The structure of the alkaline earth silicate glass CaSiO3 has been investigated using a two-dimensional 29Si NMR experiment that correlates the isotropic magic-angle-spinning (MAS) spectrum with an anisotropic off-magic-angle-spinning spectrum. Although the one-dimensional magic-angle-spinning (MAS) spectrum is completely unresolved, all five types of SiO4 tetrahedra (represented by the notation Q(n), where n = 0-4 representing the number of bridging oxygen) can be resolved and quantified on the basis of the separated anisotropic line shapes in the 2D spectrum. The distribution of isotropic chemical shifts derived from the 2D spectrum suggests that in the case of CaSiO3 glass the conventional approach of fitting the one-dimensional MAS spectrum with overlapping Gaussian line shapes would lead to significant errors in Q(n) quantification. The equilibrium constants for the disproportionation reaction Q(n) \rightleftharpoons Q(n-1) + Q(n+1) with n = 1, 2, and 3 were determined from the 2D spectrum to be 0.105 ± 0.019, 0.156 ± 0.005, and 0.106 ± 0.022, respectively. These results clearly indicate a significantly greater deviation from a binary model of Q(n) species disproportionation in alkaline earth silicate melts when compared to alkali silicate melts and thus suggest a relatively more disordered structure.
identified mainly by their isotropic position, $\delta_{\text{iso}}$, which approximately ranges from $-70$ ppm for $Q(0)$ to $-110$ ppm for $Q(4)$. In crystalline silicates, the isotropic line widths are usually on the order of 1 ppm or less, and it is often possible to resolve not only different $Q(n)$ species but also crystallographically distinct $Q(n)$ species of the same type (i.e., same $n$). In contrast, in a glass, the isotropic line widths are inhomogeneously broadened to over 10 ppm due to a continuous distribution of isotropic chemical shifts, which arise from a continuous structural distribution in local structure (e.g., Si–O–Si angles, nonbridging oxygen–alkali distances, and higher coordination sphere structures). This broadening results in considerable overlap of $Q(n)$ resonances and thus significant uncertainties when attempting to quantify the relative $Q(n)$ populations from isotropic MAS line shapes. As we have shown previously, the separation of anisotropic line shapes obtained in a two-dimensional NMR spectrum correlating isotropic and anisotropic line shapes provides a means of determining the distributions of $Q(n)$ species without any a priori assumptions about the distribution and also significantly reduces the covariances between best fit parameters, thus increasing the precision in quantifying site populations.

We have used a slightly modified version of the magic-angle-flipping NMR experiment by Bax et al. where the NMR spectrum while spinning at the magic angle is correlated with that while spinning at an axis perpendicular to the magnetic field. When spinning perpendicular to the magnetic field, the static sample anisotropic line shapes are scaled by a factor of $-0.5$, as shown in Figure 1. Our sequence differs from the original experiment of Bax et al. by the addition of an additional $\pi$ pulse before $t_2$ to improve sensitivity and to give pure absorption mode line shapes. The experiment was performed on a Chemagnetics 9.4 (79.48 MHz for $^{29}$Si) NMR spectrometer using a modified version of a home-built DAS probe described earlier. The experiment was done at ambient temperature with a sample spinning rate of 10.4 kHz. The $^{29}$Si relaxation time was measured using a saturation recovery experiment under MAS conditions, and $T_1$ values were found to be 50.3 s. A pulse delay of 300 s was chosen. No changes in peak shape as a function of delay time were observed, indicating no differential relaxation among different species. The angle pair ($90^\circ$ and $54.74^\circ$) was employed with detection made at $54.74^\circ$. $\pi/2$ times were chosen to be 4.4 $\mu$s at $90^\circ$ and 5.7 $\mu$s at $90^\circ$. The number of scans was 32; the number of $t_1 \times t_2$ points is $61 \times 256$, with a dwell time of 25 $\mu$s and 25 $\mu$s, respectively.

Sample Preparation and Characterization. The sample was synthesized from high-purity CaCO$_3$ and 95% $^{29}$Si-enriched SiO$_2$ (Oak Ridge Laboratory), with 0.1 wt % CoO added to enhance spin–lattice relaxation. The starting material was decarbonated at 900 °C and then melted for 2 h at about 1600 °C. The weight loss during synthesis was within 0.1% of nominal, indicating close to ideal stoichiometry. High-precision electron microprobe analyses on multiple grains of the glass, accounting for the isotopic enrichment, gave a molar Ca/Si ratio of 0.99 ± 0.01.

