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4 **Investigation of the effect of aging on wood hygroscopicity by 2D  $^1\text{H}$  NMR**  
5 **relaxometry**

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13  
14 **Abstract:** 2D  $^1\text{H}$  NMR relaxometry is increasingly used in the field of wood sciences due to its great  
15 potential in detecting and quantifying water states at the level of wood constituents. More precisely,  
16 in this study, this technique is used to investigate the changes induced by “natural” and “artificial”  
17 aging methods on modern and historical oak woods. Two bound water components are detected and  
18 present differences in terms of association to the different wood polymers in cell walls: one is more  
19 strongly associated to wood polymers than the other. The evolution of the two bound water types is  
20 discussed in regard to aging methods and is related to the structure of the cell wall, especially with  
21 the S2 layer and the evolution of wood chemical composition (cellulose, hemicelluloses and lignin).  
22 The evolution of hydric strains is discussed taking into account the effect of aging methods on the  
23 two bound water components too. The obtained results confirm the ability of 2D NMR relaxometry to  
24 evaluate the effect of aging at the molecular level and on hydric deformation. Furthermore, this  
25 method shows that it is possible to determine the moisture content of wood without the necessity to  
26 oven-dry the wood material.

27  
28 **Keywords:** Aging, deformation, extractibles, hydric cycles, oak wood, thermal treatment, 2D NMR  
29 relaxometry

## 31 **Introduction**

32 The built heritage shows that wood makes it possible to design sustainable and healthy buildings  
33 (Epaud 2007, Obataya 2007, Froidevaux 2012). Wood, as an envelope or structural material, is a  
34 material of interest in the field of construction both for new buildings and for the question of  
35 renovation of old buildings (Froidevaux 2012). However, to estimate lifetimes or to propose methods  
36 of maintenance, it is necessary to continue the research efforts to understand the mechanisms of  
37 physical aging of wood and its hygro-mechanical properties at the scale of its constituents.

38 Aging is a complex phenomenon that modifies physical, chemical and mechanical properties of a  
39 polymeric based material, under the effect of its proper instability, environmental parameters or  
40 mechanical strains (Fayolle and Verdu 2005). As a natural and biodegradable resource, wood is  
41 mainly constituted of three biopolymers: cellulose, hemicellulose and lignin. These components can  
42 be vulnerable to environmental factors such as temperature, solar radiation, humidity, which can  
43 degrade the wood's polymeric structure. Studies have shown that the degradation due to aging mostly  
44 affect the hemicelluloses (which are the most vulnerable polymers), resulting in a better dimensional  
45 stability of the wood material (Kranitz 2014, Gauvin 2014). A decrease of cellulosic material as well  
46 as a slight decrease in lignin content are also observed in some historical woods (Kranitz et al. 2016).  
47 Heat treatments at high temperature show a common effect with natural aging on decreasing the  
48 Equilibrium Moisture Content (EMC), leading to an improved dimensional stability of wood and are  
49 usually considered as artificial aging. Numerous studies have been conducted to develop industrial  
50 processes varying in terms of temperature (generally at high temperature between 160°C and 280°C),  
51 duration and vector (gas, water vapour, oil...) (Tjeerdsma et al. 1998, Esteves and Pereira 2008,  
52 Wentzel et al. 2018) to improve the durability of timbers. The higher the temperature of treatment -  
53 and the longer the treatment time - the greater the dimensional stability of wood (Inari et al. 2009;  
54 Chaouch 2011; Endo et al. 2016). However, these treatments' intensity considerably weakens the  
55 mechanical properties of timbers (Hill 2006, Froidevaux 2012, Candelier 2016). Thus, thermal

56 treatments at lower temperature are proposed as a better alternative as they have a lower effect on the  
57 mechanical properties of timber. However, it remains unclear if the thermal treatments in presence or  
58 absence of humidity is the closest to a ‘natural aging’ effect. Some authors show that hydrothermal  
59 treatments in precise conditions of Relative humidity, Temperature and Pressure can mimic an aged  
60 wood in terms of its mechanical characteristics, colour change and decreased swelling rate  
61 (Froidevaux 2012, Gauvin 2015, Endo et al. 2016). Whereas in terms of dry heat treatments, it seems  
62 to be a better option than steam to reduce the hygroscopic capacity of wood, and improve its  
63 dimensional stability, with a minimum of thermal degradation (Obataya 2007, Matsuo et al. 2009,  
64 Sandberg and Navi 2013).

65 The wood hygroscopicity plays a major role on the dimensional stability and mechanical properties  
66 of wood. This improved dimensional stability may be explained by a decrease in adsorption sites in  
67 the polymers chains of the wood cell walls (Hill 2006, Froidevaux 2012, Murata et al. 2013).  
68 However, in Rautkari et al. 2013, a poor correlation between EMC, sorption sites accessibility and  
69 theoretical hydroxyl group content was found following a thermal treatment and therefore additional  
70 mechanisms should exercise control over the EMC. This shows that water interactions with wood  
71 (hygroscopicity and dimensional stability) are still not completely understood, which can be  
72 explained by the difficulty to characterize adsorbed water in wood. The use of proton Nuclear  
73 Magnetic Resonance ( $^1\text{H}$  NMR) relaxometry to detect bound water in the wood’s cell walls is gaining  
74 popularity in the research field as it is a non-invasive method allowing to study the same material  
75 subjected to different loadings. Here, we investigate the state of water adsorbed on the wood’s cell  
76 walls through  $^1\text{H}$  low-field (LF) NMR relaxometry (Menon et al. 1987, Araujo et al. 1994, Labbé et  
77 al. 2002, Fredriksson and Garbrecht Thygesen 2017, Beck et al. 2018). Recent studies (Cox et al.  
78 2010, Bonnet et al. 2017) have used two-dimensional (2D)  $T_1$ - $T_2$  correlation spectra, allowing to  
79 differentiate two different types of bound water, which have been assigned to water adsorbed to  
80 different wood polymers in the hygroscopic range (Bonnet et al. 2017). So far, this technique is the

81 sole tool capable to observe two different types of bound water in wood. Thus, 2D  $^1\text{H}$  NMR  
82 correlation spectra is a great method that can provide an insight on the water environment inside the  
83 lignocellulosic matter and hints the influence of the microstructure and chemical composition on the  
84 hydrogen signal observed. Moreover, the influence of the two bound water components on  
85 dimensional properties has to be further investigated. According to Cox et al. (2010), only one  
86 component may contribute to wood swelling, whereas for Bonnet et al. (2017), the two components  
87 have an effect on the hydric strains.

