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Nuclear-spin-lattice relaxation in natural clays via paramagnetic centers

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Nuclear-spin-lattice relaxation time measurements were made on ^{29}Si nuclei in a series of 2:1 natural clay minerals. The magnetization recovery was found to be nonexponential. The nuclear relaxation arises from coupling to fixed paramagnetic impurities in the absence of spin diffusion. A theory is developed in which the nuclear spin relaxation behavior is expressed as an error function. These clays have very similar structures which allow the relative concentration of paramagnetic centers to be obtained from the fit of the magnetization recovery curves. [S0163-1829(96)03137-2]

I. INTRODUCTION

In the early stages of NMR Bloembergen proposed the concept of nuclear relaxation via spin diffusion to paramagnetic impurities to explain the abnormally short spin-lattice relaxation times observed.[1] Independently de Gennes[2] and Khutsishvili[3] developed the concepts and mathematical equations for spin difusion to relaxation centers, obtaining the same results from slightly different starting assumptions. Since those days, the concepts of spin diffusion, exponential recovery of magnetization, and expressions for T_1 under conditions where spin diffusion operates are now well understood and established. The relaxation rate is proportional to the impurity concentration, to the spin-diffusion coefficient, and to the relaxation length, whose value depends on the behavior of the nuclear spins in the vicinity of the paramagnetic centers. Nuclear-spin-lattice relaxation via paramagnetic centers in the absence of spin diffusion is not as well developed. Blumberg[4] developed a model which predicts that the nuclear magnetization grows as $\tau^{1/2}$ following saturation of the nuclear spins, where τ is the time after saturation. More recently, Tse and Lowe[5] followed by Tse and Hartmann[6] developed a multirelaxation-center model with suppressed spin diffusion. Their theory predicts that the spin system ultimately relaxes as $\exp[-(t/\tau^{1/2})]$. This expression reduces to Blumberg's $\tau^{1/2}$ result at short times. This theory has been extended to one- and two-dimensional systems by replacing the 1/2 exponent by n, i.e., $\exp[-(t/\tau)^n]$, resulting in a model generally known as a stretched exponential model. The stretched exponential has been successfully used to fit the spin-lattice relaxation of several different systems containing paramagnetic impurities.[7–9] The value of n ranges between 0.5 and 1. Higher levels of fixed impurities should tend to a limiting $n=0.5$ stretched exponential relaxation which agrees with Tse's[6] theory.

In this manuscript, we use approximations originating with Fedders *et al.*[10] to describe the relaxation of a spin-1/2 system in the absence of spin diffusion. In Fedders original work, the experimental system of interest was relaxation by rapidly relaxing protons or deuterons but the concept equally applies to relaxation by paramagnets.

The physical model for Blumberg's,[4] Tse's,[5,6] Fedders,[10] and our work is the same. The system consists of dilute, randomly distributed, fixed relaxation sinks (paramagnets). The nuclear spins must interact only weakly between themselves so nuclear spin diffusion is effectively quenched. This means that they must be separated by large distances due to structure or magnetic dilution or must have very weak magnetic moments. Thus the primary nuclear relaxation is through direct coupling between the nuclei and the paramagnets. Within this physical system, one arrives at an equation similar to our Eq. (10a) (vide infra), Eq. (12) in Blumberg,[4] and Eq. (6) in Tse and Hartmann.[6] The difference lies in the approximations used to make this equation integrable. In our work, we assume that the nucleus couples only to the nearest paramagnetic center while Tse assumes that it couples to all paramagnets in the volume of the sample. We predict that the magnetization recovery is an error function.

Philosophically, we would like to point out that mathematical models for relaxation in these slowly relaxing systems are truly just models. The stretched exponential model is a perfectly good model with its implicit model dependencies and assumptions. Our single relaxation center model is simply another way for an experimentalist to treat magnetization recovery data. The disadvantage to our model is that it may oversimplify the physics by considering only the nearest paramagnetic center. However, the stretched exponential function contains two highly correlated parameters, t and n, in the exponential. Neither model is unique and ''goodness of fit'' cannot be used as proof of correctness because it is clear that one can obtain a good fit with a polynomial with sufficient terms but such an equation would give no physical insight into the spin system considered. The advantages and disadvantages of these models will be further discussed in Sec. VI.

Our model was developed as the result of work on natural clay minerals which contain paramagnetic impurities, particularly Fe^{3+} and/or Fe^{2+}. To test the theory, we selected several clays which are chemically representative of the 2:1 layer silicates with varying amounts of paramagnetic iron. The structure of an idealized 2:1 layered clay can be described as a layer of octahedrally coordinated cations sandwiched between two layers of tetrahedrally coordinated silicon atoms. The tetrahedra and octahedra have oxygen as the charge balancing anions. Aluminum is the usual octahedral action in which case, for charge balance, one-third of the octahedral sites are vacant. Since each half unit cell contains three octahedral sites these are referred to as dioctahedral

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TABLE I. Characteristics of the 2:1 layer silicate samples used in this study. The symbol χ^+ in the structural formula indicates a monovalent interlayer cation.

