

Study of Bakken and Three Forks Formations using NMR Core Analysis

Mohamed M. Awad^{1,3,4,*}, Philip M. Singer¹, Z. Harry Xie², Maura Puerto¹, Hui pu³, and George Hirasaki¹

¹Rice University, Department of Chemical and Biomolecular Engineering, Houston, TX, USA 77005

²Core Laboratories, Houston, TX, USA 77040

³University of North Dakota, Petroleum Engineering Department, Grand Forks, ND, USA 58202

⁴Egyptian Petroleum Research Institute, Production Department, Cairo, Egypt 11727

Abstract. NMR has proven to be a valuable tool in the petrophysical analysis of unconventional plays such as shale-gas and tight-oil formations. In this study, we use NMR T_1 - T_2 measurements at 2.3 MHz and 22 MHz to provide key insights into the wettability, presence of bitumen, surface-relaxation mechanism, and internal gradient effects in cores from the Bakken and Three Forks formations. We determine the NMR wettability index of the Bakken and Three Forks formations by comparing the NMR response of octane saturated and formation-brine saturated cores (without cleaning the cores prior to saturation). The results indicate that the Upper Bakken cores are strongly oil-wet, the Middle Bakken cores are water-wet to intermediate-wet, and the Three Forks cores are strongly water-wet. In the case of the Upper Bakken cores, the presence of bitumen is detected at 22 MHz where a short echo-spacing is possible. We used the temperature dependence (25 °C to 100 °C) of T_2 at 2.3 MHz to determine the origin of the NMR surface-relaxation mechanism in the saturated nanometer-sized pores. The results indicate that NMR surface relaxation in the Upper Bakken is dominated by enhanced ^1H - ^1H dipole-dipole relaxation, while in the Three Forks it is dominated by paramagnetic surface relaxation. In the case of the Middle Bakken, NMR surface relaxation for the octane saturated cores is dominated by enhanced ^1H - ^1H dipole-dipole relaxation with surface water film, while for brine saturated cores it is dominated by paramagnetic surface relaxation. Finally, we vary the echo-spacing of the T_2 measurement to check for internal gradient effects, which (if present) would complicate the interpretation of wettability and surface-relaxation mechanism from T_2 . While no internal gradients were found at 2.3 MHz, we find strong internal gradient effects in the specific case of octane-saturated cores in the Middle Bakken and Three Forks at 22 MHz.

1 Background

Unconventional reservoirs are any reservoir that requires utilizing special recovery operations outside the conventional recovery operations. According to the U.S. Geological Survey in 2013, the Bakken reservoir is considered one of the world largest unconventional resources with approximately 7.4 billion barrels estimated recoverable oil [1] with an API gravity of 42°. The Bakken formation was deposited from the Late Devonian to Early Mississippian age. The new Bakken wells have high decline rate from the initial production rate, sometimes as high as 85% per year, this high decline rate is because of the complex nature of the Bakken formation, and the formation porosity ranges from 4 ⇔ 8 pu (porosity units) with low permeability 0.001 ⇔ 0.01 mD.

There are three members in the Bakken formation, the Upper Bakken and Lower Bakken are organic shale, separated by dolomitic siltstone and sandstone called Middle Bakken [2]. The Bakken formation lies above the Three Forks and below the Lodgepole limestone. The Upper Bakken and Lower Bakken are organic-rich and the hydrocarbon source rocks with total organic carbon (TOC) content range from 12 ⇔ 36 wt% [3, 4]. The Middle Bakken lithology is highly variable, where it includes interbedded siltstone, sandstone, siliceous limestone, limestone, and sandy dolomite. The dominant lithology of the Middle Bakken in most of the Williston basin is calcareous, dolomitic, or argillaceous siltstone [5]. The upper layer of the Three Forks is located under the Lower Bakken, and consists of a well-sorted very fine-grained layer of Sanish sand. Laminations of illite-rich clay with dolomitized limestone is the main composition

* Mohamed M. Awad: mohamed.awad91990@yahoo.com, mmmohame@cougarnet.uh.edu

of the Three Forks. The TOC of Middle Bakken and Three Forks formations ranges from 0.1 ⇔ 0.3 wt% [4].

NMR core-analysis is a powerful technique for characterizing unconventional plays such as shale-gas and tight-oil formations. Previous NMR studies have provided unique information such as bitumen and kerogen content, wettability, pore-size distribution, movable vs. bound fluid, and water vs. hydrocarbon saturation [6, 7, 8, 9, 10, 11, 12, 13, 14, 15]. For instance it was previously shown in the Barnett shale that $(T_1/T_2)_o \approx 4$ for oil-saturated cores was larger than $(T_1/T_2)_w \approx 2$ for water-saturated cores [6]. It was also previously shown for conventional cores that $(T_1/T_2)_o \approx 4$ for oil-wet cores was larger than $(T_1/T_2)_o \approx 1$ for water-wet cores [16].

In this report, we build on previously reported techniques and show how NMR core-analysis can give a wealth of information about wettability and the presence of bitumen in the Bakken formation. We also show how the NMR surface relaxation mechanism and presence of internal gradients can be determined using a combination of frequency and temperature dependence of the NMR response.

2 Experimental Work

All core samples tested in this study are from one well. The core samples were 2.54 cm (1") diameter, not preserved and left to equilibrate with the core-lab moisture. All the cores are twin cores. The twin cores consisted of one ≈ 4.8 cm (1.89") in length, and the other is ≈ 3.1 cm (1.22") in length. Both ends of all core samples tested in any of the experiments were trimmed with an electrical saw to eliminate the effect of the inverted drilling mud (oil-based mud) used in the coring process.

