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^{29}Si MAS NMR relaxation study of shocked Coconino Sandstone from Meteor Crater, Arizona

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Abstract ^{29}Si nuclear magnetic resonance (NMR) spectroscopy was used to characterize the silica phases in a moderately-shocked Coconino sandstone from Meteor Crater, Arizona. The spectra were recorded using direct polarization, magic-angle spinning, and variable delay times in a saturation recovery pulse sequence. Resonances observed at -97.3, -107.1, -113.9 and -191.2 ppm were assigned to a densified hydrous form of amorphous silica (D phase), quartz, coesite and stishovite phases, respectively. The relative percentages were estimated as 1.7, 80.6, 16.4 and 1.3% for the D, quartz, coesite, and stishovite phases. The power-law recoveries of the magnetization for the quartz and coesite phases can be interpreted in terms of their phase geometries.

Introduction

Coconino sandstone from Meteor Crater, Arizona is ideally suited for examination of naturally shocked quartz. Unshocked Coconino sandstone is an exceptionally pure quartzite, consisting almost entirely of quartz. Shocked samples representing a wide range of degrees of shock metamorphism are easily collected in and around the crater. It has been one of the most extensively studied of all naturally-shocked rocks.

Shocked Coconino sandstone at Meteor Crater was described by Shoemaker (1960, 1963) as one of the main components of the fused, crushed, and shocked rock distributed in and around the crater that provided the geological basis for the first description of modern impact mechanics. Interest in shocked Coconino sandstone accelerated with the discovery of coesite (Chao et al. 1960) and later with the detection of stishovite (Chao et al. 1962) in samples from Meteor Crater. These discoveries provided a means by which impact structures could be recognized; it was also quickly demonstrated that shocked rocks were present at many other sites (Stöffler 1971).

The first extensive quantitative analysis of shocked Coconino sandstone was performed by Kieffer (1971), who used X-ray diffraction techniques to determine relative abundances of the silica polymorphs quartz, coesite, stishovite, and glass over the entire range of shock metamorphism. She created a classification scheme based on the amount of quartz remaining in the rocks after having been shocked, and microscopically examined thin sections of the specimens to characterize the extent of shock metamorphism. Kieffer et al. (1976) followed up the earlier work with a transmission electron microscopy examination of the same samples that she used to develop the classification method. This analysis was the first systematic transmission electron microscope (TEM) characterization of the microstructure of a shocked rock, and provided information on the occurrences and textural relationships of the various silica polymorphs.

The development of advanced nuclear magnetic resonance (NMR) methods making use of high-field superconducting magnets and magic-angle spinning (MAS) techniques provided a new capability for probing the local environment of silicon sites in crystalline solids, and was quickly applied to as many polymorphs of silica as possible. Coconino sandstone provided the source for coesite and stishovite in the first examination of these phases by NMR spectroscopy (Smith and Blackwell 1983). Yang et al. (1986) used Coconino sandstone to show that MAS NMR spectroscopy could be used not only to detect coesite and stishovite in shocked whole-rock samples, but to determine the relative abundance of these phases.

As part of a project to develop NMR spectroscopic methods for examination of shocked quartz (Cygan et al. 1990, 1992), Cygan et al. (1994) obtained aliquots of the original samples that Kieffer (1971) used to define the classification scale. The spectra obtained from these samples were fully consistent with Kieffer's interpretation, and further demonstrated the usefulness of MAS

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NMR spectroscopy in characterizing shocked quartz. In addition, Cygan et al. (1994) identified an additional resonance and associated it with a new densified form of hydrated amorphous silica tentatively dubbed the "D phase". They proposed that the presence of this phase is evidence for a shock-induced reaction between quartz and steam under high pressure conditions, and further suggested that it is the same substance as the vesicular "froth" that Kieffer et al. (1976) had observed in TEM images of the same samples.

In related work, Assink et al. (1994), developed NMR relaxation methods for analyzing experimentally shocked quartz powders, and used them to determine fractal dimensions of crystalline and amorphous components and to estimate their relative abundances. The present work applies these relaxation methods to the Kieffer samples of Coconino sandstone with the purpose of (1) independently determining relative polymorph abundances in whole-rock samples, and (2) characterizing the relaxation behavior of the various phases.

