

DETECTION OF HIGH-PRESSURE SILICA POLYMORPHS IN WHOLE-ROCK SAMPLES FROM A METEOR CRATER, ARIZONA, IMPACT SAMPLE USING SOLID-STATE SILICON-29 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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High-resolution solid-state silicon-29 nuclear magnetic resonance spectroscopy using "magic-angle" sample-spinning can readily detect the presence of the high pressure silica polymorphs coesite and stishovite in whole-rock samples from a Meteor Crater, Arizona, impact sample, and yields accurate coesite/stishovite ratios. Such determinations are being carried out by partially suppressing (saturating) intense quartz signals (which have long spin-lattice relaxation times) by means of short experimental recycle-times. This method enhances the signal-to-noise ratios of coesite and stishovite (which have relatively short spin-lattice relaxation times). For the sample examined, the coesite/stishovite ratio is about 27.

INTRODUCTION

Coesite and stishovite are high-pressure silica polymorphs which are important diagnostic minerals for the recognition of meteor impact and for the examination of the pressure and temperature paths which individual samples follow during impact. Stishovite occurs naturally only at meteor impacts; coesite is by far most common at impact sites. The traditional methods used to detect these phases are optical examination followed by powder x-ray diffraction of the residue left after digestion in an HF-containing acid (Chao *et al.*, 1960, 1961, 1962; Bruce and Cohen, 1963; Fahey, 1964). Coesite and stishovite are concentrated by this acid digestion method, although if sufficient reaction time is allowed, the coesite will also dissolve, leaving only stishovite. The disadvantages of the method are that HF is unpleasant to use, that very small grains can be lost during filtration and that glass (containing silicon in either 4- or 6-fold coordination) is destroyed in the process.

We present in this paper the results of a high-resolution solid-state silicon-29 "magic-angle" sample-spinning (MASS) nuclear magnetic resonance (NMR) spectroscopic study of a sample of shocked Coconino sandstone from Meteor Crater, Arizona. Our results indicate that MASS NMR can easily detect the presence of both coesite and stishovite in whole rock samples, and yields quantitative values for the coesite/

stishovite ratio, an important parameter in examining the pressure and temperature history of shocked samples (Kieffer, 1971; Stöffler, 1971). The method also permits, in principle, the quantitative determination of quartz, and of glassy phases, when present.

NUCLEAR MAGNETIC RESONANCE

Discussions of the theory of solid-state silicon-29 NMR spectroscopy, the methods used (including magic-angle sample spinning), and the presently available background data for silicates have been presented by Lippmaa *et al.* (1980, 1981), Smith *et al.* (1983) and Mägi *et al.* (1984). We note here only that the NMR experiment measures the radiofrequency emissions from nuclei which have been excited to some higher-energy spin state while the sample is located in a very strong magnetic field. In the pulse Fourier transform method we use, the nuclei are first excited by a short burst of radiofrequency radiation, typically about ten microseconds, and then the re-emissions from the sample are monitored for some longer period, typically about one second. These signals are first detected in the time domain, and are then Fourier transformed to yield spectra in the frequency domain. This method is chemically useful because the frequencies of the signals detected are a strong function of the type of chemical environment in which the nuclei exist. These frequencies are by convention reported as the chemical shift, which is the ppm deviation of the resonance frequency of the sample from that of some standard reference (in our case tetramethylsilane). More details are to be found in the book by Farrar and Becker (1971).

A description of the silicon-29 MASS NMR behavior of the silica polymorphs has been presented by Smith and Blackwell (1983). Chemical shifts of the silica polymorphs relevant to impact sites are -107.1 ppm for quartz, -108.1 and -113.9 ppm for coesite, and -191.1 ppm for stishovite. The chemical shift of stishovite is so far removed from the others because it contains silicon in six-fold coordination. Differences of 0.5 to 1.0 ppm are readily resolved by modern MASS NMR spectrometers. Accuracy and precision are probably about 0.3 ppm, and are a function of the linewidth of the resonance under observation.