The formation brine was prepared with the same salinity (309,612 ppm) and composition as the formation brine in the well analysis reports in the well files. The sodium bicarbonate and sodium sulfate were replaced with sodium chloride with the same ionic strength to prevent precipitation. No precipitation was observed in the collected brine samples from the wells because all the salts were in equilibrium with the reservoir rock.

For the as-received twin cores tested in this study, one was saturated with Bakken formation brine and the other was saturated with octane as a model oil. In order to preserve wettability, the cores were not cleaned prior to saturation. All core samples in this study were saturated using the same method. The saturation setup consisted of vacuum pump, two vacuum gauges, saturation cell, pressure gauge, hand pump for saturation fluid, and saturation fluid tank. The cores were saturated with CO₂ after the vacuum to replace any air inside the pores with CO₂. Since CO₂ is more soluble in both brine and oil, this leads to the highest possible saturation [17].

Figure 1 shows the flowchart of the experiments work flow. Specifically, the core samples were exposed to vacuum for 1 ⇔ 1.5 hours (-29.5 in-Hg), then saturated

with CO₂ for 4 hours at one atmospheric pressure, again exposed to vacuum for 1 ⇔ 1.5 hours (-29.5 in-Hg) followed by saturation with CO₂ for 4 hours, then exposed to vacuum (-29.5 in-Hg) again for 1 ⇔ 1.5 hour, and finally saturated with either formation brine or octane at 2,000 psi using a hand pump. During the saturation process, the pressure was monitored in order to maintain the pressure at 2,000 psi by hand pump. The saturation process lasted for approximately 4 days, one day for vacuuming and CO₂ saturations, and 3 days for pressurizing the cell at 2,000 psi. The saturation process was stopped when no pressure change was noticed for one day.

NMR T_1 - T_2 measurements of the as-received, octane-saturated and brine-saturated cores were acquired at 30 °C with a Larmor frequency of 2.3 MHz, and an echo spacing (t_E) of $t_E = 0.2$ ms and 0.4 ms, using a GeoSpec2 by Oxford Instruments, located at Rice University. T_1 - T_2 measurements of the saturated cores were then acquired at 22 MHz with $t_E = 0.06$ ms and 0.2 ms at CoreLab using a custom-built instrument.

Since the NMR hydrogen index (HI) of the fluids in the as-received cores are unknown, all the NMR porosities are reported assuming $HI = 1$, which we report in units of "pu1". In other words, "pu1" is short for porosity units (i.e. percent of bulk volume) assuming $HI = 1$. The change in fluid filled porosity after saturation was also measured by the change in weight of the core samples after saturation, which agreed well with the NMR porosity change after saturation.

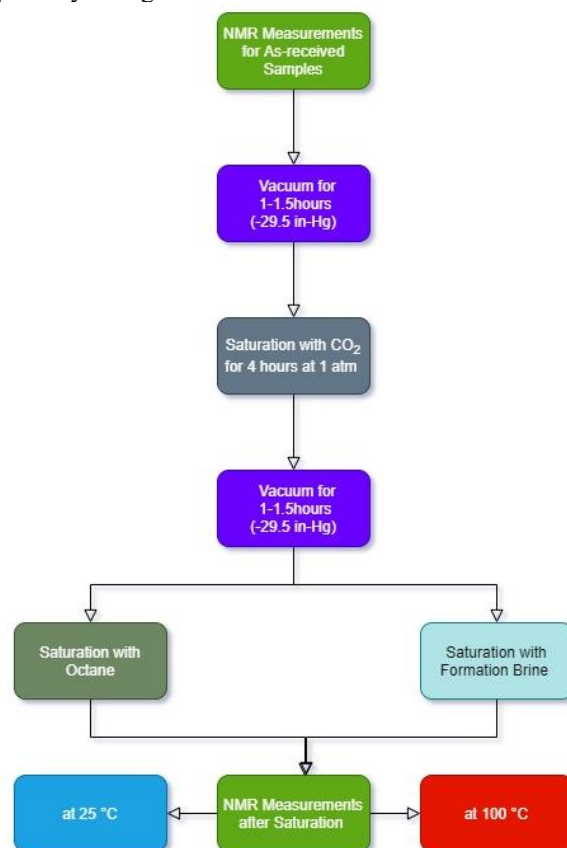


Fig. 1 Flowchart of the Experiments Workflow

NMR T_2 measurements at ambient (25 °C) and elevated temperature (100 °C) were then acquired at 2.3 MHz with $t_E = 0.2$ ms, using a Temco core-holder for 1” cores. The core holder was sealed with the core inside, and then heated in an oven to 105 °C. After 2 hours heating in the oven, the core holder was quickly inserted into the GeoSpec2. A thermocouple connected to the sample space indicated a drop from 102 °C to 98 °C during the 4 minute-long T_2 measurement. Repeatability of the measurement indicated no fluid loss. The empty Temco core-holder indicated ≈ 2 pu1 of background signal. The magnetization decay (i.e. the echo train) of the background signal was subtracted from the saturated core signal before inverting for the T_2 distribution.

