Beyond Speciation: A Study of Modifier Cation Clustering in Silicate Glasses by $^{29}$Si Magic Angle Flipping NMR

A Thesis

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Abstract

To elucidate trends in the chemical shift anisotropy and quantify the abundances of $Q^{(n)}$-species in silicate glasses, glasses modified with the alkali and alkaline earth cations, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$, Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$, were studied using Magic Angle Flipping on the $^{29}$Si. The Mg$^{2+}$ ion was found to be most effective at depolymerizing the glass network, leading to the most random distribution of species, whereas large alkali cations (K$^+$, Rb$^+$, and Cs$^+$) were found to most closely follow the binary distribution model. We observed a general decreasing linear trend in the magnitude of the chemical shift anisotropy of $Q^{(3)}$, $\zeta^{(3)}$, with increasing cation potential ($Z/r$). Interestingly, among glasses with the same modifier but at different molar compositions, there is a general increasing trend in $\zeta^{(3)}$ with decreasing modifier content. This behavior suggests that the Si-NBO bond length becomes shorter [100] as modifier content decreases, suggestive of changing cation cluster sizes or packing patters. In glasses containing Rb$^+$ or Cs$^+$, two unique $Q^{(3)}$ environments were observed, suggestive of two unique clustering patterns. Eleven different cesium silicate glasses were studied to probe this behavior; a general increasing trend in $\zeta^{(3)}$ as cesium content decreases is observed, possibly due to a change in cation coordination number. This trend may also be indicative of $Q^{(3)}$ sites existing in three-membered rings. The constrained and unfavorable geometry of these structures may also give rise to two unique CSA patterns; however, we determined that CSA alone cannot be
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I dedicate this work to my parents, Jeffrey and Chris Sanders.
Acknowledgments

“The most exciting phrase to hear in science, the one that heralds new discovies, is not ‘Eureka!’ but ‘That’s funny...’ ”

∼ Isaac Asimov

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is an incredible source of information and logic, and who was there for our “That’s funny...” moment upon our observation of two distinct $Q^{(3)}$ environments. Finally, I must thank my advisor, Dr. Philip Grandinetti. He has been very supportive of me over my four year stay in his lab, and allowed flexibility in my schedule to allow me to explore other passions of mine. He also provided me with a priceless education of NMR, for which I am incredibly grateful. Thank you, everyone, for helping me become who I am, and for helping me get to where I am today.
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* The $x = 2$ sample was acquired using PIETA [108] acquisition. All experiments were performed with true 90° and 180° pulses that were sufficiently short enough to fully and equally excite the entire spectrum.
Chapter 1: Introduction

1.1 The glassy state

1.1.1 The history of glass

Throughout the ages, glasses have played a particularly important role in the technological advances of the human species. Glasses are ubiquitously used today due to their relatively low cost, easy workability, and high usefulness, with uses such as kitchenware, windows, lab equipment, jewelry, and nuclear waste containment [1–3]. The glassy state and melts (composed primarily of silicate melts) play pivotal roles in geological processes such as volcanism [1]. The glass state also plays an important role in biological processes, such as anhydrobiosis [4], as well.

Before the production of glasses was understood, early humans used volcanic glasses, such as obsidian, as basic tools and weapons to complement stone and metal [5–7]. Glasses were one of the earliest manmade materials, produced in the Middle East by Mesopotamians, Egyptians, or Syrians, approximately five thousand years ago. Due to a poor understanding of glass chemistry, early synthetic glasses were cloudy and quite brittle due to the significant presence of metals within the glass [1,8]. By the addition of very fine metal powders, typically silver or gold, glass was the first material used whose color could be changed at will [1]. Due to the difficulty and relative high cost of producing them, early synthetic glasses were typically reserved
for royalty and used as jewels and amulets [1,5]. The evolution of glass blowing in the third century B.C.E. opened the floodgates for an industrial revolution, after which glasses were very cheap to make and a valuable trade commodity [1,9,10]. Without glasses, the considerable scientific progress of the 16th-18th centuries would probably not have been possible. Galileo’s telescope, Hooke’s microscope, Newton’s prism, and Boyle’s test tubes would not have existed [1,5,7,11]. Today the production of glass is among the largest industries in the world.

1.1.2 Glass formation and definition

The definition of what constitutes a glass has been a point of contention for scientists, thus there are many definitions that exist today [1,7]. A commonly accepted definition is that a glass is made when a melt is rapidly cooled, forming a liquid-like solid called a super-cooled liquid [2]. This rapid cooling, colloquially called quenching, prevents the melt’s species from rearranging into a lower energy, lower volume crystalline state; however, this definition is not all-encompassing as glasses can be formed through a variety of other means, such as precipitation, polymerization, and deposition [12–20]. Often, glasses are described as being amorphous solids with considerable atomic-level disorder; however, this definition is misleading. It is true, that unlike crystals, glasses have no discernible long-range order, but glasses are remarkably ordered in the short and even intermediate-range. In order to avoid confusion, the structural determination of non-crystalline solids, which include glasses [7], will be explored in this body of work.
1.1.3 Structural models of silicate glasses

Non-crystalline solids are inherently amorphous in nature and as such, techniques that elucidate long-range bonding constraints in crystals have been of little benefit to the study of the structure of glasses [21–23]. Due to the lack of long-range structural order, glass must first be characterized by its short range bonding order, which consists of a central atom coordinated to ligands, constituting the first coordination sphere. Many techniques have been used to modify the ever-evolving theory of glass structure and each technique brings with it unique information about the structure of glass; these techniques will be explored in the following sections.

X-ray scattering studies of glasses

One of the earliest techniques used to study glasses was X-ray scattering. In this technique, X-rays of a characteristic wavelengths are shined on to a solid material, and if any planes of symmetry exist in the sample, X-rays of the same wavelength are diffracted back and detected. Crystals, which must comply to long-range periodicity constraints, contain many identical symmetry planes, and thus produce a very ”clean” diffraction pattern, containing very narrow peaks at characteristic positions. Glasses, on the other hand, must not comply to any long-range periodicity, and as such contain a multitude of symmetry planes at seemingly random orientations. As such, the diffraction patterns of glasses contain, on first glance, very little information.

This result was used to develop one of the first models of glass structure by Zachariasen in 1932 [24]. This model proposes that oxide glasses are composed of a polymerized network of silicate tetrahedra interlinked through bridging oxygen atoms (BOs) as shown in Figure 1.1; In this case, silicate would be referred to as the network
Figure 1.1: The structure of glass (right) from the model proposed by Zachariasen [24]. The glass structure is described as having local order but lacking long-range periodicity. The structure is shown in contrast to the structure of a crystalline solid (left), which contains long-range structural periodicity.

former, that is, it is responsible for the polymerized network of the glass. However, unlike crystals, there are no long-range periodicity constraints. Whereas a crystal of the formula A$_2$O$_3$ consists entirely of six-membered rings, the glassy analog with the same composition is composed of smaller and larger rings, or chains of glass formers. As such, the local order is retained, but the long-range order is lost. Recent work by Huang et al. [25] and Lichtenstein et al. [26] has supported the Zachariasen model by directly imaging two-dimensional silica crystal and glass using atomic force microscopy (AFM) and scanning tunneling microscopy (STM). The images acquired by both groups look very much like the Zachariasen model in Figure 1.1.

Warren and Biscoe [27] continued the work of Zachariasen by studying glasses modified with metal oxides. As metal oxides, referred to hereafter as network modifiers, are introduced to the melt, Si-O-Si bonds are broken to form non-bridging
Figure 1.2: As a network modifying cation is introduced to the glass structure, the bridging oxygen bonds within the glass structure are broken. The terminating oxygen sites within the glass are called non-bridging oxygen (NBO) sites. The network modifying cations cluster near the NBO sites within the glass.

As such, it can be considered that the network modifying cations interrupt, or depolymerize, the network. The results achieved by Warren and Biscoe showed that there is not an ordered distribution of modifying cations within the glass structure, but a random distribution. This observation led to the introduction of the random network model, shown in Figure 1.3.

Later studies by Mozzi and Warren [28] on vitreous silica expanded on the work of Zachariasen. Using improved X-ray scattering techniques, they found that the Si-O-Si bond angle in pure silica glass ranges anywhere from 120° to 180°, with an average value around 144°. Additionally, they showed that each silicon atom was tetrahedrally coordinated by four oxygen atoms, with an average bond length of 1.62 Å. This study showed more definitively that glass is different from a crystal due to a distribution of parameters such as bond lengths and angles.

By applying a Fourier transform to diffraction data, Neuefeind and Liss [29] were able to extract the radial distribution function (RDF) of pure silica glass, shown in Figure 1.4. The RDF shows that the first coordination sphere around silicon is filled...
Figure 1.3: The random network model as proposed by Warren and Briscoe [27]. The network modifying cations cluster randomly throughout the glass structure.

exclusively by oxygen atoms at a distance of about 1.7Å from silicon. Further away from silicon, there are O-O interactions, Si-Si interactions and a second shell of Si-O interactions. This technique is limited, though, to studying single-phase glasses, i.e. glasses without network modifiers. The RDF becomes incredibly complicated upon the addition of network modifiers due to a broad distribution of distances between the cations and the NBOs, which eliminates any observable resolution in the RDF. However, this technique as been valuable to the study of glasses of other compositions, such as germanium [30], titanium [31], and boron [32] oxide glasses. More advanced X-ray techniques like EXAFS have also been routinely used to study silicate glasses [33].

Extended X-ray Absorption Fine Structure

X-ray Absorption Spectroscopy (XAS) is a very sensitive technique used primarily to measure the abundance of trace materials in a sample. This technique works by shining X-rays with tunable energy on a sample, and measuring the absorbance as a
Figure 1.4: The radial distribution function \(T_x(r)\) of silica glass [29]. This provides a reliable measure of average distances in the glass structure, at some distance \(r\) from the atom of interest.

function of X-ray energy. As soon as the energy of the incident X-ray matches the binding energy of an electron in the atom of interest, a sharp increase in absorption is measured. As the energy of the incident light increases beyond this first absorption peak, backscattered electrons interfere with forward-propagating photoelectrons, which generates an oscillating interference pattern in the measured absorbance profile. Extended X-ray Absorption Fine Structure (EXAFS) relies on this behavior; a Fourier transform of the oscillating pattern reveals information similar to the radial distribution function. Using EXAFS, one can determine the distance of atoms from the atom of interest, the number of atoms, the type, and as such, any structural disorder in the material.
In 1985, Greaves et al. [34] studied modified glasses using EXAFS to try to elucidate the local environment of the cations within the glass structure. Based on these results, he found that cations do not just randomly cluster within the glass as proposed by Warren and Biscoe, but instead form channels in the glass structure. The channels are made up of cations coordinated to NBOs. These results suggested the modified random network model, shown in Figure 1.5.

**Raman Spectroscopy**

Vibrational techniques have been used extensively to study the atomic-level structure of amorphous solids, specifically silicate glasses [35]. Raman scattering was of primary importance in the early studies of silicate glasses [1], which gave information about the state of polymerization within a silicate glass as a function of modifying
cation content [35]. Additionally, the short- and intermediate-range bonding order in silicate glasses has been studied using Raman scattering by observing different $Q^{(n)}$ species within the glass [1, 36–39]. Moreover, Raman can be used to elucidate information about the clustering of $Q^{(n)}$ species within the glass; it has been used to show that silicate tetrahedra form 4-to-6 member rings, and even planar 3-membered rings at high salt content [37, 38, 40–42].

Unfortunately, X-ray techniques and Raman spectroscopy are not commonly quantitative in determining the speciation within silicate glasses due to the introduction of metal oxides, with the exception of the recent onset of quantitative Raman spectroscopy [40, 43, 44]; however, nuclear magnetic resonance (NMR) spectroscopy has been of paramount importance in the accurate speciation by separating the resonance of each silicon based on its resonant shift [45–50]. Since NMR can be used quantitatively, the relative proportions of each species in the glass can be determined by simply integrating the area under each resonance [49–51].

1.2 Nuclear Magnetic Resonance and early studies of glass

First described in 1938 by Rabi, NMR is a powerful quantitative spectroscopic technique used to discriminate between atoms in different bonding environments. Each NMR-active atom has a characteristic observable frequency; this difference is exploited to identify and quantify the amount of nuclei present in different bonding environments.

Since there are no long-range bonding constraints in glasses, a convenient way to gain information about the structural disorder within the glass would be to study the local bonding environment around the silicon nucleus. The coordination of silicon is
commonly denoted as $Q^{(n)}$, where $Q$ denotes tetrahedral coordination (i.e. Silicon coordinated to four oxygens), and $n$ denotes the number of bridging oxygens per silicate tetrahedron, as described by Bray et. al [48, 52] in their early NMR studies of single-phase and modified glasses.

