

## NOTES

# ASSESSMENT OF CATION BINDING TO CLAY MINERALS USING SOLID-STATE NMR

DAVID J. SULLIVAN, JAY S. SHORE AND JAMES A. RICE

South Dakota State University, Department of Chemistry & Biochemistry, Brookings, South Dakota 57007-0896

**Key Words**— $^{113}\text{Cd}$ , 2D-Exchange, Montmorillonite, NMR, SEDOR.

### INTRODUCTION

A significant characteristic of clay minerals is their ability to bind and exchange cations, yet no clear picture of the structure of the cation exchange sites exists. The main reason for this lack of information is that the cation exchange sites comprise only a small percentage of a clay. Most spectroscopic techniques detect the whole sample, and information about the exchange sites is lost in the overwhelming signal from the bulk material. Clay minerals are complex, heterogeneous materials, with random patterns of atomic substitution, particle size and broken bonds. As a result, the spectra obtained by most methods are very complicated, with many broad, overlapping signals. Any information about species' near exchanged cations or of the cations themselves is essentially unresolved. A more direct approach to this problem is to use a technique that will selectively observe the exchangeable cation itself, such as solid-state nuclear magnetic resonance (NMR). A cation that is NMR observable and not present in the bulk clay structure acts as a discrete probe of the exchange sites. There will be no signal from the clay, and the signal from the exchanged cation will depend upon the influence of neighboring clay atoms. The spectra that result will provide information about the environment and motion of the cation only. If the cation is rigidly bound to the clay, the spectra will be solely dependent on the structure of the exchange sites.

There have been several studies using solid-state NMR of nuclei such as  $^7\text{Li}$ ,  $^{23}\text{Na}$ ,  $^{113}\text{Cd}$  and  $^{133}\text{Cs}$  adsorbed onto clays (Chu et al. 1987; Bank et al. 1989; Luca et al. 1989; Laperche et al. 1990; Liang and Sherriff 1993; Weiss et al. 1990a, 1990b; Tinet et al. 1991; Kim, Cygan and Kirkpatrick 1996; Kim, Kirkpatrick and Cygan 1996). These studies base all structural assignments on chemical shift and line-shape in-

formation. For example, Weiss et al. (1990b) observed 2 peaks in the  $^{133}\text{Cs}$  MAS spectrum of a Cs-exchanged hectorite that was dried at 500 °C. The more shielded peak was assigned to a 12-coordinate Cs cation, and the other to a 9-coordinate species, possibly in the pseudo-hexagonal holes in the tetrahedral layer. Luca et al. (1989) used the measured  $^7\text{Li}$  and  $^{23}\text{Na}$  linewidths from exchanged montmorillonites to describe differences in the electric field gradient of the quadrupolar  $^7\text{Li}$  and  $^{23}\text{Na}$  nuclei. As the hydration of the clay was changed, the observed trends in the linewidths led to the conclusion that as the clay was dried, the cations migrated into the pseudo-hexagonal holes in the tetrahedral layer. While these studies have provided a great deal of insight into the environment of cations on clay minerals, the information obtained only allows generalizations to be made about the location of the cation. The cations will almost certainly be bound through oxygen ligands, and because the surface of the clay is disordered, the peaks in the spectra will be broadened by chemical shift distribution. As a result, small changes in the chemical shift due to differences in structure beyond the coordinated oxygens are not resolved.

Information about the second coordination sphere is what is needed to determine more specifically where a cation resides on a clay mineral. Multiple-resonance experiments have proven very useful for studying long-range interactions in many materials. There have been several studies using X-Y double-resonance,  $^{27}\text{Al}$ - $^{31}\text{P}$  and  $^{27}\text{Al}$ - $^{29}\text{Si}$  for example, to determine if there is coupling between the 2 species in materials such as zeolites (Grey and Kumar 1995; Grey and Vega 1995; Kao and Grey 1996; van Eck et al. 1990). Because the coupling is proportional to their separation, it is possible to calculate internuclear distances if the coupling can be measured quantitatively with NMR (Mueller

1995; Mueller et al. 1995; Jarvie et al. 1996). The simplest of these double-resonance techniques is spin-echo double-resonance (SEDOR) (Kaplan and Hahn 1958; Emshammer et al. 1960), which is used here to demonstrate  $^{27}\text{Al}$ - $^{113}\text{Cd}$  coupling in a Cd-exchanged montmorillonite.

