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13 **Reversible and irreversible effects of a moderate heat treatment on the**
14 **moisture sorption and swelling behavior of modern and historical oak wood**

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31 **ABSTRACT**

32 The reversibility of a moderate thermal treatment (TT) at 120°C on modern and historical oak
33 wood samples was investigated by ¹H nuclear magnetic resonance (NMR) relaxometry,
34 equilibrium moisture content (EMC) determination and volumetric deformations'
35 measurements. The EMC values showed full reversibility after conditioning the samples at 65%
36 relative humidity (RH) for one week, in agreement with previous research using moderate TTs.
37 However, ¹H NMR relaxometry evidenced an irreversible effect on water mobility (i.e.
38 molecular tumbling) for both wood samples. This result is compared with volumetric
39 deformations determined by considering two reference states. When using, as reference, the dry
40 volume at each state, volumetric deformations are consistent with EMC values. However, when
41 using the dry volume of the sample before TT, the volumetric deformations are found to be
42 higher than the ones before TT for modern wood but remain lower for historical wood. The
43 irreversible changes in water dynamics suggest that some modifications of the wood structure
44 have not been completely recovered but are not linked to the changes of volumetric
45 deformations. In addition, ¹³C solid-state NMR spectroscopy allowed the comparison of the
46 composition between both wood samples, suggesting that their different behaviour concerning
47 volumetric deformations could be explained by a lower proportion of acetyl groups from

48 hemicelluloses for historical wood due to its natural aging. We showed that combining
49 macroscopic observations such as EMC and volumetric deformations with molecular-level
50 information gained from ^1H and ^{13}C NMR leads to a deeper understanding of the effects of
51 thermal treatments and reversibility tests.

52
53 **Keywords:** Thermal treatment; Reversibility; Wood aging; Oak wood; ^1H NMR relaxometry;
54 ^{13}C NMR spectroscopy; Volumetric deformations
55

57 INTRODUCTION

58 Thermal treatments (TTs) are nowadays widely applied to wood materials for the sake of
59 improvement of their performances. In particular, the effect of thermal modifications on some
60 wood properties has been found more than 100 years ago, when it was observed that drying
61 wood at high temperature increased its dimensional stability and reduced its hygroscopicity
62 (Sandberg et al. 2017). Such treatment not only improves the dimensional stability and reduces
63 the hygroscopicity of wood but also other properties such as resistance against fungi and insects,
64 and characteristics including colour, odour, gluability, and coating performance (Sandberg et
65 al. 2017). In addition, TTs considered as “artificial” aging may also be used to mimic and study
66 “natural” wood aging (Rostom et al. 2020).

67 Due to the potential of TTs, many protocols have therefore been developed varying in length,
68 temperature or atmosphere (inert gas, dry air, and vapour) (Hill et al. 2021) to improve some
69 wood properties, to mimic “natural” aging and also to better understand the underlying
70 mechanisms involved by TTs. At high temperatures, TTs are known to reduce the equilibrium
71 moisture content (EMC) of wood mainly because of the chemical degradation of wood polymer
72 components and mass loss, which reduces the quantity of hydroxyl (-OH) adsorption sites.
73 Recently, it has been shown that the hygroscopicity of wood decreases in relation to the mass
74 loss, resulting from thermal modifications (Borrega and Kärenlampi 2010), but that this
75 reduction in hygroscopicity is also influenced by another mechanism related to irreversible
76 hydrogen bonding. Some authors (Suchy et al. 2010a, b,) suggested that this mechanism relates
77 to the irreversible aggregation of cellulose microfibrils and irreversible stiffening of the
78 hemicelluloses/lignin matrix during the drying of green wood. Moreover, Kato and Cameron
79 (1999) showed that during a TT, irreversible formation of new hydrogen bonds can take place
80 in the amorphous regions of cellulose and hemicelluloses. On the basis of these works, more
81 recent studies have investigated this phenomenon showing that the reduction in water content
82 following a TT cannot be explained by the decrease in hydroxyl sites (Rautkari et al. 2013) and
83 that the reduction in hygroscopicity and swelling could also be result from an increased stiffness
84 of the polymer matrix (Boonstra and Tjeerdsma 2006; Rautkari et al. 2013). Concerning the
85 loss of mass induced by TTs, this can lead to a reduction in strength and a change in the mode
86 of failure (Borrega and Kärenlampi 2008), making the mechanical behaviour of thermally-
87 modified woods a widely investigated question. Thus, other researches focused on moderate
88 TTs (lower than 150°C), which do not lead to an important loss of mass, as an alternative to
89 high temperature TTs. In the case of moderate TTs, the decrease of the EMC could be explained
90 by the loss of extractives and also by structural modifications leading to restricted space
91 between polymers (Rostom et al. 2020).

92 In general, there is still ongoing work to understand the mechanisms involved in TTs of wood
93 and their relative importance, for which reversibility tests are a complementary and interesting
94 tool to study reversible and irreversible modifications (within the time frame of the study)
95 induced by TTs. This tool, which has been increasingly used over the recent years, consists in
96 studying the reversibility of the reduction of both EMC and swelling after TTs by placing the

97 sample in contact with water (e.g. soaking, wet (soaking)-drying cycling, high relative humidity
98 (RH) conditioning) for long periods of time. Some studies used repeated cycles of wetting-
99 drying, carried out in air or under vacuum conditions or re-humidification, which could be
100 performed either by soaking in water for a certain time or by exposure to high RH. Other studies
101 used conditioning at intermediate or high RH for a certain duration, generally several weeks or
102 months (Čermák et al. 2015; Gauvin 2015; Obataya and Higashihara 2017; Sahin and Guler
103 2018; Wentzel et al. 2018). These works contributed to get a better understanding of the
104 underlying mechanisms involved by TTs.

105 For instance, reversibility tests suggested that, following drying of green wood, the hydrophilic
106 chain portions within the amorphous phase get additionally constrained and this local stress is
107 released by a dry TT, due to the thermal activation of the segmental motions of the amorphous
108 chain portions (Obataya 2007). This "stabilized" structure, referred to as "annealed", reduces
109 water sorption at low RH, but on the contrary, at higher RH, it was hypothesized that amorphous
110 chain portions return to their initial conformational state while their segmental mobility
111 increases (Obataya 2007; Endo et al. 2016). A similar is observed when wood is heat-treated at
112 high temperature (higher than 150°C), since exceeding the glass transition temperature related
113 to the amorphous domains causes their annealing and reorganization (Endo et al. 2016; Wentzel
114 et al. 2018). Residual stresses in the cell wall matrix upon cooling the material appear and can
115 be released by humidification at high RH or by saturation with water, which completely or
116 partially eliminates the effects induced by drying (Obataya et al. 2002; Altgen et al. 2016; Endo
117 et al. 2016; Obataya and Higashihara 2017). This recovery of the hygroscopic behaviour was
118 also observed for naturally-aged wood (279 years after cutting), following a conditioning at
119 100% RH for several weeks (Obataya 2017). In general, humidification-drying cycles on heat-
120 treated wood, under dry or humid conditions, lead in both cases to a complete or partial removal
121 of the TT-induced effects (Altgen et al., 2016; Endo et al., 2016; Majka et al., 2016). For high
122 TT temperatures, part of the decrease in hygroscopicity and swelling of wood is due to the
123 chemical degradation of the chains in the amorphous domains and another part was assigned to
124 the physical aging of the polymers, which turns out to be reversible (Endo et al., 2016; Obataya
125 and Higashihara, 2017). Concerning the reversible modifications following dry TTs, recent
126 studies on the accessibility of hydroxyl sites proposed models to account for the reversibility
127 and irreversibility of TT in the presence or absence of humidity (Altgen et al., 2018; Willems
128 et al., 2020). They propose that sorption sites for water are composed of pairs of functional
129 groups along the polymer chains, involving at least one –OH group. At high temperature and
130 under dry conditions, the sites that were removed by chemical degradation of wood polymers
131 could not rearrange to reform adsorption site pairs, in contrast to the case of hygro-thermal
132 treatments. Thus, for TTs under a dry atmosphere only re-humidification by soaking samples
133 in water would allow a rearrangement of these sites and would then be the cause of EMC
134 recovery.