1.2.1 One-Dimensional Nuclear Magnetic Resonance (1D NMR)

The first NMR studies of glasses were used to explore the speciation of $Q^{(n)}$-species, and to develop models to describe this speciation. Bray et. al [48, 52] determined that one way to model the proportions of each $Q^{(n)}$ species is through thermodynamic disproportionation equilibrium. The reaction,

$$2Q^{(n)} = Q^{(n+1)} + Q^{(n-1)}, \text{ where } n = 3, 2, 1,$$

represents this model. The mole fractions of each $Q^{(n)}$ species are used to calculate the disproportionation constant, $k_n$, by the equation,

$$k_n = \frac{[Q^{(n+1)}][Q^{(n-1)}]}{[Q^{(n)}]^2}.$$  \hspace{1cm} (1.2)

Two extremes of this model exist. The binary model, first observed using NMR by Dupree et. al [53] using Magic Angle Spinning (MAS) assumes that only two types $Q^{(n)}$ species exist within the glass, thus every disproportion constant is zero. The other extreme assumes a statistically random distribution. The probability of observing each $Q^{(n)}$ site at any given molar concentration of modifying salt is determined by the constraints of charge and mass balance. If $k_3 \approx 0.375$, $k_2 \approx 0.495$, $k_1 \approx 0.311$ then the distribution of $Q^{(n)}$ species within the glass is considered to be random [52, 54]. It is not realistically practical to observe these values for $k_n$, so any significant deviation away from $k_n = 0$ is considered to give rise to a somewhat
Figure 1.6: The thermodynamic model of a binary model (left) and a random model (right) for the $Q^{(n)}$-species distribution in silicate glasses as a function of modifier content.

random distribution of $Q^{(n)}$ species. The distribution $Q^{(n)}$ species as a function of mole fraction of both extremes are given in Figure 1.6.

While this approach is useful, it suffers from inherently low resolution due to significant overlap of the NMR resonances of each $Q^{(n)}$ site, as shown in Figure 1.7. Unconstrained simulations of MAS spectra often lead to non-sensical results which violate charge and mass balance. This problem was partially remedied in 1987 by Stebbins [51], who discovered that each $Q^{(n)}$-species has a unique pattern in static experiments, as shown in Figure 1.8 as their 90° spinning patterns.

As a result of Stebbins’ result, not only could the relative proportions be determined, but the local geometry of the $Q^{(n)}$-species could be probed as well. By performing static experiments or by spinning the sample away from the magic angle, the chemical shift anisotropy of each site in the sample can be observed, as shown
Figure 1.7: The chemical shift range of each $Q^{(n)}$-species, adapted from Davis et. al. [46]
Figure 1.8: The distinct anisotropic lineshape of each $Q^{(n)}$-species for $^{29}$Si NMR (shown as spinning at 90° with respect to the magnetic field, which scales the anisotropy by $-\frac{1}{2}$) as shown by Stebbins [51].
Figure 1.9: The contributions of the nuclear shielding tensor parameters on the anisotropic lineshape.

in Figure 1.9, which is a probe of how the local geometry of the site deviates from tetrahedral. This allows us to probe the local electronic environment of each site, which in turn can be used to measure bond lengths and angles in each site. This result paved the way for two-dimensional NMR experiments, which improve upon the resolution of 1D experiments by separating each site not only by their anisotropy, but by their isotropic frequencies as well.

1.2.2 Two-Dimensional Nuclear Magnetic Resonance (2D NMR)

Many experiments have been developed to correlate the isotropic and anisotropic frequencies of each site in glasses, such as 2D Phase Adjusted Spinning Sidebands (2D PASS) [55,56], Magic Angle Turning (MAT) [57], Magic Angle Hopping (MAH)
[58], and Magic Angle Flipping (MAF) [59]. The remainder of this document will focus on using the MAF experiment to measure the speciation and CSA of the $Q^{(n)}$-species within a series of binary silicate glasses. The experimental details of the MAF experiment will be explained in the following chapters.

The first use of MAF to study silicate glasses was performed by Zhang et. al [45], to measure the speciation in a silicate glass of composition $2Na_2O\cdot3SiO_2$. The relative proportions of the $Q^{(2)}$, $Q^{(3)}$, and $Q^{(4)}$ sites were measured, and the disproportionation constant, $k_3$, was measured to be $0.0129 \pm 0.0001$. This value indicates a very binary distribution, consistent with Dupree et. al’s work on sodium silicate glasses.

Zhang et. al followed this with a study of a binary glass with the composition $CaO\cdotSiO_2$ [47], which is expected to disproportionate in a more random fashion than a glass modified with sodium. Indeed, while the binary model predicts only the presence of $Q^{(2)}$ in a glass of this composition, contributions from each $Q^{(n)}$-species were detected in this MAF experiment. The calculated disproportionation constants were measured to be, $k_1 = 0.105 \pm 0.019$, $k_2 = 0.156 \pm 0.005$, and $k_3 = 0.106 \pm 0.022$. These values indicate the the distribution of $Q^{(n)}$ species is indeed quite random, due to the ability of smaller, higher charged cations like $Ca^{2+}$ to depolymerize the glass network.

Finally, Davis et. al [46] studied a binary silicate glass of the composition $K_2O\cdot2SiO_2$ and found that, much like sodium silicate glasses, the distribution of sites was quite binary. The disproportionation constant, $k_3$, was calculated to be $0.0103 \pm 0.0008$. This value for $k_3$ was slightly smaller than what was calculated by Zhang et. al [45] for the sodium-modified silicate glass. This indicates that potassium is less effective
than sodium at disrupting the polymerized network, suggesting that even more binary distributions would be expected for glasses modified with larger alkali like Rb\(^+\) and Cs\(^+\).

It is worth noting, though, that these experiments are limited due to a number of factors. First and foremost, these early studies relied on samples to be enriched in the \(^{29}\)Si nucleus. Due to it’s low natural abundance (\(\approx 4.7\%\)) and intermediate gyromagnetic ratio the \(^{29}\)Si is inherently insensitive, so performing experiments at natural abundance were, at the time, impractical; however, isotopically enriched SiO\(_2\) is quite expensive, so samples had to be chosen carefully. Additionally, these experiments suffered from inherently long relaxation times, often on the order of 30 minutes. As such, these early MAF experiments often took up to four weeks to complete, which makes studies of the compositional dependence of the glass structure very impractical.
The following chapters will detail the work I have completed and improvements that have been made on studying silicate glasses with MAF. The second chapter will focus on work done on $^{29}$Si-enriched binary glasses modified by magnesium, and the improvement made to the MAF experiment by the addition of CPMG acquisition [60, 61]. The third chapter will detail further improvements made on the MAF experiment, such as the clever use of paramagnetic dopants in glasses to dramatically reduce relaxation times, which allows the study of glasses at natural-abundance $^{29}$Si. This chapter will also focus on the results of MAF experiments on various other alkali- and alkaline-earth-modified glasses. Finally, chapter four will focus on the study of cesium oxide modified silicate glasses and our observation of different clustering patterns in the glass through NMR investigations.
Chapter 2: Magic-Angle Flipping NMR of magnesium silicate glasses

2.1 Introduction

The atomic level ordering of silicate melts dictate their bulk thermodynamic and transport properties such as heat capacity, thermal conductivity, and viscosity [1,2,62]. Structurally, silicate melts are composed of a network of silicate tetrahedra that are interlinked through oxygen bonds [24]. As network modifying cations are introduced into the melt, Si-O-Si bonds are broken and non-bridging oxygen (NBO) sites are formed. Silicate melts quenched as glasses can be studied at room temperature, since the structure of the melt is preserved at the glass transition temperature. In a glass with composition $\alpha\text{MO} \cdot (1 - \alpha)\text{SiO}_2$, we will assume that the following anionic equilibria [63,64] takes place in the melt:

$$2Q^{(n)} \rightleftharpoons Q^{(n-1)} + Q^{(n+1)}, \quad (2.1)$$

and

$$2Q^{(0)} \rightleftharpoons 2Q^{(1)} + (O)^{2-}, \quad (2.2)$$

where $(O)^{2-}$ refers to the free oxygen anion, and $Q^{(n)}$ refers to a silicate tetrahedron and $n$ is the number of bridging Si-O-Si linkages per tetrahedral unit, where $n$ ranges
from 0-4. Calculating the corresponding equilibrium constants,

\[ k_n = \frac{\chi_{Q_{n+1}} \cdot \chi_{Q_{n-1}}}{(\chi_{Q_n})^2}, \quad (2.3) \]

and

\[ k_0 = \frac{(\chi_{Q_1})^2 \cdot \chi_{(O)^2-}}{(\chi_{Q_0})^2}. \quad (2.4) \]

where \( \chi_{(O)^2-} \) is the mole fraction of free oxygen anion and \( \chi_{Q_n} \) is the mole fraction of the \( Q^{(n)} \) species, one can infer how the \( Q^{(n)} \) anions are distributed in the bulk glass. When \( k_n \) is zero the distribution of silicate tetrahedra within the glass is binary, that is, the glass contains a maximum of two \( Q^{(n)} \)-species with the sequential appearance of other \( Q^{(n)} \)-species as the modifier cation content increases [24]. In contrast, calculated values of \( k_n \) assuming a statistically random distribution, neglecting the formation of free oxygen anion, would give \( k_1 = 0.311, k_2 = 0.439, \) and \( k_3 = 0.375 \) [65]. Thus, one can view the equilibrium constants as a measure of frozen-in disorder or configurational entropy of the glass.

For amorphous materials, where there is a distribution of isotropic chemical shifts for each site, lineshapes can be poorly resolved due to a large degree of overlap when multiple sites are present. Typically, multiple sites are resolved in 1D \( ^{29}\text{Si} \) MAS NMR experiments by assuming the chemical shift distribution for each site can be represented as a Gaussian function. Areas obtained through unconstrained fitting of the 1D spectrum alone, however, cannot always be used to satisfactorily predict the necessary charge balance, and the associated uncertainty on the areas can be on the order of several percent. An alternative approach is to discriminate between \( Q^{(n)} \)-species by their CSA, as described by Stebbins [49]. These anisotropic \( ^{29}\text{Si} \) lineshapes can be deconvoluted using known nuclear shielding tensor anisotropy parameters for each.
$Q^{(n)}$-species to determine the relative contributions from each site. This approach applied to one-dimensional static sample NMR spectra, however, is limited by low sensitivity and strong overlap of anisotropic lineshapes for different $Q^{(n)}$-species. In previous work [45–47], it was demonstrated that Magic Angle Flipping (MAF) [58] provides an order of magnitude improvement in quantifying $Q^{(n)}$-species compared to fitting 1D static or MAS NMR lineshapes alone. This 2D NMR approach has been successfully applied in quantifying the relative populations of $Q^{(n)}$ in silicate glasses of composition $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ [45], $\text{K}_2\text{O} \cdot 2\text{SiO}_2$ [46], and $\text{CaO} \cdot \text{SiO}_2$ [47].

In this work we employ 2D MAF to investigate the structure of two magnesium silicate glasses with composition $\text{MgO} \cdot \text{SiO}_2$ and $2\text{MgO} \cdot \text{SiO}_2$. Magnesium silicates are the primary constituents of terrestrial mantles [66]. The simplest crystalline magnesium silicate by composition is forsterite, $\text{Mg}_2\text{SiO}_4$, which has a single silicon site with $Q^{(0)}$ coordination [67]. In contrast, studies of forsterite ($2\text{MgO} \cdot \text{SiO}_2$) glass by Raman [68] and NMR [69] spectroscopy have detected multiple $Q^{(n)}$-species, indicating a significant degree of polymerization within the glass network. Similarly, in NMR studies by Sen et al. [70] on a $\text{MgO} \cdot \text{SiO}_2$ glass, significantly higher $Q^{(n)}$ disproportion equilibrium constants of $k_2 = 0.364$ and $k_3 = 0.464$ were observed. The objective of this work is to (1) determine the mole fractions of $Q^{(n)}$-species in each glass, (2) determine structural differences between glasses with higher MgO/\text{SiO}_2 ratios, (3) determine the degree of polymerization in the 2 $\text{MgO} \cdot \text{SiO}_2$ glass, and (4) expand on previously reported trends in the anisotropic parameter $\zeta$ with changing modifier cation potential.
2.2 Experimental

Samples of $\alpha$ MgO · $(1 - \alpha)$ SiO$_2$, were synthesized with 100% $^{29}$Si-enriched SiO$_2$ using the container-less levitation technique [70]. Final spherical glass beads measured 1 - 2 mm in diameter. This work focuses on two compositions with $\alpha = 0.500 \pm 0.005$ and $0.660 \pm 0.007$, corresponding to compositions of MgO · SiO$_2$ and 2 MgO · SiO$_2$. NMR experiments were performed on a hybrid Tecmag Apollo-Chemagnetics CMX II NMR spectrometer interfaced to a 4 mm homebuilt dynamic-angle-spinning probe [71] operating at a field strength of 9.4 Tesla, corresponding to an operating frequency of 79.476 MHz for $^{29}$Si. The $^{29}$Si relaxation time was measured for both glass compositions indicating a spin-lattice relaxation time, $T_1$, of 8 s and 26 s for MgO · SiO$_2$ and 2 MgO · SiO$_2$, respectively. The difference in $T_1$ between the two samples is explained by possible paramagnetic impurities that were incorporated in the glass structure during synthesis. A recycle delay of $6T_1$ was used for each glass and no changes in peak shape as a function of recycle delay were observed indicating no differential relaxation between the $^{29}$Si resonances.

