Mechanism of NMR Relaxation of Fluids in Rock

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A theory of the nuclear magnetic relaxation of fluids in the pore spaces of sedimentary rocks at low frequencies is presented. Because the materials studied are varied in their composition and cannot be thoroughly characterized, the theory cannot be considered as universally applicable; however, it is consistent with diverse experimental observations that are in the literature, many of which have not been heretofore explained. The multiexponential character of the NMR decays has earlier been found to be correlated with the heterogeneities in pore sizes which characterize most rocks. The heterogeneity length scale is larger than the diffusion length associated with NMR relaxation times. It is found that the most important relaxation mechanism arises from hyperfine interactions with paramagnetic ions such as Mn^{2+} and Fe^{3+} at the grain surfaces. Lack of a strong temperature dependence of the rates indicates that the diffusive motion of the fluid molecules or the on–off motion at a surface site do not enter into a determination of T_1 and T_2. The ratio T_1/T_2 measured at low frequencies has been generally found to be significantly greater than 1. It is proposed that the explanation for this phenomenon lies in the fact that the scalar part of the hyperfine interaction is comparable to the dipolar part, because the latter is partially averaged due to the restricted rotational motion of the molecules at a surface site. © 1994 Academic Press, Inc.

INTRODUCTION

It has long been known that the enhancement of NMR relaxation rates of fluids in porous media is due to relaxation at the pore–grain interface (1, 2). Fluid molecules diffuse, eventually reaching a grain surface where there is a finite probability that they will be relaxed. It has been generally believed that this relaxation process in porous rocks is associated with the presence of paramagnetic ions, such as iron or manganese, on or near the grain surfaces (2–4). However, the details of the surface relaxation mechanism have not been elucidated.

Over the past few years many experimental relaxation time data on various fluids in rocks have been accumulated, for a variety of reasons on a variety of rock samples and pore fluids. Each of these studies was directed toward answering one or more specific technical questions, and no attempt has

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been made to account for the disparate data in terms of an underlying relaxation mechanism. The purpose of this work is to explain the diverse experiments. The reader is cautioned that the natural materials used in the experimental studies are heterogeneous and cannot be as thoroughly characterized as synthetic samples or pure materials. Thus the theory presented here is to be regarded as semiquantitative.

The NMR magnetization decays of fluids in rocks are invariably nonexponential. The most general way of describing these decays is by a sum of exponentials. We refer to the set of coefficients of such an expansion as a spectrum or distribution of decay times. We show that this behavior cannot be explained by intrinsically nonexponential decay processes, but must arise from heterogeneities in the structure or chemical composition of the porous medium. Our theory describes the relaxation in a small region of the medium in which the magnetization decay of the pore fluid has a single-exponential character. The size of this region, which is defined below, is small compared to the size of laboratory samples. When the magnetization decays of all such regions are summed, the experimentally observed distribution of relaxation times results.

REVIEW OF EXPERIMENTAL OBSERVATIONS

The correspondence between heterogeneities in pore structure and the distribution of NMR relaxation times was explored by Straley et al. (5). Rock specimens were fully saturated with water and the spectrum of longitudinal relaxation times was determined. Then each rock was centrifuged at a number of rotor speeds. At successively higher speeds, water was progressively expelled from the samples, as the centrifugal pressure overcame the capillary pressure of successively smaller pore spaces. At each step, the NMR relaxation spectrum was remeasured. At low centrifuge speed, the components with the longest T_1 disappeared from the spectrum while the short T_1 components were unaffected. As the centrifuge speed was increased, progressively shorter components disappeared. This indicated that the populations of water molecules with longer lifetimes were in relatively larger pores which were easier to drain. Since the publication of

(5), this analysis has been performed on more than a hundred diverse rock samples, with the same results (C. Straley, personal communication).

The connection between pore size and NMR relaxation time has also been probed with mercury-injection porosimetry. The pressure required to push a nonwetting fluid such as mercury into a pore is inversely proportional to the size of the pore opening. Using a single scale factor to relate mercury entry pressure to NMR longitudinal relaxation rate, Kenyon et al. (6) found reasonable agreement between the NMR- and mercury-derived size spectra for most, although not all, of the 11 sandstone samples measured. Similar results were found by Morriss et al. (7), who measured the mercury and transverse relaxation time spectra of 28 sandstone samples. Agreement between the techniques is not expected to be exact since mercury porosimetry measures pore opening, whereas NMR relaxation depends on the surface-to-volume ratio, as discussed below. The results suggest that there is a fixed relationship between these microgeometric quantities for many sandstones. This is not likely to be true for carbonates, whose microgeometries are much more diverse.

Borgia et al. (8) measured the distribution of relaxation times of three synthetic porous ceramics and two natural rocks. Each material had a distribution of pore diameters that ranged over an order of magnitude or more. The ceramics were characterized by monoexponential NMR decays, while the rocks had broad distributions of relaxation times.

