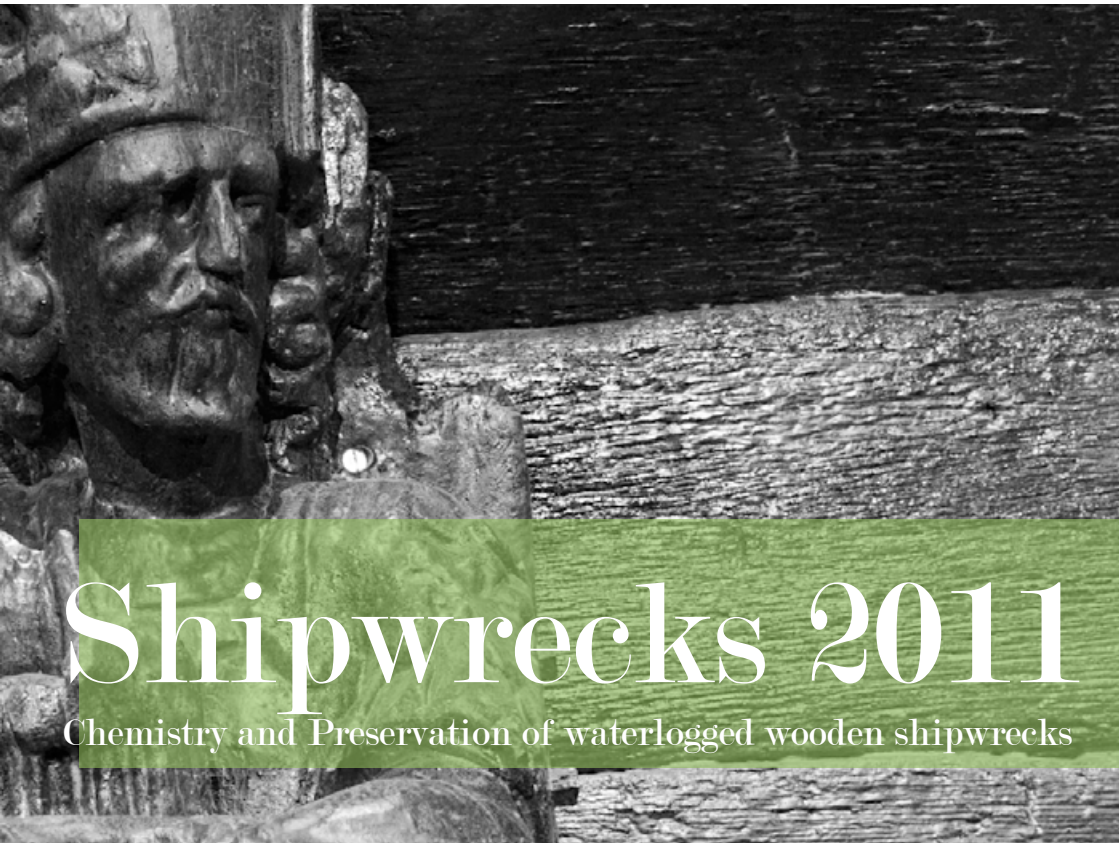

SHIPWRECKS 2011

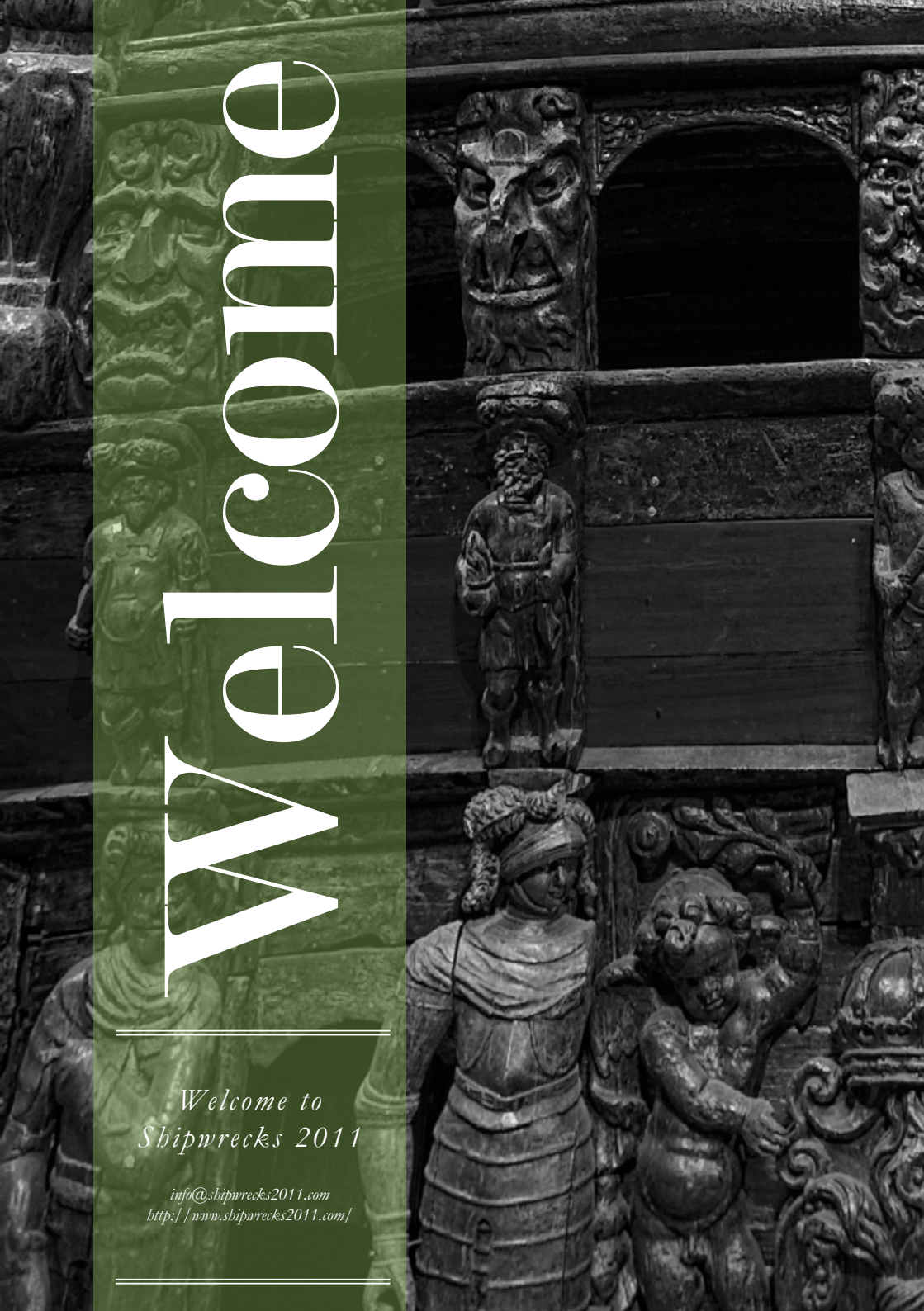
18-21 OCTOBER, STOCKHOLM



Shipwrecks 2011

Chemistry and Preservation of waterlogged wooden shipwrecks





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SHIPWRECKS 2011

18-21 OCTOBER, STOCKHOLM

PROCEEDINGS

CHEMISTRY AND PRESERVATION OF
WATERLOGGED WOODEN SHIPWRECKS

18-21 October

Stockholm

ROYAL INSTITUTE
OF TECHNOLOGY

ISBN 978-91-7501-142-4

Editor - Monica Ek

j o i n t l y o r g a n i z e d b y :



SHIPWRECK

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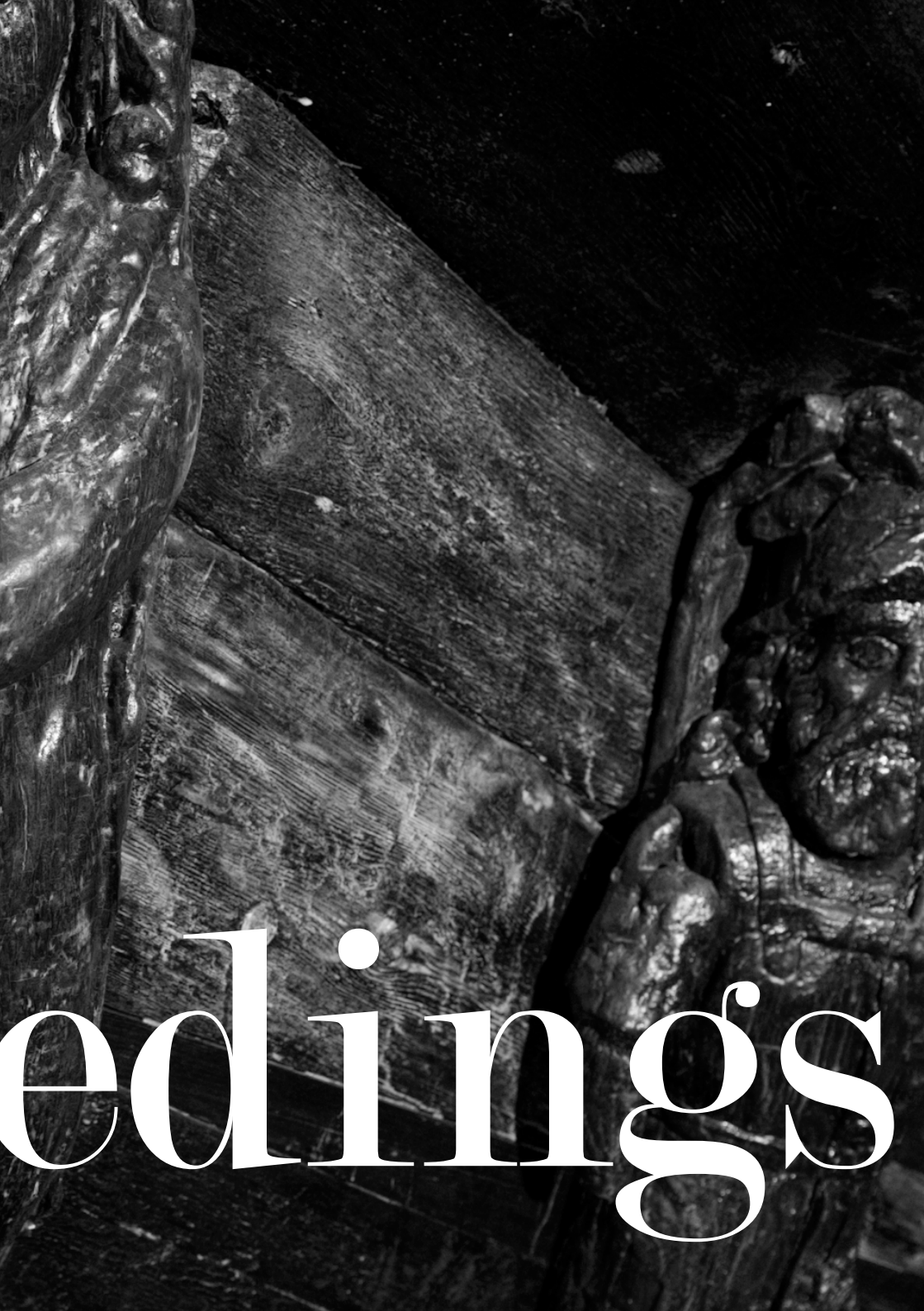
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01.

FROM THE SKULDELEV TO THE ROSKILDE SHIPS - 50 YEARS OF SHIPWRECK CONSERVATION AT THE NATIONAL MUSEUM OF DENMARK

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SUMMARY

Two large archaeological ships finds, the Skuldelev ships and the Roskilde ships, both from the Viking age and the medieval period were conserved at the National Museum of Denmark, nearly 50 years apart. The conservation methods applied to the two finds, reflect the conservation practice which prevailed during these periods and also the progress in conservation methods and scientific knowledge.

The different methods used for conservation reflect the extensive technical and economic resources required for the conservation of ship wrecks. When resources are limited, large archaeological finds often lead to development of new, less resource demanding methods when scientific and technical progresses made over a period of time evolve into new and better conservation methods.

The Skuldelev ships were excavated between 1957 and 1962 and conserved in the period from 1962 to 1975. When the conservation of the wrecks started, the most used methods were still alum and creosote/petroleum treatments. As these methods were quite inadequate, the Skuldelev ships were the first wooden archaeological finds to be conserved with Polyethylene glycol (PEG) in Denmark and thereby opening a whole new era in conservation at the National Museum. New conservation methods, such as 100% PEG impregnation and freeze-drying from tertiary butanol, were introduced.

50 years later a new large archaeological find, the Roskilde ships, was discovered during excavation of a new museum harbour at the Viking Ship Museum in Roskilde. The excavation took place from 1996 to 1997 and when the conservation started in 1998, PEG was still the most frequently used impregnation agent for waterlogged wood. However,

its application has changed over the years due to the progress in the conservation skills and technical developments. For example wood has been impregnated with 45% aqueous PEG solutions and freeze-dried in moulds to obtain the correct shape in order to minimize handling and destruction of the surface of the wood.

Although nearly 50 years apart, the Roskilde ships will follow nearly the same steps during their conservation as the Skuldelev ships. These steps include: field conservation, temporary storage and packing, assessment of the state of preservation of the wood, selected impregnation and dehydration methods, recommended exhibition climate, mounting for exhibition, maintenance and evaluation of long term stability. The presentation will discuss, compare and the present stages of conservation experience and scientific knowledge in relation to the above mentioned steps in the conservation process for the two finds.

THE SKULDELEV SHIPS THE ROSKILDE SHIPS

THE FINDS

In 1962 the Skuldelev ships were excavated from Roskilde Fjord under supervision of Olaf Olsen and Ole Crumlin-Pedersen. The ships were known to the public as a nuisance to the fishermen when sailing through the fjord at low tide. The ships were from Viking age and not medieval as the legend had told. They date from 1030-1050 AD. The find consists of two war ships, two cargo ships and one fishing boat. The timber used for planks and frames are oak, pine and ash. The completeness of the ships differs from 15% to 80%.

In 1996-97 the Roskilde ships were excavated from Roskilde Harbour. The find, being the largest ship find in Northern Europe for half a century, turned up during the construction of a museum harbour for the Viking Ship Museum in Roskilde. The ships date from 1030-1335 AD. The find consists of one war ship and seven cargo ships. The timber used for planks and frames are oak and pine. The completeness of the ships differs from 30% to 60%.

FIELD CONSERVATION/TEMPORARY STORAGE AND PACKING

Investigations were done under water from 1957-59 by frogmen and pieces from the ships were brought to the National Museum for further examination. In 1962 the ships were excavated. A sheet piling was placed around the ships in the fjord in order to excavate the find on land. A water system was established to keep the timber wet until fully excavated. The labelling to identify the objects was done with numbers cast in plastic, fastened to the object with a metal nail. The ships were taken apart and each object was placed in large plastic bags where the pieces were kept moist and held together. Each object was supported on wooden stretchers for transport, and brought to the newly equipped department of Conservation at the National Museum. In 4 months the excavation was completed. When the excavation started no one knew that eight ship wrecks were to be found under the Museums' ground. Seven ships were excavated on land. One ship was excavated under water by diving archaeologists and conservators. A water system was established in the excavations on land to keep the timber wet. The labelling was done with plastic labels, fastened to the object with a stainless steel nail, on which the number of each part was written with a pencil. The ships were taken apart, each object were held together with textile and plastic foil bandages supported on wooden stretchers and placed in water tanks

beside the excavation and kept securely wet until documentation. The documentation took place in a workshop on the museum island. In 10 months the excavations were completed.

ASSESSMENTS OF THE STATE OF PRESERVATION

The frames and planks, keelsons etc. were mainly made of oak (*Quercus* sp.) and smaller amounts of pine (*Pinus sylvestris*). Without treatment, most of these wooden objects would suffer from collapse, shrinkage and surface checks if not conserved properly. The conservator Borge Brorson Christensen discovered during his research on conservation methods for the timbers from the Skuldelev ships, that the degree and pattern of degradation heavily influenced the success of the conservation treatment. Thus, a classification system for waterlogged archaeological wood in relation to its degradation pattern was developed. The system was used for selection of conservation treatment for the timbers of the find. Light microscopy was used to determine the wood species and the degradation at a cellular level. The wet weight, oven-dry weight and volume of small samples were used to determine the density and water-content at a macroscopic level. The demands to assess waterlogged archaeological wood has increased over the years as a correct assessment is not only necessary in relation conservation but also for in situ preservation. A Pilodyn wood tester is used for proxy determination of wood density in the field both under water and at terrestrial sites. An increment borer is used both in the field as well as in the laboratory for taking small core samples up to 15 cm into the wood for density determination. Larger wood samples are taken by sawing of by hollow drills. The wet sample volumes in combination with wet and dry weights are used to estimate: densities, water contents, cell wall densities, porosities and diffusivities. Moreover, electrical conductance is used to estimate diffusion coefficients in the wood. In addition to the density determination, light microscopy, scanning electron microscopy, EDAX, XRF and IR are used to characterize the wood.

DOCUMENTATION

All the ships were documented photogram-metrically in situ. The plotting of the plans and sections of the ships was done from this documentation after the excavation, but very accurate all the same. Instead of paper drawings of the site each element of the ships was photographed in detail. All known data from excavation to storage were recorded by hand, on a card with photographs and sketches: position in excavation, description of element and fragments, species of wood, conservation treatment and place of storage.

After cleaning, the elements of the ships were documented in scale 1:1. The drawings were made with colour codes on transparent polyester foil supported on a glass-plate over the timber differentiating between original edges (black) and fractures (red) on the inside of the plank. The plank and the folio were turned and features of the other side were marked in yellow on the drawing. The reflecting surface of the folio indicated when the feature of the object, tip of the pencil and the mirrored image of the eye of the draftsman were merging, showing the projection was perpendicular to the glass-plate. The precision is within a few millimetres, especially with the planks, while the frame timbers were added more cross sections to make up for the curviness of the element. Full-scale documentation proved to be an important part of the analysis and reconstruction of the ships.

All the ships were documented in traditional drawing in situ, except for the ship excavated under water that was digitally documented using a total station. A database was designed to hold all the information. The 1:1 drawings were done in the traditional way except for the pencils being replaced with felt-tip pens, and in two colours: original edges (black, the outer edge being a broad line, the inner a thin line) and fractures (green) on the inside of the plank. When the plank and the folio were turned the features of interest on the other

side were marked in a stitched line on the drawing. The 1:1 drawing progressed and became digital during the documentation of the ships. A FaroArm connected to a pc with a 3D programme, Rhino, was introduced.

Three ships were almost completely documented in 3D. The precision is within very few millimetres and it is possible to measure the wood whatever shape or form it has. The drawings are 3D, but can be printed to be used for reconstruction. The reconstruction in 3D, however, is still being worked on. Every single element was photographed, in the beginning as analogue photos later as digital. The computer became an integrated part of archaeology and conservation in the years where the Roskilde ships were documented and most information are now digital, from the documentation made in situ to the drawing and description of each element.

SELECTED METHODS FOR IMPREGNATION

When the Skuldelev ships were excavated, the very first timbers were treated with alum, being the most used impregnation agent at the time. However, the use of Polyethylene glycol (PEG) for conservation of waterlogged wood had just taken its beginning, starting with the impregnation of the Vasa.

With the conservation of the Skuldelev ships in mind, Brorson Christensen started his investigations on the possible use of PEG. The first processes were carried out with PEG 4000 at 60°C, impregnation increased stepwise from 10 by 15 % until 95% was reached. This treatment was successful on small pieces of soft timbers, whereas osmotic collapse was observed on the well preserved oak timbers.

Based upon these experiences, impregnation with cold PEG solutions increasing from 25 to 50% (w/w) was introduced. The concentrations of the impregnation baths were controlled using a refractometer. The impregnation lasted from 7 to 24 months.

The ability of PEG 4000 to penetrate into the wood has been investigated and it is clear that the molecular size of high molecular mass PEG is too big to enter the cell wall of the wood. However, to some extent PEG 2000, still a solid impregnation agent at room temperature, can penetrate into the cell lumen and to some extent in the cell wall.



The PEG 2000 acts as a stabilising agent during and after the drying process and works as a cryoprotector during the freezing process. Models for the diffusion of PEG into waterlogged wood according to dimensions and degree of degradation have been developed. The freezing characteristics of the most frequent PEGs have been analysed. Based upon these results, PEG 2000 was selected as impregnation agent for the Roskilde ships. The concentration is increased from 10 to 40% (w/w) at room temperature for at least 3 years depending of the dimensions and degree of degradation of the wood. The concentrations of the impregnation baths are controlled by weighing samples of solution dry them out and calculate the concentration.

SELECTED METHODS FOR DRYING

Brorson Christensen decided to use PEG 4000 for impregnation of the waterlogged wood. Most of the wood was, depending on the degradation pattern, treated in two ways:

- Full impregnation, 95% (w/w) at 60°C
- Partial impregnation, 50% (w/w) at 20°C

The method of impregnating to 95% (w/w) at 60°C works by lowering the temperature of the impregnated object to 20°C, where upon solid PEG precipitates and supports the structure of the wood. A minor part (5%) of the PEG stays liquid in the remaining 5% of the water. The PEG of this solution precipitates upon evaporation of the water during air-drying. This method was used for the more degraded objects, with a tendency to collapse. The 50% (w/w) impregnation was used for lesser degraded objects, like frames. As the solid PEG first precipitates upon removal of the water by air-drying, the method only prevents collapse to a minor degree.

The drying period depended on the thickness of the objects and lasted from a few months to more than half a year. The treated objects were dark, heavy and brittle.

The wood from the Roskilde ships will all be conserved by vacuum freeze-drying. Shipwrecks conserved for exhibition will be freeze-dried in shape. The PEG impregnated objects will be placed in moulds in order to obtain the correct shape. Moulds and wood will be placed in the vacuum freeze-dryer and frozen to temperatures below the eutectic (-25 to -35°C).

The frozen aqueous PEG solution in the wood precipitates in a eutectic structure consisting of ice and solid PEG, both supporting the wood. As no liquid phases are present, the ice can be sublimed by vacuum freeze-drying at a temperature below the eutectic.

The freeze-drying processes take from 4 to 6 months, depending of the thickness of the objects. The treated objects are light in colour and weight, and have the correct shape for later mounting.

SHAPING AND MOUNTING

After conservation, the planks were dry, but not shaped to fit into the reconstructed ship. A fibreboard mould based upon the shape of the original 1:1 documented plank was created. The curvature of the plank was measured and with the fibreboard held in the right shape, a dock with the right curvatures was built. The dry, full PEG impregnated plank was placed on the mould in the dock and heated to 60°C in a humid chamber for several hours until the PEG melted and the wood became flexible. While still warm, the plank in the mould was given the right curvature, fragments were connected with tooth picks or thin wooden and metal sticks and the wood left to cool and solidify. While still in the dock, the plank was lifted to the supporting frame and mounted.

In order to enable mounting of misshapen or flat ship parts for display, all timbers are fixed in the right shape while wet and impregnated. Keel parts and frame timbers are fastened in steel frames, fractures are fixed in the right position and moulds or wedges are placed under the planks before freezing. The curvatures and shapes used in this process are based upon the initial 1:1 documentation and the full reconstruction of the ship. The fixed frozen shapes and positions are preserved during the drying process. Shaping of the timbers while the wood is still in wet, impregnated and flexible condition minimises the risks of the

surface being damaged upon mounting for display. Moreover, the degrading heating of the PEG during mounting is avoided.

REQUIREMENTS TO THE ENVIRONMENT AND LONG TERM STABILITY

The Skuldelev ships were nearly all conserved with PEG 4000, which under normal museum climate (20°C, 50% RH) is a very stable material, as it first starts to absorb water at RH above 85%. As the heating processes in the conservation of the Skuldelev ships have resulted in some degradation of the PEG, the sorption of water can start at a lower RH.

As most archaeological wood, the planks and frames from the Skuldelev ships contained both sulfur and iron in various chemical compositions. During the conservation and exhibition, these chemicals reacted with moisture and oxygen, and at the beginning of the 1980th salt/corrosion products became visible around the original holes for iron nails. These outbreaks, analysed as iron sulfate by Kirsten Jespersen, are mainly believed to be caused by uncontrolled high RH in the exhibition hall. The salts outbreaks did also push solid PEG to the surface, where it became visible as bluish precipitations. Thorough cleaning in 1984 and establishing of a stable climate with a RH close to 50% has stopped further outbreaks.

The Roskilde ships are all being impregnated with PEG 2000 at 20°C, which ensure that the PEG will not be thermally degraded. Undamaged PEG 2000 will first start to absorb moisture at a RH of 80%, far above that of a normal museum climate (20°C, 50% RH). As the dry PEG does only contain a minimal amount of sorbed water, migration of salts and dissolved PEG in the wood should be very limited.

The open structure of the PEG-treated and freeze-dried wood allows a fast access of oxygen into the wood and to the iron and sulfur containing chemical agents. Therefore, eventual problems with salt outbreaks are expected to take place in the first years after the vacuum freeze-drying. Until now there has been no signs of salt outbreaks.

Beside a stable climate (it goes for the Skuldelev ships as well), it is important that the wood is not exposed to high intensity of visual and UV light, and that the air is free from dust, as cleaning of surfaces reduces the life span of the boats.

MAINTENANCE

Museum visitors come close to the artefacts in the building specially designed to exhibit the five Viking ships, and the stealing of fragments from the wrecks has been a problem. Cords have now been put up around each ship as a simple fence and the problem is nearly solved. The dust is a major problem as can be expected in an open exhibition hall, built in the late 60'ies. Once a year, conservators have to remove the dust from the ships.

At the moment, all but one ship have a future in the storage after conservation. One is chosen to be the first archaeological Viking age ship in a travelling exhibition. The frequent moving prevents the dust to settle. However, the extra handling of the archaeological wood will create problems with wear and tear of the surface. Protection against the public is a challenge, as the size of the ship makes it difficult to keep the appropriate distance between the public and the ship.

CONCLUSION

The conservation of the Skuldelev ship was a pioneer project. All parts of the projects had to be developed, new methods invented, exploited, revised and improved. When the

project started in the early 1960's, the tradition for conservation of waterlogged wood in Denmark was 100 years old. Still, this was the first time such a spectacular find was revealed. The find was very different from the previous finds of archaeological wood, the type of degradation was different and the type of objects was new. The amount of wood received at the conservation department called for new conservation procedures, new equipment and an extension of the conservation laboratory. The public awareness and enthusiasm justified allocation of resources and very soon it was clear that all of the ships should be conserved and mounted for permanent display in a museum built for the purpose.

The demands to the conservators were to preserve the wood to a stable condition and with dimensions enabling reassembly of the original wrecks. Not all treatments fulfilled the demands completely, but considering the conditions, the work of Brorson Christensen and Jespersen was a success, it created the base upon which later methods and research was founded and stands today as a milestone in the conservation of shipwrecks.

The conservation of the Roskilde ships is founded on the experiences from the Skuldelev ships, but also the work with other large finds of waterlogged wood mainly in the decade from 1990 to 2000 has increased knowledge and techniques in the field. When new types of finds or large amount of objects are sent to the conservation laboratory, it seems to inspire and initiate the research and development of methods. In the treatment of the Roskilde find, the conservators can apply results from the research in the assessment techniques, new technology in documentation, models for diffusion mechanisms and vacuum freeze-drying processes. The developments in the use of data based monitoring and processing techniques have improved the possibilities for data logging and control.

The progresses have also increased the demands to the result. After conservation, the wood is expected to have a light appearance with only little shrinkage and no collapse. Over the years, the demand regarding public accessibility to a find has changed. And finds are prioritised. This means that no museum will be built for the find, but one of the ships will be conserved, supported and mounted with the intention to travel for exhibition worldwide. This is a new approach to the conservation of shipwreck, but probably not the final one.

02.

THE BATAVIA – PAST, CURRENT AND FUTURE CONSERVATION

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HISTORY

The Batavia, a Dutch East Indiaman, was wrecked on its maiden voyage (1629) when it struck a reef in the Houtman Abrolhos, approximately 400 km north of Perth and 50 km off the Western Australian coast. These waters are warm tropical to sub-tropical and promote high levels of biological activity. The wreck site lies in shallow water subjected to strong surges and heavy surf which promotes physical degradation. The wreck lay undisturbed until its discovery in 1963 and its excavation by staff of the Western Australian Museum in the early 1970s. The only structural timber remains from the Batavia, those of a small section of the stern and lower port side, were protected by burial under a mass of stone blocks, cannon and other assorted artefacts and subsequent coverage by marine sediment and concretion. The anaerobic burial environment, while affording physical and biological protection to the timber remains was responsible for the incorporation of significant amounts of sulfides into the timber. This, combined with the inward diffusion of iron corrosion products from nearby ferrous artefacts, contributed significantly to the post-treatment deterioration of the timbers when subjected to periods of high relative humidity in the display gallery.

CONSERVATION AND RECONSTRUCTION

The timbers were documented and excavated individually, wrapped in wet hessian and placed in large plastic bags filled with seawater and a fungicide, Panacide (2,2'-dihydroxy-5,5'-dichlorodiphenyl methane) prior to being transported to the conservation laboratories in Fremantle. The timbers were desalinated for approximately two years in large tanks filled with tap water. The maximum water content of selected timbers indicated that generally, the exterior of the timbers were moderately degraded (the outer 0-3 cm = 170-250 %)

overlying a relatively undegraded core (40-50 % in the inner regions). Other timbers were more degraded however, with maximum water contents of up to 600 %. The timbers were impregnated by total immersion in heated (60°C) polyethylene glycol (PEG) 1500 solutions. Over a 2-3 year impregnation period the concentration of the PEG, initially 5-10 % (weight/volume), was slowly raised to 90% with an average equilibrium time of 2-4 months between increases in PEG concentration to avoid osmotic shock. The PEG concentration was increased at a rate such that the weight ratio of PEG to water in solution was never more than 20% greater than in the timber (MacLeod 1990).

Because of the size of the timbers freeze-drying was not possible. The impregnated timbers were therefore slowly dried in a dehumidifying chamber in which the initial temperature and relative humidity (RH) were $5 \pm 3^\circ\text{C}$ and $90 \pm 5\%$ respectively. Over a six to twelve month period, the temperature and RH were slowly altered to $22 \pm 2^\circ\text{C}$ and $60 \pm 5\%$ to dry and acclimatise the timbers to the conditions in the display gallery. Shrinkages of approximately 2 % and 3 - 4 % were recorded in the radial and tangential directions respectively. Following treatment, the remains of the Batavia were reconstructed, using the timbers as a guide for the shape and form of the Dimet coated steel support structure. Each timber was fitted to this framework, attached to the support through original bolt holes. This arrangement has proven to be highly beneficial when individual timbers have had to be removed for remedial post-conservation treatment (MacLeod 1990).

ANALYSES AND ACID FORMATION

Although the display environment was temperature ($22 \pm 2^\circ\text{C}$) and relative humidity ($60 \pm 5\%$) controlled, occasional plant breakdowns caused extended periods of high relative humidity ($>80\%$). After display for many years in this environment some of the timbers were encrusted with an acidic white/yellow precipitate. In 1985, investigations related to alleviating these problems were initiated (MacLeod and Kenna 1991). The results of more than 100 surface pH measurements are summarised below (Table 1), with the major minerals present on the surface of the acid affected timbers, identified by X-ray diffraction (XRD) analysis, listed in Table 2.

Table 1. Surface pH and general description of Batavia timbers.

