EXTENDING THE LIMITS OF TRADITIONAL 2 MHZ NMR T1-T2 MAPS FOR SOURCE ROCK CHARACTERIZATION

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RESUMEN

La Resonancia Magnética Nuclear (RMN) es una de las técnicas más aplicadas para la medición de porosidad y saturación de fluidos en roca. En particular, en laboratorio las mediciones de RMN de campo bajo (2 MHz) permiten una caracterización no destructiva de las muestras en el mismo rango de frecuencia que las herramientas de pozo. Sin embargo, las aplicaciones tradicionales de esta técnica están limitadas a la detección de componentes de tiempos de relajación largos y no permiten el análisis de las componentes sólidas incluyendo la materia orgánica – parte fundamental en el estudio de una roca madre.

En este trabajo se discute cómo esta limitación puede superarse implementando una secuencia de pulsos novedosa para adquirir mapas T1-T2 que puede ejecutarse en equipamiento comercial estándar de RMN de laboratorio. Se presenta la aplicación de esta metodología a muestras de afloramiento de la Fm. Vaca Muerta y se muestra como las diferentes regiones en el mapa T1-T2 correlacionan con las propiedades geoquímicas y composicionales de la roca – especialmente el contenido de materia orgánica y de filosilicatos.

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 in pore sizes. In this context, Nuclear Magnetic Resonance (NMR) has shown a significant importance in shale characterization. NMR 2D relaxation maps enable fluid typing, porosity measurements and sometimes 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 (Carr-Purcell-Meiboom-Gill) pulse sequence (Carr and Purcell 1954; Meiboom and Gill 1958). This is adequate to measure fluid components inside the rock with long signal decays, 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. The sequence combines an FID to measure the fast decay signals and a CPMG for the slow decay signals, in one 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 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.

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 of any kind. Since the main objective of this work is to characterize solid organic matter and clay content inside the rock using NMR

measurements, samples were 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 and clay types are obtained from clay fraction XRD (D8 Advance Bruker X-ray diffractometer; Ni-filtered CuKα, 40 kV, 40mA). The average mass of the samples ranged from 50 to 80 g.

A novel pulse sequence, introduced by Acosta et al. (2020) and Silletta et al. (2022), 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 µs 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 µs to increase this time interval; a CPMG pulse sequence of 500 echoes, with an echo time of 200 µs 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 Teal and Eccles (2015). The interpretation of the different signals in the T1-T2 maps is done following previous works from Silletta et al. (2022).

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 clay content of the rock. The results of both studies can be seen in Figure 1.

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

Figure 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.

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 (Acosta et al. 2020; Silletta et al. 2022). The data was inverted with exponential kernels to obtain NMR T1-T2 maps. In Figure 2, 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.

