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Nuclear Magnetic Resonance and Electron Paramagnetic Resonance as Analytical Tools To Investigate Structural Features of Archaeological Leathers

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Archaeological waterlogged leathers dated from the 13th to 17th century have been analyzed using carbon-13 high-resolution solid-state nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR). The NMR and EPR spectra have been compared to modern vegetable-tanned leathers and crude hide. Both techniques allowed us to fully characterize the samples and better understand the changes occurring during aging in water environment. The main features of the archaeological leathers are the high contents in iron and the absence of residual vegetable tannins. Traces of lubricants could not be detected either. The accumulation of iron oxides may have played a role in the conservation of the archaeological objects and explain the surprising good conservation state of the leather samples as was observed in the NMR spectra. The absence of tannins and lubricants in the studied archaeological samples is also discussed. It may be a consequence of aging in water-rich environment. The analysis strategy described in this paper can be systematically applied to characterize archaeological or historical leather samples.

Leather production is certainly one of the most ancient industrial activities still in operation.[1] The chemistry involved in leather making and its deterioration over time has been an important field of study for a long time. As a matter of fact, both historical and archaeological leathers represent an important part of the cultural patrimony all over the world that must be transferred from generation to generation. The preservation of artifacts made entirely or partially of leather is very challenging, as it is a particularly difficult material to conserve. This difficulty arises undoubtedly from the nature of the raw hide itself and from the different processes involved in its transformation into leather. Macroscopic properties of leather, making it suitable for artifact manufacturing, rely mainly on the applied tanning processes. These latter involve either organic compounds, such as natural tannins extracted from different woody plants, or mineral tannins, such as different varieties of native alum mainly used before the 18th century. They are all known to create molecular covalent or van der Waals interactions with the collagen moiety of skins. One of the targets of the tanning process is to favor molecular interactions inside the entire volume of the starting hide. Lubricants, such as oils or fats, can be also introduced into the leather directly as a tanning agent or at the end of the tanning process in order to increase and maintain its flexibility and softness properties. Lubricants also reduce water absorption. At room temperature lubricants are either liquids or soft solids, and even after their incorporation in the leather, they generally keep a high degree of molecular mobility.

In this article we illustrate the potential of solid-state ^{13}C NMR spectroscopy[2−5] to investigate the structural properties of archaeological leathers and to follow their changes under aging. Surprisingly, up to now only a very few high-resolution solid-state NMR studies have been devoted to historical or archaeological leathers compared to other bio-organic compounds such as lignocellulosic materials,[6−11] although the analysis strategy is very similar in both cases. Only a few NMR studies are reported on historical parchments.[12,13] In this work, electron paramagnetic resonance (EPR) was used as well to gain valuable information on the presence and the role of iron and manganese oxides in

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the archaeological samples. It is worth noting that in archaeological sciences EPR has been used several times to study inorganic materials[14,15] but never, as far as we know, for organic materials such as woods and leathers.

High-resolution solid-state NMR leads to structural information on organic compounds through qualitative analyses, quantitative measurements, and molecular dynamic studies.[16] It can readily be applied to investigate tanning and post-tanning treatments, as well as aging of leathers under different external conditions. In this work we focus on the qualitative approach of solid-state NMR using mainly two basic experiments. On the one hand, the commonly used CP-MAS experiment, which combines proton-to-carbon cross-polarization transfer (CP) and magic-angle sample spinning (MAS), allows the carbons of rigid domains to be selectively observed. On the other hand, carbons of mobile domains can be selectively observed through direct ^{13}C observation by single-pulse excitation (SP) and high-power decoupling applied during signal acquisition. To obtain high-resolution spectra, the SP experiment is also combined with MAS, and the full experiment is denoted the SP-MAS experiment. In modern leather, collagen and tannin moieties are typical rigid polymers on the NMR point of view and appear in CP-MAS spectra, whereas all lubricants used to soften the leather are selectively observed with the SP-MAS experiment. As a consequence carbons belonging to different domains of mobility can be edited in separated spectra by combining CP-MAS and SP-MAS experiments.[17] As we have already shown on other organic materials, typical solution NMR experiments such as DEPT (distortionless enhancement by polarization transfer) can be as well directly applied when molecular mobility is high enough for MAS alone to completely average to zero the reduced proton−proton dipolar interactions and the magnetic susceptibility tensor. DEPT allows specific editing of subspectra of CH, CH_2, and CH_3 carbons.[18]

