Effect of Paramagnetic Mineral Content and Distribution on Surface Relaxivity in Organic- Rich Niobrara and Haynesville Shales

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Effect of Paramagnetic Mineral Content and Distribution on Surface Relaxivity in Organic-Rich Niobrara and Haynesville Shales

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Summary

Surface relaxivity (SR) is required to convert nuclear magnetic resonance (NMR) relaxation times to pore size distributions (PSD).Current methodology uses a constant value of SR for an entire well, formation, or rock type, regardless of compositional and textural variations. This approach might result in significant errors in PSD calculation in the presence of paramagnetic minerals that affect SR values. We present SR calculations for Niobrara and Haynesville samples calculated from measurements of surface to volume ratio (SVR) and from measurements of the average pore radius. We measured the transverse relaxation time (T_2) with a low field (2 MHz) NMR instrument. We also measured porosity and PSD using nitrogen adsorption (N2). The total specific surface area (TSSA) was measured using N2 and cation exchange capacity (CEC) equivalent surface area.

We find that paramagnetic impurities, chlorite and illite in the Haynesville and illite-smectite in the Niobrara, dominate the NMR response and the calculated SR. There is a linear relation between the paramagnetic clay content and SR. The value of SR depends on the calculation method and on the measurement technique for TSSA and TPV. Presence of smectite increased the uncertainty in TSSA and TPV and consequently SR calculations in Niobrara. This uncertainty is lower for high maturity (gas window) Haynesville samples since smectite is absent in these samples. Our SR - clay correlations can be used to calculate SR from mineralogy and invert NMR logs and laboratory NMR data to PSD.

Introduction

NMR logging is widely used to measure porosity and pore size distribution (PSD) both at laboratory and downhole conditions. NMR time distributions are considered as a representation of PSD (Kenyon et al., 1997). Surface relaxivity (SR) is required to transform the time domain NMR data to size domain PSD. The surface relaxation is due to the interaction of paramagnetic sites with the hydrogen nuclei in the pore space (Korringa et al., 1962) and increases when paramagnetic minerals are present (Saidian and Prasad, 2015a).

Foley et al. (1996) showed that the paramagnetic ion content, magnetic susceptibility, and the surface relaxivity are linearly correlated for synthetic unconsolidated sand packs. Increasing the concentration of the paramagnetic ions and minerals increases the SR in unconsolidated sand packs (Keating and Knight, 2007; 2008; 2010). The SR cannot be calculated directly for rock grain surfaces since there is no information available for spin-electron interaction on the surface of the rocks (Kleinberg et al., 1994). As a result, a practical approach is to calculate SR using indirect methods e.g. by measuring the surface to volume ratio (SVR) (Hossain et al., 2011; Keating and Knight, 2007) or correlating NMR time distributions with PSD assessed by other techniques such as mercury intrusion (MI) (Marschal et al., 1995; Rivera et al., 2014) and nitrogen adsorption (N2) (Saidian and Prasad, 2015a). Commonly, SR is calculated using these methods for limited number of samples and an average value is used for the entire well, formation or rock type regardless of any mineralogical variations. This constant value approach results in significant errors since reported values of SR for similar rock types can vary up to two orders of magnitude (Dunn et al., 2002).

We calculated the SR by measuring the T_2 and SVR as well as measuring the average pore radius using N2 technique for organic rich Niobrara and Haynesville samples. We calculated the SVR using the total specific surface area (TSSA) measured by cation exchange capacity (CEC) and N2 techniques. Then we investigated the effect of paramagnetic mineral content and distribution on the SR.

Materials

We used 19 Niobrara and 16 Haynesville samples sets from oil and gas producing organic rich shales, respectively. Table 1 highlights the physical properties of the sample sets (For more information about these samples sets see, Kuila, 2013; Saidian et al., 2015).

Methods

We used porosity, PSD, CEC, and mineralogy of Haynesville and Niobrara sample sets published by Kuila (2013).

