

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/318020611>

Estimating the surface relaxivity as a function of pore size from NMR T2 distributions and micro-tomographic images

Article in *Computers & Geosciences* · June 2017

DOI: 10.1016/j.cageo.2017.06.016

CITATIONS

37

READS

542

5 authors, including:



Francisco Benavides

National University of Costa Rica

8 PUBLICATIONS 72 CITATIONS

[SEE PROFILE](#)



Ricardo Leiderman

Universidade Federal Fluminense

59 PUBLICATIONS 363 CITATIONS

[SEE PROFILE](#)



Andre Souza

43 PUBLICATIONS 776 CITATIONS

[SEE PROFILE](#)



Giovanna Carneiro

Schlumberger Limited

26 PUBLICATIONS 349 CITATIONS

[SEE PROFILE](#)

1 **Estimating the surface relaxivity as a function of pore size**
2 **from NMR T2 distributions and micro-tomographic images**

3 Francisco Benavides^{a)1)}, Ricardo Leiderman^{a)}, Andre Souza^{b)}, Giovanna Carneiro^{b)c)}, Rodrigo
4 Bagueira^{c)}

5 a) Computer Science Department, Fluminense Federal University, Av. Gal. Milton Tavares de
6 Souza, s/no, Niterói, RJ, Brazil, 24210-346. fbenavides@id.uff.br; leider@ic.uff.br.

7

8 b) Schlumberger Brazil Research & Geoengineering Center, Rua Paulo Emidio Barbosa, 485,
9 quadra 7B, Parque Tecnológico do Rio de Janeiro, Rio de Janeiro, RJ, Brazil, CEP 21941-907.
10 ASouza19@slb.com; giovannaafc@gmail.com

11

12 c) Institute of Chemistry, Fluminense Federal University, Outeiro de São João Batista, s/no,
13 Niterói, RJ, Brazil, 24020-141. rbagueira@vm.uff.br.

14

15

16

17

18

19

20 1) Author to whom correspondence should be addressed. Electronic mail: fbenavides@id.uff.br

21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37

Abstract

In the present work, we formulate and solve an inverse problem to recover the surface relaxivity as a function of pore size. The input data for our technique are the T_2 distribution measurement and the micro-tomographic image of the rock sample under investigation. We simulate the NMR relaxation signal for a given surface relaxivity function using the random walk method and rank different surface relaxivity functions according to the correlation of the resulting simulated T_2 distributions with the measured T_2 distribution. The optimization is performed using genetic algorithms and determines the surface relaxivity function whose corresponding simulated T_2 distribution best matches the measured T_2 distribution. In the proposed methodology, pore size is associated with a number of collisions in the random walk simulations. We illustrate the application of the proposed method by performing inversions from synthetic and laboratory input data and compare the obtained results with those obtained using the uniform relaxivity assumption.

Keywords: Surface relaxivity; NMR magnetization decay; Digital Petrophysics; Random walk; Pore size distribution.

38 **1 - Introduction**

39 ^1H Nuclear Magnetic Resonance (NMR) is a powerful tool for studying reservoir
40 rock properties, based on the responses of protons in fluid molecules filling the formation
41 pore space. Porosity, pore size distribution, permeability, capillary pressure curves and
42 wettability are examples of important petrophysical deliverables that can be accessed *via*
43 laboratory and field (downhole and surface) NMR realizations (Coates et al., 1999)(Dunn
44 et al., 2002).

45 According to the basic theory, the NMR transversal relaxation rates ($1/T_2$) of protons
46 in molecules of the wetting phase can be enhanced by contact or quasi-contact
47 interactions with the solid/fluid interfaces. In the limit of the fast diffusion regime, the solid-
48 fluid interaction is the dominant relaxation mechanism and the relaxation rate of a fluid
49 occupying the pore space can be approximated by (Brownstein and Tarr, 1979):

$$\frac{1}{T_2} = \rho_2 \left(\frac{S_p}{V_p} \right) = \rho_2 \frac{c}{R_p} , \quad (1)$$

50 where (S_p/V_p) is the ratio of surface area to pore volume; ρ_2 (ρ , from now on) is the
51 surface relaxivity, a proportionality constant that characterizes the strength of relaxation
52 induced by the solid/fluid interfaces; R_p is the pore radius and c is the shape factor (1,2
53 and 3 for planar, cylindrical and spherical pores, respectively). When an estimate for the
54 surface relaxivity parameter is available, the measured relaxation time distribution can be
55 converted into a pore size distribution using the equation above. In the formation
56 evaluation context, the pore size distribution is one of the distinctive NMR deliverables
57 when compared to the other available geophysical methods.

58 The importance of accessing surface relaxivity values for improving the accuracy of
59 NMR deliverables is described in several papers, such as for example in (Souza et al.,
60 2013), where the authors demonstrated how to calibrate the relaxation term of a classical
61 NMR permeability model to improve its performance. According to (Saidian and Prasad,
62 2015), there are three primary types of methods to estimate the surface relaxivity:

- 63 i. Iterative variation to match NMR relaxation times with independent measurements
64 of pore or throat size distribution;
- 65 ii. Estimations using rock surface area;
- 66 iii. Estimations based solely on NMR measurements;

67 All of them rely upon the assumption that the surface relaxivity can be represented by a
68 uniform value. However, as stated in (Keating and Knight, 2012), it is highly unlikely that
69 all the pore surfaces in a sedimentary rock sample have the same relaxivity value.

70 In (Arns et al., 2006), the authors cite multiple physiochemical factors that cause the
71 surface relaxivity to vary in sedimentary formations. Considering the rock formation
72 depositional, diagenetic, and hydrocarbon-filling mechanisms, it is a reasonable
73 conjecture that, for at least some cases, some of these factors may be related to pore
74 size. For example, we can cite mixed wettability reservoirs in which the wettability for
75 larger pores has been altered to oil-wet due to heavier oil fraction deposition, while the
76 wettability in smaller pores has remained unaltered (water-wet) (Looyestijn and Hofman,
77 2006). In this case, the surface relaxivity would be larger for the smaller pores and vice
78 versa. Another example we can cite are rock formations in which clay and heavy minerals
79 have been deposited differently according to the pore size. In fact, in (Boggs, 2009) the
80 author mentions that for sandstones, smaller pores will more likely contain higher

81 amounts of clay mineral, while larger pores will have more quartz grains in their
82 surroundings. In this case, again, the surface relaxivity would be larger for the smaller
83 pores. The results presented in (Liu et al., 2014) corroborate what is stated here; as for
84 the investigated sandstone, the authors observed that the surface relaxivity was larger
85 for the smaller pores, although they offered no justification for such behavior. In the
86 author's own words: "The slope of the result in sandstone varies in the different pore
87 regimes, which implies heterogeneous surface properties in the pores. The surface
88 relaxivity was estimated to be around 30 $\mu\text{m/s}$ in the pore length ranging from 10 μm to
89 70 μm , and was continuously increasing in the pores smaller than 10 μm ". To the best of
90 our knowledge, this is the first and only study reported in the literature that attempted to
91 investigate the surface relaxivity variation in rock samples. At this point, we would like to
92 mention that the results obtained in the present work for the investigated carbonate also
93 indicated a clear tendency of the surface relaxivity to vary with pore size.

94 Based on the above concept, in this study we formulate and solve an inverse
95 problem to recover the surface relaxivity as a function of pore size. To the best of our
96 knowledge, there is no work reported in the literature treating the same inverse problem.
97 The input data for our technique are the T_2 distribution measurement and the micro-
98 tomographic image of the rock sample under investigation, and the inverse problem under
99 consideration is precisely that of (iteratively) finding the surface relaxivity function whose
100 corresponding T_2 distribution best matches the T_2 distribution measurement. To that end,
101 we simulate the transversal NMR relaxation signal (and the corresponding T_2 distribution)
102 for a given surface relaxivity function using a random walk implementation developed in
103 house and that runs in the sample tomographic image, and rank different surface

104 relaxivity functions based on the correlation of the resulting simulated T_2 distributions with
105 the reference (measured) T_2 distribution. The heuristic method used for the optimization
106 is genetic algorithms. The proposed methodology is suitable for the experimental
107 characterization of surface relaxivity on preserved pores and also provides the ability to
108 probe the surface alterations that are chemically induced by alkaline, surfactant and
109 polymer flooding in enhanced oil recovery (EOR) studies.

110 The continuation of this article is structured as follows: In Section 2 we formulate
111 the inverse problem and present the solution strategy, where we describe how we perform
112 the NMR relaxation simulation from digital images and introduce the concept of
113 associating the number of collisions in the random walk simulations to pore size. In
114 Section 3, we illustrate the application of the presented method performing inversions
115 from (noisy) synthetic and laboratory input data, discuss the obtained results, and
116 compare them to those obtained with the uniform relaxivity assumption. Then, we
117 conclude in Section 4.