The waterlogged leather samples studied in this work were collected from an excavation in Lyon, France during the building of a car parking at the St-Georges area. They were clearly identified to soles of shoes and were dated from the 13th to 18th century. They constitute a valuable set of well-identified archaeological samples that have allowed us to illustrate the interest in archaeological sciences of solid-state NMR and EPR spectroscopies. Their structural features, obtained from NMR and EPR, are compared here to those of modern leathers.

EXPERIMENTAL SECTION

Sample Preparation. The waterlogged leather samples, dated from the 13th to 18th century, were collected during the years 1996−1998 from an excavation in Lyon, France at the St-Georges area. The samples were washed with fresh water to remove any mud particles and kept at 5 °C in water with antiseptics to prevent biological degradation. Before analyses, they were washed again and dried for 1 week inside a fume hood under strong ventilation until they reached constant weights. The amount of water contained in the wet sample was measured from these experiments. The commercially available crude tannins and the modern leather samples tanned with vegetable tannins were kindly provided by Guy Lumia at CEA-Marcoule, France. Among them, a first sample was treated with tannins extracted from quebracho and a second one with oak leaf tannin. They are denoted in the following "quebracho leather" and "oak leather", respectively. A third sample, denoted "moroccan leather", whose vegetable tannin process is not known, was provided from a small-scale leather production. Crude collagen was purchased from Sigma. The corium-layer sample was directly prepared at the laboratory from the salted hide of a 17 month old beef obtained at the slaughterhouse.

NMR Experiments. For each sample, 300−400 mg of dried material was cut in a small cube of 2−3 mm edge and filled in 7 mm diameter (340 μL) cylindrical double-bearing rotors made of zirconia. The rotors were closed with Kel-F end caps. All high-resolution solid-state ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance DSX 200 spectrometer operating at a proton frequency of 200.13 MHz (carbon frequency at 50.3 MHz). The ^1H radio frequency field strength used both for pulses and proton dipolar decoupling was set to give a 90° pulse length of about 2.5 μs. For each spectrum, 1600 transients were added. MAS spinning rate was set to 4000 Hz. The chemical shift values were referenced with respect to tetramethylsilane (TMS) using the carbonyl signal of glycine set at 176.03 ppm as intermediate reference. DEPT spectra were recorded with a polarization-transfer pulse length of $3\pi/2$ in order to record CH and CH_3 resonances in opposite sign with respect to CH_2.

EPR Experiments. X-band EPR spectra were recorded at room temperature on a Bruker EMX spectrometer equipped with an ER-4116 DM Bruker cavity. Leather or corium-layer fibers were cut in less than 1 mm edge pieces and introduced in a synthetic Suprasil quartz EPR tube under argon. Radical spin quantifications were obtained using the Bruker weak pitch as a rough "standard". For all spectra, the microwave frequency was set to 9.66 GHz (except for the corium-layer sample, 9.65 GHz) and microwave power to 12.6 mW. In this condition, the radical signals are saturated, and their intensity cannot therefore be compared. The modulation frequency and amplitude were 100 kHz and 1.04 mT, respectively. The one scan experiment took 6 min for each sample, except for corium-layer sample (3 min).

Elemental Analyses. Fe, Cu, Mn, and Al contents were determined by elemental analyses performed by the "Service Central de Microanalyse du CNRS" (Solaize, France) using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Thermo Fisher 3580. Al and Cu represent less than 0.01% for all analyzed samples.

RESULTS AND DISCUSSION

In order to facilitate the interpretation of archaeological samples, we first ascertain the main NMR and EPR features of modern leather tanned with vegetable tannins followed by a lubricant application.

