High-resolution ^{27}Al and ^{29}Si NMR spectroscopy of glasses and crystals along the join CaMgSi$_2$O$_6$-CaAl$_2$SiO$_6$

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Abstract

We present in this paper high-resolution magic-angle sample-spinning (MASS) ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR) spectroscopic data for glasses and crystals along the join CaMgSi$_2$O$_6$-CaAl$_2$SiO$_6$ (Di-Cats). For the glasses, our results indicate the following: (1) No ^{27}Al NMR signal is detected for other than tetrahedrally coordinated Al, and all ^{27}Al can be quantitatively accounted for. (2) For the glasses there is a systematic deshielding (more positive chemical shift) at Al with increasing Al content, paralleling the variation observed for crystals. (3) There is only a very small (about 2 ppm) nonsystematic variation in ^{29}Si chemical shift across the join. (4) The ^{29}Si peak breadths of the glasses are much greater than for typical crystals and become narrower with increasing Al content. (5) The observable ^{27}Al resonances of the glasses do not change in line width with changing composition. We interpret these results as indicating that the glasses become increasingly polymerized with increasing Cats content, that Cats glass is fully polymerized, and that the lack of variation in the ^{29}Si chemical shift is due to the opposing effects of increasing polymerization, which increases shielding, and the increasing number of Al next-nearest neighbors, which decreases the shielding.

Introduction

The structure of silicate melts and glasses is a field of research that cuts across a number of scientific and engineering disciplines. In recent years, advances in X-ray diffraction (Taylor and Brown, 1979a, 1979b), EXAFS (Greeves et al., 1981), thermochemical measurements (Navrotsky et al., 1982), and vibrational spectroscopy (Brawer and White, 1977; Mysen et al., 1982; McMillan et al., 1982; Furukawa and White, 1980) have greatly improved our understanding of at least the local arrangement of atoms in melts and glasses.

Much still needs to be learned about glass structure, however, and there is considerable controversy about the interpretations of some of the vibrational spectra. New methods are clearly needed to examine glass structure. High-resolution magic-angle sample-spinning (MASS) nuclear magnetic resonance (NMR) spectroscopy (Andrew, 1971) is one such method.

In this paper we present high-resolution ^{27}Al and ^{29}Si MASS NMR data for crystals and glasses along the join CaMgSi$_2$O$_6$-CaAl$_2$SiO$_6$ (Di-Cats) and a novel way of determining the amount of ^{27}Al (or any other quadrupolar nuclide) that is detected in the NMR spectrum. There have been a number of previous investigations of these and similar glass compositions using Raman, calorimetric, and X-ray diffraction methods. Mysen et al. (1982 and references therein) and McMillan and Pirou (1983 and references therein) have interpreted their Raman

spectroscopy data to indicate that Di glass contains Q^0, Q^1, Q^2, Q^3, and Q^4 Si sites and that all the Al in Cats glass is in tetrahedral coordination. Negative enthalpies of mixing for glasses along the Di-Cats join are consistent with these ideas (Navrotsky et al., 1983). X-ray radial distribution study of CaAl$_2$Si$_2$O$_8$ (An) glass, which like Cats is on the SiO$_2$-CaAl$_2$O$_4$ join, also indicates that glasses along this join contain only tetrahedrally coordinated Al and are fully polymerized (Taylor and Brown, 1979a, 1979b).

Previous studies of the MASS NMR behavior of aluminosilicate glasses have been reported by de Jong et al. (1983), who examined the ^{27}Al NMR behavior of a variety of aluminosilicate crystals and glasses; by Thomas et al. (1983), who examined the ^{27}Al NMR behavior of a sodium aluminosilicate glass and Al$_2$O$_3$-SiO$_2$ gels; by Lippmaa et al. (1982), who examined the ^{29}Si NMR behavior of lead silicate glasses; by Kirkpatrick et al. (1985a), who examined the ^{23}Na, ^{27}Al, and ^{29}Si NMR behavior of some feldspar glasses; and by Murdoch et al. (1985), who examined the ^{29}Si NMR behavior of a variety of silicate glasses.

