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NMR at Different Temperatures to Evaluate Shales

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Summary

One of the most important elements in reservoir characterization is identification of fluids present. Fluid typing tests on rock core samples can give a good indication of fluids present in a reservoir. NMR logging and NMR rock core analysis have had success in fluid typing of unconventional reservoirs where other methods had limited success (i.e. Dean Stark extraction). A variety of NMR techniques, including T_2 relaxation, T_1 relaxation, T_1-T_2 correlation maps, T_2-Diffusion correlation maps, and T_2-Store-T_2 correlation maps, have successfully been used in the past to determine different fluid types in reservoir rock. All but diffusion can be easily applied to shale reservoirs. Even so, these techniques often do not provide a complete picture of the fluid make up in the sample, due to difficulties identifying all the different fluids present in a sample.
In this work, we describe and demonstrate, how NMR techniques can be used, at different temperatures, to identify the different fluids present in a shale sample. Several examples will be shown at a variety of temperatures. Two different temperature techniques will be employed; 1) NMR measurements of samples at three temperatures (35°C, 60°C, and 110°C); 2) An Eagleford shale sample was tested in an overburden pressure and temperature cell at the following temperatures: 30°C, 40°C, 50°C, 60°C and 70°C. These techniques yield interesting results in relation to measuring not only fluid types but also the presence and quantity of different fluids in the sample.

Introduction

In this paper, T_2 relaxation as well as $T_1 - T_2$ maps and ratios were used to identify and quantify the amount of fluids present in shale samples. Ignoring diffusion effects, due to short echo times being used in this experiment, T_2 relaxation of a fluid in a pore is related to pore size as follows [1]:

$$\frac{1}{T_2} = \frac{1}{T_{2-Bulk}} + \rho \frac{S}{V} \qquad (1)$$

Where S/V is the surface to volume ratio of the pore, ρ is the relaxivity parameter and T_2-bulk is the T_2 relaxation time of the fluid.
Similarly, the T_1 relaxation of the fluid in the pore is related to pore size as follows [1]:

$$\frac{1}{T_1} = \frac{1}{T_{1-Bulk}} + \rho \frac{S}{V} \qquad (2)$$

In addition to T_2 and T_1 one dimensional measurements, a two-dimensional NMR measurement has been developed and proven useful for fluid typing in shales. This is a T_1-T_2 measurement which acquires both relaxation times at once [2]. T_1-T_2 data is usually displayed as a color 2D map with T_1-T_2 ratio lines shown. An example of T_1-T_2 map is shown below.

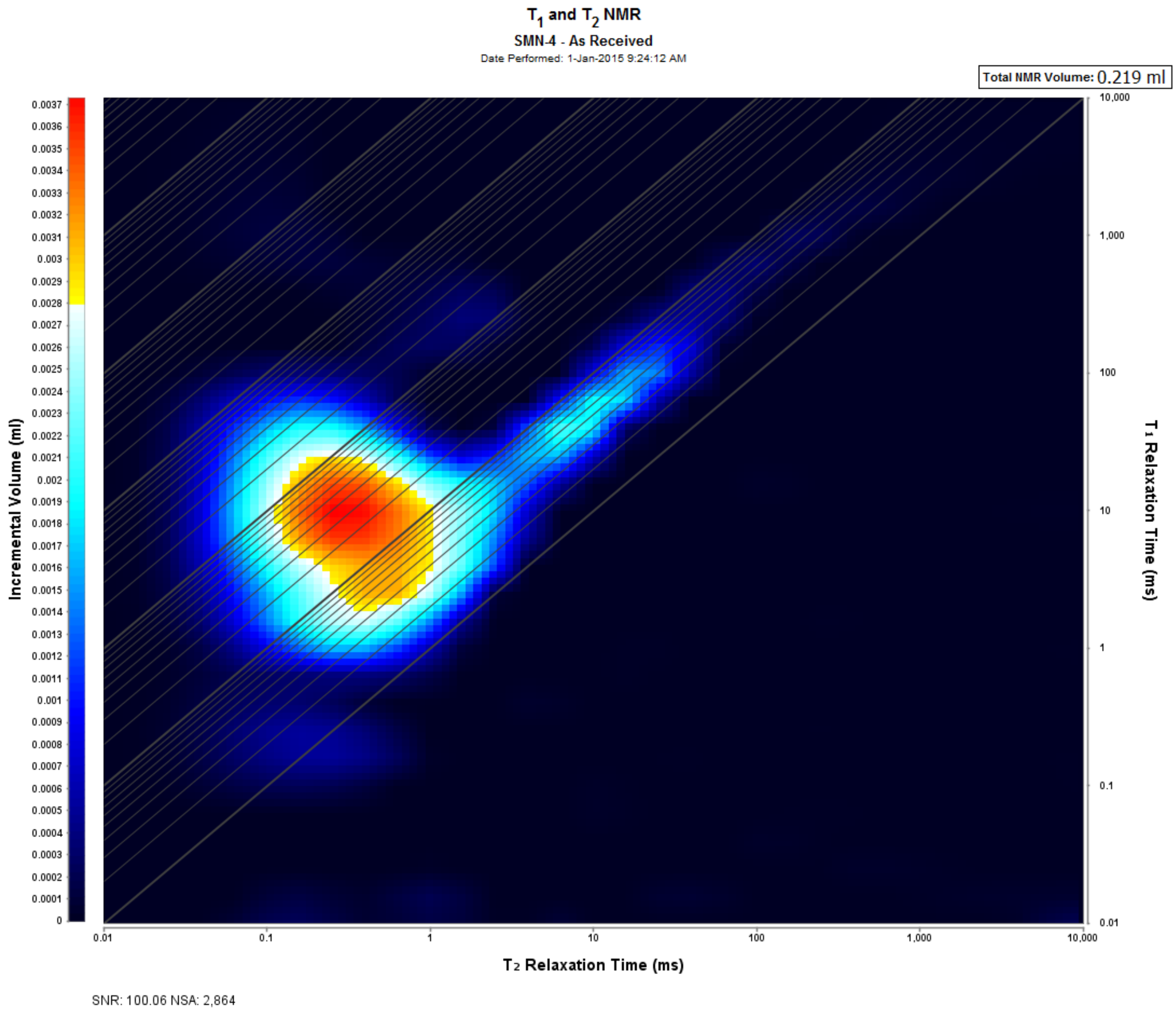


Figure 1: T_1-T_2 map of a shale with ratio lines spaced logarithmically. The diagonal corresponds to a T_1-T_2 ratio of 1.

T_1-T_2 ratio of a fluid is related to its viscosity, the higher the ratio the higher the viscosity [2], as shown in Figure 2. This idea was used to detect and quantify fluids (water and bitumen) in “as received” shale samples subject to different temperatures.

