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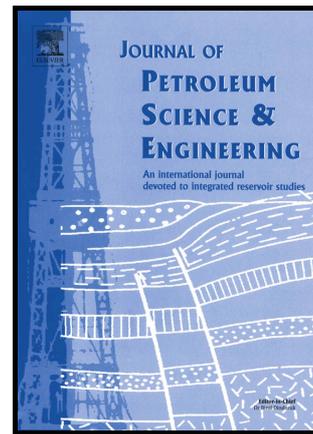
Cite this article as: M. Nadia Testamanti and Reza Rezaee, Determination o NMR T_2 cut-off for clay bound water in shales: A case study of Caryngini: Formation, Perth Basin, Western Australia, *Journal of Petroleum Science an Engineering,* http://dx.doi.org/10.1016/j.petrol.2016.10.066

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Determination of NMR T_2 cut-off for clay bound water in shales: A case study of Carynginia Formation, Perth Basin, Western Australia

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Abstract

Low-field Nuclear Magnetic Resonance (NMR) has proved to be a valuable tool for the petrophysical characterization of conventional reservoirs, but its effective application to unconventional reservoirs is still under research. Pore structure characterization of shales is particularly challenging due to the complexity of the pore network and the small size of pores.

Using low-field NMR, we performed transverse relaxation (T_2) experiments on samples from the Perth Basin, Western Australia. The samples were initially saturated with KCl brine to obtain the total NMR porosity and T_2 distribution, then centrifuged and finally oven-dried at increasing temperatures. T_2 spectra were also acquired after centrifuging and heating the samples. Our results indicate that most of the transverse relaxation occurs below 3 ms in saturated samples and that a conventional centrifuge cannot remove water from the smaller pores, making the commonly accepted clay bound water cut-off unsuitable for shales. Furthermore, the results from NMR experiments performed on the oven-dried shale samples suggest that the water content remains relatively constant after heating them above 65°C. The calculated T_2 cut-off for clay bound water is between 0.22 and 0.26 ms for the samples studied.

The methodology presented in this paper can be replicated in other formations to find a suitable T_2 value for clay bound water, which can be a good indication of potentially producible porosity and can also be used for permeability estimation.

Keywords: Shale reservoir; Nuclear magnetic resonance; Pore structure; T_2 cut-off; Clay bound water

1. Introduction

Gas in conventional reservoirs is stored in medium to high permeability formations, making it relatively easy to produce in a profitable way. Production from these types of reservoirs is in decline and new ones are becoming harder to find. In this scenario, unconventional reservoirs are becoming increasingly important. Following the success of the United States in the development of shale plays, other countries have begun to explore basins with unconventional resource potential and restudy those formations that were once considered as prospective source or seal rocks only.

Shales are very heterogeneous, both in their mineralogical composition and fabric (Chalmers et al., 2012; Ghanizadeh et al., 2014; Josh et al., 2012; Loucks et al., 2012). An accurate laboratory characterization will be of critical importance in the estimation of Original Gas In Place (OGIP), understanding flow mechanisms (Bustin et al., 2008) to forecast production and ultimately, decide on the best development strategy for shale plays.

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Pore sizes in shale rocks are on the scale of nanometers to micrometers and its permeability can be as low as a few Nano-Darcies, making petrophysical characterization a challenging task (Gensterblum et al., 2015; Loucks et al., 2012). Mercury injection and Nitrogen adsorption are some of the most widely used laboratory methods for characterization of pore structure, however, they have some limitations and may not be suitable for shale pore characterization (Bustin et al., 2008; Clarkson et al., 2011; Loucks et al., 2012; Lu et al., 1995; Sondergeld et al., 2010b).

Over the past decades, the NMR (Nuclear Magnetic Resonance) technique has been improved, becoming a reliable tool to measure and estimate petrophysical properties of the reservoir rocks and fluids. Its application in formation evaluation includes the estimation of pore size distribution, free fluid, and irreducible volume and ultimately permeability calculation (Coates et al., 1999b; Hinai et al., 2014; Kenyon, 1997a; Rezaee et al., 2012). When it comes to pore size distribution, the NMR technique has the ability to detect water stored in a wider range of pore sizes, provided the right equipment and settings are used (Behroozmand et al., 2014; Sondergeld et al., 2010a; Sulucarnain et al., 2012).

1.1   NMR Basics

The T_2 (transverse relaxation) experiment is one of the most valuable sources of information for petrophysical characterization in an NMR measurement. The T_2 time depends on bulk fluid processes, surface relaxation and diffusion mechanisms (Coates et al., 1999a) described by the following equation:

$$\frac{1}{T_2} = \frac{1}{T_{2\,bulk}} + \rho_2 \frac{S}{V} + \frac{D(\gamma G T_E)}{12} \tag{1}$$

where $T_{2\,bulk}$ is the bulk relaxation, ρ_2 is the surface relaxivity of the pore surface, S/V is the ratio of pore surface to fluid volume, D is the molecular diffusion coefficient, G is the gyromagnetic ratio of a proton and T_E is the inter-echo spacing.