88 The main purpose of this study is to analyse the effect of two aging methods on the hygroscopicity of  
89 wood material by using the 2D  $^1\text{H}$  NMR relaxometry to evaluate the interactions between water and  
90 the cell wall's physical and chemical changes that may have occurred. A method to evaluate the 'true  
91 dry mass' of wood material is also proposed, enabling the calculation of the "true equilibrium  
92 moisture content" without the need of drying the samples at 103°C in an oven (which can lead to  
93 irreversible damages or misinterpretations). The evolutions/modifications are also discussed against  
94 hydric strains, as well as the possible contribution of the two water components on the volume  
95 deformation. A parallel objective of this work is to compare these changes between historical and  
96 modern oak woods.

97

## 98 **Materials and Methods**

99 **Materials:** The experiments were carried out on modern and historical oak wood samples to compare  
100 the effect of aging on two types of wood. The historical wood (350-year-old oak) was provided by  
101 Atelier Perrault, and comes from a wooden door's frame of an old building of the 17<sup>th</sup> century in Saint  
102 Georges street in Rennes, France. The historical oak wood has been subjected to natural aging. The  
103 modern oak wood was recently provided from a sawmill located in the North of France and may be  
104 considered without aging. Figure 1 provides an optical microscopy image of the transversal cross-  
105 section (plane RT) of both wood materials. The chemical composition and the proportion of the

106 different kinds of cells (vessel, fiber, parenchyma...) were not quantified in this study, but these  
107 images allowed confirming differences between these two oak materials.

108 Small specimens of approximately 1 cm<sup>3</sup> were prepared as 1 cm is the maximum height for optimal  
109 NMR measurements. This was done using a band saw and they were all clear from visible defects.  
110 They were sawn along the anisotropic directions (Longitudinal L, Radial R and Tangential T). All  
111 the samples were taken side by side, to minimize the variability between samples of the same type  
112 (modern wood or historical wood). The average density of all specimens was measured at 2% relative  
113 humidity (RH) and is 0.64 (±0.02) g cm<sup>-3</sup> for modern oak wood and 0.47 (±0.02) g cm<sup>-3</sup> for historical  
114 oak wood. The lower density of the historical wood is in accordance with the fact that there are more  
115 vessels.

116 All samples were subjected to a common cycle of adsorption-desorption to equalize their hydric  
117 history, using saturated salt solutions at 2% RH (silica gel) and 97% RH (potassium sulphate: K<sub>2</sub>SO<sub>4</sub>).  
118 They were kept in desiccators until constant mass (about one week). All the experiments were carried  
119 out at 20°C and on an adsorption cycle (starting from 2% RH) to avoid the influence of the hysteresis  
120 in the observed phenomena.

121  
122 **Aging protocols:** Two aging methods were conducted, on the one hand repeated hydric cycles  
123 (considered as a “natural aging” method with gentle impact) and on the other hand mild thermal  
124 treatment (considered as an “accelerated aging” method). To compare the effect of these aging  
125 methods, the samples were all characterized through 2D <sup>1</sup>H NMR at equilibrium moisture content  
126 (Eq. 1):

$$EMC_{x\%RH} = \frac{M_{x\%RH} - M_{dry}}{M_{dry}} \times 100 \quad (1)$$

127 where EMC<sub>x%RH</sub> is the equilibrium moisture content at x% RH [%], M<sub>x%RH</sub> the mass of the equilibrated  
128 sample at x% RH [g] and M<sub>dry</sub> the mass of dry sample [g].

129 Repeated hydric cycles consist in applying repeated cycles of adsorption and desorption to wood  
130 specimens. In this study, three samples of modern wood and three samples of historical wood were  
131 subjected successively to 2% RH and 97% RH using the method of saturated salt solutions to attain  
132 EMC at room temperature (20°C). These hydric cycles were repeated during 6 months (corresponding  
133 to a total of 12 cycles of adsorption-desorption) and samples were studied at 1, 3 and 6 months. In  
134 order to study the evolution of the samples at each period, they were conditioned at 65% RH, 20°C  
135 (using sodium nitrite (NaNO<sub>2</sub>)) and analysed through <sup>1</sup>H NMR at EMC. In parallel, control samples  
136 of modern and historical wood (three of each) were conditioned at 65% RH, 20°C, over the entire  
137 period of the experiments. Deformation measurements and mass measurements were carried out  
138 regularly on all samples to assess the EMC by weighing and the evolution of the hydric strains.

139 Thermal treatments (TT) were conducted in an oven at a temperature of 120°C (where RH is close to  
140 0%) for three periods of time (24 hours, 3 days and 7 days). Prior to the TT, the initial state of each  
141 specimen conditioned at 65% RH was characterized through 2D <sup>1</sup>H NMR at EMC at 20°C. After TT,  
142 the specimens were again conditioned at 65% RH, 20°C for one week before a second <sup>1</sup>H NMR  
143 analysis. This protocol allows to compare the EMC evolution for the same sample and to determine  
144 the mass loss induced by the TT. Dimensions were also measured before and after treatment to assess  
145 the change in volume deformation as this provides information on the stability of the wood. Three  
146 specimens of each wood were considered for the 24 hours TT to take into account the variability of  
147 wood material and to test the reproducibility and the repeatability of the used method. As the  
148 variability was statistically tested with a Student T-test and showing significant changes after 24h TT,  
149 only one specimen of each wood type was analysed for the 3 and 7 days TTs.

150

151 **NMR methods:** The samples were measured by 2D <sup>1</sup>H NMR and to do so they were inserted in  
152 18mm NMR tubes. The RH was controlled with a saturated salt solution at 65% RH during the NMR  
153 experiments (Bonnet et al. 2017, Fourmentin 2015) placed in a small container on the top of the NMR

154 tubes. As the temperature of the magnetic unit is 40°C, a cooling system is used to maintain the  
155 samples at 20°C (at the bottom of the NMR tubes). The temperature in the area of the saturated salt  
156 container (outside the instrument) corresponds to a temperature of 25±2°C (measured during NMR  
157 analysis). The theoretical variation of the saturated salt solution used is up to 2% decrease of RH at  
158 30°C. To take into account possible variations on EMC, all samples were weighed before and after  
159 NMR measurements and the mean value of these two measurements was used to calculate the EMC.  
160 The difference in EMC calculated with the mass before NMR and the mass after NMR measurement  
161 was evaluated and resulted to be lower than 0.1%. Therefore, it is considered of a minor effect and  
162 does not affect the obtained results and interpretations. The device used was a BRUKER MINISPEC  
163 MQ20 spectrometer that operates at 0.5 T, corresponding to a resonance frequency of 20 MHz for  
164 <sup>1</sup>H.

165 The principle of NMR is based on the intrinsic nuclear spin that some atomic nuclei have (with an  
166 odd number of protons, neutrons, or both). When an atomic nucleus with a nonzero spin is placed in  
167 a magnetic field **B**<sub>0</sub>, the nuclear spin can be aligned in the same direction or in the opposite direction  
168 to the field. These two types of nuclear spin alignment are characterized by different energies, and  
169 their sum is called the magnetization ( $\vec{M}$ ). When a second magnetic field (with a characteristic energy)  
170 **B**<sub>1</sub>, perpendicular to **B**<sub>0</sub> is applied as a pulse, this magnetization is disturbed and the relaxation (=time  
171 needed for the magnetization to come back to its initial state) is characteristic of the atom and of the  
172 local environment (Kekkonen 2014). The two main relaxation times measured are: T<sub>2</sub>, the spin–spin  
173 or transversal relaxation time and T<sub>1</sub>, the spin–lattice or longitudinal relaxation time.

