Communication

Detection of intermolecular homonuclear dipolar coupling in organic rich shale by transverse relaxation exchange

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ABSTRACT

The mechanism behind surface relaxivity within organic porosity in shales has been an unanswered question. Here, we present results that confirm the existence of intermolecular homonuclear dipolar coupling between solid and liquid phases in sedimentary organic matter. Transverse magnetization exchange measurements were performed on an organic-rich shale saturated with liquid hydrocarbon. Liquid and solid constituents were identified through both sample resaturation and through their T_1/T_2 ratios. Extensive cross peaks are observed in the T_2-T_2 exchange spectra between the solid and the liquid constituents, indicating an exchange of magnetization between the two phases. This result cannot arise from physical molecular diffusion, and the dissolution energies are too high for chemical exchange, such that the magnetization exchange must arise from intermolecular homonuclear dipolar coupling. These results both confirm a possible source of surface relaxivity in organic matter and emphasize caution in the use of standard porous media interpretations of relaxation results in shales because of coupling between different magnetization environments.

1. Introduction

In the past decade, numerous investigations of unconventional petroleum resources [1–13] by nuclear magnetic resonance (NMR) have been conducted. The low permeability of shales makes traditional core analysis characterization difficult and unreliable [14], such that a non-invasive method such as NMR is appealing. Despite its extensive use, many unanswered questions still exist regarding the interpretation of the NMR results in shale and mudrocks.

One of these questions is the mechanism of surface relaxivity in organic matter [15]. Surface relaxivity in conventional petroleum reservoirs [16–23] has been well established as arising from the presence of paramagnetic impurities on the pore surface. When a fluid molecule encounters a paramagnetic ion, the interaction between the electron and nuclear spins causes the rapid relaxation of the nuclear spin. Shales may contain a significant quantity of paramagnetic impurities; however, in organic matter itself, the amount of paramagnetic impurities is extremely low [24,25]. Given their low concentrations, it does not seem plausible that

the dominant mechanism of surface relaxivity in organic porosity is due to fluid interaction with paramagnetic impurities.

A significant difference between unconventional shale resources and conventional petroleum resources is the presence and potentially high concentrations of organic hydrogen in solids. For conventional resources, the pore matrix consists predominantly of either sandstone or carbonate, neither of which contain significant quantities of hydrogen. Therefore, any hydrogen in the sample is assumed to be in fluid-filled porosity. However, organic matter is rich in hydrogen and, in many cases, it is the organic matter that contains most of the porosity in the sample [26]. Several researchers have hypothesized that the surface relaxivity arises from the homonuclear dipolar coupling [2,9,15] between the hydrogen in the organic matter and the saturating fluid. Korringa, Seevers, and Torrey presented the theory of longitudinal surface relaxation for the interaction between fluid molecules and paramagnetic ions [16]. This was later adapted for transverse relaxation by Kleinberg et al. [17]. This has been adapted to surface relaxation due to homonuclear dipolar coupling [27]. If two spins are undergoing dipolar coupling, this will cause an enhancement in their relaxation rate. For a fluid molecule adsorbed on the pore surface, the two spins will be in the rigid lattice regime and this enhancement will be inversely proportional to the strength of their coupling [28]:

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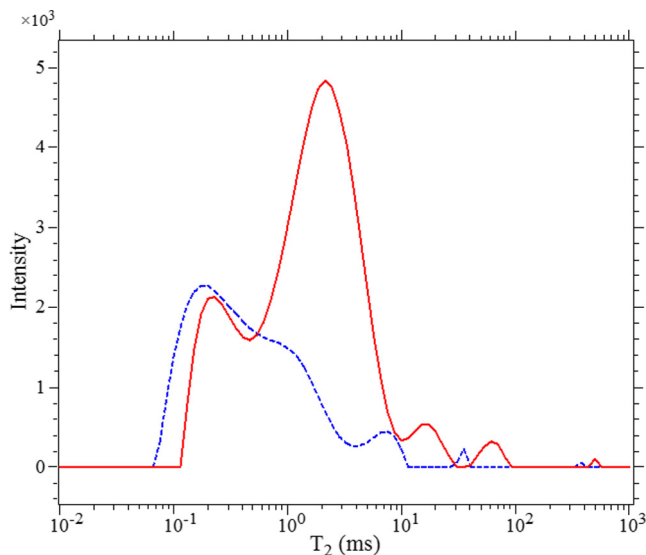 *E-mail address:* Kathryn.washburn@nofima.no (K.E. Washburn).

