**Monitoring Shale Water Uptake Using 2D Magnetic Resonance Relaxation Correlation and SPRITE MRI**

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# Highlights

* Introducing, for the first time, a magnetic resonance imaging method for shales.
* The imaging method can provide water and oil images on a macroscopic scale.
* Water and oil saturations depend on the macroscopic scale heterogeneity of bedding planes.
* technique permits differentiating shale fracture and matrix pore water.
* Monitoring shale water imbibition using a combination of MR Imaging and techniques.

# Abstract

Fluid storage and transport in shale and clay formations is important in many areas of application, including hydrocarbon recovery from, and waste fluid storing in, these reservoirs. The multiscale heterogeneous nature of shales is largely responsible for these rocks being considered unconventional and complicated. Researchers often rely on imaging methods to provide spatial information to characterize their heterogeneity.

SEM and nano-CT are powerful methods that have been used to give images of shale nanopores with fields of view (FOV) of 100 . However, this limited FOV has raised questions about the validity of simulations based on these methods to scale up and represent macroscopic shale properties. Here, we have used, for the first time, SPRITE Magnetic Resonance Imaging (MRI) methods to give core plug size shale images. The imaging method resolves water and oil signals to give separate images of each in shales.

“As received” shale samples were used to acquire 1D and 3D oil and water images to characterize natural fluid distribution. Water uptake experiments were conducted to probe fluid displacement in shales. Measurements included gravimetric, Magnetic Resonance (MR) relaxation correlation, and SPRITE imaging methods. Water and oil images showed that sample scale heterogeneities are imposed by the shale beddings. Water uptake experiments (1) showed the capability of the method to identify MR signals from shale fracture water and matrix pore water, and (2) illustrated wettability control of spatial water distribution in shales during spontaneous imbibition.

# Keywords

Shale formations

Magnetic resonance imaging

Magnetic resonance relaxation

Water imbibition

Tight porous media

2D relaxation correlation maps

# Introduction

Low permeability geological formations include shales, clay-rich rocks, mudstones, fine-grained siltstones, coals, and chalks [1]. Understanding fluid storage and fluid transport in these rocks is imperative in many areas such as hydrology, geoscience, petroleum engineering, and petrophysics. Scientists and engineers seek either to store waste materials permanently in [2], or to free valuable hydrocarbon from [3] the complex pore structure of such rocks. While low permeability is an advantage for underground repository of hazardous wastes, it impairs the production of hydrocarbons from organic shales. Hydraulic fracturing operations substantially overcome the permeability issue in shales by inducing pathways for fluid flow. This makes numerous shale hydrocarbon reserves accessible for economic production [4].Furthermore, potential contamination of aquifers by the fracking fluid can be avoided by a better understanding of fluid flow in the induced and natural fractures [5]. This will lead to environmental-friendly development of shale reservoirs, safe and permanent storage of waste materials, and avoid potential geohazards while supporting energy-security [6,7].

Multiscale heterogeneity is inherent to shales and mudstones [8]. Their heterogeneity evolves from depositions under initial sedimentation conditions through compaction and to diagenesis during burial. Imaging technologies such as field emission-scanning electron microscopy (FE-SEM) and nano-computed tomography (nano-CT) have been used to report on spatial heterogeneity, morphology, and the pore structure of shale rocks [9,10,11,12]. Many shales, at centimeter and millimetre scale, show laminae that result from episodic sedimentation during deposition [13]. At the microscale, spatial structures of the mineral skeleton and inclusions, organic matter, and microfracture developments are evident [12,14]. It is only at the nanoscale that pore heterogeneity, pore connectivity, and organic and clay pore distributions can be distinguished. This information is fundamental to simulation efforts that are being used to characterize fluid flow in these nanopores and to estimate shale petrophysical properties [15,16,17,18,19,20,21,22].

Given the shale pore system heterogeneity, conventional core analysis methods are inadequate for proper characterization [6,23,24]. For shale fluid saturation measurement, these methods include the retort method, the two-phase extraction method, and the Dean Stark apparatus. These methods which rely on fluid extraction and evaporation are destructive and offer no spatial information.

Application of current rock visualization methods in simulations encounters challenges that limits their performance in shales. First, simulations should be conducted on representative elementary volumes (REV) to properly reflect macroscopic properties of the rock. However, Kelly et al. [25] showed that significant variations in properties such as porosity and organic matter distribution makes these high spatial resolution methods subjective for quantitative analysis due to their limited field of view (FOV). Second, to investigate flow characteristics in shales, these methods must bridge from morphological variation to fluid behavior. This requires high computational power and commonly ignores wettability variations [15]. Third, these methods involve sample destruction and elaborate sample preparation through mechanical crushing, laser or, ion milling techniques.

