

## **NMR T1-T2 Response of Moveable and Non-Moveable Fluids in Conventional and Unconventional Rocks.**

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### **ABSTRACT**

Recent publications have shown that liquid rich shales can also contain a significant proportion of high viscosity hydrocarbons that are not producible in tight rocks such as shales [1], [2]. NMR theory of fluid relaxation suggests that the ratio of T1/T2 can be used to differentiate low viscosity fluids (moveable) and highly viscous fluids. In the present study we have investigated the NMR response of moveable and non-moveable fluids in conventional and unconventional reservoir rocks using T1-T2 correlation maps obtained with a TE = 100 $\mu$ sec.

Berea sandstone, Lyons sandstone, and Bossier tight sands were saturated at 3000 psi with 2.5% KCl brine. The corresponding T1-T2 maps show that T1/T2= 1.5. In two Wolfcamp shale samples from an oil producing well, we observed for the “native” state a NMR signal with a T1/T2 ratio of 1.3. An increase in amplitude of the “native” state NMR signal was observed after the shale samples imbibed 2.5% KCl brine for 24h. However, the imbibition of dodecane for 24h by the shale samples gave rise to a NMR signal with a T1/T2 ratio of 3 for one shale sample and 2.5 for the other sample. These experiments show that moveable brine in rocks has a T1/T2 ratio close to 1.5 while the T1/T2 ratio for moveable oil is close to 3.

The study of non-moveable hydrocarbons was conducted on solid bitumen and wax. In their bulk solid state, solid bitumen and wax have T1/T2 ratios of 20 and 400, respectively. However, these ratios decreased and approached a value of 2 to 3 after the hydrocarbons were liquefied. Liquid wax was also introduced in a Berea sandstone sample, and allowed to solidify within the rock. The NMR T1-T2 map of Berea saturated with solid wax show a T1/T2 ratio of 400. These results imply that non-moveable hydrocarbons are not affected by surface relaxivity and have T1-T2 ratios higher than moveable hydrocarbons.

### **Introduction**

Inspired by the success story of the Barnett shale, the oil and gas industry has produced a considerable amount of natural gas from various shale formations since 2000. However, the low natural gas price has shifted the interest from natural gas to oil rich shales. Liquid rich shales present more complexity in the quantification of producible hydrocarbons. Some of the quantification issues arise from the presence of non-negligible quantity of high viscosity bitumen, which is considered to be non-moveable hydrocarbon.

Rylander et al., (2013) [2] reported that high viscosity bitumen constitutes over half of the hydrocarbon in place in some part of the Eagle Ford shale. Solid bitumen and moveable oil have the same signature on neutron and density log. Therefore solid bitumen can be misinterpreted as producible hydrocarbon.

To overcome this shortcoming of conventional logs, Ramakrishna et al., (2012) [3] and Rylander et al., (2013) [2] have used NMR to detect the proportion of non-moveable hydrocarbons respectively in the Green River formation and the Eagle Ford shale. In the present study we have conducted a systematic study on the 2D NMR response of moveable and non-moveable fluids which can be used as guideline to differentiate moveable and non-moveable fluids in laboratory and downhole conditions.

### **Materials and Experimental procedure**

For the purpose of this study, we acquired the T1-T2 maps of various fluid saturated rocks, wax and solid bitumen at an echo spacing (TE) of 100 $\mu$ sec, with a 2 MHz Oxford Geospec 2 NMR instrument. The fluids used are deionized water, 2.5% KCl brine, dodecane and crude oil. Sandstones and shales plugs of approximately one inch (length and diameter) were used. The sandstones were Berea, Lyons and Bossier, having porosities of 18%, 6% and 8%, respectively. We used 2 Wolfcamp shale samples whose properties are summarized in Table I.

The wax sample was a commercial canning wax and the solid bitumen sample was an Ozocerite sample provided Dr. Cardott from the Oklahoma Geological Survey.