Mineral name	Origin	Structural formula (unit cell)	Impurity concentration N_p in 10^{19} cm $^{-3}$
SWy-1	Wyoming	$(Si_{7.84}\,Al_{0.16})\,(Fe_{0.43}\,Al_{3.17}\,Mg_{0.40})\,O_{20}\,(OH)_4\,\chi^+_{0.68}$	9.24
SAz-1	Cheto, Arizona	$(Si_{7.86}\,Al_{0.14})\,(Fe_{0.16}\,Al_{2.84}\,Mg_{1.00})\,O_{20}\,(OH)_4\,\chi^+_{1.14}$	3.53
STx-1	Texas	$(Si_{7.84}\,Al_{0.16})\,(Fe_{0.07}\,Al_{3.53}\,Mg_{0.40})\,O_{20}\,(OH)_4\,\chi^+_{0.56}$	1.52
SHCa-1	Hector, California	$(Si_{7.98}\,Al_{0.02})\,(Al_{0.04}\,Mg_{5.19}\,Li_{0.66}\,Fe_{0.11})\,O_{20}\,(OH)_4\,\chi^+_{0.66}$	2.02
Talc	Malinkrodt Chem. Company	$(Mg_{3.81}\,Fe_{0.19})\,Si_8\,O_{20}\,(OH)_4$	4.10
Barasym SYN-1	NL industries	$(Si_{6.4}\,Al_{1.6})\,(Al_{3.98}\,Fe_{0.016})\,O_{20}\,(OH)_4\chi^+_{1.6}$	0.34

clays. Trioctahedral silicates are constructed from divalent octahedral cations, usually magnesium, thus all three octahedral sites are occupied. Some of the octahedral cations may be naturally replaced by Fe^{2+} or Fe^{3+}. In this description, the layers are electrically neutral but isomorphous replacement of cations confers a net negative charge, e.g., replacement of Si^{4+} by Al^{3+} in the tetrahedral layer or Al^{3+} by Mg^{2+} in the octahedral layer. The negative charge is compensated by interlayer cations, usually Na^+, K^+, or Ca^{2+}. We had originally embarked on a study of Li^+ exchange and diffusion in clays but discovered that it was critical to understand the general properties of nuclear relaxation due to the paramagnetic ions in these clay minerals. We chose to study the magnetization recovery of ^{29}Si, instead of ^{7}Li because ^{29}Si is a simpler spin system with an angular moment of $h/4\pi$ and thus no electric quadrupole moment to complicate the nuclear spin relaxation. Additionally, ^{29}Si is only 4.70% abundant which makes it a magnetically dilute nucleus. Therefore each ^{29}Si nucleus is essentially isolated and spin diffusion between ^{29}Si sites in the clay is negligible.

There are several other NMR experiments reported in the literature where relaxation by paramagnets has been effectively exploited. In particular, Devreux and co-workers[11] developed a theory for obtaining fractal dimensionality from the detailed magnetization recovery of ^{29}Si in synthethc silicates. Sen and Stebbins[12] used this theoretical approach to obtain fractal dimensionality and information about phase separation in glasses. These approaches are natural outgrowths of the work by Tse.

II. EXPERIMENTAL SECTION

A. Samples

Measurements were made on five natural clay minerals and a synthetic barasym sample. All samples were obtained from the Source Clay Repository of the Clay Minerals Society except the talc sample which was obtained from Malinkrodt Chemical Company. Table I lists representative chemical analysis, localities, and structural formulas for these samples. Samples have iron contents ranging from 0.3 $\times 10^{19}$ to 9×10^{19} cm^{-3}. Hectorite (SHCa-1) is a trioctahedral smectite with layer charge developed by the substitution of Li^+ for Mg^{2+} in the octahedral sheet. This material contains carbonates as impurities which must be removed prior to sedimentation of the clay fraction. A 10 g sample of SHCa-1 was treated with pH=5, sodium acetate/acetic acid buffer to remove carbonates. The sample was washed with deionized water to remove excess salts. The resulting SHCa-1 clay was $Na+$ exchanged by several washes with 0.5 M NaCl and then washed free of excess salt by repeated centrifugation with deionized water. The $<2\,\mu$m size fraction was collected by centrifugation. The montmorillonite samples, SAz-1, SWy-1, and STx-1, are dioctahedral smectites with Al^{3+} partially substituted by Mg^{2+}. The layer charge ranges from 0.2 to 0.6, and most of the charge is located in the octahedral layer. Na^+ exchanged montmorillonites were prepared using the procedure described for hectorite, except that these samples have negligible carbonate content and were not washed with the buffered acetic acid. Barasym is a pure synthetic dioctahedral clay with Si^{4+} partially substituted by Al^{3+}. Thus the layer charge is located in the tetrahedral layers. The interlayer cation was exchanged for Na^+ using the same procedure described above. Talc is a trioctahedral 2:1 clay with negligible layer charge. The sample was used as received because it has a very small exchange capacity. All samples were dried in a 60° C oven overnight and then powdered in a mortar and pestle and stored over phosphorus pentoxide for at least three days to dry. The reason for careful and reproducible sample drying is that these clays contain interlayer water which may provide additional relaxation mechanisms via dipolar couplings to mobile protons in the water. Although the procedure described does not remove all water of hydration, the remaining water is immobile and does not produce significant relaxation.