One important feature of MASS NMR spectroscopy that is necessary to understand the data presented in this paper is the concept of the experimental "recycle time". For a nucleus to fall from a higher energy spin state to a lower energy spin state, it must lose a quantized amount of energy. This so-called spin-lattice (T_1) interaction takes place at different rates in different materials, even for the same nuclide, and is a function of a number of factors, including the presence of paramagnetic centers, atomic motion in the crystal, the presence of protons, and so on. To obtain optimum signal to noise, the sample is usually irradiated with the radiofrequency radiation at time intervals of about five times T_1 , the time for an essentially equilibrium Boltzmann population to be (re)established. If the recycle time is significantly less than about $5T_1$, less signal is seen, because not all the nuclei have time to fall to the lower energy state after excitation. If the recycle time is sufficiently short, the signal is almost entirely suppressed, a condition called saturation (Farrar and Becker, 1971).

We find that coesite and stishovite have much shorter T_1 's than quartz, and have taken advantage of this fact to suppress the signal from quartz and greatly enhance the signal-to-noise ratios from the other phases. This method allows the detection of very small amounts of the higher pressure phases.

The experimental methods used are those described by Smith *et al.* (1983). The spectrometer is "home-built" and is based on an 8.45 Tesla superconducting magnet (Oxford Instruments, Osney Mead, U.K.) and a Nicolet 1280 (Madison, WI) computer system. The sample probe is also homebuilt, and uses mushroom-shaped (Andrew-Beams) sample rotors for MASS.

SAMPLE DESCRIPTION

The sample examined is a piece of Coconino sandstone from Meteor Crater, Arizona. Powder X-ray diffraction of the whole rock sample (CuK α radiation) using a Siemens D-500 x-ray diffractometer (goniometer scan rate = 1° 2 θ /m; range = 200 counts/s; time constant = 1 s; 35 kv, 30 ma), shows only quartz and coesite. Stishovite is not detected, and there is no broad band of intensity in the range of 20° 2 θ , indicating the absence of glass. At a decreased scan rate of 0.1° 2 θ /minute with computer control of the scan, however, a small peak at 30.2° 2 θ was repeatedly observed (Fig. 1). This peak corresponds to a d-spacing of 2.959Å, which is the (110) spacing of stishovite, and its most intense peak. This careful x-ray diffraction examination indicates clearly that stishovite is present, but without a very slow scan rate and an automated diffractometer, the stishovite peak is not discernible from background noise. Because of the presence of coesite and stishovite and the lack of glass, our sample falls into class three of Kieffer (1971).

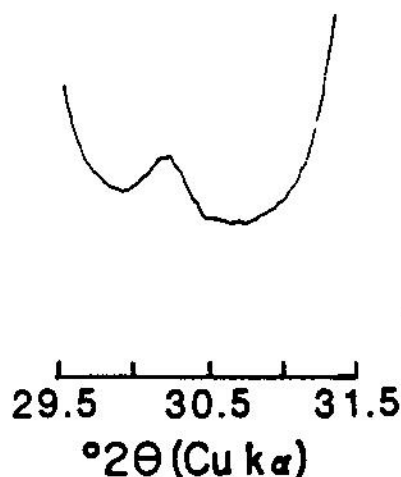


Fig. 1 Portion of automated slow-scan powder x-ray diffraction pattern showing the stishovite (110) peak. The largest quartz and coesite peaks are at least two orders of magnitude larger.

RESULTS AND DISCUSSION

We show in Figure 2 the silicon-29 MASS NMR spectra of the Meteor Crater sample obtained at recycle times of 5 seconds, 20 seconds, and 15 minutes. In addition to the true centerband resonances, these spectra also contain small peaks at about -68, -74, -151 and -157 ppm. These peaks are not true resonances, but are spinning sidebands, which are a result of the magic-angle spinning process (Smith *et al.*, 1983).

The spectrum obtained with a recycle time of 15 minutes consists of a large peak at -108.3 ppm, which we attribute to overlapping peaks of quartz and coesite; a peak at -114.9 ppm, which we attribute to coesite; and a peak at -192.4 ppm, which we attribute to stishovite. These peaks are displaced about 0.8 ppm upfield (to more negative values) from those of Smith and Blackwell (1983), and are also quite broad. Both the difference in peak position and peak breadth are probably due to magnet drift during the five days it took to collect this spectrum.

