The Structure of Oxide Glasses: Insights from ^{17}O NMR

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As a probe of local structure in network forming oxide glasses, ^{17}O nuclear magnetic resonance (NMR) spectroscopy has been an invaluable tool [1–10]. The analysis of oxygen in these glasses is vital because their structure predominately consists of well-defined corner-sharing SiO_4 tetrahedra connected in a continuous infinite three-dimensional network lacking long-range order. The interconnection of two tetrahedra involves a Si–O–Si bond angle, and two dihedral angles, and the variation in these angles is considered to be one of the main sources of disorder in a conventional melt quenched silicate glass.

The best approach for measuring Si–O–Si bond angle distributions is to use methods that provide a detailed and direct measurement of the local environment around oxygen. Unfortunately, the information obtainable from X-ray absorption spectroscopies has been limited for light backscattering atoms like oxygen [11]. In contrast, solid-state ^{17}O NMR, specifically, the ^{17}O quadrupolar coupling and chemical shift parameters provide a simple and direct probe of electronic structure, and is well suited for measuring the local structure around bridging oxygen [12–21].

With the development of 2D NMR methods that separate and correlate anisotropic and isotropic lineshapes [22–24], it is becoming increasingly possible to obtain local structural information for glasses via ^{17}O NMR. In 1992, Farnan *et al.* [4] first demonstrated how the distribution of ^{17}O NMR parameters can be measured in a silicate glass using 2D dynamic-angle spinning (DAS) NMR without any assumptions about the shape of the NMR parameter distributions. Additionally, they demonstrated that the ^{17}O quadrupolar coupling parameter distribution can, in principle, be mapped into the Si–O–Si bond angle distribution in the glass.

A crucial aspect in these structural determinations is an understanding of the relationship between the measurable NMR parameters and the variations in local structure that influence the NMR parameters. The development of such relationships has been an ongoing task for oxygen in oxide glasses, with significant gains being made by the combination of computational methods and experimental investigation of a variety of oxygen environments in crystalline silicates.

For bridging oxygen, a number of structural features play a role in determining the ^{17}O quadrupolar coupling parameters, with the most significant features occurring in the first coordination sphere of the bridging oxygen. In the mid-1980's Oldfield and coworkers [25–27] clearly established on the basis of their ^{17}O magic-angle spinning (MAS) NMR measurements that the electronegativity of the cations coordinated to a bridging oxygen atom is a primary factor influencing the magnitude of the C_q-parameter for the bridging oxygen. In a series of *ab initio* calculations on model clusters focusing on the silicate bridging oxygen linkage Tossell and coworkers [12–14] predicted simple trends for the ^{17}O quadrupolar coupling parameters with Si–O–Si angle. These trends were later experimentally confirmed by Grandinetti *et al.* [17] in ^{17}O DAS measurements on coesite.

Vermillion *et al.* [19] and Clark *et al.* [20] further refined this understanding by examining the effect of additional coordination of the bridging oxygen by network modifier alkali cations. Their findings, obtained using *ab initio* methods on model clusters representing typical bridging oxygen environments in lithium, sodium, and potassium silicates, suggested that the previously established trend in ^{17}O C_q with Si–O–Si angle is systematically shifted to lower magnitudes with increasing number and field strength of coordinating alkali cations. They also found that the previously established trend [12–15] in ^{17}O quadrupolar coupling asymmetry parameter, η_q, with Si–O–Si angle is systematically shifted to higher values by the presence of one coordinating alkali cation, and only slightly shifted to higher values by the presence of two coordinating alkali cations.

In two related papers, Clark and Grandinetti [18, 28] used *ab initio* methods to study a number of clusters with the coordinating cations varied from Group III to Group VI and from Periods 2 to 4, while simultaneously varying the network forming cation–oxygen distance. A general trend, shown in Figure 1A, was observed that the magnitude of C_q increases linearly with increasing network forming cation–oxygen bond distance, and also increases with cation group number, as shown Figure 1B. These findings suggest that group number and cation-bridging oxygen distance can serve as a better predictor of the bridging oxygen quadrupole coupling constant than electronegativity differences [26, 27].

