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LETTER

The structure of $NaAlSi_3O_8$ liquid at high pressure: New constraints from NMR spectroscopy

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ABSTRACT

The structure of $NaAlSi_3O_8$ glass has often been studied as an analogue for that of silicic magmas. We describe here ^{29}Si and ^{27}Al MAS-NMR spectra for glasses quenched from pressures of 8 and 10 GPa. Unlike in our recent studies of alkali silicate glasses, we see no suggestion of a coordination number increase for Si. We do find some evidence for five-coordinated aluminum, but the narrow, discrete $^{[6]}Al$ peak reported by Ohtani et al. (1985) is not present in our spectra. Coordination changes in tectosilicate liquids may occur by a mechanism different from that in liquids containing abundant nonbridging O.

INTRODUCTION

Increases in the coordination numbers of Al and Si are among the most significant changes that occur in silicate mineral structures with increasing pressure. Similar changes in silicate liquids have often been postulated in order to explain effects of pressure on density, viscosity, and thermodynamic activities. Evidence from in situ infrared spectroscopy on glasses at room temperature and high pressure has suggested such changes more directly (Williams and Jeanloz, 1988).

Magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy has proved to be a very useful way of detecting and quantifying coordination numbers of Si and Al in silicates because of the method's sensitivity to local structure (Kirkpatrick, 1988; Stebbins and Farnan, 1989). Recently, we have reported ^{29}Si MAS-NMR results on alkali silicate glasses quenched from liquids at high pressure that allow quantification of the abundance of octahedrally coordinated Si ($^{[6]}Si$) and a species that is most likely five-coordinated Si ($^{[5]}Si$) (Stebbins and McMillan, 1989; Xue et al., 1989a, 1989b). Concentrations of each of these species reach 6–8% in $Na_2Si_4O_9$ glass produced at 12 GPa.

The composition $NaAlSi_3O_8$ has often been studied as an analogue for granitic magmas. A number of previous Raman spectroscopic (Mysen et al., 1980, 1983; McMillan and Graham, 1981) and X-ray scattering (Hochella and Brown, 1985) studies of glasses quenched from high pressure liquids have concluded that the Al coordination number does not change at pressures below 4 GPa in this composition. Ohtani et al. (1985) reported the presence of a substantial quantity of six-coordinated Al ($^{[6]}Al$) in $NaAlSi_3O_8$ glasses quenched from liquids at 6 and 8 GPa, observed as relatively narrow peaks at −16 ppm in ^{27}Al MAS-NMR spectra. We describe here both ^{29}Si and ^{27}Al MAS-NMR spectra of samples from 8 and 10 GPa that do not support the specific results of that study, but do agree with its general conclusion.

EXPERIMENTAL METHODS

Previous studies of $NaAlSi_3O_8$ glass quenched from 8 GPa (Ohtani et al., 1985) were complicated by the formation of quench crystals of jadeite. We have been able to quench crystal-free glasses from 8 and 10 GPa by modifying the capsule and furnace design. In brief, glass powder was placed into an inner capsule of Re foil, which was then placed in an outer Re capsule packed with W metal powder to prevent oxidation of the Re. High pressure experiments were made with the USSA 2000 multianvil apparatus at the C. M. Scarfe Laboratory for Experimental Petrology at the University of Alberta. Three-section $LaCrO_3$ heating elements (Kanzaki, 1987; Wei et al., 1990) reduced thermal gradients to less than 20 °C across the 2.5-mm length of the sample. Pressure was calibrated using the fayalite-spinel (5.3 GPa, 1000 °C; Yagi et al., 1987) and coesite-stishovite (9.2 GPa, 1000 °C; Yagi and Akimoto, 1976) phase transitions. Experimental temperatures were 2000 °C at 8 GPa and 2200 °C at 10 GPa.

The starting glass was synthesized from high purity oxides and carbonates as previously described (Liu et al., 1987). 95% ^{29}Si SiO_2 (Oak Ridge National Laboratory) was used, and 0.1 wt% FeO and 0.2 wt% Gd_2O_3 were added to speed spin-lattice relaxation and data measurement. After high pressure experiments, glasses were transparent but red in color, probably because of reduction of Gd^{3+} to a lower valence state. Microprobe analyses confirmed the added transition metal levels, and detected 0–0.3% rhenium oxide, some of which was present as discrete opaque inclusions. No W was detected

(<0.02%). Optical examination (400×) and the NMR data described below show that these samples are indeed free of silicate crystals.