135 In conclusion, the literature shows that the origins of the decrease in hygroscopicity and
136 swelling of wood after TT are not yet well understood. In addition, these interpretations are
137 issued from high processing temperatures where both reversible and irreversible changes occur.
138 In the case of TT carried out at low or moderate temperatures (i.e. lower than 150°C), one may
139 expect a complete reversibility of the effects induced by the thermal treatment, as there is little
140 or no chemical degradation of the polymers. Thus, this temperature regime should simplify the
141 study and understanding of these phenomena occurring after TTs. In this contribution, EMC,
142 dimensional measurements and ¹H 2D NMR relaxometry (which allows studying the
143 interactions between wood and bound water) will be used to investigate the reversibility
144 following a moderate TT. The ¹H 2D NMR T₁-T₂ correlation experiments, allowing to quantify
145 and study the dynamics (i.e. molecular tumbling) of two types of adsorbed water in wood, have

146 shown interesting applications in wood sciences in recent years (Cox et al. 2010; Bonnet et al.
147 2017; Courtier-Murias 2019; Rostom et al. 2020, 2021; Mikac et al. 2021; Stagno et al. 2021;
148 Goñi-Urtiaga et al. 2022). Nevertheless, this powerful approach has never been used to
149 investigate wood reversibility consecutive to a moderate TT. The aim of this work is to improve
150 the understanding of the mechanisms behind TT by studying wood reversibility after a
151 moderated TT (120°C). Such experiments will be carried out on modern and historical wood
152 samples, thus allowing a comparison between similar materials but with differences in their
153 chemical composition, as characterized by ¹³C solid-state NMR.

154
155

156 MATERIALS AND METHODS

157 Materials

158 The experiments were carried out on modern and historical oak wood materials, which were
159 used in Rostom et al. (2020) to investigate the effect of aging on wood hygroscopicity by
160 applying a moderate TT (120°C). The historical wood (about 250-year-old oak after tree
161 cutting) comes from a wooden door's frame of a building from the 17th century in Saint Georges
162 street in Rennes, France (provided by Atelier Perrault), which was subjected to natural aging.
163 The modern oak wood, considered without aging, was provided from a sawmill located in the
164 North of France in 2018.

165 Small samples of approximately 1 cm³ were cut from those two oak wood boards and were
166 collected, as possible, side-by-side to minimize the variability between samples. They were
167 sawn along the anisotropic directions (Longitudinal L, Radial R and Tangential T) and were all
168 cleared from visible defects. Before TT experiments, complete water adsorption/desorption
169 cycles were imposed to the samples to avoid differences in the moisture history. For this
170 purpose, they were alternately stored for one week in desiccators at a RH of 97% (using
171 potassium sulfate) and 2% RH (using silica gel) at 20°C. After the initial dry state at 2% RH,
172 samples were stabilized at 65% RH and subjected to NMR measurements.

173 Then, the samples were thermally treated in an oven at 120°C (where the RH is close to 0%)
174 for 1 day, 3 days and 7 days. The results related to the effect of the TT were described in a
175 previous work (Rostom et al. 2020). Here, the same samples are used to investigate the
176 reversibility of such a TT. It should be noted that two out of the three samples used for the 24h
177 TT in the previous work have been used for the reversibility test as one of them has been used
178 for microscopic observations in a parallel work. The average density of all the samples before
179 TT was measured at 65% RH and found to be 0.67 (±0.01) g.cm⁻³ for modern oak wood and
180 0.50 (±0.02) g.cm⁻³ for historical oak wood.

181 Similarly to what has been previously done by Rostom et al (2021), both mass and volume of
182 each sample were normalized to their initial volume (here, the one obtained at 2% RH before
183 TT experiments) to allow comparisons between samples with slightly different volume and
184 mass. Thus, for simplification, normalized units will be used (mg* referring to mg/cm³ for the
185 mass and mm³* referring to mm³/cm³).

186

187 Reversibility protocol

188 The study of the reversibility of the TT at 120°C was carried out according to an experimental
189 protocol in three steps:

190 (1) Before TT: all samples were analysed at 65% RH (using a saturated ammonium nitrate
191 solution) through ¹H NMR, mass and dimension measurements;

192 (2) After TT (carried out in a standard oven at 120°C): all samples were conditioned in a
193 desiccator at 65% RH until constant mass (about one week) and were left for about one year

194 and two months prior to the reversibility tests due to constraints related to COVID-19 pandemic
195 without observing significant evolution of mass and volume deformations;
196 (3) The reversibility test is performed by conditioning all samples at about 97% RH, 20°C
197 for two weeks in a desiccator filled with a saturated potassium sulphate solution. As for previous
198 analysis, the samples were conditioned at 2% RH (using silica gel) for a week, then conditioned
199 at 65% RH for a week. This allows to be in an adsorption cycle (starting from 2% RH) to avoid
200 the influence of the hysteresis in the observed phenomena. After 14 weeks, samples were again
201 analysed to prove their possible evolution after reversibility test. This second analysis was only
202 conducted for step 3, as wood is anticipated to be less stable compared to steps 1 and 2.

203 At each equilibrium moisture content (EMC), the specimens were analysed by means of ¹H
204 NMR relaxometry and their dimensions and masses were measured. The results before and after
205 TTs are explained in Rostom et al. (2020) and are used here for the sake of comparison to the
206 reversibility tests.

207 **Determination of EMC**

209 The EMC is determined as the ratio of the water mass to the dry wood mass. As shown in
210 Rostom et al. (2021), the dry wood mass may be deduced thanks to ¹H NMR. Here, the EMC
211 values from 2D ¹H NMR relaxometry have been obtained based on this previous work showing
212 the relationship between the 2D ¹H NMR signal intensity and water content in wood samples:

$$213 \text{EMC}_{\text{NMR},x\%RH} = \frac{M_{\text{water,NMR},x\%RH}}{M_{\text{drywood,NMR}}} * 100 \quad (1)$$

214 where $\text{EMC}_{\text{NMR},x\%RH}$ is the equilibrium moisture content at x% RH, $M_{\text{water,NMR},x\%RH}$ is the mass
215 of water at x% RH and $M_{\text{drywood,NMR}}$ is the mass of dry wood, all these quantities being deduced
216 from NMR measurements. It has recently been shown that this NMR approach, which can be
217 used to obtain the dry mass of wood, provides accurate values for EMC without the need to
218 oven-dry the samples at 103°C (Rostom et al. 2021).

219 It should be noted that the EMC values used here are the average values over 4 samples used in
220 a previous work (Rostom et al. 2020) in which different TT durations have been used (1, 3 and
221 7 days) as the effect of TT was similar for the studied TT durations. Moreover, mass losses
222 using moderate TT were small and thus similar for all samples.

223 **Volumetric deformations' measurements**

225 The dimensions of the samples were measured using a calliper with a precision of 0.01 mm, at
226 each step of the experiments.

227 Volume deformations can be evaluated by the following equation:

$$228 \Delta \varepsilon_{x\%} = \frac{V_{x\%} - V_{dry}}{V_{dry}} \quad (2)$$

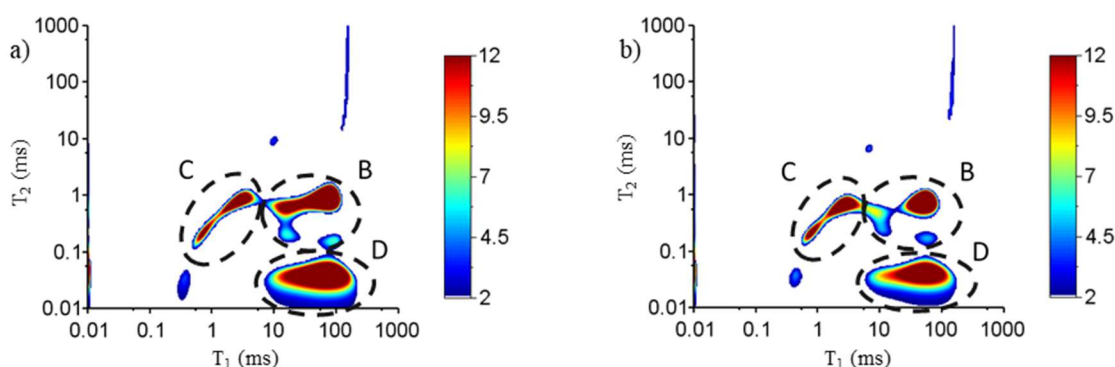
229 where $V_{x\%}$ is the humid volume at a given value of x% RH and V_{dry} is the dry volume.

230 In this study, the volume deformations have been calculated using two reference states: either
231 the dry volume before TT or the dry volume state at each state (e.g. after TT or reversibility) as
232 both calculations have been used in the literature to study wood properties (García Esteban et
233 al. 2005; Obataya and Higashihara 2017).

