

Pushing the boundary of traditional 2 MHz NMR T1-T2 maps for source rock characterization

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Abstract. In rock samples, NMR measurements are commonly associated with characterization of porosity and fluid saturation. Low-field laboratory NMR allows for a nondestructive measurement of *as received* samples using the same frequency as well logging NMR tools. Unfortunately, the organic solid-like components of the rock, crucial in the characterization of source rocks, cannot be probed using standard pulse sequences. In this paper we will discuss how this limitation can be overcome by implementing a new pulse sequence to acquire T1-T2 maps that can be implemented in a standard commercial NMR laboratory benchtop analyzer. Source rocks were analyzed with this new methodology, showing how different components in the NMR T1-T2 maps correlate to geochemical and compositional properties of the rock. Among such properties, we focus our attention on solid organic matter, clay content and typing and fluid allocation inside the rock.

1 Introduction

In recent years, unconventional plays have contributed to an increase in oil and gas production. Contrary to conventional reservoirs, shales are much more complex and require the development of new techniques to fully characterize them. This is due to its extremely low permeability, different types of pores (organic and inorganic), and a wide range of pore sizes. In this context, Nuclear Magnetic Resonance (NMR) has shown significant importance in shale characterization. NMR 2D relaxation maps enable fluid typing, porosity measurements, and in some cases the identification of organic matter.

Standard laboratory NMR measurements on rocks use low-field (2 MHz) equipment for several reasons. First of all, this frequency matches the NMR-logging tool, allowing for a comparison between measurements. The relatively low cost and ease of use is also relevant. Furthermore, NMR is a non-destructive technique that allows whole rock inspection, and in the case of low field NMR, fitting rocks up to 1.5 inches in diameter and greater than 2 inches long. This is useful for *as received* rock analysis.

To characterize porosity using low-field NMR, the usual methodology is to acquire a 1D T₂ spectrum using a CPMG pulse sequence. This is adequate to measure fluid components inside the rock with long decaying signals (greater than 100 μs, which corresponds to half the echo-time used). However, solid-like components with short decay signal times, cannot be detected. A Free Induction Decay (FID) sequence can be used to characterize the short-time decay signals but is not adequate for studying

the dynamics of fluid components. An additional limitation of 1D measurements is that they may not be able to separate the contribution of different fluid types with similar relaxation times. To solve this, a second relaxation time is measured, and 2D T₁-T₂ maps are used.

In the present work, a novel 2D low-field NMR sequence, that can be applied to any commercial analyzer, is used to characterize both solid and fluid components inside the rock [1,2]. The sequence combines an FID to measure the fast decaying signals and a CPMG for the slow decaying ones, in a single measurement. This will allow for solid-like and fluid components to be visible on the same T₁-T₂ NMR map. Since shale rocks present a wide variety of components with different relaxation times, both short and long, the application of a single sequence that can characterize the whole range of T₂ times becomes essential.

The proposed NMR methodology was applied to shale outcrop samples in order to understand the origin of different components in the 2D NMR T₁-T₂ maps. This was done by using complementary geochemical and composition information of the rock. In particular, the focus was put on organic matter and clay-associated water.

2 Experimental Methodology

Samples from an outcrop section of Huincul High, Vaca Muerta Formation, were studied using a low-field NMR laboratory analyzer (Oxford Geospec2 analyzer at 2.27 MHz). The samples were measured *as received*, with no previous treatment. Since the main objective of this work is to characterize solid organic matter and clay content inside the rock using NMR measurements, samples were

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chosen specifically to cover a wide range of Total Organic Carbon (TOC) and clay content values. Seven samples were chosen with TOC values from 2 wt% to 10 wt%, and clay contents between 14% and 32%. The TOC values were obtained from RockEval 6 pyrolysis, while the clay content derives from whole rock XRD measurements. Clay types are obtained from clay fraction XRD (D8 Advance Bruker X-ray diffractometer; Ni-filtered CuK α , 40 kV, 40mA). The average mass of the samples ranged from 50 to 80 g.