General Description	pH Measurements	
	Range	Average
dark grey with waxy PEG 1500 surface	7.0 - 9.0	7.8 ± 0.7
dark waxy	5.4 - 6.8	6.1 ± 0.5
extensive regions of iron (III) corrosion products	4.5 - 4.8	4.6 ± 0.1
light grey timber, poor condition	2.5 - 5.0	4.1 ± 0.9
light grey wood, patches of rich mineralisation	2.0 - 3.5	2.7 ± 0.5
yellowish, mineralised regions extremely poor condition	1.7 - 4.4	2.8 ± 1.0
light wood, extensive mineralisation, poor condition	1.2 - 3.2	2.2 ± 0.7
extreme degradation, very rich mineralisation	1.3 - 2.3	1.7 ± 0.4

The surface acidity could arise from a number of sources. The degradation of PEG molecules gives rise to formic acid which, with a pKa of 3.75 could produce surface pH readings in the 4-7 range. In addition, saturated solutions of ferric oxy hydroxides exhibit solution pH values around 2 to 3. These latter minerals were the predominant iron corrosion products present on the wood surfaces. Hydrolysis of iron (III) species could also contribute to the timber acidity. It is important to note, however, that none of the previous explanations could account for the extremely acidic wood surfaces where the pH was less than 2.0. These lower pH values were attributed to the presence of sulphuric acid as a result of pyrite oxidation.

Pyrite oxidation can occur via either microbiological or chemical routes. Both these processes however, are dependent on the relative humidity, with a rapid increase in the reaction rate at relative humidities greater than 60%. In order to clarify the major mechanism causing the high surface acidity on the Batavia timbers, swabs of the timber surfaces were taken and cultivated. The timber surfaces were essentially sterile. These results indicated that the primary rate determining step in the pyrite oxidation mechanism was more likely to be chemically and not microbiologically controlled (MacLeod and Kenna 1991).

Table 2. Minerals identified by XRD on acid affected Batavia oak wood.

Name	Chemical Formula	Index Number
Goethite	α -FeO.OH	17-536
Lepidocrocite	FeO.OH	8-98
Iron (II) hydroxide	Fe(OH)2	13-89
Orthorhombic sulphur	S	8-247
Pyrite	FeS2	26-801
Rozenite	FeSO4.4H2O	16-699
Siderotil	FeSO4.5H2O	22-357
Natrojarosite	NaFe3(SO4)2(OH)6	11-302
Jarosite	KFe3(SO4)2(OH)6	22-827
Bilinite	Fe3(SO4)4.22H2O	25-1153
Butlerite	FeSO4(OH).2H2O	23-304
Roemerite	FeFe2(SO4)4.14H2O	13-530

The major white sparkling mineral was identified as rozenite. Pyrite has a molar volume of 24 cm³ while its oxidation product, rozenite, has a molar volume of 98 cm³. This four times expansion in crystal volume during oxidation is likely to cause extreme physical damage to the internal wood structure. Jarosite and natrojarosite, commonly observed oxidation products also have much larger molar volumes than their precursor iron (II) sulphides. The presence of elemental sulphur and so many iron (II) and iron (III) sulphates strongly indicated that oxidation of pyrite had occurred in the Batavia timbers. After this problem was identified (MacLeod and Kenna 1991) and since it was well known that the rate of pyrite oxidation increases dramatically at relative humidities greater than 60%, the RH of the display gallery was reduced to 55% in the late 1980s.

In the late 1990s, another extensive study was undertaken using some of the treated Batavia oak and pine timbers that were unsuitable for inclusion on the reconstructed hull (Ghisalberti et al 2001). XRD analysis of minerals recovered from the surface and from the inner regions of the wood samples identified the usual suite of iron oxy hydroxides, hydrated iron sulphates and pyrite (as per Table 1). In addition to the previously reported compounds (MacLeod and Kenna 1991), melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), siderite (FeCO_3) and magnetite (Fe_3O_4) were also identified in the Batavia timbers. The average surface pH measurements were lower in areas that possessed higher iron contents and the pine samples were more acidic than the oak samples. In addition, the pine samples (% ashav = 30.6 %) were significantly more mineralised than the oak samples (% ashav = 2.5 %), a factor that was considered to contribute to the higher acidity in the pine timbers.

Other experiments involving the impregnation of modern and archaeological samples of oak and pine with degraded PEG 1500 from the original Batavia treatments and with fresh PEG 1500 indicated that the presence of deteriorated PEG is unlikely to be the main contributing factor to the lower pH of the Batavia timbers. Although solution carbon-13 nuclear magnetic resonance spectroscopic (^{13}C NMR) analysis of the extracts from Batavia timbers revealed signals attributable to PEG and to formate/formic acid degradation products (δ 172 ppm), the lower pH of archaeological pine is due primarily to its higher level of mineralisation.

The addition of water to the archaeological samples caused significant recrystallisation of the soluble minerals present in the wood structure, leading to the formation of larger crystals and the conversion of rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) to melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). As with the oxidation of pyrite mentioned previously, these changes in crystal size and hydration state have the potential to physically damage wood structures.

Accelerated ageing experiments, which involved the incubation of shavings of modern *Pinus sylvestris* with goethite and melanterite for a few months in warm, aqueous solutions, followed by analysis of the wood particles by Fourier transform infrared (FT-IR) and solid state ^{13}C NMR spectroscopy, indicated that both melanterite and goethite caused fresh wood to decay. Not surprisingly, melanterite appeared to have a greater overall effect on wood deterioration, most likely due to its much greater water solubility, the acidity of its aqueous solution (pH = 3.48) and the ability of its oxidation product (ferric ion) to catalyse cellulose degradation (Ghisalberti et al 2001).

In addition to the analysis of incorporated corrosion products, acid-affected and non-acid Batavia timbers have been examined to determine the extent of deterioration of the timber components. While line broadening, due to the presence of paramagnetic species, complicated interpretation of some of the solid state ^{13}C NMR spectra, these spectra, combined with FTIR, pyrolysis gas chromatographic and elemental analyses demonstrated that there is significant carbohydrate loss from the Batavia timbers with only traces of acetate present in timber samples taken from the outer wood surfaces (MacLeod and Richards 1997; Wilson et al 1993). There was no evidence in the ^{13}C NMR for a 146 ppm resonance, suggesting that the β -O-4 lignin linkages were intact and, as expected, there was significantly less carbohydrate in the outer parts of the samples. Interestingly, correlation of the maximum water content values of a series of shipwreck timbers, including those of the Batavia, demonstrated an inverse relationship with the % carbon assigned as O-alkyl in their respective NMR spectra (Wilson et al 1993). This is reasonable in light of water saturating spaces previously occupied by hydrophilic carbohydrate components.

DEACIDIFICATION

As the immediate problem was acidic attack on the timbers, it was essential to find a way of reducing acidity levels and slowing the associated degradation processes that led to these elevated acid levels. The preferred deacidification method was non-aqueous, as there were neither the resources nor the inclination to re-immersion the timbers in a water-based deacidification system and then re-impregnate and dry the timbers again. Initially four non-aqueous deacidification methods and two aqueous solutions were tested (MacLeod and Kenna 1991). Use of a methyl magnesium carbonate (3 %) aqueous spray, urea (2 %) in methylated spirits and sodium hydroxide (0.05 M) in methylated spirits had minimal effect on the timber acidity. Gaseous ammonia, saturated ammonia solution and diaminoethane however, were effective in lowering the surface pH of the timber. Given the high toxicity of diaminoethane, the acidic timbers were treated with gaseous ammonia at a local pest control facility. Approximately 200 kg of affected timber were removed from the reconstruction and treated in bulk under a gas-proof membrane. This decision by MacLeod and Kenna (1991) proved fortuitous as subsequent investigations showed that surface treatment of the acidic archaeological timber samples with diaminoethane degraded the wood components, particularly the hemicellulose and holocellulose fractions of the wood (Ghisalberti et al 2001).

The ammonia vapour technique converted acidic iron sulphates to iron oxy hydroxides and a range of less acidic hydrated iron hydroxy sulphates. The surface colour changed to the characteristic red/brown colour of iron oxy hydroxide minerals. Three kilograms of neutralised oxidation products were removed from the surfaces by dry blasting the formerly acidic Batavia timbers. The ammonia neutralisation method has also been successfully applied to selected Vasa timbers (Fors and Richards 2010).

Over the next seven years, the surface pH values were monitored of 28 deacidified and non-deacidified timbers on the Batavia reconstruction. The deacidified timbers did not become more acidic over time, with the average surface pH remaining around 4.0, while the surface pH of the non-deacidified timbers decreased slightly with time. This was attributed to way in which the surface pH readings were taken (drops of distilled water and a flat surface pH meter) and the fact that the surface pH was measured in exactly the same positions over the monitoring period. Surface pH readings on new areas indicated more neutral pH values, indicating that the repeated addition of small amounts of water was promoting chemical reactions in the wood. This decrease in pH with repeated additions of water to the same position on acidic timbers was confirmed in subsequent tests (Ghisalberti et al 2001).

CONSOLIDATION OF FRIABLE, DEACIDIFIED TIMBERS

Surface pH monitoring of the ammonia treated Batavia timbers from the outer and inner port side of the reconstruction continued for over seven years, with the average pH (4.25) not far outside the pH range of seasoned, natural undegraded European oak (4.5 to 5.5). It was observed however, that some of the previously deacidified Batavia timbers were becoming increasingly friable over time. The major mineral identified on the surface of one of these friable, deacidified timbers (F0) was melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). The major mineral identified in the samples of corrosion products collected from the surface of acid-affected timbers prior to deacidification with gaseous ammonia was rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$). It was obvious that the ferrous sulphates on the timber surfaces were becoming increasingly hydrated by the uptake of ambient water from the atmosphere

and/or bound water from the internal wood structure, with the latter mechanism likely to lead to internal desiccation of the timber (Richards 1990). As stated previously, the molar volume expansion of these hydrated corrosion products that occupied void spaces and wood cells, was also likely to result in further physical damage to the internal structure of the timber.

Experiments were carried out to ascertain the most appropriate consolidation treatment to apply to these deteriorating timbers (Richards 1990). Different consolidants, concentrations and solvent mixtures were tested, with the success of the treatment determined by the dimensional and colour changes experienced by the samples. Of the variety of consolidation regimes that were tested, the most effective was vacuum impregnation with 10% (w/v) polyvinylpyrrolidone (PVP) in n-butanol. This treatment was successfully applied to timber F0, which had been removed from the Batavia reconstruction. Dimensional and weight changes were minimal and the average surface pH did not change significantly. There was a decrease in the lightness and yellow-red colour of the timber after consolidation. In order that the timber more closely match the rest on the reconstruction, the timber was coated with colour-matched, tinted 40% (w/v) PEG 3350 in ethanol to offer some cosmetic assistance and to also minimise the detrimental effects of any future changes in relative humidity in the display gallery. The application of this PEG coating also assisted in reducing the residual n-butanol odour, which was pungent even after months of off-gassing in a fume cupboard. Despite some of the issues associated with this consolidation process the results were very pleasing and the wood surface remains stable after many years on display in the gallery environment.

COSMETIC TREATMENT OF THE BATAVIA TIMBERS

One very important advantage of the compatibility of PVP with PEG is that direct application of PEG/pigment mixtures to the timber surfaces was possible, thereby the colour aesthetics of the overall Batavia reconstruction to be improved. Although past deacidification and consolidation of previously deteriorating Batavia timbers have stabilised the reconstruction to a large extent the display remained in urgent need of some extensive aesthetic improvements. After experimenting with different adhesives for repairing broken timbers and filling solutions for covering the very large, visible saw cuts on the reconstruction it was ascertained that the most successful adhesive was 75 % (w/v) PVP in ethanol and the most appropriate filler was a pigmented paste comprising 80 % PEG 3350/8 % PVP in ethanol (w/w) (Richards 2002). These solutions were applied to the reconstruction in 2000 and the repairs and filled areas remain stable eleven years after their application.

FUTURE CONSERVATION / RESEARCH DIRECTIONS

Much research over the past 10 years has been devoted to gaining an understanding of the past and present deterioration and conservation of acid-affected waterlogged wood. Studies on Vasa timbers have been at the forefront of many of these research efforts (Almkvist 2008; Fors 2008; Lindfors et al 2007; Sandström et al 2003) with staff from the WA Museum also contributing (Fors and Richards 2010, Godfrey et al in press). Major differences between Vasa and Batavia timbers include the presence of significantly more iron corrosion products in the Batavia timbers, varying amounts of sulfur and

differences concentrations and molecular weights of PEG used in their respective treatments. Thus, while a very good understanding has been gained of the impacts of iron, sulfur and PEG on the past and current degradation of Vasa wood, much less research has been conducted on the Batavia timbers. Further analyses of the Batavia timbers are therefore planned in the hope that these will shed more light on the impact of contaminants, treatment chemicals (primarily PEG) and the storage environment on acid development and on-going degradation of treated, waterlogged archaeological wood.

Additional work is also planned to investigate the in situ treatment of isolated acidic outbreaks on conserved timbers. This will be of direct benefit to timbers from ships like the Vasa, Mary Rose and the Shinan ship in Korea that generally cannot be easily removed for individual treatment in the laboratory. While it is preferable to maintain appropriate storage and display environments to minimise future acid development, it is an unfortunate reality that occasional acidic outbreaks will continue to occur.

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03.

THE FIRST FIVE YEARS AND FUTURE PERSPECTIVES OF YENIKAPI SHIPWRECKS PROJECT

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Certainly the location of Istanbul at the crossroads of the waterway connecting the Mediterranean and the Black Sea as well as the land route connecting Asia and Europe has contributed greatly to the cultural development and wealth of the city. Due to her location Istanbul has always been, since her early days, a city of higher wealth level where various cultures developed together. Archaeological remains and finds uncovered in the excavations for the subway and Marmaray projects on both the European and Asian sides of Istanbul are of great importance for the cultural history of the world. Particularly the 36 Byzantine shipwrecks uncovered at the Theodosian Harbor known to have been located at Yenikapı is one of the most important discoveries of the recent years (Fig. 1).



Fig. 1 View of excavations at Yenikapı, former Theodosian Harbor and shipwrecks.

The shipwrecks uncovered at the Theodosian Harbor, a well-protected commercial harbour, have survived in pretty good condition as they were buried in the silt brought by the Lycus Stream. The Istanbul Archaeological Museums turned to Istanbul University's Department of Conservation of Marine Archaeological Objects to deal with most of the shipwrecks. Department President and project director Professor Ufuk Kocabaş and a hard-working team of Department assistants, full time specialists and Istanbul University graduate students have been working for over five years in the active construction site in tent-covered pits to document and carefully recover the shipwrecks (Fig. 2).



Fig. 2 On site recording and drawing (YK 22).

Excavations still going on have brought to light thousands of archaeological artefacts. Among these artefacts the 36 shipwrecks constitute the largest ancient shipwreck collection of the world and provide us with invaluable information regarding the Byzantine period seafaring, sea trade and shipbuilding technology. The dimensions of the excavation site as well as the widest ancient ship repertory of the world uncovered are considered the most important project of the recent times and have found great reflection both in domestic and international media and public as well as academia (Fig. 3).



Fig. 3 - Lifting of ship members using carriers (YK 27).

One of the foremost important finds that the Yenikapı excavations have contributed is the discovery of galleys, rarely encountered in archaeological excavations under the water. Archaeological evidence for rowing ships with sails known as galleys dating to the Middle Byzantine period within the Mediterranean world have been obtained for the first time at the Yenikapı excavations. Other known examples of this ship type date to the 14th century and thereafter, i.e. later than those at Yenikapı. To date, six galleys have been identified among the Yenikapı shipwrecks and four of them were studied by the Istanbul University's team. Trade ships of various sizes and possible fishermen's boats uncovered at Yenikapı clearly show the daily activities of the harbour. Our preliminary observations and examinations of the ships uncovered have shown that the ships, whose lengths vary from 8-9 m. to 35-40 m were used for carrying cargo (Fig. 4).

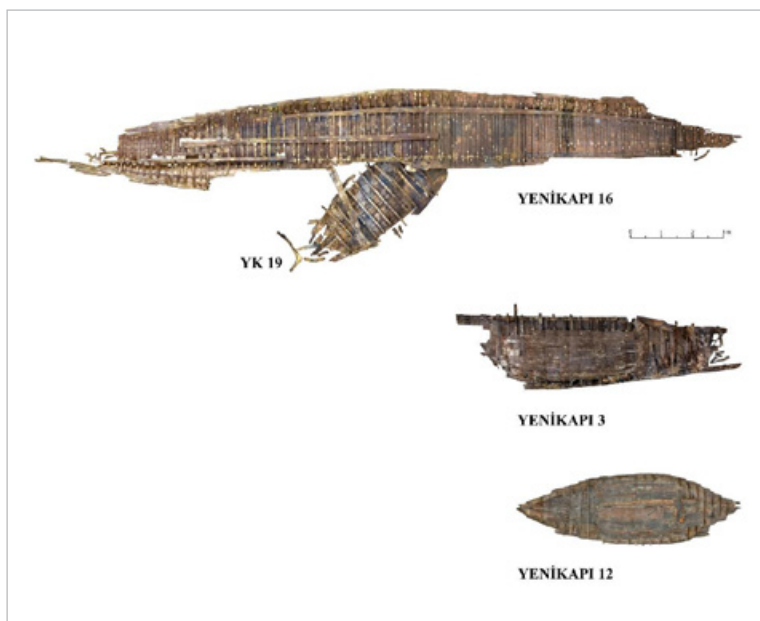


Fig. 4 Scaled photo-mosaics of YK 16, YK 3 and YK 12

The first stage of our project has been going on since March 2006 with the on-site recording, documentation and lifting, a principal rule of archaeology; to date, 26 shipwrecks have been recorded and lifted by our team of 31 experts. Recording and lifting work of the shipwrecks still continue. The second stage of our project covers the 3D drawings of each ship member lifted from the site. Our team implements this stage with the FaroArm device procured by IU's Scientific Projects Unit. Studying the ship members via 3D drawings will allow identification of ancient shipbuilding technologies and their presentation of the national and international academia. Through our work at Yenikapi on behalf of IU since 2006, we have completed the on-site 3D digital drawings of 26 shipwrecks in total using Total Station equipment. Before lifting, full scale drawings on clear acetate as well as high resolution photo-mosaic photographic recording were completed. Two FaroArm 3D drawing equipments procured with the support of IU's Scientific Research Fund in early 2009 has come into use for rendering detailed full scale drawings of dismantled ship timbers in the laboratory. Using these devices, it was possible to draw all the details of YK 12, including coaks and nails, the finest tool marks, original joints, cross-sections etc. that will cast light on its construction technique.

The third stage of our project involves the conservation and restoration of the waterlogged wooden members of the shipwrecks implemented by IU's Shipwrecks Conservation and Reconstruction Laboratories. This work will be carried out by Turkish scientists for the first time and the method involves the wooden ship members getting saturated with the synthetic resin polyethylene glycol (PEG) and Kauramin. With the completion of this stage the wooden members will be reinforced and will be ready for display at the museum foreseen to be established (Fig. 5).



Fig. 5 Istanbul University Ship Restoration and Reconstruction Laboratory

Our work at Yenikapı not only is the first ship archaeology work conducted by Turkish scientists on land but also can be considered the turning point for ship and boat archaeology in Turkey. Utmost care has been paid to make contributions to the scientific literature as well as building up the necessary infrastructure. The first ship conservation and reconstruction laboratory of Turkey has been inaugurated in 2007 at Istanbul University Beyazıt campus.

As a result of the efficient presentation of our project in international platform, the International Symposium on Boat and Ship Archaeology (ISBSA), one of the foremost organizations of the field in the world held every three years, will be held in Istanbul, for the first time, on 12-16 October 2009.

In addition to international presentations, nationwide ones were made at universities, symposia and meetings, particularly underlining the richness of our cultural heritage through press and media contributions were made to the development of public awareness for the protection of cultural heritage.

The first volume of our monograph series foreseen to be published since the beginning of our project has come out with the title “Yenikapı Shipwrecks, Volume 1, The ‘Old Ships’ of the ‘New Gate’” in late 2008. Targeting both national and international audience, our book has been published bilingual in Turkish and English presenting the raw data obtained until then, methodology and preliminary evaluations.

Experts and students from abroad join our team for certain periods of time exchanging knowledge and scientific collaboration. In this frame, our work has become a scientific bridge between Istanbul and various other countries across the world, especially the European countries.

2011 project activities include the removal of last in situ shipwreck, Yenikapı (YK 35) and put an end to the long term fieldwork. It is also planned to complete 1:1 scale detailed drawings of YK 3, YK 6, YK 27, YK 20 timbers and to focus on the conservation procedure of those vessels respectively. In addition, the ongoing renovation of the Istanbul University Ship Conservation and Reconstruction Laboratory is expected to be finished by the end of 2011.

Lecture series will be organized between 2012-2014 with the participation of project team members who continue research on Yenikapı shipwrecks. The second volume of Yenikapı Shipwrecks series will be published by Asst. Prof. Dr. Işıl Özsait-Kocabaş under the title of “Yenikapı 12 Shipwreck”. Besides the second book of the first volume, “Old Ships of the New Gate Volume 1.1”, will be released in 2013. “The First International Maritime Congress of Eurasian Maritime History”, between 5-9th November 2012, will be supported by our institution, also the 12th ICOM-CC WOAM (Wet Organic Archaeological Materials) will be held under the auspices of Istanbul University. Our team also involves replica studies of Yenikapı ships which will begin with the construction of YK12 by the end of 2012 (Fig. 6).



Fig. 6 Illustration of Yenikapı 12 shipwreck after 3D documentation

It is planned to start 1:1 drawings of galley type vessels YK 13, YK 16, YK 25, YK 36, and to complete conservation procedures of YK 1 and YK 12 in 2013 and of YK 3, YK 6, YK 27, YK 20 in 2014. The future aim of the project is to complete 1:1 drawings and conservation procedures of all vessels in 2025.

Our ultimate goal is to make Istanbul own the largest ancient shipwreck collection in the world. No doubt, this collection to attract numerous Turkish and foreign visitors will contribute to the national economy when displayed in a museum to be founded in the future, adding a new value to the cultural heritage of Turkey.

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04.

MICROBIAL DEGRADATION IN THE 18TH CENTURY SHIPWRECK VROUW MARIA

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INTRODUCTION

On the day the Vrouw Maria sank in 1771 she was about 30 years old. She has now been lying on her keel on the bottom of the Baltic Sea for another 240 years in the Finnish archipelago close to the island of Nauvo. Altogether, for about 270 years she has been, in one way or the other, subject to physical, chemical and above all microbial degradation. During her “active” years as a merchant vessel any biological degradation was directed by the presence of air, in other words of oxygen. When still sailing, she was subject to large variations in the ambient temperature, although they were generally higher than the temperature at the seafloor where she has been lying since she sank. The change in the surrounding conditions after the shipwreck would have exerted an influence on the microbial flora present at that time and which could have been introduced either by men or simply distributed through air and water. Vrouw Maria’s situation changed dramatically when she sank 1771 in an autumn storm despite salvage attempts by the crew. Since then she has been lying at a depth of about 40 meters where water is slightly saline, very cold (below 4°C) and where low oxygen-levels prevail. These circumstances now regulate the metabolic activity of any microorganism degrading the wooden structure of Vrouw Maria. Her hull is made of oak, which is more durable whereas the mast parts are made of pine. Different types of wood very likely show different resistance to microbial degradation, an important part of evaluating the possible life span of this valuable shipwreck.

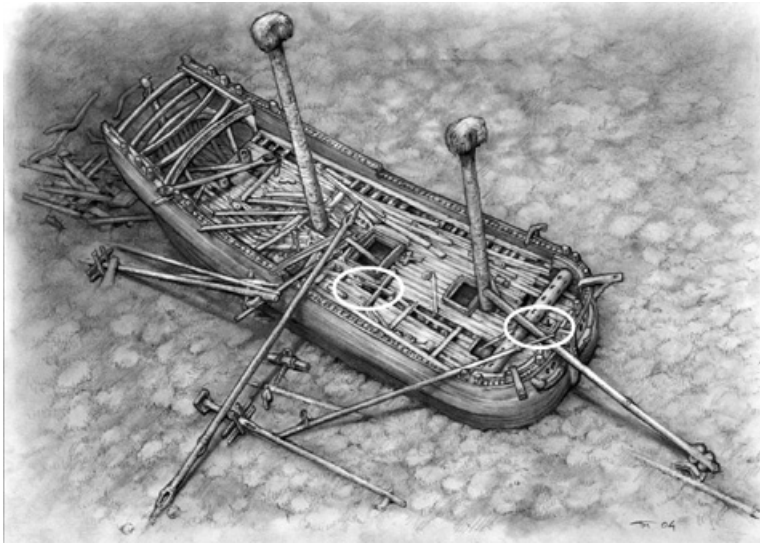


Figure 1: Drawing of the *Vrouw Maria*. Circles mark the original place of the samples. (Drawing by Tiina Miettinen, Finnish National Board of Antiques)

MATERIALS AND METHODS

Two pieces of wood lying loose on the deck of *Vrouw Maria* have been lifted by divers in the past years for research purposes. One is an approx. 80 cm long and 20 cm thick piece of pine wood, possibly part of the rigging, the other the anchor winch stopper, a 1.30 m long 30 cm thick piece of oak wood. Samples for DNA analyses were taken within hours of the lifting from three different depths of the wood, the outmost biofilm layer, the soft degraded wood underneath and the harder, less degraded wood beneath the very soft layer. These subsamples were immediately frozen and kept at -20°C until further use.

We analysed the microbial populations in the wood samples by molecular methods, isolated total DNA, amplified, cloned and sequenced fungal, bacterial and archaeal 16/18S ribosomal genes. The quality of the sequences was checked using the programme 4Peaks highly similar sequences were searched for using BLASTN. Sequences were aligned in SINA, alignments manually adjusted and phylogenetic trees constructed in ARB 5.1.

RESULTS

The fungal sequences obtained belong mainly to aquatic ascomycetal groups with wood-degrading abilities. The majority clustered with an aquatic *Acremonium*-like sequence that has a manganese (II) oxidising enzyme with laccase activity. Sequences belonging to lignicolous clades of *Lulworthia*-like and *Nais inornata*-like fungi were also retrieved. Surface samples also yielded a few chytridiomycetal sequences, which represent a group of lower fungi with versatile degradation abilities.

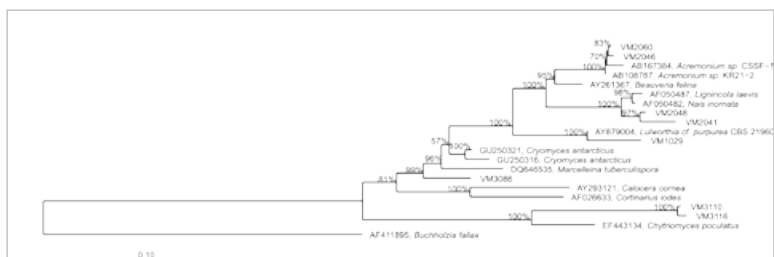


Figure 2: A phylogenetic maximum likelihood tree based on 18S rRNA gene data showing the position of the Vronn Maria (VM) fungal sequences. Bootstrap values over 50% are indicated in the tree. The analysis was conducted with the RAxML programme as implemented in the ARB package.

The bacterial sequences belonged to at least 6 different phyla, many which are previously known to be present in marine sediments, activated sludge and polluted environments. The largest groups of clones clustered with uncultured nonthermophilic marine Chloroflexi bacteria, uncultured Acidobacteria, and with different taxa of Planctomycetes, including clusters Pirellula, Nostocoida and uncultured groups. Some Nitrospira, Verrucomicrobia and Deltaproteobacteria were also present. The majority of the Vrouw Maria bacterial sequences fell into clusters containing mainly uncultured environmental clones, and some lacked close relatives. Thus one has to be cautious when inferring anything regarding their function in the environment.

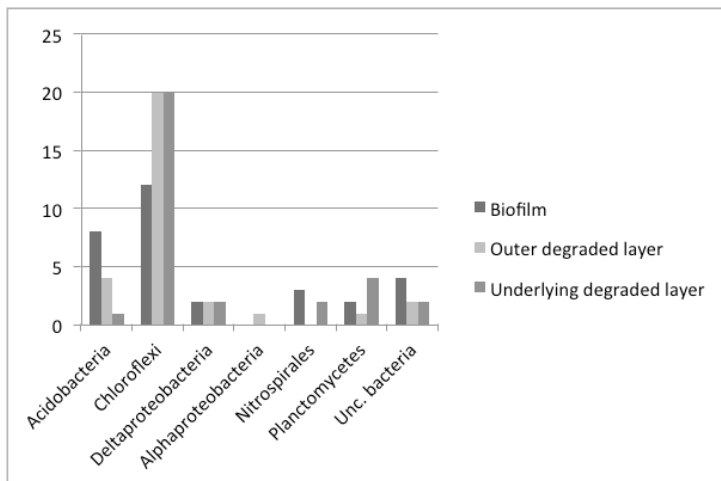


Figure 3: Bacterial diversity in three subsamples of the oak wood sample. Y-axis shows the number of sequences.

The archaeal sequences all belong to the phylum Thaumarchaeota, previously called “mesophilic Crenarchaeota”. They cluster, with one exception, with the marine group I.1a ammonia oxidizing *Candidatus Nitrosopumilus maritimus*. One single clone clustered in the soil crenarchaeotic group (SCG) to which the ammonia oxidizer *Nitrososphaera viennensis* belongs.

DISCUSSION

The wood of the Vrouw Maria remains still in good condition. She was built mainly of oak and a clear influence of microbes was only observed down to about 1 cm in the piece of oak-wood studied. In the pine-wood sample biological degradation was observed down to 4 cm but only the outer layer was heavily degraded. Microscopy, ultrasound, x-ray and molecular biology studies all support these findings. Biological degradation under current circumstances apparently proceeds, but at a slow rate. An indication for this is also the finding that aggressive wood decaying fungi are absent. However most of the Vrouw Maria fungi are probably actively participating in the degradation of the wood.

We did not retrieve sequences that can be associated with erosion and tunnelling bacteria that are generally associated with the degradation of waterlogged wood. These are reported to be early colonisers of wet wood and could be outcompeted by fungi later on. However, when sampling we might simply have missed them, as living organisms would not be evenly distributed throughout the wood. It is most likely though, that the bacteria present in the wood are also participating in its degradation. A sunken wooden ship can be seen as a huge carbon source lying on the seafloor.

The bacterial groups found represent taxa generally associated with low oxygen, nutrient-rich or polluted habitats such as marine sediments, biofilms, polluted water and sludge treatment plants. The most common phyla found were Chloroflexi, Acidobacteria and Planctomycetes. Bacteria belonging to these groups usually produce slime and exoenzymes. Many are to be able to feed on sugars and complex carbohydrates, such as xylan, hemicellulose, cellulose and pectin, all present in wood. Many Chloroflexi and Planctomycetes, are filamentous and form flocs and biofilms. The Vrouw Maria sequences may also be important actors in the global nitrogen cycle. Many of the bacterial groups found in Vrouw Maria are able to reduce nitrate to nitrite, some also to N₂ (denitrification). The ammonia oxidising Thaumarchaeota, to which all the Vrouw Maria archaea belonged, catalyse the first part of nitrification where ammonia is oxidized to nitrite, which is the rate-limiting step in nitrification.

Many of the bacterial and archaeal Vrouw Maria sequences clustered with sequences retrieved from heavy-metal rich habitats. Interestingly enough, some Acidobacteria are reported to oxidize ferrous iron when oxygen is present and catalyze dissimilatory ferric iron reduction under oxygen limited conditions. The number of acidobacterial sequences was highest in the biofilm. This is in closer contact with the seawater, which at the wreck-site has a natural elevated iron content, and gets more oxygen than the inner parts. The wooden surface of the wreck also shows a raised iron content. Only very few sequences of sulphate reducing bacteria were retrieved. This is probably due to the fact that they require stricter anaerobic conditions than those present in our samples. The situation could be different in the parts of the wreck that are in contact with the seafloor.

