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Characterization of wood components of Portuguese medieval dugout canoes with high-resolution solid-state NMR

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Abstract

High-resolution nuclear magnetic resonance of carbon 13 was employed to characterize archaeological wood samples from Portuguese medieval dugout canoes. Structural and chemical modifications were assessed by comparing the structural features of archaeological wood samples with modern wood. The main results concern the strong decrease of sugar moiety with a complete disappearance of hemicelluloses. During ageing in water environment, the *β-O-4* inter-unit linkages of lignins have not been degraded. The features of the ^{13}C NMR spectra clearly reveal that the products of degradation of the carbohydrates occurring during depletion of sugars were not recombined inside the lignocellulosic matrix. Finally, this article gives a clear illustration that although the water contents of archaeological wood can certainly be used as a good criterion concerning their state of degradation, solid-state ^{13}C NMR lead to unambiguously data as far the structural properties of archaeological waterlogged woods are concerned.

Keywords: Waterlogged woods; Archaeological woods; Lignins; Celluloses; Solid-state NMR; Portuguese medieval dugout canoes

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1. Introduction

^{13}C high-resolution solid-state NMR is a powerful analytical tool for chemical characterization of natural materials such as wood (Gil & Neto, 1999; Mannu, 2002). Its impact on archaeology until nowadays has not been important (Ghisalberti & Godfrey, 1998; Lambert, Shawl, & Stearms, 2000; Paci, Federici, Capitani, Perenze, & Segre, 1995). In a previous work, we showed that NMR was a worthwhile analytical tool to investigate archaeological wood, both to obtain qualitative and quantitative data (Bardet, Foray, & Trân, 2002). Indeed we showed that quantitative measurements could be performed on such samples to get reliable structural data on the two main wood components, lignins and celluloses. In the present work, we applied such strategy on different wood samples that were taken out from three archaeological Portuguese dugout canoes named Geraz Do Lima I and II, and Mazarefe. The general shapes and the wood materials themselves have been well preserved for both Geraz Do Lima artefacts; on the other hand the Mazarefe dugout is very fragile in its structure made of wood that appears heavily degraded. These artefacts are presently stored up in water at the National Centre for Nautical and Subaquatic Archaeology at Lisbon, Portugal, before restoration. Another goal of this paper is to compare the information concerning the structural features of wood that can be obtained with NMR and with the measurements of their water content. Indeed, water content is still widely used as a criterion of the degradation of archaeological artefact made in wood. However, even if it is an easy measurement to perform, its interest remains limited to infer changes in the chemical composition of wood, its reproducibility is also questionable as soon as wood samples are taken out deeply inside a wooden artefact (Hedges, 1990). These structural features are very important to define the appropriate restoration processes of waterlogged wood (De Jong, 1979). As an example, the most commonly used conservation treatment for waterlogged wood is the polyethylene glycol (PEG) impregnation process, which relies on the formation of hydrogen bonds between PEG and the carbohydrates of the wood. Therefore, the content of carbohydrates in the starting archaeological material to be restored may

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significantly impact the success of any PEG treatment (Grattan & Clarke, 1987; Rowell & Barbour, 1990).

2. Experimental

2.1. Sample preparation

For the little degraded Geraz Do Lima canoe, archaeological samples were collected by two ways: firstly, by core sampling at one end of the object to get surface and inside samples (dimensions of the total sample: about 30-mm length, 2–3-mm diameter); secondly, by taking a bigger sample from the bottom of the canoe in order to do various analysis such as chemical components, NMR or water contents. Regarding the Mazarefe dugout, no core sampling was necessary because the whole structure of the artefact is already highly deteriorated. Water contents based on oven-dried wood, pre-saturated with water under vacuum, were obtained by weighing the wood sample before and after oven drying at 105 °C: from 100 to 200%, the wood can be considered as little degraded; over 400%, it is heavily degraded. Table 1 lists the archaeological ages of the three canoes and their maximum water contents.

2.2. NMR experiments

The samples were prepared by grinding, moderately, a predetermined amount of dry wood in order to reduce them into powders. Seven-millimeter diameter (340 μl) cylindrical double bearing rotors made of zirconia were filled with the dried sample (200–400 mg) retained with kel-F end caps.