3 Theory

The measured T_1 and T_2 relaxation times are composed of the following components:

$$\frac{1}{T_1} = \frac{1}{T_{1B}} + \frac{1}{T_{1S}}, \quad (1)$$

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}. \quad (2)$$

$T_{1B,2B} (\propto T/\eta)$ are the bulk-fluid relaxation times. $T_{1S,2S}$ are the surface-relaxation times, which are defined by the following expressions in the “fast-diffusion regime”:

$$\frac{1}{T_{1S,2S,W}} = \rho_{1,2,W} \frac{S}{S_W V} \quad \& \quad \frac{1}{T_{1S,2S,O}} = \rho_{1,2,O} \frac{S}{S_O V} \quad (3)$$

S_W and S_O are the saturation for water and oil, respectively, in the empty pores of the as-received cores. The saturation of the total pore volume is not known since the saturation of the as-received cores is not known. S/V is the surface to pore-volume where $S/V = 6/d$ for spherical pores of diameter d . $\rho_{1,2,W}$ ($\rho_{1,2,O}$) are the surface-relaxivities for water and oil, respectively, which depend on wettability but do not depend on saturation. We use $T_{1S,2S} = T_{1,2}$ throughout given that bulk-fluid relaxation is negligible (i.e. $T_{1B,2B} \gg T_{1S,2S}$) in the present case. We used Eq. (3) to determine the surface relaxivity ratios $\rho_{1,W}/\rho_{1,O}$ and $\rho_{2,W}/\rho_{2,O}$ from the $T_{1,2,W,O}$ distributions peaks (i.e. modes) shown in Figure 2 at 2.3 MHz, and the measured values of S_W and S_O . The only exception is for $T_{1,2,W}$ in the Upper Bakken where the log-mean, is used instead of the peak in the region above $T_{2,W} > 1$ ms to avoid the as-received signal $T_{2,AS} \approx 0.2$ ms.

We find a large contrast in $\rho_{1,W}/\rho_{1,O}$ between the Upper Bakken, the Middle Bakken and the Three Forks, where $\rho_{1,W}/\rho_{1,O} \gg 1$ indicates strongly water-wet conditions, and $\rho_{1,W}/\rho_{1,O} \ll 1$ indicates strongly oil-wet conditions (similarly for $\rho_{2,W}/\rho_{2,O}$). We also report NMR wettability indices $I_{W,1,2}$ which range from $I_{W,1,2} = +1 \Leftrightarrow -1$ as such [16]:

$$I_{W,1} = \frac{\rho_{1,W}/\rho_{1,O} - 1}{\rho_{1,W}/\rho_{1,O} + 1} \quad \& \quad I_{W,2} = \frac{\rho_{2,W}/\rho_{2,O} - 1}{\rho_{2,W}/\rho_{2,O} + 1}. \quad (4)$$

We assume that there is no difference between the intrinsic water and oil relaxivities (i.e. $\rho_{\text{ratio}} = 1$) [16] given that we are using a pure alkane (octane) rather than a crude-oil. We also assume there is no diffusive coupling between the saturating fluids and the as-received fluids.

In nanometer-confined pores, surface relaxation originates from (1) enhanced ^1H - ^1H dipole-dipole relaxation, where the enhancement is due to hindered rotational and translational motion of the fluid at the surface [7, 18], and/or (2) paramagnetic surface-relaxation induced by 2D diffusion of the fluid in the proximity of a paramagnetic site at the surface [9]. In the case of enhanced ^1H - ^1H dipole-dipole relaxation, $T_{1,2,W,O}$ are expected to increase with increasing temperature since the fluid’s correlation time or residence time at the surface decreases with increasing temperature [19, 20]. In the case of paramagnetic surface-relaxation, the absence of any observable temperature dependence in $T_{1,2,W,O}$ is attributed to the lack of temperature dependence in the electron relaxation time [20]. In this report, we therefore use the observation of an increase in $T_{2,W,O}$ with temperature as a sign of enhanced ^1H - ^1H dipole-dipole relaxation, and constant $T_{2,W,O}$ with temperature as a sign of paramagnetic surface-relaxation.

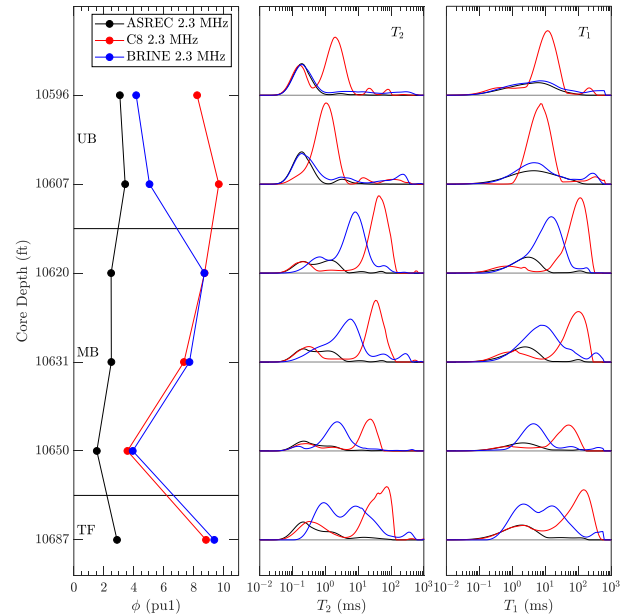


Fig. 2 Porosity, T_2 , and T_1 at 2.3 MHz ($t_E = 0.2$ ms) at 30 °C for as-received (black), octane-saturated (red) and brine-saturated (blue) cores, across the Upper Bakken, Middle Bakken, and Three Forks.

For fluids under nano-confinement, an increase in $T_{1,W,O}$ with increasing frequency can occur from both relaxation mechanisms. In the case of enhanced ^1H - ^1H dipole-dipole relaxation, an increase in $T_{1,O}$ with

frequency was previously observed in polymer-heptane mixes, where the viscous polymer acts like a kerogen surface for heptane [21]. In the case of paramagnetic surface-relaxation, the frequency dependence in $T_{1,W,O}$ can be explained by 2D diffusion of the fluid in the proximity of a paramagnetic site [9]. We note that the observed frequency dependence in $T_{1,W,O}$ is much weaker than predicted by the traditional Bloembergen-Purcell-Pound model for bulk fluids in the slow-motion regime.

