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Explaining Nuclear Magnetic Resonance T_2 shifts in sandstones with anomalous porosity

Marta Henriques Jácomo (IAG/USP)*, Ricardo Ivan Ferreira da Trindade (IAG/USP), Everton Lucas-Oliveira (IFSC/USP), Tito J. Bonagamba (IFSC/USP)

Abstract

Some sandstones present anomalously high porosities after burial, which result from different mechanisms including the early growth of quartz and clays on host quartz grains (Bloch et al., 2002). These rocks typically show a macroporosity and some microporosity well identified by Nuclear Magnetic Resonance (NMR) relaxometry. However, the comparison between NMR and petrophysics measurements show a systematic mismatch in pore-size estimations in most samples expressed as a shift in NMR T_2 to lower relaxation times. Here we show the results obtained on three sedimentary units that present anomalous porosity: the clay-coated sandstones from Água Grande (Recôncavo Basin), the microcrystalline quartz-coated sandstones from Fontainebleau Formation (Paris Basin), and the sandstones coated with illite either microcrystalline quartz from Uerê Formation (Solimões Basin). Hematite-coated sandstones from Juruá Formation (also from Solimões Basin) were also studied to characterize the effects of magnetic minerals in the rock matrix on NMR data.

Introduction

During progressive burial a trend of porosity-loss with depth is observed on sandstone units due to the increase in mechanical compaction and quartz cementation. However, the porosity can be preserved in special conditions, for example, when fluid overpressure occurs in rocks with low thermal maturity, due to early hydrocarbon emplacement or through clay or quartz grain-coating (Bloch et al., 2002). Anomalously high porosity caused by coatings of microcrystalline quartz and clay in sandstones have been studied by many authors in different depositional settings (Pittman et al., 1992; Mc Kinley et al., 2003; Worden et al., 2012; Ajdukiewicz and Larese, 2012; French & Worden, 2013). However, their microporosity structure has not been studied, including the micropore families associated with coatings. The NMR is a non-destructive tool well suited for the study of these pores, since it provides information about pore size distribution and can be performed in well log exploration, i.e. *in-situ*. In the present study we characterized the pore space of samples from Fontainebleau and Uerê Formation, which show anomalous porosity due to the presence of microcrystalline quartz coatings, and Água Grande Formation, which shows chlorite coatings. The complete dataset was published in Jacomo et al. (2018, 2019).

Method

NMR is a noninvasive technique applied in the characterization of porous media, particularly in sedimentary reservoir rocks.

The NMR signal provides information about the amount of fluid located within porous media, since the signal is proportional to the number of molecules bearing 1H nuclei. Some porous media properties, such as pore size distribution, porosity, permeability, saturation, and capillary adsorption can be obtained by NMR (Vincent et al., 2011). Among the most important parameters measured by NMR, the transverse relaxation time T2 is the most used in the well-logging exploration (Kenyon et al., 1995; Kenyon, 1997).

Three main mechanisms govern the NMR transverse relaxation time in a fluid within a porous medium: (i) bulk relaxation (T_{2B}), which is related to the intrinsic relaxation of molecules in each type of fluid, being mostly controlled by viscosity and dissolved paramagnetic ions Fe^{+3}; (ii) diffusion relaxation (T_{2D}), which is controlled by the dynamic behavior of fluid molecules bearing 1H nuclei under magnetic field gradients; and (iii) surface relaxation (T_{2S}), which is connected with the grain mineralogy and surface-to-volume ratio (SVR) (Kenyon, 1997, Coates et al., 1999; Keating & Knight, 2007; Mitchell et al., 2010).

The NMR transverse relaxation times T_2 can be expressed by the sum of these three mechanisms. However, the surface relaxation is generally predominant over the others; and, besides that, the relaxation rates depend on the chemical composition of the porous matrix and the surface/volume ratio, as follows:

$$1/T_2 = \rho_2 \, (S/V)$$

where ρ_2 is the pore surface relaxivity for transverse relaxation time T_2; S/V is the surface/volume ratio. Surface relaxivity can be interpreted as a measurement of how much the proton magnetization can relax when it encounters a pore surface and depends on the concentration of paramagnetic impurities and magnetic particles on it.

Under the fast diffusion regime (Brownstein and Tarr, 1979), the transverse relaxation time T_2 is directly associated with pore size. Consequently, T2

measurement provides pore size distributions for the analyzed samples.