A novel pulse sequence, introduced by Acosta *et al.* [1] and Silletta *et al.* [2], was implemented to obtain T₁-T₂ maps. This so-called SR-FID-ECHO-CPMG sequence allows for simultaneous measurement of solid-like and liquid components present in the rock. T₁ is encoded using a saturation recovery (SR) technique with delay times from 21 μ s to 390 ms in 50 logarithmic steps. For the T₂ dimension, a mixed acquisition scheme is used: data points are acquired during the FID prior to the first 180° pulse of the CPMG, using a spin echo of 200 μ s to increase this time interval; a CPMG pulse sequence of 500 echoes, with an echo-time of 200 μ s with single data point acquisition at the top of the echo is used. A numerical inversion of the measured data is required to obtain T₁-T₂ maps. Exponential kernels are applied to both dimensions, and the inversion is performed using the algorithm presented by [3]. The interpretation of the different signals in the T₁-T₂ maps is done following previous works [2].

3 Results

A detailed geochemical and mineralogical characterization of seven outcrop samples was performed. RockEval 6 pyrolysis measurements were used to derive TOC values for each of the samples. XRD measurements were also performed on the same samples to obtain the clay content of the rock. The results of both studies can be seen in Table 1.

Table 1. TOC data from pyrolysis and clay content and clay type from XRD measurements. The clay illite/smectite content is a percentage of the whole rock clay content.

Sample	TOC [wt%]	Clay Content [%]	Illite/Smectite [%]
1	8.32	14	100
2	9.96	24	89
3	4.80	29	92
4	2.36	16	96
5	4.27	25	84
6	2.48	22	87
7	1.97	32	85

NMR measurements were performed on each of the seven samples. The Oxford Geospec2 analyzer has two different diameter probes (43 and 53 mm, inner diameter) and can measure samples up to 8 cm in length. The total amount of rock mass used for this study ranged from 50 to 80 g. This allowed for a high SNR in reasonable time frames. T₁-T₂ maps of the seven outcrop samples were measured using a SR-FID-ECHO-CPMG sequence [1,2].

The data was inverted with exponential kernels to obtain NMR T₁-T₂ maps. In Figure 1, a T₁-T₂ map of one of the samples is shown. The signal is normalized by the number of scans and the mass of the sample. Eight different zones in the map are separated by red lines and each zone is identified with a letter from A to H. The signal in each of the zones is integrated, which allows for a quantitative study to be performed.

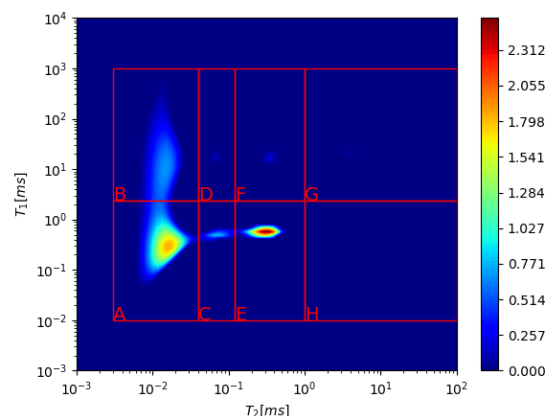


Fig. 1. T₁-T₂ 2 MHz NMR map using a SR-FID-ECHO-CPMG sequence for one of the outcrop samples. The map was inverted using exponential kernels for both dimensions. Using red lines, 8 different zones are identified and labeled from A to H.

The allocation of zones within the NMR maps is based on previous works [4-8]. The zones F and G are associated with fluid components in inorganic pores inside the rock; zone D is associated with fluid in organic pores; and zone H is a non-physical region (T₁ < T₂). Zone B falls on short T₂ times on the order of 10⁻² ms. These short relaxation times indicate solid-like components. Using the same pulse sequence, it has been shown that zone B correlates with the TOC present in the rock [1,2]. For the samples analyzed in this work, a comparison between TOC values and quantification of zone B is shown in Figure 2. A linear trend is observed which is supported by performing a least squares linear fit with a R² value of 0.877.

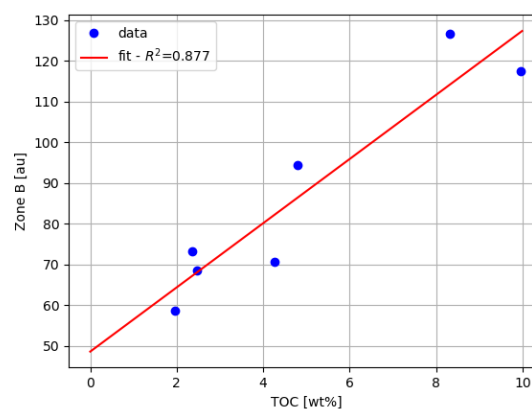


Fig. 2. NMR signal from zone B is plotted against TOC value from RockEval6 pyrolysis. A linear fit is performed. R² stands for the coefficient of determination of the least-squares.

