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Application of NMR Shock Barometer to Naturally Shocked Minerals

Randall T. Cygan, Mark B. Boslough

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APPLICATION OF NMR SHOCK BAROMETER TO NATURALLY SHOCKED MINERALS

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ABSTRACT

The shock-loading of natural materials by an impact, such as a comet or meteorite, can result in the formation of modified and altered phases in the target rock. In order to characterize the resulting material and to evaluate the extent of shock modification, we have used nuclear magnetic resonance (NMR) spectroscopy to examine several natural and experimentally shocked minerals. We use NMR spectroscopy to characterize the formation of high pressure silica polymorphs and amorphous material associated with the shocked Coconino Sandstone from Meteor Crater, Arizona. Five samples of the sandstone were obtained from several locations at the crater to represent a range of shock conditions associated with the hypervelocity impact of a 30 meter-diameter meteorite. The NMR spectra for these powdered materials exhibit peaks assigned to quartz, coesite, stishovite, and glass. A new resonance, identified as a densified form of amorphous silica with silicon in tetrahedra with one hydroxyl group, is observed for two of the moderately shocked samples. Experimental shock-loading of dry and water-saturated Coconino Sandstone powders provides shock-metamorphosed material that exhibit broadening of NMR resonances with increasing shock pressure, but no evidence of the new dense silica phase.

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ACKNOWLEDGMENTS

Roger Assink and R. James Kirkpatrick are acknowledged for their major contributions regarding NMR spectroscopy. Roger performed and evaluated the NMR relaxation experiments and Jim provided invaluable expertise in the interpretation of the NMR spectra. We are grateful for the efforts of Gary Turner in obtaining the MAS NMR spectra and Marvin Banks and Edward Dunbar in performing the shock recovery experiments. Additional technical support and scientific comments were provided by Martin Carr, William Casey, Michael Eatough, Mary Gonzales, Robert Graham, Charles Hills, Paul Hlava, Susan Kieffer, John McHone, Bruno Morosin, and Henry Westrich. Patrick Brady and Henry Westrich provided comprehensive reviews and suggestions for improving the final report. This research was supported by the U.S. Department of Energy under contract DE-AC04-94AL85000 with funding from the Planetary Materials and Geochemistry Program of the National Aeronautics and Space Administration.

SUMMARY

The objective of the present research is to quantify the effect of shock-loading experienced by silicate minerals subjected to natural impact. NMR spectroscopy is used to analyze natural samples, primarily quartz, obtained from known impact sites. The NMR spectral characteristics of the minerals is used to estimate the peak shock pressures and compare the results to a previous experimental calibration of the NMR shock barometer. NMR spectroscopy can also identify high pressure mineral polymorphs, the hydration state of amorphous phases, and evaluate the structural state of diaplectic and fused glasses associated with the terrestrial impacts. The primary objectives of this project have been: 1) determine if and how the method can be applied to shocked quartz specimens form natural impacts, and 2) investigate the usefulness of NMR spectroscopy as a screening tool to identify shocked material in samples of unknown origin.

The initial phase for this project has emphasized the characterization of shocked samples from Meteor Crater, Arizona and a comparison with samples obtained by the experimental shock-loading of Coconino Sandstone under dry and wet conditions. Our NMR results of the naturally-shocked Coconino Sandstone support the initial classification scheme of Kieffer based on X-ray diffraction and TEM analyses. We were able to characterize the different states of shocked amorphous silica associated with five different levels of shock loading. A new phase (a densified form of hydrated amorphous silica) has been identified by the NMR technique for a moderately-shocked sample. The experimentally-shocked samples exhibit NMR spectral broadening for both quartz and clay with increasing shock pressure. Deconvolution analysis suggests the amorphous component associated with the wet samples is more dense than the dry samples. Raman spectroscopic analysis indicates the formation of a hydrated silica phase represented by vicinal silanol groups.

This NASA project was started in June 1992 with funding from the Office of Space Science and the Planetary Materials and Geochemistry Program. The project was renewed the following year with funding provided through May 1994. This final report covers the research performed during this funding period. Additional funding to renew this project starting in June 1994 has been approved by the Washington DC NASA office. Randall T. Cygan (Sandia National Labs)

and Mark B. Boslough (Sandia National Labs) are the principal investigators with assistance from Roger A. Assink (Sandia National Labs) and R. James Kirkpatrick (University of Illinois).

PROJECT RESULTS

Under the present funding from the Planetary Materials and Geochemistry Program at NASA, we applied NMR spectroscopy to five naturally-shocked Coconino Sandstone samples from Meteor Crater, Arizona. Figure 1 provides a summary of these ^{29}Si NMR results and notes the presence of the silica polymorphs and the dense hydrated phase (D) (see reprints). Over the past year, we have also collected cross-polarization NMR data, we obtained spectra using different pulse delay times for gross comparison of relaxation times of various phases, and we have applied extensive deconvolution analysis. The spectra strongly correlate with Kieffer's (1971) classification scheme for various stages of shock metamorphism. They also yield strong evidence for a new shock-produced amorphous phase, as discussed in the accompanying reprints (Boslough *et al.*, 1993; Cygan *et al.*, 1994a).

We have now performed six more shock recovery experiments on Coconino Sandstone, at peak pressures of 7.5, 16, and 22 GPa. For each pressure level, we shocked two samples, one dry and one fully saturated with water. We obtained NMR spectra from the shocked specimens, and found very little difference between the initially wet and dry samples (see Figure 2 and reprints; Cygan *et al*, 1994b). We also found that the peaks broaden as a function of shock pressure, independent of water content, in much the same way as the synthetic quartz powders do in our earlier shock barometry work.

Kieffer (1971) provided a strong argument that many of the shock metamorphic features in Coconino Sandstone are attributable to the presence of groundwater. However, our experimentally-shocked sample spectra bear very little resemblance to the spectra from naturally-shocked samples from Kieffer, in that none of the high pressure phases nor dense hydroxylated glass are present. We suspect that the strongest parameter responsible for this difference is the duration of the shock pulse, which is measured in microseconds for the experimental shock, and tens or more of milliseconds for the natural shock at Meteor Crater (and it is worth noting that quartz grains at the K/T impact may have experienced high pressure for times of several seconds). Laser Raman spectroscopy of the experimentally-shocked wet sandstone, however, does suggest the occurrence of a phase characterized by coordinated silanol groups.