The 2D MAF $^{29}$Si experiment correlates isotropic MAS frequencies to anisotropic frequencies obtained while spinning off the magic angle during the $t_1$ evolution period. The magnitude of the chemical shift anisotropy scales by the second-order Legendre polynomial,

$$P_2\cos(\theta) = \frac{3\cos^2(\theta) - 1}{2},$$

and as such we achieve correlation between the isotropic and anisotropic dimensions by effectively acquiring at both angles. Here, the off-magic angle, $\theta_R$, is set at $\theta_R =$
Figure 2.1: (A) Shifted-echo Magic-Angle Flipping pulse sequence with spin transition and spatial symmetry pathways. (B) Magic-Angle Flipping pulse sequence using CPMG acquisition ($m = 80$) with spin and spatial symmetry pathways. In both experiments the rotor axis angle, $\theta_R$, during $t_1$ evolution is set to $\theta_R = 90^\circ$. The period, $\tau_{\text{hop}}$, during which the magnetization is stored as Zeeman order (i.e. the magnetization decays only by $T_1$) while the rotor is switched between angles, is set to 80 ms. The echo shift period, $\tau_{\text{echo}}$, is set to 3.95 ms. Hypercomplex acquisition is performed to obtain positive and negative $t_1$ quadrants in the 2D time domain signal [74]. Four dummy scans are performed prior to acquisition to ensure the system reached steady state prior to the start of the experiment.

$90^\circ$ away from the external magnetic field direction, where the averaged frequency anisotropies are scaled [72,73] by a factor of $-1/2$.

The 2D MAF spectrum of the MgO · SiO$_2$ glass, shown in Fig. 2.2, was obtained using the shifted-echo MAF pulse sequence [59,75], illustrated in Fig. 2.1A. The number of $t_1 \times t_2$ points was $128 \times 256$ with dwell times of 62.5 $\mu$s in both dimensions. The total acquisition time was 16 days for MgO · SiO$_2$. The 2D MAF spectrum of
Figure 2.2: Experimental 2D $^{29}$Si MAF NMR spectrum of MgO · SiO$_2$ with representative experimental (black lines) and simulated (green dashed lines) cross sections at selected isotropic chemical shifts (χ$^2_{\text{reduced}} = 1.8$). All frequencies (in ppm) are referenced to TMS.
2 MgO · SiO$_2$ glass is shown in Fig. 2.3. To improve sensitivity the MAF sequence with Carr-Purcell-Meiboom-Gill (CPMG) [60,61] acquisition, illustrated in Fig. 2.1B, was used. The number of loops, $m$, in the CPMG acquisition was set to acquire 80 echoes. An echo spacing of 8 ms between $\pi$ pulses was used with dwell times of 62.5 $\mu$s in $t_1$ and 20 $\mu$s in $t_2^{(m)}$. The use of CPMG acquisition provided a sensitivity enhancement of 4.5 over the MAF sequence of Fig. 2.1A. Utilizing CPMG acquisition has proven effective in analyzing both static and spinning samples because the acquisition of multiple echoes in the time domain can reduce experimental time for samples with long $T_1$ [76–79]. Previous studies [80, 81] have already demonstrated that the acquisition dimension of other 2D correlation techniques such as Magic Angle Turning (MAT) can be enhanced by adding CPMG acquisition by increasing sensitivity. The MAF CPMG spectrum was processed using the TOP approach to CPMG as outlined by Dey et al. [82]. The total acquisition time was 3 days for 2 MgO · SiO$_2$. A Gaussian apodization was applied along the anisotropic dimension with a half width at half height (HWHH) of 235 Hz to enhance the sensitivity of the 2D spectra of both samples.

As acquired, the signal from both sequences in Fig. 2.1 correlate a $t_1$ dimension containing both isotropic and anisotropic frequencies to a $t_2$ dimension containing only isotropic frequencies, as presented in previous MAF investigations of silicate glasses [45–47]. The 2D MAF spectra presented here, however, have been transformed to correlate a purely isotropic spectrum to a purely anisotropic spectrum through the application of an affine transformation [83], consisting of a shear parallel to $t_2$ using a shear factor of 1.
Figure 2.3: $^{29}$Si MAF NMR spectrum of the 2 MgO · SiO$_2$ glass with representative experimental (black lines) and simulated (green dashed lines) cross sections at selected isotropic chemical shifts ($\chi_{\text{reduced}}^2 = 1.7$). All frequencies (in ppm) are referenced to TMS.
In this study we employ the IUPAC definitions for nuclear shielding and chemical shift interactions [84] where the isotropic nuclear shielding is defined as

$$\sigma_{\text{iso}} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}),$$

with corresponding isotropic chemical shift

$$\delta_{\text{iso}} = \frac{(\sigma_{\text{ref}} - \sigma_{\text{iso}})}{(1 - \sigma_{\text{ref}})},$$

where $\sigma_{xx}$, $\sigma_{yy}$, and $\sigma_{zz}$ are the components of the nuclear shielding tensor in its principal axis system and $\sigma_{\text{ref}}$ is the isotropic nuclear shielding of the reference compound (TMS). The shielding anisotropy, $\zeta$, and asymmetry parameter, $\eta$, are defined as

$$\zeta = \sigma_{zz} - \sigma_{\text{iso}},$$

and

$$\eta = \frac{\sigma_{yy} - \sigma_{xx}}{\zeta},$$

respectively. Based on the results of previous MAF studies on silicate glasses [45–47], we assume that the nuclear shielding anisotropy, $\zeta$, and asymmetry parameters, $\eta$, are identical for each $Q^{(n)}$ site. Thus, we will use the notation, $\zeta^{(n)}$ and $\eta^{(n)}$, to represent the nuclear shielding parameters for a $Q^{(n)}$ site in a magnesium silicate glass. Additionally, we assume the distribution of isotropic chemical shifts for $Q^{(n)}$ species in the glass will be Gaussian, with a mean value, $\langle \delta_{\text{iso}}^{(n)} \rangle$. The 2D MAF spectrum was analyzed using the nonlinear least-squares fitting routine built into the Optimization toolbox of MATLAB®. The analysis incorporates the NMR simulation package SIMPSON [85] to generate an anisotropic lineshape for each $Q^{(n)}$ with a given $\zeta^{(n)}$ and $\eta^{(n)}$. Up to five anisotropic $Q^{(n)}$ lineshapes are used to generate a 2D MAF lineshape with a Gaussian distribution of isotropic chemical shifts. Thus, the
parameters used to model the 2D spectrum were (1) the mean $Q^{(n)}$ isotropic chemical shift position, $\langle \delta_{iso}^{(n)} \rangle$, in the isotropic dimension, $\omega_2$, (2) the standard deviation of each $Q^{(n)}$ isotropic chemical shift distribution in $\omega_2$, (3) the nuclear shielding tensor anisotropy, $\zeta^{(n)}$, for each $Q^{(n)}$, (3) the nuclear shielding tensor asymmetry parameter, $\eta^{(n)}$, for each $Q^{(n)}$, (4) the integrated 2D MAF lineshape intensity for each $Q^{(n)}$, and (5) the Gaussian line broadening along $\omega_1$, the anisotropic dimension, identical for all $Q^{(n)}$ anisotropic lineshapes.

The best-fit values for $\zeta^{(n)}$ and $\eta^{(n)}$ were determined by analyzing 1D anisotropic cross sections in the 2D MAF spectrum where each $Q^{(n)}$ dominates, and are given in Table 2.1 along with previously measured values. Additionally, the best-fit line broadenings obtained from the least-squares fit of the 1D anisotropic cross sections corresponded to Gaussian function with HWHH equal to 528 Hz (6.6 ppm) for both 2 MgO · SiO$_2$ and MgO · SiO$_2$. A challenge in presenting uncertainties for the shielding parameters arises from a strong covariance with the Gaussian line broadening that is also used in the least-squares analysis of anisotropic lineshapes. After subtracting the 228 Hz of Gaussian apodization applied during signal processing, only 293 Hz (3.7 ppm) of the line broadening found during least-squares analysis of the anisotropic cross sections can be attributed to structural disorder, intrinsic excited state lifetime, and uncertainty in the tensor parameters. The uncertainties in the shielding tensor, therefore, can range from values as low as those reported in table 2.1 to as high as 3.7 ppm. The best fit values for the mean and standard deviation of each $Q^{(n)}$ isotropic chemical shift distribution, as well as the integrated intensity for each $Q^{(n)}$ were determined by analyzing the full 2D MAF spectrum, and are given in Table 2.2.
To calculate the equilibrium constants of Eqs. (2.3) and (2.4) one needs the \((O)^{2-}\) mole fraction,

\[
\chi_{(O)^{2-}} = \frac{n_{(O)^{2-}}}{n_{Q_0} + n_{Q_1} + n_{Q_2} + n_{Q_3} + n_{Q_4} + n_{(O)^{2-}}},
\]

as well as the \(Q^{(n)}\) mole fractions,

\[
\chi_{Q_n} = \frac{n_{Q_n}}{n_{Q_0} + n_{Q_1} + n_{Q_2} + n_{Q_3} + n_{Q_4} + n_{(O)^{2-}}},
\]

where \(n_{Q_n}\) are the total number of moles of \(Q_n\), and \(n_{(O)^{2-}}\) is the total number of moles of the anion \((O)^{2-}\). From the analysis of our \(^{29}\)Si NMR 2D spectra one can measure the fraction of silicon in each of the five \(Q_n\) forms, \(y_{Q_n}\), that is,

\[
y_{Q_n} = n_{Q_n}/n_{Si},
\]

where \(n_{Q_n}\) is the number of moles of the species \(Q^{(n)}\), and \(n_{Si}\) is the total number of mole of silicon. If the anion \((O)^{2-}\) is not present in the glass, then

\[
\chi_{Q_n} = y_{Q_n},
\]

and the calculation of the \(Q^{(n)}\) disproportionation constants, \(k_n\), is straightforward. When the glass network is sufficiently depolymerized, near the orthosilicate composition, however, there may be significant \((O)^{2-}\) anion present. In this situation, Eq. (2.13) will no longer be valid [54,86–90]. Combining the relative \(Q^{(n)}\) abundances of Eq. (2.12), obtained by \(^{29}\)Si NMR, with the constraint of charge balance, as derived in the Appendix, the mole fractions of all species in the equilibria of Eqs. (2.1) and (2.2) are calculated according to

\[
\chi_{(O)^{2-}} = \frac{(\frac{\alpha}{1-\alpha}) - 2y_{Q_0} - 1.5y_{Q_1} - y_{Q_2} - 0.5y_{Q_3} - 0.5y_{Q_4} + y_{Q_4}}{(\frac{\alpha}{1-\alpha}) - y_{Q_0} - 0.5y_{Q_1} + 0.5y_{Q_3} + y_{Q_4}},
\]
and

\[ \chi_{Q_n} = \frac{y_{Q_n}}{\left( \frac{\alpha}{1-\alpha} \right) - y_{Q_0} - 0.5y_{Q_1} + 0.5y_{Q_3} + y_{Q_4}}. \]  

(2.15)

Using the expressions above with the $^{29}\text{Si}$ NMR relative $Q^{(n)}$ abundances given in Table 2.2, the mole fractions, also shown in Table 2.2, were calculated.
Figure 2.4: Reconstructed 1D NMR lineshape from the least-squares analysis of the 2 MgO · SiO₂ ²⁹Si MAF NMR spectrum with (A) the isotropic projection of the 2D MAF spectrum (gray circles) with the best fit (dashed line) and (B) Gaussians representing the relative areas of $Q^{(1)}$ and $Q^{(1)}$. All frequencies (in ppm) are referenced to TMS.

