

EXPERIMENTALLY SHOCKED QUARTZ, NMR SPECTROSCOPY, AND SHOCK WAVE BAROMETRY*

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Shock recovery experiments performed on synthetic quartz powders provided samples shock-loaded to mean pressures of 7.5, 16.5, and 22 GPa. All of the shocked powders and the starting material exhibit similar values for the refractive indices. X-ray diffraction analysis of the (101) quartz peak indicates a limited increase in broadening for the shocked material relative to the unshocked. By comparison, the ^{29}Si NMR spectra exhibit a nearly five-fold increase in relative broadening for the primary peak with shock pressure. This broadening effect is the result of disordering and residual strain in the quartz lattice and the formation of an amorphous silica phase. The calibration of the NMR peak widths with shock pressure provides a very sensitive shock barometer for the determination of pressures associated with natural impacts, as well as materials subjected to shock by nuclear tests.

1. INTRODUCTION

The shock-loading of natural materials by impact or explosive loading can result in the formation of highly modified and altered phases. Shocked minerals often exhibit fracturing, planar deformation, comminution, disordering, and lamellae. The extent of these modifications will strongly depend upon the peak pressures and temperatures associated with the shock event^{1,2}. New phases are also frequently observed as a result of shock-loading. Diaplectic glasses and other amorphous phases, including shock-fused glass, have been observed at shock pressures greater than 5 GPa. Coesite and stishovite, crystalline polymorphs of silica, are often seen in quartz samples shocked to higher pressures².

Examination of shock features in minerals has traditionally relied upon the qualitative examination of microstructures by optical and

electron microscopies. Density and X-ray measurements are also performed in order to quantify the physical state of shocked minerals and glasses. However, one of the most convenient and useful diagnostic techniques is that of optical refractivity³. Measurements of the refractive indices of experimentally shocked minerals have provided useful calibration curves for deriving approximate shock pressures of unknown samples. Figure 1 provides the results of refractivity measurements completed on samples of shocked single crystals of quartz⁴. Refractive indices and birefringence ($n_o - n_e$) decrease with increasing shock pressure until the quartz becomes isotropic and transforms to a diaplectic glass. There are no changes in the refractive indices at shock pressures below 25 GPa.

Due to the limitations of these more traditional methods of examining shock

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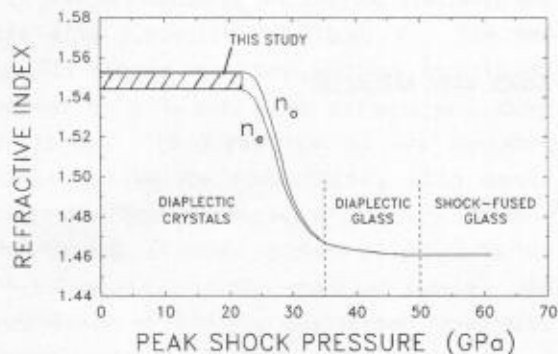


FIGURE 1

Refractive indices of shocked quartz as a function of shock pressure.

features, we have utilized nuclear magnetic resonance (NMR) spectroscopy to characterize quartz powders shocked to pressures up to 22 GPa. This study demonstrates the usefulness of this modern analytical technique in quantifying the changes in the chemical and structural state of the shocked phases.

2. EXPERIMENTAL METHOD

Shock recovery experiments on synthetic quartz powder were performed using the Sandia "Bear" explosive loading fixtures to provide well-characterized shock states⁵. Peak shock pressures (mean values of 7.5, 16.5, and 22 GPa) and temperatures were determined by numerical calculations⁶. The use of different packing densities for each shock pressure provided two data sets: low T (mean values of 175°C to 450°C) and high T (mean values of 350°C to 600°C).

X-ray diffraction analysis, and optical and scanning electron microscopic examination of the starting material indicate a pure and single phase of α -quartz with no amorphous or glassy material. The same techniques were used to characterize the material recovered from the bulk of the sample fixture (off-axis) following shock-loading. The X-ray diffraction analysis

of the major (101) quartz reflection was used to characterize the extent of residual strain associated with the recovered samples⁷.

²⁹Si NMR spectroscopy, using pulse Fourier transform and "magic angle" sample spinning (MASS) techniques, was implemented to examine the shocked quartz powders^{7,8}. The NMR experiment measures the radio frequency emission from ²⁹Si nuclei (4.7% natural abundance) which have been excited to a higher energy spin state while the sample is located in a very strong magnetic field (8 to 11 Tesla). The resonance frequencies are sensitive to the local electronic structure about the nuclei and therefore are useful in determining the chemical bonding and, ultimately, the extent of shock modification.

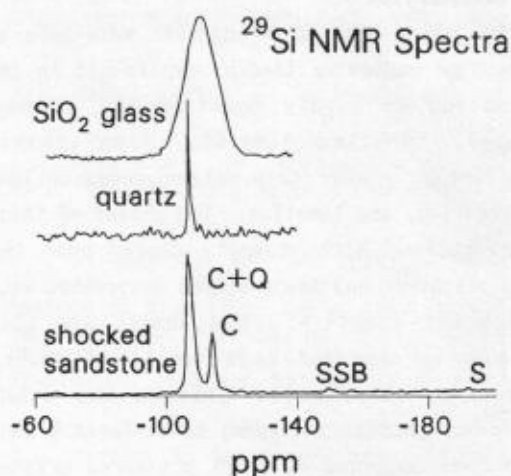


FIGURE 2

MASS NMR spectra for ²⁹Si. Coesite (C), quartz (Q), stishovite (S), and spinning sidebands (SSB) occur in the shocked sandstone spectrum.