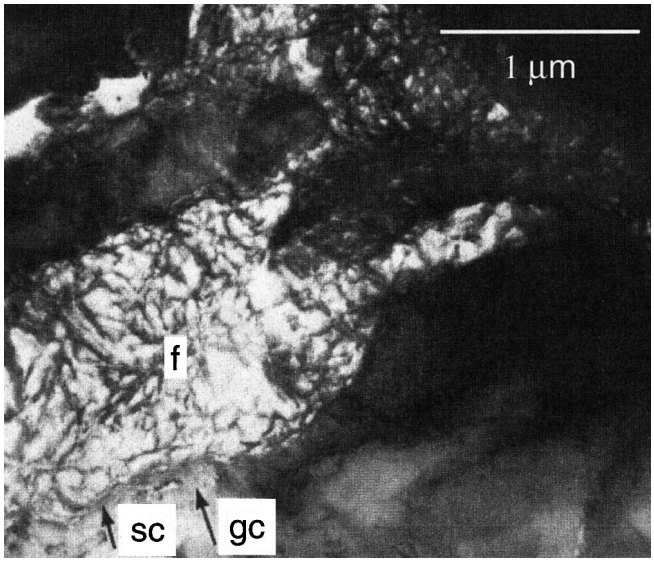

Fig. 1 Transmission electron micrograph of froth phase (*f*) in a crystalline quartz grain for class 3 Coconino sandstone (sample #33) as modified from Kieffer et al. (1976); *sc* sharp contact, *gc* gradational contact

Materials

Approximately 2 g of powdered sample #33 from Meteor Crater, Arizona were obtained directly from S. Kieffer, and is the same material examined in her early studies of shock metamorphism at Meteor Crater (Kieffer 1971; Kieffer et al. 1976). Sample #33 was chosen for the NMR relaxation study due to the presence of quartz, coesite, stishovite, and the D-phase as identified by ^{29}Si MAS NMR (Cygan et al. 1994). In addition, this sample was extensively examined by TEM (Kieffer et al. 1976). Kieffer (1971) identified this shocked Coconino sandstone sample, collected in alluvium formed from mixed debris on the crater rim on the southeast side of the crater, as a low class 3 sample. Class 3 materials represent a moderately shocked sandstone that is typically composed of 45% to 85% quartz with the remainder being high pressure silica polymorphs or glass. Five shock classes were identified based on decreasing quartz content (Kieffer 1971).

Based on quantitative X-ray diffraction analysis, Kieffer (1971) determined that sample #33 is composed of approximately 72% quartz, 21% coesite, 7% glass, and a trace (between 0.25% and 1% by weight) of stishovite. Due to limitations of the method and the existence of an amorphous phase, Kieffer (1971) estimated the relative error in the abundances to be approximately 10%. The diameters of quartz grains are typically 0.1 mm to 0.3 mm and are often characterized by a wavy extinction under crossed Nicols. Planar deformation features (PDF) are observed in about 5% of all quartz grains. PDFs are considered diagnostic of an impact event (Grieve et al. 1990). Class 3 rocks from Meteor Crater generally are identified by quartz grains and high pressure regions that include symplectic, or intergrown, regions on quartz boundaries, opaque regions grading into the symplectic regions, and high-refractive index cores within some of the opaque regions. These cores are usually 60 μm to 100 μm in length but can be as large as 200 μm. The cores are composed of coesite grains that are generally less than 20 μm in diameter.

Kieffer et al. (1976) describes the textural relationships of these different shocked regions based on TEM evidence. Additionally, the authors identify an amorphous material characterized by a fine network of angular vesicles that they call "froth" (Fig. 1). This froth phase occurs close to or within the high pressure region of sample #33, typically at a boundary with quartz, coesite, or stishovite. The froth occurs in veins, in irregular open fractures, or in PDFs within grains. The froth constitutes approximately 20% to 40% areal extent of the symplektic phases, and forms a network of vesicles that range in size from 10 Å to 500 Å. Kieffer et al. (1976) suggested that the petrographic opacity observed for the shocked material is related to the occurrence of submicroscopic veins of froth observed in TEM images. Furthermore, they suggest that the froth was produced by the violent separation of a water vapor phase from a silica liquid phase, occurring at shock pressures between 10 GPa and 20 GPa.