The observation that the magnitude of C_q increases linearly with increasing network forming cation–oxygen

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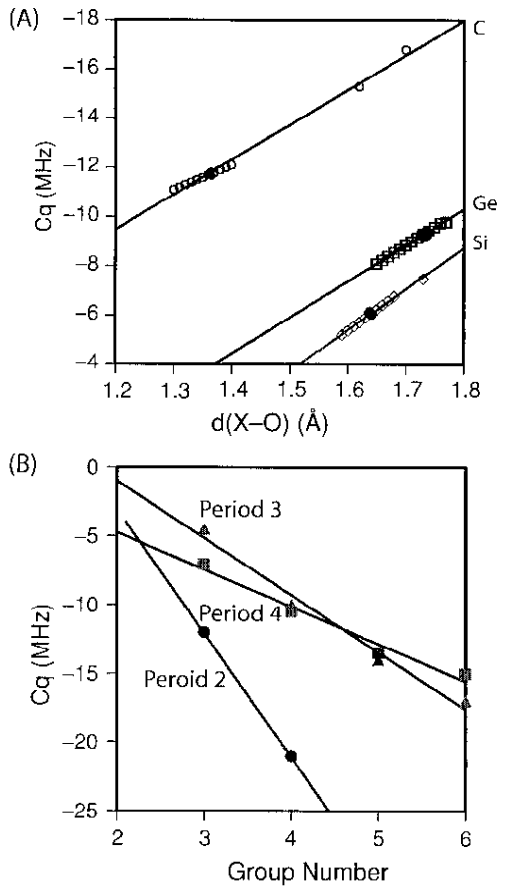

Fig. 1. (A) Comparison of bridging oxygen ^{17}O C_q values for the clusters $(OH)_3T–O–T(OH)_3$, where T = carbon, silicon, and germanium, as a function of d(T–O). (B) Bridging oxygen C_q dependence on the group number of coordinating cations for each period. C_q values are calculated for identical cation–oxygen distances and a bridging oxygen angle of 180°.

bond distance was investigated in more detail by Clark and Grandinetti for bridging oxygen atoms in silicates [21]. In this work, *ab initio* calculations were performed for model clusters to examine the dependence of ^{17}O quadrupolar coupling parameters on both Si–O distance and Si–O–Si angle. This work demonstrated that the ^{17}O quadrupolar coupling constant is dependent on both of these structural features, while η_q is primarily dependent on the Si–O–Si angle. Also, it is noteworthy that the strong linear dependence of C_q on Si–O distance helped explain the rather different angular trends for C_q found in coesite [17] and ferrierite [29], since the Si–O–Si angle and Si–O distance correlations for these two materials are quite different [21].

Relationships between ^{17}O quadrupolar coupling parameters and structure in silicates have also been examined using periodic density functional theory (DFT) calculations. These calculations, which are capable of describing quite accurately a system's electronic structure, have been performed for crystalline sodium silicates, the siliceous zeolite ferrierite, and also for plausible sodium silicate glasses that were generated using molecular dynamics [30,31]. These calculations generally support the previously established trends, i.e. C_q decreases in magnitude with decreasing Si–O–Si angle and Si–O distance, whereas η_q depends only on Si–O–Si angle. Additionally, these investigations found no dependence of the bridging oxygen C_q upon the number of coordinating alkali cations, a finding in contrast to that reported using modeling clusters [19,20].

Overall, it has become clear that first coordination sphere structural features that appear to be most important in determining the ^{17}O quadrupolar coupling parameters of the bridging oxygen are the nature of the two coordinating network forming cations, the T–O–T′ linkage angle, the T–O bond distances, and the nature and number of coordinating network modifier cations. Contributions from beyond the first coordination sphere of the bridging oxygen appear to be secondary in importance. For example, Xue and Kanzaki [16] performed *ab initio* calculations employing clusters expanded out to four coordination spheres to model each of the silicate bridging oxygen linkages in coesite and obtained a slightly improved agreement with the experimental trends, with corrections on the order of a few percent in the ^{17}O C_q and η_q values.

