hydraulic sorting of the spherules during fall.

O'Keefe and Ahrens (*20*) have argued that the radius of droplets condensing from impact-produced rock vapor clouds is a function of projectile diameter and, to a lesser extent, velocity. Spherules from the K-T boundary are invariably less than 1 mm in diameter. Based on their results [figure 22 in (*18*)], our largest spherules, about 3 mm in diameter, would correspond to projectiles between about 20 and 50 km in diameter.

Over virtually the entire Barberton belt, S2 lies within 1 m stratigraphically of the transition from volcanic to sedimentary stages of greenstone belt evolution. This lithologic break marks a profound tectonic, sedimentological, and petrologic change in the history of the Barberton belt. Its coincidence with S2 may be just that, a fortuitous coincidence of unrelated events, or it may indicate that major tectonic and crust-forming events on the early earth were controlled or strongly influenced by meteorite impacts.

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Silicon Coordination and Speciation Changes in a Silicate Liquid at High Pressures

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Coordination and local geometry around Si cations in silicate liquids are of primary importance in controlling the chemical and physical properties of magmas. Pressure-induced changes from fourfold to sixfold coordination of Si in silicate glass samples quenched from liquids has been detected with ^{29}Si magic-angle spinning nuclear magnetic resonance spectrometry. Samples of $Na_2Si_2O_5$ glass quenched from 8 gigapascals and 1500°C contained about 1.5 percent octahedral Si, which was demonstrably part of a homogeneous, amorphous phase. The dominant tetrahedral Si speciation in these glasses became disproportionated to a more random distribution of bridging and nonbridging oxygens with increasing pressure.

INFORMATION ABOUT THE STRUCTURE of liquid silicates is necessary for understanding the bulk chemical and physical properties of magmas. The best known and most fundamental aspect of this structure is the regular coordination of Si by four O atoms (Si^{IV}). All evidence indicates that at ambient pressure for geologically important compositions, Si^{IV} predominates in silicate melts and glasses, as it does in crystalline minerals (*1*).

At the pressures that are present throughout most of the earth's interior, on the other hand, Si in crystalline silicates is evidently six-coordinated (Si^{VI}), and the transition to the higher coordination occurs between 8 and 25 GPa (about 240- to 750-km depth) (*2*). Analogous transitions from Si^{IV} to Si^{VI} in silicate liquids have been postulated to account for high-pressure phase equilibria and liquid densities and viscosities (*3*) and were predicted from molecular dynamic simulations (*4*). However, direct spectroscopic evidence for Si^{IV} in high-pressure liquid silicates is limited. Both Raman and infrared absorption spectroscopy on silicate glasses at room temperature and pressures to nearly 40 GPa have demonstrated that significant structural changes do occur (*5*). The infrared data have been interpreted as indicating the disappearance of well-ordered SiO_4 tetrahedra and the formation of species with higher coordinations, but the Raman data showed no clear evidence for Si^{IV}. However, these results may not be directly applicable to equilibrium liquids because such liquids have much higher thermal energies than glasses at room temperature, possibly allowing additional mechanisms of structural response to pressure.

The development of large volume high-pressure apparatus has allowed samples of up to 10 mg to be synthesized at pressures to 25 GPa and temperatures above 2000°C (*6*) then rapidly quenched for spectroscopic work at ambient conditions. The structure of a quenched glass is generally assumed to record that of the equilibrium liquid at its glass transition temperature (T_g), although some local displacive change may take place during decompression (*5*). A coordination increase for Al^{3+} (structurally analogous to Si^{4+}) has been reported in a ^{27}Al NMR (nuclear magnetic resonance) study of such samples (*7*). Recent solid-state ^{29}Si NMR work has demonstrated that the technique is useful in detecting and characterizing both Si^{IV} and Si^{VI} (*8*), as well as for distinguishing amorphous from crystalline materials. We have applied this technique to find

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evidence for increased coordination of Si in glasses quenched from liquids equilibrated at high pressures and to investigate the effects of pressure on the structure of the tetrahedral network.

