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Analysis of Experimentally Shocked Minerals by NMR Spectroscopy

Randall T. Cygan, Mark B. Boslough

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ANALYSIS OF

EXPERIMENTALLY SHOCKED MINERALS

BY NMR SPECTROSCOPY

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ABSTRACT

The shock-loading of natural materials by an impact or explosion can result in the formation of modified and altered phases. 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 experimentally shocked minerals. In three related NMR studies we have 1) examined shocked clinoptilolite, 2) performed a preliminary analysis of shocked quartz, and 3) reproduced our shocked quartz results with detailed spectral deconvolutions, and extended it with NMR analysis of shocked feldspar powders.

We subjected clinoptilolite, a common zeolite mineral associated with the alteration of volcanic glass by meteoric waters, to a series of controlled shockloading experiments. These recovery experiments were performed by shocking powdered natural clinoptilolite samples from Rainier Mesa, Nevada to mean peak pressures of 7.5, 16.5, and 22 GPa using chemical explosives. Silicon-29 magic-angle spinning NMR spectra were obtained for the unshocked material and each of the powders recovered from the shock experiments. The unshocked clinoptilolite NMR spectrum exhibits several overlapping resonances with chemical shifts ranging from -96 ppm to -112 ppm (center of resonance). NMR spectra of the shocked samples exhibit dramatic peak broadening with increasing pressure. In addition, the chemical shift becomes less negative suggesting a decrease in the Si-O-T angles (T = tetrahedral cation). Transmission electron microscopy (TEM) and cross polarization NMR examination of the 22 GPa sample also indicate the formation of a hydrous amorphous phase. These results suggest that the zeolite structure undergoes progressive changes with increasing shock pressure, including compression of the structure and partial transformation to a disordered phase.

Our first ²⁹Si magic-angle spinning (MAS) NMR spectra of synthetic quartz powders recovered from shock experiments at mean pressures of 7.5, 16.5, and 22 GPa indicate that the NMR technique is very sensitive to shock pressure. All of the shocked powders and the starting material have similar values for the refractive indices. The (101) X-ray diffraction peak of quartz broadens only slightly with shock pressure, at most by a factor of 1.7. By comparison, the ²⁹Si

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NMR spectra exhibit a nearly five-fold increase in relative peak width at the highest shock pressure. We concluded that the NMR peak is most likely the result of disordering and residual strain in the quartz lattice and the formation of an amorphous silica phase, and that the calibration of the NMR peak widths with shock pressure provides a very sensitive shock barometer for the determination of pressures associated with experimentally-shocked quartz powders. This work led us to seek potential applications including shock barometry using minerals from natural impacts, as well as materials subjected to shock by nuclear tests.

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Further work on annealed samples replicates the preliminary work and confirms that MAS NMR spectroscopy is an extremely sensitive and reproducible probe of disorder in synthetic quartz powder samples that have been experimentally shock-loaded to peak pressures up to 22 GPa. Curve fitting and deconvolution of ²⁹Si NMR spectra of shocked quartz led to four primary observations: 1) the width of the resonance increases systematically with shock pressure, indicating a greater distribution of local silicon environments caused by shock-induced disorder; 2) a much broader peak component appears indicating the presence of highly disordered material, which TEM observation indicates may be due to very high dislocation densities; 3) the inferred disordered material appears to have a significantly shorter T_1 relaxation time than the crystalline material; and 4) there is no evidence for the presence of high pressure silica phases (coesite or stishovite) in the shocked samples. The net effect of shock-loading on the ²⁹Si NMR spectrum of quartz is an increase in peak width that strongly and consistently correlates with known shock pressure. Peak width is therefore a useful "shock barometer" for quartz in this pressure range for the experimental loading conditions. By contrast, ²³Na, ²⁷AI, and ²⁹Si MAS NMR spectra of shocked and unshocked An₆₀ plagioclase feldspar powders do not change significantly with increasing shock pressure. There is no evidence for either amorphous or high pressure phases in the plagioclase spectra for shock pressures up to 22 GPa.

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PART I EXAMINATION OF SHOCKED CLINOPTILOLITE BY NMR SPECTROSCOPY

INTRODUCTION

Highly modified phases can result from the shock-loading of minerals, in particular, those minerals associated with natural impact or nuclear testing. Shocked minerals typically exhibit fracturing, planar deformation, comminution, disordering, lamellae, and possibly new phases. The new phases may include fused glass, diaplectic (shock-induced) glass, high pressure polymorphs, or other reaction products. The extent to which these shock-induced features form strongly depends on the peak shock pressure. Shock temperature, rate of shock compression, composition, and density (porosity) of the material also contributes to the shock metamorphism of the target material.

Studies of the effect of shock in minerals have traditionally relied on the qualitative examination of microstructures by optical and electron microscopies (for example, Chao, 1968; Hörz, 1968). Additional determinations including refractivity, density, X-ray diffraction, infrared absorption, X-ray photoelectron spectroscopy, and electron paramagnetic resonance (EPR) have been used to characterize the physical and chemical state of the shocked mineral. Stöffler (1984) provides a comprehensive summary of these different diagnostic techniques. Additional details are provided in Part II and by Cygan *et al.* (1990, 1992).

One goal of many of these previous diagnostic and characterization studies was to develop a sensitive technique for quantifying the extent of shock deformation in the mineral — the development of a shock barometer. Although most of this work has examined materials recovered from experimental shocks and from natural impacts sites such as Meteor Crater, Arizona and Vredefort Dome, South Africa, little emphasis has been placed on the examination of shocked minerals associated with nuclear testing sites. The accurate scaling of stress decay

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associated with nuclear testing would be a significant contribution to the development of a shock barometer based on shocked minerals. Such a technique would be helpful in the post-test analysis of shock pressure exposure of rock samples. It could be used in conjunction with real-time stress probes and sensors that collect data during the test, or for post-test analysis when real-time evaluation is lacking or has failed.

There is only one previous study that has considered the use of natural minerals for quantifying the extent of shock loading associated with a nuclear test. Vizgirda *et al.* (1986) recently examined the hyperfine EPR splitting of Mn²⁺ in calcite from shocked coral samples from Cactus Crater at the Pacific test site. It was hoped that EPR would provide a basis for a shock barometer for examining the shock effects of the nuclear test. However, their results do not conclusively define a reproducible trend between hyperfine peak splitting and shock pressure.

The goal of the present study is to examine the zeolite mineral clinoptilolite obtained from the Nevada Test Site and test the possible use of nuclear magnetic resonance (NMR) spectroscopy as a diagnostic tool for shock modification. Based on the success of a NMR shock barometer for experimentally-shocked quartz (see Part II and Part III), we intend to determine the usefulness of the technique for examining a more complex mineral such as clinoptilolite. We use solid state ²⁹Si NMR spectroscopy to examine clinoptilolite powders shocked to pressures of 7.5 to 22 GPa. The NMR technique involves monitoring radio frequency re-emissions from ²⁹Si nuclei while the sample is in a very strong magnetic field (see Kirkpatrick, 1988). The resonance frequencies are sensitive to the local electronic (that is, structural) environment of silicon in the material, and provide information about the range of silicon environments resulting from shock modification. NMR frequencies are particularly sensitive to the nearest and next-nearest neighbor environment of the ²⁹Si.

Clinoptilolite is probably the most abundant natural zeolite in crustal rocks. It occurs as an alteration product of silicic volcanic glass associated with the rhyolitic tuffs of the Great Basin and Basin and Range physiographic provinces of the western United States (Smyth *et al.*, 1990). Clinoptilolite is a major component of the tuffs at the Nevada Test Site located in southern Nevada and can compose up to 90 % of the geologic media in which underground testing of

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nuclear weapons is done. In addition, Yucca Mountain, also in Nevada and the site for the United States high-level radioactive waste repository, is dominated by clinoptilolite-rich tuff at the proposed repository horizons (Broxton *et al.*, 1987).

EXPERIMENTAL METHODS

The starting material for the shock recovery experiments is a natural clinoptilolite collected from Rainier Mesa at the Nevada Test Site. Rainier Mesa is the site of numerous nuclear tests and is predominantly comprised of Tertiary-age argillaceous volcanic tuff that has been extensively zeolitized (Ekren, 1968). The clinoptilolite sample was obtained from core stored at the United States Geological Survey Core Library located in Mercury, Nevada. A 12-cm section of the 5-cm diameter core was selected and corresponds to a depth of 14.6 m (47.9 feet) for the U12 n.18 UG-2 horizontal pre-shot drill hole associated with the Middle Note test of 1990.

The core sample was processed by first crushing it by hand in an alumina mortar and then sieving the resulting grains to a size range 70 to 150 μ m. Powder X-ray diffraction analysis suggests that the Rainier Mesa sample is composed of approximately 85 % clinoptilolite, 12 % sanidine, and the remainder cristobalite and possibly phlogopite. Heavy liquid separation using bromoform and acetone mixtures was used to isolate the clinoptilolite material from the remaining core minerals. The clinoptilolite mineral is less dense (observed density = 2.15 g/cm³) than the other phases and is easily separated. The separated clinoptilolite phase was washed successively in acetone, deionized water, then again in acetone; all in a sonic cleaning bath. Approximately 60 grams of the processed clinoptilolite powder were obtained. X-ray diffraction analysis of this starting material indicated that the sample was comprised of clinoptilolite with no evidence of contaminating phases.

The chemical analysis of the clinoptilolite used for the shock experiments is presented in Table 1. A general analysis was performed by XRAL Activation Services of Ann Arbor, Michigan using X-ray fluorescence technique for the major elements and a variety of methods for the trace elements: direct current plasma emission for B and Mn, combustion and spectroscopic titration (LECO method) for S, standard wet chemistry for Cl, F, and Li, and X-ray fluorescence for the other trace elements. In addition, several electron microprobe analyses were obtained with a JEOL JXA-8600 microprobe using a 1-16 μ m² rastered beam at 15 kV and 4 nA current, and standard data reduction techniques (Bence

Oxide	XRF and Wet Analysis (Weight %)	Electron Microprobe Analysis ¹ (Weight %)	Cation	per 72 Oxygens ²
Major Elements				
SiO ₂	67.5	64.61	Si	29.64
TiO ₂	0.12			
Al ₂ O ₃	12.1	12.12	AI	6.55
Fe ₂ O ₃ (total Fe)	0.93			
FeO (total Fe)		0.13	Fe	0.05
MnO	0.05			
MgO	0.22	0.10	Mg	0.07
CaO	1.12	1.24	Ca	0.61
Na₂O	2.91	2.47	Na	2.19
K₂O	3.97	3.67	к	2.15
P ₂ O ₅	0.02			
H₂O (loss on ignition)	10.3			
Total	99.30	84.34		
H ₂ O (difference)		15.66	H₂O	24.00
Trace Elements (ppm)				
В	10			
Ba	150			
CI	1200			
Cr	<10		Note: Si/AI = 4.5	53
Li	10		(Na + K) >	> Ca
Nb	30			
Rb	170			
S	<100			
Sr	60			
Y	20			
Zr	90			

Table 1. Chemical analysis of Rainier Mesa clinoptilolite

¹Average of 13 analyses ²Recalculated for charge balance

and Albee, 1968). The rastered beam and fairly low current were used to minimize the loss of alkali elements during analysis. The electron microprobe values were used to determine a structural formula for the clinoptilolite based on 72 oxygen atoms; the formula values are provided in Table 1. The calculated density based on this structure is 2.18 g/cm³ and is in good agreement with the observed value of 2.15 g/cm³.