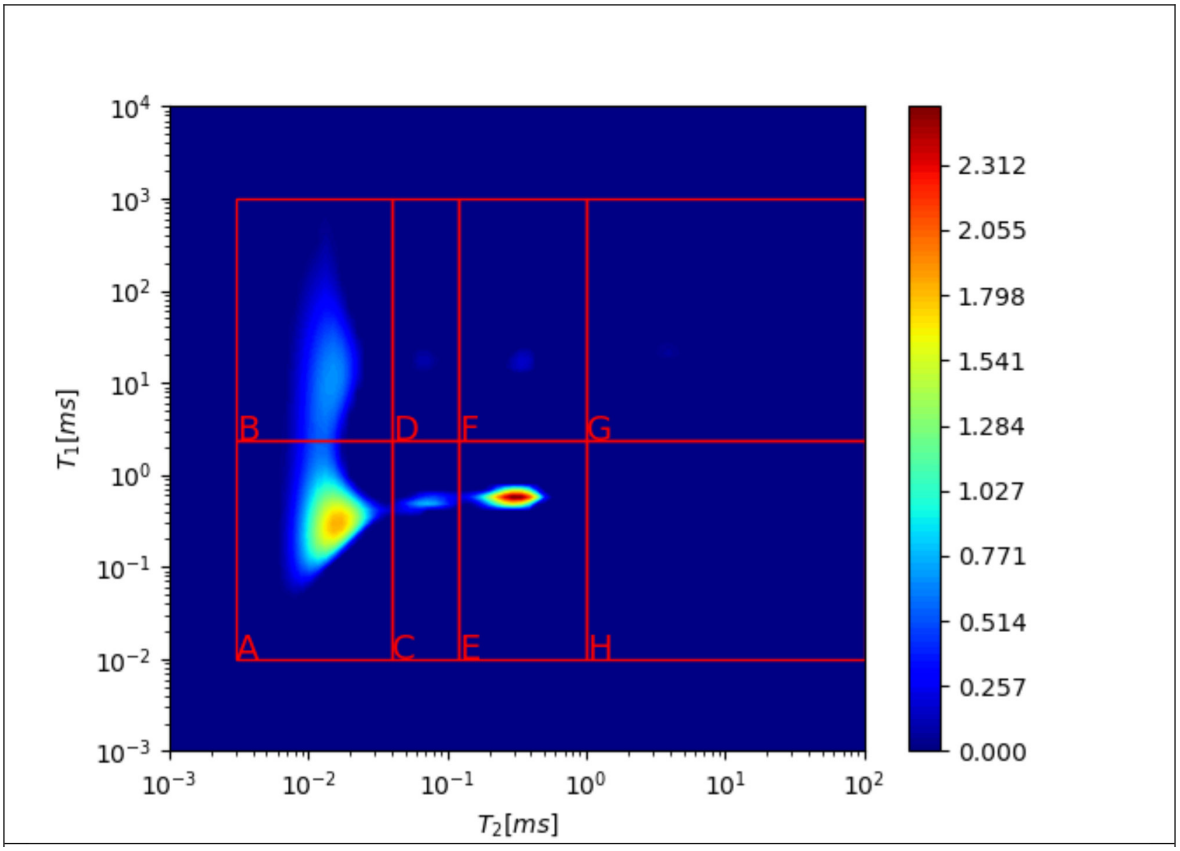

Figure 2. T1-T2 2 MHz NMR map using a SR-FID-ECHO-CPMG sequence for one of the outcrop samples. The map was inverted using exponential kernels for both dimensions. Using red lines, 8 different zones are identified and labeled from A to H.

Allocation of zones within the NMR maps is based on previous works (Elsayed et al. 2022; Liu et al. 2021; Song and Kausik 2019; Khatibi et al. 2019; Fleury et al. 2016). The zones F and G are associated with fluid like 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, Silletta et al. (2022) have shown that zone B correlates with the TOC present in the rock. For the samples analyzed in this work, comparison between TOC values

and quantification of zone B is shown in Figure 3. A strong linear trend is observed which is supported by performing a least squares linear fit with a R2 value of 0.877.