234 **¹H NMR measurements**

236 ¹H NMR relaxometry measurements were carried out using a BRUKER MINISPEC MQ20
237 spectrometer that operates at 0.5 T, corresponding to a resonance frequency of 20 MHz for ¹H.
238 The samples were inserted in an 18 mm NMR tube in which the RH was controlled with a
239 saturated salt solution placed in a small container in the upper part of the tube during the NMR

240 experiments. For more details about the conditions of measurements see Rostom et al. (2020).
 241 2D ^1H NMR correlation spectra of T_1 and T_2 relaxation times were acquired using the Inversion
 242 Recovery (IR) sequence coupled with the Carr-Purcell-Meiboom-Gill (CPMG) sequence (Carr
 243 and Purcell 1954; Meiboom and Gill 1958). The data computation was performed using an in-
 244 house software, which reproduces the 2D-Inverse Laplace Transform (ILT) algorithm of Song
 245 et al. (2002). The 2D ^1H NMR correlation spectra allow to display the components of the NMR
 246 signal as a function of their NMR relaxation, T_1 and T_2 . In the present case, different regions
 247 corresponding to adsorbed water (bound water) in different wood compartments (peaks B and
 248 C) or to wood polymers (peak D) as shown in Figure 1 are clearly detected (Cox et al. 2010).
 249 This NMR approach also leads to T_1/T_2 ratios for the different kinds of H atoms, which are
 250 characteristic of the extend of reorientational motions (i.e. molecular tumbling) and therefore
 251 of the interactions of water with polymers matrix of the wood cell walls. As previously
 252 explained (Bonnet et al. 2017), the volume under each peak of the 2D spectra is proportional to
 253 an amount of H atoms, which is used to quantify adsorbed water and the T_1 and T_2 values of
 254 each peak are determined by means of the coordinates of their respective maxima.



255
 256 **Figure 1.** T_1 - T_2 correlation spectra of modern oak wood (a) and historical oak wood (b) samples by 2D ^1H T_1 - T_2
 257 NMR relaxometry at 65% RH. Peaks B and C are attributed to ^1H detected from bound water and peak D is
 258 attributed to ^1H from wood polymers. It should be noted that to follow previous notation (Cox et al. 2010) peak
 259 A is not included here, which correspond to free water and it is not present in these samples. All the T_1 - T_2
 260 correlation spectra acquired in this work can be found in Figures S3 and S4.

261 262 ^{13}C solid-state NMR measurements

263 ^{13}C solid-state NMR spectroscopy measurements were carried out at room temperature on a
 264 300 MHz (7 T) Bruker Avance III HD NMR spectrometer equipped with a 4 mm ^1H -X double
 265 resonance MAS probehead. All the spectra were recorded using a magic angle spinning (MAS)
 266 frequency of 5 kHz and the $^1\text{H} \rightarrow ^{13}\text{C}$ cross polarization (CP) experiment. The $90^\circ(^1\text{H})$ pulse
 267 length was equal to $3.2 \mu\text{s}$ and the radiofrequency field used during the $^1\text{H} \rightarrow ^{13}\text{C}$ magnetization
 268 transfer was set to 62 kHz. A ^1H dipolar decoupling of 90 kHz was applied during the
 269 acquisition of the ^{13}C NMR signal. Three different contact time (CT) values were used, 50 μs ,
 270 1 ms and 4 ms. The recycle delay was fixed at 3 s, in agreement with the ^1H spin-lattice
 271 relaxation time $T_1(^1\text{H})$ of the wood samples considered. The ^{13}C chemical shift values were
 272 referenced with respect to tetramethylsilane, by calibrating the peak related to the carbonyl
 273 carbon of α -glycine at 176.03 ppm.

274 For these ^{13}C NMR measurements, native samples of 1 cm^3 of each oak wood (modern and
 275 historical) were considered as control samples and conditioned at 65% RH, 20°C until
 276 equilibrium, then powdered using a manual grater and reconditioned at 65% RH to be consistent
 277 with the analysis conditions used in this study.

278 Regarding treated samples, 1 cm³ samples of each oak wood were also equilibrated at 65% RH
279 and 20°C, then thermally treated at 120°C in an oven-dry for 7 days. These samples are
280 considered to be similar to the ones used in (Rostom et al. 2020), and in particular their density
281 was identical. After TT, the samples, in a cubic shape, were stabilized at 65% RH, 20°C. After
282 stabilization, the samples were ground using a manual grater and conditioned at 65% RH until
283 their insertion into the NMR rotor to perform the measurements. The powdering of the samples
284 was therefore subsequent to the TT. The protocol indicated here for treated samples is very
285 important since the effect of TT on cubic samples of wood is different from its effect on a
286 powdered wood.

287 ¹H → ¹³C CP MAS NMR is generally used to get quantitative or, under certain conditions,
288 semi-quantitative information on the chemical composition of environmental samples,
289 including wood (Willis and Herring 1987), studied under similar conditions. In this work, ¹H
290 → ¹³C CP MAS will be used to compare the composition of modern and historical wood
291 samples and correlate this feature to the water absorption behavior and the performance of the
292 reversibility tests. In addition, various ¹³C CP MAS NMR spectra were obtained using different
293 CT values as it may allow investigating whether structural changes of cell wall polymers
294 occurred during the reversibility tests (Košíková et al. 1999).

295
296

297 RESULTS AND DISCUSSION

298 Dry masses

299 Table 1 shows the evolution of the mass measurements performed by weighing and through ¹H
300 NMR analysis (Rostom et al. 2021) in the dry state and at 65% RH for modern and historical
301 oak wood samples at each step of the study (initial state, before TT, after TT, after reversibility
302 test and after 14 weeks). If we focus on the dry masses obtained by NMR, which provides more
303 accurate values than the usual drying methods (Rostom et al. 2021), we observe that there is
304 almost no sample degradation during TT's (about 1%) and reversibility tests carried out. This
305 is consistent with previous works which reported that oak wood degradation begins only at 130-
306 150°C (Esteves and Pereira 2008). Thus, degradation of the polymer components should not
307 occur under the TT conditions used in this work and the dry mass loss observed may be due to
308 a relatively small loss of extractives, which could impact water adsorption behaviour (Mantanis
309 et al. 1994). Furthermore, other chemical changes without significant degradation may have
310 occurred.

311 By comparing the evolution of the dry masses and the masses at 65% RH determined by
312 weighing, we can observe that they are following the same trend as they decrease due to TT
313 (samples were “dried” at 120°C) and then increase due to the reversibility tests but without
314 coming back to their initial values. In addition, these results emphasized the limitation of drying
315 methods (in comparison to NMR) to obtain accurate dry masses of wood as values obtained by
316 weighing are always higher than the ones obtained by NMR with the exception of completely
317 dry samples where both techniques provide the same results. Thus, dry masses obtained by
318 NMR will be used in the following sections to discuss the relevance of various parameters (i.e.
319 EMC and volumetric deformations) to study wood reversibility.

320

321 **Table 1.** Dry masses and masses at 65% RH (in mg*, obtained by weighing and by ¹H NMR) of wood samples at
 322 the initial state, before TT, after TT, after reversibility test (after 2 weeks at 97% RH and after 14 weeks at 65%
 323 RH) for both modern and historical oak woods. The standard deviations are indicated in parenthesis.

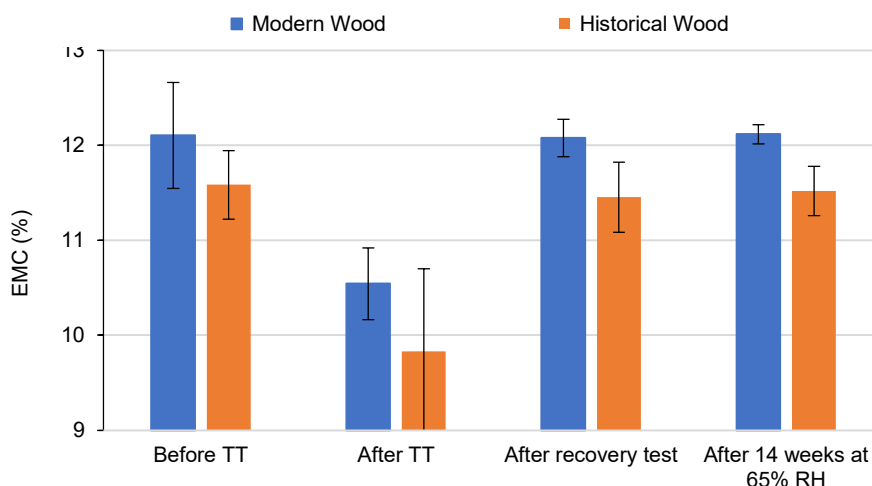
		Before TT	After TT	After reversibility test	
				2 weeks	14 weeks
Modern wood	Dry state, NMR data	629.8 (10.9)	628.3 (12.1)	624.5 (13.2)	622.5 (16.1)
	Dry state, weighing	641.6 (11.5)	628.9 (12.7)	636.6 (17.1)	636.6 (17.1)
	65% RH, Weighing	706.6 (14.8)	694.5 (15.7)	699.9 (15.2)	697.8 (18.0)
Historical wood	Dry state, NMR data	463.4 (21.7)	459.7 (26.3)	458.5 (24.6)	456.6 (26.0)
	Dry state, Weighing	473.1 (23.5)	459.8 (25.0)	466.8 (26.9)	466.8 (26.9)
	65% RH, weighing	517.3 (25.7)	505.2 (32.6)	510.6 (29.7)	509.2 (30.1)