174 The Inversion Recovery (IR) sequence coupled with the Carr-Purcell-Meiboom-Gill (CPMG)  
175 sequence (Carr and Purcell 1954, Meiboom and Gill 1985) was used to obtain 2D NMR correlation  
176 spectra of the T<sub>1</sub> and the T<sub>2</sub> relaxation values. The calculation of T<sub>1</sub>-T<sub>2</sub> correlation spectra from NMR  
177 data was performed with an in-house software, which essentially reproduces the 2D-Inverse Laplace  
178 Transform (ILT) algorithm of Song et al. (2002). For more details about this and about the acquisition

179 method and parameters, see Bonnet et al. 2017. The  $T_1$ - $T_2$  correlation spectra allow to show the NMR  
180 signal as a function of the two relaxation times,  $T_1$  and  $T_2$ , obtaining two different peaks for the  
181 adsorbed water (which is not possible with 1D  $T_1$  or  $T_2$  spectra due to peak overlapping). The volume  
182 under each peak of the 2D spectra is proportional to the amount of hydrogen (H) atoms. The  $T_1$  and  
183  $T_2$  values of each peak are determined by means of the coordinates of their respective maxima. 2D  
184 spectra also give unambiguous access to  $T_1/T_2$  ratios. The latter is characteristic of H atoms mobility  
185 and confinement and greatly helps spectrum interpretation.

186

187 **Determination of EMC:** The moisture content can be calculated from the  $T_1$ - $T_2$  spectra, as the area  
188 under the peaks is proportional to the amount of H atoms. Thus, the total moisture content can be  
189 evaluated through NMR as the sum of the area under the two peaks corresponding to bound water.  
190 In order to convert the NMR signal into a mass of adsorbed water, a standard curve is performed with  
191 different quantities of water. The bound water mass ( $M_{\text{NMR},x\%RH}$ ) determined by  $^1\text{H}$  NMR at  $x\%$  RH  
192 is defined by (Eq. 2):

$$q_{\text{NMR},x\%RH} = \alpha \cdot M_{\text{NMR},x\%RH} \quad (2)$$

193 Where  $q_{\text{NMR},x\%RH}$  is the NMR signal intensity of peaks of interest and  $\alpha$  the proportional coefficient  
194 determined through the standard curve (in this study,  $\alpha = 164.77$  NMR signal/g of water).

195 To calculate  $\text{EMC}_{\text{NMR},x\%RH}$ , it is necessary to determine the mass of the dry sample,  $M_{\text{dry}}$ . To avoid  
196 irreversible structural damages or misinterpretations (in particular for thermal treatment), the studied  
197 materials are never oven-dried at  $103^\circ\text{C}$  as usually done before heat treatments (Rajohnson 1996,  
198 Obataya 2007, Candelier 2013). Therefore,  $^1\text{H}$  NMR can be of good use to determine the “true dry  
199 weight” of wood. Total mass of wood is weighed at EMC with a scale of precision  $\pm 0.0002\text{g}$  and the  
200 amount of bound water at EMC is calculated through  $^1\text{H}$  NMR as depicted previously. Thus, the mass  
201 of dry wood  $M_{\text{dry}}$  [g] can be calculated as follows (Eq. 3):

$$M_{dry} = M_{w,x\%RH} - M_{NMR,x\%RH} \quad (3)$$

202 Where  $M_{w,x\%RH}$  [g] is the total mass (dry wood and bound water) determined by weighing at x% RH  
 203 (which corresponds to the average value of weighing before and after NMR experiments) and  
 204  $M_{NMR,x\%RH}$  [g] is the bound water mass determined by NMR at x% RH. The moisture content  
 205 determined through  $^1H$  NMR measurements ( $EMC_{NMR,x\%RH}$ ) is defined as  $M_{NMR,x\%RH}$  divided by  
 206  $M_{dry}$ . The moisture content determined by weighing at x% RH ( $EMC_{w,x\%RH}$ ) is defined as  $M_{w,x\%RH} -$   
 207  $M_{w,2\%RH}$  divided by  $M_{w,2\%RH}$ . These two moisture contents verify the following relationship (Eq. 4):

$$EMC_{NMR,x\%RH} = EMC_{w,x\%RH} \frac{M_{w,2\%RH}}{M_{dry}} + \frac{M_{w,2\%RH} - M_{dry}}{M_{dry}} \quad (4)$$

208 The obtained data for  $EMC_{NMR,x\%RH}$ ,  $EMC_{w,x\%RH}$ ,  $M_{dry}$  and  $M_{w,2\%RH}$  are given in SI. Uncertainties  
 209 on measurements for EMC are determined through the standard deviation values; they take into  
 210 account the possible variability between samples' results and the precision of the balance (0.36% for  
 211 the modern wood and 0.28% for the historical wood).

212

213 **Volume measurements:** In order to assess the changes in regard to the two aging methods, the  
 214 samples' dimensions were measured with a Mitutoyo electronic calliper with a precision of  $\pm$   
 215 0.01mm. These measurements were performed at each step of the experiments for the three directions  
 216 R, T and L allowing the calculation of the samples' volume: during the conditioning, at EMC, right  
 217 before and after NMR measurements.

218 Measurements of the samples' dimensions allow to determine the deformation between two states,  
 219 2% RH and x% RH (with x=65% or 97% RH). Hydric strains at x% RH ( $\varepsilon_{x\%}$ ) are related to the state

220 at 2% RH, as the volume of the dry wood was not experimentally measured as previously explained,  
221 according to (Eq. 5):

$$\varepsilon_{x\%} = \frac{V_{x\%RH} - V_{2\%RH}}{V_{2\%RH}} \times 100 \quad (5)$$

222 Where  $V_{x\%RH}$  and  $V_{2\%RH}$  are the volumes of a sample at x% RH and 2% RH respectively.

223 Note that the determination of the volume deformations was done using the state at 2% RH right  
224 before the conditioning at 65% RH for samples subjected to hydric cycles.

225 Uncertainties on deformation measurements are determined through standard deviation values; they  
226 take into account the possible variability between samples' results and the precision of the electronic  
227 calliper. For these experiments, the variability is about 0.39% for the modern wood and 0.30% for  
228 the historical wood. Also note that the EMC values for hydric strains may slightly differ from those  
229 during the NMR experiments due to possible variations of RH and temperature and because the  
230 dimension measurements are performed outside the desiccators.