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ACKNOWLEDGEMENTS

We thank the following bodies for their support:

The University of Helsinki Funds

The Unit of Maritime Archaeology, Finnish National Board of Antiquities

The Wihuri Foundation

The Swedish Cultural Foundation in Finland

The Otto A. Malm Foundation

05.

THE SWASH CHANNEL WRECK - IN SITU PROTECTION AND PRESERVATION

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FOREWORD AND AIM

The Swash Channel Wreck lies in approximately seven meters of water on a flat sand and shingle seabed immediately adjacent to the eastern edge of the dredged section of the Swash Channel in the approaches to Poole Harbour in Dorset, U.K. Environmental monitoring undertaken by Bournemouth University since 2005 produced results indicating that the site is under threat from both physical and biological degradation that is causing a loss of archaeological material, and consequently information, in a very short period of time. The site is exposed to relatively extreme water movements as a combination of natural tidal- and wind-generated currents and vessel movements, with serious influence to the physical state of the hull structures resulting in mechanical damage and superficial erosion.

Due to that a research project was financed having the aim to undertake a programme of in situ experimentation to determine the most effective way of stabilizing and protecting in situ the Swash Channel Wreck versus the most financial way.

The results of this research is it hoped will inform the management party on which could be the most suitable and scientific method for the protection of this site as well as other maritime sites with similar characteristics to the Swash Channel Wreck.



Figure 1 - The location of the Swash Channel Wreck.

THE WRECK

The Swash Channel Wreck is an early 17th century high status armed merchantman lying in approximately 7 meters of water.

The site covers an area of some 50m×40m with extensive structural remains covering an area 40m×20m. The portion of the hull that have been found expose, so far, include the port upper bow, up to and including the top rail, the lower midships area and lower stern.

Archaeological objects raised to this stage include silver spoons, pottery, butchered cattle bone, a copper alloy hand bell, a copper alloy skillet, a wooden carving of a merman, leather shoes, lead shot, rigging elements and a wooden tool handle and a gun carriage. Material known to exist on site (in addition to ship's structure) includes an 8m long rudder with a carved human face at its head, a further small carving, seven iron guns, three barrels, numerous elements of rigging including pulley blocks (with running rigging still rove through them) and standing rigging, cannon balls, ballast, the remains of a galley and possible pump elements.

IN SITU PROTECTION

The protection of the site involved the deployment of various site preservation methods to evaluate those that are the most effective. The methods tested were Netting, Geotextile and Artificial sea grass.

More in depth, the first is a scaffolding net deployed following already published methodologies, aimed to trap the sediment supposed to build up;

the second is a thermally bonded non woven polypropylene/polyethylene which has been utilised as a mat barrier to keep the sediment in place and as a filter by avoiding or limit the passage of woodborer larvae;

the latter is synthetic mat with artificial floating fronds to encourage sediment deposition, similarly to the natural sea grass.



Figure 2 – Site plan showing the location of the trials

The aim of the project was to undertake a program of in situ experimentation to determine which was, among the three methods, the most effective way of stabilizing and protecting in situ the wreck through the analysis of wood decay on sacrificial and hull samples.

The methodology was designed on the experience of several international projects, with the added aspect of scientifically studying the original timber decay and degradation and efficacy of different protective methods, rather than being focused only on sacrificial samples which could offer localised and limited results.

MATERIALS AND METHODS

Sacrificial samples were placed on top of the original hull structure, freely floating in the water column as control samples, and below the protective trials; sacrificial samples were deployed in triplicates for scientific validity and analyzed after twelve months deployment; the analytical method used is the same used for the original wood structure. The selected species were Oak, Elm and Scots pine.

The hull samples were cut off the hull structure prior to the deployment of the three trials. A second series of hull samples was cut off twelve month later in proximity to the previous samples.

The characterization of wood decay was based on four different analyses:

marine borers attack: the degree of attack on behalf of marine wood borers on the sacrificial samples and on the archaeological hull was evaluated utilising the BS EN 275:1992 Wood preservatives. Determination of the protective effectiveness against marine borers, which establishes the degradation by the number of galleries dug by these organisms inside standard measure sacrificial samples. Towards the assessment of the level of attack, all samples were X-rayed;

micromorphological characterisation: investigations were carried out on all wood deployed or collected from the wreck, by means of transmission light microscope on thin wood sections, along the three diagnostic anatomical directions; furthermore it was possible to investigate the conservation state of the cell walls of the wood samples and observe their microbiological attack through a scanning electron microscope; decay classified on 4 grades.

physical analysis: the estimation of decay by means of physical parameters was made through the following measurements: Maximum Water Content (MWC%), Basic Density (BD), Residual Basic Density (RBD%) and, when possible, total shrinkages along the three fundamental directions.

chemical characterisation: it was carried out according to established procedures, following international standard methods routinely used on fresh wood, with minor modifications due to the small amount of available material (TAPPI 1996-7); the following components were obtained from the sieved material: organic and water extractives, lignin, holocellulose, ashes.

During the same period (12 months) the efficacy of the in situ protection methodology was also determined through the measurement of the sediment levels by means of sediment rods controlled each month.

RESULTS

MARINE BORERS ATTACK

The analysis of the X-Ray films allowed evaluating the absence of any attack on the sacrificial samples coming from the Geotextile and Artificial sea grass test fields, while heavy attacks from both *Teredo* and *Limnoria* were found on the samples from the scaffolding net test area, very similar to those showed by the control samples. Some attacks are also visible on the samples from the hull.

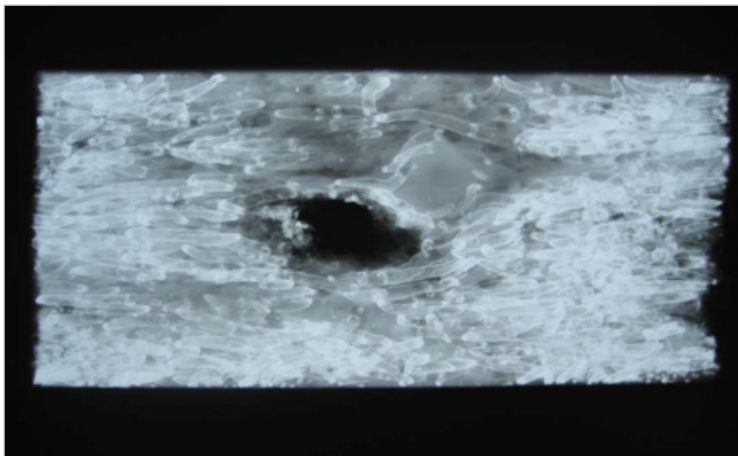


Figure 3: x-ray of sample showing level of degradation by wood borers graded 4 (from netting test)

MICROMORPHOLOGY

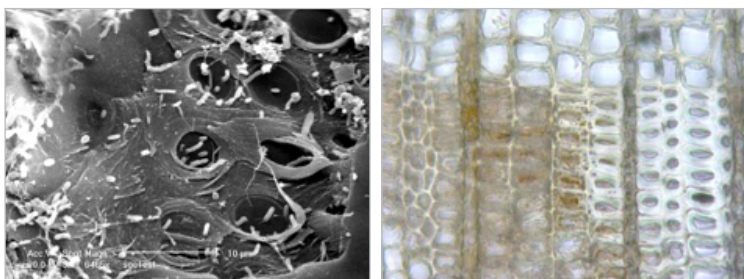


Figure 4: on the left a SEM picture showing the presence of bacteria inside bordered pits (oak wood) ; on the right the red box underline the presence of bacterial and fungal attacks close to a marine borer tunnel (Scots pine)

The worse situation was recorded on hull samples, in particular on oak sapwood samples,

highly decayed. The sacrificial samples coming from the control and from the trials have been deployed underwater for only 10 – 12 months, thus at this stage the decay grading made by morphological characterisation is only able to distinguish if the attack has already started (presence of bacteria or fungal hyphae) or not. The marine borers attack is crucial also as a starting point for bacterial and fungal attacks, because the tunnels are a mean for the introduction of oxygen and pathogens.

PHYSICAL CHARACTERISATION

All the sacrificial samples coming from the control and the trials show parameters establishing a very good state of preservation. The variation of the MWC values are linked to the anatomical features of the different species and to the permeability of wood (e.g. oak samples have not been completely filled by water after 1 year of deployment). The Residual basic density is always very close to 100%, sign of the absence of any important decay, measurable through physical methods. The samples from the hull, on the contrary, showed sensible decay, with an average RDB of 50%.

CHEMICAL ANALYSES

The results from chemical analyses are comparable to those from the previous analyses, except the marine borers attack. No sensible decay is measurable on the complete set of sacrificial samples, where the ratio between lignin and holocellulose is perfectly comparable to that of the sound wood.

CONCLUSIONS

It is granted that anaerobic conditions can be achieved by limiting the provision of oxygen, and a way to do this is by deployment of a consistent and a stable layer of sediment. The other aim is to avoid attack by marine wood borers and the geotextile helps, showing very good results for medium/long term preservations. The system provided the maintenance of the protective sediment layer during the whole trial period. On the contrary the scaffolding net completely failed, because no deposition happened and the sacrificial samples were completely prone to the borer attacks, while the synthetic sea grass appeared good only for short term preservations on such a dynamic site.

During the short deployment period the attack by macro organism seems more crucial to measure wood decay than the classical methodologies utilised for the diagnosis of waterlogged archaeological wood: the bacterial and fungal attack has already started, but the effects are not yet measurable.

06.

SULFUR AND IRON OXIDATION PROCESS IN THE TUDOR WARSHIP MARY ROSE.

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ABSTRACT

Acid production in marine waterlogged archaeological timbers is a major conservation concern relating to the preservation of historic ships. Reduced iron and sulphur compounds, such as FeS₂, are present throughout the Mary Rose timbers; making this ship an ideal model to study iron and sulfur oxidation processes in marine archaeological wood. Sulfate production derived from the oxidation of reduced Fe and S compounds can be a chemical or biological process. However, at low pH values the biological mechanisms of iron oxidation predominate. Acidophile, chemolithotrophic cultures have been enriched using a range of Mary Rose samples as the inocula. Starting material included PEG preserved Mary Rose timbers; biofilm samples associated with the ship, and an unpreserved timber previously containing an iron bolt. A range of halotolerant, chemolithotrophic and heterotrophic organisms have been observed attached to reduced sulfur compounds, suggesting associations between species from different trophic levels are involved in sulphur cycling. Molecular characterisation of the enriched acidophile microbial communities and those of the original inocula has been achieved using 16S ribosomal DNA sequences derived from clone libraries. Experimental data using XANES (X-ray absorption near edge spectroscopy) analysis of FeS₂ impregnated wood (oak) demonstrates the sulphate production at low pH catalysed by halotolerant Fe and S oxidising chemotrophic bacteria enriched from the Mary Rose warship.



STUDY OF BACTERIAL WOOD DEGRADATION BASED ON LABORATORY MICROCOSM- EXPERIMENTS

Jana Gelbrich

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ABSTRACT

Within the EU-Project BACPOLES (EVK4-CT-2001-00043) bacterial wood degradation could be simulated in laboratory experiments to investigate the living conditions of the up to now unknown bacteria consortia, named erosion bacteria (EB), which cause considerable decay on waterlogged archaeological wood. In these Microcosms (MCs) experiments the role of oxygen and chemical composition of the sediment were investigated. Therefore, the microcosms were subjected to different gassing treatments. In further experiments the chemical composition of the sediment was verified to investigate the influence of different nutrient concentrations to the degradation process by EB.

From the findings it can be concluded that bacterial wood decay can proceed without free oxygen present but that it is more intense if oxygen is available. A water flow like streams in the sea, simulated by vertical water circulation, seem to stimulate the degradation activity and the degradation of wood by EB seems to be a result of low nutrient levels of the surrounding.

Most of these results can be used directly as basics for improvements of in situ, reburial or preventive conservation strategies which will be presented here at the example of preventive conservation of two river barges at the German Maritime Museum.

INTRODUCTION

Two partially preserved river barges of late 17th century were excavated in 2007 in Bremen and transported to the German Maritime Museum in Bremerhaven. They should be conserved but at first, a detailed documentation and investigation of these shipwrecks is necessary. There are different reasons, which prevented and still prevent the documentation

and investigation of these barges. Therefore the storage period in water has to continue for an uncertain time. Due to the responsibility in preservation of cultural heritage a preventive conservation concept for the water storage period as well as a monitoring system for EB activity was developed based on the method and results of the laboratory experiments of the EU-Project BACPOLES (EVK4-CT-2001-00043).

In this presentation the methods and results of these already finished and published laboratory experiments will be summarized and it will be exemplified how useful this methodical approach can be for practical monitoring of preventing conservations of wooden cultural heritage

METHODS AND RESULTS OF THE LABORATORY EXPERIMENTS

Within this presentation the methods as well as the results of the laboratory experiments will be summarized based on the already existing publications (Kretschmar 2007, Kretschmar et al. 2008a, Gelbrich 2009, Gelbrich et al. 2010).

MATERIAL AND METHODS

To simulate the bacterial wood degradation under laboratory conditions naturally occurring bacteria consortia are necessary. The source medium of bacteria was sediment and ground water from a heavily decayed pine pile foundation site in the Netherlands as well as already moderately infected pine sapwood sticks. As microcosms (MCs), acrylic glass cylinders or glass jars were used and filled with sediment. The already infected wood was placed in the middle. To stimulate decay, sound pine sapwood sticks were added. All wood samples were completely submerged into the sediment and finally, MCs were filled with water until the sediment column was overlaid by water for a completely water saturated system. The MCs were incubated in dark at 20 °C.

To investigate the influence of available oxygen on the bacterial degradation process different gasses or gas mixtures were supplied in the overlaying water layer of the MCs - 1. Air (21% vol. O₂), 2. Air + Oxygen (app. 50 % vol. O₂), 3. Nitrogen (0% vol. O₂) - and as fourth treatment the Air inflow was combined with a vertical circulation of the water through the sediment column of the MCs as simulation of water current. A scheme of a MC of this experiment is shown in Figure 1. MCs were examined after 120, 150, 195, 350 and 400 days by microscopic investigations described in detail in Gelbrich 2009.

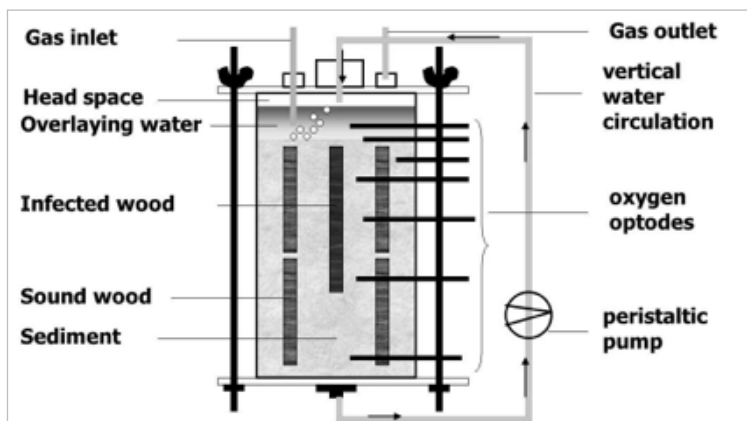


FIGURE 1: Microcosm scheme of the first experiment with gas supply, oxygen optodes and water circulation.

In a second experiment the influence of chemical composition of the sediment was investigated. Therefore, on the one side, the sediment nutrient concentration was lowered by “dilution” with silica sand or pure silica sand. On the other side nitrate, ammonia, phosphorus or sulphate were added to change the sediment composition.

RESULTS

In all but two (nitrogen and sulphate added) treatments bacterial wood attack was found at least after 5 month but with differences in decay intensities and incubation time. Every addition of nutrients resulted in a reduced bacterial activity in wood degradation from which it can be concluded that the wood degrading process by bacteria is attended by nutrient poor surroundings.

All treatments with different gases showed bacterial decay, even the nitrogen treatment, which mean the oxygen free variant. That means that bacterial wood degradation can proceed without free oxygen but it seem to be more intense if oxygen is available. In all gassing treatments, except the circulated one, the bacterial degradation seem to be stagnated or slowed down, because from 195 days onwards, there was no further increase in decay pattern detectable up to the end of the experiment after 400 days. That means on the other hand that exchanges of surrounding material seem to support the bacterial wood degradation process because at all samplings the highest observed bacterial decay intensity was found in the circulated treatment. Thus, it can be concluded, the environments with fluctuating conditions, leading to cycling of various elements, may lead to higher decay rates compared to environments with stable conditions. This is confirmed by Klaassen (2008), who investigated the water flow through wooden foundation piles: “However, if wooden piles are enclosed in water saturated soils with no water-pressure gradient along the piles and hence no water flow through the stem, bacterial wood degradation should be (almost) inactive.

PRACTICAL USE

Two river barges of late 17th century were excavated in 2007 in Bremen/ Germany. The excavation site was on the former island of the river Weser, which was a shipbuilding site for centuries. Due to the location within a river the used bulkhead had to be stabilized by cross bracings of steel to bear up against the water pressure of the river. The distances of these cross bracings were too small for a complete excavation. Therefore the founded 17 and 11 m long shipwrecks had to be cutted in several parts.

STORAGE CONDITIONS

For the storage of the two river barges at first a steel basin of approximately 4 m x 10 m x 1,4 m was built in which the shipwrecks were completely submerged in tapwater and a storehouse was erected around the basin. For the storage conditions it was decided, based on the experiences from the laboratory experiments, to use stable conditions. All fluctuation of water should be prevented and water refillings, which are necessary if you want to investigate the objects, should be minimized or even completely prevented until a detailed concept of handling exist.

The storehouse has no climatic control, except a heating system to prevent the freezing of the water in winter. The water temperature should be as cold as possible but the storehouse is made of steel plates without any insulation and there is a window front in south west direction. To prevent the fast and intensive warming up of the water, especially during summer time, the steel tank was insulated by covering with styrol.

MONITORING

To monitor if wood degrading bacteria are active and in which intensity at our storage conditions, easily degradable, water saturated pine sapwood sticks were used according the laboratory experiments. Due to the well known depth gradient (Björdal et al. 2000, Gelbrich 2009) the samples were arranged in two different depths, 5-7cm and 17-19 cm, under water level (Figure 2). Since December of 2010 every other month samples of each depth were investigated by light microscopy.

Additional monitoring parameters are temperature and pH values of the storage water (Figure 3).



FIGURE 2: Hanging construction of the samples in two different depths (left) and installation in the storage basin (right).

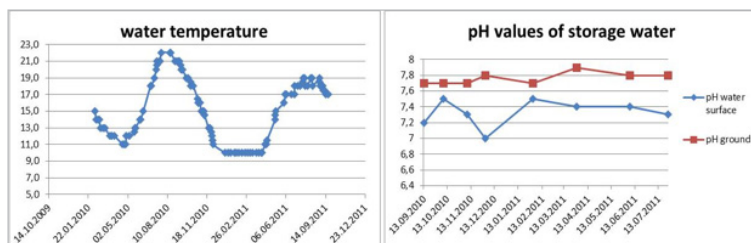


FIGURE 3: Temperature gradation of the storage water since February 2010 which reflects the seasonal changes (left) and pH values of the storage water in two different depths (right).

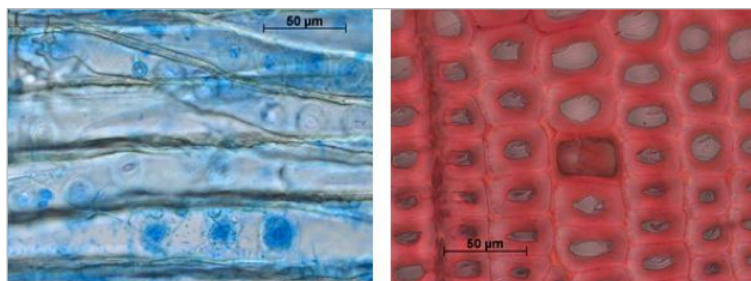


FIGURE 4: Bacterial degradation of the pits in longitudinal section without decomposing ligneous cells (left) and bacterial wood degradation in a tracheid cell, shown in transverse section (right).

Microscopic investigations showed up to 6 month, that there is bacterial activity but no wood degrading activity. The active bacteria of this first stage are cellulolytic ones which decompose parenchyma and pit structures (Figure 4). But at the fourth sampling after 8 month first signs of bacterial wood degradation were detectable (Figure 4).

CONCLUSION

The monitoring system based on the method of the laboratory experiment showed that within our storage conditions bacterial wood degradation can occur. It was detected in easily degradable fresh pine sapwood which stored in the upper part of the basin. Therefore, in this stage no serious threat should be expected for the archaeological remains of oak heartwood. Nevertheless for a longer storage period the conditions have to be changed and the parameter with the best potential to improve the storage condition is the water temperature which has to be lowered before biocides should be used.

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08.

CHARACTERIZATION OF WATERLOGGED ARCHAEOLOGICAL WOOD WITH UV-MICROSPECTROPHOTOMETRY

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INTRODUCTION

Waterlogged archaeological wood is a heterogeneous material. Material characteristics and composition are dependent on; the wood species, the burial environment, type of degrading organisms, and degree of degradation. Erosion bacteria are the main degraders of waterlogged archaeological wood, which erode the cellulose rich secondary wall leaving behind the lignin rich compound middle lamella and a residual material (Björda et al. 1999; Blanchette et al. 1990; Kim and Singh 2000). In waterlogged condition the wood retains the original size and shape since the compound middle lamella remains intact even at very advanced stages of decay. The typical erosion decay pattern is of intact cells distributed among decayed cells. The challenge for conservators is to find suitable treatments that will hinder both shrinkage in intact cells and collapse in decayed cells upon drying of the material. Conservators can benefit from a deeper understanding of the chemical and physical properties of decayed waterlogged archaeological wood at the sub-cellular level. This will be a valuable contribution for development of suitable and effective conservation treatments. To this end cellular UV-microspectrophotometry has been used to characterize the lignin distribution at the sub-cellular level in waterlogged spruce and pine solely decayed by erosion bacteria.

MATERIAL

The examined material was three spruce (*Picea abies*) poles and one pine (*Pinus*) pole. The spruce poles were situated in the moat which surrounded Copenhagen (Denmark) in the medieval period. The poles are estimated to be from the first two decades of the 16th century. The pine pole was part of a well, dated to the 17-18th century and found in Nibe at the northern part of Jutland (Denmark).

Light microscopy investigations of both spruce and pine show a typical erosion decay pattern. No fungal decay or other types of bacterial decay are observed. The surface layers of the spruce poles are heavily decayed with only very few sound tracheids left. Approximately 1 cm from the surface, up to one third of the tracheids are sound. Approximately 4 cm from the surface the majority of the tracheids are sound. The pine heartwood shows only initial decay whereas the sapwood is totally disintegrated at the surface with no sound tracheids left in the material. The inner part of the sapwood is heavily degraded with few sound tracheids.

METHODS

CELLULAR UV-MICROSPECTROPHOTOMETRY

Cellular UV-microspectrophotometry is an established technique for determining the distribution of lignin at the sub-cellular level in wood tissue (Koch and Kleist 2001). In this study a Zeiss UMSP 80 microspectrophotometer equipped with a scanning stage was used to create 2D and 3D image profiles at defined wavelength (280 nm) to visualize the absorbance intensities of lignin in the different cell wall components. The scanning program digitizes rectangular fields of the tissue with a local geometrical resolution of 0.25 μm^2 . The method was used to compare: the waterlogged decayed material to reference material of *Picea abies* and *Pinus sylvestris* sapwood; material with different stages of decay from the same pole; and the decay pattern between the four selected poles.

The wood samples were embedded in Spurr's resin (Spurr 1969). 0.99 μm thick sections were cut with a diamond knife (Ultramicrotome, Reichert Jung) and fixed to a quartz glass slide. The sections were immersed in non-UV absorbing glycerine and covered with a quartz cover slip.

TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy (TEM) was used to characterize the sample material. 0.1 μm thick sections of the Spurr's embedded material were cut with a diamond knife (Ultramicrotome, Reichert Jung), collected on grids and stained for four minutes in 1 % potassium permanganate dissolved in 0.1 % sodium citrate. The samples were examined with a Philips CM 12 transmission electron microscope at 40 kV with magnification from 1.800 to 8.000.

RESULTS

TRANSMISSION ELECTRON MICROSCOPY

TEM analysis of the material confirms that the decay is solely due to erosion bacteria. There are no traces of typical decay patterns from soft rot fungi, tunnelling or cavitation bacteria. The general decay pattern in tracheids is seemingly sound tracheids distributed among degraded tracheids. The decay pattern of individual tracheids is identical in replica samples from the same pole and in samples with different stages of decay. The only difference is that the samples taken close to the surface contain less sound tracheids than samples taken closer to the core of the poles. It is not possible to see any change in cell corners and middle lamella in decayed tracheids. The S1 cell wall is preserved and the S3 cell wall is often only partly decayed. The S2 cell wall is decayed and a residual material is left in the tracheid. The lumina are often filled up with this residual material. Two types of residual material have been observed. Type 1 is light gray and granular. Type 2 is darker gray with transparent perforations. Normally the two types are not observed in the same tracheid but in adjacent tracheids. Type 1 is more frequently observed than type 2.

CELLULAR UV-MICROSPECTROPHOTOMETRY

Cellular UV-microspectrophotometry of sound tracheids distributed among decayed tracheids show the same UV absorbance pattern as tracheids from the sound reference material. This is valid both for sound tracheids from samples taken from the heavily decayed surface layer and for samples closer to the core where the wood is less decayed.

Overall two different UV-absorbance patterns are observed in the S2 cell wall of decayed tracheids. Type A: The residual material from the S2 cell wall fills out the whole cell including the lumen. The absorbance of the residual material is lower than the absorbance of an un-decayed S2 cell wall but contains lignin. Type B: The residual material of the S2 cell wall shows randomly distributed areas with normal absorbance, lower absorbance, and higher absorbance. The lumen is often preserved as a separate unit but may have a low absorbance.

Observations on cell corners in decayed tracheids show that the absorbance pattern is similar to the sound reference material. This is also the case for the absorbance pattern for the radial middle lamella. The tangential middle lamella however has a drop in absorbance intensity compared to the reference material. This is especially the case for tracheids with the described type A decay pattern.

The degradation pattern is similar in latewood and earlywood tracheids. But due to the thin S2 cell wall the pattern is harder to observe in earlywood. The only observed difference between earlywood and latewood is the fact that the lumen is often empty even at severe decay stages in earlywood.

CONCLUSIONS

The sound tracheids distributed among decayed cells do not show any signs of decay that can be observed with light microscopy, TEM or UV-microspectrophotometry.

The more lignified parts of the wood tracheids (cell corners, compound middle lamella) do not show any sign of decay when viewed by light and transmission electron microscopy. However, UV-microspectrophotometry reveals that especially the tangential middle lamella has a lower absorbance than the reference material in decayed tracheids. This shows a so far unknown change in the middle lamella of heavily decayed tracheids.

The UV microspectrophotometry analysis confirms that the residual material left after erosion bacterial decay of the S2 cell wall contains breakdown products of lignin. Even at severe stages of decay the lumina are filled with lignin containing residual material.

Two types of erosion bacterial decay are observed. This might be due to two different types of erosion bacteria or two stages of decay of the residual material.

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09.

CHARACTERIZATION OF ARCHEOLOGICAL WATERLOGGED WOODS BY NUCLEAR MAGNETIC RESONANCE AND GEL PERMEATION CROMATOGRAPHY

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ABSTRACT

In this study, archaeological woods and reference sound woods of the same taxa (*Quercus* and *Arbutus Unedo*), along with the corresponding extracted lignin, were fully characterized by means of phosphorus NMR spectroscopy, two dimensional NMR spectroscopy and GPC analysis. The samples were collected from the Site of the Ancient Ships of San Rossore (Pisa, Italy), where many shipwrecks dating from 2nd century BC to 5th century AD have been discovered.

INTRODUCTION

Historical or archaeological wooden objects are generally better conserved in wet environments respect to other contexts. Nevertheless, waterlogged wood is slowly degraded by the action of anaerobic erosion bacteria, which cause the loss of cellulose and hemicellulose, leading to the formation of cavities filled with water. During this process, lignin can be also altered. The result is a porous and fragile structure, poor in polysaccharides and mainly composed of residual lignin, which can easily collapse when drying and needs specific consolidation treatments. Due to this reason, the chemical characterization of archaeological wood and lignin are aspects of primary importance in the diagnosis and conservation of waterlogged wood artifacts. High resolution nuclear magnetic resonance (NMR) spectroscopy has been one of the most important analytical techniques for 40 years, nevertheless its impact on archaeology until recently has been

minimal for some clear reasons well described by Lambert [1]. Recent developments have dramatically changed this situation and now this technique is used with good results also in the field of cultural heritage. In particular, the possibility to determine and quantify functional groups and intermonomeric bonds in lignin by NMR is demonstrated and the high-resolution nuclear magnetic resonance of ^{13}C , developed in the field of geochemistry to characterize fungal degraded wood[2] and to evaluate lignin in organic matter [3] and sediments [4], was employed to characterize archaeological wood samples from the 11th century excavation site in the lake Paladru at Charavines, France [5]. The main result observed was the preservation of the most abundant intermonomeric bond in lignin structure, so called $\beta\text{-O-4}$. The solid state ^{13}C -NMR is not enough sensible to characterize and quantify the other important intermonomeric bonds present in lignin structure, and with this technique is not possible to observe and quantify the important functional groups such as carboxylic and alcoholic moieties. In order to avoid this problem new NMR analytical tools have been adopted, such as qualitative 2D-HSQC, ^{31}P -NMR analysis which permit to achieve a complete picture of lignin chemical features [6,7]. Another important goal in elucidating wood structure is the preservation of informations about the presence and the extent of any additional interaction between lignin and different biopolymer found in wood. Both GPC [8] and ^{31}P NMR analyses using ionic liquid in order to dissolve wood may provide evidence about the presence of elusive lignin carbohydrate complexes (LCCs) [9] that may be altered to some extent during chemical modifications. In this study we investigated the chemical alteration of archaeological woods samples, along with the corresponding extracted lignin, collected from the archaeological site of the Ancient Ships of San Rossore (Pisa, Italy), where over the last 10 years 31 Roman shipwrecks dating between 2nd century BC to 5th century AD have been discovered [10,8]. The taxa of the examined woods were: *Arbutus unedo* (Strawberry tree) and *Quercus* (Oak).

RESULT AND DISCUSSION

The ageing effects on the structure of archaeological waterlogged wood were at first evaluated by GPC analyses in order to detect possible increase/decrease in the average molecular weights of the extracted lignin.

GPC of extracted lignins after acetylation

Figure 1 shows the GPC profiles of the extracted reference lignin (black line) versus the corresponding isolated archaeological lignin (grey line) for the two wood taxa under examination. Both the archaeological lignins underwent a limited delignification process since no sensible shift towards low molecular weights is observed with regard to reference lignin specimen. Assuming the reference sound sample representatively, it seems that *Quercus* lignin has been subjected to a depolymerization process which mainly affected the high molecular weight fraction while *Arbutus Unedo* lignin underwent a comprehensive consumption.