Latour, Kleinberg, and Sezginer (9) measured the temperature dependence of T_1 and T_2 for about a dozen water-saturated rocks. Half were sandstones and half were carbonates. They found that the distributions of relaxation times were almost independent of temperature between 25 and 175°C.

Kleinberg, Farooqui, and Horsfield (10) measured the frequency dependence of T_1. Eight rocks including both sandstones and carbonates were measured at 5, 40, and 90 MHz. T_1 varies modestly with frequency in this frequency range for the materials considered.

Kleinberg et al. (10) also determined the T_1/T_2 ratio. The measurements were made at 2 MHz. At this frequency, and for the CPMG pulse spacing used, the transverse relaxation is unaffected by diffusion in magnetic field gradients (11, 12), and T_2 is dominated by relaxation at the grain surfaces. For almost all rocks studied, the T_1 and T_2 distributions had remarkably similar shapes, and T_1/T_2 was determined by cross-correlating the two relaxation time distributions. Based on measurements on 48 rocks it was found that T_1/T_2 is in the range of 1 to 2.6, with a median value of 1.59.

As shown below, the longitudinal relaxation rate in a homogeneous region of porous material is proportional to the surface-to-volume ratio of the pore space. The constant of proportionality, ρ_1, is called the longitudinal surface relaxivity. Howard, Kenyon, and Straley (13) measured ρ_1 for a variety of sandstones. Howard et al. pointed out some uncertainties in evaluating the surface relaxivity parameter for natural materials. For example, the presence of clay minerals can make determination of the surface-to-volume ratio difficult. For "clean" sandstones, i.e., siliceous rocks with a relatively low clay content, they found $\rho_1 \approx 3 \times 10^{-3}$ cm/s.

Almagor and Belfort (14) and D'Orazio et al. (15) measured the NMR relaxation times of water adsorbed on porous silica glasses. The results of the two groups were similar. D'Orazio et al. found the longitudinal surface relaxivity parameter $\rho_1 = 5 \times 10^{-7}$ cm/s. This is orders of magnitude smaller than ρ_1 found in clean sandstones composed almost entirely of silica (13). D'Orazio also found $T_1/T_2 = 58$, in distinct contrast to the small values of T_1/T_2 found by Kleinberg et al. (10).

Straley et al. (5) measured the relaxation time distributions of water and kerosene mixtures in rocks. They found that when a rock was wetted by water, subsequently introduced kerosene relaxed at its slow bulk liquid relaxation rate, while the water in contact with the grain surfaces relaxed rapidly. However, when the rock was dried for five weeks at 60°C and then saturated with pure kerosene, the kerosene relaxation was accelerated by the grain surfaces.

Latour et al. (9) repeated this experiment with two hydrocarbon viscosity standards. They used the same drying protocol as Straley et al. (5). Explicitly taking into account the temperature-dependent distribution of relaxation times of the bulk hydrocarbon liquids, they found that the distribution of relaxation rates deduced from hydrocarbon-saturated rocks matched the distribution of relaxation rates found when the rocks were fully water-saturated. However, they also found that the grain surface was less efficient in relaxing the oils than it was in relaxing water: ρ_1(water)/ρ_1(oil) was 17 for one of the viscosity standards and 31 for the other.

ORIGIN OF MULTIEXPONENTIAL RELAXATION

The NMR decay of longitudinal magnetization of water in rocks is nonexponential (16, 17). A typical example is shown in Fig. 1. The top of the figure shows the longitudinal NMR relaxation of water in Berea sandstone at a proton resonance frequency of 2 MHz. Dots are experimental data and the line drawn through them is the best fit to the expression

$$M(t) = \sum_i A_i[1 - 2\exp(-t/T_{1i})]. \quad [1]$$

The spectrum of A_i is shown in the bottom of the figure. Each A_i is proportional to the number of protons with relaxation time T_{1i}. In this example, regularization (18) has been used to smooth the spectrum. A main peak one or two decades wide and a tail extending to small values of T_{1i} are commonly observed features in the distribution of relaxation times of water in porous rocks.
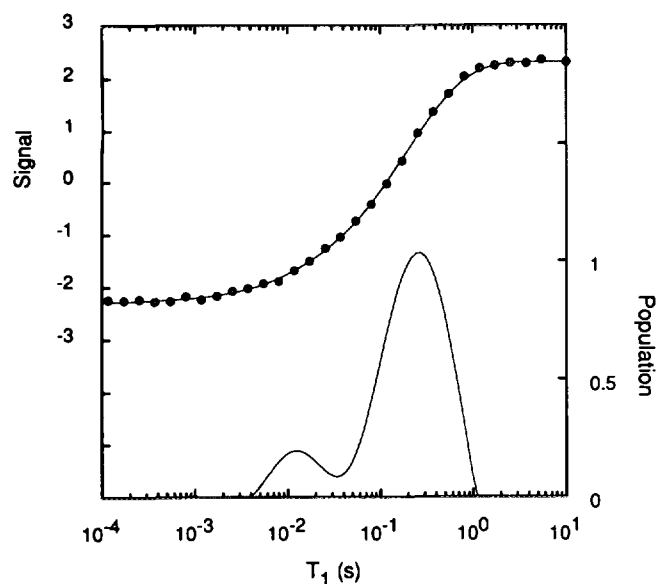
FIG. 1. Longitudinal relaxation of water protons in porous Berea sandstone. At the top is the inversion-recovery signal as a function of recovery time; dots, data; curve, fit to Eq. [1]. The bottom line is the corresponding distribution of relaxation times.