T_{2D} is the relaxation time from diffusion in internal gradients, where higher magnetic fields B_0 (i.e. higher NMR frequencies, $\omega_0 = \gamma B_0$) or longer t_E (echo-spacing) result in shorter T_{2D} , assuming the “free diffusion” or “short-time regime” [22]:

$$\frac{1}{T_{2D}} = \frac{1}{12} (\gamma G t_E)^2 D \quad \text{where} \quad G \approx \Delta\chi B_0 / d. \quad (5)$$

G is the approximate strength of the internal gradient in a pore of size d . $\Delta\chi$ is the magnetic susceptibility contrast between fluid and matrix, or between fluid and fluid for oil-water emulsions (for instance). γ is the gyro-magnetic ratio, and D is the diffusion coefficient of the fluid in the pore. In cases where internal gradients are present, caution must be taken when interpreting wettability or pore-size from T_2 . The lack of t_E dependence on T_2 at 2.3 MHz indicates no internal gradient effects at 2.3 MHz. However, at 22 MHz we observe a decrease in T_2 with increasing t_E for certain cases, which indicates internal gradients for those cases.

4 Wettability

For the Upper Bakken, the total NMR porosity, T_2 , and T_1 distributions at 2.3 MHz are shown in Figure 2, for as-received, octane-saturated and brine-saturated cores. The as-received data indicate ≈ 3 pu1 at short $T_{2,AR} \approx 0.18$ ms and large $(T_1/T_2)_{AR} \approx 14$, which is most likely from bitumen [23]. Even though the same saturation process and pressure was used for octane and brine saturation, the NMR data indicate that the octane saturation (≈ 6 pu1, $S_O = 1$) is much higher than the brine saturation (≈ 2 pu1, $S_W = 0.24$) of the twin cores, in agreement with the weight change of the core after saturation. This indicates that the Upper Bakken is resistant to brine saturation of oil-wet nano-pores. More specifically, brine saturation at 2,000 psi was insufficient to overcome capillary forces in oil-wet pores of size $d < 10$ nm. Using Eq. (3) we find that $\rho_{1,2,W}/\rho_{1,2,O} \approx 0.026$ (defined as the log-mean of $\rho_{1,W}/\rho_{1,O}$ and $\rho_{2,W}/\rho_{2,O}$ in Figure 3(a)). Using Eq. (4) we find that $I_W \approx -0.94$ (defined as mean of $I_{W,1}$ and $I_{W,2}$ in Figure 3(b)), indicating that the Upper Bakken is strongly oil-wet.

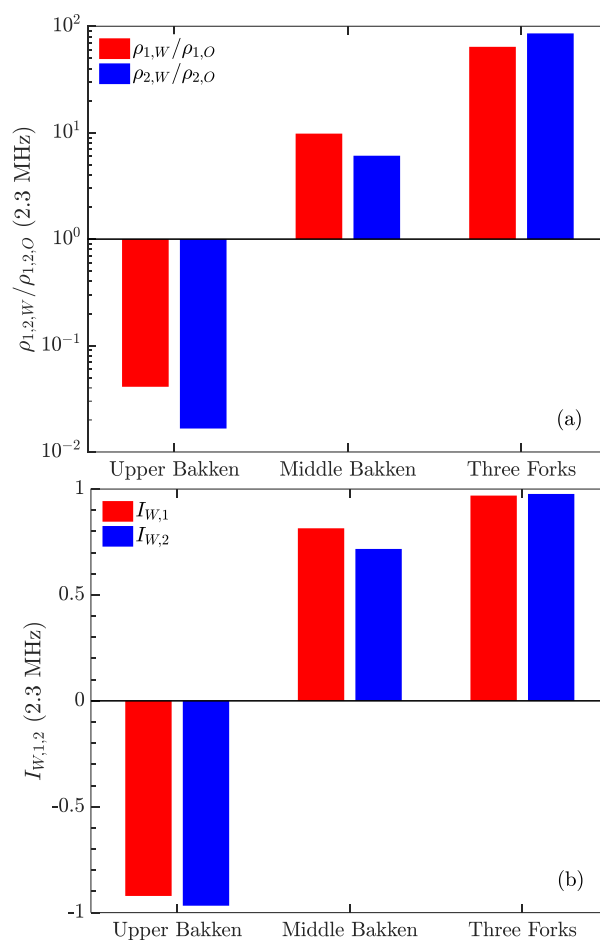


Fig. 3 (a) Ratio of surface relaxivities $\rho_{1,W}/\rho_{1,O}$ and $\rho_{2,W}/\rho_{2,O}$ and (b) NMR wettability indices $I_{1,W}$ and $I_{2,W}$ for the Upper Bakken, Middle Bakken, and Three Forks, all at 2.3 MHz.

For the Middle Bakken, the as-received data indicate ≈ 3 pu1 at short $T_{2,AR} \approx 0.6$ ms and moderate $(T_1/T_2)_{AR} \approx 3.2$, which is most likely from clay-bound water [7]. The pore volume saturated in both the octane and brine saturations in the twin cores was approximately the same (≈ 6 pu1) according to NMR, in agreement with the weight change of the core after saturation. We find that $\rho_{1,2,W}/\rho_{1,2,O} \approx 7.7$ and $I_W \approx +0.77$, indicating water-wet to intermediate-wet conditions.

The Three-Forks as-received is similar to the Middle Bakken. The Three Forks saturated cores show $\rho_{1,2,W}/\rho_{1,2,O} \approx 74$ and $I_W \approx +0.97$, indicating strongly water-wet conditions.