To study the NMR response as function of viscosity, the wax and solid bitumen samples were heated to their melting point by flowing heated nitrogen through the sample tube.

Table I: Properties of the Wolfcamp shale samples.

sample ID	Crushed helium porosity (%)	Total clays (wt%)	Total carbonates (wt%)	TOC (wt%)
W-xx03	6.4	71	5	1.7
W-xx18	7.3	36	10	8.5

## **Results**

### **T1-T2 maps of moveable bulk fluids**

Figure 1 shows the NMR T1-T2 maps of the moveable fluids in their bulk states. We observed that for all the bulk fluids studied T1=T2. This result is in agreement with the BPP theory developed by Bloomberg et al., (1948) [4].

### **T1-T2 maps of saturated rocks**

The T1-T2 maps on Figure 2 show that for all the sandstones saturated with 2.5 % KCl, T1/T2=1.5. However, when we saturated the Berea sample with methane at 4000 psi, T1/T2=3.

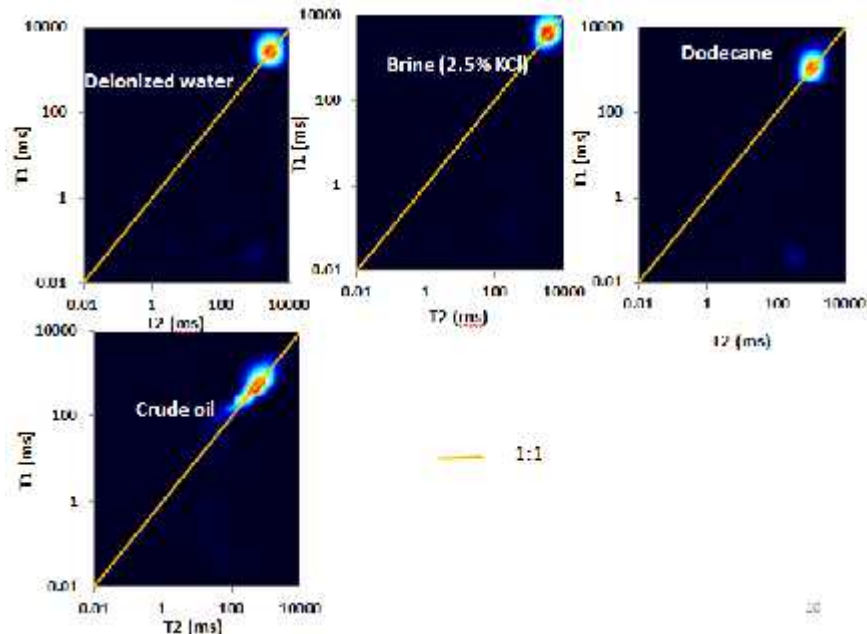


Figure 1: T1-T2 maps of moveable fluids in bulk state. For bulk moveable fluids  $T1=T2$ . A range of  $T1=T2$  values is observed for crude oil because of the different components forming this crude oil sample.

We acquired the T1-T2 maps for the Wolfcamp shale samples in the “native” state, after brine imbibition, and dodecane imbibition (Figure 3). The “native” state is equivalent to an “as received” state, fundamentally unknown saturation state. We observe after brine imbibition an increase in amplitude at the same location as the “native” state signal. This amplitude has  $T1/T2=1.3$ , which is close to the value of  $T1/T2=1.5$  obtained for sandstone. This implies that the fluid contained in the native samples was residual brine. However, after dodecane imbibition, an amplitude increase is noticed at longer time than the brine amplitude. This amplitude has a  $T1/T2$  ratio of 3 for sample W-xx03, and 2.5 for sample W-xx18.