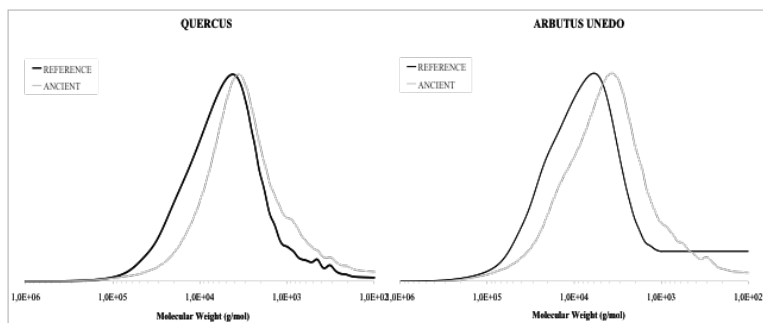


Figure 1. GPC profiles of acetylated lignin, reference sample (black line) compared to ancient sample (grey line), extracted from *Quercus* (left) and *Arbutus unedo* (right).

GPC analyses were also carried out on benzoylated pulverized woods to facilitate the detection of all wood components by UV detection [8]. The materials recovered after planetary milling were dissolved in ionic liquid, resulting in an homogeneous phase, and benzoylated with benzoyl chloride in the presence of pyridine.

GPC of woods after benzoylation

Figure 2 reports the GPC profiles of the unprocessed reference sound wood (black line) versus the analogue archaeological wood (grey line) for the two wood taxa examined after benzoylation.

Generally, the molecular weight distributions show a bimodal trend, due to the contemporary presence of a fraction containing cellulose and lignin carbohydrate complexes (LCCs) and a fraction composed by lignin. For all the ancient samples a significant decrease in the wood molecular weight is detected, mostly related to carbohydrates cleavage. These results demonstrated a deeper and faster degradation of the polysaccharide matrix compared to a limited delignification process, as also clearly conceivable from the Klason lignin data (Table 1). The GPC profiles of *Arbutus Unedo* reference wood highlighted the presence of partially free lignin whereas *Quercus* sound wood chromatogram showed an uniform composition of the analyzed samples. Overall, these results may account for lignin-carbohydrate complexes (LCC) of different chemical type and strength that could influence the degradation process as well as the wood deterioration extent.

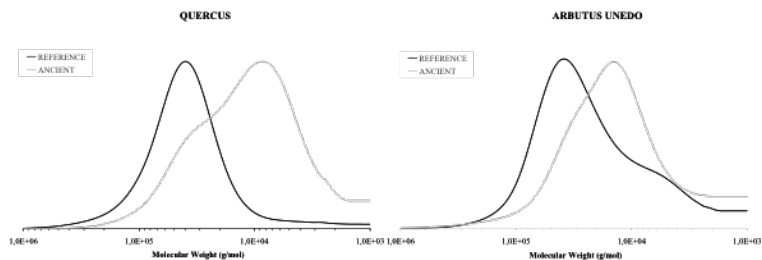


Figure 2. GPC profiles of benzoylated wood, reference sample (black line) compared to ancient sample (grey line), for *Quercus* (left) and *Arbutus unedo* (right)

Sample	Klason Lignin (%)
Arbutus Unedo - reference	32,5
Arbutus Unedo - ancient	73,9
Quercus - reference	31,4
Quercus - ancient	58,7

Table 1. Klason lignin content in archaeological and sound reference wood.

NMR analysis of extracted lignin after acetylation

Lignin and archaeological wood samples were further analyzed by 2D-HSQC spectroscopy Figure 3 to identify the principal intermonomeric bonds and evaluate any significant changes in the lignin chemical structure. The main intermonomeric units in lignin include: arylglycerol- β -arylether (β -O-4), phenylcoumaran (β -5), pinoresinol (β - β), and dibenzodioxocine (5-5'-O-4).

The results, highlighted that lignins extracted from archaeological and reference sound woods were both rich in arylglycerol- β -arylether units (β -O-4). Cross-peaks relating to other principal intermonomeric bonds (β -5, β - β) were also identified.

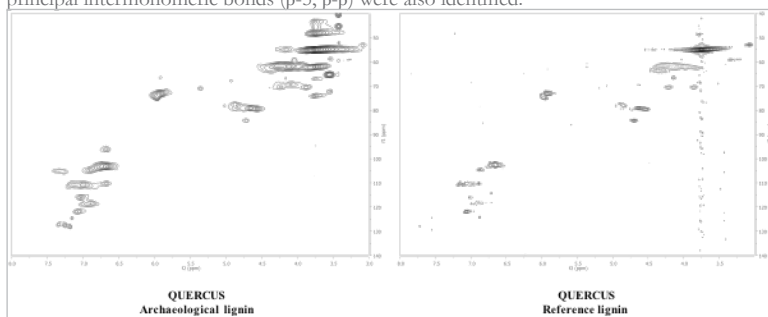


Figure 3. 2D-HSQC-NMR spectra of acetylated lignin extracted from archaeological (left) and reference sound (right) *Quercus* wood.

Lignins extracted from both archaeological and reference sound woods were further analyzed by quantitative ^{31}P NMR spectroscopy to determine p-hydroxycumaryl (P-OH),

guaiacyl (G-OH), syringyl (S-OH) and condensed free phenolic units, as well as carboxylic acids. Table 2 reports the ^{31}P NMR quantification (expressed as mmol/g of lignin) of different phenols and acidic moieties for extracted lignins. All data were normalized on the Klason lignin content. The free phenolic content did not appear notably affected by the ageing process whereas a slight increase in total acidic moieties was observed, according to an oxidative delignification. Such a comprehensive conservation of lignin structure and functionalities was in agreement with literature data [11, 8]. The random trend of syringyl content was attributed to the limited reliability of our reference specimens

	Quercus reference	Quercus archaeo- logical	Arbutus Unedo reference	Arbutus Unedo archaeo- logical
Condensed Ph-OH	0,53	0,54	0,50	0,43
S-OH	0,34	0,64	0,31	0,21
G-OH	0,61	0,58	0,67	0,68
P-OH	0,11	0,08	0,08	0,12
COOH	0,11	0,23	0,24	0,32

Table 2. Extracted lignin – ^{31}P NMR : content values of different free phenols (condensed, syringyl, guaiacyl, *p*-hydroxyphenyl) and total acidic groups, expressed as mmol/g of lignin, normalized on Klason lignin content.

CONCLUSION

The chemical structure of lignin in archaeological woods from Pisa, which after a prolonged period in an aquatic environment have lost most of their original holocellulose content, is still very similar to the chemical structure of lignin specimens isolated from reference sound wood.

The use of innovative solvent system as the ionic liquid [amim]Cl and complementary techniques based on NMR and GPC enables to highlight chemical and morphologic changes in native wood avoiding further degradation. The analyses pointed out a deeper and faster consumption of the polysaccharide matrix along with a limited degradation of the polyphenolic fraction. Besides, it is possible to assess the presence of lignin-carbohydrate complexes which may be altered to some extent during the lignin extraction procedure .

Altogether, chromatographic, spectroscopic and Klason analyses demonstrated a severe degradation concerning archaeological Arbutus Unedo wood. Ancient Quercus wood, instead, showed an overall recalcitrant behaviour towards chemical and/or biological degradation which could be related to the pronounced LCC content highlighted by GPC and quantitative ^{31}P NMR analyses for both archaeological and reference sound wood.

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10.

WOODEN FOUNDATIONS IN VENICE: A PRELIMINARY STUDY

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THE FOUNDATION SYSTEM IN VENICE

The foundation soils in Venice are composed of sand, silt, clay and peat which are often mixed in different proportions; all these layers are relatively compact and show a low bearing capacity. The poles used in the foundation system were made of larch, oak, alder and elm with diameters varying from 10 to 25 cm: normally there were 9 poles per square meter, driven proceeding from outside to the core of the foundation. Poles length ranged from a maximum of 3.50 m to less than 1 m. Once the poles were driven, the heads were sawed to get a regular surface on which two or more layers of wood boarding (“zatteroni”) were set (Figure 1). The interposition of cross-boards upon the palisade favored homogeneous behaviors of the whole foundation system.



Figure 1: poles and boarding, on the left at Rio Acque Dolci, right, Rio San Martino

The basic knowledge of the foundation building system of Venice is quite well known [1, 2]. However, despite this fact scientific investigations on their effective state of preservation are substantially missing. Analogously to what found in the Netherlands [3], a situation of decay emerged from a series of analyses executed on the wooden poles of two ancient Venetian belfries [4], although with a certain extent of variability between the two cases. These occurrences, together with the relevant variability observed, put some questions on the effective behavior of the whole foundation system (i.e. the combination of wood, soil and water) [5].

Present research project was planned starting from these points. Although its outcomes do not allow answering all questions, it establishes a reference for the future.

EXPERIMENTAL

The sites chosen for the sampling were those where Insula S.p.A. was performing interventions: two sites in the insula of San Felice, in the Cannaregio district (at the confluence of Rio delle Acque dolci and Rio dei Gozzi) and one site in the insula of San Martino di Castello (Rio Ca'di Dio) (Table 1).

Site	Wood samples	Typology	Soil samples	Depth of soil sampling
Ca' di Dio	A	boarding	C1_1	0-10 cm
	A	boarding	C1_2	10-20 cm
	B	log	C1_3	25-40 cm
	B	log	C1_4	40-55 cm
	C	pole	C1_5	55-70 cm
	D	pole	C1_6	70-90 cm
	D	log	C1_7	90-100 cm
	E	log	C2_1	0-15 cm
	F	log	C2_2	15-30 cm
	G	log	C2_3	30-45 cm
			C2_4	45-60 cm
			C2_5	60-75 cm
			C2_6	75-80 cm
Acque dolci	H	boarding	C3_1	0-17 cm
	H	boarding	C3_2	18-30 cm
	H	boarding	C3_3	21-45 cm
	H	boarding	C3_4	46-60 cm
	J	boarding	C3_5	61-75 cm
	L	pole		
	L	log		
	M	pole		
	N	pole		
	P	pole		
San Martino	R	pole		
	S	pole		
	T	pole		

Table 1: sampling sites and samples characteristics.

Analyses carried out on wood were focused to evaluate its characteristics at the moment of the extraction from excavation, according to what provided in standard UNI 11205:2007

[6]. Characterization of waterlogged archaeological wood consisted in the:

- analysis of anatomical characteristics, by means of optical and electronic microscopy (SEM and ESEM),
- measurement of: basic density (Db, g/cm³), Maximum Water Content (MWC, %), total substances extractable in organic solvents and in water (%), ash content (%), acid lignin (%) according to the methodology described by standard TAPPI T222 [7], and calculation of holocellulose (%).
- for the soil analysis, organic carbon, total lime content and texture were determined [8], and Fourier-Transform Infrared Spectrometry (FT-IR), thermo-gravimetric analysis coupled with differential scanning calorimetry (TG-DSC), X-ray fluorescence (XRF) and X-ray diffraction (XRD) were carried out.

RESULTS AND DISCUSSION

There was an elevated uniformity in species used in each foundation: in the Rio Ca' di Dio site every analyzed element, independently on the typology, was in larch (*Larix decidua* Miller) whereas in Rio delle Acque Dolci there was a difference according to typology: all poles were of alder (*Alnus glutinosa* (L.) Gaertn.) and boards above piling were made of oak (*Quercus* sp.). Finally, all poles analyzed in Rio San Martino were in Scots pine (*Pinus sylvestris* L.).

Anatomical analyses also allowed evaluating the state of preservation of cell walls as related to the eventual typology of biological attack.

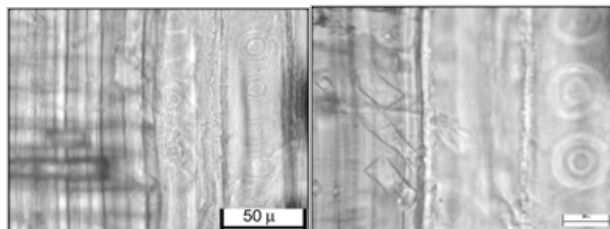


Figure 2: Rio Ca' di Dio. Left, radial section of sample C. Right, radial section of sample D. Both samples were larch (*Larix decidua* Miller). Arrows indicate signs of bacterial attack.

In Figure 2 arrows show clear traces of erosion bacteria attacks. This fact was confirmed from both the presence of diamond-shaped grooves (longer arrow) and thin erosions around border pits (shorter arrow). Traces of bacterial attacks were also visible on transversal sections of softwoods. Also on *Alnus* the traces of the bacterial attacks were evident, reaching in some cases the collapse of the wooden tissue.

Some substantial differences were observed in wood samples taken in the considered sites. In Rio Ca' di Dio, where all samples were of larch, the state of preservation is on average quite good, mainly when compared with values often found in archaeological excavations. Measured average basic density was 0.35 g/cm³ against a literature average value of 0.56 g/cm³ for non-degraded wood, and values of holocellulose-to-lignin ratio (H/L) for samples taken from poles ranged from 1.6 to 2.4 (Figure 3), corresponding to approximately 60-80% of the analogous value for non-degraded wood. Instead, samples from boarding were in a worse state of preservation, with H/L of the order of 40% of that for non-degraded

wood, associated with a high variability among the analysed portions. A similar occurrence was also found for another larch sample, also taken from a board in Rio delle Acque Dolci site. This let suppose an effect of the different lying position in which samples have been preserved in service conditions (horizontal for boarding, vertical for poles).

In the Rio delle Acque Dolci site more wood species were used. Concerning oak, the analyses evidenced a quite good durability, with H/L ratio of 60% of that for non-degraded oak wood. Conversely, alder samples appeared generally decayed. In these cases the low measured values of MWC (thus apparently indicating materials in good conditions) were imputable to collapse of cells, which in fact increased the basic density of samples. This occurrence demonstrated the importance of a multidisciplinary approach for a correct diagnosis. Finally, in Rio San Martino site all samples, made of Scots pine, were in a uniform state of preservation, corresponding to a basic density of 0.2 g/cm^3 (40% of that for non-degraded wood), which evidenced an appreciable level of decay.

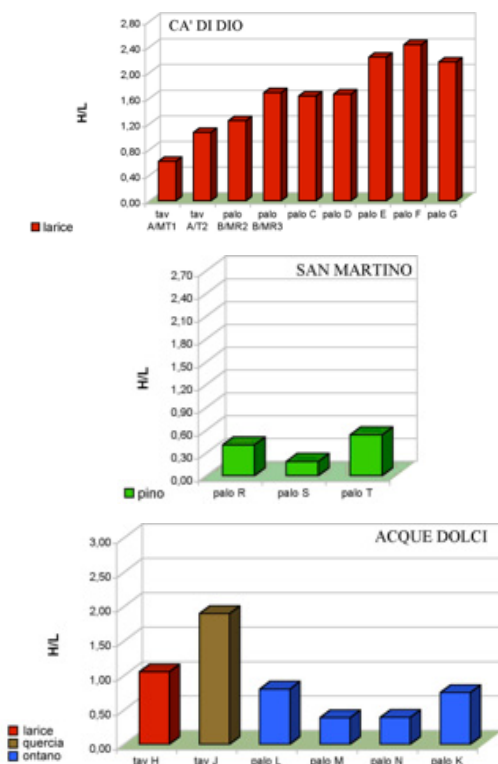


Figure 3 a,b,c: values of Holocellulose-to-Lignin ratio (H/L) for samples taken from the considered sites. The maximum values in the y-axes correspond to the H/L ratio for non-degraded wood of the considered species.

To analyse soil characteristics, during sampling, pH and redox potential (Eh) measurements were performed in situ on foundation soils.

The pH values were typical of the slight alkalinity condition: pH values tended to decrease slightly as the depth increased. In the foundations system, soil is completely immersed in water and therefore the absence of oxygen leads to reducing conditions. Eh measurements confirmed the status of strong reduction in soils in contact with foundation poles: the Eh values were all negative, between -16 and -90 mV.

The percentage of organic matter in soil samples was around 3-4%. This value increased with increasing depth and this was probably due to the lagoon sediments that are rich in organic matter and their accumulated layers in the canals.

All samples contained between 8 and 15% of carbonates: as shown for the organic matter, the quantity of limestone seemed to be correlated with the sampling depth. Consequently, big amounts of limestone influenced directly the increase of pH values up to 8.5 (as recorded in situ).

According to the triangle of soil texture by USDA (United States Department of Agriculture), foundation soil textures have been classified by the fractions of each soil separate (sand, silt, and clay) and they were on the average all included in the classes sandy clay and sandy clay loam. In particular, while the depth increased, the percentage in the amount of sand increased too and the percentage of clay and silt, which were the smaller fractions in soil, decreased.

The presence of calcium, iron, silicon, potassium, aluminum, sulfur and traces of titanium, chromium and manganese were detected by XRF analysis (Figure 4). FT-IR and termogravimetric analysis results showed that carbonates (in particular calcite, dolomite and siderite), silicates and clay (as illite and albite) were present in the soils samples. It's important to underline that the formation of siderite, FeCO_3 and pyrite, FeS , occur only when redox potential values are negative (reduction condition): that was the case for the Venetian sites as already shown.

These results were confirmed by XRD analysis which evidenced the presence of calcite, dolomite, albite, sepiolite, illite and quartz in foundation soils.

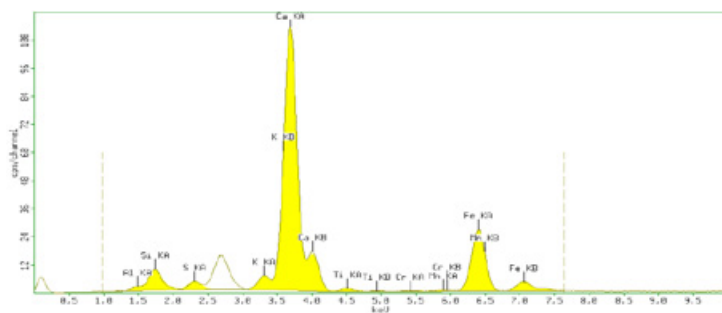


Figure 4 : XRF spectrum of sample C1_1

CONCLUSIONS

This research allowed for the first time to get a range of information on the behavior of the Venetian foundation system: this can be considered the beginning of a scientific knowledge based on the conditions and characteristics of the wooden foundations of buildings.

The analyses carried out on wood samples confirmed that, in the service conditions of foundations, the material was subjected to decay processes. However, kinetics of decay were apparently slow, although this aspect needs to be further evaluated.

The identified wooden species (namely larch, Scots pine, oak and alder) are in agreement with those found in previous investigations carried out for tower bells of Frari and S. Stefano, in Venice [4], and also with those reported in the Bacpoles Project [9]. Decay was essentially of biotic origin, and more specifically it was imputable to the action of erosion bacteria, identified by means of microscopic analyses. These organisms attack wood in almost total absence of oxygen.

The analyses on foundation soils allowed defining the most significant parameters for the characterization and the comprehension of the behavior of soils in contact with wooden foundation. In particular, the state of slight alkalinity, the negative redox potential, the significant amount of organic material are fundamental to understand the state of preservation of Venetian foundations.

ACKNOWLEDGEMENTS

This research was funded by Corila (Consorzio per il coordinamento delle ricerche sul sistema lagunare di Venezia) and it was included into the “Secondo Programma di ricerca” of Corila (Architecture and Cultural Heritage).

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11.

THE WATERLOGGED WOOD OF THE SHIPWRECKS FOUND IN PISA (ITALY). DIAGNOSIS AND CONSERVATION

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FOREWORD

The recovery of well-preserved ancient wooden artifacts of historical value gives rise to several questions pertaining to their preservation, the extent of degradation and the way for their conservation. This situation arose when in Pisa (Tuscany-Italy), in the first years of 2000, during infrastructural works for the realization of the Tyrrhenian railway control station, several shipwrecks were discovered not far from the Leaning Tower (Giachi et al., 2000; Giachi et al., 2006). The shipwrecks were found in a disordered state probably because of the many floods of the Arno river which occurred over the centuries, and are dated back from II cent. BC to VI cent. AD (Figure 1).

All the ships (at the present time 31, entire and fragmented hulls) were covered by sediments of clay and sand, which have different contents of interstitial water and different degrees of permeability, despite both are saturated with water. Wood elements appeared completely waterlogged and with spongy consistency, even if the aspect and the shape of the wooden artifact seemed very good.

The concern that arose from this discovery was not only the one created by the removal of the hulls from the site but, obviously, also that of their conservation and the better way to plan the conservation treatments. While the excavation went on, a diagnostic study was realized to point out the state of preservation of the wood of the Pisan ships.

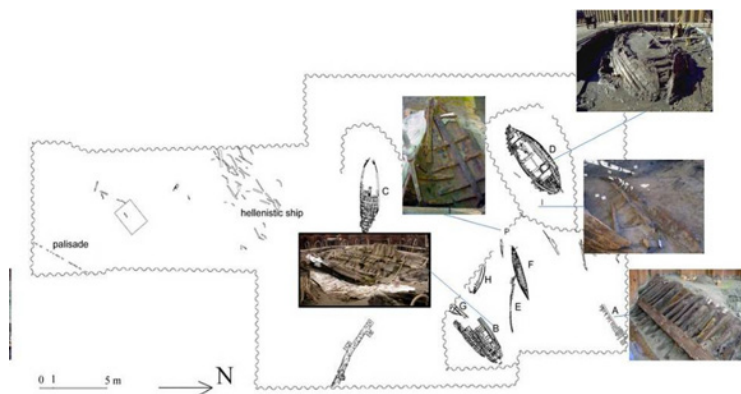


Figure 1. The excavation area in Pisa and some of the shipwrecks here found.

WOOD DECAY CHARACTERISATION

Wood characterisation was performed following Italian standard UNI 11205:2007. and consisted in:

- micro-morphological analysis on wood sections along the three diagnostic directions (transverse, longitudinal-radial and longitudinal-tangential), aimed to identify the wood species, analyse the state of preservation of the cell walls and to obtain as much as possible information about the organisms that caused the decay (Bjorndal et al., 2000; Blanchette et al., 1990);
- physical analysis, with simple methods. It allows obtaining the following parameters: Maximum Water Content, MWC%; Basic Density, Db; Residual Basic Density, RD_b, which are the most utilised parameters available on the literature to measure the decay of waterlogged archaeological wood (Macchioni, 2003);
- chemical analysis. It followed the methodology set-up for sound wood for the pulp and paper industry (TAPPI standards, 1996-97), but modified in order to give reliable results also for the small amount of material available from archaeological samplings (Pizzo et al. 2010). The obtained results (in particular the determination of the residual amounts of Holocellulose and Lignin, and evaluation of their ratio H/L) represent a time-consuming, but reliable method to chemically show the extent of the decay of cell walls (Capretti et al., 2008).

The result is not only a series of separated analyses, but also a complete diagnosis coming out from an integrated evaluation of the obtained results.

The results put in evidence that lot of wood species were used for the construction of the ships: some of these were entirely realized with hardwoods; in other hulls the planking was entirely made using coniferous wood, but the frames were of different hardwoods. Figure 2 shows, as an example, the distribution of wood species on the ship “C”.

The decay of wood of the Pisan shipwrecks, mainly due to erosion bacteria, is extremely severe: MWC values are mostly between 450 and 550%, but often reaching 700%; RDb is mostly ranging between 20 and 30%. In most cases the H content is as low as 10%, thus the H/I ratio, that should be included between 2.5 – 3, is frequently below 0.5. The inorganic content of wood is very high (ash > 10%) and derives from calcite, gypsum, pyrite and iron oxides. The direct consequence is the absolute need for a consolidation of the material, in order to avoid the collapses and the loss of the shape of the artefacts.

Sample	Specie	MWC (%)	RDb (%)	H/L
A1	Oak	261	46	0.08
A2	Maritime pine	483	35	0.44
A3	Oak	506	26	0.11
A4	Elm	543	29	0.12
A5	Walnut	462	31	0.13
A6	Oak	633	21	0.13
A7	Maritime pine	362	45	0.33

Table 1. Example of the principal results obtained from the samples from the ship *A*.

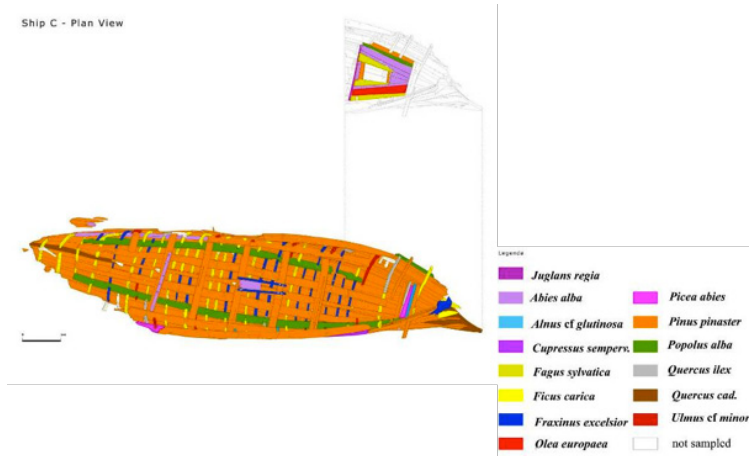


Figure 2. Plan view of the Ship C and the wood species utilized for its construction.

TRIALS FOR THE CONSERVATION

Conservation of highly degraded archaeological wooden artefacts is a big issue. In Pisa's Centre of Restoration different treatments have been realised, based on consolidation by impregnation mostly with colophony.

An experimentation regarding the impregnation treatments of wood was carried out, in order to improve the knowledge on methodologies and consolidating materials for impregnation, and on the behaviour of the new composite made of decayed wood and consolidant.

Esterified colophony (Rosin 100 and Rosin 459) in addition to PEGs mixtures were tested (Giachi et al., 2011), whereas tests with other treatments are still on going. Tests with esterified colophony were performed in order to evaluate commercially available chemically modified types of rosin. They possess excellent stability to thermal and oxidative degradation, and allow setting the treatment temperature closer to room temperature (thanks to their slightly lower viscosity), thus decreasing the energy consumption. A mixture of colophony and PEG 3400 was also tested, to increase the plasticity of the only colophony. Moreover, solutions of PEGs and PPG (i.e., without the presence of water) and solutions of PEGs with the addition of trehalose were considered (Giachi et al. 2010). Finally, a few specimens were treated by using Klucel and a copolymer of vinyl acetate and vinyl versate.

The waterlogged archaeological wood utilized were rests of trees found in the same area of the ships, thus transported by the same floods that covered the ships, but having no archaeological interest. Thanks to that we had the opportunity of having a good amount of sufficiently big samples for a large test campaign. The decay of those samples was measured with the same methodology and gave results comparable to the decay measured on the samples of the ships. Wood species were representative of both softwoods and hardwoods.

In order to evaluate movements and deformations of the samples, specimens were prepared as cuboids of size 5 cm, oriented according to the principal anatomical directions of wood.

The different treatments were evaluated on the base of Equilibrium moisture contents, dimensional stability at different relative humidity (at constant temperature), retention of impregnating products and macroscopic and microscopic evaluations.

Results highlighted that, for the experimental conditions used for tests, the PEG/PPG mixtures and the natural and modified colophony treatments gave the most satisfactory results both in the maintenance of shape and dimensions of samples and in the stabilization with respect to RH variations (Table 2). Moreover, the Equilibrium moisture contents of samples treated with R100 and R459 were much reduced in comparison to the other consolidating substances and to untreated archaeological wood. This fact was related to the high retention values of those products that occluded most of the porosity, including the micro-porosity of cell walls, and to the lower interaction with environmental moisture as compared to rosin. Moreover, this occurrence was considered helpful in contrasting the moisture-related negative effects in cases of eventual faults in the climate control during e.g. exhibition and in protecting treated wood from the risks of new fungal attacks.

Interestingly, for some of the samples treated with Klucel and the vinyl copolymer some promising results were obtained: their treating efficacy resulted high (i.e., their stabilizing effect was high if compared to the amount retained by the samples, which was very

low). However, further research is needed in these cases in order to be the results more reproducible.

Sample	Specie	MWC (%)	tangential shrinkage variation (%)	retention (%)
colophony	hardwoods	580 (141)	0.2 (0.0)	327 (95)
	conifer	504 (90)	0.0 (0.3)	272 (90)
R100	hardwoods	580 (141)	-0.4 (0.6)	290 (90)
	conifer	504 (90)	0.9 (0.7)	293 (28)
R459	hardwoods	580 (141)	3.2 (1.0)	214 (83)
	conifer	504 (90)	0.2 (0.3)	164 (45)

Table 2. Example of the main results obtained for the treatment with the resin-related products. Results are averages (standard deviation in brackets). The tangential shrinkage variation represents the difference in tangential deformations calculated after exposure of treated samples to climates at 85% and 35% RH (negative values = swelling).

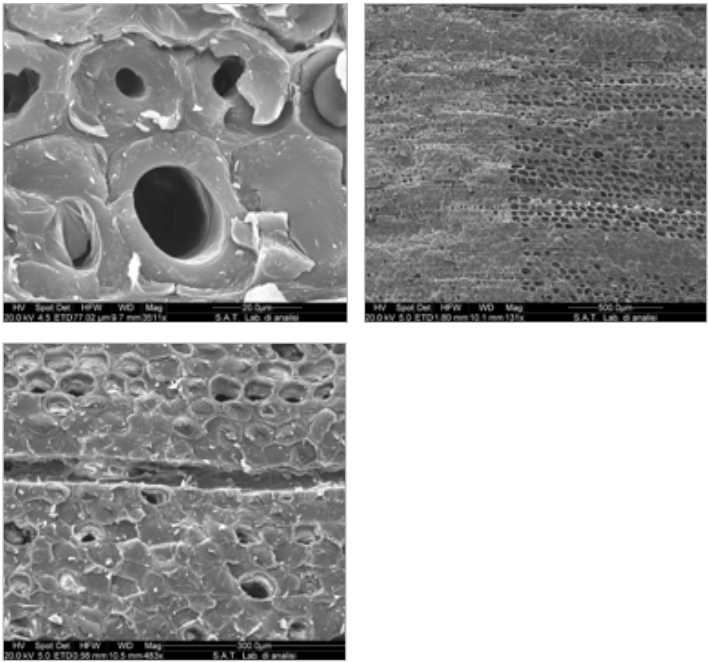


Figure 3. SEM images of the transversal section of pine treated with Rosin 100: the way of deposition is similar to that of colophony and Rosin 459.

CONCLUSION

In the first years of 2000, during infrastructural works for the realization of the Tyrrhenian railway control station, several shipwrecks were discovered not far from the Leaning Tower Pisa (Tuscany-Italy). The wood elements constituting the ships were in a bad state of preservation, as evidenced by a comprehensive diagnostic analysis carried out on some samples taken from the ships. This occurrence gave the opportunity to start a test campaign focused to compare different treatments, both among those most commonly used for the conservation of waterlogged archaeological wood (PEGs and rosin) and also including new products, such as PPG/PEGs combinations and esterified colophonies. Results of some of the new treatments were acceptable and encouraging. However, considering that the considered methods did not evidence an optimal combination in order to achieve in the same time good consolidation and stabilization of the wood, low costs, safety, and easily manageable procedures, further research is going on at present. In this case, other different products and methodologies are being considered, such as sugar alcohols and melamin resin (kauramin® BASF).

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12.

TEN YEARS OF VASA RESEARCH –REVIEW AND OUTLOOK

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INTRODUCTION

VASA sank in 1628 in Stockholm harbor during her maiden voyage. The shipwreck was relocated during the 1950s and was raised to the surface in 1961 [1]. The absence of shipworm in the brackish waters of the Baltic Sea, the anaerobic conditions and low temperature in the bottom sediments 30 m below the surface contributed to its preservation. Several tons of iron compounds from rusting cannon balls and iron bolts and sulfur compounds from the water and polluted effluents from the town impregnated the wood. Erosion bacteria attacked the wood surfaces. During conservation 1962 to 1979, the hull was treated with aqueous polyethylene glycol (PEG) solutions and then dried for another ten years. Loose objects were PEG conserved in tanks. Large amounts of PEG and boron compounds were added to the timbers in this process [2]. Since 1989, the ship and its collections are kept under controlled climate conditions in the present museum.