It is also important to understand the dynamic nature of the cation on the clay mineral under different hydration conditions. When a swelling clay like montmorillonite is highly hydrated, the adsorbed cations are present in the interlayers, separated from the clay surface by water molecules. Cations in this state are able to move freely throughout the interlayer, and may be exchanging rapidly between a surface-bound and hydrated species (Grim 1953; Weiss et al. 1990a, 1990b). The motion may range from free, solution-like tumbling to a rigid, surface-bound complex, varying either continuously or in steps as the amount of water present decreases. If the cations are very mobile, it is not possible to observe couplings between the cations and the clay. In this case, it is more useful to characterize the motion of the cations. Weiss et al. (1990a, 1990b) used variable-temperature  $^{133}\text{Cs}$  NMR to study the motion of  $\text{Cs}^+$  adsorbed on several clays, particularly hectorite.  $\text{Cs}^+$  was found to be very mobile in all samples containing interlayer water and motionally averaged peaks were resolved at very low temperatures, which were assigned to  $\text{Cs}^+$  on or near the surface (Stern layer) and  $\text{Cs}^+$  in the interlayer water (Guoy layer).

There are also other solid-state NMR methods commonly used to study the motion of a particular species, such as relaxation measurements and 2-dimensional exchange (2D-exchange) experiments (Schmidt-Rohr and Spiess 1995) that have not yet been applied to clay minerals. It is expected that the spin-spin relaxation time ( $T_2$ ) is shorter for a rigidly bound, immobile nucleus than for one able to move freely (Bloembergen et al. 1948). For this reason, the changes in the  $T_2$  relaxation time of a cation adsorbed onto a clay mineral under different hydration conditions could be used to observe changes in the motion of the cation. Also, if the cation is mobile, its resonance frequency will change as it moves between different surroundings, which can be detected using static 2D-exchange NMR.

SEDOR, 2D-exchange and  $T_2$  experiments have yet to be applied to the study of cation interactions with clay minerals despite the specific information that they could provide on the nature of bound cations and cation binding sites on clay minerals. The purpose of this study is to demonstrate that Cd-clay binding can be observed through  $^{27}\text{Al}$ - $^{113}\text{Cd}$  coupling via a SEDOR experiment when the cations are rigidly bound to the clay, and that  $^{113}\text{Cd}$   $T_2$  and 2D-exchange experiments can be used to study the mobility of the cations.

#### MATERIALS AND METHODS

The Source Clay Minerals Repository's Ca-montmorillonite (Stx-1), from Gonzales County, Texas, was

used as received with no pretreatments except as noted. Isotopically enriched  $^{113}\text{Cd}$  (95 atom %) was purchased from Isotec, Inc., as the oxide, and dissolved in a minimum volume of 0.1 M HCl. Three grams of the clay sample were first  $\text{Na}^+$ -exchanged by adding 250 mL of 1-M NaCl to the clay and stirring for 24 h. The sample was then centrifuged and rinsed repeatedly with deionized water until the supernatant tested negative for chloride ion with  $\text{AgNO}_3$ . Any colloidal material that did not settle out during centrifugation was discarded. The  $\text{Na}^+$  exchange procedure was repeated once. The montmorillonite was then exchanged with the enriched  $^{113}\text{Cd}$  solution (total of 200 mg  $^{113}\text{Cd}^{2+}$ ) for 24 h, centrifuged and rinsed repeatedly with deionized water until the supernatant tested negative for chloride ion with  $\text{AgNO}_3$ . The  $^{113}\text{Cd}$ -exchanged sample was then freeze-dried. Half of the freeze-dried clay was then allowed to rehydrate at 100% humidity for 24 h, while the remainder was stored in a desiccator.

