Correlations between $^{17}$O NMR parameters and local structure around oxygen in high-pressure silicates: Implications for the structure of silicate melts at high pressure

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**Abstract**

In order to understand the correlations between $^{17}$O NMR parameters and the local structure around O in high-pressure silicates, we have obtained $^{17}$O MAS and static NMR spectra on several crystalline alkali silicate and silica phases, as well as on ambient pressure glasses. Our results show that $^{17}$O NMR is capable of distinguishing nonbridging O atoms (NBO), bridging atoms (BO: $^{14}$Si-O-$^{12}$Si), O atoms in the $^{14}$Si-O-$^{14}$Si linkage, and O atoms coordinated to three $^{14}$Si ($^{14}$O). NBO are characterized by small quadrupolar coupling constants ($e'qQ/h$, $\sim$2.3 MHz), but their isotropic chemical shifts ($\delta_0$) are very sensitive to the type of network-modifying cations. The $^{14}$O (in stishovite), on the other hand, has by far the largest $e'qQ/h$ value (6.5 MHz) and a larger $\delta_0$ (109 ppm) than any BO in silicates. BO and $^{14}$Si-O-$^{14}$Si both have intermediate $e'qQ/h$ values ($\sim$4.5–5.7 MHz), and the $\delta_0$ value of the latter (97 ppm in wadeite-$^{14}$Si,$^{14}$O) is larger than those of the former ($\sim$50–65 ppm).

We have also applied $^{17}$O NMR to study the structure of alkali silicate glasses quenched from melts at high pressure. The $^{17}$O NMR spectra of a $^{28}$Si,$^{14}$O glass quenched from 6 GPa and of Na$_2$Si$_2$O$_5$ glasses quenched from 6 to 10 GPa are consistent with the presence of O sites in the $^{14}$Si-O-$^{14}$Si (and possibly also $^{14}$Si-O-$^{12}$Si) linkage, supporting our previous model developed from $^{29}$Si NMR. In addition, $^{17}$O static NMR also reveals the development of another new type of O site, possibly one that is connected with two or three $^{14}$Si or $^{12}$Si atoms, in the Na$_2$Si$_2$O$_5$ glass quenched from 10 GPa. Thus, $^{14}$Si and $^{12}$Si may be largely isolated from one another below 10 GPa, whereas at higher pressure, clustering of these Si species may become significant in Na$_2$Si$_2$O$_5$ melts.

**Introduction**

The high pressures of the Earth’s mantle are known to have large effects on the physical and chemical properties of magmas, including phase equilibria, density, viscosity, and diffusivity. In order to gain the fundamental understanding needed to generate accurate predictive models of igneous processes, geophysical inferences and laboratory measurement of macroscopic properties must be complemented by studies of atomic-scale structure and dynamics of melts. Spectroscopic studies are playing an increasingly important role in the understanding of pressure-induced changes in the bonding and structure of silicate liquids and glasses. The latter are generally assumed to contain the structure of the liquid quenched in at the glass transition, which is usually many hundreds of degrees to more than a thousand degrees below the liquidus temperatures. Studies of glasses are thus the traditional first step in inferring the structure of liquids, but the possibility of large temperature effects above the glass transition cannot be neglected (e.g., Brandriss and Stebbins, 1988; Stebbins, 1991). Because in-situ, high-temperature, and high-pressure studies remain very difficult, further assumptions about the effects of ambient temperature depressurization of glass samples must also be made. It is clear that many effects of pressure are retained in quenched glasses, but it has also become apparent that some structural changes can be rapidly reversible (e.g., Wolf et al., 1990). Despite these complications, results on glasses produced by quenching stable liquids at high pressure (such as those presented here) provide a qualitative starting point for understanding the actual liquids at high $T$ and $P$.

Most spectroscopic studies of glasses have been on simplified analogues of geological compositions. Particularly for NMR, most easily interpretable results have come from binary or ternary compositions, for which structural effects can be much more clearly distinguished than in more complex systems. Alkali di- and tetrasilicates, for example, although far from magmatic in composition, do have ratios of nonbridging O atoms to tetrahedral cations (1 and 0.5, respectively) that are similar to those of mafic...
to intermediate magmas and thus probably capture many of the general effects of composition, temperature, and pressure that are important to igneous processes. The results presented here are part of an ongoing study to characterize the structure of such compositionally simple silicate glasses quenched from melts at high pressure.

In silicate glasses and melts at ambient pressure of geologically important compositions, almost all Si and Al are coordinated by four O atoms ([\textsuperscript{4}Si] and [\textsuperscript{4}Al]). Spectroscopic studies on silicate glasses quenched from melts at pressures <3 GPa have revealed several types of pressure-induced changes in the tetrahedral structure, such as reduction of intertetrahedral angles and changes in the second neighbor connectivity of the SiO\textsubscript{4} and AlO\textsubscript{4} tetrahedra (e.g., Myssen et al., 1983; Hochella and Brown, 1985; Dickinson et al., 1990; Myssen, 1990). It has been predicted from molecular dynamics simulations that, at even greater pressure, the dominant structural change for silicate melts could be an increase in the coordination of nonbridging O atoms, which are forced to connect with the network formers (Si and Al), with accompanying changes in density and viscosity (e.g., Angell et al., 1982, 1983, 1987, 1988; Matsui et al., 1982; Matsui and Kawamura, 1980, 1984). In our earlier papers (Xue et al., 1989, 1991; Stebbins and McMillan, 1989), we have reported \textsuperscript{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopic results on alkali silicate and silica glasses quenched from melts at pressures up to 12 GPa. These data yielded strong evidence for the presence of significant amounts of five- and sixfold-coordinated Si ([\textsuperscript{5}Si] and [\textsuperscript{6}Si]) in alkali silicate melts at high pressure. More recent \textsuperscript{31}Si NMR studies have also identified the presence of a small amount of [\textsuperscript{5}Si] in alkali silicate glasses quenched from melts at 1 bar (Stebbins, 1991; Stebbins and McMillan, 1993).

