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# Understanding mechanisms of drying of a cellulose slurry by Magnetic Resonance Imaging

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**Abstract:** This study concerns the spatial evolution of the internal components of a macroscopic sample of cellulose slurry during its convective drying. In a first stage, some water is extracted which induces a shrinkage of the structure, the sample remaining saturated, i.e. the solid porous structure made of fibers in contact remains filled with water. In a second stage, when capillary effects are unable to induce further shrinkage, the porous structure formed by the cellulose network homogeneously desaturates and all bulk water is extracted. All along these two stages the drying rate remains constant. Confined water (i.e. likely between macrofibrils) and possibly bound water start to be extracted in a third final stage, during which the sample somewhat further shrinks. In that case a dry front tends to develop from the free surface of the sample, but the water content still decreases homogeneously in the wet region, which suggests that a connected hydraulic network for the confined and bound water persists. This network in fact already ensured the full extraction of bulk water at the end of the second stage keeping a constant drying rate, in contrast with simple porous media.

## Introduction

Water-cellulose suspensions, pastes or slurries, are dried at various steps of industrial processes (Hubbe et al. 2007, Sinquefield et al. 2020) or when they are used as poultices for salt removal from ancient walls (Vergès-Belmin et al. 2011). The best technique for water removal through drying is the object of intense research (Posada et al. 2020, Peng et al. 2012, Lovikka et al. 2016), in particular to avoid hornification or other mechanisms by which the local structure is affected by drying (Hubbe et al. 2017, Beaumont et al. 2017, Weise et al. 1996). The evolution of the porous structure and/or the pore size distribution, considering both free and bound water, has also been studied by NMR (Nuclear Magnetic Resonance) (Häggkvist et al. 1998, Topgaard and Söderman 2002) and DSC (Differential Scanning Calorimetry) (Park et al. 2006). In this context, Topgaard and Söderman (2002) showed that three types of water disappear successively, first bulk water, then water in pores with at least one dimension on the micron scale, and finally water in nanometric pores. These three types of water might correspond respectively to the bulk water, the “freezing bound water”, and the non-freezing bound water, identified by DSC (Weise et al. 1996).

We emphasize that in previous studies the possible spatial heterogeneity of the system, i.e. the development of regions with different water contents, and possibly water types, inside the sample, has generally been neglected. Yet, this is a critical question as soon as one considers the drying of a porous medium, since the extraction of water from the interior of the sample is induced by evaporation resulting from a gradient of RH (relative humidity) between the sample surface and the ambient air. Under these conditions, it would not be surprising that a gradient of water content develops inside the medium. On another side, the different regimes of drying depend on the processes at the origin of water transport and extraction, which can inform on the cellulose structure, water types and exchanges inside the medium.

43 Thus, it is useful to appreciate the way a cellulose slurry dries and look at the internal distribution of  
44 water content in time, the distribution of water types, the mechanism of water transport, and the  
45 possible shrinkage of the structure.

46 The mechanisms of drying of non-deformable, homogeneous porous structures initially filled with a  
47 liquid (perfectly wetting the solid) and submitted to a constant air flux along one of its external surface  
48 usually follows a well admitted scenario (Van Brakel 1980, Prat 1993, Coussot 2000, Tsimpanogiannis  
49 et al. 1999, Lehmann et al. 2008, Shokri et al. 2009, Yiotis et al. 2012). During a long first period, the  
50 drying rate remains constant and the saturation (i.e. the liquid to pore volume ratio) decreases  
51 homogeneously in the sample. This regime is capillary-driven, i.e. any withdrawing of liquid leads to a  
52 homogeneous redistribution of the liquid throughout the sample due to capillary effects. This  
53 maintains a sufficient density of small liquid patches around the sample free surface, which keeps  
54 approximately constant the boundary conditions in terms of vapor field in this region, which in turn  
55 induces a constant drying rate. In the next regime, i.e. when the liquid film size is too thin or,  
56 equivalently, the external evaporation rate is too large, capillary effects are unable to re-equilibrate  
57 sufficiently rapidly the liquid network, which tends to induce a complete drying of some region situated  
58 below the free surface. For model porous systems, such a scheme remains qualitatively valid down to  
59 nanometric pore size (Thiery et al. 2017).

60 With a cellulose slurry, there is first a major complication regarding this scheme: the elements  
61 composing the structure, i.e. the cellulose fibers, can deform when submitted to some stress such as  
62 the capillary stresses which typically develop during drying; as a consequence the apparent volume of  
63 the solid structure of the porous medium may vary, so that we are dealing with a compressible porous  
64 medium. In that case, some water content gradient can develop, as was for example observed for  
65 emulsions (Goavec et al. 2018), microgels (Keita et al. 2016 a) or polymeric bi-porous media (Lerouge  
66 et al. 2020).

67 Here we study a relatively thick cellulose slurry sample initially containing a relatively small volume  
68 fraction of cellulose, and we follow its characteristics by NMR and MRI (Magnetic Resonance Imaging)  
69 all along its drying process. The data analysis provides a full scheme of the mechanisms at work during  
70 drying of such a material. We start by presenting the materials and procedures (Section II), then we  
71 present the results (Section III) and finally we discuss these data (Section IV).

72

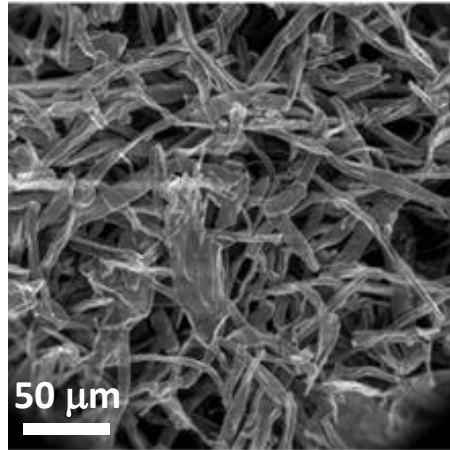
## 73 **Materials and procedures**

### 74 **Material**

75 The cellulose paste was prepared as follows: cellulose fibers (Arbocel® BC1000, supplied by *Kremer*  
76 *Pigmente*), were mixed (at a weight solid fraction of 7%) with distilled water at room temperature for  
77 twenty minutes until obtaining a homogeneous paste. Arbocel® BC1000 is composed of natural  
78 crystalline cellulose fibers (with 99.5% cellulose content), of hydrophilic nature, which is only partly  
79 swollen by water without dissolving and is insoluble in most solvents. The average fiber thickness and  
80 length are respectively about 20  $\mu\text{m}$  and 700  $\mu\text{m}$  (see Fig. 1). The fiber density is  $1500\text{kg m}^{-3}$ . It follows  
81 that the initial volume fraction of the cellulose in the sample is 5.3%. With such a compressible material  
82 of complex porous structure, we can appreciate the porous structure and estimate the pore size from  
83 a view of the compressed fiber packing after the paste shrinkage due to drying (see Fig. 1). In that case  
84 the typical pore size is a few tens of microns, and we can expect that the effective pore size at the  
85 beginning of the test is slightly larger. The drying of a cellulose paste was also observed using

86 Environmental Scanning Electron Microscopy (ESEM). The experiment was performed on a FEI  
87 QUANTA 200 ESEM FEG device. The temperature in the ESEM chamber was fixed at 5°C and the vapor  
88 pressure and the relative humidity was varied from 870 Pa to 176 Pa and from 100 % to 20 %  
89 respectively.