High-resolution solid-state ^{13}C NMR spectra using proton dipolar decoupling, magic angle spinning (MAS) and cross-polarization (CP) were recorded on a BRUKER Avance 400 MHz spectrometer operating at 100.6 MHz at room temperature. The ^{1}H radio-frequency field strength was set to give a 90° pulse duration around 2.5 μs. For each spectrum, 1600 scans were collected. The chemical shift values were measured with respect to tetramethylsilane via glycine as a secondary substitution reference with the carbonyl signal set at 176.03 ppm. The amplitude of the ^{13}C NMR signal in a CP experiment was dependent on the contact times (Pines, Gibby, & Waugh, 1973). In order to get quantitative data, dynamic studies of the carbon magnetization build-up were performed by varying the contact values from 10 μs to 20 ms. From the variable contact time experiments, the different signal intensities were plotted versus the contact times, t_{cp}, and fit to the classical and simplified equation

$$M = M_0(1 - \exp(-t_{cp}/T_{CH}))\exp(-t_{cp}/T_{1\rho H})$$

where M is the measured intensity, M_0 is the initial intensity of magnetization, T_{CH} and $T_{1\rho H}$ are two characteristic relaxation times of the system. From the above equation it is possible to extract M_0. M_0 is directly proportional to the number of spins, and consequently, it can be used for quantitative analysis. Unfortunately, this parameter can never be measured directly and the values M_0, T_{CH} and $T_{1\rho H}$ were computed by fitting the experimental intensities M recorded at different contact times t_{cp} with the above analytical expression.

Therefore for a given contact time, the correction factors to be applied on the different signal intensities and their corresponding integrals are easily calculated. It appears that a spin lock time of 1 ms is optimal for reaching the maximal polarization of all the wood carbons and that the maximum expected errors for the signal intensities are below 5%. The correction factors can be even be lower if one considers longer t_{cp} such as 3–5 ms, but the price to pay is a significant decrease in signal to noise ratio. Therefore, a 1 ms contact time was considered as a good compromise and no correction was applied to the measured integrals in the present case.

Table 1
Properties of Portuguese medieval dugout canoes

Name	Age (cal AD)[a]	Maximal water content (%)[b]
Geraz do Lima I	998–1031	189,57
Geraz do Lima II	674–891	201,69
Mazarefe	778–991	804,14

[a] Reports to 2 sigma (98%) interval.

[b] Calculated from dry wood.

3. Results

3.1. Qualitative analyses

In order to support the qualitative analyses of these archaeological wooden artefacts, series of spectra are given in Figs. 1 and 3. In Fig. 1, a representative spectrum of each

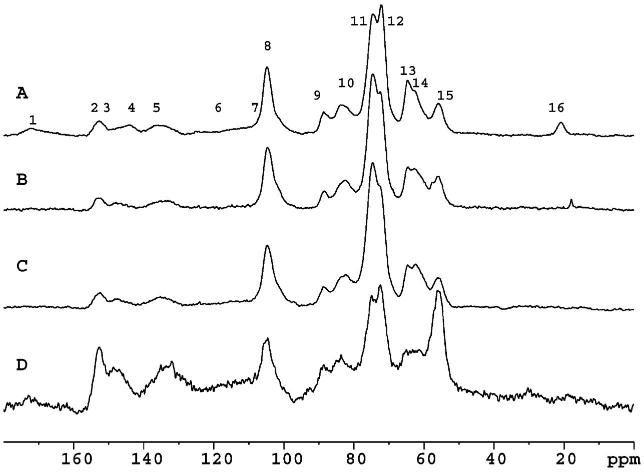

Fig. 1. 100 MHz CP/MAS ^{13}C high-resolution solid-state NMR spectra of moderm wood (A) and of archaeological wood from different canoes: Geraz do Lima II (B), Geraz do Lima I (C) and Mazarefe (D) with water contents of 71, 61 and 831%, respectively.

