of Chemical Physics 131, 104504-1-10.

Xue, X., & Stebbins, J. F. (1993) ^{23}Na NMR chemical shifts and local Na coordination environments in silicate crystals, melts and glasses. Physics and Chemistry of Minerals 20, 297-307.

Yarger, J. L., Smith, K. H., Nieman, R. A., 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.

Figure Captions

Figure 1. Pressure cell schematic. External pressure is applied to advance a piston and compress a PTFE cup containing a pressure transmitting fluid. A sample suspended in the fluid experiences hydrostatic pressure and a custom NMR coil placed around the sample allow for in-situ HP-NMR experiments. All component materials are chosen such that the pressurizing cell is completely non-magnetic. **Cell components shown are not to scale.*

Figure 2. Static ^{23}Na NMR spectra of albite glass collected *in situ* up to 2.0 GPa shown on a frequency scale relative to the peak position at 0 GPa. Spectra collected at 0, 1, and 2 GPa are shown as black lines labeled in order of increasing pressure from bottom to top with the spectrum collected after decompression to room pressure (red line) shown first in the sequence. Inset shows magnified view of the peak positions of spectra collected at 0 (black line), 0.5 (red line), 1.5 (blue line), and 2.0 GPa (green line). Spectra labeled in order of increasing pressure from bottom to top).

Figure 3. *Top*) Relative shift of the ^{23}Na NMR peak maximum (filled squares) and calculated average Na-O bond distance (open squares) for albite glass as a function of pressure. *Bottom*) Percent volume change calculated from reduction in the average Na-O distance only (filled circles-This study) and reported for bulk albite glass (open circles-Kuryaeva and Surkov, 2010) as a function of pressure.