B. NMR procedures

The ^{29}Si MAS NMR spectra were recorded on a Varian Unity 400 Spectrometer operating at 79.459 MHz. A Varian

MAS probe was used, with 7 mm rotors and spinning speeds of about 6.2 kHz. Spectra were obtained with 2048 data points, and a spectral width of 100 kHz. The 90° pulse width was ~ 6 μs. The inversion recovery method $(180°-\tau-90°)$ was used for magnetization recovery experiments. Approximately fifteen recovery delays, τ, were used ranging from 0.001 to 65 s. For each delay, ~ 128 scans were accumulated. For the montmorillonite SWy-1 sample, 4096 transients were collected per delay because of the poor signal to noise ratio. The delay times, τ, for the barasym sample varied between 0.032 to 1048 s because of the slow magnetization recovery in this sample. The recycle delay, between repetitions of the inversion recovery pulse sequence, ranged from 3 to 300 s depending on the magnetization recovery rate for the particular sample. Chemical shifts were obtained using tetramethylsilane as an external standard.

C. EPR spectroscopy

The spectrum of the sample with the highest concentration of iron (SWy-1) was recorded on a Bruker ER 200 D-SRC EPR sepctrometer operating at 9.6 GHz.

III. BLUMBERG'S MODEL (NO SPIN DIFFUSION)

Blumberg[4] proposed a model of a diffusionless spin system relaxed by paramagnetic impurities. We use essentially the same model but use different assumptions in the mathematical treatment and arrive at slightly different equations. Since elements of Blumberg's model are required in our treatment we will summarize his description.

The system is described by very dilute paramagnetic impurities and nuclei with a large internuclear spacing or which are magnetically dilute. He defines a barrier radius, b, as the distance from the paramagnetic ion at which the magnetic field due to the paramagnetism is equal to the local dipolar field of the crystal. Nuclear spins within the barrier radius are shifted and broadened so they do not contribute to the NMR line and since they have different local fields, they do not undergo mutual spin flips with neighboring spins. If the correlation time for the electron spin, $\tau_c \gg T_2$, the transverse relaxation time of the nucleus, then b is given by

$$b=(\mu_p/\mu_n)^{2/3}a, \quad \tau_c \gg T_2. \tag{1}$$

When the reverse obtains, the z component of the electron spin is motionally averaged and b is

$$b=(\mu_P{}^2 B_o/\mu_n KT)^{1/3}a, \quad \tau_c \ll T_2, \tag{2}$$

where a is the characteristic lattice spacing between nuclei, μ_n and μ_p are the nuclear and electron magnetic moments, respectively, B_o is the applied magnetic field, τ_c is the correlation time for the paramagnetic ion, and T_2 is the transverse relaxation time of the nucleus.

If the internuclear distances are large or the nuclei are magnetically dilute, the effect of spin diffusion is negligible. Thus the only change in nuclear magnetization is due to direct interaction with the paramagnet which is assumed to be a dipole-dipole interaction with r^{-3} dependence. After saturation or inversion, the nuclear magnetization grows by direct relaxation with an initial rate proportional to $\tau^{1/2}$, where τ is the time after saturation. At very long times after saturation, spin diffusion will start to contribute to the recovery of magnetization, i.e., spin diffusion cannot be completely eliminated but it is negligible compared to direct relaxation at short times. Blumberg's formula for the initial magnetization recovery is

$$M_Z(t)=(4\pi^{3/2}/3)N_p C^{1/2}\tau^{1/2}, \quad \text{when} \quad \tau > b^6/C, \tag{3}$$

where N_p is the number of paramagnetic centers per unit volume and C is a constant,

$$C=\frac{3}{2}\gamma_p^3\gamma_n^2\left(\frac{h}{2\pi}\right)\sin^2\theta\ \cos^2\theta S(S+1)\frac{2\tau_c}{1+(\omega_n^2\tau_c^2)}, \tag{4}$$

where θ is the angle between the line joining the nucleus and the paramagnet and the applied field direction, γ_n and γ_p are the magnetogyric ratios of the nucleus and the paramagnet, respectively. S is the spin quantum number of the paramagnet, τ_c is the longitudinal electron relaxation time, and ω_n is the Larmor frequency of the nucleus. The radial dependence in Eq. (4) is much stronger than the angular one so the angular dependence can be neglected resulting in a simplified equation:

$$\overline{C}=\frac{2}{5}\gamma_p^2\gamma_n^2\left(\frac{h}{2\pi}\right)^2 S(S+1)\frac{\tau_c}{(1+\omega_n^2\tau_c^2)}. \tag{5}$$

