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LETTER

Five- and six-coordinated Si in $K_2Si_4O_9$ glass quenched from 1.9 GPa and 1200 °C

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ABSTRACT

It has often been suggested that at high pressure, Si in silicate melts should change from four to higher coordination. Transition states involving five-coordinated Si have often been observed in molecular dynamics simulations even at low pressure and have been given a key role in configurational change and viscous flow. Using ^{29}Si MAS NMR, we have definitively observed small amounts of both five- and six-coordinated Si in a $K_2Si_4O_9$ glass quenched from a liquid at 1200 °C and 1.9 GPa. Such results provide new constraints for models of density, viscosity, and thermodynamics of silicate melts.

INTRODUCTION

Si is the archetypical tetrahedral, network-forming cation in silicate liquids at low pressure. With the one exception of alkali silicate glasses containing more than 30% P_2O_5 (Dupree et al., 1987), only four-coordinated Si ($^{[4]}$Si) has been spectroscopically observed in glasses quenched from equilibrium liquids. However, several types of evidence have suggested that higher coordination states of Si may be very important in melts and magmas. The first of these consists of the results of ion-dynamics simulations (Woodcock et al., 1976; Soules, 1979; Brawer, 1985; Angell et al., 1983, 1988). In work on the network liquids SiO_2 and its analogue BeF_2, as well as on systems containing network-modifying cations, five-coordinated Si ($^{[5]}$Si) has commonly been observed as a short-lived intermediate state during the exchange of oxygen from one tetrahedron to another. The role of such higher coordinations has been stressed in the mechanism for viscous flow (Brawer, 1985; Hochella and Brown, 1984), although the total number of such sites at any given instant is probably very small. Computer simulations have also suggested that populations of $^{[5]}$Si and $^{[6]}$Si should increase with pressure and eventually dominate over $^{[4]}$Si (Angell et al., 1983, 1988), as expected by analogy with crystalline silicates.

The second line of evidence for Si with a coordination number higher than four is thermodynamic. Studies of densities of silicate melts at high pressure have shown that most Si could be six-coordinated at 25 GPa (Rigden et al., 1988). Crystalline silicates are dominated by $^{[6]}$Si at pressures above 8 to 24 GPa (e.g., Knittle and Jeanloz, 1987; Hazen, 1985), and the reduction in volume accompanying this change should prevail at some pressure in liquids as well. According to ab initio molecular orbital calculations, $^{[6]}$Si is not inherently unstable at low pressure (Gibbs, 1982). Solution calorimetry has shown that the $K_2{}^{[6]}Si^{[4]}Si_3O_9$ (wadeite-type) structure is, in terms of enthalpy, more stable than the phase containing only $^{[4]}$Si (Geisinger et al., 1987), although the latter does have an unusual and perhaps highly strained structure. A similar situation prevails for the four- and six-coordinated polymorphs of GeO_2 (Navrotsky, 1971).

Direct evidence for coordination increases of Si or its analogue Al in silicate liquids is, however, very limited. In glasses on the Al_2O_3-SiO_2 binary, both Raman spectra (McMillan and Piriou, 1982) and ^{27}Al MAS NMR results (Risbud et al., 1987) have suggested the presence of Al in high coordination. Pressure-induced coordination changes for both Al and Si have been sought in samples quenched from pressure to about 3 GPa, but with negative results (Sharma et al., 1979; McMillan and Graham, 1981; Mysen et al., 1983; Fleet et al., 1984; Hochella and Brown, 1985). In samples of $NaAlSi_3O_8$ glass quenched from above 6 GPa, however, Ohtani et al. (1985) reported $^{[6]}$Al observed by ^{27}Al MAS NMR. Pressure-induced changes in Raman spectra of $K_2Si_4O_9$ glasses quenched from liquids up to 2.4 GPa have been suggested to be consistent with the presence of $^{[6]}$Si (Dickinson et al., 1989).

Infrared and Raman spectra collected at high pressure but room temperature in diamond-anvil pressure cells have shown that severe distortions in glass structure are caused by pressures from about 10 to 40 GPa (Hemley et al., 1986; Williams and Jeanloz, 1988). The IR data have been interpreted as indicating the destruction of regular SiO_4 tetrahedra and the formation of higher coordinations (Williams and Jeanloz, 1988). Both types of studies showed that most or all of the pressure-induced changes

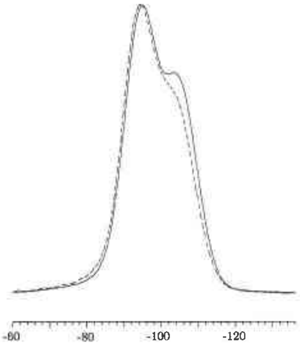

Fig. 1. ^{29}Si MAS NMR spectra for $K_2Si_4O_9$ glass quenched from 1 bar and 1200 °C, and 1.9 GPa and 1200 °C. Only the $^{[4]}$Si peak regions are shown. For the 1-bar sample, about 90 mg of sample and 8000 signal averages were used, with a 10-s delay between pulses. For the high-pressure sample (dashed curve), about 35 mg of sample and 10000 signal averages were run, with the same delay time. 20-Hz (0.13 ppm) exponential line broadening was applied to both spectra. Scale here and in Fig. 2 in ppm relative to TMS.

relaxed immediately on decompression, and models have been proposed to account for this rapid reversibility (Stolper and Ahrens, 1987). It is likely, however, that liquids respond in more ways to pressure than do glassy solids: diffusive motion should allow a much greater range of configurations to be explored.

