CATION ORDERING AT AMBIENT PRESSURE AND STRUCTURAL 
DENSIFICATION MECHANISMS OF HIGH-PRESSURE SILICATE GLASSES 
AND MELTS

A DISSERTATION

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS 
FOR THE DEGREE OF 
DOCTOR OF PHILOSOPHY

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March 2006
I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

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(Gordon Brown)

Approved for the University Committee on Graduate Studies.
Abstract

This work uses silicate glasses as structural proxies for measuring the structure of ambient and high-pressure (up to 10 GPa) silicate melts. Two general themes characterize this work: cation ordering in ambient pressure glasses and pressure-induced structural changes in glasses. The ambient pressure studies utilize oxygen ($^{17}$O) nuclear magnetic resonance (NMR) to investigate structural ordering around non-bridging oxygen (NBO) in silicate and aluminosilicate glasses. In calcium aluminosilicate glasses, $^{17}$O NMR clearly shows that silicon cations are more favorable hosts for NBO than aluminum cations. A study of calcium-magnesium and potassium-magnesium silicate glasses shows that the size and charge of the modifier cation affect the mixing around NBO. This work demonstrates that the similar size and charge of the Ca and Mg makes the cations randomly mix around the NBO. In contrast, the differences in size and valence between K and Mg are large enough to produce a site preference where NBO are mostly associated with the higher field strength Mg$^{2+}$ while the K$^+$ cations mostly associate with the bridging oxygen. The high-pressure studies focus on determining changes in the atomic structure of silicate glasses with increasing pressure. The compression mechanisms of depolymerized silicate and aluminosilicate glasses were investigated with $^{17}$O, $^{27}$Al, and $^{29}$Si NMR and the quantification directly shows that NBO are consumed by the mechanism that generates high-coordinated network formers (e.g. $[^{5}]$Si, $[^{6}]$Al, etc.) at high pressure. Also, this work illustrates that the type of modifier cation drastically affects the Al-coordination and density of high-pressure glasses because Ca-aluminosilicate glasses contain more high-coordinated Al and pressure-induced density changes than Na- and K-aluminosilicates. The average Al-coordination and density are correlated and show that there are two distinct compression regimes that occur up to 10 GPa. Both regimes show a density increase; however, the high-pressure mechanism(s) show a prominent increase in the Al coordination. The magnitude of the pressure induced density changes at low pressure are dependent on the type of modifier cation present, which suggests that this initial regime, in addition to a small increase in the Al-coordination, likely involves compressing modifier cation polyhedra.
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Chapter One

Introduction
Background

Silicate melts have played a vital role in many events of the early Earth and lunar histories and continue to shape the evolution of the Earth. It is thought that the large amount of heat energy generated by the core formation likely raised the temperature of the entire proto-Earth by 1500 K (Verhoogen, 1980). This large temperature increase would have induced massive amounts of melting in the deep interior and created a magma ocean (Taylor, 1989; Tonks and Melosh, 1990). Another large-scale massive melting event likely occurred shortly after core formation (about 4.4 to 4.5 Ga) when a Mars-sized planetesimal impacted the proto-Earth (Melosh, 1990; Lunine, 1999; Canup and Righter, 2000). This impact formed the Moon and had profound effects on the thermal state of the early Earth by melting a large portion of the planet and creating a magma ocean (Benz and Cameron, 1990; Melosh, 1990; Pritchard and Stevenson, 2000; Solomatov, 2000). Also, it is well accepted that a magma ocean several hundred meters deep existed on the Moon shortly after this event (Ringwood, 1990; Ryder et al., 2000). Crystal ascent in these large magma oceans is thought to be responsible for the creation of the initial lithosphere (Ryder et al., 2000). The occurrence of igneous rocks with a large range of ages and compositions (e.g. komatiites, flood basalts, mid-ocean ridge basalts, etc.) suggests that terrestrial melts generated at elevated pressures have been shaping the Earth's surface and interior for most of its history. Recent geophysical models have proposed that gravitationally stable silicate melts may also reside deep inside the Earth at the 410 km transition zone (Revenaugh and Sipkin, 1995; Suzuki and Ohtani, 2003; Bercovicci and Karato, 2003) and at the core-mantle boundary (Williams and Garnero, 1996). Therefore, knowledge of the properties of high-pressure silicate melts remains crucial to understanding the evolution of our planet as well as those of other silicate planets and satellites.

The rate of magma ascent (or descent) is dependent on the buoyancy of the melt relative to the surrounding crystalline material, and therefore, dependent on melt viscosity and the density contrast between the minerals and melts. However, since early work has shown that these macroscopic properties are highly dependent on composition, temperature and pressure, there has been a considerable effort to
understand how these variables affect melt properties (Kushiro, 1978; Rigden et al., 1984; Richet and Neuville, 1992; Agee and Walker, 1993; Poe et al., 1997; Ohtani and Maeda, 2001; Reid et al., 2001; Tinker et al., 2003). It has been well documented that the density of melts increases with pressure and that the compressibility of silicate melts is about an order of magnitude greater than that of most crystalline materials (Bass, 1995). Ambient pressure silicate melts are commonly less dense than the surrounding minerals, but as the pressure increases the volume of the two phases approach comparable values and eventually may become equal. This is referred to as the “density crossover” (Stolper et al., 1981; Agee and Walker, 1993; Suzuki and Ohtani, 2003) and, while its presence is uncertain in the Earth, the consequences of this hypothesis are that there would be a maximum depth for eruptible magmas. It is also the basis for the previously mentioned geophysical models that suggest that melt layers are located at the 410 km transition (Revenaugh and Sipkin, 1995; Suzuki and Ohtani, 2003; Bercovicci and Karato, 2003). Unlike the positive pressure dependence observed for density, viscosity has been shown to have either a positive or negative pressure dependence, depending on the composition of the melt (Scarfe et al., 1987; Wolf and McMillan, 1995; Ohtani et al., 2005). In general, the viscosity of ultramafic compositions has been shown to increase with pressure, whereas, the viscosity of felsic, andesitic, and basaltic compositions have been shown to decrease with pressure. Recent studies have also shown that the viscosity of CaMgSi2O6 and peridotite melts eventually reach a maximum near 8 GPa and then decrease at even higher pressures (Reid et al., 2001; Liebske et al., 2005). The changes in the pressure dependence of viscosity based on composition and the presence of a maximum suggest that there are significant changes occurring in the atomic-structure of high-pressure melts (Poe et al., 1997; Liebske et al., 2005). Because their structures are approximately that of melts at the glass transition temperature, glasses are commonly used as the starting point in structural studies of melts (Seifert et al. 1981; Stebbins 1995; Richet and Bottinga 1995). The structure of glasses has also been shown to be highly dependent on pressure (Yarger et al., 1995; Matsui, 1996; Poe et al., 2001) and the abundance of five-coordinated aluminum ([5]Al) and non-bridging oxygen (NBO) have been
suggested to control the viscosity of high-pressure melts (Poe et al., 1997; Lee et al., 2004).

Silicate melts and glasses, unlike crystalline silicates, possess no long-range structural periodicity or symmetry. However, silicate glasses and melts contain short-range structural order, which means that, like crystalline materials, the structure is dominated by cation-oxygen bonds like Si-O. Further discussion of oxide glass structure relies heavily upon the principle that there are network formers (e.g. Si, Al, B) and network modifiers (e.g. Ca, Na, K, etc.), although certain cations can play both roles. Network formers are commonly associated with 4 oxygen neighbors to form tetrahedral species (e.g. \(^{[4]}\)Si, \(^{[4]}\)Al, etc.) and these tetrahedral species share oxygen with other tetrahedral species to provide the framework and rigidity of the silicate glass structure. These shared oxygen are referred to as bridging oxygen as they connect two network formers (e.g. \(^{[4]}\)Si-0-\(^{[4]}\)Si, \(^{[4]}\)Si-O-\(^{[4]}\)Al, etc.). The addition of network modifier oxides breaks up this interconnected structure by creating non-bridging oxygen (NBO). NBO are oxygen bonded to only one network former, where the remainder of the bond valence is coordinated by neighboring network modifier cations (e.g. \(^{[4]}\)Si-O-3\(^{[6]}\)Ca). In systems with a variety of modifier cations and network formers (e.g. natural melts, industrial glasses, etc.), it has been shown that there is a competition for “preferred sites” with the ultimate goal of lowering the bulk free energy of the melt. This ordering has been shown to occur for network formers and modifiers and is thought to be dominated by the field strength of the cations \((Z/R^2)\), where \(Z\) is the valence charge of the cation and \(R\) is the cation-oxygen bond length), relative to the available valence charge of the anion site (Kirkpatrick et al. 1983; Navrotsky et al., 1985; Farnan et al., 1992; Stebbins et al., 1997); Lee et al., 2005). In the melt literature, the average NBO/tetrahedron ratio (NBO/T) is the measure of the average network connectivity of the melt/glass structure. Most natural magmas and igneous rocks have an average NBO/T ratio between 0 and 1.4 (Mysen, 1988; Mysen and Richet, 2005) where lower and higher values represent felsic and basic melts, respectively. Additionally, this value has also been shown to have a large influence on pressure-induced structural transitions, where values closest to NBO/T=0.5 have been
found to generate the most high-coordinated Si in binary silicates (Wolf et al., 1990; Xue et al., 1991).

**Application of NMR spectroscopy to the study of silicate glass structure**

The lack of long-range order in glasses and melts minimizes the effectiveness of conventional crystallographic techniques for structural determinations (e.g. X-ray diffraction). Solid-state nuclear magnetic resonance (NMR) is one of many approaches that have been used to investigate the structure of disordered materials like silicate glasses. NMR is a nuclide specific technique and most sensitive to the first nearest neighbor. This allows the study of the short-range structure by measuring the immediate bonding environment of a specific atom (Engelhardt and Michel, 1987). NMR is quantitative; integration of peak areas can determine the relative percentages of different structural species surrounding a specific nuclide (i.e. Si, Al, O, … etc.), making data from NMR very useful for determining cation ordering and coordination numbers in disordered materials like silicate glasses.

One of the major breakthroughs in the application of NMR to solids was the advent of magic-angle spinning (MAS) (Engelhardt and Michel 1987). Spinning the sample about a specific angle (54.7°) relative to the magnetic field averages out the dipolar-dipolar coupling and the first-order quadrupolar effects resulting in narrower peak widths. Most of the earlier work of solid-state NMR was done on spin-1/2 (I=1/2) nuclides like \(^1\text{H}, \text{^13C},\) and \(^{29}\text{Si}\) because of their importance in solids and the relatively narrow NMR linewidths. Many geologically and technologically important nuclides (\(^{11}\text{B}, \text{^17O}, \text{^23Na}, \text{^27Al}, \text{^35Cl}\)) are considered quadrupolar nuclides (I = 3/2 and 5/2) and despite spinning the sample, still suffer from second-order quadrupolar broadening. This effect broadens the linewidths significantly, sometimes to the extent where the resolution can be too poor to observe low abundance species. As shown in a recent study (Stebbins et al., 2000), using larger external magnetic fields can reduce the extent of this broadening. For instance, the \(^{27}\text{Al}\) peak in \(^{27}\text{Al}\) MAS NMR spectra of NAS glasses collected at 18.8 Tesla (Allwardt et al., 2005a) is much more Gaussian and more than 3 times narrower than those in spectra collected at 7.1 Tesla (Lee et al., 2004). This effect drastically reduces peak overlap and allows a robust quantification
of the peak area. For this reason, most $^{27}\text{Al}$ MAS NMR spectra in this dissertation are collected at ultrahigh (18.8 Tesla) external magnetic field.

Other NMR techniques like dynamic-angle spinning (DAS) (Baltisberger et al., 1992), double-orientation rotation (DOR), and triple-quantum MAS (3QMAS) (Frydman and Harwood, 1995; Baltisberger et al., 1996) have been devised to eliminate second-order quadrupolar broadening. DAS and DOR physically change the angle of rotation during the experiment, while 3QMAS accomplishes this by using multiple, well-timed pulses. This non-mechanical process makes 3QMAS much less challenging and inexpensive to implement than DAS and DOR because it can use standard equipment (Frydman and Harwood, 1995). The 3QMAS spectra are presented as two-dimensional contour plots where the addition of the second dimension can typically obtain more information than the conventional, 1-D MAS spectrum. In 3QMAS spectra, the isotropic dimension is free of second-order quadrupolar broadening and the projection of the MAS dimension portrays a somewhat distorted view of the conventional 1-D MAS spectra. However, the major drawback to 3QMAS is that measured intensities are also dependent on the excitation and reconversion efficiency, which depend on the structural symmetry of the site. This prevents a truly quantitative assessment of structural sites with drastically different quadrupolar coupling constants ($C_q$) (Baltisberger et al., 1996).

**Questions to be addressed by this thesis**

1. How do the size and charge of cations affect the atomic structure surrounding NBO in silicate and aluminosilicate glasses?
2. What are the structural mechanisms of densification in silicate and aluminosilicate glasses?
3. How does pressure and composition affect the density and network former coordination in high-pressure glasses?

**Contents of this Thesis**

*Chapter 2:*

This chapter utilizes $^{17}\text{O}$ MAS and 3QMAS NMR to investigate structural
preferences of NBO in aluminosilicate glass structure. The spectra clearly show that Al-NBO can be clearly distinguished from Si-NBO and the latter is strongly preferred in Ca-aluminosilicate glasses, except in compositions where Al is much more abundant than Si. An equilibrium constant formulation was used to predict the abundance of Al-NBO and Si-NBO and suggests that, while Al-NBO are likely absent in most glasses (and melts?) of geologic importance, they are likely to be present in low-silica slags produced during the steelmaking process. The NMR spectra of the CAS0 and CAS20 glasses were collected by Dr. Sung Keun Lee, while I synthesized the samples, collected the spectra for CAS10, and analyzed the data/spectra. This work has been published in American Mineralogist (Allwardt et al., 2003).

Chapter 3:

Many thermodynamic models of silicate and aluminosilicate melts assume that the modifier cations mix randomly. In this chapter, NBO mixing in several Ca-Mg and K-Mg silicate glasses is experimentally investigated with $^{17}$O 3QMAS NMR. These spectra show that Ca$^{2+}$ and Mg$^{2+}$ cations mix randomly in pyroxene composition glasses (e.g. [Ca,Mg]SiO$_3$), which agrees with a previous viscosity study along the same join (Neuville and Richet, 1992). On the other hand, this study also found that K-Mg mixing is ordered in silicate glasses as the smaller and more highly charged Mg$^{2+}$ cations out-compete the K$^+$ cations for ionic bonds to NBO in the glass structure. I synthesized the glasses and collected the NMR spectra for this study. However, 3 of the 8 samples were remelted from previous studies (Farnan et al., 1992; Stebbins et al., 1997) to avoid remaking $^{17}$O-enriched glasses. This work has been published in American Mineralogist (Allwardt and Stebbins, 2004).

Chapter 4:

This study utilized Raman, $^{29}$Si MAS NMR, and $^{17}$O 3QMAS NMR spectroscopies to investigate structural mechanisms that create high-coordinated Si in K$_2$Si$_4$O$_9$ glasses quenched from melt at pressures up to 8 GPa. These mechanisms were determined to be $\text{NBO} + [4]\text{Si-O-}[4]\text{Si} = [4]\text{Si-O-}[5]\text{Si}$ and $\text{NBO} + [4]\text{Si-O-}[5]\text{Si} = [4]\text{Si-O-}[6]\text{Si}$ where the right hand side of both “equations” are favored at higher
pressure. Also, crystalline materials were used to provide robust peak assignments for the $^{17}\text{O}$ 3QMAS spectra and show that $^{17}\text{O}$ NMR should not be used to determine the Si-speciation in high-pressure glasses. Additionally, this study utilized a rapid decompression technique (~1 second) to investigate how the conventional decompression time (12 hours) affects the recoverable high-pressure glasses. This approach shows that the some of the high-pressure signature (e.g. [\text{^{5}}\text{Si} and \text{^{6}}\text{Si}]) is lost during the longer decompression time. Collection of Raman spectra and the high-pressure glass synthesis were done by Dr. Burkhard Schmidt (Bayerisches Geoinstitut, Germany). I collected all NMR spectra, synthesized ambient pressure glasses (starting materials), analyzed the bulk of the data, and wrote the majority of the manuscript. This work has been published in the Silicate Melt Workshop special issue of Chemical Geology (Allwardt et al., 2004).

**Chapter 5:**

This chapter combined $^{27}\text{Al}$ MAS NMR, conventional high-pressure techniques, and density measurements to investigate the pressure dependence of structure and density for aluminosilicate glasses. Additionally, this study very clearly showed that higher field strength modifier cations (e.g. \text{Ca}^{2+}) clearly induce a greater number of high-coordinated Al than the lower field strength modifier cations (e.g. \text{Na}^{+} and \text{K}^{+}). This increase in the Al-coordination appears to be well correlated to the increase in density of the recovered glass. Additionally, the measured density of the high-pressure glasses show that a large portion of the total densification observed in-situ in melts by others is preserved by the decompressed glasses. This chapter was mostly the result of a 2-month internship at the multianvil lab at the Bayerisches Geoinstitut and a week visiting the piston-cylinder lab at the University of Minnesota. I synthesized all glasses, wrote the manuscript, and, with the assistance of Dr. Lin-Shu Du and Prof. Jonathan Stebbins, collected the high-field $^{27}\text{Al}$ MAS NMR spectra. Additionally, I measured the density of the glasses with heavy liquids using glasses of known density as internal standards. Drs. Anthony Withers, Marc Hirschmann, Dan Frost and Burkhard Schmidt assisted this study by showing me how to use the high-
pressure equipment and answering technical questions. This work has been published in American Mineralogist (Allwardt et al., 2005a).

Chapter 6:

This chapter represents the first attempt to determine the temperature dependence of the Al-coordination at high pressure. It utilizes $^{27}\text{Al}$ MAS NMR and the spectra suggest that for NBO-containing aluminosilicate glasses and melts, an increase in temperature would yield a greater abundance of high coordinated Al. However, for NBO-poor glasses, the opposite effect is observed where there is a drastic decrease in the Al-coordination in the high temperature sample. This opposite temperature dependence, along with the lack of NBO, likely suggests that NBO-poor melts rely on different compression mechanisms than NBO-containing melts. Most high-pressure glasses were synthesized at Bayreuth by Dr. Brent Poe (INGV-Rome) from starting materials provided by Prof. Jonathan Stebbins. With the help of Dr. Lin-Shu Du, I collected the high field NMR spectra and wrote the manuscript. This work has been published in American Mineralogist (Allwardt et al., 2005b).

Chapter 7:

This chapter begins with a fairly lengthy review of recent high-pressure glass research and presents some of my original research that investigates compression mechanisms in Ca- and K-aluminosilicate glasses up to 5 GPa using $^{17}\text{O}$ 3QMAS and $^{27}\text{Al}$ MAS NMR. Quantification of the spectra suggests that high-coordinated Al are formed by a similar mechanism as is observed for Si in binary silicates (Xue et al, 1991; Allwardt et al., 2004). This chapter also investigates some technical aspects of quantifying the structure of glasses at high pressure like effects of decompression and the reproducibility. This work has been published as a chapter in the Elsevier book: Advances in High-Pressure Technology For Geophysical Applications (Allwardt et al., 2005c).

Appendix 1:
This appendix details how to measure the density of small glass samples using heavy liquids. It includes safety precautions and a step-by-step method for making the measurements. The precision was assessed by using glasses of known density (CaMgSi$_2$O$_6$ and NaAlSi$_3$O$_8$) and has been shown to be approximately 0.02 g/cm$^3$, which, for the small sample sizes, is considerably better than the 0.05g/cm$^3$ reported for weighing in air and ethanol (Poe et al., 2001). This technique is modified from a version used by Dr. Steve Feller at Coe College (personal communication).

Appendix 2:

Chapter 5 clearly shows that glasses synthesized at increasing pressures have a greater density and also contain more high coordinated Al. Additionally, it shows that a relatively small compositional differences like the type of modifier cation (K, Na, and Ca) drastically affects Al-coordination and glass density. Appendix 1 is a natural extension of this work and investigates how the presence of multiple modifier cations (Ca-K, Ca-Mg, and Ca-Mg-K) affects the pressure dependence of both the Al speciation and the density. The quantification of the $^{27}$Al MAS NMR spectra clearly shows that the effect of composition on the Al speciation is not linear. Additionally, the comparison of the density and average Al-coordination clearly show that there are two distinct compression regions for each of the 7 compositions for glasses up to 10 GPa. Everyone’s role is similar to that detailed for Chapter 5. The data from this appendix will be written up as a manuscript and submitted for publication after my defense.

Appendix 3:

Chapter 3 details how modifier cations associate with NBO in silicate glasses and this appendix is a natural extension of that study to aluminosilicate compositions. More specifically, it utilizes $^{17}$O MAS and 3QMAS NMR to investigate mixing of Mg-Ca and Mg-Ca-K cations around NBO in ambient pressure aluminosilicate glasses. The spectra for the mixed modifier cation glasses show that there is modifier cation ordering in both systems. Similarly to chapter 7, $^{17}$O MAS spectra were collected for four high-pressure samples to investigate compression mechanisms. The
abundance of Ca-NBO species in the high-pressure samples appears to be equal to that measured for the ambient pressure glasses, which suggests that there is a strong preference for Mg-NBO in the generation of $[5]Al$ and $[6]Al$. I synthesized all ambient and high-pressure glasses and collected all NMR spectra for this study. The data from this appendix will be written up as a manuscript and submitted for publication after my defense.

Appendix 4:

In addition to the high-pressure glass research contained in this thesis, I have also collaborated with Prof. Eiji Ohtani (Tohoku University) and his research group (Drs. Hidenori Teresaki and Akio Suzuki) to measure the viscosity of high-pressure melts. These measurements utilize synchrotron radiation (SPring 8, Japan) and multianvil presses to measure the terminal velocity of metallic spheres in high-pressure and temperature melts. The results of this work show that the melt viscosity contains a minimum at a pressure below 5 GPa and, based on the results of the structural studies, this suggests that this minimum is likely a result of a maximum in the abundance of $[5]Al$. I initiated the collaboration w/ Dr. Teresaki and since this was my first experience using synchrotron radiation and this style of multianvil, he ran the experiments. I assisted during the experiments, assembled the multianvil assemblies and chose the composition and conditions for the three experiments (temperature and pressure).

Additional collaborative work not presented in dissertation:

In addition to the research presented in the chapters and appendices of this dissertation, I have synthesized high-pressure glasses for two different collaborative studies where I was involved in a secondary role. The first study is primarily in collaboration with Dr. Lin-Shu Du, Prof. Jonathan Stebbins (Stanford) and Dr. Burkhard Schmidt (Göttingen) and investigated the glass structure of Na-borosilicate glasses at 5 GPa. This study revealed that $[4]B$ is formed from $[3]B$ and an NBO, which is a similar mechanism to that observed in our studies of silicates and aluminosilicates. It was published in the Journal of Non-Crystalline Solids as Du et al., (2004). The
second collaborative study is still in progress and involves room-temperature compression of $^{17}$O-enriched silica glass to 8 and 15 GPa. The preliminary analysis of the NMR spectra done by Dr. Lin-Shu Du and Prof. Jonathan Stebbins show that there is an increase in the range of bond angles with a smaller average angle at elevated pressure, but there is no change in the coordination state of the Si. Previous work has shown that glasses from these pressures might be up as much as 20 to 30 % more dense than the ambient pressure glass (Hemley et al., 1994). Prof Sabayachi Sen (UC-Davis) synthesized the ambient-pressure SiO$_2$ glass at Corning Incorporated and $^{17}$O DAS spectra will be collected by Prof. Phillip Grandinetti (The Ohio State University). The DAS spectra may be able to quantify the bond angles of these glasses.

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Chapter Two

Bonding preferences of non-bridging oxygen: Evidence from $^{17}$O MAS and 3QMAS NMR on calcium aluminate and low-silica Ca-aluminosilicate glasses

Modified version published in American Mineralogist
Abstract

The fraction of oxygen as non-bridging oxygen (NBO) can be well approximated based on composition alone in many silicate glasses, but the NBO preference for specific network forming cations is much less well known. Using oxygen-17 ($^{17}$O) NMR on low-silica calcium aluminosilicate (CAS) glasses, this study shows that Al-NBO (155 ppm) can be readily distinguished from Si-NBO (110 – 120 ppm), and that there is a strong preference for the latter. This study also presents a consistent equilibrium constant formulation that indicates that for thermodynamic modeling of most CAS melts with Si$>$Al, Al-NBO are of minor importance, although they could be significant in some models of dynamics. Al-27 one pulse NMR and analyses of spinning side bands show that AlO$_5$ and AlO$_6$ species are below detection limits (<0.5%) in the low-silica (SiO$_2$ $\leq$ 20 mol%) glasses of this study (NBO/T=0.6 to 0.8). In addition, $^{17}$O MAS NMR does not detect any obvious (<2%) Al$_3$O triclusters; hence calculations of T-NBO/T assignments (where T=Si or Al) can be assigned unambiguously.
Introduction

Discussion of oxide glass structure relies heavily upon the principle that there are network formers (i.e. Si, Al, B) and network modifiers (i.e. Ca, Na, K etc.). The network formers provide the framework and rigidity of the glass while the network modifier oxides break apart this structure through the formation of non-bridging oxygen (NBO). An NBO is an oxygen bonded to only one network former leaving the network modifiers to balance the remaining valence charge.

Network connectivity plays a significant role in the thermodynamic (Navrotsky 1995; Hess, 1995) and transport properties (Hess et al. 1995, 1996) of magmas and glasses. For instance, the orthosilicate composition (33 mol% SiO$_2$) of the binary compositions of SiO$_2$-alkali or alkaline earth glasses is thought to contain the most NBO of any composition (Hess 1980). In binary silicate glasses, as the amount of silica is increased from the orthosilicate composition (increasing the network connectivity and reducing the number of NBO), enthalpies, free energies, component activities and viscosity are all strongly affected (Hess 1995; Navrotsky 1995; Hess et al. 1995, 1996). This is the result of increasing the network connectivity as $Q^0$ species are being converted to $Q^1, Q^2$ and even more connected species, where 0, 1, and 2 represent the number of bridging oxygen (BO) bonded to the Si tetrahedron. Similar effects are expected for other network cations. The average degree of network connectivity is relatively well known for silicate and aluminosilicate glasses, but the distribution of NBO on different network cations is much less well understood.

Certain combinations of framework cations in some composition ranges show no preference in competing for NBO, such as B and Si in the Ba-borosilicates (Zhao et al 2000). In contrast, there is much indirect evidence that suggests that Si has a strong preference over Al for NBO in the alkali and alkaline earth aluminosilicate systems (Mysen 1988 and references therein).

Most previous studies of NBO preferences in aluminosilicates have used relatively indirect methods for NBO detection such as Raman spectroscopy (Mysen et al. 1981,1985; Domine and Pirou 1986), X-ray and/or neutron scattering (Petkov et al. 1998, 2000; Cormier et al. 2000), and $^{27}$Al and $^{29}$Si magic-angle spinning (MAS) NMR (Engelhardt et al. 1985). For instance, the study of Engelhardt et al. (1985) used
the observed $^{29}$Si chemical shifts to estimate the average Q speciation for Si and Al in "low silica" (<10% SiO$_2$) glass as Q$^0$ and Q$^4$, respectively. However, the uniqueness of such conclusions is uncertain because of the lack of resolution among $^{29}$Si peaks for different network species and the dependence of $^{29}$Si MAS chemical shift on both the average Q speciation, and next nearest neighbor effects (Si vs. Al).

Oxygen-17 NMR can provide a much more direct evaluation of this issue. Previous $^{17}$O NMR spectra have shown the presence of NBO in several calcium aluminosilicate (CAS) glasses on the CaAl$_2$O$_4$-SiO$_2$ join (Stebbins and Xu 1997; Stebbins et al. 1999; Oglesby et al. 2002; Lee et al. 2002). The observed $^{17}$O MAS chemical shifts for NBO in these glasses are similar to those found in calcium silicate glasses (Stebbins 1995; Stebbins et al. 1997). In addition, a recent $^{17}$O MAS study of an NBO-containing impurity phase in crystalline CaAl$_2$O$_4$ showed that the Al-NBO peak is shifted to a higher frequency by 30 to 40 ppm from that of the NBO peak of the CAS and Ca-silicate glass spectra (Stebbins et al. 2001). These findings further suggested that Si is the preferred network cation of NBO in aluminosilicate glasses and thus in melts at the glass transition temperature.

An intriguing complication to the conventional network picture of the melt structure is the possible presence of minor concentrations of "triclusters" containing three tetrahedral network formers linked to a single oxygen (Lacy 1963). These have been suggested by Toplis et al. (1997) and others on the basis of viscosity anomalies in Na-aluminosilicate liquids near the charge-balanced (NaAlO$_2$-SiO$_2$) join, and could increase the predicted fraction of NBO. Although $^{17}$O NMR data on crystalline CaAl$_4$O$_7$ indicated a distinct set of NMR parameters for at least Al$_3$O triclusters, overlap with bridging oxygen peak intensity in the Ca-aluminosilicate glasses has not yet allowed unambiguous detection of this species (Stebbins et al. 2000). Low-silica glasses provide an opportunity to more clearly resolve such groups.

The observation of small amounts of high-coordinated Al ($^{[5]}$Al and $^{[6]}$Al) in some alkaline earth aluminosilicates of glasses (Toplis et al. 2000; Stebbins et al. 2001) and in the calcium aluminate glasses (Shelby et al. 1985) can also complicate the calculation of average Q speciation and the NBO to tetrahedra ratio (NBO/T). For instance, are oxygen bonded to $^{[5]}$Al and $^{[6]}$Al considered bridging (BO) or non-
bridging (NBO) in aluminosilicate glass structure? If a high coordinated Al is considered network forming, should they be counted in the number of tetrahedra? In order to make an unambiguous assignment of NBO/T, it must be shown that concentrations of high coordinated Al in the glass structure are negligible. Aluminum-27 MAS NMR data are thus a useful compliment to $^{17}$O spectra.

By investigating Si-poor Ca-aluminosilicates with $^{17}$O NMR, it is thus possible to observe to what extent NBO ‘prefer’ Si as a framework host compared to Al, because Al-NBO can be directly observed and quantified. Here we describe results for Al-NBO and Si-NBO in calcium aluminate and low-silica (10, 20 and 33 mol%) calcium aluminosilicate glasses utilizing $^{17}$O MAS and $^{17}$O triple-quantum MAS (3QMAS) NMR, where for the first time both species can be directly quantified, and the ‘preference’ for Si-NBO rigorously defined.

**Experimental Procedure**

The eutectic composition of calcium aluminate (62 CaO · 38 Al$_2$O$_3$) was chosen due to its low liquidus temperature (1360 °C) and relatively good glass-forming ability; calcium aluminosilicate (CAS) compositions were selected to keep the ratio of NBO/T (0.62) and the percentage of total oxygen as NBO (27%) near constant to aid in the direct comparison of spectra.

Glass samples were made using CaO, ~45% $^{17}$O-enriched SiO$_2$ (Stebbins et al. 1997), and ~20% $^{17}$O-enriched Al$_2$O$_3$. Some of the latter was made by hydrothermal exchange between $^{17}$O-enriched water and Al(OH)$_3$ as in Stebbins et al. (2001). The remainder of the enriched Al$_2$O$_3$ was made using a new method, by slowly injecting 1 mL of 40% $^{17}$O-enriched H$_2$O (Icon Stable Isotopes) into a water-cooled flask containing the stoichiometric amount (4.6 g) of Al-tri-sec-butoxide. The reactants were stored in a sealed flask for a week to allow ample time for the reaction to occur. The resulting Al(OH)$_3$ was then rinsed with isopropanol, dried at 120°C, and slowly heated to 1000°C in Ar to form Al$_2$O$_3$. Calcium oxide was used in place of CaCO$_3$ to avoid loss of $^{17}$O during decarboxonation. Due to the hygroscopic behavior of CaO, it was dried overnight at 1000°C and used immediately. No significant weight gain occurred during the weighing of this reagent.
To speed spin-lattice relaxation, 0.2 wt % cobalt oxide was added to the oxide powders. The 200 mg samples were then melted in Ar (Table 1) and quenched by dipping the bottom of the Pt crucible in water. Samples were found to be entirely amorphous when examined with a 400X petrographic microscope. Compositions were measured by electron microprobe using mineral standards (Table 1). This analysis showed small amounts of unexpected MgO (<0.5 mol %), which when compared to the amount of CaO in the sample will cause errors in data analysis much less significant than some of the other uncertainties. Additionally, the microprobe data of the CA glass showed that there is 0.6 mol % SiO$_2$ from an unknown source.

