

Shocked quartz: A ^{29}Si magic-angle-spinning nuclear magnetic resonance study

PETER S. FISKE,^{1,*} WILLIAM J. NELLIS,¹ ZHI XU,² and JONATHAN F. STEBBINS²

¹Physics and Space Technology Directorate, L-045, Lawrence Livermore National Laboratory, Livermore, California 94550, U.S.A.

²Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305-2115, U.S.A.

ABSTRACT

Quantitative ^{29}Si NMR spectra of single-crystal α -quartz, shock compressed to 12–38 GPa and recovered, provide new information about the complex response of quartz to shock loading. Spectra from samples recovered from shock pressures of 12–20 GPa show a broadening of the ^{29}Si NMR peak and the development of asymmetry toward lower NMR frequency (indicating an increase in the mean Si-O-Si intertetrahedral bond angle). NMR spectra of samples shock compressed above ~ 25 GPa show increasing amounts of a separate amorphous phase of SiO_2 with a mean Si-O-Si bond angle roughly 5° narrower, and 10–15% denser, than fused SiO_2 . Small amounts of crystalline material remain with a mean Si-O-Si bond angle up to 3° larger than unshocked α -quartz. The recovery of dense glass indicates that post-shock temperatures were sufficiently low to also preserve stishovite, had any been created in our experiments. The paucity of stishovite or ^{29}Si in an amorphous phase in our recovered samples suggests that the formation of stable, high-coordinated Si is kinetically hindered in shock compression experiments up to about 35–40 GPa, except in regions of high temperature, such as planar deformation features (PDFs), microfaults (pseudotachylites), or voids.

INTRODUCTION

For nearly 40 years, physicists, chemists, and mineralogists have studied quartz recovered from shock experiments in an effort to understand the behavior of silicates during shock compression and release. Although shock recovery experiments are limited in pressure, can produce complicated stress histories, and preserve only the structural changes that can be rapidly formed and quenched, these studies have nevertheless improved our understanding of the effects of shock waves on solids and have been applied to a diverse set of problems including modeling of impact and explosion cratering and the unambiguous identification of meteorite impact craters. However, our understanding of the behavior of quartz under shock loading is still evolving.

DeCarli and Jamieson (1959) reported that quartz shocked to 60 GPa became amorphous. Wackerle (1962) published equation-of-state data for quartz shocked up to 60 GPa and noted a kink in the Hugoniot suggesting a phase transition over the shock pressure range of 14–35 GPa. A note added in proof mentions the discovery of stishovite and suggests that it may be the shock-induced high-pressure phase suggested by the Hugoniot data. McQueen and coworkers (1963) proposed that quartz transforms directly to stishovite or a stishovite-like amorphous phase (i.e., with Si in sixfold coordination) that reverts on decompression. Subsequent studies have

shown that quartz shocked to pressures above about 40 GPa compresses to a density similar to that of stishovite at the same pressure (see Hemley et al. 1994 for a thorough review of the high-pressure behavior of silica). That quartz transforms directly to stishovite, or a stishovite-like amorphous material during shock compression to 20–35 GPa remains a widely held view, and numerous shock experiments on quartz or amorphous SiO_2 at pressures >40 GPa have assumed to be studying stishovite or a material thermodynamically equivalent to stishovite (e.g., McQueen et al. 1963; Davies 1972; Grady et al. 1974; Lyzenga et al. 1983; Schmitt and Ahrens 1989). The recovery of trace quantities of stishovite in shock experiments is cited as evidence of this phase transformation.

Microscopic analyses of shocked quartz from experiment and nature suggest a more complicated set of phenomena than a simple solid-state phase transformation of quartz to stishovite or an amorphous material with Si in sixfold coordination. Stishovite observed in quartz experimentally shock recovered from pressures >20 GPa is found mainly associated with planar deformation features (PDFs), voids, or pseudotachylites (microfaults)-sites of intense local heating (e.g., Goltrant et al. 1991; Goltrant et al. 1992; Gratz et al. 1992). Similarly, stishovite found in shocked quartz from impact craters is also generally associated with PDFs, voids, or pseudotachylites (e.g., Stöffler 1971; Kieffer 1971; Kieffer et al. 1976; Martini 1991).

In this paper, we present ^{29}Si NMR analyses of single

* E-mail: fiske1@llnl.gov

TABLE 1. List of single-crystal quartz shock experiments

| Sample | Capsule composition | Impactor composition | Peak pressure* |
|---------|---------------------|----------------------|----------------|
| QD2 | 304 Steel | Lexan | 12 GPa |
| QD3 | 304 Steel | Cu | 33 GPa |
| SQ2-1 | 6061 Ti-6Al | Al | 13 GPa |
| SQ2-3 | 6061 Ti-6Al | Al | 21 GPa |
| SQALA-1 | 304 Steel | Cu | 21 GPa |
| SQALA-3 | 304 Steel | Cu | 27 GPa |
| SQALA-4 | 304 Steel | Cu | 28 GPa |
| SQALA-5 | 304 Steel | Cu | 30 GPa |
| SQALA-6 | 304 Steel | Cu | ~38 GPa† |

* Pressure is calculated using the impedance-match method. Two dimensional computer modeling of similar experimental configurations (Gratz et al. 1992) predict peak pressures that are lower than those given by the impedance-match technique. Impedance-match values of 12, 24, and 32 GPa correspond to computer model predictions of 14, 22, and 27 GPa.