All NMR experiments were performed on a Bruker ASX-400 spectrometer, operating at 88.78 MHz for  $^{113}\text{Cd}$ . Spin-echo MAS experiments were performed using a Bruker 7-mm MAS probe. Samples were packed in 7-mm-o.d. zirconia rotors, and were spun at 7 kHz. SEDOR and 2D-exchange experiments were performed on a home-built double-resonance static probe with a 10-mm receiver coil. The probe was double-tuned to  $^{113}\text{Cd}$  and  $^{27}\text{Al}$  (88.78 and 104.5 MHz, respectively). Samples were packed in 10-mm-o.d. glass tubes and sealed with stoppers. The pulse sequences used are illustrated in Figure 1. The  $^{113}\text{Cd}$   $\pi/2$  and  $\pi$  pulses were 4.25 and 8.5  $\mu\text{s}$  for spin-echo and  $T_2$  experiments, and 9.5 and 19  $\mu\text{s}$  for SEDOR and 2D-exchange; the  $^{27}\text{Al}$   $\pi$  pulse was 8.2  $\mu\text{s}$ . For MAS experiments, the spin-echo was obtained at integral multiples of the rotor period ( $1/\omega_r$ ). Typically, 1000 to 5000 scans were acquired for spectra of the hydrated sample, while 5000 to 20,000 scans were acquired for spectra of the freeze-dried sample. A recycle delay of 200 ms was used for all 1D spectra; a delay of 500 ms was used for all  $T_2$ , 2D-exchange and SEDOR experiments. All spectra were externally referenced to a 0.10-M  $\text{CdSO}_4$  solution.

#### RESULTS AND DISCUSSION

Spin-echo  $^{113}\text{Cd}$  MAS and static spectra of the freeze-dried and hydrated montmorillonite samples are shown in Figure 2. The signals from the hydrated sample are much narrower, and the static spectrum lacks any structure or powder pattern. This suggests that the cations in the hydrated sample are very mobile, resulting in a narrow, motionally averaged peak. The signals for the freeze-dried sample are much broader and the static spectrum has a distinct powder pattern, indicative of a more rigidly bound species. The cations may or may not be mobile in this sample, as there is

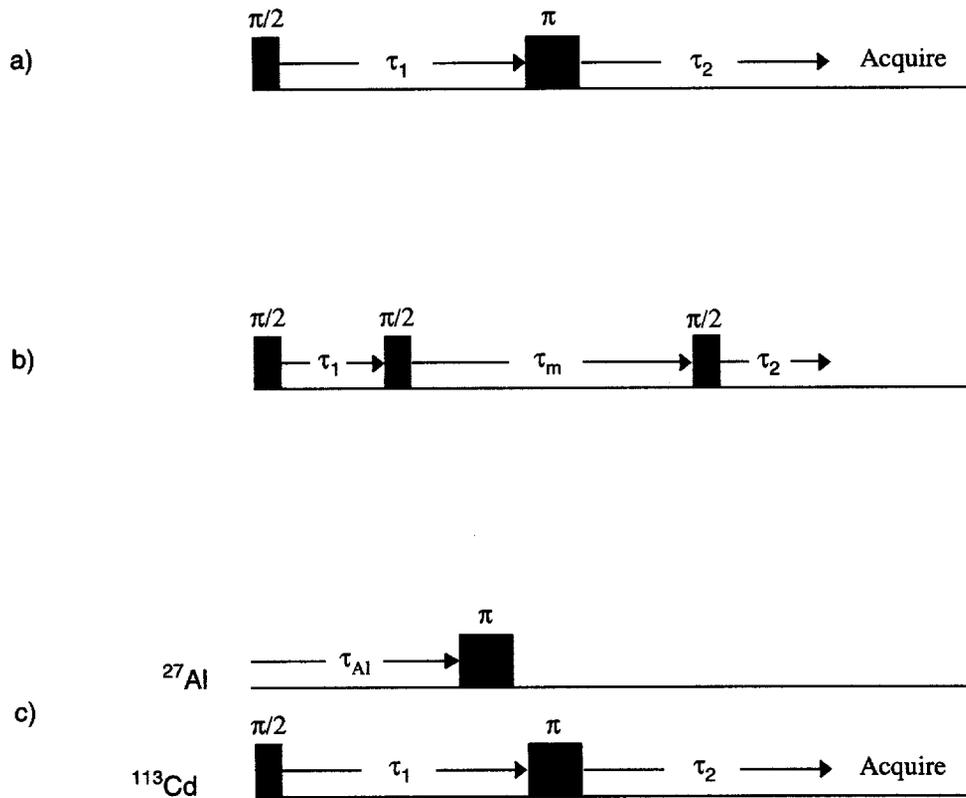


Figure 1. a) Spin-echo pulse sequence; for MAS with  $\omega_s =$  spinning speed,  $\tau_1 = \tau_2 = 1/\omega_s$ . For  $T_2$  measurements,  $\tau_1 = \tau_2 = n/\omega_s$ ,  $n = 1, 2, \dots$ . b) 2D-exchange pulse sequence;  $\tau_m =$  mixing time = 10 ms,  $\tau_1$  and  $\tau_2$  are the acquisition times in first and second dimension, respectively. c) SEDOR pulse sequence; spin-echo on  $^{113}\text{Cd}$  channel,  $\tau_{\text{Al}}$  varied from 0 to  $\tau_1$ .