The $^{17}$O and $^{27}$Al MAS NMR spectra were collected on a Varian Unity/Inova 600 spectrometer (14.1 Tesla) using a Chemagnetics ‘T3’ probe with 3.2 mm zirconia rotors spinning at 18 kHz. The $^{17}$O and $^{27}$Al frequencies are reported relative to tap water and 0.1M acidified Al(NO$_3$)$_3$, respectively. Single pulse acquisition was used with pulse widths corresponding to approximately 30° rf tip angles for the solid (about 0.3 and 0.2 μs for $^{17}$O and $^{27}$Al, respectively); one second delays between pulses were used to optimize the signal to noise ratio and to ensure a nearly fully relaxed sample. The 3QMAS NMR spectra were collected on a modified Varian VXR/Unity 400S spectrometer (9.4 Tesla), using a Doty Scientific Inc., ‘Supersonic’ probe with 5 mm silicon nitride rotors spinning at 15 kHz. The 3QMAS spectra used a shifted echo pulse sequence consisting of two hard pulses (5.0 μs and 1.5 μs, respectively) followed by a soft pulse (26 μs) similar to that used by Lee and Stebbins (2000). Delay times of 2 s and 37 μs were used. Processing of the 3QMAS data was done with the software package, RMN (FAT) (P.J. Grandinetti, The Ohio State University). The resulting 3QMAS spectra are two-dimensional plots in which the isotropic dimension is free of second order quadrupolar broadening and the MAS dimension portrays a somewhat distorted view of the 1-D MAS spectrum.

For nuclides with nuclear spin $I=5/2$, such as $^{27}$Al and $^{17}$O, the spinning sidebands for the ‘inner satellite’ ($\pm 1/2 - \pm 3/2$) transition are much less affected by quadrupolar broadening than the central transition (-1/2 – +1/2) (Jäger 1994), often providing enhanced resolution. For each of the $^{27}$Al spectra of this study, six inner satellite sidebands were stacked to enhance the signal to noise ratio and compared to
the main peak to investigate the presence of higher coordinated Al, as in Stebbins et al. (2000). The largest noise ‘peak’ in the summed spectrum was integrated and compared to the integral of the main peak to obtain a minimum detection limit for $^{[5]}$Al and $^{[6]}$Al sites of about 0.5 atomic percent.

**Results**

The $^{17}$O MAS spectra for the calcium aluminate (CA) and aluminosilicate (CAS) glasses are shown in Figure 1. For the calcium aluminate, there are two main peaks: a large Al-O-Al peak at 72 ppm (Stebbins et al. 1999) and a smaller peak at 155 ppm. This smaller peak can be uniquely assigned to Al-NBO because this is the only other major oxygen species present. There is also a small shoulder at about 120 ppm, which can be assigned to Si-NBO (Stebbins 1995; Stebbins et al. 1997). This peak was not expected but was later shown to be due to a small amount of silica contamination of the CA glass. From the CA glass data and the previously mentioned work, the peak assignments of the other CAS glasses are straightforward, as both Si-NBO and Al-NBO peaks at these same positions are clearly, if only partially resolved. As silica is added, the peak assigned to Si-NBO increases in intensity and the peak assigned to Al-NBO decreases in intensity. The BO peak in the CA glass spectrum shifts to lower relative frequencies as more SiO$_2$ is added and more Si-O-Al sites are formed (Lee and Stebbins 1999, 2000). The spectrum of the CAS33 glass may also contain a small, broad shoulder, possibly due to Al-NBO, but its relative area is difficult to assess accurately.

Several recent reports (Xu and Stebbins 1998 and Lee and Stebbins 2000) describe the interpretation of $^{17}$O 3QMAS NMR spectra of aluminosilicates in detail. Here such data serve to extend the conclusions drawn from the MAS spectra. For example, the BO peak in the MAS spectrum for CAS20 contains no discernible components, but the 3QMAS (Fig.2) data partially resolves the Al-O-Si and Al-O-Al peaks that are expected from the MAS data and also from previous work in this ternary system (Lee and Stebbins 1999,2000; Cormier et al. 2000). In the $^{17}$O 3QMAS spectra of the CAS10 and CAS20 glasses, no Si-O-Si peak is seen, indicating that less than a few percent of the total oxygen are Si-O-Si. The peak assigned to Al-NBO is
slightly offset from the Si-NBO peak, which further lends support to the presence of two distinct types of NBO.

The quantitative nature of MAS NMR allows the percentage of each type of oxygen to be determined from the relative area of each peak. For $^{17}$O spectra at 14.1 T, for sites with relatively low values of quadrupolar coupling constant ($C_q$), quadrupolar peak shapes are not obvious and are often well approximated by Gaussians, which were used to fit the spectra (Fig. 3). The average network connectivity of each framework cation can then be obtained from the fitted areas, because the total number of Al and Si are known from electron microprobe analysis (Table 1). As silica is added, the network connectivity of the Al increases markedly (decreasing Al-NBO/Al).

An equilibrium constant formulation with species concentrations measured from MAS NMR, can be used to predict percentages of Al-NBO and Si-NBO for glasses based on composition. In determining the relevant equilibrium expression, Si-O-Si was neglected because of its low abundance in the systems of this study:

$$\text{Si-O-Al + Al-NBO } \leftrightarrow \text{ Al-O-Al + Si-NBO}.$$  \hspace{1cm} (1)

The resulting idealized equilibrium constant, $K_1$, (ignoring activity coefficients) is $[\text{Al-O-Al}][\text{Si-NBO}]/[\text{Si-O-Al}][\text{Al-NBO}]$, where brackets denote the fraction of oxygen in each site type. Atomic percentages of Al and Si-NBO were measured by fitting $^{17}$O MAS NMR spectra. Atomic percentages of Si-O-Al and Al-O-Al were then calculated from composition using the approximation that $[\text{Si-O-Si}]=0$. For the CAS10 glass, in which the two large NBO peaks made peak fitting relatively straightforward, the calculated value of $K_1$ is $4.1 \pm 1.1$, where the uncertainty reflects the propagated fitting errors (Table 1). By assuming $K_1$ is constant, predictions of the percentages of Si-NBO and Al-NBO can be made for CA (+ 0.6 mol% SiO$_2$), CAS20 and CAS33 and compared to the measured values (Table 2). These predictions show good agreement with those measured from fitting $^{17}$O MAS NMR spectra. The equilibrium constant formulation can then be used to predict the amount of Al-NBO in compositions where there are no suitable data (Fig. 4). An apparent slight, systematic excess of total NBO (Table 1) may result from a small difference in the spin-lattice relaxation rate of the NBO vs. the BO.
Of all BO, Al-O-Al groups have the highest frequency chemical shifts in $^{17}$O spectra (Stebbins et al. 1999), allowing a more definitive look for Al$_3$O triclusters than has previously been possible in higher silica glasses (Stebbins et al 2000). Such groups should produce a peak with a maximum at about 35 ppm at a magnetic field of 14.1 T (Stebbins et al. 2001). The absence of an obvious feature (other than the “tail” of the Al-O-Al peak) in this region of the spectrum for CA glass indicated that at least in this composition range, triclusters concentrations are below the detection limit of about 2%. This finding does not, however, constrain the concentrations of the other triclusters species such as (Si$_2$Al)O, or their concentrations in glasses with higher Al/Ca ratios, or their possible effects on producing a slight excess of NBO above that estimated from composition (Toplis et al. 1996).

As is typical for glasses, the $^{27}$Al MAS spectrum for the CA glass (Fig. 5) is broad and unresolved and shows only one peak centered at 74 ppm, which suggests that most Al are Q$^3$ and Q$^4$ species (Stebbins 1995). The peak maximum of the CAS20 spectrum is shifted about 10 ppm to a lower frequency, which suggests that most Al is present as Q$^4$ species and is consistent with the $^{17}$O results. Within detection limits (~0.5 atomic percent), only $^{[4]}$Al was detected in the $^{27}$Al MAS stacked sideband spectra of the CA, CAS10 and CAS20 glasses (Fig. 5), because there was no obvious signal in the regions expected for $^{[5]}$Al (30 to 45 ppm) or $^{[6]}$Al (0 to 16 ppm) (Poe et al. 1994; Stebbins 1995).

**Discussion**

Both the qualitative changes in the proportions of the Al-NBO and Si-NBO peaks with silica content (Fig.1), and the calculated value of $K_1$, support and quantify previous conclusions that there is a strong preference for NBO to be localized on Si (Engelhardt et al. 1985; Mysen et al. 1981,1985; Domine and Pirou 1986; Petkov et al. 1998, 2000; Stebbins et al. 2001), presumably because there is less tendency for oxygen ‘underbonding’ (insufficient charge compensation) to occur with the higher charge network forming cations.
To further extend the equilibrium constant formulation and make it applicable to more silica-rich, and hence, more geologically relevant systems, the interaction of all three BO species should be considered with the reaction:

$$2\text{Si-O-Al} \leftrightarrow \text{Al-O-Al} + \text{Si-O-Si}. \quad (2)$$

The work of Lee and Stebbins (1999, 2000), which models the results of detailed $^{29}\text{Si}$ and $^{17}\text{O}$ NMR studies, has shown that there is a significant disproportionation in reaction 2. This leads to, for example, about 14% of the total oxygen as Al-O-Al in CaAl$_2$Si$_2$O$_8$ (anorthite) glass (Lee and Stebbins 1999). If Si-O-Si linkages are formed by reaction 2, additional Al-O-Al is also formed and the fraction of Si-O-Al decreases, resulting in an increased estimated value for K, as calculated above. However, the model for network speciation developed by Lee and Stebbins (1999, 2000) predicts that there will be only about 0.5 atomic % of Si-O-Si for the CAS10 composition, which would lead to a small correction in K, which makes $K_1 = 4.6 \pm 1.1$ and the predicted Al-NBO = 18.6 instead of 19.0 atomic %. In contrast, for a $K_1$ value based on low silica glasses, as is derived here, neglecting Si-O-Si in higher silica compositions will lead to an underestimation of the predicted fraction of Al-NBO.

In Figure 1, the CAS33 $^{17}\text{O}$ MAS spectrum has a small shoulder at about 150 ppm that might be due to the presence of a small fraction of Al-NBO, although the presence of this species is not clearly required by the data. Our estimated equilibrium constant ($K_1$) predicts that this composition could contain about 3 % Al-NBO (Table 2). However, the accuracy of this prediction from very low silica glasses is probably reduced by the increase in the Si-O-Si fraction at higher silica contents.

By subtracting Eq. 2 from Eq.1, one obtains:

$$\text{Si-O-Si} + \text{Al-NBO} \leftrightarrow \text{Al-O-Si} + \text{Si-NBO}. \quad (3)$$

Although Eq. 3 is more directly applicable to natural systems, its "equilibrium constant" cannot be calculated directly from the present data set due to difficulties in measuring very small concentrations of Si-O-Si and Al-NBO with high accuracies. As more data become available on the thermodynamics of such reactions, especially the effects of temperature on them, a consistent, predictive formulation of their free energies should become feasible.
The contour line in Fig. 4, denoting regions where the fraction of oxygens as Al-NBO is less than a few percent, indicates that for most or all geologically "interesting" Ca-aluminosilicate compositions, these species are probably of low enough concentration to be excluded from thermodynamic models of overall free energies and chemical potentials. However, small fractions could remain important in models of dynamics. This conclusion also has important implications to the way thermodynamic models of melts are formulated. If, for example, mixing of estimated “Q⁰” species populations enter into the formulation of configurational entropy, the distribution of such species over Si and Al will be quite different (most Al will be in Q⁴ groups). Similarly, if silica activity is related to the fraction of SiO₄ groups with 4 Si neighbors (Stebbins and Farnan 1989), then it will be overestimated if NBO are assumed to be equally distributed over Si and Al.

Even with the enhanced resolution provided by the “inner satellite” spinning side bands, (Fig. 5) we see no evidence for [⁵]Al and [⁶]Al in the calcium aluminate glass. This agrees with the ²⁷Al MAS NMR study of McMillan et al. (1996) at 7.4 T, but contradicts the study of Shelby et al. (1989), which was also done at the relatively high frequency of 14.1 T. The latter showed a small shoulder (~ 1%) at 9 ppm, which we did not detect. It is possible that this peak may have resulted from octahedral Al in a crystalline phase due to the difficulty in quenching large batches of calcium aluminate glasses.

The lack of measurable concentrations of high-coordinated Al and triclusters supports our study’s assignment of Al-NBO/Al and Si-NBO/Si ratios (Table 1) because there is no ambiguity in the assignment of NBO and tetrahedral species. However, the observation that higher-coordinated Al is undetectable in the glass (which represents the melt at Tₜₙ) does not necessarily mean that such groups are not present in the melts at higher T. Ion dynamics has shown that as the temperature of the melt increases, the Al-coordination increases slightly (Poe et al. 1994). However, probably a more important factor in the average Al coordination of aluminosilicate melts is the effect of the percentage of Al₂O₃. Poe et al. (1993, 1994) have utilized ion dynamics and in situ high-temperature ²⁷Al MAS NMR of calcium aluminates to show that the average aluminum coordination increases with an increasing percentage of
Al₂O₃. For instance, ion dynamics predicts that there would be an increase in the average coordination of Al by 0.2 when the percentage of Al₂O₃ is increased from 37% (this study) to 50% (charge-balanced join) (Poe et al. 1994). This is the same trend as that seen when these samples are compared to the amount of higher-coordinated Al in measured in samples along the CAS “charge balanced” join (Toplis et al. 2000; Stebbins et al. 2000). In general, temperature effects on all aspects of melt structure should be carefully considered before extrapolating results on glasses to liquidus temperatures.

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The authors would like to thank Dr. L.-S. Du for assistance in collecting the ⁷⁷Al MAS spectrum for CAS10 and the ¹⁷O MAS spectrum for CAS20 and Bob Jones for assistance in the collection of microprobe data. We would also like to thank B.O. Mysen, M.J. Toplis and an anonymous reviewer for their constructive comments on the original manuscript. This work was supported by NSF grant EAR-0104926.

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Petkov, V., Gerber, Th. and Himmel, B. (1998) Atomic ordering in Ca$_{x/2}$Al$_x$Si$_{1-x}$O$_2$ glasses (x=0,0.34,0.5,0.68) by energy-dispersive x-ray diffraction, Physical Review B, 58, 11982-11989.


Table 2.1 Composition, synthesis temperatures, and MAS fitting results for the three samples of this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO (mole %)</th>
<th>Al₂O₃ (mole %)</th>
<th>SiO₂ (mole %)</th>
<th>T°C</th>
<th>%NBO</th>
<th>NBO/T</th>
<th>%NBO</th>
<th>%Si-NBO</th>
<th>%Al-NBO</th>
<th>NBO/AI</th>
<th>NBO/Si</th>
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<tbody>
<tr>
<td>CA</td>
<td>61.5</td>
<td>37.9</td>
<td>0.6</td>
<td>1470</td>
<td>26.8</td>
<td>0.62</td>
<td>28.4</td>
<td>-0.9</td>
<td>27.6</td>
<td>0.6</td>
<td>2.5</td>
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<tr>
<td>CAS10</td>
<td>58.5</td>
<td>29.4</td>
<td>11.8</td>
<td>1606</td>
<td>34.17</td>
<td>0.82</td>
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<td>17.0</td>
<td>19.0</td>
<td>0.5</td>
<td>2.3</td>
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<tr>
<td>CAS20</td>
<td>52.0</td>
<td>28.0</td>
<td>20.3</td>
<td>1542</td>
<td>27.2</td>
<td>0.63</td>
<td>32.4</td>
<td>21.6</td>
<td>10.8</td>
<td>0.3</td>
<td>1.6</td>
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</table>

Notes: “Nominal” values are based on stoichiometry only.

*: The estimated uncertainties in the measured percentages of NBO peak areas are about 1% absolute, based on sensitivity to fitting and baseline corrections.
Table 2.2 Comparison of measured and predicted NBO percentages based on fits of $^{17}$O NMR data for CAS10. $R_{NBO} = [\text{Si-NBO}]/[\text{Al-NBO}]$

<table>
<thead>
<tr>
<th>CA</th>
<th>measured</th>
<th>calculated</th>
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</thead>
<tbody>
<tr>
<td>$R_{NBO}$</td>
<td>0.03</td>
<td>0.03</td>
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<tr>
<td>% Si-NBO</td>
<td>~0.9</td>
<td>0.9†</td>
</tr>
<tr>
<td>% Al-NBO</td>
<td>27.6</td>
<td>27.5†</td>
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</table>

**CAS20**

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<table>
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<tbody>
<tr>
<td>$R_{NBO}$</td>
<td>1.9</td>
<td>2.4</td>
</tr>
<tr>
<td>% Si-NBO</td>
<td>21.6</td>
<td>23.0†</td>
</tr>
<tr>
<td>% Al-NBO</td>
<td>10.8</td>
<td>9.6†</td>
</tr>
</tbody>
</table>

**CAS33**

<p>| | | |</p>
<table>
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<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>$R_{NBO}$</td>
<td>$9-\infty$</td>
<td>10.6</td>
</tr>
<tr>
<td>% Si-NBO</td>
<td>36–40</td>
<td>36.6</td>
</tr>
<tr>
<td>% Al-NBO</td>
<td>0–4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

*: The estimated uncertainties in the measured component peak areas are about 1% absolute, based on sensitivity to fitting and baseline corrections.

†: The sum of the percentages for NBO species has been normalized to the total NBO measured from peak fitting (Table 1) to aid in comparison.
Figure 2.1 $^{17}$O MAS NMR spectra for calcium aluminate and low-silica calcium aluminosilicates glasses collected at 14.1T. Sample compositions are given in Table 1, except for CAS33 (nominal composition: 50 mol% CaO, 17%Al$_2$O$_3$, 33% SiO$_2$, CAS312 in Lee and Stebbins, in preparation).
Figure 2.2 $^{17}$O 3QMAS spectra for CA and CAS20 glasses where the contour lines are from 7% to 97% spaced at intervals of 10% with an extra interval placed at 10% to emphasize the peak maximum of Al-NBO.
Figure 2.3 Peak fits for the $^{17}$O MAS NMR spectra for calcium aluminosilicate glasses (CAS10 and CAS20), in which peak shapes are assumed to be Gaussian.
Figure 2.4 Ca-rich portion of the CAS ternary showing predictions for the fraction of total oxygen as Al-NBO, assuming $K_i = 4.1$. The dotted lines “A” and “B” reflect the $(\text{Si-NBO})/(\text{Al-NBO})$ ratios ($R_{NBO}$) of 1 and 10, respectively. The solid, curved line shows compositions where Al-NBO are ~2% of the total oxygen and where the ‘lack of Si-O-Si’ assumption is relatively accurate. This model neglects the NBO that have been measured in the CAS charge balanced join compositions so the “2% Al-NBO” predictions will likely be pushed to more Al-rich compositions. The extrapolated, dashed line, is the prediction of Al-NBO in the region where the Si-O-Si species become more significant.
**Figure 2.5** $^{27}$Al MAS spectrum at 14.1T of the calcium aluminate glass showing the central transition (ct), and the sum of the six consecutive (±1/2-±3/2) satellite spinning sidebands (ssb), shifted to their central frequency for comparison.
Chapter Three

Ca-Mg and K-Mg mixing around non-bridging oxygen in silicate glasses: An investigation using Oxygen-17 MAS and 3QMAS NMR

Modified version published in American Mineralogist
Abstract

In an effort to improve the physical accuracy of models of the thermodynamics of silicate melts, we describe a systematic study of the extent of modifying cation mixing, using $^{17}$O 3QMAS NMR, in series of Ca-Mg and K-Mg silicate glasses. The spectra for the mixed cation $\text{Ca}_{2-2x}\text{Mg}_{2x}\text{Si}_{2}\text{O}_6$ glass show that only one large non-bridging oxygen (NBO) peak occurs that encompasses the entire range of chemical shifts ranging from Ca-NBO to Mg-NBO. Comparison of the isotropic projections from 3QMAS NMR to spectra predicted by a random model show that mixing in these glasses is highly disordered, but may contain a small amount of ordering at the glass transition temperature. In contrast, cation mixing in K-Mg silicate glasses is very ordered, confirming previous results; however, the results of this study disagree with the interpretation of the previous study and show that the NBO in K-Mg silicate glasses contain mostly Mg-NBO, not a highly ordered K-Mg-NBO species. These order-disorder results have direct implications in constraining entropy models and therefore allowing better predictions of mineral-melt equilibria in silicate melts.
Introduction

The atomic-scale structure of silicate melts dictates the macroscopic properties (i.e. viscosity, density, diffusivity, silica activity, entropy, etc.) that directly influence igneous processes (Kushiro 1980; Mysen et al. 1985; Liu et al. 1988; Richet and Neuville 1992). However, the compositional complexity and variety of magmatic liquids will often require extrapolation of structural information from simpler systems. An important aspect of this process is characterizing how structural units defined by network forming cations (e.g. Si, Al) and network modifiers (e.g. Mg, Ca, K, etc.) interact. Cooling a melt quickly and quenching it into a glass can capture the approximate structure at the glass transition temperature ($T_g$) (Seifert et al. 1981; Dingwell 1995; Moynihan 1995; Richet and Bottinga 1995; Stebbins 1995). Structural analysis of glasses avoids certain difficulties of measurements made at elevated temperatures (e.g. temperature corrections of absorption parameters (McMillan and Wolf 1995), anharmonic vibrations (Brown et al. 1995; Daniel et al. 1995; McMillan and Wolf 1995), motional averaging (Stebbins 1995)) and often can allow more accurate results. Glasses are thus the logical starting point when investigating the atomic structure of silicate and aluminosilicate melts, although caution must be exercised in extrapolating data on glass structure to that of the liquid because structural variations with temperature are often poorly understood.

Discussion of oxide glass structure often relies upon the distinction between network formers and network modifiers. Network formers bonded to oxygen provide the framework and rigidity while the addition of network modifier oxides breaks apart this structure through the formation of non-bridging oxygen (NBO). A NBO is bonded to only one network former leaving the surrounding network modifying cations to balance its remaining valence charge, while bridging oxygen (BO) are bonded to two network formers (e.g. Si-O-Si).

Most thermodynamic models of silicate and aluminosilicate melts assume that the modifier cations and the network forming cations each mix randomly on two types of sites (Weill et al. 1980; Hon et al. 1981; Navrotsky 1995). This approach has been used to successfully predict melting temperatures for the diopside (CaMgSi$_2$O$_6$) saturation surface of the CaMgSi$_2$O$_6$-NaAlSi$_3$O$_8$-CaAl$_2$Si$_2$O$_8$ ternary (Weill et al.
The assumption of ideal mixing for the network formers was known to not be entirely correct, but the authors limited the ranges of compositions of the model to those with $\text{Al/(Al+Si)} < 0.25$ to minimize the inaccuracies created by neglecting Al-avoidance. Recent spectroscopic work has quantified the degree of Al-avoidance for aluminosilicate glasses (Lee and Stebbins 1999, 2000), and it has been shown that the NBO in these systems are almost entirely associated with Si instead of Al (Mysen 1988; Stebbins et al. 2001; Allwardt et al. 2003)). These findings are both examples of non-trivial deviations from random mixing for network formers in aluminosilicate glasses.

The framework cations are however not the only contributors to the configurational entropy (and enthalpy) of a glass. Mixing of network modifier cations creates additional complications to the structure because, as was the case for network formers, each cation may have specific “site” preferences, which contribute to the bulk thermodynamic properties. For instance, the configurational entropy (at constant $T$) of $\text{CaMgSi}_2\text{O}_6$ liquid is about 150% higher than that of either end-member ($\text{Mg}_2\text{Si}_2\text{O}_6$ and $\text{Ca}_2\text{Si}_2\text{O}_6$) melt at temperatures just above $T_g$ (Neuville and Richet 1991). Modifier cations are generally assumed to mix randomly (i.e. no ordering) on their specific type of sites, as in the “two-lattice” model (Weill et al. 1980). Previous studies have shown that this assumption seems accurate for systems like Ca-Mg silicates (Kirkpatrick et al. 1983; Neuville and Richet 1991; Allwardt and Stebbins 2002), Ca-Mg aluminosilicates (Neuville and Richet 1991), Ba-Ca silicates (Stebbins et al. 1997) and K-Na silicates (Richet 1984; Florian et al. 1996). On the other hand, this assumption is clearly not entirely correct for some systems with larger differences among cation size and charge. For example, Farnan et al. (1992) found from $^{17}\text{O}$ DAS NMR that K-Mg mixing is highly ordered in silicate glasses. More recently, using $^{17}\text{O}$ 3QMAS NMR, Lee and coworkers have found that several ternary silicate glasses with two different modifier cations show a non-random preference for dissimilar pairs of modifier cations. In other words, these systems show a preference for NBO that are coordinated by both types of modifier cations rather than being entirely coordinated by a single type of modifier cation. Among the cation pairs of Na-Ca (Lee and Stebbins 2003), Ba-Mg, and Ba-Na (Lee et al., 2003), Ba-Mg shows the most preference for
dissimilar pairs and Ba-Na shows the least. The effect of Al on the mixing of alkali-
alkaline-earth modifiers in aluminosilicate glasses and melts has not yet been
determined, but it has been suggested that the alkali cations preferentially associate
with Al due to their low cation field strengths (Richet and Neuville 1992), which could
add even more order to these already ordered systems. Temperature effects on
modifier cation mixing remains largely unknown, but more mixing (higher entropy) is
expected at higher temperatures (Richet and Neuville 1992). For this reason,
configurational entropies of melts that show ordering at Tg are likely be somewhere
between those predicted from a random model and those derived from measurements
on glasses.

In this study, we have investigated Ca-Mg and K-Mg mixing in silicate glasses
using 17O 3QMAS NMR with the ultimate goal of placing atomic-scale constraints on
thermodynamic models of silicate melts. From past experimental work in Ca-Mg
(Kirkpatrick et al. 1983; Neuville and Richet 1992) and K-Mg (Farnan et al. 1992)
silicate systems, these pairs of modifier cations were chosen to represent the largest
differences in ordering (disordered (Ca-Mg) vs. ordered (K-Mg)) among
petrologically significant (and non-paramagnetic) modifier cations (Mg2+, Na+, Ca2+,
K+) as well as to optimize separation of NBO peaks in 17O 3QMAS NMR.
Additionally, these glasses can be used as an independent test of the Adam-Gibbs
(1965) method for relating viscosity measurements to configurational entropy as both
NMR and viscosity measurements investigate the entropy of systems in similar
temperature ranges.

**Experimental Procedures**

Glass samples were made using appropriate amounts of CaO, MgO, K2CO3,
and ~45% 17O-enriched SiO2 (Stebbins et al. 1997). The CaO, MgO, and K2CO3 were
dried overnight (1000 °C, 1000 °C, and 250 °C, respectively) and used immediately. In
addition, 0.2 wt % cobalt oxide was added to the oxide powders to speed spin-lattice
relaxation. The 200 mg samples (Table 1) were melted in Ar (to minimize the loss of
17O) and quenched by dipping the bottom of the Pt crucible in water. The enstatite
(MgSiO3) composition glass required the use of a “drop quench” technique to attain a
faster quench rate. This consisted of melting the sample inside a sealed, 5 mm Pt-tube and dropping it directly from the furnace into a container of water. The powder for the KM2S9 sample was held at 750 °C in Ar for 16 hours to decarbonate the sample prior to melting. The KS4 and KMS8 samples are from Farnan et al. (1992) and were remelted (1080 °C) and quenched, again in Ar. All samples were found to be entirely amorphous when examined with a 400X petrographic microscope. The compositions of glasses made for this study were measured by electron microprobe using mineral standards (Table 1).

The $^{17}$O MAS NMR spectra were collected on a Varian Unity/Inova 600 spectrometer (14.1 Tesla) using a Varian/Chemagnetics 'T3' probe with 3.2 mm zirconia rotors spinning at 20 kHz. The $^{17}$O frequency is reported relative to tap water. Single pulse acquisition was used with pulse widths corresponding to approximately 30° rf tip angles for the solid (about 0.2 µs for $^{17}$O); two second delays between pulses were used to optimize the signal to noise ratio and to ensure a fully relaxed sample. The triple-quantum magic-angle spinning (3QMAS) spectra that were used for detailed structural analysis were collected on a modified Varian/Unity 400S spectrometer (9.4 Tesla) using a Doty Scientific Inc, 'Supersonic' probe with 5 mm silicon nitride rotors spinning at 15 kHz and an rf power of 63 kHz. A shifted-echo pulse sequence was employed, consisting of two hard pulses (6 µs and 2 µs respectively) followed by a delay of typically 1.33 milliseconds (20 rotor periods) and a soft "echo" pulse (28 µs) (Massiot et al. 1996; Du and Stebbins 2003). A delay of 10 to 20 seconds was used between acquisitions to ensure spin-lattice relaxation. Processing of the 3QMAS data was done with the software package, RMN (FAT) (P.J. Grandinetti, The Ohio State University). The resulting spectra are two-dimensional plots in which the isotropic dimension is free of second order quadrupolar broadening and the projection of the MAS dimension yields a similar spectrum to that measured with conventional 1-D MAS NMR. Several different conventions have been used in plotting of MQMAS spectra, affecting both the scaling of the axes and their orientations: for example, a vertical orientation of the $\omega_I$ (isotropic) axis is more standard in 2D NMR spectroscopy (McKenzie et al. 2002; Ashbrook et al. 2002). However, for consistency with previous reports on related systems (Stebbins et al.
1997; Stebbins and Xu 1997; Lee and Stebbins 2000), and to allow ready comparison of the "interesting" isotropic dimension in vertically stacked plots of spectra for different compositions, we have plotted our data with the \( \omega_2 \) (MAS) axis vertical. We note also that our choice of axis scaling (Baltisberger et al. 1996) leads to a sign difference in the frequencies of the isotropic dimension when compared to that used by some others (Ashbrook et al. 2002).

Results

The \(^{17}\)O MAS spectra of the five glasses studied on the Ca-Mg pyroxene join (\( \text{Ca}_{2x}\text{Mg}_{2-2x}\text{Si}_2\text{O}_6 \), where \( x = 0, 0.25, 0.5, 0.75, 1 \)) are similar to previous work (Kirkpatrick et al. 1983) and are shown in figure 1. The MAS spectrum of Wo glass ((\( \text{CaO} \))\(_{0.45}\)\((\text{SiO}_2)_{0.55}\) in Stebbins et al. 1997) contains peaks that can be uniquely assigned to Si-O-Si (~35 ppm) and Ca-NBO (100 ppm) species (Stebbins et al. 1997). As the ratio of Ca:Mg decreases, the maximum of the NBO peak shifts to lower frequencies. Finally for the end-member MgSiO\(_3\) (En) glass composition, very little unique information can be determined from the \(^{17}\)O MAS spectra due to severe overlap of the Mg-NBO peak (-10 to 60 ppm) with the Si-O-Si peak (Kirkpatrick et al. 1983). In contrast, the \(^{17}\)O 3QMAS spectra of these glasses have much a higher resolution and thus contain much more direct information (Fig. 2), as was also recently reported for crystalline pyroxenes (Ashbrook et al. 2002). As in the MAS spectra, the 3QMAS spectra show a systematic shift in the peak maximum of the "NBO ridge" as the Ca:Mg ratio is decreased. This suggests that a variety of structural environments ranging from pure Ca-NBO and Mg-NBO to Ca-Mg-mixed NBO are present. There is no additional resolution in the NBO peak at higher magnetic field (Fig. 3), however, both the Si-O-Si and NBO peaks show decreased peak widths in the MAS dimension due to the reduction of second-order quadrupolar broadening with increasing field.

Since there is no additional information about the NBO peak in the higher field spectra, the 9.4 T data were used to investigate the NBO peak of the Ca-Mg silicate glass in detail. This was done by projecting the spectra in the isotropic dimension and subtracting out the Si-O-Si peak to isolate the NBO peak. The Si-O-Si peak is non-Gaussian in both the MAS and isotropic dimensions, but in the spectrum for the Wo
glass, there is enough separation between the two that the Si-O-Si peak can be isolated from the Ca-NBO peak simply by projecting a subset of the data (Fig. 4). The isotropic projection of this peak was then fit with 3 Gaussians (no structural significance) in order to accurately portray its shape and, since the Wo sample contained more silica than the others (55 mol% vs. 50 mol%), the intensity Si-O-Si composite "peak" was scaled to reflect the differing amounts of silica. After the subtraction of the scaled Si-O-Si peak from the isotropic projection of each sample (Fig. 5), the spectra for the En and Wo glasses consist only of Gaussian peaks, which suggest that this method can accurately remove the BO contributions. The widths and locations of the Mg-NBO and Ca-NBO peaks were fixed and used in a least squares fitting analysis of the distribution of NBO species in the mixed cation glasses. Two other mixed modifier cation peaks (2Ca:1Mg and 1Ca:2Mg) were needed, whose widths and positions were derived by fitting the isotropic spectrum of the CaMgSi2O6 glass. Peak widths and locations were held constant for all fits. The assumption of constant component peak positions was necessary to carry out numerically well-constrained fits and to test a simple model, and is sensible as a first approximation. However, it is possible that composition (e.g. longer-range effects of structure on chemical shift) has a minor effect on peak position, leading to additional uncertainties in the relative areas of the fitted peaks. The projections and fits can be seen in figure 5 and the relative percentages of each species are shown in Table 2. The derived relative Ca-Mg-NBO peak locations agree well with those for mixed cation O2 and O1 sites of crystalline diopside found by Ashbrook et al. (2002). We note that although 3QMAS intensities are not strictly quantitative (varying with CQ-dependent excitation and reconversion efficiency), the relatively small variations in CQ from one type of NBO site to another (about 2 to 2.5 MHz) indicate that at least a semi-quantitative interpretation of such intensities is justified.

