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NMR Characterization of Shocked Quartz* *CONF-940380-03280*

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ABSTRACT

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We have characterized experimentally and naturally-shocked quartz (both synthetic and natural samples) by solid state nuclear magnetic resonance (NMR) spectroscopy. Relaxation analysis of experimentally-shocked samples provides a means for quantitative characterization of the amorphous/disordered silica component. NMR spectra demonstrate that magnetization in both the amorphous and crystalline components follows power-law behavior as a function of recycle time. This observation is consistent with the relaxation of nuclear spins by paramagnetic impurities. A fractal dimension can be extracted from the power-law exponent associated with each phase, and relative abundances can be extracted from integrated intensities of deconvolved peaks. NMR spectroscopy of naturally-shocked sandstone from Meteor Crater, Arizona (USA) led to the discovery of a new amorphous hydroxylated silica phase. Solid state NMR spectra of both experimentally and naturally-shocked quartz were unexpectedly rich in microstructural information, especially when combined with relaxation analysis and cross-polarization studies. We suggest solid state NMR as a potentially useful tool for examining shock-induced microstructural changes in other inorganic compounds, with possible implications for shock processing of structural ceramics.

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 hypervelocity 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. We have performed NMR analysis of both laboratory-shocked synthetic quartz powders, and of naturally-shocked quartz from Meteor Crater, Arizona, USA.

NMR analysis of the recovered products from controlled explosive shock-loading experiments was performed to investigate shock-induced amorphization processes. Si-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 materials 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 second to 83 hours.

We have also collected spectra from five naturally-shocked Coconino Sandstone samples from Meteor Crater, with the goal of examining possible correlations between NMR spectral characteristics and shock level. We had previously found a strong correlation between the width of the Si-29 resonance and peak shock pressure for experimentally-shocked quartz, due to the shock-induced formation of amorphous silica, which increases as a function of shock pressure between 7.5 and 22 GPa [1,2]. We had suggested that NMR spectra could be used as a "shock barometer", or at least as a screening tool and sensitive method for identifying shocked quartz. However, because the duration of shock loading can be many orders of magnitude longer for natural impacts than for laboratory experiments, we examined the naturally-shocked specimens as well.

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 National Laboratories "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 [3]. The peak shock pressure was 22 GPa. The starting material was synthetic α -quartz sieved to a mean grain size of less than 38 μm (-325 mesh). The quartz was annealed at 900°C for 20 hours to minimize the initial defect densities that initially broadened the (101) X-ray diffraction peak [1].

The NMR spectra of the experimentally-shocked samples were recorded on a Chemagnetics spectrometer, which detects radio-frequency re-emissions from active Si-29 nuclei that have been excited to a high-energy state while the sample is immersed in a magnetic field of 4.7 T. Direct polarization, a comb saturation sequence, and magic angle spinning (MAS) at 4 kHz were employed to provide spectra with significantly reduced dipolar interactions and improved signal-to-noise ratio. The number of scans ranged from 36,000 for short pulse delays to 1 for long pulse delays.

The five samples of shocked Coconino Sandstone were obtained from Meteor Crater to represent the range of shock pressures associated with the impact. The samples are identical to those first examined by Kieffer using X-ray diffraction and optical microscopy [4]. The NMR spectra were obtained at a frequency of 71.5 MHz with an applied magnetic field of 8.45 T. The MAS frequencies were typically at 3.5 kHz, and the pulse recycle time was 30 s. Approximately 200 to 300 mg of sample powder was used for each NMR analysis.

RESULTS

Experimentally-Shocked Synthetic Quartz:

Representative spectra collected at two widely different pulse delay times are shown in Figure 1 for the unshocked and shocked synthetic quartz samples. Resonance frequencies are provided in terms of chemical shift (ppm relative to an external standard) and are related to the local bonding environment of silicon-29 nuclei and to the Si-O-Si bond angle distribution. The two spectra of 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 times, the spectra of the shocked sample exhibit both broad and narrow components. The narrow component corresponds to the normal ordered phase and is similar to that observed for the unshocked sample, while the broad component corresponds to a disordered phase produced by the shock wave. For short 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 complex material.