We chose the composition $Na_2Si_2O_5$ for study because of its chemical simplicity, low melting point, and good glass-forming ability. This material has an average number of nonbridging oxygens per tetrahedron of 1, similar to that of basaltic magmas; therefore, it is at least a crude analog of geologically interesting materials. We obtained completely crystal-free glass samples quenched from 1500°C at 5 and 8 GPa, and for comparison a crystalline sample quenched from about 1150°C at 8 GPa (*9*). Samples of 5 to 7 mg were studied by ^{29}Si magic angle spinning (MAS) NMR (*10*).

The ^{29}Si MAS NMR spectrum (Figs. 1 and 2) for the crystalline sample quenched from 8 GPa showed four distinct peaks at -94.4, -97.9, -199.8, and -200.4 ppm. The first two signals are from Si in sites with four oxygen neighbors, the latter two from Si in sites with six oxygen neighbors (*11, 12*). These Si^{VI} NMR peaks do not match those of any known crystalline phases. Powder x-ray diffraction confirmed that this is a previously unknown high-pressure polymorph of $Na_2Si_2O_5$. The observed Si^{VI} doublet has a full width at half height of about 1 ppm, which is typical of an aluminum-free silicate crystal.

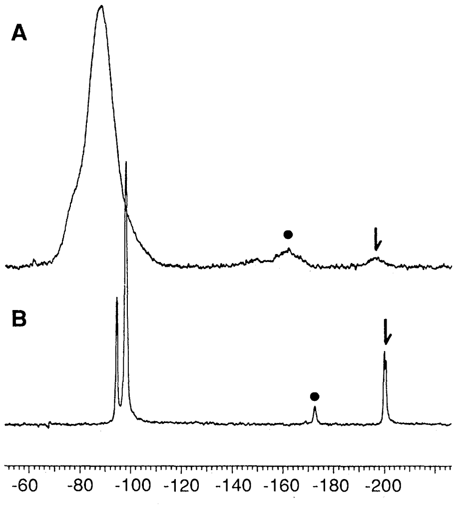

Fig. 1. ^{29}Si MAS NMR spectra of $Na_2Si_2O_5$ samples quenched from 8 GPa; (**A**) 1500°C, glassy; (**B**) 1150°C, crystalline. Peaks marked with dots are spinning side-bands; peaks marked with arrows are attributed to Si^{VI}. Sample spinning rates were about 6 kHz; 25,000 signal averages with a delay of 10 s between pulses were used for the upper spectrum; 2,000 signal averages with the same delay were used for the lower spectrum. Exponential line broadenings of about 20% of the peak widths (20 and 100 Hz) were applied to enhance signal to noise ratios. Scales for all ^{29}Si spectra are in parts per million relative to tetramethyl silane (TMS).

The spectrum of the starting glass sample (1 bar) (Fig. 3) had a single peak about 13 ppm wide, centered at -88.5 ± 0.2 ppm; this peak is essentially identical to those reported on large samples, both with and without paramagnetics added to speed spin-lattice relaxation (*13–15*). The bulk of this peak is attributed to Si in Q^3 sites (*16*). Small shoulders on both sides of the main peak may be attributed to small amounts of both Q^4 and Q^2 species (*13, 14*). Even with a signal to noise ratio of 800 to 1, no other features were detected.

The spectra of the glasses quenched from 1500°C at 5 and 8 GPa were also dominated by a single broad peak, centered at -87.5 ± 0.5 ppm (Figs. 1, 2, and 3). Two distinct features were, however, noted in these spectra. Most significantly, an obvious Si^{VI} peak at -197 ppm with a relative area of about 1.5% appeared in the spectra of the 8-GPa glasses. Its width of about 8 ppm is indicative of substantial local disorder in bond distances and angles, much greater than has been observed in aluminum-free silicate crystals (*17*). This obvious disorder, as well as the peak position and lineshape, were also quite different from those of the crystalline $Na_2Si_2O_5$ phase stabilized at this pressure (Fig. 1). These glass samples thus lacked detectable crystals, consistent with optical and transmission electron microscopic observations (*18*). The Si^{VI} sites are clearly part of the glass structure, and therefore were probably present in the liquid at its glass transition temperature T_g. The lack of a Si^{VI} peak in the glasses quenched at 1 bar and 5 GPa indicates that the formation of Si^{VI} at 8 GPa was pressure-induced. These interpretations have since been confirmed by similar NMR studies of $K_2Si_4O_9$ and $Na_2Si_4O_9$ glasses (*19*). Si^V has also been detected in these tetrasilicate samples.