The accuracy of this fitting process can be independently tested by calculating the Ca/(Ca+Mg) ratio from the relative areas of the fitted peaks. As shown in Table 2, there is excellent agreement with the actual compositions. We note also that any such analysis of the 3QMAS isotropic projections assumes there is at least an approximately unique correlation between the 3Q isotropic peak position and the
structural variable of interest (here, the ratio of Ca to Mg among the NBO first neighbors). Such peak positions are affected not only by the isotropic chemical shift $\delta_{CS}$, but also by the quadrupolar coupling constant ($C_Q$) and asymmetry parameter ($\eta$), which respond somewhat differently to the local structure (Massiot et al. 1996). Particularly for the data analyzed here, however, we do not consider this to be a significant limitation, as $C_Q$ values for NBO are relatively small and do not vary widely. Isotropic peak positions for NBO thus are dominated by $\delta_{CS}$.

A simple model was developed to compare the fitting results to a random mixing of Ca and Mg, which assumes that there are statistical distributions of three Ca and Mg cations surrounding each NBO. This means that there are four possible "species," which are the same as those used in fitting the isotropic projections. The predicted percentages of each of the structural species are:

$$X_{3Ca} = x^3$$  \hspace{1cm} (1)
$$X_{2Ca:1Mg} = 3x^2(1-x)$$  \hspace{1cm} (2)
$$X_{1Ca:2Mg} = 3x(1-x)^2$$  \hspace{1cm} (3)
$$X_{3Mg} = (1-x)^3$$  \hspace{1cm} (4)

where $x=Ca/(Ca+Mg)$ and is based on composition. The results of equations 1 through 4 are plotted in figure 6 and compared to the values obtained from the peak fitting of the NBO peaks. These equations were also used to predict spectra for purely random mixing of Ca and Mg around NBO. These were then compared to the NBO peaks of the experimental isotropic projections (Fig. 7).

The $^{17}O$ MAS spectra of K-Mg silicate glasses are shown in figure 8. The two peaks in the spectrum of the KS4 ($K_2Si_4O_9$) glass can be uniquely assigned to K-NBO (70 ppm) and Si-O-Si (-50 to 50 ppm) (Xue et al. 1994; Florian et al. 1996). Unlike for the Ca-silicate, the Si-O-Si peak in this spectrum has a distinct quadrupolar lineshape. In marked contrast to the Ca-Mg system, the K-NBO peak simply seems to disappear with the replacement of K$^+$ by even a small percentage of Mg$^{2+}$. This can be seen more clearly in the $^{17}O$ 3QMAS NMR spectra (Fig. 9). Here, the NBO peak in the mixed cation glasses is similar to that in the K-free MgSiO$_3$ glass, indicating a strong preferential association of Mg with NBO. Changing the MgO:K$_2$O ratio does not significantly change the NBO peak shape or the bonding preferences as evidenced by
comparison of the $^{17}$O 3QMAS spectra of KMS8 and KM2S9. In detail, the Mg-NBO peak appears narrower in the K-Mg silicate spectra than for the En glass, possibly suggesting that the presence of K$^+$ allows the Mg-NBO environment to be even more ordered. Another interesting observation is that the peak maximum (in the MAS dimension) for the Mg-NBO species moves to slightly lower frequency with the addition of K$^+$, possibly suggesting that the Mg-O bonds in the K-Mg silicates are slightly shorter than those in the Mg-silicate (Turner et al. 1985). The lack of much intensity in the region associated with K-NBO peak suggests that the K$^+$ is primarily coordinated by the BO. Further support for this is that the Si-O-Si peaks of the K-Mg silicate spectra are similar to those found for KS4, which are distinctly different from that observed for En.

**Discussion**

The fundamental connection between viscous flow and configurational changes led to the development of the Adam-Gibbs theory of relaxation processes (1965), which hypothesizes that changes in the viscosity of glass-forming liquids can be quantitatively related to changes in the configurational entropy. This was later shown to be quantitatively applicable to silicate melts when Richet (1984), Richet et al. (1986) and others found values for the configurational entropy derived from Adam-Gibbs analysis to be similar to those derived calorimetrically. In a detailed study of the CaSiO$_3$-MgSiO$_3$ binary, Neuville and Richet (1991) showed that at temperatures about 100 K above $T_g$, strong, non-linear variations in melt viscosities were well predicted by a model of configurational entropy assuming random mixing of Ca and Mg. The NMR data presented here provide a relatively direct way of testing this structural conclusion.

In the present study, comparison of experimental NBO peak projections with spectra predicted from a random model (Fig. 7) suggest that the modifier cation mixing, although highly disordered, may not be entirely random for all compositions along the CaSiO$_3$-MgSiO$_3$ join at the glass transition temperature (718-766 °C along this join (Neuville and Richet 1991)). This slight ordering observed at $T_g$ does not necessarily disagree with the ideal mixing that was observed in the viscosity study of
Neuville and Richet (1991) because the viscosities were measured at temperatures somewhat above $T_g$, where a greater amount of mixing and therefore more ideality is expected (Richet and Neuville 1992). In addition, analysis of the NMR data is complicated by the fact that $T_g$ is systematically lower in the mixed cation compositions, again as a consequence of the added configurational entropy (Neuville and Richet 1991). Thus, the structure sampled for the CaMgSi$_2$O$_6$ composition may represent that of a melt at as much as 50° below that of the end member glasses.

The random model appears to be adequate for approximating the projections of the Di and DE50 samples, but is inadequate for DW50 (Fig. 7). It is possible that the BO peak of the DW50 was not subtracted entirely, but this seems unlikely as the contours of the NBO peak of the 3QMAS spectrum reveal the same approximate shape as that seen in the isotropic projection after the Si-O-Si peak subtraction. One possible contribution to the differences between the random model and data for DW50 may be that its accuracy is reduced by a decrease in the Mg coordination number. This would allow fewer possibilities for an oxygen to be bonded to a Mg and may be observed (from the oxygen’s perspective) as a preference for Ca-NBO. Additionally, a $^{25}$Mg NMR study has shown that as the Ca:Mg ratio increases for Ca-Mg aluminosilicate melts (~1400 °C) the isotropic chemical shift moves in the direction of a lower coordination number (George and Stebbins 1998). Support for a decreasing Mg-coordination is also seen in the structures of the minerals diopside (CaMgSi$_2$O$_6$) and akermanite (Ca$_2$MgSi$_2$O$_7$); as the amount of Ca is increased, the coordination number of the Mg decreases from 6 to 4. However, this coordination change in the DW50 glass needs to be confirmed by $^{25}$Mg NMR or Mg-XAS (X-ray absorption spectroscopy) as inferring cation coordination changes based solely on changes in the environment of the anion is problematical.

Magmas that are rich in both Mg and alkalis are unusual in nature, but, even for normal basaltic systems, thermodynamic mixing models are important for understanding activity coefficients for alkalis, which are in turn an important part of modeling mineral-melt partitioning. Previous work on K-Mg mixing in silicate glasses has revealed that there is a significant amount of ordering at $T_g$ (Farnan et al. 1992). Similar to the results presented here, the two-dimensional, $^{17}$O DAS NMR spectra
from that study showed that the location of the NBO peak shifted by \( -40 \) ppm (in the anisotropic dimension, \( \omega_2 \)) between the spectra for \( \text{K}_2\text{Si}_3\text{O}_9 \) and \( \text{KMg}_{0.5}\text{Si}_4\text{O}_9 \) glasses, which, in this study, are referred to as KS4 and KMS8, respectively (Fig. 9). The DAS spectra were interpreted to mean that NBO in the K-Mg silicate glasses were coordinated by fixed numbers of \( \text{K}^+ \) and \( \text{Mg}^{2+} \) and are highly ordered (narrow NBO peak width). Our new \(^{17}\text{O} \) 3QMAS spectra also show that K-Mg mixing is highly ordered. However, based on the locations of the NBO peaks for the K-Mg silicates and for the Mg-silicate (En), we can now confidently conclude that most of the NBO in K-Mg silicate glasses are Mg-NBO, not a mixed K-Mg-NBO species. It also seems that \( \text{K}^+ \) mostly associates with the BO as evidenced by the similar peak shape and locations of the Si-O-Si peaks for spectra of the KS4 and KMS8 and KM2S9 glasses, which are distinctly different from that seen in the En spectrum.

The large contrast in the mixing of \( \text{K}^+ \) with \( \text{Mg}^{2+} \) when compared to that of \( \text{Ca}^{2+} \) with \( \text{Mg}^{2+} \) can be rationalized in terms of the differences in the field strengths of the cations. The field strengths for \( \text{K}^+ \), \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) are about 0.12, 0.36, and 0.5 respectively, when defined as \( z/d^2 \), where \( z \) is the formal charge and \( d \) is the typical cation-oxygen distance (Brown et al 1995). The large differences in both charge and radius between \( \text{K}^+ \) and \( \text{Mg}^{2+} \) effectively results in an “outcompetition” by the latter for coordination by the NBO with their highly concentrated effective negative charges. For the more similar pair \( \text{Ca}^{2+} - \text{Mg}^{2+} \), the entropic contribution of more random mixing apparently is enough to overcome the relatively slight energetic differences indicated by the field strengths.

The suggested coordination of \( \text{K}^+ \) primarily by bridging oxygens seems somewhat paradoxical in terms of the formal zero valence charge on Si-O-Si oxygens. However, such oxygens are common in the coordination spheres of large, low-charge cations in crystalline alkali silicates, and in fact are required when the coordination number is large and the alkali content low enough to result in an insufficient number of NBO to fully coordinate the modifiers. In such cases, Si-O-Si angles are typically somewhat reduced, and Si–O bond distances slightly lengthened, resulting in a net partial negative bond valence localized on the bridging oxygen (deJong and Brown 1980). Each mole of \( \text{M}_2^{2+}\text{O} \) or \( \text{M}^{2+}\text{O} \) added to \( \text{SiO}_2 \) produces an equal total number.
of NBO; in a mixed system a cation with much higher field strength can bond to an increased fraction of the total NBO, actually reducing its mean coordination number from that in its pure end member system. This coordination change has been measured by various spectroscopic techniques. For instance, the Mg-O distances are similar for CaMgSi$_2$O$_6$ and MgSiO$_3$ glasses, suggesting a similar Mg-coordination number (Taniguchi et al. 1997) but Mg-EXAFS (extended X-ray absorption fine structure) (Henderson et al. 1992) and $^{25}$Mg NMR spectra of glasses (Kroeker and Stebbins 2000) show that the Mg-coordination of K$_2$MgSi$_5$O$_{12}$ is less than that observed for CaMgSi$_2$O$_6$. The combination of these results suggests that the Mg-coordination in K-Mg silicates is, in fact, less than that of the Mg-silicates. Additionally, to balance the total valance charge of the system there needs to be a constant number of modifier to oxygen bonds, (Prewitt and Downs 1998) so the K$^+$ coordination would increase in K-Mg silicates relative to that seen in K-silicate glasses. Similar reasoning can explain the shift of large alkali cations to larger sites when mixed with smaller cations, and vice versa, which in turn is an important structural cause of the “mixed alkali” effect (Stebbins 1998).

The coordination of K$^+$ primarily by BO in the K-Mg silicate glasses has implications for the intermediate-range as well as the local structure. Overall local charge balance cannot be maintained in a region of the glass that has only BO and K$^+$, suggesting that on a scale larger than the coordination spheres of individual NBO, Mg- and K-rich regions must be closely associated. For example, in a silicate glass with on average three BO and one NBO per silicon tetrahedron, one could imagine a mica-like local structure in which Mg$^{2+}$ cations, entirely coordinated by NBO, are located between pairs of tetrahedral sheets, which are in turn separated by layers of K$^+$ ions, predominantly coordinated by BO. Confirmation of such speculations will, however, require methods that provide data more directly on longer-range correlations. This ordering of the K$^+$ and Mg$^{2+}$ cations around specific oxygen in silicate glass structure has implications for the thermodynamics of these systems. As mentioned previously, models of the free energies of silicate melts typically assume that there is random mixing of modifier cations. This assumption seems at least approximately accurate for Ca-Mg mixing (as strengthened by this study), but is obviously not appropriate for K-
Mg mixing in silicate glasses as the mixing is likely closer to zero (complete ordering) than ideal at $T_g$. However, to extend these conclusions to petrologically more relevant conditions, considerable work to assess temperature effects and the effect of the presence of $\text{Al}^{3+}$ on disorder remains.

**Acknowledgements**

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**References**


Table 3.1 Sample names and compositions (in mol%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO₂</th>
<th>MgO</th>
<th>CaO</th>
<th>K₂O</th>
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<tbody>
<tr>
<td>Wo*</td>
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<td>0</td>
<td>45</td>
<td>0</td>
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<tr>
<td>DW50‡</td>
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</tr>
<tr>
<td>Di†</td>
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<td>24.6</td>
<td>24.9</td>
<td>0</td>
</tr>
<tr>
<td>DE50‡</td>
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<td>37.8</td>
<td>11.9</td>
<td>0</td>
</tr>
<tr>
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<td>49</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>14.7</td>
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<td>8.1</td>
</tr>
<tr>
<td>KMS8*</td>
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<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>KS4*</td>
<td>80</td>
<td>0</td>
<td>0</td>
<td>20</td>
</tr>
</tbody>
</table>

*: Nominal compositions for samples from previous studies (Farnan et al. 1992; Stebbins et al. 1997)

‡: Compositions represent the average of three or more microprobe analyses
Table 3.2 Percentage of species measured by fitting the isotropic projections of the “NBO peaks”

<table>
<thead>
<tr>
<th>NBO species</th>
<th>3Mg</th>
<th>2Mg:1Ca</th>
<th>1Mg:2Ca</th>
<th>3Ca</th>
<th>Ca/(Ca+Mg) from fit composition</th>
</tr>
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<tbody>
<tr>
<td>Wo</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>1</td>
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<tr>
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<tr>
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<td>19</td>
<td>29</td>
<td>31</td>
<td>21</td>
<td>0.51</td>
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<tr>
<td>DE50</td>
<td>54</td>
<td>27</td>
<td>19</td>
<td>1</td>
<td>0.23</td>
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<tr>
<td>En</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Frequency (ppm)</td>
<td>-31</td>
<td>-41</td>
<td>-51</td>
<td>-62</td>
<td></td>
</tr>
</tbody>
</table>

Note: "Frequency (ppm)" indicates the peak position (in the isotropic dimension) used in fitting the "NBO peaks". See text for a discussion of the peak fitting procedure.
Figure 3.1 O-17 MAS NMR spectra (14.1 Tesla) of glasses on the Ca$_{2-2x}$Mg$_{2x}$Si$_2$O$_6$ join. Sample compositions are given in Table 1 (note that sample “Wo” has a slightly higher silica content).
Figure 3.2 O-17 3QMAS NMR spectra (9.4 Tesla) of glasses on the Ca$_{2.2x}$Mg$_{2x}$Si$_2$O$_6$ join where the contour lines are from 5% to 95% spaced at intervals of 5%
Figure 3.3  O-17 3QMAS NMR spectra of CaMgSi$_2$O$_6$ composition glass at 9.4 T and 14.1 T (same contours as figure 2).
Figure 3.4 3QMAS spectrum (9.4 T) of “Wo” glass showing how the Si-O-Si peak was isolated and projected in the isotropic dimension. The dark line is the projection and the dashed line is the fit (see text).
Figure 3.5 Isotropic projections of the 3QMAS spectra (9.4 T) showing the “NBO peak” after subtraction of Si-O-Si peak. Peak fitting is described in the text; results are given in Table 3.2.
Figure 3.6 NBO species predicted by a random model, compared to experimental results (Table 3.2).
Figure 3.7 Predicted spectra (not fits) of the NBO peaks (in the isotropic dimension) based on composition using the random model shown in Figure 3.6. The thin lines are the predicted species while the bold line is the projection from the 3QMAS spectra.
Figure 3.8  O-17 MAS NMR spectra (14.1 Tesla) of K-Mg silicates glasses. Sample compositions are given in Table 3.1.
Figure 3.9 O-17 3QMAS NMR spectra (9.4 Tesla) of K-Mg silicates glasses. Contour lines range from 5% to 95% spaced at intervals of 5%.
Chapter Four

Structural mechanisms of compression and decompression in high-pressure K$_2$Si$_4$O$_9$ glasses: An investigation utilizing Raman and NMR spectroscopy of glasses and crystalline materials

Reprinted from Chemical Geology, 213, Jeffrey R. Allwardt, Burkhard C. Schmidt, and Jonathan F. Stebbins, Structural mechanisms of compression and decompression in high-pressure K$_2$Si$_4$O$_9$ glasses: An investigation utilizing Raman and NMR spectroscopy of glasses and crystalline materials, 137-151, 2004, with permission from Elsevier.
Abstract

This study uses Raman, $^{29}$Si magic-angle spinning nuclear magnetic resonance (MAS NMR) and $^{17}$O triple quantum (3Q) MAS NMR spectroscopies on K$_2$Si$_4$O$_9$ glasses quenched from high pressure melts (5.7 and 8 GPa) and on high-pressure crystalline phases of K$_2$Si$_4$O$_9$—wadeite and CaSi$_2$O$_5$ to investigate the structural mechanisms that create high-coordinated silicon. The effect of decompression on the glass structure was also investigated by varying the decompression rates after temperature quench. The spectrum of crystalline triclinic CaSi$_2$O$_5$ phase clearly demonstrates that the $^{[4]}$Si-O-$^{[5]}$Si species do not show a distinct signature in $^{17}$O 3QMAS NMR and their signal can either be represented as "$^{[4]}$Si-O-$^{[4]}$Si-like" or "$^{[4]}$Si-O-$^{[6]}$Si-like" species, depending on the local environment of the oxygen. This suggests that Si-coordination should be directly investigated by $^{29}$Si NMR and not inferred from $^{17}$O NMR spectra. Additionally, based on the comparison of percentages of structural species measured with $^{17}$O NMR to those expected from the $^{29}$Si spectra, it seems that most, if not all, $^{[4]}$Si-O-$^{[5]}$Si in rapidly decompressed K$_2$Si$_4$O$_9$ glasses are represented as $^{[4]}$Si-O-$^{[4]}$Si, not $^{[4]}$Si-O-$^{[6]}$Si. These results were used to successfully test previously proposed mechanisms for the generation of high-coordinated Si ($Q^3 + Q^4 = [5]Si+Q^4$ and $2Q^3 + Q^4 = [6]Si+2Q^4$) when NBO are present. Spectra from glasses that were decompressed more slowly (conventionally) show that there are small structural differences between the glasses with different rates of decompression. Based on $^{29}$Si and $^{17}$O data, a small percentage of $^{[6]}$Si converts to $^{[5]}$Si (~1% of the total Si) by the reversal of the previously mentioned mechanism. Interestingly, this small structural change shows a relatively large effect on the Raman spectra, which suggests that the effect of decompression on silicate glass structure may need re-evaluation with additional in-situ studies.
Introduction

Macroscopic properties of silicate melts (e.g. viscosity, density, diffusivity, etc.) control many of the igneous processes that have dictated the chemical evolution of planetary bodies (e.g. magma ascent, partial melting, crystal fractionation, and mineral-melt elemental diffusion) (Kushiro, 1976; Stolper et al., 1981; Ghiorso et al., 1983; Scarfe et al., 1987; Xue et al., 1994; Wolf and McMillan, 1995; Farber and Williams, 1996; Hirschmann et al., 1998; Poe et al., 2001; Kushiro and Mysen, 2002). The effect of pressure on the melt properties is highly dependent on how the structure of the melt accommodates increasing pressure (decreasing bond angles and distances, increasing the coordination number of constituent elements). Information on high-pressure melt structure is thus essential to fundamentally understanding the pressure dependence of these properties and how these affect igneous processes (Wolf and McMillan, 1995). However, quantitatively studying the structure of high-pressure melts directly at conditions above the melting temperature while at the pressure of interest is experimentally very difficult. It can be complicated by uncertainties in the determination of pressure and temperature (e.g. accuracy of temperature measurements, corrections for thermal pressure due to localized heating etc., (Gillet et al., 1998) and references therein) as well as the spectroscopic uncertainties resulting from conducting experiments at high-temperatures, such as temperature corrections of absorption parameters (McMillan and Wolf, 1995), anharmonic vibrations (Brown et al., 1995; Daniel et al., 1995; McMillan and Wolf, 1995), etc. Because their structures are approximately that of melts at their glass transition temperatures ($T_g$), glasses are commonly used as the starting point in structural studies of melts.

Discussion of oxide glass structure relies heavily upon the principle that most cations can be described as either network formers (e.g. Si, Al, B) or network modifiers (e.g. Ca, Na, K etc.). Network formers are often four-coordinated and bonded to oxygen (e.g. $^{[4]}$Si-O bonds) in ambient pressure silicate and aluminosilicate glasses. The framework and rigidity of the glasses is provided by oxygen that are bonded to two network formers (e.g. Si-O-Si) which are called bridging oxygen (BO). Network modifier oxides break apart this structure through the formation of non-bridging oxygen (NBO), which are bonded to only one network former leaving
network modifiers to balance the remaining valence charge of the NBO.

In almost all crystalline silicates formed at ambient pressure, Si is entirely four-coordinated ($^{[4]}$Si). At higher pressures, relevant to the Earth's mantle, crystalline phases become stable that contain six-coordinated Si ($^{[6]}$Si) (Prewitt and Downs, 1998; Finger and Hazen, 2000), and in rare cases five-coordinated Si ($^{[5]}$Si) (Stebbins and Kanzaki, 1991; Angel et al. 1996). This conversion occurs until about 20 GPa, when the structures become dominated by six-coordinated Si ($^{[6]}$Si) for all known silicate compositions (Finger and Hazen 2000). Due to the long-range order in crystalline solids, these coordination changes generally take place with first-order phase transitions at a single, temperature-dependent pressure. However, long range order is absent in silicate melts and their structures contain large variations in bond angles and distances, suggesting that cation coordination changes are distributed over a wide range of pressures (Waff, 1975; Stolper and Ahrens, 1987). This was shown in studies of glasses quenched from high pressure melts where, the average Si (or Al)-coordination gradually increases to values greater than four with increasing pressures (Xue et al., 1991; Yarger et al., 1995). Additionally, since melts are not bound by translational symmetry, four-coordinated species can be transformed into either five- or six-coordinated species at increased pressures. Such structural transitions have been demonstrated in the conversion of $^{[4]}$Si to $^{[5]}$Si and $^{[6]}$Si (Wolf et al., 1990) (Xue et al., 1989, 1991, 1994; Farber and Williams, 1996; Stebbins and Poe, 1999) and $^{[4]}$Al to $^{[5]}$Al and $^{[6]}$Al (Stebbins and Sykes, 1990; Yarger et al., 1995; Lee, 2004; Allwardt et al., 2003a). Mechanisms for the generation of high coordinated Si (from the Si-perspective) have been suggested to be (Wolf et al., 1990; Xue et al., 1991):

$$Q^3 + Q^4 = [^{[5]}Si + Q^4^*]$$  \hspace{1cm} (1)

$$2Q^3 + Q^4 = [^{[6]}Si + 2Q^4^*],$$  \hspace{1cm} (2)

where 3 and 4 represent the number of bridging oxygen bonded to tetrahedral Si and $Q^4^*$ represents a $Q^4$ species bonded to a high-coordinated Si.

Silicon-29 NMR studies of high and ambient pressure glasses have shown that both the ratio of NBO to the number of tetrahedra (NBO/T) and the type of modifier cation are important factors in the percentage of high-coordinated Si that is recovered on quench (Xue et al., 1991; Stebbins and McMillan, 1993). Tetrasilicate
compositions (e.g. Na$_2$Si$_4$O$_9$) show a greater percentage of high-coordinated Si than disilicates (e.g. Na$_2$Si$_2$O$_5$), likely because Q$^3$ and Q$^4$ species are abundant and in approximately equal proportions in tetrasilicates (NBO/T=0.5), which would favor mechanisms 1 and 2. Disilicates (NBO/T=1), on the other hand, contain mostly Q$^3$ species and smaller amounts of Q$^4$ and Q$^2$ species. Previous studies have also found that K$_2$Si$_4$O$_9$ contains more high-coordinated Si than Na$_2$Si$_4$O$_9$ at similar pressures (Xue et al., 1991; Stebbins and McMillan, 1993). The larger ionic radius (increased coordination number) of K$^+$ relative to Na$^+$ results in an increased underbonding of the NBO, as less valence charge can be supplied by the larger modifier cation (Stebbins and McMillan, 1993), which would offer a greater opportunity for NBO to interact with neighboring Q$^4$ species to form high-coordinated Si.

In recent years oxygen-17 ($^{17}$O) NMR has become increasingly important in studying ambient pressure glass structure, as it provides an oxygen-centered perspective, thus giving complementary information to the cation-centered point of view of $^{29}$Si or $^{27}$Al NMR. Oxygen-17 NMR has been used in a few studies of high-pressure glasses (Xue et al., 1994; Lee et al., 2003; Lee 2004; Allwardt et al., 2005). In addition, very few crystalline high-pressure phases have been studied, which are typically used to provide information on peak locations necessary for the interpretation of high-pressure glass spectra. In this study, we have measured the $^{17}$O triple-quantum (3Q) MAS NMR spectra of the triclinic phase of CaSi$_2$O$_5$ (CS2-tri, containing 4-, 5-, and 6-coordinated Si) and the wadeite structure type of K$_2$Si$_4$O$_9$ (KS-4 wadeite, containing 4- and 6-coordinated Si). These results are then used to investigate the structure of high-pressure K$_2$Si$_4$O$_9$ glasses, which was chosen because this composition has been shown to contain relatively large amounts of high coordinated Si at high-pressure (Stebbins and McMillan, 1989; Xue et al. 1991). Additionally, by studying high-pressure glasses with different rates of decompression with NMR, it may be possible to determine how the structure of the glass changes during decompression, although not necessarily the total extent of such changes. The $^{17}$O 3QMAS spectra of these glasses, used in conjunction with Raman and $^{29}$Si MAS NMR spectra, can then be used to quantitatively test proposed mechanisms of decompression in potassium silicate glasses. Finally, by comparing the $^{17}$O 3QMAS
and $^{29}\text{Si}$ MAS spectra of the rapidly decompressed sample to those of the ambient pressure sample, models of the mechanism for the generation of five and six-coordinated Si in melts at high pressure can be tested.

**Experimental procedures**

*Sample synthesis*

Starting materials for the $\text{K}_2\text{Si}_4\text{O}_9$ and $\text{CaSi}_2\text{O}_5$ high-pressure samples were ambient pressure glasses made from $\text{K}_2\text{CO}_3$, $\text{CaO}$, and ~45% $^{17}\text{O}$-enriched $\text{SiO}_2$ (Stebbins et al., 1997) as has been described elsewhere (Allwardt and Stebbins 2004). Unlike previous studies of $^{29}\text{Si}$ NMR on small, high-pressure glass samples, $^{29}\text{Si}$-enriched materials were not used for this study. About 0.2 wt % cobalt oxide was added to speed spin-lattice relaxation. The high-pressure samples were synthesized in the 1000 and 1200-ton multi-anvil presses at the Bayerisches Geoinstitut, Bayreuth, Germany, as described in Rubie (1999). Experimental conditions are summarized in Table 1. The dried glasses were loaded in welded Pt- or folded Re-capsules that were placed in 25/17 or 18/11 type assemblies (edge lengths of the MgO octahedron / truncated edge lengths of the tungsten carbide anvils). For the larger 25/17 assembly, the capsules had an outer diameter of 4 mm and a length of 4 mm; while the capsules for the 18/11 assembly had an outer diameter of 2 mm and a length of 3.5 mm. Each sample was first compressed at room temperature to the desired pressure and then heated at a rate of 200-300° C/min to 1000° C and from 1000° C to the final T in about one minute. The temperature was controlled using a D-type thermocouple, located at the top of the sample capsule. The relationship between load and sample pressure at high temperature was calibrated using the phase transformations of quartz-coesite and coesite-stishovite. The experiments were held at the experimental temperatures for 1 to 5 minutes until the heater was turned off, which isobarically quenched the melts to glass within a few seconds. To investigate the mechanism of decompression, two 5.7 GPa experiments were conducted where the only difference was the rate of decompression. The decompression times for the two samples were about 14 hours (standard) and about 1 second (rapid). Rapid decompression was accomplished by opening an electric valve in the oil pressure system (Langenhorst et
al., 2002) after the temperature quench. Glass compositions were verified by electron microprobe using mineral standards.

The triclinic phase of CaSi$_2$O$_5$ was produced from an experiment that was compressed to 10 GPa and then heated to 1350° C for 4 hours. Contrary to previous studies (e.g. (Angel et al., 1996; Kudoh and Kanzaki, 1998; Stebbins and Poe, 1999)), x-ray diffraction showed that this did not produce the triclinic phase, which contains $^{[4]}$Si, $^{[5]}$Si, and $^{[6]}$Si, but had preserved the monoclinic high-pressure phase that contains only $^{[4]}$Si and $^{[6]}$Si. The monoclinic phase has been shown to undergo a displacive-like phase transition to the triclinic low-pressure phase during decompression, where the Si in half of the SiO$_6$ octahedra move off-center to effectively lose one Si-O bond, and as a result, form an NBO and a SiO$_5$ group (Angel, 1997). To transform the recovered monoclinic phase to the desired triclinic phase, the sample was heated at 460° C for 2 h in an Ar atmosphere at ambient pressures. X-ray diffraction revealed that the heat-treated sample was almost entirely transformed to triclinic CaSi$_2$O$_5$.

**Spectroscopic techniques**

The $^{29}$Si MAS and $^{17}$O 3QMAS NMR spectra were collected on a Varian Unity/Inova 600 spectrometer (14.1 Tesla) using a Varian/Chemagnetics ‘T3’ probe with 3.2 mm zirconia rotors spinning at 20 kHz. The $^{17}$O and $^{29}$Si frequencies are reported relative to tap water and tetramethyl silane (TMS), respectively. For the $^{29}$Si MAS experiments, single pulse acquisition was used with pulse widths corresponding to approximately 30° rf tip angles (about 1 μs); one second delays between pulses were used to optimize the signal to noise ratio. The triple-quantum magic-angle spinning (3QMAS) spectra were collected with the same equipment and an rf power of 145 kHz. A shifted echo pulse sequence was used, consisting of two hard pulses (3.0 μs and 1.0 μs, respectively) followed by a soft pulse (21 μs) (Massiot et al., 1996). Delay times of 20 s were used between acquisitions and the $^{17}$O 3QMAS data were processed using the software package, RMN (FAT) (P.J. Grandinetti, The Ohio State University). The resulting 3QMAS spectra are two-dimensional plots in which the
isotropic dimension is free of second order quadrupolar broadening and the MAS dimension portrays a somewhat distorted view of a conventional 1-D MAS spectrum.

Raman spectra were collected on an Olympus microscope attached to a Dilor XY confocal Raman spectrometer equipped with a charge coupled detector (Spectrum One). The excitation wavelength was $\lambda = 514$ nm using an Ar$^+$ laser (Coherent Innova). The laser power was 500 mW and the beam was focused a few $\mu$m into the unpolished sample (objective x100) with a confocal aperture of 850 $\mu$m. Spectra were collected in 3x120s per spectral window with a resolution of about 0.5 – 0.6 cm$^{-1}$ (1800 g/mm holographic grating). Raman spectra were collected on different pieces of the high-pressure glass before and after sample crushing and NMR experiments. These spectra were identical, suggesting that there was no change in the structure of the glass over a time scale of 4 months and that grinding and spinning the sample does not affect the atomic structure.

