# The ArCo Project - Ageing Study of Treated Composite Archaeological Waterlogged Artefacts - preliminary results

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## Abstract

Collections of archaeological treated wood are often affected by phenomena of degradation, mainly due to the presence of unstable salts. After drying and exposure to air, inorganic components crystallize and oxidize, causing swelling and cracking of wood, and often leading to a dramatic increase in acidity.

The ArCo project, funded in the framework of JPI - JHEP Joint Pilot Transnational Call for Joint Research Projects on Cultural Heritage, is carried out by 5 European research groups. It intends to develop and apply a characterization protocol to understand the decay of archaeological wood containing unstable salts and to investigate the interactions between applied consolidant/bulking agents, wood and unstable salts. The purpose is to provide a list of recommendations for the storage and the preventive conservation of treated wood artefacts.

Several analytical techniques (Py-GC/MS, FT-IR, SEM-EDX, XRF, ICP-OES, XRD, Raman) were employed to investigate wood treated with different methods from different archaeological findings: the alum-treated wood from the Oseberg collection (Norway); the "L'aimable Grenot" and the "Lyon 2nd"ships (France), post-treated with a solution of PEG 20% and disodium sebacate 10%; the Skuldelev and the Nydam ships (Denmark), respectively treated with PEG 4000 and PEG 2000.

The results highlighted the presence of different salts, in particular iron compounds. Wood presented different degrees of degradation depending on the samples and on the applied treatments. The distribution of the consolidating agents into the wood structure was investigated, showing differences in penetration. Further investigations will be performed after artificial ageing to study the stability of the materials.

*Keywords: ArCo project, archaeological wood, unstable salts, SEM-EDX, Py-GC/MS*

## 1. INTRODUCTION

The problem of the unstable reduced compounds in the wooden archaeological artefacts from submarine excavations has been investigated in famous case studies, such as the Vasa, Mary Rose, Batavia and Bremen Cog shipwrecks [1-3]. In particular, in these studies the presence of S compounds potentially dangerous for wood preservation was proven to be mainly related to the action of specific sulphate-reducing bacteria in the marine environment (anoxic water). The reduced sulphur, originally in the form of

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hydrogen sulphide, spreads in the porosity of the wood to form either deposits of elementary sulphur, or of iron sulphide FeS2 (pyrite) in the presence of dissolved Fe II resulting from the iron corrosion. Moreover, after removing from the burial environment and drying, concretions stability is affected by the contact with oxygen and humidity. Sulphur compounds can thus undergo oxidization to produce iron sulphates and some sulphuric acid, and these reactions are catalysed by the presence of iron ions. The final result is the occurrence, on the surface of objects, of mineral rashes which can cause cracks and deformations (Figure 1) and an irreversible acidic attack of the cellulose and lignin of the wood by hydrolysis. [4]. Recently these observations have been confirmed also for other important shipwrecks found in the Baltic sea [5].

**Figure 1** An example of efflorescence in archaeological waterlogged wood.

Conservation treatments are often needed for archaeological waterlogged wood, mainly to prevent the collapse of the structure during the evaporation of water. Polyethylene glycol (PEG) treatment followed by freeze-drying or controlled air drying remains the worldwide standard for preserving degraded waterlogged archaeological wood [6]. Nevertheless, its main limit is the excessive sensitivity of PEG to moisture, making it necessary to install expensive air conditioning systems to control temperature and above all, air humidity. Furthermore, sensitivity to moisture may increase the corrosion of iron and the instability of salts-based concretions in the case of composite artefacts [1, 4]. Recent innovative ideas about consolidating agents aim to create an open porous structure instead of a solid bulk, lighter in weight, with available volume for future re-treatment without removal of the old consolidant. The proposed materials are ‘artificial wood’ type, e.g. using lignin and cellulose mimic compounds to obtain a material which could possibly stabilize/neutralize the dangerous inorganic compounds present in wood [7].