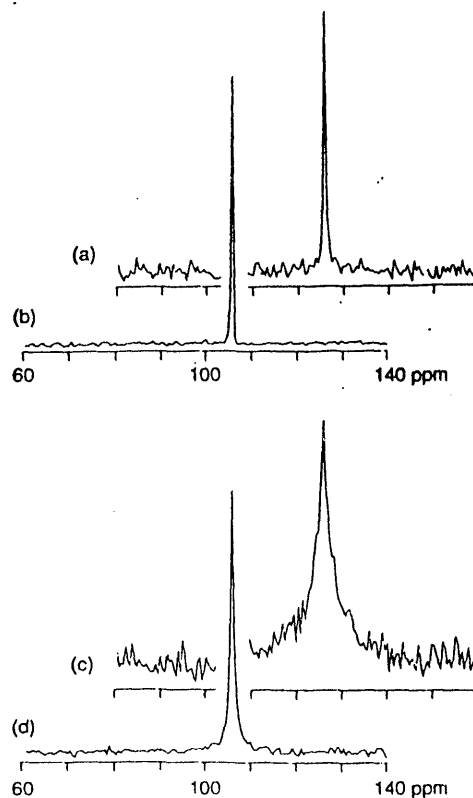


Figure 1. Spectra of unshocked α -quartz at (a) 10 s and 100,000 s and of shocked α -quartz at (c) 10 s and (d) 90,000 s delay time.

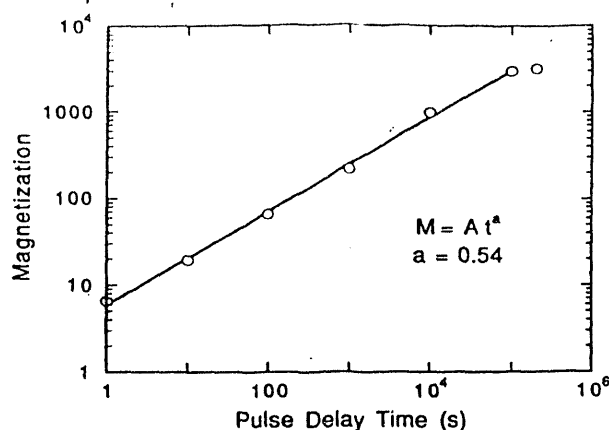


Figure 2. The magnetization recovery of an α -quartz sample on a log-log scale, which follows power-law behavior over 5 decades of time.

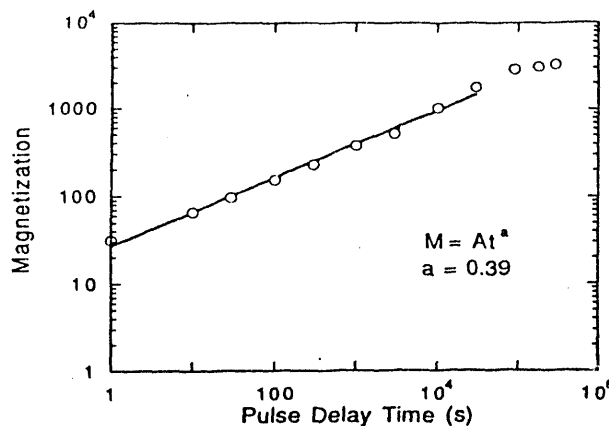


Figure 3. The magnetization recovery of α -quartz shocked to 22 GPa, which consists of components with differing relaxation behavior.

Figure 2 shows the magnetization recovery for a sample of the unshocked α -quartz. The recovery is plotted as a function of pulse delay time on a log-log plot, from which it is clear that the magnetization follows a power-law behavior over 5 decades of time. Calibration of the spectrometer with other silicate samples having shorter relaxation times confirms that the magnetization is near equilibrium for the longest pulse delay times recorded. A least-squares fit to the magnetization data yields a power-law exponent of 0.54. Figure 3 shows the magnetization recovery of an α -quartz sample which has been subjected to a 22 GPa shock wave. The recovery again displays a power-law dependence on pulse delay time, only now the exponent has been reduced to 0.39.

Naturally-Shocked Quartz Sandstone: Figure 4 provides the MAS NMR spectra for the five naturally-shocked samples; numbers in the figures are the same as those used by Kieffer [4]. The spectra are presented in relative order of increasing shock pressure. The ability of MAS NMR to discriminate among the silica polymorphs and amorphous phases is demonstrated by these results. The following is a summary of our observations: Sample #8: mostly quartz, small amounts of coesite and possibly amorphous silica, no stishovite. Sample #4: mostly quartz, more coesite than sample #8, some amorphous silica, and stishovite. Sample #33: same as sample #4, but with an additional peak, due to Q3 (one OH) silicon sites in a dense form of hydroxylated amorphous silica. Sample #7: mostly amorphous silica, with some quartz and coesite, no stishovite, contains a less intense peak associated with the same Q3 site as in sample #33. Sample #9: almost entirely amorphous silica, no stishovite. A representation of the different tetrahedral silicon sites is presented in Figure 5.

DISCUSSION

Experimentally-Shocked Synthetic Quartz: By analyzing the spectra of the experimentally-shocked quartz, we were 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 crystalline 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 6 shows the relative intensity of each component as a function of pulse delay time. As stated earlier, each component can be described with a power-law pulse delay time dependence. The exponent of the broad Gaussian component equal to 0.32 and the exponent of the narrow Lorentzian component equal to 0.49.