5 Frequency Dependence and Presence of Bitumen

For the Upper Bakken, Figure 4 shows an example of the T_1 - T_2 maps for the octane saturated and brine saturated core samples using 2.3 MHz ($t_E = 0.2$ ms) and 22 MHz ($t_E = 0.06$ ms), at 30 °C. In the octane saturated core samples, $T_{1,O}$ increased by a factor of ≈ 6 with increasing frequency. In both octane and brine saturated core samples, there was also an additional ≈ 6 pu1 observed at

short T_2 as a result of the shorter t_E used for 22 MHz compared to 2.3 MHz. The additional signal at $T_2 < 0.1$ ms at 22 MHz shows a large $T_1/T_2 \approx 100$, and is therefore attributed to bitumen (Yang et al. 2012). Given the short $T_2 < 0.1$ ms, there is most likely more bitumen signal which is not detectable even at $t_E = 0.06$ ms.

frequency indicates strong internal gradients at 22 MHz. In both octane and brine saturated core samples, there was an additional ≈ 2 pu1 at short $T_2 < 0.1$ ms and $T_1/T_2 \approx 10$, which is most likely from hydroxyls in the clay-bound water signal [8].

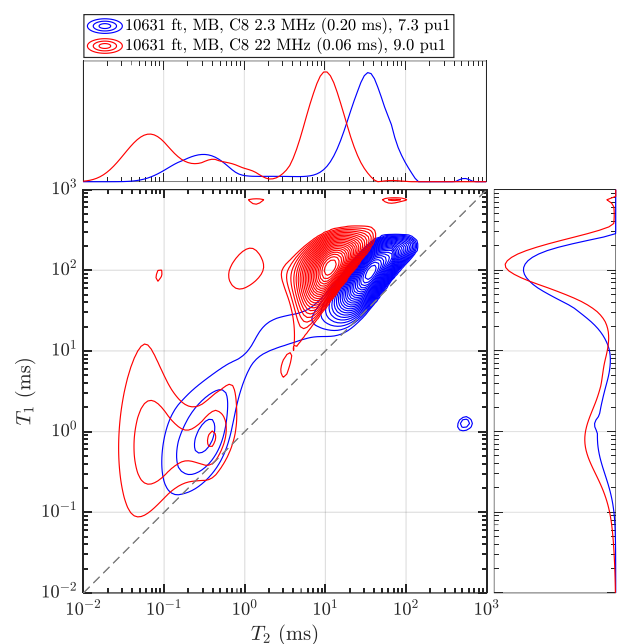
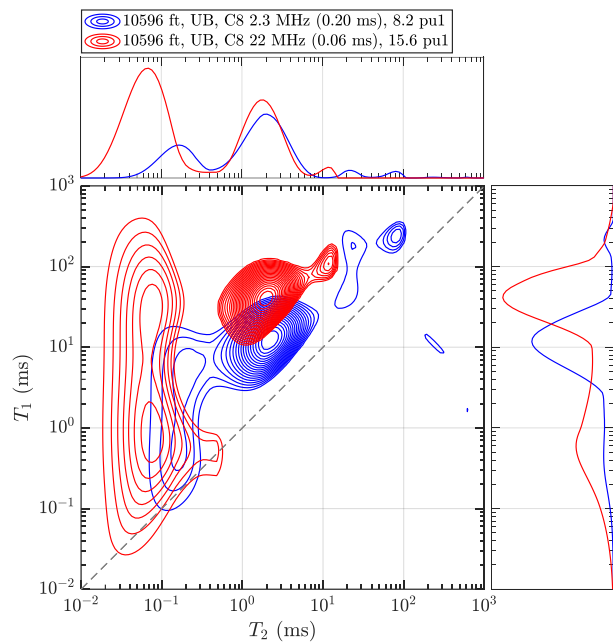


Fig. 4 T_1 - T_2 maps at 2.3 MHz (blue, $t_E = 0.2$ ms) and 22 MHz (red, $t_E = 0.06$ ms) at 30 °C, for octane-saturated (upper) and brine-saturated (bottom) core in the Upper Bakken.

Fig. 5 T_1 - T_2 maps at 2.3 MHz (blue, $t_E = 0.2$ ms) and 22 MHz (red, $t_E = 0.06$ ms) at 30 °C, for octane-saturated (upper) and brine-saturated (bottom) core in the Middle Bakken.

For the Middle Bakken and Three Forks, Figures 5 and 6 show examples of the T_1 - T_2 maps for the octane saturated and brine saturated core samples using 2.3 MHz ($t_E = 0.2$ ms) and 22 MHz ($t_E = 0.06$ ms), at 30 °C. For both saturating fluids, there was only a minor increase in $T_{1,W,O}$ with increasing frequency. In the case of octane saturated cores, the decrease in $T_{2,O}$ with increasing