Table 2
Resonance assignment of ^{13}C CP/MAS spectrum of modern and archaeological woods

Resonance number	Chemical shift (ppm)	Assignments
1	172	Carbohydrate; $-\underline{C}OO-R$, $CH_3-\underline{C}OO-$
2	152.6	Lignin; S3(e), S5(e)
3	147	Lignins; S3(ne), S5(ne), G1, G4
4	136	Lignins; S1(e), S4(e), G1(e)
5	134.3	Lignins; S1(ne), S4(ne), G1(e)
6	121	Lignin; G6
7	114–106	Lignins; G5, G6, S2, S6
8	104.8	Carbohydrates; C1
9	88.7	Carbohydrates; C4
10	83.8	Lignins; Cβ carbohydrates; C4
11	74.75	Lignins; Cα carbohydrates; C2,3,5
12	72.17	Carbohydrates; C2,3,5
13	64.7	Carbohydrates; C6
14	61.58	Lignins; Cγ
15	55.65	Lignins; $O\underline{C}H_3$
16	21	Carbohydrates; $\underline{C}H_3-COO-$

S, syringyl (aromatic unit with two methoxyl groups); G, guaiacyl (aromatic unit with only one methoxyl); ne, in non-etherified arylglycerol β-aryl ethers; e, in etherified arylglycerol β-aryl ethers.

dugout was chosen and can be compared to the spectra of a modern oak sample. In Fig. 3, we give a selection of three spectra of wood taken out at different places in the same dugout. It allows to evaluate whether the localisation of wood in a dugout influences the features of their NMR spectra.

In Fig. 1, the ^{13}C CPMAS NMR spectra of the archaeological can be fully interpreted on the basis of the literature data (Bardet, Emsley, & Vincendon, 1997; Bardet, Gagnaire, Nardin, & Vincendon, 1986; Davis, Schroeder, & Maciel, 1994; Gil & Neto, 1999). Table 2 reports the assignments of the NMR signals to the different components of wood. The major structures of wood are recalled in Fig. 2. The main features of NMR spectra of wood can be recalled. They exhibit three main interesting regions. The first area, between 20 and 30 ppm, is relating to a signal for the acetyl methyl group of the hemicellulose carbon at 21 ppm. The second region, between 40 and 160 ppm, is assigned to cellulose, hemicellulose and lignin carbons with mainly lines involved in cellulose and hemicellulose carbons. A well-resolved peak 8 is assigned to the anomeric C-1 carbon at about 104.8 ppm and other peaks to the C-6 carbon at 64.7 ppm with an upfield shoulder, the C-2, C-3 and C-5 carbons at about 72–74 ppm, respectively, and C-4 doublet carbons at 84 ppm.

Several resonances are observed for the lignin component. The resolved peak at 56 ppm arises from the methoxyl substituents, in the frequency region between 60 and 100 ppm for the three-carbon side chains with different types of substitution. The aromatic structures of lignins give rise to a set of resonances between 120 and 160 ppm. In this frequency range, the intense signal at about

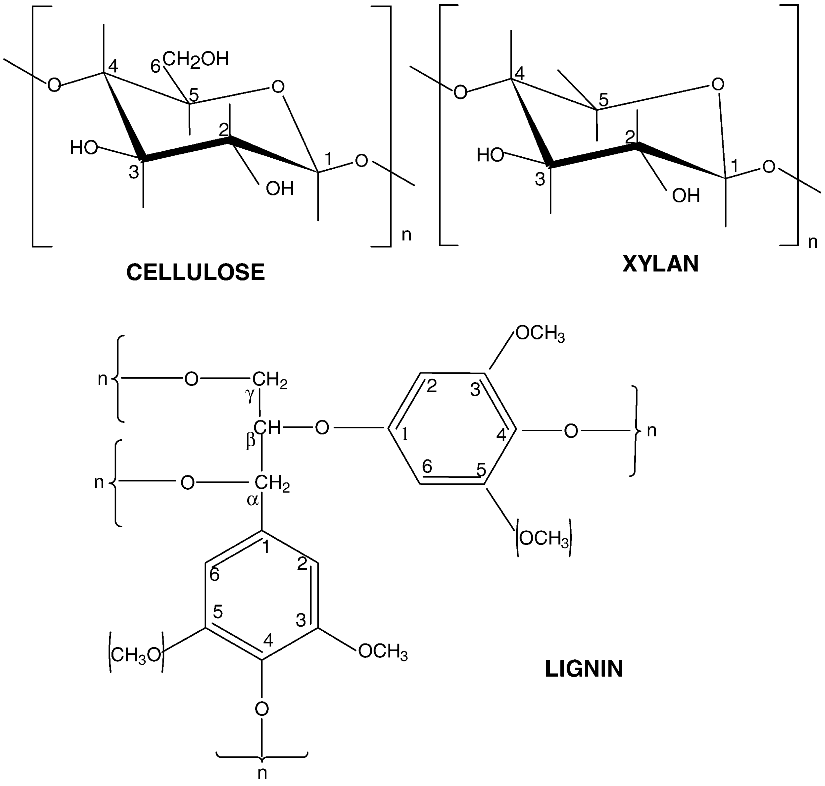

Fig. 2. Formulae of the main components of wood.