To evaluate the dynamic response of clinoptilolite to shock-loading, it is helpful to first examine the crystal structure of this fairly complex aluminosilicate phase. Additionally, the crystal chemistry behavior is important for understanding how clinoptilolite reacts with bound molecular water under high dynamic pressures. The crystal structure of clinoptilolite has recently been examined by Smyth et al. (1990) and Armbruster and Gunter (1991). Clinoptilolite is isostructural with the mineral heulandite and has a chemical formula that is characterized by cation substitution: (Ca, Na, K)₄₋₆ Al₆ (Al,Si)₄ Si₂₆O₇₂•24H2O. It belongs to the monoclinic crystal system with a = 17.633 Å, b = 17.941 Å, c = 7.400 Å, and β = 116.39° (Smyth et al., 1990). Clinoptilolite is distinguished from heulandite by having the alkali content dominant (Na + K > Ca) and Si/Al value greater than 4 (Boles, 1972) (see Table 1). The structure of clinoptilolite is defined by a primary frame made up of SiO₄ and AIO₄ tetrahedra that link together by corner sharing to form a connected three-dimensional network. The negative charge of the zeolite frame is balanced by cations that occupy the cavities. Some of these interconnected cavities are large enough to accommodate molecular water. Clinoptilolite possesses two open cavities that are defined by ten and eightmembered tetrahedral rings. Figure 1 provides a schematic of the structure of clinoptilolite showing these large cavities for the exchangeable cations (Na⁺, K^+ , and Ca²⁺) and waters.

The shock recovery experiments on the clinoptilolite powder were performed using the Sandia "Momma Bear" explosive loading fixtures to provide wellcharacterized shock states. The recovery fixtures allow samples to be shocked in a controlled and reproducible manner. A schematic of the explosive loading fixture is presented in Figure 2. Peak shock pressures and temperatures are determined by numerical simulations based on the geometry of the sample holder and the impedance of the powder. Graham and Webb (1984, 1986) provide details of the shock-loading experiment and the numerical simulations.

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Figure 1. Clinoptilolite structure as viewed down the c-axis showing the two cavities for exchangeable cations and water. The framework is comprised of silicon and aluminum tetrahedra. Crystal structure data taken from Smyth *et al.* (1990).



Figure 2. Schematic of "Momma Bear" explosive loading fixture for sample recovery.

Mean-bulk shock temperatures are determined in part by the initial packing density of the clinoptilolite powders. The mean peak shock pressures are 7.5, 16.5, and 22 GPa, and the mean bulk temperatures range from 75°C to 675°C. The range of pressures and temperatures presented in Table 2 are due to nonuniaxial loading; the variables have a radial dependence as determined by the numerical simulations. Samples to be analyzed were taken from a region with weak radial dependence (according to the simulations) and with pressures and temperatures close to the mean values. The use of two different packing densities for each shock pressure provided a low (75°C to 450°C) and a high temperature (250°C to 675°C) set of shocked samples. These temperatures are below the thermal stability limit for clinoptilolite as determined by Koyama and Takeuchi (1977). General details on the use of shock recovery fixtures are provided in the comprehensive review of Graham (1993).

Numerous analytical techniques, in addition to optical microscopy, were used to examine the starting material and the shock-loaded clinoptilolite. The X-ray diffraction patterns were obtained using Cu K_{α} X-ray radiation and a Phillips diffractometer with powders prepared on aluminum slides. Diffraction scans were performed from 5° to 60° 20 at scan rate of 1° 20/min. A JEOL JSM-T300 scanning electron microscope (SEM) at 25 kV was used to examine the morphologies of the shocked clinoptilolite powders. Transmission electron microscope (TEM) images were obtained using a JEOL 2000FX microscope operating at 200 kV. Sample mounts for the TEM work required thin foils prepared by mixing 0.5 g of the powder with Epon 828 epoxy. The mixture was poured into a cylindrical mold, centrifuged, ground, cut, then ion thinned. Electron diffraction was used for identification of crystalline phases. Semi-quantitative analyses for both SEM and TEM samples were obtained using X-ray energy dispersive spectroscopy.

The ²⁹Si NMR spectra were obtained at a frequency of 71.5 MHz ($H_o = 8.45$ T) under magic-angle spinning (MAS) conditions (see Yang *et al.*, 1986; Kirkpatrick *et al.*, 1986a; Oestrike *et al.*, 1987; Kirkpatrick, 1988). MAS frequencies were typically 2.8 kHz. A pulse Fourier transform method was used to obtain the NMR spectra by first detecting signals in the time domain, then transforming the data to yield spectra in the frequency domain. The resonance frequencies are reported as chemical shifts, which are ppm deviation of the resonance frequency

Shot	Fixture	Explosive	Sample Compact Density (Mg/m ³)	Sample Compact Density (%)	Peak Pressure (GPa)	Estimated Mean Bulk Temperature (°C)
1B917	Momma Bear	Baratol	1.16	53	5-10	250-300
2B917	Momma Bear	Comp B	1.15	52	13-20	450-600
3B917	Momma Bear-A	Comp B	1.17	53	18-26	425-675
4B917	Momma Bear	Baratol	1.50	68	5-10	75-100
5B917	Momma Bear	Comp B	1.48	67	13-20	150-350
6B917	Momma Bear-A	Comp B	1.48	67	18-26	225-450

Table 2. Schedule of shock recovery experiments for clinoptilolite

from that of standard (tetramethylsilane in this case). ²⁹Si occurs at a natural abundance of only 4.7 % and requires significant number of NMR scans in order to obtain a good spectrum with the appropriate signal-to-noise ratio. Approximately 6 hours of MAS NMR time are required to obtain each ²⁹Si spectrum.

RESULTS

The unshocked clinoptilolite sample provides a baseline for interpretation of the six powders resulting from the experimental shock loading. The unshocked sample is representative of one of the principal mineral phases that would be expected in the zeolitized tuff at the Nevada Test Site prior to any test detonation. Figure 3 provides the MAS NMR spectrum for the unshocked clinoptilolite. Intensity of the magnetization is recorded as a function of the chemical shift as noted in the ppm change relative to the tetramethysilane reference. The position of a resonance is related to the local bonding and the extent of magnetic shielding associated with the ²⁹Si nuclei in the sample. Therefore, the coordination number of the silicon and the association of nearest neighbors determine the chemical shift. Because silicon occurs primarily in the four-coordinated tetrahedral sites in almost all minerals, the silicate minerals such as clinoptilolite will have NMR spectra determined by the nearest neighbor effects (Kirkpatrick et al., 1985). An additional effect related to the Si-O-Si or Si-O-Al angle will also determine the chemical shift associated with silicate minerals (Pettifer, et al., 1988). In general, the larger the Si-O-T angle, where T represents either Si or Al, one can expect more shielding of the ²⁹Si nuclei, a lower density, and a chemical shift to lower frequencies (a greater negative chemical shift). Conversely, for a smaller Si-O-T angle, the ²⁹Si NMR spectra will be shifted to higher frequencies.

The unshocked clinoptilolite is characterized by a ²⁹Si MAS NMR spectrum with overlapping resonances having measurable intensity ranging from -86 ppm to -118 ppm. A least-squares deconvolution of the spectrum using Gaussian peak shapes suggests the existence of four distinct resonances. The resonance centered at the low frequency chemical shift of -113 ppm represents a silicon site associated with a tetrahedron that is bonded to four other silicon tetrahedra. We use the notation of Si(0AI) to distinguish this type of silicon from others that are coordinated to aluminum tetrahedra. The additional resonances occur at smaller chemical shifts (greater frequencies) and represent the Si(1AI), Si(2AI), and Si(3AI) sites in clinoptilolite for coordination with respectively one aluminum and three silicon tetrahedra, two aluminum and two silicon tetrahedra, and three aluminum and one silicon tetrahedra. Due to the relatively high Si/AI value for the Rainier Mesa clinoptilolite (Table 1) the other silicon sites are less common



Figure 3. ²⁹Si MAS NMR spectrum for unshocked clinoptilolite starting material and deconvolution of spectrum with four Gaussian peaks. Assignment of deconvolved peaks to silicon tetrahedral sites is indicated.

and therefore the Si(1AI) centered at -106 ppm will dominate the NMR spectrum.

We follow the convention and assignments of Nakata et al. (1986) and Wilson (1987) in identifying the silicon sites for the unshocked clinoptilolite, however, based on the structural analysis of Koyama and Takeuchi (1977) these assignments may be misleading (Kirkpatrick, personal communication). The Xray refinement of the clinoptilolite structure indicates there are five Si-O-T bond angles that would occur for each of the five unique silicon sites. Therefore one would expect a distribution of sites associated with these different bond angles for Si(OAI), Si(1AI) and so on. The chemical shift range associated with the angle distribution will be similar to the chemical shift expected for the nextnearest-neighbor differences (approximately 5 ppm for each additional Al tetrahedra). As an example of this interpretation, the large broad peak centered at -107 ppm in Figure 3 would represent the overlap of signals from silicon associated with two different bond angles at a Si(1AI) site and with two different bond angles at a Si(0AI) site. The additional broad peaks of Figure 3 can be similarly analyzed and the net result would be a complex overlap of silicon site distributions and a considerably broadened spectrum with no unique solution for a deconvolution.

Additional evidence for the disputed peak assignments for the clinoptilolite spectrum is found in the analysis of the integrated areas of the deconvolved peaks. Assuming that there are no Al-O-Al linkages present in the material (Lowenstein's rule) it is possible to calculate the Si/Al ratio from these data (Fyfe *et al.*, 1983; Klinowski, 1988):

$$(Si / AI)_{NMR} = \sum_{n=0}^{4} I_{Si(nAI)} / \sum_{n=0}^{4} 0.25 n I_{Si(nAI)}$$
(1)

Isi(nAI) is the integrated intensity of the NMR signal attributed to Si(nAI) units from OAI to 4AI. The calculation for the Rainier Mesa clinoptilolite provides a Si/AI value of 2.94 and is significantly smaller (and more appropriate for a heulandite zeolite) than that obtained by chemical analysis (Si/AI = 4.53; Table 1). Certainly, the distribution of bond angle chemical shifts among the next-nearest neighbor assignments would confuse this analysis (see above); the AI-O-AI linkage assumption is probably valid due to the low aluminum content of the

clinoptilolite. A complete analysis of this distribution of silicon sites is quite complex, probably non-unique, and is beyond the scope of this study. The following discussion will rely on the spectral characteristics and not the peak assignments. Therefore, we provide the original interpretation of Nakata *et al.* (1986) in Figure 3 as a first order evaluation of the silicon sites in the clinoptilolite structure.

Figures 4 and 5 provide, respectively, the ²⁹Si MAS NMR spectra for the low and high temperature samples of the shocked clinoptilolite. The unshocked spectrum from Figure 3 is provided in each figure for reference. The NMR spectrum is observed to broaden significantly with shock pressure in both cases. This broadening is somewhat more significant for the high temperature samples where also the signal-to-noise ratio has been considerably degraded. The 22 GPa high temperature sample fails to exhibit any of the resolvable structure associated with any of the other spectra. The measurable NMR signal for the 22 GPa sample at both shock temperatures ranges from approximately -80 ppm to -120 ppm, considerably expanded from the chemical shift range associated with the unshocked clinoptilolite. In addition, there is a shift in the NMR intensity to higher frequencies (centered on -100 ppm) with increasing shock pressure.