Blumberg noted that it is possible to compute $\overline{C}$ from a nuclear magnetization recovery experiment and thus determine the electronic relaxation, τ_c, for the paramagnetic center without doing a paramagnetic resonance experiment.

IV. SINGLE RELAXATION CENTER MODEL

The general diffusion equation to be solved for the behavior of the nuclear spin system is[1]

$$\frac{\partial p}{\partial t}=D\nabla^2 p-\overline{C}(p-p_0)\left(\sum_n R-R_n\right)^{-6}-2A_p, \tag{6}$$

where $p(\mathbf{R},t)$ is the magnetization of a nuclear spin located at a point $\mathbf{R}$, p_o is the thermal equilibrium value of p, and D is the spin-diffusion coefficient. It will be assumed that the nuclear spins and the paramagnetic centers occupy fixed positions in space, i.e., there is no physical diffusion. The term $C(\mathbf{R}-\mathbf{R}_n)^{-6}$ represents the probability of transition due to the nth impurity. Finally, the last term, $2A_p$, is the probability of transition due to a saturating radiofrequency field. The constant $\overline{C}$ is defined as in Eq. (5).

If spin diffusion is negligible and in the absence of a radiofrequency excitation equation (6) reduces to

$$\frac{\partial p}{\partial t}=\overline{C}(p-p_0)\left(\sum_n |\mathbf{R}-\mathbf{R}_n|\right)^{-6}. \tag{7}$$

The physical model used assumes that the paramagnetic centers are dilute and homogeneously distributed throughout the sample. The simplifying assumption is made that each nucleus under consideration is dipole coupled only to the nearest paramagnet. This is justifiable in a system with very dilute paramagnets and because of the strong r^{-3} dependence of the dipole coupling. Then, we can consider that each paramagnet influences all nuclei within a sphere with a radius which is one-half the distance to the next paramagnet, i.e., an average radius R:

$$R=\left(\frac{3}{4\pi N_p}\right)^{1/3}, \tag{8}$$

where N_p is the number of paramagnetic centers per unit volume. In reality, the impurities are distributed randomly over the lattice. If we now take the origin as the paramagnetic center, the solution to Eq. (7) is

$$p_0-p(r,t)=np_0\exp(-\overline{C}t/r^6), \tag{9}$$

where r is the distance of the nucleus under consideration from the nearest paramagnetic center and n is equal to 1 or 2 depending on whether it is a saturation recovery or inversion recovery experiment, respectively.

Conceptually, we note that the magnetization recovery of a given nucleus is dependent on its distance from the nearest paramagnet. Thus there is a distribution of exponential magnetization recovery rates and the overall nuclear magnetization recovery will be nonexponential. The total magnetization $M_Z(t)$ at any time is given by the following equation:

$$M_z(t)=\int p(r,t)dv. \tag{10a}$$

As noted in the Introduction, this integral cannot be solved analytically without making simplifying assumptions. Our assumption of a single relaxation center places limits on the integral from the barrier radius to R, the point at which the next paramagnetic center becomes the relaxation center,

$$\frac{M_z(t)}{M_0}=-nK\int_b^R \exp(-\overline{C}t/r^6)4\pi r^2dr+1. \tag{10b}$$

In this solution, M_0 is the observed equilibrium magnetization, the radius, b, is the barrier radius defined in Blumberg's model and K is a constant to be determined. The local field due to the paramagnetic center broadens the NMR line for nuclei within the critical radius, b, to the extent that their contribution to the measured NMR signal is negligible. The main difference between this model and Blumberg's calculation is that the limits of the volume integral in Eq. (10b) are different. In his model, the integral is carried out over the entire crystal, excluding only nuclei that are inside the radius b. Tse and Hartmann[6] evaluated an integral similar to that in Eq. (10b). However, in their model, they consider that all impurity sites are important to the problem. They obtain a complicated expression that reduces to $\exp[-(\tau/\tau_1)^{1/2}]$ when $b\rightarrow 0$, where $(\tau_1)^{-1/2}=(2.31\pi^{3/2}N_pC^{1/2})$. The exponential has been further generalized to $\exp[-(\tau/\tau_1)^n]$. This expression, known as a stretched exponential, has been used recently to fit the relaxation of a nuclear spin system by paramagnetic inpurities.[7]