Power-law behavior of the magnetization recovery has been observed previously for paramagnetically doped sol-gel derived silicate samples [5]. Power-law dependence for spin-1/2 nuclei is

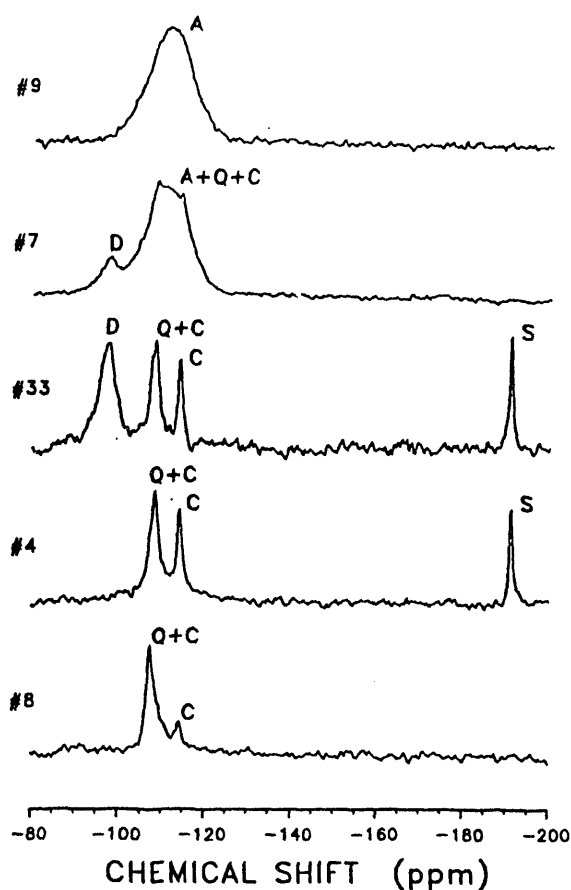


Figure 4. Si-29 NMR spectra of shocked sandstone, where Q=quartz, C=coesite, S=stishovite, A=amorphous (Q4 sites), and D=densified form of hydroxylated amorphous silica (Q3 sites). Sample numbers are those of Kieffer [4].

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 [6]. The power-law exponent was shown by Devreux et al. [5] to be equal to 1/6 of the fractal dimension of the material containing the observed nuclei. The power-law exponent of 0.54 for unshocked quartz is reasonably close to the value of 0.50 predicted for a three-dimensional material. The narrow Lorentzian component, corresponding to relatively undisturbed crystalline material, has a power-law exponent of 0.49--consistent with relaxation controlled by a three-dimensional morphology. By contrast, the power-law exponent of 0.32 for the broad Gaussian component is suggestive of relaxation in a two-dimensional system, implying the amorphous phase is lamellar in structure.

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 can not be quantitatively determined; however, because the spectra were difficult to fit in the 1000 to 3000 s time regime. We estimate that the disordered phase accounts for less than 10% of the shocked quartz.

Naturally-Shocked Quartz Sandstone: Of particular interest in these results are the strong stishovite resonances in samples #4 and #33; the stishovite peak observed by Yang et al. [7] is significantly weaker. We also observe a more intense X-ray diffraction line ($2\theta = 30.2^\circ$) for stishovite, implying

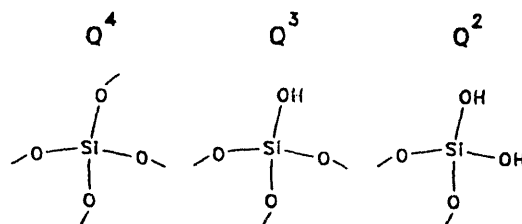


Figure 5. Silicon sites that are distinguished by Si-29 NMR spectroscopy using MAS and CPMAS methods

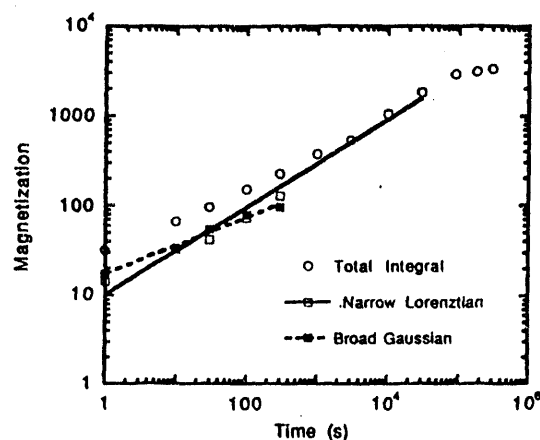


Figure 6. Magnetization recovery of α -quartz sample shocked to 22 GPa. Each spectrum was deconvolved into a narrow Lorentzian (ordered phase) and a broad Gaussian (disordered phase) component.

there is more of this phase in our samples. The only samples for which we observe stishovite are those from the intermediate shock pressures.