324

325 Equilibrium Moisture Content

326 The EMC values obtained by 2D ¹H NMR relaxometry measurements at 65% RH are presented
 327 in Figure 2 and Table 2. These measurements allow to compare the state of the samples before
 328 TT, after TT, after reversibility test and after 14 weeks of conditioning at 65% RH following
 329 the reversibility test. The two first states (before and after TT) have already been studied
 330 previously to understand the effect of aging in wood (Rostom et al. 2020) and here are used as
 331 references to investigate wood reversibility.

332 The results obtained after reversibility tests show that the EMC values of both modern and
 333 historical materials are totally recovered after conditioning at 97% RH for two weeks.
 334 Moreover, EMC remains constant, within the experimental accuracy (0.5%), over the 14 weeks
 335 of conditioning at 65% RH after reversibility test. The same trend was observed for both modern
 336 and historical oak samples. These results are consistent with previous works which have shown
 337 that conditioning the samples at high RH values leads to a complete recovery of the EMC values
 338 of woods being subjected to moderated TT (Obataya and Higashihara 2017; Willems et al.
 339 2020; Mastouri et al. 2021) when there is no or little degradation of wood polymers.



340

341 **Figure 2.** Evolution of the mean EMC at 65% RH derived from ¹H NMR relaxometry measurements for modern
 342 and historical oak woods.

343 In addition to providing a non-invasive manner to investigate samples and obtaining accurate
 344 EMC values (Rostom et al. 2021), another interest of 2D ¹H NMR relaxometry relies on its
 345 ability to detect and quantify water in two different chemical environments in the wood cell
 346 walls (Cox et al. 2010; Bonnet et al. 2017; Rostom et al. 2020). For instance, it has been shown
 347 that a moderate TT on modern and historical wood specimens results in a more important
 348 decrease of the strongly associated water to wood polymers in the modern wood than in the

349 historical wood (Rostom et al. 2020). This different extent of reduction of water adsorption
 350 could be explained by the variations in the chemical composition of both samples. Here, we
 351 hypothesized that the reversibility could also be different for water adsorbed to different wood
 352 polymers (and with different interaction strength). Thus, we have compared the evolution of
 353 both types of adsorbed water (B and C in Figure 1) after reversibility tests. However, our results
 354 show that the amounts of adsorbed water in the environments B and C (Table 2) follow the
 355 same behaviour as the total EMC (Figure 2): a full recovery of the moisture content values is
 356 observed. This feature indicates that the effect of the moderate TT performed on these oak wood
 357 samples is completely reversible in terms of EMC and that we do not observe clear differences
 358 between the two types of water associated to different wood polymers. This type of analysis
 359 should prove to be useful to investigate whether one of these two types of water is, or not, more
 360 influenced by reversible and irreversible changes. Moreover, 2D ^1H NMR relaxometry also
 361 allows a comparison of the behaviour displayed by modern and historical wood samples and to
 362 assess the influence of their composition as we will see in the following sections.

363
 364 **Table 2.** Moisture content values at 65% RH determined by 2D ^1H NMR relaxometry at each step of the
 365 experiment for both modern^a and historical^b wood samples. The reported values are averaged over all samples and
 366 the three durations of TT while the standard deviations are indicated in parenthesis.

	Before TT	After TT	After reversibility test	14 weeks at 65% RH
MC(B+C) ^a [%]	12.1 (0.6)	10.5 (0.4)	12.1 (0.2)	12.1 (0.1)
MC(B) ^a [%]	9.3 (0.5)	8.1 (0.2)	8.9 (0.2)	8.3 (1.3)
MC(C) ^a [%]	2.8 (0.0)	2.4 (0.2)	3.1 (0.2)	3.8 (1.2)
MC(B+C) ^b [%]	11.6 (0.4)	9.8 (0.9)	11.5 (0.4)	11.5 (0.3)
MC(B) ^b [%]	7.1 (0.4)	6.4 (0.2)	6.8 (0.7)	7.2 (0.5)
MC(C) ^b [%]	4.4 (0.7)	3.4 (0.9)	4.6 (0.8)	4.2 (0.6)

367
 368 **^1H NMR relaxometry**

369 2D ^1H NMR relaxometry experiments and, in particular, the T_1/T_2 NMR relaxation time ratios
 370 provide additional important information concerning the wood samples. These ratios allowed
 371 to investigate the dynamics (i.e. molecular tumbling) of adsorbed water (Bonnet et al. 2017;
 372 Rostom et al. 2020; Goñi-Urtiaga et al. 2022) which may be affected by the structural
 373 modifications of wood polymers. Although full EMC recovery was observed, we wanted to
 374 investigate whether the water dynamics are also similar to the ones in the initial state before
 375 TT. The evolution of the T_1/T_2 ratios before and after reversibility test is presented in Table 3.
 376 These results show a significant increase of T_1/T_2 ratios after TT (a feature already discussed
 377 in (Rostom et al. 2020)), which indicates a decrease in the reorientational motions of the water
 378 molecules. This trend is clearly observed for the water molecules related to both peaks B and
 379 C. After reversibility test, the T_1/T_2 ratios decrease but do not come back to their initial value,
 380 determined before TT, even after 14 weeks of conditioning at 65% RH. This trend is clearly
 381 observed for the peak B for both modern and historical oak woods but is less obvious for the
 382 peak C (especially for historical wood). This result indicates that water in both wood samples
 383 does not exactly display the same mobility as in the initial state: a slowing-down of the
 384 reorientational motions is detected in comparison to its initial state before TT. These trends
 385 suggest that physical aging induced by the TT, partly irreversible and not detected by EMC
 386 analysis occurs, could lead to more restricted motions of the water having stronger interactions
 387 with the wood polymers.

388 **Table 3.** T_1/T_2 ratios measured at 65% RH by 2D 1H T_1 - T_2 NMR experiments. These results are obtained for both
 389 modern^a and historical^b wood samples subjected to TT at 120°C for three durations. The values reported average
 390 our results from all the samples thermally-aged during three different durations and the standard deviations are
 391 indicated in parenthesis.

	Before TT	After TT	After recovery test	14 weeks at 65% RH
Peak B ^a	88.6 (3.0)	118.8 (12.8)	93.9 (3.1)	94.8 (3.1)
Peak C ^a	3.4 (0.0)	4.0 (0.2)	3.3 (0.3)	4.1 (0.9)
Peak B ^b	70.3 (2.3)	106.6 (18.7)	75.6 (2.2)	85.1 (8.6)
Peak C ^b	3.6 (0.7)	4.2 (0.5)	3.5 (0.8)	3.7 (1.0)