† Projectile velocity measurements failed during this experiment. Projectile velocity is estimated by comparing to another shot that used identical experimental parameters. Based on the reproducibility of projectile velocities given identical experimental parameters ($\pm 5\%$) we estimate an uncertainty in impedance-match pressure of $\pm 10\%$.

crystal quartz, shock compressed and recovered from pressures up to ~ 38 GPa. Our samples were produced using identical conditions and materials to those used by Gratz and coworkers (1992) to directly compare the microstructural data presented in that study with quantitative atomic-level structural information provided by NMR. In particular, we investigated the nature of “diaplectic glass” produced by shock compression and searched for evidence of a solid-state transformation of quartz to crystalline or amorphous stishovite.

EXPERIMENTAL METHODS

Disks of doubly polished single-crystal synthetic quartz (17 or 30 mm in diameter and 1.5 or 3 mm thick) were held in steel fixtures of the same design used in previous studies (see Gratz et al. 1992 and references therein). Shock pressures were generated by the impact of 5 or 2 mm thick Cu, Al, or Lexan impactors at velocities up to 2 km/s using the 6.5 m long two-stage light gas gun at Lawrence Livermore National Laboratory (see Table 1 for experimental parameters). The density mismatch between quartz and the steel container causes the shock compression to be applied by a series of 3–5 closely spaced shock waves rather than a single pulse. Previous numerical modeling of this experimental configuration shows that the initial shock wave compresses the sample to roughly half the final pressure and, in the case of the higher-pressure experiments, the sample remains at the peak pressure for roughly 0.1 μ s (Gratz et al. 1992). Peak shock pressures were calculated using the impedance match method for the projectiles and the sample capsules. However, numerical models suggest that peak pressures may be lower than those estimated by the impedance match method by as much as 20% at the highest pressures (Gratz et al. 1992). The central portion of each recovered specimen, which experiences a uniform stress history, was removed and disaggregated in a BC mortar.

Samples were handled in air and stored in a vacuum desiccator. A sample of SiO₂ glass compressed at room temperature to 18 GPa (provided by R. Liebermann) was also studied for comparison.

²⁹Si NMR spectra of the resulting polygranular material were acquired using a modified Varian VXR/Unity-400 spectrometer with a ²⁹Si Larmor frequency of 79.459 MHz and a Varian MAS probe. Frequencies were referenced to external tetramethyl silane (TMS). Samples were contained in a ZrO₂ rotor and spun at 4–4.5 kHz. Spectra were acquired using a 1.5–2 μ s pulse width (corresponding to a radio frequency tip angle of 30°) and a 1000–3000 s delay between excitation pulses. Previous experiments on quartz and silica glass suggest that these delay times are sufficient to avoid differential saturation and accompanying distortion of spectral intensities but still obtain spectra with sufficient signal-to-noise ratios. Individual samples were run for 24 to 120 h to achieve a high ratio of signal-to-noise.

EXPERIMENTAL RESULTS AND INTERPRETATION

²⁹Si NMR peaks for quartz shocked to 12–28 GPa become increasingly broader with pressure (Fig. 1). The samples shocked to 12 and 21 GPa have a full width at half maximum (FWHM) of 0.9 and 0.6 ppm, respectively, and show a pronounced asymmetry with increased intensity at lower frequency (more negative chemical shifts). For comparison, the NMR peak for unshocked quartz is symmetric and <0.6 ppm wide.

Spectra of single crystal quartz shocked to pressures of 30 to ~ 38 GPa consist of a single major peak (Fig. 2) with an increasing broad shoulder to higher frequency. No features are seen at frequencies of -190 or -150 ppm, corresponding to ¹⁶Si or ¹⁵Si. Signal-to-noise calculations for these spectra suggest that the detection limit for ¹⁶Si and ¹⁵Si is 3%.

Shocked quartz recovered from pressures of 20–35 GPa and from static compression experiments at room temperature up to 40 GPa (e.g., Kingma et al. 1993), has been shown by a variety of techniques (Gratz et al. 1992; see Stöffler and Langenhorst 1994 for a review) to consist dominantly of two distinct phases of SiO₂: highly deformed crystalline quartz and an amorphous phase, sometimes referred to as diaplectic glass. In addition, minor amounts of friction-melted glass is found along pseudotachylite-like microfaults between crystallites. The spectrum for sample QD-3, recovered from 33 GPa, most clearly shows two distinct peaks which we interpret to correspond to deformed crystalline quartz and diaplectic glass. Fitting of this spectrum, assuming two Gaussian line shapes, shows one peak centered at -109.8 ppm (FWHM 4.4 ± 1 ppm) and another at -107.8 ppm (FWHM 17 ± 3 ppm) (Fig. 3). Spectra of samples recovered from 30 and 38 GPa also show asymmetry to higher frequency, but fitting these spectra with two distinct peaks is less unique.

The position of the broad peak presumably representing diaplectic glass (-107.8 ppm) is roughly 4 ppm high-