90



91

92 **Fig.1:** ESEM Image of the cellulose paste microstructure

93

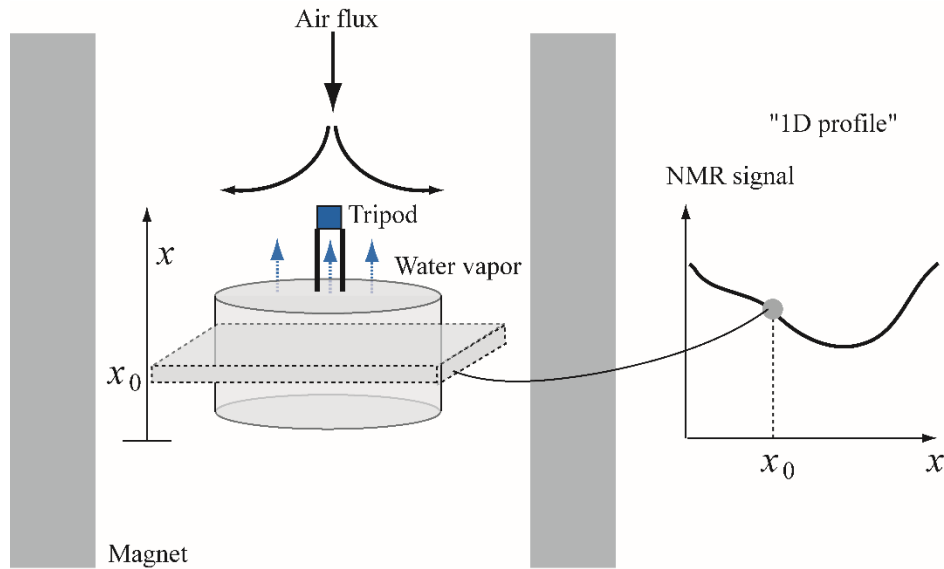
94 Set up

95 The cellulose paste was placed in a cylindrical glass dish ( $D = 9\text{cm}$ ,  $H = 5\text{cm}$ ) up to a height of 4 cm.  
96 Under these conditions, only the top surface of the paste is in contact with air (see Fig. 1). A small  
97 container enclosing water was placed over a tripod lying on the center of the paste. At the very  
98 beginning of the test it slightly sinks (see Fig. 3) in the very soft paste, but then it remains at a fixed  
99 distance from the free surface of the paste, so that MRI measurements allows to determine the  
100 effective position of the free surface above the solid structure of the slurry. We then induce a constant  
101 dry air flux (relative humidity below 0.5%) vertically against the sample free surface and we follow the  
102 water amount distribution in time with NMR.

103

104 NMR

105 All measurements are performed at a 24/80 DBX 0.5-T  $^1\text{H}$  MRI spectrometer by Bruker (20 cm open  
106 diameter in the sample area), operating at 20MHz. We look at the evolution of the water distribution  
107 in time with the help of MRI measurements, either from qualitative 2D images of a sample cross section  
108 along the vertical axis, or from quantitative 1D projections of the liquid content on the vertical axis,  
109 hereunder referred to as 1D profiles, where each data point represents the integrated NMR signal  
110 (proportional to the water mass) in a 1 mm thick layer. During the whole drying process, which usually  
111 took 2 weeks, the sample was simply left at the magnetic center of the MRI system and submitted to  
112 the dry air flux (see Fig. 2).



113  
114

**Fig.2:** Conceptual scheme of the set up and the 1D MRI profile measurement (one point along the profile corresponds to the total NMR signal in a thin layer of sample)

117

#### 118 Profile measurements (1D MRI)

119 The distribution of apparent water along the sample vertical axis ( $x$ ) (see Fig. 2) was measured by  
 120 means of the Single Point Imaging (SPI) sequence (Emid et al. 1985, Bogdan et al. 1995). In addition to  
 121 other purposes such as removing susceptibility and chemical shift artifacts, this sequence is dedicated  
 122 for studying materials with very short spin-spin  $T_2$  relaxation times, i.e. shorter than typically 1 ms, in  
 123 contrast with more classical spin-echo sequences. As a consequence, here this sequence will a priori  
 124 allows us to follow the water amount in almost any pore type in the system, in particular possible  
 125 bound water or thin liquid films possibly formed in the ultimate stages of drying.

126 The detailed parameters of the MRI sequence used were described in a previous study (Ben  
 127 Abdelouahab et al. 2019). Our implementation allows the recording of a series of MRI profiles (Prado  
 128 et al. 1997) as a function of time ( $\tau$ ) over some time interval. The different  $T_1$  values were estimated  
 129 from independent measurements with a spectrometer, and the parameters of the sequence (in  
 130 particular the repetition time) for 1D profiles were adjusted to have a minor influence of  $T_1$  over the  
 131 whole range of water states in the sample. The local NMR signal is then extrapolated based on an  
 132 exponential model ( $s = s_0 \exp(-t/T_2^*)$ ) in which  $t$  is the time and  $T_2^*$  the relaxation time) to provide a  
 133 profile  $s_0(x)$  compensated for the effect of spin-spin relaxation and possibly field inhomogeneities.  
 134 The representation of the signal relaxation with a monoexponential function is an approximation  
 135 which may be shown to provide a reliable estimate of the amount of water present even in slight  
 136 multiexponential cases (note that in any event the distribution of  $T_2^*$  is in a range of values lower than  
 137 the  $T_2$  values presented below). We then yield the distribution of water in small cross-section layers  
 138 (1 mm thickness) along the sample axis (see Fig. 2) at different positions and time. Note that the  
 139 measured profiles are also sensitive to the geometry of the sample and its container, which can explain  
 140 the appearance of ramps on the edge of the profiles, i.e., a progressive decrease of the NMR signal  
 141 over the millimeter order even if the saturation in the sample is homogeneous.