In the framework of the Oseberg’s research biomimetic materials, such as bakelite, crystalline cellulose, chitosan, synthesized lignin have been taken into consideration as possible wood consolidants [7]. In 2006, ARC-Nucléart studied fatty acid systems with the aim to stabilize soft degraded archaeological wood. Azelaic acid was tested because

of its resistance to both hydrolysis and oxidation, its hydrophobicity at room temperature and water-solubility at high temperature (> 70°C), as well as high consolidation capability [8]. Nevertheless, it was observed that azelaic acid was not suitable for stabilising degraded archaeological wood, due to the acidity of the treatment solution (lower than pH = 3), which with high temperature leads to significant chemical attack of wood by azelaic acid [9]. An alternative was the use of salts of sebacic acid (HNaSeb, $Na_2$Seb). In this way, the acidity of the treatment solutions can be easily controlled. The obtained buffer effect leads to pH values between 4 and 7, i.e. close to the pH observed for PEG solutions [10].

The common aspect of these innovative materials is that no available ageing studies exist, and providing them is one of the main aims of the ArCo project. In fact, in the framework of the project different samples from several archaeological findings are under investigation: the alum-treated wood from the Oseberg collection (Norway); the "L'aimable Grenot", the "Lyon 2$^{nd}$"ship and the "La Lomellina" shipwreck (France), originally treated with PEG and then post-treated with a solution of PEG 20% and disodium sebacate 10%; the Skuldelev and the Nydam ships (Denmark), respectively treated with PEG 4000 and PEG 2000. A wide range of analytical techniques were used to investigate both the organic and the inorganic components present in these treated composite archaeological wooden artefacts: pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS), infrared spectroscopy (FT-IR), scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX), X-ray fluorescence (XRF), X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES). The analyses have been performed on archaeological wood samples "as they were", and they will be repeated after about a year of ageing in a climate chamber where the relative humidity is periodically changed.

This paper reports some SEM-EDX, Py-GC/MS and FT-IR results obtained on the unaged samples. The final aim of the project is to investigate degradation patterns in composite materials and to provide a list of recommendations for the preventive conservation of treated composite wooden artefacts.

## 2. SAMPLES

The list of the samples analysed and their description is reported in Table 1.

**Table 1 List of samples analyzed.**

| Provenience | Sample name | Description |
|---|---|---|
| Oseberg collection | 5-AR<br>5-AP | Alum rich (AR) and alum poor (AP) samples taken from fragment 5. Probably birch wood. |
| Oseberg collection | 1B-AR<br>1B-AP | Alum rich (AR) and alum poor (AP) samples taken from fragment 1B. Probably birch wood. |
| Oseberg collection | 1C-AR<br>1C-AP | Alum rich (AR) and alum poor (AP) samples taken from fragment 1C. Probably birch wood. |
| Oseberg collection | 1D-AR<br>1D-AP | Alum rich (AR) and alum poor (AP) samples taken from fragment 1D. Probably birch wood. |
| Lyon 2$^{nd}$ | Ly-A0 | Softwood contaminated by iron salts, untreated |
| Lyon 2$^{nd}$ | Ly-A1 | Oak wood contaminated by iron salts treated with PEG 20% |

| | | |
|---|---|---|
| | | + $SebNa_2$ 10% solution and freeze-dried |
| Lyon 2nd | Ly-A2 | Mineralised softwood, untreated |
| Lyon 2nd | Ly-A3 | Iron nail with concretions |
| L'Aimable Grenot | SM-A0 | Oak wood contaminated by iron salts treated with PEG 4000 |
| L'Aimable Grenot | SM-A1 | Oak wood contaminated by iron salts treated with PEG 4000 and post-treated with PEG 20% + $SebNa_2$ 10% solution and freeze-dried |
| L'Aimable Grenot | SM-A2 | Mineralised oak wood sample treated with PEG 4000 |
| L'Aimable Grenot | SM-A3 | Mineralised oak wood sample treated with PEG 4000 and post-treated with PEG 20% + $SebNa_2$ 10% solution and freeze-dried |
| L'Aimable Grenot | SM-A4 | Oak wood contaminated by iron salts and with beginning of acidification treated with PEG 4000 |
| La Lomellina | Lo-A0 | Softwood contaminated by iron salts, treated with PEG 4000 |
| La Lomellina | Lo-A1 | Softwood contaminated by iron salts, treated with PEG 4000 and post-treated with PEG 20% + $SebNa_2$ 10% solution |
| Skuldelev | Sk-1 | Oak wood treated with PEG 4000 |
| Skuldelev | Sk-2 | Oak wood treated with PEG 4000 |
| Skuldelev | Sk-3 | Oak wood treated with PEG 4000 (dark part) |
| Nydam Bog | Ny-1 | Oak wood treated with PEG 2000 |
| Nydam Bog | Ny-2 | Oak wood treated with PEG 2000 |
| Nydam Bog | Ny-3 | Ash wood untreated and freeze dried. |