Alternatively, magnetic resonance (MR) imaging has provided a powerful tool for visualizing fluids in porous media [26]. Pure phase encoding single point ramped imaging with -enhancement (SPRITE) method [27,28], in particular, has been used in quantitative imaging of pore-filling fluids in various porous media [29,30,31,32]. In shale rocks, bulk MR relaxation measurements are the leading approach for characterization [33,34,35,36,37,38], given the drawbacks with the conventional core analysis methods. This is mainly due to the ability of MR to detect small quantities of hydrogen-bearing components in shale nanopores non-destructively [33]. Current bulk MR methods include 2D relaxation correlation measurements such as and diffusion measurements that are used for fluid typing in shales. In previous work by the authors [38], a new relaxation correlation measurement, was introduced that allowed not only fluid typing but also quantification of fluids that commonly exist in shales (oil and water) and a kerogen assessment. Despite improvements in methods measuring the shale MR response, methods have so far focused on resolving whole-sample signal components rather than obtaining spatially resolved data. This is due to the short-lived MR signal lifetimes (, , and ) in shale that present difficulty in signal acquisition and detection. SPRITE however is robust for short lifetime systems and, as we demonstrate in this work, offers an effective solution for imaging of shales.

In the present work, the SPRITE MRI method with a magnetization preparation is employed to, for the first time, give 3D images of fluids in shale samples at a core plug scale. The image signal is resolved to give oil and water images. This method is employed for bedding identification of four shale samples based on distribution of oil and water in the samples’ layers. The results show the laminated structure of the shale samples on a core plug scales and reveal that different beddings of the shale sample have different affinities for water and oil. Based on this observation, it was hypothesized that core scale heterogeneities play an important role in water/oil flow in shales. To test this hypothesis water uptake measurements were conducted on two shale core plug samples. Measured data included gravimetric, relaxation correlation, and 1D and 3D SPRITE measurements. The water signal in measurements showed strong sensitivity to water content in shale. A combination of 3D SPRITE measurements and resolved water signal peaks in measurements provided evidence for the capability of the measurement to distinguish water in fractures and water in rock matrix pores. Imaging of water uptake also demonstrated the key role of wettability in determining the water spatial distribution in shales.

The significance of this type of measurement is that it provides, for the first time, core plug scale spatial information and suggests future investigations of fluid storage and fluid flow on a REV of shale sample, especially at reservoir conditions. Another advantage of the MR methods presented in this work for shale samples is that they directly measure the fluids that naturally or forcefully occur in shale samples rather than simulating the flow in a measured morphology. Lastly, these methods are non-destructive and involve minimum sample preparation.

# Experimental section

## Instrumentation

The MR measurements were conducted on a Nalorac (Martinez, CA) 32 cm i.d. horizontal bore superconducting magnet operating at a frequency of 100 MHz for nuclei. The custom-built birdcage RF probe with a 4.5 cm diameter was driven by a 2 kW Tomco (Tomco Technologies, Stepney, Australia) RF amplifier, with a 90° pulse duration of 10.5 μs and probe deadtime of 24 μs. The water-cooled 7.5 cm id Nalorac gradient set driven by Techron (Elkhart, IN) 8710 amplifiers provided maximum gradient strength of 25 G/cm in the three principal directions. The console was a Tecmag (Houston, TX) Apollo. The MR measurements were performed at ambient magnet temperature of approximately 10° C in the sample region of the magnet.

## Resolving shale signal components

Bulk sample measurements were provided by the 2D relaxation correlation method. Details of measurement can be found elsewhere [38,39]. The relaxation correlation measurement is performed by acquiring a free induction decay (FID) after a saturation recovery.

*SaturationFID*

Saturation ensures the sample magnetization is zero as recovery commences. The magnetization partially recovers during . A 90 ̊ pulse measures the recovered longitudinal magnetization with an FID measurement wherein transverse magnetization is measured as a function of time. Signal, in the measurement can be described by a Fredholm integral of the first kind, shown in Eq. 1.

Eq. 1

The joint probability distribution, is the resolved signal in the 2D relaxation correlation map, with signal from -bearing species such as oil, water, and solid matter in the shale sample. Magnetization relaxation decay was predominantly exponential for the samples used in this study. An example FID for an Eagle Ford sample can be found in [40]. Hence, exponential functions were used in Eq. 1 to describe the signal.

Spatially resolved measurements were conducted with centric-scan single point ramped imaging with -enhancement (SPRITE) and with magnetization prepared centric-scan SPRITE. The SPRITE method is described elsewhere [27,41,42,43]. Here, a brief description of this method adapted for the multicomponent signal of shale samples is given.

***Encoding***

***pulse***

***Dephasing***

***RF***

***G***

***Recovery time,***

***Centric-scan SPRITE Readout***

***-pulses***

Fig. 1. encoding magnetization preparation with centric-scan SPRITE readout. The imaging scheme consists of two parts. The first part imposes a weighting on the sample magnetization. The second part, the centric-scan SPRITE, spatially encodes the prepared magnetization which is then used to construct the images.

Fig. 1 shows the imaging scheme used to spatially resolve oil (long and relaxation times) and water (short and long relaxation times) signal components. This scheme was implemented for 1D and 3D images. For simplicity, only one gradient direction used for 1D images is shown in the Fig. 1. For 3D images, gradients in three principal directions were used. Solid matter signals were excluded based on contrast (). The water and oil images were selectively acquired based on their difference. The measurement consists of a encoding magnetization preparation part followed by a SPRITE readout. In the first part of Fig. 1, the 90̊ pulse tips the longitudinal magnetization into the transverse plane and the spoiling gradient pulse dephases this magnetization to ensure zero sample magnetization. During the variable recovery time , the magnetization partially recovers with the spin-lattice time constant, . In the readout part, the MR SPRITE imaging method measures multicomponent signal, a fixed encoding time, , after the -pulses. is the signal amplitude as a function of position, , the encoding time for which is , and the encoding time for .