142

#### 143 *Imaging*

144 2D Images were obtained in a vertical (radial) cross section of the sample by means of a spin-echo  
145 sequence with a slice selection (Callaghan 1993). The sequence tuning used a vertical and horizontal  
146 (read out) field of views of 6.5 cm and 20 cm respectively, with a space resolution of 1mm in both  
147 directions. The slice thickness is 1cm. The whole imaging process was repeated 8 times on purpose of  
148 phase cycling and signal accumulation, with  $TR=1$  s and  $TE=4.2$  ms, and lasted about 9 minutes. The  
149 measurements are weighted by spin-spin relaxation so as to well observe the various parts of the  
150 sample. The signal intensity on the MRI picture is therefore not directly proportional to the local water  
151 amount, but instead reads  $s = s_0 \exp(-TE/T_2)$ . However, we can remark that the local relaxation time  
152  $T_2$  in a desaturating porous medium decreases with the local water amount (as the liquid volume  
153 decreases more rapidly than the area of the liquid interface with air or solid). Indeed, according to the  
154 fast exchange Brownstein and Tarr (1977) model the relaxation time essentially varies with the  
155 volume/surface ratio. In a desaturating porous medium, air penetrates the liquid network, thus  
156 inducing new liquid-air interfaces and forming thinner liquid films along the solid surface, which  
157 decreases with the ratio of the volume of liquid in a pore to the wetted surface of this pore. This implies  
158 that, in any event, the apparent signal intensity in such images slightly decreases when the water  
159 amount decreases, which allows to follow qualitatively the 2D distribution of water in time.

160

### 161 *Relaxometry*

162 We also measured the complete NMR relaxation through a Carr-Purcell-Meiboom-Gill (CPMG)  
163 sequence composed of a first  $\pi/2$ -pulse and 2000  $\pi$ -pulses during 5000 ms distributed in logarithmic  
164 intervals. The repetition time is 10 s to get a complete relaxation of all protons. This sequence is  
165 repeated 24 times to increase the signal to noise ratio. The distribution of the relaxation time  $T_2$  is then  
166 resolved by means of ILT (Inverse Laplace Transform) with a non-negative least square fit to the data  
167 with Tikhonov regularization, similar to the 'Contin' method (Whittall and MacKay 1989, Provencher  
168 1982), and described in more details in Faure and Rodts 2006. We finally get an apparent statistical  
169 distribution of  $T_2$ , expressed in terms of signal intensity associated with each possible value of  $T_2$ . Note  
170 that the exact shape of this "T-distribution" depends on the technique of regularization used, and in  
171 particular on the value of one specific factor used in the procedure (Faure and Rodts 2006), but the  
172 positions of the peaks and the amount of liquid associated with these peaks are robust values.

173 Roughly speaking the relaxation time is related to the mobility of water molecules, and specific  
174 interactions of water with their environment (e.g. adsorption, proton exchange with other species, or  
175 magnetic interactions at nanoscale). In the particular case of water embedded in a pore cavity, within  
176 the usual hypothesis of biphasic fast exchange (Philippot et al. 1998), the general property is that, for  
177 a given pore shape, the relaxation time decreases when the pore size decreases (Korb 2018). As a  
178 consequence, if the T-distribution presents some peaks, they indicate different classes of pore sizes  
179 and/or water in different "states" (e.g. bound or free water), and the amount of liquid in each class  
180 may be estimated from the integral of the T-distribution around the peak.

181

### 182 *Compression test*

183 In order to estimate the force needed to compress the solid structure of the sample we placed the dry  
184 cellulose in a cylindrical container (diameter: 4 cm, initial height of cellulose: 15 cm) with a piston free  
185 to move in the cylinder on its top. The initial cellulose concentration in air was 7%. We then applied an  
186 increasing force to the piston, which induced its displacement to a new position. Thus the normal stress  
187 could be estimated by dividing the force by the area of the cylinder section, and the corresponding  
188 mean concentration of the cellulose sample could be computed from the loss of volume. More  
189 precisely the volume fraction of cellulose is equal to the cellulose volume (mass to density ratio)  
190 divided by the current sample volume. Note that the data obtained from such a test can only provide

191 a rough evaluation of the normal stress vs concentration. Indeed, although we expect the shear stress  
192 along the (smooth) walls to be low due to wall slip effect we ignore its exact contribution to the  
193 measured force. Moreover, the stress and concentration are computed assuming the compression is  
194 homogeneous, which might not be strictly the case.

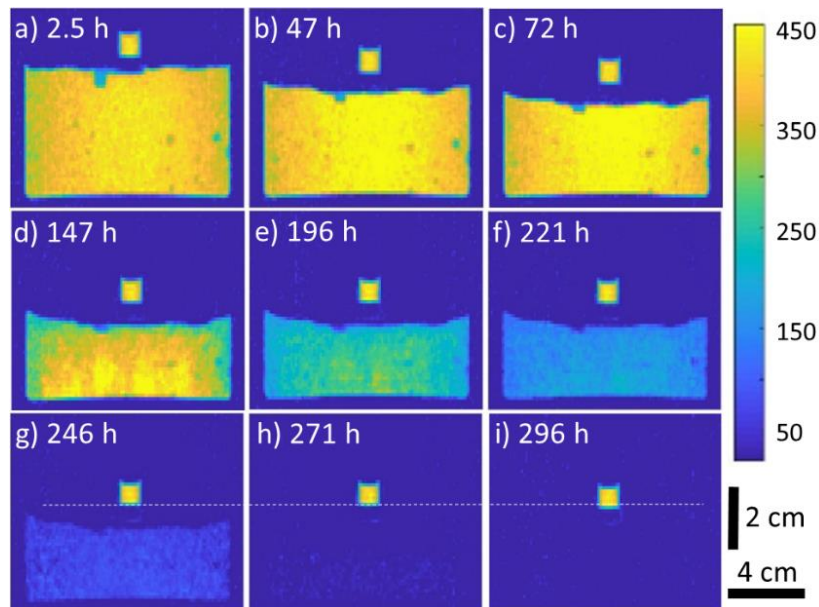
195

## 196 Results

197 We observe first a decrease of the level of the cellulose paste (see Fig.3 a,b,c,d) with an NMR signal  
198 remaining almost constant in the paste volume, while the distance between the small water container  
199 and the paste surface remains constant. This means that, during this stage, water is extracted from the  
200 paste by evaporation from the free surface and the paste drying induces a homogeneous longitudinal  
201 shrinkage. The NMR signal remains approximately constant because the water fraction remains close  
202 to 1.

203 In the next stage the apparent paste volume remains constant, which means that no more contraction  
204 occurs, while the NMR signal starts to decrease, first somewhat heterogeneously (see Fig.3 d,e), then  
205 homogeneously (see Fig.3 e,f,g). We have no clear explanation for this initial heterogeneity, in  
206 particular for the faster desaturation along the cylinder walls. Neglecting this phenomenon, we can  
207 consider that during this phase the solid structure of the cellulose paste is kept fixed and the water is  
208 extracted homogeneously from this structure. In the last stage (see Fig.3 h,i) a region with no apparent  
209 NMR signal develops from the sample top, while some slight contraction occurs (see dashed line in  
210 Fig.4).