Results and spectral interpretation

*NMR spectroscopy of crystalline phases*

The CS2-tri phase contains two $^{[4]}$Si sites, one $^{[5]}$Si site (distorted square pyramid) and two $^{[6]}$Si sites (Kanzaki et al. 1991; Angel et al. 1996), which makes it an ideal structure to investigate the $^{17}$O 3QMAS peak positions relevant to high-pressure glasses. The $^{17}$O 3QMAS spectrum of the triclinic phase of CaSi$_2$O$_5$ (CS2-tri) contains 4 distinct peaks (Fig. 1). Comparison of this spectrum to previous work shows that peak A of the CS2-tri phase is similar in position and shape to that typical of $^{[4]}$Si-O-$^{[4]}$Si groups, which we can then label as "$^{[4]}$Si-O-$^{[4]}$Si-like" (30 to 60 ppm in the MAS dimension, (Stebbins et al., 1997)), while peak B is similar to that for the $^{[4]}$Si-O-$^{[6]}$Si peak in wadeite-structured K$_2$Si$_4$O$_9$, which can then be denoted as "$^{[4]}$Si-O-$^{[6]}$Si-like" (60 to 90 ppm, (Xue et al., 1994)). The peak centered at 117 ppm can be uniquely assigned to an NBO surrounded by Ca$^{2+}$ modifier cations (Kirkpatrick et al., 1983; Stebbins et al., 1997), but that centered at about -85 ppm (in the isotropic dimension, "C") has not previously been observed with $^{17}$O 3QMAS NMR. We also note that although 3QMAS intensities are not strictly quantitative (varying with C$_q$-dependant excitation and reconversion efficiency), they can be considered semi-
quantitative (see discussion below of ambient pressure KS4 glass data) and therefore used to differentiate between models with drastically differing relative percentages. Because the isotropic dimension is free of second-order quadrupolar broadening and individual peaks are typically Gaussian in shape, Gaussians were used to fit the isotropic projection of the 2D spectrum to obtain relative percentages of 13% (A, \textsuperscript{4}Si-O-\textsuperscript{4}Si-like”), 61% (B, \textsuperscript{4}Si-O-\textsuperscript{6}Si-like”), 9% (NBO) and 17% (“C”). Similar results were obtained when integrating the two-dimensional 3QMAS spectrum directly. The relative abundances and structural species, however, do not agree with the known crystal structure of the triclinic phase of CaSi\textsubscript{2}O\textsubscript{5}, which contains 4 types of oxygen sites: \textsuperscript{4}Si-O-\textsuperscript{5}Si, \textsuperscript{4}Si-O-\textsuperscript{6}Si, NBO and \textsuperscript{5}Si-O-\textsuperscript{6}Si, with relative percentages of 30:40:10:20, respectively (Angel et al., 1996). Based on its intensity (and the lack of other valid options), peak “C” is very likely the \textsuperscript{5}Si-O-\textsuperscript{6}Si species.

To assign the corresponding oxygen structures to the other two peaks (“\textsuperscript{4}Si-O-\textsuperscript{4}Si-like” and “\textsuperscript{4}Si-O-\textsuperscript{6}Si-like”) requires a more in-depth look at the structure of CS\textsubscript{2}-triclinic as it contains three distinct types of \textsuperscript{4}Si-O-\textsuperscript{5}Si sites: two with \textsuperscript{5}Si-O bond distances (1.781\,\text{Å} and 1.824\,\text{Å}) that are similar to typical \textsuperscript{6}Si-O distances and a third that is more like a typical \textsuperscript{4}Si-O bond (1.696\,\text{Å}). If the oxygen percentages are recalculated with the assumption that the short \textsuperscript{5}Si-O bond affects the \textsuperscript{17}O NMR spectrum similarly to a typical \textsuperscript{4}Si-O bond, and the longer \textsuperscript{5}Si-O bonds are represented as \textsuperscript{6}Si-O, the expected percentages become 10% (A, \textsuperscript{4}Si-O-\textsuperscript{4}Si-like”), 60% (B, \textsuperscript{4}Si-O-\textsuperscript{6}Si-like”), 10% (NBO) and 20% (C, \textsuperscript{5}Si-O-\textsuperscript{6}Si), which agree with the measured values of 13, 61, 9, and 17%. This observation suggests that \textsuperscript{17}O NMR cannot always distinguish Si coordination so the \textsuperscript{4}Si-O-\textsuperscript{4}Si –like” peak (A) is likely the \textsuperscript{4}Si-O-\textsuperscript{5}Si with the short \textsuperscript{5}Si-O distance (O2oo), while the intensity of \textsuperscript{4}Si-O-\textsuperscript{6}Si –like” site (B) is the remaining \textsuperscript{4}Si-O-\textsuperscript{5}Si (O3ao and O3ax) species combined with the conventional \textsuperscript{4}Si-O-\textsuperscript{6}Si species. 

Si-29 MAS spectra (not shown) were also collected on the triclinic and monoclinic phases of CaSi\textsubscript{2}O\textsubscript{5} (CS\textsubscript{2}-tri and CS\textsubscript{2}-mono) and the K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9}-wadeite phase (KS\textsubscript{4}-wadeite) and are consistent with previously published results (Stebbins and Kanzaki, 1991; Stebbins and Poe, 1999). The peak widths in the spectra of CS\textsubscript{2}-mon and CS\textsubscript{2}-tri are slightly broader than the peaks reported in Stebbins and Poe.
(1999), presumably due to the addition of a small amount of cobalt oxide to the samples of this study. The peak positions of the $^{[4]}$Si peaks (Q$^{4*}$ and Q$^{3*}$) in the $^{29}$Si MAS spectra of the three crystalline materials are shown in Table 2 and clearly indicate that the replacement of some $^{[4]}$Si next nearest neighbors (NNN) by $^{[5]}$Si and $^{[6]}$Si causes the $^{[4]}$Si peak to shift to less negative frequencies, which has also been previously noted by Stebbins and Kanzaki (1991). This shift appears to be significant as a comparison to the $^{[4]}$Si peak positions of the $^{4}$ species in crystalline SiO$_2$ phases (107-114 ppm, Stebbins 1995) indicates that the effect of $^{[5]}$Si and $^{[6]}$Si as a NNN can shift the peak position of the $^{[4]}$Si by up to about 25 ppm (Table 2).

Raman spectroscopy of crystalline phases

The three crystalline high-pressure samples were also studied with Raman spectroscopy (Fig. 2). Due to the complexity of the structures, it seems impossible to give unique peak assignments for the various Raman bands, however some conclusions may be drawn from a comparison of the spectra. The Raman spectra can be separated into two regions: low frequency ($< 850$ cm$^{-1}$) and high frequency ($> 850$ cm$^{-1}$). In low-pressure silicates, where silicon is generally four-coordinated, Raman peaks between 400 and 600 cm$^{-1}$ are generally assigned to symmetric bending modes of $^{[4]}$Si-O-$^{[4]}$Si units and their frequency increases with decreasing T-O-T angle. High-frequency bands between 850 and 1200 cm$^{-1}$ are assigned to Si-O stretching vibrations of SiO$_4$ tetrahedra with various degrees of polymerization where the higher the frequency indicates a higher the degree of polymerization.

The low frequency bands of KS4-wadeite between 500 and 600 cm$^{-1}$ (Fig. 2) are difficult to assign to a specific vibration, but they could be due to T-O-T bending of the $^{[4]}$Si sublattice or octahedral bending motions while the peak at 645 cm$^{-1}$ may be due to the breathing motion of the 3-membered siloxane rings. Previous work has suggested that the Raman band at 606 cm$^{-1}$ in silica glass is due to the presence of 3-membered siloxane rings. (McMillan and Wolf, 1995). However, the Raman spectra of both high-pressure CS2 phases (Fig. 2) also contain bands near 650 cm$^{-1}$ and the CS2 crystal structures do not contain 3-membered siloxane rings or even T-O-T linkages. Williams et al. (1987) proposed that peaks in the 540 to 680 cm$^{-1}$ region of
the Raman spectra of stishovite, MgSiO₃-perovskite and MgSiO₃-ilmenite are due to the bending motion of octahedral Si. Although the Raman study of Fleet and Henderson (1997) reported that they did not observe a peak that was directly attributable to the presence of [⁶]Si, all spectra of the Na-silicate high-pressure phases where the structure contained octahedral Si yielded at least one peak in this region. This implies that the peaks near 650 cm⁻¹ are likely due to a vibration involving SiO₆ octahedra. In addition to the evidence from high-pressure silicate materials, a peak has also been reported at 613 cm⁻¹ in the Raman spectrum of crystalline SiP₂O₇ and has been assigned to the stretching mode of SiO₆ (Chakraborty et al., 1987).

The high frequency region of the Raman spectrum of the K₂Si₄O₉-wadeite shows a band at 1100 cm⁻¹ while the dominant band(s) in the CS₂ phases are located between 900 and 970 cm⁻¹. In low-pressure silicates, the 1100 cm⁻¹ band is attributed to the presence of Q⁴ species while the bands between 900 and 980 cm⁻¹ are usually indicative of the presence of Q¹ and Q² species. However, the structures of KS₄-wadeite and CS₂ do not contain these Q-species, which may indicate that these bands are related to the presence of SiO₆ groups. An assignment of these bands to SiO₆ stretching vibrations also seems unlikely as Raman bands do not appear above 800 cm⁻¹ for MgSiO₃ perovskite (Williams et al., 1987) or MgSiO₃ ilmenite (McMillan and Ross, 1987), where all the Si are octahedrally coordinated. For this reason, these bands are probably due to Si-O stretching modes of SiO₄ tetrahedra that are linked to SiO₅ and SiO₆, where the high-coordinated Si decrease the vibrational frequency of the Q⁴* and Q³* species relative to conventional Q⁴ and Q³ species. Such a shift in frequency may be expected as [⁶]Si-O bonds are longer and weaker than [⁴]Si-O bonds and the vibration should behave more like a that of [⁴]Si-NBO groups. The dominant high frequency peaks in the high-pressure CS₂ phases are located at lower frequencies (900 to 970 cm⁻¹) relative to KS₄-wadeite (1100 cm⁻¹), which suggests that the increased number of [⁵]Si and [⁶]Si NNN in these phases (Table 2) decreases the vibrational frequency. The CS₂-tri structure contains two distinct types of SiO₄ tetrahedra, where one is corner linked to two SiO₆ octahedra, a SiO₅ pyramid, and a NBO and the other is linked to two SiO₆ octahedra and two SiO₅ pyramids. The former is likely responsible for the 900 cm⁻¹ band if one considers that Q⁴ bands are at higher
frequencies than $Q^3$ bands, which would mean that the 960 cm$^{-1}$ band is due to the latter $Q^4$ species.

NMR spectroscopy of $K_2Si_4O_9$ glasses

The $^{29}$Si MAS NMR spectra for the four $K_2Si_4O_9$ glasses are shown in Figure 3. The spectra were obtained from samples with natural isotopic abundance (no $^{29}$Si-enrichment), which required acquisition durations of 24 to 48 hours to obtain spectra with reasonable signal/noise ratios from the small samples (17 to 35 mg) of the high-pressure experiments. The spectrum of the ambient pressure glass comprises one composite $^{[4]}$Si peak with frequencies ranging from $-80$ to $-120$ ppm, which is dominated by overlapping peaks for $Q^4$ and $Q^3$ species (Stebbins, 1995). The spectra of the high-pressure glasses contain two additional peaks associated with $^{[5]}$Si ($-147$ ppm, Stebbins and McMillan, 1989)) and $^{[6]}$Si ($-198$ ppm, Xue et al., 1989)). The results from the integration of the spectra can be seen in Table 3. Peak areas in the spectrum of the rapidly decompressed, 5.7 GPa $K_2Si_4O_9$ glass indicate that the structure contains 5% $^{[5]}$Si and 5% $^{[6]}$Si. When this sample is decompressed more slowly, some of the $^{[6]}$Si (about 1% of the total Si) apparently converts to $^{[5]}$Si. The uncertainty in the peak areas of about ±1% was estimated from multiple peak fittings with various methods of data processing (baseline corrections, linear prediction to reduce truncation artifacts, etc.). Therefore, the relative errors for the comparison of two spectra with identical processing are likely to be smaller.

As the synthesis pressure increases, the shape of the $^{[4]}$Si peak in the $^{29}$Si MAS spectra changes as intensity in the $Q^4$ region ($-106$ ppm, Xue et al., 1991) shifts to less negative frequencies. In ambient pressure glasses this would imply that the abundance of $Q^3$ ($-93$ ppm, Xue et al., 1991) and possibly even $Q^2$ species ($-73$ to $-85$ ppm, Stebbins, 1995) are increasing; however, high-coordinated Si NNN have been shown to also affect the positions of $^{[4]}$Si peaks (Stebbins and Kanzaki, 1991; this study). Xue et al. (1991) showed that the Q-species distribution favored more disorder at higher pressure (e.g. $2Q^3 \rightarrow Q^2 + Q^4$). For a $K_2Si_4O_9$ glass (avg. Q-species of 3.5), the ambient pressure structure should contain mostly $Q^3$ and $Q^4$ species so the abundance of $Q^3$ should decrease with increasing pressure, which is contrary to the first
impression given by comparison of the spectra of the ambient and high-pressure glasses. Additionally, since the $^{17}$O 3QMAS spectra (see below) directly shows that the abundance of NBO decreases with increasing pressure, the shifts in $^{4}$Si peak position must be due to the presence of $Q^{4*}$ (and potentially $Q^{3*}$) in the high-pressure glass structure. This is further supported by the information in table 2 that shows that an increasing coordination of the NNN causes a shift in the position of the $Q^{4}$ peak to less negative frequencies. The abundance of the $Q^{4*}$ species cannot be reliably quantified from the present spectra (Fig. 3) as the spectra from previous studies have better signal to noise ratios (e.g. Xue et al. 1991), having been collected on $^{29}$Si-enriched materials.

Figure 4 shows the $^{17}$O 3QMAS NMR spectra of the $K_2Si_4O_9$ glasses. The ambient pressure sample (KS4-1atm) contains only two peaks, which can be uniquely assigned to $^{4}$Si-O-$^{4}$Si (BO) and NBO (Farnan et al., 1992). The integrated peak areas from the isotropic projections of 81% BO and 19% NBO are close to the values of 78% and 22% expected from the composition. This suggests, that despite the rather large difference in quadrupolar coupling constant ($C_q$) for BO and NBO in this type of material (about 4.9 and 2.3 MHz, Xue et al., 1994), the use of $^{17}$O 3QMAS peak areas, uncorrected for $C_Q$ effects (Zhao et al., 2000; Lee and Stebbins, 2002), is at least a good first approximation to oxygen species concentrations.

In the $^{17}$O 3QMAS NMR spectra of the high pressure KS4 glasses, another peak appears that coincides with that reported for the $^{4}$Si-O-$^{6}$Si species of crystalline wadeite-$K_2Si_4O_9$ (Xue et al., 1994), but this peak is much wider in the glass due to disorder. A relatively robust assignment of the 3QMAS peaks for the high-pressure glasses can be reached by comparing the $^{17}$O NMR results with the results from the $^{29}$Si NMR peak fitting. The rapidly decompressed 5.7 GPa glass sample contains 5% $^{5}$Si and 5% $^{6}$Si (Table 3). If one assumes that there are negligible amounts of $^{6}$Si-O-$^{5}$Si and $^{6}$Si-O-$^{6}$Si as is suggested by Lee et al. (2003), the $^{17}$O NMR spectrum should contain 11% $^{4}$Si-O-$^{5}$Si (5% (percentage of $^{5}$Si) * 5 (coordination number)$^4/9$ (silicon/oxygen ratio) =11%) and 13% $^{4}$Si-O-$^{6}$Si (5%*6*4/9=13). The latter agrees well with the measured value of 14% for the "$^{4}$Si-O-$^{6}$Si-like" peak (Table 1) in KS4-5.7GPa-rapid (Table 2), suggesting that, at least for the rapidly
decompressed sample, this peak is due mainly to $^{[4]}\text{Si-O-[6]}\text{Si}$. If this assignment is correct, the signal of the $^{[4]}\text{Si-O-[5]}\text{Si}$ species (11%) likely overlaps with the BO ($^{[4]}\text{Si-O-[4]}\text{Si}$) peak. The peaks in the $^{17}$O 3QMAS NMR spectrum of the KS4-5.7GPa-conv glass (Fig 4) seem to be slightly broader, relative to the KS4-5.7GPa-rapid sample, possibly indicating a higher degree of disorder. The spectrum of the conventionally decompressed glass appears to contain an extension of the NBO ridge to lower isotropic frequencies (−53 to −56 ppm), which is not observed in the spectrum of the rapidly decompressed glass. This suggests that intensity in this region of the NBO ridge may represent structural species that are a by-product of the slower decompression rate, not a signature of species present in the glass structure at pressure. This also suggests that the NBO created during decompression are structurally distinct from those present at equilibrium in high-pressure melts. Furthermore, the spectrum shows a “bridge” between the BO and $^{[4]}\text{Si-O-[6]}\text{Si}$ peaks that accounts for roughly 3% of the total oxygen species. So far it is not clear what structural species this signal represents. In the $^{17}$O 3QMAS NMR spectrum of the KS4-8GPa-conv glass (Fig. 4), the peak broadening and the bridge between the BO and $^{[4]}\text{Si-O-[6]}\text{Si}$ peaks are even more pronounced. Based on the $^{29}$Si NMR data, there should be 11% and 13% $^{[4]}\text{Si-O-[6]}\text{Si}$ for the KS4-5.7GPa-conv and KS4-8GPa-conv samples, respectively, which is lower than the measured relative intensity of the $^{[4]}\text{Si-O-[6]}\text{Si}$ peaks in the 3QMAS spectra (15% and 17%, respectively, Table 3). This may suggest that the $^{[4]}\text{Si-O-[6]}\text{Si}$-like" peaks in the spectra of the conventionally decompressed KS4 glasses also contain some signal from the $^{[4]}\text{Si-O-[5]}\text{Si}$ species, which further supports that $^{17}$O NMR cannot independently measure Si-coordination.

*Raman spectroscopy $K_2Si_4O_9$ glasses*

The Raman spectrum of the KS4-1atm glass (Fig. 5) is similar to those previously reported (e.g. Brawer and White, 1975; Matson et al., 1983). The composite high frequency peak contains a maximum at 1100 cm$^{-1}$ and a less intense band at around 1155 cm$^{-1}$. These are commonly assigned to the symmetric stretching vibrations of $Q^3$ units and the asymmetric stretching vibrations of fully polymerized $Q^4$ species, respectively. Additionally, there may also be some intensity at 940 cm$^{-1}$
that would be due to a small percentage of Q\(^2\) groups. The low frequency region of the spectrum of the ambient pressure glass is commonly assigned to T-O-T bending vibrations of the silicate network and shows two resolved and relatively sharp peaks at 516 and 593 cm\(^{-1}\) and. The peak at 516 cm\(^{-1}\) represents a site with larger T-O-T angle than the one at 593 cm\(^{-1}\). The smaller T-O-T angles may be associated with three-membered siloxane rings or with the presence of Q\(^2\) species. The peak at 778 cm\(^{-1}\) is often assigned to motions of Si against its tetrahedral oxygen cage (e.g. Xue et al. 1991).

The Raman spectra of the high-pressure K\(_2\)Si\(_4\)O\(_9\) glasses are consistent with those of Xue et al., (1991). When comparing the spectra of the ambient pressure and the high-pressure glasses two obvious differences are observed: the broadening of the high frequency peak towards the low frequency side and a strong increase in the relative intensity near 600 cm\(^{-1}\) relative to that near 516 cm\(^{-1}\). At first glance, the increase in intensity in the region between 850 and 1050 may suggest an increasing fraction of Q\(^2\) species (and potentially Q\(^1\)) as a small increase in the Q\(^2\) region is seen in the \(^{29}\)Si MAS spectra (Xue et al., 1989, 1991; this study). However, this interpretation does not explain the broadening of the high frequency composite peak as the \(^{29}\)Si MAS spectra of KS4-5.7GPa-rapid and KS4-5.7GPa-conv show no changes in frequency ranges relevant to such structural species. As mentioned above, bands in these regions are observed in spectra of high-pressure crystalline materials that contain both tetrahedral and octahedral Si (Fleet and Henderson 1997; this study), but are absent in the spectra of structures where all Si is octahedrally coordinated (Hemley et al. 1986; Williams et al. 1987). This may suggest that, in addition to the symmetric stretching of Q\(^2\) and Q\(^3\) species, Raman bands in this region of the spectrum may have contributions from \(^{[4]}\)Si-O-\(^{[6]}\)Si species. The Raman spectra of the 5.7 GPa glasses also show that intensity in the region near 600 cm\(^{-1}\) depends on the decompression rate. Some have assigned this region to represent the presence of SiO\(_6\) groups in silicate glasses (Wolf and McMillan, 1995; Farber and Williams, 1996). Based on the comparison of the \(^{29}\)Si MAS and Raman spectra of these samples, either the intensity near 600 cm\(^{-1}\) is not solely due to the presence of SiO\(_6\) groups (e.g. enhanced number of 3-membered rings of SiO\(_4\) tetrahedra) or small changes in the amount of SiO\(_6\) can
have a large effect on the relative intensities in this region. Interestingly, the relative heights of the high and low frequency composite peaks are drastically different between the KS4-5.7GPa-rapid and KS4-5.7GPa-conv spectra. Also, a comparison of the Raman spectra of the KS4-5.7GPa-rapid and KS4-8GPa-conv seems to suggest that there is not a distinct signature for SiO$_5$ groups, as the two samples are shown by $^{29}$Si MAS NMR to contain similar amounts of $^{[6]}$Si (5%) and different percentages of $^{[5]}$Si (5 and 10, respectively), but are roughly similar in the low-frequency region. Additionally, a small peak is present at 1300 cm$^{-1}$ in spectra for both the KS4-5.7GPa-rapid glass and the CS2-tri crystalline sample, which, to the authors’ knowledge, has not been previously reported; however, this frequency lies outside of the frequencies typically reported in Raman spectroscopic studies of high-pressure glasses (Wolf and McMillan, 1995).

**Discussion**

**Mechanism for the formation of high-coordinated Si in high-pressure silicate melts**

The mechanisms responsible for the formation of high-coordinated Si have been indirectly investigated in previous studies (Wolf et al., 1990; Xue et al., 1991). These studies observed that more high-coordinated Si are created when NBO are present in the ambient pressure glasses, so it was concluded that one important mechanism must involve NBO. These mechanisms have also been proposed for ambient-pressure alkali germanate glasses, which were found to contain $^{[5]}$Ge and $^{[6]}$Ge and fewer NBO than would be expected based on composition (Ueno et al., 1983). From the oxygen perspective, these “reactions” can be re-written as:

\[
\text{NBO} + 4 \text{BO} \rightarrow 5^{[4]}\text{Si-O-}^{[5]}\text{Si} \quad (3)
\]

\[
2 \text{NBO} + 4 \text{BO} \rightarrow 6^{[4]}\text{Si-O-}^{[6]}\text{Si} \quad (4)
\]

and are visualized in figure 6a. The validity of mechanisms 3 and 4 for the generation of high-coordinated Si in high-pressure glasses can be tested using $^{17}$O 3QMAS NMR, but robust peak assignments for oxygen bonded to high-coordinated Si must first be determined. Our data on two known crystalline structures (CS2-tri and KS4-wadeite) are useful for this purpose, as they contain several structural species that may be expected in high-pressure glasses ($^{[4]}$Si-O-$^{[4]}$Si, $^{[4]}$Si-O-$^{[5]}$Si, $^{[4]}$Si-O-$^{[6]}$Si, and $^{[5]}$Si-O-$^{[6]}$Si).
The $^{3}$QMAS spectrum of the KS4-wadeite phase (not shown) is fully consistent with previous 1-D MAS data and the derived NMR parameters (Xue et al., 1994). As shown above for the CaSi$_2$O$_5$-triclinic phase (Fig. 1), $^{17}$O 3QMAS NMR signals for oxygens linked to $^{[5]}$Si may in some cases be unresolved from those linked to other Si coordinations. O-17 NMR is primarily sensitive to the immediate environment of oxygen, so it is not directly dependant on the Si-coordination, which is best determined directly from $^{29}$Si NMR.

The $^{29}$Si MAS results for the high-pressure glasses can predict the expected values for concentrations of oxygen species, yielding about 11% $^{[4]}$Si-O-$^{[5]}$Si and 13% $^{[4]}$Si-O-$^{[6]}$Si species for the 5.7 GPa-rapid glass, if mixing among the Si polyhedra is assumed to be random. Assuming mechanisms 3 and 4, the percentages of the total oxygen made up by BO ($^{[4]}$Si-O-$^{[4]}$Si) and NBO should decrease by 17% (11%* 4/5 + 13%* 4/6) and 7% (11%* 1/5 + 13%* 2/6), respectively. However, since $^{[4]}$Si-O-$^{[5]}$Si seems to be unresolvable from conventional BO in the $^{17}$O NMR spectra of rapidly decompressed glasses, the total change in the percentage for the intensity of the BO peak should only be ~6% (17%-11%). These numbers compare favorably with those determined from integrating the spectra (Table 2). Thus, within error, our data confirm the mechanisms proposed by Wolf et al. (1990) and Xue et al. (1991). We see no evidence to support the model proposed by Sakida et al. (2000), which, based on $^{29}$Si MAS spectra of multi component glasses with much less silica, suggested an increase in NBO content (decreasing average Q-species) as $^{[4]}$Si-O-$^{[4]}$Si bonds are broken with increasing pressure. The effect of high-coordinated Si as NNN was discussed above (Table 2) and seems like a plausible alternate explanation. High-coordinated species were not observed by Sakida et al., however the spinning sidebands, which ranged from –140 to –165 ppm, would likely mask the presence of the $^{[5]}$Si peak (~145 ppm), and the abundance of $^{[6]}$Si could have been below the detection limit. However, the very different range of compositions for glasses in that study could mean that the structural response to pressure may indeed be different.

In aluminosilicate melts, network Al and Si can both respond to pressure changes by increasing coordination, and may in a sense “compete” with each other. We can thus use the results presented here to try to extrapolate to aluminosilicates.
Known effects of pressure on crystal structures had suggested that AlO₆ should appear at lower pressures than SiO₆ species in high-pressure melts (Waff, 1975). This was later confirmed by ²⁷Al and ²⁹Si NMR of sodium aluminosilicate glasses (Yarger et al., 1995). Additionally, as in silicate glasses, the percentages of NBO in the ambient pressure glasses is important in the formation of high-coordinated Al, where more [⁵]Al and [⁶]Al can form when NBO are present (Yarger et al., 1995; Lee, 2004). This may suggest that the mechanism for the formation of [⁵]Al and [⁶]Al in “depolymerized” aluminosilicate glasses may be similar to those discussed here for Si coordination change. At ambient pressures, the products (right hand side) of the reactions: Al-O-Al + Si-O-Si = 2Si-O-Al (Lee et al., 1999, 2000) and Al-NBO + Si-O-Si = Si-O-Al + Si-NBO (Allwardt et al., 2003b) seem to be energetically favorable. If this structural ordering continues at elevated pressures, the most likely mechanism for the formation of high-coordinated Al would be:

\[
\text{Si-NBO} + 4 \text{Si-O-Al} \rightarrow 5 \left[ ⁴\text{Si-O-[⁵]Al} \right] \tag{5}
\]

\[
2 \text{Si-NBO} + 4 \text{Si-O-Al} \rightarrow 6 \left[ ⁴\text{Si-O-[⁶]Al} \right] \tag{6}
\]

because both “reactants” are likely to be relatively abundant. The quantification of very recent ²⁷Al and ¹⁷O MAS and ¹⁷O 3QMAS NMR spectra of high-pressure aluminosilicate glasses supports these mechanisms (Allwardt et al., 2005).

**Effect of decompression on the structure of high-pressure glasses**

The ²⁹Si MAS spectra reveal that a small amount of [⁶]Si (~1%) reverts to [⁵]Si during slower decompression of 5.7 GPa KS4 glasses. Additionally, the percentage of NBO increases, which may suggest that a reversal of mechanism 4 may occur during decompression (Fig. 6b); however, this is complicated by the appearance of the bridge between the [⁴]Si-O-[⁴]Si and [⁴]Si-O-[⁶]Si peaks in the spectra of KS4-5.7GPa-conv and KS4-8GPa-conv (slowly decompressed over 14 hours). This mechanism would imply that one of the oxygens associated with the [⁶]Si species moves away from the high coordinated Si to form an NBO on a tetrahedral Si, as is seen in the monoclinic to triclinic phase transition of CaSi₂O₅ (Angel, 1997). Additionally, tetrahedral NBO species generated during decompression seem to be the most probable explanation for the extension of the NBO ridge into the -53 to -56 ppm region of the isotropic
dimension for glasses with different decompression histories. We note that another very recent $^{17}$O 3QMAS study of high pressure Na-silicate glasses has interpreted the growth of intensity in a similar region of the spectrum to NBO linked to high-coordinated Si (${}^{[5,6]}$Si-NBO) (Lee et al., 2003). The reversal of mechanism 4 would also require additional local structural rearrangements, which may suggest that the $^{[5]}$Si-O bonds formed during decompression may retain the approximate lengths of the original $^{[6]}$Si-O bonds. This would account for the similar percentages of "$^{[4]}$Si-O-$^{[6]}$Si-like" species with decreasing percentages of $^{[6]}$Si between samples with different rates of decompression, although the bridge makes the accurate determination of $^{[4]}$Si-O-$^{[6]}$Si species difficult for spectra of conventionally decompressed glasses. As mentioned previously, this could explain why the $^{29}$Si and $^{17}$O data do not entirely agree with each other for the conventionally decompressed samples as some $^{[4]}$Si-O-$^{[5]}$Si are being measured as $^{[4]}$Si-O-$^{[6]}$Si (not $^{[4]}$Si-O-$^{[4]}$Si) by $^{17}$O NMR. Support for this was shown in the $^{17}$O 3QMAS NMR spectrum of the CS2-tri (Fig. 1), as it does not show a specific signature for $^{[4]}$Si-O-$^{[5]}$Si species, but these species are measured as either $^{[4]}$Si-O-$^{[4]}$Si or $^{[4]}$Si-O-$^{[6]}$Si, depending on the local environment of the oxygen.

Vibrational spectroscopy is an important complement to NMR, and has the advantage that it can be applied in-situ at high pressure and temperature. Two studies have utilized Raman spectroscopy to investigate the magnitude of decompression effects on the structure of glasses that have been annealed at $T_g$ while at pressure (Robinson, Wolf and McMillan, unpublished data as referenced in McMillan and Wolf, 1995; Farber and Williams, 1996); however, while both studies agree that decompression affects the structure, they disagree about the amount of structural relaxation. The present study benefits from using $^{29}$Si MAS NMR to constrain the interpretation of the Raman spectra of the KS4 glasses. This has shown that a small difference in $^{[6]}$Si ($\sim 1\%$) in the $^{29}$Si MAS spectra between glasses with different rates of decompression (5.7 GPa) is correlated with a noticeable effect on the intensity in the region of the Raman spectra that many previous studies have suggested is related to the presence of SiO$_6$ species (540-680 cm$^{-1}$), which suggests that relatively large increases in intensity in this region (Fig. 5) do not necessarily indicate a large increase
in the percentage of SiO₆ species (Table 3). This observation either means that this region is not due directly to the presence of SiO₆ species or that Raman spectroscopy is very sensitive to the presence of SiO₆ species in silicate glasses. A comparison of the Raman spectra (Fig. 5) also indicates that the relative intensity of the high-frequency region (roughly 850 to 1220 cm⁻¹) is greatly reduced in KS4-5.7GPa-rapid relative to the KS4-5.7GPa-conv. It is not entirely clear what causes the decrease in the relative intensity of the high-frequency peak, but the ²⁹Si MAS spectra (Fig. 3) indicate that it is not due to a change in the Q-species or a dramatic difference in the percentage of [⁵]Si and [⁶]Si NNN. Interestingly, the magnitude of the differences in the Raman spectra of glasses with differing decompression rates (540 to 680 cm⁻¹ and 850 to 1220 cm⁻¹) are surprisingly similar to that observed between the in-situ (T,P) spectrum and the spectrum measured at ambient conditions (decompressed glass) on Na₂Si₄O₉ high-pressure glasses (Robinson, Wolf and McMillan, unpublished, referenced in Wolf and McMillan, 1995). This likely suggests that the rapidly decompressed glasses retain more of the structure of the high-pressure melts than the conventionally decompressed samples and may possibly even retain the high-pressure glass structure. However, further investigations are required to clarify the extent of the structural rearrangements that occur during decompression in silicate glasses. If more reliable peak assignments can be determined for Raman spectra of glasses, and using relative percentages measured from NMR, it is possible that (T,P)-in-situ Raman spectra could be used to semi-quantitatively investigate the percentages of structural species at the temperatures, pressures and compositions of direct interest to magmatic systems.

