

NMR Spectroscopy of Experimentally Shocked Single Crystal Quartz: A Reexamination of the NMR Shock Barometer. P. S. Fiske (Department of Geology, Stanford University, Stanford, CA 94305-2115, fisko@pangea.stanford.edu) A. J. Gratz and W. J. Nellis (Institute of Geophysics and Planetary Physics, Lawrence Livermore National Laboratories, L-413, Livermore, CA 94550)

Cygan and others [1,2] report a broadening of the ^{29}Si NMR peak for synthetic quartz powders with increasing shock pressure which they propose as a shock wave barometer for natural systems. We expand on these results by studying single crystal quartz shocked to 12 and 33 GPa using the 6.5 m two-stage light-gas gun at Lawrence Livermore National Laboratories. Our NMR results differ substantially from those of Cygan and others and suggest that the proposed shock wave barometer may require refinement. The difference in results between this study and that of Cygan and others is most likely caused by different starting materials (single crystal vs. powder) and different shock loading histories. NMR results from single crystal studies may be more applicable to natural systems.

Peak Position and Line Shape Studies

The spectrum for the 12 GPa sample consists of a single asymmetric peak with an intensity maximum at -107.3 ppm (relative to TMS) and a line width (FWHM=full width at half max) of 0.8 ppm. XRD shows the sample to consist solely of quartz, although its XRD peaks are broader than those for unshocked quartz. Transmission electron microscope investigations of samples shocked to similar pressures suggest that this sample contains less than 1% of an amorphous material. The shock wave barometer of Cygan and others predicts a two-fold increase in the line width at these pressures but the peak width we observe is statistically unchanged from that observed for unshocked quartz. These results suggest that any shock wave barometer using NMR peak widths may not be able to resolve differences below about 10 GPa, the region that most needs a good shock wave barometer for natural systems, because obtaining ^{29}Si NMR spectra for quartz with peaks narrower than about 1 ppm is experimentally difficult.

The spectrum for the 33 GPa sample (figure 1) consists of a symmetric peak centered at -109.6 ppm (FWHM 5 ppm) and a high frequency broad peak centered at -106.1 ppm (FWHM 20 ppm). XRD peaks are about twice as broad as for the 12 GPa sample. Results from previous shock experiments suggest that this sample contains about 30% of an amorphous material [3]. In their highest pressure samples (22 GPa), Cygan and others found a single NMR peak with a four-fold increase in line width but no shift in peak position.

The shift in the narrow peak to lower frequency is consistent with a 3° increase in the mean Si-O-Si bond angle [4]. The broad peak is similar to those obtained for SiO_2 glass quenched at high pressure (6 GPa, peak position: -108.5 ppm, FWHM: 13 ppm [5]) and SiO_2 glass statically densified at room T to 18 GPa (peak position: -105.6 ppm, FWHM: 17 ppm [6]), suggesting that the amorphous material is substantially denser than 1 bar SiO_2 fusion glass, with a reduction in the mean Si-O-Si bond angle of 5 to 8° .

Relaxation Time Studies

Spectra were acquired using a range of delay times between excitation pulses (up to 3000 sec), and intensities were calibrated using a fully relaxed standard. Despite the use of small tip angles, the spectra with the longest delays represent only 40% of the total expected intensity due to the long relaxation time of this material.

Unlike the results of Cygan and others [7], we observe the amorphous material (found only in the 33 GPa sample) to have a longer relaxation time than the crystalline phase. This suggests that if the mechanism for relaxation is the presence of paramagnetic centers associated with structural defects [2] the amorphous material has a lower concentration of these defects than

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the crystalline material. Signal intensity measurements show that the total amount of signal obtained at each delay time is independent of shock pressure. This suggests that if paramagnetic defects are controlling relaxation in these samples, their overall concentration is not a strong function of shock pressure. However, we caution that the mechanism of relaxation in these materials is uncertain.

Finally, in order to obtain fully relaxed, quantifiable NMR spectra we are carrying out a series of experiments using single crystal amethyst. The paramagnetic Fe in amethyst has been shown to greatly reduce the relaxation time in single crystal quartz thus allowing for quicker signal acquisition and a higher ratio of signal to noise [8].

Conclusions

The differences in these results compared to the work of Cygan and others suggest that shock experiments on compact targets produce different end products than experiments on powders, and may be more comparable to naturally shocked materials.

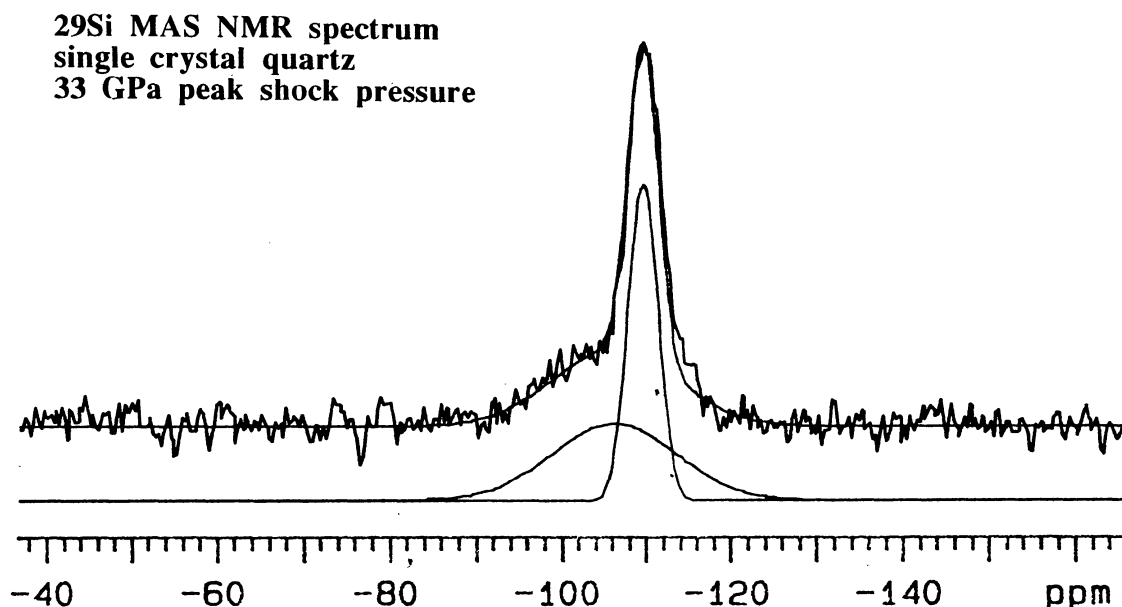


Figure 1

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