211



212

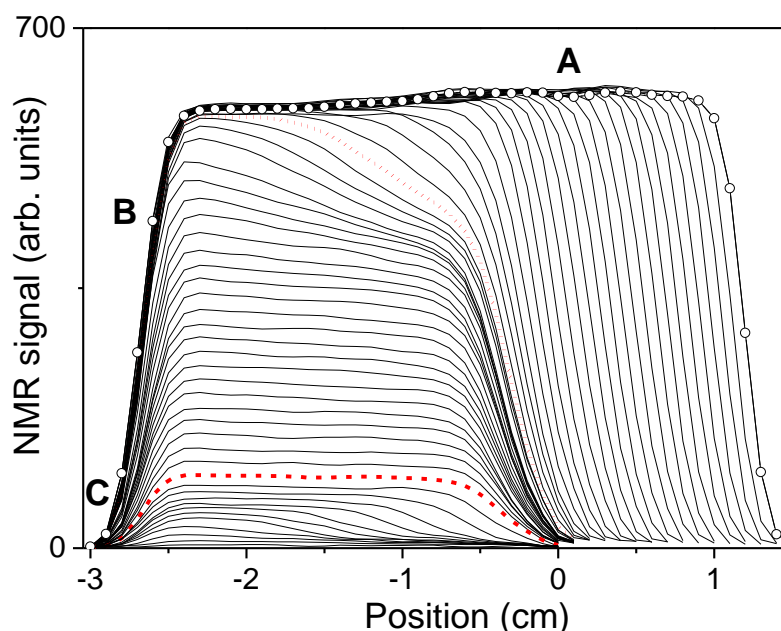
213 **Fig. 3:** 2D MR images of the cellulose paste at different times during drying. Note the  
214 « tripod » (cubic volume filled with water) lying at a given distance over the sample free  
215 surface. The NMR signal on the color scale (in arbitrary units) is for each phase an  
216 increasing, but non-linear, function of the local water amount (see Section II)

217

218 The quantitative 1D profiles (see Fig.4) evolve in agreement with this description. As drying progresses  
219 the total amount of water, corresponding to the integral of the signal over each profile, decreases. We  
220 can observe first a shrinking period (up to the dotted line), that we call here Regime A, during which  
221 the wet thickness of the sample, i.e. the length of the profile along the abscissa axis in Fig.4, decreases.  
222 We here interpret this effect as shrinkage rather than the growth of a dry region starting from the top  
223 surface of the sample thanks to the 2D images showing a constant distance between the small water  
224 container and the apparent sample top surface (see Fig.3). It may be noticed that despite this  
225 shrinkage, which induces an increase of the cellulose concentration in the sample, the signal level  
226 (plateau) in the sample does not vary significantly. This results from the fact that the volume fraction  
227 of cellulose remains small, i.e. typically less than 10%, so that the impact of the presence of cellulose  
228 remains negligible on the signal. As a corollary, it is not possible to extract some reliable information  
229 about the evolution of the distribution of cellulose concentration in the sample.

230 In the next stage (between the dotted and the dashed line in Fig. 4), i.e. Regime B, the thickness of the  
231 sample does not change any more, meaning that no more shrinkage occurs. Instead the sample  
232 desaturates, first somewhat heterogeneously, with a gradient of concentration (first profiles after the  
233 dotted curve in Fig. 4), then homogeneously up to the end of this regime: the profiles evolve parallel  
234 to each other; more precisely, two of them are similar by a given factor of the NMR signal, which means  
235 that the concentration of water decreases homogeneously throughout the sample.

236 In the last stage, i.e. Regime C, after the dashed curve, the top edge of the profile seems to move  
237 progressively towards the left, as if some dry region was growing from the free surface of the sample  
238 (see Fig. 4). It is worth noting that at the same time the level of the profile below this apparent dry  
239 region goes on decreasing, indicating that the material goes on desaturating homogeneously in the  
240 lower part of the sample. This process (dry front and desaturation below) continues until complete  
241 disappearance of the signal.



242  
243 **Fig. 4:** Successive NMR water amount profiles (from top to bottom) along sample axis at  
244 different times (time interval 5 h) during drying of a cellulose paste. Transition to regime  
245 B at 124 h (red dotted line); transition to regime C at 248 h (red dashed line). The dry air



246 flux is imposed along the sample top. For the first profile we also plot the data points  
 247 (corresponding to NMR signal in a cross-sectional layer) to illustrate the resolution of the  
 248 measurement

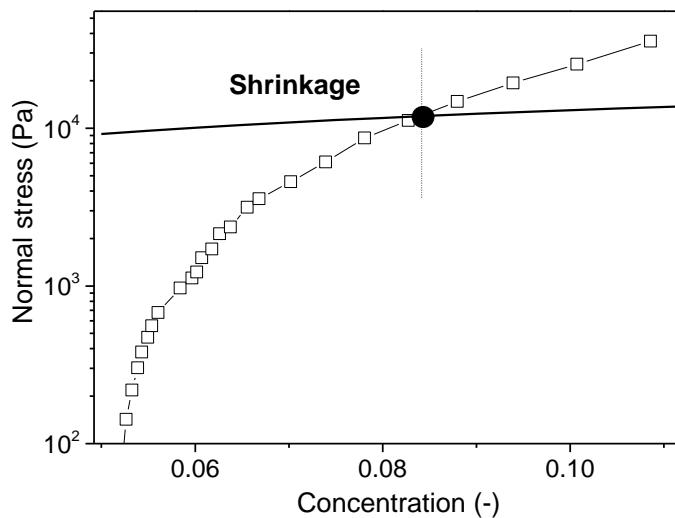
249

250 **Discussion**

251 Regime A

252 In this regime the extraction of water due to evaporation along the free surface causes a shrinkage of  
 253 the sample. The only possible force at the origin of such an effect is the Laplace pressure induced by  
 254 the formation of liquid menisci around the sample top and resulting from water extraction. Menisci  
 255 formed in this way have a characteristic radius of the order of half the pore size. This induces a Laplace  
 256 pressure in the liquid, which acts on the fiber matrix and tends to shrink it (to reduce the area of the  
 257 menisci). We thus can estimate the capillary stress as  $2\gamma/R$  in which  $R$  is the typical pore radius in  
 258 the network and  $\gamma = 0.07 \text{ N m}^{-1}$  the surface tension of water.