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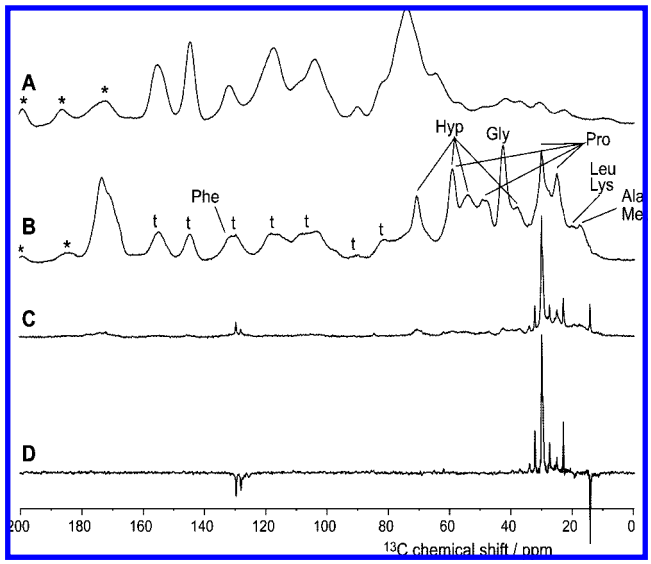

Figure 1. 50 MHz ^{13}C high-resolution solid-state NMR spectra of pure quebracho tannin (A) and modern quebracho leather (B−D). The sequences used were CP-MAS for spectra A and B, SP-MAS for spectrum C, and DEPT-MAS for spectrum D. For all spectra, the recycling delay was set to 5 s and the MAS spinning speed to 4000 Hz. In spectrum D, CH_2 groups are positive and CH and CH_3 sites are negative. Spinning sidebands are noted with a star symbol.

NMR Assignment of Modern Leather. CP-MAS and SP-MAS spectra recorded on different samples are shown in Figure 1. The spectrum A corresponds to the CP-MAS spectrum of crude tannin extracted from quebracho. By comparing this spectrum with the CP-MAS spectrum B of the quebracho leather, one can easily distinguish and assign the signals of tannin on the one hand and of collagen on the other. The ^{13}C NMR peaks of major amino acid residues have been readily assigned on the basis of data obtained in isolated amino acids, model polypeptides, and different types of collagens.[19−21] They are indicated on the spectrum with the IUPAC three-letter abbreviations for amino acids. In the present work, no attempt was done to assign precisely the different signals of tannins, noted with the symbol "t" on the CP-MAS spectra, since the structural study of tannins is beyond the scope of this article. However, different types of tannins were recorded (not shown); they all give specific NMR signals that can be used as fingerprints for their identification. Due to the aromatic nature of tannins, there is almost no overlapping with signals of collagen. Molecular interactions between collagen and vegetable tannins consist mainly in hydrogen bonds and hydrophobic interactions. Consequently, it is not expected to see significant changes in the NMR chemical shifts of crude collagen and collagen interacting with vegetable tannins as found in leather. Therefore, it can be easily evidenced if tannins are present in a sample. This point is clearly illustrated by comparing the spectrum of quebracho leather (Figure 1B) with the one of a nontanned crude skin shown in the inset of the Figure 3 (spectrum K). The two relevant spectral regions corresponding to collagen and tannins are easily identified on the spectra of modern leather

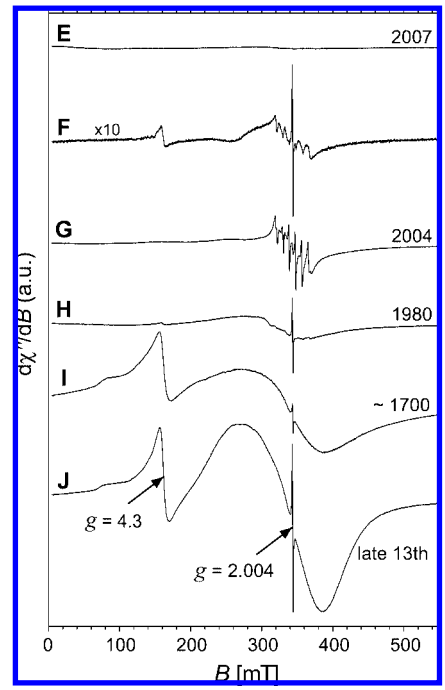

Figure 2. X-band EPR spectra at room temperature of 142 mg of corium layer (E), 135 mg of mimosa tannin (F), 105 mg of oak leather (G), 153 mg of moroccan leather (H), and 83.9 and 89 mg of waterlogged archaeological leather (I and J, respectively). Samples I and J were dated from the 18th and 13th century, respectively. For comparison, all spectra are normalized.