## 3. METHODS

SEM-EDX: a JEOL JSM-840 scanning electron microscope was used at the Museum of Cultural History, University of Oslo (Norway). The samples were sputtered using carbon before observation. The accelerating voltage was 20 KeV.

FT-IR: spectra in ATR mode were recorded on a Thermo Fisher FT-IR spectrometer (Nicolet iS50) at the Museum of Cultural History, University of Oslo (Norway). 64 scans and 4 $cm^{-1}$ resolution were adopted. The range was 4000-400 $cm^{-1}$.

Py-GC/MS: analytical pyrolysis was performed at the Department of Chemistry and Industrial Chemistry, University of Pisa (Italy) using 1,1,1,3,3,3-hexamethyldisilazane (HMDS), chemical purity 99.9%, Sigma Aldrich Inc., USA) as a silylation agent for the *in situ* derivatisation of pyrolysis products. The instrumentation consisted of a Multi-Shot Pyrolyzer® EGA/PY-3030D (Frontier Lab) connected to a gas chromatograph 6890 Agilent (USA) equipped with an HP-5MS fused silica capillary column (stationary phase 5% diphenyl and 95% dimethyl-polysiloxane, 30 m x 0.25 mm i.d., Hewlett Packard, USA) and with a deactivated silica pre-column (2 m x 0.32 mm i.d., Agilent J&W, USA). Before instrumental analysis the samples were dried in the oven for 24 hours at 50-60 °C, and after that they were ground with a ball mill. After analysis, the pyrolysis products were identified by comparing their mass spectra with spectra reported in the Wiley and NIST libraries and in the literature [11, 12]. The peak areas were normalized for each chromatogram, and the data from three replicates were

averaged and expressed as percentages, in order to calculate the relative amount of wood components and evaluate the degradation state.

## 4. RESULTS

SEM investigations were useful to observe the preservation state of the morphology of wood and the distribution of consolidating materials. Figure 2 shows some SEM images from six samples taken from the Oseberg collection, the Lyon 2nd, the L'Aimable Grenot, the Skuldelev and the Nydam Bog ships.