When saturated porous samples are measured, the porosity will be directly proportional to the amplitude of the T_2 curve, whereas pore sizes and fluid type will be related to the decay rate (Anovitz and Cole, 2015). In shales, most of the T_2 signal decay occurs at shorter times due to the abundance of small pores, which causes the saturating water to relax much faster than it would in larger pores.

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When the applied electromagnetic field in the NMR experiment is homogeneous, only bulk relaxation and surface relaxation can occur in the fluids. For pores that are fully saturated with water, the bulk relaxation rate (T_{2bulk}) is usually negligible (Coates et al., 1999a). In this case, if surface relaxivity is known or can be estimated, the T_2 relaxation time can indicate pore size (Looyestijn, 2001) following the simplified equation:

$$\frac{1}{T_2} = \rho_2 \frac{S}{V} \tag{2}$$

Then, a cut-off T_2 value could be chosen to discriminate between the free water and the capillary bound water.

In this study, shale samples in various saturation states are studied using a low-field NMR equipment and a novel approach to establish a T_2 cut-off value to distinguish between producible porosity and irreducible bulk volume is proposed.

2. Methodology

2.1 Samples

The Perth Basin, located in Western Australia, has been estimated to hold up to 32.7 Tcf of technically recoverable shale gas (U.S. Energy Information Administration, 2015). The break-up of Gondwana and the formation of the Indian Ocean were preceded by a long rifting process, which also contributed to shaping the Perth Basin (Cadman, 1994). This Basin trends north-south covering an area of almost 100,000 km^2, delimited by the Darling fault to the east and reaching the edge of the continental crust to the west (DMP-WA, 2014; Thomas, 2015). Its location is shown in **Figure 1**.

The Permian Carynginia formation is found in the northern section of the Perth Basin, at a depth of 2200 to 2500m, and is thought to hold most of its technically recoverable shale gas. It contains mostly black to gray micaceous siltstone and shale, with some minor conglomerate and interbedded sandstone, deposited in a shallow marine environment. Most of the Carynginia formation is in the dry gas window, with a kerogen Type III. It's low in clay content and has an average Total Organic Content (TOC) of 4% (Mory, 2011; U.S. Energy Information Administration, 2015).

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A set of six shale samples from the middle section of the Carynginia formation was used in this study. The mineralogical characteristics and TOC from geochemical studies performed on three of the samples (AC-1, AC-4 and AC-5) are summarized in **Table 1**. The TOC for these samples ranges between 0.64 and 3.03 Wt. %. While their lithological composition is a mixture of shale and siltstone, sample AC-1 is rich in clay whereas the other two samples are rich in quartz. The most abundant type of clay identified in the samples analyzed is mixed layer illite/smectite (I/S), followed by illite. The smectite content was low in all three samples.

2.2   NMR

Low-field NMR measurements were made using a 2 MHz Magritek Rock Core Analyzer. Before placing them inside the equipment, each sample was tightly wrapped to prevent water evaporation and moisture absorption. The background signal from the plastic wrap was also obtained and later subtracted from all core measurements.

All the (T_2) experiments were carried out using the Carr-Purcell-Meilboom-Gill sequence (CMPG), where the inter-experiment delay was set at 10,000 ms and 10,000 echoes were acquired with an echo time of 100 μs, the minimum available for this equipment.

The raw T_2 decay was processed using the 1D inverse Laplace transform, applying the Lawson-Hanson algorithm. With this algorithm, the T_2 distribution is obtained by a nonnegative least squares fit. Noise is present in every experimental decay, which leads to multiple possible solutions. To minimize this effect, the signal to noise ratio was set at 200 for all T_2 experiments. The smoothing parameter was selected after calculating the chi-square (χ^2), so as to find the best fit to the experimental data which was also the least sensitive to noise. More detailed information about this procedure can be found in Sorland (2014).

T_2 spectra were acquired for samples fully saturated, centrifuged and oven dried in the following order:

1) All samples were initially saturated with 30 g/l KCl brine under 2000 psi hydrostatic pressure and their weights were monitored until they reached a constant value. T_2 measurements were made on all samples at fully saturated state.

2) After the initial measurements, four of the samples were centrifuged at 4500 rpm for a total of 26 hours. These samples were subsequently weighted and then T_2 experiments were performed.

3) The last step of the experiment consisted of drying the same four samples in a vacuum oven at ten set temperatures: 50°C, 60°C, 80°C, 90°C, 100°C, 110°C, 120°C, 130°C, 140 °C, 150°C and 160°C. All

samples were heated until a no further weight reduction was observed. After removing them from the oven, the samples were placed in a glass vial and allowed to cool down to room temperature before T_2 measurements were made.

Upon completion of the steps previously described, two of the samples were selected to test the repeatability of the experiment and critically evaluate the results. These samples were re-saturated following the same protocol and oven-dried at increasing temperatures. Each sample was again heated at a set temperature until a constant weight value was achieved, then T_2 experiments were repeated.