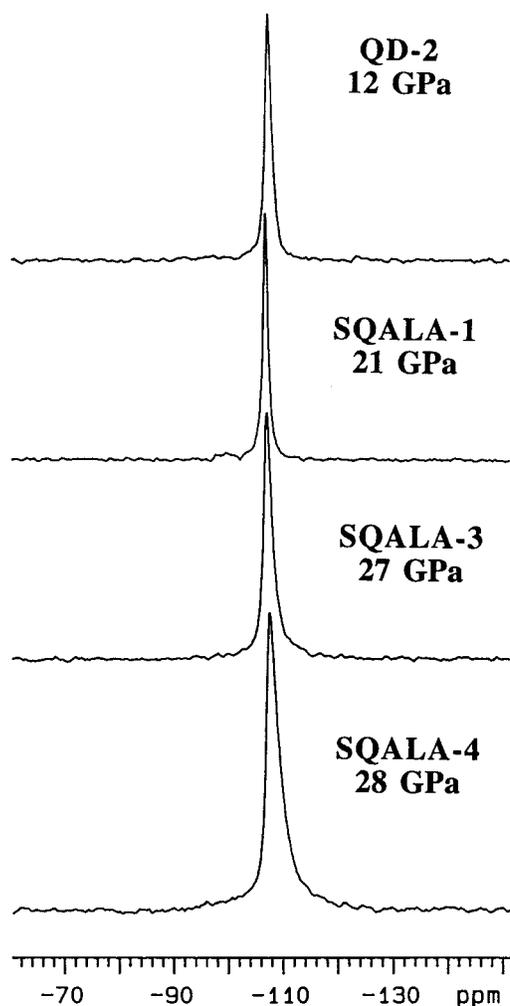


FIGURE 1. ^{29}Si MAS NMR spectra of quartz shocked to 12, 21, 27, and 28 GPa.

er in frequency than that of SiO_2 glass fused at 1 bar (-111.5 ppm; Oestrike et al. 1987). This peak position is similar to that of SiO_2 glass quenched from a liquid at high pressure (Xue et al. 1991) or compressed at room temperature (Devine et al. 1987) (see Table 2). Correlations between ^{29}Si NMR peak positions and Si-O-Si bond angle (e.g., Engelhardt and Michel 1987) suggest that the diaplectic glass produced in our experiments has a mean Si-O-Si bond angle roughly 5° narrower than fused glass. Neutron diffraction studies of SiO_2 glass compressed to 16 GPa show a decrease in the Si-O-Si bond angle of 2° and a slight narrowing of the Si-O-Si bond angle distribution (Susman et al. 1991). These small structural changes correspond to a density increase of 20%. By comparing the peak position for Si in the diaplectic glass in our samples (-107.8 ppm) to the peak position for Si in glass compressed to 18 GPa at room temperature (-105.6 ppm; sample provided by R. Liebermann) and given the results of Susman and coworkers, we estimate

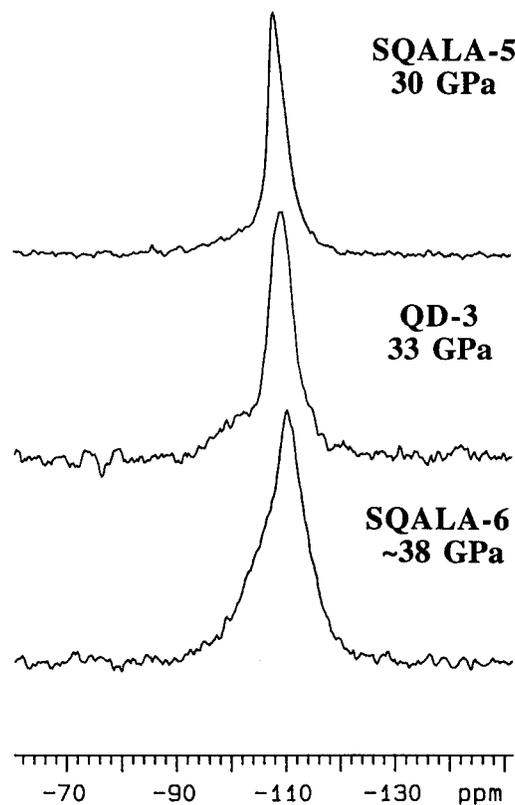


FIGURE 2. ^{29}Si MAS NMR spectra of quartz shocked to 30, 33, and 38 GPa. In this pressure range, the NMR spectra shows the presence of a dense amorphous phase (broad shoulder centered at -109 ppm) and the progressive broadening of the signal from the crystalline phase. In addition, the position of the peak for the crystalline phase shifts 3 ppm to lower frequency.

the diaplectic glass in our samples has a density of roughly 2.4 to 2.5 g/cm^3 (10–15% denser than fused SiO_2).

Langenhorst and Deutsch (1994) measured the density and refractive index of grains of shocked quartz and found that quartz recovered from shock pressures of 33 GPa has a bulk density of 2.3 g/cm^3 . Although this value is similar to our estimation based on NMR data, our estimation is only for the diaplectic glass (roughly 50% of the sample). If the deformed crystalline material has a density similar to crystalline quartz, the bulk density of our sample would be roughly 2.6 g/cm^3 . This discrepancy could be a result of incorrect estimates of pressure for our experiments (2-D hydrocode calculations of quartz held in our recovery fixture suggest peak pressures may be 5 GPa lower than those derived from shock impedance calculations (see Gratz et al. 1992 for details). In addition, the measurements of Langenhorst and Deutsch (1994) are on bulk shocked quartz, which, at these pressures, may be composed of a mixture of diaplectic glass, melt glass, and deformed crystalline material.