certainly still a significant amount of adsorbed water present. The  $T_2$  values measured for the samples as well as the measured ( $w_{1/2}$ ) and homogeneous ( $1/\pi T_2$ ) linewidths (full-width at half-height) are shown in Table 1. The  $T_2$ 's of the hydrated sample are much longer than for the freeze-dried sample, as expected for a more mobile species. In addition, contributions to the linewidths from weak dipolar couplings and chemical shift anisotropy are averaged to zero by rapid spinning about the magic-angle in the MAS experiments. The width of the peak for a single species should then be equal to the homogeneous linewidth, which is the resolution limit due to  $T_2$  relaxation. The measured width of the peak for the hydrated sample is within experimental error of the homogeneous linewidth, indicating a single or motionally averaged species present in the sample. The width of the peak from the freeze-dried sample is much larger than  $1/\pi T_2$ , however, suggesting that there actually exists a distribution of chemical shifts rather than a single resonance. This is not surprising considering the structural disorder present in the sample, and supports results regarding the non-uniformity of cation binding properties obtained by kinetic studies (Haber-Pohlmeier and Pohlmeier 1997).

Using static 2D-exchange NMR, it is possible to measure the frequency of a cation at one time ( $\omega_1$ ), and then measure it again a short time later ( $\omega_2$ ). If the frequency changes, it is observed in the 2-dimensional plot as off-diagonal intensity ( $\omega_1 \neq \omega_2$ ). If no motion is present, only signal intensity at  $\omega_1 = \omega_2$  is observed, with the width of the diagonal no greater than the homogeneous linewidth for the static sample (Table 1). The 2D-exchange plots of the samples are shown in Figure 3. While multiple resolved cation exchange sites are not observed, this experiment is useful for determining whether the cations are mobile. If they are mobile, they will be able to change orientation and/or location with respect to the external magnetic field during the mixing time,  $\tau_m$  (Figure 1b), and as a result will change frequency to one within the envelope of the chemical shift anisotropy. For the hydrated sample, there is a large amount of off-diagonal intensity with a mixing time of 200  $\mu\text{s}$ , indicating very mobile cations in this sample. For the freeze-dried sample, there is very little off-diagonal intensity even when a much longer mixing time is used (10 ms), indicating very rigidly bound, immobile cations. These results suggest that coupling should be observed in a SEDOR exper-