Methods

NMR spectroscopy

Modern Fourier transform NMR spectroscopy is well described at an elementary level in the book by Farrar and Becker (1971). Applications to solid silicates and aluminosilicates and brief reviews of the theory and methods are discussed by Lippmaa
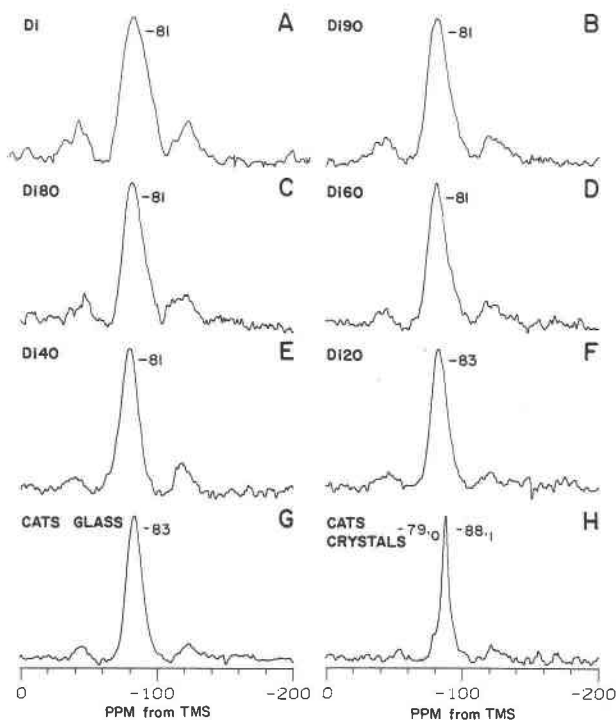
Fig. 1. ^{29}Si MASS NMR spectra along the join CaMgSi$_2$O$_6$-CaAl$_2$SiO$_6$ (Di-Cats) obtained at 8.45 T. Compositions are in mole percent Di.

et al. (1980, 1981), Müller et al. (1981a, 1981b), Smith et al. (1983), and Kirkpatrick et al. (1985a).

Of the nuclei investigated here, ^{29}Si has spin $I = \frac{1}{2}$, does not suffer from quadrupolar line broadening, and for a single structural environment produces a narrow NMR resonance (peak). Thus, the broad ^{29}Si peaks observed with the glasses *must* be due to a range of structural environments. ^{27}Al, on the other hand, has spin $I = \frac{5}{2}$ and thus possesses a nuclear quadrupole moment, and its peak breadth is in general dominated by quadrupolar broadening (Kirkpatrick et al., 1985a). Because of this, peak breadths for ^{27}Al are more difficult to interpret.
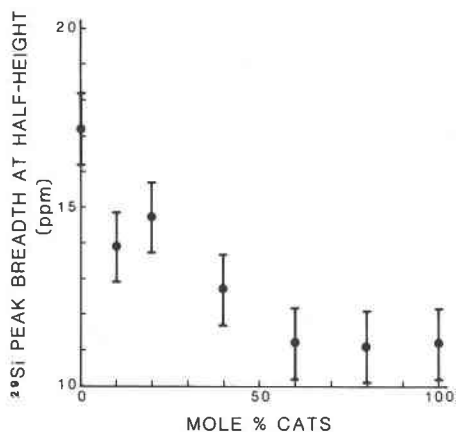

Fig. 2.   Variation in peak breadth at half-height for ^{29}Si MASS NMR spectra along the Di-Cats join. Decreasing peak breadth with increasing Cats content indicates a reduction in the types of polymerization state for Si.

Spectrometers

The NMR spectra reported here were collected on one of two "home-built" Fourier transform spectrometers as discussed by Smith et al. (1983). These instruments are based on 8.45- and 11.7-T superconducting magnets (T = tesla; Oxford Instruments, Osney Mead, Oxford, UK), are equipped with home-built Andrew-Beams type magic-angle sample-spinning assemblies, and are automated with Nicolet (Madison, Wisconsin) 1180 or 1280 computers. The ^{27}Al spectra were obtained on the 11.7-T instrument using a small (120 μL) high-speed (5 kHz) rotor, while the ^{29}Si data were obtained on the 8.45-T instrument using a large (800 μL) rotor at 2–3 kHz. ^{27}Al chemical shifts are relative to an external reference sample composed of 1 *M* AlCl$_3$ solution; ^{29}Si chemical shifts are relative to external tetramethylsilane. Because the glass peaks are so broad, we estimate the precision and accuracy to be about 1.0 ppm for both nuclei. More positive values of the chemical shift corresponds to a deshielding, or downfield shift.