118

119 **2 – Methods**

120 We start this section by highlighting that what we call “inverse problem” in the
121 present work is the whole problem of recovering the surface relaxivity as a function of
122 pore size. Likewise, what we call “inversion procedure” (or simply “inversion”) is the entire
123 computational process to recover the surface relaxivity as a function of pore size. This is
124 not to be confused with the inverse Laplace transform employed to obtain the T_2
125 distribution from the (simulated) magnetization exponential decay.

126 2.1 NMR decay simulation

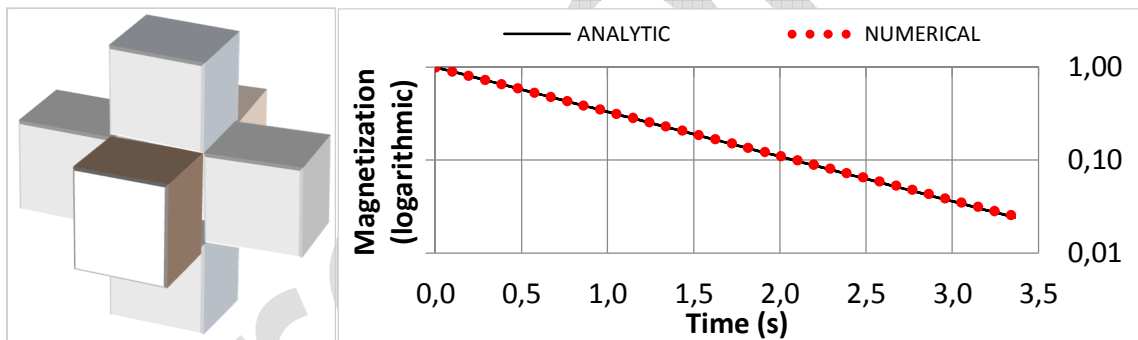
127 We use the voxel-based approach of the random walk method (RW) to simulate the
128 NMR T_2 magnetization decay $M(t)$ in a rock sample. The sample is described by a 2D or
129 3D digital image in which the pores are identified in the discrete picture elements that can
130 be voxels or pixels. The value of $M(t)$ decays according to two relaxation mechanisms:
131 non-uniform and bulk relaxation. The fluid's contact with the pore space solid walls
132 produces non-uniform relaxation $M_{NU}(t)$. The bulk relaxation is a fluid property and does
133 not depend on any property of the confining formation. It is given by $M_B(t) = e^{-t/T_{2,B}}$,
134 where $T_{2,B}$ is the bulk time. The magnetization at any time t is given by $M(t) = M_{NU}(t) \cdot$
135 $M_B(t)$.

136 In the RW simulation, each fluid particle is placed randomly in the pore space and
137 diffuses in discrete steps across neighboring voxels (Talabi et al., 2009). Whenever the
138 particle hits the solid wall, it is penalized by a factor δ that depends on the surface
139 relaxivity $\delta = 2\Delta\rho/3D$, where Δ is the image voxel resolution and D is the fluid diffusion
140 coefficient (Bergman et al., 1995). There are at least two ways to apply this penalization:

- 141 i. Every fluid particle makes the same contribution to the non-uniform
142 magnetization $M_{NU}(t)$. When the walker hits the solid surface, its contribution is
143 reduced by multiplying it by $(1 - \delta)$ (Jin et al., 2009)(Tan et al., 2014).
- 144 ii. The walker has a probability δ of being flagged as "killed"
145 whenever it hits the surface. At time t , the value of $M_{NU}(0)$ is reduced by a
146 factor N_t/N_0 where N_0 is the total number of walkers and N_t is the number of
147 walkers that have not been killed at time t (Valfouskaya et al., 2006).

148 We use the first relaxation scheme although the difference of the computational costs and
149 resulting decays associated with both is negligible.

150 We observe that the digital image representation of the rock sample can only provide
151 a discrete approximation of the pore shapes. This may induce inaccuracies in the
152 estimated decay, as the discretization slightly increases the contact area for the walkers
153 (Jin et al., 2009). However, we restrict the walker's motion to perpendicular directions, as
154 described in (Watanabe and Nakashima, 2002)), obtaining an accurate fit to analytical
155 results, as shown in Fig. 1. In the figure, the numerical results were obtained with the aid
156 our RW implementation employed in a discrete approximation of a sphere with radius
157 twenty-voxel, while the analytical results were obtained with the aid of Eq. (1).



158
159 **Figure 1.** In the Random Walk simulations we restrict the walker's motion to perpendicular directions, obtaining
160 an accurate fit to analytical results (right). The numerical results were obtained with the aid our RW
161 implementation employed in a discrete approximation of a sphere with radius twenty-voxel (radius 20 μm and
162 $\Delta = 1 \mu\text{m}$) using $\rho = 5 \mu\text{m/s}$ and $T_2 = 2.8\text{s}$, while the analytical results were obtained with the aid of Eq. (1).

163

164 The result of the RW simulation is the value of the magnetization $M(t)$ at discrete
165 times $t_k = k\Delta t, k = 1, 2, \dots, n$. To interpret the information embedded in this signal, the
166 inverse Laplace transform is applied. This consists of finding the coefficients $c_j, j =$
167 $1, 2, \dots, m$ that provide the best fit for the relation:

$$M(t_k) = \sum_{j=1}^m c_j e^{-\frac{t_k}{T_{2,j}}} . \quad (2)$$

168 The plot of coefficients c_j as a function of the corresponding times $T_{2,j}$ is typically called
 169 the T_2 distribution. Obtaining these coefficients can be stated as a least squares problem
 170 and its ill conditioned nature is associated with the presence of noise in the measured
 171 signal $M(t)$ (Prange and Song, 2009). Different noise levels associated with the same
 172 measurement may result in different T_2 distributions, which may reveal features
 173 associated with the noise and not with what was probed in the sample. This effect is
 174 limited by the Tikhonov regularization (Day, 2011), which consists of solving the
 175 optimization problem:

$$\min_{\mathbf{c}} \|\mathbf{Ac} - \mathbf{m}\|^2 + \lambda^2 \|\mathbf{c}\|^2, \quad (3)$$

176 where \mathbf{A} is a matrix whose entries are given by $A_{k,j} = e^{-\frac{t_k}{T_{2,j}}}$, \mathbf{m} is a vector whose entries
 177 are the discrete values $M(t_k)$, \mathbf{c} is the vector of coefficients c_j , and λ is a regularizer that
 178 controls the weight of the solution vector \mathbf{c} relative to the minimization of the error
 179 $\|\mathbf{Ac} - \mathbf{m}\|$. In the present work we use the L-curve criterion to determine the regularization
 180 value (Hanke, 1996)(Hansen, 1999)(Hansen and O'Leary, 1993).

181 **2.2 - Inverse problem methodology**

182 We state the inverse problem as follows: with the aid of RW simulations performed
 183 on the rock sample digital image, determine the surface relaxivity function whose
 184 corresponding T_2 distribution best matches the reference (measured) T_2 distribution. If

185 the surface relaxivity function is parametrized, the inverse problem may be stated as an
186 optimization task in which these parameters must be adjusted.