2.3 Discussion

2.3.1 2 MgO · SiO₂

The one-dimensional ²⁹Si MAS spectrum of 2 MgO · SiO₂ glass is shown in Fig. 2.4A. This spectrum has a broad resonance peaking at $\delta_{iso} = -67$ ppm, consistent with the presence of $Q^{(0)}$ species. The MAS lineshape is also skewed towards an isotropic chemical shift of $-80$ ppm, suggesting the presence of $Q^{(1)}$ species. A sharp low intensity peak was also observed at $\delta_{iso} = -62$ ppm in the isotropic dimension, which has been previously observed in ²⁹Si NMR investigations [69] of the same material and corresponds to a small crystalline forsterite impurity.
Table 2.1: Nuclear shielding anisotropy parameters, $\zeta^{(n)}$ and $\eta^{(n)}$, for $Q^{(n)}$ in magnesium silicates studied in this work and compared to previous 2D $^{29}$Si MAF NMR studies of other silicate glasses. Nuclear shielding parameters reported in this study were obtained from spectral fits of a 1D data slice of the MAF spectrum where the mole fraction of a particular $Q^{(n)}$ was expected to dominate. As explained in the main text the uncertainties in the shielding anisotropy can range from the values reported above to as high as 3.7 ppm.
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<tr>
<td>$Q^{(2)}$</td>
<td>-83.9</td>
<td>12.6</td>
</tr>
<tr>
<td>$Q^{(3)}$</td>
<td>-94.2</td>
<td>13.2</td>
</tr>
<tr>
<td>$Q^{(4)}$</td>
<td>-107.2</td>
<td>14.9</td>
</tr>
<tr>
<td>$(O)^{2-}$</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 2.2: Mean, standard deviation, silicon mole fraction ($y_{Q_n}$) and mole fraction ($\chi$) for each of the five $Q^{(n)}$ isotropic chemical shift distributions that compose the $^{29}$Si MAF NMR spectra of 2 MgO · SiO₂ and MgO · SiO₂ and the calculated free oxygen anion. Values from this work are presented with previously reported values by Sen and Tangeman [69] and Sen et al. [70]. Because of the low relative area, the value of $\langle \delta^{(4)}_{\text{iso}} \rangle$, indicated with asterisks in the table, was constrained to the $\langle \delta^{(4)}_{\text{iso}} \rangle$ value reported by Sen et al. [70] prevent the $\chi^2$ minimization from converging on unphysical values.
In recent work on 2MgO·SiO\textsubscript{2} glass by Kalampounias et al. [68] and Sen and Tangeman [69], a significant degree of polymerization was proposed to exist within magnesium silicate glasses at high magnesium concentrations, with silicon existing as \( Q^{(0)} \), \( Q^{(1)} \), and perhaps \( Q^{(2)} \). The conclusions by Sen and Tangeman [69] were based on analyses of static \( ^{29}\text{Si} \) NMR spectra where they found two sites attributed to \( Q^{(0)} \) with \( \zeta^{(0)} = 0 \) ppm and \( \eta^{(0)} = 0.0 \) and \( Q^{(1)} \) with \( \zeta^{(1)} = 45 \) ppm and \( \eta^{(1)} = 0.9 \). The \( ^{29}\text{Si} \) 2D MAF spectrum of 2MgO·SiO\textsubscript{2} glass, shown in Fig. 2.3, reveals a broadening along the anisotropic dimension as the isotropic frequency increases from \( \delta_{\text{iso}} = -62 \) to \(-80 \) ppm, confirming the presence of a second site, which is consistent for silicon with \( Q^{(1)} \) coordination. Analysis of the 2D MAF spectrum yields nuclear shielding parameters \( \zeta^{(0)} = 0.0 \) ppm, \( \eta^{(0)} = 0.0 \), \( \zeta^{(1)} = 33.0 \pm 0.1 \) ppm, and \( \eta^{(1)} = 0.4 \pm 0.1 \). The discrepancy with Sen and Tangeman’s nuclear shielding parameters for \( Q^{(1)} \) is likely due to an error in their analysis arising from the large degree of spectral overlap in the 1D static NMR lineshape. Spectral fits of the 2D MAF spectrum of 2MgO·SiO\textsubscript{2} glass were also undertaken using the \( \zeta^{(1)} \) value of Sen and Tangeman [69], but the chi-squared value obtained was significantly larger than the value obtained using the shielding tensor parameters in Table 2.1. Because of the resolution improvement of 2D MAF over 1D static NMR experiments we believe the tensor parameters obtained in this study are more accurate.

It is also worth noting that measurements of the nuclear shielding tensor of \( Q^{(0)} \) in crystalline forsterite by Weiden and Rager [91] and Ashbrook et al. [92] gave values of \( \zeta^{(0)} = -32.2 \) ppm and \( \eta^{(0)} = 0.51 \). Given the amorphous nature of the glass, such discrepancies with shielding parameters in crystalline materials are not unexpected. In crystalline silicates, the local bonding around silicon has to fulfill long
range structural order constraints, causing silicon in $Q^{(0)}$ to reside in slightly more distorted tetrahedra leading to non-zero $\zeta$ and $\eta$ values. In contrast, glasses have no such long-range structural constraints, and the $Q^{(0)}$ silicon atoms tend to adopt more symmetric local structures allowing the assumption that the values of $\zeta$ and $\eta$ are equal to zero as observed in previous investigations of silicate glasses by 2D MAF NMR [45–47].

Attempts were made to analyze the 2D MAF spectrum of 2 MgO·SiO$_2$ glass with contributions from $Q^{(0)}$, $Q^{(1)}$, and $Q^{(2)}$ but only the inclusion of $Q^{(0)}$ and $Q^{(1)}$ gave satisfactory fits. The distributions of isotropic chemical shifts for $Q^{(0)}$ and $Q^{(1)}$ are shown in Fig. 2.4B. A comparison of the relative abundances of $Q^{(0)}$ and $Q^{(1)}$ to those by Sen and Tangeman [69] are also given in Table 2.2. As noted above, however, disagreements with Sen and Tangeman [69] arise from their use of $Q^{(1)}$ nuclear shielding parameters that were significantly larger than the true values.

Using the relative abundance of each $Q^{(n)}$-species obtained from spectral fits of the 2D MAF spectrum, given in Table 2.2, and Eqs. (2.14) and (2.15), the mole fractions were calculated for each $Q^{(n)}$ and $(O)^{2-}$. These results, also shown in Table 2.2, indicate $\chi_{Q_0} = 0.56 \pm 0.03$, $\chi_{Q_1} = 0.33 \pm 0.02$, and $\chi_{(O)^{2-}} = 0.11 \pm 0.05$ for the 2 MgO·SiO$_2$ glass. The presence of $(O)^{2-}$ is not unreasonable given oxide ion activities determined at lower SiO$_2$ contents in MO-SiO$_2$ liquids, where M can be Mg, Fe, Ni, etc., by thermochemical means [89,93,94], although it is difficult to extrapolate such data down in temperature from the liquidus to the glass transition. Additionally, it is noteworthy that several magnesium silicates, including crystalline $\beta$-Mg$_2$SiO$_4$ [95], contain OMg$_n$ groups, i.e., oxygen not bound to silicon.
The mole fractions were used in Eq. (2.4) to calculate a disproportionation constant $k_0 = 0.04 \pm 0.02$ for the 2 MgO · SiO$_2$ glass. The nonzero $k_0$ for 2 MgO · SiO$_2$ indicates a tendency for silicon to polymerize within the glass melt at large modifier cation concentrations. Of course, from charge balance alone, an increase in free oxygen anion concentration would require a decrease in the number of non-bridging oxygen in the glass structure. This $k_0$ value is consistent with values of $k_0 = 0.0016$ for CaO · SiO$_2$, obtained by Masson et al. [87] in applications of polymer theory to free energy of mixing data.

2.3.2 MgO · SiO$_2$

In the 1D $^{29}$Si MAS NMR spectrum of MgO · SiO$_2$ shown in Fig. 2.6A a single broad resonance centered at -82 ppm was observed, indicative of a structure predominantly composed of $Q^{(2)}$-species. While the 1D lineshape is completely unresolved, the width and shape of the peak indicate the presence of multiple overlapping sites. Deconvoluting this lineshape, assuming the chemical shift distribution for each site is Gaussian, indicates that the spectrum is composed of five separate sites for each possible $Q^{(n)}$-species.

The 2D $^{29}$Si MAF NMR spectrum of MgO · SiO$_2$ is shown in Fig. 2.2. In a previous study of alkali silicate glasses [46], the magnitude of $\zeta^{(n)}$ for $Q^{(2)}$ and $Q^{(3)}$ was observed to be proportional to cation potential, which is defined as the charge of the cation divided by its atomic radius, for silicate glasses with different modifying cations (K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$), as shown in Fig. 2.5, where nuclear shielding tensor parameters are given in Table 2.1. This trend was related to results of Grimmer and coworkers [96,97] who observed that by aligning the principal component of the nuclear shielding
tensor \((\sigma_{zz})\) along the Si-NBO bond for a \(Q^{(3)}\) site, a decrease in the magnitude of the nuclear shielding was observed, indicating that as the length of the Si-NBO bond approaches the length of a bridging Si-O-Si bond the magnitude of the nuclear shielding will decrease to zero. This trend in nuclear shielding versus cation potential is used to explain the diminished resolution along the anisotropic dimension compared to previous MAF studies of alkali silicate glasses and the similarities between the anisotropic lineshape for each \(Q^{(n)}\) species. While similar, however, distinct trends are noticable in the 2D \(^{29}\)Si MAF NMR spectrum of the MgO \(\cdot\) SiO\(_2\) glass including a narrowing of the lineshape towards higher frequency and a shift in the symmetry of the lineshape around -80 ppm indicating multiple \(Q^{(n)}\) sites with different nuclear shielding parameters arising from different bonding environments.

Analysis of the 2D MAF spectrum requires accurate values for the nuclear shielding parameters for each \(Q^{(n)}\) site. Since \(Q^{(0)}\) and \(Q^{(4)}\) reside in a tetrahedron with uniform symmetry, the values of \(\zeta\) and \(\eta\) for \(Q^{(0)}\) and \(Q^{(4)}\) can be fixed at zero. Values of \(\zeta^{(1)}\) and \(\eta^{(1)}\) are known from spectral fits presented earlier in this study of the 2 MgO \(\cdot\) SiO\(_2\) and set equal to \(\zeta^{(1)} = 33.0 \pm 0.1\) ppm and \(\eta^{(1)} = 0.4 \pm 0.1\) leaving only \(Q^{(2)}\) and \(Q^{(3)}\) to be determined. These values were found by fitting respective cross sections of the 2D lineshape where those sites were believed to dominate and determined to be \(\zeta^{(2)} = -36.0 \pm 0.5\) ppm, \(\eta^{(2)} = 0.99 \pm 0.07\), \(\zeta^{(3)} = -27.5 \pm 0.5\) ppm and \(\eta^{(3)} = 0.45 \pm 0.11\). It should be noted that the \(Q^{(n)}\) abundances are sensitive to the nuclear shielding parameters used to model the anisotropic dimension of the 2D MAF spectrum. Using these values for \(\zeta^{(n)}\) and \(\eta^{(n)}\) the entire 2D spectrum was fit to obtain relative abundance for each \(Q^{(n)}\)-species, as shown in Fig. 2.6.
Figure 2.5: Plot of $\zeta$ versus cation potential (Table 2.1) for $Q^{(2)}$ and $Q^{(3)}$. Values for the interatomic radii ($r$) were taken from work by Whittaker and Muntus [98].

Shown in Fig. 2.2 are selected $\theta_R = 90^\circ$ cross sections with the associated least-squares best fit simulation. The relative areas of each of the Gaussian functions projected along the isotropic dimension provide a reconstructed 1D MAS NMR lineshape with the relative area under each Gaussian corresponding to the mole fraction, given in Table 2.2, of each of the five $Q^{(n)}$-species. Using the relative abundance for spectral fits of the 2D MAF spectrum, the mole fraction for each $Q^{(n)}$-species and the free oxygen anion were calculated. All spectral fits are based on the assumption that the values of $\zeta^{(n)}$ and $\eta^{(n)}$ do not change as a function of the isotropic chemical shift and the chemical shift distribution is purely Gaussian. These assumptions have been used successfully in previous investigations [46] using the same analysis.
Figure 2.6: Reconstructed 1D $^{29}$Si MAS NMR lineshape from obtained relative areas of each $Q^{(n)}$ in the MgO · SiO$_2$ glass with (A) the isotropic projection of the 2D MAF spectrum (gray line) and the least squares best fit (dashed line) and (B) Gaussians representing integrated areas for each each $Q^{(n)}$ obtained from least-squares fitting of the 2D $^{29}$Si MAF NMR spectrum. All frequencies (in ppm) are referenced to TMS.
The calculated mole fractions, as reported in Table 2.2 for each species in the MgO · SiO$_2$ glass are $\chi_{Q^{(0)}} = 0.014 \pm 0.001$, $\chi_{Q^{(1)}} = 0.185 \pm 0.004$, $\chi_{Q^{(2)}} = 0.51 \pm 0.01$, $\chi_{Q^{(3)}} = 0.245 \pm 0.005$, $\chi_{Q^{(4)}} = 0.013 \pm 0.001$, and $\chi_{(O)^{2-}} = 0.03 \pm 0.02$. These results indicate that $\chi_{(O)^{2-}}$ is significantly smaller than in 2 MgO · SiO$_2$ and approximately the same as $\chi_{Q^{(0)}}$ within the reported uncertainty.

The mole fraction for each site were then applied to known thermodynamic disproportionation models given in Eq. (2.3) and (2.4) to calculate equilibrium constants of $k_1 = 0.19 \pm 0.02$, $k_2 = 0.174 \pm 0.009$, and $k_3 = 0.11 \pm 0.01$. The high uncertainty in $\chi_{(O)^{2-}}$ precludes calculation of $k_0$ for this composition. The disproportionation constants $k_1$, $k_2$, and $k_3$ indicate a more random distribution of $Q^{(n)}$ species within the glass structure, compared to previously studied silicate glasses, with values given in Table 2.2. These $k_n$ values are lower than previously reported values of $k_2 = 0.364$ and $k_3 = 0.464$ by Sen et al. [70], obtained from unconstrained fitting of 1D $^{29}$Si MAS NMR linshapes. Again, given the improved resolution of 2D MAF over 1D MAS NMR experiments, we believe the $k_n$ values obtained in this study are more accurate.

