[29]SI NMR SPECTROSCOPY OF NATURALLY-SHOCKED QUARTZ FROM METEOR CRATER, ARIZONA: CORRELATION TO KIEFFER'S CLASSIFICATION SCHEME* M. B. Boslough[1], R. T. Cygan[1], and R. J. Kirkpatrick[2], [1]Sandia National Labs, Albuquerque, NM 87185 and [2]U. of Illinois, Urbana, IL 61801.

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

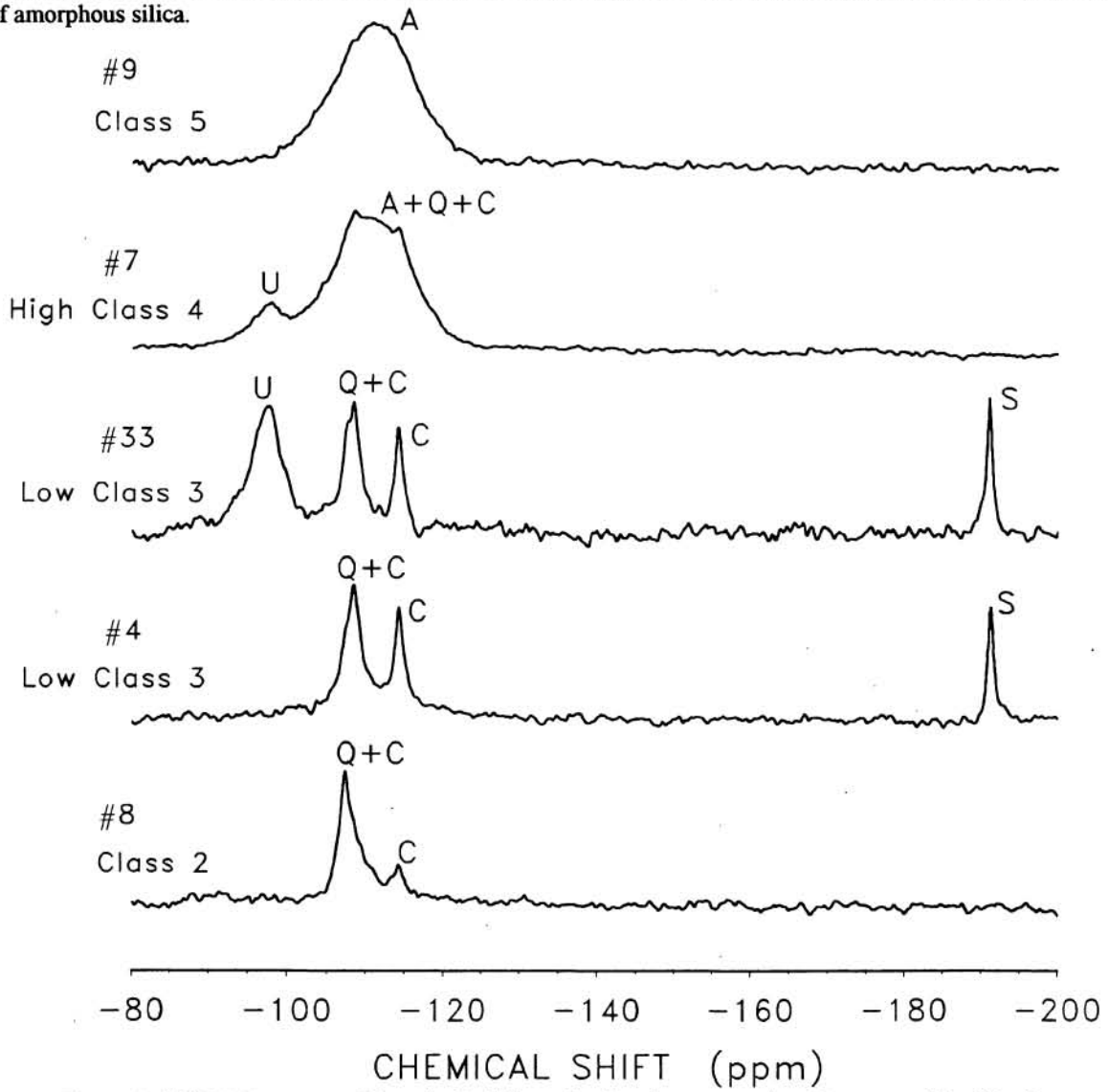

Figure 1. [29]Si NMR spectra of five shocked Coconino Sandstone samples. Resonance identifications are (Q) quartz, (C) coesite, (S) stishovite, (A) Q^4 sites in amorphous silica, and (U) unknown site tentatively identified as Q^3 (one OH) Si sites in a densified form of hydroxylated amorphous silica.

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

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

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

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

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