Sample preparation

The glasses discussed here were prepared from General Electric fused quartz and reagent-grade CaCO$_3$, MgO, and Al$_2$O$_3$. Each sample, of approximately 15 g, was prepared by fusing the constituents in the appropriate proportions in a platinum crucible at about 100°C above the liquidus, followed by quenching and grinding in an agate mortar and pestle. The process was repeated three times. Glasses were finally quenched by pouring into a silicone oil, which is significantly faster than a water quench. The samples are the same ones for which Kirkpatrick (1974) obtained crystal growth rates and for which Navrotsky et al. (1983) obtained thermochemical data. Analyses are reported in both these papers and, within analytical precision, are the nominal compositions. The diopside crystals were made by crystallizing the diopside melt at about 1200°C in air. The Cats crystals were grown from Cats glass in air at 1 atm and 1010°C and are the apparently metastable H-Cats polymorph (Kirkpatrick and Steele, 1973).

RESULTS

We show in Figure 1 the ^{29}Si MASS NMR spectra for our glasses and crystals, and we summarize the results in Table 1. The spectrum of the diopside crystals consists of a single narrow peak at −84.7 ppm, which is in the range for silicons in Q^2 sites (Lippmaa et al., 1980) and in excellent agreement with the ^{29}Si chemical shift versus total cation-oxygen bond strength relationship of Smith et al. (1983). The spectrum of the H-Cats crystals consists of a peak at −88.1 ppm and perhaps a weak shoulder at about −79 ppm, suggesting one major and one minor crystallographically distinct Si site. The weak shoulder may represent residual glass, although we can detect none optically or by X-ray diffraction. The site represented by the −88.1 ppm peak is apparently about 20 times more abundant than the other. The peaks are very broad for a crystalline material, indicating that the phase is highly disordered, in agreement with previous X-ray work (Kirkpatrick and Steele, 1973) and as expected from a metastable phase grown at large undercoolings. The peak at −88.1 ppm is in the range expected for Q^4 silicons with four Al next-nearest neighbors (Lippmaa et al., 1981). The shoulder at

Table 1. ^{27}Al and ^{29}Si chemical shifts and peak breadths of crystals and glasses along the join CaMgSi$_2$O$_6$-CaAl$_2$SiO$_6$ (Di-Cats)

Composition (mole % of end members)	Aluminum–27 Chemical Shift (ppm)	Silicon–29 Chemical Shift (ppm)	Silicon–29 Peak Breadths (ppm at half–height)
Di$_{100}$ Glass	––	−81.1	17.1
Di$_{90}$ Cats$_{10}$ Glass	56	−81.0	13.9
Di$_{80}$ Cats$_{20}$ Glass	59	−81.1	14.7
Di$_{60}$ Cats$_{40}$ Glass	62	−81.1	12.7
Di$_{40}$ Cats$_{60}$ Glass	61	−81.4	11.2
Di$_{20}$ Cats$_{80}$ Glass	64	−83.0	11.1
Cats$_{100}$ Glass	64	−83.5	11.2
Diopside Crystals	––	−84.7	$\lesssim 1$
H–Cats Crystals	60.5	−79.0,−88.1	6.0

−79 ppm would be at less shielded values than observed previously for this type of Si site.

The ^{29}Si spectra of all the glasses consist of a single broad peak, along with smaller spinning sidebands that are a result of the MASS experiment. The positions of the sidebands vary with the spinning speed (Smith et al., 1983). Any apparent structure in the peaks is, we believe, within the noise level. The asymmetry of the peaks, however, probably reflects the range of Si sites present (Murdoch et al., 1985). As noted above, these broad peak widths indicate a wide range of electron distributions around the Si nuclei in the glass phases. The peak maxima vary from −81 to −83 ppm, but in a nonsystematic way, this small chemical shift range being within the 1 ppm experimental uncertainty. This is an insignificant change for peaks so broad. The widths at half-height of the ^{29}Si peaks do, however, decrease systematically from about 17 ppm for Di$_{100}$ to about 11 ppm for Cats$_{100}$ (Fig. 2). The spectra contain about 1 ppm line-broadening due to data processing (exponential multiplication), but this has been subtracted to give the FWHH.