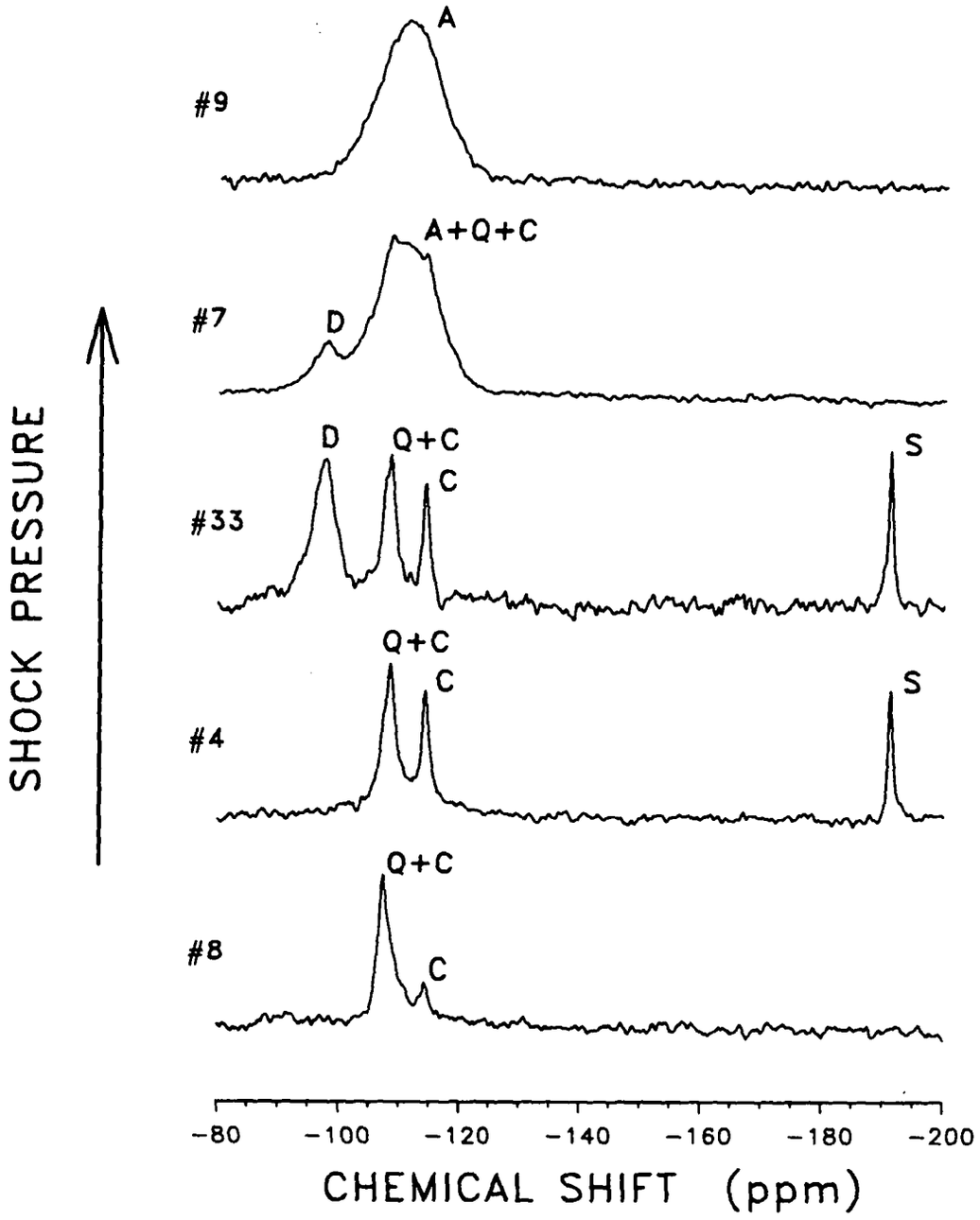

Figure 1. ^{29}Si NMR spectra of five shocked Coconino Sandstone samples. Resonance identifications are (Q) quartz, (C) coesite, (S) stishovite, (A) Q^4 sites in amorphous silica, and (D) Q^3 (one OH) silicon sites in a densified form of hydroxylated amorphous silica. Sample numbers are those of Kieffer (1971).

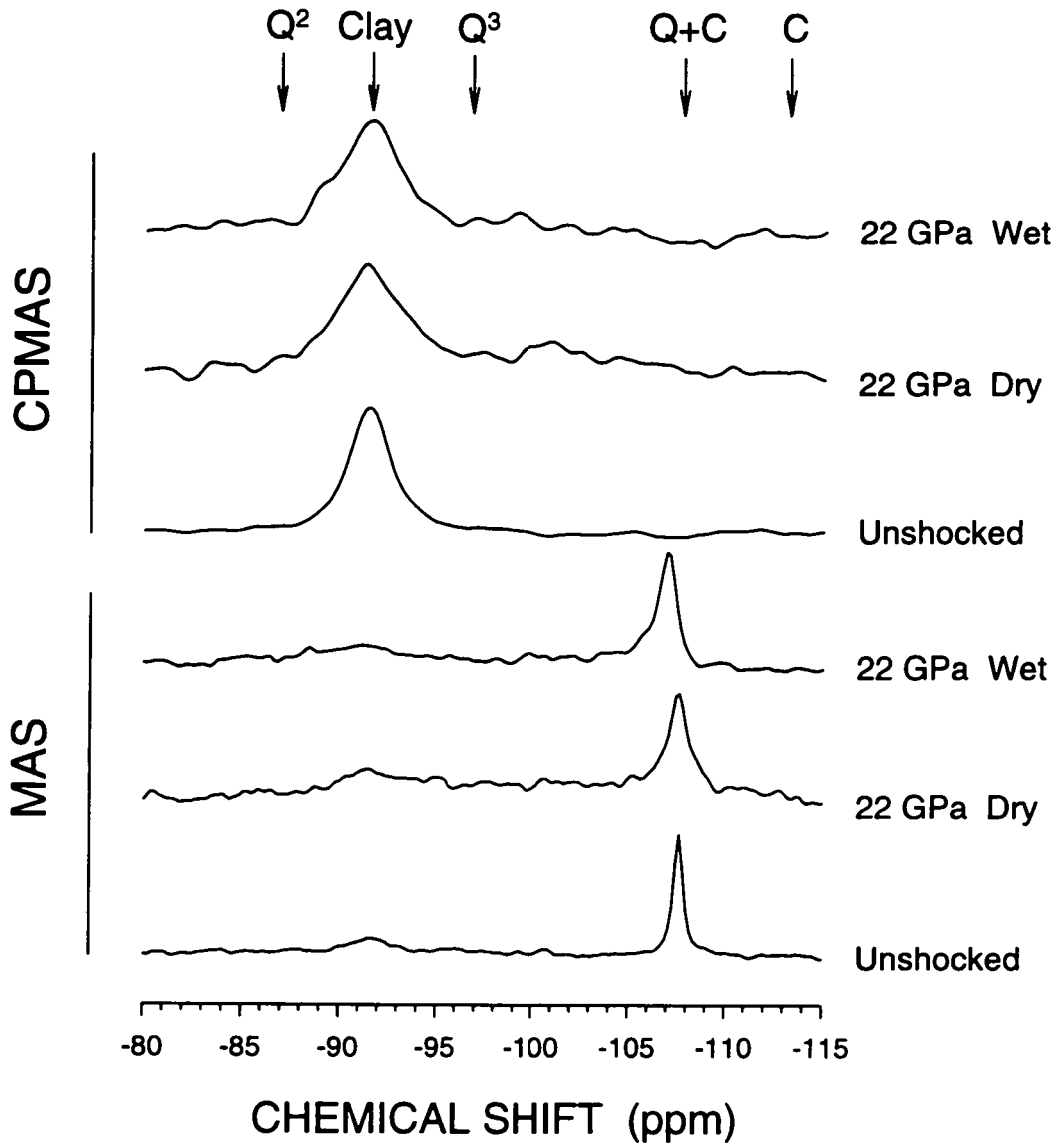

Figure 2. ^{29}Si NMR spectra of unshocked and experimentally-shocked (dry and wet) Coconino Sandstone samples. MAS (all Si sites) and CPMAS (hydrated Si species) spectra are presented for each sample. Arrows denote approximate chemical shift observed in Boslough *et al.* (1993) and Cygan *et al.* (1994a) for quartz (Q), coesite (C), clay, and hydrated amorphous silica, including Q^3 (one OH) and Q^2 (two OH) silicon sites.

Figure 3 notes the presence of vicinal silanol groups associated with the silica phase.

We also performed two more recovery experiments on the synthetic quartz powder of our original study. These experiments were done on a 30-mm-bore propellant gun. Peak pressures obtained were 19 and 39 GPa. NMR spectral analysis of these samples is pending; we will use them for independent confirmation of our peak-width *versus* peak pressure dependence, and for intercomparison of various shock recovery methods.

Detailed summaries of the experimental procedures, results, and applications of NMR spectroscopy for examining shocked minerals are provided in the attached eight (8) reprints of conference abstracts and journal articles.