3.   Experimental results

3.1   Fully saturated

NMR data were acquired for the six fully saturated samples. Their T_2 spectra are shown as solid lines in **Figure 2**. The mean peak and dominant T_2 time are found below 3 ms in all cases, which indicates small pores sizes. The T_2 distribution is unimodal for three of the samples (AC-1, AC-2, AC-5), corresponding to a single dominant pore type, which is characteristic of shales with high clay content.

A different distribution shape and relatively larger porosity values are observed in the remaining three samples (AC-3, AC-4, AC-8), where three modes can be identified. The dominant peak value of the T_2 distribution occurs between 0.4 and 0.85 ms, which corresponds with the small pores in the shale matrix. An NMR response consistent with the larger pores present in silty shale can also be identified, with a significant amount of hydrogen protons relaxing after 4 ms. NMR incremental porosity for these three samples can also be detected at longer T_2 times, even after 100 ms, which could correspond to micro-fractures present in the core samples. These micro-fractures can be induced while the re-saturation process takes place and are most likely due to clay swelling.

NMR porosity for the fully saturated samples ranged from 8 to 10% for the three core samples exhibiting unimodal T_2 distribution and from 12.5 to 18% for the remaining three samples.

3.2   Centrifuged samples

A small weight reduction was observed in the four samples after they were centrifuged. The T_2 spectra for the four samples in their initial fully saturated state, after being centrifuged and oven-dried at different temperatures is shown in **Figure 3**.

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Using a centrifuge in shales poses the difficulty of not knowing if the capillary pressure achieved by the equipment is enough to remove all the free water in the sample. The NMR spectra after the samples were centrifuged showed a decrease in the incremental porosity at larger relaxation times, typically associated with larger pores. At shorter relaxation times, the T_2 distribution remained mostly unaltered for samples AC-1, AC-2 and AC-5, so while the water that filled larger pores and micro-fractures had been expelled from the rock, the matrix pores remained filled with water. No brine was collected after this experiment, so it's possible that the minor weight decrease observed in the samples corresponded to water evaporation due to the heat produced by the centrifuge.

For the brine-air drainage in a centrifuge, capillary pressure can be calculated as:

$$P_C = \frac{1}{2}\Delta\rho\omega^2\left(R^2 - r_i^2\right) \tag{3}$$

where P_C is the capillary pressure at a particular radial distance r_i, $\Delta\rho$ is the difference between the densities of the two phases, ω is the rotational speed and R is the radius of rotation. The maximum capillary pressure achieved at a rotational speed of 4500 rpm was calculated to be 315 psi, which is insufficient to remove the water from the smaller pores. This is also evident from the T_2 spectra of sample AC-8 acquired after centrifugation: while the capillary pressure achieved seems to have been enough to force the fluid out of the larger pores and micro-fractures, it was not enough to expel it from the matrix pores. This is plausible based on the almost constant value of cumulative NMR porosity at T_2 time of 2.4 ms (where the T_2 distribution reaches zero for the centrifuged sample) before and after the sample was centrifuged. The slight increase observed in the amplitude of the dominant peak could also be interpreted as a redistribution of the water in the matrix pores.

3.3   Oven-dried samples

For the heated samples, as the temperature increases, water inside the sample becomes harder to remove and it can be inferred to be clay bound. The T_2 spectra acquired after heating the samples show a clear shift of the T_2 peak towards the left, centered on 0.1 ms for all the samples. This is consistent with the water evaporating from the sample, which leads to fewer hydrogen protons remaining inside the sample, hence the drop in the porosity detected by NMR.

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NMR porosity for all the samples heated at 80°C was found to be abnormally low. After analyzing the raw T_2 decay and acquisition parameters, the applied magnetic field was found to be unusually high for this NMR equipment. Since the T_2 experiment couldn't be repeated at that stage, the data for this temperature step was disregarded.

After the samples were heated beyond 120°C, no further weight reduction was observed. Although T2 experiments were performed, the final data analysis after oven-drying the samples up to 160°C revealed that the acquisition parameters for the samples heated between 130ºC and 160ºC were different from those previously used. Since the nature of this study requires constant acquisition parameters to achieve consistent results and draw comparisons, the NMR data from samples heated between 130ºC and 160ºC was not considered for further analysis.

4.   Discussion

4.1   *T_2 cut-off and Shale Fluid Distribution*

The ability of the NMR to distinguish between free and bound fluid has been widely used to estimate permeability for sandstones and carbonates (Chang et al., 1994; Freedman, 2006). The technological advances in low-field NMR equipment and log interpretation, paired with the interest behind unconventional resources have made measurements in shales more attractive. However, more uniform criteria are still needed for the effective application of NMR to the reservoir characterization of shales. One of the most common applications of NMR is the estimation of BVI, which is the bulk volume of irreducible water saturation, by establishing a threshold T_2 value (T_2 cut-off) to discriminate between the free fluid and the capillary bound fluid present in the rock.