Transverse relaxation time (T_2) distributions were measured using Carr-Purcell-Meiboom-Gill (CPMG) (Carr and Purcell, 1954; Meiboom and Gill, 1958) pulse sequences. The samples were fully water saturated and the measurements were performed using a 2 MHz Magritek Rock Core Analyzer®. T_2 distributions were generated

Table 1. Niobrara and Haynesville sample properties. QPF: Quartz, Plagioclase and Feldspar, Carb: Carbonates, I-S: Illite-Smectite Mixed Layer

Sample Set	Mineralogy (Content wt%, Average)	Clay Type (Content wt%,Average)	Pyrite wt% [Average]	TOC wt% [Average]	Maturity (Kerogen Type)	Average HI
Haynesville	QPF (20-34,27) Carb (2-35,10)	Illite (27-60,45) Chlorite (5-16,10)	1-5[2.2]	0.5-6.3[2.8]	Gas Window (II)	36
Niobrara	Carb (38-91,63)	I-S (3-35,18) Chlorite (0,0)	0-10.3[3.4]	0.1-5.3[2.15]	Oil Window (II)	342

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using inverse Laplace non-negative least square fitting of echo train raw data (Lawson and Hanson, 1974; Buttler et al., 1981).

Results and Discussion

We measured the T_2 distribution for all samples and calculated SR using Equation 1 from T_{2LM} and either the SVR from N2 data or the average pore radius from N2 PSD measurements.

$1/T_{2LM} = \rho_2 (TSSA/TPV) = \rho_2(c/R)$, ... Equation 1

where ρ_2 is the T_2 SR, c is a constant that can be 1, 2 or 3 for planar, cylindrical and spherical pores, respectively, R is the pore radius.

NMR Response and Mineralogy

Assuming slow bulk relaxation, negligible diffusion induced relaxation, and fast diffusion regime in the pores, the T_2 relaxation is dominated by surface relaxation. Thus, the SR and SVR are the main parameters that control the T_2 response. As mentioned earlier, surface relaxivity is a function of the paramagnetic impurities on grain surfaces. In Niobrara and Haynesville samples, the paramagnetic minerals are pyrite, chlorite and illite-smectite. Saidian and Prasad (2015a) have shown that iron content, magnetic susceptibility and mineral distribution affect SR values. Correlations between T_{2LM} and different paramagnetic minerals shows the dominant paramagnetic constituents are chlorite and, to a smaller extent, illite for Haynesville samples (Figure 1a to 1c) and illite-smectite for Niobrara samples (Figure 2a and 2b). In both sample sets, pyrite does not correlate with the T_{2LM} (Figure 1d and 2b). Figure 3a show how chlorite and illite are distributed in pore space in a Haynesville sample. Figure 3b shows the distribution of illite-smectite mixed layers in the pore space for a Niobrara sample. Pyrite particles are not distributed in the pore space and form nodules in between other grains.

To incorporate the effect of distribution of the paramagnetic minerals, we defined apparent mass magnetic susceptibility (MMS) by calculating the weighted average of MMS only for paramagnetic minerals that are distributed in the pore space such as chlorite and illite for Haynesville samples and illite-smectite for Niobrara samples, using MMS values of 0.3×10^{-6} SI m^3/kg for illite (illite-smectite) and 0.9×10^{-6} SI m^3/kg for and chlorite (Dearing, 1999). An inverse correlation between the T_{2LM} and apparent MMS was observed for both sample sets (the apparent MMS for Niobrara is not shown since illite-smectite is the only distributed paramagnetic mineral in these samples).