Eq. 2

is the prepared magnetization imposed by the encoding part of the measurement. Phase encoding time, was set long enough to suppress solid matter signal but short enough to detect oil and water signals (). , at each , gives -weighted signal in the image. One should recall that there is a distribution associated with the relaxation time. Therefore, results from a superposition of all signal components producing the multi-exponential magnetization recovery during at each voxel position, . can be described by the integration below:

Eq. 3

is weighted signal resolved as a function of position, . At each position, , the short component corresponds to the water signal and the long component yields oil signal. If a water image is of interest, the long signal component corresponding to oil species can be suppressed by acquiring an image with a recovery time, that allows only water signal to recover.

The MR acquisition parameters for the measurements outlined above are as follow: For measurements, in the recovery part, varies logarithmically from 50 μs to 2 s with 47 discrete values. 4096-time domain points were acquired during the FID, each separated by a dwell time of 1 μs. 32 signal averages were performed for a total measurement time of 35 mins and a typical signal-to-noise ratio (SNR) of 3500. varied logarithmically from 1.2 ms to 2 s forty-seven and ten times for 1D and 3D SPRITE measurements, respectively. Both 1D and 3D SPRITE measurements were acquired using an image encoding time, of 60 μs and -pulses of 13̊. After each -pulse, commencing at , nine-time domain points were recorded with a dwell time of 1.4 μs. A typical image SNR was 100 in the prepared magnetization centric-scan SPRITE measurements. 1D and 3D images comprise 64 pixels and voxels, respectively with FOV of 80 mm.

## Data processing

A Fast Laplace Inversion algorithm (Laplace Inversion Software, Schlumberger-Doll Research) written in the MATLAB environment (MathWorks, Natick, MA) was used to produce 2D relaxation correlation maps according to Eq. 1 and distribution in each image voxel according to Eq.3.

The Chirp-z Transform algorithm was applied to reconstruct images using the Acciss program developed in-house (University of New Brunswick MRI Centre) written in the MATLAB environment.

## Methods

“As-received” shale samples were measured by MR relaxation correlation and SPRITE MRI measurements. relaxation correlations helped identify shale signal components. SPRITE measurements were used to obtain images of oil and water in the samples. This allowed characterization of common heterogeneity types that exist in the shale samples under study.  
To investigate the effect of sample size heterogeneities on fluid flow in shales, two samples, EG10 and EG11, were chosen for water uptake experiments. The initial sample conditions were established by storing them in a chamber providing a relative humidity (RH) of 30% and a controlled temperature of 24̊ C. This left the samples unsaturated with water. MR measurements conducted at the sample initial condition included FID, relaxation correlation measurement, and magnetization preparation followed by 3D centric-scan SPRITE readout in order to resolve oil and water in relaxation time. After mass and MR measurements of the shale samples at equilibrium, water uptake experiments began. Heat shrink tubing was applied to the samples to ensure a 1D fluid displacement in the samples. Samples were not confined during water uptake experiments. The RH and temperature were also controlled during water uptake experiments. The bottom face of the shale samples was brought in contact with the water phase. During the water uptake process, sample mass, and MR response were measured regularly. The MR measurement suite included FID, relaxation correlation measurement, and oil suppressed magnetization preparation followed by 3D centric-scan SPRITE readout to image water. A summary of experiments performed on various shale samples is given in Table 1.

Table 1. Summary of experiments conducted on various shale samples.

|  |  |  |
| --- | --- | --- |
| **Experiments** | **MR measurements** | **Sample ID** |
| **As received** |  | M5  B5  EG10  EG11 |
| 1D SPRITE | M5  B5  EG10  EG11 |
| 3D SPRITE | M5  EG10  EG11 |
| **Water uptake** | 3D SPRITE | EG10  EG11 |

## Materials

Samples were selected from various shale formations, including Eagle Ford, Marcellus, and Barnett. These formations are vast shale plays and major gas and oil producers in the United States. Table 2 describes the basic physical properties of the core plugs used in this work. These outcrop organic-rich shale samples, Kocurek Industries Inc. (Caldwell, TX), were cylindrical in shape. The shale core plugs had previously discharged any native hydrocarbon gas. Throughout the text, samples from Eagle Ford, Marcellus, and Barnett Formations are referred to with acronyms EG, M, and B with a sample index number.

Eagle Ford shale samples EG10 and EG11, used to study water uptake in the shale pore system, had bedding orientations parallel to the direction of water uptake. A 3 wt% KCl brine was degassed and used as the water phase. KCl acts as a clay control agent to mitigate the micro-fractures caused by clay swelling. A saturated salt solution of CaCl2 was used to generate an RH of 30 % in the sample chambers at the controlled temperature of 24̊ C [44]. Reference sample composition was 17.0 wt% H2O, 82.9 wt% D2O and 0.07 wt% CuSO4. All salts were purchased from Sigma-Aldrich (St. Louis, MO) with purity > 93%.  
Table 2. Physical properties of shale core plugs.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample ID** | **Formation** | **Dimensions (LD)**  **(mm)** | **Bedding orientation with respect to the sample’s length** |
| **EG10** | Eagle Ford | 38 | Parallel |
| **EG11** | Eagle Ford | 38 | Parallel |
| **B5** | Barnett | 3838 | Parallel |
| **M5** | Marcellus | 3838 | Parallel |