The width of the NMR peak for the diaplectic glass in our samples gives a rough measure of the Si-O-Si bond angle distribution in the material. The width of the peak

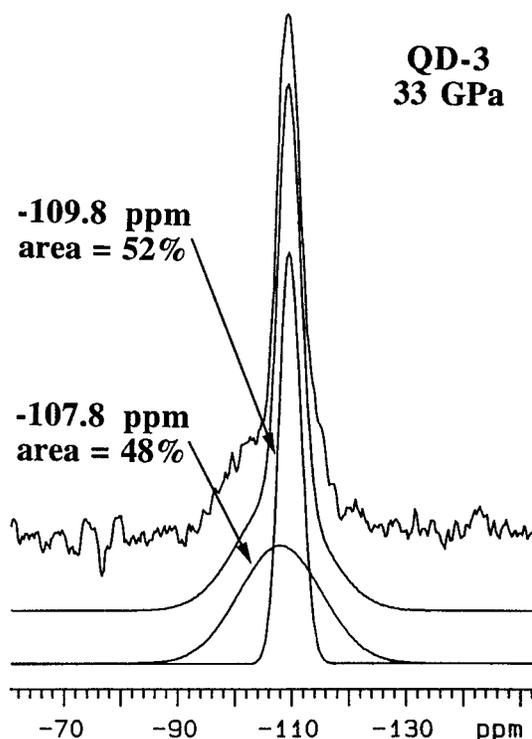


FIGURE 3. Deconvolution of the ^{29}Si MAS NMR spectrum of quartz shocked to 33 GPa (sample QD-3) clearly shows the presence of a broad feature centered at -108 ppm. This peak represents dense fourfold-coordinated glass with a mean Si-O-Si bond angle roughly 5° narrower than that in fused SiO_2 glass.

is somewhat larger than that of 1 bar SiO_2 glass (17 ± 3 ppm vs. 12 ± 1 ppm for 1 bar SiO_2 glass), suggesting that the diaplectic glass in our samples has a short-range structural disorder comparable to, or slightly larger than, that in fused SiO_2 glass. This result is contrary to previous studies suggesting that diaplectic glass has significantly less structural disorder than fused glass. For example, electron diffraction patterns of diaplectic glass show diffraction rings that are absent in patterns from fused glass, and recrystallization experiments show that diaplectic glass recrystallizes more quickly than fused glass (see Stöfler and Langenhorst 1994 for a review). A possible explanation for this discrepancy may be that the electron diffraction technique, which, though capable of analysis at magnifications of 10^5 g still averages over many atoms, possibly yielding an overall measurement of disorder that includes the contribution from nano-crystalline regions. Similarly, recrystallization experiments can be drastically affected by the presence of nano-crystalline nuclei or water. NMR, on the other hand, is sensitive only to local structure, and is able to resolve each phase clearly and shows that diaplectic glass in our samples has a bond angle distribution, and thus intermediate-range order, similar to or greater than that of fused glass.

The narrow peak in these spectra, which we interpret as representing highly deformed crystalline quartz,

TABLE 2. ^{29}Si NMR data for amorphous SiO_2 synthesized by various techniques

| Process | Peak position ppm | FWHM ppm | Source |
|--|-------------------|------------|------------------------|
| Fused at room P | -111.5 | 12 | Oestrike et al. (1987) |
| Quenched at 6 GPa | -108.5 | 13 | Xue et al. (1991) |
| Compressed to 18 GPa at room temperature | -105.6 | 17 | This study |
| Compressed to 5 GPa at 600°C | -108.5 | 15 | Devine et al. (1987) |
| Amorphous phase produced by partial sub- T_g reversion of stishovite | -108.4 | 12 | Xue et al. (1993) |
| Diaplectic glass | -107.8 | 17 ± 3 | This study |

changes in two ways with shock pressure. First, the peak broadens considerably, from 1 ppm at 27 GPa to as much as 5 ppm at 33 GPa. It is difficult to uniquely resolve this peak in the highest pressure sample. Second, the peak shifts in position from -107.4 ppm (as for unshocked quartz) at 27 GPa to lower frequency (-109.8 ppm at 33 GPa). With increasing destruction of the crystalline quartz, the mean Si-O-Si bond angle for the material shifts apparently to wider angles (up to 3° in the 33 GPa sample), opposite in behavior to the diaplectic glass. X-ray studies of shocked quartz by Schneider and Horne-mann (1976) show an expansion of the quartz lattice after shock loading above 20 GPa, mainly through a stretching of the chains of SiO_4 tetrahedra, consistent with these results.

These results are also in agreement with the work of McMillan et al. (1992) who used Raman spectroscopy to study single-crystal quartz shocked to pressures as high as 31.4 GPa. Their Raman spectra of samples shocked to 31.4 GPa show peaks consistent with amorphous SiO_2 that is at least 20% denser than 1 bar SiO_2 glass. The cell parameters for the crystalline material in their samples correspond to crystalline quartz under roughly 0.75 GPa of tension. The shift of the NMR peak for the crystalline material in our samples to lower frequency is consistent with an expanded quartz structure.

DISCUSSION

Comparison to past ^{29}Si NMR studies of experimentally shocked quartz

Our results significantly differ from previous NMR studies of experimentally shocked quartz. Cygan et al. (1994) and Boslough et al. (1996) used ^{29}Si NMR to study the effects of shock on quartz powders and compared their results to NMR spectra of shocked quartz from impact craters (Cygan et al. 1990, 1992; Cygan and Boslough 1994). Their spectra of powders shocked to 7–22 GPa show a pronounced asymmetric broadening of the peak for quartz. They attributed this broadening to the presence of an amorphous phase with a bond angle distribution intermediate between that of crystalline quartz and fused quartz.

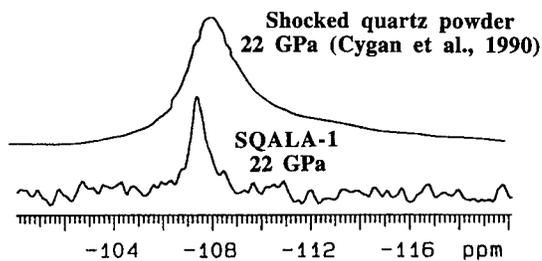


FIGURE 4. A comparison of ^{29}Si MAS NMR spectra of single crystal quartz shocked to 21 GPa (this study) and synthetic powdered quartz shocked to 22 GPa (Cygan et al. 1990).