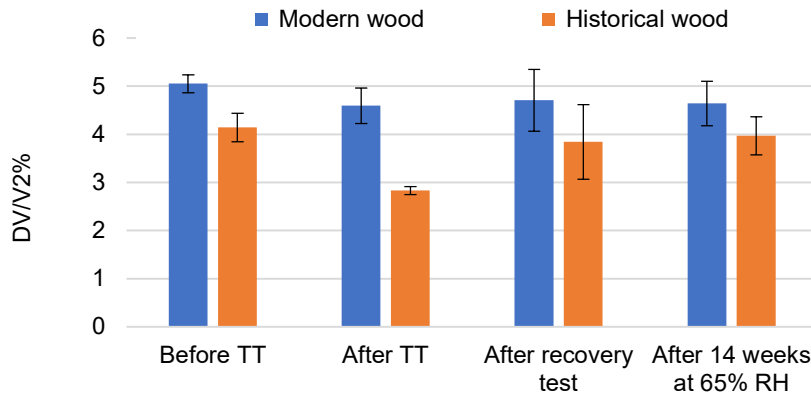
392 The exposure of the materials to high RH following TT's may lead to a structural evolution of
 393 the cell wall polymers. Indeed, the increase of RH in their environment (due to reversibility
 394 tests) may induce conformational changes within the amorphous regions of these polymers by
 395 lowering their glass transition temperature (T_g). Such a plasticizing effect may promote their
 396 segmental motions and therefore, their rearrangement. This new organization of the
 397 macromolecular chains would allow the adsorption of water on the adsorption sites - which
 398 were made inaccessible because of the changes of the cell wall polymers and the obstruction of
 399 adsorption sites already engaged in intramolecular bonds. However, the increase of T_1/T_2 ratios
 400 in comparison to the initial state suggest that water behaves in a slightly different way since its
 401 mobility has decreased. This interpretation of NMR results is similar to the assumptions made
 402 in the literature on the reduction of the annealing of polymers following drying (Obataya 2007,
 403 2017). Other authors have also proposed that the adsorption of water molecules on polymer
 404 chains could involve pairs of polar groups (thus forming an adsorption site) which could lead
 405 to reorganized pairs and then, form recomposed sites when wood is re-humidified at high RH
 406 (Willems et al. 2020). In conclusion, after the reversibility protocol, the structure of the wood
 407 cell walls has changed while its EMC is completely recovered. As a result, it could be supposed
 408 that new rearrangements of the adsorption sites have enabled the global EMC recovery but with
 409 a new repartition of the adsorbed water molecules in more confined areas, corresponding to the
 410 same spatial location and chemical environment, as the intensities of the B and C peaks have
 411 not changed. To discuss the results concerning the mobility of water, we will analyze the
 412 volumetric deformations using two reference dry status in the following sections.

413

414 **Volumetric deformations using a dry reference at each state**

415 Figure 3 presents the volumetric deformations of modern and historical oak woods calculated
 416 at 65% RH using a dry reference at each state (i.e. before TT, after TT, after recovery test and
 417 after 14 weeks of conditioning at 65% RH). The volume deformations decrease after TT and
 418 then increase following the reversibility test for both modern and historical woods. For these
 419 two samples, and within the error of measurements, we can conclude that the reversibility test
 420 produces a complete recovery in terms of volumetric deformations for both types of wood
 421 samples but this recovery is less clear for historical wood in comparison to modern wood.

422 The evolutions of both EMC and volume deformations, using a dry reference at each state,
 423 show a full recovery after TTs which is consistent with previous works using moderate TTs.
 424 However, as T_1/T_2 NMR data suggested some irreversible effects so we have further
 425 investigated the volumetric deformations by calculating them using a single dry reference which
 426 corresponds to the dry initial state before TT (Obataya and Higashihara 2017).

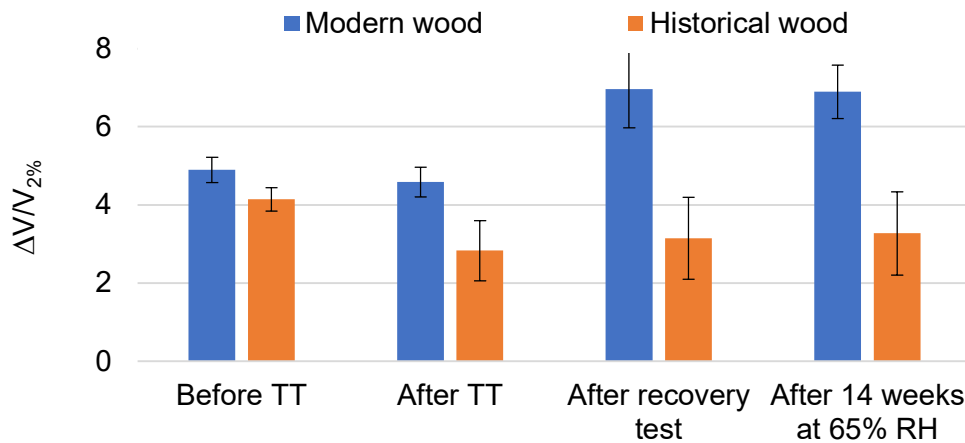


427
428 **Figure 3.** Volume deformations at 65% RH, using a dry reference at each state, estimated before TT, after TT,
429 after reversibility test and after 14 weeks at 65% RH following reversibility test for modern and historical oak
430 woods.

431

432 Volumetric deformations using a dry reference before TT

433 Figure 4 shows the volumetric deformations calculated with respect to the dry state at 2% RH
434 occurring at the very beginning of the experiment (before TT). For modern wood, a significant
435 increase of the volume deformation is observed following the reversibility test and the
436 prolonged conditioning at 65% RH and clearly overcomes the initial value before TT. However,
437 the historical wood does not follow the same behaviour as the volume deformation remains
438 lower than the initial value before TT. This feature confirms our previous observations by T₁-
439 T₂ NMR correlation experiments showing that some irreversible effects could remain after a
440 moderate TT, which seem more important for modern wood samples. It is also important to
441 note that this effect has only been detected when conditioning the samples at 97% RH for two
442 weeks whereas samples did not display further evolution over the following three months of
443 conditioning in a desiccator at 65% RH after TT.

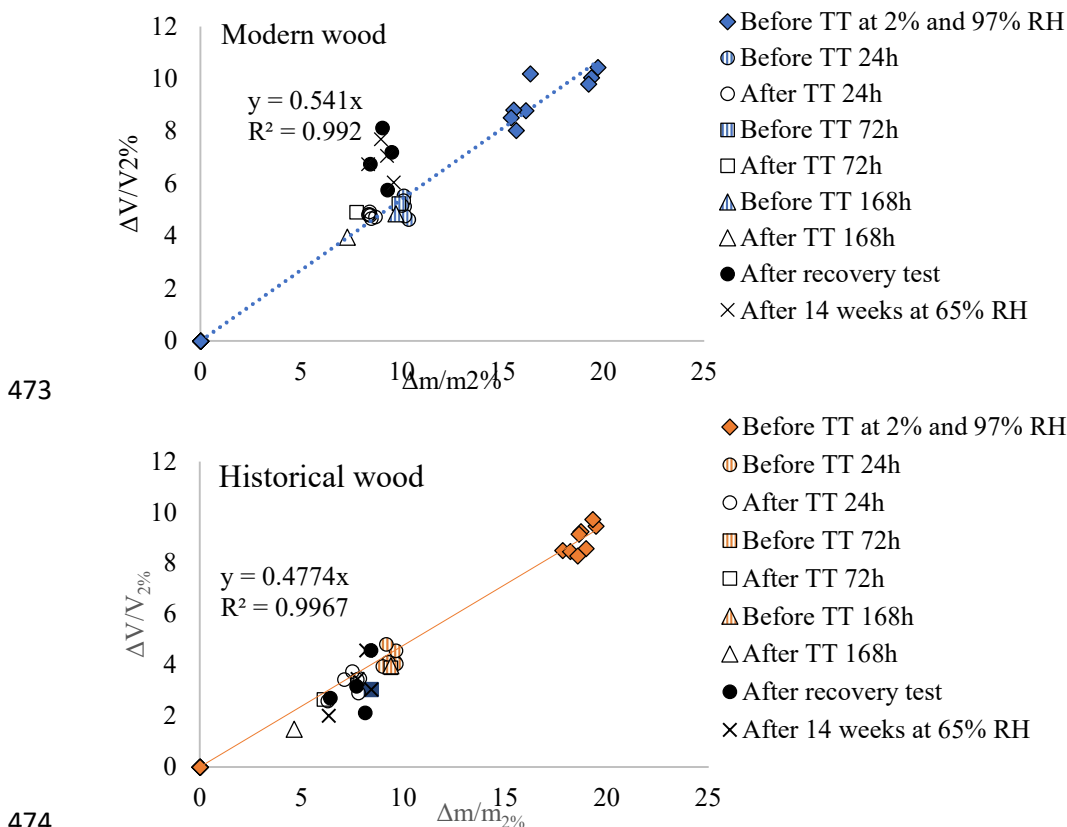


444
445 **Figure 4.** Volume deformations at 65% RH, using a dry reference before TT, estimated before TT, after TT, after
446 reversibility test and after 14 weeks at 65% RH following reversibility test for modern and historical oak woods.