In order to establish a T_2 cut-off, two NMR measurements should be made with the sample fully saturated and partially saturated. A centrifuge is usually used to desaturate core samples from conventional reservoirs, reaching irreducible water saturation (Kenyon, 1997b). For sandstones, the standard cut-off for capillary bound fluids is usually 33 ms and for carbonates, 90-100 ms is commonly used. The smallest pores in shales will need higher capillary pressure to expel the water than what most laboratory centrifuges can achieve, thus making this technique generally unsuitable for this type of reservoir. Overlooking this effect could result in underestimation of the effective porosity and ultimate gas recovery of a shale reservoir. Furthermore, a second cut-off of 3 ms is commonly used to identify clay bound water, but since most of the T_2 relaxation for the samples studied occurs below 3 ms, this standard cut-off value cannot be applied.

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In this paper, the T_2 relaxations for the shale samples oven-dried at increasing temperatures were used to establish a clay bound water cut-off. When permeability measurements cannot be made in shales, this value can be useful to get an idea of the pore space that can be occupied by a producible fluid.

The plot of NMR cumulative porosity for the samples oven-dried against temperature, revealed two distinct trends (**Figure 4a**). The intersection between these trendlines was calculated for all four samples, which indicated the minimum temperature at which the sample has to be heated so that only the clay bound water remains. At these temperatures, the NMR porosity was considered to be irreducible and it ranged between 2% and 3.86%. The average T_2 cut-off was 0.25 ms and 61°C was the approximate minimum oven temperature to evaporate all free fluid. With this T_2 cut-off, it is possible to discriminate between the clay bound water (CBW) and the pore space that could be occupied by free gas (Free Gas Index, FGI) in shales. The results for each sample are presented in **Table 2**.

The data analysis from samples heated above 100°C revealed that, even though minor variations were still observed in the cumulated NMR porosity after each heating stage, these differences were within the expected porosity calculation error. Furthermore, the T_2 distribution peak value was centered on a constant time after heating the samples above 90°C. At low saturation levels, it has been observed that water can form puddles and surface layers in the corner of small pores (Allen et al., 2001; Allen et al., 1998). Once heated above the boiling point, vaporized water molecules confined in small pores are unable to escape the sample and instead condense again into the liquid phase due to the cohesive forces of attraction (Gregg and Sing, 1982; Rouquerol et al., 1999). This could explain the observed T_2 signal even after heating the samples above 100°C. In addition, the inversion algorithm used allows the detection of signal coming from protons in the smaller pores, but it can also enhance any noise in the system and may introduce error into porosity interpretation. That's why for samples heated above 100°C, the NMR signal after 1 ms is disregarded as artificial porosity induced by the software's inversion process.

Based on the analysis of results for the four oven-dried samples, the two samples remaining were oven-dried at 65°C and T_2 measurements were made. The T_2 distribution for the six samples in their irreducible saturation state is shown as green dotted lines in **Figure 2**. The T_2 cut-off for samples AC-3 and AC-4 was calculated to be 0.22 ms and 0.23 ms respectively. The median and average T_2 cut-off for the six samples was 0.25 ms. Based on the analysis conducted on shale samples, a T_2 cut-off of 0.25 ms is proposed (**Figure 4b)** to discriminate between CBW and FGI (free gas index).

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Using Prospa © software from Magritek, the signal from the water at irreducible saturation level (S_{wirr}) was subtracted from the fully saturated spectrum. The resulting T_2 decay was then inversed using the same algorithm to obtain the T_2 distribution for the free fluid spectrum, shown as blue dashed lines in **Figure 2**.

The laboratory re-saturation process can often induce micro-fractures in shale cores and part of the porosity detected by NMR could be in fact water stored in them. Therefore, in order to get a better understanding of the fluid distribution in the rock, the acquisition of T_2 spectra after centrifuging the core samples at low speed is recommended.

4.2   Repeatability and Effect of High Temperature on Shale Structure

After heating the first set of four samples up to 160°C, two of the samples (AC-1 and AC-2) were re-saturated and oven-dried for repeatability. The saturation and drying process were replicated following the same protocol and the same vacuum oven was used to dry the samples at 14 different set temperatures: 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C, 120°C, 130°C, 140°C, 150°C, 160°C and 200°C. After a constant weight was achieved for each sample at each set temperature, NMR measurements were made and T_2 distributions were obtained.

After NMR measurements were made, the cumulative NMR porosity for the oven-dried samples was again plotted against temperature and two trends were identified (**Figure 5**). The minimum temperature at which the sample has to be heated to reach irreducible saturation level was calculated to be 59.6°C for sample AC-1 and 59.5°C for sample AC-2. The T_2 cut-off was calculated to be 0.14 ms for sample AC-1 and 0.13 ms for sample AC-2. Again, the signal from the water at irreducible saturation level shown as green dashed lines in **Figure 6** was subtracted from the fully saturated spectrum. The resulting T_2 decay was then processed using the same algorithm to obtain the T_2 distribution for the free fluid spectrum, shown as blue dashed lines in **Figure 6**.