Figure 1

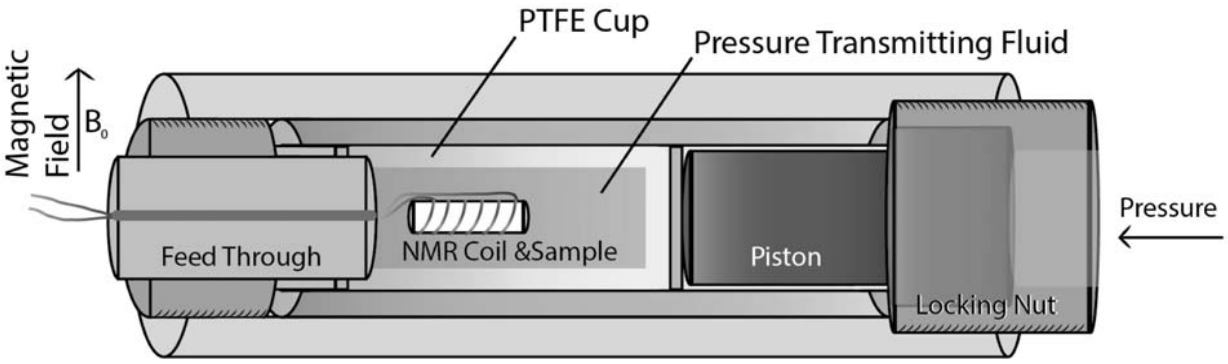
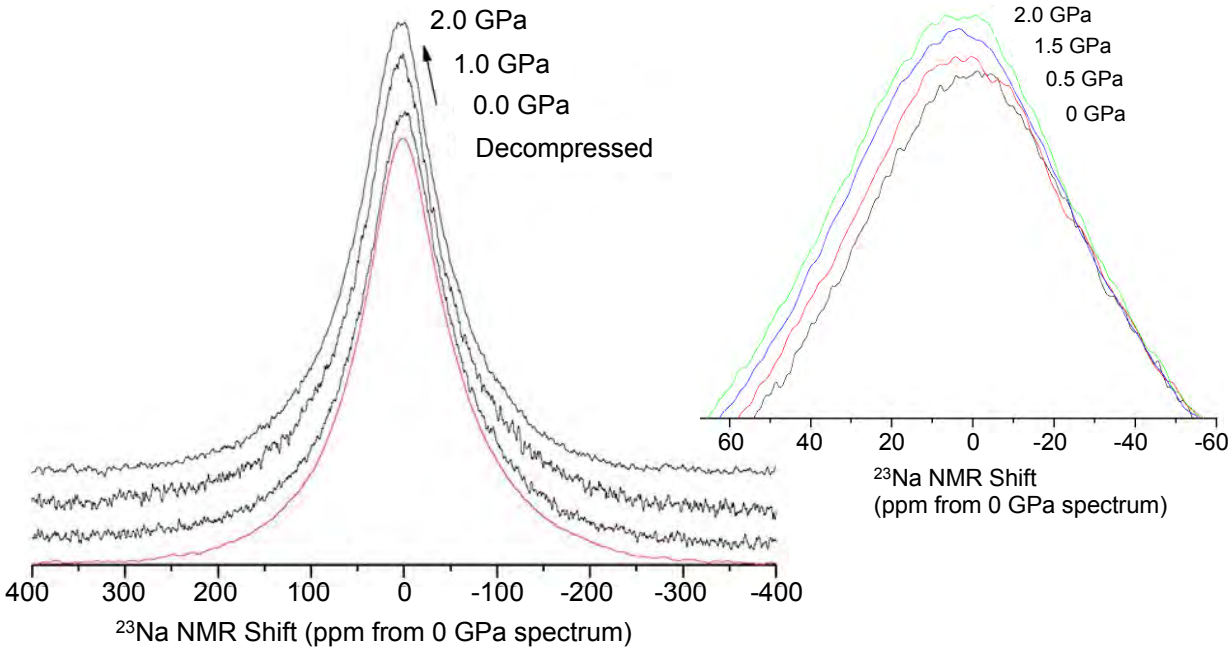
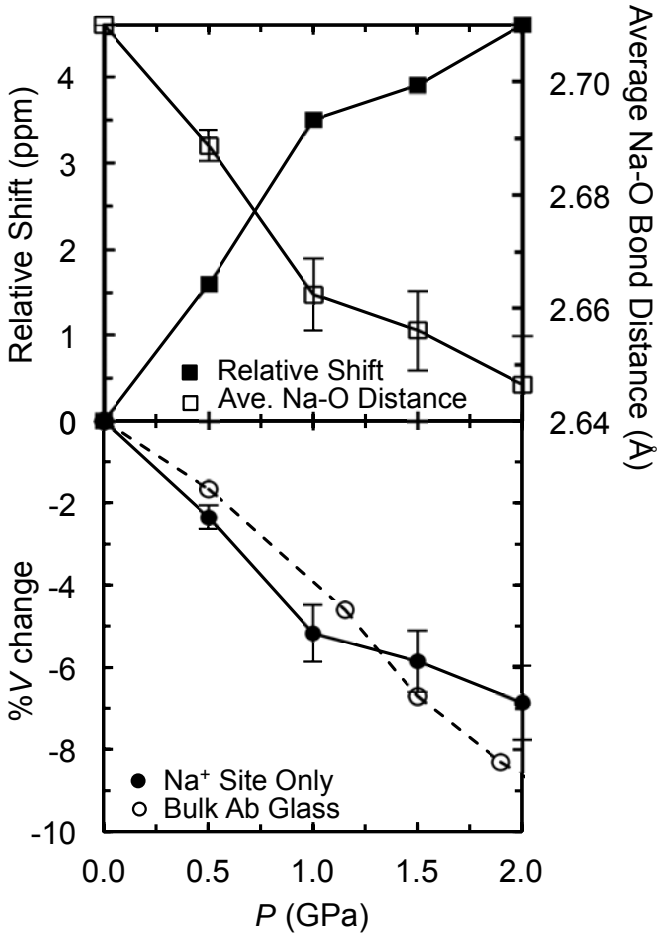