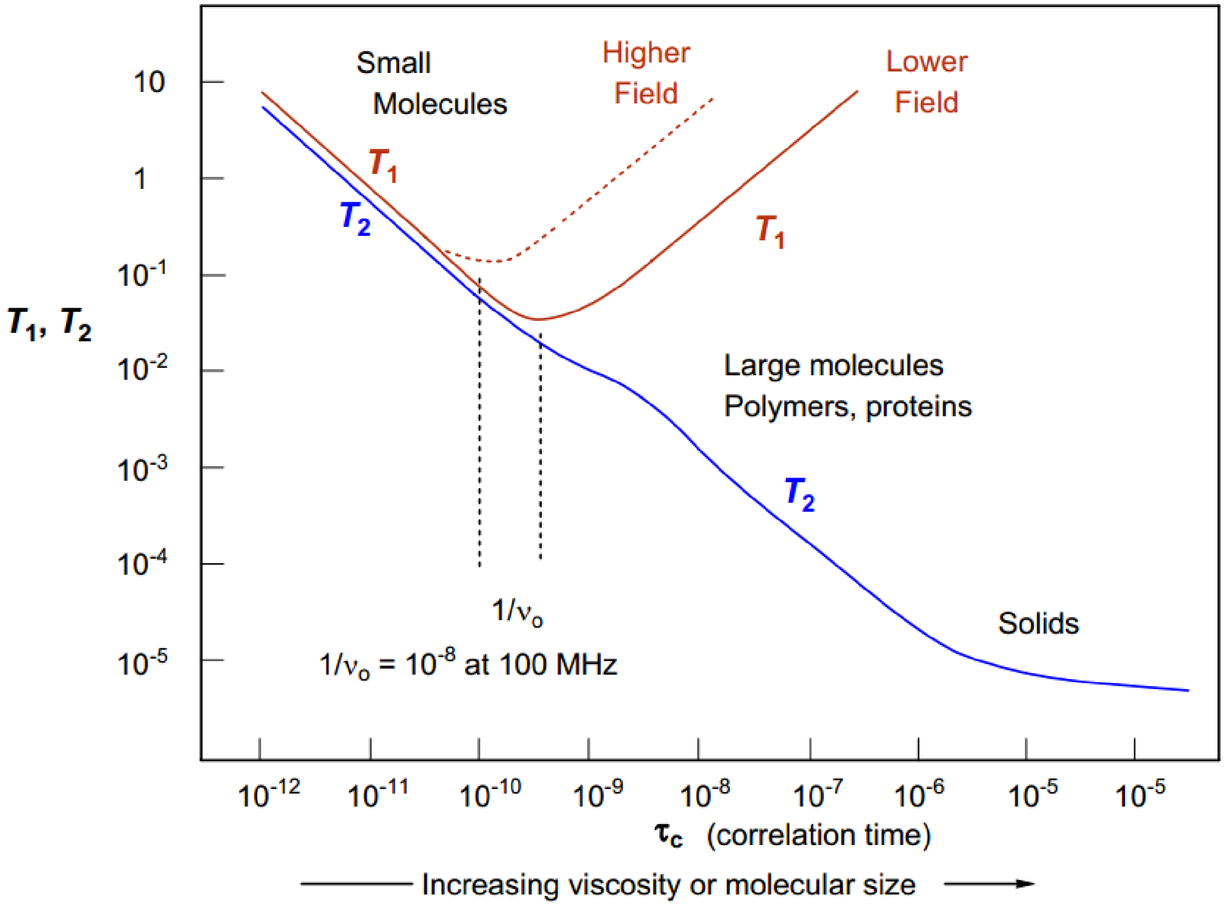


Figure 2: Effect of viscosity on T_1 and T_2.

Experiment

Nine samples were studied in a non-preserved fresh state. It was assumed that all mobile fluid and gas had escaped from the samples but heavier oil and bound/trapped fluids remained.

Table 1: Sample Identification

Well	Sample Number	Depth (ft)	Diameter (cm)	Length (cm)	Bulk Volume[1] (cc)
Shale 1	DF-1	12209.00	2.54	2.78	13.68
	DF-2	12228.20	2.54	4.4	20.38
	DF-3	12241.80	2.54	3.35	16.50
	DF-4	12250.00	2.53	3.59	14.50
Shale 2	SMN-1	13269.00	2.54	3.08	13.72
	SMN-2	13283.50	2.4	3.7	13.62
	SMN-3	13290.00	2.5	2.7	17.37
	SMN-4	13298.60	2.5	3.5	13.10
Eagleford Shale	EF-1		3.81	4.79	54.61

[1] Sample bulk volumes were calculated using Archimedes method.

T_2 and T_1-T_2 data was acquired at different sample temperatures using Oxford Instruments Geospec 2 MHz NMR spectrometer equipped with a 29 mm probe [3]. Data acquisition and processing was done using GITSystems Advanced software package [5]. Echo time (TE) used in the experiments was 0.1 ms. The short TE ensures most of the hydrogen (water in clays, bitumen, etc) was accounted for. This test does not provide information related to gas filled (or previously gas filled) pores. The temperatures for sample EF-1 were achieved by heating the confining fluid (fluorinated oil) used in a specialized high temperature and pressure probe. For all others, temperatures were achieved by blowing hot air over the sample.

Results

The T_2 data for as received samples at 35 C are shown below.