The total NMR porosity for the samples fully saturated remained relatively unchanged in the repeated experiment, being 10.18% for sample AC-1 (+0.12%) and 10.28% for sample AC-2 (+0.24%). As a result, the decrease in the calculated T_2 cut-off can be directly correlated to an increase of the free gas porosity, confirmed by the decrease in the calculated CBW volume. Furthermore, the T_2 distribution of the samples in their fully saturated state (S_w=100%) after being heated up to 160°C and then re-saturated shows a shift towards the left, suggesting that the high temperature may have affected the structure of the matrix pores. While the maximum temperature used in

this study was not high enough to produce a dehydroxylation of clays, a mechanism of dehydration-rehydration has been identified below 200°C (Bray et al., 1998; Drits and McCarty, 2007; Hall et al., 1986; Hueckel, 2002). Although this process is reversible at low temperatures, the temporary loss of water in the interlayer of clays produces a permanent change in the pore structure of shales.

This experiment has been found to be repeatable, but shale samples should not be heated above the recommended temperature of 65°C to avoid changes in the pore structure.

5.   Conclusion

This study presented a simple approach to determine a T_2 cut-off for shales to discriminate between producible and total porosity.

Micro-fractures can be induced across the core samples while the re-saturation process takes place, so the type of brine should be cautiously selected to minimize clay swelling. Analysis of the data shows that while a conventional centrifuge doesn't provide enough capillary pressure to remove water from the matrix pores of shale samples, it can help to expel water stored in larger pores and micro-fractures.

Due to the small nature of the pores in shales and the complexity of the pore network, some water remains in the rock after heating it at high temperature. This results in detectable NMR T_2 signal even after exposing the sample to a temperature above the water boiling point.

High temperature can induce the temporary loss of interlayer water in clays, affecting the shale pore structure permanently. Therefore, shales should not be heated above the recommended temperature of 65°C. Oven-drying shale samples at this temperature can be a feasible method to determine a cut-off between free gas porosity and clay bound water. This procedure allows a more accurate characterization of fluid distribution in shales, crucial for a good petrophysical characterization, and can be replicated in any other sample. The average and median T_2 cut-off for this set of six samples from the Carynginia formation was found to be 0.25 ms. The use of this T_2 cut-off for permeability estimation is currently being investigated.

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Table 1. Mineralogical composition and TOC from geochemical studies for three samples from the Perth basin.

Sample	Quartz (Wt. %)	Clay (Wt. %)	Carbonates (Wt. %)	Other Minerals (Wt. %)	TOC (Wt. %)
AC-1	24.5	55.7	4.8	15	3.03
AC-4	53	31.1	2.1	13.8	0.64
AC-5	41.3	40.7	2.8	15.1	1.82

Table 2. NMR total porosity, minimum heating temperature, calculated bulk volume irreducible NMR porosity, T2 cut-off and calculated free gas index (FGI) NMR porosity for each sample.

Sample	Minimum Temperature (ºC)	BVI (%)	$T_{2 \text{ cut-off}}$ (ms)	FGI (%)
AC-1	63.8	3.3	0.26	6.7
AC-2	60.6	3.3	0.24	6.7
AC-5	60.1	2.4	0.24	5.7
AC-8	59.2	2.1	0.24	11.0

Figure 1. Map of the Perth Basin (DMP-WA, 2014)

Figure 2. NMR T_2 distribution for shale samples studied.

Figure 3. NMR T_2 distribution for shale samples before and after being oven-dried

Figure 4. a) NMR total porosity plotted against temperature at which the sample was heated previous to the measurement. b) NMR measurement of sample fully saturated (S_w=100%) and at irreducible saturation level (S_{wirr}) to calculate a T_2 cut-off value (T_{2c})

Figure 5. NMR total porosity of samples AC-1 and AC-2 plotted against temperature at which the sample was heated for the repeated experiment.

Determination of NMR T2 cut-off for clay bound water …..

Figure 6. NMR T_2 distribution for shale samples AC-1 and AC-2 at different saturation levels. Results from the first experiment are shown as solid lines and results from the repeated experiment are shown as dashed lines.

Highlights

- This study presents a simple approach to determine a T_2 cut-off for shales to discriminate between producible and total porosity.

- Oven drying shale samples at 65°C can be a feasible method to determine a cut-off between free gas porosity and clay bound water.

- The average and median T_2 cut-off was found to be 0.25 ms.

- The use of this T_2 cut-off for permeability estimation is currently being investigated.