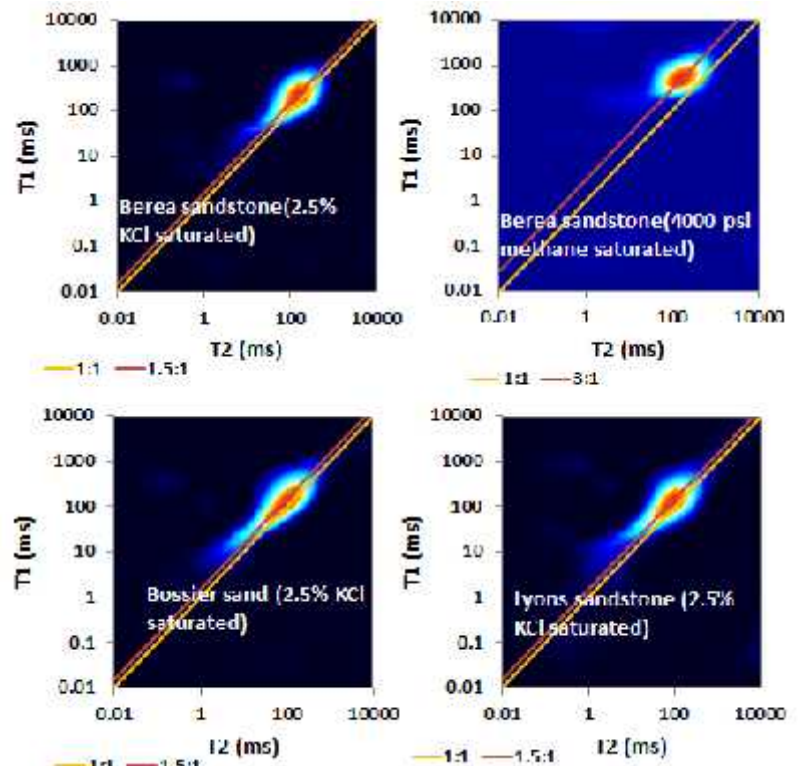
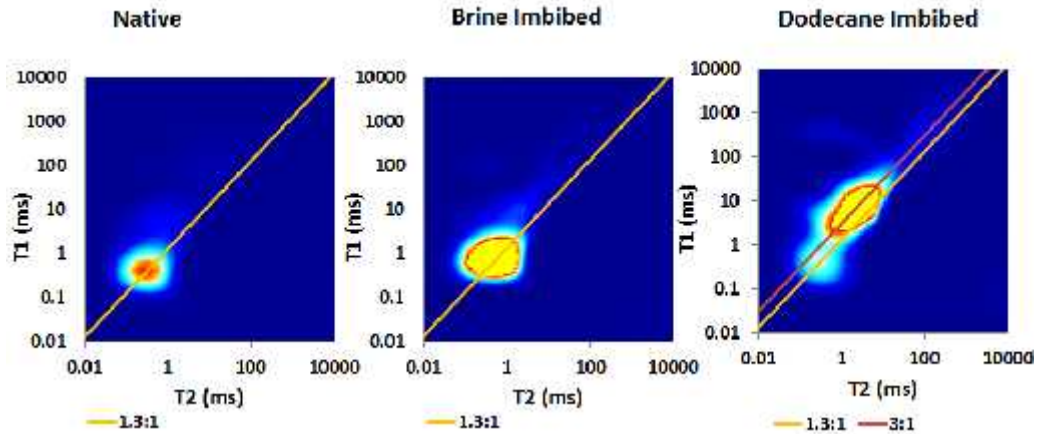
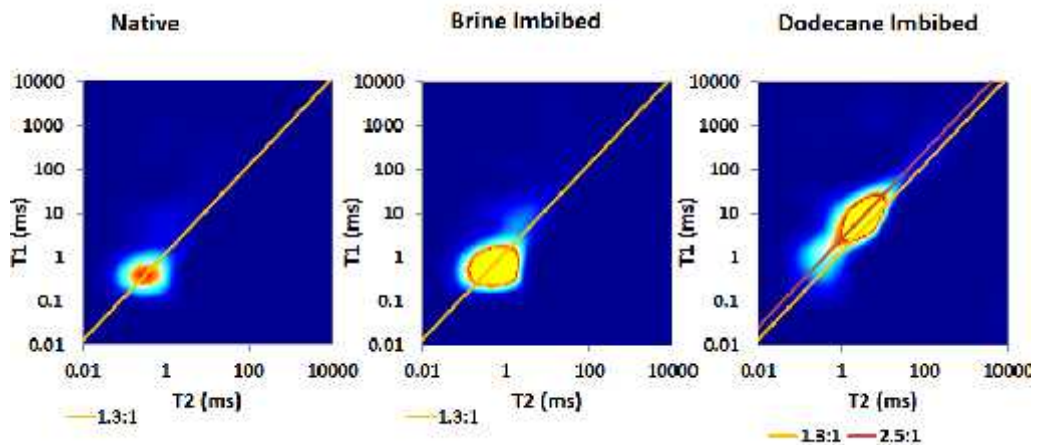