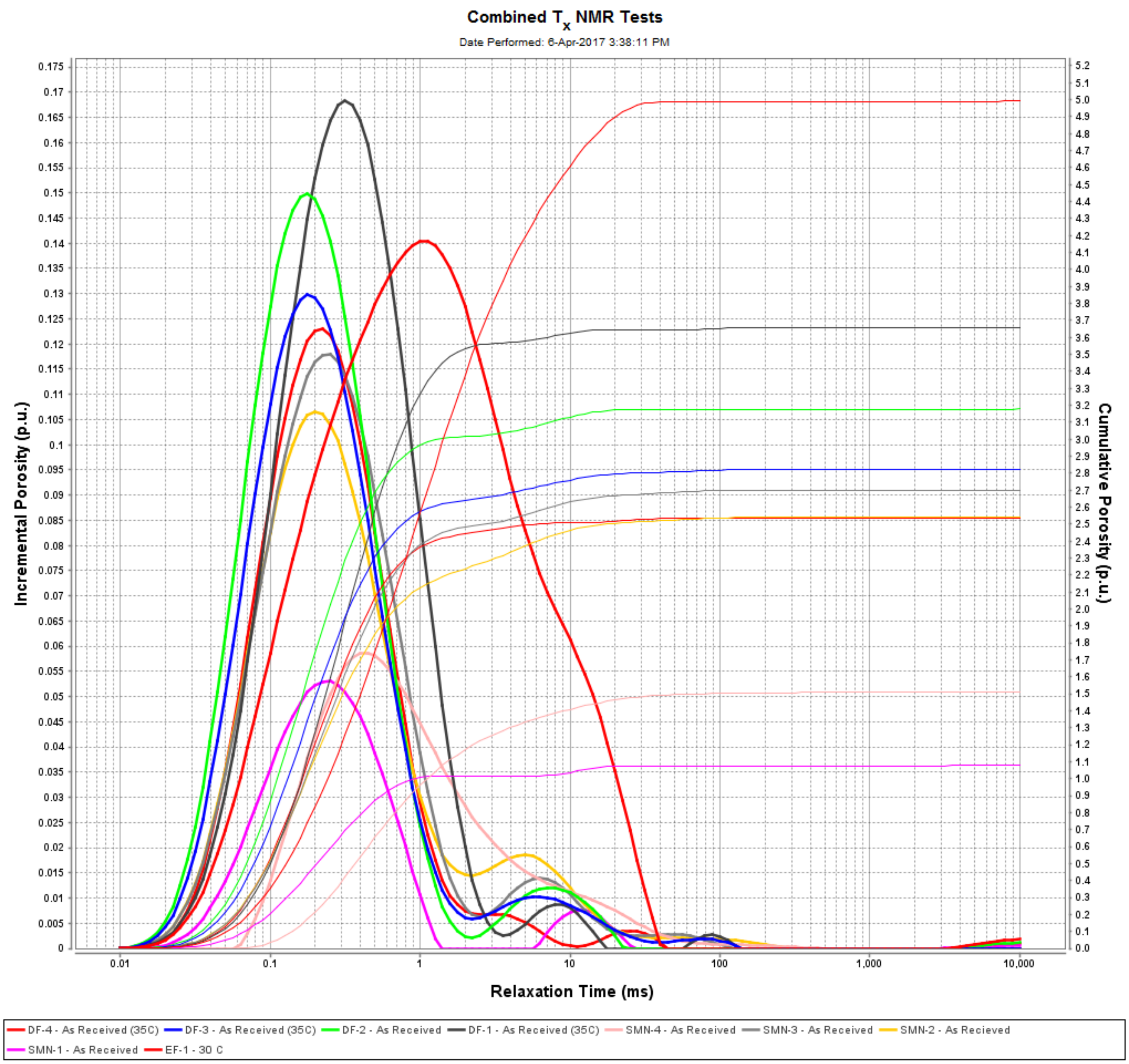


Figure 3: T_2 distributions of as received samples at 35 C

From Figure 3 we can see that sample NMR porosities are in the range of ~1 p.u. to ~5 p.u. T_2 data acquired at different temperatures yields the following results:

Table 2: NMR Porosity and T_2 log mean at different temperatures.

Sample No.	NMR Porosity, 35 C (p.u.)	NMR Porosity, 65 C (p.u.)	NMR Porosity, 110 C (p.u.)	NMR Log Mean, 35 C (ms)	NMR Log Mean, 65 C (ms)	NMR Log Mean, 110 C (ms)
DF-1	3.7	4.7	6.0	0.324	0.435	0.422
DF-2	3.2	3.3	3.0	0.217	0.225	0.222
DF-3	2.8	3.0	3.1	0.239	0.169	0.210
DF-4	5.0	4.8	4.1	1.038	0.849	1.426
SMN-1	2.6	3.6	3.3	0.190	0.156	0.207
SMN-2	2.5	2.6	2.4	0.330	0.250	0.267
SMN-3	2.7	2.4	1.9	0.306	0.247	0.306
SMN-4	1.5	1.5	1.3	0.849	0.453	0.597

Table 3: NMR Porosity and T_2 log mean at different temperatures.

Sample No.	NMR Porosity, 30 C (p.u.)	NMR Porosity, 40 C (p.u.)	NMR Porosity, 50 C (p.u.)	NMR Porosity, 60 C (p.u.)	NMR Porosity, 70 C (p.u.)
EF-1	2.5	3.3	3.6	3.9	5.9

Sample No.	NMR Log Mean, 30 C (ms)	NMR Log Mean, 40 C (ms)	NMR Log Mean, 50 C (ms)	NMR Log Mean, 60 C (ms)	NMR Log Mean, 70 C (ms)
EF-1	0.246	0.281	0.306	0.454	0.394

For a more visual presentation, data from the above tables is plotted in the following figures.

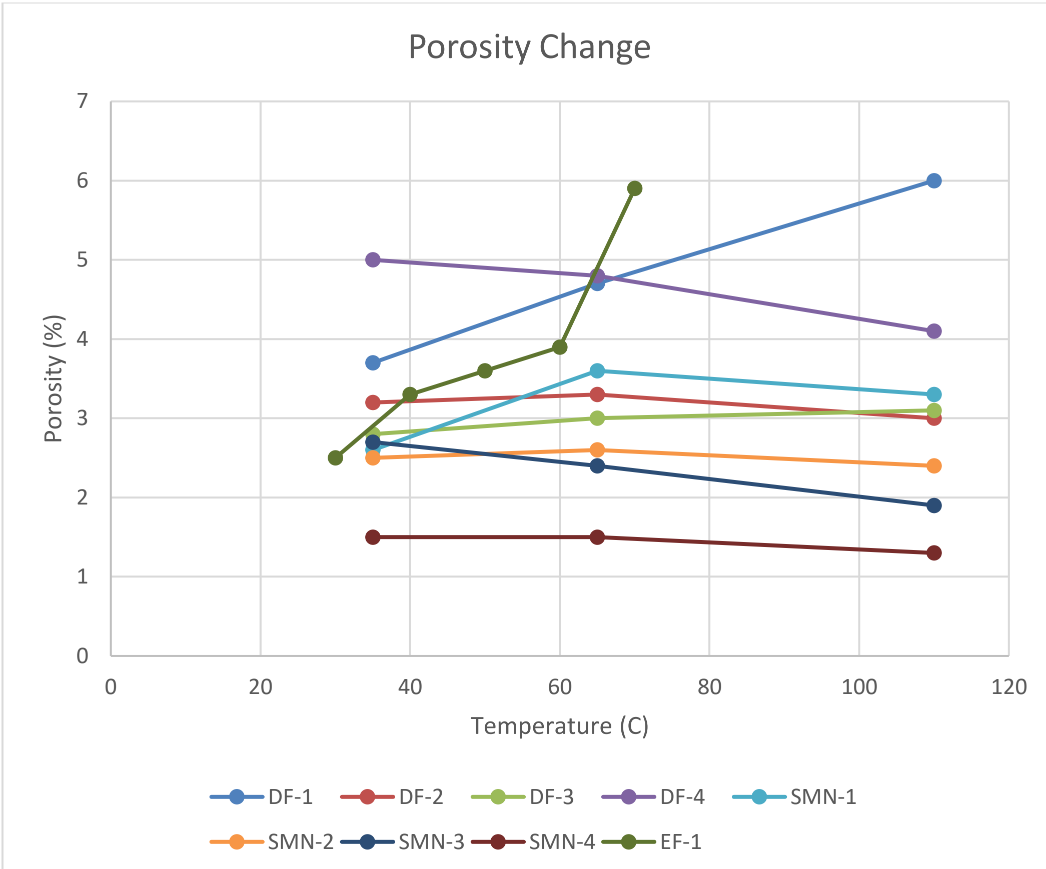


Figure 4: NMR Porosity change as a function of temperature.