shown in Figure 1. The spectra also show spinning sidebands that have to be carefully identified in order not to be assigned to isotropic chemical shifts. Indeed, due to the strong chemical shift anisotropy of the aromatic and carbonyl carbons, magic-angle spinning in the range of 4000−5000 Hz is not high enough to completely average this interaction, and consequently, spinning sidebands, indicated by star symbols in the spectra, appear. These spinning sidebands are unambiguously identified either with the TOSS (total suppression of sidebands) experiment[22] or by recording spectra at different spinning rates.

As mentioned in the introductory section, signals of carbons belonging to molecular domains with a high degree of mobility can be selectively edited by using direct carbon excitation (SP-MAS) and a short repetition delay. This experiment applied on the quebracho leather is shown in spectrum C of Figure 1. Broad signals attributed to collagen and tannins are almost not detected any longer, and new narrow signals are observed, corresponding to the lubricant used in the leather treatment. These sharp signals are typical of triacylglycerol. By increasing the vertical display of spectra it is possible to detect the signals at 62 and 69 ppm assigned to Cα and Cβ of glycerol, respectively. As the molecular mobility of the lubricant is high enough, the dipolar coupling can be completely averaged to zero under MAS. This allows the use in the solid state of sequences originally designed for solution NMR. In the present case, the DEPT sequence was applied on the quebracho leather (spectrum D of Figure 1), allowing the discrimination of CH, CH_2, and CH_3 sites of the lubricant. With the experimental parameters used, CH_2 signals are positive in

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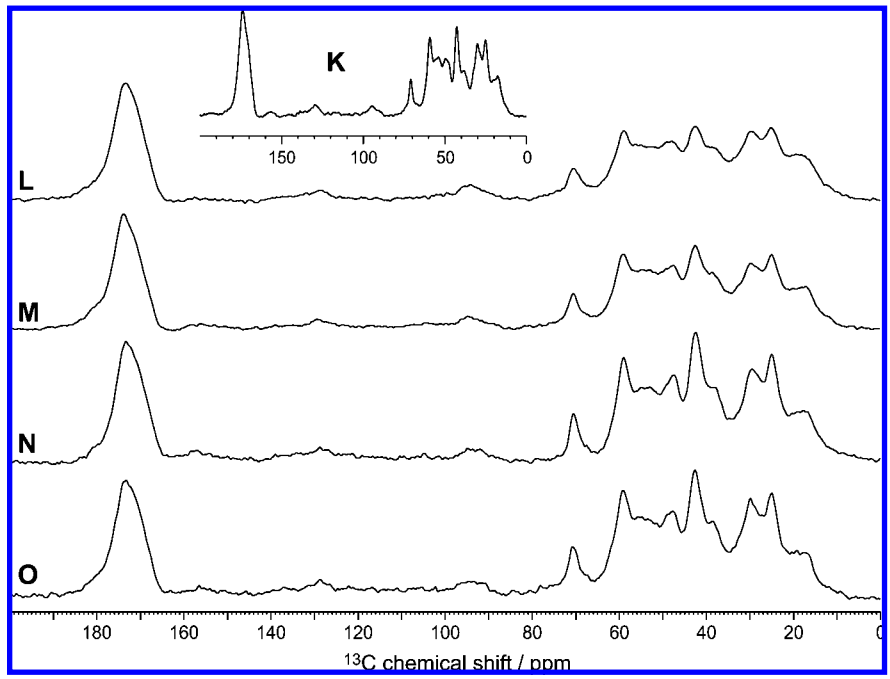