Determination of NMR T2 cut-off for clay bound water …..
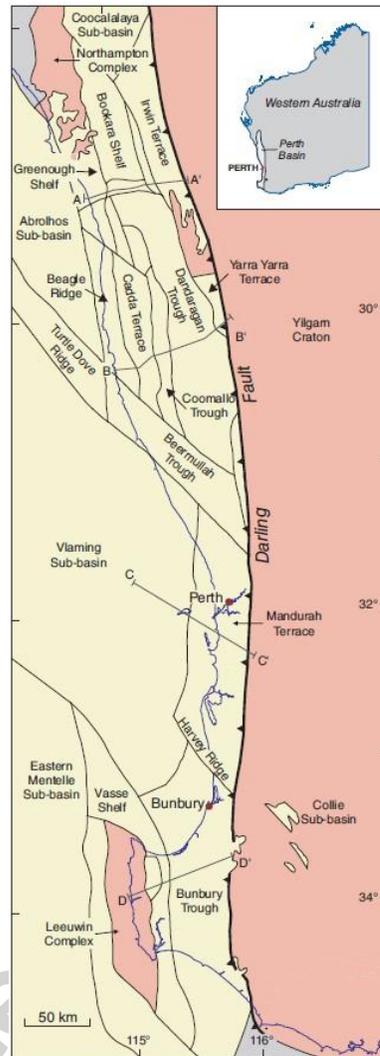
Figure 1. Map of the Perth Basin (DMP-WA, 2014)

Determination of NMR T2 cut-off for clay bound water …..
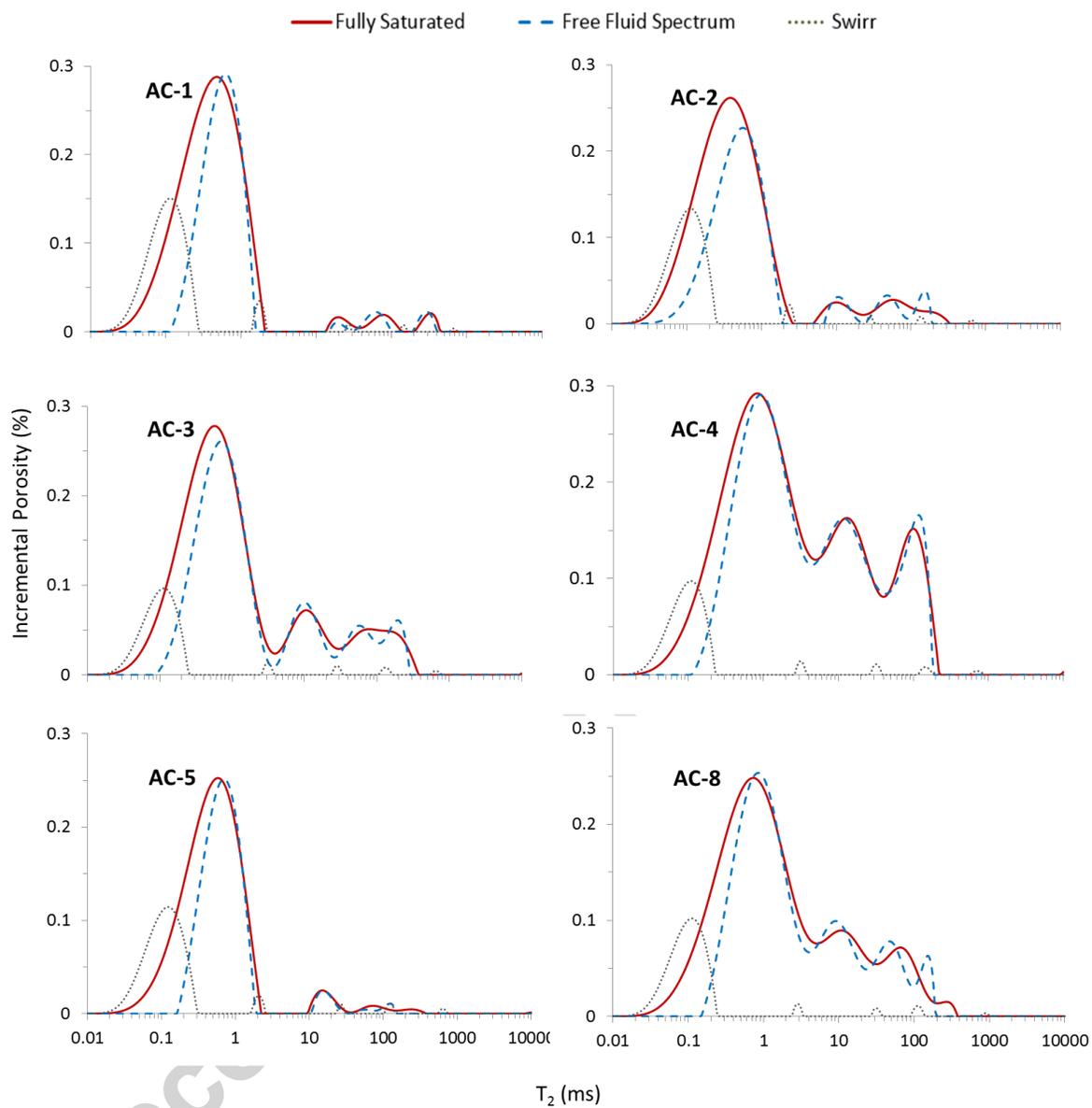
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Determination of NMR T2 cut-off for clay bound water …..
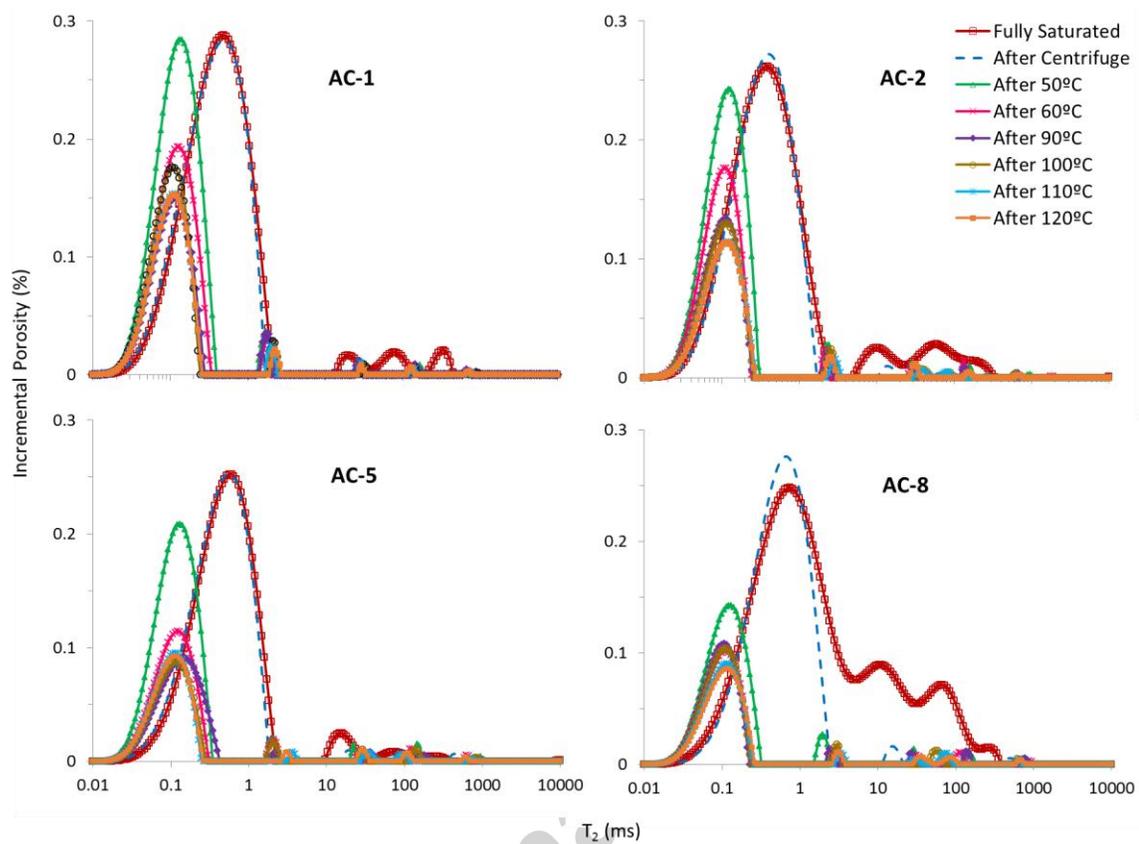
Figure 3. NMR T_2 distribution for shale samples before and after being oven-dried