It is commonly believed that nonexponential magnetization decays arise from the wide distribution of pore sizes found in natural sedimentary materials (19–26). According to this view, the spins carried by fluid molecules relax at pore–grain interfaces. The rate-limiting step is relaxation at the surface, not the transport of magnetization to the surface. The rate of magnetization decay in an individual pore is thereby monoexponential and does not depend on pore shape but only on the surface-to-volume ratio. The time evolution of the magnetization of a sample having a distribution of pore sizes can be expressed as a sum of exponential decays. Thus there is a direct mapping from the spectrum of pore sizes, or more precisely the spectrum of surface-to-volume ratios, to the spectrum of relaxation times. This is referred to as the "fast-diffusion" (24) or "surface-limited" (26) regime.

In the opposite case magnetic relaxation occurs at the grain surface, but the decay of macroscopic magnetization is controlled by the transport of molecules to the surface. This is likely to be the case when pores are relatively large and/or surface relaxation is strong. This is called the "slow-diffusion" (24) or "diffusion-limited" (26) regime. In this regime there is a time-dependent nonuniform spatial distribution of magnetization in the pore. This gives rise to a magnetization decay which even in a single pore has multiexponential character and which depends on the shape of the pore. It should be noted that even for strongly diffusion-limited relaxation, the lowest mode is often dominant (24, 27).

The papers cited above implicitly assume that the inherent strength of the surface relaxation is uniform throughout the

material. However, natural materials are often mineralogically inhomogeneous. The above models are unaffected when heterogeneities occur within pores. In the surface-limited case, fluid molecules sample the entire pore volume on the NMR time scale, thereby averaging the relaxing effects of the bounding surfaces. In the diffusion-limited case, the strength of the surface relaxation does not affect the observed NMR decay.

Mineralogy can also vary from pore to pore, and thereby the rate of surface relaxation can vary from pore to pore. In this case, a distribution of relaxation times would reflect heterogeneities that are not necessarily correlated with pore size.

Note that the decay of magnetization at a surface site may itself be nonexponential (28). However, since the fraction of fluid molecules at surface sites is very small, the overall decay of magnetization will not reflect the detailed time dependence at a surface site, but will be sensitive only to the mean lifetime of decay at surface sites. If the surface relaxivity is weak, so that the magnetization in a homogeneous sample decays uniformly, then the magnetization will show single-exponential behavior irrespective of any nonexponential decay at a surface site. This is demonstrated by a model calculation in the Appendix. The nonexponential behavior of relaxation in rocks is therefore not related to any intrinsic behavior at a surface site and must be related to the heterogeneous nature of the rock itself.

No doubt sedimentary rocks can be found that satisfy the slow-diffusion conditions or that are mineralogically heterogeneous from pore to pore. However, there is considerable evidence that for the large majority of rock materials studied, there is a linear correspondence between the relaxation time spectrum and "pore size" distribution. The best evidence is from the centrifugation measurements discussed earlier (5). These measurements show there is a direct link between pore capillary pressure and NMR relaxation time in rock materials.

Further evidence in support of the surface-limited hypothesis comes from measurements of temperature dependence (9). If NMR relaxation were in the diffusion-limited regime, the relaxation time would depend on the diffusion coefficient of the pore fluid, which is very temperature-dependent. The lack of temperature dependence is a mark of the surface-limited regime.

The distribution of relaxation times indicates there is a distribution of the quantity $\rho S/V$. This quantity is averaged over the volume explored by a diffusing molecule during the NMR measurement. The concept of a length scale over which $\rho S/V$ is averaged is illustrated in experiments of Borgia et al. (8), who measured the magnetization decays of three synthetic porous ceramics and two natural rocks. The pore size distributions of all samples were more than an order of magnitude in width, and all materials were in the fast-diffusion (surface-limited) regime. T_1 decays were monoexponential for the synthetic materials and multiexponential

for the natural materials. It appears that diffusion effectively averaged the pore sizes in the synthetic samples and failed to do so in the natural materials. This indicates that microgeometric heterogeneities of the synthetic materials occur over length scales small compared to the distance molecules diffuse during the NMR experiment. In contrast, in the rocks examined, the heterogeneity length scale must be larger than the diffusion length.

Thus the existence of temperature-independent relaxation time distributions implies that the heterogeneity length scale of the rocks heretofore examined is larger than the diffusion length at temperatures as high as 175°C (9). This is consistent with the observation that the time-dependent diffusion coefficient of water in many rocks, measured at diffusion times several times greater than T_1, does not approach asymptotically the tortuosity (29), in contrast to the situation in bead packs (30). Local distributions of geometrical quantities have been proposed in the past (31).