For simplicity in the derivation below, we define two parameters:

$$\alpha\equiv\overline{C}/b^6 \quad \text{and} \quad c\equiv b^3/R^3.$$

We note that the barrier radius, b, and the coupling constant, C, are independent of the concentration of paramagnetic centers in the sample. Therefore, c is the only parameter that is a function of the number of paramagnetic centers:

$$c=(4\pi/3)b^3N_p. \tag{11}$$

When $t=0$, Eq. (10) reduces to

$$\frac{M_z(t)}{M_0}=-nK\frac{(1-c)}{N_p}+1. \tag{12}$$

Thus, to normalize Eq. (12),

$$K=\frac{N_p}{(1-c)}.$$

The solution to Eq. (10) yields the magnetization at any time:

$$M_z(t)=M_0[1-nG(t)], \tag{13a}$$

where

$$G(t)=\frac{c\sqrt{\alpha t}}{1-c}\{F(c\sqrt{\alpha t})-F(\sqrt{\alpha t})\} \tag{13b}$$

and the function F is defined as

$$F(s)=\frac{\exp(-s^2)}{s}+\sqrt{\pi}\ \mathrm{erf}(s). \tag{13c}$$

In this notation, erf (s) is the standard error function. The experimental data can be fit to these equations to estimate the paramagnetic concentration, c, and the relaxation rate, α. In general, we get excellent fits to these equations.

Since the magnetization within the barrier radius is not observable, Eq. (13b) results in the constraint that $\alpha t>1$. The magnetization recovery is nearly complete when $c^2\alpha t\sim 2$. When the concentration of paramagnets, c, is greater than 0.2, a fit of the nuclear magnetization recovery data provides a reasonable estimate of the paramagnetic relaxation rate, α, and concentration, c. However, the magnetization recovery does not fit the equations at very short times. In a standard NMR saturation recovery experiment, Eq. (13a) reduces to Blumberg's result when $b\rightarrow 0$. Expanding Eq. (13a) and only keeping the constant and terms in $\sqrt{\alpha t}$ results in

$$M_z(t)\approx M_0c\sqrt{\pi\alpha t} \tag{14a}$$

or

$$M_z(t)=M_0\left(\frac{4\pi^{3/2}}{3}\right)N_p\overline{C}^{1/2}t^{1/2}. \tag{14b}$$

Also, there is a large magnetization at very short time. Therefore, using Blumberg's expression for large c without accounting for the magnetization offset results in underestimation of $c^2\alpha$.

V. RESULTS AND DISCUSSION

A. Fitting the NMR data to different magnetization recovery functions

Equation (13) above and the stretched exponential function are slightly different mathematical models, resulting

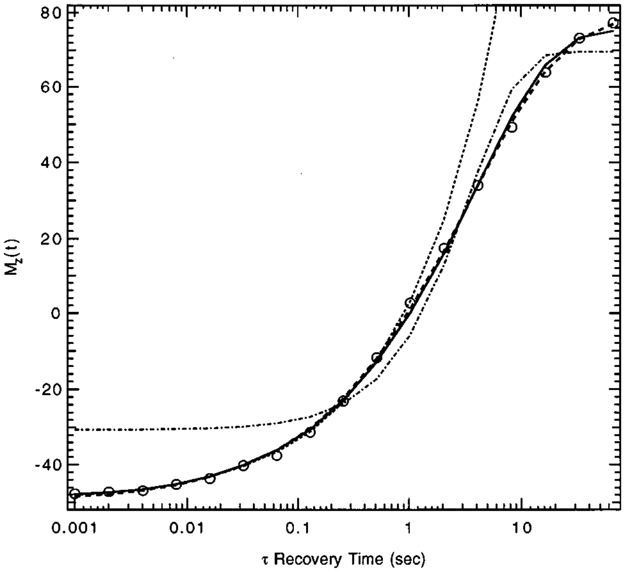

FIG. 1. Magnetization recovery vs $\log_{10}$ of time in a ^{29}Si inversion recovery experiment with hectorite. The open circles are the experimental data. Curves representing the fit of $M_Z(t)$ were obtained using four different functions: (— · — · —) = single exponential , (—) = Eq. (13), (— — —) = stretched exponential, and $[\cdots] = \tau^{1/2}$.