Figure 4 shows the NMR spectrum of our sample of single crystal quartz shocked to 21 GPa and the spectrum published by Cygan et al. (1990) of powdered quartz shocked to 22 GPa. Identical parameters were used in both experiments (rf tip angle = 90° and $d1 = 30$ s). The frequency, width, and symmetry of the two peaks are significantly different. The peak width of the single crystal sample is roughly a third of the powder sample, the frequency is 2 ppm greater and the peak is roughly symmetrical.

Shock compression of powders is known to produce large heterogeneities in energy deposition, crushing of grains, and at these pressures, melting and jetting of SiO_2 into pore spaces and it is not surprising that our results using single crystal quartz differ substantially from those of Cygan and Boslough (1994). An additional source of discrepancy may arise from their use of synthetic quartz powder which showed substantial initial structural disorder. Cygan and Boslough (1994) showed that the ^{29}Si NMR peak widths for their starting powder narrowed measurably after annealing at 900°C for 20 hours, indicating significant structural disorder. It is likely that this heat treatment did not fully anneal their materials. The results of Cygan and coworkers can only be applied to impacts into loose and porous materials, such as regolith or porous sandstone, whereas our results are more applicable to impacts into non-porous materials such as quartz-bearing crystalline rocks.

Absence of ^{16}O evidence of reversion, or lack of formation?

Stishovite is the stable phase of SiO_2 above about 8–12 GPa and $500\text{--}2000^\circ\text{C}$. However, most shock compression and recovery experiments on quartz have failed to produce more than a trace of stishovite or an amorphous phase with Si in a coordination >4 . DeCarli and Milton (1965) first reported the synthesis of stishovite by the shock compression and recovery of porous sandstone, novaculite and single crystal quartz. Recovered samples were dissolved in HF and the residue (0.02 wt%) showed trace amounts of stishovite but no coesite (DeCarli and Milton 1965). Initial materials with the highest porosity yielded more stishovite. Kleeman and Ahrens (1973) carried out further shock recovery experiments on porous

mixtures of SiO_2 and copper (6% SiO_2 by weight) and found trace amounts of stishovite in most samples. The highest yield of stishovite (“almost pure” according to Kleeman and Ahrens) was found in a sample that used fused SiO_2 as a starting material rather than quartz. Ashworth and Schneider (1985) studied samples of single-crystal quartz shocked to pressures of 22–30 GPa using TEM and found stishovite only in rare glassy patches in two samples.

The general interpretation of these results has been that quartz transforms to stishovite, or a stishovite-like amorphous phase on compression, but rapid reversion kinetics cause it to back-react to an amorphous phase with Si in fourfold coordination on decompression. Several diamond anvil cell spectroscopic studies seem to support this model. Williams et al. (1993) reported powder infrared spectra of quartz and amorphous SiO_2 collected at pressure in a diamond anvil cell that seemed to confirm this interpretation: Vibrations associated with tetrahedral stretching decrease with pressure and a low frequency vibrational feature, consistent with octahedral vibrations, grows with pressure. Upon decompression, the tetrahedral stretching vibrations return and the recovered sample has spectral features similar to statically densified SiO_2 glass or diaplectic glass. Meade et al. (1992) measured the X-ray structure factor for SiO_2 glass in a diamond anvil cell to 42 GPa and found an increase in the Si-O bond distance with pressure, which they interpreted as a gradual increase in the coordination of Si. Evidence of rapid and reversible coordination change also comes from studies of GeO_2 , a SiO_2 analog that undergoes many of the same phase transitions as quartz. Raman and EXAFS studies of GeO_2 glass indicate a pressure-induced coordination change for Ge (Itie et al. 1989; Durben and Wolf 1991).

However the spectroscopic evidence of rapid and reversible coordination number increase in SiO_2 glass is problematic. The observed spectral features interpreted by Williams et al. (1993) have been ascribed by others not to coordination number increase but to baseline problems and duplicate spectral positions of the Si-O octahedral stretching and tetrahedral bending overtones (Hofmeister, personal communication) due to the large particle sizes used in that study (Hofmeister 1995). The work by Meade et al. (1992) suggests an increase in Si-O bond length, but this is only a necessary and not sufficient condition for a change in coordination number. While the work on GeO_2 glass indicates changes in coordination of Ge with pressure (Itie et al. 1989; Durban and Wolf 1991) this provides only indirect evidence of the possibility of similar behavior in SiO_2 glass. Finally, high-temperature diamond anvil cell studies of SiO_2 show rapid transformation between phases only at high temperature [e.g., above 2000°C (Zhang et al. 1993)]. In summary, the spectroscopic evidence of rapid coordination change in SiO_2 at high pressure and low temperature are somewhat ambiguous.

In contrast, microscopic analysis of shocked quartz from experiments, and from impact craters, suggests that

sluggish kinetics of nucleation, rather than rapid kinetics of reversion, may be principally responsible for the paucity of crystalline stishovite in shock recovery experiments (e.g., Stöffler 1971; Stöffler and Langenhorst 1994). The texture and association of stishovite with PDFs, voids, and pseudotachylite veins suggests a scenario in which quartz is locally melted, due to pore collapse, PDF formation, or friction on microfaults, and stishovite nucleates and grows from the high-pressure melt (e.g., Martini 1991). Upon decompression, some of the stishovite, and all of the high-pressure melt, would revert to fourfold coordination.