Figure 2

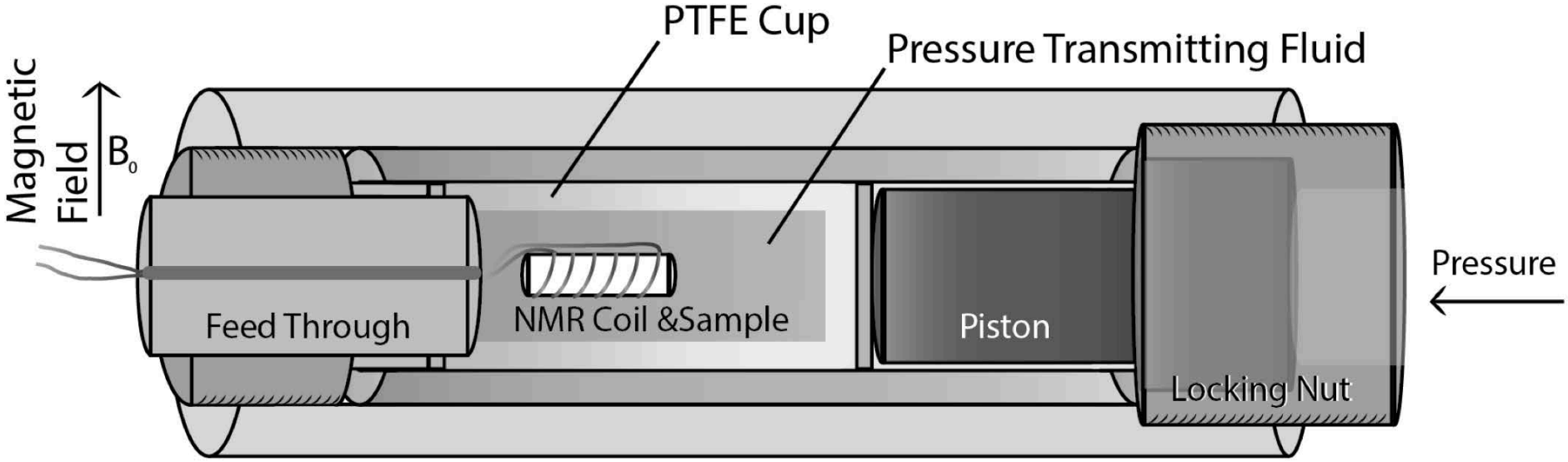


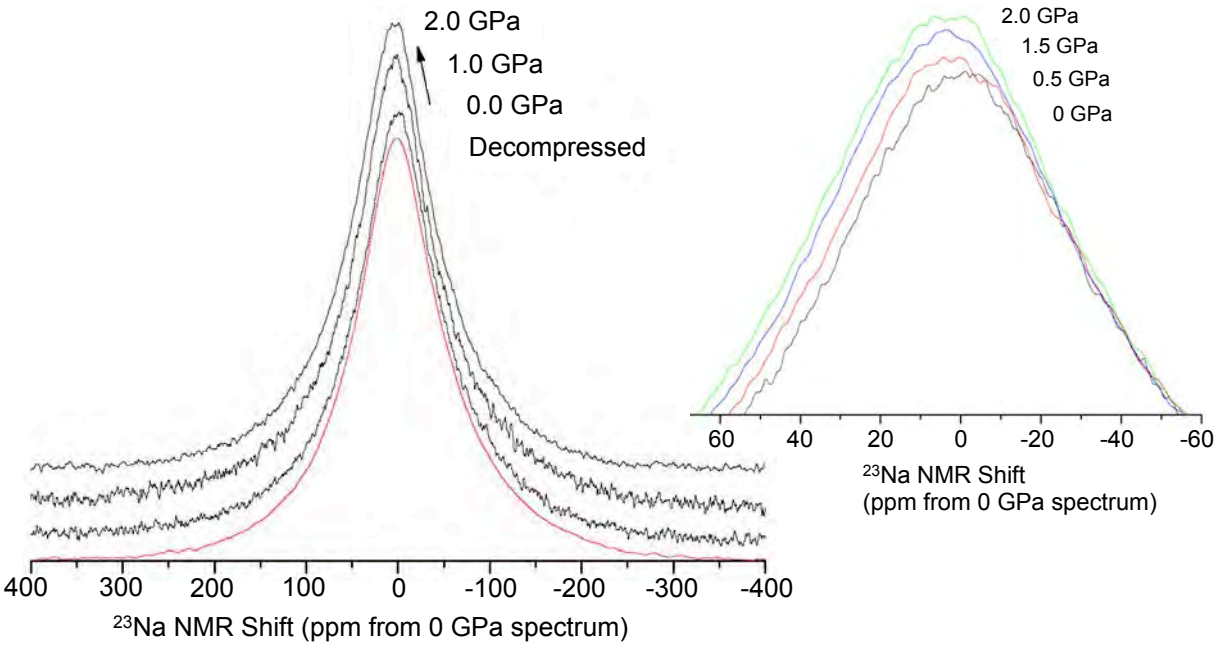
345
346 **Figure 3 top and bottom**

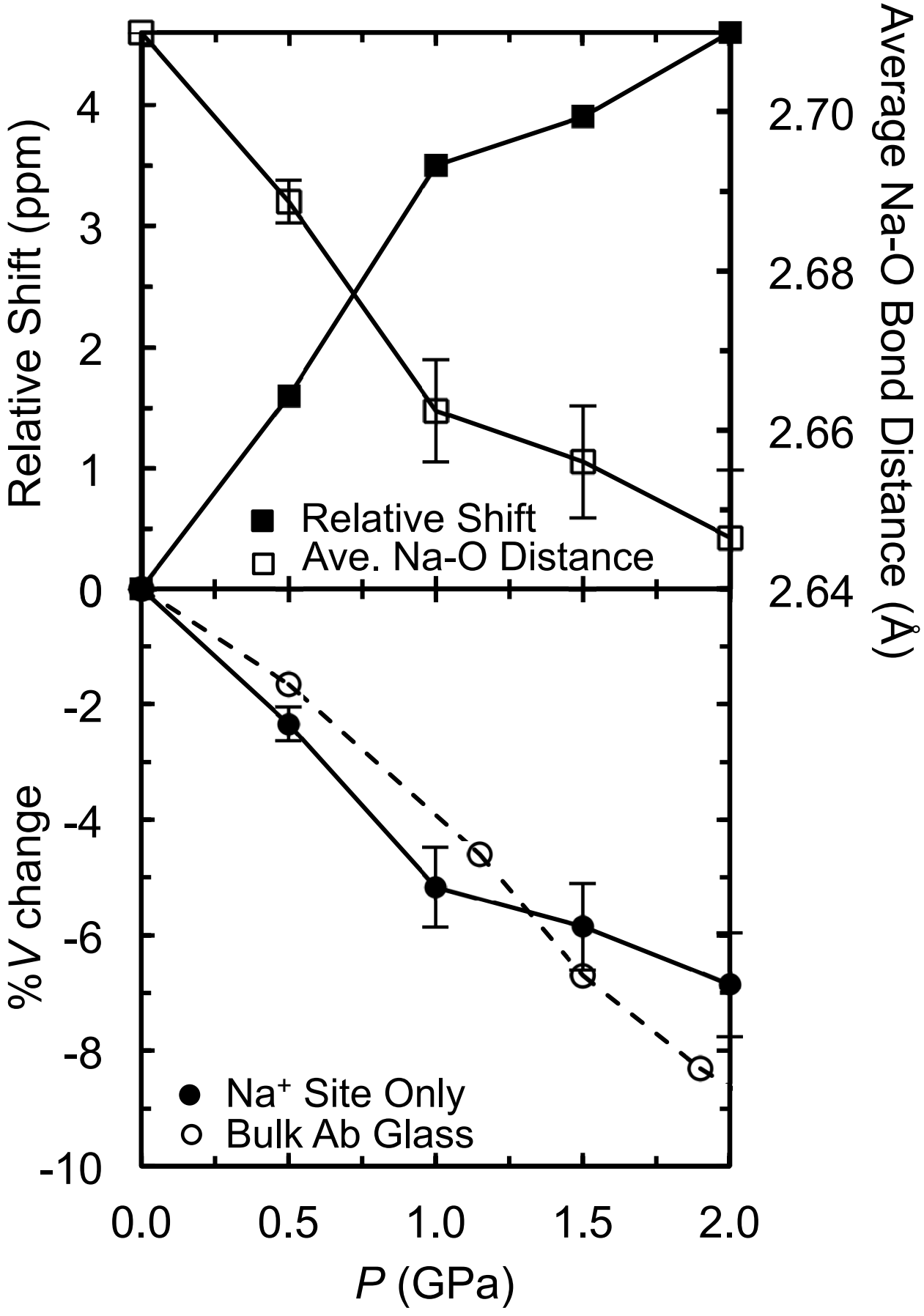
347
348
349
350



351
352


PTFE Cup
Pressure Transmitting Fluid
Magnetic Field
B_0
Feed Through
NMR Coil &Sample
Piston
Locking Nut
Pressure


2.0 GPa
1.0 GPa
0.0 GPa
Decompressed
400
300
200
100
0
-100
-200
-300
-400
23Na NMR Shift (ppm from 0 GPa spectrum)
2.0 GPa
1.5 GPa
0.5 GPa
0 GPa
60
40
20
0
-20
-40
-60
23Na NMR Shift
(ppm from 0 GPa spectrum)


Relative Shift (ppm)
Average Na-O Bond Distance (Å)
%V change
P (GPa)
Relative Shift
Ave. Na-O Distance
Na+ Site Only
Bulk Ab Glass
4
3
2
1
0
-2
-4
-6
-8
-10
2.70
2.68
2.66
2.64
0.0
0.5
1.0
1.5
2.0