from different assumptions in the mathematical solution for nuclear magnetic relaxation due to coupling to dilute paramagnetic impurities. Both can be used to described magnetization recovery in an NMR experiment. In Fig. 1, we plot the magnetization recovery of ^{29}Si in hectorite and the nonlinear fits from Eq. (13), a stretched exponential with $n=0.5$, a "normal" exponential recovery, and a recovery with $\tau^{1/2}$. It can be seen that both the stretched exponential and erf(s) functions do a credible job of fitting the data. However, we should point out that Eq. (13) might not be a good function to fit data when $\alpha t \gg 1$. In this case, the term $F(\sqrt{\alpha t})$ in Eq. (13c) is essentially equal to 1 and consequently thus the parameters α and c are very dependent on one another. Similarly with the stretched exponential function, the values of τ_1 and n are often strongly correlated, so there may be large errors in both parameters.[13] One thing is clear from Fig. 1: the magnetization does not follow an exponential recovery, indication that spin diffusion is not the major mechanism for the overall relaxation process. Additionally, the $\tau^{1/2}$ function works well at short recovery times but not well at long recoveries, as is implicit in the assumptions in Blumberg's derivation.[4]

Nonexponential relaxation is also known in the general literature of chemical reactions and other physical relaxation process in disordered systems such as glasses.[14,15] As an example, Siebrand and Wildman[14] relate nonexponential decays to structural disorder. They propose an equation to describe the relaxation in disordered systems that is very similar to the stretched exponential function, except at short times. In the case considered in our work, the random distribution of fixed paramagnetic centers introduces a structural disorder. Since the electron-nuclear interaction is distance dependent ($1/r^3$) and there is a distribution of nuclear-paramagnet distances there will be a distribution of spin-lattice relaxation times; one for each nuclear-paramagnet distance. Therefore the nonexponential relaxation is interpreted as a linear superposition of exponentials, each arising from a particular Si-paramagnet distance.

B. Dependence of the nuclear-spin-lattice relaxation time on paramagnet concentration

The ^{29}Si MAS-NMR spectra of all samples studied have a single peak ranging from -83 to -98 ppm (except for barasym), depending on the sample. This suggests the existence of only one environment for the Si atoms. The difference in chemical shift between the samples is a consequence of both structural distortions in the tetrahedral sheets and compositional variations in the octahedral sheet.[16] Chemical shifts due to the composition of the octahedral sheet are the consequence of substitutions, for example, the montmorillonites, SAz-1, STx-1, SWy-1, have layer charges due to Mg^{2+} substitution for Al^{3+} in the octahedral sheet, while hectorite has Li^{+} partially substituting Mg^{2+} as the octahedral cation. Weiss *et al.* discussed the effects of structural distortions on ^{29}Si chemical shifts.[16] These structural distortions can be relatively large and arise because tetrahedral sheets are larger than the octahedral ones and must be distorted to match at the shared oxygen planes.[17] Aluminum substitution in the tetrahedral layer increases the distortion by increasing the ideal dimensions of the tetrahedral b axis. In calculating N_p, the concentration of paramagnetic centers per cm^3, we have considered structural differences between the samples. Although small, the structural differences change the volume per unit cell and thus affect the concentrations significantly. Unit cell dimensions, a, b, c axes, are taken from the literature.[16,18,19]

The ^{29}Si MAS-NMR spectrum of barasym has three components at -83, -88, and -92 ppm. Since all of the layer charge in barasym is due to Al substitution in the tetrahedral sheet, there exist four possible distinct environments for Si, i.e., SiO_4 surrounded by three SiO_4, two SiO_4, and one AlO_4, one SiO_4 and two AlO_4, and three AlO_4. These sites have chemical shifts which increase in field (larger negative values) as the number of Al next nearest neighbors increases.[20] In barasym the Si/Al ratio per unit cell is near 4 so statistically, the probability of an Si with three AlO_4 neighbors is very low. Figure 2 shows ^{29}Si spectra of barasym and talc. Talc has no Al substitution in the tetrahedral layer and consequently all Si atoms have three Si next neighbors, and a single ^{29}Si peak at -98 ppm. The NMR lines for talc are broader than for barasym due to a distribution of dipolar couplings to the paramagnets.

The magnetization recovery curves for all clay samples studied exhibited nonexponential decay. Results of the inversion recovery experiments for these clay minerals are shown in Fig. 3. The ordinate of Fig. 3 is $M_Z(t)/M_Z(o)$, where $M_Z(o)$ is the signal intensity at equilibrium mangetization. The abscissa is plotted on a logarithmic scale. This method of plotting the data is useful to see deviations from exponentiality at short recoverty times. The sample with the highest paramagnetic concentration, SWy-1, contains almost 27 times more iron than that with the lowest paramagnetic concentration (barasym), and the recovery times span four decades in magnitude. Although the ^{29}Si NMR spectrum of