We obtained most of the NMR data with a Varian VXR400S spectrometer (9.4-T field). We used zirconia MAS rotors in a high-speed 5-mm probe from Doty Scientific, Inc. Background signals for ^{27}Al were significant with the very small samples used (7–8 mg) but were eliminated by recording background spectra under carefully matched spectrometer conditions and subtracting. Relative intensities were monitored by aqueous and crystalline Al standards to allow comparisons among glasses from different pressures. A spectrum of the 8-GPa glass was also recorded at 11.7 T by H. Eckert (University of California, Santa Barbara).

NMR RESULTS

The ^{29}Si spectra for the 8-GPa and 10-GPa samples and the 1-bar glass are shown in Figure 1. Unlike previous results for alkali silicate glasses from these high pressures (Xue et al., 1989a, 1989b), no peaks near −150 ppm ($^{[5]}Si$) or −200 ppm ($^{[6]}Si$) are observed. The main peak for $^{[4]}Si$ is shifted slightly to a less negative chemical shift, consistent with a slightly decreased mean T-O-T bond angle, as previously suggested by vibrational spectroscopy (Sharma et al., 1979; Mysen et al., 1980; McMillan and Graham, 1981). The peak position for the 1-bar sample is −97.8 ± 0.2 ppm, the line width (FWHM) is 16.6 ± 0.3 ppm. Corresponding data for the 8- and 10-GPa samples are −96.3, 17.5, and −96.2, 17.1, with similar error levels. The observed increase in line width with pressure is somewhat similar to that observed in alkali silicate glasses with increasing pressure (Xue et al., 1989a, 1989b), which may in turn be related to increased disorder due to greater interaction between network modifying cations and bridging O atoms (Murdoch et al., 1985).

One significant change in the ^{27}Al spectra between the 1-bar and high pressure samples was the loss of roughly half of the total signal intensity, as determined by integration, over the central 30 kHz of the spectra. The most likely cause of this signal loss is distortion of a substantial fraction of the Al polyhedra, sufficient to increase the quadrupolar coupling constant (e^2qQ/h or QCC) for these sites enough so that they are not observed (Kirkpatrick et al., 1986; Engelhardt and Michel, 1987). This effect has often been observed in defect-rich materials, but its specific structural implications are generally poorly understood (DeJong et al., 1983).

More visible pressure effects are a noticeable increase in the width of the main peak and the development of pronounced asymmetry toward smaller chemical shifts, leading to shoulders at about 20 ppm stretching to −10 ppm (Fig. 2). These changes could be caused by increases in QCC similar to, but less drastic than, those described above, or to changes in the distribution of chemical shifts. The spectrum at 11.7 T of the 8-GPa sample has essentially the same line shape as the spectrum at 9.4 T. This finding suggests that the latter interpretation may be correct: the effect of the second-order quadrupolar coupling is substantially reduced at higher magnetic fields, but chemical shifts are field independent. The most likely reason for the development of more shielded (more negative) chemical shifts is the formation of more highly coordinated Al sites. The position of the shoulders seen in the 8- and 10-GPa samples suggests that the primary change is the formation of $^{[5]}Al$, although a small amount of $^{[6]}Al$ could also be present. We consider this conclusion to be somewhat less than definitive, however, because of the relatively poor signal-to-noise ratios of the spectra obtainable on such small samples and the lack of clearly resolvable peaks for the high-coordinate species. An MAS-NMR study at even higher magnetic field strength could help to eliminate this uncertainty.