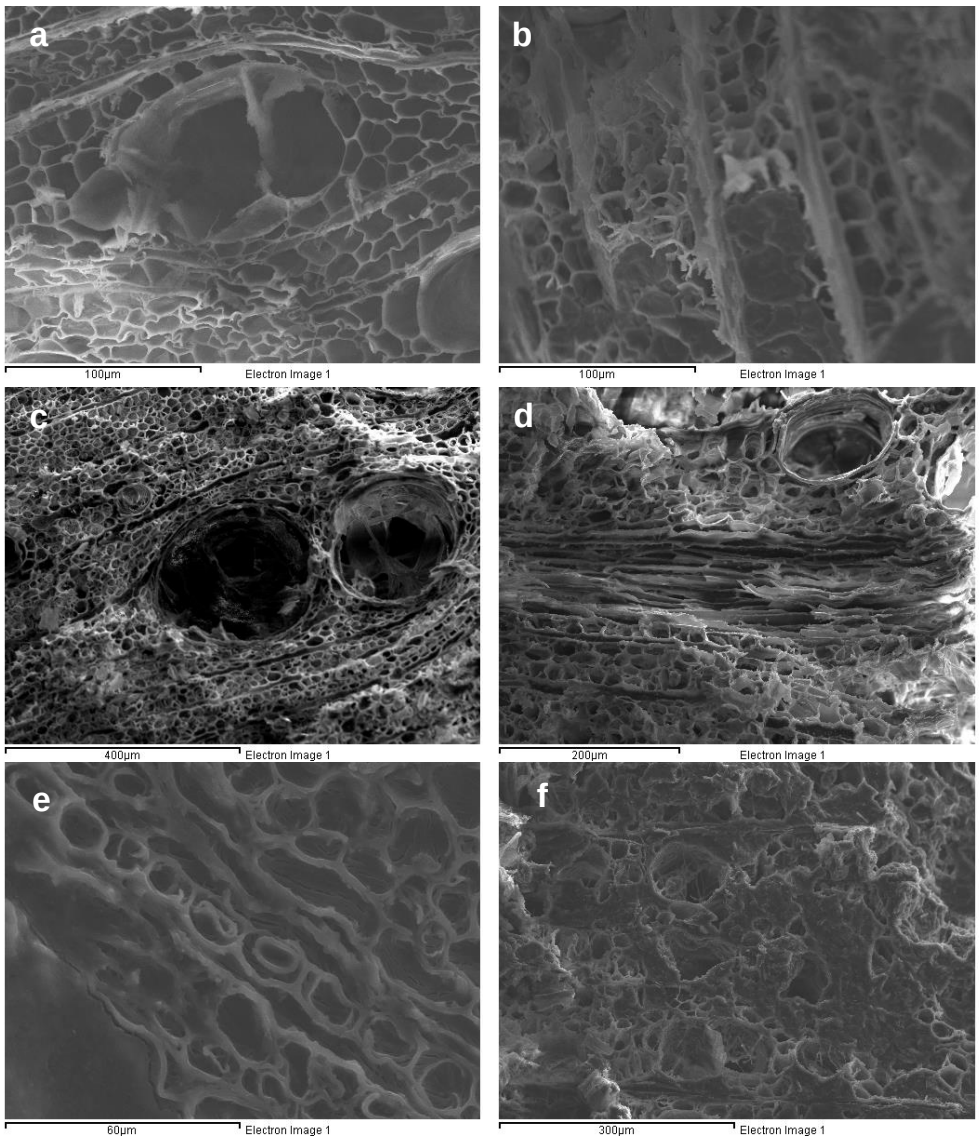


**Figure 2** SEM images for sample **a)** 1C-AP, **b)** 1C-AR, **c)** Ly-A1, **d)** SM-A4, **e)** Sk-3, **f)** Ny-2. The images are taken at different magnifications. Bar scales are reported under each image.

In sample 1C-AP (internal part of fragment 1C, alum poor region) a partial collapse/shrinkage of wood cell wall was evident. The middle lamella appeared to be the only part of cell wall which survived. In sample 1C-AR (external part of fragment 1C, alum rich region) the structural integrity of cell walls appeared almost completely compromised in some areas: the detachment of cell wall was evident, and some cells

were completely collapsed. Spare fragments were also noticed in the cavities, attributable to alum crystals. Similar observations were obtained for the other Oseberg samples. In sample Ly-A1, treated with PEG 20% + $SebNa_2$ 10% solution and freeze-dried, wood structural integrity was quite well preserved, even if partial detachment of the cell walls was noticed at higher magnifications. The wood resulted just partially impregnated. Sample SM-A4 was the only sample from L'Aimable Grenot which showed a not homogeneous impregnation. Where wood structure was visible, it appeared highly compromised, as highlighted by shrinkage of the cell, thinning of the cell walls and detachment phenomena. The samples from the Skuldelev ships were fully impregnated, as shown by sample Sk-3, in which the cell walls were completely covered by a PEG film. Similar observations were obtained for samples from the Nydam Bog.