There are, however, many questions unanswered by our earlier \textsuperscript{29}Si NMR studies. For example, the \textsuperscript{29}Si NMR spectra do not have enough resolution to yield information about the connectivities of [\textsuperscript{5}Si] and [\textsuperscript{6}Si], i.e., whether they are isolated or linked to each other in the silicate melt structure, and, if the latter is the case, whether they are connected by edge sharing or corner sharing. On the basis of the compositional dependence of the abundances of [\textsuperscript{5}Si] and [\textsuperscript{6}Si] and by analogy with the structure of alkali germanate melts and glasses at 1 bar (cf. Ueno et al., 1983), we have proposed a model that [\textsuperscript{5}Si] and [\textsuperscript{6}Si] are formed in silicate melts at high pressure at the expense of nonbridging O atoms, which are forced to connect with the highly coordinated Si (Xue et al., 1991). Quantification of this model relies on answers to the above questions. These questions may be answered to some extent by directly studying the O environments, which naturally led us to apply \textsuperscript{17}O NMR to these systems.

The \textsuperscript{17}O isotope has a natural abundance of 0.037%. Because its spin quantum number is \(\frac{1}{2}\), the \textsuperscript{17}O NMR peaks are typically broadened by second-order quadrupolar interactions between the nuclear quadrupole and the electric field gradient at the nucleus, and the broadening can only be partially removed by magic angle spinning. The nuclear quadrupole interactions are described by two parameters: the quadrupolar coupling constant (\(e'\text{\(\tilde{Q}\)/h}\), where \(e'\text{\(\tilde{Q}\)}\) is the nuclear quadrupolar coupling constant, \(e\) is the principal component of the electric field gradient at the nucleus, and \(h\) is Planck's constant) and the asymmetry parameter, \(\eta\), for the electric field gradient tensor. Although the breadth of the \textsuperscript{17}O NMR spectra yields less resolution for different O sites compared with those of spin-\(\frac{1}{2}\) nuclei (e.g., \textsuperscript{29}Si), it has the advantage that in addition to the isotropic chemical shift parameter \(\delta\), two more parameters (\(e'\text{\(\tilde{Q}\)/h}, \eta\)) can be used for structural characterization.

O is the most abundant element in silicates and oxides. The study of O structural environments is thus an important complement to studies of cation coordination. It has been shown that \textsuperscript{17}O NMR is a promising method for studying the structure and bonding in these materials (Schramm et al., 1983; Schramm and Oldfield, 1984; Turner et al., 1985; Timken et al., 1986a, 1986b, 1987; Walter et al., 1988; Janes and Oldfield, 1986; Bastow and Stuart, 1990; Mueller et al., 1992; Farnan et al., 1992). In particular, bridging O atoms linked to different types of network formers (e.g., Si-O-Si, Si-O-Al, Al-O-P), as well as nonbridging O atoms in crystalline silicates, have been found to have distinctly different \textsuperscript{17}O NMR characteristics in terms of the \(\delta\), and \(e'\text{\(\tilde{Q}\)/h}\) parameters (Timken et al., 1986a, 1986b, 1987; Walter et al., 1988; Mueller et al., 1992). These results are useful for interpreting spectra of disordered phases. Kirkpatrick et al. (1986) have applied \textsuperscript{17}O MAS NMR to study the order-disorder of cations in alkaline earth silicate glasses quenched at 1 bar. More recently, Farnan et al. (1992) were able to quantify the cation disorder in K\textsubscript{2}SiO\textsubscript{3} and K\textsubscript{2}Si\textsubscript{2}O\textsubscript{5} glasses quenched at 1 atm using dynamic angle spinning (DAS) \textsuperscript{17}O NMR.

As discussed above, new types of local O environments, especially those connected to \textsuperscript{5}Si and \textsuperscript{6}Si, must exist in silicate melts and glasses at high pressure. Therefore, in order to apply \textsuperscript{17}O NMR to study the structure of silicate glasses quenched from high pressure, it is necessary first to understand the \textsuperscript{17}O NMR characteristics of these new local O environments. In the first part of this paper, we present \textsuperscript{17}O MAS and static NMR spectra for several low- and high-pressure alkali silicate and silica crystalline phases, as well as alkali silicate glasses quenched from melts at 1 bar, and discuss the characteristics of \textsuperscript{17}O NMR spectra for different types of local O sites. We find that some pressure-induced changes in O environments are readily distinguished. We then report \textsuperscript{17}O MAS and static NMR data for alkali silicate glasses quenched from melts at high pressure and discuss the structural changes in these glasses with pressure.

**Experimental procedures**

Approximately 10 or 50% \textsuperscript{17}O-enriched SiO\textsubscript{2} (cristobalite) powders prepared from hydrolysis of SiCl\textsubscript{4} with H\textsubscript{2}\textsuperscript{17}O (Cambridge Isotope Laboratories) were used for synthesizing the starting materials. The alkali silicate glass
starting materials were prepared by the melt quench method described previously (Xue et al., 1991) from alkali carbonate and $^{17}$O-enriched SiO$_2$ in a clean N$_2$ atmosphere to prevent O isotopic exchange with air. About 0.2 wt% of Gd$_2$O$_3$ (0.1 wt% Gd$_2$O$_3$ + 0.1 wt% MnO for the Na$_2$Si$_2$O$_5$ sample) was added to shorten the spin-lattice relaxation time.

The synthesis conditions for the crystalline phases and for glasses quenched from melts at high pressure are tabulated in Table 1. Most of the high-pressure samples were synthesized using a MA8 type multianvil high-pressure apparatus at Tokyo University. The Na$_2$Si$_2$O$_5$ glass sample quenched from melt at 10 GPa and the K$_2$Si$_2$O$_5$ glass sample quenched from melt at 6 GPa were produced using a USSA-2000 multianvil apparatus at the University of Alberta (see Xue et al., 1991, for a description of the experimental procedure). The wadeite-K$_2$Si$_2$O$_5$ sample was synthesized using a piston-cylinder apparatus at the U.S. Geological Survey, Menlo Park. The identity, purity, and crystallinity of the crystalline phases have been confirmed by powder X-ray diffraction and $^{29}$Si or $^{23}$Na MAS NMR. The quenched glass samples have been examined under a polarizing microscope (400 x) and were all found to be homogeneous and crystal free. Alkali loss during synthesis was monitored by careful weighings and was found to be insignificant.