Acknowledgements

The authors would like to Heinz Fischer for the production of parts for the multi-anvil assemblies and Dr. Sung Keun Lee for a preprint of Lee et al., (2003). The authors would also like to thank Dr. Mike Toplis and two anonymous reviewers for helpful suggestions to improve the original manuscript. JRA and JFS thank the NSF for grant number: EAR-0104926 and BCS acknowledges funding from the Bayerisches Geoinstitut.
References


Table 4.1 Experimental conditions for the high-pressure samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>P [GPa]</th>
<th>T [°C]</th>
<th>Duration at T [min]</th>
<th>Decompression time</th>
<th>Decompression rate [MPa/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS4-5.7GPa-rapid</td>
<td>K₂Si₄O₉</td>
<td>5.7</td>
<td>1850</td>
<td>4</td>
<td>1s</td>
<td>5700</td>
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<tr>
<td>KS4-5.7GPa-conv</td>
<td>K₂Si₄O₉</td>
<td>5.7</td>
<td>1850</td>
<td>1</td>
<td>14h</td>
<td>0.113</td>
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<tr>
<td>KS4-8GPa-conv</td>
<td>K₂Si₄O₉</td>
<td>8</td>
<td>2200</td>
<td>2</td>
<td>15h</td>
<td>0.148</td>
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<tr>
<td>KS4-wadeite</td>
<td>K₂Si₄O₉</td>
<td>9</td>
<td>2000</td>
<td>5</td>
<td>15h</td>
<td>0.167</td>
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<tr>
<td>CS2-mon</td>
<td>CaSi₂O₅</td>
<td>10</td>
<td>2000</td>
<td>240</td>
<td>8h</td>
<td>0.347</td>
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<tr>
<td>CS2-tri³</td>
<td>CaSi₂O₅</td>
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<td>2000</td>
<td>240</td>
<td>14h</td>
<td>0.198</td>
</tr>
</tbody>
</table>

a: obtained from CS2-mon after heat treatment at 460°C for 2h in Ar at 1 atm.
Table 4.2 Position of the Q$^4*$ species in the $^{29}$Si MAS spectra of high-pressure crystalline materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Q-species</th>
<th>Next nearest neighbor</th>
<th>$^{29}$Si $^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS4-wadeite</td>
<td>Q$^4*$</td>
<td>$2^{[4]}$Si + $2^{[6]}$Si$^a$</td>
<td>98$^b$</td>
</tr>
<tr>
<td>CS2-mon</td>
<td>Q$^4*$</td>
<td>$4^{[6]}$Si$^c$</td>
<td>88$^d$</td>
</tr>
<tr>
<td>CS2-tri</td>
<td>Q$^4*$</td>
<td>$2^{[5]}$Si + $2^{[6]}$Si$^c$</td>
<td>88$^d$</td>
</tr>
<tr>
<td>CS2-tri</td>
<td>Q$^3*$</td>
<td>$1^{[5]}$Si + $2^{[6]}$Si + NBO$^e$</td>
<td>80$^d$</td>
</tr>
</tbody>
</table>

$^\dagger$ negative peak position for $^{29}$Si MAS NMR peaks

$^a$ Kinomura et al., 1975

$^b$ Stebbins and Kanzaki, 1991; This study

$^c$ Angel, 1997

$^d$ Stebbins and Poe, 1999; This study

$^e$ Angel et al., 1996
Table 4.3  Quantification of $^{29}$Si MAS and $^{17}$O 3QMAS spectra

<table>
<thead>
<tr>
<th>$^{29}$Si MAS NMR</th>
<th>[4]$^{1}$Si (%)</th>
<th>[1]$^{1}$Si (%)</th>
<th>[8]$^{1}$Si (%)</th>
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<td>&lt;1</td>
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<td>5</td>
<td>5</td>
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<td>rapid</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>KS4-5.7GPa-</td>
<td>90</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>conv</td>
<td></td>
<td></td>
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<tr>
<td>KS4-8GPa-conv</td>
<td>85</td>
<td>10</td>
<td>5</td>
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</table>

<table>
<thead>
<tr>
<th>$^{17}$O 3QMAS NMR</th>
<th>NBO (%)</th>
<th>[4]$^{1}$Si-O-[4]$^{1}$Si</th>
<th>[4]$^{1}$Si-O-[6]$^{1}$Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS4-1atm</td>
<td>19</td>
<td>81</td>
<td>-</td>
</tr>
<tr>
<td>KS4-5.7GPa-</td>
<td>11</td>
<td>75</td>
<td>14</td>
</tr>
<tr>
<td>rapid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KS4-5.7GPa-</td>
<td>12</td>
<td>73$^a$</td>
<td>15$^{ab}$</td>
</tr>
<tr>
<td>conv</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>KS4-8GPa-conv</td>
<td>13</td>
<td>70$^a$</td>
<td>17$^{ab}$</td>
</tr>
</tbody>
</table>

Error in absolute quantification is ± 1% (absolute).

a: A “bridge” is present between these peaks, which increases the uncertainty in the quantification of these peaks to ± 2 to 3%. Although it is unclear what structural species the bridge represents, its intensity is included with the intensity for the BO species.

b: Comparison of the $^{17}$O data with what would be expected based on $^{29}$Si spectra suggests that this peak represents some intensity from [4]$^{1}$Si-O-[5]$^{1}$Si in addition to [4]$^{1}$Si-O-[6]$^{1}$Si (see text for further discussion).
Figure 4.1 O-17 3QMAS NMR spectra (14.1 Tesla) of the high-pressure triclinic phase of CaSi$_2$O$_5$ (CS2) where the contour lines are drawn at intervals of 10% and range from 10% to 100%. Peak assignments are discussed in the text.
Figure 4.2 Raman spectra of the KS4 and CS2 high-pressure crystalline phases. Sample names and synthesis conditions are in table 4.1.
Figure 4.3 Si-29 MAS spectra of $\text{K}_2\text{Si}_4\text{O}_9$ (KS4) glasses
Figure 4.4 O-17 3QMAS NMR spectra of the KS4 glasses shown in Figure 3. Justification for the peak assignments is discussed in text. Contours are drawn at intervals of 5% and range from 5% to 95%.
Figure 4.5 Raman spectra of the KS4 glasses
Figure 4.6 Schematic models showing the mechanisms for the (a) generation of high-coordinated Si in high-pressure glasses and (b) a potential structural alteration resulting from slow decompression of silicate glasses. Non-bridging oxygen are denoted by black circles and other oxygens are white circles. Cations are not shown.
Chapter Five

Aluminum coordination and the densification of high-pressure aluminosilicate glasses

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Abstract:

To better understand the relationship between atomic-scale structures and densities of aluminosilicate glasses and liquids, we used $^{27}$Al MAS NMR to determine the speciation of aluminum ions in $K_3AlSi_3O_9$, $Na_3AlSi_3O_9$, and $Ca_3Al_2Si_6O_{18}$ glasses quenched from melts at 3 to 10 GPa. These data are a first approximation of high-pressure melt structure and illustrate the effects of the type of modifier cation. High field strength modifier cations (i.e., Ca) clearly induce more high-coordinated Al than lower field strength cations (i.e., Na and K). Measured glass densities show that, especially with rapid decompression, a significant portion of the total densification observed in-situ in melts is retained on return to ambient temperature and pressure. Observed increases in Al coordination are well correlated with decreased volume, which suggests that this structural change is a major part of the mechanism for recovered densification of high-pressure melts. Additionally, $^{23}$Na MAS NMR, combined with the $^{27}$Al MAS spectra and density determinations, reveal that other changes, such as the compression of modifier cation sites and/or decreased network bond angles, must also be significant, especially at low pressure.
**Introduction**

In mantles and crusts of terrestrial planets, magma transport rates are controlled by viscosity and density, both of which are affected by atomic-scale melt structures at high pressure. Magma densification with pressure may have contributed to planetary-scale stratification early in the history of the Earth (Stolper et al., 1981; Agee and Walker, 1993) and to the possible continued presence of neutrally buoyant melts above the transition zone (Revenaugh and Sipkin, 1994; Bercovici and Karato, 2003; Suzuki and Ohtani, 2003) and the D” layer (Williams and Garnero, 1996).

Magma buoyancy has a key influence on igneous processes, which in turn are critical to heat and mass transfer out of the Earth's mantle. If reliable, predictive models of melt density are to be formulated, structurally realistic constraints are needed, as large variations in temperature, pressure and melt composition make it impractical to measure density directly at all relevant conditions and compositions.

At high pressure, aluminosilicate glasses and liquids are known to have markedly different structures from those formed at ambient pressure. For example, formation of high-coordinated aluminum (\([5]Al\) and \([6]Al\)) from four-coordinated Al (\([4]Al\)) has been measured with \(^{27}Al\) magic-angle spinning (MAS) nuclear magnetic resonance (NMR) of high-pressure glasses (Yarger et al., 1995). Molecular dynamics simulations suggest that densification occurs by increases in network forming cation coordination (Nevins and Spera, 1998), combined with increases in modifier cation coordination (Matsui, 1996) and decreases in mean network bond angles (Kubicki and Lasaga, 1991; Suzuki et al., 2002). Because melts lack long-range order and contain large variations in bond lengths and angles, abrupt density increases with pressure are unlikely (Waff, 1975; Stolper and Ahrens, 1988), a conclusion supported by experiments (Agee and Walker, 1993; Ohtani and Maeda, 2001; Suzuki and Ohtani, 2003).

Most reports on high-pressure glasses and melts have described changes in either structure or properties; few studies have quantitatively and systematically documented the effects of composition on both the structure and the density of the same samples in order to directly correlate microscopic with macroscopic effects of pressure. Because of structural relaxation during cooling and possibly during
decompression, glasses are not identical to melts at high temperature and pressures. However, glasses quenched from melts at high pressure do record a significant fraction of the total densification, and thus presumably important aspects of the structural response to pressure of the melts (Poe et al., 2001). Structural measurements on glasses are also often more straightforward, precise and less assumption-dependent than those made under the challenging constraints of in-situ, high P/T conditions. Here we report density and high-field MAS NMR measurements on a series of high-pressure glasses roughly analogous in composition to basalts, at least in terms of ambient pressure ratios of non-bridging oxygen to tetrahedral cations (NBO/T) of 0.5, molar Al/Si ratios of 0.33, and a wide range of modifier cation field strengths (Table 1).

Experimental Procedures

Ambient pressure K$_3$AlSi$_3$O$_9$, Na$_3$AlSi$_3$O$_9$ and Ca$_3$Al$_2$Si$_6$O$_{18}$ glasses were used as starting materials for the high-pressure samples. The ambient pressure glasses were prepared by melting appropriate amounts of K$_2$CO$_3$, Na$_2$CO$_3$, CaO, Al$_2$O$_3$, and SiO$_2$ with about 0.2 wt % cobalt oxide (to speed spin-lattice relaxation) and dipping the bottom of the crucible into a dish of water to quench the liquid into a glass. High-pressure glasses were prepared in a piston-cylinder (P=3 GPa, Dept. of Geology and Geophysics, Univ. of Minnesota, US) or in a multi-anvil apparatus (P $\geq$ 5 GPa, Bayerisches Geoinstitut, Univ. of Bayreuth, Germany). The experimental conditions are reported in Table 1. The 3 GPa samples were melted for 10 minutes in a welded platinum capsule and the multi-anvil experiments were melted for ~5 minutes in Re-foil capsules with either a 25/17 (5 GPa) or an 18/11 (8 and 10 GPa) type assembly (edge lengths of the MgO octahedron / truncated edge lengths of the tungsten carbide anvils). Glasses were quenched from melts at high pressure by turning off the power to the furnace, which resulted in quench rates on the order of $10^2$ °C/sec (Dingwell, 1995; Allwardt et al., 2005a). Further details of the piston cylinder and multianvil procedures and assemblies are given in Xirouchakis et al., (2001) and Allwardt et al., (2004), respectively. To investigate the effect of decompression on density and glass structure two 5 GPa experiments were conducted for CAS, where the only difference
was the rate of decompression. The decompression times for the two samples were about 14 hours (standard) and about 1 second (rapid). Rapid decompression was accomplished by opening an electric valve in the oil pressure system (Langenhorst et al., 2002) after the temperature quench.

The $^{23}$Na and $^{27}$Al MAS NMR spectra were collected with a Varian/Chemagnetics ‘T3’ probe and the Varian 18.8 Tesla spectrometer in the Stanford Magnetic Resonance Laboratory. The $^{23}$Na and $^{27}$Al frequencies are reported relative to aqueous NaCl and Al(NO$_3$)$_3$, respectively. The $^{23}$Na and $^{27}$Al MAS experiments consisted of a single pulse acquisition with pulse widths corresponding to approximately 30° radiofrequency tip angles (solid); delays of 0.05 and 0.2 seconds, respectively, 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 in 3.2 mm zirconia rotors at 22 kHz. The $^{27}$Al MAS spectra were also background subtracted to remove a small signal due to substitution of $[^6]$Al into the zirconia rotors. The resulting MAS spectra were fit with 2 Gaussian peaks for each of the Al-coordinations (4, 5, and 6) to account for the slightly non-Gaussian peak shapes, which are apparent even at 18.8T. Absolute measurements of glass density were made by the sink-float method with diiodomethane-acetone solutions. To avoid errors introduced by acetone evaporation, the proportions of the two solution components were determined by weighing. Accuracy was confirmed by reproducing the well-known densities of ambient pressure NaAlSi$_3$O$_8$ and CaMgSi$_2$O$_6$ glasses.

**Results and Discussion**

The $^{27}$Al MAS NMR spectra (Fig. 1), in which the peak areas relate directly to the percentages of the Al species (Table 1), show that all of the high-pressure glasses contain $[^4]$Al, $[^5]$Al and $[^6]$Al. Peaks in the spectra of the CAS glasses are broadened relative to those for the KAS and NAS glasses, perhaps owing to a greater amount of structural disorder, as has been suggested from $^{29}$Si spectra (Stebbins, 1995). Glasses synthesized at ambient pressure (CAS0, KAS0, NAS0) contain mostly $[^6]$Al, but also small amounts of $[^5]$Al. This has also been observed in an ambient pressure Na$_3$AlSi$_7$O$_{17}$ glass (Allwardt et al., 2005a) as well as for several aluminosilicates with
much lower NBO contents (Toplis et al., 2000; Stebbins et al., 2000; Neuville et al., 2004). The abundance of high-coordinated Al increases with pressure for all three compositions, as illustrated by the trend in average Al coordination (Fig. 2a). The CAS glasses contain markedly more \([5]\)Al and \([6]\)Al than the NAS and KAS glasses; remarkably, the high-coordinated species become predominant in CAS at 10 GPa. This trend has also been observed in both ambient pressure alkaline-earth aluminate melts (Poe et al., 1993) and alkaline-earth aluminoborate glasses (Bunker et al., 1991), where the higher modifier cation field strength (Mg > Ca > Sr > Ba) yields more high-coordinated Al. This likely occurs as a result of the high field strength modifier cations (i.e., Mg and Ca) out-competing the Al for the available “strong” (i.e., short) bonds to oxygen, which would force the Al to associate with a greater number of oxygens that have smaller amounts of available valence (Bunker et al., 1991). This observation implies that a more compositionally realistic basalt analog, \(\text{Mg}_3\text{Al}_2\text{Si}_2\text{O}_{18}\), should contain even more high-coordinated Al than the CAS composition, but we have not yet succeeded in quenching a crystal-free glass of this composition at high-pressure. Si-29 MAS spectra of the CAS8 glass (not shown) and spectra from Yarger et al. (1995) indicate, even for compositions that contain large amounts of \([5]\)Al and \([6]\)Al species, only \([4]\)Si are observed at a detection limit of 0.5 to 2%. A broad range of Al:Si ratios exist in typical aluminosilicates so the average Al-Si coordination (Table 1) is likely a more important parameter when comparing the structures of glasses and melts with different compositions.

Densities of glasses synthesized at 10 GPa are 8% (KAS) to 16% (CAS) higher than those quenched at ambient pressure (Table 1). Previous in-situ studies have shown that mafic melts at 10 GPa and temperatures far above the glass transition are roughly 20 to 30% denser than at 1 bar (Agee and Walker, 1993; Suzuki and Ohtani, 2003). Precise comparisons of recovered glass densifications with in-situ, high P/T data are difficult because of incomplete data on the pressure derivatives of expansivities and compressibilities derived from ambient pressure measurements. A rough approximation can be made that thermal expansivities and \(T_g\) are not strongly affected by pressure. In this case, the fractional volume decrease in the glass, when quenched to ambient temperature but still at high pressure, would approximate that of
the high temperature liquid. However, on decompression of the glass at ambient temperature, the elastic ("vibrational") component of the compressibility will cause a partial return to the uncompressed state, even if high-pressure configurational changes are retained. For Ca silicates and aluminosilicates, this reversible component is typically 30 to 40% of the total high temperature liquid compressibility (Askarpour et al. 1993). Thus, the glass densifications reported here indicate that a significant fraction of the high-pressure melt density increase, owing to configurational change is retained on return to ambient temperature and pressure. For the CAS glasses, the shape of the dependence of density on pressure is similar to that reported for mafic melts (Ohtani and Maeda, 2001; Suzuki and Ohtani, 2003), and is distinctly different from the curves for NAS and KAS (Fig. 2b). To investigate how decompression affects the density of a high-pressure glass, an additional CAS glass was synthesized at 5 GPa and rapidly decompressed (≈ 1 s, CAS5R) using the same experimental conditions as the conventionally decompressed glass (14 h decompression time, CAS5). Table 1 indicates that the CAS5R sample was densified by about 14 % relative to the ambient pressure sample, compared to 11 % for the slowly decompressed glass. These values are similar to the 20% densification that has been observed for the compositionally more complex MORB melts at 5 GPa (Ohtani and Maeda, 2001), which suggests that the rapid decompression can retain much or even most of the total densification and structural changes found in the high-pressure glasses.

Although the extent of structural relaxation due to decompression is not completely understood for aluminosilicate glasses (Allwardt et al., 2005b), the data presented here place some of the first available constraints on how a specific, fundamental structural change affects the recoverable densification of high-pressure melts. The average Al coordinations of the CAS, NAS, and KAS glasses are strongly correlated with the density (Figs. 2 and 3), which suggests that increasing the coordination of aluminum cations is an important component of the densification mechanism for aluminosilicate melts over these pressure ranges. Figure 3 indicates as well that at least two mechanisms occur in the KAS composition as the initial densification (up to 3 GPa) does not yield a large increase in the Al coordination. In addition, for both alkali aluminosilicates (NAS and KAS) relative to the Ca
aluminosilicate (CAS), the compression of the glass to a given relative molar volume 
(V/V₀) requires less increase in the average Al coordination. Since K-O and Na-O  
bonds are likely to be more compressible than Ca-O bonds (Shannon and Prewitt, 
1969), a reasonable explanation is that the recovered densities in at least the alkali 
cation glasses are in part affected by compression of the modifier cation site and 
accompanying network bond angle changes. This effect might also occur in the other 
glasses, but may be obscured by the densification due to the increasing Al  
coordination. The linear trends of the data and the similar slopes for the different 
compositions at pressures greater than 3 GPa suggests that Al coordination change 
may be the predominant structural record of the densification in these melts. Figure 3  
also suggests that an increase in the average Al coordination of one (e.g. from [4]Al to  
glass and presumably the melt by roughly 0.3 to 0.4 g/cm³. However, a simple 
calculation using the partial molar volumes for CaO, SiO₂, and Al₂O₃ of glasses from  
Lange (1997), indicates that the observed decrease in the molar volume of the CAS10  
glass from 24 to 20 cm³/gfw cannot be solely due to the increase in the average Al  
coordination, as this change is about equal to the contribution from the partial molar  
volume of the alumina component, accounting for its mole fraction in this composition  
(4 cm³/gfw). This implies that increasing Al coordination, while the clearest structural  
signature of densification, is not the only mechanism, further suggesting a 
compression of the network modifier site and/or a reduction in the average network  
bond angle. Further evidence for this is seen in the ²³Na MAS NMR spectra of the  
NAS0, NAS5, and NAS10 glasses collected at 18.8 T (not shown), where chemical  
shift distribution predominates over quadrupolar broadening (Lee and Stebbins, 2003).  
These nearly Gaussian-shaped spectra show that the relative frequency of the peak  
maximum measured in NAS10 increases by roughly 3.5 ppm relative to NAS0, which  
was also suggested from lower field data (Yarger et al., 1995). If this is primarily a  
chemical shift effect, it corresponds to roughly a 0.005 nm decrease in the mean Na-O  
bond distance compared to the range in silicates of 0.24 to 0.3 nm (Stebbins, 1998).  

The observations that alkaline-earth aluminosilicates have a higher average Al  
coordination than the NAS and KAS glasses and that KAS and NAS glasses contain
detectable fractions of pressure-induced high-coordinated Al at pressures as low as 3 GPa, suggest that $^{[5]}$Al and $^{[6]}$Al may have important influences on the properties of common, modern basaltic magmas arising in the shallow parts of the Earth's mantle, not just on very high pressure partial melts of importance to the early Earth. Further, detailed determinations of structural changes of basaltic melts with changes in temperature, pressure and composition are essential for accurate models of density for buoyancy driven igneous processes.

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The authors thank Professor Steve Feller (Coe College) for technical advice on measuring density, Dr. Lin-Shu Du for assistance in the collection of NMR data, and Professors Pascal Richet and Eiji Ohtani for helpful discussions and insightful reviews. We also thank the US National Science Foundation for grant numbers EAR-0104926 (JRA and JFS) and OCE 9876255 (MMH) and the Bayerisches Geoinstitut (BCS and DJF) for continued funding. We are especially grateful to the Bayerisches Geoinstitut visitor's program for additional funding (JRA).

References:


Table 5.1 Experimental conditions, Al-speciation, and density of ambient and high-pressure glasses.

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<tr>
<th>Sample</th>
<th>Composition</th>
<th>P [Gpa]</th>
<th>T [°C]</th>
<th>Decompression rate [MPa/s]</th>
<th>[(\text{Al})]</th>
<th>[(\text{Al})] avg</th>
<th>[(\text{Si+Al})] avg</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAS0</td>
<td>K₂Al₂Si₃O₈</td>
<td>0.0001</td>
<td>1450</td>
<td>-</td>
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Notes: Density is measured on glasses at ambient conditions and the measurement error is about 0.02 g/cm³, which is estimated using the difference between the measured and known densities for the standards.
Figure 5.1 Background-subtracted $^{27}$Al MAS NMR spectra (18.8 T). The "**" indicate signal resulting from a small amount of crystalline impurity (~0.6 % of total Al). The spectra labeled "X5" show sections of the spectra for the ambient pressure glasses, enlarged by 500% to show the small $^{5}$Al peaks.
Figure 5.2 Pressure dependence of the (a) average Al coordination and the (b) density for quenched and decompressed glasses. The arrow represents the volumetric change that occurs during a longer decompression time relative to data for the CAS5R glass (solid circle).
Figure 5.3 Average Al coordination vs. densification high-pressure glasses relative to the ambient pressure glass. Error bars on the CAS glasses are typical for all compositions. The segmented trend of the KAS glasses suggest the possibility that two different compression regimes occur in this composition.
Chapter Six

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

Modified version published in American Mineralogist
**Abstract**

Typical liquidus temperatures can be over 1000 degrees 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 “freezes in” to that of the glass) on the percentage of $[^5]{Al}$ and $[^6]{Al}$ species in two high-pressure (10 GPa) Na-aluminosilicate glasses (Na$_3$AlSi$_7$O$_{17}$ and NaAlSi$_3$O$_8$) 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$_3$AlSi$_7$O$_{17}$ samples show that the higher $T_f$ (quenched) glass has more high-coordinated Al than the lower $T_f$ (annealed, 475 °C) glass. However, the $^{27}{Al}$ spectra of the NaAlSi$_3$O$_8$ 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$_2$O and Al$_2$O$_3$ are equal) or peralkaline (e.g. mole fractions of Na$_2$O are greater than Al$_2$O$_3$) (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. B, Al, Si) gradually increases with increasing pressure (Xue et al. 1991; Yarger et al. 1995; Du et al., 2004). 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 changes are likely to be 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$_3$O$_8$, 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 Tesla) 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\(_3\)O\(_8\) glasses quenched from a liquid at 8 and 10 GPa (Stebbins and Sykes 1990). The presence of \([5]Al\) have been confirmed in glasses synthesized at 8GPa in very recent work (Lee 2004). Additionally, Al-K edge XANES spectra have been used to suggest that the average Al-coordination is greater than 4 in several high-pressure (4.4 GPa) glasses along the NaAlSi\(_3\)O\(_8\)-NaAlSi\(_2\)O\(_6\) join (Li et al. 1996).

Non-bridging oxygen (NBO) are oxygen 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; Allwardt et al., 2005a) 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 increasing pressure in high-pressure peralkaline (Na\(_3\)AlSi\(_7\)O\(_{17}\)) glasses (Yarger et al. 1995), as has been 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 Tesla, 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 Tesla) to investigate compositions and experimental conditions that have been previously studied at lower magnetic fields: Na\(_3\)AlSi\(_7\)O\(_{17}\) (Yarger et al. 1995) and NaAlSi\(_3\)O\(_8\) (Ohtani et al. 1985; Stebbins and Sykes 1990) to more directly assess the distribution of Al coordinations in these high-pressure glasses. Glass is commonly used as a
structural analog for geologic melts because the structure of glass is that of the corresponding liquid at the fictive temperature ($T_f$), so any structural differences between glasses with different $T_f$'s represent the configurational dependence of the structure with temperature (Richet and Neuville 1992). The $T_f$ is dependent on the quench rate where a faster quench rate yields a glass structure that represents a melt at a higher temperature (higher $T_f$) (Dingwell, 1995). For this reason, this study also collected spectra on 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 extrapolate structural data on 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, neither of which contained cobalt oxide. 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, CA (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 1000K/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 2mm (diameter) by 3.5 mm (length) cylindrical capsule. Each sample was first compressed at room temperature to the desired pressure and then heated to the experimental temperature for 5 to 10 minutes. The temperature was controlled using a D-type thermocouple located at the top of the sample 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 LaCrO₃ furnace, yielding a quench rate of approximately 200-400 K/s. The lower \( T_f \) glasses were annealed at 10 GPa and near to slow-cooling glass transition temperatures \( (T_g) \), which were approximated from ambient pressure \( T_g \) data for annealed glasses and \( T_g(P) \) trends for NaAlSi₃O₈ and CaAl₂Si₂O₈ compositions (Bagdassarov et al., 2004). Although the starting materials for the annealed glasses were powdered, all samples were recovered from the high-pressure runs as single cylindrical pieces of glass. This suggests that the annealing experiments were indeed done at or slightly above the temperature of transition to supercooled liquid at 10 GPa. The two NaAlSi₃O₈ glass samples were annealed at somewhat different temperatures to test for effects of uncertainties in estimating the high-pressure \( T_g \). The Ab-1 was used for the quenched sample and the 715°C annealing experiment (Ab-715) while Ab-2 was used as the starting material 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 the Na-migration. A small amount of an unknown crystalline impurity was detected in the Ab-715 sample using x-ray diffraction (XRD), optical microscopy, and \(^{27}\)Al MAS NMR. These techniques were 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 NMR results (see next section) for both annealed Ab samples are not due to crystallization, but reflect the actual structure of the NaAlSi₃O₈ glass.

The \(^{27}\)Al MAS NMR spectra were collected on both a Varian Unity/Inova 600 spectrometer (14.1 Tesla) and a Varian 18.8 Tesla 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(NO₃)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, but this
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 the spectra collected at 18.8T. 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 18.8T.

**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 Tesla (Fig. 1). These spectra have greater peak resolution, but are consistent with the previous $^{27}$Al MAS NMR work collected at 9.4 Tesla on this composition (NaAlSi$_3$O$_8$) and pressure (10 GPa) by Stebbins and Sykes (1990) and are consistent with their suggestion that there are $^{[5]}$Al and $^{[6]}$Al species in glasses quenched from pressures as low as 8 GPa. A very recent $^{27}$Al MAS (7.1 T) study observed the presence of $^{[5]}$Al in Ab glasses quenched at 8 GPa (Lee, 2004). 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 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$_3$O$_8$ (Ab) 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 ppm lower at the fields used here (Du and Stebbins, 2005). Previous studies have shown that charge-balanced Ca- and Mg-aluminosilicate glasses contain one to eight percent of the total aluminum present.
as \[^{5}\text{Al}\] (Stebbins et al., 2000; Toplis et al., 2000; Neuville et al., 2004). These differences between the charge-balanced Na-, Ca- and Mg-aluminosilicate glasses are completely consistent with a recent \(^{27}\text{Al}\) 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 pressures to 10 GPa (Allwardt et al., 2005b). Additionally, the lack of \[^{5}\text{Al}\] and \[^{6}\text{Al}\] 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 \[^{5}\text{Al}\] or \[^{6}\text{Al}\] is responsible for a shift of viscosity maxima away from the charge balanced join in Na-aluminosilicate glasses. This observation may suggest that triclusters exist in charge-balanced Na-aluminosilicate 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 \(^{27}\text{Al}\) MAS NMR spectrum of the ambient pressure \(\text{Na}_3\text{AlSi}_7\text{O}_{17}\) (NTS-Ab) glass (Fig. 2) shows that about 1% of the aluminum in the sample is five-coordinated. The previous \(^{27}\text{Al}\) 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 \[^{4}\text{Al}\] peak in the region of the \[^{5}\text{Al}\] peak; especially since the \[^{5}\text{Al}\] 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 \[^{6}\text{Al}\], 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 \[^{5}\text{Al}\] have also been detected in \(^{27}\text{Al}\) MAS NMR spectra (18.8 T) of ambient pressure \(\text{Na}_3\text{AlSi}_3\text{O}_9\), \(\text{K}_3\text{AlSi}_3\text{O}_9\), and \(\text{Ca}_3\text{Al}_2\text{Si}_6\text{O}_{18}\), glass (Allwardt et al. 2003, 2005b).

Two high-pressure \(\text{Na}_3\text{AlSi}_7\text{O}_{17}\) 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-Q) and the other was annealed (NTS-Ab-475) near \(T_g\). 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 structure that is from a slightly higher temperature because of its rapid quench rate. The peaks in the ^27^Al MAS NMR spectrum (Fig. 3) for NTS-Ab-quenched 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, which has a lower T_f than the quenched glass (Table 1). Yarger et al. (unpublished, but reported in Wolf and McMillan, 1995, pp.543) used ^27^Al MAS NMR (9.4 T) to measure the Al speciation in a Na_3AlSi_7O_17 glass that is pressure-cycled to 12 GPa at room temperature and found that it contained 5% [5]Al and 6% [6]Al. This is significantly lower than the Al-coordination of both of the Na_3AlSi_7O_17 glasses of this study. Although it is not clear what the structural implications are for annealing below T_g in high-pressure glasses, this may suggest that 475 °C is greater than or equal to T_g at 10 GPa. (or something like that…. Suggestions? I don’t particularly like this, but the reviewer (and Toplis) were concerned about our annealing T for this sample and this is the best I could do…) This suggests that for Na_3AlSi_7O_17 glasses, the amount of 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 depolymerized 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 percentage of high-coordinated Al was determined by peak fitting the ^27^Al MAS NMR spectra (Fig. 3) 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 as the relative heights of the glass peaks in both spectra are quite similar. The longer annealing time of the Ab-630 glass (10 vs. 5 minutes) and similarity of the spectra for the annealed glasses suggests that 5 minutes is enough time for structural relaxation to occur.

NBO have been shown to be an important component in the generation of five- and six-coordinated Al (Yarger et al. 1995; Lee 2004; Allwardt et al., 2005a), however the Ab glass contains little or no NBO (Mysen 1988; Lee et al. 2000). This would require that a different mechanism is responsible for generating high-coordinated Al in high-pressure metaluminous glasses than that observed in depolymerized high-pressure glasses (Allwardt et al, 2005a). 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 (e.g. Si-O-Al or Si-O-Si) into the coordination sphere of an AlO$_4$ species, resulting in a $^{[5]}$Al bonded to a three-coordinated oxygen (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 Al may be lost during decompression after the isobaric quench (Allwardt et al., 2005a). This, combined with the temperature effects observed for the depolymerized Na$_3$AlSi$_7$O$_{17}$ glass in the present study, suggest that the average Al-coordination measured in glasses should be considered a minimum value with respect to the high-pressure liquid state. 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). The Al speciation resulting from fitting the NTS-Ab-Q glass (Table 1) indicates that the previous low field NMR study (Yarger et al., 1995) overestimates the percentage of $^{[6]}$Al due to the severe overlap at 9.4 T of the different Al-coordination peaks, which
would result in an underestimation of the amount of $^{[5]}$Al species. This would likely shift the maximum in the percentage of $^{[5]}$Al to pressures greater than 8 GPa and suggest that the melt would contain a higher average Al-coordination than the glass, which would also support this study’s observed temperature dependence for Na$_3$AlSi$_7$O$_{17}$ composition glasses. (I don’t like this either, but do you think that this is clear enough?)

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 some 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$_3$O$_8$ glasses, however, as we would expect similar behavior for the Na$_3$AlSi$_7$O$_{17}$ glasses. In fact, Na$_3$AlSi$_7$O$_{17}$ has a greater thermal expansivity (Lange and Carmichael 1987), at least at ambient pressure, and a greater pressure drop on quench would be expected, yet more $^{[5]}$Al and $^{[6]}$Al is observed in the quenched glass.