The MASS ²⁹Si NMR spectra obtained for quartz⁹, silica glass⁹, and shocked sandstone¹⁰ are provided in Figure 2. Resonance frequencies are presented in terms of chemical shift (ppm relative to an external standard).

MASS NMR is able to distinguish among the various lattice sites and coordinations of ^{29}Si in these samples based upon the characteristic resonance frequencies and shapes. Coesite contains two unique tetrahedral silicon sites (-108 ppm, as in quartz, and -114 ppm) while silicon in stishovite (trace amount) is coordinated by six oxygens and has a chemical shift of -192 ppm. The silica glass is characterized by a broadened resonance representing the large distribution of Si-O-Si bond angles in the amorphous phase¹¹.

3. RESULTS AND DISCUSSION

SEM examination of the shocked quartz powders indicates that substantial brittle disaggregation, comminution, deformation, and fracturing to have occurred with shock-loading. Refractive indices, obtained using the method of central illumination, exhibit no change over the range of shock pressures (Figure 1). X-ray diffraction measurements of the powders failed to detect any amorphous phase. However, an increase in lattice disorder was suggested by a broadening of the (101) quartz peak with increasing shock pressure⁷.

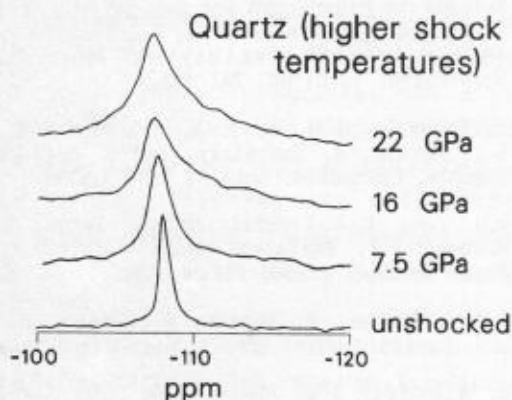


FIGURE 3
 ^{29}Si MASS NMR spectra for unshocked and high temperature shocked quartz powders.

Figure 3 provides the MASS NMR spectra of the high temperature shocked samples along with that for the unshocked starting material. The unshocked quartz is characterized by a single narrow resonance at -108 ppm, but with increasing pressure, this peak broadens as spectral intensity develops in the -110 to -120 ppm range. Best-fit Gaussian simulations of each NMR spectrum suggest the existence of two overlapping resonances⁷. The broad secondary peak is consistent with that of 4-coordinated silicon in SiO_2 glass. The intensity of the secondary peak increases with increasing shock pressure. We interpret the broadening of the quartz peak to result from defects, dislocations, and residual strain in the quartz lattice.

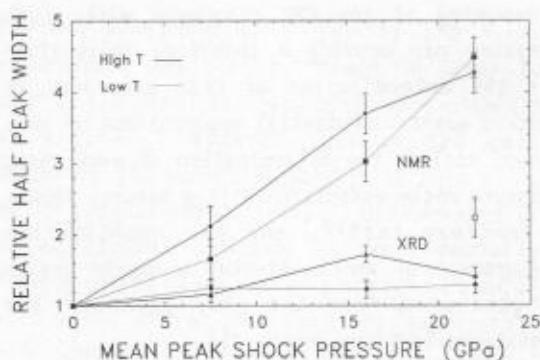


FIGURE 4
Comparison of relative changes in peak widths as a function of shock pressure for NMR and X-ray diffraction (XRD) measurements. Open square indicates a questionable data point.

Figure 4 provides a comparison of the broadening effects associated with the NMR peak for each of the shocked quartz samples relative to that for the unshocked sample. The full-width at half-peak-maximum is used to quantify the amount of peak broadening. Data are presented for both the high and low temperature shock experiments. The results of the (101) X-

ray peak measurements are treated similarly and are also presented in Figure 4. The NMR results suggest a strong positive correlation between relative peak width and mean peak shock pressure. The X-ray results are somewhat inconclusive in correlating with shock pressure. Peak broadening effects are not well defined and, at most, increase by only a factor of 1.7 relative to the unshocked sample. The comparison of the two analytical techniques suggests that considerably more sensitivity can be obtained by the NMR method for evaluating shock pressures in this range for quartz.

4. CONCLUSION

The MASS NMR results provide considerable evidence for the potential use of the technique as a shock wave barometer. The systematic broadening of the NMR resonance with shock pressure may provide a sensitive calibration for the determination of peak pressures in shocked quartz. Potential applications of this method include the determination of peak shock pressure decay associated with a natural impact or nuclear test¹², and the quantitative measurement of shock effects in quartz grains concentrated from the clay layer of the Cretaceous-Tertiary boundary¹³.

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