Recently, the first definitive observation of $^{[6]}$Si in a silicate glass quenched from a liquid at high temperature and pressure, has been reported (Xue et al., 1989). In that study, approximately 1% of the Si sites in an $Na_2Si_2O_5$ glass quenched from 1500 °C and 8 GPa were shown by ^{29}Si MAS NMR to be $^{[6]}$Si. No such species were observed in a 5-GPa sample. In this report, we extend these findings and document the presence of both $^{[6]}$Si and $^{[5]}$Si in $K_2Si_4O_9$ glass quenched from a liquid at a much lower pressure of 1.9 GPa. To our knowledge, this is the first observation of $^{[5]}$Si in any silicate.

EXPERIMENTAL DETAILS

$K_2Si_4O_9$ glass was synthesized from K_2CO_3 and 95% ^{29}Si SiO_2 (Oak Ridge National Laboratory) by repeated fusion at 1200 °C and grinding. Gd_2O_3 was added (0.2 wt%) to decrease the spin-lattice relaxation time. The glass was welded into a Pt tube and heated for ½ h at 1.9 GPa and 1200 °C in a non–end-loaded piston-cylinder apparatus (Patera and Holloway, 1978), using an NaCl pressure medium and graphite heater. This temperature is well above the liquidus of the wadeite polymorph (Kinomura et al., 1974). The sample was quenched isobarically at about 500 °C/s, producing a homogeneous mass of glass with only a few fractures. This was crushed lightly to fine sand size in a BN mortar, and the MAS NMR spectrum was collected. Optical examination showed a homogeneous, single-phase glass with minor strain birefringence along some fragment edges. The Raman spectrum of the 1.9-GPa glass is identical to that obtained previously on similar samples (Dickinson, McMillan, and Scarfe, in preparation), except for small (5–10 cm^{-1}) isotopic frequency shifts, confirming the composition. No evidence for crystals was seen in the Raman spectra.

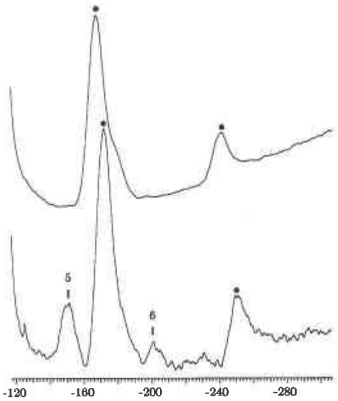

Fig. 2. Same spectra as in Fig. 1, with vertical scales enlarged about 15 times. Upper spectrum is 1-bar glass; lower spectrum is 1.9-GPa glass. Spinning sidebands for the main, $^{[4]}$Si peak are marked by dots. The small feature at −125 ppm is an instrumental artifact, as are the baseline slopes. 100-Hz line broadening (1.3 ppm) was applied to both spectra to enhance signal-to-noise ratio. Numerals show peaks for $^{[5]}$Si and $^{[6]}$Si, whose areas are about 0.4% and 0.2% of the total, respectively.

NMR measurements were made at a ^{29}Si Larmor frequency of 79.5 MHz with a Varian VXR-400 spectrometer and MAS probe, and frequencies were calibrated to ±0.2 ppm against an external standard of tetramethyl silane (TMS). Sample spinning speeds of about 6 kHz were used, with a 1-μs (about 15°) rf pulse. Spinning speed was varied to distinguish small peaks from spinning sidebands. Delay times between pulses were long enough so that relative intensities would be quantitative. The coarse grain size of the MAS sample, together with a sealed rotor, ensured that hydration during the long NMR runs was insignificant (no detectable weight changes). The relatively low surface area of the glass also indicates that surface sites made no negligible contribution to the spectra.

RESULTS

As shown in Figure 1, the major feature of the NMR spectra for the 1-bar glass is a broad double peak with maxima at −95.2 and −103.8 ppm, similar to previously published results on unenriched samples (Dupree et al., 1986; Grimmer and Müller, 1986; Schneider et al., 1987). These can be attributed with near certainty to the tetrahedral Q^3 and Q^4 species that make up most of the sample. The 1.9-GPa glass spectrum is similar, but the Q^4 peak is reduced slightly in height, and the Q^3 peak is shifted slightly to −94.4 ppm. The extremely high signal-to-noise ratio made possible by the isotopically enriched material (about 800:1 for the main peak) allows several very small additional features to be seen between the spinning side bands. An obvious peak at −150 ppm (S/N = 11), and a smaller feature at −200 ppm (S/N = 4), have areas that are about 0.4% and 0.2% of the total, respectively. The very small additional feature at about −230 ppm is probably also a real peak, but is just above noise level. It may be a spinning sideband related to the −150 ppm peak or an independent feature.