Equations proposed to summarize the important structural features for the determination of the ^{17}O quadrupolar coupling parameters are

$$C_q(\Omega, n_M) = a\left(\frac{1}{2} + \frac{\cos\Omega}{\cos\Omega - 1}\right)^{\alpha} + n_M \Delta C_q^M + m_d(d_{TO} - d_{TO}^o) \quad (1)$$

$$\eta_q(\Omega) = b\left(\frac{1}{2} - \frac{\cos\Omega}{\cos\Omega - 1}\right)^{\beta} + \Delta\eta_q^M(n_M), \quad (2)$$

where Ω is the Si–O–Si bond angle, d_{TO} is the average silicon–oxygen bond distance, and the terms $n_M \Delta C_q^M$ and $\Delta\eta_q^M(n_M)$ account for contributions from modifier cations coordinated to the bridging oxygen. These expressions are not unique in their ability to describe these relationships, and other expressions have been used previously [4,14,15].

Clark and Grandinetti [21] performed a least-squares fit of Equations (1) and (2) to the experimental values for coesite [17], cristobalite [32], and α-quartz [33] as

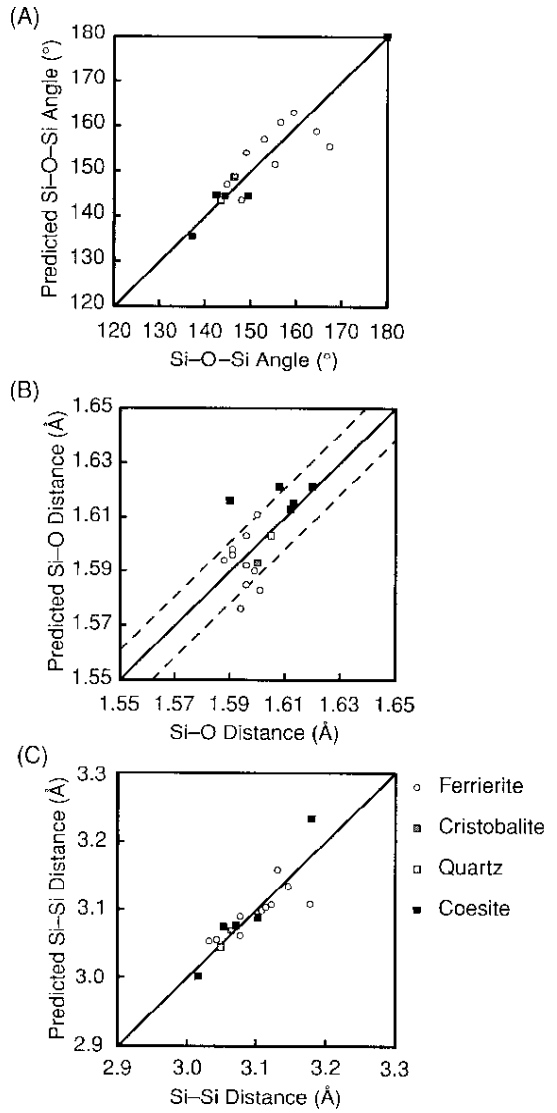

Fig. 2. Comparison between ^{17}O quadrupolar coupling predicted (A) Si–O–Si angle, (B) Si–O distance, and (C) Si–Si distance with corresponding quantities reported from X-ray crystallography [40–42]. Solid diagonal lines represent perfect agreement. Best fit parameters for Equations (1) and (2) are $a' = -6.53\,\text{MHz}, \alpha' = 1.80, m_d = -12.86\,\text{MHz/Å}, d^{\circ}_{T\,O} = 1.654\text{Å}, b = 4.73, \beta = 1.12$.