Using EDS, it was possible to record some mapping of the most abundant elements present in the samples. Regarding the "alum poor" Oseberg samples, K and S were distributed quite evenly and appeared to be penetrated in the cell lumen (Figure 3). No Al was detected, due to the low sensitivity of the technique. Nevertheless, preliminary ICP-OES measurements showed that Al is indeed present in the "alum poor" Oseberg samples, even with less abundance than K and S. This suggests that alum has undergone decomposition or that differences in penetration/diffusion occurred, and further investigations are needed to clarify this aspect. Regarding the "alum rich" Oseberg samples, the observations were similar, with the exception of the general detection of Al, which was mainly present in the same areas as K and S, indicating in this case the presence of recrystallized alum.

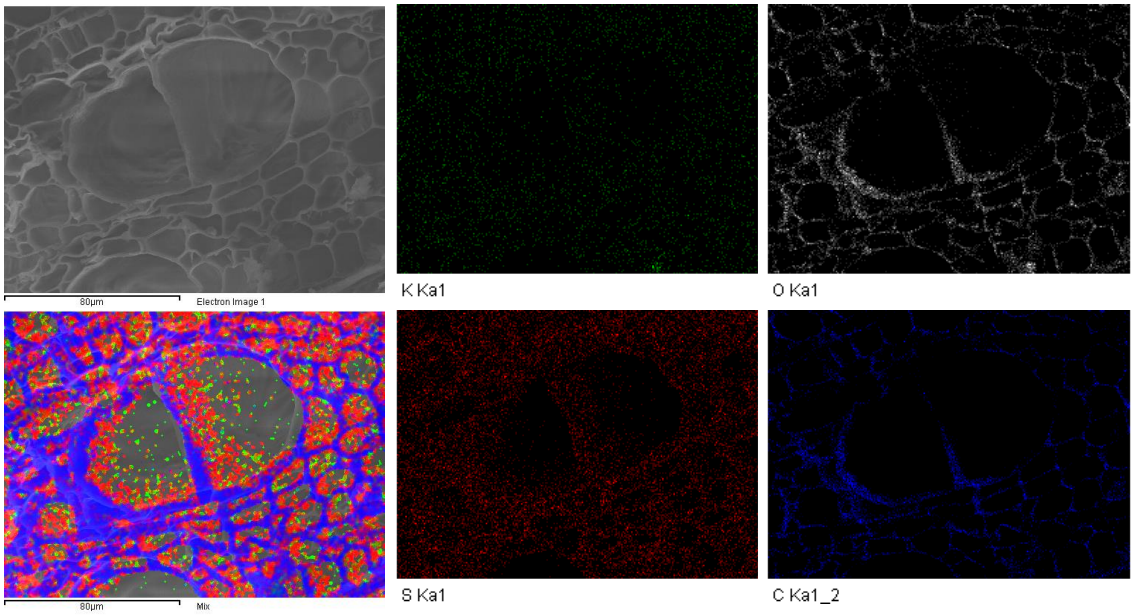


**Figure 3** EDS mapping for sample 1C-AP.

The samples from the Lyon 2nd and L'Aimable Grenot ships showed some partially mineralized areas. The EDS mapping highlighted the presence of Fe, S and Ca as major elements (Figure 4) and crystals with different shapes were observed. Some preliminary XRD analyses confirmed pyrite and gypsum to be present in these samples, likely formed as products of reactions occurred in the marine environment.