**Acknowledgements**

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References


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Table 5.1 Aluminum speciation of high-pressure glasses

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<th>NaAlSi$_3$O$_8$ (Ab), 10 GPa</th>
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</table>

NOTE: 2% of the Al in the annealed sample is $^{[6]}$Al in the crystalline phase.
Figure 6.1 $^{27}$Al MAS NMR spectra showing the effect of the external magnetic field (14.1 T versus 18.8 T) on the spectrum for the NaAlSi$_3$O$_8$ (Ab) glass quenched from a liquid at 10 GPa.
Figure 6.2 $^{27}$Al MAS NMR spectra (18.8 Tesla) of the ambient pressure Ab and Na$_3$AlSi$_7$O$_{17}$ (NTS-Ab) glasses.
Figure 6.3 $^{27}$Al MAS NMR spectra (18.8 Tesla) 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.
Chapter Seven

The effect of composition, compression, and decompression on the structure of high-pressure aluminosilicate glasses: An investigation utilizing $^{17}$O and $^{27}$Al NMR

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Abstract

This contribution reviews recent work on the determination of the structure of high-pressure aluminosilicate glasses and presents new $^{17}$O and $^{27}$Al magic-angle spinning (MAS) and $^{17}$O triple-quantum (3Q) MAS NMR spectra that investigate the structure of K$_3$AlSi$_3$O$_9$ (KAS) and Ca$_3$Al$_2$Si$_6$O$_{18}$ (CAS) glasses quenched at 5 GPa. Comparison of the $^{27}$Al MAS spectra for the high-pressure and ambient pressure CAS and KAS glasses shows that the average Al-coordination increases with increasing pressure and that there is a strong compositional dependence to the amount of high-coordinated Al, as the CAS glass contains significantly more $^5$Al and $^6$Al than the KAS glasses. The spectra of the 5 GPa and the ambient pressure glasses were compared and show that high-coordinated Al are formed by the mechanisms: $[^4]$Si-NBO + 4 $[^4]$Si-O-$[^4]$Al $\rightarrow$ 5 $[^4]$Si-O-$[^5]$Al and 2 $[^4]$Si-NBO+ 4 $[^4]$Si-O-$[^4]$Al $\rightarrow$ 6 $[^4]$Si-O-$[^6]$Al, which are similar to the mechanisms for the generation of $[^5]$Si and $[^6]$Si in high-pressure silicate glasses. Decompression times were varied (14 hours and 1 second) and longer times are shown to reduce the average Al-coordination. Additionally, the reproducibility of glass making in a multi-anvil apparatus was investigated by comparing the $^{27}$Al MAS spectra of two glasses made in the same high-pressure experiment, but in separate capsules. This suggests that the reproducibility of the average Al-coordination is about 0.1 (e.g. 5.0 ± 0.1) for glasses with an Al/(Al+Si) ratio of 0.25.
Introduction

Pressure has been shown to drastically affect macroscopic properties of melts, such as density, viscosity, and diffusivity (Rigden et al., 1984; Scarfe et al., 1987; Reid et al., 2001). A fundamental understanding of the pressure effect on the melt structure is required to formulate structurally realistic models for the pressure dependence of macroscopic melt properties. For this reason, there has been considerable effort to understand structural transitions in high-pressure glasses and melts. However, results have been somewhat controversial because of uncertainties in the structural interpretations of in-situ data from Raman spectroscopy and the apparent structural relaxation that occurs during decompression of quenched glasses. The purpose of this paper is to review aspects of what is known and suspected about the pressure effects on the structure of aluminosilicate melts and glasses and to provide new data on several aspects of these important questions. These include: the large and obvious effects of composition, the effect of temperature and thermal history, and the effect of decompression on quenched high-pressure samples. First, we briefly review some of the recent work on the pressure dependence of physical properties.

Pressure dependence of viscosity and density of silicate melts

Melt density (and hence buoyancy) and viscosity have direct consequences for magma ascent and therefore the chemical evolution of the Earth and other planetary bodies (Stolper et al., 1981). There has been a significant amount of work to determine the pressure dependence on pressure of both properties, which can be quite significant (Kushiro, 1976, 1978; Rigden et al., 1984, 1988; Scarfe et al., 1987; Agee and Walker, 1993; Reid et al., 2001, 2003; Suzuki et al., 2002; Lange, 2003). The pressure dependence of viscosity has been shown to vary strongly with composition and can be either positive or negative. For example, the viscosity of NaAlSi$_3$O$_8$ melts seems to decrease with increasing pressure (Wolf and McMillan, 1995; Suzuki et al., 2002). However, two recent studies have observed a minimum in the viscosity of albite and MORB melts at 8 and 3 GPa, respectively (Poe and Rubie, 2000; Ando et al., 2003), while Reid et al. (2003) reports a maximum in viscosity of diopside melt at 10 GPa.
These studies suggest that important structural changes occur in these melts as a function of pressure.

The qualitative pressure dependence of the density seems to be much more straightforward, as it has been shown to increase with pressure. At ambient pressure, silicate melts have long been known to be less dense than the corresponding crystals, however, melts are also much more compressible. This means that the densities of melts and source rocks become more similar as pressure increases, which could lead to neutral buoyancy and a higher probability that the melt becomes trapped and solidifies in the surrounding mineral assemblage (Stolper et al., 1981). Additionally, through the use of shock wave measurements and olivine floatation experiments, it has been shown that at pressures corresponding to the Earth’s upper mantle, melts can become more dense than typical mantle minerals, which would cause olivine and other crystalline materials to float (Rigden et al., 1984; Agee and Walker, 1993; Ohtani et al., 1993). These and other experiments have experimentally documented the increasing melt density with increasing pressure (Agee and Walker, 1988; Miller et al., 1991; Suzuki et al., 1995; Knoche and Luth, 1996; Ohtani et al., 1998; Suzuki et al., 1998; Ohtani and Maeda, 2001; Suzuki and Ohtani, 2003). Additionally, studies have measured the densities of glasses quenched from high-pressure liquids and confirmed that they, like the densities of the melts, increase with increasing pressure of synthesis (Kushiro, 1978; Poe et al., 2001). For example, very recent data (Allwardt et al., 2005b) indicates that rapidly (1 second) and conventionally (~14 hours) decompressed Ca$_3$Al$_2$Si$_6$O$_{18}$ glasses quenched at 5 GPa (CAS5R2 and CAS5S in table 1 of this study) are densified by 15 and 11% relative to the ambient pressure glass (CAS0), which is similar to that suggested by the pressure-density relationships shown for basaltic composition melts (Ohtani and Maeda, 2001). At least some of the high-pressure melt structure is thus preserved in the decompressed glasses; especially when the decompression is rapid (~1 second). This suggests that although these measurements cannot be directly applied to the density of high-pressure melts, density determination of glasses at ambient conditions can be used as at least a first approximation for the percentage of densification that occurs. Very recently, densities of some high-pressure melts have been directly determined by the X-ray absorption
method using synchrotron radiation (Urakawa et al., 2003; Ohtani et al., this volume), which may represent a real breakthrough in this field. Knowledge of how the structure of a melt changes with pressure is essential to obtaining a fundamental understanding of why these macroscopic properties are significantly affected by pressure and how this might affect the buoyancy and ascent rate of mantle melts.

Aluminosilicate glass and melt structure: background and terminology

To understand the structure of high-pressure glasses and melts, one must first describe their structure at ambient pressure, which begins with defining the network forming cations (e.g. Si and Al) and network modifying cations (e.g. Mg, Ca, Na, K, etc.). The network formers provide the structural framework of the glass and are predominantly tetrahedrally coordinated in aluminosilicate glasses when the molar percentage of modifier oxides (e.g. CaO, K_2O, etc.) are greater than or equal to the molar percentage of alumina (Al_2O_3) (Mysen, 1988). Modifier oxides in excess of the alumina break up this framework and create non-bridging oxygen (NBO). A NBO is an oxygen bonded to only one network former, leaving the network modifiers to balance the remaining valence charge, while bridging oxygen (BO) are bonded to two network formers (e.g. Si-O-Si, Si-O-Al, Al-O-Al). The mixing of Si and Al (and its accompanying charge balancing modifier) is not random in aluminosilicate glasses, because there is an energetic penalty for oxygen bonded to a pair of aluminum atoms (aluminum avoidance, Navrotsky et al., 1985). Al-O-Si linkages are generally more energetically favorable than a combination of Si-O-Si and Al-O-Al linkages (Loewenstein, 1954), although the penalty is small enough that the higher energy species can exist in silicate glasses (Stebbins et al., 1997; Lee and Stebbins, 2000, 2001). Raman and nuclear magnetic resonance (NMR) spectroscopies have illustrated that Si is almost exclusively the host for NBO in aluminosilicate melts (Mysen et al., 1981, 1985; Stebbins et al., 2001; Allwardt et al., 2003a). Therefore, the structural framework of "geologically relevant" depolymerized aluminosilicate glasses (for SiO_2 > 40mol%) generally consists mostly of Si-O-Si and Si-O-Al linkages in tetrahedral coordination where the NBO are located on the Si.

The average NBO/tetrahedron ratio (NBO/T) is often taken as a measure of the
average network connectivity in melts and glasses. Most natural magmas have an average NBO/T ratio between 0 and 1.4 (Mysen, 1988), where lower values represent rhyolites and higher values represent more alkali basalt type compositions. Another way to convey the connectivity of a glass is through the use of the Qₙ notation, where n is the number of BO bonded to the tetrahedral network former (Mysen, 1988). This notation concentrates on the immediate environment of the tetrahedrally coordinated network former (i.e. Si, Al) and its average value can be determined by the equation: \( n = 4 - (\text{NBO/T}) \). Even for integer average values of n, however, multiple Q-species have been shown to exist. For instance, if \( n = 3 \), \( Q^3 \) will not be the only Q–species present in the structure, but there will also be \( Q^4 \) and \( Q^2 \) species (Brawer and White, 1975, 1977; Murdoch et al., 1985; Brandriss and Stebbins, 1988; Zhang et al., 1997).

As more network modifiers are added to the melt, the NBO/T ratio increases and in general the viscosity decreases due to a decrease in the network connectivity of the melt (Hess et al., 1995, 1996). However, recent work has shown that the use of NBO/T and mean Q-species notations is not always appropriate for aluminosilicates as \(^{[5]}\text{Al} \) have been detected in both charge balanced (Stebbins et al., 2000; Toplis et al., 2000; Neuville et al., 2004) and depolymerized glasses (Allwardt et al., 2003b).

Additionally, triclusters, which are oxygen bonded to three instead of two tetrahedrally coordinated network formers, have been suggested as a structural species to explain anomalous ambient pressure viscosity data near the NaAlO₂-SiO₂ join (Toplis et al., 1997) and CaAl₂O₂-SiO₂ (Toplis and Dingwell, 2004).

**Pressure effects on network cation coordination**

Known effects of pressure on the structures of crystalline silicates and aluminosilicates led to the suggestion that the most obvious effect of pressure on molten silicates would be an increase in the coordination numbers of network forming cations (Al and Si), although such structural transitions would be expected to be continuous because melts lack the long-range order of crystalline materials (Waff, 1975; Stolper and Ahrens, 1987). This would also suggest that there are not likely to be first-order discontinuities in macroscopic properties with increasing pressure resulting from network former coordination changes in aluminosilicate melts (Stolper
and Ahrens, 1987). Recent evidence from experimental work and molecular dynamics simulations confirms that such changes occur in high-pressure silicate melts, which has led to proposing several types of mechanisms for the generation of high-coordinated Si (Wolf et al., 1990; Xue et al., 1991; Diefenbacher et al., 1998). Much of this work is based on data from glasses that were quenched at high pressures and subsequently decompressed. However, one must realize that at best, such results record the structure at the glass transition temperature ($T_g$) and pressure, not the experimental temperature and pressure, because the large configurational component to the heat capacity ($C_p$) necessitates that the structure changes with temperature (see below). Also, another potential pitfall of measuring the structure at ambient conditions for glasses quenched from high-pressure melts is the problem of structural relaxation during decompression, (see below). However, even with these experimental difficulties, these studies can help us understand the mechanisms of "permanent" (i.e. quenchable) densification, which must be an important part of the densification of melts at high pressure and temperature. Additionally, they are also likely to identify important, qualitative effects of compositional changes on densification mechanisms that will be useful in comparing different types of magmas.

Most early experimental work on the structure of high-pressure aluminosilicate glasses concentrated on glasses along the NaAlO$_2$-SiO$_2$ join due to their relatively good glass-forming ability and the low melting temperatures relative to other aluminosilicates (Kushiro, 1976, 1978; Sharma et al., 1979; Mysen et al., 1980, 1983; McMillan and Graham, 1981; Hochella and Brown, 1985). One early study used infrared spectra and aluminum x-ray absorption lines to suggest that the average Al-coordination of NaAlSi$_3$O$_8$ and NaAlSi$_2$O$_6$ increases between 1 atm and 3 GPa (Velde and Kushiro, 1978); however, further work in these systems with Raman and x-ray spectroscopies observed no evidence to support this increasing Al-coordination at pressures to 4 GPa (Sharma et al., 1979; Mysen et al., 1980, 1983; McMillan and Graham, 1981; Hochella and Brown, 1985). More recently, Al-K edge XANES studies of several high-pressure (4.4 GPa) glasses along the NaAlSi$_3$O$_8$-NaAlSi$_2$O$_6$ join has been used to suggest that high-coordinated Al exist in these glasses (Li et al., 1996). Al-27 magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra (9.4
and 11.7 Tesla) of glasses quenched from a liquid at 8 and 10 GPa consisted of a tetrahedral Al peak that appeared to contain intensity in the “tail” at approximately 25 and 0 ppm which were used to suggest the presence of \(^{[5]}\text{Al}\) and \(^{[6]}\text{Al}\) species, respectively (Stebbins and Sykes, 1990). A recent \(^{27}\text{Al}\) triple-quantum (3Q) MAS spectrum (7.1 T) confirmed the presence of \(^{[5]}\text{Al}\) in Ab glasses quenched at 8 GPa (Lee, 2004) while a very recent \(^{27}\text{Al}\) MAS (18.8 T) study has quantified the amount of \(^{[5]}\text{Al}\) (15%) and \(^{[6]}\text{Al}\) (6%) in the 10 GPa glass (Allwardt et al., 2005). Additionally, results from molecular dynamics simulations have also long suggested that the average coordination of network formers increases in high-pressure melts with increasing pressure (Angell et al., 1982, 1987; Nevins and Spera, 1998; Suzuki et al., 2002).

Five- and six-coordinated silicon (\(^{[5]}\text{Si}\) and \(^{[6]}\text{Si}\)) were first definitively observed in alkali silicate glasses quenched from high pressure melts by Stebbins and McMillan (1989) and Xue et al. (1989). In subsequent Raman and \(^{29}\text{Si}\) NMR studies, high-coordinated Si have been suggested to be generated by the mechanisms:

\[
Q^3 + Q^4 = ^{[5]}\text{Si} + Q^4^* \quad (1)
\]

\[
2Q^3 + Q^4 = ^{[6]}\text{Si} + 2Q^4^* \quad (2)
\]

(Wolf et al., 1990; Xue et al., 1991), where \(Q^4^*\) is a \(^{[4]}\text{Si}\) with three \(^{[4]}\text{Si}\) and one \(^{[5]}\text{Si}\) or \(^{[6]}\text{Si}\) neighbor. In this model, NBO associated with a \(Q^3\) species are consumed to form high coordinated silicon (\(^{[5]}\text{Si}, ^{[6]}\text{Si}\) and \(Q^3\) and \(Q^4\) species are transformed to \(Q^4^*\) species during this process. The work of Xue et al. (1991) and Stebbins and McMillan (1993) showed that glass compositions with an average \(Q\)-species of 3.5 (NBO/T = 0.5) contain the most high-coordinated Si, presumably because these compositions contain large amounts of \(Q^3\) and \(Q^4\) species. If mechanisms 1 and 2 are put in terms of the oxygen environment, they become:

\[
\text{NBO} + 4 \text{BO} \rightarrow 5 ^{[4]}\text{Si-O-}^{[5]}\text{Si} \quad (3)
\]

\[
2 \text{NBO} + 4 \text{BO} \rightarrow 6 ^{[4]}\text{Si-O-}^{[6]}\text{Si} \quad (4).
\]

This approach recently confirmed that mechanisms 3 and 4 create the \(^{[5]}\text{Si}\) and \(^{[6]}\text{Si}\) in potassium tetrasilicate composition (\(\text{K}_2\text{Si}_4\text{O}_9\)) by combining \(^{17}\text{O}\) 3QMAS and \(^{29}\text{Si}\) MAS NMR spectra of quenched high pressure and ambient pressure glasses, where the loss of NBO corresponded to the increase in the fraction of \(^{[5]}\text{Si}\) and \(^{[6]}\text{Si}\) (Allwardt et al., 2004). Consequently, the decrease in the percentage of NBO would also likely
increase the coordination number of the modifier cations due to the replacement of higher charge density bonds to NBO with lower charge density bonds to BO. Five- and six-coordinated Si were also observed in a high-pressure CaSi₂O₅ glass (Stebbins and Poe, 1999). Additionally, a very recent study used in-situ high-temperature and pressure x-ray diffraction of CaSiO₃ and MgSiO₃ melts up to 6 GPa to show that changes occur in Ca²⁺ and Mg²⁺ environments and the intermediate range order (Funamori et al., 2004). These authors then stated that these were likely the dominant compression mechanisms, while the increase in the Si-coordination is the secondary mechanism for melts of this composition and experimental conditions.

In aluminosilicate melts an additional complication is introduced as network Al and Si can both respond to pressure by increasing coordination and may, in a sense, “compete” with each other. Poe et al. (2001) used Raman and XANES spectroscopies to investigate compression mechanism(s) in aluminosilicate glasses and found evidence to suggest that there are two separate mechanisms. A loss of intensity in the low frequency region of the Raman spectra for the 44 CaO- 12 Al₂O₃- 44 SiO₂ glasses was used to suggest that at pressures below 6 GPa the oxygen was increasing its average coordination by either forming triclusters or having Ca²⁺ cations inhibiting the vibrations of the T-O-T species. At higher pressures, the increase in intensity in the 1570 eV region of the XANES spectra was used to suggest that either the T-O-T angle was narrowing or there was an increase in the average Al-coordination. Known effects of pressure on crystal structures led to the suggestion that AlO₆ appears at lower pressures than SiO₆ species in high-pressure melts (Waff, 1975), which was later confirmed by ²⁷Al and ²⁹Si MAS NMR of Na₃AlSi₇O₁₇ glasses (Yarger et al., 1995). The data from the glasses of Yarger et al. (1995), when compared to the results from metaluminous composition (NaAlSi₃O₈) of Stebbins and Sykes (1990), clearly demonstrates that more [⁵]Al and [⁶]Al occur in depolymerized NAS aluminosilicate glasses, which suggests that the presence of NBO somehow facilitates the generation of [⁵]Al and [⁶]Al. As mentioned previously, this agrees with previous studies of silicates where NBO have been shown to be important for the generation of [⁵]Si and [⁶]Si (Xue et al., 1991; Allwardt et al., 2004). Si-NBO (Allwardt et al., 2003a) and Si-O-Al (Loewenstein, 1954; Lee et al., 1999, 2000) species are the energetically
favorable structural species in depolymerized aluminosilicate glasses, which, combined with the observation that the generation of high-coordinated Al is dependent on the number of NBO in the system, led Allwardt et al. (2004) to propose that the mechanisms that create high-coordinated Al are most likely:

\[
\text{Si-NBO} + 4 \text{Si-O-Al} \rightarrow 5 [^{4}\text{Si-O-}^{5}\text{Al} \quad (5)
\]
\[
2 \text{Si-NBO} + 4 \text{Si-O-Al} \rightarrow 6 [^{4}\text{Si-O-}^{6}\text{Al} \quad (6)
\]

As in the silicate glasses, these mechanisms would likely increase the average coordination number of the modifier cations. Even though mechanisms 5 and 6 are reasonable for depolymerized glasses, they may not be valid for charge-balanced aluminosilicate glasses due to the lack of an adequate percentage of NBO to drive the mechanism (Stebbins et al., 1997; Lee and Stebbins, 2000). Recently, two different mechanisms were proposed for charge-balanced systems (Allwardt et al., submitted). The first involves the formation of triclusters by the mechanism proposed by Toplis et al. (1997) for ambient pressure glasses to create the NBO that could then be used in mechanisms 5 and 6. The other possibility forces a BO into the coordination sphere of an AlO₄ species to form the high-coordinated Al. Both mechanisms yield a \(^{3}\text{O}\), but the \(^{3}\text{O}\) in the “tricluster mechanism” is bonded to three tetrahedral network formers while the other mechanism results in a \(^{3}\text{O}\) bonded to one or more high-coordinated Al.

Despite being possibly the most applicable system to geologic melts due to the percentage of Al and the NBO/T ratio (Mysen 1988), relatively little work has been done on determining the structure of high-pressure aluminosilicate glasses containing significant concentrations of NBO. An early study used changes in a portion (850 to 1300 cm⁻¹) of Raman spectra to confirm that the reaction: \(2Q^3 = Q^2 + Q^4\), favored more disorder (right) at high-pressures (Mysen, 1990) as suggested previously by \(^{29}\text{Si}\) NMR on a Na-silicate glass quenched at pressure (Xue et al., 1989). The NBO/T ratio at ambient conditions has been shown to be an important factor in the average Al-coordination in high-pressure glasses where more NBO in the ambient pressure glass seems to yield more high-coordinated Al (Yarger et al., 1995; Lee, 2004; Allwardt et al., submitted). However, more studies are needed on high-pressure aluminosilicate glasses to determine whether an initial average Q-species of 3.5 (NBO/T = 0.5) yields
a maximum in the amount of high-coordinated Al as is the case for Si in Al-free compositions (Wolf et al., 1990; Xue et al., 1991). A very recent $^{27}$Al MAS NMR (18.8 T) study (Allwardt et al., 2003c) managed to isolate the effect of the type of modifier cation in high-pressure $\text{M}^{x+}(9-3x)\text{Al}_2\text{Si}_6\text{O}_{18}$ glasses (M= Mg$^{2+}$, Ca$^{2+}$, Na$^+$, or K$^+$) and clearly showed that the cation type significantly affects the average Al-coordination (Figure 1), where the alkaline earth aluminosilicates contain more high-coordinated Al than the alkali aluminosilicates. Additionally, this study directly showed that the Al-coordination begins to increase at pressures as low as 3 GPa, which was the minimum pressure explored. These findings suggest that actual mantle melts may contain significant amounts of $[^5] \text{Al}$ and $[^6] \text{Al}$ species at the modest pressures relevant to typical mantle melting, which would mean that density predictions based on values for the bulk modulus and its first pressure derivative measured at ambient conditions are problematic as they would not account for this structural change and could systematically underestimate the density.

**Effects of temperature and thermal history on structure**

Because melting temperatures of melts can be over 1000 degrees higher than the glass transition temperature in high-pressure aluminosilicate melts, determining the effect of temperature on melt structure is essential to extrapolating data from glasses to the structure of silicate liquids. NMR and molecular dynamics simulations of ambient pressure, NBO-containing aluminosilicate glasses and melts have suggested that the average Al-coordination increases with increasing temperature (Stebbins and Farnan, 1992; Poe et al., 1993, 1994). Recently, this work was extended to high-pressure (10GPa) NaAlSi$_3$O$_8$ (Ab) and Na$_3$AlSi$_7$O$_{17}$ (NAS) glasses (Figure 2, Allwardt et al., submitted) by synthesizing glasses that represent slightly different temperatures. The spectra for the Na$_3$AlSi$_7$O$_{17}$ glasses showed that the amount of $[^5] \text{Al}$ and $[^6] \text{Al}$ increases with increasing temperature, which is in agreement with previous ambient pressure studies of depolymerized melts and glasses. Since the $T_g$ is below the melting temperature and the Al-coordination of depolymerized glasses increases with temperature, it appears that depolymerized glasses quenched from the high-pressure liquid represent a minimum value for the percentage of high-coordinated Al species.
present in high temperature melts. However, the NMR spectra indicate that NaAlSi$_3$O$_8$ glasses show the opposite effect at 10 GPa, as the amount of $^{[5]}$Al and $^{[6]}$Al drastically decreases with increasing temperature (Figure 2). Further experiments are required in this area to determine if this is an anomalous system or if other charge-balanced glasses behave similarly to NaAlSi$_3$O$_8$.

The effect of decompression on the structure of high-pressure glasses

Another important factor to consider when relating the structure of high-pressure glasses to the structure of high-pressure melts is whether relaxation occurs during the decompression of high-pressure glasses, which would affect the structure that can be measured at ambient conditions. Two different approaches have utilized Raman spectroscopy, combined with the diamond anvil cell, to measure the effect of compression and decompression in silicate glasses by collecting spectra of the sample at the pressure of interest and collecting another spectrum after decompression. The first method involved compressing an ambient pressure glass to the desired pressure and measuring the spectrum without ever heating the sample (Hemley et al., 1986; William and Jeanloz, 1988; Wolf et al., 1990; Sharma et al., 1996). The results of this method have been extensively reviewed by Wolf and McMillan (1995) and, for the most part, are beyond the scope of this brief review. The second method involves annealing the glass at $T_g$ (and pressure) and collecting a spectrum (Farber and Williams, 1996; Robinson, McMillan and Wolf, in McMillan and Wolf, 1995, Figure 25). The compression mechanisms occurring during the two types of experiments seem to be similar (Wolf et al., 1990; Xue et al., 1991). However, the NMR data (Yarger et al., discussed in Wolf and McMillan, 1995, pp. 543) and Raman spectra of decompressed glasses clearly show that glasses that were annealed at high pressure or quenched from a high pressure melt (Farber and Williams, 1996; Robinson, McMillan and Wolf, in McMillan and Wolf, 1995, Figure 25; Yarger et al., discussed in Wolf and McMillan, 1995, pp. 543) are structurally distinct from those that were compressed at room temperature only. This is not surprising as the increased temperature of the latter method would provide additional energy to allow structural transitions to occur. Although the exact amount of structural relaxation that occurs
during decompression is still uncertain and debated, it is obvious that the measured structures of decompressed high-pressure glasses are different from ambient pressure glasses (before densification) indicating that at least some of the high-pressure melt structure is retained. Additionally, it is extremely difficult to quantify the amount of high-coordinated species with Raman and infrared (IR) spectroscopies due to the strong overlapping character of bands and the uncertainties in peak assignments. For this purpose NMR spectroscopy is much more robust in the quantification of the structure of high-pressure glasses than Raman or IR spectroscopies, but has the disadvantage that it currently cannot be applied in-situ at high pressure to study inorganic glasses (or melts at high temperature).

In a recent $^{29}$Si NMR and Raman spectroscopic study on high-pressure $K_2Si_4O_9$ glasses, Allwardt et al. (2004) approached the problem of determining the decompression effects on the glass structure by performing multi-anvil experiments at 5.7 GPa using two different decompression times (14 hours and 1 second). The $^{29}$Si MAS NMR spectra of the recovered samples suggest that a small fraction of $^{[6]}$Si reverts to $^{[5]}$Si (~1% of the total Si) during the slower decompression. The effect of varying decompression rates was also visible in the Raman spectra where the spectrum of the rapidly decompressed glass resembled that of a conventionally decompressed glass synthesized at 8 GPa. More importantly, the differences between the Raman spectra of the conventionally and rapidly decompressed glasses (5.7 GPa) mimicked the differences between the Raman spectra collected in-situ and that collected on the decompressed glass (Robinson, McMillan, and Wolf, in McMillan and Wolf, 1995, Figure 25). Structural determination at ambient conditions offers the opportunity for a much more robust quantitative approach with fewer assumptions as there are fewer spectroscopic uncertainties compared to measurements at extreme conditions, such as temperature and pressure effects on IR absorption coefficients and Raman scattering cross-sections (McMillan and Wolf, 1995), and anharmonic vibrations (Brown et al., 1995; Daniel et al., 1995; McMillan and Wolf, 1995).

*NMR and structural studies of high-pressure glasses*
Most recent work on the structure of high-pressure glasses has used solid-state NMR as it is quantitative and nuclide specific, so it can measure percentages of specific structural species surrounding specific types of atoms (e.g. Al, Si, O, etc.). One difficulty of early NMR investigations of high-pressure aluminosilicate glass structure was that $^{27}$Al is a quadrupolar nuclide, so peak widths and positions are dependent on the external magnetic field used. Al-27 MAS spectra from lower fields are difficult to quantify due to this effect as their interpretation can depend on accurately representing the unconstrained, overlapping peaks and their low-frequency tails for the different Al-coordinations (Stebbins et al., 2000; Gan et al., 2002). However, technological advances in high-field NMR spectroscopy have greatly increased the available external magnetic fields and sample spinning rates, which allows a more reliable approach to quantifying $^{27}$Al MAS NMR spectra as the peaks are more Gaussian in shape and contain a significantly smaller "tail" that is not prone to overlap as those observed in spectra from lower fields (Stebbins et al., 2000). Figure 3 shows how the external magnetic field affects the spectra as even the peaks in the relatively high field spectrum collected at 14.1 T are overlapping and difficult to quantify compared to the spectrum from 18.8 T. Aluminum speciation can also be quantified at lower fields by utilizing the narrower peak widths of satellite transitions (Jäger, 1994). However, as can be seen in Figure 3, the relative intensity of the spinning sidebands is significantly smaller than that of the central transition, which makes collecting spectra with an adequate signal to noise ratio much more time consuming, especially for small, high pressure samples. Another approach to quantifying Al-species is to use $^{27}$Al triple-quantum (3Q) MAS NMR as this technique produces a two dimensional spectrum where the second dimension is free of second-order quadrupolar broadening, which allows peak fitting of the projections of the 2nd dimension. The quantification of 3QMAS NMR spectra, however, is dependent on the quadrupolar coupling constant ($C_Q$) of the structural species, which is dependent on the local charge symmetry (Baltisberger et al., 1996). This does not appear to be a significant issue for $^{27}$Al NMR as the $C_Q$ of the relevant species ($^{[4]}$Al, $^{[5]}$Al, $^{[6]}$Al) are similar. However, more work is required to verify that small differences in the $C_Q$ of the different Al species is not introducing systematic quantification errors for $^{27}$Al
3QMAS spectra. The major advantage of 3QMAS is that it offers an alternative to high magnetic field spectrometers and allows at least a semi-quantitative treatment of \(^{27}\text{Al}\) spectra with "low" field spectrometers; however, it takes significantly more time to collect a spectrum with an adequate signal to noise ratio to detect small percentages of high-coordinated Al.

O-17 NMR has been used extensively to investigate the structure of ambient pressure glasses; however, the use of \(^{17}\text{O}\) NMR to determine the structure of high-pressure glasses is still in its infancy (Xue et al., 1994; Lee et al., 2003; Lee, 2004; Allwardt et al., 2004). As a result, relatively little is known about peak assignments of species that are not present in ambient pressure glasses. Xue et al. (1994) used a \(\text{K}_2\text{Si}_4\text{O}_9\)-wadeite crystalline model compound to aid in peak assignments for high-pressure glasses and found that the peak location of the \(^{[4]}\text{Si}-\text{O}^{-[6]}\text{Si}\) species overlaps with the peak for \(^{[4]}\text{Si}-\text{O}^{-[4]}\text{Si}\) species. This peak location was, however, well resolved in the \(^{17}\text{O}\) 3QMAS spectrum (Allwardt et al., 2004). Additionally, to further constrain peak assignments in \(^{17}\text{O}\) NMR for high-pressure silicate glasses, a 3QMAS spectrum of the crystalline \(\text{CaSi}_2\text{O}_5\)-triclinic phase was collected to determine how oxygen bonded to \(^{[5]}\text{Si}\) are represented in \(^{17}\text{O}\) NMR spectra. This spectrum clearly demonstrated that the \(^{[4]}\text{Si}-\text{O}^{-[5]}\text{Si}\) species do not show a distinct signature, but appear to be either \(\text{"[4]}\text{Si}-\text{O}^{-[4]}\text{Si-like"}\) or \(\text{"[4]}\text{Si}-\text{O}^{-[6]}\text{Si-like,}\) depending on the local environment of the oxygen (Allwardt et al., 2004). This strongly indicates that Si-coordination, and presumably Al-coordination, can not be reliably inferred from \(^{17}\text{O}\) NMR, but must be measured directly with \(^{29}\text{Si}\) or \(^{27}\text{Al}\) NMR.

We also note that the development of new types of small volume NMR probes, coupled with the higher sensitivity provided by higher field magnets, have greatly improved obtainable signal to noise ratios for the small samples typically made in multi-anvil high-pressure apparatus (Stebbins and Poe, 1999).

*Motivation and methodology of the present study*

Here we present new data on several high-pressure Ca- and K-aluminosilicate glasses, to illustrate the type of information that can be obtained from quenched samples. We demonstrate large effects of composition on the extent of structural
changes, explore decompression effects, and help constrain the mechanisms of densification in high-pressure glasses. Compositions \((K_3AlSi_3O_9\) and \(Ca_3Al_2Si_6O_{18}\) were chosen as simple models of mafic magmas in terms of the NBO/T ratio (0.5) and the percentage of alumina (Mysen, 1990; McDonough and Rudnick, 1998). By studying high-pressure glasses with different rates of decompression using \(^{17}\text{O}\) and \(^{27}\text{Al}\) NMR, it may be possible to mechanistically determine how the structure of a glass is affected by longer decompression times, although not necessarily the total extent of such changes. The \(^{17}\text{O}\) 3QMAS and \(^{27}\text{Al}\) MAS NMR spectra of these glasses can then be used to quantitatively test proposed mechanisms of decompression. Finally, by comparing the \(^{17}\text{O}\) 3QMAS and \(^{27}\text{Al}\) MAS spectra of the rapidly decompressed sample to those of the ambient pressure sample, models of the mechanism for the generation of five and six-coordinated Al in melts at high pressure can be compared to the previously proposed structural compression mechanisms.