The spectrum obtained with a 20 second recycle time consists of two peaks of equal intensity at -108.8 ppm and -114.7 ppm, which we attribute to the two silicon sites in coesite, a shoulder at about -107.5 ppm, which we attribute to quartz, and a small peak at -191.9 ppm, which we attribute to stishovite. The broad peak with maximum chemical shift around -102 ppm may be due to the signal from amorphous material or clay. Because this spectrum has a higher signal/noise ratio, all the sidebands are visible. At this shorter recycle time, the signal from the coesite and stishovite is greatly enhanced relative to that from the quartz.

The spectrum obtained with a recycle time of five seconds consists of two equal size peaks at -108.0 ppm and -113.8 ppm, which we attribute to coesite; and a peak at -191.0 ppm, which we attribute to stishovite. These chemical shift values agree with those of Smith and Blackwell (1983) to within 0.1 ppm, although the spectrum is quite noisy. The peak at -108.0 ppm is also broader than that at -113.8 ppm, indicating some contribution from quartz, even at this rapid recycle rate. The intensity of the broad peak with maximum chemical shift around -102 ppm is enhanced relative to that obtained with a 20 sec recycle time, indicating a short recycle time of silicon in the amorphous material or clay.

Because silicon-29 has spin $I = 1/2$, as long as a particular silicon site is not saturated, the relative area of its peak should give good quantitation of the relative abundance of that site in the sample. Thus, simulation of the spectra and calculation of the relative peak areas should give good coesite/stishovite ratios if both have relatively short T_1 's, and are thus not saturated. The coesite/quartz and stishovite/quartz ratios are not likely to be accurate because of the long T_1 of quartz.

Figure 3 presents the observed spectra (top) along with total simulations of the spectra (middle) and the individual contribution to each simulation (bottom). Table 1 summarizes the positions and areas of the peaks in the simulations. These simulations were done using the Nicolet computer program CAP, which is an interactive peak fitting program. For the 20 second and 15 minute recycle-time-spectra, the coesite/stishovite ratio (C/S) has been calculated as the ratio of the total area of the coesite peak plus the area of the sidebands indicated in the table divided by the stishovite peak area. This relationship takes into account the intensity of the sidebands associated with the coesite, but the 15 minute recycle-time-spectra does not include the area of

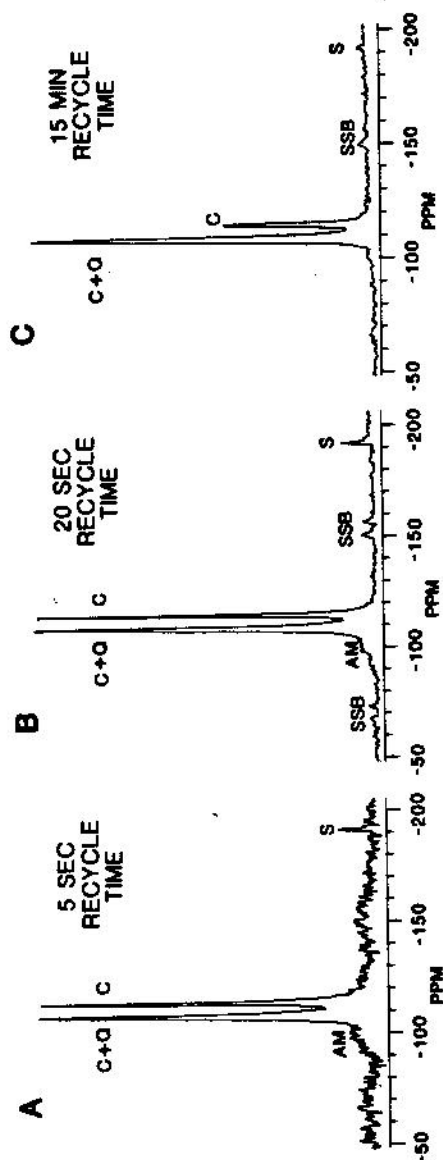


Fig. 2 71.5 MHz silicon-29 MASS NMR spectra of Meteor Crater, Arizona, sample [quartz (Q), coesite (C), stishovite (S), and amorphous material (AM)] with various recycle times, using a 5.0 μ sec 90° pulse excitation, 50 kHz spectral width, and 25 Hz line broadening due to exponential multiplication. A) 2.6 kHz MASS, 3601 scans with 5 sec recycle time. B) 2.8 kHz MASS, 3430 scans with 20 sec recycle time. C) 2.5 kHz MASS, 420 scans with 15 min recycle time.