153 ppm is assigned to oxygen substituted (−OCH3 and −OH) aromatic carbons.

The low-field spectral region is dominated by the acetyl carbonyl group of hemicellulose component at 172 ppm and several minor lines at about 180 ppm may be assigned to the carboxyl groups of 4 *O*-methylglucuronic acid residues attached to the xylan chain. As usually in CPMAS spectra, the occurrence of spinning sidebands were tracked down by varying the spinning rate or by recording the spectra with the TOSS sequence which allows to record spectra without spinning sidebands (Dixon, Schaefer, Sefcik, Stejskal, & McKay, 1982). In the NMR spectra of wood samples, the carbons of carbonyl and aromatic structures are known to give spinning sidebands due to their expected strong chemical anisotropies.

On the first hand, as a general statement concerning the spectra B and C of archaeological woods, from the Geraz Do Lima canoes, shown in Fig. 1, is that they are sharing many features with modern wood, spectrum A, since both lignin and cellulose signals are present. On the other hand, the spectrum D of the wood from the Mazarefe dugout canoe differs significantly since it appears to be almost pure lignin. The comparison with the spectrum of modern wood indicates a complete depletion of the hemicellulose moiety as indicated by disappearance of the signal at 21 ppm. Moreover a careful examination of the spectra, by comparing the intensities of the different signals of celluloses using for instance the signal at 61.58 ppm assigned to the methoxyl groups in lignins as a reference, reveals that all the spectra differ from each other. It shows that cellulose moiety decreases in a more or less important proportion from one sample to another. Differences also appear when comparing different parts of a dugout as shown in Fig. 3. These changes in the spectrum features clearly indicate changes in the relative proportions of the main compounds of wood.

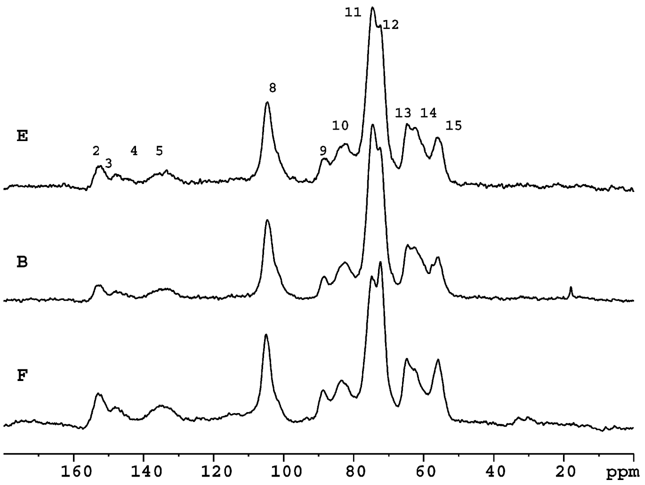

Fig. 3. 100 MHz CP/MAS ^{13}C high-resolution solid-state NMR spectra of archaeological woods collected from drilling at different positions of the same canoe, Geraz do Lima II: bottom part (E) medium part (C) and internal part (E). Their respective water contents are of 145, 71 and 142%, respectively.

Such structural changes clearly indicate that even if the dugouts were found close to each other they were not degraded to a same extent. Structural differences depending on from where the dugout wood samples were taken out are also clearly revealed in this study.

Concerning the structural features of these archaeological woods, one can conclude to an almost complete depletion of hemicelluloses and to a decrease in the amounts of celluloses that are more or less important among the samples. The extent of the deterioration of cellulose seems mostly to depend on the conditions of storage, and of the localisation of wood in the dugout. It is worth noting that the spectra of severely degraded samples present a poor signal to noise ratio samples, see spectrum D for instance. For these samples, most of the carbohydrate polymers were depleted, therefore, after drying most of their volume is occupied by air. As the wood samples were not finely grinded, the amount of solid material filling the rotor decreased significantly. It induced smaller signal to noise ratios since identical number of transients was accumulated. In the present work, we chose to record all the spectra with the same number of scans in order to record spectra under identical conditions.