An alternative scenario also leading to the weak temperature dependence of the relaxation time spectrum is that the pore space consists of almost isolated pores, each with a separate value of $\rho S/V$. However, there is no independent evidence for isolated pores; transport measurements indicate a relatively well-connected pore space, and pulsed-field-gradient NMR measurements of diffusion are clearly inconsistent with a closed-cell pore structure (29).

EQUATIONS FOR T_1 AND T_2

The basic principles of surface relaxation in porous media were laid down by Korringa, Seevers, and Torrey (KST) (3). They considered spins diffusing to and relaxing on a surface. Two surface processes and a bulk process were identified. The bulk process has the relaxation time T_{1B}. The first surface process occurs at all sites on the surface and is associated with a relaxation time T_{1S}. The second surface process is associated with dilute paramagnetic metal ion impurities and is associated with a relaxation time T_{1M}.

The KST picture can be considerably simplified using the experimental information at hand. Because the relaxation time of water in rocks is much shorter than the relaxation time of bulk water, the bulk terms in the equations can be neglected. Moreover, from the work of Almagor and Belfort (14) and D'Orazio et al. (15), it is known that the relaxation process associated with nonmagnetic sites on the surface is much too weak to affect the observed relaxation of water in rocks. Thus the process studied by D'Orazio et al., nuclear–nuclear dipolar coupling modulated by hindered molecular reorientation, does not dominate NMR relaxation in rocks. This is perhaps not totally unexpected. Mineralogy handbooks (32) report that rocks generally contain approximately 1% iron. At this concentration, paramagnetic relaxation mechanisms can be expected to overwhelm the relaxation mechanisms associated with pure diamagnetic solid surfaces.

Therefore the KST equations for surface relaxation in a single pore reduce to

$$\frac{1}{T_1} = \left(\frac{Sh}{V}\right)\frac{n_M}{T_{1M} + \tau_M} = \rho_1 \frac{S}{V}. \qquad [2]$$

S and V are the surface area and volume of the pore, h is the thickness of the surface layer within which relaxation can take place, n_M is the proportion of surface sites occupied by paramagnetic metal ions, T_{1M} is the relaxation time of protons in molecules coordinated with paramagnetic ions, and τ_M is the residence time of the fluid molecules in that coordination complex. All material constants are included in the surface relaxivity parameter ρ_1 introduced earlier.

Equation [2] assumes that all relaxing surface sites are identical; the extension to multiple site properties (e.g., multiple paramagnetic ion species) is trivial. KST assumed that relaxation at each site is exponential and characterized by a time constant T_{1M}. The appendix demonstrates that an equation of the same form results when site relaxation is nonexponential.

KST do not discuss T_2 in porous media. T_2 is shortened by diffusion in the inhomogeneous magnetic field arising from the magnetic susceptibility contrast between grains and pore fluid (11, 12), which is unrelated to surface relaxation. However, Kleinberg and Horsfield (11) found that for proton Larmor frequencies below 5 MHz and for Carr–Purcell echo spacings less than about one millisecond, the enhancement in T_2 decay coming from diffusion in the inhomogeneous local fields is negligible compared to the surface relaxation mechanism. In this regime (33),

$$\frac{1}{T_2} = \left(\frac{Sh}{V}\right)\frac{n_M}{\tau_M}\frac{T_{2M}^{-2} + (T_{2M}\tau_M)^{-1} + \Delta\omega_M^2}{(T_{2M}^{-1} + \tau_M^{-1})^2 + \Delta\omega_M^2}. \qquad [3]$$

$\Delta\omega_M$ is the change of spin precession frequency which occurs when the molecule is coordinated to the paramagnetic ion. The other symbols are defined analogously to those in Eq. [2].

Swift and Connick (33) discussed the temperature dependence of $1/T_2$. As explained below, τ_M is expected to have a very strong temperature dependence. $1/T_2$ is independent of temperature, as observed (9), when chemical exchange is fast compared to the surface relaxation process and to the dephasing effect of the paramagnetic moment, i.e., $(T_{2M}\tau_M)^{-1} \gg T_{2M}^{-2}, \Delta\omega_M^2$. In that case,

$$\frac{1}{T_2} = \left(\frac{Sh}{V}\right)\frac{n_M}{T_{2M}} = \rho_2 \frac{S}{V}. \qquad [4]$$

PARAMAGNETIC RELAXATION MECHANISM

The dominant mechanism of surface relaxation in typical rock specimens is the fluctuating hyperfine interaction of the

fluid protons with paramagnetic centers at the rock surface. To correctly calculate the magnitude of this interaction, it is necessary to account for anisotropic motions of the water molecules at a surface site.