X-ray diffraction patterns of the shocked clinoptilolite powders were obtained to monitor the mineralogical changes that may have resulted from the shock loading. None of the shocked samples exhibits any diffraction evidence of reaction or breakdown as a result of the shock. No additional peaks are observed relative to the diffraction pattern for the starting material. Measured patterns were compared to the standard pattern for a clinoptilolite zeolite from Agoura, California (JCPDS #39-1383). Significant broadening of the diffraction peaks in the 20° to 30° 20 range is observed for the shocked powders, in particular for the 16.5 GPa and 22 GPa samples. This is the result of residual strain, increase in dislocation densities, and decrease of crystal domain size due to shock loading (Hörz and Quaide, 1973; Schneider *et al.*, 1984). There is also a significant decrease in the signal-to-noise ratio and related decrease in the quality of the diffraction patterns with increasing shock pressure. There is no obvious distinction between the X-ray diffraction patterns obtained for the low and high shock temperature samples.



Figure 4. ²⁹Si MAS NMR spectra for unshocked starting material and shocked clinoptilolite powders obtained for the low shock temperature set of recovery experiments.



Figure 5. ²⁹Si MAS NMR spectra for unshocked starting material and shocked clinoptilolite powders obtained for the high shock temperature set of recovery experiments.

Optical microscopy and SEM examinations of the shocked clinoptilolite indicate a moderate amount of disaggregation occurred during shock loading. No apparent change in the refractive index was observed. TEM observation of the 22 GPa high temperature shocked clinoptilolite sample indicates that some of the material has transformed to an amorphous phase with shock loading. This sample has a significant proportion of amorphous material although it was difficult to estimate the exact amount due to the heterogeneity of the shockinduced deformation. No amorphous material was observed for the unshocked sample. Energy dispersive analysis of the amorphous material confirms that the composition is the same as for the crystalline clinoptilolite. Electron beaminduced amorphization is a typical response of hydrated minerals with TEM analysis. Although both unshocked and shocked samples display this behavior, beam exposure time was usually limited to less than ten seconds. Electron diffraction patterns were obtained during this short period to confirm crystallinity before the transformation to an amorphous material occurred. Using this approach we were able to conclusively determine the occurrence of the amorphous material in the 22 GPa high temperature sample to be the result of shock loading. No TEM examination of the other shocked clinoptilolite powders was performed.

DISCUSSION

Shock-Induced Broadening of NMR Peaks

The broadening of the ²⁹Si MAS NMR peaks of the shocked clinoptilolite may be due to several different causes, but the most important reason is the increase in the range of mean Si-O-T bond angle per silicon tetrahedron in the samples. Numerous researchers have described the excellent relationship between the mean Si-O-T bond angle and the ²⁹Si chemical shift for silicate phases (Smith and Blackwell, 1983; Dupree and Pettifer, 1984; Oestrike *et al.* 1987). Additional causes for the broadening include the extensive disorder and residual strain introduced into the clinoptilolite by shock loading. Dupree and Pettifer (1984) and Devine *et al.* (1987) have suggested that such NMR peak broadening in silica ultimately results from the redistribution of Si-O-Si bond angles in response to stress. This point is discussed in much greater detail later in Part II and Part III for the case of dynamic stressing. A similar argument can be made for the case of the Si-O-Al bond angles in aluminosilicate phases such as clinoptilolite.

Another important reason for the observed NMR peak broadening is the formation of an amorphous phase during shock. Typically this type of phase is referred to as diaplectic glass (Stöffler, 1984). Evidence for the existence of significant amorphous material is obtained from the TEM examination of the 22 GPa high temperature sample. The ²⁹Si MAS NMR spectrum for this highly shocked material (Figure 5) has no obvious structure to suggest unique silicon sites in clinoptilolite. The broad peak is probably a superposition of the spectrum for a disordered clinoptilolite with that for an amorphous phase of clinoptilolite composition. We would expect the NMR signature of the amorphous component to be similar to the broadened NMR spectrum of amorphous silica (Part II, Oestrike *et al.*, 1987). The NMR contribution of this amorphous component increases with increasing shock pressure. Although there is no evidence to suggest that this amorphous material is the result of melting, NMR spectroscopy cannot readily discern between fused and diaplectic glasses of similar compositions or silicon coordinations unless there is a large density difference.

Clinoptilolite NMR Shock Barometer

In order to develop an empirical shock barometer based on clinoptilolite it is necessary to obtain a simple metric of the changes in the NMR spectra observed with increasing shock pressure. Because of the complexity of the clinoptilolite spectra resulting from the significant number of Si-O-T bond angles and tetrahedra coordinations, this is no simple matter as compared to the quartzbased shock NMR barometer (Part II and Part III). The difference between the use of guartz and clinoptilolite for a basis of a shock barometer is best demonstrated by Figure 6.²⁹Si MAS NMR spectra are presented for both the unshocked and 22 GPa high temperature shock samples. The quartz data are taken from Part III and demonstrate the technique used to quantify the NMR spectral broadening associated with the shock loading of the relatively simple quartz structure. Although an amorphous silica phase results from the shock experiments, the fairly simple distribution of silicon sites in quartz and the amorphous phase provides a direct quantification of the spectral changes. A single peak width provides an empirical measure of the shock-induced changes and correlates directly with shock pressure (Part III, Cygan *et al.*, 1992). The transference of this approach to the clinoptilolite NMR spectra is not straightforward as noted above. The use of an n-parameter fitting model to obtain meaningful deconvolutions would be very difficult in practice and probably would not provide a unique solution.

One approach for evaluating spectral broadening based on a simple metric is the use of the first moment of the ²⁹Si NMR spectra. Due to the shift in the maximum intensity to smaller chemical shift values with increasing shock pressure, it was hoped that the first moment, as a measure of the spectrum centroid, would be a useful tool. Moments for all clinoptilolite spectra were determined by the numerical integration of the NMR spectra. First moment values range -104.8 ppm for the unshocked clinoptilolite spectrum to -101.6 ppm for the spectra for both 16.5 GPa samples. A strong correlation of first moment with shock pressure occurs up to 16.5 GPa but then fails at 22 GPa when the moments increase to -102 ppm. A similar correlation is exhibited by the second moment, a measure of spectral skewness. It is possible that the formation of the amorphous phase at the high shock pressures modifies the ²⁹Si NMR spectra



Figure 6. Representation of methods for measuring the NMR spectral broadening associated with the shock-loading of minerals. ²⁹Si MAS NMR spectra for a) unshocked quartz and b) shocked quartz (see Part III) and c) unshocked clinoptilolite and d) shocked clinoptilolite. The overlapping of multiple peaks for clinoptilolite precludes the use of a single peak width for defining the spectral changes associated with the shocked samples.

An alternative approach for measuring NMR spectral broadening for shocked clinoptilolite is based on the observation that with increasing shock pressure, the four peaks in the original spectrum become progressively less resolved (Figures 4 and 5). The intent of the new approach is to take this property, that is obvious by inspection, and develop a quantitative metric. To do this, we make use of standard errors from the deconvolutions. This technique involves the use of multiple peak deconvolutions for each of the clinoptilolite NMR spectra. By examination of the spectra presented in Figures 4 and 5, we observe a trend in the number of peaks that would be required to obtain the best fit. The unshocked clinoptilolite spectrum can best be deconvolved using four peaks whereas the significantly broadened 22 GPa spectra are best fit by a single peak. A single Gaussian peak is used for the basis of one deconvolution, and then the deconvolution is repeated using four Gaussian peaks as the basis. We use a Marquardt-Levenberg non-linear curve-fitting program (Press et al., 1986) to perform the deconvolutions and monitor the standard error associated with each fit.

Figures 7 and 8 provide a summary of the deconvolution analysis for the ²⁹Si MAS NMR spectra for unshocked and 22 GPa high temperature shocked clinoptilolite using this approach. The standard error, for a single peak and for four peaks, is related to the least-squares goodness-of-fit for each of the deconvolutions. These errors can be used to discriminate between separate/distinct and overlapping/lumped NMR peaks. The use of four peaks to fit the spectra of the highly shocked samples is useful only as a means of analysis and clearly does not have any direct physical basis. The smallest errors are obtained for the four peak deconvolution of the unshocked clinoptilolite spectrum and for the four peak deconvolution of the 22 GPa shock spectrum. Although the latter result is not entirely unexpected (better fits are possible with multiple term functions used like a Taylor series *versus* a single term function), it is the relative values of σ_1 and σ_4 that are critical in comparing the spectral deconvolutions.

The results of this deconvolution analysis are best represented by a plot of the standard error ratio as a function of the mean peak shock pressure (Figure 9). A small value σ_4/σ_1 implies an NMR spectrum with four resolvable peaks, whereas a large value suggests an NMR spectrum with broad and overlapping peaks. A

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Figure 8. Deconvolution analysis of ²⁹Si MAS NMR spectrum for clinoptilolite recovered from high temperature 22 GPa shock using a) single Gaussian peak and b) four Gaussian peaks. Standard error values are determined by analysis of residuals from curve fit.



Figure 9. Ratio of standard error values for single peak (σ_1) and four peak (σ_4) deconvolutions for the ²⁹Si MAS NMR spectra of shocked clinoptilolite plotted as a function of peak shock pressure. A small value for this ratio implies an NMR spectrum with four resolvable peaks, whereas a large value suggests an NMR spectrum with broad and overlapping peaks.

four-fold increase in this ratio is exhibited in the given shock pressure range for the high temperature data and a two-fold increase for the low temperature data. This general increase in σ_4/σ_1 is observed with increasing shock pressure and provides an empirical basis for the development of a shock barometer. An estimate of the overall error associated with the standard error ratio is of the same order as the symbol size. This correlation also potentially provides a tool for discriminating temperature effects associated with the shock loading of clinoptilolite, especially at high shock pressures,.

Cross Polarization NMR and Amorphous Phase

Although we have not directly addressed the specifics of the NMR broadening associated with the shocked clinoptilolite, it would be helpful to better characterize the amorphous phase associated with the 22 GPa high temperature powder. NMR spectroscopy provides an additional tool that can provide structural information on the hydration state of the material and possibly explain the behavior of this shocked phase. The cross polarization (CP) technique involves the transfer of nuclear spin from protons to other NMR-active nuclei, in this case between ¹H and ²⁹Si (Yannoni, 1982). Structural information is obtained from nuclei closest to the protons while preferentially eliminating the spectrum signal from anhydrous phases. Spectra are usually obtained under MAS conditions, and due to shorter relaxation times (see Part III) the cross polarization experiments provide NMR spectra that have improved signal-to-noise ratios and better sensitivity than standard MAS NMR spectra (Kirkpatrick, 1988).

The results of ²⁹Si CPMAS NMR experiments on the unshocked and 22 GPa samples are presented in Figure 10. The most noteworthy result of this analysis for the 22 GPa powder is the occurrence of a broad peak with a chemical shift centered at -98 ppm and ranging from -76 ppm to -124 ppm. This peak corresponds to the primary peak at -100 ppm exhibited in the standard MAS NMR spectra for the shocked clinoptilolite samples, and that increased in intensity with increasing shock pressure (see Figure 4 and 5). The chemical shift of the CPMAS peak corresponds to a silanol group (Si-OH) and the breadth of the peak is similar to that associated with an amorphous phase. The silanol group is a silicon coordinated with a single hydroxyl group (OH) and three silicon



Figure 10. Cross polarization MAS NMR spectra for unshocked and high temperature 22 GPa shocked clinoptilolite samples. The CPMAS intensity corresponds to ²⁹Si nuclei coupled to next-nearest-neighbor protons (*i.e.*, -Si-OH groups). No measurable signal is observed for the unshocked sample.

tetrahedra, also referred to as a Q³ silicon site (see Farnan *et al.*, 1987). This interpretation supports the observed shift in MAS NMR signal to -100 ppm with increasing shock pressure and the observation of amorphous material of clinoptilolite composition by TEM analysis. In contrast to the CPMAS results for the shocked clinoptilolite, the CPMAS spectrum for the unshocked material displays no measurable signal implying that there are no hydrated silicons present and that the normal MAS NMR spectrum (Figure 3) represents silicon tetrahedral sites coordinated to other silicon and aluminum tetrahedra. We are unable to determine whether the source of the silanol water in the shocked material is the structural water of the clinoptilolite or the sorbed water on the mineral surfaces and grain boundaries. Also, in a water-saturated environment such as the zeolitized tuff of Rainier Mesa, the shock-induced transformation of clinoptilolite to a hydrated amorphous phase may be accelerated and occur across a greater pressure range.