Determination of NMR T2 cut-off for clay bound water …..
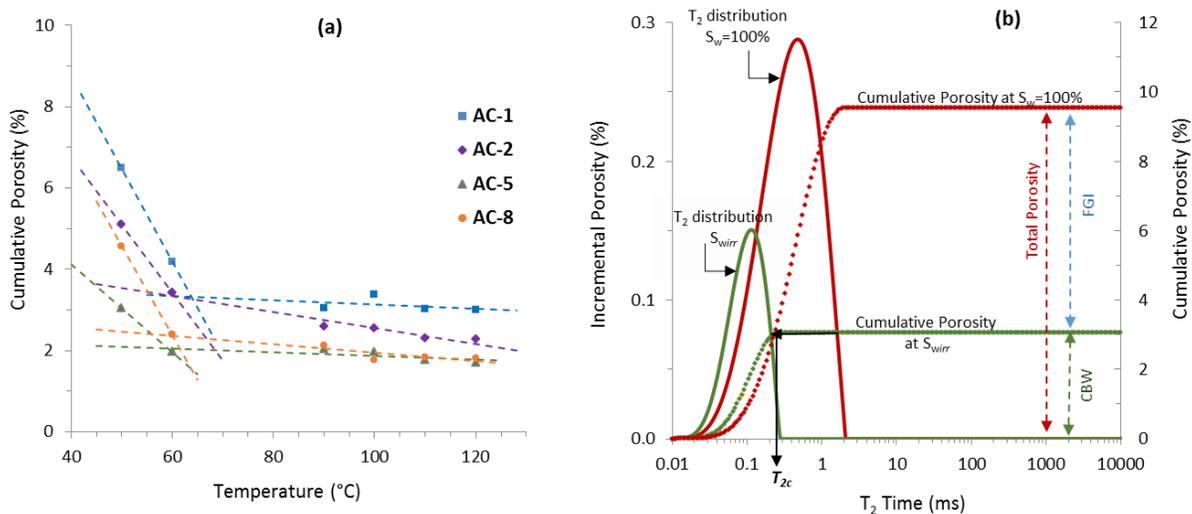
Figure 4. a) NMR total porosity plotted against temperature at which the sample was heated previous to the measurement. b) NMR measurement

of sample fully saturated (S_w=100%) and at irreducible saturation level (S_{wirr}) to calculate a T_2 cut-off value (T_{2c})