187 **2.2.1 - Surface relaxivity function parametrization**

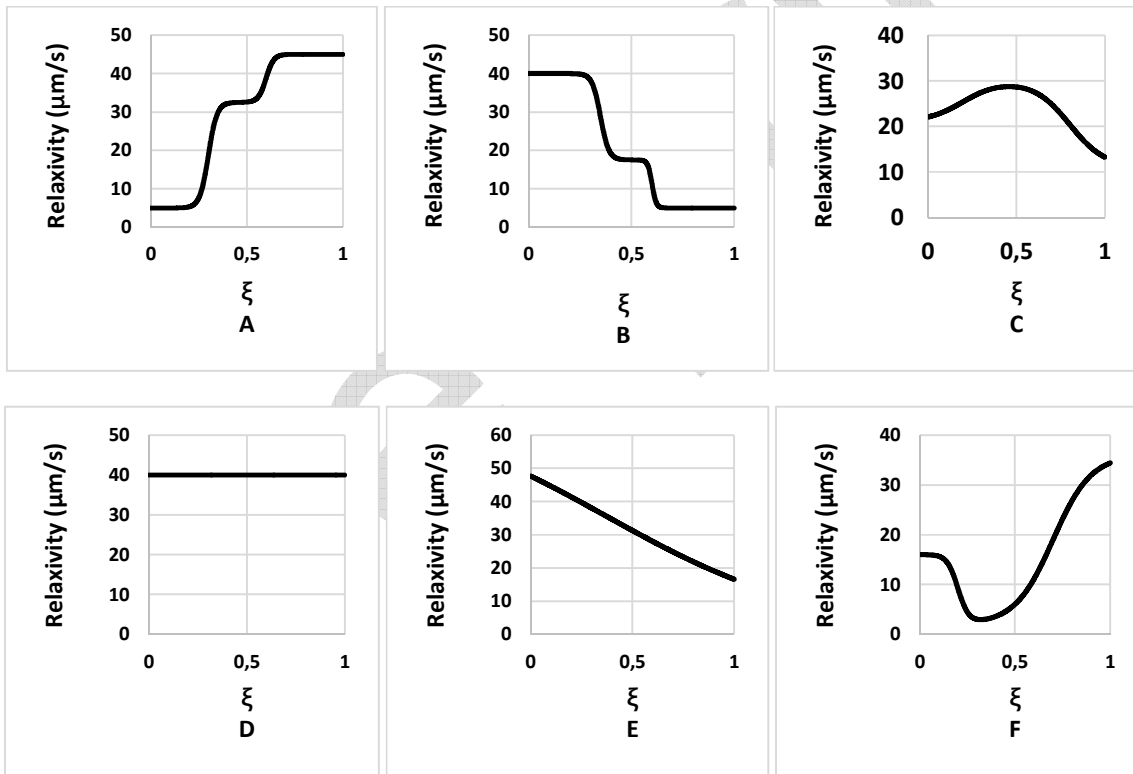
188 We benefit from the fact that in a RW simulation the total number of wall collisions
189 of a walker is proportional to the size of the pore in which it resides (the larger the pore
190 is, the smaller the total number of wall collision is, and vice versa), and instead of directly
191 associating a surface relaxivity value with each portion of the solid/fluid interface
192 according to the pore size (which would be impossible in practical implementations), we
193 associate a surface relaxivity value to each total number of wall collisions. In other words,
194 the surface relaxivity $\rho = \rho(\xi)$, where ξ is the total number of wall collisions normalized
195 to the total number of iterations in the RW simulation, as seen in more details in Section
196 2.2.2.

197 In the present work, we assume that the surface relaxivity function $\rho(\xi)$ is a linear
198 combination of basic shape functions. We choose Sigmoid shape functions with four
199 parameters to adjust:

$$\rho(\xi) = \sum_{i=1}^n A_i + \frac{K_i - A_i}{1 + e^{-B_i(\xi - \xi_i)}} \quad (4)$$

200 The values of K_i and A_i control the minimum and maximum values of the sigmoid, the
201 value of ξ_i defines the transition point (from minimum to maximum or vice-versa) and the
202 value of B_i controls the slope of the curve. This choice for the shape functions is suitable
203 to find piecewise continuous functions, establishing $n + 1$ different horizontal relaxivity
204 asymptotes for different pore size intervals. Notably, it would be suitable to approximate

205 the experimental results found in (Liu et al., 2014), for instance. The sharpness of the
 206 relaxivity transitions is controlled by the slope. We limited the number of shape functions
 207 here to $n = 2$, reducing our search to 8 optimization parameters. We emphasize that with
 208 this choice for the shape function we have increased flexibility and can represent relaxivity
 209 functions that either increase or decrease with the pore size, as well as to represent a
 210 uniform value, as shown later in Section 3.2. Examples of different surface relaxivity
 211 functions, illustrating some of the different tendencies that we can recover using the sum
 212 of two Sigmoid functions, are given in Fig. 2.



213

214

215 **Figure 2. Examples of different surface relaxivity functions, illustrating some of the different tendencies that**
 216 **we can recover using the sum of two Sigmoid functions. The vectors of parameters $(K_1, A_1, \xi_1, B_1, K_2, A_2, \xi_2, B_2)$**
 217 **are chosen as follows: $A = (30, 2.5, 0.3, 45, 15, 2.5, 0.6, 50)$, $B = (2.5, 15, 0.6, 100, 2.5, 15, 0.35, 50)$, $C =$**
 218 **$(1, 20, 0.8, 10, 10, 1, 0.2, 10)$, $D = (20, 20, 0.5, 25, 20, 20, 0.2, 900)$, $E = (0.5, 35, 0.25, 2, 0.5, 35, 0.5, 2)$, $F =$**
 219 **$(35, 1, 0.7, 10, 1, 15, 0.2, 35)$.**

220 We end this section by making two final comments: First, we expect that a
221 distribution of total number of wall collisions (and not a single value) is associated with
222 each pore size (range). This is why we consider the Sigmoid functions for the surface
223 relaxivity function, because it provides the flexibility to associate the same surface
224 relaxivity value to an entire ξ range. Even if the distributions of total number of wall
225 collisions associated with the different pore size ranges partially overlap, we expect that
226 to have a residual impact in the inversion results. This is exactly what the example in
227 Section 3.3 indicates because we could precisely recover the original surface relaxivity
228 function. Second, in principle, in actual rocks, pores of the same size can present different
229 surface relaxivities. Accordingly, assuming that only one exact surface relaxivity value will
230 be associated with each ξ is an idealization, and we make this assumption to formulate a
231 treatable inverse problem. Realistically, we expect that for each pore size range the
232 surface relaxivity value fluctuates around an average value. In that sense, we do not
233 expect that the sum of two Sigmoid functions perfectly fits the actual surface relaxivity
234 variation, but that it well represents the eventual overall tendency of the surface relaxivity
235 to vary with pore size.

236 **2.2.2 - The Mapping Simulation**

237 As we will see next, our inverse method evaluates a candidate function $\rho_c(\xi)$ by
238 executing a RW simulation based on it. To that end, it is crucial to associate a value ξ to
239 each walker. This is done only once, in the beginning of the optimization procedure, with
240 the aid of a preliminary RW simulation, in which every walker is associated with a variable
241 that is increased by 1 whenever it hits a solid wall. At the end of the simulation, we have
242 the normalized set of pairs $\left(k, \frac{y_k}{n_{st}}\right)$, $k = 1, \dots, N$, where N is the total number of walkers, k

243 is the walker identification, y_k is its corresponding total number of collisions, and n_{st} is
244 the total number of iterations. As mentioned earlier, we define $\xi_k = y_k/n_{st}$. We will refer
245 to this preliminary RW simulation as the Mapping Simulation (MS), because it provides a
246 classifier value ξ to each walker. Notice that no surface relaxivity (or bulk relaxivity) needs
247 to be associated with the pores for the MS. Typically, in the MS we consider $n_{st} = 15,000$
248 for an image resolution of $1\mu\text{m}$, which corresponds to around 2.8 seconds (the usual
249 relaxation time measured in the laboratory experiment).

250 According to what is said above, we note that we assign the same ξ value to
251 walkers that remained the entire time within pores of the same size and to those that
252 visited pores of different sizes, as long as they have had the same number of wall
253 collisions in the MS. It is impossible at this point to precisely predict the impact of this
254 approximation in the inversions, but, according to our preliminary tests, it is residual.

255 **2.2.3 - Shape function optimization**

256 To simulate a random walk decay based on a candidate function $\rho_c(\xi)$ we proceed
257 as follows: We assign to each walker (indexed by k) a relaxivity value ρ_k according to its
258 ξ_k , computed during the MS, i.e., $\rho_k = \rho_c(\xi_k)$. Then, the walker k starts its motion at the
259 same position it started in the MS (carrying its own relaxivity value ρ_k) and is penalized
260 by the factor $\delta = 2\Delta\rho_k/3D$ whenever it hits a solid wall. We perform this with all of the
261 walkers individually and sum the individual magnetization contributions at each time step.
262 At the end of this procedure we have the exponential decay and the corresponding T_2
263 distribution (applying the inverse Laplace transform to the simulated exponential decay)
264 associated with the function ρ_c .

265 We use genetic algorithms (GAs) to find the surface relaxivity function whose
 266 corresponding simulated T_2 distribution best matches the reference T_2 distribution. We
 267 expect them to be robust to treat noisy and incomplete input data, and to reduce the
 268 probability of becoming trapped at local minima. The purpose of GAs is to apply
 269 environmental pressure (survival of the fittest) to a set of possible solutions to the problem
 270 (Eiben and Schoenauer, 2002). In our case, a possible solution (that is typically called
 271 an individual) is encoded as a vector of 8 parameters $(K_1, A_1, \xi_1, B_1, K_2, A_2, \xi_2, B_2)$ that
 272 characterize the candidate relaxivity function $\rho_c(\xi)$ (see Eq. (4)). For each individual, a
 273 RW simulation is performed as described above, and an associated T_2 distribution L^i is
 274 obtained. Each individual is then ranked according to the correlation between its
 275 associated T_2 distribution and the reference T_2 distribution, i.e., $L \cdot L^i / (\|L\| \|L^i\|)$, where
 276 L is the reference T_2 distribution. A perfect match corresponds to a correlation equal to 1.