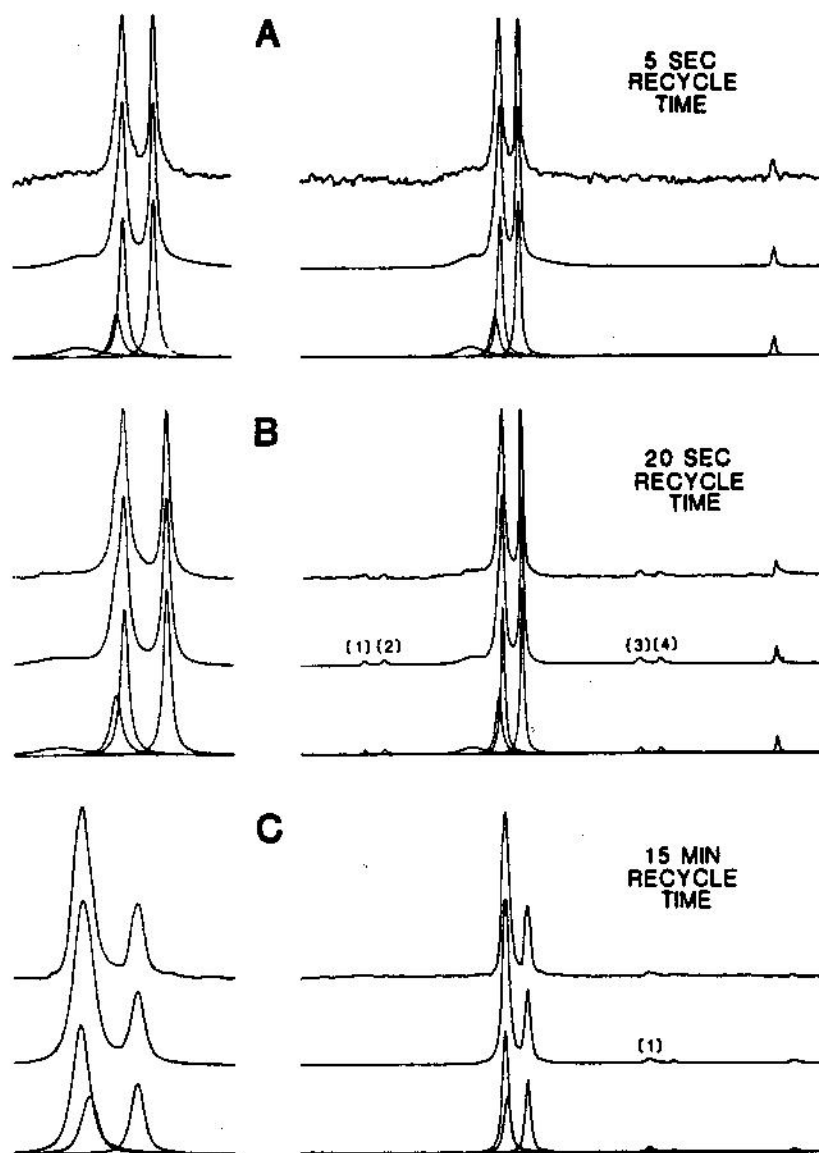


Fig. 3 Spectra (top), simulations (middle), and deconvoluted peaks (bottom) of the silicon-29 MASS NMR spectra of the sample shown in Figure 2. A) 5 sec recycle time, 80% lorentzian, 20% gaussian peaks. B) 20 sec recycle time, 100% lorentzian peaks. C) 15 min recycle time, 70% lorentzian, 30% gaussian peaks. The figures on the left correspond to the enlarged portion of quartz, coesite, and amorphous material peaks in the spectra to their right, respectively.

Table 1
Results of spectral simulations

Peak	Chemical shift (ppm)	Relative area	Coesite/Stishovite
5 sec recycle			
Quartz	-107.2	14.6	
Coesite	-108.0	35.8	
Coesite	-113.8	35.8	26.5
Stishovite	-191.0	2.7	
Amorphous material		11.1	
20 sec recycle			
Quartz	-107.5	18.9	
Coesite	-108.8	32.0	
Coesite	-114.7	32.0	26.7
Stishovite	-191.9	2.6	
Amorphous material		9.1	
Sidebands (1)		0.8	
(2)		1.1	
(3)		2.0	
(4)		1.5	
15 min recycle			
Quartz	-107.0	51.1	
Coesite	-108.3	22.4	
Coesite	-114.9	22.4	27.8
Stishovite	-192.4	1.7	
Sidebands (1)		1.9	
(2)		0.5	

the sidebands on the left of the coesite peaks that are barely above ground intensity. All the sideband intensity is assumed to be due to coesite, because quartz has essentially no sidebands (Smith *et al.*, 1983). For the noisier 5-second-recycle-time spectrum, the area of the sidebands has not been included, because they cannot be distinguished from noise.