Spectroscopy

^{29}Si magic-angle spinning (MAS) NMR spectra were acquired at 79.5 MHz on a Bruker AMX-400 spectrometer. All spectra were recorded using direct polarization and a MAS speed of 4 kHz. The ^{29}Si NMR relaxation experiments were conducted with a saturation recovery pulse sequence consisting of a train of $\pi/2$ pulses, a delay for magnetization recovery, and a $\pi/2$ acquisition pulse. The spectra were acquired at ambient temperatures and were externally referenced to octakis(trimethylsiloxy)silsesquioxane (downfield resonance at 12.0 ppm).

Results and discussion

The ^{29}Si NMR spectra of sample #33 from Meteor Crater, Arizona were acquired using recovery delays ranging from 0.25 s to 200,000 s. Spectra for selected delay times are shown in Fig. 2. The number of acquisitions ranged from 1024 for short delays to a single acquisition for the longest delays. Four resonances, -97.3, -107.1, -113.9 and -191.2 ppm, are observed in Figs. 2b, c and d which correspond to intermediate delay times. Fewer than four resonances are observed in spectra acquired at very short or very long delay times. For short delay times, Fig. 2a, the resonances at -107.1 and -113.9 ppm are not observed because their long relaxation times have pre-

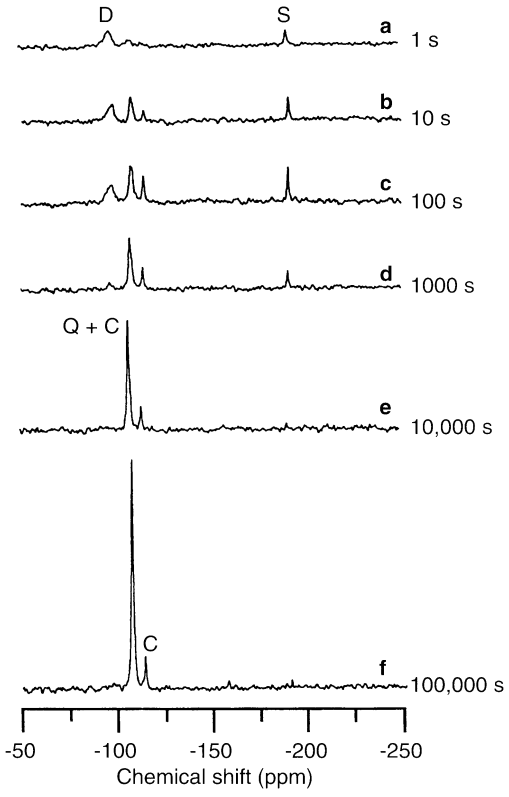

Fig. 2 ^{29}Si MAS NMR spectra of Meteor Crater, Arizona sample #33 acquired with a saturation recovery pulse sequence, delay times shown, and MAS=4 kHz. Resonance assignments are for quartz (Q), coesite (C), stishovite (S), and D-phase (D). An arbitrary vertical scale is used for each spectrum in order to emphasize the particular resonances