Let us first analyze the effects of the jittery motion of a water molecule when it is at a surface site. In all of the following, the coordinate system will be the laboratory frame, with the magnetic field oriented along the z axis. The hyperfine tensor describing the magnetic interactions between a water proton moment I and the paramagnetic moment S can be divided into dipolar and scalar terms,

$$ H = A_s \mathbf{I} \cdot \mathbf{S} + \mathbf{I} \cdot \{ \mathbf{A}_d(\mathbf{\Omega}) + \mathbf{A}_d(\delta\mathbf{\Omega}(t)) \} \cdot \mathbf{S}. \quad [5] $$

$\mathbf{A}_d(\mathbf{\Omega})$ is the time average of the dipolar tensor at the surface site. It is characterized by the angle $\Omega \equiv (\theta, \phi)$ joining the mean position of the proton to the center of the paramagnetic ion. $\mathbf{A}_d(\delta\mathbf{\Omega}(t))$ is the fluctuating part of the dipolar tensor. Its time dependence arises from thermal jitter of the proton about its mean position.

The actual motion at a surface site is unknown and may be quite complicated. For illustrative purposes, we adopt a model in which the dipolar vector joining the proton to the center of the paramagnetic ion performs rotational Brownian motion confined to a cone of angle $2\theta_0$ around Ω. We further assume this motion is sufficiently rapid so that the time-dependent part of the dipolar coupling does not contribute significantly to the NMR relaxation. Then the relevant dipolar tensor is simply $\mathbf{A}_d(\mathbf{\Omega})$, with its amplitude reduced from the limit of a rigidly attached fluid molecule by the factor $\alpha = \cos(\theta_0)\cos^2(\theta_0/2)$. Thus, for the purposes of calculating the relaxation rate at a surface site, the magnitude of the dipolar coupling is αA_d, where $A_d = \gamma_I\gamma_S\hbar^2\langle r^{-3}\rangle$.

The scalar hyperfine coupling, A_s, is invariant under rotation and therefore unchanged by rotational jitter. A_s does depend on the distance between the proton and the paramagnetic center. Thermal jitter causes this distance to have a small time-dependent variation, but the effect of this modulation on the scalar coupling is commonly neglected (34).

In the limit of uniformly decaying magnetization, the observed relaxation rate will be an average over the rates for various possible orientations at surface sites. For isotropic porous media, the relaxation rates obtained from the Hamiltonian, Eq. [5], are isotropically averaged. We assume that the correlation functions decay exponentially in time, with two different rate constants, one each for the longitudinal and transverse degrees of freedom. This leads to the usual equations of paramagnetic relaxation, with the minor modification that the dipolar constant is reduced by the factor α.

$$ \frac{1}{T_{1M}} = \left(\frac{\alpha A_d}{\hbar}\right)^2 \frac{S(S+1)}{15} $$

$$ \times \left[\frac{6\tau_{C1}}{1 + (\omega_I\tau_{C1})^2} + \frac{14\tau_{C2}}{1 + (\omega_S\tau_{C2})^2} \right] $$

$$ + \left(\frac{A_s}{\hbar}\right)^2 \frac{S(S+1)}{3} \left[\frac{2\tau_{C2}}{1 + (\omega_S\tau_{C2})^2} \right] \quad [6] $$

$$ \frac{1}{T_{2M}} = \left(\frac{\alpha A_d}{\hbar}\right)^2 \frac{S(S+1)}{15} $$

$$ \times \left[4\tau_{C1} + \frac{3\tau_{C1}}{1 + (\omega_I\tau_{C1})^2} + \frac{13\tau_{C2}}{1 + (\omega_S\tau_{C2})^2} \right] $$

$$ + \left(\frac{A_s}{\hbar}\right)^2 \frac{S(S+1)}{3} \left[\tau_{C1} + \frac{\tau_{C2}}{1 + (\omega_S\tau_{C2})^2} \right]. \quad [7] $$

Each of the relaxation rates is a sum of two terms. The first term comes from the dipolar coupling and the second term from the scalar coupling. Note that the electron spin S = $\frac{5}{2}$ for both Fe^{3+} and Mn^{2+}, the paramagnetic ions most commonly found in rocks. T_{1M} and T_{2M} depend on the two correlation times τ_{C1} and τ_{C2}. These correlation times are combinations of the amount of time a fluid molecule spends in contact with the paramagnetic ion and the relaxation times of the electron spin of the paramagnetic ion,

$$ \frac{1}{\tau_{C1}} = \frac{1}{\tau_M} + \frac{1}{\tau_{S1}} \quad [8] $$

$$ \frac{1}{\tau_{C2}} = \frac{1}{\tau_M} + \frac{1}{\tau_{S2}}. \quad [9] $$

Here τ_M, the same quantity as that used in Eqs. [2] and [3], is the residence time of the fluid molecule at the paramagnetic site, τ_{S1} is the electron longitudinal relaxation time, and τ_{S2} is the electron transverse relaxation time. Unlike the case of paramagnetic ions in solution, the dipolar and scalar interactions are controlled by the same correlation times.

The residence time is commonly assumed to be controlled by an activation energy Δ and thus has the Arrhenius form

$$ \tau_M = \tau_0\exp(\Delta/kT). \quad [10] $$

From the experiments of Latour et al. (9), it is known that the processes controlling relaxation must be independent of temperature at and above room temperature. For T_1 and T_2 to be independent of temperature, the correlation times must be dominated by the electron relaxation times, which are relatively independent of temperature in the range investigated (35).