Figure 2: T1-T2 maps of various brine saturated sandstones. All the sandstones saturated with 2.5% KCl have  $T1/T2=1.5$ , while Berea sandstone saturated with methane at 4000 psi has  $T1/T2=3$ .



W-xx03



W-xx18

Figure 3: NMR T1-T2 maps of Wolfcamp samples. Dodecane and brine can be distinguished by their T1/T2 ratios. Brine has T1/T2=1.3, while dodecane has a T1/T2 ratio of 3 for sample W-xx03 and 2.5 for sample W-xx18.

### T1-T2 maps of wax and bitumen as a function of temperature

Figure 4 and Figure 5 show the T1-T2 maps for wax and solid bitumen as a function of temperature. We observed that solid wax and bitumen have high T1/T2 ratios, 20 for bitumen and 400 for wax. However, after the samples are heated to their melting points this ratio decreases to 2 for wax and 3 for bitumen.

### Berea sample

To study the response of solid hydrocarbon within porous media we have injected melted wax within a Berea sample at 1000 psi. The molten wax was allowed to solidify within

the Berea sample under pressure. Figure 6 shows the NMR response of solid wax within a Berea sample as well as the NMR T1-T2 map of melted wax within the same Berea sample. The NMR T1-T2 map of the solid wax within Berea is identical to the map of bulk solid wax (Figure 4). Therefore, solid hydrocarbons are not affected by surface relaxivity. The melted wax within the Berea sample shows a T1-T2 ratio of 1.2. This value is close to the T1/T2 ratio of brine saturated sandstone.

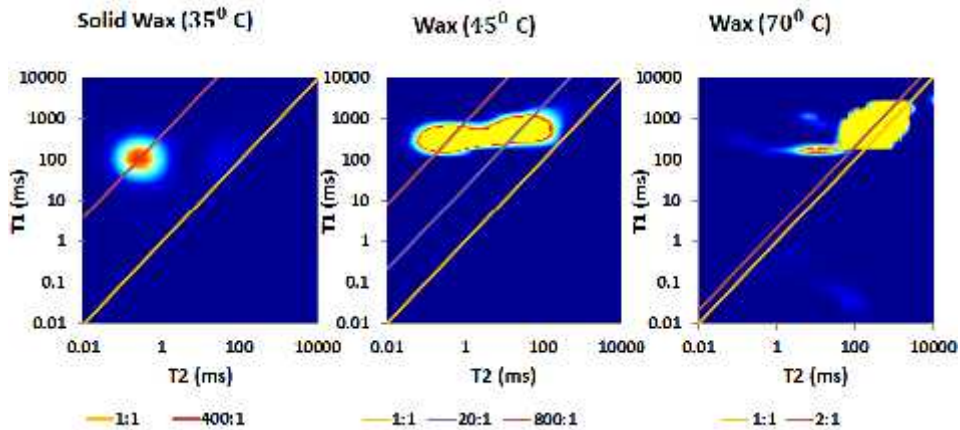


Figure 4: NMR T1-T2 maps of wax as function of temperature. At 45°C we observe two amplitudes reflecting a temperature gradient within the sample.