During the 50 years since 1961, the ship has been exposed to atmospheric oxygen and various degrees of humidity, which has created favorable conditions for chemical and biological degradation processes and transport of chemicals in the wood. During the 1990's, conservators observed acidic salt deposits on the surfaces of some timbers and loose objects [3], indicating transport of chemicals from the interior to the surface. After a rainy summer in 2000, when the museum climate by far exceeded the recommended relative humidity values, the situation became alarming. The salt outbreaks were identified as hydrated iron sulfates, gypsum and elemental sulfur [4]. It was concluded that hydrogen sulfide in the timbers, formed during the anaerobic conditions on the seafloor, was oxidized under museum conditions to sulfuric acid in iron-catalyzed processes. Degradation of the wood due to the action of sulfuric acid was an obvious threat [3,4]. This pioneering work is the basis and rationale for the comprehensive research efforts on the processes in the wood of Vasa and other ships during recent years.

RESEARCH PROJECTS

PRESERVE THE VASA

In 2003, research on the chemical and microbial processes occurring in the timbers of Vasa was initiated. Little was then known about the nature of these processes in PEG-treated archaeological water-logged wood. The research aimed at a fundamental understanding as a basis for practical preservation work. The transformation of sulfur compounds to sulfuric acid, either by iron-catalyzed reactions involving atmospheric oxygen and humidity, or by action of sulfur-oxidizing bacteria, and the possible degradation of PEG, should be elucidated.

Microbial activity - It was soon concluded that microbial activity during the prevailing dry museum conditions was of minor importance. Samples taken from interior Vasa wood failed to provide any signs of current microbial activity. But DNA analysis afforded interesting information on the microbial history of the ship and the species present during the wet periods [5]. Based on these results, all research and preservation efforts were concentrated to the chemical processes. The processes involving erosion bacteria and sulfate-reducing bacteria and the mechanisms for accumulation of organic lignin-bound sulfides and inorganic iron-sulfur compounds under seabed conditions were elucidated in laboratory simulations [6].

Sulfur and iron chemistry - Studies of speciation and distribution of sulfur and iron compounds in Vasa and some other ships by use of synchrotron-based methods, i.e. XANES (X-ray Absorption Near Edge Spectroscopy) and SXM (Scanning X-ray Microscopy), together with X-ray fluorescence, ESCA, SEM and X-ray powder diffraction showed accumulation of reduced sulfur as thiols bound to lignin and as iron sulfide particles [7-9]. High concentrations of sulfur and iron, in some cases up to 10% by weight, were observed in the bacterially degraded surface regions down to 1-2 cm [7-9].

Iron extraction - Removal of iron impurities was identified as important to minimize their assumed catalytic action. Extraction by use of sequestering agents (EDDHMA and DTPA) was initiated early [10]. The washing out of iron requires long exposure times, and the interior of massive oak pieces is in practice inaccessible for wet chemical methods. The treatment removes water-soluble compounds including PEG, and it neutralizes acids, since the aqueous extraction solutions are alkaline. Extracted objects have to be re-conserved. Successful extractions of pine species have been performed [10].

PEG degradation - Initially, it could not be excluded that degradation of PEG to for instance formic acid also contributed to the observed acidity. Studies of the distribution of PEG in Vasa wood and its stability and degradation mechanisms indicated that the half-life of PEG under museum conditions might be sufficiently long (thousands of years) for all practical purposes [11,12]. It was hypothesized, however, that PEG in the interior wood might degrade due to free radical attack [13-16]. The stability of the conservation agent is of great importance per se, in that even a very slow decomposition of PEG to shorter fragments will increase the hygroscopicity and impair the efficiency of the PEG stabilization.

Wood chemistry and stability - A comprehensive study of the chemical and mechanical properties of Vasa oak compared to reference wood (fresh wood and waterlogged, non-conserved contemporary oak) was launched in 2005. The aim was to answer the most important question for the long-term preservation of the ship: Is there a continuous decrease of the mechanical properties of the wood under present museum conditions, as a

result of chemical processes in the timbers?

Analysis of organic acids and other degradation products by NMR and of cellulose and hemicellulose by Size Exclusion Chromatography (SEC) [17] indicated that most of the observed cellulose degradation most likely has occurred after the salvage as a result of the iron rich and humid wood being exposed to air, creating possibilities for oxidative degradations and/or acid-initiated hydrolysis reactions. pH measurements and proton-NMR data for D₂O extracts of finely divided wood samples also indicated the presence of organic acids and degradation in the interior [16]. Positive correlations between high concentrations of iron(II), increasing acidity and signs of degradation of PEG and cellulose were observed [13-16].

In parallel to these studies, a program on the mechanical properties of Vasa wood was initiated, including measurements of fundamental physical properties of Vasa wood in comparison with fresh wood and of correlations between moisture and PEG content and radial and tangential compression [18-19]. A reduction by ca 50% of compressive strength of Vasa oak compared to fresh oak was derived. There was an obvious need to further extend these wood mechanical studies and to correlate the physical properties of Vasa oak with its chemical condition.

A FUTURE FOR VASA

Based on conclusions from the “Preserve the Vasa” project [20], A Future for Vasa was launched in 2006, with the following main objectives:

- Understand and if possible arrest the decay processes occurring in Vasa wood
- Elucidate the time dependence of these processes
- Clarify the relations between the chemical status of the wood and its physical-mechanical properties
- Elucidate the effect of PEG conservation on long-term wood mechanical properties
- Apply research results to new methods for practical preservation work, including a new support

Elucidate the consequences of re-conservation compared to the effects, if no such actions are undertaken

Investigate possibilities of future non-destructive monitoring of ship and loose artifacts

Wood chemical properties – Analysis of Vasa wood indicates that cellulose degradation also occurs in the interior wood [14-17]. Comparison with non-conserved reference wood indicates that degradation has occurred since the Vasa wood was exposed to air [17]. Based on carbon-13 NMR, high concentrations of oxalic acid in the interior wood was observed. This is a strong acid (pK_a 1.3) that will initiate hydrolysis of cellulose. The relative contribution from oxidative degradation (Fenton chemistry) and hydrolysis due to oxalic acid is still an open question. Interior wood samples containing rather high concentrations of sulfur in relation to iron show less degradation [14-16]. This has been interpreted as a possible inhibition of free radical processes by reduced sulfur compounds acting as scavengers [16].

To conclude, the original hypothesis [4] of a sulfuric acid mediated hydrolysis of cellulose might be important in the bacterially degraded sulfur-rich surface regions. However, the cellulose/hemicellulose is already depleted there due to bacterial degradation. In the interior wood, sulfur concentrations are low and other processes and other acids are probably more important. Attempts to neutralize acids in Vasa wood by nanotechnology [21] or ammonia gas treatment [22] have been performed with some success.

Accelerated ageing – Model experiments in which fresh oak is exposed to iron compounds, PEG and various oxygen pressures and temperatures have been reported [15]. The conditions of authentic Vasa wood can be reproduced quite well, and the experiments indicate that the degradation is rather rapid initially and then decelerates to become rather slow. The chemically treated model samples have been subjected to mechanical testing in order to establish relations between chemical status and mechanical properties.

Wood mechanical properties – Based on the early work [18-19], methods for determination of mechanical properties of hardwoods and PEG-impregnated waterlogged wood have been further developed [23-25]. Axial tension of Vasa oak as well as fresh oak treated in accelerated ageing experiments have been determined by use of miniaturized samples. There is a good correlation between the observed longitudinal tensile strength and the chemical degradation status as expressed by the average molecular weight. A relatively good mechanical stability is observed in the wood below the soft bacterially degraded PEG-rich surface region, but further inside the timbers, the mechanical properties get worse, in agreement with the chemical results indicating interior degradation processes. Current results indicate a decrease of mechanical strength of interior Vasa wood compared to fresh oak of up to ca 50 %, sometimes even more [25]. The lignin status of Vasa wood, on the other hand, is not very different from fresh wood.

Reaction rates – Most chemical reactions in archaeological wood consume oxygen, directly or indirectly. Oxygen consumption rates can be used to determine reaction rates. Oxygen consumption and diffusion in Vasa wood has been studied [26]. Diffusion rates in wood seem to be fast, and concentrations inside wood are lower than in the atmosphere, indicating interior oxygen consumption. Iron(II) impregnated samples consume more oxygen, indicating possible iron(II) catalyzed processes.

CONCLUSIONS AND PERSPECTIVES

Microbial activity under the present dry conditions is negligible, but was important during the time on the seabed and possibly also during the wet phases of the conservation; previously active microbial species have been identified by DNA and RNA analysis. Current cellulose degradation is caused by chemical processes, involving sulfur and iron compounds in combination with the humidity of the wood and atmospheric oxygen. The degradation chemistry consumes oxygen, and methods for measurement of oxygen consumption in wood have been developed. Acidic salt deposits on wood surfaces, indicating transport of chemicals from the interior to the surface, have been characterized and the mechanism for their formation has been studied in climate chamber experiments. Speciation and distribution of sulfur and iron compounds in the timbers has been elucidated in detail. High concentrations of sulfur and iron in the bacterially degraded surface regions of the timbers, in some cases up to 10% by weight, favor sulfuric acid dependent hydrolysis of cellulose in this region. Deep below the surface, sulfuric acid concentrations are negligible, and cellulose degradation as observed by means of size

exclusion chromatography and axial tension measurements might be due to free radical reactions of Fenton type and/or acid hydrolysis caused by other acids, in particular oxalic acid. A positive correlation between the mechanical weakening and the extent of chemical degradation as expressed by average molecular weight is observed. Chemical degradation and mechanical weakening are important also in the deep interior of the timbers. The long-term changes of the complex wooden structure of the ship are monitored by use of a precise geodetic positional system in the museum. The observed changes so far are slow and most probably also not linear over time.

Still unknown key parameters are the exact nature of the various possible chemical degradation reactions, their individual rates and their relative contributions to the over-all ageing of the wooden material. These basic data will affect the expected life-time of the ship. Attempts to determine the time dependence of the chemical processes by oxygen consumption measurements are not conclusive due to the heterogeneity of the material. Simulation experiments of the time-dependent changes of the real material by accelerated ageing experiments on fresh oak exposed to various well-defined chemical treatments have given some information, but are inherently difficult to interpret. The origin of the high concentrations of oxalic acid observed in the interior wood is also not clear.

Methods for evaluation of the precise nature and rate of the chemical degradation processes have to be further developed, as well as methods to stop or at least decelerate these processes under museum conditions. The occurring chemical processes are inherently slow, and there is a big problem in determining their absolute rates. An alternative to accelerated ageing or oxygen consumption measurements would be to quench reactions for a long period of time by low temperature and inert gas for future analysis, comparing the result with wood aged under museum conditions.

The heavy ship construction is subject to gravitational forces and its long-term preservation and stability will depend on the mechanical properties of the wooden construction details and their change with time. These in turn depend on the chemical degradation status, and the time dependence of the chemistry. Since this is still not sufficiently well known, the rate of the mechanical weakening of the hull is also not known. Moreover, mechanical properties have been determined on a microscopic level. To be practically useful, this knowledge has to be extrapolated to the complex, heterogeneous and heavy hull structure, which is not a trivial operation.

Quantitative evaluation of the correlations between the chemical processes and the mechanical properties of the wood has to be further developed. The recorded microscopic mechanical properties have to be extrapolated to the properties of macroscopic timbers and the complex hull structure and have to be supported by systematic observations of the movements of the hull structure and with complementary experiments on creep properties of wood species under well defined loads. Computer simulations involving finite element methods will be important for decisions on future actions to support the hull.

Wet chemical methods for neutralization of acids, removal of iron compounds and preventing free-radical processes should be further developed, as well as gas treatments for neutralization or for exclusion of atmospheric oxygen, in particular for loose objects. For the hull, environmental parameters such as relative humidity, temperature, light, and support structure have to be optimized. A Hi-tech climate system in the museum is a necessity for successful preservation.

In a more general context, future development of novel conservation and stabilization agents should be of high priority. These could be based on spontaneous assembly to supramolecular structures, and be given properties allowing neutralization of acids, free-

radical capture or complexation of detrimental metal ions. This will be an important field for future advanced research in organic synthesis and supramolecular chemistry. Chemical analysis of archaeological wood, based on a wide spectrum of instrumental methods, has been successfully developed during the last 15 years and has afforded a lot of novel information. New technologies that might offer further possibilities for elucidation of the status of archaeological wood might involve fast laser spectroscopy, ultrasound studies, neutron diffraction and X-ray scattering.

ACKNOWLEDGEMENTS

Financial support from The Swedish Research Council (VR), The Swedish Foundation for Strategic Research (SSF), The Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS), The Swedish Agency for Innovation Systems (VINNOVA), The Bank of Sweden Tercentenary Foundation, the Swedish National Heritage Board and K. & A. Wallenberg foundation is gratefully acknowledged.

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13.

X-RAY SPECTROSCOPY REVEALS THE CHEMISTRY OF WATERLOGGED ARCHAEOLOGICAL WOOD

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X-RAY ABSORPTION SPECTROSCOPY

THEORY OF X-RAY ABSORPTION SPECTROSCOPY

X-ray absorption spectroscopy includes a series of methods where the amount of X-rays absorbed by a material is studied as function of the energy (wave-length) of the incoming X-ray radiation. The energy of X-rays corresponds to the binding energy of inner-core electrons in an atom. When an atom is irradiated with X-rays with a wave-length corresponding to, or slightly shorter, than the binding energy of the inner-core electron the X-rays will be absorbed. At the absorption process an inner-core electron is excited to a higher orbital, with lower energy, or most likely, ejected from the atom. This is a very unstable situation for the atom, and an electron from a higher orbital will immediately fill up the core-hole formed, and at this process X-ray fluorescence radiation is sent out. When one irradiate a sample with X-rays of energies corresponding to the binding energy of inner-core electron and systematically increase the energy, decrease the wave-length, of the X-rays an X-ray absorption spectrum is obtained, Figure 1. The abrupt increase in the absorption, the absorption edge, corresponds to the minimum energy required to excite an inner-core electron. By subtracting the slope of the pre-edge and normalizing the edge step to unity the X-ray absorption spectrum is obtained, Figure 2. The X-ray absorption spectrum is divided into different regions dependent on the kind of physical events taking place and the information which can be extracted. The pre-edge contains normally no information. However, for some elements, as iron, there is a small peak/shoulder

corresponding to an allowed electron transition from inner orbitals to empty higher orbitals, which can be used to determine the oxidation state of the element, Figure 2 and vide infra. The XANES (X-ray absorption near edge structure) region contains information about geometry around the absorbing atoms as well as distances to surrounding atoms. The theory for the XANES region is still under development, but it can be used on empirical basis as will be shown for sulfur, vide infra. The EXAFS (extended X-ray absorption fine structure) region contains information about distances to the neighboring atoms around the absorbing atom. The theory for EXAFS is well established and is used in many areas as chemistry, biology, physics and cultural heritage. Further reading about the theory of X-ray absorption spectroscopy can be found in ref. 1 or on internet, ref. 2.

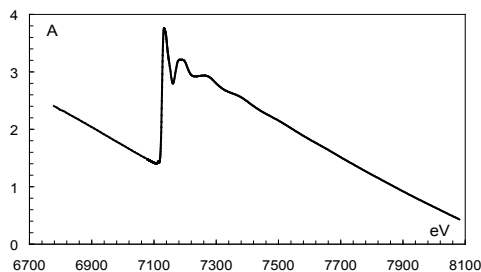


Figure 1. Raw X-ray absorption spectrum of the hydrated iron(III) ion in water.

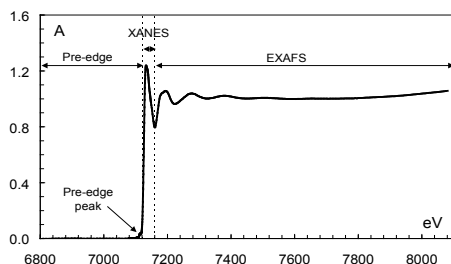


Figure 2. Normalized X-ray absorption spectrum of the hydrated iron(III) ion in water showing the pre-edge, XANES and EXAFS regions.

SYNCHROTRON LIGHT

In order to perform accurate X-ray absorption spectroscopy measurements very intense X-ray radiation in a broad energy range is required. To achieve this synchrotron light is strongly preferred. Synchrotron light is produced in a storage ring for electrons where they are traveling with the speed of light. This storage ring consists of straight sections and curves where the electron orbit is steered by strong magnets. When charged particles, as electrons, are forced to accelerate, as they do when they change direction, intense electromagnetic radiation is formed. By tuning the magnets in the corners and the insertion of light intensity magnifying devices, as wigglers or undulators, very intense X-ray radiation within a broad energy range is obtained. The light used in the experiments is

monochromatized by a set of two parallel large single crystals of elemental silicon. A short history and back-ground of synchrotron-light is found in ref. 3.

SPECIATION OF SULFUR COMPOUNDS

METHOD - SULFUR K-EDGE XANES SPECTROSCOPY

Sulfur compounds display very different X-ray absorption edge energies and features depending on oxidation state and kind of sulfur compound, Figure 3. An internal calibration was performed by measuring the pre-edge and XANES region of two compounds with the same concentration in the same solution, and thereby getting the relative absorption of the two compounds.

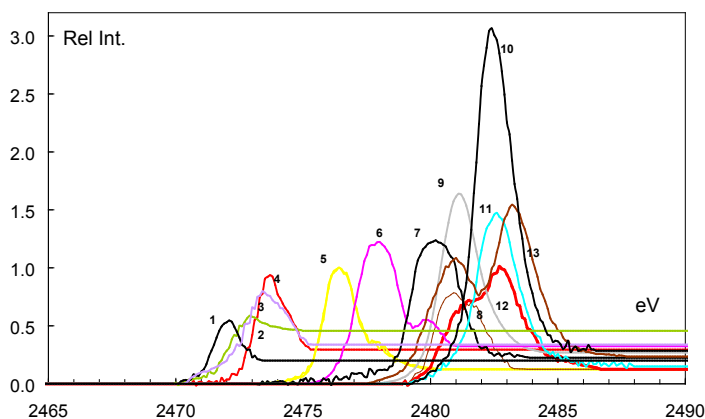


Figure 3. Sulfur K-edge XANES spectra of individual sulfur containing compounds normalized versus dimethylsulfoxide.

The relative intensity dimethylsulfoxide is set to 1.0. The following compounds are calibrated in dilute aqueous solution, (1) hydrogen sulfide ion, HS⁻ (maximum intensity at 2472.1 eV; maximum intensity: 0.545; post-edge intensity: 0.200), (2) 2-thioglycolic acid, 2-HS-C₆H₄-COOH (2473.0 eV; 0.586; 0.458), (3) L-cystein, HS-CH₂CH(NH₂)COOH (2473.4 eV; 0.797; 0.338), (4) methionine, CH₃-S-CH₂CH₂CH(NH₂)COOH (2473.7 eV; 0.935; 0.295), (5) dimethylsulfoxide, (CH₃)₂SO (two spectra) (2476.4 eV; 1.000 (by definition); 0.125), (6) dimethyl sulfite, (CH₃O)₂SO (2478.0 eV; 1.222; 0.325), (7) dimethyl sulfon, (CH₃)₂SO₂ (2480.2 eV; 1.237; 0.225), (8, thin line) sodium trifluoromethanesulfonate, NaCF₃SO₃ (2480.9 eV; 0.784; 0.125), (9) sodium methanesulfonate, NaCH₃SO₃ (2481.1 eV; 1.638; 0.270), (10) sodium sulfate, Na₂SO₄ (2482.4 eV; 2.915; 0.285), (11) sodium hydrogensulfate, NaHSO₄ (2482.6 eV; 1.472; 0.150), (12, thick line) chondroitin sulfate ester, sodium salt, NaC₁₂H₁₂O₁₀N*HSO₄ (2482.7 eV; 1.010; 0.125), (13) sodium peroxodisulfate, Na₂S₂O₈ (2483.3 eV; 1.544; 0.235).

Dimethylsulfoxide was chosen as the standard compound, and its maximum absorption was set unity and the maximum absorption of all other compounds was set in relation to this, Figure 3. As a general trend the absorption increases, and the post-edge absorption decreases with increasing oxidation state of sulfur, and the very strong absorption by sulfate (spectrum 10 in Figure 3) is explained by the high symmetry of the sulfate ion [4].

The analysis of a sulfur K-edge XANES spectrum of an unknown sample is made by fitting the experimental spectrum with the library spectra in Figure 3, and some more not shown in Figure 3 for clarity, and there each spectrum included in the fit is given a fraction of the spectrum of the pure sample. In this way the relative concentration of the sulfur species present in the sample can be determined within some percent as shown in Figure 4. The method is described in detail in ref. 4.

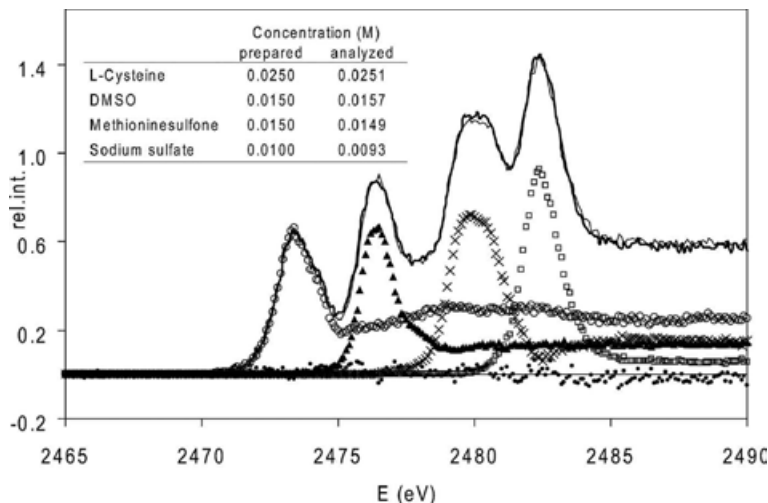


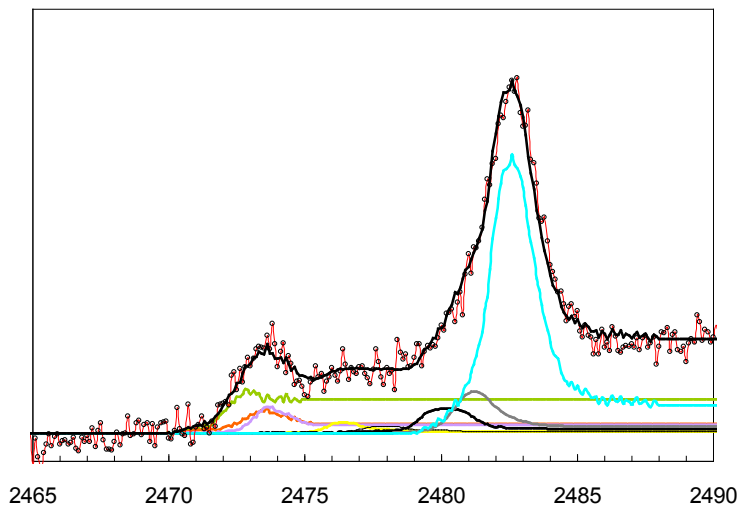
Figure 4. Sulfur K-edge spectrum of a solution containing L-cysteine, DMSO, L-methionine sulfone and sodium sulfate (thick line) and fitting by linear regression with the individual normalized spectra of L-cysteine (open circles), DMSO (filled triangles), L-methionine sulfone (crosses), sodium sulfate (open squares), sum of fit (thin line) and residuals (filled circles).

The prepared and calculated concentrations of the different species are given in the inset table.

QUALITATIVE AND QUANTITATIVE ANALYSIS OF SULFUR COMPOUNDS IN THE VASA

The sulfur K-edge absorption edge spectra of a number of wood samples from the Vasa were recorded without any pre-treatment in order to determine the sulfur speciation. One example is shown in Figure 5 where the distribution of sulfur species is determined. It is important to stress that this method only gives the relative concentration, and in order to get the absolute concentrations a separate determination of the total sulfur content must be performed. However, the quantitative analysis of sulfur species present as particles,

larger than 10 micron, is more uncertain due to self-absorption [4], while the qualitative information remains.



Fit of sulfur Kedge XANES spectrum of wood from the Vasa. The fit gave 27% thiols (orange and purple lines), 7% organic sulfide (green line), 3% sulfoxide (yellow line), 1% organic sulfite (thin black line), 5% sulfon (thick black line), 7% sulfonate (grey line) and 49% hydrogen sulfate (light blue line).

SPECIATION OF IRON COMPOUNDS

METHODS - XANES AND EXAFS SPECTROSCOPY

In the X-ray absorption spectra of iron compounds a pre-peak just before the edge is present, see Figure 2. The position of this pre-peak is a strong indicator of the oxidation state. The position of this peak is found around 7111.5 and 7113.0 eV for iron(II) and iron(III) compounds, respectively. The EXAFS method allows determination of metal-ligand bond distances within ± 0.02 Å [1]. Iron(II) and iron(III) complexes and compounds have in most cases octahedral configuration with mean Fe-O bond distances of 2.10 and 2.00 Å for iron(II) and iron(III), respectively.

SPECIATION OF IRON COMPOUNDS IN THE VASA

X-ray absorption spectra of untreated wood samples from the Vasa have been collected and data treated. The oxidation state has been determined from the position of the

pre-peak just below absorption edge and the mean Fe-O bond distance obtained from EXAFS. The EXAFS spectra and the corresponding Fourier transforms (the experimental data are converted to real space) of three samples from the Vasa, together with data of the hydrated iron(II) and iron(III) ion in aqueous solution as standard samples, are given in Figure 6. HS10_110 is a sample 110 mm below the surface into a large beam on the Vasa, HS10_ext is an aqueous solution where another piece of wood from the same area has been extracted, and 65518 is a surface sample from the Vasa. The pre-peak analysis did show that the iron in sample 65518 is dominated by iron(III), HS10_ext by iron(II), and in HS10_110 both iron(II) and iron(III) are present in significant amounts. The EXAFS data did give the same information with mean Fe-O bond distances of 2.00, 2.10 and 2.05 Å in the samples 65518, HS10_ext and HS10_110, respectively. In the samples HS10_110 and HS10_ext no further distances to iron was observed, while in sample 65518 a significant peak at ca. 3.0 Å was observed, Figure 6 left panel. This peak is most probably carbon atoms in a second scattering shell indicating that iron(III) in this sample binds to carboxylate and/or phenolate groups in organic ligands.

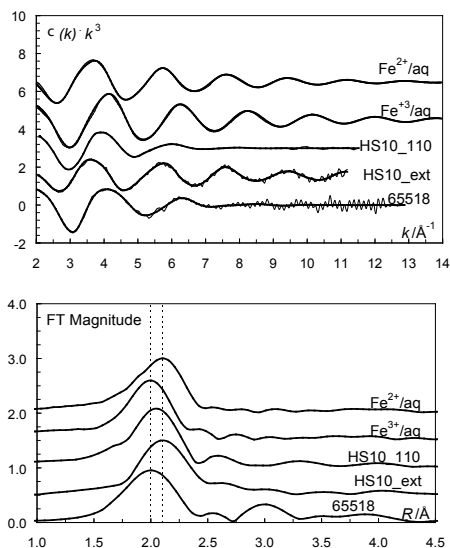


Figure 6. (Left panel) Fitted EXAFS wave functions of hydrated iron(II) and iron(III) ions in aqueous solution, an inner sample (HS10_110), an aqueous extract from this sample (HS10_ext), and sample 65518 from the surface region. (Right panel) Phase corrected Fourier transforms of the same samples. Dashed help lines are shown at 2.0 and 2.1 Å corresponding to the Fe-O bond distances expected for oxygen coordinated iron(III) and iron(II) complexes, respectively.

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14.

HIERARCHICAL STRUCTURE OF OAK WOOD FROM THE SWEDISH WARSHIP VASA

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X-ray scattering and imaging methods are excellent tools for studying the hierarchical structure of both recent and archaeological wood. Wide angle x-ray scattering (WAXS) gives information on the preferred orientation and dimensions of crystalline regions of cellulose microfibrils. Small angle x-ray scattering (SAXS) gives information on the porosity and microfibrillar short range order and imaging methods on the cellular structures. Here recent WAXS, SAXS, and microtomography results on the degradation of oak wood of the historical warship Vasa are reviewed [1] and possibilities to enlarge these studies using synchrotron radiation based imaging methods are discussed.

The samples were solid pieces of the Vasa oak and the results were compared to those of recent oak.[1] The cellular structure of the Vasa oak was surprisingly well preserved at micrometer level. The fraction of crystalline cellulose was lower for the Vasa samples compared to that of recent oak, but the average length and width of cellulose crystallites (25 ± 2 nm and 3.0 ± 0.1 nm) and the mean microfibril angle ($4-9^\circ$) were about the same for Vasa and recent oak. This indicated that the crystalline parts of the cellulose microfibrils were well preserved in the Vasa oak samples. The SAXS results indicated a decrease in the short range order between the cellulose microfibrils and higher porosity for the Vasa oak compared to recent oak, which may be explained by changes in the hemicellulose-lignin matrix.

[1] Kirsi Leppänen, Ingela Bjurhager, Aki Kallonen, Marko Peura, Ritva Serimaa. Structure of oak wood from the Swedish warship Vasa revealed by x-ray scattering and microtomography. *Holzforschung*, 2011, DOI: 10.1515/HF.2011.157

15.

STATE OF DAMAGE IN VASA OAK – MECHANICAL PROPERTIES AND MOLAR MASS OF CELLULOSE

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In all considerations of degradation of Vasa oak, the practical consequences of degradation mechanisms have to be assessed. The mechanical integrity of the ship is perhaps the most critical question. This integrity depends strongly on the mechanical properties of the oak material itself. What is the degradation state of the mechanical properties of Vasa oak? If the properties are degraded; what type of structural degradation is causing this property degradation? Then follows; what is the mechanism for reduced mechanical properties?

The early work was focused on Vasa oak damage not from any environmental effects but from the support structure itself. Analysis of the ship demonstrated the insufficiency of the current structure and the consequences for Vasa oak damage by transverse compressive loading in primarily the radial direction of the oak (Ljungdahl and Berglund, 2007). Effects from moisture and polyethyleneglycol (PEG) impregnation were also discussed.

The environmental degradation effect on mechanical properties is a more difficult problem. The anisotropic structure of wood means that one can easily define more than 50 different mechanical properties, depending on type of loading, direction of loading and property of interest. The goal was from the very early stages to connect any biological or chemical degradation of the wood cell wall to a measurable mechanical property. It means strength properties are more meaningful than stiffness characteristics. Furthermore, the crucial load-bearing component of the wood cell wall is the cellulose microfibril. Although this was questioned at some of the early meetings in the research program, the literature is clear on this point. The cellulose microfibril component is essentially a tensile material in plant structures. The cell wall tensile strength is therefore a good candidate as the mechanical property to focus on. It is furthermore likely to be the most critical Vasa oak property with respect to the safety and mechanical integrity of the Vasa ship. The large beams and other structures in Vasa are subjected to bending, and again, tensile strength is likely to be the critical event in wood beam failure due to bending moments.

One then has to realize the relevance of other plant fibers to the issue of longitudinal wood tensile strength. The literature is clear on the importance of cellulose structure for tensile strength of plant fiber cell walls. The average molar mass of the cellulose is the key parameter discussed in the scientific literature.

This analysis was then enough to jointly with other groups in the program set up a hypothesis that could be tested experimentally. "Cellulose degradation is a key event in Vasa oak degradation process, and it influences tensile strength of Vasa oak". The difficulty then is that the tensile strength of oak is influenced by other factors than average molar mass of cellulose. For this reason, a model study was carried out on recent oak (Bjurhager et al, 2010), where the following primary factors were identified: PEG content and location, microfibril angle and relative density of the wood.