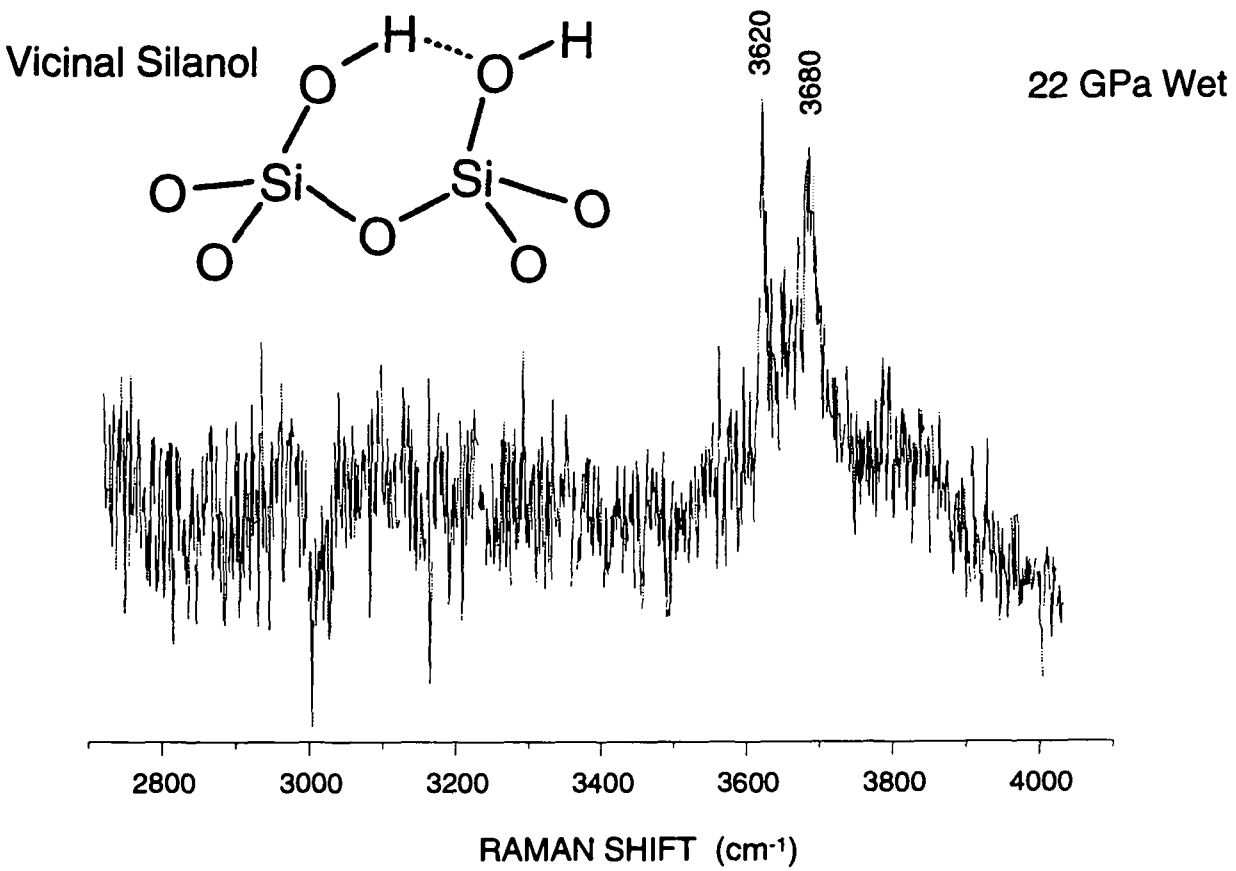

Figure 3. Laser Raman spectrum for material recovered from the high temperature 22 GPa shock of water-saturated Coconino Sandstone. The presence of vicinal silanol groups is suggested by the bands in the 3600 cm^{-1} region.

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Cygan, R. T., Boslough, M. B., and Kirkpatrick, R. J. (1994a) NMR spectroscopic examination of shocked sandstone from Meteor Crater, Arizona. In S. C. Schmidt, Ed., **High Pressure Science and Technology - 1993**, Elsevier, Amsterdam, in press.

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Boslough, M. B., Cygan, R. T., Assink, R. A., and Kirkpatrick, R. J. (1994) NMR characterization of shocked quartz. **Proceedings of NIRIM International Symposium on Advanced Materials '94**, in press.

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JOURNAL OF MAGNETIC RESONANCE, Series A 106, 116–118 (1994)

Power-Law Relaxation of Spin-$\frac{1}{2}$ Nuclei in Solids*

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Received April 5, 1993; revised June 22, 1993

We are using ^{29}Si NMR spectroscopy to characterize the chemical structure of a variety of silicate materials (*1, 2*). Since these studies usually require the recording of quantitative spectra, a direct polarization experiment with magic angle spinning (MAS) is employed. We have found that many samples do not possess a well-defined T_1, but rather exhibit a power-law relationship between the magnetization intensity and pulse delay time. This behavior is the result of relaxation of spin-$\frac{1}{2}$ nuclei by paramagnetic impurities under MAS conditions (*3*). This Note describes the complications one must consider when spectra of spin-$\frac{1}{2}$ nuclei in solids are recorded, how the relaxation by paramagnetic impurities may be used to characterize the spatial structure of a material, and some proposals by which the very long recovery times of these materials can be circumvented.

Figure 1 shows the magnetization recovery for an α-quartz powder from Alfa Products recorded at 4.7 T using a comb saturation sequence, direct polarization, and MAS at 4 kHz. The solid line is a theoretical fit assuming a 37 s exponential recovery of the magnetization. The fit is reasonable and considering the effort needed to acquire additional data (3600 scans recorded at 10 s and 360 scans recorded at 100 s), one is tempted to conclude that the 100 s pulse delay is adequate for a reasonably quantitative spectrum. This conclusion would lead to serious error.

Figure 2 shows the magnetization recovery for the same α-quartz sample for much longer delay times. The recovery is plotted on a log–log scale from which it is obvious that the magnetization follows power-law behavior over five 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 Fig. 2. Spectra recorded at 100 s would have accounted for only 2% of the equilibrium magnetization and the relative intensities of a multicomponent spectrum could have suffered serious distortion.

When recording the spectra of samples which exhibit exponential recovery, one can predict the equilibrium magnetization on the basis of experiments employing delay times on the order of T_1. Note that there is no such analogy when the sample exhibits power-law behavior. The data for delay times ranging from 1 to 100,000 s give no indication of the equilibrium magnetization. For this reason, we routinely calibrate the response of the spectrometer so that if the spin density and mass of the sample are known, we can predict when the recorded magnetization is approaching equilibrium.

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-$\frac{1}{2}$ 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 of 0.54 is reasonably close to the value of 0.50 predicted for a three-dimensional material.

Figure 3 shows the magnetization recovery of an α-quartz sample which has been subjected to a 22 GPa shock wave (*5*). 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 Fig. 4. The spectra for the unshocked sample have qualitatively similar features, independent of recovery time. The spectra for the shocked sample 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 crystalline 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. By analyzing the spectra of the shocked quartz, we are able to estimate the proportion of disordered to ordered phase and determine the fractal dimension of each phase (*6*).

* This work performed at Sandia National Laboratories, supported by the U.S. Department of Energy under Contract DE-AC04-76DP00789.

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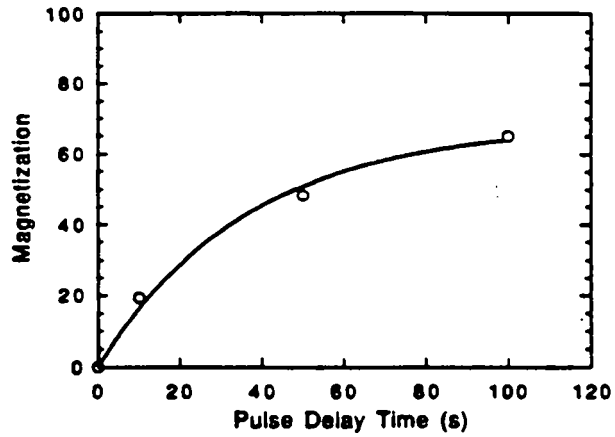

FIG. 1. The magnetization recovery of an α-quartz sample for times up to 100 s. The solid line is a theoretical fit assuming a 37.2 s exponential recovery. $M = M_0[1 - \exp(-t/T_1)]$.

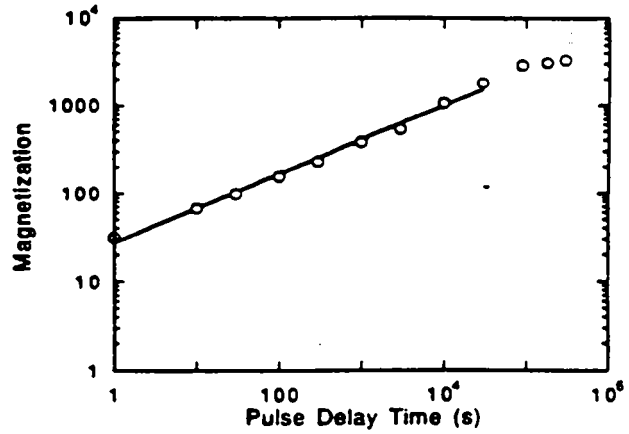

FIG. 3. The magnetization recovery of an α-quartz sample subjected to a 22 GPa shock wave. A power-law fit is shown, although the magnetization consists of components with differing relaxation behavior (see Fig. 4 and text). $M = At^a$, $a = 0.39$.