2.4 Conclusions

We present a structural investigation of two magnesium silicate glasses with composition 2 MgO · SiO$_2$ and MgO · SiO$_2$. For the MgO · SiO$_2$ glass we observe contributions in the $^{29}$Si 2D MAF spectrum from all $Q^{(n)}$-species, whereas, for the 2 MgO · SiO$_2$ glass we only observe contributions from $Q^{(0)}$ and $Q^{(1)}$, confirming observations by Sen and Tangeman [69] and Kalampounias et al. [68]. Using charge balance constraints, the presence of significant free oxygen anion, $(O)^{2-}$, was inferred in the 2 MgO · SiO$_2$ glass. The presence of free oxygen anion in the MgO · SiO$_2$
was also inferred but with significantly lower abundance than in the 2 MgO · SiO₂ glass. Thus, from the calculated mole fractions 2 MgO · SiO₂ glass the \( Q^{(0)} \) disproportionation constant, \( k_0 \), for 2 MgO · SiO₂ was obtained for the first time. While free oxygen anion is not directly observed in the \( ^{29}\text{Si} \) NMR, the predicted abundance in magnesium silicate glasses suggest that the free oxygen anion may be observable in \( ^{17}\text{O} \) solid-state NMR studies of \( ^{17}\text{O} \)-enriched silicate glasses.

Using the relative abundances of \( Q^{(n)} \) measured in the \( ^{29}\text{Si} \) 2D MAF spectrum of the MgO · SiO₂ glass the \( Q^{(n)} \) disproportionation constants, \( k_1 \), \( k_2 \), and \( k_3 \) were calculated. Fits of anisotropic cross sections of the \( ^{29}\text{Si} \) 2D MAF spectrum also allowed the nuclear shielding parameters for \( Q^{(1)} \) to be determined and applied to better understand the nuclear shielding tensor parameters for each \( Q^{(n)} \)-species in the MgO · SiO₂ glass. The observed \( \zeta^{(2)} \) and \( \zeta^{(3)} \) values were consistent with trends reported in a previous MAF study [46], where the magnitude of \( \zeta \) is observed to decrease as the cation potential increases. Based on results of Grimmer and coworkers [96, 97], this trend of \( \zeta \) versus cation potential indicates the increased ability of smaller more highly charged cations, such as Mg\(^{2+}\), to withdraw electron density from the \( ^{29}\text{Si} \) nucleus as the Si-NBO bond length increases, ultimately approaching a bridging Si-O-Si bond. Future investigations using NMR techniques that rely on differences in the anisotropic lineshapes to better resolve multiple \( Q^{(n)} \) sites of glasses with larger modifying cation potential than Mg\(^{2+}\) are expected to be problematic since, as the modifying cation potential increases, \( \zeta \) for each \( Q^{(n)} \) decreases and the nuclear shielding tensor parameters for each \( Q^{(n)} \)-species are increasingly similar.
2.5 Appendix

In a glass with composition $\alpha$MO·$(1-\alpha)$SiO$_2$, we assume the following anionic equilibria are present in the melt:

\[2Q^{(n)} \rightleftharpoons Q^{(n-1)} + Q^{(n+1)}, \tag{2.16}\]

with

\[K_n = \frac{A_{Q_{n-1}}A_{Q_{n+1}}}{(A_{Q_n})^2}, \tag{2.17}\]

and

\[2Q^{(0)} \rightleftharpoons 2Q^{(1)} + (O)^{2-}, \tag{2.18}\]

with

\[K_0 = \frac{(A_{Q_1})^2A_{(O)^{2-}}}{(A_{Q_0})^2}, \tag{2.19}\]

where $A_Y$ is the activity of species $Y$. The activity of each species is related to its mole fraction, $\chi_y$, according to

\[A_Y = \gamma_Y \chi_Y. \tag{2.20}\]

Substituting Eq. (2.20) into Eqs. (2.17) and Eqs. (2.19) we obtain

\[k_n = \frac{\gamma_{Q_n}^2}{\gamma_{Q_{n-1}} \cdot \gamma_{Q_{n+1}}} \cdot K_n = \frac{\chi_{Q_{n-1}} \cdot \chi_{Q_{n+1}}}{\chi_{Q_n}^2}, \tag{2.21}\]

and

\[k_0 = \frac{\gamma_{Q_1}^2 \cdot \gamma(O)^{2-}}{\gamma_{Q_0}^2} \cdot K_0 = \frac{\chi_{Q_1}^2 \cdot \chi(O)^{2-}}{\chi_{Q_0}^2}. \tag{2.22}\]

The mole fractions used in calculating these equilibrium constants of our anionic thermodynamic equilibrium model requires

\[\chi_{Q_0} + \chi_{Q_1} + \chi_{Q_2} + \chi_{Q_3} + \chi_{Q_4} + \chi(O)^{2-} = 1. \tag{2.23}\]
In \(^{29}\text{Si}\) NMR experiment on the glass we measure the fraction of silicon in each of the five \(Q_n\) coordination states, \(y_{Q_n}\), given by Eq. (2.12). Additional information is then needed to obtain the \((O)^{2-}\) mole fraction,

\[
\chi_{(O)^{2-}} = \frac{n_{(O)^{2-}}}{n_{Q_0} + n_{Q_1} + n_{Q_2} + n_{Q_3} + n_{Q_4} + n_{(O)^{2-}}}.
\] (2.24)

as well as the \(Q^{(n)}\) mole fractions,

\[
\chi_{Q_n} = \frac{n_{Q_n}}{n_{Q_0} + n_{Q_1} + n_{Q_2} + n_{Q_3} + n_{Q_4} + n_{(O)^{2-}}},
\] (2.25)

where \(n_{Q_n}\) are the total number of moles of the anionic species \(Q_n\), and \(n_{(O)^{2-}}\) is the total number of moles of the anion \((O)^{2-}\). Substituting Eq. (2.12) into the expressions above one obtains

\[
\chi_{(O)^{2-}} = \frac{(n_{(O)^{2-}}/n_{Si})}{y_{Q_0} + y_{Q_1} + y_{Q_2} + y_{Q_3} + y_{Q_4} + (n_{(O)^{2-}}/n_{Si})},
\] (2.26)

and

\[
\chi_{Q_n} = \frac{y_{Q_n}}{y_{Q_0} + y_{Q_1} + y_{Q_2} + y_{Q_3} + y_{Q_4} + (n_{(O)^{2-}}/n_{Si})}.
\] (2.27)

By combining the charge balance equation, given by

\[
2n_{M^{2+}} = 4n_{Q_0} + 3n_{Q_1} + 2n_{Q_2} + n_{Q_3} + 2n_{(O)^{2-}},
\] (2.28)

where \(n_{M^{2+}}\) is the total number of moles of the cation \(M^{2+}\), with the stoichiometric ratio

\[
\frac{n_{M^{2+}}}{n_{Si}} = \frac{\alpha}{1 - \alpha},
\] (2.29)

one obtains

\[
2\left(\frac{\alpha}{1 - \alpha}\right) = 4\frac{n_{Q_0}}{n_{Si}} + 3\frac{n_{Q_1}}{n_{Si}} + 2\frac{n_{Q_2}}{n_{Si}} + \frac{n_{Q_3}}{n_{Si}} + 2\frac{n_{(O)^{2-}}}{n_{Si}},
\] (2.30)
which can be rewritten as

\[
\frac{n(O)^{2-}}{n_{Si}} = \left( \frac{\alpha}{1 - \alpha} \right) - 2y_{Q_0} - 1.5y_{Q_1} - y_{Q_2} - 0.5y_{Q_3}.
\]  

(2.31)

Substituting this expression into Eqs. (2.26) and (2.27) one obtains the expressions in Eqs. (2.14) and (2.15).

The following chapter will expand on the work of Davis et. al [99](Figure 2.5) by studying the dependence of the CSA parameter \( \zeta^{(3)} \) on the glass modifier.
Chapter 3: MAF NMR of binary alkali and alkaline earth silicate glasses

3.1 Introduction

As explained in the previous chapters, silicate glasses, quenched from a melt, are composed of a network of silicate tetrahedra that are interlinked by bridging oxygens (BOs), or Si-O-Si bonds. As network modifiers are introduced to the melt, Si-O-Si bonds are broken to form two Si-O\(^{-}\) bonds, called non-bridging oxygens (NBOs). We assume that an equilibrium exists in the glass:

\[ 2Q^{(n)} \rightleftharpoons Q^{(n-1)} + Q^{(n+1)}, \] (3.1)

which can be modeled by the equilibrium constant, \( k_n \),

\[ k_n = \frac{\chi_{Q^{(n+1)}} \cdot \chi_{Q^{(n-1)}}}{(\chi_{Q^{(n)}})^2}. \] (3.2)

Most studies of silicate glasses using NMR to measure the distribution of \( Q^{(n)} \) species have been performed using magic angle spinning (MAS). However, two-dimensional techniques (MAF, PASS, MAT, MAH) provide more information than MAS, particularly about the chemical shift anisotropy tensor. This information can be used to probe the coordination environment of the \( Q^{(n)} \) species in the glass. One challenge with the MAF experiment is that a specialized probe is required, which is not available
Experiments like PASS and MAT can be performed using commercial MAS, as they do not require a DAS probe; however, these experiments have much more complicated pulse sequences than MAF and require very careful calibration, whereas the pulse sequence for MAF is very simple and robust to use, if a DAS probe is available.

Work by Eric Keeler [100] using *ab initio* calculations on an Si(OH)$_4$ tetrahedron has shown that the magnitude of the chemical shift anisotropy, $\zeta$, is related to the Si-NBO bond length, $r_{\text{Si-NBO}}$. Two dimensional MAF will be used to probe $r_{\text{Si-NBO}}$ in a series of silicate glasses using the results of Keeler [100]. However, there are several challenges to studying silicate glasses using MAF, outlined below.

Previous MAF investigations of silicate glasses [45–47, 99] have been of limited impact because these experiment often took several weeks to a month to complete, so a broad range of compositions could not be systematically studied in a reasonable time frame, due to the very long inherent relaxation time, $T_1$, of the $^{29}\text{Si}$ nucleus in glasses. While Davis et al. [99] improved upon the MAF experiment with the addition of CPMG acquisition which allowed the MAF experiment to be collected in only three days, this experiment was still limited by requiring the samples to be enriched to $\sim$100% in $^{29}\text{Si}$, which is quite expensive. The cost of making $^{29}\text{Si}$ enriched samples makes systematic studies difficult as well.

Due to this high cost, systematic compositional studies of silicate glasses must be performed at natural abundance $^{29}\text{Si}$ ($\sim$4.7%); however, these experiments are limited by low spin density and long relaxation times. By the addition of CPMG acquisition to the MAF experiment, the sensitivity is improved 3-to-5 fold, but long
relaxation times remain a problem. One possible way to mitigate this problem is by the addition of paramagnetic dopants, used to greatly reduce the $T_1$ of the $^{29}\text{Si}$ nuclei.

In this work, further improvements made upon the MAF experiment by using CPMG acquisition and the paramagnetic dopant Cu$^{2+}$ will be detailed, which allowed for the MAF analysis of silicate glasses at natural abundance $^{29}\text{Si}$ in just 4-6 days, not 3 or more weeks.

3.2 Experimental
3.2.1 Sample Preparation

Approximately 2 g of each sample was synthesized from high-purity metal carbonates (Aldrich 99+%), natural abundance silicon (IV) oxide (Aldrich 99.99+% metals basis), and copper (II) oxide (Mallinckrodt). Approximately 0.5 wt% CuO was added to decrease the relaxation time. Before synthesis, all reagents were kept in a drying oven at 150$^\circ$C to eliminate absorbed water due to the hygroscopic nature of SiO$_2$ and metal carbonates. The reagents were quickly moved from the drying oven and massed, then combined and ground in an alumina mortar and pestle for approximately ten minutes to ensure reagent homogeneity. The mixed reagents were then transferred to a platinum crucible and decarbonated at 700$^\circ$C overnight, followed by melting for about 2 h at approximately 100$^\circ$C above their respective liquidus temperatures. The melt was then quenched by placing the bottom of the crucible into water. The resulting glasses were brilliant blue in color, completely transparent, and free of bubbles. The samples were immediately placed in a desiccator due to their inherent hygroscopicity. When ready for analysis the samples were quickly moved to a nitrogen-filled glovebag, crushed using an alumina mortar and pestle, and subsequently packed in a
4mm zirconia rotor. The sealed rotors were spun with compressed air dried to a dew point of \(-40^\circ F\). We observed no considerable \(^1\)H signal in the samples.

**Paramagnetic doping**

Doping with paramagnetic compounds is commonplace in NMR in order to dramatically decrease the spin-lattice relaxation time, \(T_1\), of the nucleus of interest. However, many dopants (Gd\(^{3+}\), Fe\(^{3+}\)) are so powerful that the spin-spin relaxation time, \(T_2\), is strongly decreased as well; this leads to artificially broad lineshapes, as the width of these lineshapes is inversely proportional to \(T_2\). The Cu\(^{2+}\) ion was chosen because it contains only one unpaired electron which has a very short \(T_{1,e}\), and we found that doping to \(\sim 0.5\) wt\% with Cu\(^{2+}\) drastically decreased \(T_1\) without considerable effect on \(T_2\). Recent work by Inagaki et al. [101] on mesoporous silica and zeolites has confirmed that the Cu\(^{2+}\) ion is a desirable dopant in NMR, with a drastic effect on the spin-lattice relaxation time, \(T_1\), but without any peak broadening due to the decrease of the spin-spin relaxation time, \(T_2\).