Figure 3. 50 MHz CP-MAS ^{13}C high-resolution solid-state NMR spectra of waterlogged archaeological leather from different soles found in the St-Georges excavation site in Lyon, France. They are dated from the 13th (O and N), 16th (M), and 17th (L) century. Spectrum K shown in the inset corresponds to the corium-layer sample (crude modern hide).

the spectrum, whereas CH and CH_3 resonances appear with negative phases. Quaternary carbons are not observed with the DEPT sequence, but they can be assigned by comparing SP-MAS and DEPT-MAS spectra. Signals originating from the more rigid part of the sample, e.g., collagen and tannins, are completely filtered out by the DEPT-MAS sequence. DEPT-type experiments are very important to detect the presence and even identify the lubricants that were employed. The assignments presented here for modern leather will be very helpful as a starting point to interpret NMR spectra of any new types of leather.

EPR Features of Modern Leather. EPR spectra of the oak and moroccan leathers are shown in Figure 2, spectra G and H, respectively. The main characteristics of these spectra are the following: first, the presence of radicals, corresponding to about 0.2×10^{13} and 3.8×10^{13} spins/mg, with a very intense thin line at $g = 2.004$ saturating at ca. 0.8 mW, and second, the presence of paramagnetic metal ions with broad lines, also centered at about $g = 2$. These broad lines remain out of saturation even at the maximum microwave power available on our spectrometer, 200 mW, which indicates that they correspond to fast relaxing species. One of these broad signals is characteristic of Mn^{II} ions either with its six typical thin lines (spectrum G)[23] or with a broad line (spectrum H). Spectrum H of moroccan leather shows an additional small broad line centered at $g = 4.3$ that is attributed to Fe^{III}.[24] The large signal that could be expected for iron oxides[14] if they were present in the samples was not observed in any of the modern leather samples tanned with vegetable tannins. In order to better understand the EPR features of vegetable-tanned leathers, crude corium-layer fibers and crude tannins were also studied by EPR (spectra E and F, respectively). As expected for collagen,[25] the EPR spectrum E of corium-layer fibers shows only very small concentrations of paramagnetic species compared with other leather samples (spectra G−J). Moreover, EPR signal of radicals have never been detected either. To complete this study, three different types of crude tannins were also analyzed by EPR. The first one is a chestnut tannin, an ellagitannin, hydrolyzable tannin with castalagin and vescalagin structures, the second one is a quebracho tannin, a profisetinidin, condensed tannin, and the third one is a mimosa tannin, a prorobinetinidin, condensed tannin.[1] To simplify the reading of the Figure 2, only the spectrum F of the mimosa tannin is shown. As a matter of fact, the three tannin spectra show only small radical signals corresponding to about $1-2 \times 10^{13}$ spins/mg. However, significant differences can be noticed in their EPR spectra. Indeed, the six typical hyperfine lines of Mn^{II} are well resolved in the spectra of the chestnut and mimosa tannins, but not in the spectrum of quebracho tannins. This can be tentatively attributed to a different Mn^{II} chemical or geometrical ligand structure. Indeed, the two first tannins have trihydroxyphenyl moiety allowing complexation with metal ions, whereas the quebracho tannin has only a dihydroxyphenyl moiety which is not reactive toward metal salts.[1] Very interestingly, we observe the similar EPR features for isolated vegetable tannins and modern vegetable-tanned leathers (spectra G or H). The EPR signals observed for leather samples can be unambiguously attributed to the incorporated tannins since the broad

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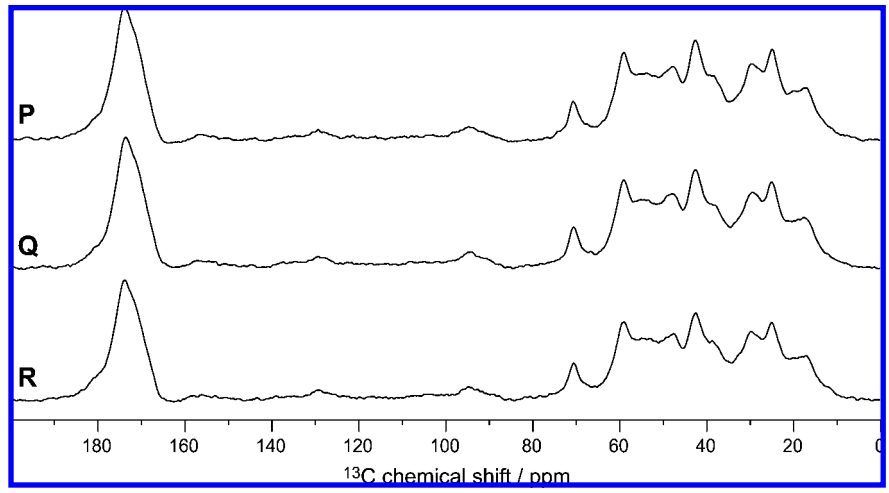