We show in Figure 3 the 11.7-T ^{27}Al MASS NMR spectra of the H-Cats crystals and the Al-containing glasses and summarize the chemical shift results in Table 1. In all cases there is a centerband resonance between 55 and 65 ppm, indicative of tetrahedrally coordinated Al (Müller, 1981a, 1981b). In addition, there are spinning sidebands that are spaced at the spinning frequency, but no observable resonance in the 0 ppm range, which would indicate octahedrally coordinated Al. The ^{27}Al chemical shift increases systematically from 56 ppm for Di$_{90}$Cats$_{10}$ to about 64 ppm for the most Cats-rich compositions. There is no systematic variation in the ^{27}Al peak breadths. The ^{27}Al resonance for H-Cats crystals (at 60.5 ppm) is about 3 ppm more shielded than that for Cats glass. The

peak breadth for these crystals is about the same as for the glasses, again indicating a disordered structure.

The decreased shielding at Al in the glasses with increasing tetrahedral Al content is the same as the variation observed for zeolites by Fyfe et al. (1982) and for clay minerals by Kinsey et al. (1985).

ALUMINUM QUANTITATION

One of the potential difficulties with the analysis of pulse-Fourier-transform NMR spectra of quadrupolar nuclides of solid samples is the possibility of the loss of some or all of the signal due to "dead-time" of the NMR receiver, and to the problem of the extent of the excitation of the quadrupolar-broadened NMR spectrum. These phenomena are not a problem with $I = \frac{1}{2}$ nuclides, such as ^{29}Si, because they do not suffer from quadrupolar broadening.

For the samples examined here the possibility exists that some of the Al atoms could be in very distorted sites and their signal lost or ineffectively excited. In particular, some of the Al could be in octahedral sites, pentahedral sites (as in andalusite), or in highly irregular sites. We show here that this is not the case, that within experimental uncertainty we see all the Al signal, and, thus, that essentially all the Al in these samples must be in sites that have NMR chemical shifts in the range characteristic of tetrahedrally coordinated Al. Some of these sites are probably quite distorted.

The method we use to determine the amount of signal actually detected depends on the results of a recent theoretical analysis of the expected signal intensities for quadrupole nuclides under different excitation conditions (Fenzke et al., 1984), and the fact that the free induction decay under static (nonspinning) conditions for these samples appears to be described by a simple exponential.
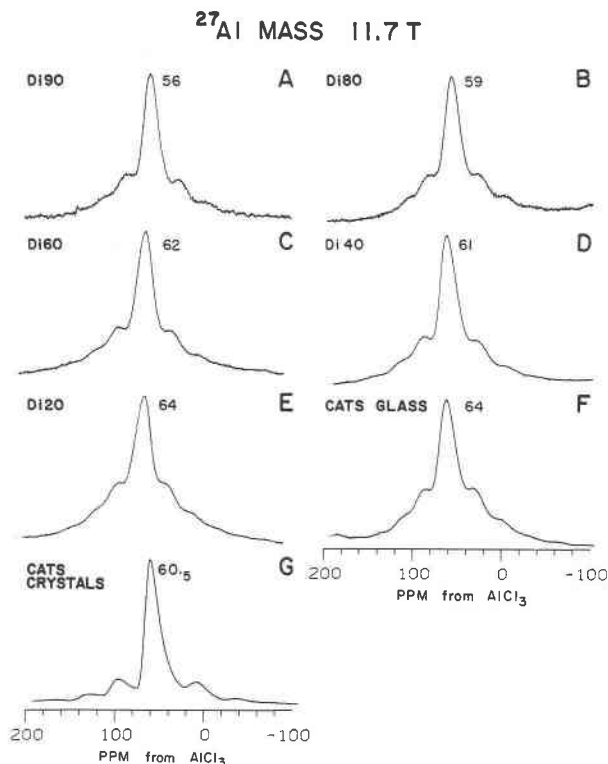
Fig. 3. ^{27}Al MASS NMR spectra along the join CaMgSi$_2$O$_6$-CaAl$_2$SiO$_6$ (Di-Cats) obtained at 11.7 T. Compositions are in mole percent Di.

Fig. 4. Both channels of the on-resonance 11.7-T free-induction decay (FID) spectrum for Di$_{40}$-Cats$_{60}$ glass. Note the exponential decay and initial pulse breakthrough period during which data are lost.