The spectra for both the unshocked and the shocked samples take a very long time to accumulate. We have considered methods by which this time can be reduced. Figure 5 shows the magnetization recovery versus pulse delay time of unshocked quartz samples with and without MAS. The recovery curve for the sample without MAS was obtained by allowing the sample to polarize while static and then applying MAS during the observation period. By eliminating MAS, nuclear spin diffusion is again effective and the relaxation rate increases dramatically. The magnetization recovery of the static sample is described reasonably well by a spin–lattice relaxation time of 3800 s. More importantly, the time to acquire a quantitatively correct spectrum is reduced an order of magnitude by application of this simple nonspin/spin sequence.

Figure 6 shows the relaxation time of the magnetization for the unshocked sample in zero field. These measurements were obtained by allowing the spins to polarize, removing the spins from the magnetic field for various periods of time, and then restoring the magnetic field and sampling their po-

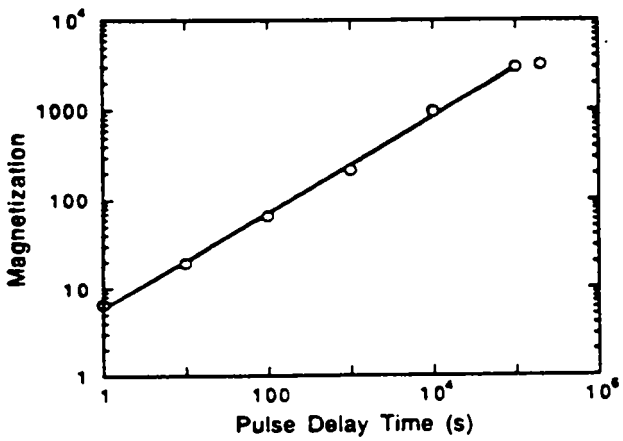

FIG. 2. The magnetization recovery of an α-quartz sample on a log-log scale. The recovery follows power-law behavior over five decades of time. $M = At^a$, $a = 0.54$.

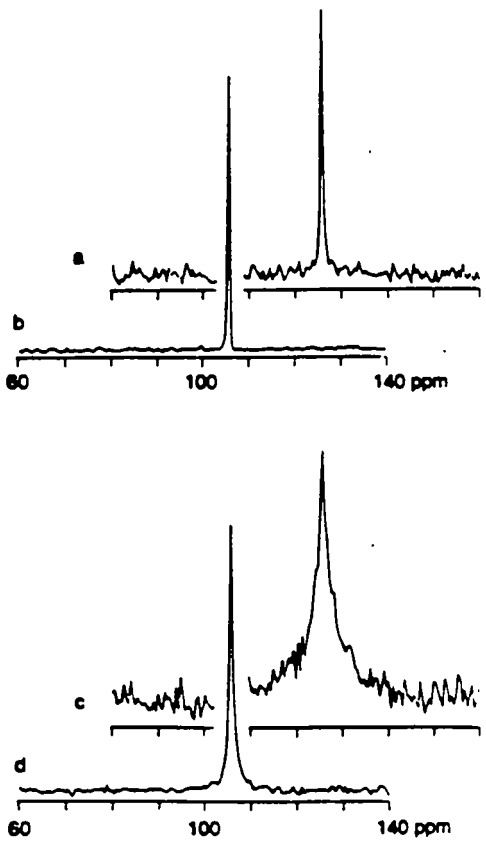

FIG. 4. Representative spectra of the unshocked α-quartz sample at (a) 10 s and (b) 100,000 s recovery times and of the shocked α-quartz sample at (c) 10 s and (d) 90,000 s recovery times.

larization. This adiabatic demagnetization/magnetization has been described previously (7). The relaxation time in zero field is approximately 130 s. This result suggests that one could simultaneously polarize several samples in a region of the magnet adjoining the probe or in a nearby magnet and then transport them to the probe for observation under MAS conditions.

MAS can quench the spin diffusion of dilute spin-$\frac{1}{2}$ nuclei in solids, thereby increasing the relaxation time and changing the functional form of the magnetization recovery. Recognition of this phenomenon is important when recording quantitative spectra and also suggests operational procedures by which the long times to record spectra of these materials may be reduced.

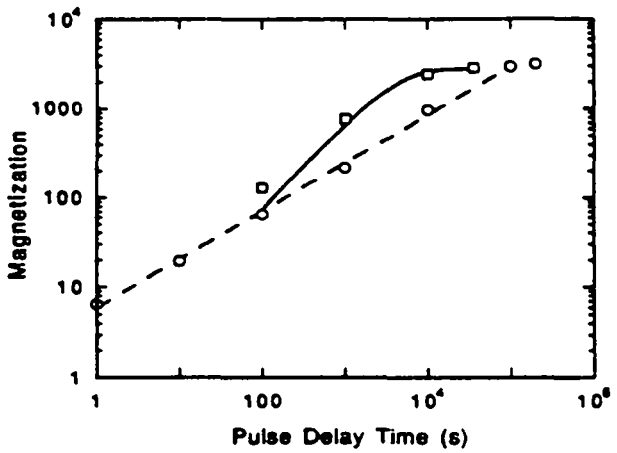

FIG. 5. The magnetization recovery of a static (——) α-quartz sample compared to that of the same sample undergoing MAS (---). The recoveries were fitted by exponential and power-law functions respectively. $M = M_0[1 - \exp(-t/T_1)]$. $T_1 = 3800$ s.

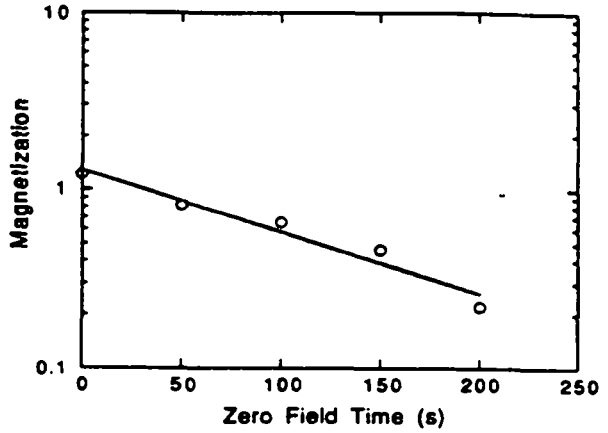

FIG. 6. The zero-field magnetization decay of an α-quartz sample. $M = M_0\exp(-t/T_1)$. $T_1 = 380$ s.

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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 offeres 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 μm (-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.

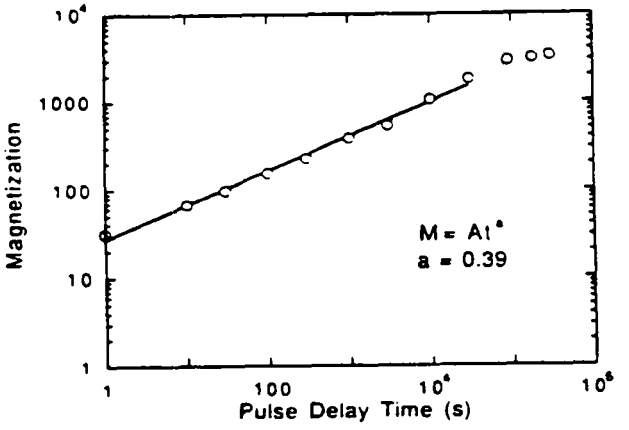

Figure 1. The magnetization recovery of an α-quartz sample on a log-log scale. The recovery follows power-law behavior over 5 decades of time.

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

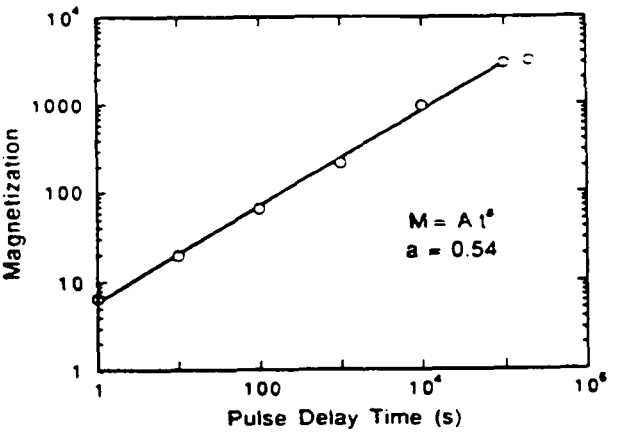

Figure 2. The magnetization recovery of an α-quartz sample subjected to a 22 GPa shock wave. A power-law fit is shown, although the magnetization consists of components with differing relaxation behavior (see Figure 4 and text).