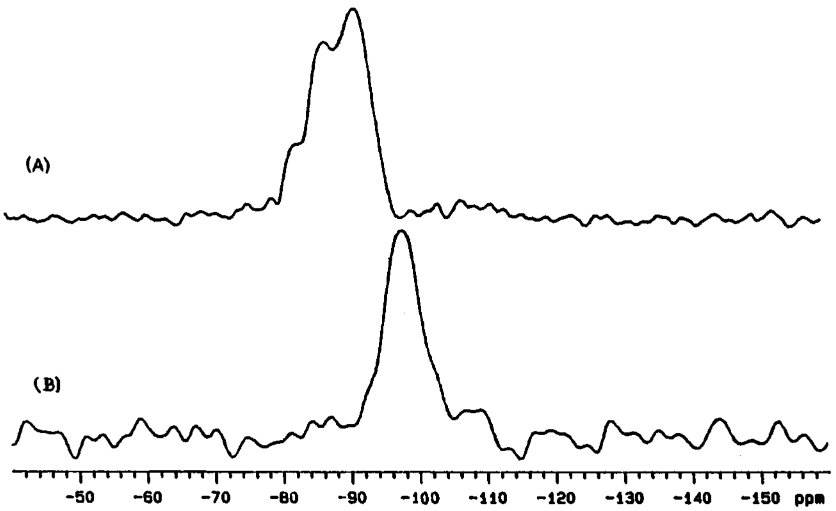

FIG. 2. ^{29}Si MAS NMR spectra of (a) barasym and (b) talc.

barasym shows three peaks, they all have the same ''spin-lattice relaxation time.'' The six experimental curves were nonlinearly fit to Eq. (13) using IGOR.[21] The parameter α should not depend on the paramagnetic concentration and although there are structural differences between dioctahedral and trioctahedral samples, α is primarily related to minor structural differences in angles, not distances [see Eq. (4)]. Therefore, we held α fixed between fitting the different curves in Fig. 3. The best value of α that fits all samples, especially those with relatively high paramagnetic concentration, is $\alpha = 280\ \mathrm{s}^{-1}$. In addition, the fit of each curve gives a different value for the parameter c, which is related to the number of paramagnetic centers per unit volume. Figure 4 contains the values of c at 300 K plotted against the concentration of paramagnets obtained from chemical analyses, N_p. The dependence is approximately linear. From Eq. (11) the dependence should be linear with a slope of $(4\pi/3)b^3$. From this data, we obtain a value for the barrier radius, b, of the order of 10 Å. Using the value for the barrier radius, b, it is possible to estimate a value for the coupling constant C. Since this factor involves the electron relaxation time τ_c as the only unknown, it may be used to obtain τ_c. Using Eq. (5), C and τ_c are calculated to be 2.8×10^{-40} cm^6/s and 8×10^{-9} s, respectively.

There are a number of relevant observations about the paramagnetic relaxation in these systems. First, we assume that all of the iron in the chemical analysis of the samples except talc is in the form of Fe^{3+}. Several papers in the literature indicate that such is the case.[22-24] However, assuming that the iron in talc is all in the ferric state made it an outlier on Fig. 4. A more careful analysis of the iron in talc resulted in an Fe^{2+} concentration of 2.7×10^{19}/c.c. and Fe^{3+} of 2.2×10^{19}/c.c. There are several EPR studies of clays, none of which explicitly addresses the question of the electron relaxation times.[25,26] However, there are clear signals from Fe^{3+} and no signals from Fe^{2+} because the relaxation time for the latter is extremely short. In an NMR experiment where the nuclear relaxation is determined by dipole coupling to a paramagnet and the time dependence causing relaxation is the relaxation of the paramagnet, the most effective nuclear relaxation occurs when the paramagnetic relaxation time is approximately the same as the nuclear Larmor frequency (T_1 minimum).[27] Thus Fe^{2+} is not an effective relaxation center for ^{29}Si nuclei because the electron relaxation times are too short. We have only included the concentration of Fe^{3+} in Fig. 4 and subsequent calculations. The electronic relaxation time, τ_c, is the longitudinal relaxation time which, to our knowledge, has not been measured for clay systems such as these.

We can roughly estimate the electron T_1 by assuming that the longitudinal and transverse relaxation times are nearly equal and that the transverse electronic relaxation time is given by the linewidth of an EPR spectrum. We measured an EPR spectrum of the most concentrated sample (SWy-1) which consists of two peaks: a broad resonance at $g = 2.0$ and a sharper signal at $g = 4.2$. In the literature, the resonance at $g = 4.2$ is assigned to iron (III) ions occupying distorted octahedral sites within the clay structure,[28] whereas the broad