259 Since the fibers, which exhibit a very large aspect ratio, are entangled (even if they are only slightly  
 260 deformed), the characteristic length ( $a$ ) of fiber portion between two successive cross points with  
 261 other fibers approximately corresponds to the pore size. By considering it corresponds to the radius of  
 262 virtual spheres occupying the whole space (in disordered packing, i.e. at an apparent concentration of  
 263 62%), it is possible to estimate the variations of  $a$  with the solid fraction. Indeed, under these  
 264 conditions the effective volume fraction of the cellulose is equal to the maximum packing fraction of  
 265 these spheres times the fiber portion to sphere volume ratio, i.e.  $\phi \approx 0.62 \times (a\pi b^2)/(4\pi a^3/3)$ , where  
 266  $b \approx 10\mu\text{m}$  is the typical fiber radius. Note that taking into account the confined water in the fiber  
 267 would induce a significant increase (see below) of  $b$  which, considering that the sample volume does  
 268 not change significantly (see below), would induce approximately an increase of  $\phi$  by a factor  $b^2$ ,  
 269 which leads to the same result:  $a \approx 0.68b\phi^{-0.5}$ . This expression predicts that, for the initial solid  
 270 fraction,  $a \approx 30\mu\text{m}$  and varies slowly when the concentration increases. The capillary stress which  
 271 tends to contract the sample writes  $4\gamma/a$ , which is rather large but slowly varies with the  
 272 concentration (see Fig. 5).



273

274 **Fig. 5:** Normal stress vs concentration (open squares) for the dry cellulose paste during a  
275 compression test (see Section Materials and Procedures), and estimation (see text) of the  
276 capillary stress for each concentration (continuous line). The dotted line marks the end of  
277 shrinkage; it is situated at the point of intersection of the two curves

278

279 On another side the resistance of the structure to shrinkage can be estimated from the force associated  
280 with the network compression in our test with dry cellulose packing (see Fig. 5). We observe that this  
281 force rapidly increases from low values with the concentration. Initially it is thus much smaller than  
282 the capillary stress, so that we expect that the first menisci resulting from water extraction will easily  
283 induce sample shrinkage. Then, as long the concentration increases the normal stress needed to reach  
284 this concentration increases, so that for some critical concentration value the capillary stress is  
285 insufficient to further induce compression, this corresponds to the point of intersection of the two  
286 curves in Fig. 4. Beyond that point the sample will essentially keep its shape and progressively  
287 desaturate. Here we find a critical concentration around 8.5%, which is close to the value (9.2%) found  
288 for the transition between Regimes A and B from MRI measurements.

289 As long as this shrinkage acts the liquid distribution around the free surface remains the same, which  
290 explains that the rate of drying remains constant (see below). Indeed, under these conditions the  
291 gradient in the vapor distribution around the free surface remains constant, which induces the same  
292 rate of vapor diffusion (Lehmann and Or 2013).

293

#### 294 **Regime B**

295 In this regime, since the sample does not shrink anymore, the extraction of water necessarily induces  
296 a desaturation of the porous network. The initial volume fraction of cellulose in this regime is now  
297 9.2%. We describe the water content through the saturation  $\psi$ , the liquid to pore volume fraction.  
298 During some initial stage the  $\psi$  decrease propagates downwards, which explains the gradient in the  
299 water profile observed at the beginning of Regime B (see Fig. 3). Then some slight gradient in water  
300 content remains but the profiles are essentially uniform and progress parallel to each other. This is the  
301 typical effect observed in simple porous media such as bead packings in a wide range of pore sizes  
302 (Thiery et al. 2017), which results from a capillary balance in the liquid network throughout the sample.  
303 For a fixed (i.e. non-shrinking) porous network initially filled by a wetting liquid the Laplace pressure  
304 increases when the saturation decreases, since the radius of the menisci decreases when the liquid  
305 films coating the structure get thinner. Some gradient of saturation in the sample then induces a flow  
306 from the more concentrated regions to the less concentrated ones, which has time to homogenize the  
307 concentration throughout the sample if the evaporation from the free surface is sufficiently slow.

308 As a consequence the drying in this regime takes the form of a liquid flow towards the free surface of  
309 the sample. Note that in this case vapor diffusion throughout the structure does not play a significant  
310 role because, as long as the air inside the sample is surrounded by liquid patches, the relative humidity  
311 inside the porous structure remains close to 100%. It follows that there is no gradient of RH along the  
312 sample length, and thus no vapor diffusion. This effect was for example demonstrated in a thin channel  
313 close on one side (see Keita et al., 2016 b): as long as there remains a continuous liquid film along the  
314 walls the RH is equal to 100% all along the channel and the liquid is drained towards the sample exit  
315 where it evaporates.

316 Moreover, as long the liquid patches are sufficiently close to each other, the relative humidity just  
317 above the free surface remains maximum, which ensures a constant rate of drying (Lehmann and Or  
318 2013) and explains our observation (see Fig. 4).

319 Note that in this frame it is assumed that gravity is negligible. Actually, the impact of gravity may be  
320 appreciated by comparing the typical capillary stress in the partially saturated sample, i.e.  $2\gamma/R$ , to  
321 the characteristic stress due to gravity, i.e.  $\rho gH$ , with  $\rho$  the liquid density,  $H$  the sample thickness  
322 and  $g$  the gravity. In all our tests the ratio between the capillary stress and the gravity stress is much  
323 larger than 1, indicating that gravity effects are negligible.

324

### 325 **Regime C**

326 In this regime a new phenomenon occurs: an apparently dry region progresses downwards while the  
327 saturation goes on decreasing homogeneously in the rest of the sample (see Fig. 4). The saturation at  
328 which this effect starts to develop can be computed by dividing the amount of water at that time to  
329 the amount of water at the beginning of regime B, i.e. when the solid porous structure is fixed (at least  
330 for Regime B). We find a critical saturation of 18 %, which is in the order of the values found for bead  
331 packings with similar pore size (Thierry et al. 2013).

332 Such a dry front develops because, in contrast with the situation in Regime B, now the rate at which  
333 the water is extracted from the sample top is too large with regards to the rate at which it can flow for  
334 re-equilibrating the saturation due to capillary effects (see e.g. Coussot 2000). Indeed, the flow rate of  
335 liquid transport driven by capillary effects decreases when the liquid film thickness decreases, i.e. when  
336 the saturation decreases.