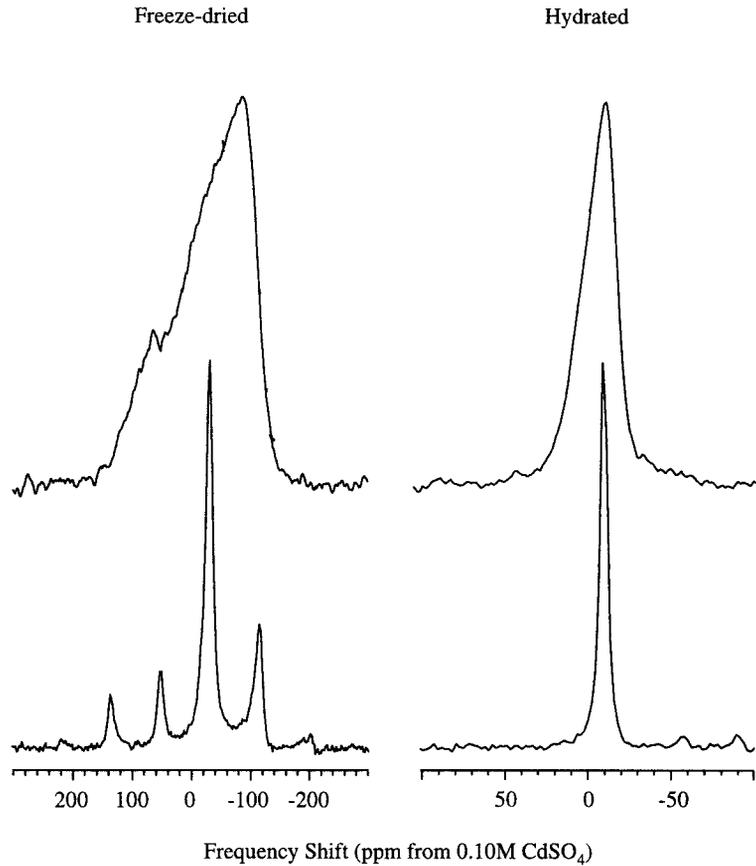


Figure 2.  $^{113}\text{Cd}$  spin-echo spectra of the freeze-dried and hydrated  $^{113}\text{Cd}$ -exchanged montmorillonite samples. Top spectra were obtained static; bottom spectra were obtained with 7 kHz MAS. Note different axes for the freeze-dried and hydrated samples.

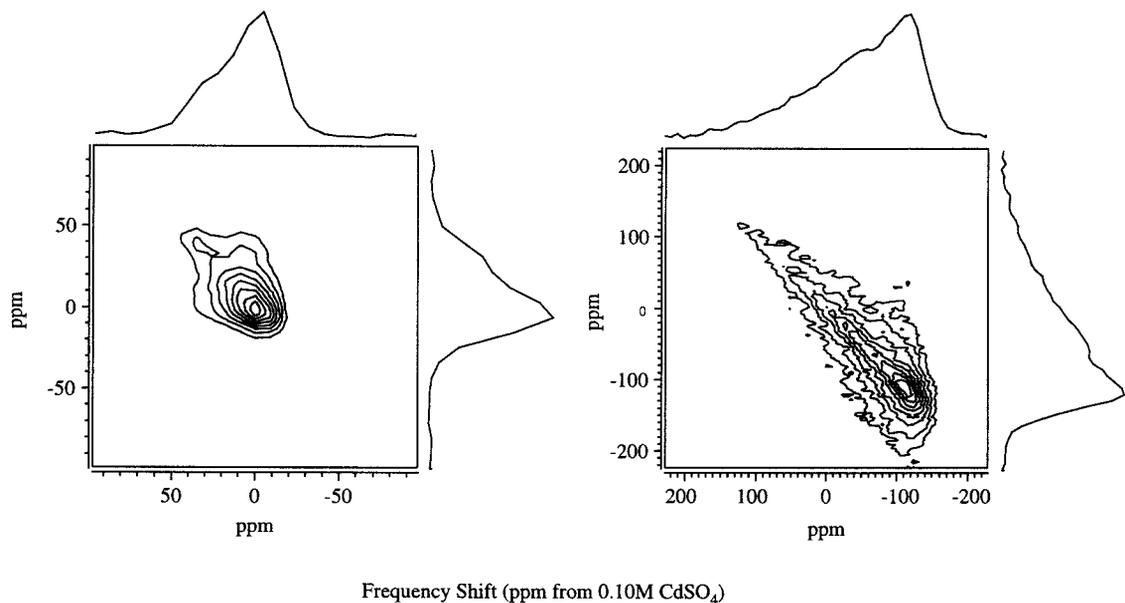


Figure 3.  $^{113}\text{Cd}$  2D-exchange plots of hydrated (left) and freeze-dried (right)  $^{113}\text{Cd}$ -exchanged montmorillonite. Note different axes for the freeze-dried and hydrated samples.