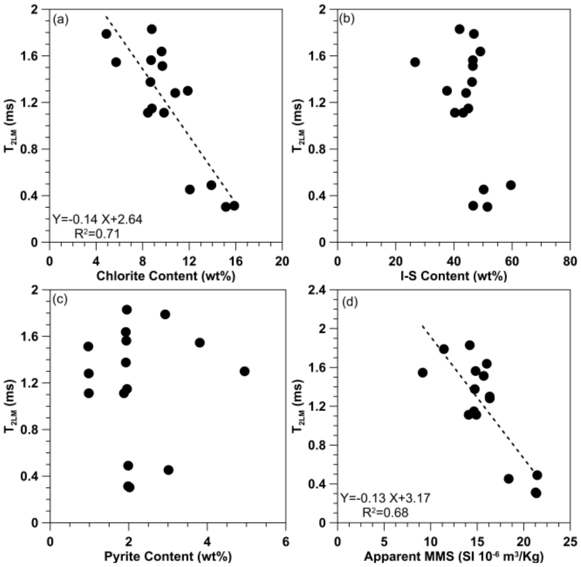

Figure 1: Correlation of T_{2LM} and (a) chlorite content, (b) I-S content, (c) pyrite, and (d) apparent MMS for Haynesville samples. T_{2LM} has strong correlation with chlorite content and apparent MMS which includes both chlorite and illite effect. The correlation is due to the distribution of clays in the pores space for Haynesville samples.

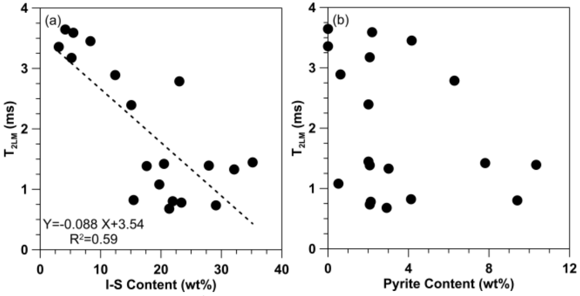

Figure 2: Correlation of T_{2LM} and (a) I-S content, (b) pyrite content. T_{2LM} has a strong correlation with I-S content because the illite and smectite clays are distributed in the pore space.

Surface Relaxivity Calculation

Saidian et al. (2015) showed that the N2 technique is reliable for porosity and PSD measurement in the Haynesville formation. They also showed that this technique can be used to measure the PSD of Niobrara marls. Other techniques such as MI can be used for chalk samples. In addition to porosity, the TSSA is required to calculate SR using Equation 1. The N2 - BET method measures external TSSA of clay minerals while the CEC method measures both internal and external TSSA. Consequently, CEC TSSA values are larger than BET-TSSA. The illitic Haynesville samples (Figure 4) show a linear correlation between TSSA values from both techniques, whereas Niobrara samples show higher scatter for clay-rich samples due to presence of smectite clays with high internal surface areas (Passey et al., 2010). XRD data confirm that smectite content is negligible for Haynesville samples because they are thermally mature (gas window); Niobrara samples with lower thermal maturity (oil window) have significant smectite content (up to 95% of the I-S mixed layer).