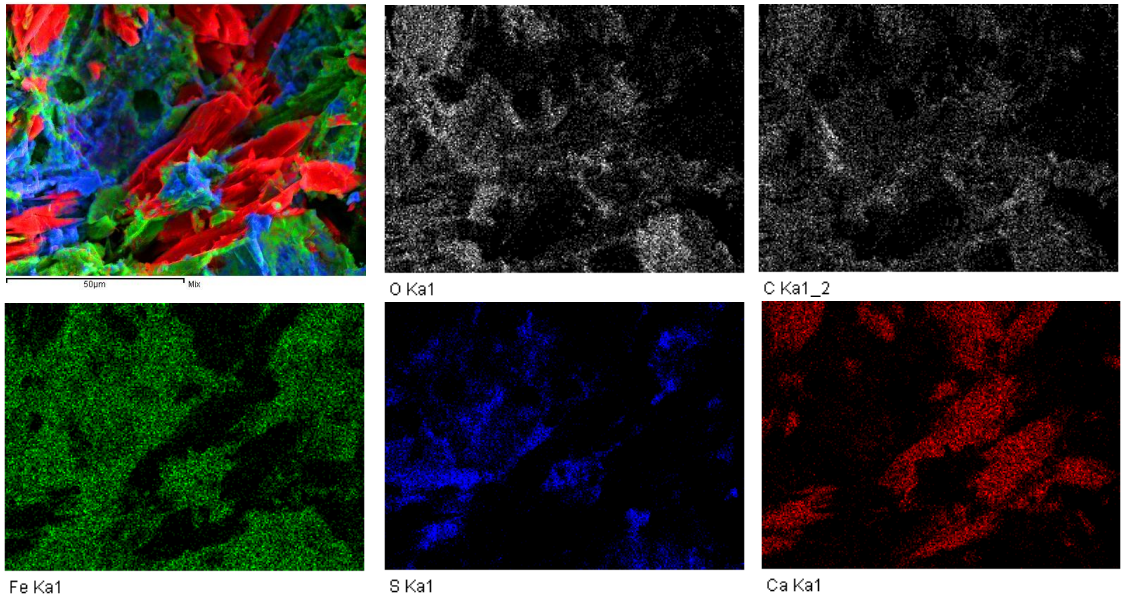


**Figure 4** EDS mapping for sample SM-A2.

In order to assess the chemical degradation state of the wood, Py-GC/MS with *in situ* silylation was applied. 113 pyrolysis products were identified in the samples and attributed to the wood components they derived from (H-holocellulose, L-lignin, G-guaiacyl lignin, S-syringyl lignin). The areas of the peaks were determined, normalised with respect to the sum of the areas of all the identified pyrolysis products and expressed as percentages. The sums of the percentage areas of the pyrolysis products from holocellulose and lignin were also calculated, together with their ratio (H/L ratio). This parameter is indicative of the degradation degree of a waterlogged wood, especially in terms of variation of the chemical composition e.g. preferential loss of holocellulose in the waterlogged environment, when it is compared with the same parameter obtained for a sample of sound wood of the same species analysed in the same conditions [13, 14]. Most of the samples were composed of oak wood, which in these analytical conditions showed a H/L ratio ca. 3.3. In addition, for the first time this coefficient was calculated for PEG-treated wooden samples. In fact, no significant overlapping between wood and PEG pyrolysis products was found in the adopted conditions, as shown in Figure 5.