# Results and discussion

### relaxation correlation measurements of as-received samples

Figs. 2a and 2b show the relaxation correlation measurements of samples EG10 and EG11 in their as-received condition. relaxation correlation measurement provides good resolution of signal components from -bearing species in shales [38]. Shale signal components marked as gray, blue, and red characterize solid matter, water, and oil in the shale samples, respectively. The log-mean relaxation times of each signal peak are shown on the relaxation correlation maps. Peak colors show signal intensity in arbitrary units. Solid matter in the shale samples had a short relaxation time of ~9 μs and long of ~110 ms. The solid matter signal may be associated with the hydroxyls in the clay minerals and kerogen since both are in the solid state. Oil in the shale samples showed a long of ~140 ms and a long relaxation time of ~150 μs. These oil relaxation times were calculated from collective signal of both oil peaks in the relaxation maps. The two water signal peaks are identified as W1 and W2 in the relaxation maps, since, as is discussed in section 3.4, the two peaks show different behaviour in the shale water uptake experiments. The water signal peak W1 had a short of ~ 2 ms and a relaxation time of 65 μs. The water signal peak W2 yielded a of ~25 ms and an even longer relaxation time of 375 μs compared to W1. In a previous paper by the authors [38], water, oil, and solid matter signal identification and quantification were undertaken via water adsorption/desorption and fluid evaporation experiments coupled with measurements. In a separate experiment, a companion shale sample was crushed and was used in an oil imbibition measurement. Increase in oil content resulted in a 50 % increase in signal intensity of the oil peak at high ratio. This unambiguously confirmed presence of oil in the shale samples.

The ratios measured in shale samples are high if compared to typical ratios reported in the literature [34]. This is because is shorter than due to the magnetic field inhomogeneities. However, as it is discussed in [38] at length, this does not prevent signal differentiation in shale species, because shale transverse magnetization is in the regime where contrast is determined by contrast. In Fig. 2, oil and water signal components show a strong contrast that has been exploited in the imaging method in section 3.2 to resolve image signal for oil and water. Moreover, solid matter shows a very short relaxation time compared to water and oil. This allowed solid matter exclusion from image signal by choosing the image encoding time, . This choice of , according to Eq. 2, ensured that solid matter signal was suppressed while the fluid signal was detected.



Fig. 2. 2D relaxation correlations of sample EG10 and EG11 in the as-received condition. Solid matter, water, and oil are shown in gray, blue, and red, respectively. measurement can resolve oil, water, and solid matter signal. Oil and water signal components show a strong contrast. Solid matter has a strong contrast with shale fluids. Projected relaxation distributions are shown on the periphery of each diagram. The diagonal lines show relaxation time ratios () of 1, 10, , , and . The values of the diagonals are the same in all subfigures.

### 1D and 3D images of as-received samples demonstrating shale bedding structure

The MR imaging method described in Fig. 1 provided oil and water images from the shale samples in the “as-received” condition. The 1D images were acquired along the diameter of the samples and perpendicular to the beddings. This allowed investigation of potential contrast in oil and water saturations between beddings of the shale samples. A 1D image of a sample with homogenous fluid saturation would appear as a half circle in the described image direction.



Fig. 3. A series of 1D -weighted images acquired for various delays, using the imaging scheme described in Fig. 1. The profiles show recovery for each pixel as increases. These data are processed using Eq. 3 to give resolved images of shale samples in Fig. 4.

1D -weighted images, , acquired for sample EG11, are shown in the stacked plot of Fig. 3. The horizontal x axis is position, the horizontal y axis is the recovery time, , and the vertical axis is the signal intensity in arbitrary units. Fig. 3 shows the signal intensity growth due to the recovery of the magnetization as increases. This data set was then analyzed using Eq. 3 to give space resolved oil and water signals,. The same procedure was followed for three more samples, EG10, M5, and B5 from different shale formations. Fig. 4 shows the 1D SPRITE images resolving relaxation times for these four samples. Water signal intensity with short relaxation times are plotted in blue and oil signal intensity with long is demonstrated in red. The projections on the horizontal axis show a bimodal distribution after the solid matter suppression with the short peak from water and the long peak from oil in the shale sample. The signal projections on the vertical axis marked in blue are the integrated signal of the water signal component (the peak with short ) while the one marked in red is the integrated signal of the oil signal component (the peak with long ).



Fig. 4. resolved 1D profiles for four shale samples of (a) EG11 from Eagle Ford Formation, (b) EG10 from Eagle Ford Formation (c) M5 from Marcellus Formation, and (d) B5 from Barnett Formation. The projections on the horizontal axes show the bulk distribution of the sample after solid matter suppression. The blue projection on the vertical axes is the projection of short component indicating water, and the red one is the projection of long component representing oil in the shale samples. The oil and water profiles spike alternatively. This demonstrates existence of water and oil rich layers in shale samples.

In Fig. 3, the first profile associated with the shortest did not show zero sample magnetization. This is because the short- water signal partially recovered during the shortest applied and before signal detection. Therefore, water signal is not well resolved in Fig. 4. However, the first is short enough for the long- oil component to reveal a full longitudinal magnetization recovery. Therefore, oil signal is well resolved in Fig. 4. The relaxation time for oil in Figs. 4a and 4b compared with that in the measurements of EG11 and EG10 in Fig. 2 is compatible and shows the same value of ~200 ms.