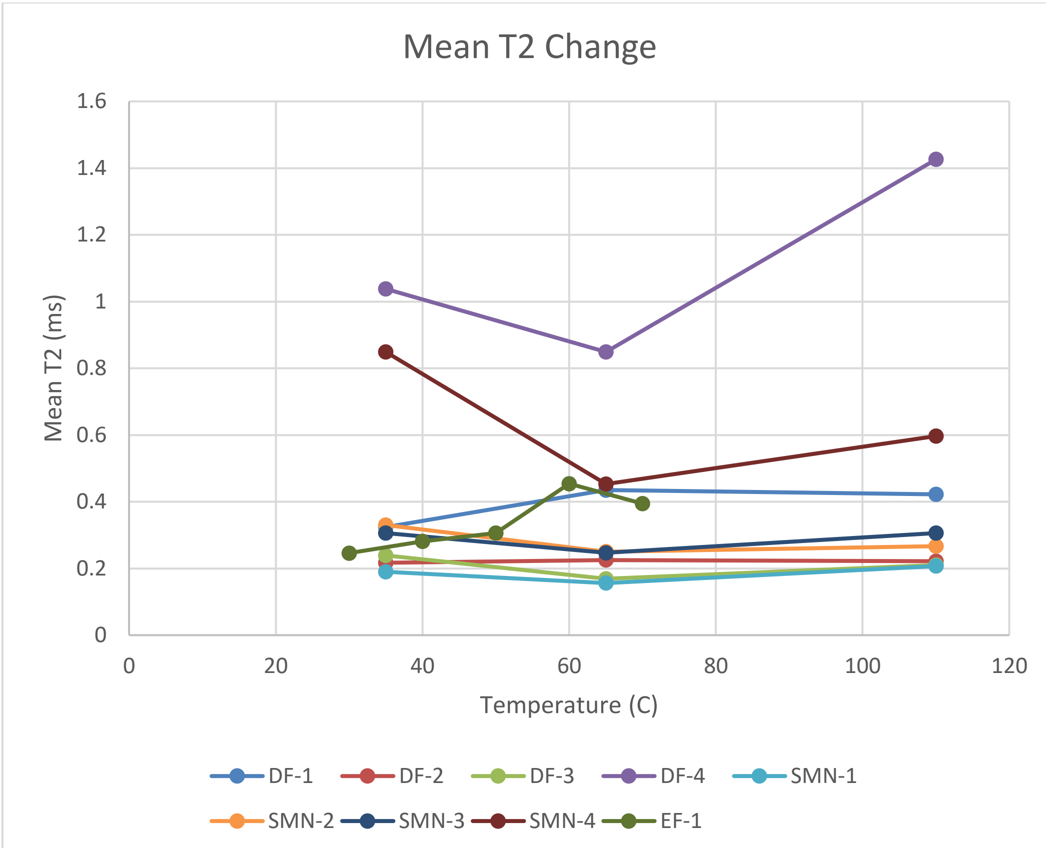
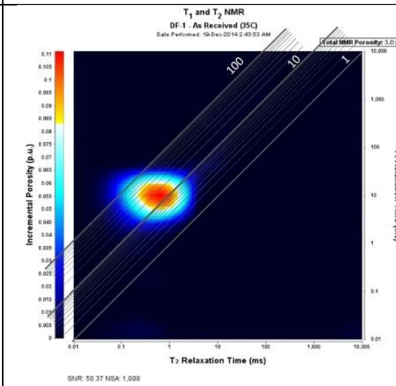
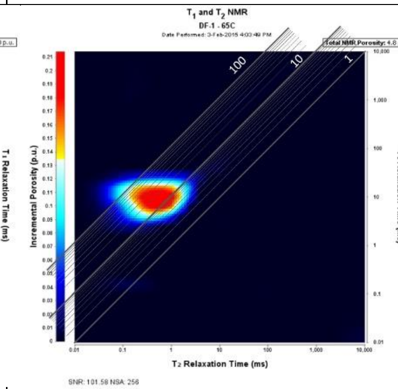
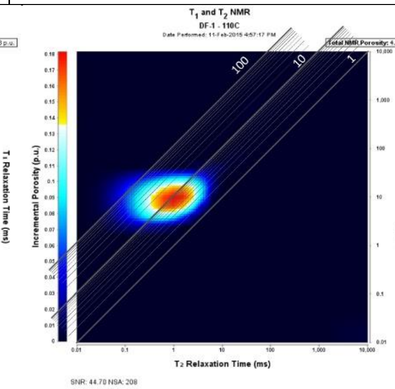
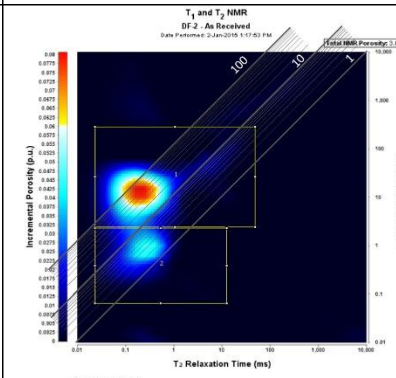
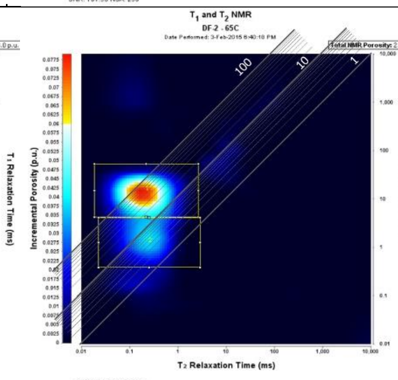
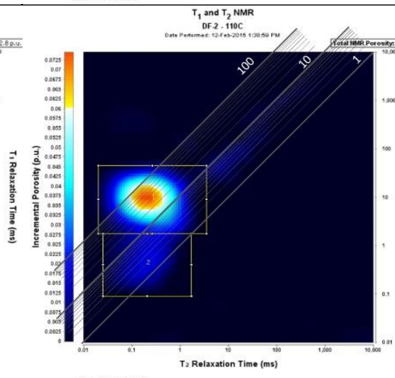