Determination of NMR T2 cut-off for clay bound water …..
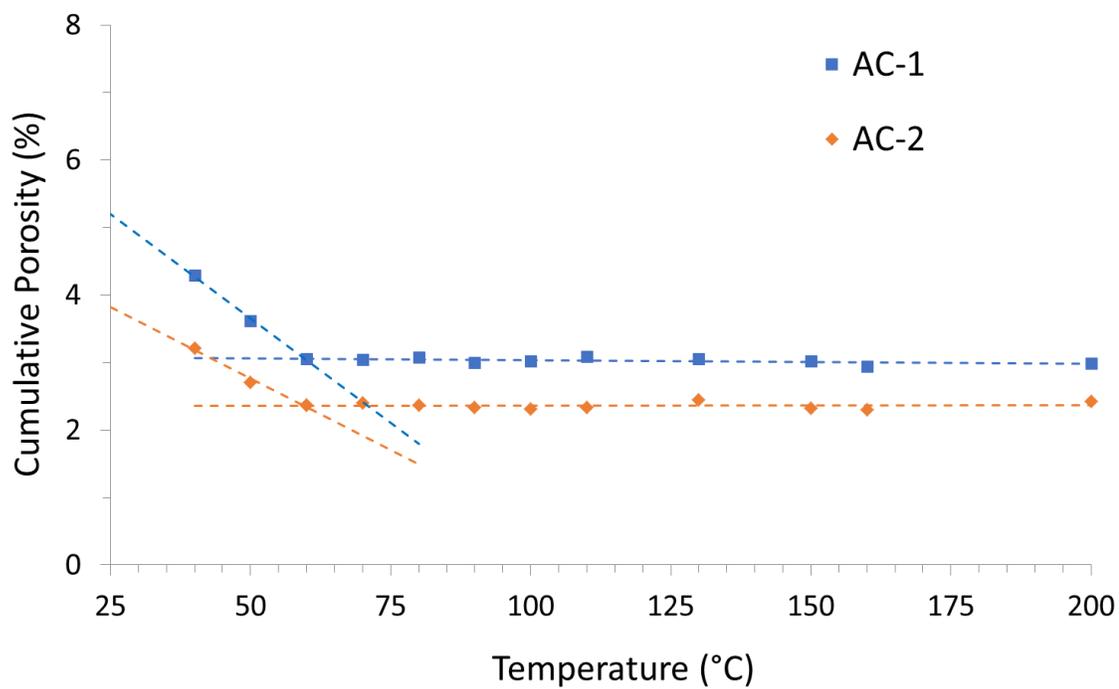
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Determination of NMR T2 cut-off for clay bound water …..
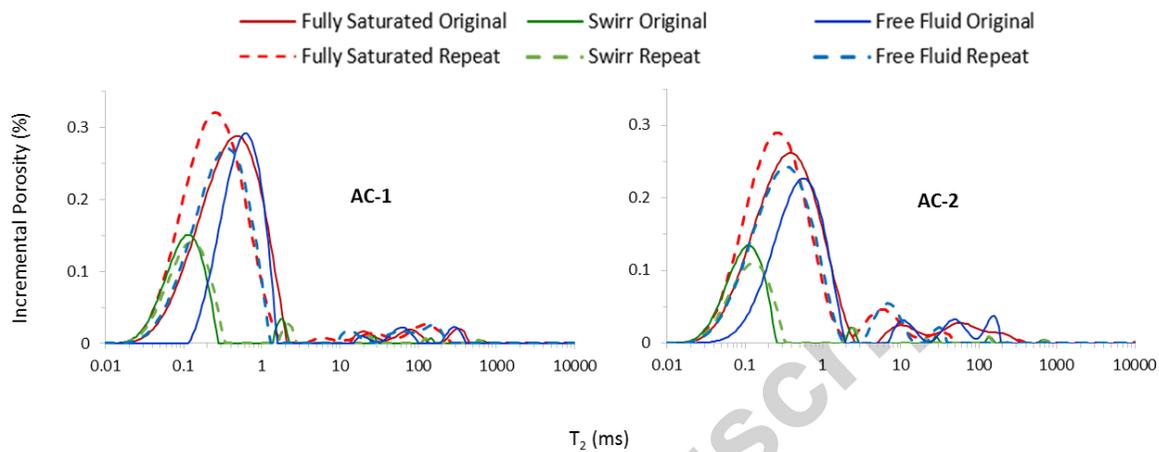
Figure 6. NMR T_2 distribution for shale samples AC-1 and AC-2 at different saturation levels. The first experiment results are shown as solid lines and the second experiment results are shown as dashed lines.