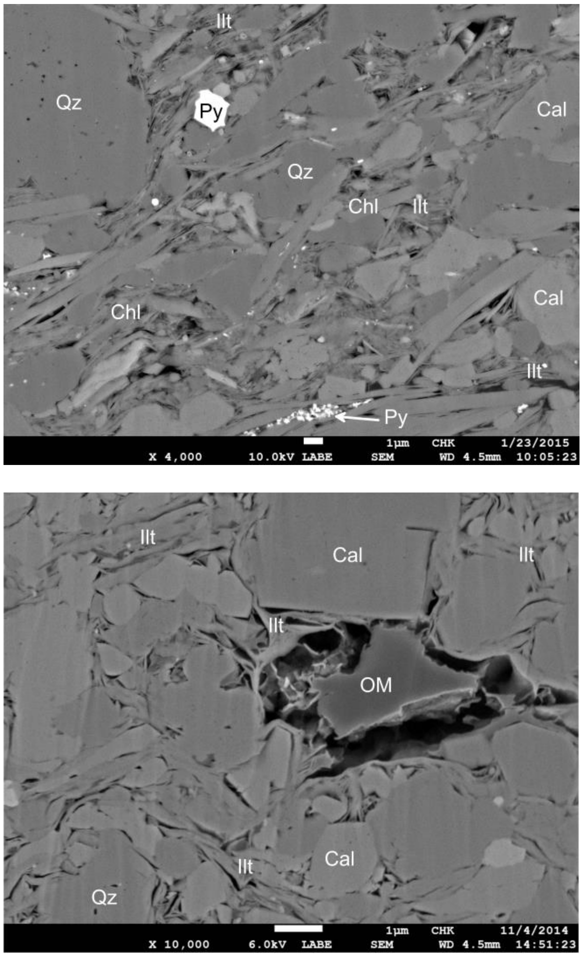

Figure 3: SEM images of (a) Haynesville and (b) Niobrara sample. Chlorite and illite fill the pores in the Haynesville samples (a) and have the highest influence on surface relaxivity. In Niobrara samples (b) the illite-smectite clays fill the pore space and are the dominant paramagnetic impurity.

For SR calculations we used both N2 and CEC TSSA values. We calculated the TPV using the recommended porosity values by Saidian et al. (2015). SR values for Haynesville samples are linearly correlated with the chlorite content, regardless of the TSSA measurement technique (Figure 5). This correlation is significantly weaker for Niobrara samples. The main reasons for this scatter are (a) uncertainty in porosity or TPV measurement (Saidian et al., 2015) (b) presence of smectite clay with significant internal surface area that cannot be measured by N2 technique (c) uncertainty in T_{2LM} measurement due to the fast relaxation of the hydrogens in pores (Saidian and Prasad, 2015b).

Effect of Organic Matter

To our knowledge, the magnetic susceptibility of kerogen is largely unknown. Using hydrocarbon fluids from different parts of the world, Ivakhnenko (2006) showed that MMS increases with increasing density and with residue yield of oil distillation. Assuming that the kerogen has a density of greater than 1 and remains unchanged at 342 ˚C (100% residue), an MMS value of -0.9×10^{-8} SI m^3/kg can be estimated based on the data from this study. Due to the diamagnetic nature of the kerogen, theoretically there should not be a significant distinction between the relaxation of hydrogen in organic matter (OM)-hosted pores and the diamagnetic mineral-hosted pores when the paramagnetic impurities are not present.

However, kerogen does not directly affect the SR value. It can affect the NMR response and SR calculation in different ways: (a) Hydrogen bearing structure of the kerogen would impose an extra relaxation due to hetro-nuclear coupling of the hydrogens in the pore space and the structural hydrogens in the kerogen (Washburn, 2014). (b) Kerogen is usually associated with pyrite and other trace minerals that usually possess a very high magnetic susceptibility (Passey et al., 2010). (c) Kerogen can host a significant portion of the pores in organic rich shales especially in gas window (Saidian et al., 2015). (d) Small OM-hosted pores can increase surface area, and with it, the surface relaxation in the rock.

Comparison of Surface Relaxivity Calculations

We calculated the surface relaxivity using Equation 1 for Haynesville samples by calculating the logarithmic mean of the radius (R) measured by N2 PSD. Due to uncertainty in Niobrara SR calculations, this analysis was not performed for Niobrara samples. Figure 7a and 7b show cross plots of SR calculated by the average radius method with SR calculated by N2 TSSA and CEC TSSA, respectively. The mismatch in SR values is due to errors in the measurements and in the method used for SR calculation. Despite the mismatch in SR values, the similar trends imply that regardless of the calculation method, SR values increase with paramagnetic mineral content.

Conclusions

We have present SR calculations for organic rich Niobrara and Haynesville shale samples by combining NMR and calculated SVR. Our results show that:

- Both the concentration and the distribution of paramagnetic minerals affect the SR value.