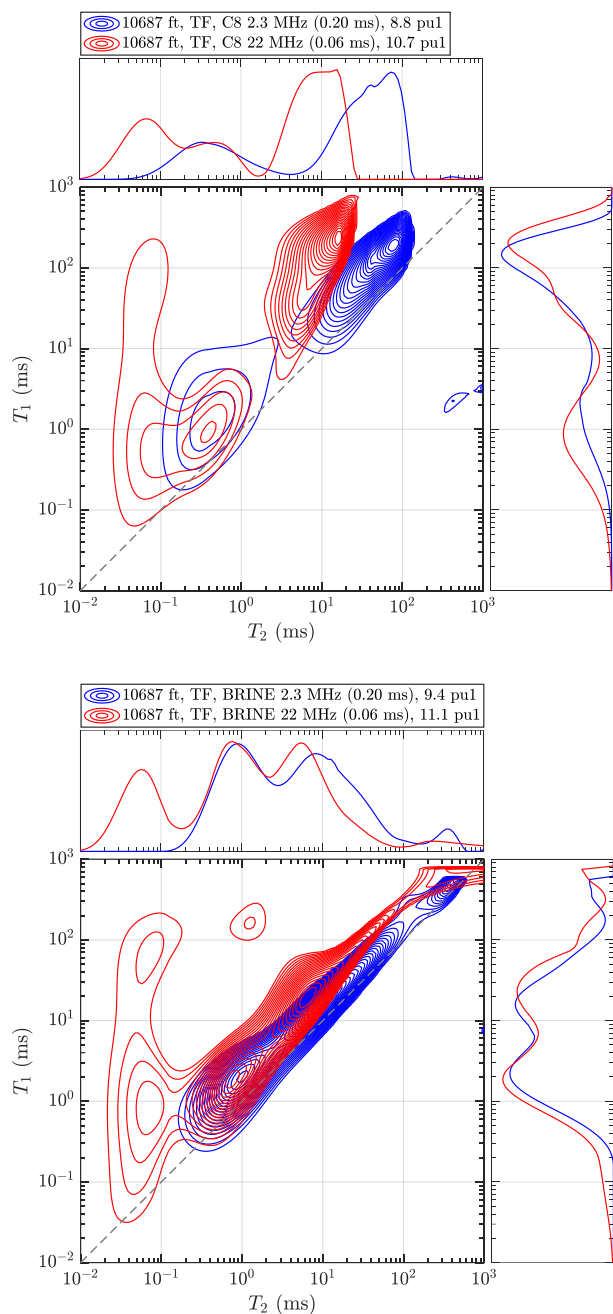


Fig. 6 T_1 - T_2 maps at 2.3 MHz (blue, $t_E = 0.2$ ms) and 22 MHz (red, $t_E = 0.06$ ms) at 30 °C, for octane-saturated (upper) and brine-saturated (bottom) core in the Three Forks.

6 Surface Relaxation Mechanism

Figure 7 (middle) shows the T_2 distribution for octane-saturated cores measured with 2.3 MHz at 25 °C and 100 °C with $t_E = 0.2$ ms. The surface relaxivity $T_{2,o}$ increases by a factor of ≈ 3 with increasing temperature in the Upper Bakken, indicating enhanced ^1H - ^1H dipole-dipole relaxation with the oil-wet nano-pores. $T_{2,o}$ increases by a factor of ≈ 2 with increasing temperature in the Middle Bakken core samples, indicating enhanced ^1H - ^1H dipole-dipole relaxation with the surface water film. These temperature effects are consistent with findings for oil in shale [10]. In the case of the Three Forks, there is no

change in $T_{2,o}$ with the increase of temperature, indicating paramagnetic surface-relaxation.

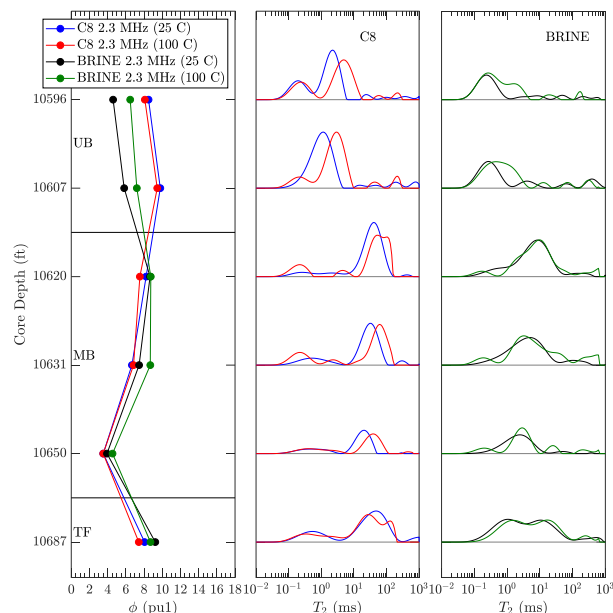


Fig. 7 Porosity and T_2 at 2.3 MHz ($t_E = 0.2$ ms) for octane-saturated cores at 25 °C (blue) and 100 °C (red), and brine-saturated cores at 25 °C (black) and 100 °C (green), across the Upper Bakken, Middle Bakken, and Three Forks.

Figure 7 (right) shows the T_2 distribution for brine-saturated cores. The Upper Bakken core samples show an increase of ≈ 2 pu1 with increasing temperature. This is attributed to a decrease in bitumen viscosity with temperature, which results in more observable NMR signal at $t_E = 0.2$ ms. Meanwhile, $T_{2,W}$ is roughly constant in both the Middle Bakken and Three Forks, indicating paramagnetic surface-relaxation.

Our data indicate that an increase in $T_{2,W,0}$ with increasing temperature correlates with an increase in $T_{1,W,0}$ with increasing frequency, which is expected for enhanced ^1H - ^1H dipole-dipole relaxation [21]. Our data also indicate that a constant $T_{2,W,0}$ with increasing temperature correlates with a constant $T_{1,W,0}$ with increasing frequency, which is expected for paramagnetic surface relaxation [20]; a different interpretation for the frequency dependence is given by Nicot *et al.* 2016 [9].

7 Internal Gradients

While we have already indicated the presence of internal gradients in T_2 at 22 MHz for octane-saturated cores by comparing 2.3 MHz to 22 MHz in Figures 4,5, and 6. Another (more common way) to test for internal gradients in T_2 is to increase t_E . Figure 8 shows how increasing t_E has minimal effect at 2.3 MHz, while it has a large effect at 22 MHz in the case of octane-saturated cores. In the case of brine-saturated cores (not shown), increasing t_E has minimal effects at both 2.3 MHz and 22 MHz. The difference in internal gradients between octane and brine saturated cores at 22 MHz is a result of the difference in magnetic susceptibility contrast between the fluid and the

matrix. In the case of brine-saturated cores, the magnetic susceptibility of brine is closer to that of the matrix. For octane-saturated cores, the magnetic susceptibility of octane is significantly different to that of the matrix.