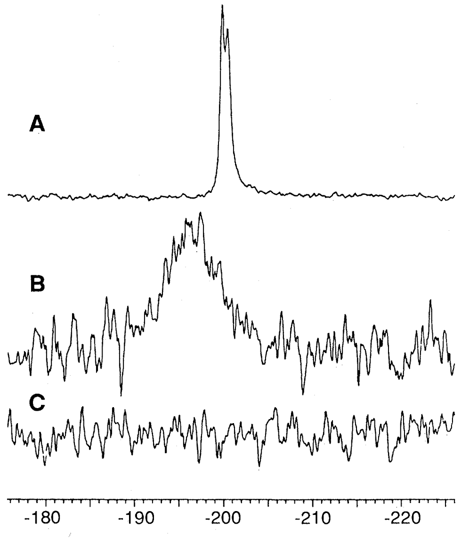

Fig. 2. Enlarged sections of spectra from Fig. 1 showing the region where six-coordinated Si peaks are known to occur. (**A**) Eight gigapascals, crystalline; (**B**) 8 GPa, glassy; (**C**) 5 GPa, 1500°C, glassy.

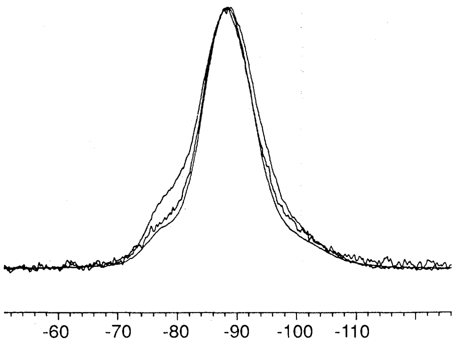

Fig. 3. ^{29}Si MAS NMR spectra of $Na_2Si_2O_5$ glasses quenched from 8 GPa and 1500°C (broadest peak), 5 GPa and 1500°C (middle), and 0.1 MPa (1 bar) and 1200°C (narrowest). Spectrometer conditions as in Fig. 1 except that a 20-Hz line broadening was applied to all spectra. The region of the spectra corresponding to four-coordinated Si is shown. Spectra for the 5- and 8-GPa glasses have been shifted to the right by 1 ppm for clarity.

Pronounced changes with pressure also occurred in the dominant Si^{IV} NMR peak of the quenched glasses (Fig. 3). From 1 bar to 5 GPa to 8 GPa, the peak became substantially wider and developed more pronounced high- and low-field shoulders. These changes probably indicate that as pressure increases, positional disorder around the Si sites increases, and the number of Q^3 sites decreases because of disproportionation to a mixture of Q^2 and Q^4 species (*20*):

$$2Q^3 = Q^2 + Q^4 \qquad (1)$$

However, application of these data to understanding the effect of pressure on speciation in the liquid is complicated by possible variations of T_g with quench rate and pressure, accompanied by known variations of liquid structure with temperature (*21*). An increase in T_g could result in a similar disproportionation (*21*). However, the estimated size of the difference in the quench rates between our high-pressure glasses and 1-bar glass (*22*) indicates that this effect is probably not significant in the MAS NMR spectra of these samples (*21*). Increasing pressure possibly lowers T_g, because the viscosity of $Na_2Si_2O_5$ liquid decreases as pressures rises above 1.5 GPa (*23*). A pressure-induced change in T_g should thus produce an effect on Q speciation opposite to that detected in the glasses by NMR. The observed changes in speciation therefore probably reflect an intrinsic effect of pressure on the liquid structure.

In NMR as in other types of spectroscopy, extreme disorder or distortion of local site geometry can cause signals to be broadened to such an extent that they are difficult to observe. We have examined this possibility by comparing the sum of the areas of all peaks in the spectrum for the 8-GPa glass with that of the 1-bar glass. Total areas, per gram of sample, are the same within ±5% for both; therefore, most or all Si is in sites with well-defined tetrahedral or octahedral geometry.

Our data show that pressure-induced coordination and speciation changes can be preserved by rapid cooling at pressures as high as 8 GPa, followed by decompression at room temperature. However, the possibility of some structural relaxation in our samples, particularly of local site distortion (*5*), cannot be excluded. In situ study at both high pressure and temperature is necessary to ultimately resolve this question.