277 A common issue in GAs is premature convergence (Pandey et al., 2014). Here, we
 278 use a variant of the island methodology to avoid it (Whitley et al., 1998). Our GA
 279 implementation divides the population of N individuals (a set of N surface relaxivity
 280 functions) in p subpopulations (islands) of the same size N/p . Each of these
 281 subpopulations is optimized locally, recombining the information of its individuals using a
 282 whole arithmetic operator (described in (Eiben and Smith, 2007)). This recombination is
 283 executed in pairs, such that two random individuals (K_1^1, A_1^1, \dots) , (K_1^2, A_1^2, \dots) are combined
 284 to produce another two individuals $\alpha(K_1^1, A_1^1, \dots) + (1 - \alpha)(K_1^2, A_1^2, \dots)$ and $(1 -$
 285 $\alpha)(K_1^1, A_1^1, \dots) + \alpha(K_1^2, A_1^2, \dots)$ where α is chosen randomly in the interval $[0, \frac{1}{2}]$. After
 286 calculating the correlation of the T_2 distributions associated with these new individuals

287 with the reference T_2 distribution, the individuals whose associated T_2 distributions result
288 in the poorest correlations are discarded, keeping the subpopulation size constant at each
289 island. This procedure is repeated iteratively, allowing all individuals to recombine only
290 once in each step. After a certain number of iterations g , the individuals with the best
291 correlations migrate to another island. We also apply a mutation operator when the entire
292 island population becomes very similar, i.e., when the relative difference between all
293 individuals is less than 10%. The mutation operator picks one of the individual's entries
294 and alters it by a randomly chosen percentage in the interval $[0,100]$. In our tests, a
295 population of 48 individuals divided into 4 islands was enough to guarantee convergence
296 after approximately 50 iterations. A probability of 10% for mutation was considered.

297

298 **3 - Numerical results**

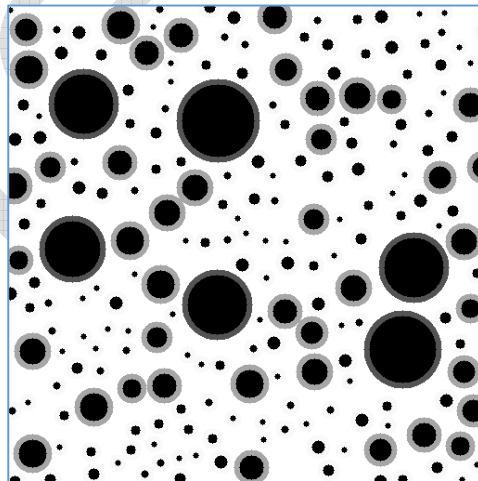
299 **3.1 - Effects of surface relaxivity variation**

300 Here we illustrate the effect of the surface relaxivity variation on the T_2 distribution
301 through a synthetic example. A random set of three circular pore families was placed on
302 a white background, as shown in Fig. 3. By pore family, we mean pores within the same
303 size range. A different gray-scale value was associated with each of the families,
304 corresponding to a different relaxivity value (a smaller relaxivity of $5 \mu\text{m}/\text{s}$ was associated
305 to the larger pores, a medium relaxivity of $20 \mu\text{m}/\text{s}$ was associated to the medium pores
306 and a larger relaxivity of $45 \mu\text{m}/\text{s}$ was associated to the smaller pores.) A 2D random
307 walk simulation was performed on this synthetic medium, such that whenever a walker

308 hits a solid wall, it picked the gray-scale value of the collision pixel, i.e., its magnetization
309 was reduced by the corresponding relaxivity value.

310 A bulk relaxation time of $T_{2,B} = 2.8s$ and a resolution of $\Delta = 2 \mu m$ was assumed. A
311 total of 54,575 walkers were used in the simulation, such that each pixel associated to
312 the pore space received one walker, filling the entire pore space. To simulate noise, we
313 synthetically added white noise to the simulated NMR magnetization decay, such that the
314 signal to noise ratio (SNR) was 368. The SNR here is estimated as $SNR = \frac{\mu_{100}}{\sigma_{100}}$, where
315 μ_{100} is the average of the first 100 decay samples (the first 100 simulated values) and
316 σ_{100} is the standard deviation of the last 100 decay samples. In addition, we used a
317 magnetization threshold stopping criterion value of 0.25%. The same stopping criterion
318 was also used in all the simulations shown in the subsequent sections. The regularization
319 was chosen according to the L-curve criterion.

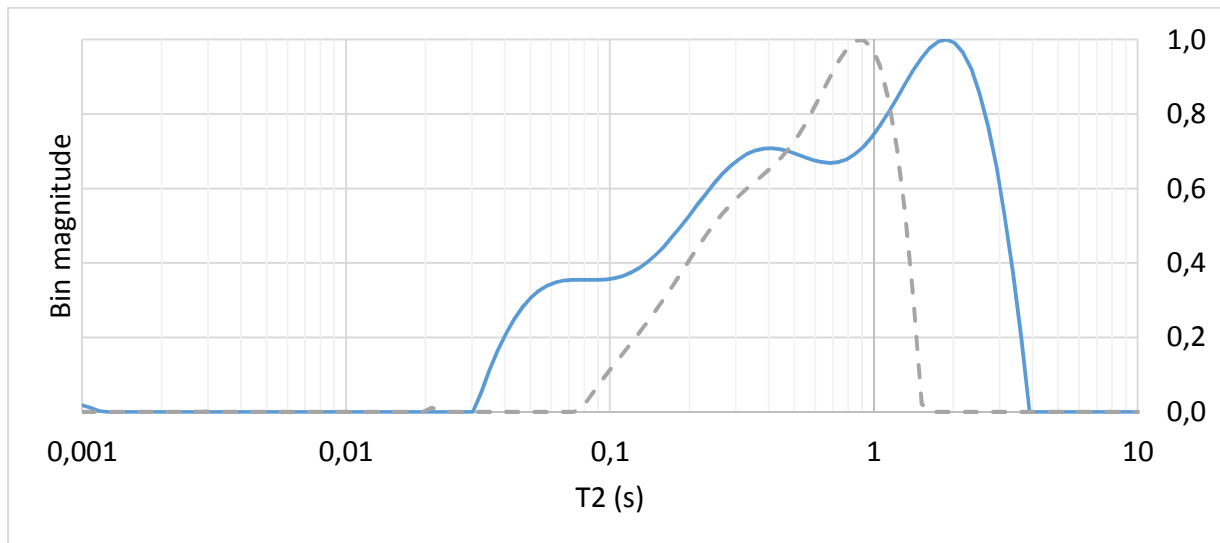
320



321

322 **Figure 3. The synthetic medium used in the simulations presented in Sections 3.1, 3.2 and 3.3. A random set**
323 **of three circular pore families was placed on a white background. A different gray-scale value is associated**
324 **with each of the pore families. For the simulation presented in Section 3.2, the same relaxivity value was**
325 **associated with all three families. For the simulation presented in Section 3.3, a different relaxivity value was**
326 **associated with each of the families.**

327



328

329 **Figure 4. The T_2 distribution obtained from the decay simulated with varying surface relaxivity (continuous**
330 **line) and the T_2 distribution obtained from the decay simulated with an average uniform surface relaxivity of**
331 **$20 \mu\text{m/s}$ (dashed line). The two curves are largely different. In particular, the simulation assuming a uniform**
332 **surface relaxivity produced a predominantly unimodal and narrower T_2 distribution.**

333

334 The T_2 distribution obtained from the decay simulated with the varying surface
335 relaxivity is shown in Fig. 4 (continuous line). The figure also shows the T_2 distribution
336 obtained from the decay simulated with an average uniform surface relaxivity of $20 \mu\text{m/s}$
337 (dashed line), i.e., the average uniform surface relaxivity of $20 \mu\text{m/s}$ was associated with
338 all the three pore families. The two relaxation curves are largely different for the same
339 pore size distribution. In particular, the simulation assuming the average uniform surface
340 relaxivity produced a predominantly unimodal and narrower T_2 distribution. The T_2
341 distribution is narrower for the uniform relaxivity case because, *at the larger pores*, the
342 relaxation occurs more rapidly in the uniform relaxivity case than in the varying relaxivity
343 case (because of the considered surface relaxivities.) Therefore, the portion of the T2
344 distribution at the right (the part associated with the larger pores) is narrower for the