447 These results show that both types of volumetric analysis do not lead to the same conclusions
448 and that EMC values may not be adequate to observe reversibility in all cases. In particular, the
449 volumetric analysis using a dry reference at each step of the study may not be suitable to study
450 reversibility of wood. This type of calculation provides information on the volumetric
451 deformations between two different RH conditions (dry samples are characterized by a RH
452 value of about 2%), which is useful to understand the behaviour of samples for real applications
453 after a TT and/or reversibility tests. In particular, it allows the estimation of the volume
454 deformation variations resulting from the changes on ambient RH but may not help to

455 understand the modifications (and reversibility) occurring within the sample. On the contrary,
 456 the volume deformation analysis using the dry state at 2% RH at the very beginning of the
 457 experiment (before TT) seems to be able to show an evolution in the sample which may be
 458 related to the irreversibility following wood TT. To further investigate this phenomenon, we
 459 have also studied the relationship between the volumetric deformations and the EMC values at
 460 all steps of the study (Figure 5) and compared it to the masses at 65 % RH shown previously
 461 (Table 1). The same type of plot as for Figure 5 but using a dry reference at each step of the
 462 study is presented in Figure S1.

463 For modern wood, an increase of the volumetric deformations was observed following the
 464 reversibility test and prolonged conditioning at 65% RH. This shows that the increase of
 465 volumetric deformations is due to a change in the correlation between the mass of adsorbed
 466 water and the volume of the sample. The values after the reversibility test fall outside the
 467 regression line between volume deformations and EMC values. However, historical wood
 468 samples do not follow the same behaviour since the deformations increase slightly after
 469 reversibility test with the increase of EMC for each sample, thus remaining on the regression
 470 line. These results could be explained by the evolution of volume (see Table S1), as volume
 471 after reversibility test is higher than the initial dry volume for modern wood.
 472



475 **Figure 5.** Volume deformations, using a dry reference before TT, vs EMC determined before TT at 2%, 97% and
 476 at 65% RH for TTs of 24h, 72h and 168h, after TT (24h, 72h and 168h), after reversibility test and after 14 weeks
 477 following reversibility test for modern and historical oak woods.

478
 479 These results confirm that, even though both EMC and volume deformations, determined using
 480 a dry reference at each step, suggested full reversibility, some modifications due to the TT were
 481 not recovered after the reversibility test. In addition, modern wood displays a larger
 482 modification of the volume after reversibility, while the historical wood undergoes a better
 483 recovery of its dimensions after TT. This may indicate an improvement of the dimensional

484 stability of the historical wood due to natural aging making it less affected by the TT. Since
485 there is no significant degradation or chemical modifications of the samples due to the moderate
486 TT, these results suggest that the TT produces some structural modifications, which may be
487 linked to differences in polymer composition between these two wood samples (the differences
488 in polymer composition are expected due to the aging of historical wood). Our results are
489 consistent with previous studies suggesting that, at higher humidity, amorphous chain portions
490 could tend to return to their initial state since their segmental mobility increases due to water-
491 induced plasticization and their residual stresses in the cell wall matrix can be released by
492 humidification, partly eliminating the effects induced by drying (Obataya et al. 2002; Obataya
493 2007, 2017; Altgen et al. 2016; Endo et al. 2016). However, we showed that even after a full
494 EMC recovery, some of these changes may be irreversible as there is still a change observed
495 on water mobility after reversibility test. We can speculate that the greater volume of 'recovered'
496 modern wood compared to the original one may be related to the 'memory' of the wood
497 associated with its green state. This effect appears to be more pronounced for modern wood
498 when compared to historic wood, likely because the polymers are not yet stabilized and are
499 prone to swelling.

500 It should be noted that the volume deformation analysis, $\Delta\varepsilon_{x\%}$, is an interesting method to study
501 wood modifications providing information about the deformation between a dry state and
502 another state at a given % RH. This is a practical parameter for understanding the behaviour of
503 wood after modifications as it allows to simulate the conditions to which wood could be
504 exposed to during its use. Nevertheless, it may have some limitations to understand the effect
505 of wood modifications in terms of the internal structure of wood at a local/molecular-level.

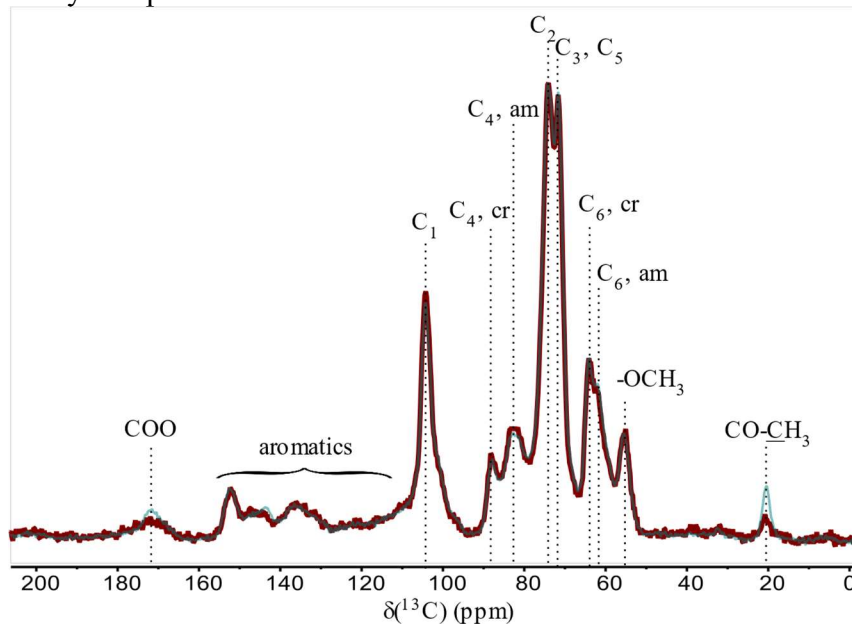
506

507 **¹³C solid-state NMR spectroscopy**

508 ¹³C solid-state NMR spectroscopy was used to study wood samples before and after a TT. For
509 each type of wood, no differences were found on the ¹H→¹³C CP/MAS NMR spectra recorded
510 before and after the TT (see Figure S2). This result is consistent with the mass analysis and
511 suggest that almost no polymer degradation occurs during the TT. For comparison, ¹³C NMR
512 experiments using different contact time values (50 μs, 1 ms and 4 ms) were performed, which
513 lead to spectra weighed by ¹H spin-lattice relaxation in the rotating frame relaxation times ($T_{1\rho}$)
514 that could be affected by structural changes of cell wall polymers (Košíková et al. 1999). The
515 ¹³C CP/MAS NMR spectra before and after TT were found to superimpose, whatever the
516 contact time used (see Figure S2). In addition, these ¹³C NMR spectra allowed us to compare
517 the polymer composition between historical and modern wood samples to determine whether
518 the differences observed in terms of reversibility could be explained by their chemical
519 composition.

520 Figure 6 shows the ¹³C NMR spectra of the native samples (initial state) from modern and
521 historical woods with the assignments of the most characteristic peaks. Though these spectra,
522 obtained by means of ¹H → ¹³C CP, are not quantitative the fact that they can be superimposed
523 leads to simply observe that their chemical composition and the relative amount of the wood
524 polymers are very similar for both wood types. The peaks mainly correspond to lignin and
525 carbohydrate carbons (cellulose and hemicellulose), as can be seen on Figure 6. Besides, one
526 may notice that the contributions from carbons involved in the crystalline and amorphous
527 phases may be clearly resolved. The only difference between these two samples stands in the
528 peaks at 20 ppm and 175 ppm which are assigned to the methyl and C=O carbons from the
529 acetyl groups of hemicellulose respectively. The intensity of these peaks is found to be
530 comparatively weaker for the historical wood than for the modern one. This feature could be
531 due to the degradation of hemicelluloses occurring during the natural aging experienced by the
532 historical wood. This interpretation is consistent with previous works suggesting that the

533 deacetylation of hemicelluloses for historical woods compared to modern woods during natural
 534 aging (Guo et al. 2018). It should be noted that it is generally difficult to compare modern and
 535 historical wood samples as it is difficult to study the same sample over a long time and because
 536 wood composition may vary due to differences in soil composition, climatic conditions, growth
 537 environment, and other factors. However, the two samples studied here seem to display the
 538 same proportions of polymers, except for the acetyl groups of the hemicelluloses, making them
 539 easily comparable.