**Experimental Procedures**

Ambient pressure \(K_3AlSi_3O_9\) (KAS) and \(Ca_3Al_2Si_6O_{18}\) (CAS) glasses were used as the starting materials for the high-pressure samples. \(K_2CO_3\), \(CaO\), \(Al_2O_3\), and \(SiO_2\) were used and all oxides and carbonates were dried at 1000 and 250 °C, respectively, prior to mixing. In addition, 0.2 wt. % cobalt oxide was added to the oxide powders to speed spin-lattice relaxation in the NMR experiments. The powder for the KAS glass was held at 750 °C for about 16 hours to decarbonate the sample prior to melting. The ambient pressure glasses were made in 400 mg batches by dipping the bottom of the Pt crucible in water to quench the melt into a glass. The glasses were also isotopically enriched by replacing conventional \(SiO_2\) with 70% \(^{17}\text{O}\)-enriched \(SiO_2\), which was synthesized as has been previously reported in Stebbins et al. (1997). All steps that involved the heating of \(^{17}\text{O}\)-enriched materials were done in argon to minimize \(^{17}\text{O}\) exchange with the environment.

The high-pressure glasses were synthesized in a multi-anvil "Kawai-type" apparatus (1000 ton) at Bayerisches Geoinstitut, Bayreuth, Germany (Rubie, 1999). A 25/17 assembly (edge lengths of the MgO octahedron / truncated edge lengths of the tungsten carbide anvil) with a LaCrO_3 stepped furnace was used. This assembly is
similar to that shown in Figure 2 of Frost et al. (2004) where the main difference is that a Re-capsule was used in place of MgO. The 25/17 assembly was chosen to maximize sample volume and allow the synthesis of two glasses per multi-anvil experiment. Two rhenium-foil capsules were stacked on top of each other, each with an outer diameter of 4 mm and a length of about 2 mm. The “high” experimental temperatures required the use of Re-capsules as 1960 °C is beyond the useful range of Pt at 5 GPa. Each experiment consisted of an initial compression to the desired pressure (at room temperature) followed by heating at a rate of 200-300° C/min to the final experimental temperature (Table 1), which was controlled using a D-type thermocouple located at the top of the sample capsule. The experiments were held at the experimental temperatures for 1 to 5 minutes until the heater was turned off, which isobarically quenched the melt to a glass within a few seconds. The P calibration was done at 1200 °C using the quartz-coesite (3.23 GPa, Hemingway et al., 1998) and the CaGeO₃ garnet-perovskite (5.94 GPa, Susaki et al., 1985) transitions. Two or more 5 GPa glasses were synthesized for each composition (KAS and CAS), where the rate of decompression was varied (~14 hours-standard and ~1 second-rapid). Rapid decompression resulted from opening an electric valve in the oil pressure system (Langenhorst et al., 2002) after the temperature had dropped below 100 °C. To investigate the best-case reproducibility of the experiments, two CAS glasses (CAS5R1 and CAS5R2) were made in the same run to ensure that the experimental conditions were nearly identical. Sample names and experimental conditions are shown in Table 1 and consist of the composition (KAS or CAS), the pressure (1 atm or 5 GPa) and the rate of decompression (rapid or standard). For instance, a KAS glass that was synthesized at 5 GPa and rapidly decompressed is referred to as KAS5R. The exception is a glass that was compressed to 6 GPa, but never heated, which was named KAS6 (Table 1). All high-pressure glasses were found to be entirely amorphous when examined with a 400X petrographic microscope, which means that any changes in the $^{27}$Al MAS spectra can thus be attributed to structural changes in the glass.

The $^{17}$O MAS and 3QMAS NMR spectra were collected on a Varian Unity/Inova 600 spectrometer (14.1 Tesla) while the $^{27}$Al MAS spectra were collected on a Varian 18.8 Tesla spectrometer operated by the Stanford Magnetic Resonance
Laboratory. Both used a Varian/Chemagnetics ‘T3’ probe with 3.2 mm zirconia rotors. The $^{17}$O and $^{27}$Al frequencies are reported relative to H$_2$O and Al(NO$_3$)$_3$, respectively. The $^{27}$Al MAS experiments used a single pulse acquisition with pulse widths corresponding to approximately 30° “solid” radiofrequency (rf) tip angles (approximately 1 $\mu$s) and 0.1 s delays between pulses were used to optimize the signal to noise ratio. No differential relaxation was observed in the reported spectra relative to experiments with longer delay times. A typical $^{27}$Al MAS NMR experiment consisted of about 15,000 transients while samples were spun at 22 kHz to separate the first spinning sideband of the tetrahedral Al peak from the octahedral Al peak. The $^{17}$O MAS and 3QMAS experiments were conducted at 14.1 T with samples spinning at 20 kHz. The MAS experiments used pulse widths of 0.25 $\mu$s and delays of 1 s between pulses. The 3QMAS spectra were collected with the same experimental equipment as the $^{17}$O MAS experiments and a rf power of 145 kHz. A shifted echo pulse sequence was used, consisting of two hard pulses (3.0 $\mu$s and 1.0 $\mu$s, respectively) followed by a soft pulse (21 $\mu$s) (Massiot et al., 1996). Delay times of 8 seconds were used between acquisitions and the $^{17}$O 3QMAS data were processed using the software package, RMN (FAT) (P.J. Grandinetti, The Ohio State University). The resulting 3QMAS spectra are two-dimensional plots in which the isotropic dimension is free of second order quadrupolar broadening and the projection of the MAS dimension yields a spectrum similar to that measured by conventional 1-D MAS NMR.

High-pressure glass samples are small by MAS NMR standards so differentiating between the signal resulting from the glass and that from the rotor becomes critical to accurately interpreting the spectra. The zirconia rotors used here contain trace amounts of $^{[6]}$Al impurities that create peaks in the $^{27}$Al MAS spectra. The signal and intensity is rotor-specific so only two rotors were used to minimize the time devoted to collecting rotor backgrounds. Signal resulting from the rotor ranges from -5 to 20 ppm in the $^{27}$Al MAS spectra with the majority of the intensity centered at about 0 ppm. To remove this signal and not introduce additional noise to the glass spectra, 75,000 transients were collected for both rotors. These were subtracted from the glass spectra to yield background subtracted $^{27}$Al MAS NMR spectra of the high-pressure glasses. These spectra were then fit with 2 Gaussian peaks for each of the Al-
coordinations (4, 5, and 6) to approximate the slight non-Gaussian peak shapes, which are apparent even at 18.8 T. Oxygen-17 MAS NMR does not have the same difficulties as $^{27}$Al NMR because $^{17}$O is of low natural abundance and the zirconia rotor background (385 ppm, Stebbins, 1995) is well outside the typical chemical shift ranges for aluminosilicate glasses (0 to 150 ppm). However, for experiments where there is either little sample or low $^{17}$O-enrichment, one should keep in mind that the first spinning sideband of this narrow peak can lie inside the range of interest. For instance, spinning the sample at 20 kHz with a 14.1 T spectrometer results in the first spinning sideband of the zirconia rotor at about 130 ppm, which is approximately the location of a Si-NBO coordinated by Sr$^{2+}$ (Allwardt, unpublished data).

New Results

The background-subtracted $^{27}$Al MAS NMR spectra (18.8 T) of the four Ca$_3$Al$_2$Si$_6$O$_{18}$ glasses are shown in Figure 4 and the results of peak fitting can be seen in Table 2. The spectrum of the ambient pressure glass (CAS0) is dominated by a peak centered at 58 ppm, which coincides with the region of the spectrum that is commonly assigned to fully polymerized (Q$^4$) tetrahedral Al ($^{[4]}$Al) in aluminosilicates (isotropic chemical shifts of approximately 56 to 64 ppm, Stebbins, 1995). A small unresolved shoulder peak (~2%) centered near 25 ppm is present. This suggests that there is $^{[5]}$Al present at ambient pressures as chemical shifts for 5 or 6-coordinated Al are in the ranges of 30 to 45 ppm and 0 to 16 ppm, respectively, which would yield expected peak maxima a few ppm lower for the external magnetic fields (18.8 T) used in this study (Du and Stebbins, 2005). Three CAS glasses were synthesized at 5 GPa. Two were decompressed rapidly (CAS5R1 and CAS5R2) while the other was decompressed more slowly over 14 hours (CAS5S). Pressure obviously affects the aluminosilicate glass structure as the spectra show that the $^{[4]}$Al peak shifts to 62 ppm and there is an increase in the intensity of the five- (25 ppm) and six- coordinated peaks (~2 ppm) (Figure 4). Peak areas derived from the two spectra show that the rapidly decompressed glasses contain between 36 to 38% $^{[5]}$Al and 28 to 31% $^{[6]}$Al, which indicates that the average Al-coordination increases from 4.0 to about 5.0 (Table 2). If all Si are assumed to be tetrahedrally coordinated, as suggested by the


$^{29}$Si MAS spectrum of a Ca$_3$AlSi$_6$O$_{18}$ glass synthesized at an even higher pressure (8 GPa, Allwardt et al., 2005b), the average coordination number of the network formers increases from 4.0 to 4.2, respectively (Table 2). Figure 4 also shows that less $^{[5]}$Al and $^{[6]}$Al are present in the CAS5S glass (31% and 22%, respectively) than the CAS5R glasses, suggesting that some high-coordinated Al are lost during the slower decompression.

The $^{17}$O MAS NMR spectra (14.1 T) of the four CAS glasses are shown in Figure 5. Previous $^{17}$O NMR work on ambient pressure Ca-aluminosilicate glasses indicates that the peak at 102 ppm is due to NBO bonded to both Si and Ca (Stebbins et al., 1997; Allwardt et al., 2003a). The spectrum of the CAS0 glass also contains a composite bridging oxygen (BO) peak, which can be separated into contributions from Si-O-Al and Si-O-Si peaks (Stebbins et al., 1997; Lee and Stebbins, 2002), although they are severely overlapping in the MAS spectrum and hard to resolve. By comparing the spectrum of CAS0 with the spectra of the CAS5R glasses, it is obvious that as pressure is increased the amount of NBO decreases, the BO composite peak decreases and shifts to higher frequency, and additional intensity appears in the region between the BO and NBO peaks (Figure 5). This additional intensity is likely related to oxygen bonded to high-coordinated Al, but the exact structural interpretation is not obvious. O-17 3QMAS NMR spectra were collected for the CAS glasses (Figure 6) in an attempt to resolve the BO peaks and the new high-pressure peak(s). Previous work using $^{17}$O 3QMAS NMR has shown that there are two predominant, distinct BO species in the ambient pressure CAS glass: Si-O-Al and Si-O-Si (Stebbins et al., 1997; Lee and Stebbins, 2002). A comparison of the spectra for the CAS0 and CAS5R glasses shows that NBO and Si-O-Al species becomes less abundant at high-pressure while there is no obvious change in the intensity of the Si-O-Si peak. As is also observed in the MAS spectra, additional intensity appears in the region between the NBO and Si-O-Al peaks in the spectrum of the CAS5R2 glass, but still cannot be resolved with 3QMAS. Figure 6 also shows that when the standard decompression is used, more Si-O-Al species are present in the structure than is seen in the rapidly decompressed glass. The peak position of the NBO observed in the spectra of high-
pressure glasses appears similar to that seen at ambient pressure although it is possible that this may be due to overlap with the high-pressure peak(s).

The background-subtracted $^{27}$Al MAS NMR spectra (18.8 T) of the three K$_3$AlSi$_3$O$_9$ glasses are shown in Figure 7. The peak widths in these spectra are narrower than those measured for the CAS glasses (Figure 4), which results in no peak overlap and therefore yields less uncertainty in the quantification of different Al-coordinations (Table 2). The KAS0 spectrum is dominated by a $^{[4]}$Al peak centered at 60 ppm, but also contains two other peaks that are the result of about 0.3% $^{[5]}$Al (25 ppm) and about 0.6% crystalline impurity. The KAS glasses also contain much less $^{[5]}$Al and $^{[6]}$Al than the CAS glasses (Table 2). Additionally, unlike the results from the CAS glasses, the $^{[4]}$Al peak of the KAS glass shifts to a slightly lower frequency (58 ppm) with increasing pressure, which is likely due to the change in the next nearest neighbor environment of the $^{[4]}$Al. Peak areas from the spectrum of the rapidly decompressed glass indicate that the structure contains 6% $^{[5]}$Al and less than 0.4% $^{[6]}$Al, which yields an average Al-coordination of only 4.09. However, the spectrum of the KAS5S glass indicates that this glass contains more $^{[5]}$Al and $^{[6]}$Al (12% and 0.7%) than the rapidly decompressed glass, which is an unexpected result as all previous studies have shown that high-coordinated species are lost, not gained during decompression (Robinson, McMillan, and Wolf as referenced in McMillan and Wolf, 1995, pp. 305; Farber and Williams, 1996; Allwardt et al., 2004).

The $^{17}$O MAS NMR spectra (14.1 T) of the three KAS glasses are shown in Figure 8. Previous studies of ambient pressure K-aluminosilicate glasses with $^{17}$O NMR have shown that the peak centered at 75 ppm is due to a Si-NBO surrounded by K$^+$ (Oglesby et al., 2002). Like the CAS glass, the ambient pressure KAS glass also contains a composite BO peak composed of both a Si-O-Al and Si-O-Si component. The intensity of the NBO peak decreases slightly in the spectra for the KAS5S and KAS5R glasses relative to that for KAS0. A small amount of additional intensity appears between 45 and 70 ppm, presumably due to the presence of oxygen bonded to high-coordinated Al, as was also suggested for the $^{17}$O NMR spectra of the CAS glasses. The 3QMAS spectra show that there are two distinct bridging oxygen peaks and an NBO peak of the KAS0 spectrum (Figure 9) and the spectra of the high-
pressure glasses show little change relative to the KAS0 glass. The KAS5R glass lost some of its $^{17}$O-enrichment either during synthesis or storage as the signal to noise ratio of the MAS spectrum is significantly reduced relative to the KAS5S glass, even though it represents twice the number of transients. This has been observed to varying degrees in all high-pressure glasses of this study and those of our previous study (Allwardt et al., 2004).

Discussion

Approximating percentages for unresolved $^{17}$O MAS peaks

The high signal-to-noise ratio and quantitative nature of conventional MAS NMR, combined with the additional resolution available from the 2nd dimension of the 3QMAS spectra can be used to better approximate changes in structure in the CAS and KAS glasses. Although there is overlap of the NBO peak with the high-pressure peak(s) in both the MAS and 3QMAS spectra, it seems reasonable to approximate the percentage of NBO by fitting a single Gaussian to this region (Table 3), as the high-frequency side of the peak is fairly well resolved and the 3QMAS spectra (Figures. 6 and 9) suggest that the peak position and width are not different at high-pressure. Beyond this, there has not been an adequate amount of work with $^{17}$O NMR with crystalline model compounds to reliably assign the additional peak(s) that are exclusive to high-pressure systems. It is apparent that the unresolved intensity between the NBO and BO peaks is related in some way to the introduction of high-coordinated Al into the glass structure, but the exact peak assignment and peak location are not obvious from the available data. To determine whether the high-pressure peak(s) is solely due to $^{[4]}\text{Si-O-[6]}\text{Al}$ or if this also includes some or all of the $^{[4]}\text{Si-O-[5]}\text{Al}$ species, the $^{17}$O MAS spectra of the high-pressure samples were subtracted from the spectra for the 1 atm glasses (Figure 10). This approach will not yield the percentage of oxygen associated with high-coordinated Al as it does not account for the decreasing intensities of the partially overlapping NBO and $^{[4]}\text{Si-O-[4]}\text{Al}$ peaks. Since the percentage of these other peaks decrease with the increase in the percentages of high-coordinated Al, the approximate value obtained from subtracting the spectra likely represents a minimum value for the $^{[4]}\text{Si-O-[5,6]}\text{Al}$ species. These difference
spectra were then fit with one Gaussian peak to approximate the peak area due to oxygen bonded to high-coordinated Al (Table 3). This value can be compared to the value expected from the $^{27}$Al MAS results (Table 3). For example, the $^{27}$Al MAS spectrum of the CAS5R2 glass shows that 38 and 28 percent of the aluminum in this glass are five- and six-coordinated, respectively (Table 2) and if one assumes that there are minimal amounts of oxygen that bridge two high-coordinated Al, as suggested by Lee (2004), the $^{17}$O NMR spectrum should contain 21% $^{[4]}$Si-$^{[5]}$Al (38% (percentage of $^{[5]}$Al) * 5 (coordination number) * 2/18 (aluminum/oxygen ratio) = 21%) and 19% $^{[4]}$Si-$^{[6]}$Al (28% * 6 * 2/18 = 19%). The minimum percentage of $^{[4]}$Si-$^{[x]}$Al measured from the difference spectrum is 25%. The predicted values for the percentage of $^{[4]}$Si-$^{[5]}$Al and $^{[4]}$Si-$^{[6]}$Al species in the other glasses are also shown in Table 3, along with the approximated percentages of $^{[4]}$Si-$^{[x]}$Al. Since the predicted values of $^{[4]}$Si-$^{[6]}$Al are less than the measured minimum values for the high-pressure peak for all samples, it seems very likely that the high-pressure peak is due at least to some degree, to the presence of both $^{[4]}$Si-$^{[5]}$Al and $^{[4]}$Si-$^{[6]}$Al species. Once again, the $^{17}$O spectra measure the immediate environment of the oxygen so it is not directly dependent on the Al-coordination. O-17 spectra for high-pressure crystalline materials like Na- and K-hollandite, (NaAlSi$_3$O$_8$ and KAlSi$_3$O$_8$, Gillet et al., 2000; Finger and Hazen, 2000) and andalusite (Al$_2$SiO$_5$) as well as quantum mechanical modeling of structures with varying Al-O distances and coordinations (Lee, 2004) will be extremely useful in the refinement of peak assignments for $^{17}$O MAS and 3QMAS NMR spectra of high-pressure aluminosilicate glasses.

Compression mechanisms in high-pressure aluminosilicate melts

Although there are uncertainties in peak assignments and difficulties with peak overlap in the $^{17}$O NMR spectra of high-pressure aluminosilicate glasses, they contain useful information for assessing structural changes that occur with increasing pressure. More specifically, by determining the differences between the spectra of the ambient pressure glasses with those for the rapidly decompressed glasses, it is possible to determine how pressure affects the structure. The results from the KAS glasses may
better enable the determination of how the structure changes prior to the formation of high-coordinated Al as it contains very few $^{[5]}$Al and $^{[6]}$Al, while the data from CAS glasses is more favorable for investigating the mechanisms for the generation of high-coordinated Al in high-pressure melts. The structural changes occurring in the glass, if any, are likely to be a decrease in the bond angles associated with the bridging oxygen and/or an increase in the K$^+$ coordination, as suggested by the molecular dynamics studies of Matsui (1996, 1998). Also, the large percentages of $^{[5]}$Al and $^{[6]}$Al species in the CAS glasses (Figure 4) indicates that the increased intensity observed in the 1570 eV region in the XANES spectra of 44 CaO-12 Al$_2$O$_3$-44 SiO$_2$ glasses of Poe et al. (2001) is more likely due to the presence of high-coordinated Al than a narrowing of the T-O-T angle.

O-17 MAS and 3QMAS NMR can measure (or at least approximate) the percentages of Si-O-Al, Si-O-Si, Si-NBO, and $^{[4]}$Si-O-$^{[5,6]}$Al species (Table 3) and the comparison of these percentages provides an excellent opportunity to directly test potential compression mechanisms. Analysis of the 3QMAS spectra from the KAS glass suggests that the percentages of Si-O-Al and Si-O-Si show little variation with pressure suggesting that Al-avoidance, at least for glasses in this compositional range, is not drastically affected by pressure. This may indicate that the decreasing T-O-T angle suggested from the Raman spectra of Sykes et al. (1993) is due to the collapse of the random network (Sykes et al., 1993). However, the depolymerized composition of this study is not an ideal system to investigate the pressure dependence of Al-avoidance due to the low percentages of Al. This indicates that the variation in the amount of Si-O-Al and Si-O-Si species resulting from the pressure dependence of Al-avoidance is negligible for glasses with similar Al/(Al+Si) ratios so changes in the $^{17}$O spectra for the high-pressure CAS glasses are due to the formation of $^{[4]}$Si-O-$^{[5,6]}$Al. Due to the uncertainty in the peak assignments and peak overlap, we used the $^{27}$Al MAS results to predict the percentages of $^{[4]}$Si-O-$^{[5]}$Al and $^{[4]}$Si-O-$^{[6]}$Al species, which allows us to avoid the inherent problems associated with estimating the percentages of these species without adequate constraints. The $^{27}$Al MAS data predicts that the CAS5R2 glass contains 21% $^{[4]}$Si-O-$^{[5]}$Al and 19% $^{[4]}$Si-O-$^{[6]}$Al species and this, combined with mechanisms 5 and 6, would predict that the percentages of the total
oxygen that are $^{[4]}\text{Si-O}^{[4]}\text{Al}$ and Si-NBO should decrease by 29% (21% * 4/5 + 19% * 4/6) and 11% (21%* 1/5 + 19% * 2/6), respectively. Considering the uncertainties in the quantification due to overlapping peaks, the difference of 9% measured for the amount of NBO seems consistent with mechanisms 5 and 6. Qualitatively speaking, the predicted percentages for the loss of $^{[4]}\text{Si-O}^{[4]}\text{Al}$ also seems reasonable for the differences observed in the 3QMAS spectra, although, once again, severe peak overlap prevents a reliable quantification. Additionally, the NBO percentages in the spectra of the KAS 1 and KAS 5R glasses should stay approximately the same (6%* 1/5 + 0.5% * 2/6 = 1%), which is observed in the minor differences between the $^{17}\text{O}$ NMR spectra. These two pieces of evidence support mechanisms 5 and 6, which were suggested by Allwardt et al. (2004) to be responsible for the creation of high-coordinated Al in high-pressure aluminosilicate glasses.

*Effect of slower decompression on the structure of high-pressure glasses*

It is clear that at least some of the high-pressure structural changes of aluminosilicate melts are captured in glasses that are measured at ambient conditions. However, a determination of the effect of decompression on the glass structure is an essential component in understanding how studies measuring structure at one bar relate to the glass structure present at high-pressure. Although studies of ambient pressure samples alone may not observe the full extent of the changes that occur during decompression, the quantitative nature of NMR can constrain the manner in which the structure changes. A comparison of the $^{27}\text{Al}$ MAS spectra of the CAS5R glasses with that for the CAS5S glass shows that 15% of the aluminum (representing about 4% of the total network formers) reverts to tetrahedral coordination during the slower decompression (Table 2). In our previous study on high-pressure $\text{K}_2\text{Si}_4\text{O}_9$ glasses, there was much less of a difference between glasses with differing decompression rates (Allwardt et al., 2004), which may suggest that Al polyhedra are more susceptible to local relaxation during decompression than Si groups. In addition to the decrease in the average Al-coordination, the $^{17}\text{O}$ NMR data show that there is a higher percentage of NBO (~2% of the oxygen) in CAS5S relative to CAS5R. Based on the reversal of mechanisms 5 and 6, one would predict that 2% of the total oxygen
would become NBO from the conversion of \([^{[4]}\text{Si-O-}^{[5,6]}\text{Al}]\) species to NBO and \([^{[4]}\text{Si-O-}^{[4]}\text{Al}]\). This indicates that the \([^{[5]}\text{Al}]\) and \([^{[6]}\text{Al}]\) that are lost during decompression are simply due to the reversal of mechanisms 5 and 6, although this is not the only way to explain the structural differences between the glasses.

An unexpected result of this study is that the KAS5R contains less high-coordinated Al than the KASS5S sample (Table 2). One explanation for this could be that the average Al-coordination increases as the sample is being held at room temperature during the gradual decompression. To test this potential explanation, a KAS glass was compressed to 6 GPa and decompressed without heating (KAS6, table 1). The peak fitting of the \(^{27}\text{Al}\) MAS spectrum of this glass (not shown) indicates that it contains 5.5\% \([^{[5]}\text{Al}]\) and less than 0.4\% \([^{[6]}\text{Al}]\) (approximate detection limit), which is significantly less than the 12.2\% and 0.7\%, respectively, measured for the KASS5S (Table 2). This suggests that this explanation cannot completely account for the increase in \([^{[5]}\text{Al}]\) and \([^{[6]}\text{Al}]\) suggested to occur during the slower decompression. However, due to structural differences, glasses quenched at pressure would likely behave somewhat differently to room temperature compression/decompression than glasses that were only compressed and decompressed without annealing/melting. Since there were no obvious experimental differences between the experiments, an alternate explanation for the differences between the 5 GPa KAS glasses is that it simply indicates problems with the reproducibility in the synthesis of high-pressure glasses, however further work remains to determine whether problems with reproducibility are the reason for this unexpected results.

Reproducibility of the structure of high-pressure glasses using a multi-anvil apparatus

To directly test the reproducibility of high-pressure aluminosilicate glasses in an ideal case, two CAS5R samples were synthesized in separate capsules during the same multi-anvil experiment (CAS5R1 and CAS5R2). Figure 4 shows that CAS5R1 contains more \([^{[6]}\text{Al}]\) and less \([^{[5]}\text{Al}]\) than CAS5R2. Quantifying the spectra reveals that the variation in the different aluminum coordinations is about 3 percent of the total aluminum for any given Al-coordination (Table 2), which translates into a variation in the average Al-coordination of about 0.1. This may result from subtle differences in
the cooling rates of different regions of the multi-anvil assembly, which would produce portions of the glass with slightly different fictive temperatures. A better way to consider these structural changes is to think about them in terms of the percentage of network formers. Realistically, the actual reproducibility of high-pressure glasses is less than that reported here as small compositional variations, temperature and pressure calibrations, and cooling characteristics of different assembly sizes can all be factors in reproducing experimental data, which could be especially true for samples synthesized at different multi-anvil facilities. These data, combined with the differences observed in the KAS5R and KAS5S glasses, could suggest that high-pressure glasses are less reproducible than previously thought and the main limitation to accurately determining the structure of high-pressure glasses lies in the reproducibility of the glasses, not in the quantification of the NMR spectra. Once again, this stresses the importance of collecting all structural measurements (e.g. $^{17}$O, $^{27}$Al, $^{29}$Si, Raman, etc.) on the same glass and not inferring structural speciation from previous work in similar systems.

Conclusions

From this and other recent studies, it is clear that there is still much to do in determining the structure of "geologically relevant" high-pressure melts. With this said, there has been significant progress toward this goal in recent years as spectroscopic methods have improved over those used in earlier studies. We conclude, based on the data presented in this study:

1. As has been observed in previous studies, the average coordination of the network formers increases with increasing pressure.

2. The field strength of the modifier cation plays a key role in the amount of high-coordinated Al present in a high-pressure aluminosilicate glass where a higher field strength (e.g. CAS) yields more $^{[5,6]}$Al than a lower field strength (KAS). This correlation between the Al-coordination and the field strength of the modifier cation is consistent with previous work on alkaline-earth boroaluminates (Bunker et al., 1991).
3. Our data supports the mechanisms proposed by Allwardt et al. (2004) for creating $^{[5]}\text{Al}$ and $^{[6]}\text{Al}$ in high-pressure aluminosilicate melts: $\text{Si-NBO} + 4 \text{ Si-O-Al} \rightarrow 5 \text{ [4]Si-O-[5]Al}$ and $2 \text{ Si-NBO} + 4 \text{ Si-O-Al} \rightarrow 6 \text{ [4]Si-O-[6]Al}$.

4. The structure of glasses with drastically different decompression rates is not the same, which suggests that decompression affects the structure of high-pressure aluminosilicate glasses.

5. More work remains to determine how reproducible high-pressure glass structure is in multi-anvil apparatuses, but it seems as though the limitation in determining the structural speciation lies in the reproducibility of the glass structure, not the detection limits of NMR.

Acknowledgements

We are indebted to Drs. Brent Poe and Marc Hirschmann for valuable discussions on high-pressure glass/melt structure and assistance in the synthesis of high-pressure glasses. We would also like to thank Drs. Eiji Ohtani, Mike Toplis and an anonymous reviewer for helpful comments on the original manuscript and Drs. Jiuhua Chen, Yanbin Wang, Tom Duffy, Guoyin Shen, and Larissa Dobrzynetskaya for organizing this review volume and offering us the opportunity to contribute. JRA and JFS thank the National Science Foundation (USA) for grant number EAR-0104926 and BCS and DJF acknowledge funding from the Bayerisches Geoinstitut. We are especially grateful to the Bayerisches Geoinstitut visitor’s program for additional funding and for facilitating the visit of JRA to their laboratories.

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Table 7.1 Experimental conditions for the high-pressure samples

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Table 7.2 Results from peak fitting the $^{27}$Al MAS NMR spectra. Columns show the relative percentages of Al species and mean coordination numbers for both Al and total network formers (Al+Si).

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Table 7.3 Measured and predicted percentages of oxygen species

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Figure 7.1 Background-subtracted $^{27}$Al MAS NMR (18.8 Tesla) showing how the choice of modifier cation affects the percentage of $[^{5,6}]$Al in $M^{x+}_{(9-3x)}Al_2Si_6O_{18}$ glasses quenched from the melt at 5 GPa (Allwardt et al., 2003c). The sample names indicate the modifier cation used in the aluminosilicate glass (e.g. CAS = calcium aluminosilicate). The "*" denotes a spinning sideband.
Figure 7.2 Background-subtracted $^{27}$Al MAS NMR spectra (18.8 T) showing the effect of temperature on the average Al-coordination in NaAlSi$_3$O$_8$ (Ab) and Na$_3$AlSi$_7$O$_{17}$ (NAS) glasses at 10 GPa. (Allwardt et al., 2005a). The high temperature samples were quenched from the liquid (2200 °C) while the low-T glasses were annealed for 12 hours near the glass transition temperature (630 °C and 475 °C, respectively).
Figure 7.3 Background-subtracted $^{27}$Al MAS NMR spectra illustrating how the external magnetic field affects the spectra for a high-pressure 10 GPa NaAlSi$_3$O$_8$ glass that was quenched from a melt (Allwardt et al., 2005a).
Figure 7.4 Background-subtracted $^{27}$Al MAS spectra (18.8 T) of the Ca$_3$Al$_2$Si$_6$O$_{18}$ glasses of this study. Experimental conditions and compositions are shown in Table 7.1.
Figure 7.5 O-17 MAS spectra (14.1 T) of the Ca$_3$Al$_2$Si$_6$O$_{18}$ glasses.
Figure 7.6 O-17 3QMAS spectra (14.1 T) of the Ca$_3$Al$_2$Si$_6$O$_{18}$ glasses. The regions for the relevant structural species are labeled, while the justification for the $^{29}$Si-O-$^{27,28}$Al peak(s) is discussed in the text. Contours are drawn at intervals of 5% and range from 8% to 98%.
Figure 7.7 Background-subtracted $^{27}$Al MAS spectra (18.8 T) of the K$_3$AlSi$_3$O$_9$ glasses of this study.
Figure 7.8 O-17 MAS spectra (14.1 T) of the $\text{K}_3\text{AlSi}_3\text{O}_9$ glasses. The "**" denotes a spinning sideband of the zirconia rotor.
Figure 7.9 O-17 3QMAS spectra (14.1 T) of the K$_3$AlSi$_3$O$_9$ glasses. The $[^{28}\text{Si}-^{16}\text{O}-^{27,28}\text{Al}]$ region is approximated based on increased intensity in this region and its similarity to that seen in the high-pressure CAS glasses. Contours are drawn at intervals of 5% and range from 8% to 98%.
Figure 7.10 The $^{17}$O MAS NMR spectra of CAS0 (dashed) and CAS5R2 (solid) shown to emphasize the differences between the spectra. The spectrum labeled “difference” is the result of subtracting CAS0 from CAS5R2 and the shaded region was used to approximate the minimum value of the $^{[4]}$Si-O-$^{[5,6]}$Al present in the spectrum.
Appendix One

Procedure for sink-float density measurements of small high-pressure glasses
Introduction

Density measurements on small (< 1 mg), high-pressure glasses have been measured with sink-float techniques using heavy liquids. The uncertainties in our measurements have been assessed by measuring the density of known materials during each set of measurements and found to be about 0.02 g/cm³. This assessment also suggests that the present technique has roughly half the error as that previously used for measuring of high-pressure glass density (Poe et al., 2001).