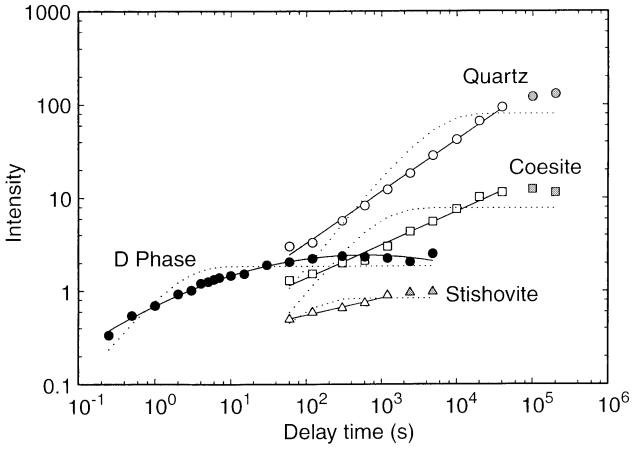

Fig. 3 ^{29}Si NMR magnetization recovery of Meteor Crater, Arizona sample #33 as a function of delay times in the saturation recovery pulse sequence. The intensities for the stishovite resonance were reduced by a factor of two to avoid interference with the data for the D-phase silica resonance. Symbol size is representative of the uncertainty in the measurement of the magnetization intensity. *Dotted lines* for quartz, coesite, and stishovite represent the best fit for an exponential recovery based on an equal weighting of the data points. The *solid lines* represent power-law fits for quartz, coesite, and stishovite with respective slopes of 0.56, 0.36, and 0.18. Magnetizations corresponding to the two longest delay times for each phase (*filled symbols*), where magnetic saturation is approached, were excluded from the power-law fits. The D-phase data are connected by a simple quadratic curve to indicate the magnetization trend with delay time

vented significant recovery of their magnetization. The resonances at -97.3 and -191.2 ppm are not apparent at the long delay times shown in Fig. 2e and f. Fewer acquisitions were recorded at long delay times, thus, the resonances of these minor components are buried in the baseline noise.

The resonances at -113.9, -107.1, and -97.3 ppm have been previously assigned to coesite (C), quartz (Q), and a densified form of amorphous silica containing one directly attached -OH group (D), respectively (Smith and Blackwell 1983; Boslough et al. 1993; Cygan et al. 1994). The hydrated phase was confirmed by ^{29}Si cross-polarization NMR. Although it is not obvious in the spectra shown, coesite has two SiO_2 tetrahedra which exist in a 1:1 ratio. As a result, two resonances are observed for coesite. One of the resonances is clearly seen at -113.9 ppm while the second resonance, at -108.1 ppm, overlaps the quartz peak. At longer repetition delays, this resonance appears as a barely noticeable shoulder on the quartz peak. The single resonance at -191.2 ppm appears in the region of the spectrum which typically corresponds to octahedrally coordinated silicon sites. This resonance has been assigned to stishovite (S). These spectral assignments are in excellent agreement with the chemical shifts previously reported for samples of quartz, coesite, and stishovite (Lippmaa et al. 1980; Smith and Blackwell 1983).

Figure 3 shows the intensity of ^{29}Si magnetization for the various silica phases as a function of delay time. The data are best viewed on a log-log plot because both the delay times and magnetization intensities vary by several orders of magnitude. The dotted lines represent exponential fits for the quartz and coesite phases. The magnetization recoveries of these phases as well as the minor D and stishovite phases were not well described by an exponential function with a simple spin-lattice relaxation time. Power-law fits to the data will be discussed later in this section. When resonances display exponential behavior, it is possible to determine the equilibrium magnetization by recording spectra with recycle delays up to one time constant and extrapolating the curve to longer times. For complex samples such as Meteor Crater, Arizona sample #33 which exhibit nonexponential behavior, such extrapolation is not possible and one can easily and mistakenly assume that an equilibrium magnetization has been reached.

As shown in Fig. 3, the magnetization recoveries for quartz and coesite reach a plateau at $\sim 10^5$ s, while for stishovite a plateau is reached between 10^3 and 10^4 s. The D-phase resonance reaches a plateau in the 10 to 100 s time region. In order to describe accurately the magnetization recovery for this peak, spectra at shorter delay times were acquired. Additionally, the D-phase exhibits a concave-down trend in the log-log plot that is distinct from the relaxation exhibited by the other phases. Figure 3 illustrates that experiments were conducted with a suffi-

Table 1 Relative percentages of the various constituents of Meteor Crater, Arizona sample #33

Peaks	Relative percentage
D phase	1.7±0.2
Quartz	80.6±2.0
Coesite	16.4±2.0
Stishovite	1.3±0.2

cient range of delay times to ensure that the spectra with the longest delay times represent the final equilibrium magnetization for that phase.