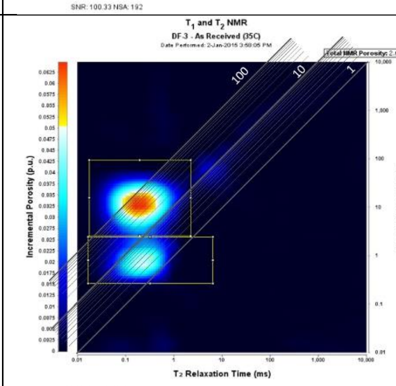
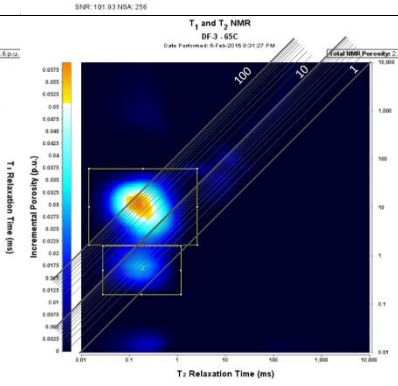
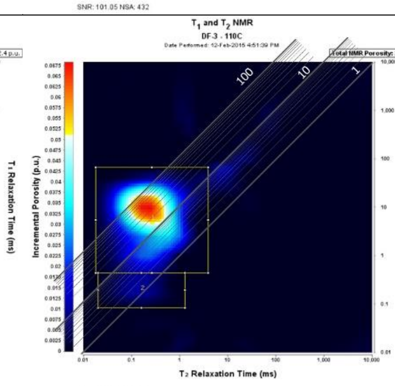
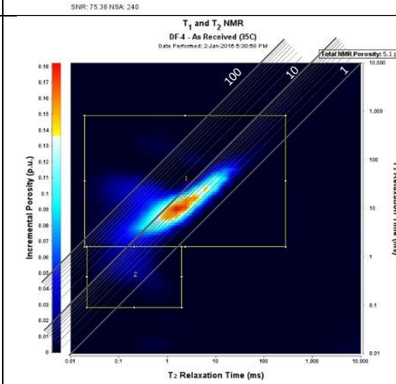
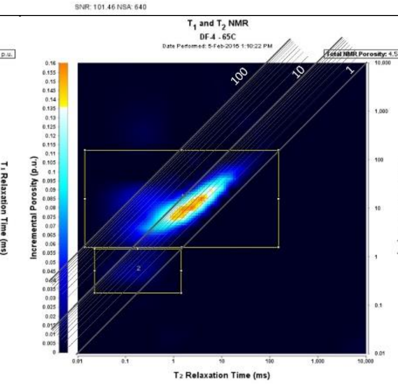
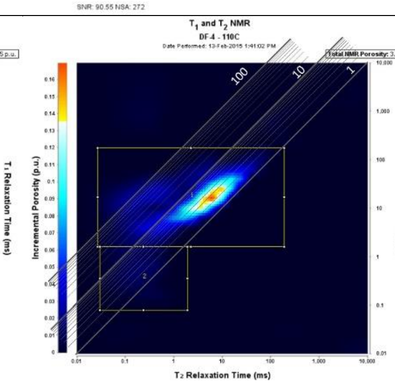
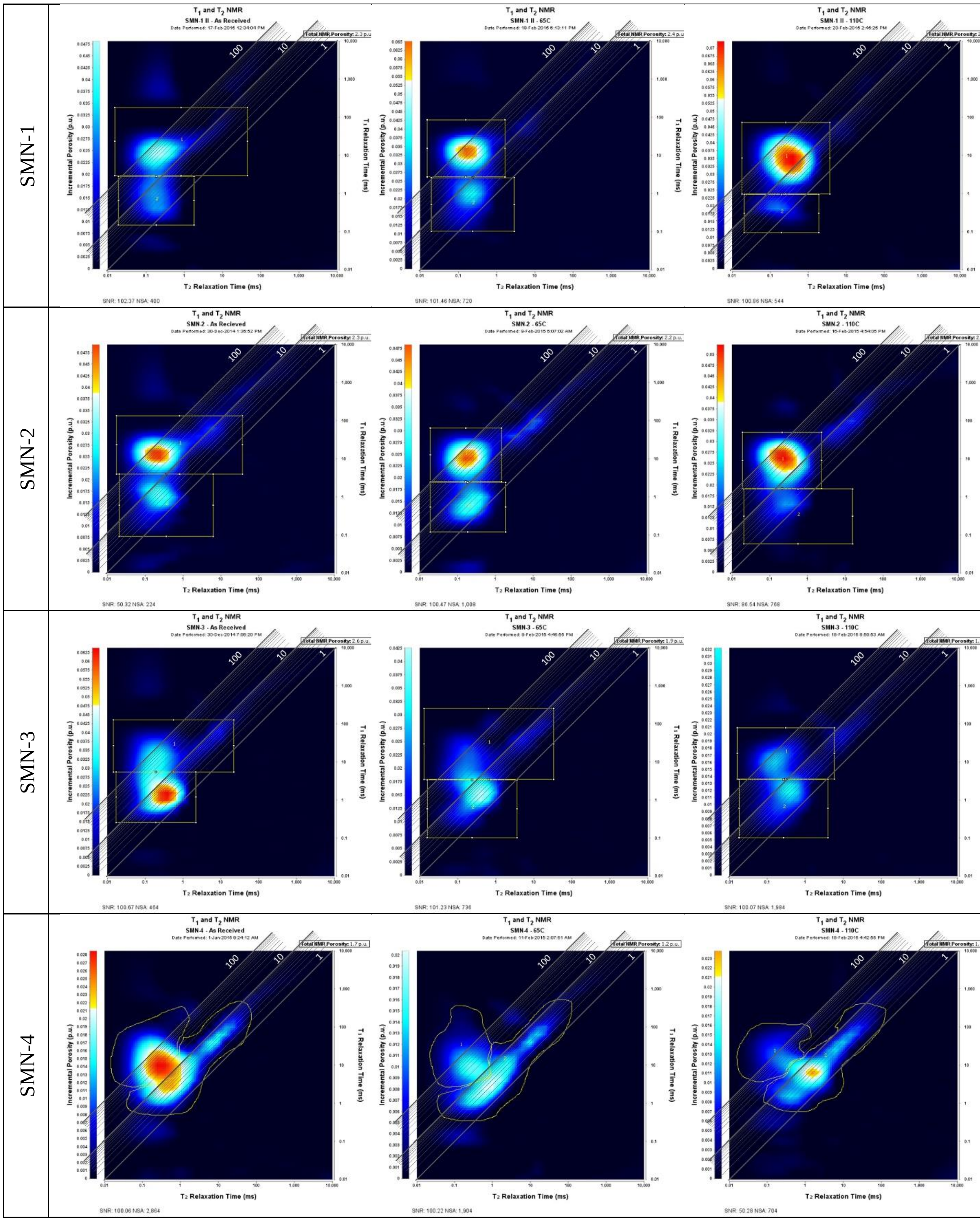