Very interestingly for all the spectra it is not possible to identify either the appearance of new signals or a broadening of residual signals. It clearly indicates that while the aging conditions induced strong depletion of carbohydrates, no chemical rearrangement inside the biopolymers network occurs. Such chemical rearrangements would have led to new chemical species with specific NMR signals and important line broadening of the signals, due to chemical shift dispersion (Leary, Morgan, & Newman, 1986; Schmidt-Rohr & Spiess, 1994). Such behaviours are widely observed in CPMAS spectra of lignocellulosic materials after chemical treatments and molecular rearrangements occurring in pulping processes (Barron, Frost, Dolmo, & Kennedy, 1985; Haw, Maciel, & Schroeder, 1984).

In the spectral region between 125 and 160 ppm are localised the signals 2 at 156.2 ppm and its low-frequency shoulder 3, respectively, assigned to syringyl moieties in etherified and non-etherified structure β-O-4. By comparing these regions on Figs. 1 and 3 for the different samples, archaeological and modern woods, it is not possible do detect significant change in their relative intensities. It clearly indicates that these β-O-4 inter-unit linkages, the most frequent in lignin polymers, were not degraded during aging.

3.2. Quantitative analyses

Quantitative treatment of the spectra can be carried out provided that if the following precautions are taken. As mentioned previously, the spinning sidebands of aromatic carbons have to be considered in integrals. The spinning rate

Table 3
Quantitative treatment of CPMAS spectra of archaeological and modern woods

Wood sample	H_2O (in %)	Integrals (in %)		Carbons (in %)		Weight (in %)	
		A_{high}	A_{low}	Lign.	Carb.	Lign.	Carb.
Contemporary oak	28	16	84	28.8	71.2	22.8	77.2
Drilling inside the bottom part of the Geraz do Lima II canoe	145	33	67	58.1	41.9	50.2	49.8
Drilling inside medium part of the Geraz do Lima II canoe	71	20	80	35.1	64.9	28.2	71.8
Drilling inside internal part of the Geraz do Lima II canoe	142	22	77	39	61	31.7	68.3
Drilling inside medium part of the Geraz do Lima I canoe	57	22.7	77.3	39.8	60.2	32.5	67.5
Drilling inside external part of the Geraz do Lima I canoe	61	25.1	74.9	44	56	36.4	63.6
Drilling inside external part of the Geraz do Lima I canoe	148	24.6	75.4	43.2	56.8	35.5	64.4
Non-identified sample from the Mazarefe canoe	831	52.3	47.7	91.9	8.1	89.2	10.8

Lign., lignins; Carb., carbohydrates; see the text for the definition of A_{high} and A_{low}.

used to record the spectra was set to 5000 Hz; therefore the spinning sidebands of the aromatic carbons, mostly signals 2 and 3, appear at high-frequency in a region without any other signals which facilitate their integration. On the other hand, the low-frequency spinning sidebands appear in the area assigned to carbohydrates and will contribute to enhance the area of this region. Therefore for the quantitative treatment, the integrals of the two high-frequency spinning sidebands were added twice to the area assigned to lignins and subtracted once to the area of carbohydrates, the corrected integrals are noted A_{high} and A_{low}, respectively.

The measured integrals can be either directly compared or used in the formulas proposed by Haw et al. (1984) that allow to calculate either the percentages in carbons or in weight by taking into account average empirical formula of lignins and sugars. In our case, we used the formula $C_9H_{7.72}O_{2.75}(OMe)_{01.53}$ proposed for hardwood lignins with a molecular mass of 207 g mol^{-1}, respectively, and for sugars the formula $C_6H_{10}O_5$ was assumed with a molecular mass of 183 g mol^{-1}.

Moreover, it has been shown from the qualitative analyses of the spectra, carried out in Section 3.1, that no new structure was formed during aging of the canoes in a saturated water environment. This feature of the archaeological material was undoubtedly due to the fact that in such conditions, the different products arising from the degradation of celluloses and hemicelluloses are leached out from the dugout canoes. Therefore, it is fully relevant to directly quantify, from the recorded spectra, the amounts of residual lignins and residual celluloses, as reported in Table 3. The water contents of different samples were also given. These data not only confirm the general observation, concerning the more or less important decrease of the amount of celluloses, made previously but they allow to evaluate very accurately the extent of the degradation. If we compare the archaeological wood composition made with NMR with the water content, the general trends appear to be rather good with regression coefficient around 0.9 as shown in Fig. 4. The highest water contents are effectively found for the most degraded wood. Nevertheless, some discrepancies can be underlined and could be misleading if they are further used to decide restoration process. For instance, three samples have very similar water contents between 142 and 148% but their amounts of lignin and celluloses differ significantly, varying from 31.7 to 50.2% in the case of lignin moiety.