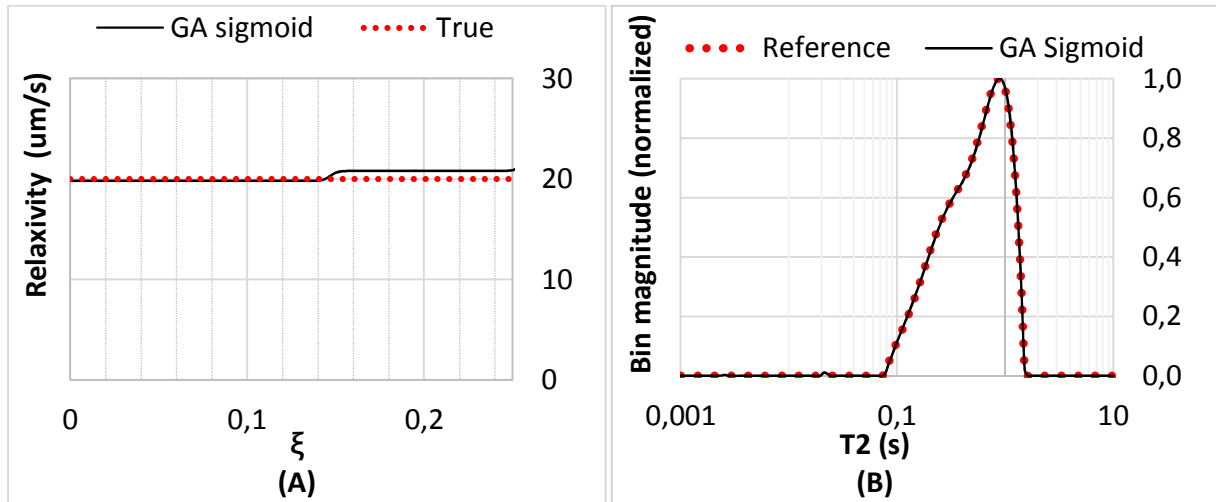
345 uniform relaxivity case than for the varying relaxivity case (we recall that relaxation time
346 increases to the right). On the other hand, *at the smaller pores*, the relaxation occurs
347 more slowly in the uniform relaxivity case than in the varying relaxivity case (again,
348 because of the considered surface relaxivities). Therefore, the portion of the T2
349 distribution at the left (the part associated with the smaller pores) is again narrower for
350 the uniform case than for the varying case. As a result, the T2 distribution as a whole is
351 narrower for the uniform case than for the varying case.

352 This is an example of how erroneous or incomplete assumptions regarding the
353 surface relaxivity can affect the NMR simulation. The effect of varying surface relaxivity
354 on petrophysical deliverables derived from NMR relaxation distributions has been
355 discussed in other works (e.g. (Arns et al., 2006) and (Ryu, 2008)).

356 **3.2 - Synthetic case with uniform relaxivity**

357 We now evaluate the performance of our method to estimate the surface relaxivity
358 for the uniform relaxivity case. For this purpose, we associate $\rho = 20 \mu\text{m}/\text{s}$ with all the
359 three pore families shown in Fig. 3. Our reference T_2 distribution comes from a RW
360 simulation executed, again, with 54,575 walkers (filling the entire pore space). To check
361 the robustness of the method for noisy input data, we considered two different SNRs in
362 the simulated decay, a SNR of 298, compatible with NMR experiments performed in the
363 lab (Fig. 5), and a SNR of 31, compatible with logging operations (Fig. 6). In Figs. 5(A) &
364 6(A) we show the surface relaxivity function obtained with the aid of our method and in
365 Figs. 5(B) & 6(B) we show the match of the resulting simulated T_2 distribution with the

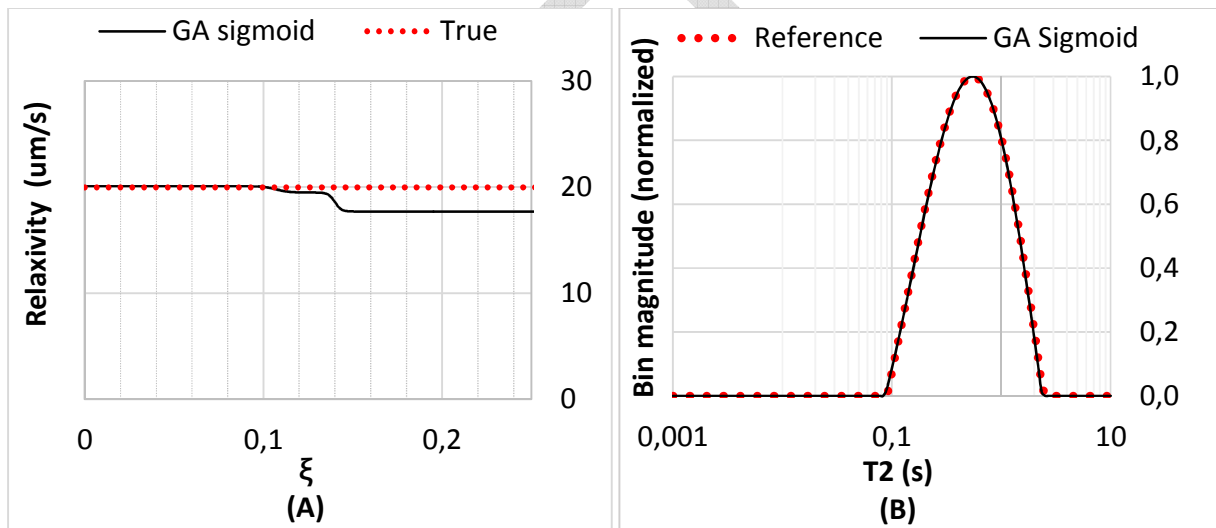
366 reference. A total of 148 generations were iterated (in general, each optimization took
 367 approximately 30 generations to converge).



368

369 Figure 5. (A) Comparison between the surface relaxivity function obtained from the inversion procedure and
 370 the “true” one. (B) The corresponding T_2 distributions. The SNR considered here is 298, which is compatible
 371 with NMR experiments performed in the lab. $\lambda = 0.11$

372



373

374 Figure 6. (A) Comparison between the surface relaxivity function obtained from the inversion procedure and
 375 the “true” one. (B) The corresponding T_2 distributions. The SNR considered here is 31, which is compatible
 376 with NMR logging operations. $\lambda = 3.19$

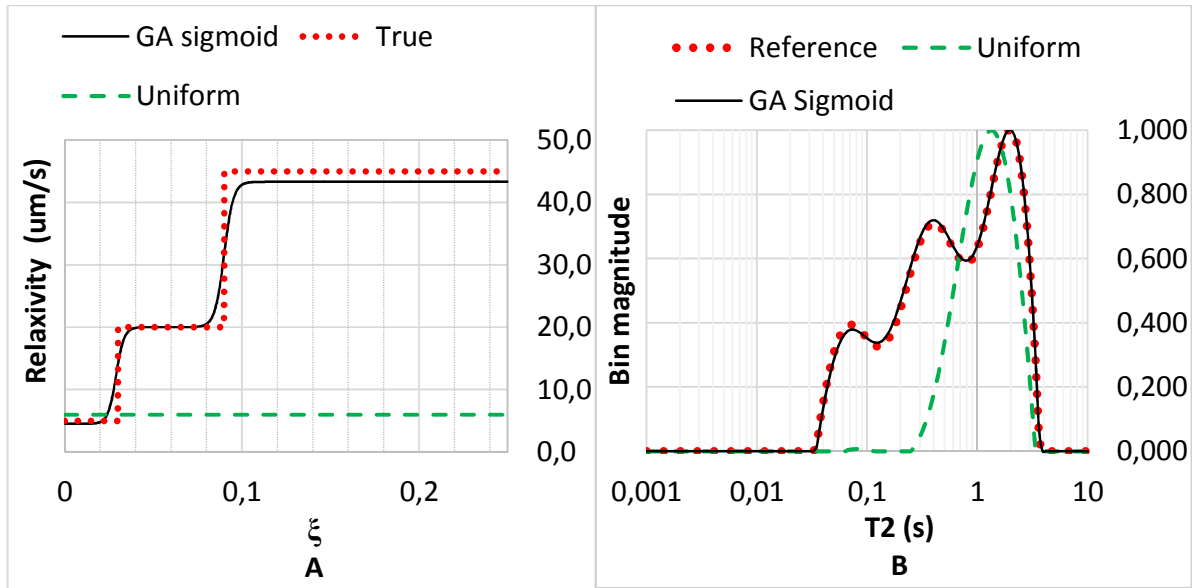
377

378 The results validate our implementation and show that our method performs well for
379 the uniform relaxivity case, where the obtained two-sigmoid combination adapted very
380 well to the uniform relaxivity value even for the noisiest case. We repeated each inversion
381 4 times and obtained the same results, indicating that the problem has only one global
382 minimum.