The relative percentage of each phase was calculated from the integrated intensity of the magnetization in the plateau region for that phase. The results have been tabulated in Table 1. The resonance at -107.1 ppm was assumed to consist of both quartz silicon and a contribution from coesite equal to the coesite resonance at -113.9 ppm. The major constituent of the Meteor Crater, Arizona sample #33 is quartz at 80.6% abundance. The second major constituent is coesite at 16.4% followed by amorphous silica and stishovite at 1.7% and 1.3%, respectively. These abundances provide a significant improvement in accuracy compared to the X-ray diffraction-based method used by Kieffer (1971) in which the glass determination is difficult. Also, we observe a coesite to stishovite ratio of approximately 13 which is about half of the value determined by Yang et al. (1986) using a limited range of delay times (5, 20, and 900 s) in their NMR relaxation experiments on a class 3 sample.

The solid lines in Fig. 3, represent power-law fits, $m(t)=Ae^{\alpha t}$, to the magnetization recoveries of the quartz, coesite and stishovite phases. The magnetization intensities corresponding to the two longest delay times for each phase were ignored for the purposes of these calculations. The fits appear excellent and the correlation coefficients are equal to or greater than 0.99 for each of the recovery curves. Power-law behavior has been used to describe the magnetization recovery of silica aerogels doped with paramagnetic impurities (Devreux et al. 1990). The relaxation of spin-1/2 nuclei dominated by paramagnetic impurities is expected to display power-law behavior when magic-angle spinning is used. In a previous contribution, Assink et al. (1994) showed that the recoveries of ^{29}Si magnetization for samples of shocked and unshocked synthetic quartz are accurately fit by a power-law function. Thus, power-law behavior for these silica phases is not surprising since they are known to contain low levels of paramagnetic impurities.

The power-law exponent is related to the fractal dimension of the phase (Devreux et al. 1990). The fits shown in Fig. 3 predict fractal dimensions of 3.3, 2.2 and 1.1 for the quartz, coesite, and stishovite phases respectively. A three-dimensional structure is certainly reasonable for the dominant quartz phase. Coesite has a two-dimensional characteristic that might be ascribed to its occurrence in part along fractures through a grain or in parallel cleavages as observed in class 3 samples from Meteor Crater (Kieffer et al. 1976). We hesitate to attach physical significance to the linear structure predicted for the stishovite phase. It should be noted that the signal intensity of this minor phase is much less than that of the quartz and coesite phases. Also, the logarithmic span of delay times for the stishovite phase is less than half those for the quartz and coesite phases.

The magnetization recovery of the D-phase cannot be described by either an exponential or power-law function. The fast recovery and unique time behavior suggests that the D-phase relaxation mechanism is dominated by a mechanism distinct from the mechanism governing the other phases. We believe that the D-phase relaxation mechanism likely includes contributions from both paramagnetic impurities and, more importantly, heteronuclear dipolar interactions between the silicon nuclei and the reservoir of ^{1}H spins. The magnetization recovery of spins subjected to multiple relaxation mechanisms cannot be described by a simple functional form.

Conclusion

The examination of the NMR relaxation behavior of shocked natural materials provides an additional tool for characterizing the complex phases that make up a shocked rock. NMR can simultaneously identify quartz and the high pressure silica polymorphs that occur in Meteor Crater samples. In addition to the existence of quartz, coesite, and stishovite, sample #33 is also noteworthy in the presence of a densified and hydrated amorphous silica (D phase) that we suggest corresponds to the froth described by Kieffer et al. (1976). Relaxation experiments performed over a wide range of experimental delay times indicate a significant range of times associated with the silica phases before magnetic saturation is achieved. Visualization of the recovery curves on a log-log plot provides evidence that equilibration has been reached and that the phase composition can be calculated. The power-law relaxation behavior also provides fractal dimensions that might be related to the geometry of the silica phases. The NMR methods used in this study provide a convenient analytical approach for the direct identification and quantitative determination of crystalline-glass mixtures that can occur in shocked rocks.

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