

Characterization of Amorphous Material in Shocked Quartz by NMR Spectroscopy*

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Nuclear magnetic resonance (NMR) analysis of the recovered products from a series of controlled explosive shock-loading experiments on quartz powders was performed to investigate shock-induced amorphization processes. Silicon-29 NMR spectroscopy is an excellent probe of the local bonding environment of silicon in minerals and is capable of detecting and characterizing amorphous and disordered components. NMR spectra obtained for the recovered material exhibit a narrow resonance associated with the shocked crystalline material, and a broad component consistent with an amorphous phase despite the absence of evidence for glass from optical microscopy. The NMR measurements were performed over a range of recycle times from 1 to 3×10^5 s. The results demonstrate that the magnetization in both the crystalline and amorphous material follows power-law behavior as a function of recycle time. The amorphous component dominates the spectra for short NMR recycle times due to its shorter relaxation time relative to the crystalline material. Fractal analysis of the power-law relations suggests a fractal dimension of 2 for the amorphous phase and 3 for the crystalline phase.

INTRODUCTION

Identification of shocked minerals and determination of their degree of shock metamorphism has become an increasingly important problem in earth and planetary science as the relative importance of impact processes has been recognized. Diagnostic methods for examining shock features in minerals have traditionally relied on qualitative examination of microstructures by optical and electron microscopy. Silicon-29 NMR spectroscopy offers the potential for quantitatively assessing the degree of shock metamorphism in silicates by probing the local bonding environment of silicon. This paper describes its application to structural studies of amorphous material in shocked quartz powder.

EXPERIMENTAL

The shock recovery experiments using quartz powder samples were carried out in the same

manner as those for the study of Cygan et al. [1]. The experiment made use of the Sandia "Momma Bear" explosive loading fixture to achieve a well-characterized shock state. These recovery fixtures allow samples to be shocked in a controlled, reproducible manner. Shock pressure and temperature histories were determined numerically by two-dimensional computer simulations [2]. The peak shock pressure was 22 GPa. The starting material was synthetic α -quartz sieved to a mean grain size of less than $38 \mu\text{m}$ (-325 mesh). The quartz was annealed at 900 C for 20 hr to minimize the initial defect densities that had previously broadened the (101) X-ray diffraction peak [1].

The NMR spectra were recorded on a Chemagnetics spectrometer at a field strength of 4.7 T. Direct polarization, a comb saturation sequence and magic angle spinning (MAS) at 4 kHz were employed. The number of scans ranged from 36,000 for short pulse delays to 1 for long pulse delays.

RESULTS AND DISCUSSION

Figure 1 shows the magnetization recovery for an α -quartz sample which has not been shocked. The recovery is plotted on a log-log scale from which it is obvious that the magnetization follows power-law behavior over 5 decades of time. Calibration of the spectrometer with silicate samples having shorter relaxation times confirms that the magnetization is near equilibrium for the longest times recorded in Figure 1.

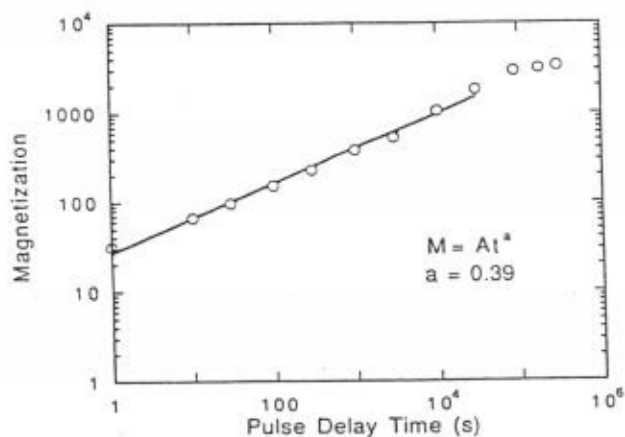


Figure 1. The magnetization recovery of an α -quartz sample on a log-log scale. The recovery follows power-law behavior over 5 decades of time.

Power-law behavior of the magnetization recovery has been observed previously for paramagnetically doped sol-gel derived silicate samples [3]. Power-law behavior for spin-1/2 nuclei is expected whenever the sample is undergoing MAS and its relaxation is dominated by randomly distributed paramagnetic impurities. Although the samples in this study were not intentionally doped, they contain low levels of paramagnetic impurities [4]. The power-law exponent was shown to be equal to 1/6 of the fractal dimension of the material containing the observed nuclei [3]. The power-law exponent of 0.54 is reasonably close to the value of 0.50 predicted for a 3-dimensional material.

Figure 2 shows the magnetization recovery of an α -quartz sample which has been subjected to a 22 GPa shock wave. The recovery again displays power-law characteristics. However, the power-law exponent of the shocked sample is only 0.39.