In the key study (Bjurhager, Nilsson et al (2011)), specimens for mechanical testing (Berglund group) and molar mass analysis (Iversen group) are sampled from several locations on the ship. The mechanical property study on Vasa oak shows that the longitudinal tensile strength is severely reduced in several regions of the ship, and that the reduction correlates with reduced average molecular weight of the holocellulose (cellulose+hemicelluloses). This could not have been concluded without a thorough mechanical and chemical investigation, since the Vasa wood (with exception from the bacterially degraded surface regions) is morphologically intact and with a microstructure comparable to that of recent oak. In fact, in the early project stages, experienced workmen at the museum expressed strong skepticism with respect to the degradation hypothesis.

In more quantitative terms: the average longitudinal tensile strength of recent oak is 112 MPa, whereas the average strength in interior regions of Vasa oak is in the 40-50 MPa range. Locally, the strength of individual specimens was as low as 23 MPa. The data correlate with reduced average molecular weight, AMW, of holocellulose. Severe holocellulose degradation has taken place locally, and reduction in AMW from more than 800 kDa to 200 kDa has occurred locally. Due to the excessive and robust construction of the ship, stress levels in the oak structures of the Vasa are still likely to be lower than the strength values of Vasa oak. There is no immediate danger for structural failures, but average molecular weight and tensile strength need to be measured regularly in order to assess degradation development. The lowest AMW measured in the present study, 170 kDa, could potentially be reached for an increasing volume of Vasa oak.

Finally, the fruitful collaboration between Bjurhager, Iversen and Almkvist deserves to be emphasized, since their multidisciplinary collaboration is an important reason for the interesting results.

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16.

DEGRADATION REACTIONS IN VASA WOOD

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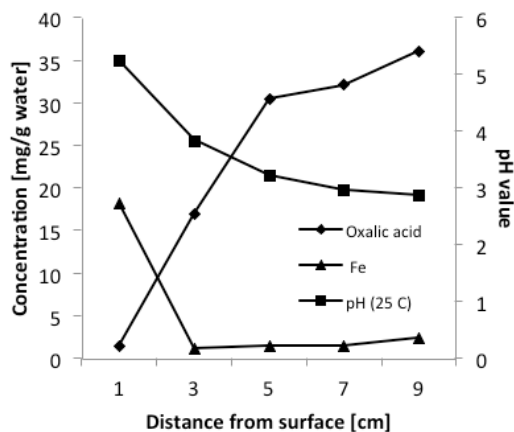
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The Vasa warship has an ongoing chemical degradation of the polysaccharides that has been linked to a decrease in tensile strength. Previous studies have shown that the dry and PEG impregnated Vasa wood is most severely degraded in the interior of the oak wood planks (ca 6-7 cm from surface). In the same interior regions, a high concentration of oxalic acid is observed in addition to low concentration of iron (rust) and a low pH. The aim of this work has been to investigate the concentration of oxalic acid at different distances from the PEG rich surface as well as to study the chemical status of lignin in the Vasa oak wood.

As oxalic acid can be formed from phenolic compounds and iron, analysis of extractives (hydrolysable tannins) and lignin in the wood has been performed. Acetone and water extracts of wood meal were analyzed by MALDI TOF spectroscopy and ¹³C NMR spectroscopy. The results indicate that no discernible amounts of hydrolysable tannins are present in dry and PEG impregnated Vasa. Waterlogged Vasa contains traces of tannins. In order to investigate the lignin, Vasa oak wood was subjected to a chemical degradation reaction (thioacidolysis) in which the most common lignin monomer linkages (β -O-4 bonds) are broken and the remaining monomers (syringyl and guaiacyl) are analyzed by GC-MS. Results obtained from the thioacidolysis coupled with GC-MS are similar to those of fresh oak. The results were confirmed by CP/MAS ¹³C NMR, since no detectable lignin oxidation was observed.

The concentration of oxalic acid was determined by High Performance Anion Exchange Chromatography, which revealed a significant increase of oxalic acid with increasing distance from the PEG rich wood surface (see figure). Our study on extractives and lignin indicates that oxidation reactions such as Fenton type reactions have not occurred to any large extent. Instead, acid hydrolysis of cellulose by oxalic acid is proposed as the main degradation mechanism. We have, furthermore, investigated the influence of iron (rust) on oxalic acid concentration and pH. Preliminary results show that iron (rust) in the surface wood of the Vasa scavenges oxalic acid and thereby raises the pH.

This is in accordance with previous chemical and mechanical testing, which shows that regions that are rich in sulfur and iron (surface regions) are better preserved.



17.

FROM CREEP CHARACTERIZATION OF VASA OAK TOWARDS DESIGN STRATEGIES OF AN IMPROVED SUPPORT SYSTEM FOR THE SHIP

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BACKGROUND

Geodetic measurements on the Vasa ship since year 2000 have shown increasing deformation. Creep in the load carrying oak members contributes to the observed global creep of the ship hull. A degradation of static mechanical properties has previously been shown to be caused by molecular degradation in Vasa oak. The molecular degradation mechanisms should also contribute to increased creep.

The ultimate goal to design a new improved support system for the Vasa ship is undeniably an ambitious enterprise. In contrast to the existing support system, modern quantitative tools in structural engineering should be employed in the design process. A natural starting point is at the lowest level where mechanical properties can be quantified and directly used as input in finite element models to predict the structural creep response, namely elastic and creep moduli of Vasa oak are then needed. It is self-evident that there is considerable scatter in these mechanical properties, depending on polyethelyne glycol (PEG) content, density and level of molecular degradation (cf. Bjurhager et al., 2010). A structural model must therefore consider the uncertainties in input variables on the material level.

With the aim to assess the performance of various support systems in numerical simulations, we have thus started out to characterize material properties, i.e. the stiffness and creep properties of Vasa oak and green reference oak in the radial, tangential and longitudinal directions. Cubic specimens of 50 mm edges are being tested in compression,

both quasi-statically and with constant load, to obtain elastic moduli and creep moduli, respectively. The strain field is measured with digital speckle photography, to allow identification of Poisson's ratios. Considerably lower stiffness and higher creep rates are being observed for Vasa oak compared with recent oak with similar densities. The inferior mechanical properties of Vasa oak can be attributed to the plasticization primarily due to PEG induced softening and molecular degradation.

Strategies on up-scaling material creep to structural creep will be presented; including reliability based modelling due to material uncertainty and to extrapolation of creep behaviour from experimental data. Finite element models can be used for modelling of creep of the ship structure, which can be compared with the geodetic measurements as a verification measure. The next step is to simulate structural creep response with various support solutions, and identify the one that minimizes creep and local stress concentrations. The boundary conditions in such simulations should be carefully selected, not to impair on ship visibility, aesthetics, cost limitations etc. in the optimization process.

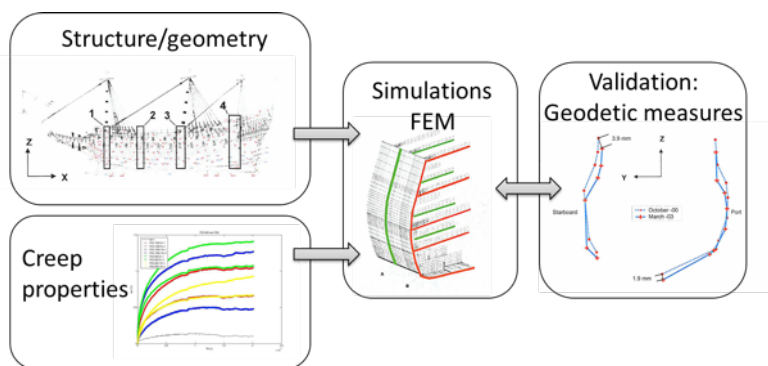


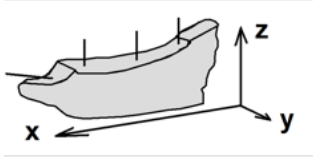
Figure 1. Schematic illustration of up-scaling approach from material properties to structural creep response.

An illustration of an engineering mechanics approach is presented in Figure 1. A first tangible goal is to conceive a structural and finite element model that is considered trustworthy. Creep data is currently being logged for Vasa oak material in various directions. These material properties will be used to extrapolate long-term creep according to evaluated strategies used for wood materials (e.g. Bond et al., 1997). Together with a geometrical model, finite element simulations may be performed on the Vasa structure and compared with geodetic measurements. The idea is that a favourable comparison would lend some confidence to such a simulation tool, although all assumptions and simplifications along the way must be carefully considered. Subsequently, a variety of support strategies could be quantitatively evaluated. An on-going investigation focuses on the calculation of strain fields over the ship's hull. The purpose is to identify localized zones of high strains and to use the obtained strains fields for future comparisons with predicted strains.

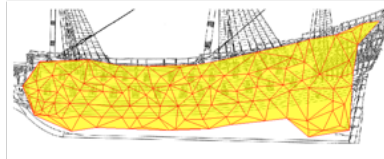
CREEP STRAIN FIELDS

The in-plane strain field over the curvilinear hulls surface is obtained as an average between three adjacent measurements nodes, using the displacement vector field and normal vector for each surface element (e.g. Brunner et al., 1981). The approach is outlined in Figure 2.

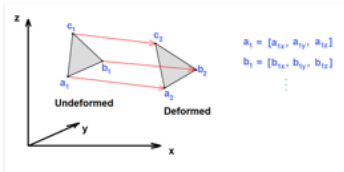
1. Reference coordinate system



2. Triangular mesh between nodes



3. Determination of displacement vectors



4. Calculation of strain field

$$\left[\begin{array}{l} \varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \\ \varepsilon = n_i \varepsilon_{ij} n_j \end{array} \right.$$

Figure 2. Determination of creep strain fields over the hull surface from geodetic position measurements since year 2000.

The starting point is year 2000, when the first position data of the nodes were recorded. The increasing strain has been determined for each time when positions were recorded. Since the humidity level was kept relatively constant during the entire time span, the estimated strains are interpreted as effective creep strains. It should be underscored, though, that some of the members are not entirely fastened to each other, and slippage may occur between load-carrying lumber planks. Hence, it is an effective creep strain covering material creep, slippage of components and damage accumulation.

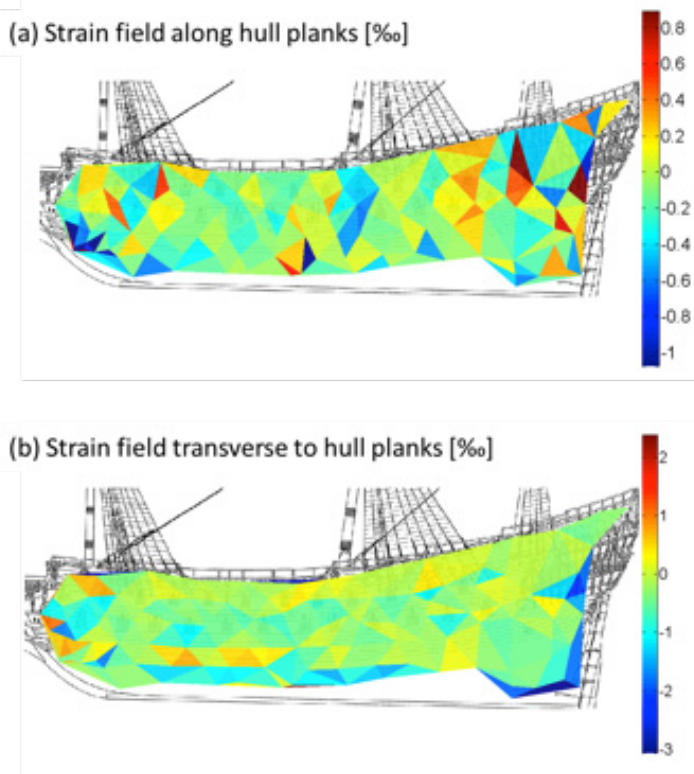


Figure 3. Surface strain field on port side from 2000 to 2010 (a) along planks, and (b) transverse to planks.

An example of calculated surface strains is presented in Figure 3. It can be observed that there is a large spatial variation in the strain field, particularly for the longitudinal strains along the hull planks. These strains are small, due to the high longitudinal stiffness. Nevertheless, the estimated strains are statistically significant and show localization in particular regions, although neighbouring regions may show strains in the opposite direction. A clear tendency in the strain transverse to the planks is that they are generally negative. This shows that the ship is setting in compression under its own weight. Again, certain zones of increased strains may be identified. The method shows the possibility to identify regions of strain localization, which can be investigated in closer detail to check if localized damage can be found and if local structural support may be necessary.

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18.

ANALYTICAL PYROLYSIS TECHNIQUES TO EVALUATE THE DEGRADATION OF ARCHAEOLOGICAL WATERLOGGED WOOD

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INTRODUCTION

The consolidation and preservation of waterlogged wooden artefacts, such as shipwrecks and archaeological objects recovered from underwater environments, is a particularly arduous conservation problem. Under favourable conditions of low temperature and low oxygen, waterlogged wood artefacts can survive in surprisingly good condition. Nevertheless, as a result of the action of biota among which the anaerobic bacteria, waterlogged wood is often deeply degraded and has undergone loss of polysaccharide components (cellulose and hemicelluloses) [1-4]. The result is a soft and fragile wood structure which presents formation of micropores filled with water, alteration of lignin, and loss of extractable compounds: this wood is likely to collapse when drying. In degraded wood the cellulose content is generally very low with respect to lignin. Thus, the chemical characterisation of residual lignin is surely an aspect of primary importance in the diagnosis and conservation of waterlogged wood artefacts. At present, the knowledge of wood degradation processes in historical and archaeological objects is extremely inadequate; in particular the chemistry of lignin is far from being understood.

This paper presents the state of art on the chemical composition of archaeological waterlogged wood, with particular attention to lignin content. The application of micro-destructive analysis based on direct exposure electron ionisation - mass spectrometry (DE-MS) and analytical pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS) also using hexamethyldisilazane (HDMS) for the in-situ thermally assisted derivatisation of pyrolysis products is presented. The DE-MS mass spectra results are interpreted by unsupervised pattern recognition analysis. Principal component analysis (PCA) is a reliable and powerful tool, which allows to estimate the degradation state of waterlogged

wood. Py-GC/MS technique elucidates the chemical modifications of lignin molecules in archaeological objects [5-7].

The assessment of the extent of wood degradation and the main lignin decay patterns in archaeological wood samples collected from the excavation of the archaeological site of San Rossore (Pisa, Italy) are presented. In this site, thirty one shipwrecks dating from 2nd cent. B.C. to 5th cent. A.D. have been discovered from 1998 until now. The analytical results show a great variability in the pyrolytic profiles of the examined wood samples. The significant degradation patterns include: extensive degradation of polysaccharides and demethylation reactions causing formation of catechols. , ,

MATERIALS AND METHODS

SAMPLES

14 archaeological wood samples (elm, pine and beech) derived from the Site of the Ancient Ships of Pisa San Rossore (Pisa, Italy), where the remains of 31 Etruscan and Roman shipwrecks have been excavated (2nd century BC - 4th century AD [8].

Native reference sound wood samples of the same species: pine (*Pinus pinaster*), elm (*Ulmus minor*), beech (*Fagus sylvatica*).

Solid micro-samples (less than 1 mg) of powdered wood were analyzed without any pre-treatment for DE-MS and Py-GC/MS analysis.

ANALYTICAL METHODS

DIRECT EXPOSURE-MASS SPECTROMETRY (DE-MS)

Samples were analysed by direct deposition on the exposure probe filament of the DE-MS. The instrumentation (Thermo Electron Corporation, USA) was made up of a Direct Probe Controller and a Direct Exposure Probe (rhenium filament, current programmed mode), coupled with a Polaris Q ion trap external ionisation mass spectrometer (electron impact ionisation 70 eV). The MS source temperature was 230 °C. After optimization of the conditions on reference wood and lignin, for each sample the analysis was repeated twice by scanning over the *m/z* range 50–500. Optimal conditions to obtain a convenient peak shape of the total ion current (TIC) curve as a function of time were achieved by programming the probe as follows: 0 mA for 20 s, from 0 to 1000 mA in 2 s and 60 s at 1000 mA. A mass spectral fingerprint was obtained by averaging the mass spectra in the desired time range.

PYROLYSIS-GAS CHROMATOGRAPHY/ MASS SPECTROMETRY PY-GC/MS

Instrumentation consisted of a Py-2020iD Double shot pyrolyzer Frontier Lab (Japan) with a sample cup, connected to an Agilent (USA) GC/MS system made up of a 6890 gas chromatograph equipped with a DB-1701 fused-silica capillary column (Agilent), and a 5973 Mass Selective Detector operating in electron impact (EI) mode at 70 eV. Pyrolysis temperature: 500 °C. Chromatographic conditions: initial temperature of 50°C, 30°C/min to 100°C, 6 °C/min to 290°C, 10 min isothermal. Carrier gas: He (purity 99.995%), constant flow 1.0 ml/min.

PYROLYSIS (HMDS)-GAS CHROMATOGRAPHY/MASS SPECTROMETRY PY(HMDS)-GC/MS

Analytical pyrolysis adopting hexamethyldisilazane (HMDS) as silylating agent for in situ thermally assisted derivatisation of pyrolysis products was also tested. In this case the instrumentation was made up of: 5150 CDS Pyroprobe 5000 Series pyrolyser with a Pt filament connected to a Agilent 6890 gas chromatograph equipped with a HP-5MS fused silica capillary column (Hewlett Packard) and with a 2m deactivated silica pre-column, coupled to an Agilent 5973 Mass Selective Detector operating in electron impact mode (EI) at 70 eV. Pyrolysis temperature: 550 °C for 20 μ s. Constant amounts (40–60 μ g) of sample and hexamethyldisilazane (5 μ l) were inserted in the centre of the pyrolysis quartz tube with glass wool, and then placed in the pyrolysis coil filament. Chromatographic conditions were as follows: initial temperature 31 °C, 8 min isothermal, 10 °C/min to 240 °C, 3 min isothermal, 20 °C/min to 300 °C, 30 min isothermal. Carrier gas: He (purity 99.995%), constant flow 1.0 ml/min.

GC/MS quantification was based on peak areas. Peak areas of the wood-degradation products were calculated, the summed areas normalized, and the data for replicated analyses averaged and expressed as percentages.

RESULTS AND DISCUSSION

DE- MS

In DE-MS technique the sample is directly introduced into the mass spectrometer by deposition on a probe filament. After the filament has been introduced into the ion source, the sample is desorbed or pyrolysed by controlled resistive heating of the filament. The main advantage is the minimal pre-treatment of the sample and the quick response (2-4 min), so our experiments aimed to explore the potential of this fast fingerprint technique in retrieving chemical information on archaeological wood materials. Figure 1 presents the mass spectra obtained for the archaeological and reference sound beech wood samples. The spectra show high complexity, and are characterized by the occurrence of peaks indicative of a guaiacyl-syringyl lignin. Polysaccharide pyrolysis products are consistently less abundant in the archaeological sample than in sound wood, and are observed at m/z 55, 69, 73, 97, 114 and 126. The fragment at m/z 69 is formed in the fragmentation of furan derivatives; m/z 114 can be attributed to xylans, while 55 and 73 are derived from levoglucosan [9].

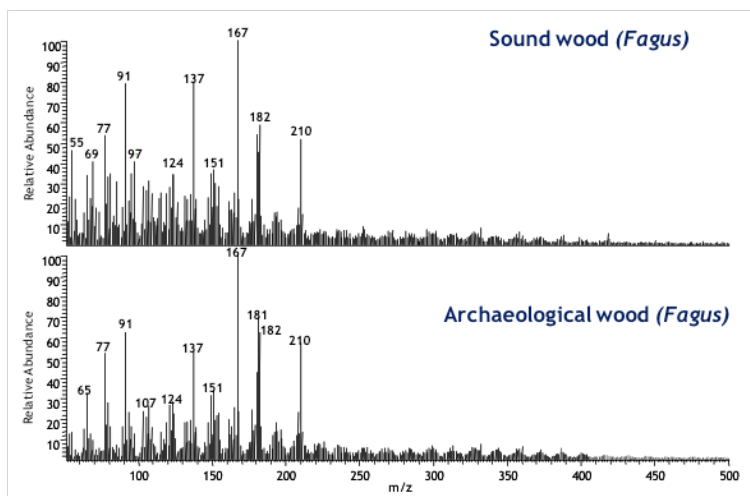


Figure 1. DE-MS spectra of archaeological and reference sound beech (*Fagus sylvatica*) wood samples

The guaiacyl-derived fragments are: m/z 124, corresponding to the molecular peak of guaiacol (2-methoxy-phenol), m/z 137 (guaiacol + CH_2 +), and m/z 151 (guaiacol + CH_2CH_2 +). The syringyl-derived fragments can be at m/z 167 (syringol + CH_2 +) and m/z 181 (syringol + CH_2CH_2 +), while the peak at m/z 210 corresponds to the molecular ion of syringyl alcohol [6, 9-11]. Due to the difficulties in the interpretation of DE-MS spectra, we submitted the data to principal component analysis (PCA) to compare, differentiate and classify the samples [8]. The mass spectral data corresponding to sound and archaeological woods (two or three replicated samples for each material) were submitted to PCA based on the covariance matrix after row normalisation of the data matrix (m/z from 50 to 500), using the XLSTAT software (Addinsoft, France).

The resulting score plot for the first two principal components shown allows to achieve the following information:

- PC1 gives a rapid indication on the type of wood, discriminating between softwoods and hardwoods, and on the ratio between the amounts of syringyl and guaiacyl fragments;
- PC2 differentiates the samples on the basis of holocellulose (cellulose and hemicelluloses) content, and gives an indication of the degree of wood decay;
- all the archaeological samples are located in the lower part of the PC2/PC1 score plot, which highlights their lower content of polysaccharides with respect to native samples of the same species.

PY - GC/MS

In Py-GC/MS, gas chromatography (GC) is used to separate the pyrolysis (Py) products of wood prior to mass spectrometric (MS) identification, permitting to obtain a complex but detailed molecular profile in which the type and amounts

of wood pyrolysis products can be evaluated (Figure 2). Solid samples can be analyzed without any pre-treatment, and analysis time is around 30 min.

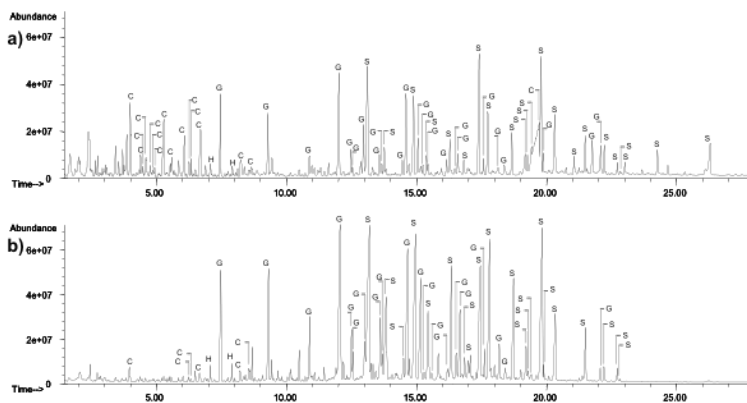


Figure 2 - Py-GC/MS profiles of a) sound beech wood (*Fagus sylvatica*) and b) archaeological beech wood from the Pisa San Rossore site. (C: carbohydrates pyrolysis products; G: guaiacyl-; S: syringyl- and H:hydroxyphenyl- lignin pyrolysis products).

The first section of the pyrograms (3-7 min) is dominated by the pyrolysis products of polysaccharides, while lignin thermal cleavage leads to a complex mixture of phenolic products (7-27 min), with a guaiacyl structure in the case of pine, and with both guaiacyl and syringyl structures in the case of elm and beech. Relative peak areas can be calculated for carbohydrate-derived compounds and for G and S type lignin products, and reflect the relative amounts of wood components.

The comparison between the pyrograms of sound wood with archaeological pine wood samples, shows a very good level of lignin preservation in archaeological wood, which gives the same pyrolysis products observed in non-aged lignin, while polysaccharides result strongly depleted. This behaviour, observed in all analysed samples of waterlogged wood, provides evidence of a substantial degradation in the wood. Pyrolysis also highlighted the partial demethylation of lignin units (both guaiacyl and syringyl monomers): small but not negligible amounts of catechols and methoxycatechols were identified among the pyrolysis products of the waterlogged wood samples.

PY(HMDS)- GC/MS

The use of hexamethyldisilazane (HMDS) for the in-situ thermally assisted silylation of pyrolysis products permits to silylate hydroxylic, phenolic and carboxylic moieties in pyrolysis products of lignin, cellulose and hemicellulose, achieving a better GC separation and detection of polar and unvolatile compounds. It is possible to highlight the silyl-derivatives of cinnamyl alcohols (E-Coniferyl alcohol-2TMS and E-Sinapyl alcohol-2TMS) as the more abundant pyrolysis products of lignin. These products are generally not observed when a furnace pyrolyser is used and also when pyrolysis is performed in the absence of a derivatising agent

From a qualitative point of view, archaeological wood samples produce silylated pyrolysis products analogous to those observed in sound wood, as already observed for

analytical pyrolysis without HMDS. The comparison between pyrograms of sound and archaeological wood clearly reflects wood degradation in archaeological wood samples.

A strongly decrease of polysaccharides content is observed, confirming the selectivity of the degradation process in underwater environment. When analysed in presence of HMDS, the degraded archaeological wood samples showed a relative high amount of acidic functionalities probably caused by an oxidative degradation step. Another parameter that suggests an oxidation process is the content of aldehydes and ketones, higher than in reference wood material.

CONCLUSIONS

Our results highlight some advantages of the pyrolysis-mass spectrometric techniques for the characterisation of archaeological wood: they allowed us to minimise the sample size and to perform the analysis in a short time, thus avoiding the long wet-chemical procedures that are commonly used in wood analysis.

DE-MS is a fast fingerprint method for the screening, evaluation and comparison of archaeological wood samples in a few minutes. This technique, coupled with PCA performed on mass spectra, enables us to achieve a rapid semi-quantitative indication of the syringyl/guaiacyl ratio and of the loss of polysaccharides as the effect of degradation in a waterlogged environment. The comparison of DE-MS results with those obtained by Py-GC/MS suggests that DE-MS can be used as a pre-screening method for selecting sub-groups of samples to be submitted to further analysis. This analytical approach has a great potential when applied to large wooden artefacts, such as shipwrecks to monitor the state of decay.

The results obtained by Py-GC/MS confirm the validity of this technique as a tool for shedding light on the chemical modifications of wood macromolecules in archaeological objects. The adopted approaches give qualitative and semi-quantitative information on the type of wood (hardwood or softwood – angiosperm or gymnosperm), on the relative amounts of lignin and holocellulose, and on the chemical transformation undergone by lignin during ageing.

Particularly, the presence of an increased concentration of carboxylic and phenolic functionalities in the lignin network of the Roman wood samples confers an enhanced polarity and cation exchange properties to archaeological wood. These changes need to be taken into account in terms of its influence on the chemical interaction between waterlogged wood and any consolidating materials that might be used for conservation.

ACKNOWLEDGEMENTS

The authors are grateful to Gianna Giachi (Restoration Laboratories of the Archaeological Superintendence of Tuscany, Florence, Italy), and to IVALSA CNR group (Florence, Italy) for providing archaeological and reference wood samples and for their valuable support and collaboration. Funding was provided by the Archaeological Superintendence of Tuscany and by the Italian MIUR (PRIN Cofin05).

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19.

LONG TERM RESPONSES IN ARCHAEOLOGICAL WOOD TO AMBIENT TEMPERATURE AND RELATIVE HUMIDITY – CASE STUDY: THE OSEBERG SHIP

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ABSTRACT

INTRODUCTION

The Oseberg ship, dated from ca 815-820 AD, is one of the most important discoveries of the Viking age period in Norway. The fact that the ship consists of 90 % original material makes it a unique find with no comparison elsewhere in the world. The ship is 21.5 meters long, built with radially cut, 3 cm thick oak planks and is 5 meters at its widest. In 1904 the waterlogged wood was conserved with linseed oil and creosote and the surface exterior was then lacquered. Over 2000 pieces were used for the reconstruction of the ship with the use of both original and modern screws together with adhesive.

The Oseberg ship, displayed at the Viking Ship Museum in Oslo, has been subjected to an

uncontrolled climate since 1926, with only heating in winter. The display area is therefore influenced by seasonal changes in relative humidity (RH), which rises above values of 70% RH in summer, and drops below 30% RH in winter. Rapid changes over the course of a few hours have also been recorded.

EXPERIMENTAL RESULTS

Continuous monitoring of dimensional change due to RH fluctuations has been carried out on two planks of the ship and on two samples free to warp. To our knowledge, it is the first example of long term hygro-mechanical monitoring on an archaeological wooden artifact. Through this approach it is possible to show the specific sensitivity to RH fluctuations; restrained planks show the least response, while unrestrained samples have highest response to RH changes.

The analysis of the data obtained after fifteen months of continuous logging allows us to quantify the specific “sensitivity” of the wood, which can be useful in determining the threshold of allowable RH fluctuations.

The results of stress on the free samples in the exhibition site will be discussed. It is also planned to measure the forces absorbed by the restrained samples so that long-term mechanical effects of absorbed stress can be understood better. These data are fundamental as a validation of future Finite Element simulations and hygro-mechanical modelling of deteriorated wood

20.

THE CLIMATE-CONTROL SYSTEM AT THE VASA MUSEUM

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The Vasa Museum, Swedish National Maritime Museums

Maintaining a stable climate in the huge internal space of the Vasa Museum has been a challenge since the museum opened in 1990 to house the newly-conserved seventeenth-century warship, Vasa. The enormous heights necessary to accommodate the ship's masts produced temperature and humidity gradients, and the unanticipated growth in visitor numbers during the 1990s affected environmental conditions inside the museum. The original climate-control system, clearly under-dimensioned, could not cope with these demands. Relative humidity fluctuations of over 15% could be recorded in some areas. It was after the appearance of acidic salt outbreaks on the ship and objects around the year 2000, believed to be caused by moisture transport within the wood, that a costly upgrade of the climate-control system was approved. The existing conditions around the ship were thoroughly documented and this data incorporated in the design of the new system. In 2004, the upgraded system became operational and since that time preservation staff and technicians have been working together to fine-tune the control parameters to obtain the most stable year-round climate around and inside the ship. Both salt outbreaks on the wood and seasonal movements of the hull structure appear to have stabilized, improving the preservation prospects of the wood itself and facilitating the design of a new cradle to support the massive weight of the hull.

This paper has been published previously: E. Hocker, Maintaining a Stable Environment: Vasa's New Climate-Control System, Bulletin of the Association for Preservation Technology 41: 2-3 (2010) 5-7.

21.

VASA – PRESENT DAY STATUS AND ONGOING WORK

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The Vasa Museum, Box 27 131, 102 52 Stockholm

Vasa has now spent 50 years on land, and the work with preservation is still – perhaps more than ever - a challenge. It has to be carried out in many areas and includes a wide range of specialists, such as conservators, engineers, archaeologists, chemists, wood scientists, carpenters and many others. Work today includes every-day maintenance as well as embracing the latest research; it goes from taking small samples from the hull to replacing 5000 corroded iron bolts with high-tech stainless steel bolts. In order to create a new support system for the ship it has been necessary to record the hidden frame-structure of the ship as well as making accurate 3-D representations of the hull. The question of size is always an issue: extracting iron or acids from a large ship is not the same as extracting these substances from a small wooden spoon. Likewise the long-term perspective is important: small deformations in the big hull can seem negligible but in a preservation perspective of 1000 years every little movement has to be followed up, measured and monitored by digital means. The museum environment adds its own limitations to the work, since most of the preservation measures have to be carried out in front of the public.