The analysis of Fenzke et al. (1984) indicates that for ^{27}Al, if only the central ($\frac{1}{2}$, $-\frac{1}{2}$) transition is excited (the usual case for all but the most symmetrical sites in solids), the signal intensity detected does not depend on the quadrupole coupling constant if the pulse width (duration of the exciting pulse) is less than or equal to $\frac{1}{6}$ of that needed to flip the spin system of ^{27}Al in solution by 90°. In solution, all five transitions are fully excited. Under these conditions, the signal detected for a solid sample should be 0.236 that of the signal from the same number of atoms in a solution that is given a 90° pulse. Thus, by comparing the signal per unit mass of Al in a solid sample at $\frac{1}{6}$ the solution 90° pulse to 0.236 times the signal per unit mass of Al in a 1 M AlCl$_3$ solution given a 90° pulse, it is possible to determine the fraction of the expected signal actually seen.

We do the quantitation experiments at 11.7 T under static conditions with a small diameter coil ($\sim$5 mm I.D.) to give a short ($\sim$6 μs) solution 90° pulse. The sample is held in a silica glass tube that fits tightly into the coil. The solid pulse length is always $\frac{1}{6}$ the solution 90° pulse length ($\sim$1 μs). The internal phasing of the spectrometer is adjusted so that as much signal as possible is in one of the two channels. In many cases, essentially all of the signal can be phased into one channel, although in others, some remains in the second. The spectra are collected exactly on resonance to avoid beat patterns. Spectra with two or
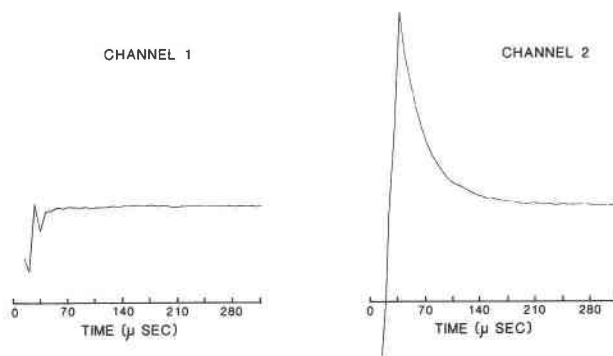
more peaks could be quantitated using more laborious peak integration and simulation methods.

Figure 4 is a typical free induction decay (FID) for our Di-Cats glass samples. Except for the initial chaotic, pulse-breakthrough period, the decay is nearly a simple exponential, as expected for Lorentzian-shaped peaks. The initial pulse-breakthrough period is due to some of the exciting r.f. pulse-ringdown leaking into the receiver after data acquisition begins. We reduce the pulse-breakthrough period by placing a 0.1-MΩ resistor in parallel with the coil.

It is this initial pulse-breakthrough period that has previously caused problems with determining the amount of signal detected, because the true signal emitted by the sample during that period is lost. Thus, the first accurate data point in the FID (at 42 μs in our data) is of much lower intensity than the point at zero time (t). The data for the sample and the standard must, however, be compared at $t = 0$, because the signal for the AlCl$_3$ solution standard decays orders of magnitude more slowly than that for a solid glass. Thus, at $t = 42$ μs the signal intensity for the standard is essentially the same as at $t = 0$ s, whereas that for the glass is less than half its $t = 0$ value.

A $t = 0$ FID intensity for a solid sample can be obtained by extrapolation to $t = 0$, if there are no broad components that have completely decayed away before the first good data point. In this case the extrapolated intensity should equal the short-pulse-width value predicted by Fenzke et al. (1984) to within experimental error, and signal from all the Al is detected and is present in the Fourier-transformed spectrum. If the extrapolated intensity is significantly less than the predicted intensity, signal from some atoms is totally lost during the pulse-breakthrough period or is not fully excited, and is not contained in the Fourier-transformed spectrum. If the extrapolated intensity is greater than the predicted intensity, some or all of the sites have such small quadrupole coupling constants that there is some signal from the satellite transitions in the spectrum. This does not seem to be the case for these glasses.
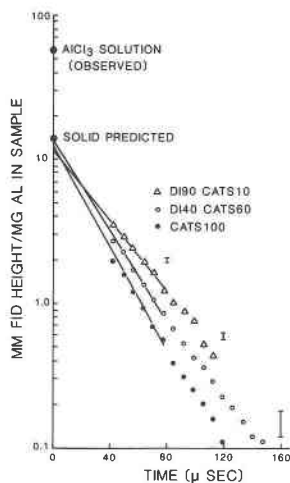
Fig. 5. Log-linear plot of normalized FID intensity versus time for Di-Cats glasses, showing AlCl$_3$ solution intensity at $t = 0$ and extrapolations to $t = 0$ for the glass data. For those glass samples for which not all the signal could be phased into one spectrometer channel, $I_{Tot} = (I_{Ch,1}^2 + I_{Ch,2}^2)^{1/2}$.