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- Calculated surface relaxivities using the TSSA measured by CEC and N2 were more consistent for Haynesville samples compared to Niobrara. The inconsistency in Niobrara was due to presence of smectite clay with high internal surface area.
- Similar to other hydrocarbons, kerogen is diamagnetic and the magnetic properties of kerogen do not affect the SR value. However the OM-hosted pores, high CEC and surface area of the kerogen affect the SR calculations.

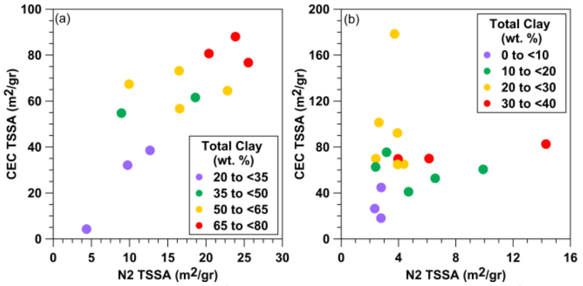

Figure 4: Cross plot of CEC TSSA and N2 TSSA for (a) Haynesville and (b) Niobrara samples color-coded with total clay content. Linear correlation for Haynesville is due to abundance of clays with minimal internal surface area. Lack of correlation for Niobrara samples is due to the presence of smectite with high internal surface area.

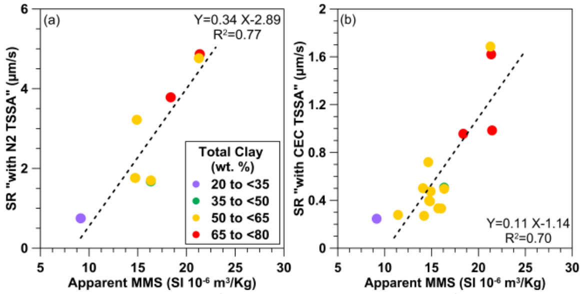

Figure 5: Cross plot of apparent MMS and surface relaxivity calculated using (a) N2 TSSA and (b) CEC TSSA for Haynesville samples. Both plots show the effect of paramagnetic impurity (chlorite and illite) on the surface relaxivity regardless of the technique that is used for TSSA measurement.

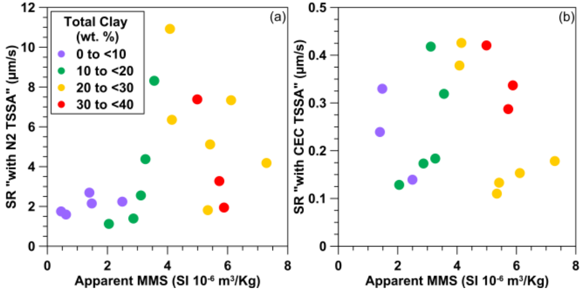

Figure 6: Cross plot of apparent MMS and surface relaxivity calculated using (a) N2 TSSA and (b) CEC TSSA for Niobrara samples. Lack of correlation is due to high uncertainty in porosity estimation for Niobrara samples (Saidian et al., 2015) as well as presence of smectite with high internal surface area.

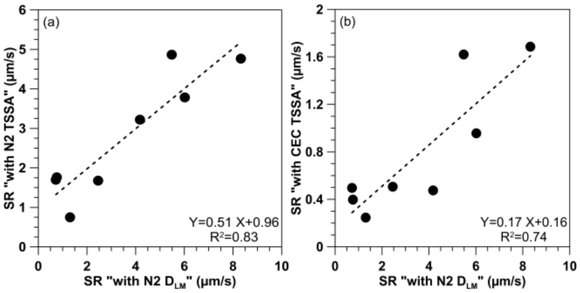

Figure 7: Correlation between the SR calculated by average radius method with (a) CEC TSSA and (b) N2 TSSA. The SR values are not consistent but show similar trends.

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