Results

Stack plots of the $^{29}$Si two-dimensional ($90^\circ$, MAS) correlation NMR spectrum of CaSiO$_3$ glass are shown in Figure 2. In Figure 2A the spectrum is plotted with the most negative isotropic chemical shifts in the MAS dimension to the front. Recalling the characteristic anisotropic line shapes shown in

![Figure 1](image1.png)

**Figure 1.** One-dimensional $^{29}$Si off-magic-angle-spinning (i.e., $90^\circ$) NMR line shapes for the five different silicate tetrahedral environments in silicate glasses. Line shape parameters are based on typical values found in crystalline compounds.

![Figure 2](image2.png)

**Figure 2.** Stack plots of the two-dimensional $^{29}$Si (MAS, $90^\circ$) correlation spectrum. In A the spectrum is plotted with the most negative chemical shifts in the MAS dimension in the front. In B the spectrum is plotted with the least negative chemical shifts in the front.
Figure 1, it is clear from the $90^\circ$ dimension that in the region of $-110$ ppm a low-intensity symmetric line shape attributed to $Q(4)$ species can be observed. Moving to less negative chemical shifts in the $-100$ ppm region, anisotropic chemical shift line shapes characteristic of negative axiality and nearly zero asymmetry parameters are observed and are attributed to $Q(3)$ species. In the region of $-85$ ppm the anisotropic line shapes are dominated by anisotropic chemical shift, and line shapes with $\eta = 0.70$ are attributed to $Q(2)$ species. In Figure 2B the same spectrum is plotted with the least negative isotropic chemical shifts in the MAS dimension to the front. In the region of $-65$ ppm a very weak symmetric line shape attributed to $Q(0)$ species is observed. Moving to more negative chemical shifts in the $-75$ ppm region, anisotropic chemical shift line shapes characteristic of positive axiality are observed and are attributed to $Q(1)$.

The anisotropic line shapes in the individual cross sections taken parallel to the $90^\circ$ dimension were least-squares analyzed to obtain the relative contribution of each $Q(n)$ species to the MAS intensity at the MAS frequency correlated to that cross section. A contour plot along with representative cross sections and best-fit simulations is also shown in Figure 3. Again, this approach has the advantage that the parameter uncertainties in each cross section are completely uncorrelated with parameter uncertainties in other cross sections. The chemical shift anisotropy line shape for each site was modeled using five parameters. These were (1) an isotropic chemical shift position $\delta_{iso}$, (2) a chemical shift tensor axiality $\Delta$, (3) a chemical shift tensor asymmetry parameter $\eta$, (4) an integrated intensity, and (5) a Gaussian smoothing function. All sites in each cross section shared the same isotropic frequency and that value was fixed by the isotropic dimension. In least-squares analyses those cross sections dominated by one $Q(n)$ species showed little variations in $\Delta$, $\eta$, and Gaussian line broadening for the line shape of the dominant species. Therefore, in the final least-squares analysis of each cross section the chemical shift tensor

Discussion

The MAS spectrum obtained from the projection of the two-dimensional spectrum onto the MAS dimension is shown in Figure 4 along with the individual component line shapes for each of the $Q(n)$ species present in the glass. The component line shapes were constructed from the integrated intensities obtained from the least-squares analyses of the anisotropic cross sections. To quantify deviations from a Gaussian shape for each of the $Q(n)$ component line shapes, we have calculated the mean...
position, variance, skewness, and kurtosis for each Q\(^{(\alpha)}\) line shape. These are given in Table 1. The skewness and kurtosis are nearly zero in all three cases, an indication that the assumption of Gaussian distributions is probably reasonable.

A simplifying assumption in our analysis of the 2D spectrum is that there is overlap of no more than two different Q\(^{(\alpha)}\) species at a given isotropic frequency. With the exception of the low-intensity Q\(^{(0)}\), we believe this assumption is valid on the basis of the tabulated ranges of Q\(^{(\alpha)}\) isotropic chemical shifts in crystalline silicates.\(^{15,16}\) Indeed, we believe this is also a strong criticism of the fit of the 1D MAS spectrum of CaSiO\(_3\) glass since the cations would necessarily be Na\(_2\)O–SiO\(_2\) liquids (M = Ca, Fe, Ni, etc.) by thermochemical means,\(^{22-24}\) although it is difficult to extrapolate such data down in temperature from the liquidus to the glass transition. It is also worth noting that several calcium silicates (e.g., Ca\(_2\)SiO\(_4\)) contain OCa\(_n\) groups, i.e., oxygen not bound to silicon.