Figure 5 is a plot of time vs. log of normalized FID intensity for several of the Di-Cats glasses we have examined. Also shown are the normalized $t = 0$ intensity for the AlCl$_3$ solution standard and the normalized $t = 0$ intensity for the solids predicted by the Fenzke et al. calculations. Because the error in measurement of the low-intensity points is large, the first five or six data points were fit with a log-linear relationship and extrapolated to $t = 0$. Because of the factor-of-about-three extrapolation, we estimate the precision and accuracy of this extrapolation to be about 10–15%. The fraction of the ^{27}Al signal detected for these samples ranges from about 0.85 to 0.99, with a mean of about 0.92 (Table 2). We have found extrapolated $t = 0$ intensities as great as 1.08 the predicted value for glasses in other systems, and we take extrapolated $t = 0$ intensities within about 10% of the expected value to indicate that all the ^{27}Al signal is detected. Thus, within the precision of the method, we interpret these data for the Di-Cats glasses to indicate that we are seeing all, or nearly all, the ^{27}Al signal for these samples, although values less than about 0.9 for some samples may indicate that signal for a low-concentration broad component is lost. In corroboration of these results, we note that signal for both tetrahedrally and octahedrally coordinated Al is readily detected in ^{27}Al NMR spectra of Al$_2$O$_3$-SiO$_2$ glasses and dehydrated peraluminous gels (Weiss et al., 1985; our unpub. data).

DISCUSSION

The primary objective of this work is to use MASS NMR to examine the structure of the glasses. The major questions that can be addressed are the coordination of the Al and the effect of Al on the polymerization state of the glass.

The Al in these glasses appears to all be in tetrahedral coordination. No signal from octahedrally or pentahedrally coordinated is detected, and within experimental error, all the ^{27}Al signal is detected. The presence of only Al(4) is in agreement with the MASS NMR results of de Jong et al. (1983). Some of the Al sites are likely to be quite irregular, but all the nuclei still resonate in the range for tetrahedrally coordinated Al. Unfortunately, because there is a range of sites in the glass, the quadrupole coupling constants cannot readily be determined.

The presence of only tetrahedrally coordinated Al is fully consistent with previous X-ray radial distribution and calorimetric data for these samples or samples of similar composition (Taylor and Brown, 1979a, 1979b; Taylor et al., 1980; Navrotsky et al., 1983). It is also consistent with our ready observation of ^{27}Al spectra for crystalline materials with large (6–9 MHz) quadrupole coupling constants (kyanite, andalusite, and sillimanite, Ghose and Tsang, 1983, and our unpub. results). The latter results, together with elementary calculations (Meadows et al., 1982), suggest that if octahedrally co-ordinated Al were present and not detected in our spectra, *all* the octahedral site would have to be characterized by quadrupole coupling constants at least this large. Because we expect glasses to contain a broad distribution of quadrupole-coupling constants, some of the less distorted octahedral sites should be detectable. Indeed, octahedral Al can be readily detected in peraluminous glasses and gels (Thomas et al., 1983; Weiss et al., 1985). We interpret out results, then, as indicating that essentially all the Al is in tetrahedral coordination.

Because all the Al appears to be in tetrahedral coordination, Cats$_{100}$ glass must be fully polymerized (i.e., contains only Q^4 tetrahedral sites) and must contain only a defect level on nonbridging oxygens. This is because the tetrahedral cation to oxygen ratio is 1:2, as it is for all compositions on the join SiO$_2$-CaAl$_2$O$_4$ if the Al is in tetrahedral coordination.

Di glass, on the other hand, has an average of two nonbridging oxygens per tetrahedral cation. The 17 ppm half-height line width of the ^{29}Si resonance of diopside glass (at 8.45 T) centered at -81 ppm is consistent with the idea that Di glass contains Q^0, Q^1, Q^2, Q^3, and Q^4 Si sites (Murdoch et al., 1985). This idea is based primarily on Raman spectra (Mysen et al., 1982; McMillan and Piriou, 1983), and ^{29}Si MASS NMR cannot resolve separate peaks for the different types of sites. If Cats glass is fully polymerized, the glasses along the Di-Cats join must become progressively more polymerized with increasing Cats content.