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.

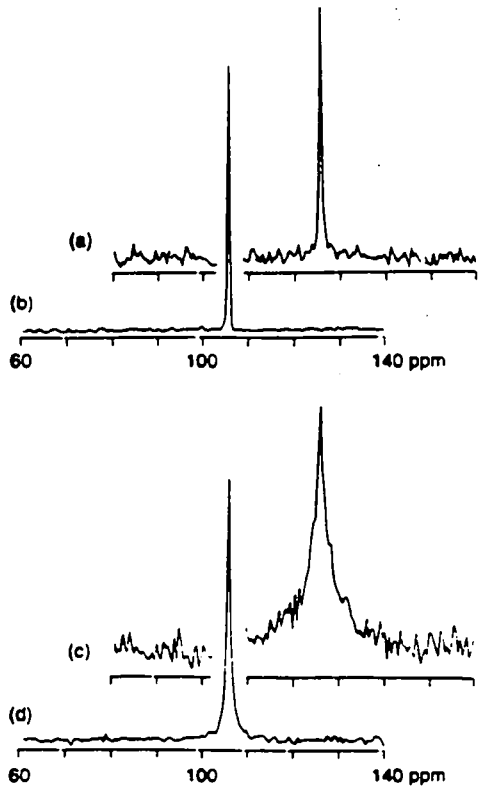

Figure 3. Representative spectra of the unshocked α-quartz sample at (a) 10 s and (b) 100,000 s pulse delay times and of the shocked α-quartz sample at (c) 10 s and (d) 90,000 s pulse delay times.

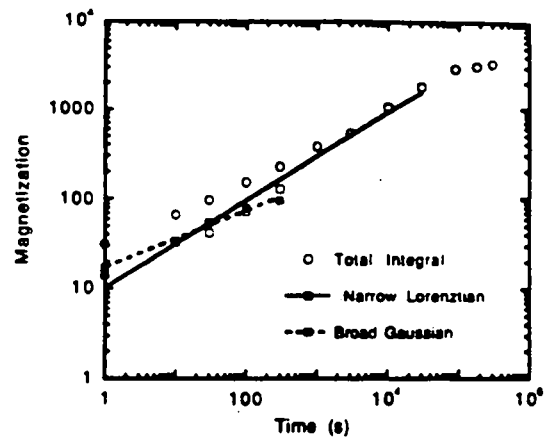

Figure 4. The magnetization recovery of an α-quartz sample subjected to a 22 GPa shock wave. Each spectrum has been deconvoluted into a narrow Lorenztian component corresponding to the ordered phase and into a broad Gaussian component corresponding to the disordered phase.

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.

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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NMR Characterization and Relaxation Analysis of Amorphous Material in Shocked Quartz*

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Amorphization can occur as a natural process when certain minerals undergo shock loading as a result of meteorite impacts. We have performed a series of controlled explosive shock-loading experiments on quartz powders. Subsequent analysis of the recovered shocked material by ^{29}Si NMR spectroscopy provides a new method for quantitative characterization of the amorphous/disordered silica component. In addition to a very narrow resonance associated with the shocked crystalline material, the spectra exhibit a broad component consistent with an amorphous phase, despite the absence of optical microscopic evidence for glass. The relative intensity of the broad resonance exhibits a strong correlation with known peak shock pressure, and can be used as a "shock barometer".

New NMR measurements over a wide range of recycle times (from 1 to 3×10^5 seconds) demonstrate that magnetization in both the amorphous and crystalline components follow power-law behavior as a function of recycle time. This observation is consistent with the relaxation of nuclear spins by paramagnetic impurities. The amorphous component has a shorter relaxation time than the crystalline phase, and therefore dominates the spectra for short NMR recycle times. It has previously been shown that a fractal dimension can be extracted from the power-law exponent associated with each phase. The fractal dimension determined in this way for the amorphous phase is about 2, as opposed to 3 for the crystalline phase.

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^{29}SI NMR SPECTROSCOPY OF NATURALLY-SHOCKED QUARTZ FROM METEOR CRATER, ARIZONA: CORRELATION TO KIEFFER'S CLASSIFICATION SCHEME

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We have applied solid state ^{29}Si nuclear magnetic resonance (NMR) spectroscopy to five naturally-shocked Coconino Sandstone samples from Meteor Crater, Arizona, with the goal of examining possible correlations between NMR spectral characteristics and shock level. This work follows our observation of a strong correlation between the width of a ^{29}Si resonance and peak shock pressure for experimentally shocked quartz powders [1,2]. The peak width increase is due to the shock-induced formation of amorphous silica, which increases as a function of shock pressure over the range that we studied (7.5 to 22 GPa). The Coconino Sandstone spectra are in excellent agreement with the classification scheme of Kieffer [3] in terms of presence and approximate abundances of quartz, coesite, stishovite, and glass. We also observe a new resonance in two moderately shocked samples that we have tentatively identified with silicon in tetrahedra with one hydroxyl group in a densified form of amorphous silica.

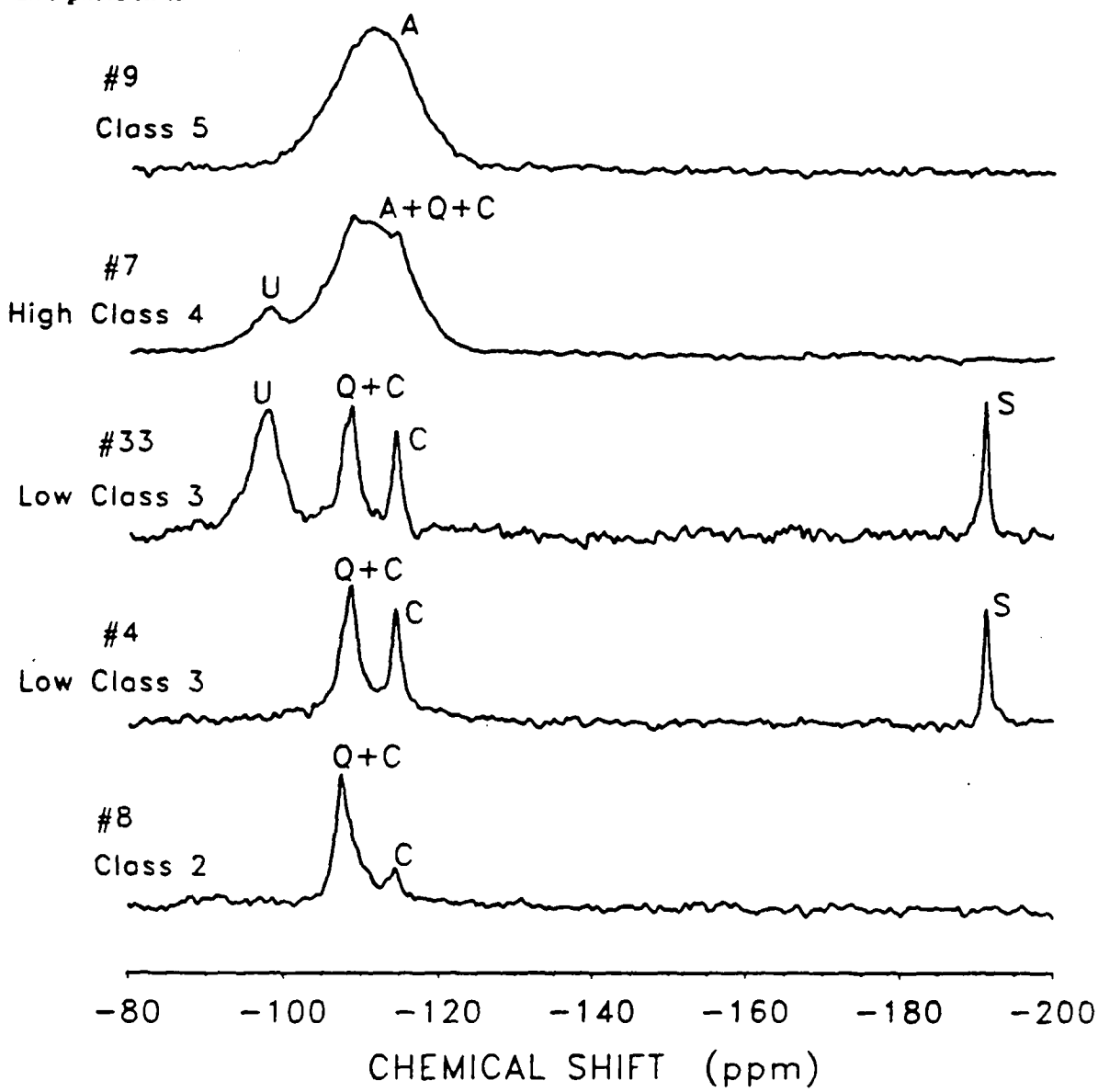

Figure 1. ^{29}Si NMR spectra of five shocked Coconino Sandstone samples. Resonance identifications are (Q) quartz, (C) coesite, (S) stishovite, (A) Q^4 sites in amorphous silica, and (U) unknown site tentatively identified as Q^3 (one OH) Si sites in a densified form of hydroxylated amorphous silica.