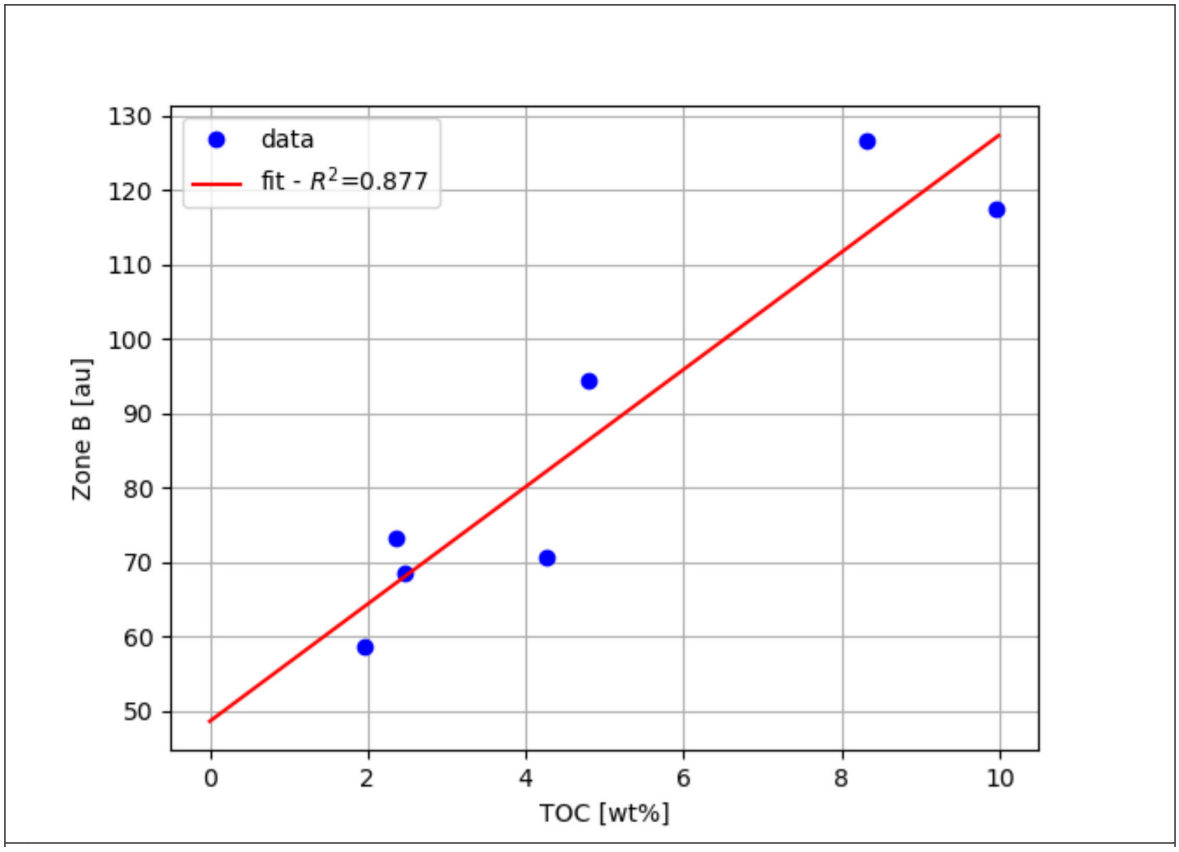

Figure 3. NMR signal from zone B is plotted against TOC value from RockEval6 pyrolysis. A linear fit is performed (red line). R2 stands for the coefficient of determination of the least-squares.

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 which are part of the clay structure); bound water (interlayer water in expandable clays and superficial water surrounding clay structures). The T1-T2 maps of the outcrop samples show a strong signal component in zone A which has both low T2 and T1 relaxation times. Fleury et al. (2021) and Fleury and Romero-Sarmiento (2016), in T1-T2 maps at 23.7 MHz, have assigned the signal at low T2 and low T1 to hydroxyls from the clay structure. This motivates the hypothesis that zone A is at least partly associated with hydroxyls in clays or other minerals. Nevertheless, further work must be performed to fully understand the origin of this signal.

The region of T1-T2 maps around ratios T1/T2 ~ 2-4 has been usually associated to clay bound water (e.g., Song and Kausik 2019; Habina et al. 2018; Fleury and Romero-Sarmiento 2016). Thus, taking these references into account, signals from zone C and zone E appear to be

related to clay bound water. To test this theory out, the addition of the signal from both zones is plotted against clay content of the rock (see Fig. 4). A least squares linear fit is performed on the data with R2 = 0.654.

