

NMR SPECTROSCOPIC EXAMINATION OF SHOCKED SANDSTONE FROM METEOR CRATER, ARIZONA

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

INTRODUCTION

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

We have previously suggested that NMR spectra be used as a "shock barometer", or at least as an identification technique for shocked quartz. However, our measurements to date have been limited to laboratory-shocked samples. Because

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

EXPERIMENTAL METHOD

Five samples of shocked Coconino Sandstone were obtained from Meteor Crater to represent the range of shock pressures associated with the impact. The samples are identical to those first examined by Kieffer using X-ray diffraction and optical microscopy [7].

The NMR experiment detects the radio frequency emission from active ^{29}Si nuclei that have been excited to a high-energy spin state while the sample is located in a very strong magnetic field. The ^{29}Si NMR spectra of the shocked Coconino Sandstone samples were obtained at a frequency of 71.5 MHz with an applied magnetic

field of 8.45 T. The NMR analysis requires magic-angle spinning (MAS) and multi-pulse Fourier transform techniques to provide spectra with significantly decreased interference from dipolar interactions and improved signal to noise ratio. MAS frequencies were typically at 3.5 kHz and the pulse recycle time was 30 s. Approximately 200 to 300 mg of sample powder were used for each NMR analysis.

RESULTS

Figure 1 provides the MAS NMR spectra obtained for the five naturally-shocked samples; sample numbers are equivalent to those used by

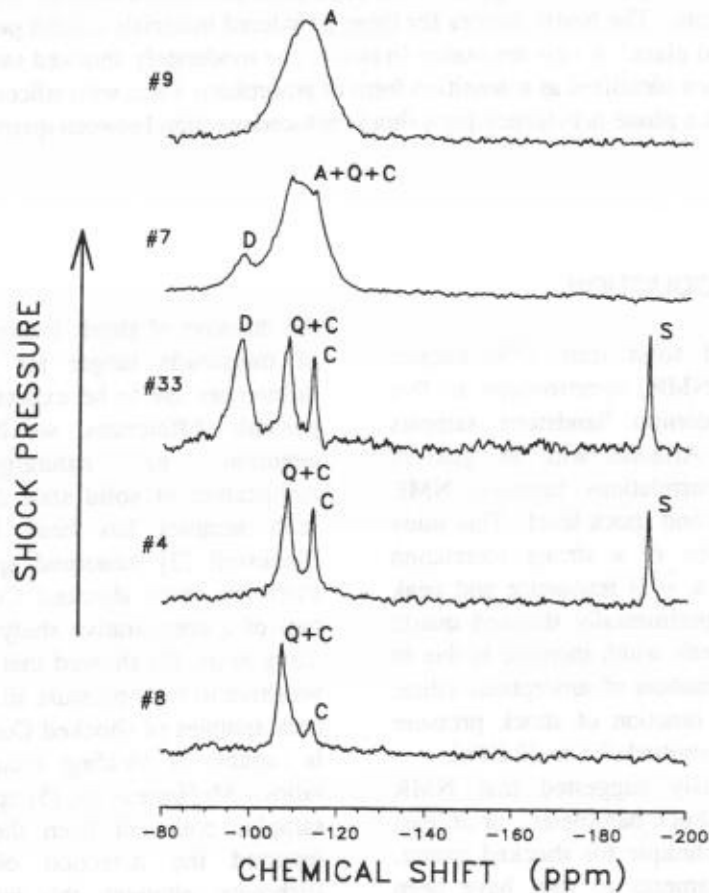


Figure 1. ^{29}Si NMR spectra of five shocked Coconino Sandstone samples. Resonance identifications are (Q) quartz, (C) coesite, (S) stishovite, (A) Q^4 silicon sites in amorphous silica, and (D) Q^3 (one OH) silicon sites in a densified form of hydroxylated amorphous silica. Sample numbers are those of Kieffer [7].

Kieffer [7]. The spectra are presented in relative order of increasing shock pressure. Resonance frequencies are provided in terms of chemical shift (ppm relative to an external standard) and are related to the local bonding environment of silicon in different coordinations and to the Si-O-Si bond angle distribution. The ability of MAS NMR to discriminate among the silica polymorphs and amorphous phases is demonstrated by these results.

The following is a summary of our observations: Sample #8: mostly quartz, small amounts of coesite and possibly amorphous silica, no stishovite. Sample #4: mostly quartz, more coesite than sample #8, some amorphous silica, and stishovite. Sample #33: same as sample #4, but with an additional peak, due to Q³ (one OH) silicon sites in a dense form of hydroxylated amorphous silica. Sample #7: mostly amorphous silica, with some quartz and coesite, no stishovite, contains a less intense peak associated with the same Q³ site as in sample #33. Sample #9: almost entirely amorphous silica, no stishovite. A representation of the different tetrahedral silicon sites is presented in Figure 2.