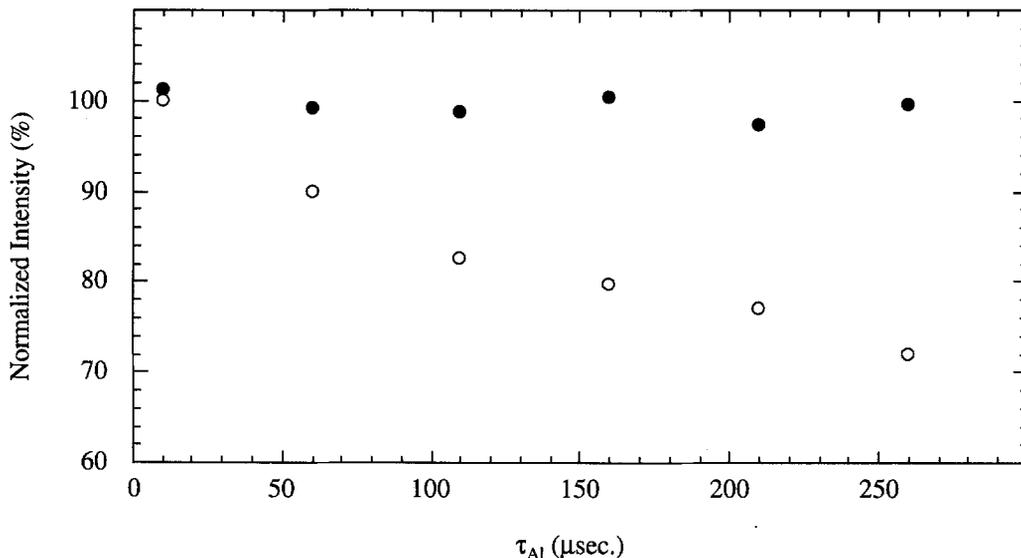


Figure 4. Plot of  $^{27}\text{Al}$ - $^{113}\text{Cd}$  SEDOR intensity vs.  $\tau_{\text{Al}}$  for the hydrated ( $\bullet$ ) and freeze-dried ( $\circ$ ) sample.

iment on the freeze-dried sample if the cations are close enough to Al atoms in the octahedral layer.

SEDOR is a static experiment in which the dipolar coupling between the 2 nuclei of interest is perturbed by a  $\pi$  pulse on the unobserved nucleus, which prevents refocusing of resonances from coupled nuclei during a spin-echo sequence on the observed nucleus (Figure 1c). Differences in signal intensity with and without excitation of the unobserved nucleus indicate coupling between the 2 nuclei. In this experiment, the  $^{27}\text{Al}$   $\pi$  pulse prevents refocusing of some  $^{113}\text{Cd}$  spins that are coupled to  $^{27}\text{Al}$ . As  $\tau_{\text{Al}}$  approaches  $\tau_1$ , the effect is the most pronounced. The results of  $^{27}\text{Al}$ - $^{113}\text{Cd}$  SEDOR experiments are shown in Figure 4. No coupling between Al and Cd is observed for the hydrated sample, even with the longest  $\tau_{\text{Al}}$ . This is explained in part by the fact that the cations are coordinated by a sphere of water molecules, keeping them well separated from the Al atoms in the octahedral layer. In addition, the cations are moving very rapidly, as shown in Figure 3a. The rapid motion averages any weak dipolar couplings between  $^{27}\text{Al}$  and  $^{113}\text{Cd}$  to zero, so no change is observed in the SEDOR experiments. Coupling is observed for the freeze-dried sample, however. The cations must be rigidly bound (Figure 3b), and must be

within 5 Å of the Al atoms (in the octahedral sheet) in order for this coupling to be observed. Currently, the detection of heteronuclear coupling using SEDOR is limited to internuclear distances up to approximately 5 Å for simple, well-defined samples, and even less for complex or disordered materials such as the clay studied here (van Wüllen et al. 1996). Because the separation between the interlayer and the Al atoms in the octahedral sheet is rather large ( $>5$  Å), the cations must migrate into the pseudo-hexagonal holes in the tetrahedral sheet in order to observe the coupling between  $^{27}\text{Al}$  and  $^{113}\text{Cd}$ .

## CONCLUSION

Double-resonance and 2D solid-state NMR experiments have been successfully applied to the study of host-guest interactions for a wide variety of materials. These same experiments, however, have never been applied to the study of cations adsorbed onto clay minerals, primarily because of the complexity of the samples and low sensitivity of the dilute cations. Using isotopically enriched  $^{113}\text{Cd}$  greatly reduces acquisition times, and has made it possible to study the cation motion using 2D-exchange NMR and to observe heteronuclear  $^{27}\text{Al}$ - $^{113}\text{Cd}$  dipolar coupling. The results presented here show the potential for the determination of Al-cation (or Si-cation) distances in clay minerals, creating a very detailed picture of the cation exchange sites.

## ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant OSR-94-52894 and by the South Dakota Future Fund.

Table 1. Comparison of measured ( $w_{1/2}$ ) and homogeneous ( $1/\pi T_2$ ) linewidths.

Sample	MAS or Static	$T_2$ (ms)	$w_{1/2}$ (Hz)	$1/\pi T_2$ (Hz)
Hydrated	MAS	878	320	363
Hydrated	Static	334	3000	953
Dehydrated	MAS	450	1250	707
Dehydrated	Static	147	13,000	2165

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(Received 30 May 1997; accepted 28 September 1997; Ms. 97-046)