The presence of the resonance with a chemical shift of about -98 ppm in two of our samples (#33 and #7) is especially noteworthy. There is no X-ray diffraction evidence for significant amounts of any crystalline material other than the three silica polymorphs. There are several lines of evidence that this resonance corresponds to silicon in tetrahedra with one hydroxyl group in a dense form of hydroxylated amorphous silica: 1) Variable recycle time NMR experiments indicate the resonance has a very short relaxation time (T_1), consistent with previous observations for shock-produced amorphous silica. 2) The shift to higher frequency (smaller negative ppm value) is consistent with a denser phase than a similar phase formed at one atmosphere for a given silicon coordination. A dense amorphous phase has been identified in NMR spectra obtained by Nellis et al. [8] from crystalline quartz shocked to 33 GPa, with a resonance centered at about -106 ppm, an upfield shift of about 6 ppm from -112 ppm for normal-density silicon glass [9]. The resonance for Q3 (one OH) silicon sites in a normal-density gel is at about -102 ppm [10]. Our observed peak position of about -98 ppm would be consistent with densification by roughly the same amount as the amorphous silica associated with shocked quartz. 3) The peak is broad, indicating a wide range of Si-O-Si bond angles typical of amorphous material, and is inconsistent with silicon in clay or feldspar. 4) The target Coconino Sandstone was wet, and there is TEM evidence for vesicular "froth" (consisting of amorphous material produced by steam separation) in the intermediate shock samples [11]. 5) We have observed in a previous NMR study of clinoptilolite that shock loading can generate hydroxyl groups [12].

The strongest evidence for the existence of a densified form of hydroxylated amorphous silica is provided by cross-polarization NMR experiments, referred to as CPMAS when using magic-angle spinning. Cross polarization transfers nuclear spin from protons to other NMR-active nuclei, thereby providing additional structural information and preferentially eliminating spectrum signal from anhydrous phases. Figure 8 provides a comparison of the CPMAS and MAS spectra for sample #33. The enhanced CPMAS signal for the -98 ppm resonance confirms the occurrence of the hydroxylated tetrahedral silicon (identified as Q3). A less intense peak at -86 ppm associated with Q2 silicon is also observed in the CPMAS spectrum. No significant CPMAS signal is observed for sample #9; the "A" peak is due to Q4 silicon in amorphous silica.

CONCLUSIONS

The silicon-29 NMR spectra of experimentally-shocked synthetic quartz consist of two components corresponding to ordered and disordered phases. The spin-lattice relaxation of each phase exhibits power-law behavior which suggests that the disordered phase has a two dimensional morphology while the ordered phase is three dimensional. The relative intensities of the fully relaxed spectra yield relative abundances of each phase; by this means, we found that the disordered phase accounts for less than 10% of the total material.

Silicon-29 NMR spectroscopy can also provide considerable microstructural information on high pressure crystalline and amorphous phases resulting from natural impacts. Cross-polarization techniques can be used to enhance silicon resonances near protons to analyze hydrated phases. Using this approach

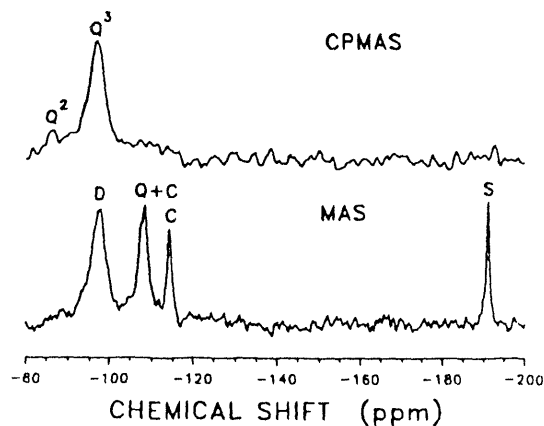


Figure 8. MAS and CPMAS Si-29 NMR spectra for Meteor Crater sample #33 exhibiting the hydroxylated Q3 and Q4 sites for silicon.

we have identified a new naturally-occurring shock-produced phase--a densified hydroxylated amorphous silica.

It is clear from these results that solid state NMR is an extremely powerful tool for examination of shock-induced microstructural changes in quartz, yielding quantitative information on existence of phases, their relative abundances, morphology, and relaxation behavior. Application of similar NMR spectroscopic techniques to the examination of shock-induced microstructural changes in other inorganic compounds--particularly structural ceramics--would be likely to yield similarly useful information.

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