231

## 232 **Results and discussion**

233 **T<sub>1</sub>-T<sub>2</sub> spectra and peak assignment:** Figure 2 shows T<sub>1</sub>-T<sub>2</sub> correlation spectra recorded from  
234 historical and modern oak wood samples (only one sample of each wood is represented here), before  
235 aging processes. Regardless of small differences in the shapes of the peaks observed in the  
236 cartographies, the global scheme is similar for both wood materials.

237 To interpret these spectra, it is necessary to understand the influence of water mobility and  
238 environment on the relaxation times T<sub>1</sub> and T<sub>2</sub>. T<sub>1</sub> and T<sub>2</sub> depend on the local environment of the  
239 measured hydrogen atoms (H) (i.e. from water molecules and wood polymers in this work), that is to  
240 say: size of the molecules they are bound to, affinity with molecules interacting and pore size. T<sub>2</sub>  
241 relaxation time decreases as pore size is reduced. Moreover, T<sub>2</sub> will also be shortened when molecular  
242 tumbling (mobility) decreases. If H atoms are in molecules with restricted mobility due to viscosity,

243 or the interactions being in macromolecules or solid phase,  $T_2$  values will decrease gradually  
244 depending on the degree of this restriction. The case of  $T_1$  is a bit more complicated than  $T_2$  as it first  
245 decreases when molecular tumbling decreases (from liquid phase) but it increases when molecular  
246 tumbling is low (in gel and solid like molecules). Fortunately,  $T_1/T_2$  ratios are characteristic of the  
247 mobility of H atoms and greatly help spectrum interpretation. Depending on the value of these ratios,  
248 water can be assigned to unconfined water, mobile water in a free or adsorbed state and bonded  
249 immobile water molecules and solid macromolecules. It can be noticed that  $T_1/T_2$  ratios lower than  
250 one are physically not permitted (Bonnet et al. 2017).

251 Based on this knowledge, the peaks observed in the  $T_1$ - $T_2$  spectra can be identified based on analysis  
252 previously done in Cox et al. (2010) and Bonnet et al. (2017). Peak A is labelled as liquid water in  
253 the lumen as it has the highest  $T_1$  and  $T_2$  values and it is close to the  $T_1=T_2$  line. In some spectra, this  
254 peak is located slightly above the  $T_1=T_2$  line, which certainly owes to the way the signal acquisition  
255 was made. Indeed, the CPMG period of the NMR sequence was deliberately truncated after 12ms to  
256 prevent excessive radio frequency (RF) power deposition in the sample and thus avoid heating the  
257 sample. As a result, the measurement of  $T_2$  value for peak A is not complete and lacks accuracy,  
258 leading to a widening and 'mislocation' in  $T_2$  direction. In our case, the amplitude of the peak is also  
259 very low and it is therefore not of interest in this study. Peaks B and C correspond to bound water in  
260 two specific and distinct water reservoirs in the wood cell walls. The  $T_1/T_2$  ratio is higher for peak B  
261 than for peak C, indicating a more restricted molecular motion in compartment B and thus more  
262 strongly bonded water molecules in that compartment. In contrary, the low  $T_1/T_2$  ratio for peak C  
263 indicates less restricted molecular motion and less strongly bonded water molecules. In some spectra,  
264 peak C seems to split into two peaks, one with lower  $T_1$  and  $T_2$  values than the other peak but having  
265 almost the same  $T_1/T_2$  ratio. This could be interpreted as two types of C-water with small differences  
266 on their environment (e.g. surface-to-volume ratio). In general, the peak with higher  $T_2$  and  $T_1$  values  
267 is most intense, but in few cases, it is the other one showing higher amplitude. Thus, for easier

268 interpretation, the peak taken into account for the calculation of  $T_1$  and  $T_2$  values of peak C is always  
269 the one with higher  $T_1$  and  $T_2$  values. It would be interesting to understand the nature of this splitting  
270 but it is out of scope of this work. Finally, peak D represents H atoms from the wood polymers since  
271 the  $T_2$  value relaxes very fast (in the order of  $\mu\text{s}$ ).

272 Among the recent results, Bonnet et al (2017) have proposed to relate the two components B and C  
273 to the structure of the S2 layer of the cell wall, because this layer may explain the mechanical  
274 properties and especially the hydric strains. Based on a schematic structure of the S2 layer inspired  
275 by Boyd (1982) and Salmén and Burgert (2009), it has been explained that the population of water  
276 from component B (strongly bonded) may be located in the microfibrils composed mainly of  
277 microfibrils of crystalline and amorphous cellulose embedded in a matrix of hemicelluloses  
278 (primarily glucomannan for softwoods). While the population of water from component C (weakly  
279 bonded) may be in a lignin and hemicelluloses (xylan) matrix corresponding to the intra-microfibril  
280 region. The attribution of the two bound water components B and C to these two regions is related to  
281 the fact that water affinity is higher in the region composed of cellulose and hemicelluloses than in  
282 the region composed of lignin and hemicelluloses. However, the proportion of polymers differ  
283 between hardwoods and softwoods (Chaouch et al. 2010). Hardwoods contain mainly glucuronoxylan  
284 and low amount of glucomannan. Thus, for our studied materials, it can be suggested that xylan  
285 (glucuronoxylan) may be present in the two regions.

286

287 **NMR results for samples at the initial state:** Table 1 presents the average results obtained from  
288 NMR measurements on the control samples of hydric cycles and on the samples at the initial state  
289 before TT. EMC values (deduced from the sum of peaks B and C) are the same order of magnitude  
290 for both woods. Furthermore, peak B reveals a higher moisture content than peak C for both woods,  
291 meaning that this compartment contains more adsorbed water than the other one. Compartment C

292 shows higher water content for the historical wood than for the modern wood, while there is less  
293 water in compartment B for historical wood.

294 These differences in terms of relative moisture content in B and C could provide new insights in terms  
295 of evolution in the structure and composition of the wood cell wall. The higher moisture content in  
296 compartment C of the historical wood appears to indicate a higher amount of available adsorption  
297 sites in that region compared to the modern wood. The higher content of adsorption sites could be  
298 due to an evolution of the polymeric structure such as a change in the polymers conformation. Indeed,  
299 the lignin undergoes structural changes due to oxidation during aging but, as shown in Kranitz 2014,  
300 the absolute amount remains the same. Therefore, these structural changes in the lignin could free  
301 some previously inaccessible hydroxyl sites for water adsorption.

302 NMR results give an additional indication in favor of the hypothesis made on the local environment  
303 of water in compartment B, which is mainly composed of cellulose and hemicelluloses. As mentioned  
304 earlier, the hemicelluloses are the first polymers to degrade during wood aging and a decrease in  
305 amorphous cellulose is observed in naturally aged woods (Kranitz 2014), thus leading to a decreased  
306 number of adsorption sites and therefore lower moisture content in that region for historical wood  
307 compared to the modern wood. However, it may be difficult to quantitatively compare these two oak  
308 wood types without chemical characterization. This is a common issue found when historical and  
309 modern wood are to be compared, as the composition and proportion of polymers in the cell wall  
310 before aging are not known. The environmental conditions and geographical location are also a source  
311 of variability in the wood development and evolution. Thus, to improve our understanding of the  
312 relative differences on the amounts of B and C ‘water’ between historical and modern oak wood, a  
313 detailed chemical analysis could be useful (e.g. characterization and quantification of wood polymers)  
314 in future works.