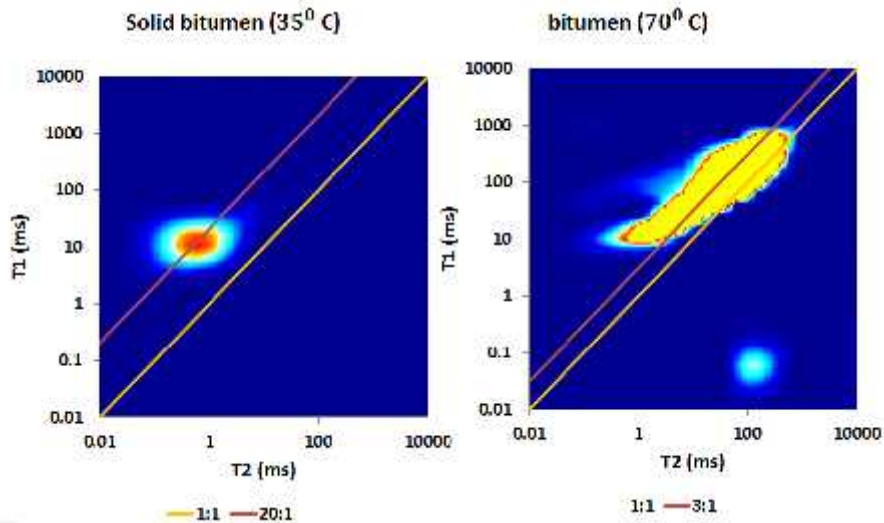


Fig. 5: NMR T1-T2 maps of bitumen as function of temperature. On the map at 70°C, we observed an amplitude around T2=100 ms and T1=0.3ms due to a numerical instability in the inversion algorithm.

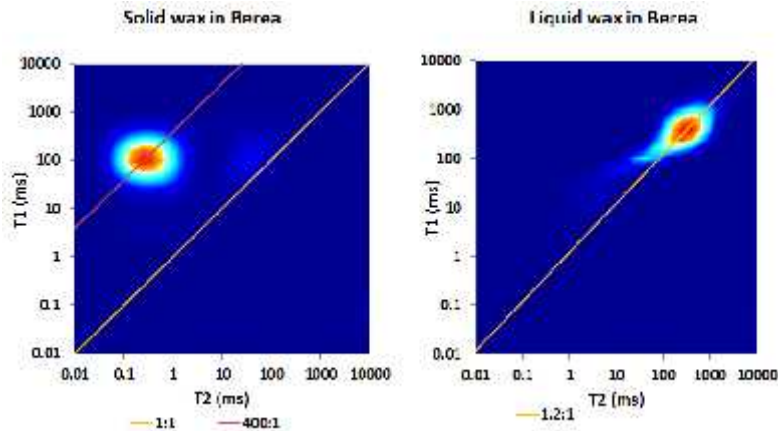


Fig. 10: NMR T1-T2 maps of solid and melted wax within a Berea sample. The liquid wax map was acquired at a temperature of 70 °C. The liquified wax inside Berea has a response similar to brine in the Berea.

### Conclusion:

The study described above shows that the NMR T1/T2 ratio can be used to distinguish between moveable and non-moveable hydrocarbons, in conventional rocks like sandstone or unconventional shales. For bulk moveable fluids we expect  $T1=T2$ . Various brine saturated sandstones have a constant T1/T2 ratio of 1.5. Non-moveable fluids have high T1/T2 ratios which depend on their molecular weight. These high viscosity fluids are not affected by surface relaxivity when they are injected in porous media. In the Wolfcamp shale samples studied, moveable oil has a T1/T2 ratio equal to 2.5-3, while the T1/T2 ratio for brine is 1.3.

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### References

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