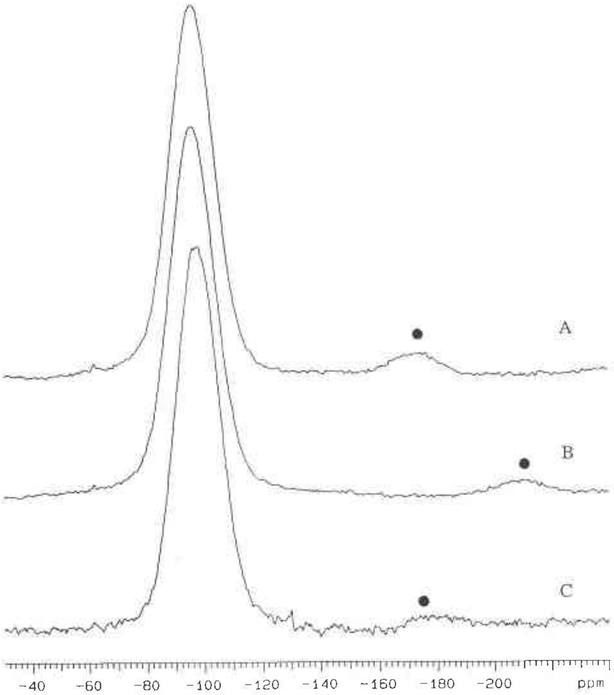

Fig. 1. MAS-NMR ^{29}Si spectra at 79.46 MHz of isotopically-enriched $NaAlSi_3O_8$ glass. Spinning sidebands are indicated by dots. Sharp features, near −128 ppm in the lower spectrum and near −62 ppm in all three, are artifacts. For each spectrum, data from about 40000 1-μs pulses (about 20–30° tip angle) were averaged, and an exponential line broadening of about 4% was applied during processing. Frequency scale is in ppm relative to tetramethyl silane (TMS). A: 10-GPa sample, spin rate about 6300 Hz. B: 8-GPa sample, spin rate about 9000 Hz. C: 1-bar sample, spin rate about 6500 Hz.

We also collected an ^{27}Al MAS spectrum for an $NaAlSi_3O_8$ glass quenched from a liquid at 8 GPa by M. Kanzaki in the laboratory of T. Fujii (University of Tokyo). The spectrum is the same as that shown in Figure 2, despite differences in the sample container (graphite), thermal gradient, and rates of quench and decompression. The spectrum of a glass-crystal mixture from the

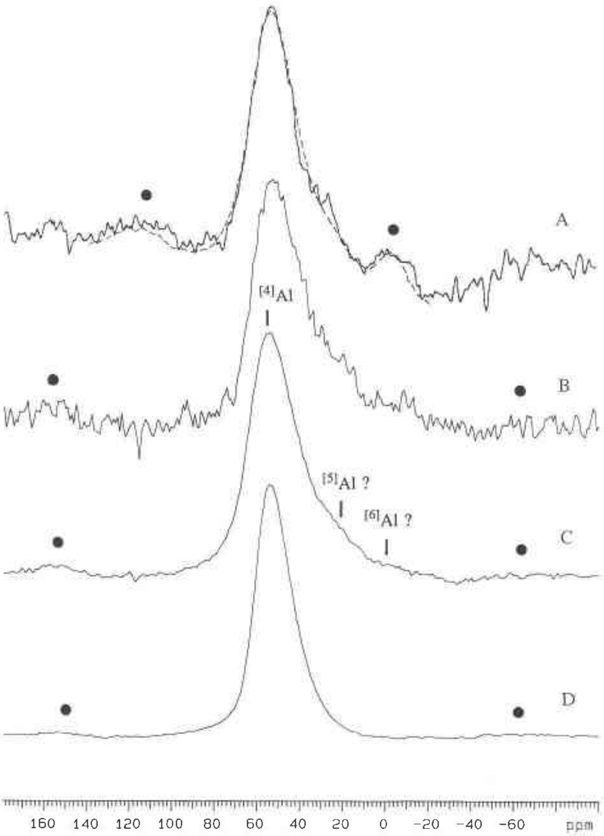

Fig. 2. MAS-NMR ^{27}Al spectra of same glasses as in Fig. 1. Frequency scale is in ppm relative to 1-*M* aqueous $Al(NO_3)_3$. Sample size for high pressure glasses was 6–8 mg and about 100 mg for the 1-bar glass. An exponential line broadening of about 7% was applied during data processing. A: 8-GPa sample at 130.3 MHz Larmor frequency (11.7-T field). Data from 4000 1 μs pulses, with a delay of 1 s, were averaged, with a spin rate of about 8 kHz. Dashed line is spectrum C (below), with sideband peaks artificially added and baseline slightly rotated to match 11.7-T data. B: 10-GPa sample at 104.2 MHz (9.4-T field). Data from about 22000 0.5 μs pulses with a delay of 0.2 s were averaged, with spin rate of about 10 kHz. C: 8-GPa sample at 104.2 MHz. Data from 200000 0.5 μs pulses, other parameters as in B. D: 1-bar sample, data from 1000 pulses, other parameters as in B.

same sample contained, in addition to the glass peak, a narrow peak at −0.9 ppm, similar to that reported earlier for crystalline jadeite (Ohtani et al., 1985).