Figure 4. 50 MHz CP-MAS ^{13}C high-resolution solid-state NMR spectra of waterlogged archaeological leather of three different samples taken at different locations on the same sole dated from the 17th century and found in the St-Georges excavation site in Lyon, France.

EPR signal observed for the corium-layer fibers presents only a very low intensity. Note that this latter signal is almost not visible on Figure 2 since the spectra intensities were normalized in order to be compared. Moreover, as the six hyperfine lines of Mn^{II} are resolved for the oak leather (Figure 2, spectrum G), the tanning agent of this sample should contain a trihydroxy moiety. This is indeed the case for the oak leaf hydrolyzable tannin used for this leather. The vegetable tannin used for the moroccan leather is unknown, but its EPR spectrum indicates a tannin with only a dihydroxyphenyl moiety, like profisetinidin in quebracho tannin or procyanidin in pine tannin.[26] This analysis illustrates the real potential of EPR in providing information about the tanning agents employed in the preparation of leather. Theses results are consistent with those obtained by quantitative elemental analysis that shows that the contents of Fe and Mn are very small, less than 0.01%, in all recent samples including mimosa tannin, oak leather, and moroccan leather.

NMR and EPR of Archaeological Leathers. The previous results gave an overview of the ^{13}C NMR and EPR features of modern leathers and of their main components. It makes the interpretation of both NMR and EPR spectra of archaeological leathers easier. All the archaeological leather samples studied here were taken from soles of shoes dated from the 13th to the 18th century and collected on one site during the same excavation campaign. They represent a very large set of soles that can be considered in rather good state since their general shapes are well preserved. In order to explore whether or not we have to face an heterogeneity among the sample set, which could be due either to the samples themselves or to their different degrees of degradation, NMR and EPR analyses were carried out on several samples collected either from different soles or inside the same one. The ^{13}C NMR spectra of samples collected on four different soles dated from the 13th to 17th century are shown in Figure 3. As can be seen, they are very alike since all the principal ^{13}C resonances appear at identical chemical shifts. However, it can be noted that the intensities of the signals are slightly different between the different spectra corresponding to different samples. This is particularly visible for resonances at 79, 59, and 43 ppm in spectra L and M compared to spectra N, O, or K. On the other hand, the NMR spectra of samples taken at different places on a same sole were perfectly identical (see Figure 4). These results show that the present leather collection, despite the small differences observed previously between different soles, is very homogeneous as far as the question of its chemical structure is addressed. This observation is quite surprising when compared to waterlogged wood samples for which we observed in previous studies a much larger heterogeneity, even for samples collected inside the same object;[10] The usually larger dimensions of wooden artifacts can explain in part this structural behavior. Additionally, the degradation of waterlogged wood is very drastic in most of cases with an almost complete depletion of the cellulose moiety. From the present study, it appears that collagen, compared to its cellulose counterpart, is less sensitive to biodegradation in anaerobic and water-saturated surrounding.