Although beyond the scope of the present project, additional experiments can be designed using D₂O to determine the source of the water involved in hydrating the clinoptilolite during the shock event. Recently, we have performed shock recovery experiments on water-saturated sandstone powders (Cygan et al., 1994b) in order to examine the formation of dense hydrated silica phases. This experimental effort was prompted by the findings of Cygan *et al.* (1994a) in which a new hydrated phase in naturally-shocked Coconino Sandstone from Meteor Crater, Arizona was identified using CPMAS NMR spectroscopy. A similar approach using deuterated water for the saturated clinoptilolite recovery experiments can be implemented. By using deuterium, an NMR inactive nuclide, rather than hydrogen, we would be unable to observe a CPMAS signal from the shocked clinoptilolite if the porewater was contributing to the hydration reaction. Conversely, if the structural water of clinoptilolite was involved in the reaction, we would obtain a CPMAS result similar to that observed in the present study (Figure 10). It would also be informative to examine the CPMAS spectra for all of the shocked clinoptilolite samples and determine the amount of broadening as a function of shock pressure. This approach would remove the complication associated with the multiple overlapping peaks in the MAS spectra since the CPMAS spectra exhibit a single broadened peak associated with the Si-OH site for the shocked samples.

CONCLUSIONS

This study provides a mineralogical basis for the examination of shock loading effects associated with the underground detonation of nuclear weapons at the Nevada Test Site. A correlation exists between ²⁹Si MAS NMR peak broadening and the mean peak shock pressure for samples of Rainier Mesa clinoptilolite shocked up to 22 GPa and 675°C using experimental recovery techniques. Chemical shifts become less negative with increasing shock pressure suggesting a decrease in the mean Si-O-T angle during the dynamic compression of the clinoptilolite structure. TEM and CPMAS evidence suggest that clinoptilolite is also partially transformed to an amorphous material (diaplectic phase) with shock compression, and comprises a significant proportion of the 22 GPa high temperature sample. The amorphous phase is characterized by a Q³ silicon site (Si-OH) and results from the interaction of the clinoptilolite with structural and/or sorbed water during shock loading. Statistical deconvolution of overlapping and broadened resonances suggest the potential use of clinoptilolite as a shock barometer and that NMR spectroscopy is more sensitive than other analytical techniques in evaluating shock effects in clinoptilolite. However, additional variables, in particular shock duration, may influence the resulting spectra; the duration of the shock pulse associated with a nuclear detonation is considerably greater than that experienced by the clinoptilolite in our standard explosives recovery experiments. Other differences may also arise if the transformation is induced in a water-saturated environment such as found in the test beds at the Nevada Test Site.

PART II

NMR SPECTROSCOPY OF EXPERIMENTALLY SHOCKED QUARTZ: SHOCK WAVE BAROMETRY

INTRODUCTION

As previously discussed in Part I, the shock-loading of natural materials by impact can result in the formation of highly modified phases. Shocked minerals typically exhibit fracturing, planar deformation, comminution, disordering, lamellae, and, frequently, new phases. These new phases may be glass (fused or diaplectic) or other reaction products which include high pressure polymorphs of the original minerals (see Stöffler, 1984). For a given material the extent to which these shock-induced features form depends upon the peak shock pressures and temperatures. These variables, in turn, are related to velocity, composition, density, and angle of impact associated with the projectile, and the original composition and density (porosity) of the target material. The modifications and changes in the original material induced by the shock are referred to as shock metamorphism.

The effects of shock metamorphism on minerals, in particular the presence of the high pressure polymorphs of SiO₂ (coesite and stishovite), have been used to identify impact events (Stöffler, 1971). For the Meteor Crater, Arizona terrestrial impact site, the occurrence and textural relationships of glass and the SiO₂ polymorphs have provided a basis for estimating the shock pressure (Kieffer, 1971; Kieffer *et al.*, 1976).

Recent interest in an extraterrestrial cause for the Cretaceous-Tertiary extinction (Alvarez *et al.*, 1980) has prompted an increase in research on shock features in quartz (for example, Bohor *et al.*, 1984; Carter *et al.*, 1986; Alexopoulos *et al.*, 1988). The Alvarez *et al.* (1980) theory proposed that a large asteroid collided with the earth 65 million years ago, resulting in mass extinctions. Observed

shock features in mineral grains and possible stishovite in clay layers from near the Cretaceous-Tertiary boundary support this idea (Bohor *et al.*, 1984; McHone, *et al.*, 1989). However, several researchers interpret shock features in minerals to be the result of volcanic eruption processes (Carter *et al.*, 1986), but this interpretation remains controversial and is not generally accepted (Izett and Bohor, 1987; Sharpton and Schuraytz, 1989). Multiple sets of shock lamellae and reduced values of the refractive indices are widely accepted as diagnostic of a shock event in the minerals.

Studies of the effect of shock in minerals have traditionally relied on qualitative examination of microstructures by optical and electron microscopies. Refractivity, density, X-ray diffraction, infrared absorption, X-ray photoelectron spectroscopy, and electron paramagnetic resonance (EPR) have been used to quantify the physical state of shocked minerals and glasses (see Stöffler, 1984). Optical refractivity has proven to be one of the most useful diagnostic techniques of shock metamorphism, especially for quartz (Chao, 1968; Hörz, 1968). Its usefulness as a shock barometer was determined by recent spindle stage measurements, which show a decrease in birefringence and refractive index for material shocked to pressures above 22 GPa (Grothues et al., 1989). Above shock pressures of 28 GPa, quartz becomes increasingly isotropic and completely transforms to diaplectic glass at 35 GPa, but, at pressures below 22 GPa there is little change in the refractive indices (Figure 11). Detailed X-ray line broadening studies of shocked powder and single crystal quartz have also been performed, and indicate a decrease in domain size and an increase in microstrain effects with increasing shock pressure (Hörz and Quaide, 1973; Schneider et al., 1984; Ashworth and Schneider, 1985). Because these microstructural properties are apparently a function of shock pressure, X-ray line broadening may also be used as a shock barometer.

In an attempt to better understand the structural changes in quartz with shockloading and to develop a better measure of shock pressure, we use solid state ²⁹Si nuclear magnetic resonance (NMR) spectroscopy to examine quartz powders shocked to pressures of 7.5 to 22 GPa. This NMR technique involves monitoring radio frequency re-emissions from ²⁹Si nuclei while the sample is in a very strong magnetic field (see Kirkpatrick, 1988). The resonance frequencies are sensitive to the local electronic (that is, structural) environment of silicon in

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Figure 11. Refractive index as a function of peak shock pressure, demonstrating the decrease in refractivity and birefringence with increasing shock pressure. The curves labeled n_o and n_e define the birefringence envelope for shocked single crystals of quartz (Grothues *et al.*, 1989). The ordinary index, n_o , and extraordinary index, n_e , begin to converge at shock pressures greater than 22 GPa and eventually coalesce at a shock pressure of about 35 GPa to indicate the formation of an isotropic phase (glass). The refractivity measurements from the present study are for shocked powder samples.

the material, and, thus, provide information about the range of silicon environments resulting from, for instance, shock modification. One aim of this research is to provide a sensitive technique for monitoring shock pressure by calibrating a ²⁹Si NMR shock wave barometer.

NMR spectroscopy is useful in the analysis of shocked quartz because of the sensitivity of the NMR frequencies to the local (nearest and next-nearest neighbor) environment of the ²⁹Si. The resonance frequencies are reported as chemical shifts, which are ppm deviation of the resonance frequency from that of standard (tetramethylsilane in this case). The ²⁹Si resonances of SiO₂ have been examined by Smith and Blackwell (1983), Oestrike *et al.* (1987), and Murdoch *et al.* (1985) among many others. These studies have determined the chemical shifts for the silicon sites in quartz, fused glass, coesite, and stishovite. Yang *et al.* (1986) examined shocked Coconino sandstone from Meteor Crater, Arizona and identified the characteristic ²⁹Si resonances of quartz, coesite, and stishovite. Figure 12 provides several NMR spectra of these materials for reference. Stishovite has a very different chemical shift because its silicon is in six-fold coordination, and the electronic shielding is much different. The coesite structure has two tetrahedral silicon sites, one of which has a chemical shift close to that of quartz.

Recently, McHone *et al.* (1989) used ²⁹Si MAS NMR to identify stishovite in a concentrated sample of a Cretaceous-Tertiary boundary clay from Raton, New Mexico. This result provides support for the hypothesis that the impact of an extraterrestrial object led to the Cretaceous-Tertiary extinction. McHone and Nieman (1988) also identified stishovite by ²⁹Si NMR in material from the Vredefort Dome of South Africa which has been proposed to be an impact feature.

Application of the NMR technique to the shocked quartz powders is, thus, attractive due to the potential of NMR to distinguish among the amorphous, cryptocrystalline, and crystalline phases which may exist in bulk samples. Early studies of the shock-loading of quartz (De Carli and Jamieson, 1959; De Carli and Milton, 1965; Deribas *et al.*, 1965) recognized the presence of stable and metastable silica phases including fused and diaplectic glasses and the high



Figure 12. ²⁹Si MAS NMR spectra of SiO₂ glass, quartz, and a naturally shocked sandstone from Meteor Crater, Arizona (modified from Yang *et al.*, 1986 and Oestrike *et al.*, 1987). The resonance frequencies are presented in ppm relative to the standard resonance of ²⁹Si in tetramethylsilane. Coesite (C), quartz (Q), and stishovite (S) are noted in the shocked sandstone spectrum. Spinning sidebands (SSB) are the result of the MAS technique.

pressure polymorphs. NMR analysis provides a unique capability for identifying these phases based upon the local structural environment of silicon.

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EXPERIMENTAL METHODS

The shock recovery experiments on guartz powder were performed using the Sandia "Bear" explosive loading fixtures to provide well-characterized shock states. The recovery fixtures allow samples to be shocked in a controlled and reproducible manner. Peak shock pressures and temperatures are determined by numerical simulations. Graham and Webb (1984, 1986) provide details of the experimental shock-loading experiment and the numerical simulations. Meanbulk shock temperatures are determined in part by the initial packing density of the mineral powders. The mean peak shock pressures are 7.5, 16.5, and 22 GPa, and the mean bulk temperatures range from 150°C to 700°C. The range of pressures and temperatures presented in Table 3 are due to non-uniaxial loading; the variables have a radial dependence as determined by the numerical simulations. Samples to be analyzed were taken from a region with weak radial dependence (according to the simulations) and with pressures and temperatures close to the mean values. The use of two different packing densities for each shock pressure provided a low and a high temperature set of shocked samples. The starting material for the shock-loading experiments was synthetic α -quartz powder (< 325 mesh) obtained from Alfa Products (lot # 88316). The material was briefly washed with deionized water and dried before insertion in the shock recovery sample holder; approximately eight grams of the quartz powder was required for each experiment. X-ray diffraction analysis of the starting material indicated pure, single phase α -quartz with no amorphous or glassy material present. Scanning electron microscopic (SEM) examination of the starting material determined a size distribution of approximately 30 to 90 microns. After removal from the recovery fixtures, the shocked material was lightly disaggregated with a mortar and pestle. Approximately 200-300 mg of powder sample are required for NMR analysis, and an additional one gram sample was used for optical, SEM, and X-ray diffraction examinations.