22.

CONSUMPTION OF OXYGEN BY CONSERVED ARCHAEOLOGICAL WOOD

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Oxygen consumption by an object is an indication that a reaction takes place that changes the chemical composition of the object. Such a change can be considered a degradation especially if it results in a reduction of mechanical strength. This is the fundamental idea behind the measurement of oxygen consumption in museum objects described here.

A technique has been developed that enables non-destructive measurement of oxygen consumption of whole pieces of conserved archaeological wood. The procedure allows measuring even very low rates of oxygen consumption corresponding to very slow reactions. The samples can be pre-conditioned at any desired relative air humidity (RH) and the measurements can be carried out at room temperature (non-accelerated ageing). In this way it has been shown that polyethylene glycol impregnated archaeological wood at 50 % RH consume approximately $1 \mu\text{g O}_2/\text{g sample/day}$ on average at room temperature. Investigations have been carried out on samples from the Vasa ship, the Skuldelev Viking ships, the Roskilde ships, the Hjortspring boat, objects from the Nydam find and fresh reference wood.

A system has been developed that allows measuring oxygen concentration inside timber. It involves the installation of glass probes with an oxygen sensor on the tip, in the wood. Such measurements have shown that the oxygen content inside conserved wood is lower than in the surrounding air in most cases. This is in agreement with oxygen being consumed inside the wood.

23.

THE BEHAVIOUR OF ALUM IN ALUM-CONSERVED WOODEN OBJECTS

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The conservation using alum salts was developed in the 1850's by C.F. Herbst in Denmark and was in use until the 1950's. The waterlogged wooden artifacts were immersed into a hot (80-100°C), concentrated solution of alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$). The alum solution penetrated the wood, replaced the water, and re-crystallized. The alum crystals stabilized the wood structure and prevented collapse. The alum conservation method was used in different variations mostly in Scandinavia but also in other countries around the world.

Approximately 10 years ago, serious damage on alum-conserved objects was observed in collections in Sweden, Denmark and Norway. A key-role in this slow but ongoing deterioration process seems to play sulfuric acid. All alum-conserved artifacts exhibit a very low pH (ca 1). The acid was probably formed by decomposition of alum during the treatment procedure.

Whereas alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, and the water-free steklite, $\text{KAl}(\text{SO}_4)_2$, are well-known compounds there is very little known about alum-like species existing in the temperature range between 20-120°C. Knowledge about behaviour and reactions of alum and alum-like compounds is important in many respects:

- Elucidation of mechanisms of the formation of sulphuric acid
- Stability of alum and alum-like compounds in treated objects
- Possible reactions between alum and other conservation materials and wood
- Interaction of alum-conserved objects with environmental humidity
- Has alum to be removed in a future re-conservation or strengthening procedures?

Our contribution will present first results in studying the decomposition of alum during heating – as in the original alum-conservation procedure – and the formation of sulfuric acid. Two different ways of decomposition could be identified: a) in solution, forming

potassium aluminum hydroxide sulfate and sulfuric acid, and b) a 'dry' decomposition with a loss of crystal water. The reactions were studied using X-ray diffraction, infrared spectroscopy, differential thermal analysis and differential thermal gravimetry. It is expected that an improved knowledge of the behaviour of alum, its decomposition and an identification and characterization of alum-like compounds ($\text{KAl}(\text{SO}_4) \cdot x\text{H}_2\text{O}$, e.g.) will help to understand better the deterioration processes in alum-treated wooden objects.

24.

ALUM-TREATED WOOD: CHARACTERIZATION USING INFRARED SPECTROSCOPY AND SOLID STATE NMR

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The Oseberg find contains a large proportion of hardwoods that had been treated about 100 years ago with hot solutions of alum salts (potassium aluminum sulfate dodecahydrate, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$). Today, the wood is characterized by a high acidity (pH 1) and is structurally highly degraded. The observed deterioration is also active. The 'alum treatment' was a method of choice for the conservation of highly deteriorated waterlogged archaeological wood found from 1850 – 1950 and has since been replaced by treatment with polyethylene glycols (PEG). The alum treatment has been mainly used in Scandinavia but also in the USA, Japan and other European countries.

Attempts to chemically characterize the alum-treated wood from the Oseberg find is one phase in the research currently being undertaken at the Museum of Cultural History as a part of the Alum Research Project. The ultimate aim of this project is to design conservation re-treatments which will stabilize and strengthen the wood. So far, we have focussed on non-destructive analytical techniques using ATR-FTIR and solid state NMR. Further chemical analyses are planned, using destructive techniques.

Analyses using infrared spectroscopy and solid state ^1H and ^{13}C NMR were undertaken on selected alum-treated samples and compared with fresh woods as well as archaeological woods from the same find not treated with alum. The advantages of these analytical techniques lie in the fact that sample preparation is minimal prior to measurement – highly deteriorated wood can be greatly modified by standard sample preparation procedures. These techniques, when used together, give an acceptable level of qualitative structural information regarding the state of the remaining polymers.

Analytical results demonstrated that all alum-treated samples are highly degraded relative to

archaeological wood from the same find not treated with alum salts. The non-alum-treated archaeological wood has carbohydrates left, which are highly reduced in the alum-treated wood. ^{13}C NMR can distinguish different lignin types, and has shown that syringyl lignin is more deteriorated than guaiacyl lignin in the most deteriorated alum-treated samples. NMR and FTIR-ATR results also show that remaining polymers in the alum-treated wood, dominated by lignins, are highly oxidized, contain carboxylic groups, and that in the most deteriorated samples even the aromatic ring in lignin appears to be deteriorated. This shows that the alum-treatment has caused extensive chemical changes in the wood, resulting in wood with a powdery consistency with almost no structural integrity relative to samples from Oseberg not treated with alum.

25.

HYDROXIDE NANOPARTICLES FOR DEACIDIFICATION OF ARCHAEOLOGICAL WOOD

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INTRODUCTION

In the last decades, some major shipwrecks underwent extensive treatments, aimed at stabilizing the wooden structure and allowing their preservation and exposition as objects whose historical importance is fundamental for cultural, social and economic aspects. The Swedish Vasa warship and the English Mary Rose represent two of the most famous examples, and share some common conservation features. [1,2] Both these shipwrecks, in fact, have remained buried for centuries in relatively anoxic waters that slowed bacterial degradation. Following their salvages, in the second half of the 20th century, the two ships underwent massive consolidation treatment, including extensive impregnation with poly (ethylene glycol), PEG. Despite the good preservation status at the moment of their rescue, however, the two ships developed, in the last decades, similar conservation issues due to the presence of sulfur compounds. While the sulfate-rich waters of the Stockholm harbor and of the southern coast of England inhibited the action of aerobic microorganisms, on the other hand they provided the perfect environment for the metabolic cycles of sulfate reducing bacteria, resulting in the production of a large amount of reduced sulfur compounds which penetrated inside the ships' timbers. After the recovery of the ships, exposition to oxygen started turning the reduced compounds into sulfuric acid, which degrades wood both chemically and mechanically by catalyzing the hydrolysis of cellulose. The presence of iron compounds inside wood, due to bolts and other parts, favors the process, since iron ions catalyze the oxidation of reduced sulfur, and degrade cellulose through Fenton-like reactions. Moreover, iron is involved in the degradation of PEG, producing organic acids (acetic acid, formic acid). Investigations on the Vasa, for example, mapped the pH values of wood in several degraded areas, reporting values below 2.

As a matter of fact, acid hydrolysis and oxidation of cellulose threaten the conservation of these important historical objects, and represent two among the main issues to be addressed by conservation strategies aimed at preserving the ships. The ideal treatment, in fact, should focus on both these synergistic degradation pathways, limiting or eliminating them in one single step.

This contribution will highlight how nanotechnology may contribute to address such severe conservation issues. Recent investigations have shown that magnesium (as well as calcium) hydroxide nanoparticles are capable to inhibit both cellulose hydrolysis and oxidation that affect historically valuable cellulose-based materials. [3] Stabilization of cellulose pH around 6-7 prevents radicals' formation due to the catalytic activity of iron (II) in acidic environment. A well-controlled deacidification treatment seems thus to give great benefits in fighting both hydrolysis of cellulose and minimizing the effects of oxidation, favored by iron salts contaminating the artworks (see figure 1). Noticeably, since the deacidified environment inhibits the activity of iron ions, the oxidation of reduced compounds of sulfur by iron, in sulfur-rich waterlogged wood, could also be limited.

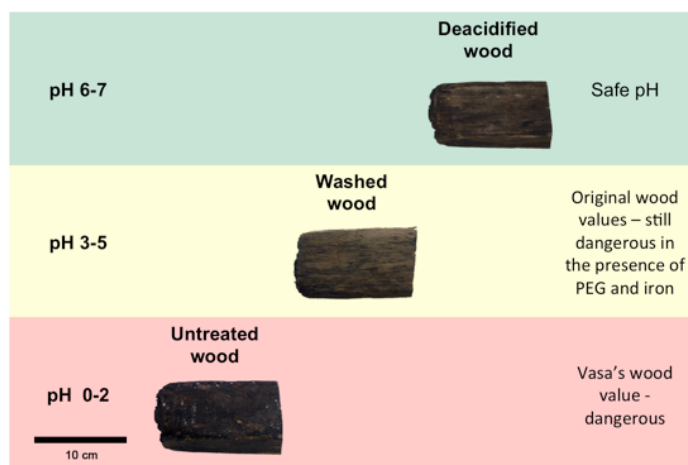


Fig. 1: pH values of *Vasa* wood before the treatment and after the deacidification with alkaline earth hydroxide nanoparticles.

Recently, samples coming from the *Vasa* hull have been considered in order to formulate methods for the treatment of acid archaeological wood, based on our previous studied on paper deacidification. [4-6] The acidity of *Vasa* wood shows a great pH inhomogeneity, with very acidic surface spots (pH 2 or less) where sulfate and iron salt precipitation occurred, and a general decreasing trend in pH (from 5 to 1.5-2) from the surface to the first centimeter in the wood bulk. The concentration of sulfates decreases from the surface up to the first centimeter, while iron is present in the surface mainly as iron (III) complexes and hydroxides. The inner part of the wood, on the other hand, shows a larger

concentration of mobile iron (II) ions. The presence of acetic acid also increases with depth, while the formic, glycolic and oxalic acids, which can also be found within the wood, are not correlated to any spatial distribution. [7,8] PEG shows a differential distribution according to the polymer molecular weight used during impregnation: a few centimeters below the wood surface for the first PEG types applied, and a constant concentration through the depth of the wood for the PEG type that was applied afterward. [9]

On such a chemically complex matrix, alcoholic dispersions of nanoparticles of earth alkaline hydroxides proved to be effective in the neutralization of acidity, and in the creation of an alkaline reserve that provides long lasting deacidification effects towards intensive and prolonged accelerated aging. Originally, calcium hydroxide with a mean size of 200-250 nm, strontium hydroxide (200-250 nm), and magnesium hydroxide (120-150 nm) were used in the preliminary tests on Vasa wood samples. Besides the deacidification effects, the chemical reactivity of calcium and strontium cations could also allow blocking soluble and partially soluble sulfate salts, which favor mechanical wood degradation.

The promising results have encouraged research efforts aimed at preparing smaller nanoparticles. The particles' size, in fact, represents a key factor in increasing their penetration inside the wood fibers, hence enhancing the beneficial effects of the treatment.

EXPERIMENTAL RESULTS

The production of nanoparticles for treating acidic waterlogged wood, can be approached in different ways, according to the desired particles' size, and to the amount of dispersion needed for the conservation issues.

By following a bottom-up procedure, hydroxide nanoparticles of earth metal ions can be synthesized with a homogeneous phase reaction in water or organic solvents. [10,11] The obtained particles must then be purified washing away reaction's by-products (e.g. sodium chloride) that would otherwise contaminate the treated wood objects. The purification steps usually do not alter the particles' size, but are time consuming, and may represent an issue for a large-scale production when deacidification of big objects, i.e. shipwrecks' timbers, is considered. A recently proposed break-down method, on the other hand, allows the production of large amounts of calcium hydroxide nanoparticles starting from lime, without requiring any purification step. [12]

After the synthesis, nanoparticles are dispersed in a proper solvent, which must be able to prevent particles' aggregation while granting, at the same time, a good wetting of the wood substrate. Characterization of nanoparticles, both before and after their dispersion in a solvent, is carried out through X-ray diffractometry, scattering techniques (DLS, SAXS), electronic microscopy (TEM), infrared spectroscopy (FTIR) and SEM-EDX. The assessment of particles's size and polydispersity, in fact, is of crucial importance when selecting the proper formulation for the treatment of wood substrates.

Promising results were obtained by using dispersions of calcium and magnesium hydroxide nanoparticles in 2-propanol. Samples of archaeological waterlogged wood, coming from the Vasa ship, were cut into cubic blocks (3 cm), which were soaked in dispersions of hydroxide nanoparticles for 13 hours. Pre-treatment of the samples in distilled water for a week, enabled the partial washing of PEG, allowing a better penetration of the alcoholic dispersions within the wood fibers. The evaluation of the deacidification treatment was carried out by monitoring two important parameters of wood's degradation status, i.e. pH and the pyrolysis temperature of wood cellulose, following the treatment of the wood samples with the nanoparticles dispersions. The measurement of pH, performed via cold

water extraction, indicated that highly acidic oak wood samples were adjusted back to less dangerous values (4-5), while pine samples reached an almost neutral value (6-7). It is worth noting that the deacidification treatment with nanoparticles can be reiterated until the samples' pH is adjusted to the desired values. The maximum pyrolysis temperature of cellulose (T_{max}) was determined through differential thermogravimetry (DTG), and provided further information about the degradation status of wood, before and after deacidification. An acid environment, in fact, causes the swelling and depolymerization of the cellulose chains, and also favors the dehydration of wood during its thermal degradation in DTG experiments. As a result, T_{max} is significantly decreased in acidic wood samples, such as the ones coming from the Vasa. Deacidification treatment with nanoparticles dispersions, on the other hand, caused the pyrolysis temperature to be reverted back to values typical of fresh wood. This result can be explained by considering that the acidic environment surrounding the cellulose fibers is efficiently neutralized by the presence of the hydroxide nanoparticles, which penetrate through the wood matrix and adhere to the fibers. The earth alkaline metal ions could also form coordination bonds with oxidized sites in the degraded cellulose, e.g. carboxylic groups that were converted to carboxylate by deacidification. The resulting coordination network would show a higher resistance to thermal degradation, justifying the increase in T_{max} . DTG experiments are only microinvasive, and are particularly important since they allow the evaluation of nanoparticles' penetration through the wood samples. As a matter of fact, deeper penetrations (up to 2 cm) were reached by applying the smallest particles (magnesium hydroxide), while bigger particles could reach depths of about 1 cm.

From the reported results, it is evident that the penetration of nanoparticles is the key factor for the improvement of the method, also in the perspective of treating large timbers. Penetration can be increased both working on the dispersing solvent and on the methodologies for the synthesis of smaller particles. While good results were obtained by using dispersions of magnesium hydroxide nanoparticles in perfluoropolyethers, an innovative approach has been developed, which allows the synthesis of calcium hydroxide nanoparticles with smaller average size and narrow size distribution. This process is an update of a bottom-up process for the synthesis of hydroxides. In particular, homogeneous phase reaction involving Ca- and Mg-precursors has recently allowed the production of hydroxide nanoparticles with average sizes starting from about 50 nm, through a very quick process (because purification step can be avoided). A comparison between calcium hydroxide and magnesium hydroxide dispersions is depicted in figure 2. This latter method could represent an important upgrade, since deeper penetrations would grant the access to the most degraded inner core of the acidic Vasa timbers, and could allow a good neutralization even when only partial pre-removal of the PEG is performed. The removal of the wood consolidant, in fact, constitutes a problematic step for several practical reasons, and all the methodologies that limit its extent could be advantageous.

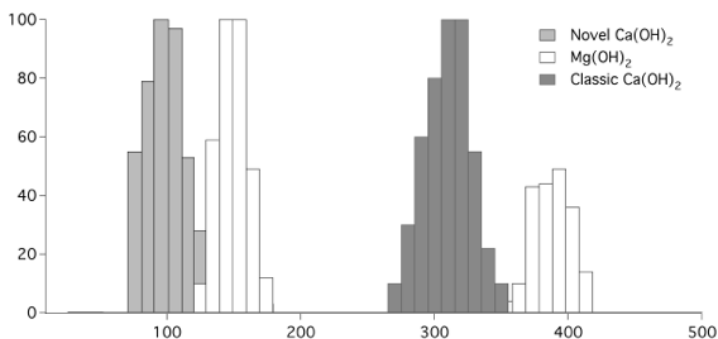


Fig.2: Comparison between calcium hydroxide nanoparticles obtained via break down method (dark grey), magnesium hydroxide nanoparticles obtained via homogenous phase reaction (white) and calcium hydroxide nanoparticles via an innovative homogenous phase reaction.

CONCLUSIONS

Formulations based on different nanomaterials provide a really innovative palette to inhibit synergistic degradation processes in acidic archaeological wood, such as hydrolysis and oxidation of cellulose. The results obtained in the last years are encouraging research efforts in order to realize feasible nanomaterials that can be produced in short times and applied even to large objects.

Recently, strontium carbonate nanoparticles have been used to neutralize acidity in samples of the Mary Rose ship's wood. [13] Promising results were obtained on cross-sections with limited depths (millimeters).

On the other hand, while dispersions of hydroxide nanoparticles can already penetrate up to significant depths, producing good neutralization effects (and a carbonate buffer to avoid future degradation), the recent preparation of smaller nanoparticles could allow the treatment of larger samples, eventually of timbers. As a matter of fact, smaller particles will enable better performances, especially when the porosity of wood is partially or completely blocked by wood consolidants that cannot be completely removed.

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26.

NEW CONSOLIDANTS IN WOOD CONSERVATION

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INTRODUCTION

In the wood lifetime, several agents can alter the chemical structure of its main components. In detail, water and biological agents can favour hydrolysis reactions which cause the prevalent loss of hemicelluloses and cellulose, which represent the backbone of the ligneous structure. In the past, several compounds and methods have been studied and used for the treatment of waterlogged wood. Out of the various compounds, poly(ethylene glycols) (PEGs) with different molecular weights are still today the most used compounds for wood consolidation. However several problems have appeared consequent to the presence of PEG into wood, because of its hygroscopicity, its relatively high cost, and the chromatic alteration of the wood manufacturing products; thus, the study of different wood consolidants is required. The goal of this study is the synthesis and characterization of wood consolidants provided with a chemical structure similar to the wood, in order to maintain its aesthetic, mechanical and physical characteristics. For this purpose, several hydroxylated compounds were synthesized and characterized in order to obtain water-soluble compounds with a high affinity for polar materials as wood, paper and natural fibres. The interest for the synthetic procedures is the use of renewable resources like cellulose, L-tartaric acid, D(+)-glucose and α,α -trehalose as starting compounds. Therefore several compounds were synthesized and characterized with the aim to obtain a library of molecules suitable for their use as consolidant agents. All the synthesized compounds have a structure similar to those of polysaccharides and in particular to cellulose in order to restore wood backbone and to improve his mechanical strength. In order to design new consolidants for wood impregnation it is necessary a rapid screening, and a diagnostic protocol was used in order to select the consolidant with the best performance between the synthesized products.

RESULTS AND DISCUSSION

SYNTHESIS OF WOOD CONSOLIDANTS

Cellulose ethers were the first class of compounds synthesized and characterized in this work, in order to be used as wood consolidants. Since cellulose is one of the most important natural polymers, several synthetic cellulose derivatives are of great industrial importance and the chemistry of cellulose derivatization has been intensively studied in the last decades in order to obtain a range of products having different chemical and physical properties. Between those, the synthesis of cellulose ethers is an important aspect of commercial cellulose derivatization. Besides, they have a high chemical stability and are toxicologically innocuous. Most cellulose ethers are water-soluble polymers. On the other hand some types are also soluble in organic solvents. Their water solubility can be controlled to a certain extent by the combination of the different ether groups, the degree of substitution and the distribution of the substituents. In the present work, water-soluble cellulose ethers like allyl-carboxymethylcellulose and allyl-hydroxypropylcellulose were obtained from cellulose with a reduced degree of polymerization (DP), in order to enhance the wood penetration ability of the synthesized products. Two kind of functional groups were introduced in the cellulose structure: a cross-linkable group (allyl), in order to reduce the mobility of the consolidant after its penetration into wood; a hydrophilic group (carboxymethyl or n-hydroxypropyl), in order to ensure a partial or complete solubility in water of the product. The syntheses of allyl-carboxymethylcellulose and allyl-hydroxypropylcellulose are reported in Figure 1.

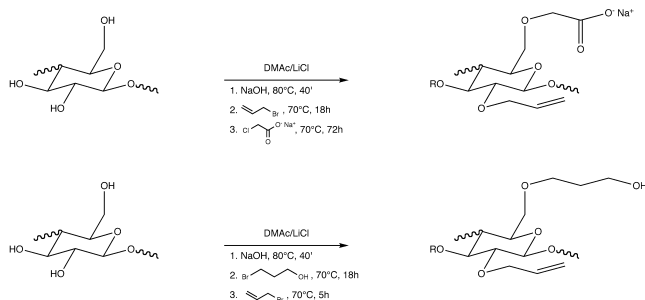


Figure 1. Synthesis of the cellulose ethers

The second class of compounds synthesized in this work is represented by hydroxylated oligoamides (m,n). The goal was to obtain water-soluble compounds with a high affinity for polar materials and lower molecular weights with respect to the cellulose ethers. The interest for the synthetic pathways is the use of renewable resources as starting compounds. In fact natural compounds or their derivatives, as L-tartaric acid, D(+)-glucaric acid and α,α -trehaluronic acid, were used as hydroxylated diacids in the polycondensation reactions in order to obtain hydroxylated oligoamides (m,n) like polyethylene-L-tartaramide, polyethylene-D(+)-glucaramide and polyethylene- α,α -trehaluronamide. The oligoamides are generally obtained as condensation products from activated hydroxylated diacids and diamines. In the present work, the polycondensation reactions between different dimethyl esters and diamines were performed in order to obtain oligoamides with different behaviour. In fact products with different molecular weight and different hydrophilic/hydrophobic ratio were obtained using aliphatic

diamines and dimethyl esters obtained from hydroxylated dicarboxylic acids. The syntheses of the oligoamides are reported in Figure 2.

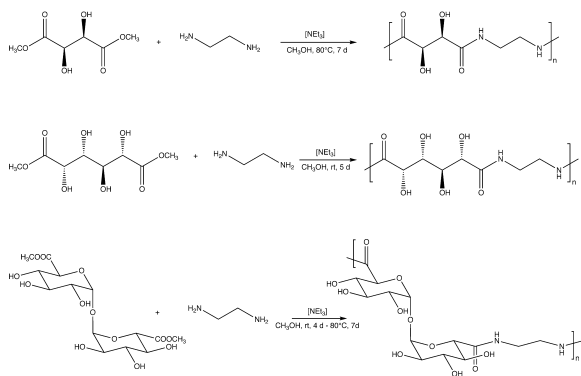


Figure 2. Synthesis of the hydroxylated oligoamides

AFFINITY OF THE CONSOLIDANTS FOR WOOD

In order to evaluate the chemical affinity of the consolidants for partially or strongly degraded waterlogged wood, preliminary tests on recent wood lignin samples were performed. In fact in degraded wood the cellulosic component is partially lost and the residue material is mainly formed by lignin. Lignin samples were prepared from wood flours following standard procedures, maintained for 24 hours into aqueous solutions or colloidal dispersions of the consolidants and magnetically stirred at room temperature. After filtration, washing and drying at 60°C, the samples were analyzed through FT-IR spectroscopy, then spectra were compared with those of untreated lignin and of the consolidants in order to evaluate the effectiveness of the treatment. Both the cellulose ethers (allyl-carboxymethyl cellulose and allyl n-hydroxypropylcellulose) and the hydroxylated oligoamides (polyethylene-L-tartaramide, polyethylene-D(+)-glucaramide and polyethylene- α,α -trehaluronamide) were tested on wood lignin samples. As an example, the FT-IR spectrum of the lignin treated with allyl-carboxymethyl cellulose is reported (Figure 3).

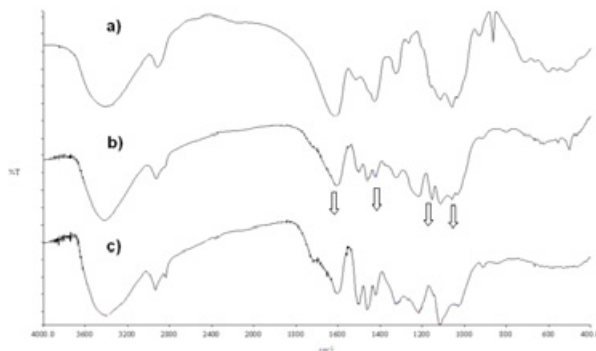


Figure 3. FTIR spectra of (a) lower DP allyl carboxymethyl cellulose (3), (b) wood lignin treated with lower DP allyl-carboxymethyl cellulose (3), and (c) wood lignin.

APPLICATION OF THE CONSOLIDANTS ON DEGRADED WOOD

Some of the synthesized products were tested on archaeological wood cubic specimens (volume 1 cm³) in order to verify their ability to penetrate inside cellular walls. The treatments were carried out by immersing every specimen in a solution of the consolidant and keeping it at room temperature for 45 days. After this treatment, the specimens were subjected to gravimetric and volumetric analyses to determine their physical properties, and the wood flours obtained from internal and external sections were analyzed using FT-IR spectroscopy. The determination of the specimens' weight was carried out by using the gravimetric method referring to the UNI ISO 3131 normative. This method allowed to evaluate the weights of the specimens treated with the different consolidants at relative humidities (R.H.) of 100%, 86%, 65% and 12%. The determination of the weight at the anhydrous state allowed to calculate the wood moisture content in the initial conditions (I.H.) and at the three hygroscopic equilibrium values (R.H. 100%, 86%, 65%) and to evaluate the basic density. In this study, in order to keep the consolidants far from the T_g, the measurement conditions at R.H. 12% were considered equivalent to those at the anhydrous state. From the data analysis it was possible to observe how all the examined samples had a higher moisture content with respect to the recent wood. The higher hygroscopicity of archaeological wood is caused by the partial or total loss of the crystalline structure of cellulose, which leads to an increase of the sites available to create bonds with water molecules. In the treated specimens the consolidants limited this phenomenon, saturating most of the hydroxyl groups of the wood. For this reason, in all the treated specimens the moisture content appeared to be lower respect to the untreated wood. The determination of specimens' volumic mass was carried out by weighing every specimen and calculating the volume through the water displacement method. In general, archaeological wood has a volumic mass lower than recent wood, due to the loss of material, in a different entity depending on its degradation state. In fact, comparing recent wood with archaeological wood this difference can be clearly noticed. The comparison with the volumic mass values of the samples treated with the consolidants showed instead a

slight variability. The volumetric shrinkage β_v of the specimens were also calculated.

$$\beta_v = (V_f - V_0) / V_f \times 100 \quad (\text{where } V_0 = \text{oven-dry volume and } V_f = \text{green volume})$$

The results related to the basic density showed how the consolidants were penetrated into the wood, leading to an increase of the density respect to the untreated wood. The volumetric shrinkages instead are clearly reduced in the treated specimens respect to the untreated one. The wood flours obtained from the external and internal sections of the specimens were then subjected to the FT-IR analysis in order to evaluate the presence of the consolidant on the surface of the specimens and inside them. As an example, the FT-IR study of the penetration of polyethylene-L-tartaramide is reported (Figure 4).

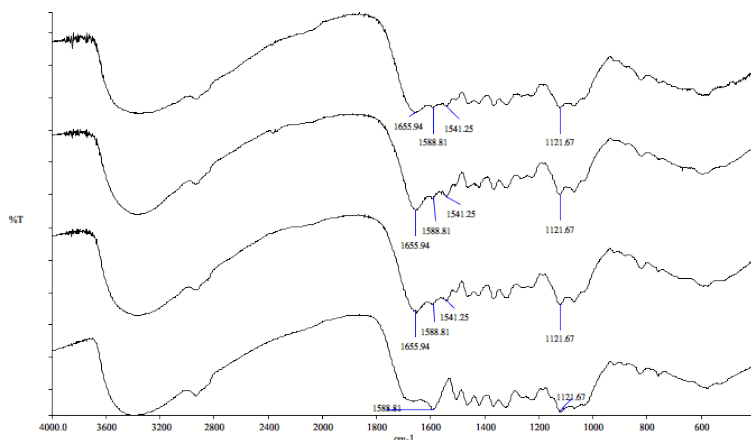


Figure 4. FT-IR study of the wood penetration for polyethylene-L-tartaramide

CONCLUSIONS

In this study, a library of functionalized polysaccharides and hydroxylated oligoamides potentially useful for waterlogged wood consolidation were synthesized and characterized. All the synthesized compounds are provided with a chemical structure similar to the one of the most degraded components of the wood, cellulose and hemicelluloses. High affinity for lignin was observed with all the consolidants. However, the amount of consolidant in the internal section of the wood specimens was only high for the hydroxylated oligoamides, probably due to their lower molecular weight respect to the cellulose ethers. Finally, the data related to the physical properties of the degraded wood specimens treated with the hydroxylated oligoamides showed an increase of the basic density and a decrease of the volumetric shrinkage with respect to the untreated wood. This behaviour clearly explains the effectiveness of these compounds in the consolidation process of waterlogged wood.

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27.

SUPRAMOLECULAR SELF- ASSEMBLED FE(III)- SEQUESTERING 3D POLYMER NETWORKS FOR THE PRESERVATION OF MARITIME ARCHAEOLOGICAL WOOD

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The Mary Rose was a Tudor warship, the flagship of what is now the British Royal Navy and a favourite of King Henry VIII (Wetherall, 2008). In 1545 she sank as she prepared to engage a French fleet in the Solent channel, near Portsmouth (UK) (Fors, 2006). She lay on the seabed, covered in silt and sand, which largely protected her from degradation for over 400 years until she was raised in 1982. The Mary Rose is a unique artefact of great cultural significance both in the United Kingdom and across Europe where she represents an age of great European exploration and sea-faring. It is imperative that artefacts of this import are preserved for future generations using modern technological advances as they represent tangible links with our past.

Chemical analyses of waterlogged wooden artefacts show loss of hemicellulose, cellulose and some loss of lignin. When the waterlogged artefact is raised from the sea, it can undergo irreversible dimensional changes due to drying which result in cracking or collapse of the wood. Conservators deal with this issue by controlled removal and replacement of the water with poly(ethylene glycol) (PEG) which improves the structural stability of the wood. The PEG is sprayed onto the wet relic for several years and impregnates the wood by diffusion, while the treatment material is rather inexpensive, the constant spraying over several years can result in the procedure becoming very costly.

While the PEG treatment deals with the issue of structural stability, there are chemical and biological processes ongoing in the wood which present further obstacles to conservators. Analysis has revealed mineral inclusions in the wood such as sulphur, from degraded

organic matter on the seabed, and Fe(III), from corroded bolts used to maintain the ship's architecture. Fe(III) can also act as a catalyst for the Fenton's type production of oxalic acid from oak wood used in the construction of the ship (Almkvist, 2008) and can cause the PEG consolidant to degrade to formic acid (Wetherall, 2008; Fors, 2006; Sandström, 2005; Jensen, 2006; Hjelm, 2005).