To investigate the effect of Cu\(^{2+}\) doping on time savings and signal-to-noise gains, we synthesized two binary barium disilicate glasses, BaO · 2SiO\(_2\): one undoped, and one doped to \(\approx 0.5\) wt\% with CuO. The results are presented in Figure 3.1. To achieve enough signal to clearly see each peak, MAF on the undoped sample was run for 64 days, achieve a signal-to-noise (S/N) ratio of 26. The MAF on the doped sample was run for only 5 days, achieving S/N of 66. To achieve a S/N of 66 in the undoped sample, the experiment would have to be run

\[
\left( \frac{66}{26} \right)^2 = 6.44
\]

(3.3)
To achieve the same S/N, the undoped sample would have to run for \textbf{410 days}.

That’s an effective factor of \textbf{time savings of 82}.

Figure 3.1: A comparison of undoped barium disilicate glass and CuO-doped barium silicate glass. We observe an effective reduction in experiment time by a factor of about 82 by simply adding 0.5wt\% CuO.
times longer, corresponding to an experiment time of about 410 days. This means that by the addition of only 0.5wt% CuO, we have effectively reduced the amount of time each experiment takes by a factor of about 82. This number will vary depending on the amount of CuO added to the sample.

### 3.2.2 NMR Spectroscopy

All experiments were performed on a Tecmag Apollo NMR spectrometer operating at a field strength of 9.4 T (79.472662 MHz for $^{29}$Si), interfaced to a home-built 4mm DAS probe based on a previous design [71]. One concern with DAS-type probes is that the rf tuning changes as a function of the rotor angle due to the coil (an inductor) moving with respect to the external magnetic field. As such, the probe was tuned and matched at the magic angle. All experiments were performed at ambient temperature and a sample spinning rate of approximately 14 kHz. The $^{29}$Si relaxation time of each sample was measured using the saturation recovery experiment under MAS conditions. The relaxation profile of each sample was multi-exponential, that is, there were a distribution of relaxation times. The relaxation profile was fit to the stretched exponential function,

$$ A(1 - e^{(-t/T_1^*)^\beta}), \quad (3.4) $$

where $T_1^*$ is the net relaxation time of the sample, and the parameter $\beta$ is a measure of the distribution of relaxation times, where $\beta = 1$ indicates a single exponential decay (i.e. the true $T_1$ is measured), and $\beta = 0.5$ indicates a very random distribution of $T_1$ values (i.e. the resulting $T_1^*$ indicates a broad distribution of relaxation times). Examples of a single exponential and stretched exponential fits are given in Figures 3.2 and 3.3. Typically for our experiments, $\beta \approx 0.55$. A recycle delay of approximately
Figure 3.2: The saturation recovery data (diamonds) for the sample Mg$_{0.375}$K$_{1.25}$·4SiO$_2$ from Keeler [100], presented with a logarithmic time axis (horizontal) fit to a single exponential function (solid line).

$5T_1$ was used for each sample with very short $T_1$ values ($\approx$1-2 seconds). For samples with particularly long $T_1$, a recycle delay of approximately $1.5T_1$ was used, which corresponds to the time it takes about 75% of the spins to fully relax. No changes in peak shape as a function of recycle delay were observed, suggesting there was no net differential relaxation among species in the glass, as observed by Keeler [100]. The measured $T_1$ values and recycle delays for each experiment are provided in the Appendix in Table 3.3.

The MAF experiment used in this work was the same as in previous chapters, shown in Figure 3.4. A summary of experimental details is given in the Appendix in Table 3.3. The number of points directly acquired will be denoted as $n_{t2}$, and the number of points indirectly acquired will be denoted as $n_{t1}$. Hypercomplex acquisition
Figure 3.3: The saturation recovery data (diamonds) for the sample Mg$_{0.375}$K$_{1.25}$·4SiO$_2$ from Keeler [100], presented with a logarithmic time axis (horizontal) fit to a stretched exponential function with $\beta \approx 0.5$

was used to obtain positive and negative time domains of the indirectly acquired data. In order to simplify the experiment, phase cycling was employed only to eliminate signals arising from the evolution of the $p = 0$ pathway during $t_1$. We assume that the remaining $\frac{\pi}{2}$ pulse and all subsequent $\pi$ pulses were perfectly efficient; however, stimulated echoes were observed, suggesting this assumption is not entirely true. This effect was probably caused by an imperfect length of the pulses.

The resulting spectra were analyzed using a modified bootstrap [102] approach written by Professor Jay H. Baltisberger, whereby the entire 2D spectrum is simulated in “one shot”. A new spectrum is generated by picking $n_{t_2} \times n_{t_1}$ points from the experimental spectrum at random, and weighing each point appropriately based on the number of times it was picked at random. The resulting spectrum is then analyzed.
using the minimization package MINUIT [103], fitting to a variety of parameters for each simulated $Q^{(n)}$-species: amplitude, area, $\delta_{\text{iso}}$, $\delta_{xx}$, $\delta_{yy}$, Gaussian broadening (used to model broadening due to a distribution of geometries), and Lorentzian broadening (used to model broadening caused by the experiment). A new spectrum is then generated by again picking points at random, and analyzed. This is repeated two thousand times to obtain a Gaussian distribution of parameters, and as such, a measure of their uncertainties.

3.3 Discussion

In order to expand on the results from the previous chapter in Figure 2.5, 2D MAF was used to study seven Cu(II)-doped binary silicate glasses of compositions SrO $\cdot$ 2SiO$_2$, BaO $\cdot$ 2SiO$_2$, Na$_2$O $\cdot$ 2SiO$_2$, Na$_2$O $\cdot$ 4SiO$_2$, Rb$_2$O $\cdot$ 2SiO$_2$, Rb$_2$O $\cdot$ 4SiO$_2$, and Cs$_2$O $\cdot$ 2SiO$_2$. The experimental 2D MAF spectra, the simulated MAF spectra, and the residuals for each sample are given in in the Appendix in Figures 3.7-3.12. The spectra were analyzed using Prof. Baltisberger's approach (as outlined in the previous section) to yield not only the mole fraction of each $Q^{(n)}$-species present in the glass, but also rich information about the chemical shift, and thus, the electronic environment around the $^{29}$Si nuclei in the glass. Every simulated parameter was allowed to vary freely. The mole fractions are given in Table 3.1, and the chemical shift anisotropy information is given in Table 3.2.

The results shown in Table 3.2 indicate that the chemical shift anisotropy, $\zeta^{(3)}$ increases with decreasing cation potential. Figure 3.5 shows a linear trend between these parameters. It is also clear from Figure 3.5 that there exists a trend for each metal cation as a function of molar composition. Interestingly, the best-fit simulation
Table 3.1: Mole fractions of anionic species in a series of glasses, as measured by Magic Angle Flipping. The glasses are sorted by cation potential (Z/r) from strongest (Mg²⁺) to weakest (Cs⁺). The results are given as an average ± the standard deviation in the simulated parameter as determined by the modified bootstrap approach written by Prof. Baltisberger.
<table>
<thead>
<tr>
<th>Glass</th>
<th>reference</th>
<th>(\zeta^{(4)}/\text{ppm})</th>
<th>(\zeta^{(3)}/\text{ppm})</th>
<th>(\zeta^{(2)}/\text{ppm})</th>
<th>(\eta^{(4)})</th>
<th>(\eta^{(3)})</th>
<th>(\eta^{(2)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO(\cdot)SiO(_2)</td>
<td>[99]</td>
<td>0.0</td>
<td>27.5 ± 0.5</td>
<td>36.0 ± 0.5</td>
<td>0.0</td>
<td>0.45 ± 0.11</td>
<td>–</td>
</tr>
<tr>
<td>CaO(\cdot)SiO(_2)</td>
<td>[47]</td>
<td>0.0</td>
<td>45.4</td>
<td>48.3</td>
<td>0.0</td>
<td>0.01</td>
<td>–</td>
</tr>
<tr>
<td>SrO-2SiO(_2)</td>
<td>this work</td>
<td>9.15 ± 0.03</td>
<td>56.94 ± 0.08</td>
<td>64.9 ± 0.2</td>
<td>0.05 ± 0.02</td>
<td>0.023 ± 0.0003</td>
<td>–</td>
</tr>
<tr>
<td>BaO-2SiO(_2)</td>
<td>this work</td>
<td>8.341 ± 0.008</td>
<td>59.55 ± 0.05</td>
<td>52.78 ± 0.08</td>
<td>0.02 ± 0.01</td>
<td>0.029 ± 0.0002</td>
<td>–</td>
</tr>
<tr>
<td>2Na(_2)O-3SiO(_2)</td>
<td>[45]</td>
<td>0.0</td>
<td>69</td>
<td>78.0</td>
<td>0.0</td>
<td>0.03</td>
<td>–</td>
</tr>
<tr>
<td>Na(_2)O-2SiO(_2)</td>
<td>this work</td>
<td>4.17 ± 0.05</td>
<td>75.34 ± 0.09</td>
<td>81.6 ± 0.9</td>
<td>0.064 ± 0.008</td>
<td>0.029 ± 0.0009</td>
<td>–</td>
</tr>
<tr>
<td>Na(_2)O-4SiO(_2)</td>
<td>this work</td>
<td>6.039 ± 0.083</td>
<td>76.79 ± 0.14</td>
<td>–</td>
<td>0.585 ± 0.026</td>
<td>0.046 ± 0.0011</td>
<td>–</td>
</tr>
<tr>
<td>K(_2)O-2SiO(_2)</td>
<td>[46]</td>
<td>0.0</td>
<td>74.9 ± 0.2</td>
<td>85.0 ± 1.3</td>
<td>0.0</td>
<td>0.030 ± 0.006</td>
<td>–</td>
</tr>
<tr>
<td>K(_2)O-4SiO(_2)</td>
<td>[100]</td>
<td>0.0</td>
<td>84.3 ± 0.1</td>
<td>–</td>
<td>0.0</td>
<td>0.0</td>
<td>–</td>
</tr>
<tr>
<td>Rb(_2)O-2SiO(_2)</td>
<td>this work</td>
<td>3.2 ± 0.8</td>
<td>82.20 ± 0.10</td>
<td>74.2 ± 0.2</td>
<td>0.8 ± 0.3</td>
<td>0.081 ± 0.0008</td>
<td>0.030 ± 0.003</td>
</tr>
<tr>
<td>Rb(_2)O-4SiO(_2)</td>
<td>this work</td>
<td>5.1 ± 0.3</td>
<td>86.09 ± 0.14</td>
<td>–</td>
<td>0.22 ± 0.12</td>
<td>0.032 ± 0.002</td>
<td>–</td>
</tr>
<tr>
<td>Cs(_2)O-2SiO(_2)</td>
<td>this work</td>
<td>0.0</td>
<td>79.12 ± 0.08</td>
<td>74.1 ± 0.4</td>
<td>64.8 ± 0.5</td>
<td>–</td>
<td>0.047 ± 0.009</td>
</tr>
</tbody>
</table>

Table 3.2: Chemical shift anisotropy parameters, \(\zeta^{(n)}\) (in ppm) and \(\eta^{(n)}\) for each \(Q^{(n)}\) of the glasses studied in this work. The results are given as an average ± the standard deviation in the simulated parameter as determined by the modified bootstrap approach written by Prof. Baltisberger.
of each sample indicates that the chemical shift tensor of the $Q^{(3)}$ site remains axially symmetric for all modifiers and each $Q^{(3)}$, i.e. the tensor has a small $\eta^{(3)}$ or stated differently, $\delta_{xx} \sim \delta_{yy}$. This indicates that the observed trend in Figure 3.5 is due largely to changes in the $\delta_{zz}$ parameter. Grimmer et al. [96,97] postulated that this correlation between the magnitude of the CSA and the identity of the modifier was largely due to the Si-NBO bond length. Based on Grimmer’s results it seems that the observed trend for each metal cation results from changes in the Si-NBO bond length as well, and we postulate this is due to cation cluster sizes. Small clusters may result in shorter Si-NBO bond lengths and as such, a larger $\zeta^{(3)}$. Larger clusters may result in longer Si-NBO bond lengths and smaller $\zeta^{(3)}$.

Using *ab initio* calculations to probe the effect of changing a single Si-O bond length in a Si(OH)$_4$ tetrahedron on the chemical shift tensor, Keeler(111,303),(708,330) showed that a decrease in one Si-O bond length leads to an increase in $\zeta$, whereas an increase in the Si-O bond length leads to a decrease in $\zeta$. A summary of his results is given in Figure 3.6. While these results are qualitative, they can be used to show that the observed trend in Figure 3.5 are due largely to a decrease in the Si-NBO bond length with decreasing cation potential. This serves as a testament to the ability of small, highly charged cations like Mg$^{2+}$ to extract electron density from the non-bridging oxygen, effectively causing it to “reach out” to the cation, thereby increasing the Si-NBO bond length to lengths approaching a fully symmetric tetrahedron, whereas large, singly charged cations like Rb$^+$ do not have this ability to extract electron density from the NBO, and thus allow the silicate tetrahedron to relax to a more electronically favorable geometry.
3.3.1 Second distinct $Q^{(3)}$ site observed in Rb$_2$O · 2SiO$_2$ glass

What began as a straight-forward compositional NMR study on binary silicate glasses led us to make an observation of great importance: the rubidium and cesium disilicate glasses exhibits *two* unique $Q^{(3)}$ environments, straying from the conventional model of silicate glasses outlined in the first two chapters. As stated in the introduction, the current glass speciation model predicts:

$$2Q^{(n)} \rightleftharpoons Q^{(n-1)} + Q^{(n+1)}; \quad (3.5)$$

however, this model does not predict what may happen to a *single* $Q^{(3)}$ site with the addition of modifier. There may exist an equilibrium such as:

$$Q^{(3)} \rightleftharpoons Q^{(3')} , \quad (3.6)$$

where $Q^{(3)}$ is the “starting” $Q^{(3)}$ environment, and with the addition of modifying cations a second site is produced, presumably due to the large size of Rb$^+$ and Cs$^+$ relative to the size of the silicate tetrahedron. A notable observation is that the cesium silicate glasses produce 2D MAF spectra with a higher degree of resolution than the rubidium silicate glasses (i.e. the $Q^{(3)}$ and $Q^{(3')}$ sites are isotropically resolved more clearly), so any future investigation on this equilibrium would be completed easier and more accurately with cesium silicate glasses. Due to the small sample size of the data in this chapter though, this equilibrium cannot be thoroughly probed.