Refractive index measurements were performed using a standard optical microscope with sodium light, standard immersion oils at 23°C, and the method of central illumination. The refractivity values are presented as a range of values because of variable orientation of the anisotropic grains. The restricted values of immersion oil standards limit the accuracy of the refractivity measurements to 0.004.

Shot	Fixture	Explosive	Sample Compact Density (Mg/m ³)	Sample Compact Density (%)	Peak Pressure (GPa)	Estimated Mean Bulk Temperature (°C)
7B866	Momma Bear	Baratol	1.6	60	5-10	150-175
8B866	Momma Bear-A	Comp B	1.6	60	18-26	325-575
9B866	Momma Bear	Comp B	1.6	60	13-20	325-475
10B866	Momma Bear	Baratol	1.3	50	5-10	325-350
11B866	Momma Bear-A	Comp B	1.3	50	18-26	475-700
12B866	Momma Bear	Comp B	1.3	50	13-20	475-600

Table 3. Schedule of shock recovery experiments for untreated quartz

The X-ray diffraction patterns were obtained using Cu K_{α} X-ray radiation and a Phillips diffractometer with powders prepared on aluminum slides. Diffraction scans were performed from 10° to 70° 20 at scan rate of 2° 20/min and from 26° to 27° 20 at a scan rate of 0.25° 20 /min. The latter scan provides more detail of the shape of the quartz (101) peak.

The ²⁹Si NMR spectra were obtained at a frequency of 71.5 MHz ($H_o = 8.45$ T) under magic-angle spinning (MAS) conditions (see Yang *et al.*, 1986; Kirkpatrick *et al.*, 1986a; Oestrike *et al.*, 1987; Kirkpatrick, 1988). MAS frequencies were typically 2.8 kHz. A pulse Fourier transform method was used to obtain the NMR spectra by first detecting signals in the time domain, then transforming the data to yield spectra in the frequency domain.

RESULTS

SEM examination of our shocked quartz powders indicates that substantial brittle disaggregation occurred due to shock-loading. Significant comminution, deformation, and fracturing is apparent. The mean grain size was reduced from 30-90 μ m to 10-60 μ m in all cases. Fine-grained (less than 1 μ m) material is more abundant in the shocked quartz samples than in the unshocked sample. Small blebs (5-15 μ m) of apparently amorphous material occur in the 22 GPa samples. Planar features (shock lamellae) were observed in only the low temperature 22 GPa sample. We found one quartz grain in the sample that contains three sets of parallel structural voids visible after hydrofluoric acid treatment. Presumably, the HF preferentially etches the diaplectic glass that fills the shock lamellae (Bohor *et al.*, 1984).

Within the precision of the measurement technique, there is no variation in the refractive indices of the shocked samples, and the measured refractive indices were all identical to the unshocked quartz sample (Figure 11). Mean peak shock pressures for these samples are below that required to affect the refractive index.

The full X-ray diffraction scans for each of the shocked powders indicate the presence of only quartz. There is no evidence of a broad glass peak near 25° 2 θ . The detailed scans of the most intense quartz peak (101) at 26.62° 2 θ show a small but measurable broadening with increasing shock pressure for both the low and high temperature runs (Figure 13). There is also a shift in peak position towards lower 2 θ values (larger d-spacing) with increased shock pressure up to 16 GPa. There is no shift in the peak position for either of the 22 GPa samples.

The NMR spectra are characterized by a single peak with a maximum of about - 108 ppm for four-coordinated ²⁹Si in quartz. However, this peak broadens substantially with increasing shock pressure (Figure 14). The unshocked quartz has a full-width-at-half-height (FWHH) of 0.8 ppm, whereas that of the high temperature 22 GPa sample is 3.8 ppm. The peaks of the high temperature samples are somewhat more broadened than those of the low temperature samples. There is no peak for stishovite which would occur at about -192 ppm (Smith and Blackwell, 1983; Yang *et al.*, 1986), consistent with the relatively low



Figure 13. Comparison of the X-ray diffraction patterns for the $26.6^{\circ} 2\theta$ peak (101) for the shocked quartz powders relative to that for the unshocked starting material: (a) low shock temperature samples and (b) high shock temperature samples. Diffraction patterns were obtained at a scan rate of $0.25^{\circ} 2\theta$ /min.



Figure 14. ²⁹Si MAS NMR spectra for shocked quartz powders relative to that for the unshocked starting material: (a) low shock temperature samples and (b) high shock temperature samples.

pressures of our shock experiments. In addition, the NMR peak maxima tend to shift upfield (to lower frequencies or less negative chemical shifts) with increasing shock pressure. The only exception to this trend is the lower temperature 22 GPa sample, which is shifted upfield relative to the unshocked sample but not as far as the 16 GPa sample. This behavior is similar to the shifts in 20 observed in the X-ray diffraction patterns for the same 22 GPa-shocked samples.

DISCUSSION

X-Ray Diffraction

Broadening of X-ray diffraction lines usually is associated with residual strain, disorder of the crystal, and decrease of crystal domain size (Hörz and Quaide, 1973; Schneider *et al.*, 1984). Shifts in diffraction peaks by lattice strain effects usually represent uniform strain whereas broadening of the peaks indicates a nonuniform strain (Cullity, 1978). We are uncertain as how to interpret the X-ray diffraction data of the 22 GPa samples (see Figure 13). It is possible that these samples experienced high enough temperatures (greater than 570°C) during (and after) shock-loading that an inversion to β -quartz occurred which later reverted to the α -quartz structure upon cooling.

The unshocked starting material possesses a fairly broad (101) X-ray peak indicating some inherent strain prior to shock-loading (Hörz, personal communication). This strain may have been generated during the initial synthesis and grinding of the material. However, all of the X-ray and NMR results are normalized relative to the starting material. A comparison of the sensitivity of the two techniques in quantifying the degree of disorder can therefore be made regardless of the initial state of the material. We hope to study this pre-shock effect in future research by examining a variety of synthetic, natural, and thermally annealed quartz samples. We address the thermal annealing effect to some extent in Part III by examining a series of temperatures and durations for the annealing of the starting material.

Nuclear Magnetic Resonance

The broadening of the NMR peak of the shocked quartz may be due to several different causes, but must be due to an increase in the range of mean Si-O-Si bond angle per silicon tetrahedron in the samples. Many workers, including Smith and Blackwell (1983), Dupree and Pettifer (1984), and Oestrike *et al.* (1987), have described the excellent relationship between this and the ²⁹Si chemical shift for SiO₂ phases.

One possible cause for this broadening is extensive disorder and residual strain introduced into the quartz lattice by shock-loading. Dupree and Pettifer (1984) and Devine *et al.* (1987) have suggested that such NMR peak broadening ultimately results from the redistribution of Si-O-Si bond angles that forms in response to stress. Although static pressures were used in the previous studies of amorphous silica phases, a similar argument can be made for the dynamic stressing of our study.

A second possible cause for the observed NMR peak broadening is formation of an amorphous phase. Vitreous silica has a ²⁹Si resonance maximum at -111 to -112 ppm, and a FWHH of about 20 ppm (Dupree and Pettifer, 1984; Oestrike *et al.*, 1987; our Figure 12). The extent of such a contribution to the NMR spectra in Figure 14 is uncertain. The asymmetrical shape of the peaks and the intensity in the -109 to -118 ppm range in the spectra of the high pressure shock samples is consistent with some contribution from a silica glass phase. The intensity of this broad component increases with increasing shock pressure. Although none of the X-ray diffraction scans provide evidence of glass, our SEM observations confirm the existence of a glass phase in the shocked samples. NMR spectroscopy may be able to discern between fused and diaplectic glasses of similar compositions or silicon coordinations based on the density difference, and therefore change in chemical shift, between the two materials.

A third possible cause of the peak broadening could be the presence of coesite, one of the high pressure polymorphs of silica (Stöffler, 1971, 1984). Smith and Blackwell (1983) and Yang *et al.* (1986) observed two ²⁹Si NMR peaks -108.1 ppm and -113.9 ppm, for this phase. Although no coesite is detected by X-ray diffraction, if coesite was formed it may have been in an amount below the detection level. It is possible that some coesite contributes to the peak broadening observed in Figure 14. This amount may be relatively small because there is no significant signal at -114 ppm associated with the downfield coesite peak.

An example of a possible deconvolution of the broadened NMR peak is presented in Figure 15 where the relative contributions of the disordered quartz and silica glass may be graphically examined. An unidentified peak of low intensity occurs upfield as a result of the optimum fitting of three Gaussian



Figure 15. Optimum curve fits for the ²⁹Si MAS NMR spectrum for the high temperature 22 GPa shocked quartz sample. The upper curve is a smoothed peak derived from the raw data. The lower curves provide the results of a possible deconvolution assuming 100 % Gaussian peak shape for quartz, glass, and a third unidentified peak.

curves to the NMR spectrum. In this model deconvolution, the optimum fit attributes about 60 % of the ²⁹Si NMR signal to the glass phase, whereas the disordered quartz accounts for 25 % of the observed NMR peak. Because of the lack of singularities for constraining the model, the resulting curves do not necessarily represent a unique solution. A more detailed investigation of deconvolution of the ²⁹Si NMR spectra is presented in Part III.

Relative Peak Changes and Shock Wave Barometry

Although the origin of the NMR peak broadening is not entirely clear, this broadening appears to be a useful empirical measure of peak shock pressures. Figure 16 shows the NMR peak broadening increases much more rapidly with increasing shock pressure than X-ray diffraction peak broadening. The NMR peaks of the 22 GPa samples are almost five times broader than that of the unshocked quartz sample. The broadening of the NMR peaks shows no strong or consistent correlation with shock temperature.

The X-ray peak broadening increases at most by a factor of 1.7 relative to the unshocked samples and is much less than for the NMR peak widths (Figure 16). This result suggests that NMR is a more sensitive measure of shock pressure. However, the synthetic quartz we used already had measurable line broadening in its unshocked state. For unstrained starting material, the X-ray line broadening may exhibit a stronger and more consistent trend than what we observed, but the NMR trend may also be enhanced.

The variation of the NMR peak widths with temperature is much smaller than that with pressure. Thus, the NMR peak width measurement can provide a shock barometer over a wide range of unknown shock temperatures. It may therefore be particularly useful in studies of naturally shocked quartz where the precise initial conditions and loading path (which dictate the shock temperature) are unknown.