This change in average polymerization state is reflected in the breadths of the ^{29}Si peaks (Fig. 2). Because ^{29}Si does not suffer from the quadrupolar line-broadening effects observed for Al, increased line widths in the glass relative to crystals are almost certainly caused by structural disorder. This disorder could be caused by a range of cation-oxygen bond distances and angles, the presence of a number of different kinds of Si sites in the glass, and Al-Si disorder in the tetrahedral sites. For Di glass, the ^{29}Si peak

Table 2. Fraction of ^{27}Al NMR signal detected for Di-Cats glasses at 11.7 T

Composition (mole % of end members)	Fraction of ^{27}Al Signal Detected
Di$_{90}$Cats$_{10}$	0.85
Di$_{60}$Cats$_{40}$	0.99
Di$_{40}$Cats$_{60}$	0.99
Di$_{20}$Cats$_{80}$	0.89
Cats$_{100}$	0.92

breadth at half-height is 17 ppm, compared to about 1 ppm or less for crystalline diopside. This increase in line width in the glass can only be due to a range of bond distances and angles and the presence of a number of different polymerization states. For Cats glass the half-height peak breadth is only 11 ppm. For this composition, only Al-Si disorder and a range of bond distances and angles can cause peak broadening. Within the precision of the measurement, the peak breadth for Cats glass is the same as for SiO$_2$ glass (Kirkpatrick et al., 1986), which also has a fully polymerized framework structure. This seems to imply that, at least for this composition, Al-Si disorder has a relatively minor effect on peak broadening. The progressive decrease in the ^{29}Si peak breadth with increasing Cats content thus appears to be due primarily to the progressive reduction in the number of different types of Si sites present.

The observation of only tetrahedral Al is also consistent with the essentially constant ^{29}Si chemical shift for the glasses. Lippmaa et al. (1981) have shown that for silicate crystals of a given polymer type, such as frameworks, increasing tetrahedral Al content (i.e., increasing number of next-nearest-neighbor aluminums) causes progressive deshielding at the Si nucleus. Lippmaa et al. (1980), however, have shown that, for crystals, progressively more polymerized structures generally have *increased* shielding at the Si nucleus (i.e., more negative chemical shifts). Smith et al. (1983) have related both these variations to changes in the total cation-oxygen bond strength sums. In the glasses examined in this work, these two effects appear to be counteracting each other. With increasing Cats content the average Si atom is in a more polymerized site but has more Al next-nearest neighbors, so there is no net chemical shift change with change in composition.

The systematic deshielding at Al with increasing Cats content is also consistent with this model of the structural variations in the glasses. Müller et al. (1981b) have shown that for aluminosilicate ions in solution, the shielding of tetrahedrally coordinated Al varies in the same way as that of Si, with increasing polymerization increasing the shielding. For framework and sheet silicates, Fyfe et al.

(1982) and Kinsey et al. (1985) have shown that shielding at tetrahedral Al decreases with increasing Al content. The progressive deshielding at Al, from 56.5 ppm for Di$_{90}$Cats$_{10}$ to 64.0 ppm for the most Cats-rich compositions, indicates that the deshielding effect of increasing Al is more important. In fact, this trend continues all the way to crystalline CaAl$_2$O$_4$, which has only tetrahedral Al, and ^{27}Al chemical shift of 78.8 ppm at 11.7 T (Table 2).

The ^{27}Al NMR results for the glasses also support the idea of Mysen et al. (1981, 1982) that Al is concentrated in the most polymerized tetrahedral sites. Fyfe et al. (1982), Kinsey et al. (1985), and Kirkpatrick (1985b) have shown that ^{27}Al chemical shifts for framework silicates (with Q^4 sites) are in the range of 52 to 64 ppm, whereas sheet silicates (with Q^3 sites) have chemical shifts in the range of 65 to 74 ppm. For Cats glass to be fully polymerized, it can have only Q^4 sites. The more diopside-rich compositions have some less polymerized sites, but the decrease in the peak maximum with increasing Di content strongly suggests that most of the Al is in Q^4 sites. The ^{27}Al peak position for Cats crystals and glasses is at the more deshielded (more positive) end of the chemical shift range for framework silicates because the Al/Si ratio is greater than one.

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