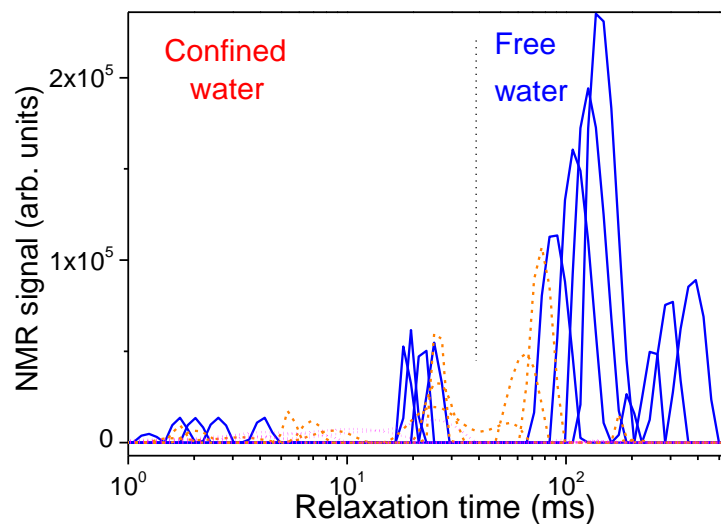
337 However, here, we have so far left aside the question of water state, assuming that we were dealing  
338 with a single type of water, in the form of free water in relatively large pores. Actually, we can get  
339 some information on the pore sizes in which water is embedded from the distribution of NMR  
340 relaxation times. Essentially four peaks are visible (see Fig. 6). Considering the relative large T2 values  
341 to which they are associated, the two peaks on the right likely correspond to free water in the pores  
342 of the structure of fibers, which would thus contain two types of pores of different characteristic sizes.  
343 It must be emphasized that the relaxation times of these two peaks are rather close, so the pore sizes  
344 too. Also note that from such basic measurements and without knowing the NMR relaxivity of the  
345 medium, it is not possible to quantify further, in a straightforward way, the exact pore size and shape.  
346 However we can usefully compare these results with those obtained with hardwood, which is a  
347 material for which we can expect a value of relaxivity close to that of cellulose, since water lies in a  
348 similar structure. We find that the T2 values of these two peaks are larger than the T2 value (around  
349 100 ms) for water in fibers, whose diameter is about 10 microns, and smaller than the T2 value for  
350 vessels (around 600 ms), whose diameter is about 100 microns (Penvern et al. 2020). This confirms  
351 that the pore size of water in this range corresponds to a few tens of microns, as described above.

352 The third peak is situated at much smaller T2 values, around 20 ms. This a priori corresponds to water  
353 situated in pore size of the order of one micron. To go on with our comparison with NMR  
354 measurements in hardwood, a peak at such a T2 value was attributed to water in the rays of poplar  
355 (Penvern et al. 2020). Indeed, it is situated above (in terms of T2 value) that associated with bound  
356 water and below that associated with free water in fibers which, from structure observations, exhibit  
357 a smaller surface to volume ratio than the rays. Moreover, the fact that it is associated with a peak  
358 clearly distinct from the others means that there are very limited exchanges between free water and  
359 this water type. This will be confirmed by the observation that the free water peak disappears first  
360 while the third peak remains intact. This leads us to suggest that this peak corresponds to some (free)

361 water situated between the microfibrils of the cellulose fibers. The fourth peak (on the left) seems to  
362 be somewhat mobile. We have no explanation for this mobility. However, the low value of the  
363 corresponding relaxation time, i.e. between 1 and 10 ms, indicates that the corresponding water is  
364 more deeply embedded than the rest of water. This might correspond to either water between  
365 microfibrils or bound water. A further analysis of this water type is provided by O'Neill et al. (2017).  
366 Note that the corresponding fraction of water is anyway rather low, as it appears from Fig. 6, which is  
367 consistent with the assumption that it corresponds to bound water. Indeed, the fiber saturation point  
368 being equal to 10%, we here expect the fraction of bound water to be equal to 0.7% of the total initial  
369 water amount.

370 These results and our analysis are consistent with those of Felby et al. (2008). The three main types of  
371 water identified here also appear to correspond respectively to the three water types identified by  
372 DSC, namely the bulk or free water, the freezing bound or capillary water, and the non-freezing bound  
373 water (Burghoff and Pusch 1979; Yamauchi and Murakami 1991; Weise et al. 1996). Finally, in the  
374 present context we will not further elaborate on these aspects but simply retain that these two peaks  
375 on the left are associated with water much more confined than the water associated with the two  
376 other peaks, and we will call them altogether "confined water". We will thus not distinguish between  
377 the two last types of water contained in micronic or nanometric pore sizes distinguished by Topgaard  
378 and Söderman (2002).

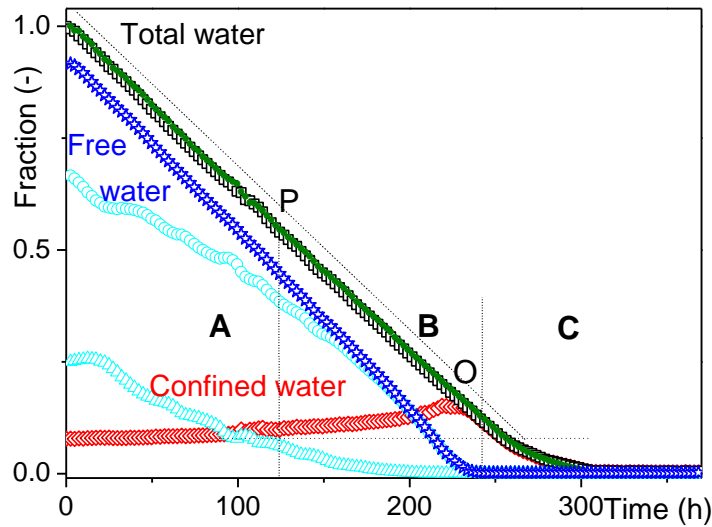
379 As drying progresses the peaks evolve differently. First the two peaks on the right at the same time  
380 decrease and move to the left, while the third and fourth peaks remain more or less the same (see Fig.  
381 6). Finally the peak on the right disappears while the second peak goes on decreasing and approaches  
382 the third peak.



383

384 **Fig. 6:** Distributions of relaxation time for the whole cellulose paste sample during  
385 drying, at different times: (blue curves) 0, 50, 100, 150 h, (orange curves) 175, 200, 225  
386 h, then every 12 h (magenta curves)

387



388

389 **Fig. 7:** Water fraction as a function of time for the different classes identified from the  
 390 distribution of relaxation times (see some of these distributions in Fig. 6): (triangles) first  
 391 peak on the right, (circles) second peak, (blue stars) total of these two peaks, i.e. free  
 392 water, (red diamonds) third and fourth peaks, i.e. confined water, (squares) total water.  
 393 The letters correspond to the different regimes identified in the text. The evolution of  
 394 the total fraction of water deduced from the integral of the water content profiles (see  
 395 Fig. 4) is also shown (small green filled circles)

396

397 We can follow more precisely the water amount associated with each class of water, by integrating  
 398 the distribution in the range associated with the corresponding type of water, i.e. below each peak.  
 399 The result of this integration should be proportional to the water mass in each class. The corresponding  
 400 fractions of water mass of each class are represented in Fig. 7. The total fraction (total water mass  
 401 divided by the initial value) is also computed from the integration of the successive profiles in time  
 402 shown in Fig. 4. The result is perfectly similar to the total fraction obtained from the T2 distribution  
 403 (see Fig.7), which confirms the validity of the technique.