The 1D water and oil projections in Fig. 4 show saturation is high in alternate layers suggesting some bedding planes are water rich while others are oil rich. This shows that while water has a strong desire to saturate some of the shale beddings, other beddings are more favorable to oil. Therefore, it is evident that core plug scale heterogeneities play an important role in water/oil distribution in these samples. Shale heterogeneities arise from variations in pore structure of its assorted mineral framework, including, but not limited to, clay mineral pores, organic matter pores, fracture space, pores associated with calcite, quartz, feldspar, and dolomite. Shale fluid images can be related to spatial distribution of its minerals. For instance, a layer with substantially more water than oil may be attributable to clay minerals which are intrinsically water wet. A layer with significantly more oil than water can be an indication of a layer which is rich in organic matter porosity. An empty fracture or a layer with insignificant porosity will appear as a void in signal in both water and oil images. In cases where both fluids are present, a mixed-wet region is inferred, provided that the layer’s thickness is greater than the imaging resolution. Shale sample B5, in contrast to other samples, has a homogeneous water saturation across its bedding. For a valid interpretation of fluid images to the wettability of shale layers, it is essential to maintain the natural fluid distribution in the shale samples. Careful coring procedure and core plug handling is recommended to achieve this.



Fig. 5. 2D cross sections from a series of -weighted 3D images acquired for various delays, using the imaging scheme described in Fig. 1. The increase in color intensity of cross sections, as increases, shows recovery. These data are processed using Eq. 3 to give the resolved images of shale samples in Fig. 6.

The high degree of shale heterogeneity demands 3D images providing more spatial information regarding fluid distribution in the samples. The imaging scheme in Fig. 1 was also performed using 3D centric-scan SPRITE method as the readout part for samples M5 and EG11. Fig. 5, analogous to Fig. 3, shows the magnetization recovery for a cross section from the 3D -weighted images of sample EG11 as increases. This dataset was then analyzed using Eq. 3 for each voxel position to resolve sample distribution after solid matter suppression. The signal at each voxel was resolved yielding a bimodal distribution. The peak with the short relaxation time was attributed to water and the one with long was associated with oil to give 3D images of oil and water. Fig. 6 shows the superimposed 3D water and oil images of samples M5 and EG11. The 3D images were sectioned to better reveal the oil/water distributions in beddings of the samples. The signal intensities of oil and water was calibrated using the reference sample to give oil and water content in porosity units (p.u.) plotted in the 2D cross sections in Fig. 6.

According to Eq. 2, the image signal intensity obtained from centric-scan SPRITE for oil and water is attenuated according to their relaxation time. In order to obtain fluid content in porosity units plotted in Fig. 6, the signal intensity was first back-extrapolated to zero using their relaxation time. The back-extrapolated signal intensity was then converted to fluid content in porosity units using the image signal intensity from the reference sample and the H2O concentration of the reference sample. In performing the conversion for oil, the oil hydrogen index was assumed to be equal to one. This means the oil hydrogen count per volume is equal to that of water. The hydrogen index is close to one for most oils.



Fig. 6. 3D superimposed images of oil and water in samples (a) M5 and (b) EG11 with cross sections showing oil and water content. The color intensity in the cross-section plots is calibrated to oil and water content in porosity units (p.u.) for each sample. Axis for 2D cross sections are pixels. Image FOV was 80 mm. The 3D images show the layered structure of the samples. Sample M5 shows a low porosity bedding plane with no water, and low oil content. Similar results were obtained for sample EG10.

In Fig. 6, 3D images of samples M5 and EG11 show the layered structure of the water/oil spatial distribution induced by samples’ beddings. Sample M5 shows a layer with signal void in water and with low oil content. This is a layer with insignificant porosity, as no fracture is visible externally. In the cross section of M5, the region to the right of the void shows a clear tendency to populate oil rather than water, and the left-hand side has a stronger tendency towards water than oil. The cross sections through oil and water content of sample EG11 show that water and oil alternatively occupy regions in the sample, forming bedding structures. Images in Figs. 4 and 6 offer clear evidence on the efficiency of the fluid-solid interactions, varying with the shale laminated structure, to determine fluid storage and distribution. This raises the question of how bedding affects fluid flow in shales. Therefore, in the next section, the effect of sample heterogeneity on fluid flow in shales was investigated using water uptake experiments on two nominally similar samples, EG11 and EG10, based on their MR response.

### relaxation correlation measurements during water uptake experiment

In this section, 2D MR relaxation correlation and gravimetric measurements during water uptake experiments are reported for two shale samples, EG10 and EG11. The water uptake process was monitored for 43 days. During the process, water entered the sample pore space due to capillary forces [45,46]. Four representative measurements of EG10 and EG11 shales as a function of time are shown in Figs. 7 and 8, respectively. Solid matter, water, and oil signal components are identified with gray, blue, and red colors, respectively. Sample EG11 was measured with a reference sample present. Signal from the reference is shown in green. This reference sample helped calibrate signal to mass. Water signal in relaxation maps for both samples bifurcates into two distinct signal peaks (W1 and W2). Figs 7 and 8 show the increase in integrated signal intensity of peaks W1 and W2 as water uptake proceeds.