DISCUSSION

We observe no evidence for five- or six-coordinated Si in $NaAlSi_3O_8$ glasses quenched from liquids at high pressure (concentration <0.5%), and no sign of spectrally well-defined, symmetrical $^{[5]}$Al or $^{[6]}$Al sites. The observability of the latter type of species in some low-pressure glasses has been demonstrated by ^{27}Al MAS-NMR studies of the Al_2O_3-SiO_2 and CaO-Al_2O_3-SiO_2 systems (Risbud et al., 1987; Sato et al., 1989). Our ^{27}Al results thus agree with the preliminary findings of Bishop (1986) but disagree with those of Ohtani et al. (1985). We are not certain of the reason for this discrepancy. Our samples and those of Ohtani et al. were melted at approximately the same temperature. The similarity of our spectra from samples prepared with different capsule materials and furnace assemblies suggests that the discrepancy is not the result of a quench-rate effect on the structure of a homogeneous glass or on the degree of relaxation on decompression. The −16 ppm peak in the spectra of Ohtani et al. (1985) cannot be due to well-crystallized jadeite, but it is possible that poorly crystalline nuclei or non-crystalline clusters could have been present. If these were small enough to contain Al octahedra sufficiently strained to raise the QCC by a few MHz, a broadened peak shifted by 15 or more ppm to more negative values could be produced. There is also the possibility of contamination of samples by a separate, Al-rich phase, which can be a particular problem with tiny high-pressure samples. An unidentified component dissolved in the glasses (e.g., H_2O) could also conceivably affect the structure and spectra.

On the other hand, the broad shoulders on the tetrahedral Al peaks suggest that some $^{[5]}$Al or $^{[6]}$Al may be present. Our results therefore do support the general conclusions of Ohtani et al. (1985) and of molecular dynamics simulations (Angell et al., 1982) that the beginning of the increase in the Al coordination number can be observed and occurs at a lower pressure than for Si. Also, the apparent overall loss of signal intensity in the ^{27}Al spectra possibly could be the result of the formation of highly distorted Al sites with coordination numbers greater than four. A greater effect of P on Al than on Si coordination is also expected, of course, from the larger size of the Al^{3+} cation, its common presence in four-, five-, or six-coordinated sites in minerals formed even at 1 bar, and the relatively low pressures at which $^{[4]}$Al-containing minerals react to form $^{[5]}$Al- or $^{[6]}$Al-bearing phases.

Finally, it is generally assumed that glasses record the structure of the liquid at the temperature of transition to the glass (T_g). We have recently shown that at least some of both $^{[5]}$Si and $^{[6]}$Si can be preserved during decompression of alkali silicate glasses (Stebbins and McMillan, 1989; Xue et al., 1989a, 1989b), although there is evidence from diamond-anvil pressure-cell studies at higher pressure than those studied here that some features of glass structure can change on decompression at room temperature (Williams and Jeanloz, 1988; Wolf et al., 1989). We have proposed a mechanism in which the high coordinate Si sites are created at the expense of nonbridging O (Xue et al., 1989b and in preparation). It is possible that in tectosilicate compositions such as $NaAlSi_3O_8$, a different mechanism for coordination change is required that becomes significant only at pressures above 10 GPa, and that requires the energetically more difficult formation of O coordinated by three Si or Al cations. On the other hand, it has been proposed that high-coordinated Si (and Al) formed in tectosilicate liquids somehow relaxes to lower coordination during decompression (Stolper and Ahrens, 1987; Williams and Jeanloz, 1988), again because a mechanism different from that in alkali silicates dominates. It is thus conceivable that subtle differences in the P-T path followed during quench and decompression could result in the differences between our results and those of Ohtani et al. (1985), although we consider this to be unlikely because of the variety of samples that we have examined. Further in situ studies at high pressure and high temperature may help to resolve these issues.

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