The $^{17}$O NMR spectra were collected on crushed samples using a Varian VXR-400S spectrometer at a Larmor frequency of 54.2 MHz. A Doty Scientific high-speed MAS probe with a 5-mm rotor was used for the MAS NMR. A Varian probe with a horizontal 5-mm rf coil was used for the static NMR. The liquid 90° pulse lengths measured on deionized H$_2$O in both probes were about 8–10 μs. For the MAS NMR experiments, single pulses of 0.5–1 μs (about a 15–30° tip angle for the central transition in solids) were used, and the sample spinning speeds were usually 9–11 kHz. Small pulse angles were used to ensure quantitative and selective excitation of the central transitions for all O sites. For the static experiments, a 90°-τ − 90°-τ solid-state echo pulse sequence with a τ value of 55 μs was applied to overcome the problem of spectrometer dead time, which is a severe problem for broad spectra. Delay times of 0.2–30 s between pulses (or pulse sequences) were used, depending on the spin-lattice relaxation time of the sample. Frequencies were externally calibrated to approximately ±0.2 ppm against deionized H$_2$O.

Values of $\delta$, $\epsilon^2qQ/h$, and η for the crystalline phases have been derived from computer simulations of the $^{17}$O MAS NMR spectra based on the algorithm of Müller (1982). In addition to the second-order quadrupolar broadening, the $^{17}$O static NMR line shape of a powdered sample is in general also affected by chemical shift anisotropy and by the relative orientations between the chemical shift tensor and the electric field gradient tensor. For two of the crystalline samples we studied (wadeite-K$_2$Si$_2$O$_5$ and stishovite), we were able to obtain the static NMR spectra. We have simulated these lines using values of $\delta$, $\epsilon^2qQ/h$, and η derived from the MAS NMR spectra to obtain the principal component values for the chemical shift tensor. Because of the quality of these spectra, we have restricted our simulations to coincident principal axes between the chemical shift tensor and the electric field gradient tensor (see below for further discussions). The coordinate system we adopted is that described in Narita et al. (1966). The principal components of the chemical shift tensor are described in this paper as $\delta_x$, $\delta_y$, and $\delta_z$, denoting the components along the x, y, and z principal axes of the electric field gradient tensor (see Fig. 1 of Narita et al., 1966).

**Table 1. Synthesis conditions for crystalline phases and glasses quenched from melts at high pressure**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Starting material*</th>
<th>Synthesis conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Na$_2$Si$_2$O$_5$</td>
<td>Na$_2$Si$_2$O$_5$ glass, 10% $^{17}$O</td>
<td>1 atm, 810 ºC, 16 h, in N$_2$</td>
</tr>
<tr>
<td>α-Na$_2$Si$_2$O$_5$</td>
<td>Na$_2$Si$_2$O$_5$ glass, 10% $^{17}$O</td>
<td>6 GPa, 900 ºC, 1 h</td>
</tr>
<tr>
<td>Wadeite-K$_2$Si$_2$O$_5$</td>
<td>K$_2$Si$_2$O$_5$ glass, 10% $^{17}$O</td>
<td>2.64 GPa, 770 ºC, 25 h</td>
</tr>
<tr>
<td>Stishovite</td>
<td>SiO$_2$ cristobalite, 50% $^{17}$O</td>
<td>9.5 GPa, 860–900 ºC, 1 h</td>
</tr>
<tr>
<td>Na$_2$Si$_2$O$_5$ glass, 6 GPa</td>
<td>Na$_2$Si$_2$O$_5$ glass, 10% $^{17}$O</td>
<td>6 GPa, 1950 ºC, 10 min</td>
</tr>
<tr>
<td>Na$_2$Si$_2$O$_5$ glass, 8 GPa</td>
<td>Na$_2$Si$_2$O$_5$ glass, 48.6% $^{17}$O</td>
<td>6 GPa, 1750 ºC, 5 min</td>
</tr>
<tr>
<td>Na$_2$Si$_2$O$_5$ glass, 10 GPa</td>
<td>Na$_2$Si$_2$O$_5$ glass, 10% $^{17}$O</td>
<td>8 GPa, 2000 ºC, 5 min</td>
</tr>
<tr>
<td>Na$_2$Si$_2$O$_5$ glass, 10 GPa</td>
<td>Na$_2$Si$_2$O$_5$ glass, 10% $^{17}$O</td>
<td>10 GPa, 2050 ºC, 5 min</td>
</tr>
</tbody>
</table>

* Percentage of $^{17}$O enrichment refers to that of SiO$_2$ used in preparing the starting material.

**Correlations between $^{17}$O NMR parameters and the local structure around O**

The $^{17}$O NMR spectra of crystalline alkali silicates and silica

Four crystalline alkali silicate and silica phases (α-Na$_2$Si$_2$O$_5$, ε-Na$_2$Si$_2$O$_5$, wadeite-K$_2$Si$_2$O$_5$, and stishovite) have been chosen for this study because these phases contain several different types of O sites. The NMR parameters derived from computer simulations of the $^{17}$O MAS NMR spectra are reported in Table 2.

- **α-Na$_2$Si$_2$O$_5$.** There are three distinct O sites in the structure: O1, O2, and O3 in the ratio of 1:2:2 (Pant and Cruickshank, 1968). O1 and O2 are both bridging O atoms (BO), whereas O3 is a nonbridging O atom (NBO).