Fig. 7. 2D relaxation correlations of sample EG10 with time as water uptake proceeds. Solid matter, water, and oil are shown in gray, blue, and red, respectively. The water peaks show an increase in signal intensity with time. Projected relaxation distributions are shown on the periphery of each diagram. The diagonal lines show relaxation time ratios () of 1, 10, , , and . The values of diagonals are the same in all subfigures.



Fig. 8. 2D relaxation correlations of sample EG11 with time as water uptake proceeds. Solid matter, water, oil, and reference sample are shown in gray, blue, red, and green, respectively. The water peaks show an increase in signal intensity with time. Projected relaxation distributions are shown on the periphery of each diagram. Diagonals indicated are as per Fig. 7.

To unambiguously identify water peaks from other shale species in relaxation maps, the changes in integrated signal intensity, for all the peaks, relative to their initial value were plotted in Figs. 9a and 9b for samples EG10 and EG11, respectively, as a function of mass gained by the sample ( vs ). S is integrated signal intensity and indexes solid matter, W1, W2, and oil. is the mass gained by the sample due to water uptake. Fig. 9 shows that the integrated signal intensities of the W1 and W2 peaks are sensitive to the change in the shale water content while signal intensities of peaks associated with solid matter and oil are essentially constant. The insets in Figs. 9a and 9b magnify the plots. It should be noted that the dramatic increase for W2 peak on Fig. 9 is because its initial value, is small. It is apparent that, as water uptake proceeds, the signal increase for W1 and W2 peaks behaves differently. Section 3.4 will further explore this.



Fig. 9. Relative signal change of water peak W1(▼), water peak W2(▲), oil (♦), and solid matter (●) peaks versus mass gained by (a) the sample EG10 based on the relaxation correlations of Fig. 7 and (b) the sample EG11 based on the relaxation correlations of Fig. 8 during water uptake experiments. Integrated water signal intensity of peak W1 increased about two-fold and that of W2 increased about nine-fold for both samples after water uptake experiment. Solid matter and oil signal intensities remained essentially unchanged. Water signal intensity in the relaxation correlations showed high sensitivity to change in water content.

### Identification of peaks related to water in fractures and pore water

This section provides evidence of the capability of relaxation correlation measurement to resolve confined water in the shale matrix pore space and fracture water. The water signal intensities in relaxation correlation maps in combination with MR imaging during water uptake experiments showed that peak W1 represents water signal from matrix pores, whereas W2 is the water signal from microfractures in shale samples.

The coordinates of peak W1 (matrix pore water) relative to that of W2 (fracture water) on the relaxation correlation maps of Figs. 7 and 8 are in agreement with water molecules in a less confined environment. Surface relaxation experienced by water molecules in the large microfractures is reduced compared to those in shale nanopores. This results in a longer relaxation times for water in fractures than matrix pore water.



Fig. 10. Water content based on integrated signal intensities of water peaks; W1 for sample EG10 (■), W1 for sample EG11 (▲), W2 for sample EG10 (♦), and W2 for sample EG11 (▼) on relaxation correlation maps during water uptake experiment.

Fig. 10 shows the integrated signal intensities of W1 and W2 peaks calibrated to water content in p.u. for EG10 and EG11 as a function of time. The quadrilateral data points on Fig. 10 are for sample EG10, and the triangle data points are for sample EG11. W1 and W2 integrated signal intensities are shown in light and dark blue, respectively. This signal calibration to p.u. for water was performed by manipulating water quantity and establishing a linear relationship between the mass change in the samples due to this manipulation and the associated signal change. Alternatively, Eq. 4 can be used to convert shale signal intensities () to their mass () using a reference sample.

|  |  |
| --- | --- |
|  | Eq. 4 |

where is mass. is signal intensity. is mass density. is hydrogen index; represents water, oil, or solid matter; denotes reference sample. Eq. 4 requires knowledge of hydrogen index and density for shale species.

The initial sample conditions before water uptake included bringing the samples to equilibrium with a relative humidity of 30 % in a desiccator. During the samples’ initialization, water occupied small pores in the sample through capillary condensation and leaves large pores unfilled. This is consistent with the MR response from measurements showing similar matrix pore water (W1) content of around 5 p.u., and fracture water (W2) of close to zero for both samples. As water uptake proceeds, water enters both fracture and pore space. In Fig. 10, W1 and W2 water content increases with time for both samples. Figs. 11 and 12 show spatially resolved water content for EG10 and EG11 shales as a function of time for a slice from oil suppressed 3D centric-scan SPRITE measurements. The images are slices perpendicular to the sample beddings. The initial conditions for EG10 (Fig. 11a) and EG11 (Fig. 12a) were similar, as observed in their response on measurements.

In Fig. 10, the fracture water curve for EG10 is placed above that of EG11. There were more microfractures in EG10 compared to EG11 for water imbibition. This agrees with the observation that EG10 showed a higher initial imbibition rate and water content during water uptake experiments. Moreover, Fig. 11 clearly shows a fracture in sample EG10. Therefore, sample EG10 was more fractured than EG11. Please note that most fractures were micrometer scale. Therefore, water occupying most fractures did not reveal the fissure structure of the fractures with the image resolution obtained in this work. However, water fracture content was detected on the relaxation correlation map as peak W2.