The EPR spectra of all archaeological leather samples revealed the presence of strong signals of metallic oxides and radicals as visible in Figure 2, spectra I and J. Indeed, the assignment of these EPR signals can be carried out on the basis of previous works;[14] signals of Fe and Mn oxides are both spread over the entire spectrum, and therefore, they strongly overlap. However, Fe oxides are the main contribution of the spectrum in the region from 60 up to 200 mT, whereas between 200 and 500 mT the spectrum is dominated by the signal of Mn oxides. Moreover, Fe^{III} gives an additional signal similar to the Fe oxides in the region of 100−200 mT. It has to be noted that the broad signals assigned to Fe and Mn oxides are not saturated even at 200 mW indicating very fast relaxation properties of the corresponding electronic spins. By comparing the EPR spectra of the different archaeological samples (only two examples are shown here), it appears that the relative concentrations of both oxides are strongly sample-dependent. These variations are smaller but still present in samples collected on the same sole. Even if oxide EPR signals are very intense, their concentration can be small as shown below.[27]

Although accurate quantitative analysis from EPR spectra is difficult with such broad overlapping lines, clear tendencies can

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be established that are consistent with the metal concentrations found by elemental analysis. Thus, only archaeological samples contain large amount of metals with, e.g., 5% Fe and 0.01% Mn for the sample of spectrum I and 1% Fe and 0.1% Mn for the sample of spectrum J. These concentrations have to be compared to those found in recent samples (spectra G and H) that are less than 0.01% Fe or Mn. When spectrum J is compared to spectrum I, the shoulder part of the broad line in the 60−100 mT region is decreased, corresponding to a decrease in the concentration of the Fe oxides. Consequently, the increase of the typical derivative signal ranging from 140 to 200 mT, that is assigned to both the broad Fe oxides and the thin Fe^{III} contributions, clearly indicates an increase of the Fe^{III} concentration. It has to be noted that as the Fe^{III} signal is much thinner than the Fe oxide one, even a small amount of Fe^{III} can give a strong 140−200 mT signal. This is in accordance with the elemental analysis results which reveal a decrease of the total Fe content from 5% to 1%. The broad derivative line in the 200−500 mT region assigned to both Fe and Mn oxides increases in the archaeological samples. As we have just shown that there are less Fe oxides, this increase of EPR signal indicates that the concentration in Mn oxide increases. This result is in agreement with the elemental analysis showing that Mn contents are 0.01% for the sample corresponding to spectrum I and 0.1% in the case of spectrum J.

When the EPR spectra of several samples taken from soles of different ages are compared, it is observed that the concentration in iron or manganese oxides varies significantly with time; however, no clear tendency can be established with the age of the samples. The concentration variations across samples taken on the same sole are much smaller. The radical signals, which are similar to those observed in recent leathers, are centered at $g = 2.004$ and saturate at ca. 0.8 mW. The variation of the radical line shape across the different measured samples, even when taken from the same sole, indicates the presence of several species. No general trend is observed for the line shape variations. However, an increase of the radical concentration is observed with time, from 1.4×10^{13} up to 6×10^{13} spins/mg for the oldest samples that were analyzed.