We have previously suggested that NMR spectra be used as a "shock barometer", or at least as an identification technique for shocked quartz. However, our measurements to date have been limited to laboratory-shocked samples. Because the duration of shock loading can be many orders of magnitude longer for large impacts, major differences are to be expected. To address these possible differences, we have now turned our attention to naturally-shocked samples. Application of solid state NMR spectroscopy to such samples has been limited. Smith and Blackwell [4] measured spectra of coesite and stishovite taken from shocked Coconino Sandstone as part of a comparative study of silica polymorphs. Yang *et al.* [5] showed that this technique is very sensitive to high-pressure silica phases from whole rock samples of shocked Coconino Sandstone, and is capable of yielding accurate coesite/stishovite ratios. McHone *et al.* [6] applied the technique to samples collected from the K/T boundary and reported the detection of trace amounts of stishovite, although this interpretation has been disputed [7].

In the present work, we obtained spectra for five samples of Coconino Sandstone representing shock classes 2-5 (Fig. 1). The following is a preliminary summary of our observations. **Class 2** (sample #8): mostly quartz, small amounts of coesite and possibly amorphous silica, no stishovite. **Class 3** (sample #4): mostly quartz, more coesite than sample #8, some amorphous silica, and stishovite. **Class 3** (sample #33): same as sample #4, but with an additional peak, possibly due to Q^3 (one OH) Si sites in a dense form of hydroxylated amorphous silica. **Class 4** (sample #7): mostly amorphous silica, with some quartz and coesite, no stishovite, contains a less intense peak possibly associated with the same Q^3 site as in sample #33. **Class 5** (sample #9): almost entirely amorphous silica, no stishovite. Of particular note are the surprisingly strong stishovite resonances in the Class 3 samples; the stishovite peak observed by Yang *et al.* [5] is significantly weaker. We also observed a more intense X-ray line ($2\theta = 30.2°$) for stishovite, implying there is more of this phase in our samples. The only samples for which we observe stishovite are those previously identified as Class 3.

The presence of an unidentified peak 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 Si in tetrahedra with one hydroxyl group in a dense form of hydroxylated amorphous silica: 1) The large intensity implies that, unless it is a major phase, it 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 Si 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 silica glass [9]. The resonance for Q^3 (one OH) Si sites in a normal-density gel is at about -102 ppm [10]. Our observed peak position of about -98 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 Si 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 Class 3 samples [11]. 5) We have observed in a previous NMR study of clinoptilolite that shock loading can generate hydroxyl groups [12].

Further work is required to confirm the identification of the unknown phase, and to answer other questions. NMR proton cross-polarization techniques can be used to enhance Si resonances near protons, as would be the case for this phase. NMR relaxation studies can provide characteristic fractal dimensions as has been done for amorphous material in experimentally-shocked quartz [13]. We are also in the process of obtaining NMR spectra for other naturally shocked samples, in particular for quartz from the K/T boundary, that may have seen a radically different loading and unloading history than the Meteor Crater samples.

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National Institute for Research in Inorganic Materials,
Tsukuba, Japan, March 14-17, 1994.

NMR Characterization of Shocked Quartz

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We have characterized experimentally and naturally-shocked quartz (both synthetic and natural samples) by solid state NMR spectroscopy. This method 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. In addition, NMR spectra have led to our discovery of a new amorphous hydroxylated silica phase in naturally shocked sandstone from Meteor Crater, Arizona.

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NMR Characterization of Shocked Quartz*

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ABSTRACT

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.

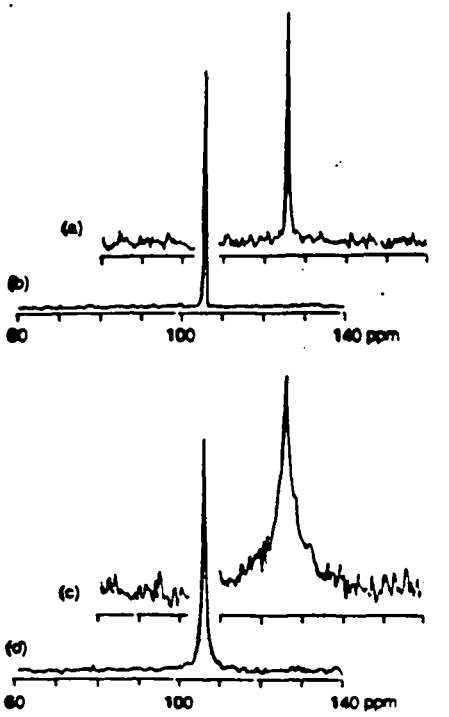

Figure 1. Spectra of unshocked α-quartz at (a) 10 s and 100,000 s and of shocked α-quartz at (c) 10 s and (d) 90,000 s delay time.

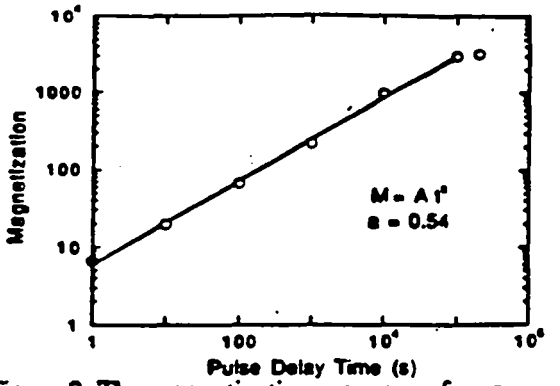

Figure 2. The magnetization recovery of an α-quartz sample on a log-log scale, which follows power-law behavior over 5 decades of time.

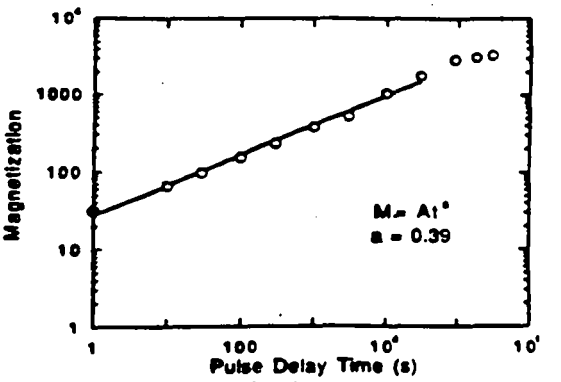

Figure 3. The magnetization recovery of α-quartz shocked to 22 GPa, which consists of components with differing relaxation behavior.

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

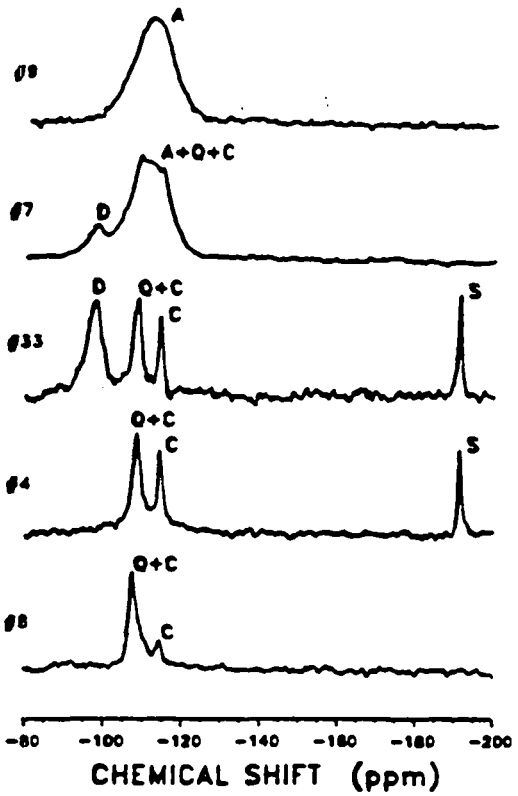

Figure 4. Si-29 NMR spectra of shocked sandstone, where Q=quartz, C=coesite, S=stishovite, A=amorphous (Q4 sites), and D=densified form of hydroxylated amorphous silica (Q3 sites). Sample numbers are those of Kieffer [4].