KST explicitly assume that fluid molecules exchange between discrete environments. Such models have been chal-

lenged by Halle (*36*), who pointed out that in confined geometries, the decay of correlation of spins on fluid molecules can be retarded by multiple contact with interfaces. Models such as Halle's are of relevance when the surface relaxation is controlled by the rate at which fluid molecules approach and depart from the surface. The temperature independence of T_1 and T_2 in rocks demonstrates that $T_{2M} \gg \tau_M \gg \tau_C$, with T_{2M} and τ_C independent of temperature. Were not τ_M so bracketed, multiple reencounters with the surface would affect the measured relaxation times. However, in rocks the NMR relaxation is insensitive to the details of the motions of fluid molecules, and therefore the experiments cannot distinguish between a simple discrete site approximation and more complex models such as that of Halle.

In general, electron-spin relaxation is multiexponential (*37*). This affects the frequency dependence of the nuclear relaxation rates. In the absence of strong dispersion, as in the present case, a single electron correlation time is adequate to represent the data. The effect of multiple electron relaxation times will be of interest when more detailed data over a wider range of frequencies become available.

The Curie spin relaxation mechanism (*38*) has not been included in Eqs. [6] and [7]. Its coupling coefficient depends on the inverse square of the temperature, and its correlation time is necessarily associated with molecular motion, which makes the temperature dependence even stronger. Thus this mechanism cannot be dominant in rocks at and above ambient temperature. Similarly, the possibility of outer-sphere relaxation (*39*) playing a role can be eliminated. Outer-sphere relaxation is controlled by the molecular diffusion coefficient, which has a strong temperature dependence.

It is very difficult to estimate the electron-spin relaxation times (*38, 40*). It is generally accepted that these relaxation times are in the range 10^{-12} to 10^{-8} seconds. To narrow that range, it is necessary to know the identity of the paramagnetic ion, its oxidation state, whether it is in the high-spin or low-spin configuration, the nature of the ligands, the ligand coordination structure, and static and dynamic distortions of the coordination structure. Usually this information is not available for the electron spins on the surfaces of rock grains.

There are also numerous uncertainties in determining the electron relaxation time from the available relaxivity measurements. Howard *et al.* (*13*) point out several problems. First, the values of ρ obtained depend on the method used to find the surface-to-volume ratio of the pore space, particularly in the presence of clay minerals. Second, the fraction of surface sites occupied by paramagnetic ions can differ from the bulk paramagnetic content as determined by elemental analysis or magnetic susceptibility measurements. However, it is possible to set a bound on the electron relaxation time. From Eq. [6] it can be seen that the absence of a frequency-squared dependence of T_1 below 90 MHz (*10*) implies that τ_{S1}, the spin–lattice relaxation time of the electron, must be less than about 2×10^{-9} s.

The oil relaxation results (*9*) provide significant additional information. A study of the literature of sonic attenuation reveals that it is extremely difficult to remove the last monolayer of water from grain surfaces. In a review of the acoustic attenuation of lunar rock material, Tittmann *et al.* (*41*) observed that it was necessary to repeatedly cycle rocks to high temperature at 10^{-11} Torr vacuum to remove the last monolayer of adsorbed water. Thus we may suppose that rocks "dried" at 60°C at ambient pressure still contain at least a monolayer of water.

In quantifying the relaxation of oil in water-wetted rock, the scalar contribution to T_1 is neglected, which will be justified below. The dipolar coupling has a $1/r^6$ dependence on electron–nuclear distance. It is known from solution studies (*38*) that this distance in $Fe^{3+}(H_2O)_6$ is 2.9 Å. The T_{1M} of oil is 17 or 31 times longer than the T_{1M} of water on rock surfaces (*9*), and we interpret this as being due to a layer of immobile water separating the oil molecules from the surface. Thus there is a greater electron–nuclear distance between the magnetic electron and protons on the oil molecule. Using the point-dipole approximation, which is excellent for atoms which are not directly coordinated to iron or manganese ions (*42*), this distance is predicted to be (2.9 Å) $\times$ (17)$^{1/6}$ = 4.7 Å, or (2.9 Å) $\times$ (31)$^{1/6}$ = 5.1 Å. These are reasonable values for the distance between the grain surface and the oil molecules, with an intervening layer of immobile water. The scalar coupling, which arises from paramagnetic electron probability density at the hydrogen nucleus, is insignificant beyond the first coordination sphere.

If the distance between the paramagnetic electron and the water protons is much different than 2.9 Å, implausible values are found for the distance between the electron and the hydrocarbon protons or for the electron-spin relaxation time. Thus these observations exclude the possibility that there was more than one monolayer of water on the surface in the Latour *et al.* hydrocarbon experiments. The possibility that paramagnetic ions buried under the surface are effective in relaxing proton spins is also excluded.