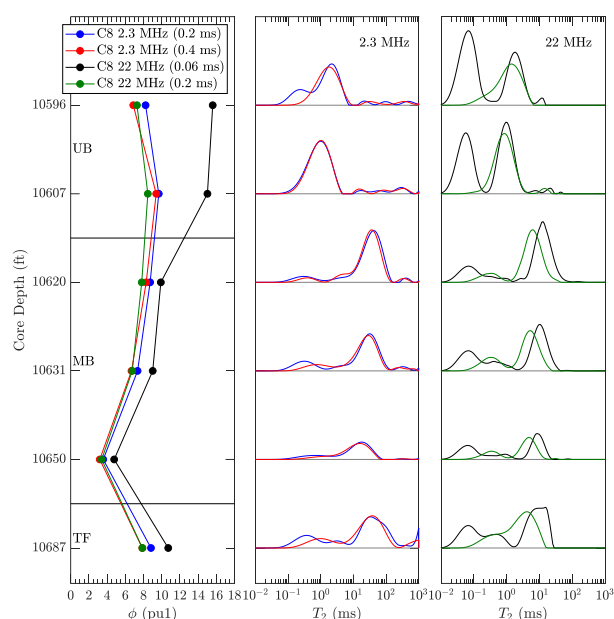


Fig. 8 Porosity and T_2 for octane-saturated cores at 30 °C, at 2.3 MHz with $t_E = 0.2$ ms (blue) and $t_E = 0.4$ ms (red), and at 22 MHz with $t_E = 0.06$ ms (green) and $t_E = 0.2$ ms (black) across the Upper Bakken, Middle Bakken, and Three Forks.

8 Conclusions

The accurate identification of the rock wettability is very crucial for improving the oil recovery using fluid injection. Previous NMR studies performed on the Bakken were focused on porosity, pore size distributions, fluid typing, the identification of the bitumen and bound water signals [24, 25, 26, 27, 28]. Previous research on native-state and post cleaning Bakken/Three Forks cores, concluded dual wettability where the small pores are water wet and the larger pores are oil wet, and the clay is oil wet [28].

In this paper, NMR measurements have shown that the Upper Bakken cores are strongly oil-wet, while the Middle Bakken cores are water-wet to intermediate-wet, and the Three Forks cores are strongly water-wet. We were able to detect the presence of bitumen in the Upper Bakken cores at 22 MHz where a short echo-spacing is possible. We investigated the origin of the NMR surface-relaxation mechanism in the saturated nanometer-sized pores by studying the temperature dependence (25 °C to 100 °C) of T_2 at 2.3 MHz. The results indicate that NMR surface relaxation in the Upper Bakken is dominated by enhanced ^1H - ^1H dipole-dipole relaxation, while in the Three Forks it is dominated by paramagnetic surface relaxation. On the other hand, the octane saturated Middle Bakken cores is dominated by enhanced ^1H - ^1H dipole-dipole relaxation with surface water film, while for brine saturated cores it is dominated by paramagnetic surface relaxation.

We checked for the presence of the internal gradient by varying the echo-spacing of the T_2 measurement. While no internal gradients were found at 2.3 MHz, we found strong internal gradient effects in the case of octane-saturated cores in the Middle Bakken and Three Forks at 22 MHz. These results suggest that the echo-spacing dependence on T_2 should be investigated on a routine basis in unconventional shale (particularly at 22 MHz), where it is often assumed that internal gradients are negligible.

Our findings are also summarized in the table below. We have shown how NMR core-analysis can give a wealth of information in the Bakken formation including wettability, presence of bitumen, surface relaxation mechanism, and presence of internal gradients. In order to preserve the wettability of the cores, our methodology *does not* involve core cleaning. Our methodology also highlights the advantages of measuring the cores at both 2.3 MHz and 22 MHz.

	Octane saturated	Brine saturated
Upper Bakken	<ul style="list-style-type: none"> Strongly oil-wet ($I_W \approx -0.94$) ^1H-^1H dipole-dipole relaxation with organic surface Presence of bitumen 	<ul style="list-style-type: none"> Strongly oil-wet ($I_W \approx -0.94$) Resistant to brine saturation ($S_W \approx 0.24$) Presence of bitumen
Middle Bakken	<ul style="list-style-type: none"> Water-wet ($I_W \approx +0.77$) ^1H-^1H dipole-dipole relaxation with surface water film Strong internal gradients at 22 MHz 	<ul style="list-style-type: none"> Water-wet ($I_W \approx +0.77$) Paramagnetic surface relaxation with minerals
Three Forks	<ul style="list-style-type: none"> Strongly water-wet ($I_W \approx +0.97$) Paramagnetic surface relaxation with minerals Strong internal gradients at 22 MHz 	<ul style="list-style-type: none"> Strongly water-wet ($I_W \approx +0.97$) Paramagnetic surface relaxation with minerals

We thank the Wilson M. Laird Core and Sample Library for providing the core samples used in this study. We also thank Zeliang Chen and Xinglin Wang for useful discussions.