One of the limitations in assessing the suitability of the NMR shock wave barometer is the uncertainty in the amount of glass and coesite generated during the experimental shock event. SEM examination of the shocked samples suggests that both fused and diaplectic glass are present. The NMR results



Figure 16. Comparison of relative half-peak widths (full-width-at-half-height) obtained for X-ray diffraction (XRD) patterns and MAS NMR spectra of the shocked quartz powders as functions of the mean peak shock pressure. The open square indicates the NMR result for a low temperature sample which we suspect was improperly sampled from the recovery fixture.

indicate that these glasses contain only four-coordinated silicon and contribute to a broad peak with a mean chemical shift of approximately -110 ppm. Any higher coordinated silicon, such as a six-coordinated silicon in a stishovite-like diaplectic glass (Chhabildas and Miller, 1985; Boslough, 1988), would yield a resonance in the -190 to -200 ppm range and is not observed. Coesite or a disordered coesite-like material with mean Si-O-Si bond angles larger than quartz, and then more negative chemical shift, might also contribute to the observed peaks. Our NMR analysis of the low temperature 22 GPa sample after treatment with hydrofluoric acid indicated an almost two-fold decrease in FWHH relative to the untreated 22 GPa sample (see Part III). The ²⁹Si NMR spectrum exhibits some spectral intensity in the -114 ppm region where coesite would have a resonance (Smith and Blackwell, 1983; Yang *et al.*, 1986). Future research will require improved NMR spectra with better signal-to-noise ratios and an analysis of standard mixtures of the quartz, coesite, and glass.

Applications of the NMR Shock Wave Barometer

In applying an NMR shock barometer to terrestrial impact events, it is important to recognize the way the impact occurs and the amounts of material that are shocked by the impact. The amount of terrestrial material shocked to a given pressure by a meteorite impact is a complex function of projectile mass, velocity, density, angle of impact, and other parameters. The highest shock pressures are in the small central region of the impact, and the material associated with the lower shock pressures is radially distant from the impact point, but represents a larger volume. The significant radial decay of shock pressure from the impact point therefore produces large volumes of material subjected to pressures less than 22 GPa (for example, Stöffler, 1984). An NMR shock barometer would be useful in determining the low shock pressures associated with this material. This is a significant advantage because refractive index-based shock barometers are limited to pressures greater than 22 GPa.

Another potential application of shock barometry using the NMR spectroscopic approach is the accurate scaling of stress decay associated with nuclear testing. The technique is amenable to post-test analysis of shock pressure exposure of rock samples. This method can be used in conjunction with real-time stress probes and sensors that collect data during the detonation, or for post-test analysis where real-time evaluation has failed or is lacking. Consequently, data from nuclear test sites can be used to calibrate natural shock events. This is similar to the approach of Vizgirda *et al.* (1986), who examined the hyperfine EPR splitting of Mn²⁺ in calcite from shocked coral samples from Cactus Crater at the Pacific test site. These results, however, do not conclusively define a reproducible trend between hyperfine peak splitting and shock pressure. We believe an NMR shock barometer would be more useful, because of the larger observed spectral changes, and because of the widespread occurrence of quartz and other silicate minerals.

Future research on shocked material using MAS NMR spectroscopy should emphasize the structural differences associated with ²⁹Si in diaplectic and fused glasses. Mineral samples should also be subjected to greater shock pressures in order to examine any coordination changes which may result. Although the present study has emphasized ²⁹Si NMR spectroscopy, there are other NMRactive nuclei (²³Na, ²⁷Al, and ³⁹K) which could provide detailed information on the disordered state of other shocked minerals that may be present on the moon and terrestrial planets. The maskelynitization of feldspar minerals could be examined in this fashion. Some of these issues are examined in Part III.

CONCLUSIONS

This study demonstrates a significant positive correlation of ²⁹Si MAS NMR peak width with mean peak shock pressure for samples of synthetic quartz shocked up to 22 GPa and 700°C. The NMR technique is more sensitive to shock pressure than X-ray diffraction methods, with the (101) quartz X-ray peak broadening much less than the NMR peak for the synthetic quartz samples. The quartz refractive indices do not change in this low pressure range, in agreement with the results of Grothues *et al.* (1989). The results of this study suggest the potential usefulness of NMR spectroscopy in providing a shock barometer that is sensitive and accurate for shock pressures below 22 GPa. No other observable parameter appears to change as much or as consistently in this pressure range.

PART III

NMR SPECTROSCOPY OF EXPERIMENTALLY SHOCKED QUARTZ AND PLAGIOCLASE POWDERS

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 (for example, Boslough, 1991). Diagnostic methods for examining shock features in minerals have traditionally relied on qualitative examination of microstructures by optical and electron microscopy. The object of much research has been to describe and characterize shock effects, thus providing criteria for recognizing and classifying various levels of shock metamorphism. Because shock features have been studied mainly with microscopic techniques, most of the descriptions have been of microstructural changes. These changes include twinning, recrystallization, glass formation, kink band formation, mosaic extinction, and formation of a number of types of planar and subplanar features called "planar deformation features", including microfault zones, fractures, glassy plates, and shock lamellae. Shock effects on mineral microstructures have been discussed extensively (for example, Carter, 1965; French and Short, 1968; Kieffer, 1971; Stöffler, 1972; Roddy et al., 1977; Grieve, 1987; Gratz, 1984; Gratz et al., 1988; Alexopoulos et al., 1988; Carter et al., 1989; Nicolaysen and Reimold, 1990, Tatevin et al., 1990)

An important use of these observations has been the identification of natural impacts on earth. For example, recognition of shocked minerals at the Cretaceous-Tertiary boundary has been essential in linking the biological extinction which occurred at that time with an impact event (Bohor *et al.*, 1984; French, 1990). There has been some controversy in this interpretation, and some workers have suggested that mineral "shock features" may result from

volcanic eruption processes (see Carter *et al.*, 1986). However, these concerns appear to have largely been laid to rest (French, 1990).

More quantitative methods including refractivity, density, X-ray diffraction (XRD), infrared absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance (EPR) have also been used to investigate the physical state of shocked minerals and glasses (see Stöffler, 1984). Most of the data from these techniques show some degree of correlation with intensity of shock-loading over some range of shock pressure in certain minerals, and have been used to identify shocked minerals and quantify their level of shock metamorphism.

We have previously shown that solid state NMR is an extremely sensitive probe of disorder brought about by shock-loading of quartz, and have suggested that it could be used over a limited range of shock pressures and loading conditions (Part II; Cygan *et al.*, 1990). That work noted a good correlation between the width of the ²⁹Si resonance and known shock pressure. This correlation has a stronger dependence on shock pressures between 7.5 and 22 GPa than quantitative data determined by refractivity and XRD. That study was preliminary and rather empirical in nature, and the shock-induced structural changes responsible for the changes in the NMR spectra were not significantly explored.

We have now expanded on the earlier work of Part II by: 1) repeating the experiments under the same conditions with annealed samples; 2) better characterizing the ²⁹Si MAS NMR spectra using more-sophisticated curve fitting and deconvolution techniques; 3) examining the effect of post-shock hydrofluoric acid etching and thermal annealing of quartz on the observed NMR spectra; 4) exploring the T₁ NMR relaxation of the shocked quartz; and 5) determining whether a more complex aluminosilicate mineral (An₆₀ plagioclase feldspar) also exhibits a useful correlation between shock pressure and NMR spectral features. Our primary purpose is to determine the degree of reproducibility of the previous experimental results of Part II, to seek a physical basis for them, and to begin to determine whether they are unique to quartz. By understanding the source of the spectral changes, we expect to gain a stronger basis for using their correlation with shock pressure as a "shock barometer".

EXPERIMENTAL METHODS

The six shock recovery experiments using quartz powder samples were carried out in precisely the same manner as those discussed in Part II. Well-characterized shock states were achieved by using the Sandia "Momma Bear" explosive loading fixtures, for which peak pressures and temperatures have been numerically determined by Graham and Webb (1984, 1986). Two sets of three experiments were performed, each to mean peak shock pressures of 7.5, 16.5, and 22 GPa. The only difference between the two sets were the initial packing densities of the powders, which lead to "low shock temperature" and "high shock temperature" conditions at the same shock pressures (Table 4). There are ranges of pressures and temperatures for each sample because the experimental shock-loading is not uniform, and according to numerical simulations has a radial dependence. The samples for which the NMR spectra were obtained were taken from the bulk region where this dependence is weak and can be approximated by its mean value.

As with the previous study (Part II), the starting material was synthetic α -quartz sieved to a mean grain size of less than 38 microns (325 mesh). The only substantive difference in preparation procedure was that in the present study the quartz was annealed at 900°C for 20 hours to minimize the initial defect densities which had previously broadened the (101) X-ray diffraction peak.

One set of three shock-loading experiments was carried out on an An₆₀ plagioclase feldspar (labradorite). The initial packing density led to relatively high shock temperatures (Table 4). The natural An₆₀ plagioclase is from a basalt flow from Pueblo Park, New Mexico, and was pre-treated by annealing at 900°C for 20 hours before shock-loading. The NMR experiment detects the radio frequency emission from active nuclei which have been excited to a high energy spin states while the sample is located in a very strong magnetic field. Wilson (1987) and Kirkpatrick (1988) discuss MAS NMR spectroscopy and its application to minerals. Our ²⁹Si MAS NMR spectra were obtained at a frequency of 71.5 MHz with an applied magnetic field of 8.45 T and the identical experimental conditions as those used in Part II. The ²³Na and ²⁷Al MAS NMR spectra for the plagioclase samples were obtained at respectively 130.3 MHz and 132.3 MHz using a similar spectrometer and an applied magnetic field of

Shot	Fixture	Explosive	Initial Sample Compact Density (Mg/m ³)	Initial Sample Compact Density (%)	Peak Pressure (GPa)	Estimated Mean Bulk Temperature (°C)	
Quartz							
8B906	Momma Bear	Baratol	1.60	60	5-10	150-175	
5B906	Momma Bear	Comp B	1.60	60	13-20	325-475	
2B906	Momma Bear-A	Comp B	1.60	60	18-26	325-575	
9B906	Momma Bear	Baratol	1.36	51	5-10	300-325	
6B906	Momma Bear	Comp B	1.36	51	13-20	475-600	
3B906	Momma Bear-A	Comp B	1.30	51	18-26	450-700	
An ₆₀ Plagioclase Feldspar							
7B906	Momma Bear	Baratol	1.30	48	5-10	325-350	
4B906	Momma Bear	Comp B	1.30	48	13-20	500-625	
1B906	Momma Bear-A	Comp B	1.30	48	18-26	500-725	

Table 4. Schedule of shock recovery experiments for
annealed quartz and feldspar

11.74 T. In all cases, the spectra were taken under magic-angle spinning (MAS) conditions to reduce the broadening associated with quadrupolar interactions. The spinning rate was approximately 3.5 kHz. Pulse Fourier transform methods were used, in which signals are detected in the time domain, and then transformed to the frequency domain.

The NMR chemical shifts are referenced to tetramethylsilane (TMS) (²⁹Si), 1 molar NaCl solution (²³Na), and 1 molar AlCl₃ solution (²⁷Al), with increased shielding for less positive or more negative values. All of the MAS NMR spectra were obtained using a pulse recycle time of 30 seconds unless otherwise noted. The effects of varying recycle times on the ²⁹Si resonance of SiO₂ minerals are briefly discussed by Yang *et al.* (1986).

RESULTS AND DISCUSSION

Thermal Annealing of Quartz

Because we were concerned that the initial defect structure could have a significant effect on the NMR spectra and X-ray diffraction patterns, we explored the effect of thermal annealing of the quartz without shock-loading. We heated the synthetic quartz to various temperatures for times of 1 hour and about 20 hours and measured the effects on the ²⁹Si resonance and the (101) X-ray diffraction peak (see Table 5). The widths of both NMR and XRD peaks decrease with heat treatment, but the decrease in NMR peak width is insignificant relative to the broadening caused by the shock-loading. The change in width of the XRD peak, however, is of the same order as the shock-induced broadening (Part II). The peak widths were determined by fitting a split Pearson VII function to the observed data (see below). The peak width values reported in Table 5 have a relative error (one estimated standard deviation) of approximately 5 to 12 % based upon the curve fitting procedure. Because of these results, we used annealed quartz as our starting material for the shock studies, but there is no effect on the comparison of the present NMR results with those of Part II.