Fig. 11. 2D cross sections (a to d) are from oil suppressed 3D centric-scan SPRITE measurements perpendicular to the beddings of the sample EG10 with time during water uptake experiment. The signal intensity is calibrated to the water content in porosity units. 2D cross section (e) is from oil suppressed 3D centric-scan SPRITE image of sample EG10 in its as received condition. 1D water profiles (f) are projections of the water content in the 2D cross section as during water uptake proceeds. The dash lines clearly demonstrate that beddings identified in the as received condition affect the water distribution during water uptake. Water uptake in the EG10 shale sample reveals the layered structure of the sample and the fracture across the sample as it fills with water.



Fig. 12. 2D cross sections (a to d) are from oil suppressed 3D centric-scan SPRITE measurements perpendicular to the beddings of the sample EG11 with time during water uptake experiment. The signal intensity is calibrated to the water content in porosity units. 2D cross section (e) is from oil suppressed 3D centric-scan SPRITE image of sample EG11 in its as received condition. 1D water profiles (f) are projections of the water content in the 2D cross section as during water uptake proceeds. The dash lines clearly demonstrate that beddings identified in the as received condition affect the water distribution during water uptake. Water invades the sample from the bottom of the core plug. Water uptake in the EG11 shale sample reveals the layered structure of the sample.

### Effect of samples’ beddings on water imbibition in shales

In Figs. 11 and 12, the water imbibition follows the layered structure of the shale samples. This can be understood through the capillary forces which act as the main force to pull water into the shale pore space. On a pore surface, the interface between two immiscible fluid with interfacial tension of and contact angle of curves due to a pressure difference across the interface. This pressure difference is called capillary pressure, . In a simplified geometry, for a cylindrical pore with radius, , capillary pressure is given by the Young-Laplace equation modified by contact angle [47]:

The wettability of the pore surface determines the contact angle, . For a fluid to wet the surface, should be . On the millimetre scale, Figs. 4 and 6 show that some layers are prone to saturate water while some other layers are prone to oil. This suggests the existence of a wettability variation on the sample scale. Layers with pore surfaces more prone to oil exhibit an increase in resulting in a lower capillary force to act in favor of water imbibition into its pores [48]. Therefore, water imbibed in the shale samples, in Figs. 11 and 12, showed a layered structure. It should be noted that the layered variation in water occupying the samples can also be explained through possible existence of a layered variation in porosity. Further shale characterization methods can confirm or reject this.

Based on Eq. 4, increases for smaller pore radius. In shale samples, however, there are several complications. At the pore level, it was found that pore accessibility plays an important role [49]. Pore accessibility includes a small pore surrounded by large pores, or a large molecule excluded from nanopores of shale. Therefore, despite having larger pores than the shale matrix, fractures fill with water from the beginning of the water imbibition [50]. Fig. 10 shows that fracture water (W2), for both samples, increases even in the early stages of water imbibition. Moreover, Fig. 11 shows accessibility on the sample scale. Fig. 11 shows that the visible fracture in shale is inaccessible by the waterfront at the beginning of the water uptake process. Once the waterfront reaches the fracture, it filled the fracture space.

MR relaxation times can report on pore-level fluid dynamics. In this work (results not shown here), relaxation time of W1 and W2 water peaks showed a strong but minor positive correlation with water content in shale samples. The relaxation time had a negative correlation with water content. This consistent behavior of MR relaxation times with shale water content motivates future research.

The acquisition of these unprecedented images from fluids in short MR lifetime shale samples invites their application for other short lifetime multicomponent signal samples such as clays. These measurements are well suited to produce experimental data on a macroscopic scale and data of this type is invaluable for simulations of fluid flow and fluid storage [51,52]. Future works will benefit from these methods undertaken with reservoir conditions.

# Conclusion

Multiscale heterogeneity of shales requires application of methods reporting on spatial information from the pore to reservoir scale. On this scale range, industry-standard core plugs are an important source of information needed to determine reservoir behaviour. We have introduced, for the first time, a quantitative MRI method for shales. The imaging method resolves water and oil signals to give separate images of each in shale core plug samples. Therefore, application of these MR imaging methods for fluid flow in shale core plugs will assist in a more reliable scale up for shale reservoirs. The MR imaging method also benefits from minimal sample preparation and direct measurement of fluids in the shale rather than simulation in a measured topology.

In this paper, 1D and 3D images with a nominal resolution of 1.25 mm were used to identify millimetre scale heterogeneities in shales imposed on water and oil porosity by samples’ laminae. Water uptake experiments monitored using the MR imaging and relaxation correlation measurements (1) proved the capability of the measurement to differentiate shale fracture water and pore water, and (2) demonstrated the key role of wettability in determining water spatial distribution in shales. These results highlight the importance of bedding planes in fluid distribution and flow.

Application of these methods offers opportunities for simulation and experimental investigations of fluid behavior in shales. This will contribute to a better understanding of fluid flow and fluid storage in shales which will aid economic production from shale hydrocarbon reserves and effective storage operations in shale and clay formations.

# Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgements

S. Zamiri thanks the New Brunswick Innovation Foundation for a scholarship. Bruce J. Balcom acknowledges NSERC of Canada for a Discovery grant [2015-6122] and the Canada Chairs program for a Research Chair in Material Science MRI [950-230894].