540 **Figure 6.** ^{13}C CP/MAS NMR spectra (contact time of 1 ms) of both modern (blue) and historical (red) wood
 541 samples and the corresponding peak assignment (Yang et al. 2014). C_1 to C_6 correspond to different carbon
 542 positions of carbohydrates while cr and am denote carbons located within crystalline and amorphous domains
 543 respectively.
 544

545 Considering the previous observations, we could expect lower water adsorption for the
 546 historical wood sample, since fewer acetyl groups from the hemicelluloses are detected in this
 547 sample. However, as previously seen using ^1H NMR, historical wood is characterized by a total
 548 water content which is very close to the one of modern wood, suggesting that the degradation
 549 of acetyl groups in hemicelluloses may not be the only (or the main) factor explaining the
 550 decrease in EMC following natural aging of historical wood. It is also interesting to note that
 551 although the EMC is very similar for both types of wood, the amount of bound water in the
 552 water compartments B and C measured by ^1H NMR is different (see B and C in Table 2). The
 553 amount of water molecules of type B, the more strongly adsorbed water, is lower for historical
 554 wood than for modern wood in the initial state. As the only difference for historical wood is a
 555 lower amount of acetyl groups in the hemicelluloses, one may propose that water molecules of
 556 type B are mainly adsorbed on hemicelluloses. Consequently, the fraction of water molecules
 557 of type C in historical wood is higher than the one measured for modern wood, indicating that
 558 this chemical environment may have experienced modifications during natural aging (chemical
 559 and/or physical changes of the polymer matrix). These modifications could allow a higher water
 560 uptake in the compartments of water molecules of type C, leading to a total amount of adsorbed
 561 water equivalent to that obtained for modern wood.

562 As explained above, a decrease of the content of acetyl groups in hemicelluloses can be due to
 563 aging and heat treatments of wood and this should imply a reduction in both hygroscopicity and
 564 volume deformations of wood. It has often been proposed that the reduction in hygroscopicity
 565 is due to the degradation of hemicelluloses, which results in a significant loss of adsorption sites
 566 (-OH). However, some studies have shown that the reduction of the EMC cannot be explained

567 solely by the decrease of hydroxyl sites. Indeed, (Rautkari et al. 2013) demonstrated that there
568 is a weak correlation between the lowering of EMC of heat-treated wood and the number of
569 accessible -OH sites. The reduction in hygroscopicity and deformations of the studied materials
570 were explained by the increase in the stiffness of the polymer matrix (Boonstra and Tjeerdma
571 2006; Rautkari et al. 2013). These conclusions were reached for high temperature heat
572 treatments (165-220°C) in a dry atmosphere or in the presence of steam. Here, we have shown
573 that a lower amount of acetyl groups in hemicelluloses does not necessarily imply a reduction
574 in hygroscopicity since the water content of historical wood is close to the one of modern wood.
575 The reduction of wood deformations after aging or TT may therefore depend on other
576 parameters such as density or other physical changes.

577 Concerning wood reversibility, our results suggest that there is a relationship between the
578 chemical composition of the sample and the irreversible effect of a moderate heat treatment on
579 the volume deformations observed for oak wood samples. We have indeed shown that
580 volumetric deformations increase after reversibility tests for modern wood whereas they come
581 back to almost their initial state for historical wood, which has a lower amount of hemicellulose
582 acetyl groups due to aging under natural conditions for about 300 years. As the historical wood
583 has experienced natural aging, the degradation of a part of its polymeric matrix in the cell wall
584 could be the cause of an improved volume stability compared to the modern wood since natural
585 aging has degraded the domains which mostly affect its dimensional variations. Besides, the
586 irreversible chemical rearrangements that may have occurred in the different chemical
587 compartments could also have an impact on the improved dimensional stability of historical
588 wood, since the content of water molecules of type C is higher than for the ones of type B for
589 the same wood after reversibility tests (see Table 2).

590
591

592 CONCLUSION

593 This research work showed that EMC values alone do not allow to fully understand the
594 mechanisms underneath TTs and wood reversibility. Moreover, the NMR data indicated that
595 water molecules possess a more restricted mobility after reversibility tests, in comparison to the
596 initial state, for both modern and historical wood samples. This modification on water mobility
597 could be explained by a structural relaxation of the cell wall polymers following the exposure
598 of the material to a high RH, which could reduce the T_g of the chain portions in the amorphous
599 phases and thus promote their rearrangement. These changes could modify the adsorption sites
600 engaged in intramolecular bonds - but in a slightly different way since the mobility of water has
601 decreased (increase of T₁/T₂ ratio in comparison to the initial state). When wood is re-
602 humidified at high RH, a reorganization of these pairs will occur, thus leading to recomposed
603 adsorption site. Therefore, after reversibility test, small residual stresses or irreversible ones in
604 the structure of the wood cell walls could limit the total return of the structure to its original
605 organization even though a full recovery of the EMC was observed.

606 Concerning volumetric deformations, we have compared two methods used to study wood
607 properties: using as a reference the dry volume at each step of the study or the dry volume at
608 the initial state (i.e. before TT). A full reversibility of the volume deformations was evidenced
609 when they are calculated using the dry volume at each step as a reference. Actually, this type
610 of analysis compares the variation of volume at two different hydric states (65% and 2% RH in
611 our case), which is useful to study the performance of wood material in a real application after
612 TT. Nevertheless, this approach does not enable to understand the mechanisms behind TTs and
613 reversibility. On the other hand, when using the dry volume of the intact sample before TT as
614 a reference, volume deformations increased after reversibility test for modern wood. Our results
615 also suggested that the observed restricted mobility of adsorbed water molecules does not have

616 a direct effect on volume deformations since the evolution of the latter is different for each oak
617 wood type, while the effect on ¹H NMR relaxometry data is similar for both modern and
618 historical wood samples.

619 Finally, ¹³C solid-state NMR spectroscopy has been used to compare the composition of both
620 historical and modern wood samples in a native state suggesting that the degradation of acetyl
621 groups in hemicelluloses may not be the only (or the main) factor explaining the decrease in
622 EMC during natural aging of the historical wood. Moreover, we hypothesized that the changes
623 observed in terms of the evolution of the volume of the specimens, and therefore, between
624 historical and modern woods could come from the rearrangement of the macromolecular chains
625 in the wood cell walls. The differences between historical and modern woods could arise from
626 the lower proportion of acetyl groups from hemicellulose for historical wood, due to aging.

627

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631

632 **Author contributions**

633 L.R., D.C.-M. and S.C. worked on developing the structure and method of the paper. L.R.
634 performed all the experiments except from the ¹³C NMR experiments which were carried out
635 by C.L. D.C.-M and S.C. wrote the manuscript. All authors provided critical feedback and
636 helped shape the research, analysis and manuscript.

637

638 **Conflict of interest**

639 The authors declare that they have no known competing financial interests or personal
640 relationships that could have appeared to influence the work reported in this paper.

641

642

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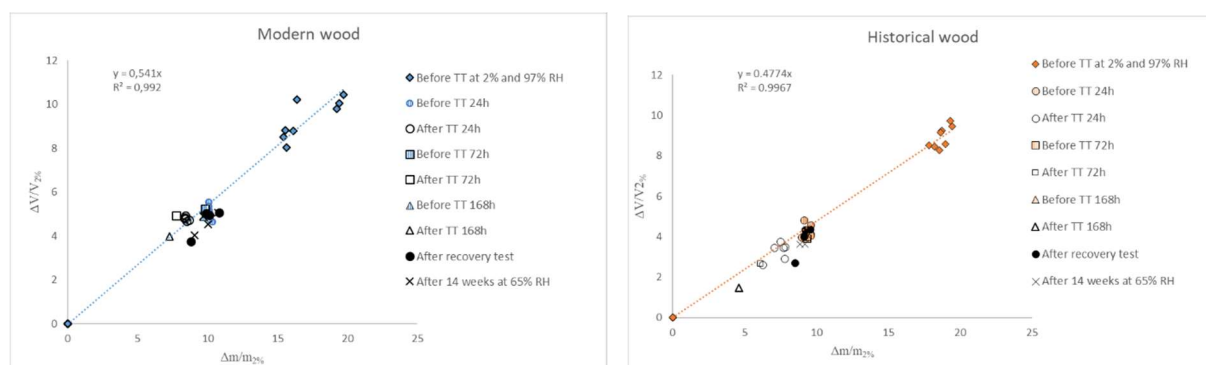
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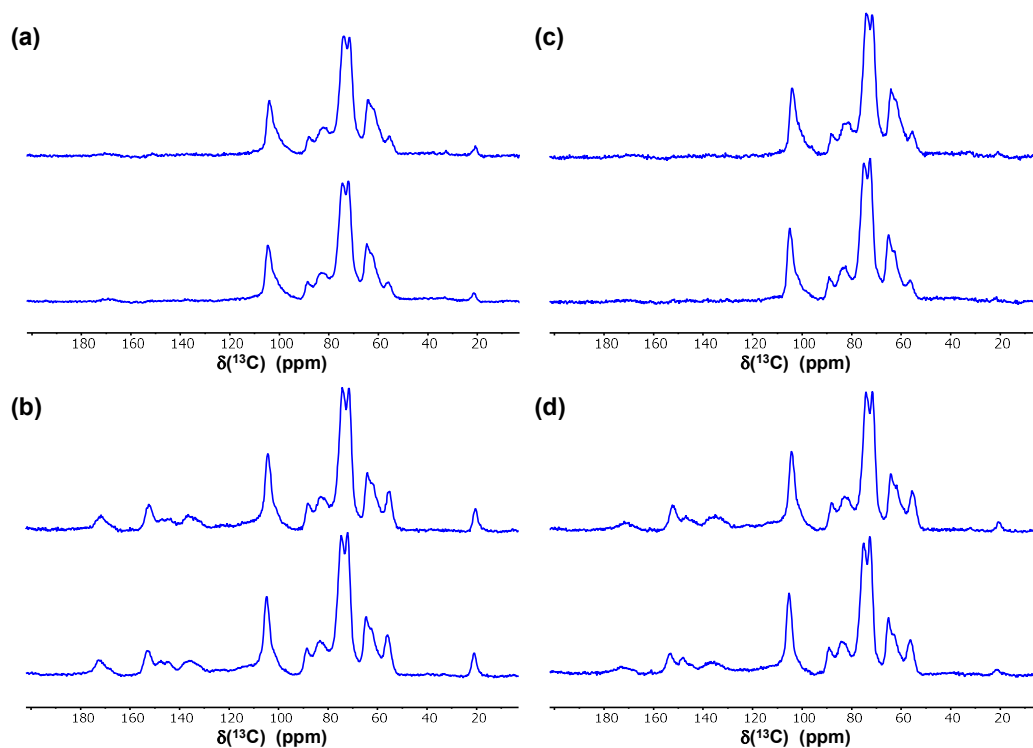
Supplementary material (SI)