Determination of Peak Width by Curve Fitting

Profile-fitting techniques are often used to accurately determine the characteristics of peaks associated with various spectroscopic methods. X-ray diffraction analysis often relies on an assortment of analytical functions for fitting to the observed diffraction pattern. Howard and Snyder (1983) and Howard and Preston (1989) provide details of the functions and discuss the benefits of each for the curve fitting of diffraction and other spectral peaks. These methods will usually provide a statistically accurate determination of peak position and intensity and a measure of the peak shape. The most commonly used fitting techniques are those that use Lorentzian and Gaussian functions. Equations (2) and (3) provide the analytical expressions used respectively for the Gaussian and Lorentzian curve fits to the observed spectral intensities:

Anneal Cor	nditions	Peak Width Relative to Initial (%)			
Temperature (°C)	Time (hr)	X-ray (101)	NMR (-107 ppm)		
700	1	93	93		
700	16	90	91		
900	1	79	85		
900	17	81	92		
900	20	81	89		
1100	1	86	89		
1100	17	80	90		

Table 5. Narrowing of measured peaks for annealed quartz powders

$$I = I_{0} \exp(-X^{2}/k)$$
 (2)

$$I = I_0 (1 + k^2 X^2)^{-1}$$
(3)

X represents the deviation $(x_i - x_c)$ in the independent variable x_i from the peak center position x_c . I_o is the intensity of the peak at x_c . The k values are related to the peak width at half-maximum (peak width or FWHH) and are unique for each equation. In practice, the Lorentzian function is used to describe peaks that are characterized by broad tails, whereas the Gaussian function provides a description of narrow peaks. Loren:zian peaks provided the optimum peak shape for the deconvolution of our ²⁹Si NMR spectra into contributing components.

An additional function that combines the Lorentzian and Gaussian attributes for the empirical fitting of spectral data is the Pearson VII expression (Brown and Edmonds, 1980):

$$I = I_{o} [1 + 4/g^{2} (2^{1/m} - 1)X^{2}]^{-m}$$
(4)

The g term represents the full width of the peak at half maximum and the m exponent value refers to the curvature of the peak. Depending upon the value of m, this equation can provide an analytical function that is a linear combination of the Lorentzian and Gaussian expressions. The Pearson VII function (Equation (4)) reduces to the Lorenztian function (Equation (3)) when m is equal to unity. For practical purposes, the Pearson VII function approximates the Gaussian function (Equation (2)) when m has a value greater than ten.

The Pearson VII function is symmetrical about x_c and is limited in its ability to describe the observed X-ray patterns and NMR spectra for the quartz powders of this study. However, the asymmetry of the observed peaks can be evaluated by using a combination of two half-profiles of Pearson VII functions such that they share common I_o and x_c values. The so-called split Pearson VII function provides this flexibility. Figure 17 presents a schematic of the split Pearson VII curve for describing the spectral characteristics of a single broadened NMR peak. Six parameters are allowed to vary during the computerized least-squares

share common I_o and x_c values. The so-called split Pearson VII function provides this flexibility. Figure 17 presents a schematic of the split Pearson VII curve for describing the spectral characteristics of a single broadened NMR peak. Six parameters are allowed to vary during the computerized least-squares fitting process in order to obtain the best fit of the split Pearson VII expression to the observed data. The peak width g will be the sum of the separate g_1 and g_2 values. This fitting technique was used here to derive the peak widths for the NMR and X-ray diffraction peaks.

Shock-Induced Broadening of Quartz ²⁹Si NMR Resonance

The ²⁹Si MAS NMR spectra for the six shocked quartz samples of the present study show systematic increases in peak width with increasing shock pressure for both the low and high shock temperature experiments (Figures 18 and 19). To better compare NMR peak widths we now make use of a systematic approach to spectral fitting that eliminates measurement error and bias. In this method the spectra are fit by a split Pearson VII function. This function has six adjustable parameters, from which one that represents the full-width at half-maximum height (peak width) can be defined. This function was used because it is asymmetrical (like the observed NMR data) and because it represents a combination of Lorentzian and Gaussian functions.

Similar broadening of the ²⁹Si resonance in shocked quartz was observed in Part II and attributed it to either extensive disordering and residual strain or formation of an amorphous phase, or some combination of these contributions. In Part II we concluded that the broadening correlates to an increase in the range of mean Si-O-Si bond angles per tetrahedron in the shocked samples. The key finding, however, was the strong correlation between peak breadth and shock pressure.

The ²⁹Si MAS NMR peaks of the annealed unshocked and shocked quartz samples are well fit by the split Pearson VII function (Figure 20). The peak widths of the shocked samples normalized to that of the starting material increase systematically with increasing shock pressure for both the high and low shock temperature data sets (Figure 21). These peak widths are in excellent agreement with the widths of the spectra of Part II recalculated using the


Figure 17. Schematic of a split Pearson VII function applied to a broadened NMR peak. The resonance is described by six fitting parameters: maximum intensity I_0 , peak center x_c , half peak widths g_1 and g_2 (peak width = $g_1 + g_2$), and curvature m_1 and m_2 .



Figure 18. ²⁹Si MAS NMR spectra for unshocked starting material and shocked quartz powders obtained for the low shock temperature set of recovery experiments.



Figure 19. ²⁹Si MAS NMR spectra for unshocked starting material and shocked quartz powders obtained the high shock temperature set of recovery experiments.



Figure 20. Comparison of ²⁹Si MAS NMR spectra with split Pearson VII curve fits: a) annealed (900°C for 20 hr) quartz starting material and (b) 22 GPa high shock temperature quartz sample.



Figure 21. ²⁹Si MAS NMR peak widths of the shocked quartz powders normalized to that of the unshocked starting material versus the mean peak shock pressure. Open symbols represent data from the initial study discussed in Part II and the filled symbols are the data from the present study (Part III). For clarity, error bars are presented only for the data from the present study. systematic split Pearson VII routine. All six measurements lie within the previously-reported error bars.

Deconvolution of Quartz ²⁹Si NMR Resonance

Although the split Pearson VII function provides good fits to the observed NMR spectra, it is entirely empirical and does not provide a basis for interpreting the asymmetry of the peaks for the shocked quartz. We have found that linear combinations of two Lorentzian functions (two-peak fits) also provide good fits to the NMR spectra (Figure 22). Because each Lorentzian has three parameters, this combination also has six free parameters.

The best two-peak fits to the spectra for the shocked samples consist of a relatively narrow peak (peak width of 1 to 2 ppm) at the quartz position of about -107.3 ppm and a broader peak (peak width of about 8 to 13 ppm) at about -108 ppm. The narrow peak can be taken to represent silicon on sites that are not greatly distorted from the original quartz structure, and the broad peak to represent silicon on more distorted sites. The two-peak fit, however, is only a useful formalism, and the observation that the split Pearson VII function fits the peaks as well probably indicates that there is a continuum of silicon environments in the shocked samples. The chemical shift of about -108 ppm for the broad peak indicates an increase of average mean Si-O-Si bond angle per tetrahedron from about 144° for unshocked quartz to about 146° for the sites represented by the peak. Pettifer *et al.* (1988) provides a discussion of this correlation of bond angle with NMR chemical shift for silica materials.

The broad peak is significantly different than that for typical amorphous silica. Silica glasses, for instance, have peak maxima at about -111 to -112 ppm and peak widths of 10 ppm or more (Dupree and Pettifer, 1984; Oestrike *et al.*, 1987; Pettifer *et al.*, 1988). Thus, the sites represented by the broad peak in our twopeak fits have a smaller average mean Si-O-Si bond angle per tetrahedron and a narrower range of mean Si-O-Si bond angles than most amorphous silica. This result is consistent with the lack of evidence for an amorphous phase in X-ray diffraction and optical microscopic observations.



Figure 22. ²⁹Si MAS NMR spectrum for the 22 GPa high shock temperature quartz sample and the deconvolution of the spectrum with two Lorentzian peaks.

There is no evidence of additional crystalline silica phases in any of the measured ²⁹Si NMR spectra for the shocked quartz powders. In particular, there are no peaks for coesite (-108.1 ppm and -113.9 ppm) or for the six-fold silicon in stishovite (-191.1 ppm) (see Smith and Blackwell, 1983; Yang *et al.*, 1986).

Effects of Post-Shock Treatment on ²⁹Si NMR Resonance

Further evidence for the association of the broad spectral component with highly distorted sites comes from the reduction in ²⁹Si NMR peak width of shocked quartz after partial dissolution in hydrofluoric acid (Figure 23). Split Pearson VII curve fit to the spectrum of the 22 GPa high shock temperature sample etched for 30 seconds in a 1:1 diluted hydrofluoric acid solution indicates a 32 % reduction in peak width after reaction. The two-peak fit indicates that the narrowing can be attributed primarily to a decrease in the intensity of the broad peak (Figure 23). Similar effects are observed for the 16 GPa high shock temperature sample. These results are consistent with the expected selective dissolution of highly deformed material.

Similar but weaker changes in the ²⁹Si resonance are caused by post-shock thermal annealing of the powders. Annealing of the 22 GPa and 16.5 GPa high shock temperature powders at 900°C for 20 hours causes the split Pearson VII peak widths to decrease by respectively 8 % and 18 %. Two peak fits of the spectra indicate decreases in the breadths of both resonance components. The relative intensity of the broad peak is also reduced by 24 % and 14 % for the 22 GPa and 16.5 GPa high shock temperature samples respectively. These observations are consistent with thermal annealing of defects in the deformed material (Langenhorst *et al.*, 1992).

Relaxation Effects

The relative intensities of the broad peaks in the two-peak fits are greater than those of the narrow peaks in the MAS NMR spectra obtained with a pulse recycle of 30 seconds. For fully-relaxed resonances, these areas should be proportional to the relative atomic abundances of the corresponding sites. If one type of site relaxes much faster than the other and if one or both of the resonances are not fully relaxed, the relative intensity of the fast-relaxing site



Figure 23. ²⁹Si MAS NMR spectrum for the 22 GPa high shock temperature quartz sample after treatment with hydrofluoric acid and the deconvolution of the spectrum with two Lorentzian peaks.

would be enhanced. To examine the effect of recycle time on the shapes and relative areas of the fit peaks, ²⁹Si MAS NMR spectra were also obtained for the 22 GPa high shock temperature sample using recycle times of 5 seconds and 300 seconds.

For our samples the relative intensity (area) of the broad peak in the two-peak fit decreases with increasing recycle time (Figure 24), indicating that the silicons on the site represented by this broad peak have a shorter T_1 average relaxation time than the silicons represented by the narrow peak. This difference can be explained by postulating a higher concentration of paramagnetic centers associated with defects near the more distorted sites. Such paramagnetic centers centers could be due to unpaired electrons associated with unsatisfied bonds or dislocations or point defects.

Similar relaxation experiments using ²⁹Si NMR spectroscopy have been used to characterize the chemical structure of a variety of silicate materials (Davis *et al.*, 1992; Nellis *et al.*, 1992; Ulibarri *et al.*, 1992). 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 (Assink *et al.*, 1993, 1994). This behavior is the result of relaxation of spin-1/2 nuclei by paramagnetic impurities under MAS conditions (Devreux *et al.*, 1990). This note describes the complications one must consider when spectra of spin-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 25 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 37.2 second exponential recovery of the magnetization. The fit is reasonable and considering the effort needed to acquire additional data (3600 scans recorded at 10 seconds and 360 scans recorded at 100 seconds) one is tempted to conclude that the 100 second pulse delay is adequate for a reasonably quantitative spectrum. This conclusion would lead to serious error.