Figure 5: Log Mean T_2 change as a function of temperature

Most samples had porosity increase with temperature increasing from ~30 C to ~70 C and a loss in porosity in the final temperature increase step, indicating drying. Two samples (DF-1 and DF-3) had porosity increase from 70 C to 110 C indicating that bitumen that was initially too heavy to appear in the NMR (i.e. too viscous) had become detectable with increasing temperatures. The average T_2 value also increased at the highest temperature for all samples after a slight decrease sometimes at the intermediate temperature. This trend confirms that the viscosity is decreasing with temperature as does the next figure with T_1 and T_2 maps.

The following plots show the T_1 and T_2 distributions for all of the samples at each temperature (30 C, 70 C for EF-1, 35 C, 65 C, 110 C for the rest).

	35 C	65 C	110 C
DF-1			
DF-2			
DF-3			
DF-4			


SMN-1
SMN-2
SMN-3
SMN-4
T1 and T2 NMR
SMN-1 II - As Received
SMN-1 II - 65C
SMN-1 II - 110C
SMN-2 - As Recieved
SMN-2 - 65C
SMN-2 - 110C
SMN-3 - As Received
SMN-3 - 65C
SMN-3 - 110C
SMN-4 - As Received
SMN-4 - 65C
SMN-4 - 110C
Incremental Porosity (p.u.)
T2 Relaxation Time (ms)
T1 Relaxation Time (ms)

EF-1

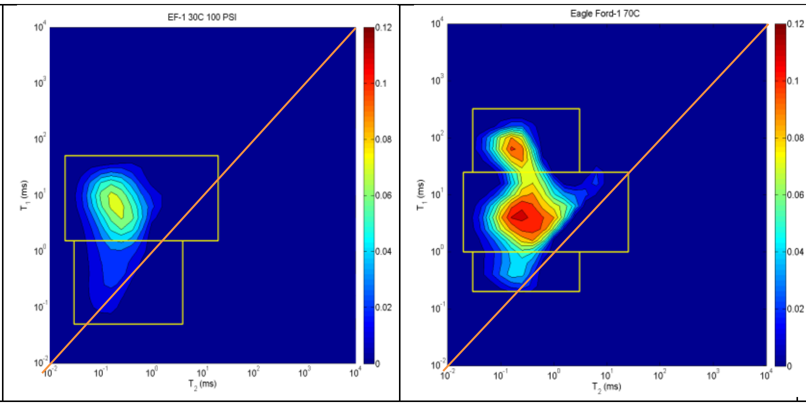


Figure 6 - T_1-T_2 results at all three temperatures, EF-1 temperatures shown are 30 C and 70 C.

The graphs show the T_2 distribution at each T_1 value. Red intensity indicates high porosity while blue is low. In shale, it is often useful to examine these types of maps because they can show two or more distinct peaks which correspond to different T_1/T_2 ratios. The T_1/T_2 ratio can be used to determine the origins of the signal in T_1-T_2 maps. Higher ratios indicate higher viscosity fluids such as bitumen, shorter ratio contributions are likely due to water (likely capillary and clay bound water).

Samples DF-1 and DF-4 had only one peak (one T_1/T_2 ratio) and thus the maps cannot be used for separation of signal from this sample (or there was only one fluid type present). For the other samples, the following tables and plots summarize the porosity of each fluid type associated with the low and high T_1/T_2 ratio. The high ratio is thought to be bitumen while the lower ratio is water. Sample EF-1 actually has three peaks at 70 C temperature. The lowest and the medium ratio peaks correspond to the visible peaks at 30 C. These are thought to be water and bitumen. The third peak only shows up once the temperature reaches 70 C. Its T_1/T_2 ratio is very high (~400), suggesting a very viscous substance that was not even visible at lower temperature. The porosity contribution of this peak is 1.14 p.u.

Table 4 - Porosity of the low T_1/T_2 ratio

Sample No.	Low $T_1 - T_2$ Ratio Porosity, 35C (p.u.)	Low $T_1 - T_2$ Ratio Porosity, 65C (p.u.)	Low $T_1 - T_2$ Ratio Porosity, 110 C (p.u.)
DF-1	-	-	-
DF-2	0.93	1.24	0.44
DF-3	0.88	0.67	0.2
DF-4	-	-	-
SMN-1	0.92	0.98	0.51
SMN-2	0.95	0.71	0.61
SMN-3	1.54	1.2	1.03
SMN-4	0.94	0.79	0.78
EF-1	0.7*	0.66**	-