Besides NMR measurements, we used other petrophysical and mineralogical tools such as X-ray microcomputed tomography (Micro-CT), Scanning Electron Microscopy (SEM), magnetic susceptibility (χ), hysteresis, isothermal remanent magnetization and thin section.

Results

The microcrystalline quartz-coated Fontainebleau sandstones were classified according to their texture, composition, and abundance of microcrystalline quartz crystals into Group 1, comprising samples with very low amounts of coatings, and Group 2, for one sample, entirely coated by microquartz (FB155).

Both groups show three (or four) peaks in NMR 2MHz T$_2$ distribution at ~1s (peak 1), 10^{-1}s (peak 2), and 10^{-2}s (peak 3); since Fontainebleau sandstones are composed almost exclusively of SiO_2 – paramagnetic impurities being absent from quartz grain surfaces – the main mechanism of magnetization of their pore-filling fluids is surface relaxation. In this condition, the transverse relaxation time T$_2$ distribution can be directly correlated with the pore size distribution. Micro-CT analyses showed that samples FB-155, FB-217 and FB-10 have similar pore size distributions. We expected the T$_2$ NMR distributions of these samples to be similar as well, but the FB-155 showed a significant displacement of T$_2$ times towards shorter times. Using Micro-CT data, the estimated transverse surface relaxivity (ρ_2), which correlates T$_2$ with pore sizes, varies from ~1 to 8 µm/s for Group 1 and is ~28 µm/s for the sample FB155 (Table 1).

Table 1: Transverse relaxation times measured at 2 MHz or 20 MHz (*), using a log-normal fitting of curves and calculated surface relaxivity (ρ_2); (1) is Group1; (2) is Group 2 Each peak corresponds to one family of pores. Note that Group 2 (FB155) and Group 1 (FB 217 and FB 10) have similar pore sizes, but the former shows much shorter T$_2$ times, therefore revealing a slight displacement towards shorter times (adapted from Jácomo et al., 2019).

Samples	T$_2$ (s) Peak 1	T$_2$ (s) Peak 2	T$_2$ (s) Peak 3	T$_2$ (s) Peak 4	ρ_2 Micro-CT (µm/s)
FB (1)	1.07	0.13	0.01	0.003	4.20
FB10 (1)	0.93	0.13	0.01	-	8.06
FB25 (1)	0.76	0.14	0.01	-	3.72
FB83 (1)	1.74	0.28	0.07	0.01	0.76
FB217 (1)	1.26	0.11	0.02	0.01	4.77
FBL2B01(1)*	0.63	0.32	0.05	0.01	7.22
FBL3B01	1.20	0.20	0.03	0.01	8.23
(1)*					
FB155 (2)	0.36	0.05	0,01	-	27.92

The chlorite-coated samples from Água Grande Formation were divided into two groups: Group 1 with low chlorite coatings contents and Group 2, which has high amounts of chlorite coatings. The NMR 2 MHz T$_2$ distributions for all samples can be interpreted in terms of three peaks (Figure 1). Thin sections and SEM images allowed us to interpret the longest T$_2$ times (>0.1 s) as due to intergranular macropores, while the intermediate T$_2$ peak in the distributions was interpreted as due to mineral dissolution (mainly feldspar). We observed an important displacement towards shorter times in 2 MHz NMR T$_2$ distributions of samples with high amounts chlorite coatings (Group 2). The chlorite coatings contain Fe, hence they can enhance relaxivity. However, this seems not to be the only reason for displacement. We observed that %Fe covering the quartz grains is correlated to the difference between the porosities estimated by petrography and Helium methods, which can estimate the microporosity value or chlorite porosity. However, the area of the NMR T$_2$ distribution curves is not proportional to the porosity measured by conventional methods. Therefore, some diffusive coupling must operate in the system bringing the T$_2$ peaks in NMR distributions towards shorter times.
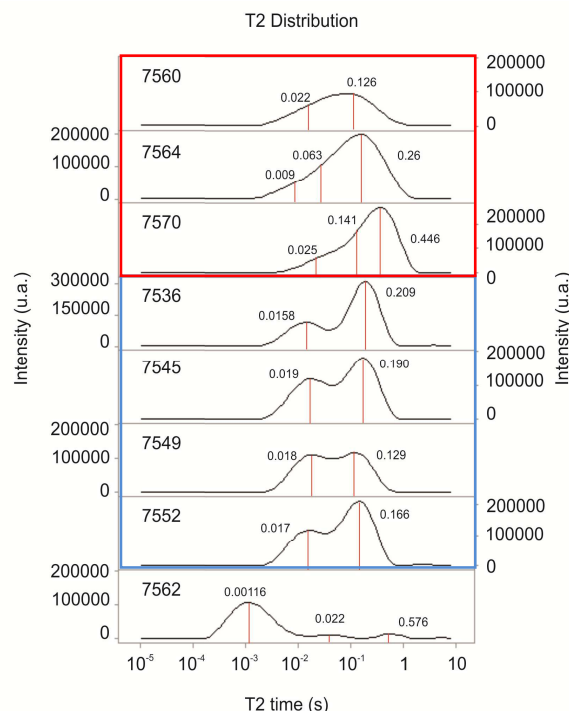