3.4 Conclusions

A structural investigation of silicate glasses using MAF is presented for a variety of binary silicate glasses: SrO · 2SiO$_2$, BaO · 2SiO$_2$, Na$_2$O · 2SiO$_2$, Na$_2$O · 4SiO$_2$, Rb$_2$O · 2SiO$_2$, Rb$_2$O · 4SiO$_2$, and Cs$_2$O · 2SiO$_2$, all doped to approximately 0.5wt%
with CuO. An inversely proportional trend between $\zeta^{(3)}$ and cation potential is observed in a variety of binary silicate glasses, and we postulate that this behavior is primarily due to changes in the Si-NBO bond length, a la Grimmer et al. [96, 97]. Moreover, we observe a trend among glasses of the same atomic composition, where $\zeta^{(3)}$ tends to increase with decreasing modifier content. This is presumably due to changes in the cation clustering pattern. In order to gain more insight into the equilibrium presented in equation 3.6, the next chapter will focus on a series of cesium silicate glasses with a variety of modifier content, $\chi_{\text{Cs}2\text{O}}$. 
Figure 3.4: (A) Shifted-echo Magic-Angle Flipping pulse sequence with spin transition and spatial symmetry pathways. (B) Magic-Angle Flipping pulse sequence using CPMG acquisition with spin and spatial symmetry pathways. In all experiments the rotor axis angle, $\theta_R$, during $t_1$ evolution is set to $\theta_R = 90^\circ$. The period, $\tau_{\text{hop}}$, during which the magnetization is stored as Zeeman order (i.e. the magnetization decays only by $T_1$) while the the rotor is switched between angles, is set to 180 ms. Hypercomplex acquisition is performed to obtain positive and negative $t_1$ quadrants in the 2D time domain signal [74]. Six dummy scans are performed prior to acquisition to ensure the system reached steady state prior to the start of the experiment.
Figure 3.5: Plotted above are the measured chemical shift anisotropy, $\zeta(3)$, values (Table 3.2) plotted versus cation potential, $Z/r$. Unless otherwise labeled, each blue box corresponds to the disilicate composition, $A_2O \cdot 2SiO_2$. The yellow boxes correspond to $\zeta(3')$, the CSA of a second $Q(3)$ site observed in rubidium and cesium disilicate glasses. The atomic radii were taken from Whittaker and Muntus [98], assuming a coordination number of 6 for each cation. The chemical shift anisotropy appears to be inversely proportional to cation potential; however, $\zeta(3)$ changes as a function of the mole fraction of modifier, so there may be a trendline for each unique molar composition as a function of modifier. The dotted red line is not a best-fit trendline; it is there to simply guide the eye.
Figure 3.6: The *ab initio* computational results from Keeler [100] describing the change in the CSA tensor as a function of Si-O bond length while retaining tetrahedral bond angles. Generally, as a single Si-O bond length is shortened, $\zeta$ increases and the nuclear shielding decrease (corresponding to a chemical shift increase.)
3.5 Appendix
Table 3.3: Experimental parameters for the MAF analysis of the listed glasses. All experiments were collected with $t_1$ dwell time of 50 $\mu$s and a $t_2$ dwell time of 12.6 $\mu$s. Hypercomplex acquisition was used to acquire positive and negative time domains in the $t_1$ dimension. The number of $t_1$ points acquired corresponds to the total number of hypercomplex points acquired; the number in parenthesis corresponds to the effective number of $t_1$ points acquired.
Figure 3.7: The experimental MAF spectrum, simulated spectrum, and residuals for the Rb$_2$O·(4)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 2.26 \pm 0.04$. 
Figure 3.8: The experimental MAF spectrum, simulated spectrum, and residuals for the Rb$_2$O·(2)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi_{\text{red}}^2 = 3.63 \pm 0.05$. 
Figure 3.9: The experimental MAF spectrum, simulated spectrum, and residuals for the Na$_2$O·(4)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 2.11 \pm 0.03$. 
Figure 3.10: The experimental MAF spectrum, simulated spectrum, and residuals for the Na$_2$O·(2)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 1.59 \pm 0.03$. 
Figure 3.11: The experimental MAF spectrum, simulated spectrum, and residuals for the SrO-(2)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 2.24 \pm 0.03$. 

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Figure 3.12: The experimental MAF spectrum, simulated spectrum, and residuals for the BaO·(2)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 1.850 \pm 0.009$. 

\[\chi^2_{\text{red}} = 1.850 \pm 0.009\]
Chapter 4: MAF study of the compositional dependence on the structure and CSA of cesium oxide-modified silicate glasses

4.1 Introduction

As explained in the previous three chapters, silicate glasses are composed of a network of silicate tetrahedra that are interlinked by bridging oxygens (BOs), or Si-O-Si bonds. As network modifiers are introduced to the melt, Si-O-Si bonds are broken to form two Si-O$^-$ bonds, called non-bridging oxygens (NBOs). The following equilibrium has been well studied using NMR previously:

\[ 2Q^{(n)} \rightleftharpoons Q^{(n-1)} + Q^{(n+1)}; \]  

(4.1)

however, as shown in the chapter 3, silicate glasses modified with large alkali (Cs$^+$, Rb$^+$) contain two unique $Q^{(3)}$ sites, suggesting another equilibrium may exist in the glass:

\[ Q^{(3)} \rightleftharpoons Q^{(3')} \].  

(4.2)

In order to more completely study the effect of modifier content on the chemical shift anisotropy, eleven cesium silicate glasses were synthesized. For the generic composition $\text{Cs}_2\text{O} \cdot (x)\text{SiO}_2$, we synthesized samples with $x = 1.5, 1.75, 2, 2.25, 2.5, 3, 3.5,$
4, 4.5, 5, and 6 to thoroughly study the $Q^{(3)}$ regime of the binary distribution model (Figure 1.6).

4.2 Experimental

4.2.1 Sample Preparation

Approximately two grams of each sample was synthesized from high-purity cesium carbonate (Aldrich 99+%), natural abundance silicon (IV) oxide (Aldrich 99.99+% metals basis), and copper (II) oxide (Mallinckrodt). Approximately 0.5wt% CuO was added to each sample to decrease relaxation time. A summary table of synthesis information is given in Table 4.1. Cesium carbonate is incredibly hygroscopic (will go from a fine powder to a paste to an aqueous solution in just a few hours) so great care was taken to keep all reagents dry, by keeping them in a 150°C drying oven prior to synthesis. The reagents were quickly moved from the drying oven and massed, then combined and ground in an alumina mortar pestle for about ten minutes to ensure reagent homogeneity. The mixture was then transferred to a platinum crucible and decarbonated at 700°C overnight. The samples were then transferred to a high-temperature furnace and melted for about two hours. A phase diagram for cesium silicates was not found so the melt temperatures were found by a trial-and-error approach, where a low temperature was first chosen, and if the synthesis failed, the temperature was increased and synthesis attempted again. Once a melt was achieved, the samples were quenched by dipping the bottom of the crucible in room temperature water. The resulting glasses were brilliant blue in color, completely transparent, and free of bubbles; this is indicative of a successful glass synthesis. The samples were immediately placed in a desiccator, crushed in a nitrogen-filled glove bag.
and subsequently packed in a 4mm zirconia prior to analysis. The sealed rotors were spun with compressed air dried to a dew point of -40°F. We observed no considerable $^1$H signal in the samples.

One problem in synthesizing binary alkali silicate glasses containing large alkali (K, Rb, Cs) is alkali volatization. Malfait et al. [43] detail an alternate synthesis approach whereby a calibrated “synthesis curve” is generated by heating a constant composition at a constant temperature for varying amounts of time before quenching, and then the samples are analyzed for elemental content. This gives a measure of the degree of volatilization of the alkali oxide as a function of temperature and time. As such, Malfait et al. can accurately describe the alkali content in their glasses. This approach, while valuable, was not used in our syntheses.

4.2.2 NMR Spectroscopy

All experiments were performed on a Tecmag Apollo NMR spectrometer operating at a field strength of 9.4 T (79.472662 MHz for $^{29}$Si), interfaced to a home-built 4mm DAS probe based on a previous design [71]. One concern with DAS-type probes is that the rf tuning changes as a function of the rotor angle due to the coil (an inductor) moving with respect to the external magnetic field. As such, the probe was tuned and matched at the magic angle, where we detect. All experiments were performed at ambient temperature and a sample spinning rate of approximately 14 kHz. The $^{29}$Si relaxation time of each sample was measured using the saturation recovery experiment under MAS conditions. The relaxation profile of each sample was, again, multi-exponential and fit to the stretched exponential function,

$$A(1 - e^{(\frac{1}{T_1^{\beta}})^{\alpha}})$$

(4.3)
Table 4.1: Synthesis information for cesium silicate glasses of the generic composition Cs$_2$O · (x)SiO$_2$. The mole fraction of cesium carbonate, $\chi_{\text{Cs}_2\text{O}}$, is given as synthesized. It is worth noting that large alkali oxides are prone to volatilization at high temperatures, so the $\chi_{\text{Cs}_2\text{O}}$ is likely smaller than as calculated, but elemental analysis was not performed on these samples. All glasses were synthesized in ambient air.

<table>
<thead>
<tr>
<th>“x”</th>
<th>$\chi_{\text{Cs}_2\text{O}}$</th>
<th>Mass Cs$_2$CO$_3$/g</th>
<th>Mass SiO$_2$/g</th>
<th>Mass CuO/g</th>
<th>Melt Temperature / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.3932</td>
<td>1.7463</td>
<td>0.4852</td>
<td>0.0156</td>
<td>1100</td>
</tr>
<tr>
<td>1.75</td>
<td>0.3546</td>
<td>1.6455</td>
<td>0.5437</td>
<td>0.0115</td>
<td>1100</td>
</tr>
<tr>
<td>2</td>
<td>0.3305</td>
<td>1.6216</td>
<td>0.5982</td>
<td>0.0099</td>
<td>1200</td>
</tr>
<tr>
<td>2.25</td>
<td>0.3048</td>
<td>1.5609</td>
<td>0.6480</td>
<td>0.0112</td>
<td>1200</td>
</tr>
<tr>
<td>2.5</td>
<td>0.2826</td>
<td>1.5060</td>
<td>0.6958</td>
<td>0.0122</td>
<td>1200</td>
</tr>
<tr>
<td>3</td>
<td>0.2477</td>
<td>1.4127</td>
<td>0.7832</td>
<td>0.0106</td>
<td>1200</td>
</tr>
<tr>
<td>3.5</td>
<td>0.2142</td>
<td>1.2750</td>
<td>0.8543</td>
<td>0.0109</td>
<td>1200</td>
</tr>
<tr>
<td>4</td>
<td>0.1983</td>
<td>1.2401</td>
<td>0.9165</td>
<td>0.0103</td>
<td>1200</td>
</tr>
<tr>
<td>4.5</td>
<td>0.1798</td>
<td>1.1775</td>
<td>0.9806</td>
<td>0.0132</td>
<td>1300</td>
</tr>
<tr>
<td>5</td>
<td>0.1667</td>
<td>1.1284</td>
<td>1.0324</td>
<td>0.0108</td>
<td>1300</td>
</tr>
<tr>
<td>6</td>
<td>0.1418</td>
<td>1.0146</td>
<td>1.1232</td>
<td>0.0125</td>
<td>1400</td>
</tr>
</tbody>
</table>
No net differential relaxation among species was observed as a function of relaxation delay, so quantitation is considered accurate. A summary of the experimental details is given in the Appendix in Table 4.4. The MAFCPMG experiment was the same as used in chapter three (Figure 3.4), and the spectra were analyzed using Prof. Baltisberger’s approach, as outlined in the previous chapter, section 3.2.2. All 2D MAF spectra are given in Figures 4.6-4.16.