315

316 **NMR results for repeated hydric cycles:** Table 2 presents the moisture content measured during  
317 the repeated hydric cycles as well as the characteristic relaxation times  $T_1$  and  $T_2$  for all samples. A  
318 graphical representation of the evolution in total moisture content is also presented in Figure 3.  
319 First observation shows that hydric cycles did not really affect the adsorption behaviour of the  
320 samples, meaning that no significant increase or decrease in EMC is observed in regards to the  
321 standard deviation values. A paired Student T-test was performed on all the moisture content  
322 measures ( $EMC_{NMR,65\%RH}(B + C)$ ,  $EMC_{NMR,65\%RH}(B)$  and  $EMC_{NMR,65\%RH}(C)$ ) showing no significant  
323 evolution of the EMC (p-values > 0.05) along the 6 months of repeated hydric cycles. Moreover, the  
324 evolution of the  $T_1/T_2$  ratio is globally constant. This indicates no change in the mobility of water  
325 pools, thus no change in the polymeric structure of the cell wall, i.e. no change in the hygroscopicity  
326 of the wood material. Such results were expected since the room temperature and humidity are fixed  
327 and controlled along the experiment, which is not the case in natural conditions of aging. Furthermore,  
328 mass of samples was recorded during the cycles and permits to estimate the mass loss through the 6  
329 months cycles, showing no significant mass loss through the whole experiment period.  
330 In conclusion, although these repeated hydric loads may have an influence on the hydric properties  
331 over the long term, we suppose that the duration of tests is not sufficient to induce a significant effect  
332 on the hygroscopic properties. This result will be discussed with the hydric deformation  
333 measurements below.

334

335 **NMR results for moderate heat treatment:** NMR data are presented in Table 3 and a graphical  
336 representation of the evolution in total moisture content before and after the heat treatments is  
337 presented in Figure 3.

338 A noticeable loss in total  $EMC_{NMR,65\%RH}(B + C)$  is observed for both modern and historical wood  
339 samples and the longer the treatment, the higher the loss in hygroscopicity, as expected. Thermal  
340 treatments also show a total higher effect on the historical wood than on modern wood. There is a

341 higher EMC loss for historical wood the longer the treatment time (13% for modern wood against  
342 19% for historical wood, in average of the 72 h and 168 h TT). The loss of water in compartments B  
343 and C can be calculated separately, showing for the 24 h TT a higher percentage of water loss in peak  
344 C (18.0%) than peak B (6.9%) for historical wood. While it seems to be the contrary for modern oak  
345 wood, with higher loss in compartment B (11.5%) than C (9.9%). The same conclusions were  
346 obtained for the 72 h and 168 h TTs.

347 A Student T-test was performed on these percentages of loss in EMC for the 24 h TT, showing no  
348 significant difference between the loss in  $EMC_{NMR,65\%RH}(B)$  and  $EMC_{NMR,65\%RH}(C)$  for modern wood.  
349 For historical wood, the statistical tests confirmed a significant difference between peaks B and C,  
350 with a higher loss for  $EMC_{NMR,65\%RH}(C)$ . As mentioned previously, the strongly bound water  
351 (component B) may be located in the microfibrils (cellulose-glucuronoxylan-glucomannan matrix) -  
352 and the weakly bound water in the lignin-glucuronoxylan matrix (component C). It is suggested in  
353 Salmén and Burguert (2009) that there might be a highly acetylated xylan which is closely associated  
354 to a less condensed type of lignin, whereas low substituted xylans are associated with cellulose and a  
355 condensed type of lignin. It can be noticed that xylan units of hemicelluloses in hardwoods are  
356 generally strongly acetylated, generating a higher sensitivity of these materials to thermal treatments,  
357 as the xylan units could lead to higher kinetic of thermo-degradation in hardwoods (Chaouch et al.  
358 2010). Therefore, one could assume that the highly acetylated xylan are linked with the component  
359 C, while the low-substituted xylan is linked to the component B. These associations could be of major  
360 importance in regard of the selective evolution of wood adsorption.

361 For the historical wood, it seems that the dry mass loss (Table 4) is greater with treatment time.  
362 Indeed, the dry mass loss for 72 and 168 h TTs was higher than for the 24 h treatment, but as only  
363 one sample was used for these two durations, observations are mostly qualitative. For the modern  
364 wood, the same observation was made except for the 168 h TT that seems to be an outlier due to its  
365 low value, but which is due to the fact that it is the dry mass loss of a single sample. Recent tests

366 confirmed an increased dry mass loss with treatment time for modern wood, up to 2.3%. Nevertheless,  
367 these percentages of dry mass loss are quite low and according to Kollmann and Fengel (1965) and  
368 Esteves and Pereira (2008) wood degradation begins only at 130-150°C for oak wood. Thus, by  
369 heating at 120°C, there should be no degradation of polymers and the dry mass loss observed may be  
370 due to a loss of extractives during heat treatment as discussed in Esteves and Pereira 2008.

371 In our case, the extractives degradation cannot fully explain the loss in EMC observed after TT,  
372 knowing that not all the extractives are volatile (Hillis 1971, Esteves and Pereira 2008, Jankowska et  
373 al. 2017). Indeed, the  $T_1$ - $T_2$  correlation spectra reveal a global increase of the  $T_1/T_2$  ratio after thermal  
374 treatments (Table 3), indicating that there are stronger bonds between adsorption sites and water  
375 molecules. The ratio increase also indicates the confinement of the H atoms detected. The evolution  
376 of H atoms mobility could be due to a restricted space between polymers therefore changing the local  
377 environment of H atoms. When wood is oven-dried in a dry atmosphere, various chemical changes  
378 take place producing a "shrunken" state for which the intermolecular space is minimized (Obataya  
379 2007). Thus, when wood is reconditioned at 65% RH, the restricted intermolecular space will not  
380 allow the adsorption of the water molecules in several layers as it used to before TT. This hypothesis  
381 can also be interpreted by looking at the evolution of peak C for instance (Figure 4), which can be  
382 divided into two parts to highlight two populations of water. The lower part corresponds to the least  
383 mobile H atoms and therefore the most strongly linked water molecules (directly linked to the  
384 adsorption sites). The upper part corresponds to the most mobile H atoms and therefore the least  
385 strongly linked water molecules (upper additional layers of adsorbed water) (see Figure 4b).