Tanning and Aging of Archaeological Waterlogged Leathers. Contrary to what is observed in modern leathers that are tanned with vegetal tannins (spectrum B in Figure 1), it was not possible to detect the presence of vegetal tannins on the NMR spectra of archaeological leathers (see spectra in Figures 3 and 4). It is clear that after aging under conditions such as those encountered in the Lyon excavation, the features of the NMR spectra are similar to those of raw collagen fibers, as found in a crude modern hide. Moreover, using the SP-MAS experiment, it was not possible to detect the presence of lubricants such as oils. These features are consistent with direct macroscopic observation of the samples which all appear very stiff with a drastic darkening of their initial brown color after their cleaning in water and drying at room temperature. The question concerning the complete absence of tanning agents and lubricants in all these different samples of shoe soles has to be addressed. Two hypotheses can be proposed. The first one could be a complete leaching of the tanning and lubricant agents either by aging in water-rich environment or by washing the samples prior to their study. The second hypothesis considers the possibility that theses shoe soles were made of leather that was treated neither with vegetable tanning agents nor with lubricants. To exclude the impact of sample washing, a leather sample was analyzed before cleaning, leading to NMR spectra identical to washed samples, without traces of tanning agent or lubricant. The slight differences observed in the EPR spectrum before and after cleaning are of the same order as to those observed for samples taken from different places in the same sole. In order to further check the hypothesis of the leaching out of tannins and lubricants during aging, we have roughly simulated the environment conditions undergone by the archaeological leather sample by applying a 2 week water extraction using a Soxhlet extractor on a modern vegetable-tanned leather treated with lubricants. By this way, about 30−50% of dry weight could be extracted. NMR analysis of the leather after extraction revealed an almost complete disappearance of the lipidic lubricants and a decrease of the tannin signal of about 10%. On the basis of EPR spectra, radical and thin Mn^{2+} signals disappeared as well, whereas Fe^{3+} and broad Mn^{2+} signals remained unchanged, indicating a stronger link to collagen. As mentioned above, these four signals are attributed to vegetable tannins. This simple extraction experiment demonstrates that aging in water surrounding can undoubtedly extract lipids and in a lesser extent tannins. Of course it cannot be excluded that fragments of collagen may be also degraded and extracted with time. But on the basis of the very similar CP-MAS spectra found for collagen, crude skin, and archaeological leather, one can conclude that there is no preferential degradation of specific amino acids during aging. However, as indicated by the increase of the radical EPR signal intensity with the age of archaeological samples, some degradation of collagens has occurred. It probably mainly concerns hydrolysis of ester bonds leading to shorter oligomers that will have been then more easily extracted. Such degradation should not modify the overall feature of the NMR spectra and is therefore not detectable. However, this type of degradation can only be very limited in the considered samples, since the water content of the as-found samples does not indicate a heavy degradation. Very interestingly, EPR measurements show that iron and manganese oxides are accumulated in the waterlogged sample during aging and appear as a specific property of archaeological samples. Such oxides were never detected on modern leathers analyzed so far. These oxides could be brought by water into the organic materials from sediment depositions surrounding the archaeological samples. Residual collagen of leather can be seen like a molecular network fixing oxides. In the literature, degradation of archaeological organic artifacts due to high metal salts concentration has been reported.[1] Transition metals are also known to catalyze the oxidation of sulfur dioxide under aerobic conditions in the presence of water.[28] Sulfur derivatives are known to be synthesized by microorganisms in archaeological waterlogged materials. We could expect a similar effect on our leather samples. However, as revealed by this study, the archaeological leather artifacts considered here are well conserved, and the presence of iron and manganese oxides seems to have had no detrimental effects. Two main reasons

(28) Bowden, D. J.; Brimblecombe, P. *Journal of Cultural Heritage* **2003**, *4*, 137–147.

could explain this apparent discrepancy. On the one hand, the artifacts studied here were conserved in anaerobic conditions. On the second hand, metal oxides may not be oxidation catalysts as is the case for metal salts. As neither tannins nor lubricants were detected to explain the surprisingly good conservation state of the studied artifacts, it is conceivable that the anaerobic conditions and the presence of either metal oxides or Fe^{3+} have played a role in the stabilization of the molecular structure, in particular of the collagen moiety itself.[1,29,30]

CONCLUSIONS

The molecular structure of waterlogged archaeological leather shoe soles has been investigated using ^{13}C solid-state NMR and EPR spectroscopy. In order to better extract the typical spectral features of archaeological leather, their NMR and EPR spectra were compared to samples of different modern leathers, tannins, and corium fibers (collagen). The artifacts, dated from the 13th to 18th century, were all coming from the same excavation site. Despite a relatively broad range of ages, the general features of their NMR and EPR spectra were conserved across the different samples. All studied artifacts were well conserved, showing a ^{13}C CP-MAS spectrum typical of pure collagen. No traces of tannins or lubricants could be detected, indicating that either nontreated leather was used for the manufacture of shoe soles at that period or aging in water environment has completely leached out the more mobile tannin and lubricant molecules. The results are consistent with the second hypothesis. EPR spectra revealed the accumulation of a significant amount of Fe and Mn oxides in the archaeological leathers, which, however, did not seem to have accelerated the degradation process. In the opposite, the surprisingly good conservation state of the leather artifacts suggested a stabilization effect of the collagen moiety by the metal oxides under these specific aging conditions. The two main characteristics of waterlogged leather artifacts as revealed by NMR and EPR, e.g., a conserved chemical structure of collagen with the presence of metal oxide impurities, can be very helpful for the scientist in charge of setting the conservation process.

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