Figure 24. Ratio of the intensities of the broad and narrow components of the two-peak fits versus reciprocal recycle time for the ²⁹Si MAS NMR spectra of the 22 GPa high shock temperature quartz sample.



Figure 25. Magnetization recovery of α -quartz sample for times up to 100 seconds. The solid line is a theoretical fit assuming a 37.2 second exponential recovery.

Figure 26 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. We know from calibration of the spectrometer with samples having shorter relaxation times, that the magnetization is near equilibrium for the longer times recorded in Figure 26. Spectra recorded at 100 seconds would have accounted for only 2 % of the equilibrium magnetization and the relative intensities of a multicomponent spectrum would 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 seconds 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.

The power-law behavior has been observed previously for doped sol-gel derived silicate samples (Devreux *et al.*, 1990). Power-law recovery was shown to be expected for samples undergoing MAS and whose 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 (Part II). The power-law exponent of 0.54 is reasonably close to the value of 0.50 predicted for a three-dimensional material.

Figure 27 shows the magnetization recovery of the α -quartz sample which has been subjected to a 22 GPa shock wave. The recovery again displays powerlaw 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 28. 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



Figure 26. Magnetization recovery of α -quartz sample on a log-log scale. The recovery follows power-law behavior over five decades of time.



Figure 27. Magnetization recovery of 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.



Figure 28. Representative spectra of the unshocked α -quartz sample at (a) 10 seconds and (b) 100,000 seconds recovery times and of the shocked α -quartz sample at (c) 10 seconds and (d) 90,000 seconds recovery times.

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 deconvolving 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.

Our data indicate that the time dependence of magnetization recovery for isotopically dilute spins such as ²⁹Si follows a power-law rather than exponential decay, and that for spins that are relaxed by interaction with paramagnetic impurities, the exponent of the power law decay is related to the fractal dimension of the associated phase (Devreux *et al.*, 1990). To explore this possibility, we have obtained preliminary data indicating that both the narrow and broad components indeed have power-law dependences, with saturation times of the order of 10^3 and 10^5 seconds for the broad and narrow components respectively. The observed power-law exponent are consistent with fractal dimensions of about 3 for the narrow component and of 1.5 to 2 for the broad component.

Using the power-law functions to fit the relaxation behavior indicates that the actual relative intensity of the broad peak may be less than 10 %, rather than the 50 to 80 % estimated from the fit to the short recycle time spectra. Thus, the opportunity to characterize the extensive distorted silicon environments represented by the broad component is a fortuitous result of the T_1 relaxation behavior of these samples.

TEM Examination of Shocked Quartz

Transmission electron microscopic (TEM) examination of the shocked quartz powders suggests the formation of nonuniform and complex deformation features (Figure 29). The dominant microstructure is characterized by a relatively high dislocation density. This phase, which likely corresponds to the broad component of the two-peak fits to the NMR spectra, is heterogeneously distributed among the bulk and relatively dislocation-free quartz material. We



Figure 29. TEM photomicrograph of the 22 GPa high shock temperature sample exhibiting heterogeneous deformation. Scale bar represents 1 μ m.

also observed a tendency for the highly deformed phase to transform to an amorphous material while being subjected to electron bombardment. Vitrification of shocked quartz in response to the electron beam is enhanced by the high-density of defects created by the shock-loading (Gratz *et al.*, 1988).

Based on the combined NMR, XRD, TEM, and optical microscopic data, we conclude that the shocked quartz samples retain the basic quartz structure and that a high density of dislocations causes the wide observed range of local silicon environments and the slight increase in the mean Si-O-Si bond angle.

Quartz NMR Shock Barometer

The results presented above indicate that the shock barometer suggested in Part II can be a useful empirical tool, albeit with a number of important qualifications, and that the peak width as determined by the split Pearson VII function is more reproducible than relative peak intensities in the two-peak fits (see Figures 21 and 30). The correlation of relative peak intensities with shock pressure is still strong, but there is significant scatter and the reproducibility is not as good as for the split Pearson VII peak widths. We believe that the larger scatter in the two-peak fits is a result of the difficulty of doing the fits and that the split Pearson VII peak widths provide a better correlation with peak shock pressure because they are less subject to statistical fitting errors.

The interpretations discussed above also provide a fundamental basis for understanding the origin of the correlation. Increasing shock-loading causes increased structural distortions and an increased amount of deformed material.

It must be emphasized that this shock barometer has only been calibrated for specific loading conditions. There has always been a tendency to relate the results of shock recovery experiments only to peak pressure. Such an interpretation neglects other aspects of the shock process that may have as much or more influence on the result (Kieffer, 1971; Stöffler, 1972). In practice the shock wave is a short stress pulse, with the shock front followed by a faster rarefaction wave that decreases the peak pressure and increases the duration of the pulse as the wave propagates. The pulse duration in laboratory experiments is typically about a microsecond, whereas large natural impacts can have



Figure 30. Ratio of the intensities of the broad and narrow components of the two-peak fits to the ²⁹Si MAS NMR spectra versus mean peak shock pressure. Open symbols are data from the initial study presented in Part II and filled symbols are the data of the present study (Part III).

pressure durations of up to a second. Comparison between laboratory-shocked and naturally-shocked samples of effects that require more than a microsecond to develop are clearly questionable. A clear difference is the formation of coesite, which is present at meteorite craters but is not produced in laboratory recovery experiments with short pressure durations (DeCarli and Milton, 1965; this study) or is only produced in minute quantities (Deribas *et al.*, 1965). We are currently carrying out a systematic study of naturally shocked quartz to determine under what circumstances, if any, the experimental NMR shock barometer can be applied (Boslough *et al.*, 1993; Cygan *et al.*, 1994a).

Another complication in applying the NMR shock barometer to natural samples is that the approach to peak pressure is in practice not an instantaneous event. For a single shock wave the true rise time depends on such material properties as yield strength, the existence of phase transitions, viscosity, and thermal transport. The geometry of our laboratory experiments leads to shock reverberations, whereby the sample is brought to the peak pressure in steps. Shock reverberations also occur in nature, because most rocks are polycrystalline and have some porosity. Stress waves can reflect off grain boundaries and free surfaces, giving rise to wide variations in local conditions. The high strain rates associated with rapid pressure release and tensile pulses following the shock wave can also generate effects which might be attributed to the shock wave.

Finally the post-shock temperature history of the material can have an affect on the observed properties. This temperature depends on the initial porosity and loading path, as well as on the peak shock pressure. The cooling time depends on details of the experimental geometry for laboratory-shocked samples and on depth of burial and thermal transport properties for a natural event. Of all these potentially complicating factors, the only ones we have significantly addressed have to do with temperature. The relative peak widths depend on shock temperature (or initial packing density) as well as on shock pressure (Figure 21). However, the initial densities of quartz powders used in this study are quite low compared to those likely to be naturally shocked, and a more complete study would require denser initial states. Because post-shock annealing of our samples at 900°C for 20 hr has some effect on the resulting NMR spectra (10 to 20 % peak width decrease), we express some concern in applying the shock barometer to material of unknown thermal history.

Another important problem is that the dependence of relative peak intensity on shock pressure (Figure 21) is only valid for NMR experiments with recycle times of 30 seconds and for samples with similar T_1 relaxation time. Figures 24 and 27 illustrates the strong dependence of this parameter on recycle time for our material. If relaxation to paramagnetic defects controls the T_1 values, relative intensities of the fit peaks and the overall peak width must also depend on the concentration of paramagnetic sites in the quartz.

Perhaps the most important result of this study is not a method of determining the shock pressure of an unknown sample, but a method of identification of shocked quartz. Even in our most highly shocked quartz sample, we found very few grains with the diagnostic optical features normally used to identify shocked quartz, and no high pressure phases are detected by XRD or MAS NMR. However, the ²⁹Si NMR resonances are significantly broadened, with the broadening strongly correlated with shock pressure. We suggest that this broadening can be effectively used as a convenient, new diagnostic technique for identifying naturally shocked quartz.

NMR Spectra of Shocked An₆₀ Plagioclase

The ²³Na, ²⁷Al, and ²⁹Si MAS NMR spectra of the shocked An₆₀ plagioclase feldspar are not significantly different from those of the unshocked sample. This sample probably has the incommensurate, modulated structure characteristic of such feldspar (see Ribbe, 1983). The ²⁹Si MAS NMR spectra of intermediate plagioclase feldspars are complex due to the large number of silicon sites and the incommensurate structure (see Kirkpatrick *et al.*, 1986b, 1987 and Kirkpatrick, 1988 for a summary of the NMR results for plagioclase feldspar). The ²⁹Si MAS NMR spectra of the unshocked and shocked samples (Figure 31) consist of multiple overlapping resonance in the range of -80 to -111 ppm and are similar to those previously observed (Kirkpatrick *et al.*, 1987). Deconvolutions of these spectra require either six or seven peaks which represent the wide distribution of silicon environments in the incommensurate



Figure 31. ²⁹Si MAS NMR spectra of the annealed (900°C for 20 hr) An₆₀ plagioclase starting material and the 16.5 GPa shocked plagioclase feldspar.

structure, and there is no significant correlation of any fit parameter with shock pressure.

The ²⁷Al peaks have maxima at about +54 ppm and widths of 28 ppm. The ²³Na peaks have maxima at about -18 ppm and widths of about 18 ppm. These NMR spectra are also similar to previously published spectra (Kirkpatrick *et al.*, 1985).

CONCLUSIONS

²⁹Si MAS NMR spectroscopy of quartz powders is exceptionally sensitive to disorder produced by shock-loading to pressures between 7.5 and 22 GPa. The level of disorder increases with shock pressure in such a way as to increasingly broaden the ²⁹Si resonance. The chemical shifts and widths of the peaks for the shocked guartz, in combination with the lack of optical and XRD evidence for an amorphous phase, suggest that the observed peak broadening is due to changes in Si-O-Si bond angles caused by large dislocation densities. For controlled shock-loading on well-characterized quartz powders, this broadening can be used as an indicator of peak shock pressure ("shock barometer"). To extrapolate this method to natural samples, more research is required to characterize the relaxation behavior of ²⁹Si in quartz and the influence of paramagnetic defects. The experimental conditions under which the NMR spectra are obtained (especially pulse recycle time) have a strong effect on the peak width. Therefore, to make use of ²⁹Si NMR spectral broadening as a quantitative measure of shock-loading, it is imperative that these conditions be carefully controlled.

Broadening of the ²⁹Si NMR peak seems to be a general feature of shocked quartz, and we believe this technique may be more useful as method for identifying naturally shocked quartz than for quantifying shock pressures. The primary contributor to the spectral broadening appears to be an amorphous-like phase. Preliminary data on the relaxation behavior of our samples indicates that the abundance of this extensively distorted material may be less than 10 %, although the effect on the peak widths of the spectra obtained at a recycle time of 30 seconds is disproportionately large. Its T₁ relaxation time appears to be much shorter than that of the less distorted material, perhaps due to a higher concentration of paramagnetic centers associated with defects.

Unlike the results for quartz, the NMR spectra for the shocked An_{60} plagioclase feldspar have no features that obviously correlate with shock-loading conditions. This result may be due to the already large peak breadth caused by the large number of silicon sites in its complex structure. There is no evidence to support the use of NMR spectroscopy of intermediate plagioclase as a shock barometer.

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