The scalar interaction must be invoked to explain the observed T_1/T_2 ratio because a pure electron–nuclear dipolar interaction is characterized by $1 \leqslant T_1/T_2 \leqslant 1.16$ when $\omega_I\tau_{C1} < 1$. Scalar coupling contributes to T_2 relaxation, but not to T_1 relaxation if either $\tau_{S1} \gg \tau_{S2}$ or $\omega_S\tau_{C2} \gg 1$. Both hypotheses are plausible. Then Eqs. [6] and [7] can be written

$$\frac{1}{T_{1M}} = \left(\frac{\alpha A_d}{\hbar}\right)^2 \frac{S(S+1)}{15} 6\tau_{C1} \qquad [11]$$

$$\frac{1}{T_{2M}} = \left(\frac{\alpha A_d}{\hbar}\right)^2 \frac{S(S+1)}{15} 7\tau_{C1} + \left(\frac{A_s}{\hbar}\right)^2 \frac{S(S+1)}{3} \tau_{C1}. \qquad [12]$$

Then the ratio T_1/T_2 is

$$\frac{T_1}{T_2} = \frac{7}{6} + \frac{5}{6}\left(\frac{A_s}{\alpha A_d}\right)^2. \qquad [13]$$

Using the point-dipole approximation to calculate A_d with $r = 2.9$ Å, and $A_s/h = 1.2 \times 10^6$ Hz, appropriate to water molecules coordinated to the Fe^{3+} ion (*38*), it is found that $5A_s^2/(6A_d^2) = 0.11$. To obtain the median experimental value of T_1/T_2 for rocks of 1.59 (*10*), one must take $\alpha = 0.51$. Within the model where the dipole vector is confined to a cone of apical angle $2\theta_0$, this value of α corresponds to $\theta_0 = 51°$. Thus, the observed value of the T_1/T_2 ratio can be reasonably explained by invoking the scalar part of the hyperfine tensor, in combination with partial averaging of the dipolar tensor. Both A_d and A_s are sensitive to the exact manner in which water coordinates to the metal ion. However, their ratio is less sensitive to changes in electron–proton interaction distance than either is individually.

Anisotropic electron motion influences the T_1/T_2 ratio. It can be shown that if the motion of the electronic moment is strongly anisotropic, then the scalar coupling makes T_1 relaxation as effective as T_2 relaxation, and then there is no longer a mechanism making T_1/T_2 significantly bigger than 1. Since Mn^{2+} and Fe^{3+} are S-state ions, the effects of crystal field splittings on the electron can be assumed to be relatively small and the electron motion isotropic.

Bounds can be placed on the time water molecules reside on the grain surface. As explained above, this residence time, τ_M, dominates the correlation times that enter into Eqs. [6] and [7] when it is shorter than the electron relaxation times. According to Eqs. [2] and [3], the residence time controls the relaxation rates when it is larger than T_{1M} and T_{2M}. Thus, for the observed NMR relaxation times to be independent of temperature, the temperature-dependent residence time must be bounded by τ_{1S} below and by T_{2M} above.

CONCLUSION

Any theory of the surface relaxation of fluids in the pore space of sedimentary rocks must be consistent with the following observations: (1) the longitudinal and transverse magnetization decays are multiexponential for rock materials, but not for some synthetic porous media; (2) the relaxation spectra are independent of temperature over the range 25 to 175°C; (3) T_1 varies much more slowly than the square of the frequency over the range 5 to 90 MHz; (4) T_1/T_2 is found to be in the range of 1.6 when relaxation by diffusion is suppressed; (5) the relaxation of water on silica glass surfaces is distinctly slower than the relaxation of water in siliceous rocks; and (6) oils in a laboratory-dry rock relax significantly times slower than does water in the same rock.

For the preponderance of rocks studied, nonexponential decay of magnetization can be confidently attributed to a broad distribution of surface-to-volume ratios. Magnetization decays are multiexponential when the heterogeneity length scale of the material is larger than the distance molecules can diffuse during an NMR measurement. Fluid molecules diffuse to the surface and exchange into the first coordination

sphere of paramagnetic ions at that surface. Nuclear relaxation at the surface is slow compared to the exchange process.

The dominant interactions between protons in the fluid and paramagnetic ions on the grain surfaces are scalar and dipolar couplings between electron and nuclear spins. The dipolar coupling is reduced by a partial averaging due to the restricted rotational Brownian motion at a paramagnetic surface site. The electron-spin relaxation time is the relevant correlation time for both interactions. Oil in rock relaxed more slowly than water in rock because a monolayer of water blocked the surface in the experiments considered. The model is consistent with a physically reasonable value for the electron–nuclear interaction distance and provides a bound on the electron relaxation time. Upper and lower bounds can be placed on the residence time of molecules on the surface.

APPENDIX

In this appendix, we show by a simple model calculation that if the number of fluid molecules at relaxing surface sites is small compared to the total number of molecules, then the detailed behavior of the magnetization at a surface site does not enter into the overall decay. In particular, we consider the weak-relaxation ("surface-limited") regime and show that the decay is exponential irrespective of the time dependence of magnetization at a surface site. Similar considerations hold in the strong-relaxation ("diffusion-limited") regime, except that the additional complication of solving a diffusion equation must be considered. The weak-relaxation limit corresponds to the experimental situation.