The rapid reversion kinetics of stishovite is often cited as the reason for a paucity of crystalline stishovite in shock-recovered samples. However, the actual reversion kinetics of stishovite appear to be much slower than originally measured. Skinner and Fahey (1963) carried out the first detailed study of the reversion kinetics of acid concentrates of stishovite from Meteor Crater. The reversion rate was measurable in the time scale of the laboratory from 300 to 800 °C. However, later experiments by Xue and co-workers (Xue et al. 1993), who used NMR spectroscopy to directly determine the amount of stishovite in their partially reverted samples, showed the kinetics of reversion to be roughly three orders of magnitude slower than that measured by Skinner and Fahey (1963). These data demonstrate that, contrary to what is widely cited in the literature, stishovite is metastable at a temperature of 500 °C and that reversion at 600 °C takes place on the order of days! An extrapolation of these reversion data suggest that much of the stishovite present in the sample at high pressure should survive decompression, which involves thermal quench rates as fast as 10^9 K/s (for copper metal; Nellis 1997). Post-release temperatures of samples shocked to 25–35 GPa are estimated to be 400–700 °C (e.g., Raikes and Ahrens 1979; Mashimo et al. 1980), and little or no thermal reversion of stishovite is possible in the few minutes the sample takes thermally equilibrating after the impact (although, if stishovite forms in regions of local heating, these zones will be hotter and some reversion is possible). Reversion of stishovite is even less likely for samples of quartz that are pre-chilled to 77 K and shock loaded into the pressure range of 20–35 GPa (Gratz et al. 1992). The fact that these pre-chilled samples do not show a significantly higher proportion of crystalline stishovite suggests that thermal reversion is not the main reason for a paucity of stishovite in shock-recovered samples of quartz.

The presence of densified glass in our samples places an important constraint on the post-shock temperature in our samples and on the potential for preserving crystalline stishovite. Grimsditch (1986) showed that SiO_2 glass irreversibly densified at room temperature and 18.2 GPa undergoes 50% relaxation to low-pressure density after 1 h at 500 °C. In contrast, Xue et al. (1993) showed that stishovite undergoes 50% reversion after 4 h at 600 °C. The relaxation kinetics of dense SiO_2 glass are significantly faster than that of stishovite. Therefore, the sur-

vival of dense glass in our samples suggests that the amount of reversion of stishovite in our experiments is small. We believe the paucity of stishovite measured in our samples must reflect the paucity of stishovite produced during compression.

It is less certain whether ^{16}Si structural units in a solid amorphous phase could be preserved in our shock recovery experiments. Other than the fact that ^{15}Si and ^{16}Si units are preserved in glasses quenched at high pressure (e.g., Xue et al. 1991), and that these glasses appear stable at ambient conditions, little is known of the reversion kinetics of high-coordinated Si species in amorphous materials. If the ^{16}Si - ^{14}Si reversion reaction is governed by the same kinetics as viscous flow in liquid silicates, then significant metastability is likely. However, the ^{16}Si -O bond is significantly weaker than the ^{14}Si -O bond and it is likely that the onset of ^{16}Si -O bond breaking would occur at a significantly lower temperatures than ^{14}Si -O bond breaking.

Spectroscopic observations of completely reversible Si coordination change at high pressure and low temperature (e.g., Williams et al. 1993) was considered to be strong evidence supporting complete reversibility of ^{16}Si and ^{14}Si at low temperatures. However, as noted earlier, these observations are somewhat ambiguous. Given the observations of sluggish kinetics in high-pressure DAC experiments at temperatures below 2000 °C, it is more likely that Si readily changes its coordination number at high pressure only when supplied with sufficient heat to overcome a kinetic barrier. The back-reaction of ^{14}Si from ^{16}Si on decompression is also kinetically hindered in at least some amorphous silicate materials: Metastable ^{16}Si units are observed at ambient conditions in alkali-silicate glasses quenched at high pressure (e.g., Xue et al. 1991).

The Hugoniot data for SiO_2 shows clear evidence that, at very high shock pressure, quartz and amorphous SiO_2 compress to materials with a density similar to stishovite. However, at the lower pressures of the “mixed phase regime,” and under the conditions of a “ring-up” experiment, the evidence of partial conversion to stishovite, or a stishovite-like amorphous phase, is scant. One possible explanation is that, on shock compression (and in a DAC at room temperature), quartz first transforms to the amorphous phase observed in room-temperature DAC compression experiments (Kingma et al. 1993). This amorphous material may allow for significant additional compression, possibly forming ^{16}Si -like defect states that are different from structurally stable ^{16}Si units, such as those observed by NMR in high-pressure glasses. These defect states may form by a rapidly reversible process, such as the closing of the Si-O-Si intertetrahedral bond angle. Stolper and Ahrens (1987) proposed such a model for the compression of silicates. But the creation of stable ^{16}Si units, and true “stishovite-like” material at high pressure, may require surmounting a kinetic barrier that may be impossible given the low temperature of DAC compression experiments or, in the case of “ring-up” shock experiments at the pressures explored in this study, a

combination of low temperature and short duration. Only at very high shock pressures (>40 GPa?) may shock temperatures be sufficient to permit a rapid transformation of ^{44}Si to ^{66}Si . Past shock experiments that assumed complete transformation of SiO_2 to stishovite on shock loading (e.g., McQueen et al. 1963; Davies 1972; Grady et al. 1974; Lyzenga et al. 1983; Schmitt and Ahrens 1989) should be treated with caution even though some results at higher pressures and temperatures match equilibrium experiments (e.g., Ahrens 1996).

ACKNOWLEDGMENTS

The authors are grateful to Neal Hinsey for his technical expertise in these experiments. The specimen of silica was densified in the Stony Brook High Pressure Laboratory of the NSF Center for High Pressure Research (CHiPR) and was provided to us by R.C. Liebermann. The authors are grateful to Dieter Stöffler and Paul McMillan for critical reviews of this work and Anne Hofmeister for editorial assistance. Part of this work was performed at Lawrence Livermore National Laboratory under the auspices of the Department of Engineering under contract number W-7405-ENG-48.