Glasses rich in modifier (1.5 ≤ x ≤ 4) were fit with two unique $Q^{(3)}$ environments; for glasses with lesser modifier content, only a single $Q^{(3)}$ environment was observed. As is most clearly evident in Figure 4.10, there appear to be two unique $Q^{(4)}$ environments in glasses more silica-rich than the disilicate composition. As such, we fit each of those samples (x ≥ 2.25) with two unique $Q^{(4)}$ sites. Upon first glance, one or both of the $Q^{(4)}$ sites appear to have non-zero CSA. For binary glasses containing large alkali, it does not seem out-of-the-ordinary for $Q^{(4)}$ sites to have non-zero CSA; large alkali demand a large coordination number (6-10), and due to the diluteness of $Q^{(3)}$, and thus, oxygen anions in the glass, the cations probably do coordinate to bridging oxygens - distorting the tetrahedral geometry of the $Q^{(4)}$ site and producing a non-zero CSA for silicon atoms in $Q^{(4)}$ sites. However, unconstrained simulations provided unsatisfactory fits and non-sensical results by allowing all the parameters for both $Q^{(4)}$ to vary freely, presumably because the simulation was fitting to noise. As such, the spectra were simulated with two $Q^{(4)}$ sites constrained to have zero CSA. This is an adequate approximation to get better quantification, but at the loss of CSA information about the $Q^{(4)}$ electronic environment. All simulations were performed with 600 Hz of Gaussian broadening on all sites, emulating a distribution of each
site. In this case, unconstrained fits produced wildly different values for Gaussian broadening, which is physically unrealistic.

4.3 Discussion

In order to investigate the effect of modifier content on $\zeta^{(3)}$, eleven silicate glasses of the generic composition Cs$_2$O·$(x)$SiO$_2$ were studied using MAF to extra chemical shift anisotropy information, as well as the relative abundances of each $Q^{(n)}$-site. The results of the spectral fits are given in Tables 4.2 and 4.3, and given graphically in Figures 4.1 and 4.2. The percent abundance of each $Q^{(n)}$-species are given in Figure 4.1 as a function of $\chi_{\text{Cs}_2\text{O}}$, and no error bars are given due to the high degree of precision of the spectra fits. The dotted lines correspond to what would be expected if the distribution were binary. We find relatively good agreement between our fits and the binary distribution model, and our results agree with speciation results from Malfait et al. [40] using Raman spectroscopy. The disproportionation constant, $k_3$, was determined for the three samples containing $Q^{(2)}$. The $k_3$ value from the analysis of Cs$_2$·SiO$_2$ glass is in relatively good agreement with the value reported by Malfait [40], 0.0019 ± 0.0005.

The primary goal of this study was to probe the equilibrium

$$Q^{(3)} \rightleftharpoons Q^{(3')}$$

but no coherent trend was observed in the speciation of each $Q^{(3)}$ site as a function of $\chi_{\text{Cs}_2\text{O}}$, shown in Figure 4.3. Figure 4.4 shows the individual isotropic contributions of each site in the glasses. There appears to be no trend in the isotropic positions, widths, or intensities of each site. This suggests that these sites occur randomly, as opposed to a linear trend we may expect from the above equilibrium. A number
Figure 4.1: The abundance of each Q-species as a function of modifier mole fraction. The dotted lines come from the binary distribution model. Points for each individual $Q^{(3)}$ and $Q^{(4)}$ sites were not included because there does not seem to be a coherent trend in speciation of those sites.
Figure 4.2: A plot of $\zeta^{(3)}$ and $\zeta^{(3')}$ as a function of mole fraction. There appears to be a step-wise trend, suggesting that this could be due to a change in the coordination environment around each $Q^{(3)}$ site as modifiers are introduced.
Table 4.2: Mole fractions of anionic species in glasses of nominal composition C$_2$O-(x)SiO$_2$. The mole fraction of the modifier, C$_2$O, are given based off of the masses used to synthesize each glass.
Table 4.3: Chemical shift anisotropy parameters, $\zeta^{(n)}$ (in ppm) and $\eta^{(n)}$ for each $Q^{(n)}$ of the glasses studied in this work. The anisotropy and asymmetry parameters of all $Q^{(4)}$ sites were constrained to zero.
Figure 4.3: The speciation results for each $Q^{(3)}$ environment in cesium silicate glasses. There is no discernable trend observed.

...of factors could explain the observed behavior, including thermal history (i.e. the melting point and melt temperature) and quench rate. There does, however, seem to be a stepwise trend in $\zeta^{(3)}$ and $\zeta^{(3')}$ as a function of $\chi_{\text{Cs}_2\text{O}}$, suggesting the existence of unique coordination environments, shown in Figure 4.2. Generally at low modifier content, $\zeta$ is larger; at high modifier content, $\zeta$ is smaller. Following the results of Grimmer et al. [96, 97], this means that $r_{\text{Si-NBO}}$ for each $Q^{(3)}$ site is increasing with increasing modifier content.
Figure 4.4: The extracted isotropic projections for each site, as simulated using Prof. Baltisberger’s approach. We see no clear trend relative proportions of each $Q^{(3)}$ and $Q^{(3)}$ site.
We postulate that this stepwise change in $r_{\text{Si-NBO}}$ is due to cation cluster sizes changing as a function of $\chi_{\text{Cs}_2\text{O}}$. We expect the cluster sizes to increase as modifier is added, and as such, $r_{\text{Si-NBO}}$ could increase in order to satisfy coordination requirements of a larger cluster. *Ab initio* calculations to investigate the effect of coordination number on $r_{\text{Si-NBO}}$ are ongoing and will hopefully show that with increasing cluster size (increasing coordination number), $r_{\text{Si-NBO}}$ increases accordingly.

### 4.3.1 Cation clustering in silicate glasses modified with large alkali

The observed result of two unique $Q^{(3)}$ environments in the glass is suggestive of two different Si-NBO bond lengths, a la Keeler [100]. Two possible explanations are shown in Figure 4.5. Due to the large size of Cs$^+$ and Rb$^+$ with respect to the silicate tetrahedra and oxygen atoms, it is possible that packing constraints due to rapid quenching of the melt could give rise to two unique clustering environments. Matson et al. [104] showed that glasses with considerable alkali ($\chi_{\text{M}_2\text{O}} \sim 0.2$) tend to form sheet-like structures. It is possible that there would be disorder in the sheets of these glasses due to the size the cations.

Alternatively, one could postulate a greater density of anionic charge around the cations is required by these cations’ need for a large coordination number. As such, planar three-membered rings could be formed in these sheets to allow for greater electron density for coordination.
Two possible explanations for 2D MAF results

(A) Different modifier cluster sizes lead to different NBO lengths which leads to different shielding anisotropies

(B) 3-rings present with distorted tetrahedral cause different shielding anisotropies

Figure 4.5: Two possible explanations of our observed results. One possibility is the existence of multiple cluster sizes, shown in cartoon form in (A). As the cluster size increases, the Si-NBO bond length can be expected to increase, leading to a decrease in \( \zeta^{(3)} \). Another possibility is the existence of three-membered rings, shown in (B). Galeener [37] showed these rings are planar, which leads to distorted geometries. Since silicate species in glasses tend to take a very locally-favored geometry, we can expected this distorted geometry in three-membered rings to lead to a different CSA and thus, different value for \( \zeta^{(3)} \).
4.3.2 Raman and NMR evidence of three-membered rings in silicate glasses

A common theme in the Raman spectroscopy analysis of silicate glasses is the discussion of planar three-membered rings containing three silicate tetrahedra. It is known that crystalline Cs$_2$O·SiO$_2$ is composed entirely of three-membered rings of $Q^{(2)}$, whereas crystalline Cs$_2$O·2SiO$_2$ is composed of 4- and 8-membered rings [105]. This suggests the possibility of the existence of three-membered rings in silicate glasses containing large alkali at relatively high content. Using Raman spectroscopy, Galeener [37] suggested that the band observed at $\sim 600$ cm$^{-1}$ corresponds to a vibrational mode of planar three-membered rings, and Matson et al. [104] showed that in binary silicate glasses, this band tends to decrease in intensity with increasing modifier content in glasses containing small modifier (Li, Na), and tends to increase in intensity with increasing modifier content in glasses containing large modifier (K, Rb, Cs). Malfait et al. [106] furthered this work by combining Raman spectroscopy with NMR to analyze the abundance of three-membered rings in glasses containing large alkali. Using NMR chemical shift arguments and double-quantum $^{29}$Si INADEQUATE correlation spectroscopy, Malfait et al. found evidence that there exist two types of $Q^{(3)}$ and $Q^{(2)}$ in silicate glasses containing large modifier at high concentrations. Generally, the absorbance peak associated with $Q^{(3')}$ and $Q^{(2')}$ environments was observed to be more narrow than the peaks associated with $Q^{(3)}$ and $Q^{(2)}$, presumably due to the constrained geometry of these species in the three-membered ring, constraining possible variations in the electronic environment around the $^{29}$Si nucleus which would give rise to a broader distribution of chemical shifts.
It may be possible to probe the existence of three-membered rings in silicate glasses using chemical shift anisotropy measurements. To check this, our colleague Pierre Florian simulated the crystal structures [105] using the CASTEP program [107] to extract NMR parameters, and found that, due to the geometry of silicate tetrahedra in each crystal being very similar (roughly tetrahedral), there was no appreciable CSA difference between $^{29}$Si nuclei in three-membered rings and those in four- or eight-membered rings in cesium-modified crystals. Since we expect glasses to generally adopt a more energetically-relaxed local environment, and since the crystals already have a roughly tetrahedral geometry, we do not expect to be able to probe the existence of three-membered rings in glasses using CSA arguments alone. To check the effect of cation on the CSA of silicate environments in three- or more-membered rings, Florian also experimentally measured the CSA and simulated both crystalline para and pseudo wollastonite, CaO·SiO$_2$ to compare the simulation to the experimental CSA results. Para wollastonite, composed entirely of three-membered rings, was found to have a very large CSA for the $^{29}$Si nucleus, approximately $\zeta=90$ ppm. On the other hand, pseudo-wollastonite contains no three-membered rings, and the CSA of was measured to be about 50 ppm. The simulated results agreed very well with the experimental results, and so we can trust with confidence the simulation results on cesium silicate crystals which show that CSA cannot be used alone to detect three-membered rings in cesium silicate glasses.
4.4 Conclusions

A series of cesium silicate glasses were studied to probe the effect of modifier content on the anisotropy of $Q^{(3)}$ environments in the glass, as well as to probe the speciation of each unique $Q^{(3)}$ environment. We found no discernable trend in the speciation of each site; however, there appears to be a stepwise trend in the CSA of each site as a function of modifier content, suggesting discreet changes in the cation clustering pattern as the content of modifier changes. To probe the existence of three-membered rings in the glasses, the CASTEP simulation package was used to simulate two cesium silicate crystals: one which contains only three-membered rings, and one that contains four- and eight-membered rings. There was no appreciable CSA difference between the two, suggest that CSA information cannot be exclusively used to probe the existence of three-membered rings in cesium silicate glasses.
4.5 Appendix
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Table 4.4: Experimental details for the MAF analysis of binary cesium silicate glasses with the generic composition Cs$_2$O · (x)SiO$_2$. Hypercomplex acquisition was used to acquire positive and negative time domains in the $t_1$ dimension. The number of $t_1$ points acquired corresponds to the total number of hypercomplex points acquired; the number in parenthesis corresponds to the effective number of $t_1$ points acquired.

* The $x = 2$ sample was acquired using PIETA [108] acquisition. All experiments were performed with true 90° and 180° pulses that were sufficiently short enough to fully and equally excite the entire spectrum.
Figure 4.6: The experimental $^{29}$Si MAF NMR 2D spectrum, simulated spectrum, and residuals for the Cs$_2$O-(1.5)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 1.63 \pm 0.11$. 

88
Figure 4.7: The experimental MAF spectrum, simulated spectrum, and residuals for the Cs$_2$O-(1.75)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{red} = 2.52 \pm 0.03$.  

89
Figure 4.8: The experimental MAF spectrum, simulated spectrum, and residuals for the Cs$_2$O-(2)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 1.488 \pm 0.010$. 
Figure 4.9: The experimental MAF spectrum, simulated spectrum, and residuals for the Cs$_2$O-(2.25)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 2.80 \pm 0.07$. 

91
Figure 4.10: The experimental MAF spectrum, simulated spectrum, and residuals for the Cs\textsubscript{2}O·(2.5)SiO\textsubscript{2} glass. Twenty contours are plotted from -2.5\% to 97.5\% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 2.32 \pm 0.03$. 
Figure 4.11: The experimental MAF spectrum, simulated spectrum, and residuals for the Cs$_2$O·(3)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 2.49 \pm 0.05$. 

93
Figure 4.12: The experimental MAF spectrum, simulated spectrum, and residuals for the Cs$_2$O-(3.5)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 2.04 \pm 0.02$. 94
Figure 4.13: The experimental MAF spectrum, simulated spectrum, and residuals for the Cs$_2$O·(4)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 2.055 \pm 0.019$. 95
Figure 4.14: The experimental MAF spectrum, simulated spectrum, and residuals for the Cs$_2$O·(4.5)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 1.68 \pm 0.04$. 

96
Figure 4.15: The experimental MAF spectrum, simulated spectrum, and residuals for the Cs$_2$O-(5)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 2.97 \pm 0.06$. 97
Figure 4.16: The experimental MAF spectrum, simulated spectrum, and residuals for the Cs$_2$O·(6)SiO$_2$ glass. Twenty contours are plotted from -2.5% to 97.5% of the maximum experimental intensity, and all spectra are plotted on the same scale. For this fit, $\chi^2_{\text{red}} = 1.95 \pm 0.03$. 
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