In earlier spectroscopic studies of glasses quenched from liquids at pressures up to 3 GPa, no pressure-induced Si coordination changes were detected (*24*). Our data indicate that even at 5 GPa, the amount of $\mathrm{Si^{VI}}$ in $Na_2Si_2O_5$ liquid is less than the detection limit of about 0.3%. At 8 GPa, the percentage of $\mathrm{Si^{VI}}$ in $Na_2Si_2O_5$ liquid is also small. Most, if not all, magmas that reach the surface of the earth at the present time come from depths where pressures are less than 8 GPa (about 240 km). Compression of these liquids therefore has probably been dominated by mechanisms other than an increase in coordination of the network-forming cations. Changes with pressure in intertetrahedral bond angles and bond lengths have been shown to occur in silicate liquids (*24*). The small shift in the $\mathrm{Si^{IV}}$ peak position with pressure in our samples indicates that the mean Si-O-Si angle decreased less than 2° (*12*), although the range of angles probably increased. The observed disproportionation of $\mathrm{Si^{IV}}$ species in $Na_2Si_2O_5$ glasses at high pressures may be a consequence of adjustments in the tetrahedral network. Such an effect is analogous to that caused by substitution of the smaller cation Li^+ for Na^+ at 1 bar: reaction 1 is displaced to the right (*20, 25*). This shift may indicate that at high pressure, Na sites are smaller, and the Na-O interaction is stronger. Changes in the $\mathrm{Si^{IV}}$ speciation in silicate liquids may also have significant effects on thermodynamic properties such as the activity of the SiO_2 component (*20, 25*). Greater disproportionation also implies a more random distribution of bridging and nonbridging oxygens (*20*).

It has been suggested that at very high pressures, magmas may actually become denser than their source rocks and thus would be unable to rise to the earth's surface. Such a density contrast at depth would have major consequences for the rates and mechanisms of heat and mass transport in the planet (*3, 26*); Si coordination changes in liquids may play a crucial role in producing this contrast. During the early history of the solar system, when substantial melting in the deep interiors of the terrestrial planets may have occurred, $\mathrm{Si^{VI}}$-bearing magmas could have been predominate.

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10. NMR measurements were made at a ^{29}Si Larmor frequency of 79.5 MHz with a Varian VXR-400S spectrometer and MAS probe. Frequencies were calibrated to ±0.2 ppm against an external standard of tetramethyl silane (TMS); MAS rotors with double o-ring seals were used to prevent sample hydration. Sample spinning speeds of about 6 kHz were used, with a 1-μs (about 15°) radio frequency pulse. The observed peaks attributed to $\mathrm{Si^{VI}}$ were well above background intensity and were shown to be neither artifacts nor spinning side bands by variation of spectrometer operating conditions. In silicates, only $\mathrm{Si^{VI}}$ is known to produce ^{29}Si chemical shifts in the range of −180 to −220 ppm (*8, 11*). Correlations between Si-O bond distance and chemical shift suggest that a tetrahedral site with a mean distance of 0.153 nm might cause a chemical shift in this range [A.-R. Grimmer, *Chem. Phys. Lett.* **119**, 416 (1985)]. However, this extreme tetrahedral compression has not been observed in minerals (*2*) and has been shown to be energetically very unfavorable [G. V. Gibbs, *Am. Mineral.* 67, 421 (1982)]. Shortened tetrahedral bonds would also be expected to relax on decompression.
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17. The ^{29}Si MAS NMR linewidths for $\mathrm{Si^{IV}}$ in crystalline Mg_2SiO_4, $CaMgSi_2O_6$, $MgSiO_3$, SiO_2 (quartz), and low-pressure $Na_2Si_2O_5$ polymorphs, for example, are all about 1 ppm or less, as is the $\mathrm{Si^{VI}}$ peak in stishovite (*11*).
18. Optical microscopic examination showed that the 5- and 8-GPa glasses were homogeneous and free of quench crystals, which were, however, observed in a 10-GPa sample. Transmission electron microscope images of crushed glass fragments at magnifications to ×100,000 revealed no sign of crystallinity, and electron diffraction produced no diffraction rings or spots. NMR results on two separate 8-GPa samples quenched from 1500°C and one sample quenched from 1700°C were essentially the same.
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