The $^{17}$O MAS NMR spectrum of this phase contains a narrow doublet and some broader peaks (Fig. 1a). The narrow doublet may be attributed to the single NBO site, O3, as it has been shown by previous studies that NBO...
Table 2. NMR parameters derived from $^{17}$O MAS NMR spectra

<table>
<thead>
<tr>
<th>Phase</th>
<th>O site</th>
<th>$\eta$</th>
<th>$e^{2}qQ/h$ (MHz)</th>
<th>$\delta$ (ppm)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cristobalite ($SiO_2$)</td>
<td>BO</td>
<td>0.125 ± 0.005</td>
<td>5.3 ± 0.1</td>
<td>40 ± 2</td>
<td>1</td>
</tr>
<tr>
<td>$\alpha$-Na$_2$Si$_4$O$_6$</td>
<td>O1 (BO)</td>
<td>0.0 ± 0.2</td>
<td>5.7 ± 0.3</td>
<td>55 ± 5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>O2 (BO)</td>
<td>0.25 ± 0.05</td>
<td>4.7 ± 0.2</td>
<td>55 ± 2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>O3 (NBO)</td>
<td>0.1 ± 0.1</td>
<td>2.35 ± 0.04</td>
<td>34 ± 1</td>
<td>2</td>
</tr>
<tr>
<td>Wadellite-$K$Si$_4$O$_6$</td>
<td>O1 (BO)</td>
<td>0.35 ± 0.05</td>
<td>4.45 ± 0.05</td>
<td>62.5 ± 1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>O2 ($^{17}$O-Si-$^{34}$Si)</td>
<td>0.20 ± 0.05</td>
<td>4.90 ± 0.05</td>
<td>97 ± 1</td>
<td>2</td>
</tr>
<tr>
<td>Stishovite ($SiO_2$)</td>
<td>$^{17}$O</td>
<td>0.125 ± 0.05</td>
<td>6.5 ± 0.1</td>
<td>109 ± 2</td>
<td>1</td>
</tr>
<tr>
<td>Na$_2$Si$_4$O$_6$ glass</td>
<td>BO</td>
<td>0</td>
<td>5.0 ± 0.3</td>
<td>65 ± 5</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>NBO</td>
<td>0</td>
<td>2.3 ± 0.1</td>
<td>40 ± 2</td>
<td>2</td>
</tr>
<tr>
<td>Na$_2$Si$_3$O$_7$ glass</td>
<td>BO</td>
<td>0</td>
<td>5.0 ± 0.3</td>
<td>60 ± 5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>NBO</td>
<td>0</td>
<td>2.3 ± 0.1</td>
<td>39 ± 2</td>
<td>2</td>
</tr>
<tr>
<td>Na$_2$Si$_4$O$_6$ glass</td>
<td>BO</td>
<td>0</td>
<td>5.0 ± 0.2</td>
<td>50 ± 4</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>NBO</td>
<td>0</td>
<td>2.3 ± 0.0</td>
<td>36 ± 2</td>
<td>2</td>
</tr>
<tr>
<td>K$_2$Si$_3$O$_7$ glass</td>
<td>BO</td>
<td>0</td>
<td>4.9 ± 0.2</td>
<td>52 ± 4</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>NBO</td>
<td>0</td>
<td>2.3 ± 0.1</td>
<td>76 ± 2</td>
<td>2</td>
</tr>
</tbody>
</table>

Note: parameters without quoted error have been fixed during simulation. Data for glasses are for samples at 1 bar.

* Data from Spearing et al. (1992).

in general have much smaller $e^{2}qQ/h$ and thus narrower $^{17}$O NMR patterns than BO (Timkin et al., 1987; Mueller et al., 1992; Farnan et al., 1992). The broad peaks may be simulated with two broad quadrupolar doublet patterns corresponding to the two BO sites. The ratios of these three O sites have been fixed during the simulation to those expected from the crystal structure. One of the BO has a rather large value of $e^{2}qQ/h$ (5.7 MHz), which may be correlated to the unusually large Si-O-Si angle of O1 (160.04° for O1 vs. 138.93° for O2; Pant and Cruickshank, 1968). Positive correlations between $^{17}$O $e^{2}qQ/h$ and Si-O-Si angle have been predicted from quantum mechanical calculations (Tossell and Lazzeretti, 1988; Tossell, 1990) and are also supported by a recent dynamic angle spinning $^{17}$O NMR study of a K$_2$Si$_4$O$_6$ glass (Farnan et al., 1992) (see below for further discussion).

$\alpha$-Na$_2$Si$_4$O$_6$. This is a high-pressure phase that we found to be stable at pressures of about 5–6 GPa (Kanzaki et al., in preparation). Although detailed structure of this phase has not yet been solved by single-crystal X-ray diffraction, the $^{29}$Si NMR spectrum contains two distinct peaks centered at -81.0 and -82.3 ppm, which from stoichiometry can be attributed to two Q$_3$ sites (Si with three other second-neighbor Si ions), suggesting that it has a sheet structure similar to the other lower pressure Na$_2$Si$_3$O$_7$ polymorphs (Kanzaki et al., in preparation). We may thus expect the ratio of BO and NBO in this phase to be 3:2. The $^{29}$Si chemical shifts of these peaks are about 10 ppm less negative than those of BO in other silicates, such as Na$_2$Si$_4$O$_6$, cristobalite ($SiO_2$) (Timken et al., 1986b; Spearing et al., 1992), and alkaline earth metasilicates (Timken et al., 1987; Mueller et al., 1992). The O2 site is unique to high-pressure silicates containing mixed fourfold- and sixfold-coordinated Si. Its $e^{2}qQ/h$ is similar to those of normal BO, but its $\delta$ is significantly larger.

The static NMR spectrum cannot be simulated well with the same parameters derived from the MAS NMR spectrum if the chemical shift anisotropy is ignored (Fig. 2b). This has been commonly observed for static $^{17}$O NMR spectra of crystalline silicates (e.g., Timken et al., 1986a, 1986b; Spearing et al., 1992). A reasonable fit is obtained by taking this anisotropy into consideration, assuming that the principal axes of the chemical shift tensor are coincident with those of the electric field gradient tensor (Fig. 2c). The derived principal components for the chemical shift tensor of O1 are $\delta_x = 81$, $\delta_y = 81$, and $\delta_z = 25.5$ ppm. Those of O2 are $\delta_x = 117$, $\delta_y = 117$, and $\delta_z = 57$ ppm. Uncertainties for all are about ±10 ppm.
Fig. 1. (a) Experimental and simulated $^{17}$O MAS NMR spectra of $\alpha$-Na$_2$Si$_5$O$_8$. The experimental spectrum (upper) was acquired on an 84-mg sample (100% $^{17}$O) with a 1-µs pulse length, 30-s delay, and 3000 signal averages. The sample spinning speed was 10 kHz. A 100-Hz exponential line broadening was applied; (b) $^{17}$O MAS NMR spectra of $\alpha$-Na$_2$Si$_5$O$_8$. The spectrum was acquired on a 17-mg sample (100% $^{17}$O) with a 1-µs pulse length, a 10-s delay, and 6300 signal averages. The sample spinning speed was 3 kHz. A 260-Hz Gaussian line broadening was applied.