Fig. 1. T$_2$ distributions for Groups 1 (red) and 2 (blue) from Agua Grande Fm. The sample 7562 is a non-reservoir sample, which is composed mainly by micropores. While Group 1 samples show a wide T$_2$ distribution, Group 2 samples show bimodal narrower distribution.

The relaxivities from Group 1 samples, which are in fast diffusion regime, vary from 32 µm/s to 43 µm/s. The samples from Group 2, which are in intermediate diffusion regime, have effective relaxivities of about 15µm/s and the relaxivity of micropores is ~100 µm/s.

The Solimões samples comprise microcrystalline quartz-coated sandstones, with and without important iron-bearing minerals. Uerê formation samples were divided in Group 1, containing Fe-illite and Group 2 containing Fe-dolomite, siderite and pyrite. Group 3 samples is composed of hematite-coated sandstones cemented by quartz overgrowths, albite, hematite and pore-filling illite from Juruá Formation.

The T_2 distributions for all studied samples showed three to four peaks (Table 2). Macroporosity in these samples is indicated by a peak above 10^{-1} s in T_2 time distributions, whereas intermediate peaks (0.1 - 0.01 s) are related to mineral dissolution. In Group 1 the shortest T_2 times do not present a shift towards values below of 0.3×10^{-2} s. In contrast, Groups 2 and 3 are characterized by a shift in the highest intensity peak towards shorter times (~5×10^{-2} s), reducing the differences between the peaks, sometimes merging all the peaks into a unimodal distribution (Group 2) or producing an extra peak close to 3.3×10^{-2} s, which makes the T_2 distributions clearly bimodal.

Relaxivity values from Group 1, which is in fast diffusion regime, vary from 14 µm/s to 37 µm/s, while the relaxivity values from intermediate diffusion regime samples from Group 2 and 3 vary from 35 µm/s to 118 µm/s. The relaxivity from 2875 sample is 443 µm/s.

Conclusions

The low magnetic field NMR distributions of coated sandstones from Fontainebleau, Água Grande, Uerê and Juruá Formation are characterized by an important displacement towards short T_2 values in samples with high amounts of clay or microquartz coatings.

Since almost all samples from Fontainebleau have pore surfaces with similar composition (devoid of paramagnetic impurities in grain surface), their T_2 values shift is related to differences in S/V ratio of pores, which may be caused by the presence of microcrystalline crystals on the pore's surface. At 2 MHZ, the shift towards short T_2 values observed for Água Grande samples is due to the variable amounts of Fe-rich chlorite, besides a contribution of intermediate diffusion coupling. The Solimões sandstones are characterized by high magnetic susceptibility, which is the main cause of the shift towards short T_2 values. (Keating and Knight, 2007). This is corroborated by the results obtained for the Juruá Formation, which is devoid of coatings but showed the displacement toward shorter times.

Although the anomalous porosity caused by presence of coatings is characterized by the drift of T_2 toward shorter times, the processes behind these shifts are different and depend strongly on the mineralogy and texture of the rocks.

Table.2. The transverse relaxation times T_2 distributions for microcristalline coated sandstones without (Group 1) and with (Group 2) important iron contribution. Group 3 forms the hematite coated sandstones. We observe important shift toward T_2 shorter times in ferrous samples.

Samples	Group	T_2 (s) Peak 1	T_2 (s) Peak 2	T_2 (s) Peak 3	T_2 (s) Peak 4
R2852	1	0.17*	0.079	0.014	0.002
R2856	1	0.24*	0.098	0.020	0.008
R2860	1	0.29	0.12*	0.014	-
R2863	1	0.44*	0.20	0.083	0.012
R2855	1	0.11*	0.050	0.022	0.008
R2853	2	0.32	0.047*	0.007	-
R2854	2	0.36	0.050*	0.016	0.007
R2877	3	1.000	0.21*	0.063	0.007*
R2875	3	0.28	0.009*	-	-

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