# Credit Author Statement

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***Encoding***

***pulse***

***Dephasing***

***RF***

***G***

***Recovery time,***

***Centric-scan SPRITE Readout***

***-pulses***

Fig. 1. encoding magnetization preparation with centric-scan SPRITE readout. The imaging scheme consists of two parts. The first part imposes a weighting on the sample magnetization. The second part, the centric-scan SPRITE, spatially encodes the prepared magnetization which is then used to construct the images.Color should be used for this figure in print.



Fig. 2. 2D relaxation correlations of sample EG10 and EG11 in the as-received condition. Solid matter, water, and oil are shown in gray, blue, and red, respectively. measurement can resolve oil, water, and solid matter signal. Oil and water signal components show a strong contrast. Solid matter has a strong contrast with shale fluids. Projected relaxation distributions are shown on the periphery of each diagram. The diagonal lines show relaxation time ratios () of 1, 10, , , and . The values of the diagonals are the same in all subfigures.

Color should be used for this figure in print.



Fig. 3. A series of 1D -weighted images acquired for various delays, using the imaging scheme described in Fig. 1. The profiles show recovery for each pixel as increases. These data are processed using Eq. 3 to give resolved images of shale samples in Fig. 4.

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Fig. 4. resolved 1D profiles for four shale samples of (a) EG11 from Eagle Ford Formation, (b) EG10 from Eagle Ford Formation (c) M5 from Marcellus Formation, and (d) B5 from Barnett Formation. The projections on the horizontal axes show the bulk distribution of the sample after solid matter suppression. The blue projection on the vertical axes is the projection of short component indicating water, and the red one is the projection of long component representing oil in the shale samples. The oil and water profiles spike alternatively. This demonstrates existence of water and oil rich layers in shale samples.



Fig. 5. 2D cross sections from a series of -weighted 3D images acquired for various delays, using the imaging scheme described in Fig. 1. The increase in color intensity of cross sections, as increases, shows recovery. These data are processed using Eq. 3 to give the resolved images of shale samples in Fig. 6.

Color should be used for this figure in print.



Fig. 6. 3D superimposed images of oil and water in samples (a) M5 and (b) EG11 with cross sections showing oil and water content. The color intensity in the cross-section plots is calibrated to oil and water content in porosity units (p.u.) for each sample. Axis for 2D cross sections are pixels. Image FOV was 80 mm. The 3D images show the layered structure of the samples. Sample M5 shows a low porosity bedding plane with no water, and low oil content. Similar results were obtained for sample EG10.

Color should be used for this figure in print.



Fig. 7. 2D relaxation correlations of sample EG10 with time as water uptake proceeds. Solid matter, water, and oil are shown in gray, blue, and red, respectively. The water peaks show an increase in signal intensity with time. Projected relaxation distributions are shown on the periphery of each diagram. The diagonal lines show relaxation time ratios () of 1, 10, , , and . The values of diagonals are the same in all subfigures.

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Fig. 8. 2D relaxation correlations of sample EG11 with time as water uptake proceeds. Solid matter, water, oil, and reference sample are shown in gray, blue, red, and green, respectively. The water peaks show an increase in signal intensity with time. Projected relaxation distributions are shown on the periphery of each diagram. Diagonals indicated are as per Fig. 7.

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Fig. 9. Relative signal change of water peak W1(▼), water peak W2(▲), oil (♦), and solid matter (●) peaks versus mass gained by (a) the sample EG10 based on the relaxation correlations of Fig. 7 and (b) the sample EG11 based on the relaxation correlations of Fig. 8 during water uptake experiments. Integrated water signal intensity of peak W1 increased about two-fold and that of W2 increased about nine-fold for both samples after water uptake experiment. Solid matter and oil signal intensities remained essentially unchanged. Water signal intensity in the relaxation correlations showed high sensitivity to change in water content.

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Fig. 10. Water content based on integrated signal intensities of water peaks; W1 for sample EG10 (■), W1 for sample EG11 (▲), W2 for sample EG10 (♦), and W2 for sample EG11 (▼) on relaxation correlation maps during water uptake experiment.

Color should be used for this figure in print.



Fig. 11. 2D cross sections (a to d) are from oil suppressed 3D centric-scan SPRITE measurements perpendicular to the beddings of the sample EG10 with time during water uptake experiment. The signal intensity is calibrated to the water content in porosity units. 2D cross section (e) is from oil suppressed 3D centric-scan SPRITE image of sample EG10 in its as received condition. 1D water profiles (f) are projections of the water content in the 2D cross section as during water uptake proceeds. The dash lines clearly demonstrate that beddings identified in the as received condition affect the water distribution during water uptake. Water uptake in the EG10 shale sample reveals the layered structure of the sample and the fracture across the sample as it fills with water.

Color should be used for this figure in print.



Fig. 12. 2D cross sections (a to d) are from oil suppressed 3D centric-scan SPRITE measurements perpendicular to the beddings of the sample EG11 with time during water uptake experiment. The signal intensity is calibrated to the water content in porosity units. 2D cross section (e) is from oil suppressed 3D centric-scan SPRITE image of sample EG11 in its as received condition. 1D water profiles (f) are projections of the water content in the 2D cross section as during water uptake proceeds. The dash lines clearly demonstrate that beddings identified in the as received condition affect the water distribution during water uptake. Water invades the sample from the bottom of the core plug. Water uptake in the EG11 shale sample reveals the layered structure of the sample.