Fig. 1. T_2 distribution for the (a) as-received state (blue dashed) and (b) resaturated state (solid red) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

$$\frac{1}{T_{2D}} = \|D_{ij}\| = \left\| -\frac{\mu_0 \gamma^2 \hbar}{4\pi r_{ij}^3} \left(\frac{3\cos^2\theta_{ij} - 1}{2} \right) \right\| \tag{1}$$

where T_{2D} is the relaxation time of two hydrogen atoms undergoing dipolar coupling, D_{ij} is the dipolar coupling constant, the brackets denote the absolute value, μ_0 is the permittivity of a vacuum, γ is the gyromagnetic ratio, $\hbar$ is Planck's constant, r_{ij}^3 is the distance between the coupled spins, and θ_{ij} is the angle they that make with the applied magnetic field. While Korringa, Seevers and Torrey theory contains a complete description of how surface correlation time affected the measured relaxation time, Kleinberg et al. [17] later found that for transverse relaxation due to paramagnetic ions, the correlation term could be neglected because the relaxation time between the nuclear spin of the fluid molecule and the electron spin of the paramagnetic ion was significantly more rapid than the surface residence time. However, the relaxation time from the dipolar coupling cannot be assumed to be much greater than the surface

residency of the fluid molecule, such that the correlation time must be taken into consideration. Therefore, the transverse relaxation rate for a single pore in the fast diffusion limit is described as:

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \left(\frac{Sh}{V}\right)\left(\frac{n_H}{T_{2D} + \tau_c}\right) \tag{2}$$

where T_2 is the measured relaxation time, T_{2B} is the relaxation time of the bulk fluid, S is the surface area, V is the pore volume, h is the layer thickness, n_H is the relative fraction of hydrogen sites on the surface of the pore surface, and τ_c is the correlation time of how long a fluid molecule remains at the surface before exchanging with the bulk. Eq. (2) can be simplified by rewriting it to include a surface relaxivity term:

$$\rho_D = \frac{h \times n_H}{T_{2D} + \tau_c} \tag{3}$$

where ρ_D is surface relaxivity due to dipolar coupling. Then, assuming the system contains a low viscosity fluid, the bulk term can be neglected and the system can be described in a form similar to that of transverse relaxation due to paramagnetic ions:

$$\frac{1}{T_2} = \rho_D \frac{S}{V} \tag{4}$$

Although there were many indications that homonuclear dipolar coupling was the source of surface relaxivity in organic matter, there was no direct evidence. For example, if the surface relaxivity is caused by homonuclear dipolar coupling, because of the presence of τ_c in ρ_D, the measured transverse relaxation time will become longer with increased temperature due to shorter correlation times. Longer transverse relaxation times with increased temperature in organic rich shales were observed [29], but other possible causes for the longer relaxation times could not be ruled out, such as that the change in relaxation time was caused by a decrease in oil viscosity with temperature. Here, the molecular rotational correlation time decreases with temperature, leading to weaker dipolar interactions within the oil molecules themselves and a longer relaxation time would be observed regardless of whether the source of surface relaxivity in the porous sample were due to interactions with paramagnetic impurities or homonuclear dipolar coupling.

Recent work by Singer et al. [30] has shown the existence of intramolecular homonuclear dipolar coupling in fluid-filled organic matter. The method used was an adaptation of the tech-
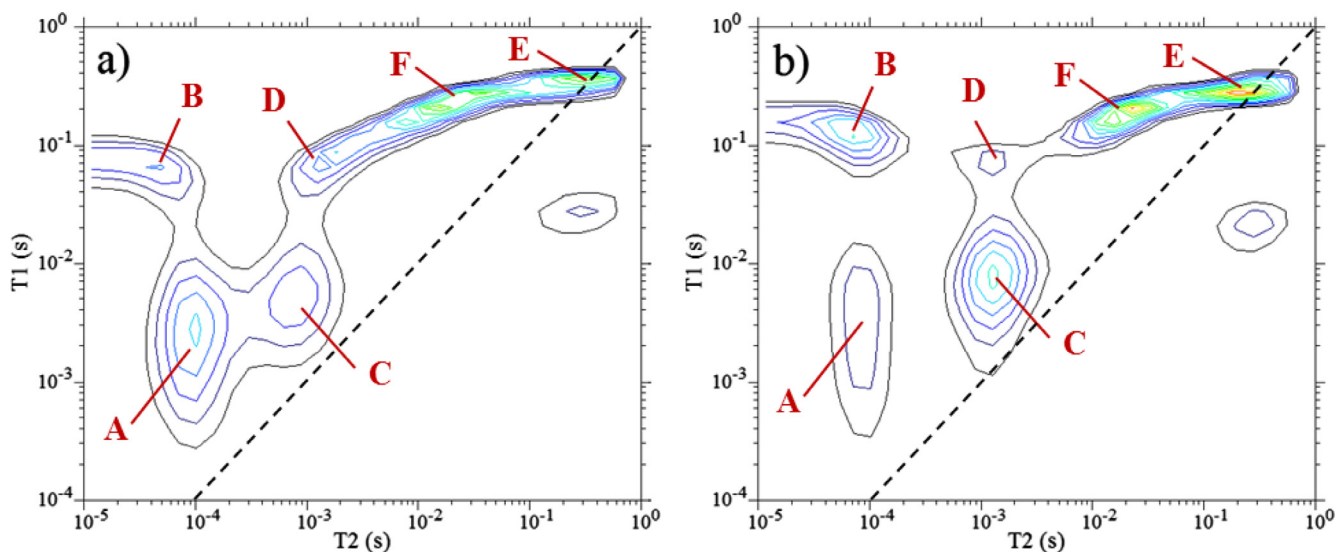

Fig. 2. T_1-T_2 correlation for the (a) as received state sample and (b) resaturated state sample. Dashed line indicates parity.