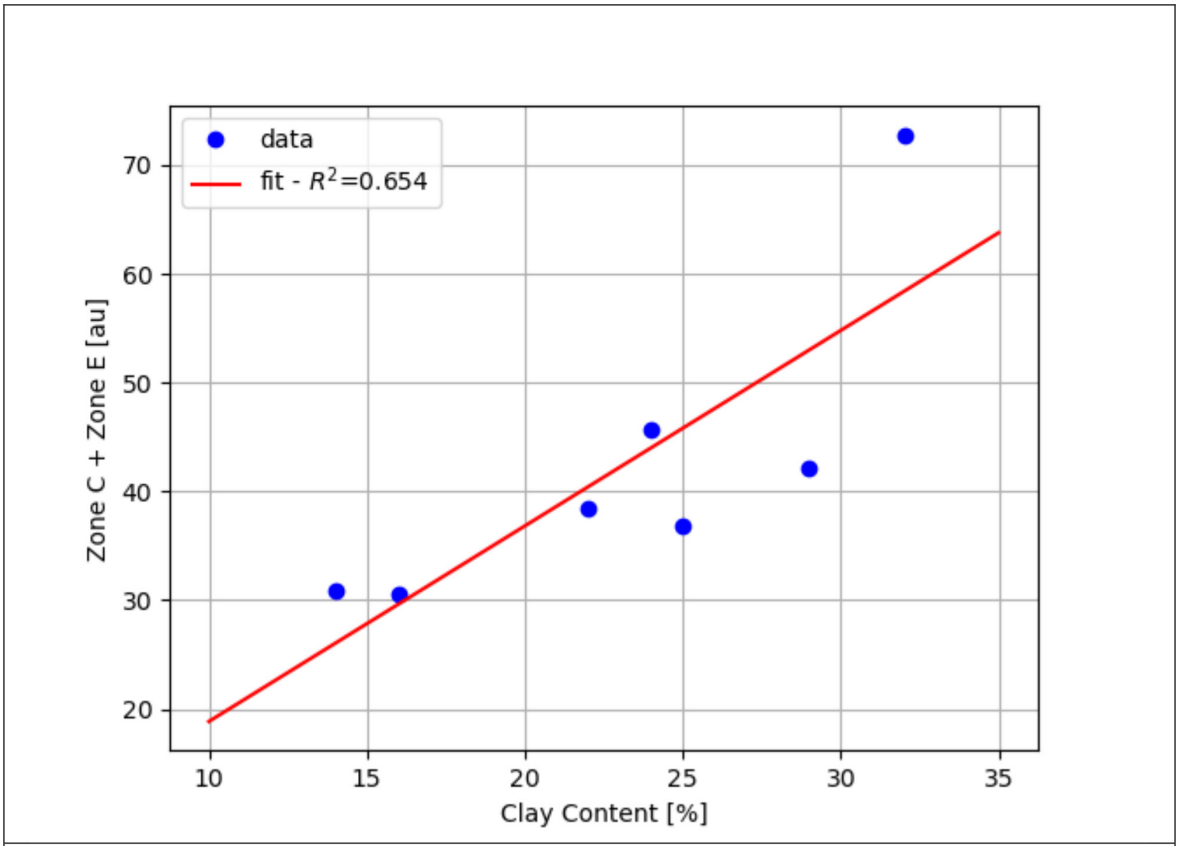

Figure 4. NMR signal of the sum of zone C and zone E is plotted against clay content from whole rock XRD. A linear fit is performed (red line). R2 stands for the coefficient of determination of the least-squares.

The signals from zone C and zone E were plotted individually against clay content to investigate if a better correlation was observed. The signal from zone E shows a very high linear correlation (R2 of 0.955) with clay content (see Fig. 5), while zone C does not correlate at all (R2 of 0.006).

The correlation analysis performed above is a first step in understanding which NMR signals in T1-T2 maps originate from the presence of water associated with clays in the rock. More samples must be measured, and further experiments are required to be able to identify for sure which zone accounts for clay bound water. What is clear is 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.