386 Following the TT, peak C is shifted downward ( $T_2$  decreases and  $T_1$  increases) showing a larger  
387 population of H atoms more strongly bound to the polymeric matrix, but there has been a loss of the  
388 less strongly bound H population. Consequently, there is a loss of additional layers of adsorbed water  
389 molecules due to the smaller intermolecular space following TT. Note that this observation is similar

390 for peak B. The shrinking of the polymeric matrix could be a plausible explanation for the increase  
391 in the confinement of bound water molecules and therefore for the decrease in water adsorption.

392

393 **Discussion in relation with deformation:** The hydric strains of studied materials either subjected to  
394 repeated hydric cycles or to thermal treatments are given in Figure 5 and are compared to those  
395 without aging (control samples and samples at the initial state). They are expressed as a function of  
396 total EMC ( $EMC_{NMR,65\%HR}(B + C)$ ) determined by  $^1H$  NMR from the components B and C. Note  
397 that, if the hydric strains (related to the state at 2% RH) are plotted against EMC (related to dry mass)  
398 it is observed that the hydric strains for modern and historical wood materials vary linearly with the  
399 moisture content, as expected for wood materials (see SI for more details). The slope  $\beta$  of the obtained  
400 linear law expressed as a function of EMC is 0.50 for modern wood 0.45 for historical wood. It can  
401 be noticed that the value of the slope is related to the density of the studied materials (Bonnet 2017)  
402 and the slope  $\beta$  decreases with decreasing density. According to the above results (see Table 2 and  
403 Table 3), the densities of the samples after “natural” or “artificial” aging do not significantly vary, so  
404 the slope remains the same after aging. Thanks to this linear law between hydric strains and EMC, it  
405 is possible to discuss the influence of each bound water compartments (B or C) on the decrease of  
406 volume deformation. This evolution is related to the decrease of EMC(B) and EMC(C) which is  
407 related to the decrease of EMC(B+C) for samples subjected to aging, see SI for more details.

408 The hydric strains for samples subjected to repeated hydric cycles seem to be “globally” stable  
409 through the 6 months cycles (Figure 5) for modern and historical wood materials. This is in coherence  
410 with a “globally” stable EMC. Note that the hydric strains of the samples at one month are higher  
411 than those of the control samples, in coherence with higher EMC (Table 2). Between 1 month and 6  
412 months cycles there is surprisingly a slight decrease of the volume deformations with no decrease of  
413 the EMC. Further studies are necessary to confirm these unexpected results (at other durations).  
414 Moreover, it seems to be more important for modern wood than for historical wood (Figure 5) in

415 coherence with the fact that the hemicelluloses are supposed to be mostly degraded in historical wood  
416 (Kranitz 2014, Obataya 2007), thus leaving a material more stable in terms of volume deformation.  
417 Concerning the samples subjected to thermal treatments, the hydric strains significantly decreased  
418 after TT and with treatment duration. However, the effect seems to be weaker for the modern wood  
419 than for historical wood. The contribution of each component (B or C) on the hydric strains is not the  
420 same for both studied materials. For historical wood material, the contribution of compartment C on  
421 volume deformation decreases with treatment time while the contribution of component B increases  
422 (see Table 5). Furthermore, the component C contributes the most in the loss of volume deformation  
423 for historical wood, which means that for higher treatment times, the lignin-xylan matrix might  
424 undergoes some chemical changes that reduces the hygroscopicity of the wood cell wall. As for the  
425 modern wood, inverse phenomena was observed with a decrease in contribution of component B in  
426 the loss of volume deformation, while component C seems to increase. Nevertheless, the contribution  
427 of compartment C in modern wood presents higher percentage meaning that it has a higher influence  
428 on the decrease in volume deformation.

429 To conclude, the use of NMR by quantifying the two components B and C and relating them to the  
430 possible modification of hygroscopicity due to aging, appears to be an available and accurate method  
431 to evaluate the decrease of hydric strains. Furthermore, these results confirm that the two components  
432 B and C have an effect on hydric deformation, especially for thermal treatments.

433

## 434 **Conclusions**

435 This study shows the potential of the 2D <sup>1</sup>H NMR correlation spectra to study modifications in wood  
436 hygroscopicity by being the sole technique able to quantify two types of adsorbed water in two

437 different chemical environments in the wood cell walls. This method also permits to determine the  
438 moisture content of wood without the necessity to oven-dry the wood material.

439 Two aging methods have been conducted on two oak wood materials (modern and historical wood),  
440 on the one hand “natural” aging with repeated hydric cycles and on the other hand “artificial” aging  
441 with mild thermal treatment. Results show that the duration of the “natural” aging seems to be not  
442 sufficient to induce evolution on the hygroscopic properties, but unexpected results over time were  
443 observed for the hydric strains. More investigations are necessary, especially with other durations.

444 Concerning “artificial” aging, a clear reduction in total moisture content was observed after heat  
445 treatment and reconditioning at 65% RH for the two types of oak wood, accompanied with low dry  
446 mass loss. The observed decrease of water content is in accordance with the decrease of the swelling  
447 strains between 2% RH and 65% RH. Moreover,  $T_1$ - $T_2$  NMR experiments allow us to measure the  
448 effect of heat treatment for the two types of adsorbed water by showing a higher percentage of water  
449 loss in one compartment than in the other for the historical oak wood. The reason of this selective  
450 loss of water adsorption can be explained in relation with the chemical composition of the studied  
451 materials. The global decrease of EMC is the result of the loss of extractives but also of structural  
452 modifications such as restricted space between polymers leading to a decrease of adsorbed water  
453 layers. This is shown by the increase of the  $T_1/T_2$  ratio which indicates a decrease on the averaged  
454 mobility of H atoms for each water pool after TT and stronger interactions (bonds) between wood  
455 and adsorbed water molecules. All these results could be completed with  $^{13}\text{C}$  NMR or IR investigation  
456 to determine the changes that occurred in wood polymers more precisely.

457

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461

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- 566

567

## TABLES

568

569 **Table 1:** Density [ $\text{g}/\text{cm}^3$ ] and 2D  $^1\text{H}$  NMR results ( $\text{EMC}_{\text{NMR},65\%}$  noted B+C [%] and the ratio  $T_1/T_2$  [-])  
 570 for the specimens at 65% RH (samples without hydric or thermal loadings). Average values (mean) and  
 571 standard deviation (SD) are given.

	Modern wood Mean (SD)	Historical wood Mean (SD)
Density $\text{g}/\text{cm}^3$	0.67 (0.02)	0.50 (0.02)
B+C [%]	12.10 (0.36)	11.51 (0.29)
B [%]	9.24 (0.34)	7.36 (0.39)
T1/T2	88.39 (3.46)	76.06 (7.39)
C [%]	2.86 (0.20)	4.15 (0.58)
T1/T2	3.34 (0.12)	3.83 (0.67)

572

573 **Table 2:** Density [ $\text{g}/\text{cm}^3$ ] and 2D  $^1\text{H}$  NMR results ( $\text{EMC}_{\text{NMR},65\%}$  noted B+C [%] and the ratio  $T_1/T_2$  [-])  
 574 of the specimens subjected to repeated hydric cycles. Average values (mean) and standard deviation  
 575 (SD) are given.