383 **3.3 - Synthetic case with varying relaxivity**

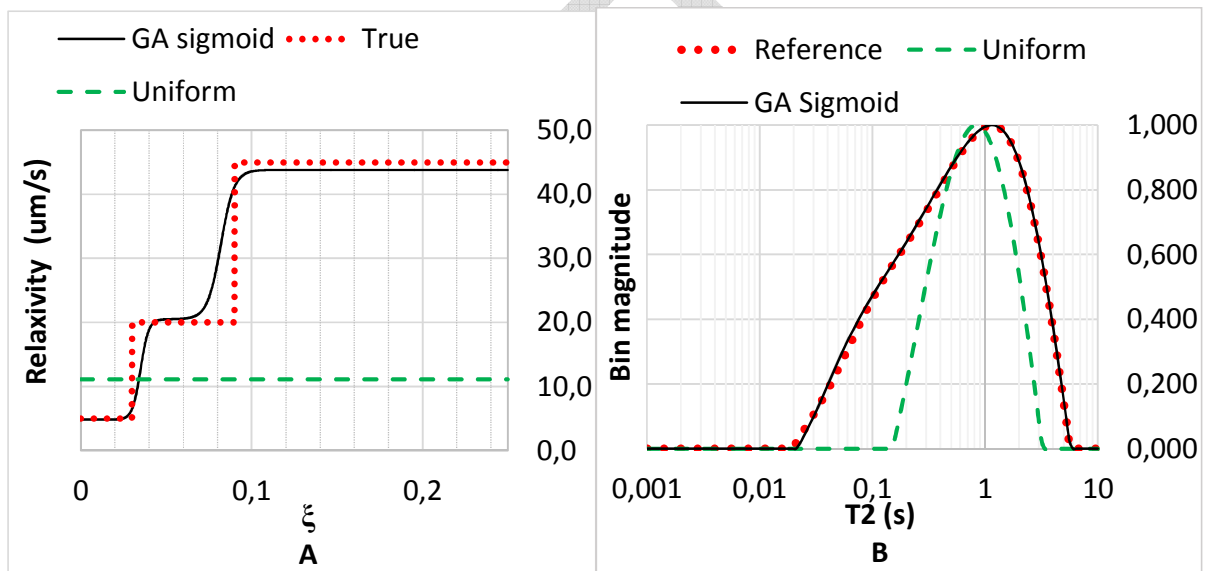
384 The second test corresponds to the scenario in Section 3.1, i.e., the medium is
385 represented in Fig. 3 and a different surface relaxivity value was associated with each of
386 the three pore families

387 . In Figs. 7(A) & 8(A) we compare the surface relaxivity function estimated with the
388 aid of our method with the original surface relaxivity variation (continuous line vs. dotted
389 line), while in Figs. 7(B) & 8(B) we show the match between the resulting T_2 distribution
390 and the reference. For Fig. 7, we have considered a SNR of 338, compatible with NMR
391 experiments performed in the lab, while for Fig. 8, we have considered a SNR of 32,
392 compatible with logging operations. As in the previous section, we repeated each
393 inversion 4 times and obtained the same results, indicating that the problem has only one
394 global minimum. The figures show that the method performed well even for the noisiest
395 case, validating both methodology and implementation. In addition, a uniform surface
396 relaxivity value does not exist that results in a good match for the reference T_2 distribution.
397 This is clearly shown by the dashed curves in Figs. 7(B) & 8(B). We emphasize that the
398 uniform surface relaxivity value used for each figure was also determined from an
399 optimization procedure, i.e., there is no other uniform surface relaxivity value that results
400 in a better match for the reference T_2 distribution than those shown in Figs. 7(A) and 8(A).



401
 402 Figure 7. (A) Comparison between the surface relaxivity function obtained from the inversion procedure and
 403 the “true” one. (B) The corresponding T_2 distributions. The SNR considered here is 338, which is compatible
 404 with NMR experiments performed in the lab. The T_2 distribution corresponding to the uniform relaxivity
 405 represented in (A) is also plotted in (B). $\lambda = \frac{1}{2}$

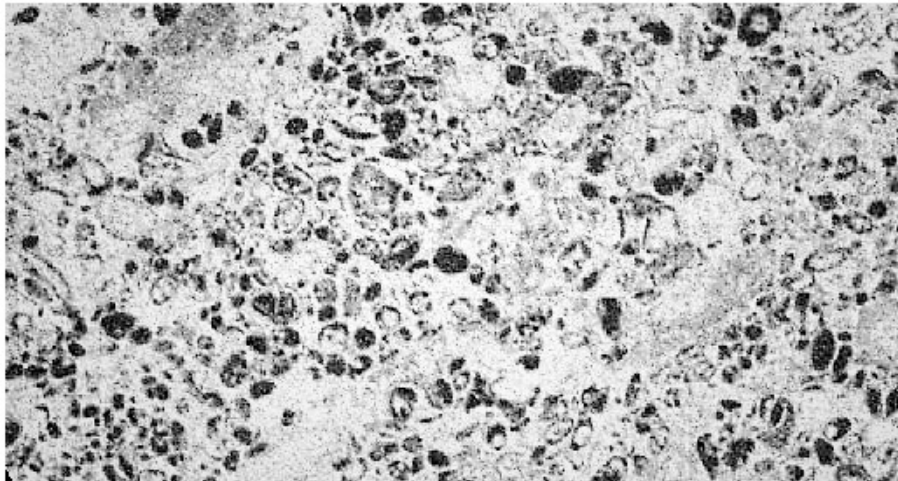
406



407
 408 Figure 8. (A) Comparison between the surface relaxivity function obtained from the inversion procedure and
 409 the “true” one. (B) The corresponding T_2 distributions. The SNR considered here is 32, which is compatible
 410 with logging operations. The T_2 distribution corresponding to the uniform relaxivity represented in (A) is also
 411 plotted in (B). $\lambda = 3.06$.

412 **3.4 - Laboratory case**

413 Now we apply the developed methodology to an actual sedimentary rock core. The
414 reference T_2 distribution is now the actual T_2 distribution from the lab. We also compare
415 the obtained results with the experimental determination of an average (uniform) effective
416 transverse surface relaxivity. The chosen sample is a calcite limestone outcrop, Edwards
417 White (EW), from the Edwards Formation located in the central-west state of Texas
418 (USA), with gas porosity and permeability of 0.28 and 5.5 mD , respectively (Silva Jr et al.,
419 2015). A slice of the sample tomographic image is shown in Fig. 9.



420

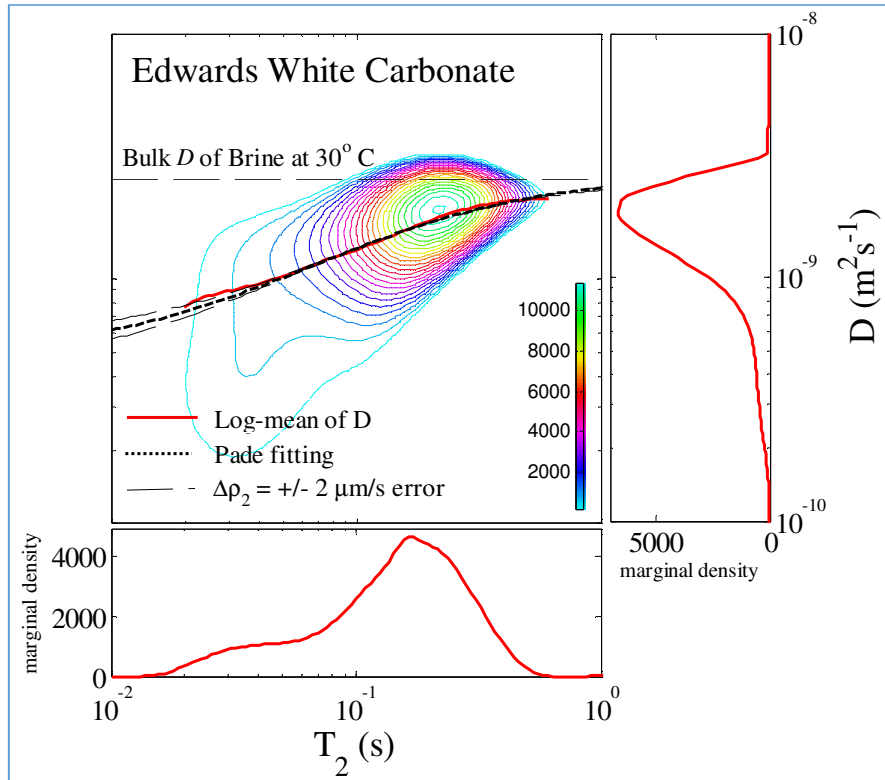
421

Figure 9. A slice of the Edwards White's tomographic image.