In the model, there are two populations of molecules, labeled by subscripts s and b, corresponding to the surface-relaxing sites and bulk sites. Since we are interested in the weak-relaxation limit, we assume that there is no spatial variation of the magnetization. Let $m_s(t)$ and $m_b(t)$ be the magnetizations of these two populations at time t. We will also assume that the bulk decay of magnetization can be neglected or has been factored out, so we need consider only the decay of magnetization due to the surface sites. In general, $m_s(t)$ and $m_b(t)$ will satisfy rate equations of the form

$$\frac{dm_s(t)}{dt} = -\frac{1}{\tau_M} m_s(t) + \frac{\epsilon}{\tau_M} m_b(t)$$

$$- \int_{-\infty}^{t} R(t - t_1) m_s(t_1) dt_1 \qquad [14]$$

$$\frac{dm_b(t)}{dt} = \frac{1}{\tau_M} m_s(t) - \frac{\epsilon}{\tau_M} m_b(t); \qquad [15]$$

$\epsilon \equiv n_M hS/V$ is the ratio of the number of molecules at surface-relaxing sites to the total number of molecules. In the experimental situations of interest, ϵ is very small, on the order

of 10^{-6}; τ_M is the residence time at a surface site. $R(t)$ is a relaxation function that characterizes the decay process at a surface site. If the decay at a surface site is exponential, then the Laplace transform $\tilde{R}(s)$ is a constant. In general, the decay at a surface site is not exponential, but may be represented by having a spectrum of relaxation rates $P(\Gamma)$, so that the decay at the site is given by $\int_0^\infty P(\Gamma)e^{-\Gamma t}$. In this case, $\tilde{R}(s)$ is given by

$$\frac{1}{s + \tilde{R}(s)} = \int_0^\infty \frac{P(\Gamma)d\Gamma}{s + \Gamma}. \qquad [16]$$

In particular, $\tilde{R}(0) = 1/T_M$, where T_M is the mean lifetime at a relaxing site.

After a Laplace transformation of the rate equations, with the initial conditions $m_s(0) = \epsilon$, $m_b(0) = 1 - \epsilon$, we obtain linear equations which may be solved for the Laplace transform of the total magnetization:

$$\tilde{m}(s) = \frac{s + \tau_M^{-1} + \tilde{R}(s)}{s^2 + s[\tau_M^{-1} + \tilde{R}(s)] + \epsilon\tilde{R}(s)\tau_M^{-1}}. \qquad [17]$$

The Laplace transform of the above equation will in general lead to nonexponential decay. However, in the parameter ranges of interest, the decay will be exponential with negligible deviations. To see this, first set $\epsilon = 0$, in which case $\tilde{m}(s) = 1/s$ consists of a simple pole at the origin, corresponding to no decay in the absence of surface sites. If we now put in a small fraction of surface sites, corresponding to $\epsilon \ll 1$, then the pole at the origin moves to slightly negative values of s in the Laplace domain. The position of the pole is given by

$$s = -\frac{\epsilon\tilde{R}(s)\tau_M^{-1}}{s + \tau_M^{-1} + \tilde{R}(s)}. \qquad [18]$$

Assuming some reasonable analytic properties of $\tilde{R}(s)$, we can find the position of the root near $s = 0$ as an expansion in ϵ,

$$s_0 = -\frac{\epsilon\tilde{R}(0)\tau_M^{-1}}{\tau_M^{-1} + \tilde{R}(0)} + O(\epsilon^2), \qquad [19]$$

or equivalently

$$s_0 = -\frac{n_M hS}{V}\frac{1}{\tau_M + T_M} + O\left[\left(\frac{n_M hS}{V}\right)^2\right]. \qquad [20]$$

The residue of this pole can similarly be shown to be $1 - O(\epsilon)$. After Laplace transformation, this pole gives rise to a simple exponential decay, whose weight is almost one in the limit that ϵ is very small. The decay of $m(t)$ therefore can be seen to have two parts: a simple exponential, with weight

$1 - O(\epsilon)$ and decay rate $|s_0|$ and an additional decay with weight $O(\epsilon)$ that is in general nonexponential [corresponding to a nonconstant $\tilde{R}(s)$]. Furthermore, the form of $\tilde{m}(s)$ shows that this nonexponential decay has a lifetime set by the lifetime at a surface site T_M and the residence time τ_M, which are both much smaller than $1/|s_0|$ in the $\epsilon \to 0$ limit.

Thus, we conclude that for $\epsilon \to 0$, which corresponds to having very few surface sites compared to the number of bulk molecules, and regardless of the detailed behavior at a surface site, the overall decay of the magnetization is single exponential with decay rate

$$\frac{1}{T_{1,2}} = \frac{n_M hS}{V}\frac{1}{T_{1M,2M} + \tau_M}. \qquad [21]$$

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