Because the quadrupolar patterns for the two O sites overlap, we cannot determine the unique relative orientations of the chemical shift tensor and the electric field gradient tensor for either site.

Stishovite. Stishovite is a high-pressure SiO$_2$ polymorph that is stable above approximately 9 GPa. There is only one crystallographically distinct site each for Si and O in the structure (Sinclair and Ringwood, 1978). Each Si ion is coordinated to six O atoms, and the SiO$_6$ octahedra share both corners and edges with neighboring octahedra. Each O atom is coordinated to three $^{18}$Si ($^{17}$O) atoms.

The $^{17}$O MAS NMR spectrum of stishovite is composed of a doublet that can be well simulated with a single O site (Fig. 3a). The $\epsilon^2 q Q / h$ value of $^{17}$O in stishovite (6.5 MHz) is by far the largest among O sites in silicates known so far. Its $\delta_1$ (109 ppm) is also larger than those of BO in any silicates, although NBO in strontium metasilicates and barium metasilicates have larger $\delta_1$ values (Timken et al., 1987).

Fig. 2. (a) Experimental and simulated $^{17}$O MAS NMR spectra of wadeite-K$_2$Si$_5$O$_9$. The experimental spectrum (top) was acquired with a 1-µs pulse length, a 1-s delay, and 14300 signal averages. The sample spinning speed was 11 kHz. A 40-Hz Gaussian line broadening was applied; (b) $^{17}$O static NMR spectrum of wadeite-K$_2$Si$_5$O$_9$ and simulations without considering chemical shift anisotropy. The experimental spectrum (top) was acquired with a solid-state echo pulse sequence (see text), a 1-s delay between pulse sequences, and 8100 signal averages. A 600-Hz Gaussian line broadening was applied; (c) $^{17}$O static NMR spectrum of wadeite-K$_2$Si$_5$O$_9$ as in b and simulations that have taken account of chemical shift anisotropy. Both the MAS and static NMR spectra were obtained on an approximately 80-mg sample (100% $^{17}$O).

For the $^{17}$O static NMR spectrum, as for that of wadeite-K$_2$Si$_5$O$_9$, the fit is poor when we simulate only with the parameters derived from the MAS NMR spectrum, ignoring the chemical shift anisotropy (Fig. 3b). When the chemical shift anisotropy is taken into consideration, again assuming coincident principal axes between the chemical shift tensor and the electric field gradient tensor, a reasonable fit can be obtained (Fig. 3b). The derived principal components for the chemical shift tensor are $\delta_{x'} = 69$, $\delta_{y'} = 95$, and $\delta_{z'} = 163$ ppm. Uncertainties are approximately ±7 ppm for all. The quality of this spectrum does not allow us to analyze further the relative orientations of the two tensors.

The $^{17}$O NMR spectra of alkali silicate glasses quenched at 1 atm

We have also obtained a $^{17}$O MAS NMR spectrum for a K$_2$Si$_5$O$_8$ glass and $^{17}$O MAS and static NMR spectra for Na$_2$Si$_5$O$_8$, Na$_2$Si$_5$O$_7$, and Na$_2$Si$_5$O$_6$ glasses, all quenched from melts at 1 atm (Figs. 4, 5, and 6). These spectra resemble those of alkaline earth silicate glasses prepared at 1 atm (Kirkpatrick et al., 1986) and have much less well defined features than those of crystalline phases as a result of structural disorder.

The MAS NMR spectrum of the K$_2$Si$_5$O$_8$ glass consists
of a narrow peak that is attributable to NBO and a broader doublet that is attributable to BO (Fig. 4). In the MAS NMR spectra of the sodium silicate glasses, these two patterns overlap, as was briefly mentioned in Kirkpatrick (1988), but the narrow component clearly increases in relative intensity with increasing Na$_2$O content, suggesting that it is the NBO peak (Fig. 5). These spectra can all be reasonably simulated with a narrow NBO and a broader BO pattern, by constraining the ratio of NBO and BO to that required by stoichiometry and by applying a large Gaussian line broadening function (500–1900 Hz) to account partially for the disorder (Figs. 4 and 5). The $\eta$ values were also fixed to 0 in these simulations owing to a lack of constraints. Because of the simplicity of these assumptions, the actual uncertainties in the mean NMR parameters (listed in Table 2) are probably larger than those associated with the simulations. The derived mean $c^2qQ/h$ and $\bar{\delta}$ values for BO are similar for both the potassium and the sodium silicate glasses. There is a slight increase in the mean $\bar{\delta}$ value of BO in sodium silicate glasses with increasing Na$_2$O content, consistent with the trend observed in crystalline silicates (e.g., cristobalite vs. $\alpha$-Na$_2$Si$_2$O$_5$; see Table 2). The mean $c^2qQ/h$ values of NBO are also similar for the potassium and sodium silicate glasses, but the NBO in the K$_2$SiO$_3$ glass has a much larger mean $\bar{\delta}$ than those of sodium silicate glasses, which is responsible for the better resolution of the NBO peak and the BO doublet in the former.

The static NMR spectra of the sodium silicate glasses may be decomposed into a broad outer doublet and a narrower inner doublet (Fig. 6). The relative height of the latter increases with increasing Na$_2$O content. We may thus attribute the former to BO that have a large mean $c^2qQ/h$ value and the latter to NBO with a smaller mean $c^2qQ/h$, consistent with the MAS NMR spectra. These static NMR spectra cannot be simulated well with the parameters derived from the MAS NMR spectra by assuming an absence of chemical shift anisotropy, as is the case for the crystalline phases. We have not attempted to further simulate these spectra, given the complications associated with the disordered nature of these materials.