Representative spectra for the unshocked and shocked quartz samples are shown in Figure 3. The spectra for the unshocked sample have qualitatively similar features, independent of recovery time. The spectra for the shocked sample, however, appear quite different for short and long recovery times. For short recovery

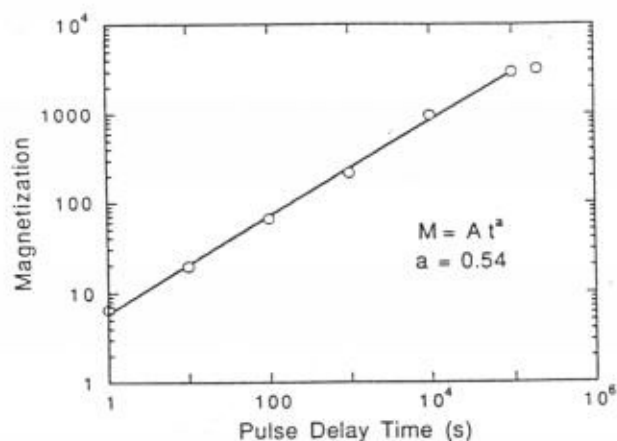


Figure 2. The magnetization recovery of an α -quartz sample subjected to a 22 GPa shock wave. A power-law fit is shown, although the magnetization consists of components with differing relaxation behavior (see Figure 4 and text).

times, the spectra of the shocked sample exhibit both broad and narrow components. The narrow component corresponds to the normal ordered phase as observed for the unshocked sample, while the broad component corresponds to a disordered phase produced by the shock wave. For short recovery times the broad component dominates, while for long recovery times the narrow component dominates to the extent that the contribution of the broad component is not observed. These spectra illustrate the importance of recognizing the relaxation characteristics of a complex material.

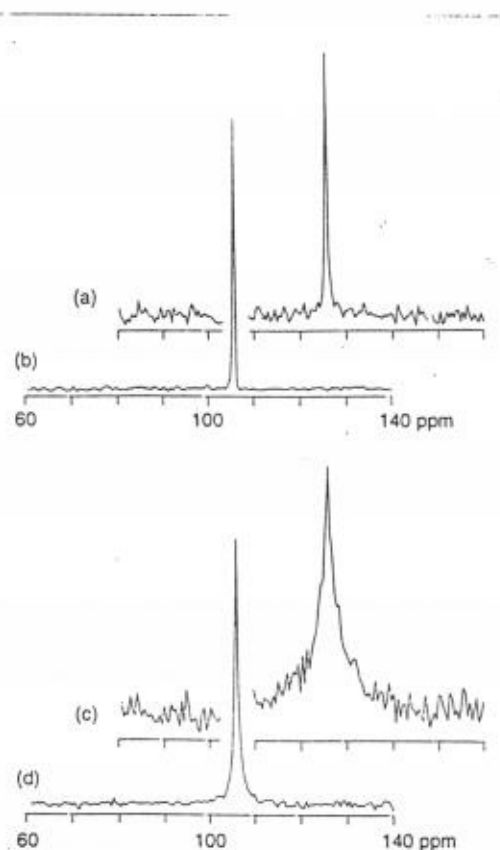


Figure 3. Representative spectra of the unshocked α -quartz sample at (a) 10 s and (b) 100,000 s pulse delay times and of the shocked α -quartz sample at (c) 10 s and (d) 90,000 s pulse delay times.

By analyzing the spectra of the shocked quartz, we are able to estimate the ratio of disordered to ordered phase and determine the fractal dimension of each phase. The spectra of the shocked quartz were numerically fit with two components: a narrow Lorentzian component corresponding to an ordered phase and a broad Gaussian component corresponding to a disordered phase. A Lorentzian lineshape provides the best fit for the entire spectrum of the unshocked material as well as the best fit for the narrow component of the shocked material. A Gaussian lineshape provides the best fit for the broad component of the shocked material. Figure 4 shows the relative intensity of each component as a function of pulse delay time.

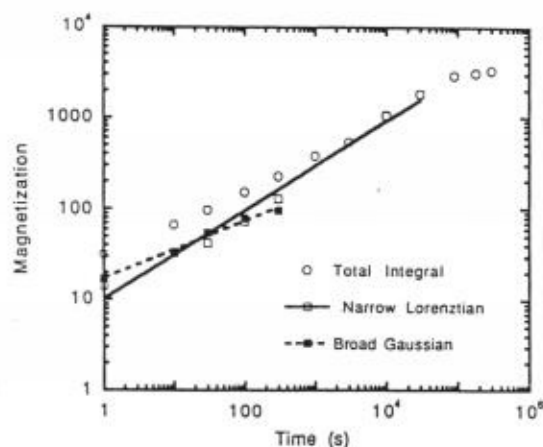


Figure 4. The magnetization recovery of an α -quartz sample subjected to a 22 GPa shock wave. Each spectrum has been deconvoluted into a narrow Lorentzian component corresponding to the ordered phase and into a broad Gaussian component corresponding to the disordered phase.

The broad Gaussian component has a power-law exponent of 0.32 which corresponds to a fractal dimension of two, while the narrow Lorentzian component has a power-law exponent of 0.49 which corresponds to a fractal dimension of three.

The equilibrium intensities of each component are proportional to the amounts of material in each phase. For times of 10,000 s and above, the broad resonance was a fairly minor component of the total signal and could be ignored. Thus, a reasonable estimation can be made of the equilibrium signal corresponding to the ordered phase. The intensity of the equilibrium signal corresponding to the disordered phase could not be quantitatively determined, however, because the spectra were difficult to fit in the 1000 to 3,000 s time regime. We estimate that the disordered phase accounts for less than 10% of the shocked quartz.

CONCLUSIONS

The silicon-29 NMR spectra of shocked quartz consist of two components corresponding to ordered and disordered phases. The spin-lattice relaxation of each phase exhibited power-law behavior which suggests that the disordered phase is two dimensional while the ordered phase is three dimensional. The disordered phase is estimated to account for less than 10% of the material.

ACKNOWLEDGMENTS

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