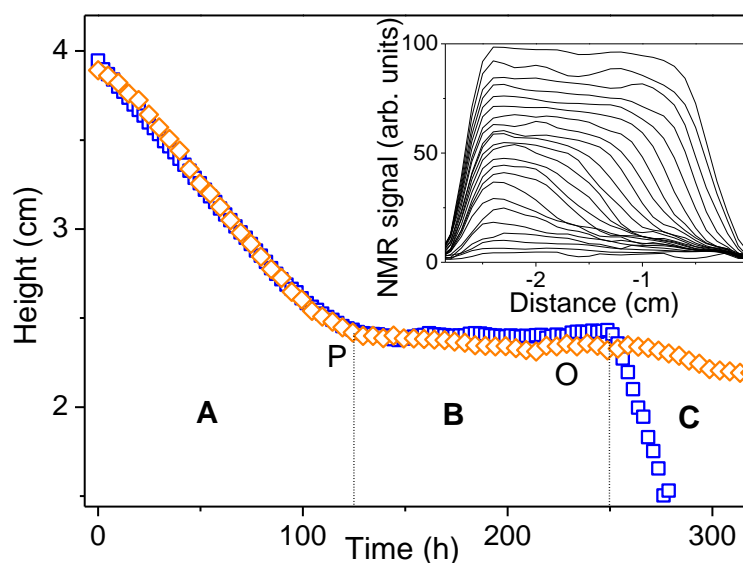
404 We see that during Regime A (i.e. shrinkage regime) the two classes of free water progressively  
 405 disappear with a similar dynamics, while the confined water remains constant. Moreover, the  
 406 relaxation times of these two free water types decrease, i.e. the T-distribution is shifted towards lower  
 407 T2 values (see Fig. 6), which is consistent with the fact that during shrinkage the pore size progressively  
 408 decreases (Häggkvist et al. 1998). The amount of these two water classes and the corresponding  
 409 relaxation times (see above) go on evolving in a similar way in Regime B, during which no more  
 410 shrinkage occurs. This now reflects the fact that, as long as the saturation decreases in the porous  
 411 network, air occupies more space in the porosity, so that the liquid volumes form thinner films in  
 412 contact with the solid (cellulosic) structure, in which the water exhibits a smaller relaxation time than  
 413 in the filled pores. Importantly, as the T-distribution shifts towards lower values, the peak shapes  
 414 remain similar, i.e. they do not spread. This further proves that the desaturation is essentially  
 415 homogeneous throughout the sample, otherwise we would have some fraction of water still exhibiting  
 416 a relaxation time close to the initial one, and the right side of the peaks would remain attached (largest  
 417 T2 value) while the peaks spread towards lower T2 values.

418 Remarkably, in this regime, the apparent amount of confined water increases (see Fig. 7). We do not  
419 see any reason for which the effective amount of water between the macrofibrils would increase at  
420 that time since the maximum amount should have been absorbed rapidly after the cellulose has been  
421 put in contact with a large amount of water. More likely, here, as long as the porous medium  
422 desaturates, leading to a complex liquid network wetting the solid structure, some thin liquid films,  
423 say of micrometric thickness, form along some portions of the fiber surfaces, connecting liquid patches  
424 of much larger volumes (which ensures the bulk water transport towards the free surface, and thus  
425 ensures a constant drying rate). These liquid films exhibit a small relaxation time, of the order of that  
426 of the (main) confined water, so that they appear as confined water in our measurements. As  
427 desaturation progresses, more liquid films are formed and finally there remains (point O) only such  
428 liquid films in addition to confined water. From that point, the confined water and water in liquid films  
429 will progressively disappear in an indistinguishable manner.

430 Although we have no definite evidence it is likely that during regime B till point O the confined water  
431 amount remains constant. The situation is less clear beyond that point: the thin water films coating  
432 the external surface of the fibers and the thin water layers between macrofibrils might behave in a  
433 similar way. It is remarkable that during the period between point O and the beginning of regime C the  
434 drying rate (associated with total water evaporation) remains constant (see Fig. 7) and the water  
435 content distribution remains homogeneous (see Fig. 4).

436 We can have further information about the time at which the confined water starts disappearing from  
437 a more thorough look at the sample size evolution. Indeed, the extraction of this confined water should  
438 induce a contraction of the fiber, which should induce a contraction of the structure. However, the  
439 shrinkage of the sample structure based on a network of fibers in contact, and resulting from fiber  
440 shrinkage, depends on the distribution of fiber orientations and on the detailed shrinkage  
441 characteristics of the fibers (in their longitudinal and radial directions). According to our assumption  
442 of fiber shrinkage due to water penetration between macrofibrils it is natural to consider that they  
443 essentially shrink radially, i.e. longitudinal shrinkage is negligible. Then, the fiber network is a priori  
444 made of fibers in any direction and in contact. Along some direction, the average amount of cellulose  
445 fibers being equal to their volume fraction, the maximum shrinkage of the network is obtained if along  
446 this direction we only find fiber radial cross-sections (which is not possible from a strict point of view,  
447 as we need some fibers oriented along their longitudinal direction). In this ideal case, the sample  
448 shrinkage is equal to the loss of volume of the fibers relatively to the sample volume. Here the fraction  
449 of confined water, with regards to the sample volume, at the beginning of regime B (point P in Fig. 7)  
450 is found from the ratio of the confined water volume (1.1 cm<sup>3</sup>) to the sample volume (equal to the  
451 total water volume (6.6 cm<sup>3</sup>) plus the cellulose volume (0.67 cm<sup>3</sup>)), which gives 15%. So, according to  
452 the above reasoning, when the confined water is extracted, we expect a maximum shrinkage of 15%  
453 of the sample volume.

454 Now using the raw data associated with the 2D images we can determine the exact position of the  
455 small water container in time (see Fig. 8). We see that, apart from some slight discrepancy at the  
456 beginning of the test (due to the fact that it slightly sinks) the container follows exactly the water  
457 profile, which corresponds to the shrinkage regime (A), then it remains constant, which exactly  
458 corresponds to the desaturation regime (B). Interestingly, in Regime C, it starts again decreasing. This  
459 process is certainly due to the disappearance of confined water and we deduce that confined water  
460 disappears mainly in regime C. As a corollary, we can consider that only confined water remains in  
461 Regime C. The corresponding shrinkage is about 10% of the sample volume, which is below but still in  
462 the order of the maximum expected shrinkage from above calculations based on the extraction of  
463 confined water from fibers in a particular structure.