**Characteristic $^{17}$O NMR parameters of various types of O sites**

We have plotted in Figure 7 the $c^2qQ/h$ parameter against $\bar{\delta}$, for the various types of O sites (NBO, BO, $^{14}$Si-
Fig. 5. Experimental and simulated $^{18}$O MAS NMR spectra of Na$_2$Si$_2$O$_5$, Na$_2$Si$_3$O$_7$, and Na$_3$Si$_4$O$_9$ glasses quenched from melts at 1 atm. These spectra were acquired on samples of approximately 100–145 mg (10% $^{18}$O), with a pulse length of 0.5–1 µs, a delay of 0.2–1 s, and 14000–54000 signal averages. The sample spinning speeds were 10–11 kHz. A 50-Hz exponential line broadening was applied to the spectrum of the Na$_2$Si$_2$O$_5$ glass, and a 100-Hz Gaussian line broadening was applied to those of the Na$_2$Si$_3$O$_7$ and Na$_3$Si$_4$O$_9$ glasses.

Fig. 6. The $^{18}$O static NMR spectra of Na$_2$Si$_2$O$_5$, Na$_2$Si$_3$O$_7$, and Na$_3$Si$_4$O$_9$ glasses quenched from melts at 1 atm. All spectra were acquired with the solid-state echo pulse sequence and a 1-s delay between pulse sequences. The spectrum of the Na$_2$Si$_3$O$_7$ glass was obtained on a 154-mg sample (48.6% $^{18}$O) with 4000 signal averages; those of the Na$_2$Si$_2$O$_5$ and Na$_3$Si$_4$O$_9$ glasses were obtained on samples 100–125 mg (100% $^{18}$O) with about 50000 signal averages. A 100-Hz exponential line broadening was applied to all.

Fig. 7. The parameter $\delta$ vs. $\epsilon_2 q Q / h$ for various types of O sites in sodium silicate, potassium silicate, and silica crystals and ambient pressure glasses. Errors are mainly smaller than the symbols. Solid symbols denote potassium silicates; open symbols denote sodium silicates; shaded symbols denote silica.

$^{18}$O in alkali silicate and silica crystals and ambient pressure glasses. Because of the known variations of these parameters with the type of network-modifying cations, we have not included the data for alkaline earth silicates reported by Timken et al. (1987) and Mueller et al. (1992). The figure clearly shows that the different types of O sites can be distinguished by one or both of the two parameters.

NBO are characterized by small $\epsilon_2 q Q / h$ values (approximately 2.3 MHz). The $\delta$ values of NBO are very sensitive to the type of network-modifying cations, and a larger cation causes a more positive $\delta$ (76 ppm for potassium tetrasilicate vs. 34–45 ppm for sodium silicates), consistent with previous studies (Timken et al., 1987; Mueller et al., 1992). In addition, out data suggest that the $\delta$ values of NBO may be sensitive to the intertetrahedral angle of the Si to which the NBO is bonded as well. The $\delta$ value of NBO in the high-pressure $\alpha$-Na$_2$Si$_2$O$_5$ phase, which we suspect has an unusually small Si-O-Si angle within the silicate sheets, is shifted by about 10 ppm to a higher frequency, compared with that of $\alpha$-Na$_3$Si$_4$O$_9$ (see Table 2).

BO and $^{18}$Si-O-$^{18}$Si sites have similar $\epsilon_2 q Q / h$ values (4.5–5.7 MHz), which are intermediate between those of NBO and $^{18}$O. The two can be distinguished by $\delta$, which is considerably higher for the latter (97 ppm for $^{18}$Si-O-$^{18}$Si vs. 40–65 ppm for BO). It might be expected that O atoms in the $^{18}$Si-O-$^{18}$Si linkages would also have similar $\epsilon_2 q Q / h$ values and perhaps $\delta$ values intermediate between those of normal BO and $^{18}$Si-O-$^{18}$Si. It has been shown previously (Timken et al., 1987; Mueller et al., 1992) that the $\delta$ and $\epsilon_2 q Q / h$ values of BO are relatively insensitive...
to the type of network modifiers compared with those of NBO. The results we obtained for ambient pressure potassium and sodium silicate glasses are consistent with that conclusion (see Fig. 7). We may expect the same for O atoms in the $[{\text{Si-O-Si}}]$ or $[^{31}\text{Si-O-}^{31}\text{Si}]$ linkages.

Both quantum mechanical calculations (Tossell and Lazzeretti, 1988; Tossell, 1990) and a $^{13}$O dynamic angle spinning NMR study (Farnan et al., 1992) have suggested that the $e_2^{gQ}/h$ value of BO increases with an increasing intertetrahedral angle. Our data are qualitatively consistent with such a conclusion, as shown in Figure 8, where we have plotted the $e_2^{gQ}/h$ value against the $\text{Si-O-Si}$ angles for $\alpha$-$\text{Na}_2\text{Si}_2\text{O}_5$, wadeite-$\text{K}_2\text{Si}_2\text{O}_6$, cristobalite ($\text{SiO}_2$: Spearing et al., 1992), and diopside ($\text{CaMgSi}_2\text{O}_6$: Mueller et al., 1992). However, the $e_2^{gQ}/h$ values of these crystals are in general slightly lower than those predicted from the curve derived by Farnan et al. (1992) from dynamic angle spinning NMR data of a Kr$\text{Si}_4\text{O}_9$ glass. This offset is not surprising, given that the absolute position of the curve was calibrated indirectly with data for a single material. There are likely to be other structural effects that perturb the dominant $\text{Si-O-Si}$ angle correlation. It is conceivable that the $e_2^{gQ}/h$ value for BO in the $[^{31}\text{Si-O-}^{31}\text{Si}]$ and $[^{31}\text{Si-O-}^{31}\text{Si}]$ linkages also vary somewhat with the $\text{Si-O-Si}$ angle.