	Modern wood Mean (SD)				Historical wood Mean (SD)			
	Control samples	1 month	3 months	6 months	Control samples	1 month	3 months	6 months
Density $\text{g}/\text{cm}^3$	0.65 (0.04)	0.66 (0.02)	0.65 (0.02)	0.64 (0.02)	0.49 (0.02)	0.48 (0.01)	0.47 (0.01)	0.47 (0.01)
B+C [%]	12.08 (0.11)	12.46 (0.04)	12.45 (0.07)	12.47 (0.02)	11.59 (0.35)	11.85 (0.23)	11.90 (0.35)	12.23 (0.36)
B [%]	9.16 (0.13)	9.20 (0.18)	9.28 (0.09)	9.36 (0.12)	7.46 (0.43)	7.83 (0.50)	7.89 (0.79)	7.12 (1.11)
T1/T2	91.16 (0.00)	82.90 (5.43)	87.84 (5.75)	84.52 (5.75)	84.61 (7.37)	81.20 (0.00)	81.29 (4.70)	75.20 (2.49)
C [%]	2.92 (0.23)	3.27 (0.15)	3.17 (0.08)	3.11 (0.10)	4.13 (0.77)	4.02 (0.35)	4.01 (0.65)	5.11 (0.99)
T1/T2	3.37 (0.20)	3.80 (0.39)	4.17 (0.28)	3.94 (0.27)	4.24 (0.97)	4.10 (0.37)	4.19 (0.52)	4.03 (0.47)

576

577

578 **Table 3:** Density [ $\text{g}/\text{cm}^3$ ] and 2D  $^1\text{H}$  NMR results ( $\text{EMC}_{\text{NMR},65\%}$  noted B+C [%] and the ratio  $T_1/T_2$   
 579 [-]) for the specimens subjected to moderate heat treatment. Average values (mean) and standard  
 580 deviation (SD) are given.

Time of treatment	Modern wood Mean (SD)			Historical wood Mean (SD)		
	24h	72h	168h	24h	72h	168h
Density [ $\text{g}/\text{cm}^3$ ]	0.68 (0.01)	0.65	0.65	0.50 (0.02)	0.48	0.46
B+C [%]	10.90 (0.21)	10.04	10.20	10.34 (0.32)	9.02	8.97
B [%]	8.34 (0.20)	7.69	8.06	6.82 (0.46)	6.34	6.30
$T_1/T_2$ [-]	111.73 (5.27)	128.99	128.99	100.38 (9.85)	114.90	128.99
C [%]	2.57 (0.16)	2.35	2.14	3.52 (0.61)	2.68	2.67
$T_1/T_2$ [-]	4.05 (0.18)	4.25	3.78	4.41 (0.29)	3.57	4.01

581

582

583 **Table 4:** Mass of specimens [g] before and after heat treatments and the relative mass loss [%].  
 584 \*this value may be an outlier.

Thermal Treatment time	Modern wood Mean (SD)			Historical wood Mean (SD)		
	Before treatment [g]	After treatment [g]	Relative % mass loss	Before treatment [g]	After treatment [g]	Relative % mass loss
24h	0.5731 (0.06)	0.5715 (0.06)	0.27 (0.19)	0.4313 (0.06)	0.4292 (0.05)	0.46 (0.54)
72h	0.5781	0.5746	0.61	0.4303	0.4265	0.87
168h	0.4634	0.4623	0.23*	0.3874	0.3783	2.36

585

586

587 **Table 5:** Contribution of components B and C [%] on the variation of hydric deformation at 65%HR  
 588 before and after aging. This contribution is given by  $\Delta\text{EMC}(\text{B or C})$  divided by  $\Delta\text{EMC}(\text{B} + \text{C})$ .

Thermal treatment time	Modern wood		Historical wood	
	B [%]	C [%]	B [%]	C [%]
24h	78.6	21.4	39.3	60.7
72h	70.8	29.2	41.3	58.7
168h	55.2	44.8	51.4	48.5

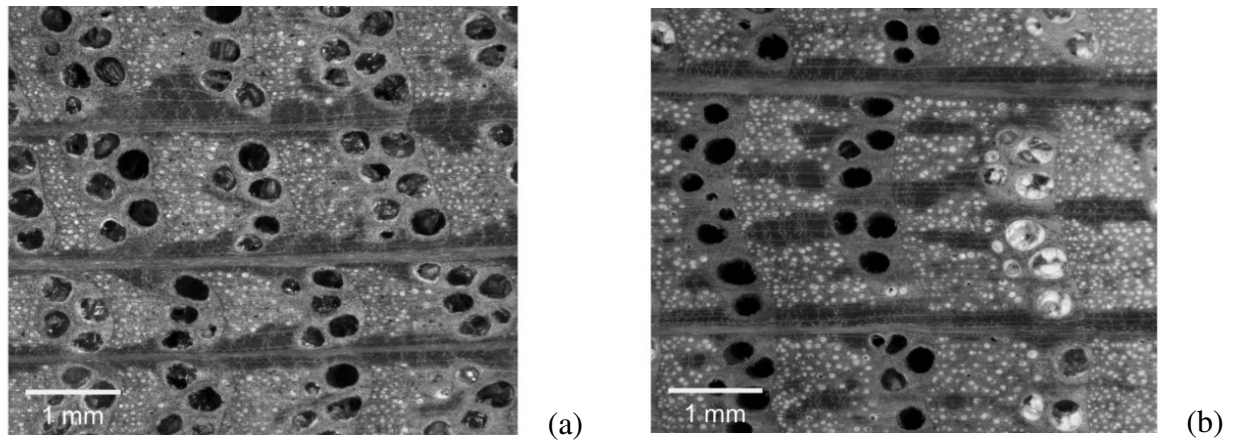
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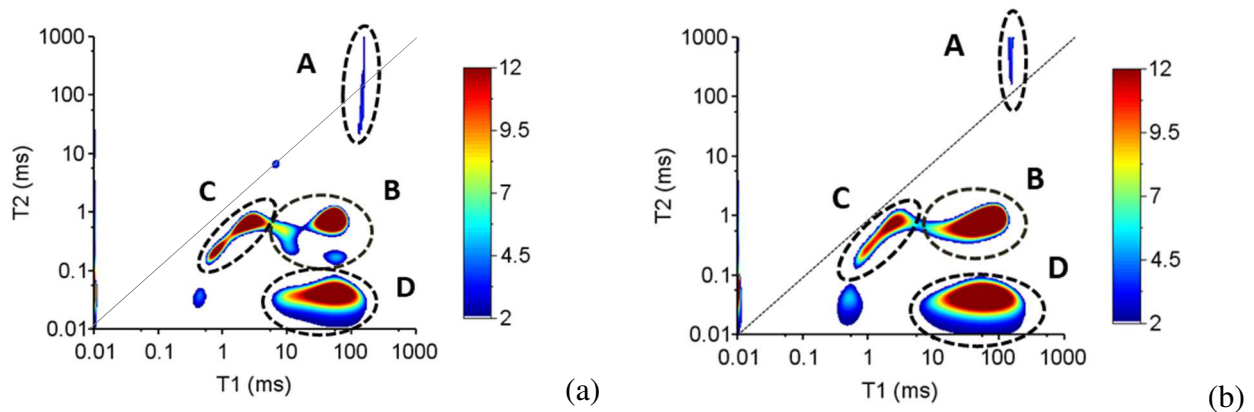
591