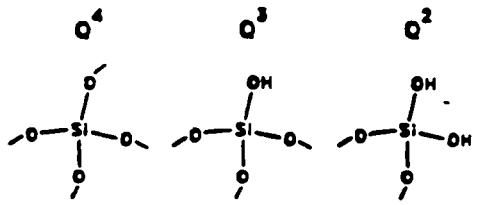

Figure 5. Silicon sites that are distinguished by Si-29 NMR spectroscopy using MAS and CPMAS methods

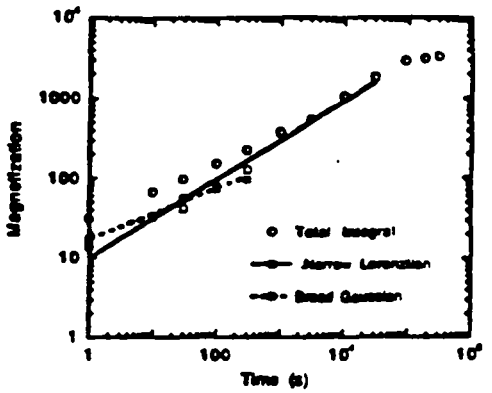

Figure 6. Magnetization recovery of α-quartz sample shocked to 22 GPa. Each spectrum was deconvolved into a narrow Lorentzian (ordered phase) and a broad Gaussian (disordered phase) component.

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

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

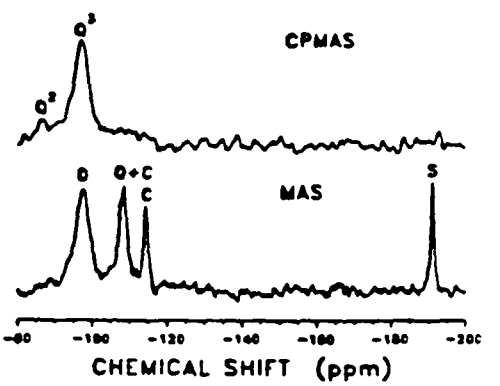

Figure 8. MAS and CPMAS Si-29 NMR spectra for Meteor Crater sample #33 exhibiting the hydroxylated Q3 and Q4 sites for silicon.

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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NMR SPECTROSCOPIC EXAMINATION OF SHOCKED SANDSTONE FROM METEOR CRATER, ARIZONA

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Solid state silicon-29 nuclear magnetic resonance (NMR) spectroscopy has been used to characterize the formation of high pressure silica polymorphs and amorphous material associated with the shocked Coconino Sandstone from Meteor Crater, Arizona. Five samples of the sandstone were obtained from several locations at the crater to represent a range of shock conditions associated with the hypervelocity impact of a 30 m-diameter meteorite. The NMR spectra for these powdered materials exhibit peaks assigned to quartz, coesite, stishovite, and glass. A new resonance in two of the moderately shocked samples is also observed. This resonance has been identified as a densified form of amorphous silica with silicon in tetrahedra with one hydroxyl group. Such a phase is evidence for a shock-induced reaction between quartz and steam under high pressure conditions.

INTRODUCTION

We have applied solid state ^{29}Si nuclear magnetic resonance (NMR) spectroscopy to five naturally-shocked Coconino Sandstone samples from Meteor Crater, Arizona, with the goal of examining possible correlations between NMR spectral characteristics and shock level. This study follows our observation of a strong correlation between the width of a ^{29}Si resonance and peak shock pressure for experimentally shocked quartz powders [1,2]. The peak width increase is due to the shock-induced formation of amorphous silica, which increases as a function of shock pressure over the range that we studied (7.5 to 22 GPa).

We have previously suggested that NMR spectra be used as a "shock barometer", or at least as an identification technique for shocked quartz. However, our measurements to date have been limited to laboratory-shocked samples. Because the duration of shock loading can be many orders of magnitude longer for large impacts, major differences are to be expected. To address these possible differences, we have now turned our attention to naturally-shocked samples. Application of solid state NMR spectroscopy to such samples has been limited. Smith and Blackwell [3] measured spectra of coesite and stishovite from shocked Coconino Sandstone as part of a comparative study of silica polymorphs. Yang *et al.* [4] showed that this technique is very sensitive to high-pressure silica phases from whole rock samples of shocked Coconino Sandstone, and is capable of yielding accurate coesite/stishovite ratios. McHone *et al.* [5] applied the technique to samples collected from the K/T boundary and reported the detection of trace amounts of stishovite, although this interpretation has been disputed [6].

Kieffer [7]. The spectra are presented in relative order of increasing shock pressure. 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 in different coordinations and to the Si-O-Si bond angle distribution. 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 Q^3 (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 Q^3 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 2.

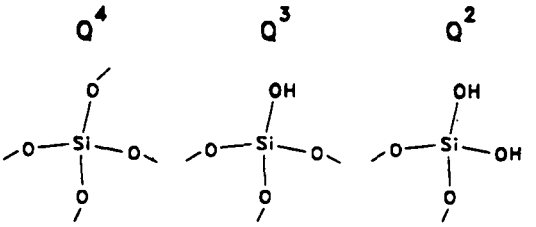

Figure 2. Silicon sites that are distinguished by ^{29}Si NMR spectroscopy using MAS and CPMAS methods.

DISCUSSION

Of particular interest in these results are the strong stishovite resonances in samples #4 and #33; the stishovite peak observed by Yang *et al.* [4] is significantly weaker. We also observe a more intense X-ray diffraction line ($2\theta = 30.2°$) for stishovite, implying 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 Q^3 (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

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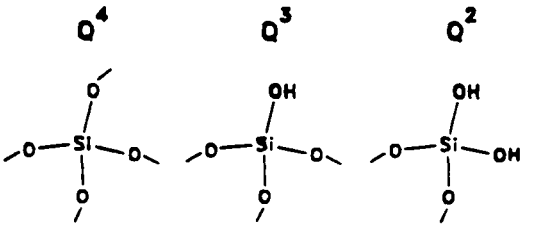

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The strongest evidence for the existence of a densified form of hydroxylated amorphous silica is provided by cross-polarization NMR experiments, referred to as CPMAS when using magic-angle spinning. Cross polarization transfers nuclear spin from protons to other NMR-active nuclei, thereby providing additional structural information and

preferentially eliminating spectrum signal from anhydrous phases. Figure 3 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 Q^3). A less intense peak at -86 ppm associated with Q^2 silicon is also observed in the CPMAS spectrum. No significant CPMAS signal is observed for sample #9; the "A" peak is due to Q^4 silicon in amorphous silica.

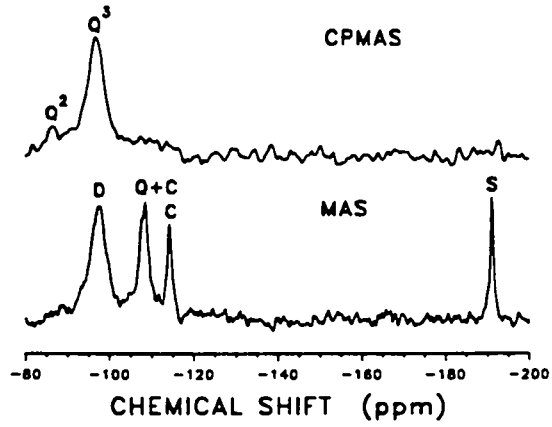

Figure 3. MAS and CPMAS ^{29}Si NMR spectra for Meteor Crater sample #33 exhibiting the hydroxylated Q^3 and Q^2 sites for silicon.