The $^{13}$O site in stishovite distinguishes itself by its large $e_2^{gQ}/h$ and $\delta$ values. Its $e_2^{gQ}/h$ value (6.5 MHz) is the largest among O atoms in all known silicates (3.7–5.8 MHz for normal BO and 1.6–3.2 MHz for NBO), and its $\delta$ is also larger than any normal BO (40–87 ppm) (Timken et al., 1986a, 1986b, 1987; Walter et al., 1988; Mueller et al., 1992; and this study). Recent quantum mechanical calculations have also suggested that threefold-coordinated O atoms (with a mean Si-O bond length and mean Si-O-Si angle similar to those of stishovite) have a significantly higher $e_2^{gQ}/h$ value and a lower O NMR shielding (larger $\delta$) than twofold-coordinated O atoms (BO) (Tossell, 1990). We may expect that in silicates where additional network-modifying cations also interact with $^{13}$O, O atoms coordinated to three Si atoms, the $e_2^{gQ}/h$ and $\delta$ values for $^{13}$O may vary somewhat. In the case of normal BO, the $\delta$ value of BO in a pure $\text{SiO}_2$ phase (e.g., cristobalite, 40 ppm: Spearing et al., 1992) is lower than those in all alkali and alkaline earth silicates (55–87 ppm: Timken et al., 1987; Mueller et al., 1992; and this study; also see Fig. 7). This may be explained by the greater deshielding of the O nuclei in the presence of additional network-modifying cations. The observed increase in $\delta$ of BO in sodium silicate glasses with increasing Na$_2$O content noted above is also consistent with the trend. If a similar trend holds for $^{13}$O, we may expect even greater values of $\delta$ for $^{13}$O sites in alkali or alkaline earth silicates than in silica (stishovite). Also by analogy with normal BO, there may be a variation in the $e_2^{gQ}/h$ value of $^{13}$O with the Si-O-Si angle.

It should be noted that there are several other types of O sites that may appear in high-pressure silicate glasses and melts, for which we do not yet know the $^{13}$O NMR characteristics. Examples of these include O ions linked to two $[^{31}\text{Si}]$ by either corner or edge sharing. The former appears in high-pressure perovskite-type Mg$\text{SiO}_3$ and Ca$\text{SiO}_3$ phases (Horiuchi et al., 1987; Liu and Ringwood, 1975), whereas the latter can be seen in the ilmenite-type Mg$\text{SiO}_3$ phase (Horiuchi et al., 1982). When there is a high concentration of $[^{31}\text{Si}]$ in high-pressure silicate glasses or melts, such O sites may become significant. It is possible that both types of O sites may have even larger $^{13}$O $\delta$ values than those of O atoms in the $[^{31}\text{Si-O-}^{31}\text{Si}]$ linkages, but their $e_2^{gQ}/h$ values could be either smaller or larger. Thus these types of O sites could be indistinguishable from $^{13}$O in $^{13}$O NMR spectra. Direct measurements on high-pressure crystalline phases containing such O sites would clearly be useful.

**The $^{13}$O NMR of Alkali Silicate Glasses Quenched from Melts at High Pressure**

$\text{K}_2\text{Si}_3\text{O}_5$ glasses

As discussed above, the $^{13}$O MAS NMR spectrum of the $\text{K}_2\text{Si}_3\text{O}_5$ glass quenched from melt at 1 atm can be simulated with a narrow NBO peak and a broader BO doublet. In Figure 9, we compare the $^{13}$O MAS NMR spectrum of a $\text{K}_2\text{Si}_3\text{O}_5$ glass quenched from melt at 6 GPa with the above. Both the narrow NBO peak and the broad BO doublet shift by about 3 ppm to a higher frequency, from 1 atm to 6 GPa. The narrow NBO peak also becomes about 20% broader, and its relative intensity increases by a similar amount for the glass quenched at 6 GPa. There is no indication of an increase in the width of the BO peak, which could result in a reduced relative intensity because of instrumental dead time. We have not attempted detailed quantification of the spectra because...
of the uncertainties in fitting broad, overlapping quadrupolar powder patterns.

The shift of both the narrow NBO peak and the BO doublet to a higher frequency may be explained by an increase in the mean intertetrahedral angle with pressure that has been suggested by our previous Raman and $^{29}$Si NMR study (Xue et al., 1991). There are at least two possibilities for the cause of the broadening of the narrow NBO peak. One possibility is simply that there is a greater disorder in the NBO sites due to an increase in the population of NBO sites that are linked to Si having small intertetrahedral angles, and there is no significant concentration of new O species. However, there is no reasonable structural model that can account for the apparent growth of NBO relative to BO without the appearance of a third type of O species. Our earlier $^{29}$Si NMR study has revealed that the sample contains about 4% $^{10}$Si, and 2% $^{30}$Si (Xue et al., 1991). Because the formation of every $^{10}$Si or $^{30}$Si site would create up to five to six O sites that are linked to them, we may expect that the concentrations of new types of O sites that are linked to $^{10}$Si or $^{30}$Si are significant, even at 6 GPa. A comparison of the $^{17}$O MAS NMR spectra of these glasses with that of wadeite-$K_{2}Si_{3}O_{8}$ shows that the high-frequency half of the doublet for the O atom in the $^{10}$Si-O-$^{30}$Si linkage overlaps with the NBO peak because such an O site has a higher $\delta_{Q}$ than normal BO (Fig. 9). Thus the increased intensity and the apparent broadening and shift to a higher frequency of the NBO peak could be caused by the formation of new O sites in the $^{10}$Si-O-$^{30}$Si (possibly also $^{10}$Si-O-$^{15}$Si) linkages. At the concentration level for $^{15}$Si and $^{30}$Si in this sample, we may expect that O atoms linked to two or more highly coordinated Si atoms are insignificant.

**Na$_2$Si$_3$O$_8$ glasses**

Comparisons of the $^{17}$O MAS and static NMR spectra of Na$_2$Si$_3$O$_8$ glasses quenched from melts at 1 atm and 6, 8, and 10 GPa are shown in Figures 10 and 11. As shown earlier, the $^{17}$O MAS NMR spectrum of the Na$_2$Si$_3$O$_8$ glass quenched at 1 atm can be simulated with a narrow NBO peak and a broader BO doublet, similar to that of the K$_2$Si$_3$O$_8$ glass, except that the resolution between these two O sites is reduced because of the smaller mean $\delta_{Q}$ for NBO in sodium silicates (see Figs. 5 and 10). The $^{17}$O static NMR spectrum of this sample is also composed of a broad doublet attributable to the BO and a narrower doublet inside it due to the NBO (see Figs. 6 and 11).