well as the *ab initio* predicted values for ferrierite [29] and obtained the parameter values given in the caption of Figure 2. The resulting parameterized equations describe the relationships between the ^{17}O quadrupolar coupling parameters and the relevant structural features in the first coordination sphere for a bridging oxygen atom in the absence of modifier cations. The precision of these relationships can be seen in Figure 2, where the Si–O–Si angles and Si–O distances predicted by these expressions are shown versus the actual values. Close agreement between predicted and reported values are demonstrated, even though only two structural variables are considered, i.e. the average bond distance and the bond angle. Here, the Si–O–Si angles in Figure 2A are predicted from η_q alone and, with the Si–O–Si angle determined, Equation (1) is used to predict the Si–O distance from C_q, as shown in Figure 2B. After having determined the Si–O distance for a given angle, it is also possible to determine the Si–Si distance.

It is noteworthy that not only the quadupolar coupling constant and asymmetry parameter can be used to measure the Si–O–Si angle and Si–O distance, but also the simultaneous measurement of C_q and η_q for each bridging oxygen site can be used to obtain the correlation between Si–O–Si angle and Si–O distance. This has significant impact for determining two-dimensional structural distributions around bridging oxygen in silicate glasses. This approach requires a good measurement of the quadrupolar asymmetry parameter, which has been historically been more difficult to measure than the quadrupolar coupling constant. Fortunately, this situation has been improved with the development of techniques such as Rotor Assisted Population Transfer (RAPT) [34–37] for enhancing the sensitivity of the MAS detected DAS [17,38,39]experiment, which allows overlapping anisotropic ^{17}O central transition lineshapes to be separated.

Figure 3A is the recently reported ^{17}O RAPT/MAS-detected DAS spectrum of silica glass [43]. From a least-square analysis of the ^{17}O 2D DAS spectrum a three-dimensional histogram, correlating the δ_{cs} (chemical shift), C_q, and η_q of ^{17}O, was obtained. A projection of this three dimensional histogram, showing the two-dimensional correlation between C_q and η_q for silica glass, along with corresponding one-dimensional projections is shown in Figure 3B. With the aid of Equations (1) and (2), the experimental C_q and η_q histograms were mapped into the two-dimensional histogram of the Si–O–Si angle versus the Si–O distance, shown in Figure 3C. This result is the first experimentally measured two-dimensional structural distributions in a glass, and illustrates nearly strong linear correlations between the Si–O–Si angle and Si–O distance in silica glass.

Significant insights into the structure of silicate glasses are now made possible by an analysis using this methodology. For example, in the case of silica glass, it is remarkable that a strong positive correlation is observed between Si–O distance and Si–O–Si bond angle. This trend was unexpected since it is *opposite* of that generally found in crystalline SiO_2 polymorphs, as shown in