See <https://link.springer.com/article/10.1007/s00226-023-01501-6>



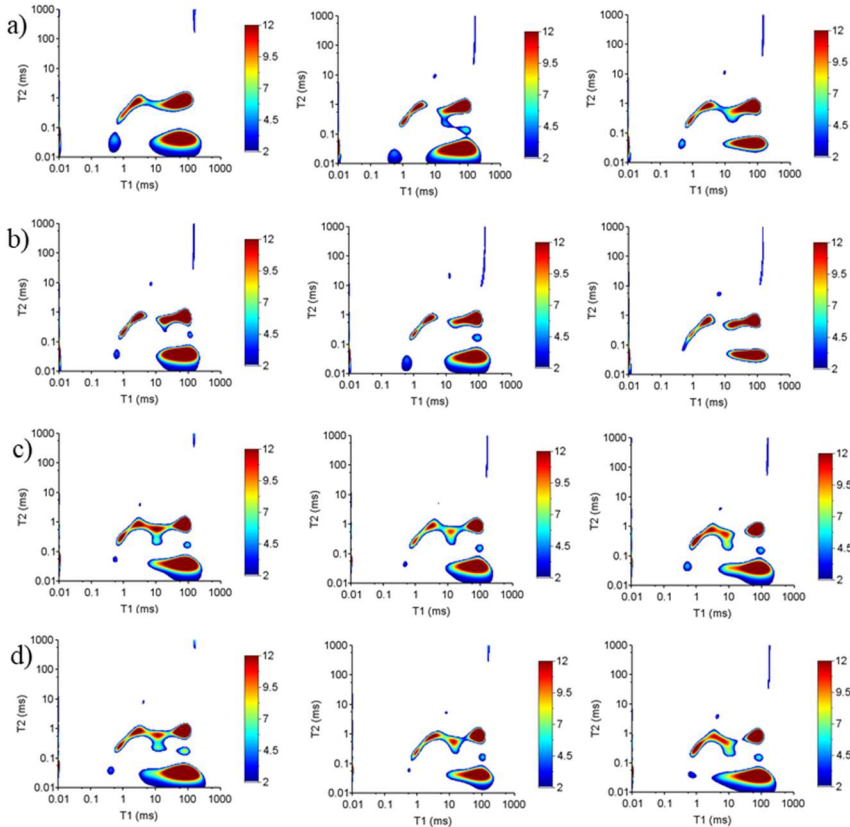
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Figure S1. Volume deformations, using a dry reference at each step, vs EMC determined before TT at 2%, 97% and at 65% RH for TTs of 24h, 72h and 168h, after TT (24h, 72h and 168h), after reversibility test and after 14 weeks following reversibility test for modern and historical oak woods.

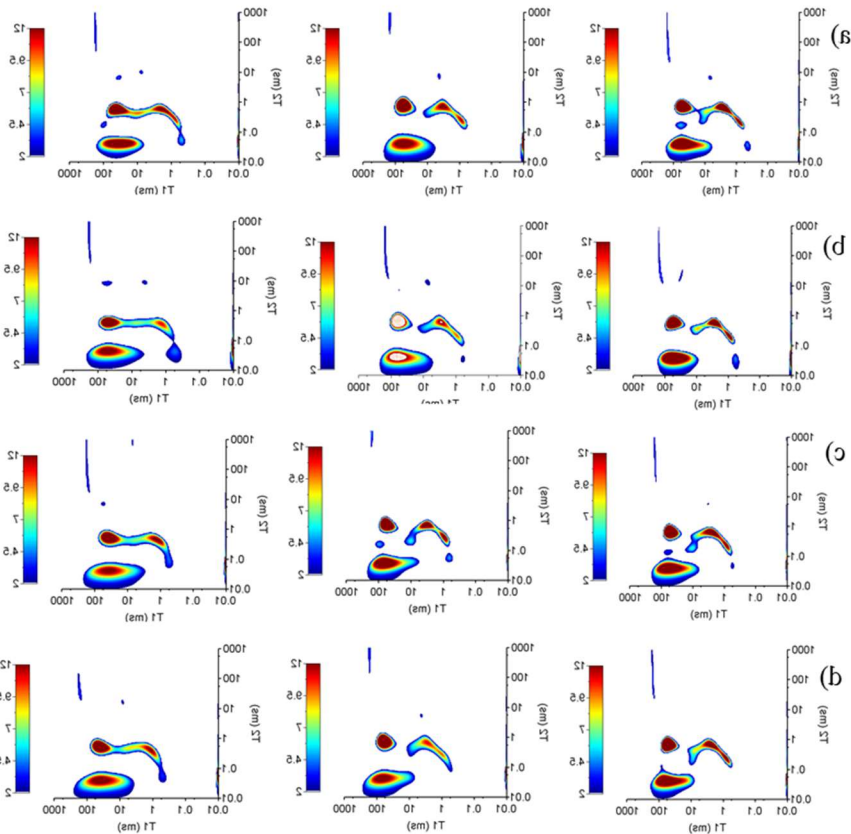


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Figure S2. Comparison of the ^{13}C NMR spectra before (top) and after (bottom) TT obtained for modern wood [(a) and (b)] and historical wood [(c) and (d)]. These spectra were obtained by means of $^1\text{H} \rightarrow ^{13}\text{C}$ cross-polarization, magic-angle spinning and ^1H high-power decoupling applied during the acquisition of the ^{13}C NMR signal. The contact time was set to 50 μs [(a) and (c)] and 4 ms [(b) and (d)]. The other experimental conditions were kept identical to the ones described in the manuscript.



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 775 **Figure S3.** 2D ^1H T_1 - T_2 NMR relaxometry spectra at 65% RH for modern wood a) before TT, b) after TT, c) after
 776 reversibility tests and d) after 14 weeks at 65% RH for the three studied at each state.
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 779 **Figure S4.** 2D ^1H T_1 - T_2 NMR relaxometry spectra at 65% RH for historical wood a) before TT, b) after TT, c)
 780 after reversibility tests and d) after 14 weeks at 65% RH for the three studied at each state.

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Table S1. Dry volumes at 2% RH and volumes at 65% RH normalized to volume data at 2% RH before TT experiments (mm³) of wood samples at the initial state, before TT, after TT, after reversibility test (after 2 weeks at 97% RH and after 14 weeks at 65% RH) for both modern and historical oak woods. Mean values for the cases are provided and standard deviations values are included in parentheses.

		Before TT	After TT	After reversibility test	
				2 weeks	14 weeks
Modern wood	Dry state	1000 (-)	999 (2)	1022 (6)	1022 (6)
	65% RH	1051 (2)	1045 (4)	1071 (3)	1069 (7)
Historical wood	Dry state	1000 (-)	994 (2)	993 (7)	993 (7)
	65% RH	1041 (2)	1029 (7)	1034 (15)	1032 (11)

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