REFERENCES CITED

- Ahrens, T.J. (1996) Application of shock compression science to Earth and planetary physics. In S.C. Schmidt and W.C. Tao, Eds., *Shock Compression of Condensed Matter-1995*, p. 3–8. AIP Press, Woodbury, New York.
- Ahrens, T.J. and Rosenberg, J.T. (1968) Shock metamorphism: Experiments on quartz and plagioclase. In B.M. French and N.M. Short, Eds., *Shock Metamorphism of Natural Materials*, p. 59–82. Mono Book Corp., Baltimore, Maryland.
- Ashworth, J.R. and Schneider, H. (1985) Deformation and transformation in experimentally shock-loaded quartz. *Physics and Chemistry of Minerals*, 11, 241–249.
- Boslough, M.B., Cygan, R.T., Crawford, D.A., and Kirkpatrick, R.J. (1996) NMR spectroscopy of shocked quartz from experimental impact craters (abstract). *Lunar and Planetary Science Conference*, 27, 137–138.
- Cygan, R.T., Boslough, M.B., and Kirkpatrick, R.J. (1990) NMR spectroscopy of experimentally shocked quartz: Shock wave barometry. In V.L. Sharpton and G. Ryder, Eds., *Proceedings of the 20th Lunar and Planetary Science Conference*, p. 451–457. Lunar and Planetary Institute, Houston, Texas.
- (1992) NMR spectroscopy of experimentally shocked quartz and plagioclase feldspar. In G. Ryder and V.L. Sharpton, Eds., *Proceedings of the 22nd Lunar and Planetary Science Conference*, 127–136.
- (1994) NMR spectroscopic examination of shocked sandstone from Meteor Crater, Arizona. In S.C. Schmidt, J.W. Shaner, G.A. Samara, and M. Ross, Eds., *High Pressure Science and Technology-1993*, p. 807–810. American Institute of Physics, New York.
- Cygan, R.T. and Boslough, M.B. (1994) Analysis of experimentally shocked minerals by NMR spectroscopy. *Sandia Report SAND94-0294*, Sandia National Laboratories, 97 p.
- DeCarli, P.S. and Jamieson, J.C. (1959) Formation of an amorphous form of quartz under shock conditions. *Journal of Chemical Physics*, 31, 1675–1676.
- DeCarli, P.S. and Milton, D.J. (1965) Stishovite, synthesis by shock wave. *Science*, 165, 144–145.
- Davies, G.F. (1972) Equations of state and phase equilibria of stishovite and a coesitlike phase from shock wave and other data. *Journal of Geophysical Research*, 77, 4920–4933.
- Devine, R.A.B., Dupree, R., Farnan, I., and Capponi, J.J. (1987) Pressure-induced bond-angle variation in amorphous SiO_2 . *Physical Reviews*, 35, 2560–2562.
- Durben, D.J. and Wolf, G.H. (1991) Raman spectroscopic study of the pressure-induced coordination change in GeO_2 glass. *Physical Reviews B*, 43, 2355–2363.
- Engelhardt, G. and Michel, D. (1987) *High resolution solid-state NMR of silicates and zeolites*, 485 p. Wiley, New York.
- Goltrant, O., Cordier, P., and Doukhan, J.-C. (1991) Planar deformation features in shocked quartz; a transmission electron microscopy investigation. *Earth and Planetary Science Letters*, 106, 103–115.
- Goltrant, O., Leroux, H., Doukhan, J.-C., and Cordier, P. (1992) Formation mechanism of planar deformation features in naturally shocked quartz. *Physics of the Earth and Planetary Interiors*, 74, 219–240.
- Grady, D.E., Murri, W.J., and Fowles, G.R. (1974) Quartz to stishovite: Wave propagation in the mixed phase region. *Journal of Geophysical Research*, 79, 332–338.
- Gratz, A.J., Nellis, W.J., Christie, J.M., Brocius, W., Swegle, J., and Cordier, P. (1992) Shock metamorphism of quartz with initial temperatures –170 to +1000 °C. *Physics and Chemistry of Minerals*, 19, 267–288.
- Grimsditch, M. (1986) Annealing and relaxation in the high-pressure phase of amorphous SiO_2 . *Physical Reviews*, 34, 4372–4373.
- Hemley, R.J., Jephcoat, A.P., Mao, H.K., Ming, L.C., and Mangani, M.H. Pressure-induced amorphization of crystalline silica. *Nature*, 334, 52–54.
- Hemley, R.J., Prewitt, C.T., and Kingma, K. (1994) High-pressure behavior of silica. In *Mineralogical Society of America Reviews in Mineralogy*, 29, 41–81.
- Hofmeister, A.M. (1995) Infrared microscopy in earth science. In H.J. Humecki, Ed., *Practical Guide to Infrared Microscopy*, p. 377–416. M. Dekker, New York.
- Itie, J.P., Polian, A., Calas, G., Petiau, J., Fontaine, A., and Tolentino, H. (1989) Pressure-induced coordination changes in crystalline and vitreous GeO_2 . *Physical Review Letters*, 63, 398–401.
- Kieffer, S.W. (1971) Shock metamorphism of Coconino Sandstone at Meteor Crater, Arizona. *Journal of Geophysical Research*, 76, 5449–5473.
- Kieffer, S.W., Phakey, P.P., and Christie, J.M. (1976) Shock processes in porous quartzite: Transmission electron microscope observations and theory. *Contributions to Mineralogy and Petrology*, 59, 41–93.
- Kingma, K.J., Meade, C., Hemley, R.J., Mao, H.-K., and Veblen, D. (1993) Microstructural observations of a-quartz amorphization. *Science*, 259, 666–669.
- Kleeman, J. and Ahrens, T.J. (1973) Shock-induced transition of quartz to stishovite. *Journal of Geophysical Research*, 78, 5954–5960.
- Langenhorst, F. and Deutsch, A. (1994) Shock experiments on pre-heated alpha and beta-quartz: I. Optical and density data. *Earth and Planetary Science Letters*, 125, 407–420.
- Lyzenga, G.A., Ahrens, T.J., and Mitchell, A.C. (1983) Shock temperatures of SiO_2 and their geophysical implications. *Journal of Geophysical Research*, 88, 2431–2444.
- Mashimo, T., Nishii, K., Soma, T., and Sawaoka, A. (1980) Some physical properties of amorphous SiO_2 synthesized by shock compression of a-quartz. *Physics and Chemistry of Minerals*, 5, 367–377.
- McMillan, P.F., Wolf, G.H., and Lambert, P. (1992) A Raman spectroscopic study of shocked single crystalline quartz. *Physics and Chemistry of Minerals*, 19, 71–79.
- McQueen, R.G., Fritz, J.N., and Marsh, S.P. (1963) On the equation of state of stishovite. *Journal of Geophysical Research*, 68, 2319–2322.
- Meade, C., Hemley, R.J., and Mao, H.K. (1992) High-pressure X-ray diffraction of SiO_2 glass. *Physical Review Letters*, 69, 1387–1390.
- Nellis, W.J. (1997) Solids, dynamic high-pressure effects. *Encyclopedia of Applied Physics*, 18, 541–554.
- Oestrike, R., Yang, W.H., Kirkpatrick, R.J., Hervig, R.L., Navrotsky, A., and Montez, B. (1987) High-resolution ^{23}Na , ^{27}Al , and ^{29}Si NMR spectroscopy of framework aluminosilicate glasses. *Geochimica et Cosmochimica Acta*, 51, 2199–2209.
- Raikes, S.A. and Ahrens, T.J. (1979) Post-shock temperatures in minerals. *Geophysical Journal of the Royal Astronomical Society*, 58, 717–747.
- Schmitt, D.R. and Ahrens, T.J. (1989) Shock temperatures in silica glass: Implications for modes of shock-induced deformation, phase transformation, and melting with pressure. *Journal of Geophysical Research*, 94, 5851–5871.
- Schneider, H. and Hornemann, U. (1976) X-ray investigations on the deformation of experimentally shock-loaded quartzes. *Contributions to Mineralogy and Petrology*, 55, 205–215.