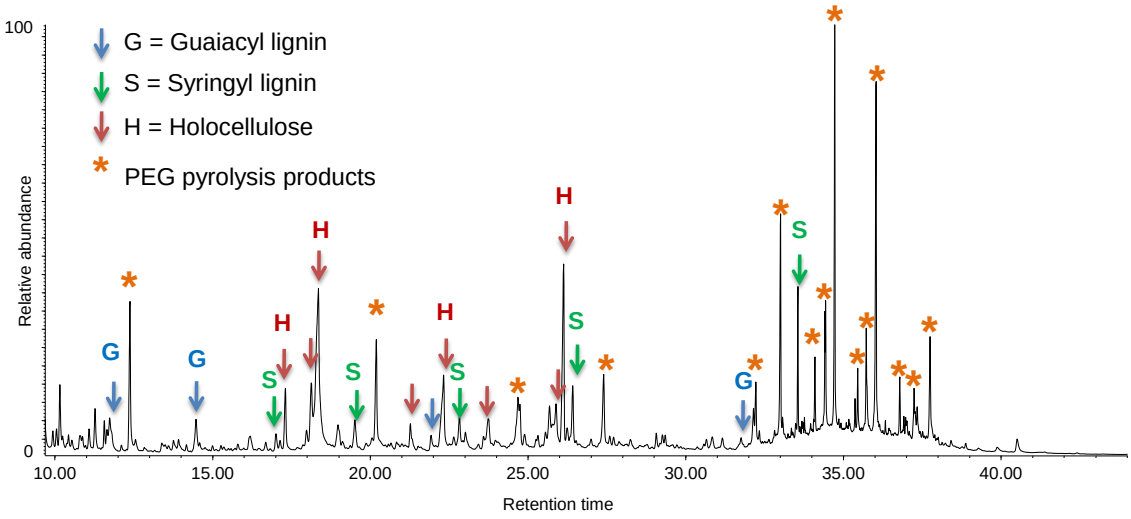


**Figure 5** Py(HMDS)-GC/MS profile of sample SM-A0.

The Oseberg samples showed an almost complete loss of the carbohydrates component, resulting in H/L ratios around 0. In addition, lignin pyrolysis products with acidic functionalities were detected with high abundances (40-80 %), indicating a high extent of lignin oxidation, which was even higher in the alum rich regions. This confirmed the poor conditions of wood in these samples. The H/L ratios for the Lyon 2nd samples were 0.47, 0.02 and 0.20 for samples Ly-A0, Ly-A1 and Ly-A2, respectively. This indicated that sample Ly-A1, post-treated with PEG 20% + $SebNa_2$ 10% solution and freeze-dried, was the most degraded in terms of loss of polysaccharides. Further investigations are needed to understand if the treatment itself could have played a role in promoting this type of degradation. Regarding the L'Aimable Grenot samples, no pyrolysis products from wood were detected for samples SM-A2 and SM-A3, which showed an almost complete mineralisation. Sample SM-A0 had a H/L ratio 2.76, indicative a very good state of preservation of this sample, in which the carbohydrates component was almost entirely preserved. Samples SM-A1 and SM-A4 had H/L ratios 0.59 and 0.79, respectively, highlighting a worse state of preservation. An interesting observation was obtained comparing the results for samples Ly-A1 and SM-A1, both post-treated with PEG 20% + $SebNa_2$ 10% solution and freeze-dried. For sample SM-A1 a peak corresponding to sebacic acid was detected in high abundance. For sample Ly-A1 no such peak was detected, in agreement with Py-GC/MS results obtained in the analysis of pure disodium sebacate, which produced a few pyrolysis products (mainly ketones) with very low abundance, since carboxylates have very low volatility. This suggested that in the sample Ly-A1 disodium sebacate was present in the carboxylate form, while in the sample SM-A1 it has been transformed into sebacic acid, as a consequence of protonation in acidic environment.

To confirm this observation FT-IR analysis in ATR mode was applied to these two samples and to pure disodium sebacate. For both sample Ly-A1 and pure disodium sebacate, an absorption band around 1560 $cm^{-1}$ was detected, corresponding to the typical C=O stretching of carboxylates. This absorption band was not present in sample SM-A1, which instead showed an absorption band around 1730 $cm^{-1}$, corresponding to the typical C=O stretching of carboxylic acids. This was taken as a proof that the

disodium sebacate was completely transformed in the corresponding sebacic acid in sample SM-A1. This was likely due to differences in acidity between the samples and further investigations are needed in order to understand if this reaction could correspond to a positive effect of the applied post-treatment on the general acidity of wood.

The Py-GC/MS results for the Lomellina ship samples are still under interpretation. The samples from the Skuldelev ships showed different results: for sample Sk-1 the H/L ratio 1.44 was indicative of an intermediate state of degradation with a partial loss of carbohydrates. For sample Sk-2, visual observations and SEM images highlighted a significant difference between the core and the surface of the sample, which were analysed separately. The H/L ratio of the core was very high (6.24), indicating a very good preservation of holocellulose and, on the other side, a preferential degradation of lignin, whereas the H/L ratio of the surface was very low, highlighting depletion of holocellulose in this part of the sample. Also sample Sk-3 showed extensive loss of carbohydrates. Finally the samples from Nydam Bog showed similar results with H/L ratios ca. 0.2, highlighting extensive degradation of carbohydrates.

## 5. CONCLUSIONS

This paper summarizes a part of the SEM-EDX, FT-IR and Py-GC/MS results obtained for a series of samples from several archaeological shipwrecks and wooden artefacts, investigated in the framework of the ArCo-JPI project. The analyses will be repeated after artificial ageing of the samples.