DISCUSSION

Of particular interest in these results are the strong stishovite resonances in samples #4 and #33; the stishovite peak observed by Yang *et al.* [4] is significantly weaker. We also observe a more intense X-ray diffraction line ($2\theta = 30.2^\circ$) for stishovite, implying there is more of this phase in our samples. The only samples for which we observe stishovite are those from the intermediate shock pressures.

The presence of the resonance with a chemical shift of about -98 ppm in two of our samples (#33 and #7) is especially noteworthy. There is no X-ray diffraction evidence for significant amounts of any crystalline material other than the three silica polymorphs. There are several lines of evidence that this resonance corresponds to silicon in tetrahedra with one hydroxyl group in a dense form of hydroxylated amorphous silica: 1) Variable recycle time NMR experiments indicate the

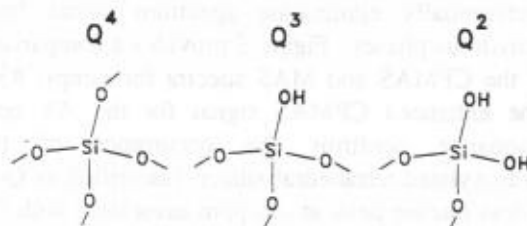


Figure 2. Silicon sites that are distinguished by ²⁹Si NMR spectroscopy using MAS and CPMAS methods.

resonance has a very short relaxation time (T_1), consistent with previous observations for shock-produced amorphous silica. 2) The shift to higher frequency (smaller negative ppm value) is consistent with a denser phase than a similar phase formed at one atmosphere for a given silicon coordination. A dense amorphous phase has been identified in NMR spectra obtained by Nellis *et al.* [8] from crystalline quartz shocked to 33 GPa, with a resonance centered at about -106 ppm, an upfield shift of about 6 ppm from -112 ppm for normal-density silicon glass [9]. The resonance for Q³ (one OH) silicon sites in a normal-density gel is at about -102 ppm [10]. Our observed peak position of about -98 ppm would be consistent with densification by roughly the same amount as the amorphous silica associated with shocked quartz. 3) The peak is broad, indicating a wide range of Si-O-Si bond angles typical of amorphous material, and is inconsistent with silicon in clay or feldspar. 4) The target Coconino Sandstone was wet, and there is TEM evidence for vesicular "froth" (consisting of amorphous material produced by steam separation) in the intermediate shock samples [11]. 5) We have observed in a previous NMR study of clinoptilolite that shock loading can generate hydroxyl groups [12].

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

preferentially eliminating spectrum signal from anhydrous phases. Figure 3 provides a comparison of the CPMAS and MAS spectra for sample #33. The enhanced CPMAS signal for the -98 ppm resonance confirms the occurrence of the hydroxylated tetrahedral silicon (identified as Q³). A less intense peak at -86 ppm associated with Q² silicon is also observed in the CPMAS spectrum. No significant CPMAS signal is observed for sample #9; the "A" peak is due to Q⁴ silicon in amorphous silica.

SUMMARY

Silicon-29 NMR spectroscopy can provide considerable microstructural information on high pressure crystalline and amorphous phases resulting from natural impacts. Cross-polarization techniques can be used to enhance silicon resonances near protons to analyze hydrated phases. Using this approach we have identified a new naturally-occurring shock-produced phase—a densified hydrated amorphous silica.

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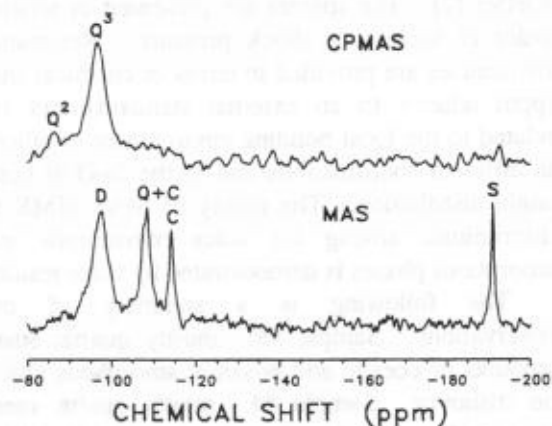


Figure 3. MAS and CPMAS ²⁹Si NMR spectra for Meteor Crater sample #33 exhibiting the hydroxylated Q³ and Q² sites for silicon.

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