Using our relative Q\(^{(\alpha)}\) populations we can calculate for the disproportionation reaction

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

the equilibrium constant at the glass transition temperature,

\[k_n = [Q^{(\alpha+1)}][Q^{(\alpha-1)}]/[Q^{(\alpha)}]^2\]

For CaSiO\(_3\) glass we obtained \(k_1 = 0.105 \pm 0.019, k_2 = 0.156 \pm 0.005,\) and \(k_3 = 0.106 \pm 0.022,\) respectively. This is the first time equilibrium constants have been measured for alkaline earth silicate glasses. In order to compare with the more studied alkali silicate glasses, we have tabulated equilibrium constant data in Table 3 of alkali silicate data from ref 10. It can be seen that equilibrium constants for calcium silicates are generally larger except in the two cases of \(k_2\) for lithium silicates and \(k_1\) for sodium silicates. Previous work has suggested that more highly charged cations such as Ca\(^{2+}\) will shift the disproportionation reaction equilibrium to the right.\(^{6}\) These results clearly confirm a significant deviation from a binary model\(^{25,26}\) of Q\(^{(\alpha)}\) species disproportionation in alkaline earth silicate melts when compared to alkali silicate melts. While a crystalline composition of CaSiO\(_3\) would contain only Q\(^{(2)}\) species with alkaline earth cations evenly distributed throughout the lattice, a high equilibrium constant implies an uneven distribution of alkaline earth cations in the glass since the cations would necessarily cluster near the more negative Q\(^{(\alpha)}\) species with more nonbridging oxygen (i.e. low \(n\)).

As a comparison, we also calculated the disproportionation equilibrium constant \(k_2\) using the fit of the one-dimensional MAS spectrum to three Gaussian line shapes. Results of the fit are also shown in Table 2. These values result in a \(k_2\) value of 0.086 ± 0.024, which is significantly lower than those obtained by analyzing the two-dimensional spectrum. Clearly, there is higher uncertainty associated with these results because of the poor resolution in the MAS spectrum compared to the two-dimensional spectrum. Again, the discrepancy in results between the two methods suggested that Gaussian fitting of one-
dimensional MAS spectra is unlikely to be reliable, especially for unresolved spectra, as the case for alkaline earth silicate glasses.

Extensive interpretations of silicate species abundances, and resulting thermodynamics, have been made for Ca-, Sr-, and Ba-silicate glasses and liquids by analyzing Raman spectra.\(^{1,13}\) Correction factors for Raman band intensities were calibrated using concentrations of Q\(^{(1)}\), Q\(^{(2)}\), and Q\(^{(3)}\) species derived by fitting a published \(^{29}\)Si MAS NMR spectrum of CaSiO\(_3\) glass\(^{6}\) to three Gaussian line shapes. This fit was, unfortunately, not consistent with the glass composition, as the area of the Q\(^{(3)}\) peak appears to be considerably larger than that of the Q\(^{(1)}\) peak. This NMR spectrum, however, may have been somewhat distorted due to the lower sample spinning speeds available at the time. The Q\(^{(3)}\) and Q\(^{(1)}\) abundances derived from the calibrated Raman intensities are quite different from those found here, resulting in a \(k_2\) value of 0.032 instead of 0.156. It is clear that the Raman-based models will need to be significantly and systematically adjusted.

Conclusions

We have found that a new two-dimensional NMR approach can give much more robust estimates of silicate species abundances in glasses than can fitting of unresolved peaks in one-dimensional NMR spectra. Using this approach we obtained for the first time the equilibrium constants for the Q\(^{(n)}\) disproportionation reaction in CaSiO\(_3\). These results confirmed a significantly greater deviation from a binary model of Q\(^{(n)}\) disproportionation in alkaline earth silicate melts compared to alkali silicate melts. Results of this kind on a few carefully chosen compositions should lead to a major improvement of structure-based thermodynamic models of silicate liquids.

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References and Notes