## FIGURES

592



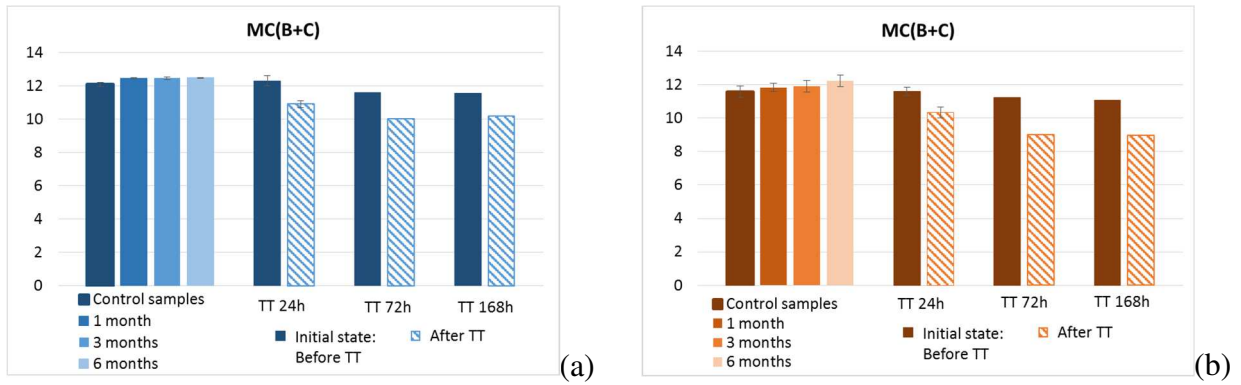
593 **Figure 1:** Optical microscopy image of transversal cross-section of the historical oak wood (a) and  
594 the modern oak wood (b). Fibers were possibly filled with wood powder during the polishing (in  
595 white in the fibers).  
596



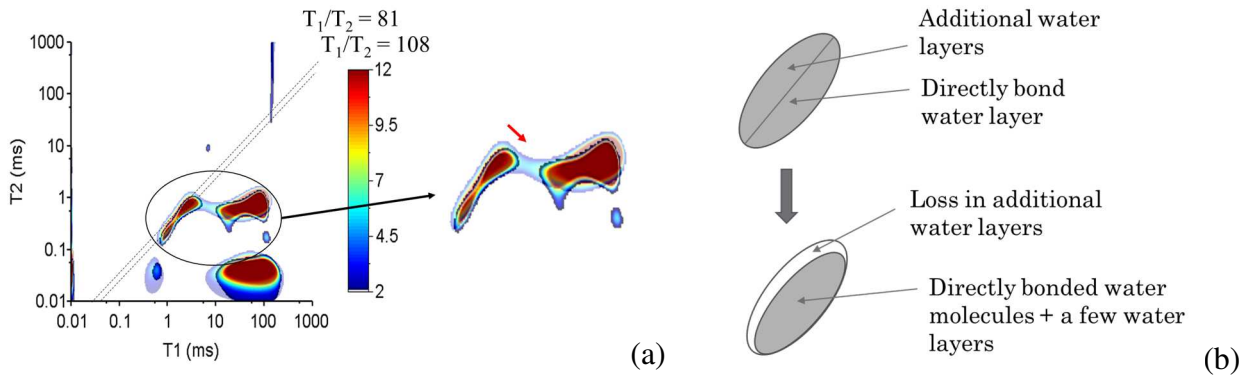
597 **Figure 2:**  $T_1$ - $T_2$  correlation spectra of the historical oak wood (a) and the modern oak wood (b) at  
598 the initial state before aging at 65% RH, 20°C. Diagonal lines correspond to  $T_1=T_2$ .  
599

600

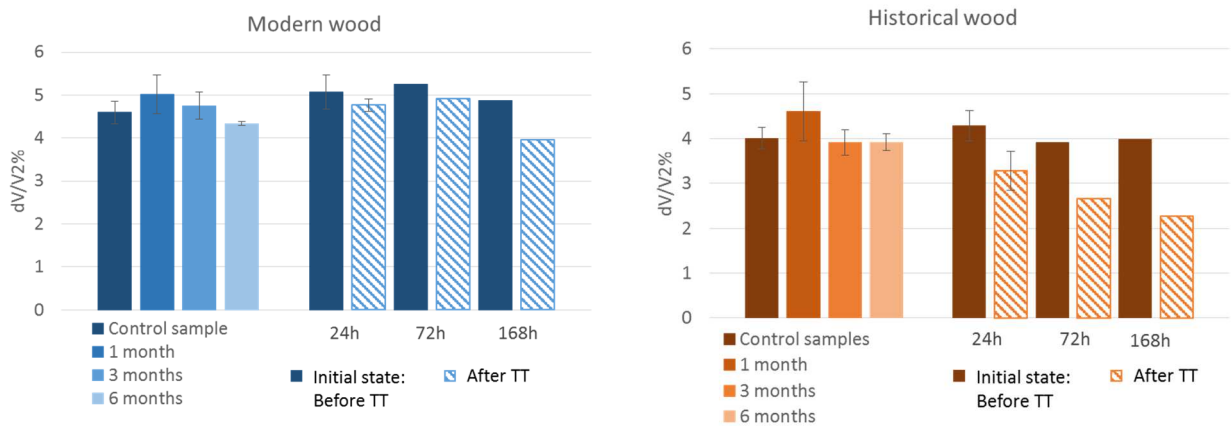
601



602 **Figure 3:** Evolution of the total moisture content  $EMC_{NMR,65\%RH}(B+C)$  noted MC(B+C) [%] for  
 603 (a) modern and (b) historical wood samples subjected to repeated hydric cycles and moderate  
 604 thermal treatment.  
 605



606 **Figure 4:** (a) Superposition of two  $T_1$ - $T_2$  correlation spectra of the same modern wood sample before  
 607 (in transparency) and after (in bright colour) heat treatment. (b) Schematic representation of the  
 608 evolution of “peak C” following a thermal treatment.  
 609  
 610



611 **Figure 5:** Volume deformations of samples (according to Eq. 5) without aging and through the 6  
 612 months repeated hydric cycles and for the thermal treatments.  
 613