422

423 In the laboratory, an average effective relaxivity can be calculated from the two
424 dimensional NMR experiment called $D - T_2$ (diffusion coefficient T_2), a technique that
425 measures the correlation between both parameters (Souza et al., 2013)(Zielinski et al.,
426 2010). Fig. 10 shows the $D - T_2$ map signal (contour lines) of the EW core. The
427 experimental details of the NMR technique used to acquire the T_2 data and to perform the
428 $D - T_2$ are outside the scope of this work and can be found in (Luo et al., 2015)(Souza et

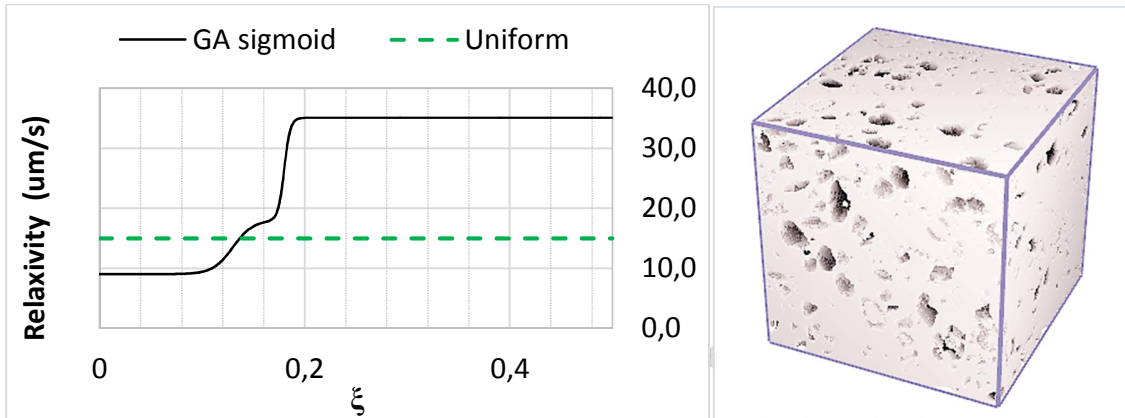
429 al., 2013) (Zielinski et al., 2010). From the $D - T_2$ experiment, we determined an average
 430 uniform surface relaxivity of $15 \mu\text{m}/\text{s}$.



431
 432 **Figure 10. 2D NMR $D - T_2$ map of the Edwards White sample, showing the Padé fitting (black dotted line) that**
 433 **resulted in an effective $\rho_2 = 15 \mu\text{m}/\text{s}$. Additional fittings (black dashed lines) considering the error on the input**
 434 **parameters: cementation coefficient (m) and bulk diffusion coefficient D_0 . The estimated error determined was**
 435 **$\Delta\rho_2 = \pm 2 \mu\text{m}/\text{s}$. All the fittings were performed considering the average of D for each T_2 bin.**

436
 437 The SNR of the decay signal measured in the lab was estimated at 378. In Fig. 11,
 438 we show the surface relaxivity function estimated with the aid of our method, and in Fig.
 439 12, we show the match between the resulting and measured T_2 distribution. As in the
 440 previous sections, we repeated the inversion 4 times and obtained the same results,
 441 indicating that the problem has only one global minimum. In Fig 12, we also plot the T_2

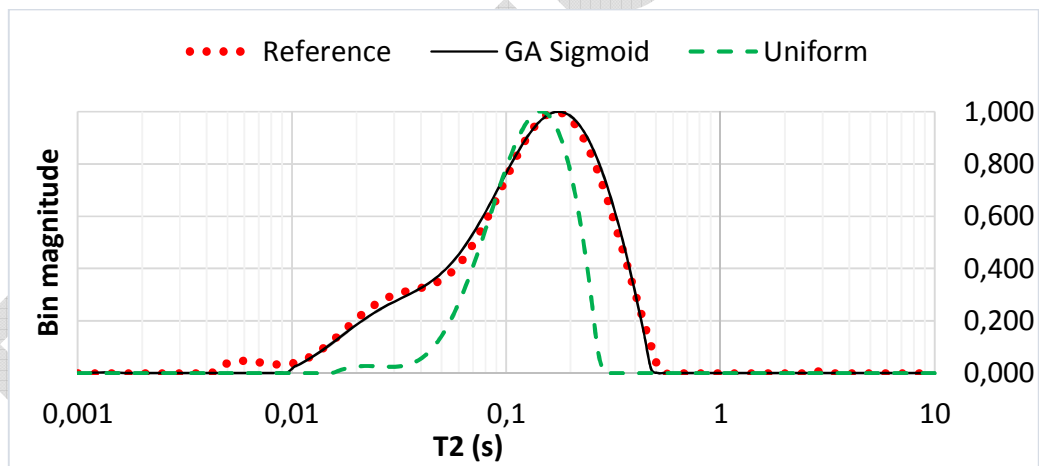
442 distribution resulting from a RW simulation performed with the uniform relaxivity of $\rho =$
 443 $15 \mu\text{m}/\text{s}$ (the value estimated in the lab.)



444

445 **Figure 11.** Edwards White's surface relaxivity function obtained from the inversion procedure. The surface
 446 relaxivity magnitude decreases with pore size. More specifically, the obtained relaxivity function suggests the
 447 existence of (approximately) two different horizontal relaxivity asymptotes associated with two different pore
 448 size intervals. The SNR of the measured NMR decay signal was estimated at 378.

449



450

451 **Figure 12.** Comparison between the T_2 distribution corresponding to the surface relaxivity function shown in
 452 Fig. 11 and the T_2 distribution measured in the lab. The T_2 distribution corresponding to the uniform relaxivity
 453 of $15 \mu\text{m}/\text{s}$ (the relaxivity value obtained from the $D - T_2$ experiment) is also plotted in the figure. $\lambda = 0.19$

454

455 The results shown in Fig. 11 indicate that the magnitude of the surface relaxivity
456 decreases as the pore size increases. More specifically, the obtained surface relaxivity
457 function suggests the existence of (approximately) two different horizontal relaxivity
458 asymptotes associated with two different pore size intervals. In addition, Figure 12Fig. 12
459 shows that the relaxivity function shown in Fig. 11 leads to a T_2 distribution that accurately
460 matches the reference. In fact, it matches the reference much more precisely than the T_2
461 distribution obtained with the uniform surface relaxivity value of $15 \mu\text{m}/\text{s}$. In that sense,
462 we truly believe that the relaxivity function obtained with the aid of the proposed
463 methodology is a better estimate for the surface relaxivity, for any practical implication,
464 than the uniform value obtained from the $D - T_2$ experiment. The T_2 distribution obtained
465 with the aid of the proposed method does not match well the reference only in a small
466 portion at the left, related to the relaxation at the smallest pores. We can think of some
467 potential explanations for this local mismatch. First, the digital image may not have
468 captured accurately the micro-porosity (we recall here that the gas porosity is 28% while
469 the porosity digitally calculated from the tomographic image is approximately 20.5%).
470 Second, the physical dimensions of the image in which we performed the RW are shorter
471 than the physical dimensions of the sample used in the NMR experiment. In that sense,
472 the image used may not be a perfect representative volume. Third, there are methodology
473 approximations, as mentioned previously in the text, that can impact the inversion results.
474 Currently, it is impossible to know for sure the reason for the small local mismatch.

475 We end this section providing a final comment. In principle, the degree of correlation
476 between the simulated T_2 distribution and the reference T_2 distribution may be indicative
477 of the error associated with the obtained surface relaxivity function. However, more tests

478 need to be performed before we can make that statement. It certainly would be valuable
479 to check the inversion result's accuracy and, for each case, determine if the surface
480 relaxivity variation is indeed linked to the pore size.

481

482 **4 - Summary and conclusions**

483 In the present work we formulated and solved an inverse problem to recover the
484 surface relaxivity as a function of pore size. The input data for our technique are the T_2
485 distribution measurement and the micro-tomographic image of the rock sample under
486 investigation. We simulate the NMR signal relaxation for a given surface relaxivity function
487 using the random walk method, and the optimization is performed using genetic
488 algorithms, where we find the surface relaxivity function that leads to the best match for
489 the T_2 distribution measurement. In the developed methodology, we use the link between
490 pore size and total number of wall collisions in the random walk simulations.