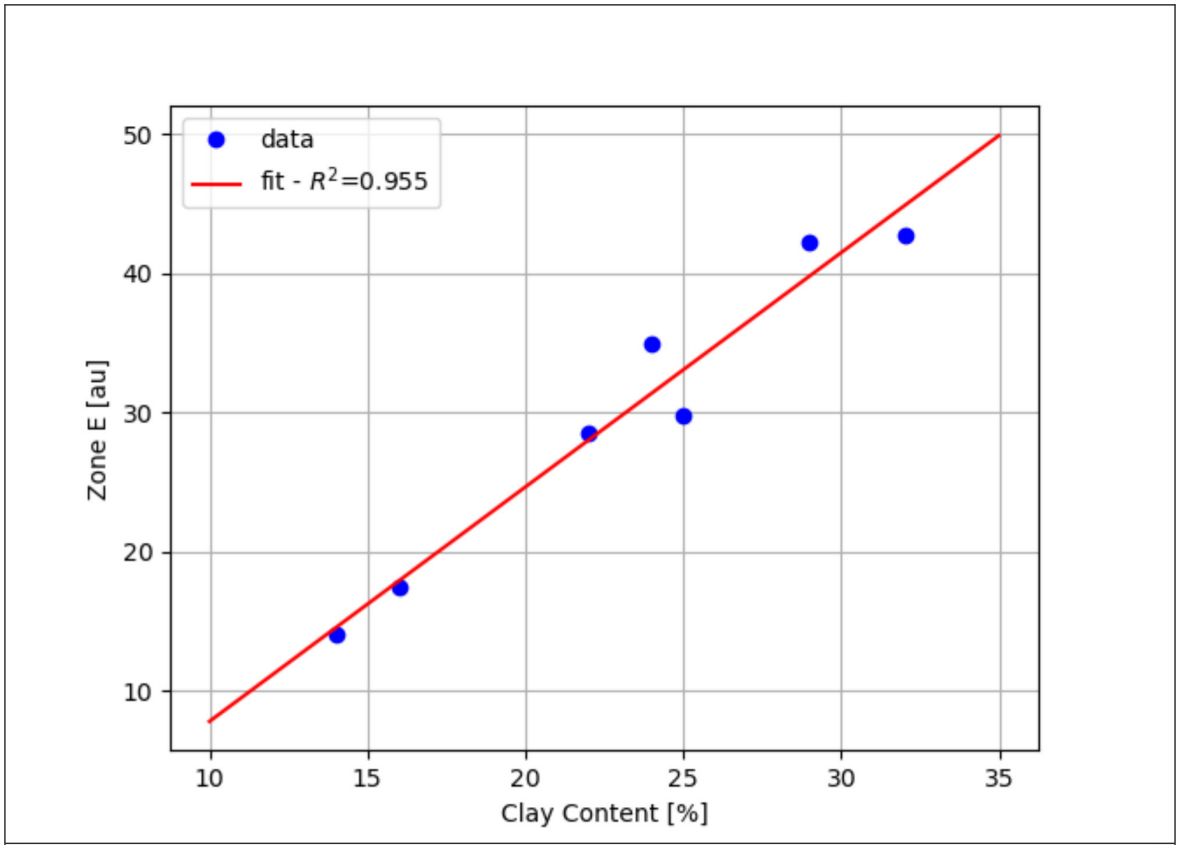

Figure 5. NMR signal of zone E is plotted against clay content from whole rock XRD. A linear fit is performed (red line). R2 stands for the coefficient of determination of the least-squares.

Clay fraction XRD results presented in Figure 1, show that all samples have more than 84% interstratified illite/smectite. Thus, no clay typing from NMR signals was attempted. NMR T1-T2 maps on pure clay samples are suggested to analyze if clay typing is possible.

CONCLUSIONS

The present study focused on understanding the origin of the signals in 2D relaxation NMR maps by applying a novel sequence which allows to probe solid like and fluid components in one single measurement. The signal at low T2 and high T1 (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 T2 and short T1 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 this region in particular.

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