- Skinner, B.J. and Fahey, J.J. (1963) Observations on the inversion of stishovite to silica glass. *Journal of Geophysical Research*, 68, 5595–5604.
- Stöffler, D. (1971) Coesite and stishovite: Identification and formation conditions in shock metamorphosed rocks. *Journal of Geophysical Research*, 76, 5474–5488.
- Stöffler, D. and Langenhorst, F. (1994) Shock metamorphism of quartz in nature and experiment: I. Basic observation and theory. *Meteoritics*, 29, 155–181.
- Stolper, E.M. and Ahrens, T.J. (1987) On the nature of pressure-induced coordination changes in silicate melts and glasses. *Geophysical Research Letters*, 14, 1231–1233.
- Susman, S., Volin, K.J., Price, D.L., Grimsditch, M., Rino, J.P., Kalia, R.K., Vashishta, P., Gwanmesia, G., Wang, Y., and Liebermann, R.C. (1991) Intermediate-range order in permanently densified vitreous SiO₂: A neutron-diffraction and molecular dynamics study. *Physical Reviews*, 43, 1194–1197.
- Wackerle, J. (1962) Shock compression of quartz. *Journal of Applied Physics*, 33, 922–937.
- Williams, Q., Hemley, R.J., Kruger, M.B., and Jeanloz, R. (1993) High-pressure Infrared Spectra of a-quartz, coesite, stishovite and silica glass. *Journal of Geophysical Research*, 98, 22,157–22,170.
- Xue, X., Stebbins, J.F., Kanzaki, M., McMillan, P.F., and Poe, B. (1991) Pressure-induced silicon coordination and tetrahedral structural changes in alkali oxide-silica melts up to 12 GPa: NMR, Raman, and infrared spectroscopy. *American Mineralogist*, 76, 8–26.
- Xue, X., Stebbins, J.F., and Kanzaki, M. (1993) A ²⁹Si MAS NMR study of sub-T_g amorphization of stishovite at ambient pressure. *Physics and Chemistry of Minerals*, 19, 480–485.
- Yang, W.H., Kirkpatrick, R.J., Vergo, N., McHone, J., Emilsson, T.I., and Oldfield, E. (1986) Detection of high-pressure silica polymorphs in whole-rock samples from a Meteor Crater, Arizona, impact sample using solid-state silicon-29 nuclear magnetic resonance spectroscopy. *Meteoritics*, 21, 117–124.
- Zhang, J., Liebermann, R.C., Gasparik, T., Herzberg, C.T., and Fei, Y. (1993) Melting and subsolidus relations of SiO₂ at 9–14 GPa. *Journal of Geophysical Research*, 98, 19785–19793.

MANUSCRIPT RECEIVED JANUARY 27, 1998

MANUSCRIPT ACCEPTED JUNE 29, 1998

PAPER HANDLED BY CHARLES A. GEIGER