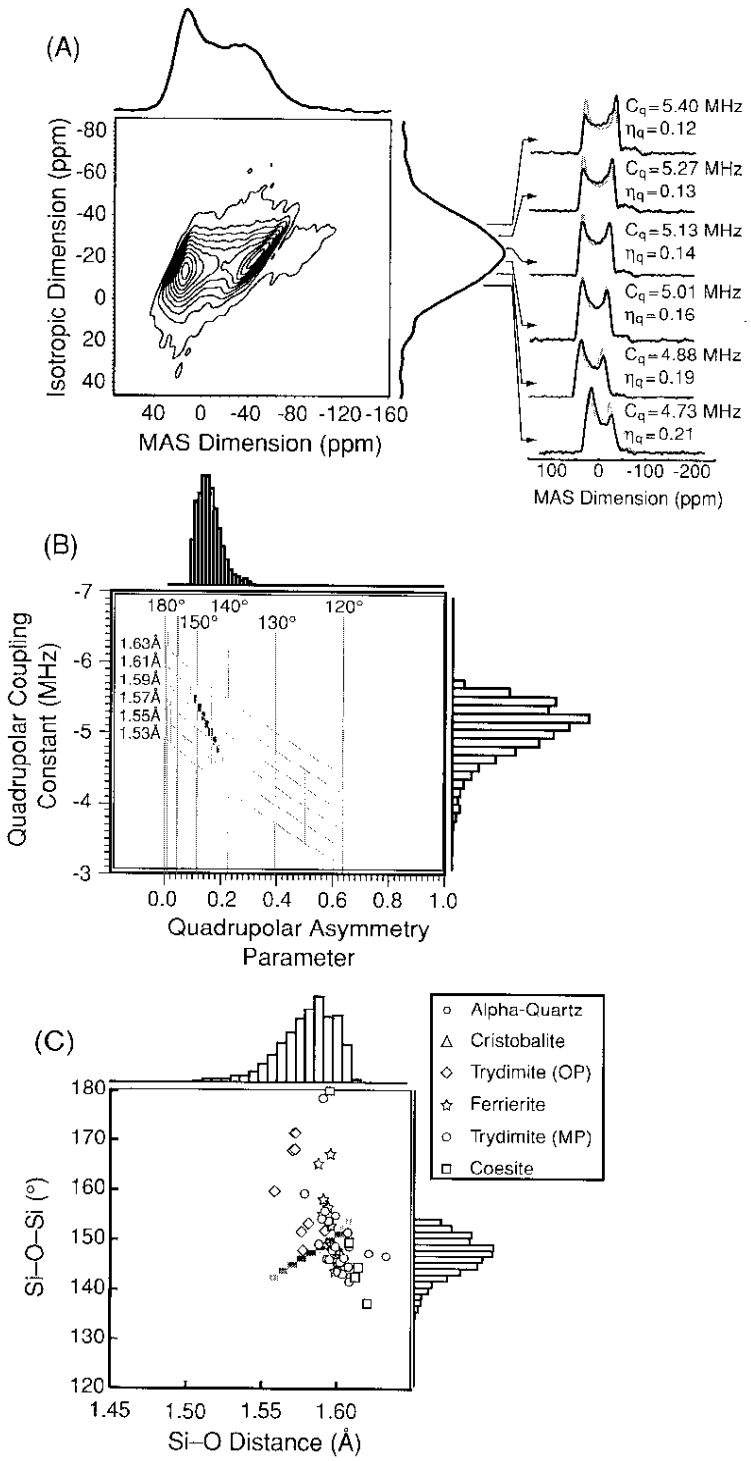

Fig. 3. (A) Experimental 2D ^{17}O RAPT/MAS-detected DAS spectrum of SiO_2 at 9.4 T along with experimental 1D projections onto the MAS and isotropic dimensions. Shown on the right are selected experimental cross sections along with best fit simulations. (B) Two-dimensional histograms along with the corresponding one-dimensional projection showing the correlation between C_q and η_q. Grid lines shown were obtained from Equations (1) and (2) by varying Si–O distance with Si–O–Si angle held constant and the Si–O–Si angle with the Si–O distance held constant. (C) 2D histograms of Si–O–Si angle versus Si–O distance for silica glass derived from NMR parameter distributions, and for various crystalline polymorphs.

Figure 3C. Also, the resulting Si–O–Si bond angle distribution, which peaks at 147° with a standard deviation of 3.8°, is noteworthy for its narrowness in comparison with distributions determined by diffraction or Si-29 NMR measurements [44–46].

In conclusion, ^{17}O NMR is proving to be an extremely robust probe of structure in silicate glasses. As the relationship between the ^{17}O NMR parameters and structure has become increasingly well-understood, it is now possible to apply this knowledge for the interpretation of the two-dimensional NMR spectra of disordered materials. This has led to the experimental determination of correlated structural distributions for oxygen sites in glasses, a significant achievement that is not presently possible by other experimental techniques. With the continued application of this methodology, it will be possible to gain a more complete understanding of many glasses of scientific and technological importance.

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