* at 30 C
** at 70 C

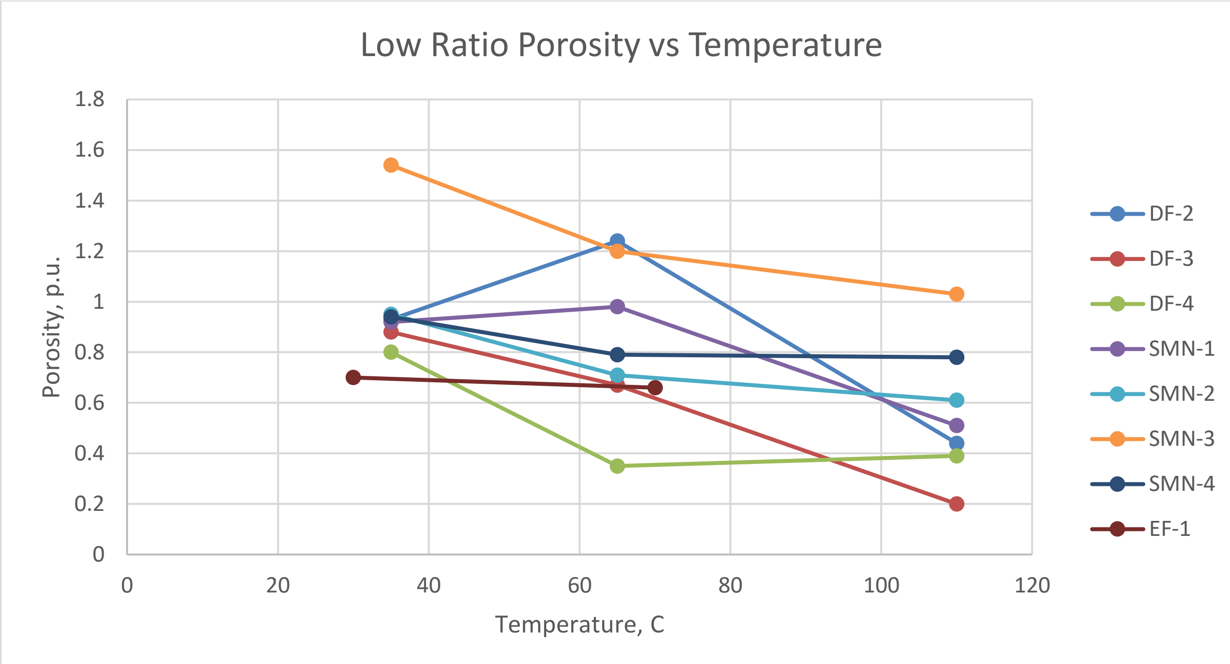


Figure 7 - Porosity of the lower T_1/T_2 ratio versus temperature

Table 5 - Porosity of the high T_1/T_2 ratio

Sample No.	High $T_1 - T_2$ Ratio Porosity, 35C (p.u.)	High $T_1 - T_2$ Ratio Porosity, 65C (p.u.)	High $T_1 - T_2$ Ratio Porosity, 110C (p.u.)
DF-1	-	-	-
DF-2	2.15	1.46	1.94
DF-3	1.49	1.54	2.1
DF-4	-	-	-
SMN-1	1.24	1.35	2.31
SMN-2	1.23	1.07	1.42
SMN-3	1.10	0.8	0.65
SMN-4	0.76	0.41	0.28
EF-1	2.2*	4.19**	-

* at 30 C
** at 70 C

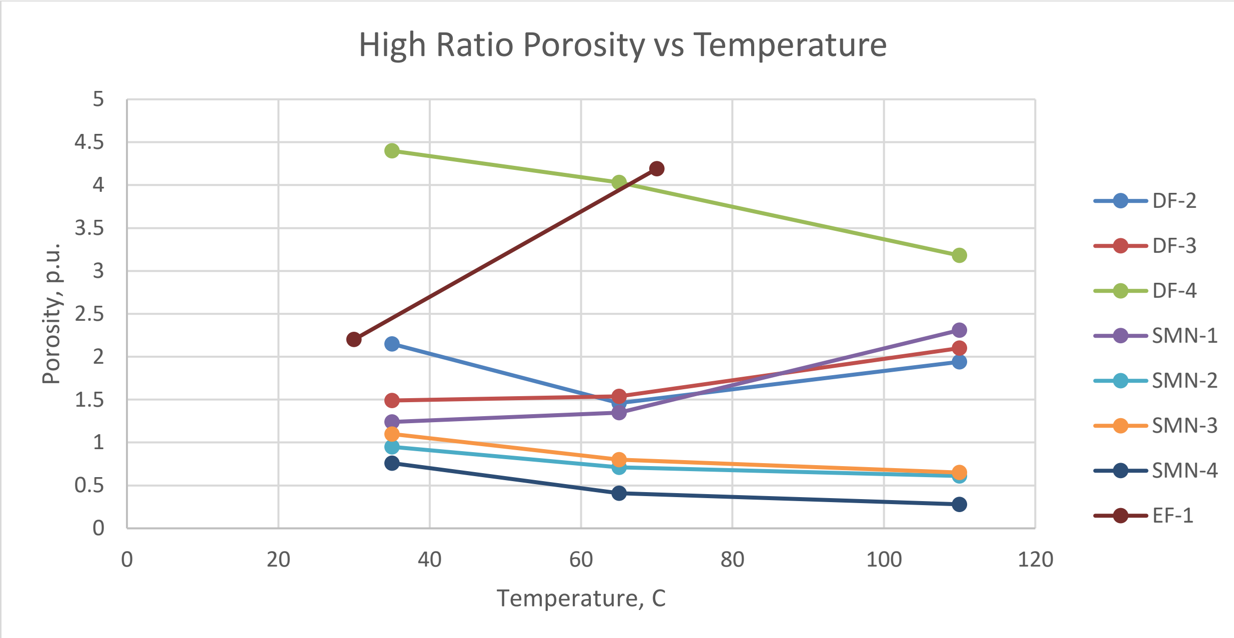


Figure 8 - Porosity of the higher T_1/T_2 ratio versus temperature

Higher T_1/T_2 ratios indicate more viscous fluids. As fluids such as bitumen are heated it is known that their viscosity lowers. Other fluids such as water have viscosities which do not change with temperatures. Examining the changes in the T_1/T_2 ratio of the different fluid populations can yield insight into the fluid. The following tables and plots show the T_1/T_2 ratio of the two populations present in the samples (lower ratio and higher ratio).

Table 6 - Lower T_1/T_2 ratio changes with temperature

Sample No.	Low $T_1 - T_2$ Ratio, 35C	Low $T_1 - T_2$ Ratio, 65C	Low $T_1 - T_2$ Ratio, 110 C
DF-1	-	-	-
DF-2	8	3	2
DF-3	3	3	1
DF-4	4	3	2
SMN-1	5	5	4
SMN-2	4	3	3
SMN-3	4	4	4
SMN-4	5	4	4
EF-1	1*	1**	-