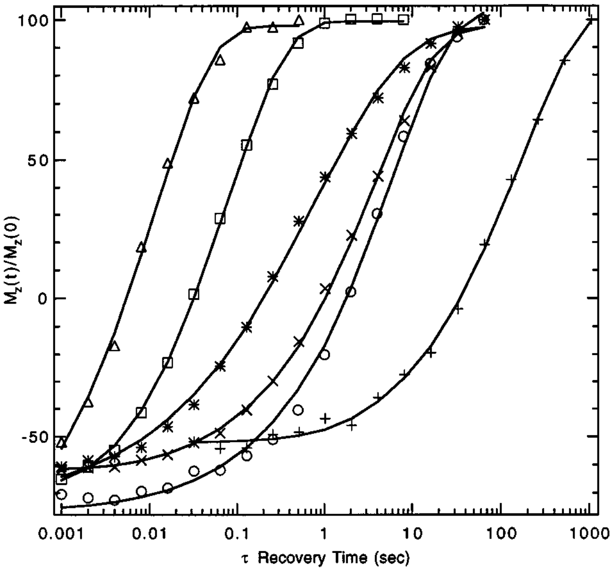

FIG. 3. Nuclear magnetization recovery vs $\log_{10}$ of time from inversion recovery experiments for the six samples studied: (+) barasym, (×) hectorite, (*) STx-1, (□) SAz-1, (δ) Swy-1, and (○) talc. The solid lines represent the fit of $M_z(t)/M_z(0)$ using Eq. (13).

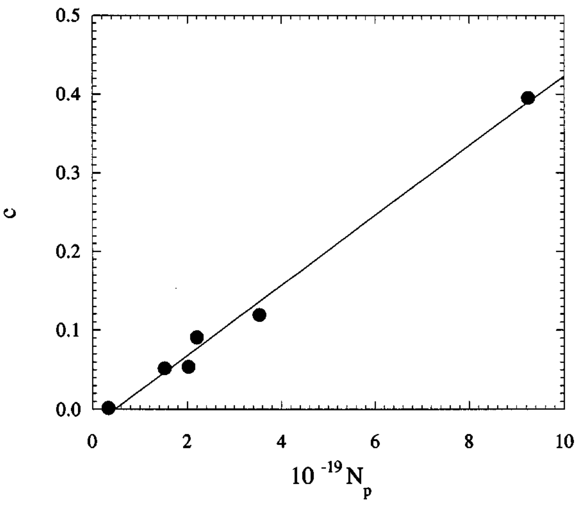

FIG. 4. The concentration of paramagnets, c, obtained from fitting the ^{29}Si magnetization recovery data using Eq. (13) vs N_p, the concentration of Fe^{3+} ions per unit volume, obtained from independent chemical analysis of the clays or from literature analyses.

signal reflects Fe-O-Fe groupings within the lattice.[25] The linewidth of the sharper peak is about 380 g, so that τ_c is of the order of 4.7×10^{-10} s. Although the agreement is not perfect, this is reasonably close to the value of 8×10^{-9} obtained from the fit of the NMR magnetization recovery curves using Eq. (12). Part of the difference may arise because of inhomogeneous broadening in the EPR signal which contributes to the total width but is not due to relaxation.

VI. CONCLUSIONS

The ^{29}Si relaxation times in many materials, including most minerals is likely determined by distant coupling to paramagnetic centers. The dilute nature of ^{29}Si, due to both isotopic and chemical dilution, means that spin diffusion will be very limited. We propose a model to describe the nuclear-spin-lattice relaxation through coupling to paramagnets where the paramagnets are dilute and nuclear spin diffusion is quenched. Using this model the recovery of nuclear magnetization is described by an error function rather than a ‘‘normal’’ exponential function. This model allows us to obtain the relative concentration of paramagnetic centers from the fit of the magnetization recovery curves. Tse and Hartmann used fewer simplifying assumptions in the mathematical treatment of the model for nuclear relaxation by coupling to dilute paramagnets, in the absence of spin diffusion. Their model results in a stretched exponential function for the magnetization recovery. The primary difference between their model and ours is the fact that they consider that a given nucleus interacts with all paramagnets in the sample while we restrict the interaction to the single nearest paramagnet. Both the stretched exponential and error function produce excellent fits to all of our data so there is no reason, based in ‘‘goodness of fit’’ to select one over the other. We believe that our model has certain advantages in that we can extract the concentration of paramagnets from fitting the NMR magnetization recovery curves. Additionally, in our hands the stretched exponential function results in a high correlation between two parameters τ_1 and n in the fit. This means that good fits can be obtained with a very different value of one parameter simply by changing the other one. Thus it is difficult to assign physical meaning to these parameters. To take this a bit farther, this correlation between parameters makes it difficult to obtain unique values of the exponent n, which can be correlated to the fractal dimension of the system. However, Tse and Hartmann’s assumption of coupling to all electron spins in the sample may be more physically realistic. To some extent the choice of which model to apply is at the liberty of the experimentalist and may depend on the detailed nature of the sample and what physical interpretation or picture she would like to obtain from the data.

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