References

- H. Pu, Y. Li, "CO₂ EOR Mechanisms in Bakken Shale Oil Reservoirs" *Carbon Management Technology Conference*, SPE-439769-MS (2015)
- North Dakota Geological Survey, "Overview of the Petroleum Geology of the North Dakota Williston Basin." *North Dakota Industrial Council* (1986) <https://www.dmr.nd.gov/ndgs/Resources/>
- T. Tran, P.D. Sinurat, B.A. Wattenbarger, "Production Characteristics of the Bakken Shale Oil." *SPE Annual Technical Conference and Exhibition*. SPE-145684-MS (2011)
- L.C. Price, "Origins and Characteristics of the Basin-Centered Continuous-Reservoir Unconventional Oil-Resource Base of the Bakken Source System, Williston Basin: EERC" *EERC Website*. (1999) <http://www.undeerc.org/News-Publications/Leigh-Price-Paper/Default.aspx>
- R.L. Webster, "Petroleum Source Rocks and Stratigraphy of the Bakken Formation in North Dakota." *Hydrocarbon Source Rocks of the Greater Rocky Mountain Region*, AAPG Bulletin (1984), **68** (7): 953
- A.E. Ozen, R.F. Sigal, "*T*₁/*T*₂ NMR Surface Relaxation Ratio for Hydrocarbons and Brines in Contact with Mature Organic-Shale Reservoir Rocks" *Petrophysics* **54** (1), 11-19 (2013)
- P.M. Singer, Z. Chen, G.J. Hirasaki, "Fluid Typing and Pore Size in Organic Shale Using 2D NMR in Saturated Kerogen." *Petrophysics*, **57** (6): 604–19 (2016)
- M. Fleury, M. Romero-Sarmiento, "Characterization of Shales Using *T*₁-*T*₂ NMR Maps" *Journal of Petroleum Science and Engineering* **137**: 55–62 (2016)
- B. Nicot, N. Vorapalawut, B. Rousseau, L.F. Madariaga, G. Hamon, J. Korb, "Estimating Saturations in Organic Shales Using 2D NMR" *Petrophysics*, **57** (1): 19–29 (2016)
- Z.H. Xie, Z. Gan, "Investigation of Physical Properties of Hydrocarbons in Unconventional Mudstone using Two-dimensional NMR Relaxometry" *SPWLA 60th Annual Logging Symposium*, SPWLA (2019)
- D. Kausik, D. Freed, K. Fellah, L. Feng, Y. Ling, G. Simpson, "Frequency and Temperature Dependence of 2D NMR *T*₁-*T*₂ Maps of Shale" *Petrophysics* **60** (1), 37-49 (2019)
- Z. Chen, P.M. Singer, X. Wang, H.J. Vinegar, S.V. Nguyen, G.J., Hirasaki, "NMR Evaluation of Light Hydrocarbon Composition, Pore Size, and Tortuosity in Organic-Rich Chalks" *Petrophysics* **60** (6), 771-797 (2019)
- I. Sulucarnain, C.H. Sondergeld, C.S. Rai, "An NMR study of shale wettability and effective surface relaxivity" SPE Canadian Unconventional Resources Conference (2012)
- R.F. Sigal, E. Odusina, "Laboratory NMR Measurements on Methane Saturated Barnett Shale Samples" *Petrophysics* **52** (1), 32-49 (2011)
- I. Gupta, C. Rai, C. Sondergeld, "Study Impact of Sample Treatment and Insitu Fluids on Shale Wettability Measurements using NMR" *Journal of Petroleum Science and Engineering* **176**, 352-361 (2019)
- A. Valori, B. Nicot, "A Review of 60 years of NMR Wettability" SCA-17 (2018)
- "Recommended Practices for Core Analysis." *American Petroleum Institute* (1998) <http://w3.energistics.org/RP40/rp40.pdf>
- K.E. Washburn, "Relaxation Mechanisms and Shales." *Concepts in Magnetic Resonance Part A* **40**: 39–65 (2012)
- C. Straley, "A Mechanism for the Temperature Dependence of the Surface Relaxation Rate." SCA-27 (2002)
- I. Foley, S.A. Farooqui, R.L. Kleinberg, "Effect of Paramagnetic Ions on NMR Relaxation of Fluids at Solid Surfaces." *JMR* **123** (1): 95–104 (1996)
- P.M. Singer, Z. Chen, L.B. Alemany, G.J. Hirasaki, K. Zhu, Z.H. Xie, T.D. Vo, "Interpretation of NMR Relaxation in Bitumen and Organic Shale Using Polymer-Heptane Mixes." *Energy & Fuels* **32**, 1534-1549 (2018)
- M.D. Hurlimann, "Effective Gradients in Porous Media Due to susceptibility Differences" *Journal of Magnetic Resonance* **131**, 232-240 (1998)
- Z. Yang, G.J. Hirasaki, M. Appel, D.A. Reed, "Viscosity Evaluation for NMR Well Logging of Live Heavy Oils" *Petrophysics*, **53** (1), 22–39 (2012)
- O.S. Tomomewo, H. Jabbari, N. Badrouchi, C. Onwumelu, M. Mann, "Characterization of the Bakken Formation using NMR and SEM Techniques" *ARMA*, 19-1875 (2019)
- C. Onwumelu, O. Kolawole, I. Bouchakour, O. Tomomewo, A. Adeyilola, "Effective Correlation between Petrophysical Characterization of Magnetic Resonance Imaging Log and Nuclear Magnetic Resonance Core Data" *ARMA/DGS/SEG International Geomechanics Symposium*, 20-001 (2020)
- C. Onwumelu, S. Nordeng, A. Adeyilola, "Rock Characterization Using Nuclear Magnetic Resonance and Scanning Electron Microscope: A Laboratory Study of Bakken Formation" *SEG International Exposition and 89th Annual Meeting*, 3354-3358 (2019)
- R. Kausik, K. Fellah, L. Feng, G. Simpson, "High- and Low-Field NMR Relaxometry and Diffusometry of the Bakken Petroleum System" *Petrophysics*, **58** (4), 341–351 (2017)

28. G. Simpson, N.S. Fishman, S. Hari-Roy, "New Nuclear Magnetic Resonance Log T2 Cut-off Interpret Parameters for the Unconventional Tight Oil of the Bakken Petroleum System Using 2-D NMR Core Laboratory Measurements on Native state and Post-Cleaned Core Samples" *SPWLA 59th Annual Logging Symposium* (2018)