SUMMARY

Silicon-29 NMR spectroscopy can 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 we have identified a new naturally-occurring shock-produced phase—a densified hydrated amorphous silica.

ACKNOWLEDGMENTS

Susan Kieffer and John McHone kindly provided us with well-documented samples from Meteor Crater. Gary Turner obtained the NMR spectra. This work was supported by the Dept. of Energy under contract DE-AC04-76DP00789, with partial funding by NASA's PMG program.

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NMR SPECTROSCOPY OF EXPERIMENTALLY-SHOCKED COCONINO SANDSTONE AND THE EFFECT OF PORE WATER; R. T. Cygan[1], M. B. Boslough[1], and R. J. Kirkpatrick[2], [1]Sandia National Laboratories, Albuquerque, NM 87185 and [2]University of Illinois, Urbana, IL 61801

We have extended our solid state ^{29}Si nuclear magnetic resonance (NMR) spectroscopic study of shocked Coconino Sandstone from Meteor Crater, Arizona. Previously we showed that the NMR spectra of naturally-shocked samples taken from the crater are in excellent agreement with the classification scheme of Kieffer [1], and we identified a new hydroxylated amorphous phase [2,3]. To follow up that work, we have now collected data on Coconino Sandstone explosively shocked to independently-known pressure-temperature states. In addition, we performed identical explosive loading experiments on water-saturated samples to characterize the effects of groundwater in a natural impact. The magic-angle spinning (MAS) spectra for the shocked sandstone powders exhibit no additional phases; resonances for coesite and stishovite are not observed. However, a broadening of the quartz resonance is exhibited for both dry and wet samples relative to the narrow resonance for quartz in the unshocked material. The cross-polarization magic-angle spinning (CPMAS) NMR experiments exhibit an enhanced single resonance, probably associated with hydroxylated silicon in kaolinite clay. This peak broadens with shock-loading for both dry and wet samples. There is no clear distinction between the NMR spectra obtained for the dry and wet samples recovered from the shock-loading experiments.

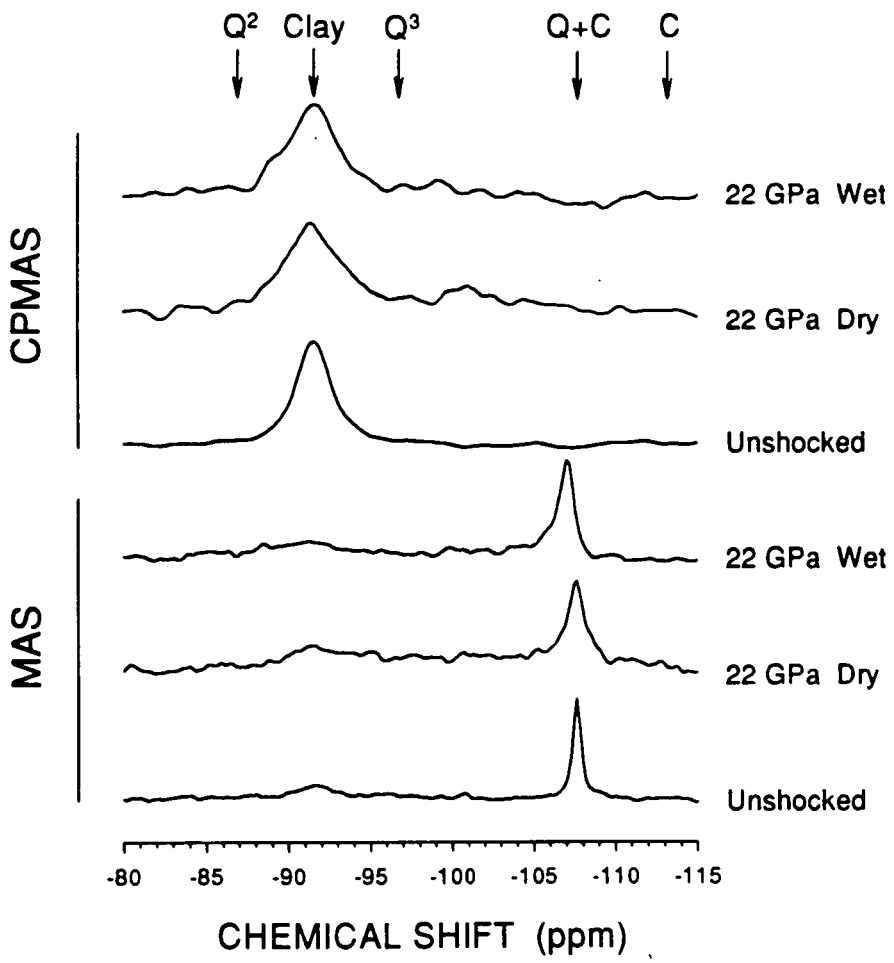

Figure 1. ^{29}Si NMR spectra of unshocked and experimentally-shocked (dry and wet) Coconino Sandstone samples. MAS (all Si sites) and CPMAS (hydrated Si species) spectra are presented for each sample. Arrows denote approximate chemical shift observed in previous studies [2,3] for quartz (Q), coesite (C), clay, and hydrated amorphous silica, including Q^3 (one OH) and Q^2 (two OH) silicon sites.

The present work is part of a continuing project to develop solid state NMR spectroscopy as a method of quantifying the effect of shock loading experienced by silicate minerals subjected to natural impact. We have previously suggested that NMR spectra be used as an unambiguous identification technique for shocked quartz, and have shown that it can be used as a "shock barometer" under some conditions [4,5]. In addition to finding a new densified amorphous phase, we have shown that NMR relaxation analysis can provide morphological information about shock-produced amorphous material [6]. However, our measurements to date have been limited to laboratory-shocked synthetic quartz samples, and to naturally-shocked sandstone. Moreover, other workers have obtained quantitatively different results using different starting materials (single crystals as opposed to powder) and different loading conditions [7]. By subjecting Coconino Sandstone to the same shock-loading histories as pure synthetic quartz in our earlier work, we are beginning to bridge the gap between natural and artificial shock-loading histories to help understand the differences. In addition, by using initially water-saturated samples, we attempt to 1) isolate the effect of the presence of water and 2) find out if the dense amorphous hydroxylated phase we found in naturally-shocked sandstone can be synthesized in the laboratory, and if so, under what conditions.

Samples of unshocked Coconino Sandstone were obtained from near Meteor Crater, Arizona and were subjected to explosive loading using the Momma Bear fixtures of Graham and Webb [8]. Wet experiments were performed by first saturating the sandstone powder with deionized water before sealing the copper sample fixture. The dry powder samples were subjected to peak shock pressures of approximately 7.5, 16.5, and 22 GPa. The corresponding pressure values for the wet sandstone samples are somewhat higher. The recovered materials were examined by optical and secondary electron microscopies, X-ray diffraction, and NMR spectroscopy. We use both standard MAS and CPMAS techniques in the NMR experiments to determine the resonances associated with ^{29}Si nuclei. Cross polarization transfers nuclear spin from protons to the ^{29}Si, thereby providing additional structural information and preferentially eliminating spectrum signal produced by anhydrous phases.

The MAS and CPMAS spectra obtained for the shocked sandstone samples do not exhibit any additional resonances compared to the spectra for the unshocked sample (Figure 1). Resonances for coesite (-108 ppm and -113 ppm) and stishovite (-192 ppm) are not observed. The strong four-fold coordinated silicon resonance, with a chemical shift of -108 ppm, dominates the MAS NMR spectra. A broadening of the quartz resonance for both dry and wet samples is observed with increasing shock pressure. These results are similar to our previous work on dry synthetic quartz powders [4,5]. A minor resonance in the MAS spectra, corresponding to the major resonance in the CPMAS spectra, is observed at -92 ppm. These resonances are associated with the hydroxylated silicon site in clay, probably kaolinite; X-ray diffraction analysis of the recovered material confirms this assignment. Some broadening of the clay CPMAS resonance occurs with increasing shock pressure for both dry and wet samples. There is no clear evidence for the formation of a dense hydroxylated amorphous phase in the material recovered from the wet shock-loading experiments. We previously observed for several naturally-shocked samples from Meteor Crater a very strong resonance with a chemical shift of -97 ppm, corresponding to Q^3 silicon [2,3]. These differences in the NMR spectra are related to the distinct loading and unloading histories associated with experimental shock-loading and natural impact events.

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