The relatively large widths of the −150 and −200 ppm peaks (6 and 8 ppm) strongly indicate that they are not due to crystalline phases, which, in Al-free silicates, are generally less than 1 ppm (Smith and Blackwell, 1983; Kirkpatrick, 1988). A chemical shift of −200 ppm is almost certainly due to $^{[6]}$Si, by analogy with crystalline phases and recent results on a $Na_2Si_2O_5$ glass quenched from 8 GPa (Xue et al., 1989). Chemical shifts near −150 ppm for Si are previously unobserved for a silicate. However, in ^{27}Al MAS NMR spectra of minerals, the progression from four to five to six coordination produces a systematic increase in chemical shielding (to more negative chemical shifts). Recent work has shown that the relationship of chemical shift to structure is very similar for ^{27}Al and ^{29}Si (Phillips et al., 1989). It is therefore most likely that a ^{29}Si MAS NMR peak midway between the ranges known in silicates for $^{[4]}$Si and $^{[6]}$Si is due to $^{[5]}$Si. The lack of any known crystalline phases containing $^{[5]}$Si supports our conclusion that we have observed high coordination states of Si that are part of a homogeneous glass structure.

DISCUSSION

It is now clear that some aspects of the high-pressure structure of silicate liquids can indeed be quenched into a glass. Our samples presumably record the structure of the liquid at its glass transition temperature, T_g. It is possible that the structure, including populations of $^{[5]}$Si and $^{[6]}$Si, changes with increasing T above T_g (Brandriss and Stebbins, 1988). Furthermore, because in situ studies at room temperature indicate that significant local relaxation can take place on decompression (Hemley et al., 1986; Williams and Jeanloz, 1988), we cannot be certain that our quenched samples record all aspects of the liquid structure at T_g and 1.9 GPa. Studies at both high T and P will be needed to further resolve this issue.

Although five-coordinated Si has been previously unknown in silicates, a wide variety of organic molecules have been prepared with this local structure (Marsmann, 1981; Coleman, 1983; Tandura et al., 1986), and the SiF_5^- complex has been stabilized and studied by matrix-isolation techniques (Ault, 1979). In general, most of these structures seem to have a trigonal-bipyramidal geometry. The only close analogue in an oxide is the $^{[5]}$Al site in andalusite, which also has a distorted trigonal-bipyramidal structure (Burnham and Buerger, 1961). Organic molecules containing $^{[5]}$Si are of particular interest as reactive intermediates during configurational change (Corriu et al., 1984), just as SiO_5 groups are of particular interest in postulated flow mechanisms in silicates.

The existence of well-defined $^{[5]}$Si and $^{[6]}$Si peaks in the 1.9-GPa glass sample indicates that at least some of the Si in high coordination is in geometrically well-defined sites, presumably because of minima in the surface of free energy vs. configuration. This is distinctly different from the situation that might arise if intertetrahedral rotation during compression coincidentally moved extra oxygens near to existing tetrahedra (Stolper and Ahrens, 1987). Si sites with a wide distribution of local geometries, bond distances, and bond angles, resulting in NMR peaks too broad to distinguish, could constitute up to about 5% of the total, however.

Our NMR data contain some hint of the mechanism by which sites with Si in high coordination may form on compression. There is a slight reduction in intensity of the Q^4 peak, suggesting that these sites may be the first to be destabilized with respect to $^{[5]}$Si. The pressure-induced disproportionation reaction among Q species, $2Q^3 = Q^2 + Q^4$, which has been documented for $Na_2Si_2O_5$ (Xue et al., 1989) and suggested previously for $K_2Si_4O_9$ (Dickinson and Scarfe, 1985), may be in part masked by this effect in more silica-rich compositions.

Perhaps the most important finding here is, however, simply that $^{[5]}$Si and $^{[6]}$Si can, in fact, be directly observed in glasses. The postulated role of $^{[5]}$Si as a transition state in viscous flow may thus be one viable mechanism for the observed decreases in viscosity with pressure in silica-rich liquids (Scarfe et al., 1987). Unfortunately, one consequence of this change could be the observed decrease in glass-forming ability, which may make glasses with large amounts of $^{[5]}$Si and $^{[6]}$Si difficult to produce. $^{[5]}$Si could also have an important role in the configuration energetics of liquids (Brandriss and Stebbins, 1988). The increases in oxygen packing that are presumed to be a major part of liquid density increases may also become quantifiable. A variety of studies over wider ranges of pressure and composition is in progress to define the role of Si in high coordination in the properties of silicate melts.

Note added in proof: J. A. Tossell (personal communication) has recently completed Hartree-Fock molecular orbital calculations of the ^{29}Si chemical shift of $^{[5]}$Si and $^{[6]}$Si that are consistent with the observations reported here.

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