SEM-EDX enabled differences in the wood structural integrity of the samples to be highlighted. In addition, the efficacy of the impregnation was assesses as well as the presence and distribution of inorganic compounds.

Py-GC/MS permitted to establish the preservation state of the wood in the samples analysed by the calculation of the H/L ratio, highlighting a significant variability of degradation /preservation conditions. The calculation of the H/L ratio was successfully obtained also in co-presence of organic material different from wood, such as the consolidating agent (PEG). Finally, the disodium sebacate post-treatment was observed to behave differently after application on different samples: for the Lyon 2$^{nd}$ ship no alteration of disodium sebacate was detected, whereas for the L'aimable Grenot ship disodium sebacate turned into sebacic acid, which was observed as one of the most abundant pyrolysis products. This observations was also confirmed by FT-IR analysis.

## REFERENCES


1. Sandström, M., et al., Deterioration of the seventeenth-century warship Vasa by internal formation of sulphuric acid. Nature 2002. **415**: p. 893-897.
2. Fors, Y. and S. Magnus, Sulfur and iron in shipwrecks cause conservation concerns. Chemical Society Reviews, 2006. **35**: p. 399 - 415.
3. Preston, J., et al., The effects of Mary Rose conservation treatment on iron oxidation processes and microbial communities contributing to acid production in marine archaeological timbers. PLoS One, 2014. **9**(2): p. 1-8.

4. Sandström, M., et al., Sulfur accumulation in the timbers of King Henry VIII's warship Mary Rose: A pathway in the sulfur cycle of conservation concern. Proceedings of the National Academy of Sciences, 2005. **102**(40): p. 14165-14170.
5. Fors, Y., et al., Sulfur and iron analyses of marine archaeological wood in shipwrecks from the Baltic Sea and Scandinavian waters. Journal of Archaeological Science, 2012. **39**(7): p. 2521-2532.
6. Grattan, D.W. and R.W. Clarke, Conservation of waterlogged wood, in Conservation of Marine Archaeological Objects C. Pearson, Editor. 1987, Butterworths London p. 164-206.
7. Christensen, M., H. Kutzke, and F.K. Hansen, New materials used for the consolidation of archaeological wood - past attempts, present struggles, and future requirements. Journal of Cultural Heritage, 2012. **13**(3): p. S183–S190.
8. Chaumat, G., L. Blanc, and C. Albino. Development of new consolidation treatments from fatty acid resin solution. in Proceedings of the 10th ICOM-CC Group on Wet Organic Archaeological Materials Conference. 2007. Amsterdam.
9. Pedersen, N.B., P. Jensen, and K. Botfeldt. A strategy for testing impregnation agents for waterlogged archaeological wood. in Proceedings of the 11th ICOM-CC Group on Wet Organic Archaeological Materials Conference. 2010. Greenville.
10. Chaumat, G., L. Blanc, and C. Albino. Study of the azelaic/palmitic acids association to treat waterlogged archaeological wood. in Proceedings of the 11th ICOM-CC Group on Wet Organic Archaeological Materials Conference. 2010. Greenville.
11. Fabbri, D. and G. Chiavari, Analytical pyrolysis of carbohydrates in the presence of hexamethyldisilazane. Analytica Chimica Acta, 2001. **449**(1-2): p. 271-280.
12. Lucejko, J.J., Wet archaeological wood: chemical study of degradation and evaluation of consolidation treatments, in Department of Chemistry and Industrial Chemistry2010, University of Pisa: Pisa. p. 178.
13. Lucejko, J.J., et al., Analytical pyrolysis vs. classical wet chemical analysis to assess the decay of archaeological waterlogged wood. Analytica Chimica Acta, 2012. **745**: p. 70-77.
14. Tamburini, D., et al., Characterisation of archaeological waterlogged wood from Herculaneum by pyrolysis and mass spectrometry. International Biodeterioration & Biodegradation, 2014. **86, Part B**: p. 142-149.