Materials:

- Glass(es) of known density (e.g. CaMgSi₂O₆, NaAlSi₃O₈, etc.)
- Glasses with unknown densities (no bubbles, metal, or crystalline material!)
- Diodomethane (MEI)
- Acetone
- watchglass
- pipette and Erlenmeyer flask
- glass cylinder with cover (liquid)
- funnel (glass)
- personal protective equipment
- hazardous waste containers (bottle and plastic bags (2), both with dated hazardous material tags!!)

General Comments:

- Read the MSDS reports for MEI and acetone
- Do not breathe the fumes and keep the solution in the fume hood whenever possible.
- Acetone evaporates so it is important to know the mass of the MEI in the solution and the total mass of the solution. From these two measurements, it is possible to calculate the mass of acetone and more importantly, the density of the solution.
• Also, please note that the solution will have density stratification if it sits long enough. To avoid this, make sure that you mix the solution by swirling the solution around before making a sink-float measurement

• **NEVER** put anything in or take anything out of the cylinder as this will remove an unknown amount of solution and render your results useless!!!

• Be very careful of the surface tension of the solution (something can float when it shouldn’t!). One way around this is to swirl the cylinder while the container is tilted (~30°).

• When mixing solutions, always keep the solution covered.

• It’s a good idea to use a glass sample with a known density as an internal standard (e.g. diopside, albite, etc). This allows you to assess the quality of the data. Remember, MEI will also evaporate if given enough time.

**Procedure:**

1. Choose pieces of glass that appear homogeneous. Keep in mind that bubbles, crystalline material and metal can affect your measurements.

2. Keep very careful notes about the details of each sample (e.g. mass, shape, color, etc.) and anything else that could be used to distinguish it from the others.

3. Try to pick samples that are distinctive from the others based on color, shape, size, etc, as this makes distinguishing the sample in the solution easier.

4. Consider the relative densities of your samples measurement (e.g. which sample should be most/least dense) as this may be an important way to distinguish them during the.

5. Make 3 columns in your lab book: **result** (sink/float, important details), **mass of glass cylinder** (containing Acetone-MEI solution), and **mass of MEI dropper** w/ bottle containing extra MEI.

6. Weigh the glass cylinder with the samples and record the mass.

7. Zero the scale, and record this in the lab book for the sample container (and glasses) mass (so you’re only recording the mass of the solution).
8. (if you need a bathroom break, now's the time because you might be here a while...) Allow ~2 hours for these measurements. It rarely takes this long, but just in case...

9. **PUT ON GLASSES, LABCOAT, AND GLOVES !!!!**

10. Add **roughly** 3 g of MEI to the container with the unknowns. Weigh this and record it under the **glass cylinder** column. This will be your initial mass of MEI and is a **VERY** important measurement.

11. Weigh the MEI dropper and bottle, record this in column 3 (mass of MEI dropper); this will be your control to assess your evaporation of MEI!!! Additionally, this is important in case you end up making another round of measurements.

12. Put the permanent MEI bottle back in chemical storage.

13. Put some acetone in the Erlenmeyer flask and pipette a few drops of acetone into the sample container, swirl the solution, and record the mass and result (what samples, if any, sink).

14. If a glass sinks, allow some time (a minute?) for acetone to evaporate and weigh the sample again; record the mass and the result. Do this until the sample floats and be careful of the surface tension concerns (see next point and general comments for more information). A general rule of thumb: for ~3 grams of MEI, 3 mg of acetone is equal to a density difference of 0.01 g/cm$^3$.

15. If the glass floats, keep in mind that the surface tension of the solution may be keeping the glass at the surface when it should have sunk. Be sure that you see the glass of interest below the surface and observe it float to the top (or sink to the bottom) before recording the measurement.

16. When you get a glass to sink and float within an acceptable range of masses (maximum of ~ 3mg for 3 g of MEI), add more acetone and repeat steps 13 to 15 until measurements have been made on all samples. At this point, all glasses should be at the bottom of the container.

17. Once all unknowns have been measured with multiple sink/float experiments, there is a choice of whether to make another round of measurements or finish and clean up. If another round of measurements are necessary, add enough
MEI so that all the glasses float (NOTE: measure the mass of the MEI container before adding MEI to assess whether MEI has evaporated and so you can get a very accurate measure of the amount of MEI in the solution). Record the mass of the cylinder AND the MEI container after the addition. Repeat steps 12-16.

Clean up:

18. Remove the glass samples with a tweezers and place them on the watchglass. Rinse the samples with acetone and move them to a clean place to dry.
19. Put the unused MEI back into the permanent storage bottle that goes in the chemical storage cabinet.
20. Dump all solutions that contain MEI into the hazardous waste bottle using a funnel.
21. Thoroughly rinse all glassware with acetone and pour this solution into the hazardous waste bottle.
22. Place all paper towels that were used during the experiment into plastic hazardous waste bags (double bagged). Additionally, if you dripped any MEI on any nearby paper, this goes into the hazardous waste bag too.
23. Take off gloves, glasses, and lab coat and wash your hands.
24. Record the results in EXCEL (see Table A.1.1) and determine the density of the unknowns (Table A.1.2).

**Relevant Equations**

\[
\rho_{\text{solution}} = \frac{(\rho_{\text{acetone}} \times \rho_{\text{MEI}}) + \rho_{\text{MEI}} \times \rho_{\text{acetone}} \times (Q))/(Q \times \rho_{\text{MEI}} + \rho_{\text{acetone}})}
\]

\[
Q = \frac{m_{\text{acetone}}}{m_{\text{MEI}}}
\]

\[
m_{\text{acetone}} = m_{\text{solution}} - m_{\text{MEI}}
\]

\[
\rho_{\text{acetone}} = 0.79 \text{ g/cm}^3
\]

\[
\rho_{\text{MEI}} = 3.32 \text{ g/cm}^3
\]
Acknowledgements
This procedure is modified from a method provided by Dr. Steve Feller (Coe College). I would also like to thank Derek Lerch (Stanford) for very useful discussions on the safe use of heavy liquids.

References
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<th>m-soln (g)</th>
<th>m acetone (g)</th>
<th>Q density-liq result (g/cm³)</th>
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Table A.1.2 Results from measurements from previous table showing minimum and maximum density of glasses

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Appendix Two

Aluminum coordination and density of 4 and 5 component high-pressure aluminosilicate glasses

The text of this appendix will be expanded and submitted as a manuscript
**Introduction**

The density of silicate melts increases with pressure and the magnitude of this change has been shown to be compositionally dependent (Rigden et al., 1988; Ohtani and Maeda, 2001). Glasses are typically used as a first approximation for the structure of melts as they represent the structure present in the liquid at the glass transition temperature. Previous MAS NMR studies have shown that Al is much more susceptible to coordination changes than Si in high-pressure aluminosilicate glasses (Yarger et al., 1995). One of our previous studies has shown that the Al speciation and densification of the compositionally similar Ca₃Al₂Si₆O₁₈ (CAS) and K₆Al₂Si₆O₁₈ (KAS) glasses are drastically different (Allwardt et al., 2005). For example, the average Al coordination of the two glasses at 5 GPa is 4.75 and 4.12, respectively. Additionally, CAS5 has twice the density increase as KAS5. Since there are such large differences between the structure and density of these compositionally similar glasses (NBO/T, Al:Si ratio, etc.), the goal of the present study is to isolate the effect that mixing of multiple modifier cations (Ca, K, and Mg) has on the Al-speciation and how this structural change affects the densification of high-pressure glass. This study represents the first attempt, from the perspective of structure, to understand how multiple modifier cations affect the compressibility of high pressure melts.

**Experimental Methods**

This study has synthesized high pressure (2 to 8 GPa) aluminosilicate glasses with multiple modifier cations (Table A.2.1) and measured the density and percentage of different aluminum coordinations (Table A.2.2). The multiple modifier glass compositions and oil pressures were chosen so our previous results (Allwardt et al., 2005) could be used as endmembers. Similar to the previous study, all glasses were quenched from high-pressure melts in piston-cylinder and multi-anvil presses and the experimental conditions are shown in table A.2.1. The details of the experimental procedures can be found in chapters 5 and 7 where the only exception is that the 8 GPa glasses for this study were made in 25/15 assemblies where two samples were synthesized in a single multi-anvil experiment. The procedures for the $^{27}$Al MAS and density measurements are described in chapter 5 and appendix 1, respectively.
Results

The $^{27}\text{Al}$ MAS NMR spectra (18.8 Tesla) indicate that most of the Al cations are four-coordinated in the ambient pressure glasses of this study (Fig. A.2.1). The $^{27}\text{Al}$ MAS spectra for the high pressure glasses (Fig. A.2.2) clearly show that more high coordinated Al are present at elevated pressures for all six compositions (Fig. A.2.3 and Table A.2.2). Similar to the findings of chapter 5, higher average field strength modifier cations (e.g. $\text{K}^+<\text{Na}^+<\text{Ca}^{2+}<\text{Mg}^{2+}$) produce more high-coordinated Al (Fig. A.2.4). Previous work has shown a similar trend for ambient pressure alkaline-earth aluminoborate glasses (Bunker et al., 1991) and suggested that this is likely due to the stronger modifier cations (e.g. $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$) out-competing some nearby aluminum cations for short, strong bonds to oxygen. When multiple modifier cations are present (e.g. Ca and K in the CKAS glasses), the $^{27}\text{Al}$ MAS spectra (Fig. A.2.5) and the quantification of the spectra (Fig. A.2.6a) indicate that the average Al-coordination predicted from the ternary glasses overestimates the measured value. This is also observed for the five component glasses (CMKAS) along the C2KAS-CMAS join (Fig. A.2.6b) and likely suggests that modifier cation mixing affects the driving forces involved in the mechanism(s) that generate high-coordinated Al. Additionally, it should be noted that $^{29}\text{Si}$ MAS NMR spectra were collected for a few samples (not shown) and indicates that, within detection limits (~2%), only $^{4}\text{Si}$ exist in these glasses.

The density of the mixed modifier glasses was also measured and are shown to increase with increasing synthesis pressure (Fig. A.2.7). Similar to the average Al-coordination, density predicted from endmember glasses appears to overestimate the density for the 3 and 5 GPa glasses. Interestingly, at 8 GPa both the predicted average Al-coordination and the glass density are similar to the measured value (Figs. A.2.5a and A.2.7a), which may indicate that at pressures above 8 GPa it is possible to predict the density and Al coordination of a melt based on the endmember values. However, it needs to be noted that this observation would be affected by the generation of $^{5}\text{Si}$ (and $^{16}\text{Si}$) at still higher pressures.
Figure 5.3 showed that the density of a high-pressure glass appears to be correlated to the abundance of high-coordinated Al in the glass structure. The results for the KAS glasses suggested that there is likely a change in the dominant compression mechanism(s) near 3 GPa so to investigate this further, we have synthesized 2 more CAS glasses (2 and 3 GPa) and added a total of 10 multiple modifier cation high-pressure glasses. The density and average $^{[8]}$Al for the glasses along the CAS-KAS join (Fig. A.2.9a) indicate that there is a very obvious change in slope for all compositions. Additionally, this is also seen in the CMAS (filled squares) and CMKAS (open squares) glasses (Fig. A.2.9b). These observations suggest that there are two distinct compression regimes in this pressure range, where the high pressure mechanism(s) is dominated by the generation of $^{[5]}$Al and $^{[6]}$Al and the low pressure mechanism(s) involves densification with little change in the Al-coordination. The pressure of this transition appears to be compositionally dependent. This observation is shown more clearly in figure A.2.9a as the CAS curve appears to change slope at a pressure below 2 GPa, while this change occurs between 3 and 5 GPa in the C2KAS and KAS glasses. Finally, the slope for the higher pressure mechanism appears to have a slight compositional dependence as CAS has the steepest slope, which likely results from compressibility differences between CaO$_x$ and KO$_x$ polyhedra.

**Discussion**

An important aspect of this work is that it shows that the pressure-induced changes in structure and density can be quite different among compositionally similar glasses. This may be one aspect of the observation that compositional differences affect the melt compressibility (Suzuki and Ohtani, 2003). Additionally, previous investigators have suggested that the abundance of $^{[5]}$Al and NBO may dominate viscous flow in high-pressure silicate melts so these results would also suggest that the differences in structure between these compositionally similar glasses may indicate that there are also large differences in the pressure dependence of melt viscosity. Further studies need to verify this prediction. Additionally, models of gravitationally stable mantle melts at 410 km usually involve volatile-rich, basic to ultrabasic melts.
(Revenaugh and Sipkin, 1995; Bercovicci and Karato, 2003), so future work in this field needs to concentrate on determining how composition affects the structure and properties of these melts at high pressure. Since the bulk of the high-pressure research presented in this dissertation was done on dry, Fe-free, “high” silica aluminosilicates, the most obvious extensions of this work would be to investigate how the structure is affected by Fe, H₂O, lower amounts of silica, and a higher NBO/T. Although they are much more relevant to the Earth, experiments in these systems all suffer from major difficulties. For instance, the presence of Fe prevents the use of NMR and the latter three decrease the glass-forming ability of the aluminosilicate liquids. Presently, the two most promising avenues around these experimental difficulties are the use of synchrotron radiation for in-situ studies and/or computer modeling for structure and property measurements.

Acknowledgements

The authors thank Dr. Corey Liu and Prof. Puglisi for access to the 18.8 Tesla NMR. We also thank the US National Science Foundation for grant numbers EAR-0104926 (JRA and JFS) and OCE 9876255 (MMH) and the Bayerisches Geoinstitut (DJF) for continued funding.

References


Table A.2.1 Composition of ambient-pressure glasses used as starting materials for the high-pressure studies

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<tr>
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<th>CaO</th>
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<th>SiO₂</th>
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Note: Average modifier cation field strength (Z/R²) values are from Brown et al., (1995).
Table A.2.2 Experimental conditions, Al-speciation, and density of glasses

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Notes: Density is measured on glasses at ambient conditions and the measurement error is about 0.02 g/cm³, which is estimated using the difference between the measured and known densities for the standards (e.g. CaMgSi₂O₆ glass).
Figure A.2.1 Background-subtracted $^{27}$Al MAS NMR spectra (18.8T) of the ambient pressure glasses. The "**" indicate signal resulting from a small amount of crystalline impurities.
**Figure A.2.2** Background-subtracted $^{27}$Al MAS NMR spectra (18.8T) of the high-pressure glasses. The "**" indicates signal resulting from a small amount of crystalline impurities.
Figure A.2.3 Pressure dependence of the average Al coordination for the aluminosilicate glasses.
Figure A.2.4 Average modifier cation field strength versus the average Al coordination of high-pressure aluminosilicate glasses.
Figure A.2.5 $^{27}$Al MAS NMR spectra collected for CKAS glasses at 5 and 8 GPa and that predicted based on KAS and CAS endmembers.
Figure A.2.6 Compositional dependence of the average Al coordination along the (a) CAS-KAS and (b) C2KAS-CMAS joins.
Figure A.2.7 Pressure dependence of density for the six aluminosilicate compositions.
Figure A.2.8 Compositional dependence of density along the (a) CAS-KAS and (b) C2KAS-CMAS joins.
Figure A.2.9  Average Al coordination versus density of the (a) CKAS and (b) other glasses. Numbers to the upper right of the data points represent the synthesis pressure for the CKAS glasses.
Appendix Three

Ca-Mg and Ca-Mg-K mixing in 4 and 5 component aluminosilicate glasses

The figures and a more thorough discussion of the data will be submitted as a manuscript

Jeffrey R. Allwardt and Jonathan F. Stebbins
Introduction

The previous viscosity study of Neuville and Richet (1991) and our $^{17}$O NMR study (Allwardt and Stebbins, 2004) have used independent methods to determine that Ca-Mg mixing is random in silicate glasses. Additionally, Neuville and Richet (1991) also measured the viscosity of Ca-Mg garnet ([Ca,Mg]$_3$Al$_2$Si$_3$O$_{12}$) composition glasses and interpreted the data as evidence that Ca and Mg mix randomly in these glasses. The present study is meant to assess Ca-Mg mixing in aluminosilicate glasses at the atomic level.

Experimental Procedures

The ambient pressure glasses were synthesized by standard melt-quench techniques. High-pressure glasses were synthesized by similar methods as previously described in chapter 5 and $^{17}$O MAS and 3QMAS NMR experiments were performed following the techniques described in chapter 3.

Results

Figure A.3.1 presents two new spectra and two previously published $^{17}$O MAS NMR spectra (14.1 Tesla). The CaMgSi$_2$O$_6$ (CMS0) and Ca$_3$Al$_2$Si$_6$O$_{18}$ (CAS0) glasses (Allwardt and Stebbins, 2004; Allwardt et al., 2005) are presented here because the glasses contain comparable structural species to the Ca-Mg (CMAS) and Ca-Mg-K aluminosilicate (CMKAS) glasses. The intensity of the CMS0 spectrum has been divided by three to normalize the percentage of NBO (22%) among spectra in the figure and shows two “peaks.” The peak centered at ~ 55 ppm represents Si-O-Si species (Stebbins et al., 1997), while the broad “peak” has been interpreted to be a result of randomly mixed Ca and Mg cations surrounding NBO ([Ca,Mg]-NBO, Allwardt and Stebbins, 2004). The spectrum for CAS0 also clearly shows two peaks. The high-frequency peak (~100 ppm) is due to Mg-free, Ca-NBO and, the low frequency “peak” is a composite resulting from overlapping Al-O-Si and Si-O-Si peaks (Stebbins et al., 1997). These features can also be seen in the $^{17}$O 3QMAS spectra (Fig. A.3.2) where the conventional MAS dimension portrays a slightly distorted view of the MAS spectra (Fig. A.3.1). A comparison of the relative
intensities of the 100 ppm region (MAS dimension) of the spectra of the CMAS0 glass (Figs. A.3.1 and A.3.2) lacks intensity relative to the CMS0 spectrum, which indicates that Ca-Mg mixing in the CMAS0 glass is not disordered at T_g as suggested by the interpretation of the viscosity experiments. This could be due to the differing compositions, slight temperature differences, or a possible over interpretation of the viscosity data. This will be investigated in future studies (see below).

The replacement of a small amount of Ca or Mg cations in the glass structure with K appears to make the Ca-Mg mixing more random. This likely occurs because the K⁺ cations associate with the BO, which allows the higher field strength Ca²⁺ and Mg²⁺ cations to associate with the more underbonded NBO. The presence of K-NBO cannot be completely excluded from the data as these species are represented by a peak at ~70 ppm in $^{17}$O MAS spectra (e.g. Fig. 7.9), which overlaps with the composite NBO peak in the CMAS system. Additional evidence for the absence of K-NBO is that the peak shape for the Si-O-Si species in the CMKAS glass resembles that measured for KAS glasses (Fig. 7.9).

The $^{17}$O MAS spectra of the high-pressure glasses (Fig. A.3.3) reveal that the relative abundance of Ca-NBO (Mg-free) remains constant with increasing pressure (and $[^{[3]}]$Al). This likely indicates that the NBO associated with the higher field-strength modifier cations (Mg-NBO or [Ca,Mg]-NBO) are involved in the generation of high-coordinated Al. Additionally, this preference may have important implications to the structural differences of compositionally similar high-pressure glasses shown in the previous appendix.

Discussion

An important aspect of this work is that it shows that one should not assume that mixing in silicates and aluminosilicates is the same and that caution should be used in extending results measured on simple systems to more complex compositions. This finding should not be surprising since aluminosilicate glasses can contain structural species (e.g. Si-O-Al and Al-O-Al) that cannot exist in silicate glasses. A more thorough investigation of Ca-Mg mixing in CMAS aluminosilicate glasses is underway in a collaboration with Kimberly Kelsey. This study consists of collecting
$^{17}$O MAS and 3QMAS spectra for 5 to 7 glasses along the garnet ([Ca,Mg]$_3$Al$_2$Si$_3$O$_{12}$) join to better determine whether Ca-Mg cations mix randomly in aluminosilicate glasses and assess whether glasses with different NBO/T and Al/(Al+Si) ratios have drastically different modifier cation mixing behaviors.

**Acknowledgements**

We would like to thank the US National Science Foundation for grant numbers EAR-0104926.

**References**


Table A.3.1 Sample names and compositions (in mol%)

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Figure A.3.1 O-17 MAS spectra (14.1 T) of the ambient-pressure glasses.
Figure A.3.2 O-17 3QMAS spectra (14.1 T) of the ambient-pressure glasses, where the contour lines are from 5% to 95%. The contour interval is 5% for the aluminosilicates and 15% for CMS0. The CMS0 peak is scaled differently to show what a randomly mixed [Ca,Mg]-NBO peak looks like in a glass with 22% NBO.
Figure A.3.3 O-17 MAS spectra (14.1 T) of the high-pressure CMAS and CMKAS glasses.
Figure A.3.4 O-17 3QMAS spectra (14.1 T) of the CMAS glasses, where the contour lines are from 5% to 95% and spaced at intervals of 5%.
Appendix Four

Falling-sphere viscosity measurements of Ca$_3$Al$_2$Si$_6$O$_{18}$ melts to 5 GPa: Possible effect of pressure-induced structural transitions on viscosity of high-pressure melts.

These are still somewhat preliminary data and results. They may be added to Appendix 2 and submitted as a manuscript

Introduction

The viscosity of high-pressure silicate melts has been shown to be highly dependent on composition, temperature, and pressure (Kushiro et al., 1976; Kushiro, 1986; Wolf and McMillan, 1995; Reid et al., 2003; Tinker et al., 2003; Liebske et al., 2005). Numerous studies have proposed that pressure-induced structural changes have direct implications to melt viscosity (Waff, 1975; Stolper and Ahrens, 1987; Poe et al., 1997; Poe and Rubie, 2000; Tinker et al., 2003; Liebske et al., 2005); however, few, if any studies have directly shown how known structural changes affect the viscosity of high-pressure melts. Most believe that the Al-speciation and the abundance of NBO may dominate melt viscosity at elevated pressures (Kushiro, 1986; Lee et al., 2004) and that an increase in the $[^{5}]$Al decreases melt viscosity while a decrease in NBO should act in an opposite manner. Since NBO are consumed to create $[^{5}]$Al at high pressure, the net viscosity change could be positive or negative. Furthermore, it’s not completely clear whether pressure-induced octahedral aluminum act as network formers (e.g. $[^{6}]$Al in garnets, spinels, corundum, etc.) or network modifiers (e.g. $[^{6}]$Al in peraluminous glasses and melts, Mysen and Richet, 2005). The presence of known structural transitions measured in the CAS compositions (Allwardt et al., 2005a, 2005b) represents an excellent opportunity to investigate how pressure-induced structural species affect melt viscosity. For this reason, we have conducted falling sphere viscometry experiments at SPring-8. These measurements utilize synchrotron radiation to image the descent of metallic spheres in a high-pressure and temperature melt. The viscosity of the melt can be determined by calculating the terminal velocity of the sphere and using Stoke’s Law.

Experimental Methods

Cobalt-free $\text{Ca}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ glass was used as starting material and synthesized by the same experimental procedure explained in chapter 7. The glass was ground and packed into a 1.4 mm ID X 2.6 mm long Mo-capsule with a 0.8 mm ID X 0.8 mm long sphere trap on the top. One Re and one Rh sphere, each roughly 150 μm in diameter, are placed in the sphere trap and another smaller Re (~130 μm) sphere is placed in the center of the capsule. The smaller Re-sphere is used as a marker sphere.
to determine when the CAS glass has melted and the other two spheres (in the sphere trap) are measurement spheres. The sphere trap is meant to maintain the two spheres outside the hottest part of the assembly during heating to decrease the probability that the spheres will fall before the temperature is stabilized. In theory, this allows a more homogeneous temperature distribution inside the capsule and, since viscosity is highly dependent on the measurement temperature, a more robust viscosity measurement. Additionally, the use of two spheres means that two independent viscosity measurements can be made during each multianvil experiment, although this was only achieved for S1333 (Table A.4.1). Sphere diameters were determined by scanning electron microscopy where the accuracy has been previously estimated to be \( \pm 2 \mu m \) (Liebske et al., 2005).

High-pressure falling spheres are imaged by x-ray radiography in the multianvil press (SPEED 1500) at beamline BL04B1 at SPring 8 in Japan. This procedure digitally records spheres falling in real time by density contrast imaging with a CCD camera (Kanzaki et al., 1987). Pressure is applied to the sample with six outer steel anvils in the DIA geometry. The outer anvils compress eight truncated tungsten carbide (WC) cubes (12 mm truncations), which push on the eight sides of a \( \text{Cr}_2\text{O}_3 \)-doped \( \text{MgO} \) pressure assembly (18 mm edge length). The \( \text{LaCrO}_3 \) heater inside the assembly is surrounded by a “pressure marker,” which consists of equal portions of \( \text{MgO} \) and hexagonal-boron nitride (h-BN) powders. Pressure is determined by measuring the lattice constants of \( \text{MgO} \) at high-pressure and temperature using the equation of state of Jamieson et al., (1982). The h-BN is used to impede \( \text{MgO} \) grain growth at high-temperature, but can react with the Mo-capsule at high temperature and pressure (Liebske et al., 2005).

Each assembly was compressed at ambient temperature to the desired pressure and then heated to 1273 K to collect the X-ray diffraction pattern of the \( \text{MgO} \) and determine the experimental pressure (Table A.4.1). After the pressure determination, the assemblies are heated to the experimental temperatures (Table A.4.1). Since there are no high-pressure phase diagrams for the \( \text{Ca}_3\text{Al}_2\text{Si}_6\text{O}_{18} \) composition, the power to the furnace is increased until the marker sphere (smaller Re-sphere) begins to fall. At this point, the power to the furnace is held constant to try to stabilize the temperature.
inside the assembly. Eventually, the CAS glass inside the sphere trap melts and the "measurement spheres" fall in the silicate melt, which is recorded by the CCD camera. The digital video of the experiment can be converted to individual digital images for processing and advanced frame-by-frame (each frame is one-thirtieth of a second) to measure the position of the sphere relative to time. This study used similar experimental procedures as those detailed in Liebske et al., (2005) so additional experimental information and diagrams of the capsule and assembly (Fig. 1b of Liebske et al., 2005) can be found there.

Results

The initial image of the interior of the assembly is shown in figure A.4.1a. This image shows the marker sphere surrounded by CAS glass, the capsule walls, and the MgO+h-BN pressure medium. The dark horizontal borders at the top and bottom of the image are the WC anvils. Shortly after the CAS glass is melted, the spheres descend in the high-pressure silicate melt (Fig. A.4.1b). Terminal velocities are determined from the time-position relationships (Fig. A.4.2), which can be used to calculate the viscosity ($\eta$) using a modified form of Stoke's Law:

$$\eta = 2g\Delta \rho r^2/9v \left[ 1 - 2.104\left( r/r_c \right) + 2.09\left( r/r_c \right)^3 - 0.95\left( r/r_c \right)^5 \right]$$

(1)

where $g$ is the acceleration due to gravity, $r$ is the radius of the falling sphere, $\Delta \rho$ is the density difference between the sphere and melt, $v$ is the terminal velocity, and $r_c$ is the internal radius of the capsule. The term in brackets is the Faxen correction factor and is meant to correct for the wall effects for the cylindrical capsule (Shaw, 1963). Table A.4.1 and figure A.4.3 show the values for these parameters and the calculated viscosity for both high-pressure experiments at the measured temperatures.

The pressure dependence of viscosity is usually reported for isothermal conditions; however, the lack of a high-pressure phase diagram in this system prevented this approach. Therefore, a temperature correction is required to compare the results of the experiments. The ambient-pressure melt viscosity at 1640 and 1740 °C are calculated from the viscosity model of Bottinga and Weill (1972). The simple
temperature correction factor was also determined from this model and applied to the results of S1330 (3.5 GPa) and consisted of a ratio of the ambient pressure viscosities at 1740 and 1640 °C (0.63/1.07=0.59), which is comparable to the viscosity ratio of high-pressure peridotite melts (0.56) in a similar temperature range. The temperature-corrected \( \eta(P) \) plot (Fig. A.4.3) suggest that there is a viscosity minimum for the Ca\(_3\)Al\(_2\)Si\(_6\)O\(_{18}\) melts (NBO/T = 0.5) at a pressure below 4.9 GPa, which is also observed for MORB melts (NBO/T ~ 0.7) at 3 GPa by Ando et al., (2004). Additionally, the qualitative trends indicate that conclusions from the T-corrected data appear correct. Both calculated ambient pressure values are greater than the measured high-pressure viscosities and the measured viscosity for S1330 is approximately the same as that for S1333 but was measured at a lower temperature (1640 C vs. 1740 C, Table A.4.1). Since viscosity always decreases with increasing temperature, the melt viscosity at 3.5 GPa must be lower than that for the CAS melts at 4.9 GPa.

**Discussion**

As stated previously, past studies have suggested that \([5]Al\), \([6]Al\), and NBO may dominate viscous flow in high-pressure silicate melts. Our previous studies on the same CAS composition (Allwardt et al., 2005a, 2005b) showed that the abundance of these structural species are highly dependent on pressure and NBO are consumed in the generation of \([5]Al\) and \([6]Al\) (Fig. A.4.4a). These data can be put into a simple structural model where \([6]Al\) and \([4]Al\) are modeled as having a linear and negative exponential pressure dependence, respectively, which allows the percentages of \([5]Al\) and NBO to be calculated. This is shown to be a reasonable approximation for the results of the conventionally decompressed glasses (Fig. A.4.4b) and, therefore, has been applied to the data from the rapidly decompressed glass (Fig. A.4.4c). Both of these structural models predict a maximum in the abundance of \([5]Al\). Since \([x]Al\) has been shown to increase with temperature for NBO containing high-pressure glasses (Allwardt et al., 2005c), the pressure of the \([5]Al\) maximum may occur at pressures below 6 GPa in the melts. Some conclusions can be drawn by relating the structural results from glasses to the melt viscosity. First, the viscosity decrease from 1 atm to 3.5 GPa is likely due to the generation of \([5]Al\), which apparently affects the viscosity
more than the reduction in the abundance of NBO. Second, the viscosity minimum is likely the result of a maximum in the abundance of $[5]$Al species in the melt. Lastly, the increase in viscosity between 3.5 and 4.9 GPa is likely the result of the decrease in $[5]$Al species and, possibly, the decrease and/or increase in the abundance of NBO and $[6]$Al, respectively. The validity of the latter two conclusions rely on whether $[6]$Al acts as a network former or modifier in high-pressure melts and may be resolved with future experiments at higher pressures.

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References


Table A.4.1 Experimental conditions, terminal velocity, and melt viscosity

<table>
<thead>
<tr>
<th></th>
<th>P (GPa)</th>
<th>T (°C)</th>
<th>radius (um)</th>
<th>v (mm/s)</th>
<th>viscosity (*) (Pa's)</th>
<th>visc, 1740 C (Pa's)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B+W(1972)</td>
<td>0.0001</td>
<td>1640</td>
<td>X</td>
<td>X</td>
<td>1.07</td>
<td>X</td>
</tr>
<tr>
<td>B+W(1972)</td>
<td>0.0001</td>
<td>1740</td>
<td>X</td>
<td>X</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>S1330-Re</td>
<td>3.5</td>
<td>1640</td>
<td>70</td>
<td>0.357</td>
<td>0.42</td>
<td>0.245</td>
</tr>
<tr>
<td>S1333-Re</td>
<td>4.9</td>
<td>1740</td>
<td>77.5</td>
<td>0.458</td>
<td>0.39</td>
<td>0.39</td>
</tr>
<tr>
<td>S1333-Rh</td>
<td>4.9</td>
<td>1740</td>
<td>82.5</td>
<td>0.3</td>
<td>0.36</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Notes: Since there is such a large density contrast between the melt and Re- and Rh-spheres, the density difference is approximated to be constant at $17.7 \pm 0.3 \times 10^3$ and $9.7 \pm 0.3 \times 10^3$ kg/m$^3$, respectively.

* viscosity measured at the experimental temperature
Figure A.4.1 X-ray shadowgraphs from S1333 showing the (a) initial experimental arrangement at 4.9 GPa and 25° C and the (b) descent of the metallic spheres in the melt.
Figure A.4.2 Falling distance versus time and the fit that determined the terminal velocity for experiment S1333.
Figure A.4.3 Pressure dependence of the viscosity of CAS melts. The dashed line represents the isothermal (1740°C) viscosity with increasing pressure. The ambient pressure values are calculated using the viscosity model of Bottinga and Weill (1972) and the error estimates rely on the uncertainties in sphere radius, terminal velocity, density contrast, and capsule radius.
Figure A.4.4 Pressure dependence of structural species (a) measured from NMR on high-pressure glasses. Filled symbols are results from conventionally decompressed samples and open symbols are from the rapidly decompressed CAS5 sample. The Al species have been modeled from the data for the (b) conventionally and (c) rapidly decompressed glasses. The $^{[4]}$Al are approximated with a negative exponential pressure dependence while the $^{[6]}$Al are approximated with a linear pressure dependence. The abundance of $^{[5]}$Al is calculated with the assumption that only four-, five-, and six-coordinated Al exist in the high-pressure glass.