When the $^{17}$O MAS NMR spectrum of the glass quenched at 1 atm with that of the glass quenched at 6 GPa are compared, the latter shows large, unresolved intensity increases on both sides of the narrow NBO peak (Fig. 10). Its relative height decreases correspondingly. The maximum of the NBO peak also shifts slightly toward a higher frequency. The $^{17}$O MAS NMR spectra of the glasses quenched at 6, 8, and 10 GPa are all very similar. Because of the base line problem associated with spectrometer dead time and the relatively small sample sizes (10–20 mg), it is difficult to resolve differences in the line shapes among these glasses. The spectral changes from 1 atm to 6 GPa cannot be simply explained as an overall shift of the spectrum to a higher frequency, associated with a decrease in the mean intertetrahedral angle, because the intensity increases on both sides of the narrow NBO peak. It is more likely that the number of O sites that have NMR peaks on one or both sides of the narrow peak has increased. As in the case of K$_2$Si$_3$O$_8$ glasses, we know from $^{29}$Si NMR that Na$_2$Si$_3$O$_8$ glasses quenched from 6 to 10 GPa contain considerable amounts of $^{10}$Si and $^{30}$Si (3–7 and 2–5%, respectively; Xue et al., 1991). An O atom in the $^{10}$Si-O-$^{30}$Si linkage in sodium silicates may have a similar $^{17}$O NMR pattern to that in wadeite-K$_2$Si$_3$O$_8$ because we expect the $\delta_{Q}$ and $\epsilon$ of such O sites to be insensitive to the type of network modifiers (see above). Such an O site would thus yield a doublet in the $^{17}$O MAS NMR spectrum that is similar in width, but displaced to a higher frequency, compared with that of the normal BO. The intensity increases on either
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Fig. 10. The $^{17}$O MAS NMR spectra of Na$_2$SiO$_3$ glasses quenched from melts at 1 atm and 6, 8, and 10 GPa. The spectrum of the glass quenched at 1 atm is identical to that in Fig. 5. The spectra of the glasses quenched at high pressure were acquired on samples of approximately 10–24 mg (48.6% $^{17}$O for the glasses quenched at 6 and 8 GPa, 10% $^{17}$O for the glass quenched at 10 GPa), with a pulse length of 0.5–0.6 µs, a delay of 0.2–1 s, 59000–304000 signal averages, and a sample spinning speed of 10–11 kHz. A 200-Hz exponential line broadening was applied to all spectra. Spinning sidebands are marked by dots.

The $^{17}$O static NMR spectra of Na$_2$SiO$_3$ glasses quenched at pressures of 1 atm to 8 GPa also show a continuous decrease in the relative intensity of the NBO doublet (Fig. 11), consistent with the development of additional O types that have broader quadrupolar patterns, as suggested by the MAS NMR spectra. In the static NMR spectrum of the glass quenched at 10 GPa, an additional feature appears on the high-frequency side of the spectrum (around 400 ppm). This peak is likely to be the high-frequency maximum of a quadrupolar pattern for an O site with an extremely large $\epsilon^2 Q/\hbar$ or large $\delta$. This new feature cannot be accounted for by the presence of O atoms in the $^{29}$Si-O-$^{40}$Si linkages, suggesting the formation of yet another new type of O site. However, we do not see any features due to such an O site with extreme NMR parameters in the MAS NMR spectrum of this sample. That is possibly because the peak is so broad that the signal was mostly lost during the spectrometer dead time, as these spectra were measured with single pulses. The latter problem has been eliminated for the static NMR spectrum by use of an echo pulse sequence. The large $\epsilon^2 Q/\hbar$ or large $\delta_{s}$ of this new type of O site would be consistent with one that is linked to three $^{40}$Si atoms (such as that in stishovite), although we cannot rule out the possibility that it may also be caused by O atoms linked to two $^{29}$Si or $^{30}$Si atoms (see above). In either case, it would suggest that some of the $^{29}$Si (and possibly also $^{30}$Si) atoms have started to connect with each other in the Na$_2$SiO$_3$ melt at 10 GPa. This is probably to be expected from the high concentrations of $^{28}$Si (7%) and $^{29}$Si (5%) in the sample known from $^{29}$Si NMR (Xue et al., 1991).

Summary and conclusions

Our study of model crystalline silicates has shown that $^{17}$O NMR is useful for studying O environments in silicates...
quenched from high pressure and that NBO, BO, \[^{[6]}\text{Si}-\text{O}–^{[6]}\text{Si}\], and \[^{[1]}\text{O}\] can be distinguished by their characteristic $e^2\eta Q/h$ and $\delta$.

The \(^{17}O\) NMR spectra of a $K_2Si_3O_6$ glass quenched from the melt at 6 GPa and $Na_2Si_3O_6$ glasses quenched from melts at pressures up to 10 GPa can be interpreted as indicating the presence of $O$ sites in the $^{[6]}\text{Si}-\text{O}–^{[6]}\text{Si}$ (and possibly also $^{[6]}\text{Si}-^{[1]}\text{O}–^{[6]}\text{Si}$) linkage. This result is consistent with our earlier model that the formation of $^{[6]}\text{Si}$ and $^{[3]}\text{Si}$ in alkali silicate melts (glasses) is accompanied by a decrease in the number of NBO that are forced to connect with these highly coordinated Si atoms, resulting in a greater polymerization of the structure. In addition, the \(^{17}O\) static NMR spectra of the $Na_2Si_3O_6$ glasses also suggest that another new type of \(O\) site, possibly one that is connected with two or three $^{[6]}\text{Si}$ (or $^{[3]}\text{Si}$) atoms, may begin to develop at approximately 10 GPa. Thus, $^{[6]}\text{Si}$ and $^{[3]}\text{Si}$ may be largely isolated form each other in the $K_2Si_3O_6$ melt at 6 GPa and the $Na_2Si_3O_6$ melt at 6–8 GPa, whereas above 10 GPa, clustering of these Si species may begin in $Na_2Si_3O_6$ melt.

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