* at 30 C
** at 70 C

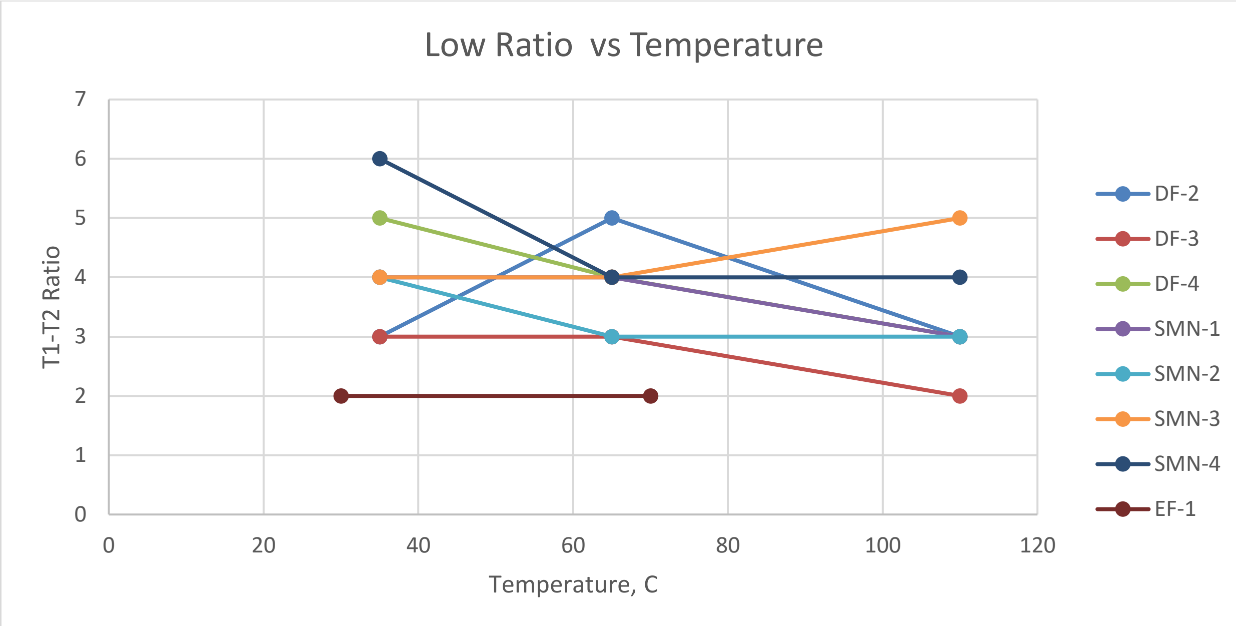


Figure 9 – Lower T_1/T_2 ratio versus temperature

Table 7 – Higher T_1/T_2 ratio changes with temperature

Sample No.	High $T_1 - T_2$ Ratio, 35C	High $T_1 - T_2$ Ratio 65C	High $T_1 - T_2$ Ratio 110C
DF-1	15	15	8
DF-2	64	64	46
DF-3	57	51	29
DF-4	6	5	4
SMN-1	57	57	21
SMN-2	51	51	45
SMN-3	51	31	64
SMN-4	80	36	80
EF-1	40*	15**	

* at 30 C
** at 70 C

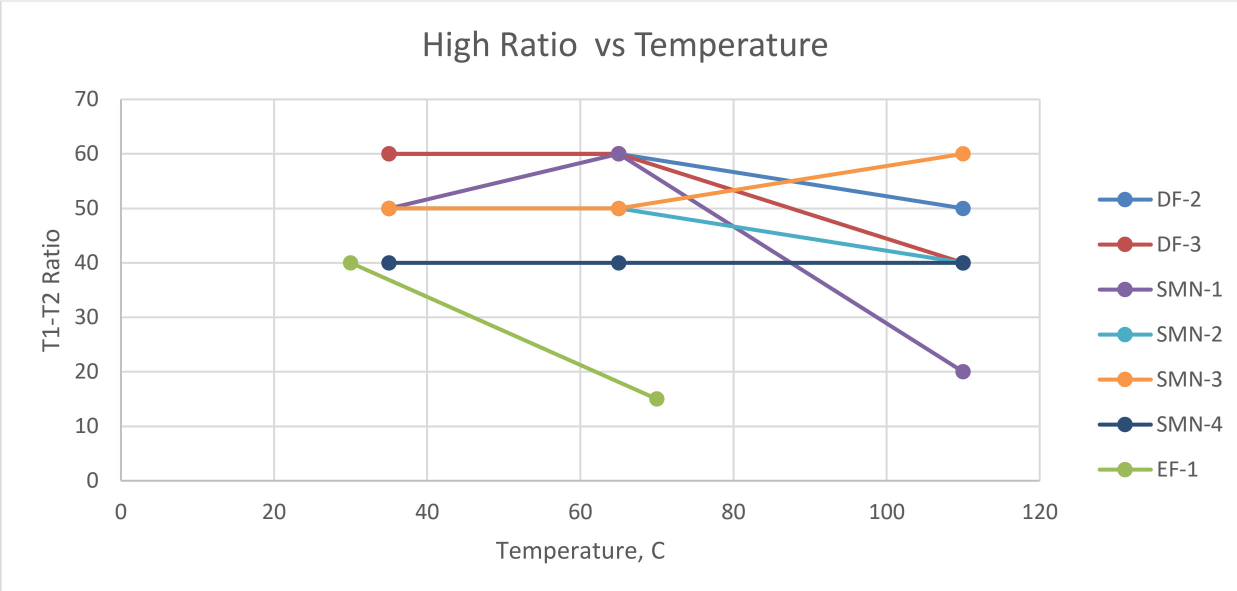


Figure 10 - Higher T_1/T_2 ratio versus temperature

Conclusions

The different fluids/clays/oils/bitumen within the sample have different NMR properties. By measuring T_1 in combination with T_2 we can distinguish between different types of components in the sample. Additionally, it has been shown that heating the sample may help separate the NMR signal more clearly. Signals with T_1/T_2 ratios between 1 and 2 are likely due to low viscosity fluid like water (bound or free). Higher ratios are from more solid like components such as bitumen.

- Two samples (DF-1 and SMN-1) had porosities that increased between 35 and 65 C. This indicates that bitumen that was initially too heavy to appear in the NMR did appear at the higher temperature.
- Samples that lost porosity as the temperature increased indicate drying.
- The porosity associated with the lower T_1/T_2 ratio generally decreases indicating drying.
- The porosity associated with the higher T_1/T_2 ratio generally stays the same or increases slightly (with the exception of DF-4).
- The T_1/T_2 ratio is unchanged for the lower ratio fluid (i.e. water) but decreases for the higher ratio fluid. This is consistent with bitumen changing viscosity. It is interesting to note that in sample EF-1 and additional high T_1/T_2 ratio peak appeared at 70 C that would otherwise not be detected at lower temperature.
- A high temperature and pressure NMR probe was successfully used to study shale at elevated temperature.

Possible sources of error associated with the measurements performed in this study are listed below.

- Short NMR relaxation times. The fluids present in shale have very short NMR relaxation times. This is due to the small pore sizes and the solid like nature of some of the hydrogen. Some hydrogen will likely not be accounted for in the measurements due to their short lifetime and equipment limitations. For a T_2 measurement the first measured point is acquired after 0.1 msec. This means signals with T_2 shorter than this become increasingly difficult to quantify.
- Grain Loss. Samples are constantly losing grain mass as a result of handling. Depending on the sample, this can be a significant source of error although it is not expected for these samples.
- Hydrogen Index. The samples are known to have more than one type of fluid present. All measurements are performed assuming a hydrogen index of one, which is known to be incorrect for fluids such as bitumen and oil.
- EF-1 sample may be drying less because it's surrounded in heatshrink and confined in OB probe with only small holes having access to air outside of the probe.

References

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