4. Discussion

After a long stay in saturated water environment, both celluloses and hemicelluloses of lignocellulosic material are almost depleted: the extent of degradation and the degradation rate are higher for the hemicelluloses than for the celluloses. On the other hand, lignins appear to be very stable under these storage conditions. These results support the fact that lignin is relatively stable and resistant to hydrolysis and also that wood polysaccharides are biologically degraded in preference to lignin at the exception that

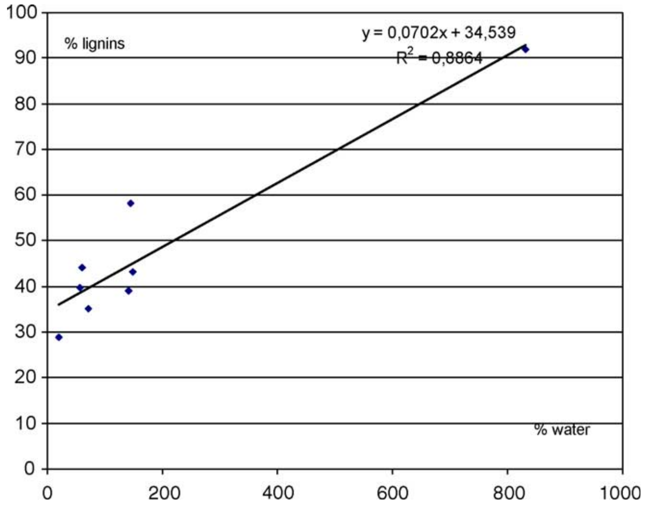

Fig. 4. Lignin content (in % of dry weight) as a function of the water content for modern and archaeological waterlogged woods.

hemicelluloses undergo hydrolysis and oxidation faster than cellulose in wood species. As it has been well established for more than 100 years, wood is a complex material. Cellulose represents the crystalline part (fibrils) of wood, which is held together by the hemicelluloses and the lignins. The main function of hemicelluloses and lignins is to buttress the fibrils. The important degradation of hemicelluloses and the leaching out of their degradation products is unambiguously the origin of the drastic weakness of these dugouts. These results give a clear explanation of the strong increase in the water content of these archaeological samples. Water enters the wood in the free space that was occupied by cellulose fibrils in the non-degraded woods.

5. Conclusions

These results clearly show that under the ageing conditions in a saturated water environment the degradation of cellulose and other sugars was enhanced. On the other hand, the overall structure of lignins does not change; the main β-O-4 inter links are still present in all the samples that were analyzed. It demonstrates that the storage conditions lead to strong degradation of celluloses and other sugars, but they do not affect lignin moieties.

Due to the high solubility of monosaccharides and their oligomers the presence of water all around the wood certainly favored their regular leaching from the wood in the environment. From a technical point of view this paper shows that quantitative analyses by ^{13}C NMR solid state should become a classical tool to characterize archaeological lignocellulosic materials and should bring complementary data to those obtained with conventional chemical analyses. In this article we have demonstrated that for the waterlogged archaeological woods, NMR is currently a powerful technique to investigate the structural features of wood and to assess the changes that the wooden artefacts have undergone under ageing in water conditions. The present work has showed that if the water content of the archeological samples is certainly a relevant parameter to characterize wood damages it can give erroneous figures certainly due to the modification of the water contents during the drilling of samples. Therefore, the strategy that we employed herein, based on quantitative analyses of the solid-state NMR provides a precise characterization of waterlogged archaeological wood. This work definitely shows the interest of the NMR method for rapid and precise structural characterization of the archaeological samples. It is clear that such a method should be adapted for wooden artefacts ageing in aerobic conditions and submitted to fungi or other microorganisms (Kim & Newman, 1995). Under such conditions, the products arising from the degradation of wood and from the parasites themselves are still present in the sample making the spectra much more complex to interpret and to exploit for quantitative analyses than those of waterlogged woods that were studied in the present work.

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