491 We evaluate the proposed method's performance using inversions from (noisy)
492 synthetic and laboratory input data. The SNRs are compatible with lab experiments and
493 field log measurements. Regarding the results obtained from synthetic input data, the
494 method could accurately recover the original surface relaxivity function for the case of
495 uniform relaxivity as well as for the case of varying relaxivity, for both SNR levels.
496 Regarding the results obtained from the laboratory input data, we verified that we could
497 precisely match the measured T_2 distribution. On the other hand, the T_2 distribution
498 resulting from the uniform relaxivity assumption did not accurately match the measured
499 T_2 distribution. This indicates that the relaxivity function obtained using the proposed

500 method is presumably a better estimate, for any practical implication, than the uniform
501 value obtained from the $D - T_2$ experiment. In principle, the degree of correlation between
502 the simulated T_2 distribution and the reference T_2 distribution may be indicative of the
503 error associated with the obtained surface relaxivity function. However, more tests need
504 to be performed before we can make that statement. It would be valuable to check the
505 inversion result's accuracy and, for each case, determine if the surface relaxivity variation
506 is linked to pore size.

507 **Acknowledgements**

508 This work was carried out in association with the ongoing NMR Project, sponsored by
509 Shell, registered as “Aplicação de técnicas avançadas de Ressonância Magnética
510 Nuclear (RMN) assistidas por ferramentas computacionais na avaliação petrofísica de
511 rochas carbonáticas” (ANP 18999-3) under the ANP R&D levy as “Compromisso de
512 Investimentos com Pesquisa e Desenvolvimento”. The authors also recognize the
513 support from CAPES, CNPq and FAPERJ. F. B. recognizes the support from National
514 University of Costa Rica (UNA).

515 **References**

- 516 Arns, C.H., Sheppard, A.P., Saadatfar, M., Knackstedt, M.A., others, 2006. Prediction of
517 permeability from NMR response: surface relaxivity heterogeneity, in: SPWLA 47th
518 Annual Logging Symposium. Society of Petrophysicists and Well-Log Analysts.
- 519 Bergman, D.J., Dunn, K.-J., Schwartz, L.M., Mitra, P.P., 1995. Self-diffusion in a periodic
520 porous medium: A comparison of different approaches. Phys. Rev. E 51, 3393–
521 3400.

- 522 Boggs, S., 2009. Petrology of Sedimentary Rocks. Cambridge University Press., pp. 137–
523 206.
- 524 Brownstein, K.R., Tarr, C.E., 1979. Importance of classical diffusion in NMR studies of
525 water in biological cells. Phys. Rev. A 19, 2446–2453.
- 526 Coates, G.R., Xiao, L., Prammer, M.G., 1999. NMR logging: principles and applications.
527 Haliburton Energy Services.
- 528 Day, I.J., 2011. On the inversion of diffusion NMR data: Tikhonov regularization and
529 optimal choice of the regularization parameter. Journal of Magnetic Resonance
530 211, 178–185.
- 531 Dunn, K.-J., Bergman, D.J., Latorraca, G.A., 2002. Nuclear magnetic resonance:
532 Petrophysical and Logging applications. Pergamon. Handbook of geophysical
533 exploration. Volume 32.
- 534 Eiben, A.E., Schoenauer, M., 2002. Evolutionary computing. Information Processing
535 Letters 82, 1–6.
- 536 Eiben, A.E., Smith, J.E., 2007. Introduction to Evolutionary Computing, in:
537 Natural Computing Series. Springer Berlin Heidelberg. Ch: 3.5, pp. 42–69.
- 538 Hanke, M., 1996. Limitations of the L-curve method in ill-posed problems. BIT Numerical
539 Mathematics 36, 287–301.
- 540 Hansen, P.C., 1999. The L-curve and its use in the numerical treatment of inverse
541 problems. IMM, Department of Mathematical Modelling, Technical University of
542 Denmark.

- 543 Hansen, P.C., O'Leary, D.P., 1993. The Use of the L-Curve in the Regularization of
544 Discrete Ill-Posed Problems. *Siam Journal on Scientific Computing* 14.
- 545 Jin, G., Torres-Verdín, C., Toumelin, E., 2009. Comparison of NMR simulations of porous
546 media derived from analytical and voxelized representations. *Journal of Magnetic
547 Resonance* 200, 313–320.
- 548 Keating, K., Knight, R., 2012. The effect of spatial variation in surface relaxivity on nuclear
549 magnetic resonance relaxation rates. *Geophysics* 77, E365–E377.
- 550 Liu, H., d Eurydice, M.N., Obruchkov, S., Galvosas, P., 2014. Determining pore length
551 scales and pore surface relaxivity of rock cores by internal magnetic fields
552 modulation at 2 MHz NMR. *Journal of Magnetic Resonance* 246, 110–118.
- 553 Looyestijn, W.J., Hofman, J., 2006. Wettability-index determination by nuclear magnetic
554 resonance. *SPE Reservoir Evaluation & Engineering* 9, 146–153.
- 555 Luo, Z.-X., Paulsen, J., Song, Y.-Q., 2015. Robust determination of surface relaxivity from
556 nuclear magnetic resonance DT2 measurements. *Journal of Magnetic Resonance
557* 259, 146–152.
- 558 Pandey, H.M., Chaudhary, A., Mehrotra, D., 2014. A comparative review of approaches
559 to prevent premature convergence in GA. *Applied Soft Computing* 24, 1047–1077.
- 560 Prange, M., Song, Y.-Q., 2009. Quantifying uncertainty in NMR spectra using Monte Carlo
561 inversion. *Journal of Magnetic Resonance* 196, 54–60.
- 562 Ryu, S., 2008. Effects Of Spatially Varying Surface Relaxivity And Pore Shape On Nmr
563 Logging. *Society of Petrophysicists and Well-Log Analysts, SPWLA-2008-BB CP*.

- 564 Saidian, M., Prasad, M., 2015. Effect of mineralogy on nuclear magnetic resonance
565 surface relaxivity: A case study of Middle Bakken and Three Forks formations. Fuel
566 161, 197–206.
- 567 Silva Jr, G.P. da, Franco, D.R., Stael, G.C., Oliveira Lima, M. da Costa de, Martins, R.S.,
568 Moraes França, O. de, Azeredo, R.B.V., 2015. Petrophysical studies of north
569 American carbonate rock samples and evaluation of pore-volume compressibility
570 models. Journal of Applied Geophysics 123, 256–266.
- 571 Souza, A., Carneiro, G., Zielinski, L., Polinski, R., Schwartz, L., Hürlimann, M.D., Boyd,
572 A., Rios, E.H., Santos, B.C.C. dos, Trevizan, W.A., others, 2013. Permeability
573 Prediction Improvement Using 2D NWR Diffusion-T2 Maps, in:
574 SPWLA54thAnnualLoggingSymposium. Society of Petrophysicists and Well-Log
575 Analysts.
- 576 Talabi, O., AlSayari, S., Iglauer, S., Blunt, M.J., 2009. Pore-scale simulation of NMR
577 response. Journal of Petroleum Science and Engineering 67, 168–178.
- 578 Tan, M., Xu, J., Zou, Y., Xu, C., 2014. Nuclear magnetic resonance (NMR) microscopic
579 simulation based on random-walk: Theory and parameters analysis. Journal of
580 Central South University 21, 1091–1097.
- 581 Valfouskaya, A., Adler, P.M., Thovert, J.-F., Fleury, M., 2006. Nuclear magnetic
582 resonance diffusion with surface relaxation in porous media. Journal of Colloid and
583 Interface Science 295, 188–201.

- 584 Watanabe, Y., Nakashima, Y., 2002. RW3D. m: three-dimensional random walk program
585 for the calculation of the diffusivities in porous media. *Computers & geosciences*
586 28, 583–586.
- 587 Whitley, D., Rana, S., Heckendorn, R.B., 1998. The Island Model Genetic Algorithm: On
588 Separability, Population Size and Convergence. *Journal of Computing and*
589 *Information Technology* 7, 33–47.
- 590 Zielinski, L., Ramamoorthy, R., Minh, C.C., Al Daghar, A., Abdelaal, A., 2010. Restricted
591 diffusion effects in saturation estimates from 2D Diffusion-Relaxation NMR maps.
592 Annual Technical Conference and Exhibition of Society of Petroleum Engineers
593 134841.
- 594