Next, the focus is set on components in the T₁-T₂ maps associated with clays. Clays contain Hydrogen in different

forms: structural water (Hydrogen atoms that are part of the clay structure); bound water (interlayer water in expandable clays and superficial water surrounding clay structures). The T_1 - T_2 maps of the outcrop samples show a strong signal component in zone A which has both low T_2 and T_1 relaxation times. Research papers by Fleury et al. [8,9], using T_1 - T_2 maps at 23.7 MHz, have assigned the signal at low T_2 and low T_1 to hydroxyls. This motivates the hypothesis that zone A is at least partly associated with hydroxyls in clays. Nevertheless, solid organic matter (kerogen) also has hydroxyls in its structure and contributes to signal A. Further work must be performed to fully understand the origin of this signal and how it correlates to components in the rock.

The region of T_1 - T_2 maps with ratios $T_1/T_2 \sim 2-4$ has been usually associated with clay-bound water [6,8,10]. Thus, taking these references into account, signals from zone C and zone E appear to be related to clay-bound water. To test this hypothesis, the addition of the signal from both zones is plotted against the clay content of the rock. A least squares linear fit is performed on the data with $R^2 = 0.823$.

To further analyze the data, the signals from zone C and zone E were plotted individually against clay content. The signal from zone E shows a linear correlation ($R^2 = 0.953$) with clay content (see Figure 3), while zone C does not correlate at all ($R^2 = 0.130$). The values of zone C, by themselves, do not appear to change with clay content and might be more associated with zone A. It is important to point out that the signal from zone C has a T_2 time lower than 100 μ s which is invisible to traditional CPMG measurements with 200 μ s echo-time.

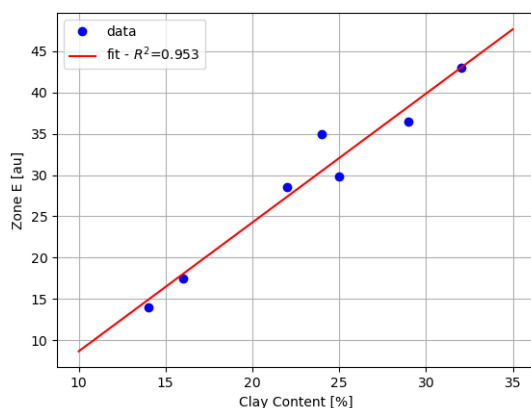


Fig. 3. NMR signal of zone E is plotted against clay content from whole rock XRD. A linear fit is performed. R^2 stands for the coefficient of determination of the least squares.

Correlation analysis represents a powerful tool for understanding the origin of NMR T_1 - T_2 maps. In previous works [1,2], we have collected abundant evidence that zone B correlates with TOC values from the rock. The signal from water associated with clays is still under continuous research. These results suggest that zone E highly correlates with clay content while zone C does not. The origin of zone C is uncertain but might be associated with another component inside the rock, the acquisition scheme, or a numerical inversion artifact.

Another research interest is clay typing using the shape and position of NMR signals from water associated with clays. Clay fraction XRD results presented in Table 1, show that all samples have more than 84% interstratified illite/smectite. Thus, no clay typing from NMR signals was attempted on these samples. NMR T_1 - T_2 maps on pure clay samples and rocks with different clay compositions could be used to analyze if clay typing is possible. Success in this venture would increase the capabilities and importance of NMR T_1 - T_2 maps for source rock characterization.

4 Conclusions

The present study is focused on understanding the origin of signals in 2D relaxation NMR maps by applying a novel sequence that allows to probe solid-like and fluid components in the sample, using a single measurement. The signal at low T_2 and high T_1 (zone B) has been shown to identify with TOC values of the rock. Regarding clay-associated water, a very strong correlation between clay content and zone E is observed. The signal in zone A, with short T_2 and short T_1 values, may be associated with structural water (hydroxyls), although further investigation is required to confirm this hypothesis. Future work involves measuring dry rock samples and pure clay samples to be able to characterize these regions in particular.

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