The simulations show that the coesite/stishovite ratio is between 26.5 and 27.8 for all three spectra. Within experimental error, these are identical.

These results clearly show that MASS NMR is an effective tool for determining the presence of coesite and stishovite and their abundance ratio. Spectra with good signal-to-noise ratios can probably be routinely obtained with recycle times of 10 to 20 seconds and run times of two to twelve hours, which are typical for silicon-29 at natural abundance. This run-time length can be readily reduced by a factor of 3 or 4 by using larger sample sizes. The method has the advantage that whole-rock samples can be used, eliminating the possibility that glass, coesite, or stishovite could be lost during acid digestion and subsequent filtration.

Because the coesite/stishovite ratio stays constant with varying recycle time, both phases must have very similar, short T_1 's. Because the apparent concentration of quartz increases with increasing recycle time, its T_1 must be considerably longer than those of coesite and stishovite.

Overall, then, the results we have obtained indicate that solid-state silicon-29 MASS NMR spectroscopy is a useful new technique for the detection of small quantities of the high pressure silica polymorphs coesite and stishovite, in whole rock samples which have been subjected to intense pressure. Further work should enable the quantitative determination of quartz/coesite/stishovite/glass compositions in both natural and synthetic samples.

REFERENCES

- Bunch, T.E. and A.J. Cohen, 1963. Coesite and shocked quartz from Holleford crater, Ontario, Canada. *Science* 142, 379.
- Chao, E.C.T., E.M. Shoemaker, and B.M. Madsen, 1960. First natural occurrence of coesite. *Science* 132, 220.
- Chao, E.C.T., J.J. Fahey, and J. Littler, 1961. Coesite from Wabar crater, near Al Hadida, Arabia. *Science* 133, 882.
- Chao, E.C.T., J.J. Fahey, J. Littler, and D.J. Milton, 1962. Stishovite, SiO_2 , a very high pressure new mineral from Meteor Crater, Arizona. *J. Geophys. Res.* 67, 419.
- Fahey, J.J., 1964. Recovery of coesite and stishovite from Coconino sandstone of Meteor Crater, Arizona. *Amer. Mineral.* 49, 1643.
- Farrar, T.C. and E.D. Becker, 1971. *Pulse and fourier transform NMR: introduction to theory and methods*. Academic Press, New York.
- Kieffer, S.W., 1971. Shock metamorphism of the Coconino sandstone at Meteor Crater, Arizona. *J. Geophys. Res.* 76, 5449-5473.
- Lippmaa, E., M. Mägi, A. Samoson, G. Engelhardt, and A.-R. Grimmer, 1980. Structural studies of silicates by solid-state high-resolution ^{29}Si NMR. *Chem. Soc.* 102, 4889-4893.
- Lippmaa, E., M. Mägi, A. Samoson, M. Tarmak, and G. Engelhardt, 1981. Investigation of the structure of zeolites by solid-state high-resolution ^{29}Si NMR spectroscopy. *Am. Chem. Soc.* 103, 4992-4996.
- Mägi, M., E. Lippmaa, A. Samoson, G. Engelhardt, and A.-R. Grimmer, 1984. Solid-state high-resolution silicon-29 chemical shifts in silicates. *Phys. Chem.* 88, 1518-1522.
- Smith, J.V. and C.S. Blackwell, 1983. Nuclear magnetic resonance of silica polymorphs. *Nature* 303, 223-225.
- Smith, K.A., R.J. Kirkpatrick, E. Oldfield, and D.M. Henderson, 1983. High-resolution silicon-29 nuclear magnetic resonance spectroscopic study of rock forming silicates. *Am. Min.* 68, 1206-1215.
- Stöffler, D., 1971. Coesite and stishovite in shocked crystalline rocks. *J. Geophys. Res.* 76, 5474-5488.

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