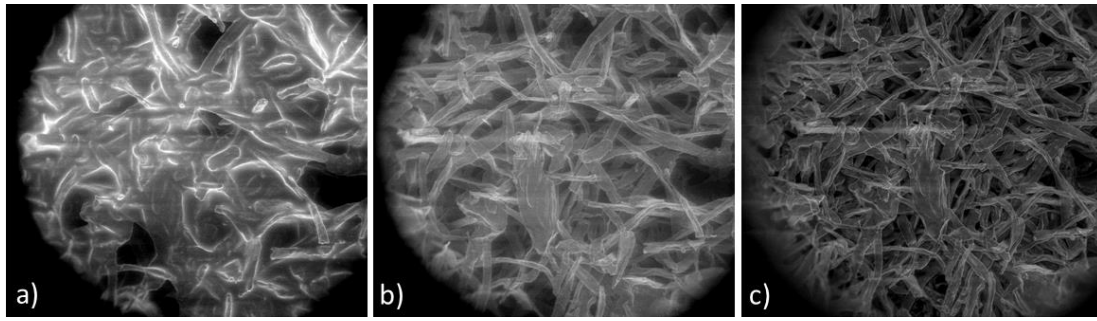
464

465 **Fig. 8:** Position of the feet of the small water tripod container (orange diamonds) and  
 466 position of the apparent front of water (blue squares), i.e. mean position of the frontal  
 467 part of the water profile, as a function of time. The inset shows the water content profiles  
 468 during regime C: (from top to bottom) every 2.5 h from 248 h after the beginning of the  
 469 drying test

470

471 From above measurements we can also estimate the shrinkage of cellulose fibers. The volume of  
 472 cellulose being 0.67 cm<sup>3</sup> and that of confined water 1.1 cm<sup>3</sup>, we deduce that the fiber volume should  
 473 turn from 1.77 to 0.67 cm<sup>3</sup>, meaning that they individually shrink by a factor 2.6: their initial apparent  
 474 volume is about 2.6 times their volume under dry conditions. In order to check this we observed the  
 475 drying of a paste sample with ESEM. We did not quantify the drying progression but were able to  
 476 observe the details of the paste structure when there remained essentially confined water. This is  
 477 proved by the fact that we distinguish the shape of the cellulose fibers all along this period until full  
 478 drying (see Fig. 9). Indeed, we can see that the shape of the fibers do not change during this period; if  
 479 some water films were covering the fibers at the beginning (i.e. in Fig. 9a), except if they are extremely  
 480 thin (a few nanometers) and then stabilized by the disjoining pressure, they could not follow exactly  
 481 the shape of the fibers as the capillary equilibrium cannot be respected by simply covering such  
 482 particles of complex shape with a film of given thickness.

483 From direct measurements on these images we find that on average the ratio between the diameter  
 484 of the fibers in the first picture and that in the last picture is about 1.4, which means that the associated  
 485 volume change is about 2. This value is lower than the expected one from above NMR measurements  
 486 (i.e. 2.6), but this may be due to the fact that here we do not control the exact state of the material,  
 487 i.e. we do not know if Fig. 9a corresponds to the first point for which there remains only confined water  
 488 or a point later. In any event, these observations confirm the large individual shrinkage of the fibers,  
 489 which further supports our interpretation of the NMR data.



490  
491 **Fig. 9:** Environmental scanning electron micrographs of a cellulose paste structure during  
492 drying  
493

494 Under these conditions, if we assume that between O and regime C the free water films are drained  
495 homogeneously while the confined water remains fixed so that it does not play any role, the surprising  
496 result here is that usually in such a case, i.e. with thin films remaining along the pore walls, a dry front  
497 develops because the rate of transport driven by capillary effects is too low (Cousot 2000). The latter  
498 phenomenon explains the second period of drying necessary to remove the final liquid amount  
499 (typically for a saturation of 10 to 20% (Thiery et al. 2017)). Here, if we consider the confined water  
500 fixed and thus a constitutive part of the solid porous structure, the saturation associated with the liquid  
501 films is 15%, in the range for which a dry front usually develops, whereas it appears that a dry front  
502 only develops from 248 hr of drying, when all these liquid films have disappeared.

503 This suggests that our assumption of a fixed confined water in the period starting from point O is  
504 wrong. There might be some simultaneous disappearance of both types of water. Instead we suggest  
505 that the films disappear first, without the development of a dry front, helped by confined water which  
506 plays a fundamental role in the process, by transporting the remaining water in the films towards the  
507 top surface of the sample. This effect is somewhat similar to that recently described in wood drying  
508 (Penvern et al. 2020). In this case the free water is partly dispersed in cavities inside the structure, with  
509 almost no connections, but a constant drying rate is observed as long as there remains bound water,  
510 which suggests that this bound water extracts free water from the interior of the sample and  
511 transports it towards the free surface.

512 The final extraction of confined water then would start only in regime C, leading to the development  
513 of a concentration gradient, looking almost like a dry front progressively invading the whole sample  
514 (see Fig. 8). It is worth emphasizing that during this process the water content below this dry region  
515 goes on decreasing homogeneously (see inset of Fig. 8). Such an effect results from some effect of re-  
516 equilibration of the water concentration in time, thanks to a transport process.

517 At this time we could assume that vapor diffusion throughout the structure could play a significant role  
518 in this water transport. However, the situation is finally similar to that for Regime B: the relative  
519 humidity inside the porous structure remains close to 100% as the air is surrounded by walls contained  
520 free water (even if this water somewhat confined, we are well above the Fiber Saturation Point). It  
521 follows that there is no gradient of RH along the sample length, and thus no vapor diffusion.

522 This is the definite evidence that this confined water can be transported through the sample. This leads  
523 to the surprising result that the water confined inside the cellulose fibers is able to be transported from  
524 fiber to fiber, through some connected hydraulic network.

525



526 **Conclusion**

527 We showed that during the drying of a cellulose paste all the bulk water, i.e. comprised between the  
528 fibers, is extracted first at a constant rate, while the drying rate remains constant. During this process  
529 the paste shrinks until capillary effects cannot induce further compression, then it homogeneously  
530 desaturates as long as gravity effects are negligible. In contrast with standard porous media, with a  
531 structure made of non-permeable solid material, the constant drying rate is maintained even when  
532 the bulk water content is very low. This is allowed thanks to the presence of free water confined inside  
533 the fibers, which can help transport the bulk water towards the sample free surface. This phenomenon  
534 exhibits some similarity to the effect observed: 1) for hardwood, in which bound water allows to  
535 transport free water almost enclosed in depth in the solid structure towards the sample free surface  
536 (Penvern et al. 2020), and 2) for model biporous systems (Lerouge et al. 2020) made of large pores  
537 dispersed in a matrix of small pores, in which the large pores are fully emptied first even in depth. In  
538 both cases a constant drying rate is observed all along these processes. In the case of the cellulose  
539 paste this extraction apparently relies on a continuous network of confined water throughout the  
540 structure, connected by fiber contacts.

541

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544

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546 **Compliance with Ethical Standards:**

- 547 - No conflict of interest  
548 - This article does not contain any studies involving human participants performed by any of  
549 the authors.

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553 **Code availability:** non applicable.

554 **Authors' contributions:** NBA, SR and BM carried out the NMR experiments, HD and XM carried out  
555 the macroscopic tests and material preparations; all authors discussed the data; BM, AG and PC  
556 wrote the paper.

557

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