Although the PEG consolidant is treated with borax to hinder biological growth, there is evidence that sulphur-reducing and iron-oxidising bacteria are present in the wood (Mitchell, 2008). These can aid the production of sulphuric acid from elemental sulphur and oxidise Fe(II), which is relatively innocuous in the wood, to Fe(III) allowing it to mediate further acid production.

Clearly the presence of Fe(III) is a major issue in the conservation of maritime archaeological wood, one that remains untreated by standard conservation techniques, however its removal from the timbers is no more straight-forward. Several options for the removal of Fe(III) or the counter-acting of the acid production caused by Fe(III) saturation have been described in the literature, for example, washing the timbers with Fe(III) chelating agents such as diethylenetriamine pentaacetic acid (DTPA) (Fors, 2006; Almkvist, 2008a). Treating areas of acid build-up with Ca(OH)₂ or Mg(OH)₂ nano-particles to reduce acidity has also been suggested (Giorgi, 2006; Giorgi, 2005). Washing the wood can, however, lead to removal of consolidants (such as the PEG supporting polymer), which can in turn lead to shrinkage and collapse of the waterlogged wood. On the other hand, using nano-particles could lead to the development of basic environments in the timbers adversely affecting the alkaline sensitive lignin, additionally it does not impede further acid production catalysed by Fe(III).

To tackle this problem from all aspects, that is structurally, chemically and biologically, with a particular focus on impeding the action of Fe(III), a supramolecular approach using novel consolidants based on biopolymers, such as cellulose derivatives and chitosan, to create a self-assembled polymer network which is capable of reinforcing the structure of the wood, chelating Fe(III) and hindering biological attack is under investigation. Two orthogonal approaches to achieve this are being developed, these two consolidants can either exist independently, depending on environment within the wood structure, or work together to create a third system, which will further enhance the stability of the archaeological wood.

An important aspect of this work is the use of biopolymer precursors in place of the traditional PEG polymers. Biopolymers such as cellulose and chitosan do not form acidic degradation products like PEG and interact favourably with the wood biopolymers. Replacing PEG removes one avenue of acid formation from the wood structure, helping to prolong the lifetime of the wood.

The first of these two systems is based on a unique host molecule, known as cucurbit[8]uril (CB[8]). This barrel shaped molecule of eight repeating glycoluril units is capable of accommodating two guest molecules, one electron poor and one electron rich, into its internal cavity to form a ternary complex, termed a 'supramolecular handcuff' (Figure.1).

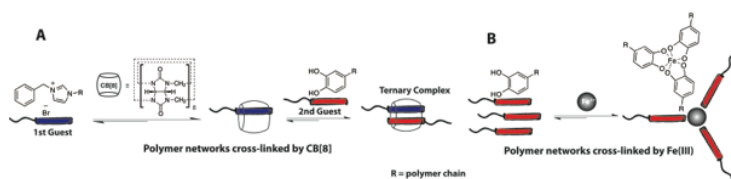


Figure 1: Graphic illustrating (A) sequential binding of the 1st and 2nd guest within the CB[8] cavity and (B) chelation of Fe(III) chelator functionalised polymer chains with Fe(III)

Previous work in our group has shown that mixing two polymer chains with appropriately chosen guest molecules in the presence of CB[8] results in the formation of a rigid polymer gel (Rauwald, 2008; Appel 2010). Functionalising polymer chains with a Fe(III) chelating guest and an anti-microbial guest to tackle biological activity will then result in a gel which can not only support the structure of the wood but also tackle two main issues effecting conservation of the wooden artefacts (Figure 2).

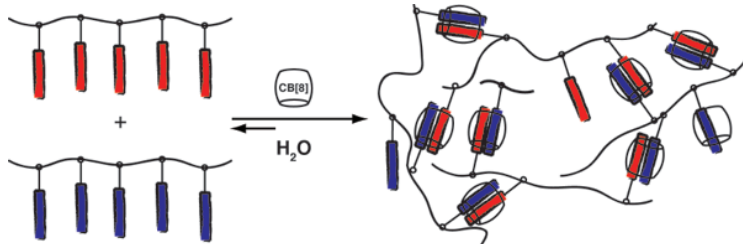


Figure 2: Idealised schematic showing the formation of a supramolecular self-assembled polymer network using an Fe(III) chelating guest (red) and an anti-microbial guest (blue) with CB[8] as the cross-linker

The second approach is the development of a metal-organic polymer network, useful in areas of high Fe(III) concentration, where Fe(III) can cross-link polymer chains functionalised with Fe(III) chelating agents to entrap the Fe(III) hindering its catalytic activity while providing an element of support (Figure 3)

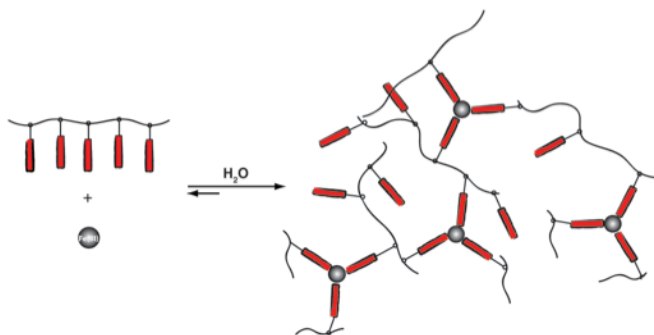


Figure 3: Idealised structure of a metal-organic polymer network cross-linked by Fe(III)

Due to the inhomogeneous nature of the wood and distribution of Fe(III) within the

timbers, it is likely that both systems will work in concert to reduce the action of the Fe(III) within the wood and support the wooden structure (Figure 4). The addition of the anti-microbial guest provides a third benefit to the use of this system over the current PEG treatment, this added functionality should also provide the wood with some resistance to rot, another cause of degradation in archaeological wood.

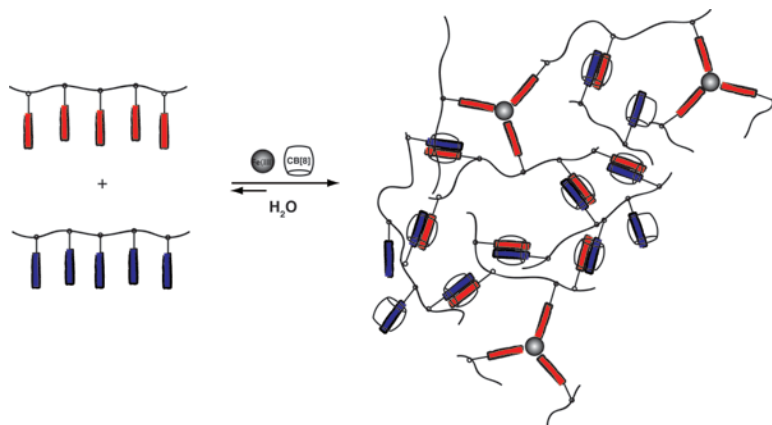


Figure 4: Idealised structure of the enhanced consolidant incorporating both the CB[8] cross-linked polymer and the metal-organic polymer network, enhancing the structural support and chemical and biological activity of the consolidant system

As a final advantage of this system, these 3D polymer networks are completely reversible, meaning that removal of the polymers from the wood should have no adverse effects on the structure of the wood. Preliminary studies involving the selection of appropriate guests, characterisation of the Fe(III) problem within the wood and demonstration of the formation of such Fe(III) chelating polymers will be presented in this talk.

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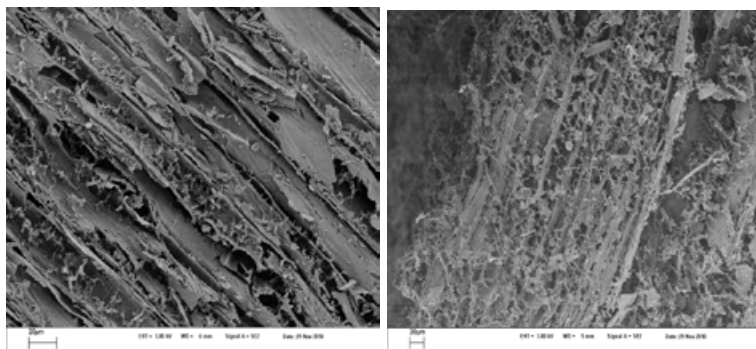
BIOMIMETIC CONSERVATION: CELLULOSE AND CHITOSAN FOR WOOD PRESERVATION

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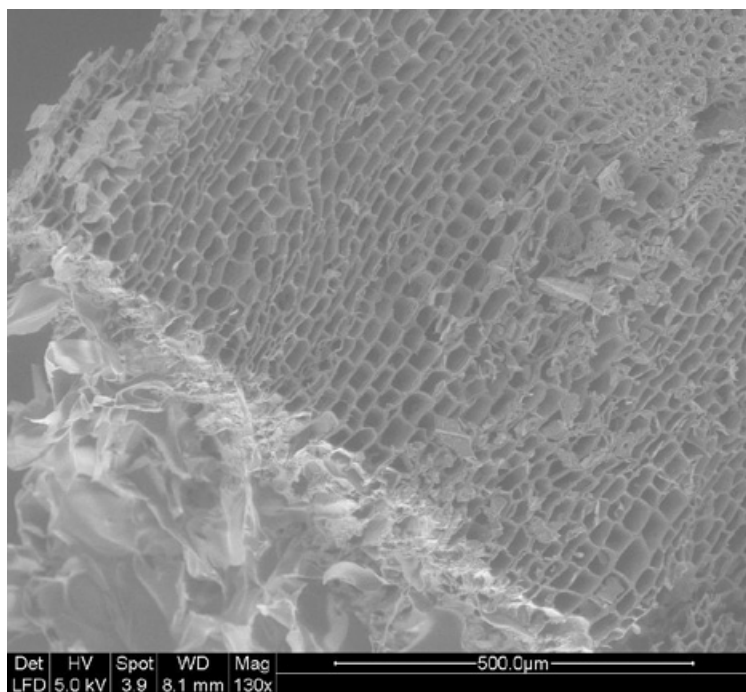
Biomimetics is a discipline which tries to utilise advantages from materials existing in nature when designing new materials to be used in engineering. Many materials are strong despite having porous structures. In conservation science, this allows the possible construction of materials which are chemically compatible with archaeological wood and offer support without bulking the artefacts fully. Cellulose is extremely important as it can already be found in wood and the crystalline parts of the cellulose are resistant to acid degradation and much less hygroscopic than regular cellulose. Using magnifications of around 25000-30000x in a SEM, it was possible to see the individual whiskers. Tests on archaeological wood fragments indicated that it was difficult to keep the fibres dispersed in water as ions from the artefacts made them coagulate rapidly. Acetylation only made the matter worse and risked turning the whiskers into cellulose acetate. Initial tests indicate that surfactants may be used to stabilise the whiskers more thoroughly. If the cellulose is not ideal, chitosan might be an alternative. The material is made from modified chitin (from crabs and other seafood) and can be dispersed in monovalent acids. Tests indicate that chitosan dispersed in acetic acid improved the strength of the wood without filling the structure.



INTRODUCTION

Due to the problems with previous and current conservation methods, it is vital to explore new possibilities for treating archaeological wooden artefacts. New conservation strategies may well have to be retreatable, leading us towards the option of having ‘open’ or ‘airy’ structures to accommodate possible future consolidants [1].

The field of biomimetics uses inspiration from natural designs when making artificial constructions. It is especially famous for bone grafts, the ‘lotus effect’ (self-cleaning surfaces) and animal functionality (surface-adhering gecko feet or motion sensors on spiders) [2]. One of the characteristics of biomimetic materials is their tendency to self-arrange in open or porous structures. If applied to conservation, this means that the treated artefacts are left ‘airy’ enough to be re-treated when the need arises sometime in the (hopefully far) future. Despite its success in design, however, no biomimetic approach has been developed for treating waterlogged wood. As the need for new consolidants increases, it is natural to look towards a discipline which offers bio-compatible light weight structures – especially when they are composed of non-toxic substances.



2 Cellulose whiskers

Cellulose is a major component in wood but pure cellulose can be treated with acid to leave highly crystalline rods, so-called ‘whiskers’, which are resistant to degradation [3]. In fact, the hydrogen bonding between individual molecules promotes such a tight structure that even water cannot penetrate into the crystalline cellulose, making the whiskers highly resistant to changes in humidity. In watery suspensions, the whiskers naturally align into a vertical nematic crystal phase. As the fibres bond to one another (for example during freeze-drying) they produce a white porous structure which can be used to bridge micro- or macroscopic cracks in archaeological wood. The structure may then be further treated with other polymers if additional strength is desired – or combined with nanoparticles (such as calcium carbonate) which can act as a reservoir of acid-neutralising material.

Cellulose whiskers may be prepared in sulphuric acid [4]. This leaves some sulphate groups on the surface of the whiskers which helps disperse them in water. It may also be possible to disperse the whiskers in other solvents if desirable. These initial tests simply used 5% wt. cellulose fibres in 66% sulphuric acid stirred at 60°C for one hour. The treated fibres were centrifuged repeatedly until a white precipitate formed and this was collected and ultrasonicated (using a tip sonicator at 30% power) to disperse the whiskers.

Archaeological wood from the Viking Age was used to test the penetration of the fibres. SEM images showed that the whiskers form large sheets upon freeze-drying when frozen in liquid nitrogen. Unfortunately the whiskers look much like existing wooden structure and it can be tricky to differentiate the two (as shown in Figure 1).

Figure 1: SEM images showing actual cellulose from the wood (left) and artificial cellulose fibres (right). Note that the structure of the original cellulose is very similar to that of the fibres.

While acetylation is sometimes used to prevent cellulose fibres from sticking – especially in nonpolar solvents – this is not desirable in conservation science as it can lead to formation of cellulose acetate which generates acidic acid upon contact with air. In stead, thin solutions and stearic hindrance through applied surfactants should be used to prevent the whiskers from sticking to one another during penetration. Initial tests using PEG as a surfactant showed that it significantly improved penetration and distribution.

CHITOSAN

Chitosan is a bio-polymer made from deacetylated chitin [5]. Since chitin from seafood such as prawn and crabs is readily available as leftover material from the food industry, this chitin is used for the bulk of chitosan production. Unlike the original chitin, the chitosan is water-soluble in dilute monovalent acids [6]. The acids may be neutralised before freeze-drying (this merely causes the chitosan to precipitate). Even using a 2%w/v solution of chitosan makes the mixture quite viscous and the freeze-dried chitosan feels somewhat like a hard foam mattress. An additional advantage to chitosan is that it may chelate certain metal ions and thus prevent them from acting as catalysts and accelerate the degradation of consolidants and treated artefacts.

Both dilute hydrochloric acid and acetic acid were tested for chitosan dispersions. It was found that the acetic acid kept the chitosan stable over longer times (it should be noted that acetic acid is generally undesirable in a museum environment, however). Archaeological pieces of waterlogged Viking Age wood were put into solutions and allowed to penetrate. The pieces were frozen in liquid nitrogen and freeze-dried. An example is seen in Figure 2. This demonstrates the structure of the chitosan outside the wood as well as the trouble with discerning the amount of chitosan adhering to the leftover wooden matrix. Even if chitosan cannot easily be identified in the structure, pieces treated with chitosan felt significantly more stable than those treated with cellulose fibres or simply freeze-dried. Chitosan-treated pieces could easily be cut with a razor blade without powdering or flaking the bits of wood. This makes it imperative to do more future experiments to determine how the chitosan is actually distributed.

CONCLUSIONS

The current state of conservaton techniques leaves some things to be desired. The ideal consolidant is compatible with wood while having excellent strength-to-weight ratio. Additionally the treated artefacts should not be bulked but maintain an ‘open’ structure to allow for future re-treatment.

Attempts to fill archaeological Viking Age wood pieces with cellulose whiskers showed that the whiskers adhere well to the remaining wooden material. Unfortunately the ions in archaeological wood makes the whiskers flocculate and thus prevents thorough penetration of large pieces of wood. The solution is to use surfactants. Although initial tests were made with PEG, more efficient surfactants might prevent the fibres from sticking over longer time frames. Even so, the cellulose should be reinforced somehow to increase its strength once inside the artefacts.

Chitosan is modified chitin. The polymer may be dissolved in dilute monovalent acids and both hydrochloric acid and acetic acid were tested. The acetic acid seemed most efficient at preventing conglomeration of chitosan. Actual pieces of archaeological wood from the Viking Age were treated and the chitosan was able to penetrate and stabilise the wood to a much higher degree than the cellulose fibres.

Although these studies are far from finished, they have demonstrated that biomimetic materials may be compatible with archaeological wood. In the future, further study should focus on enhancing the properties of the consolidants to allow them to better imbue strength to the degraded wood. In addition, the next generation of consolidants might be hybrid materials which contain acid-neutralising nanoparticles or are reinforced by durable inorganic parts.

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29.

A NEW PROTOCOL SUITABLE FOR THE TREATMENT OF COMPOSITE ARCHAEOLOGICAL ARTEFACTS: PEG TREATMENT + FREEZE- DRYING + RADIATION-CURING RESIN CONSOLIDATION

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INTRODUCTION

For 30 years, ARC-Nucléart used a specific treatment to preserve composite archaeological waterlogged artefacts that cannot be treated by the standard Polyethylene Glycol (PEG) protocols. This approach is quite suitable for very brittle objects or wooden objects that include iron parts or are contaminated by metallic salts. In each case, PEG resin can be considered as too soft and too hydrophilic for the metallic base materials, especially for long-term storage in air after drying.

The so-called “Nucleart” process enables hydrophobic resin such as styrene-unsaturated polyester (S-UP) to be used; this is polymerised in situ by gamma irradiation. Even if this technique is completely irreversible, the hardness and the final hydrophobic behaviour of the composite “plastic-wood” material obtained is very interesting for subsequent possibly hazardous environmental conditions: mechanical shocks, vibration, high humidity, etc. Since water and styrene-polyester resin are not compatible, the impregnation of wet wooden artefacts was carried out via two successive very long and costly impregnation treatments: liquid exchange of the water inside the wood by acetone, followed by another liquid exchange of acetone by S-UP resin. The treatment ends by a in situ polymerisation of the resin with gamma rays.

Since 2008, ARC-Nucléart has developed another version of the “Nucleart” treatment by associating PEG treatment and radiation-curing resin. The process consists in beginning the treatment with classical PEG 4000 permeation followed by freeze-drying.

The dried artefact is then consolidated, in the third step, by full impregnation with liquid

S-UP resin under pressure, followed by in-situ resin hardening by gamma irradiation.

DESCRIPTION OF THE NEW “NUCLEART” TREATMENT

This new “Nucleart” treatment consists in combining two current treatments already used by the workshop, PEG/freeze-drying treatment and Nucléart treatment suitable for dried artefacts. The originality of this process in comparison to other treatments of waterlogged objects lies in the order of the steps. First, it is proposed to dry the artefacts, and in a second step to complete the wood consolidation treatment by a thermoset type resin without any addition of solvent. The advantages of such an approach appear very interesting, namely high-level consolidation of the object, a free solvent method and a short duration compared to the old “Nucleart” protocol that involved two long successive liquid-liquid exchanges (Tran Q.K. 1984, 2008, 2011). The main disadvantage, which is already well known for the “Nucléart” process, is the non-reversibility of the crosslinked resin.

The main objective of archaeological wood treatment is to keep the initial shape of the object during drying, whatever the level of degradation of the wood considered. In other words, the success of the treatment depends on our capability to preserve the integrity of the waterlogged object during the freeze-drying step. Though freeze-drying prevents any collapse of the porous structure of degraded wood, it is not able to avoid fibre shrinkage due to the extraction of bound water that establishes hydrogen linkage with the polar functions of the wood components. During the vaporisation of bound water, the fibre shrinkage phenomenon leads to deformation of the wood (see Photographe N°1). Though this is generally moderate compared to collapse, it is not negligible. Secondly, another source of deformation is ice expansion as a result of the water freezing. Both phenomena induce deformations that can cause micro-cracking of very brittle degraded wood. This micro-cracking is not very spectacular (Photograph N°2), but is harmful for all subsequent handling of the object up to final polymerisation of the styrene-polyester resin. That is why it is important to reduce micro-cracking in very degraded wood coming from the drying step as far as possible.



Photograph N°1: Shrinkage effect observed on samples not treated by PEG (left) compared to sample treated with 30% wt PEG 4000 (right).



Photographie 2: Microcracks observed after freeze-drying without any PEG impregnation.

To summarise, the major question in using the new “Nucleart” protocol is assessing the quantity of PEG to inject into the wood before freeze-drying. We saw previously that PEG is absolutely necessary to limit micro-cracking effects and to obtain minimum consolidation for the wood to be handled before radio-polymerisation, but it is necessary to retain free pores in the wood to permit final densification within the second styrene-polyester base impregnation stage. A compromise has to be made between PEG and styrene-polyester resin contents. Further preliminary experiments suggest that 30%wt PEG content may be the best solution.

This present work aims to validate the 30%wt of PEG 4000 case. We used archaeological wood samples from the Charavines sites (11th century AD): 6 beech samples for very degraded grade cases and 6 further oak samples for little degraded wood. The geometry of the beech and oak samples is approximately: 47 x 27 x 25 mm. Weight and size measurements were carried out at each step of the treatment. The protocol can be described as follows:

- 1) Impregnation of samples with 20% PEG solution for 2 weeks at 70°C, followed by further impregnation for 2 weeks with 30wt% PEG 4000 solution, again at 70°C. The impregnation duration can be considered too short, but the geometry is small and heating was used to accelerate water-PEG exchange in the wood.
- 2) Freeze-drying of the sample with the following operating parameters: duration: 48h, vacuum: 8.10-2 mbar, temperature of sample at the beginning of freeze-drying: -30°C.
- 3) Nucleart densification: vacuum-pressure method: vacuum = 1 mm Hg, for 8 h, pressure = 5 bar for 24 h. Radio-polymerisation by gamma ray with a 20 kGray dose.

RESULTS - DISCUSSION

The results are given in two types of table, as follows:

-Tables 1 and 2, respectively for beech and oak samples, give the change in size and weight of the samples at different stages of the treatment. Each value is an average of 6 samples. The reference for the calculated percentage is established from the initial values for the waterlogged samples before treatment.

-Tables 3 and 4, respectively for beech and oak samples, make a comparison between samples without and with 30% PEG-treated samples in terms of variations in size and weight.

Beech	Initial state Waterlogged samples	After 30% PEG permeation	After Freezing	After freeze- drying	After resin radio- polymerisation
Volume variation (%)	Reference value	3	3	# 0	-2
Weight variation (%)	Reference value	2	# 0	-65	-6

Table 1: Variation in very degraded beech sample sizes and weights throughout the treatment.

Oak	Initial state Waterlogged samples	After 30% PEG permeation	After Freezing	After freeze- drying	After resin radio- polymerisation
Volume variation (%)	Reference value	2	2	-8	-8
Weight variation (%)	Reference value	# 0	-1.5	-45	-16

Table 2: Variation in non degraded beech sample sizes and weights throughout the treatment.

Beech	Partial treatment: only freeze-drying	Full treatment 30% PEG permeation and freeze- drying
Volume variation (%) Reference is initial state	-4.5	# 0
Weight variation (%) Reference is initial state waterlogged sample	-77	-65

Table 3: Comparison of very degraded beech samples between partial treatment without PEG and full treatment with 30% PEG permeation. All samples are freeze-dried.

Oak	Partial treatment: only freeze-drying	Full treatment 30% PEG permeation and freeze- drying
Volume variation (%) Reference is initial state	-10	-8
Weight variation (%) Reference is initial state waterlogged sample	-60	-45

Table 4: Comparison of little degraded oak samples between partial treatment without PEG and full treatment with 30% PEG permeation. All samples are freeze-dried.

In Photographs 1 and 2, it appears that 30%wt impregnation gives better results in terms of preventing micro-cracking (beech) and deformation (oak) of wood during the freeze-

drying stage, compared to no PEG permeation. This demonstrates the efficiency of PEG 4000 in limiting fibre shrinkage and encouraging cryogenic protection of wooden tissue. In Tables 1 and 2, the loss of volume is quite satisfactory in the case of very degraded wood (near 0% after freeze drying and near 2% after densification due to the contraction of resin during its polymerisation), but nevertheless remains less interesting in the case of little degraded wood, with a value of 8%.

In Table 1, the mass loss of beech just after freeze-drying is very important (-65%), unlike mass loss after resin densification (-16%). Moreover, in Table 3, the mass loss from humid state of not PEG treated sample (-77%) is close to the mass loss of PEG treated sample (-65%). Both features mean that the mass uptake due to the PEG is limited compared to uptake due to S-UP resin. This is because the vacuum-pressure technique used for styrene-polyester permeation is more efficient than for natural PEG impregnation. Furthermore, PEG is not an inhibitor of radio-polymerisation. It is therefore possible to conclude that the presence of PEG does not prevent resin permeation and in-situ polymerisation of the resin in the wood.

With regard to the final appearance, there is no major difference between the new method and the old one. We noticed a darker colour due to the presence of styrene-polyester in the wood, which is usual with Nucleart method.

CONCLUSION AND PERSPECTIVES

Experiments were performed with waterlogged samples and demonstrated the interest of this new approach compared to the old one. Even if the old method with acetone solvent gave the best results, without any micro-cracking, the results obtained with PEG are sufficiently interesting and should enable the old protocol to be abandoned completely. Over the past year, the protocol has begun to be implemented successfully on several collections by the ARC-Nucleart workshop.

Though the results are promising with this new Nucleart protocol, ARC-Nucléart does not intend to change its "treatments" policy. The Nucleart process is used mainly for exceptional cases, especially those involving severe constraints, as mentioned in the introduction: high consolidation rate and hardness, protection against active chemical changes in composite artefacts. Indeed, the cost of the Nucleart treatment and its irreversibility mean that its use must be limited. "PEG + freeze-drying" treatment remains the main and standard protocol used by ARC-Nucléart to treat archaeological collections.

Further research work is foreseen to explore the original idea of two-stage treatment involving first drying waterlogged material, followed by a second stage of consolidation from a dry state. It could be possible to replace the radiation-cured resin by a traditional resin applied in its melting state. For instance a paraffin-based resin, i.e. a neutral and very hydrophobic resin with a melting point range of 50-60°C.

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30.

TIME- AND WAVELENGTH RESOLVED DIFFUSE OPTICAL SPECTROSCOPY FOR NONINVASIVE CHARACTERIZATION OF WOOD

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In this work we propose the use of time-resolved diffuse optical spectroscopy in the near-infrared range as an effective mean for non-invasive analysis of wood in depth. Different types of wood have been investigated including spruce, pine and oak. Hardwood and softwood show different bulk absorption and scattering spectra which vary according to chemical and structural composition and are related to the orientation of the fibers, highlighting the strong anisotropy of the wood. The technique can be used both to assess waterlogged wood, and for the monitoring of dynamic changes in the moisture content of wooden samples. Investigations are underway to assess the applicability of the technique for the assessment of conservation treatments.

INTRODUCTION

Wood is frequently found in excavated and waterlogged shipwrecks. However, the conservation of excavated waterlogged wood is particularly complex due to the natural processes of degradation which, prior to excavation underwater, lead to modifications of the physical and chemical properties of wood. In addition, the deterioration of consolidated or treated wood and the interaction of wood with the environment are central issues for the ongoing preservation of excavated materials. Normally chemical analysis is needed which necessitates sampling for a thorough understanding of the

chemical composition of waterlogged wood. In addition, the conservation of recovered wood has been subject to significant study for the assessment both of condition and treatment, but there are few non-invasive methods for the assessment of the physical and chemical properties of bulk wood following treatment. Various methods for the non-invasive analysis of wood and its moisture content have been proposed which include, e.g. permittivity, electrical impedance and Nuclear Magnetic Resonance. Another promising method, which has the advantage of being able to probe the optical properties of the material in depth at the bulk level, and can be used for the assessment of the condition and components in wood is based on the propagation of radiation in the visible and near infrared [1], which is the focus of this work.

We propose a non-invasive method based on Time-Resolved Diffuse Optical Spectroscopy (TRS) in the visible-NIR region for the analysis of the composition, structure and water content of wood. The measurement of the absorption of photons yields information which can be related to the lignin and cellulose content of wood, or to its moisture content, while the measurement of the scattering spectrum provides information of wood structure.

MATERIALS AND METHODS

EXPERIMENTAL SET-UP

Figure 1 shows a schematic of the system set-up employed for time-resolved diffuse optical spectroscopy on wood samples. Illumination was provided by a supercontinuum fiber laser source emitting in the wavelength range 450-1750 nm, with a mean power over all the spectrum of 5W and pulse duration less than 30 ps. The laser repetition rate can be adjusted from 2 to 80 MHz; for these measurements it was set at the maximum value available.

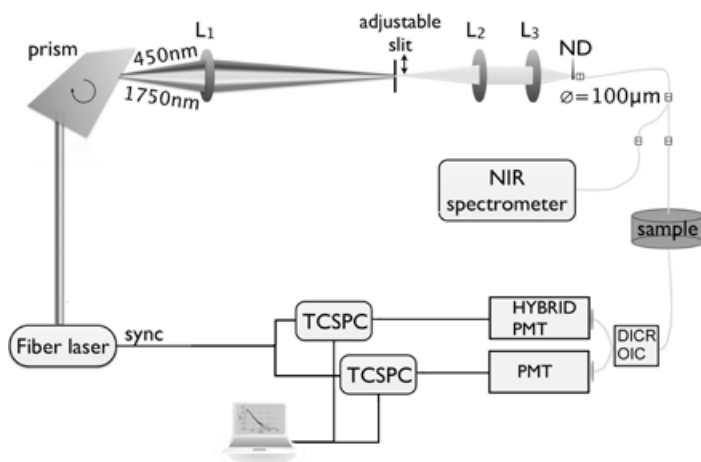


Fig.1 Block diagram of the set-up for TRS.

Spectral selection was achieved through computer controlled rotation of a prism; the dispersed radiation was then focused onto an adjustable slit, acting as a bandpass filter, to improve the spectral purity and thus obtaining a full-width at half maximum (FWHM) of about 10-15 nm in the spectral range 600-1200 nm used in the measurements.

Multimodal step-index optical fibers delivered the laser light to the samples and collected the diffused light. A dichroic filter allowed us to send the collected light either to a hybrid photomultiplier tube (PMT) sensitive up to 930 nm or to a PMT with sensitivity in the range 930-1200 nm. The temporal resolution, limited by the temporal response of the detectors, was around 180 ps for the Hybrid PMT and around 300 ps for the other detector. The system is fully automated for data acquisition and analysis. Measurements were performed from 600 nm to 1200 nm in steps of 5 nm, with a Time-Correlated Single-Photon Counting board as processing electronics. Both reflectance and transmittance geometry can be chosen for the measurements. In the first case, the fiber delivering the source and the one collecting the diffused light from the sample are on the same side of the sample itself, while in the second case the two fibers are placed on opposite sides of the sample.

WOOD SAMPLES

Measurements were performed on different types of wood: pine and spruce as examples of softwood and balsa and oak as examples of hardwood. To account for the strong anisotropy of wood, samples have been measured in two different geometries: with the line connecting the tips of the two optical fibers parallel to the direction of the wood vessels and with the same line perpendicular to the vessels. In the following these two geometries will be referred to as the par-configuration and the per-configuration. Furthermore, to evaluate time-resolved diffusion spectroscopy for the determination of the dynamic change in moisture content, a wooden sample (spruce) was conditioned under an environment with RH set at 84% at an ambient temperature of about 25 °C and changes in the absorption spectrum of the sample were monitored during forced drying to 10% RH. During drying, the weight and volume of the sample were measured.

DATA ANALYSIS

For each wavelength, the optical parameters in terms of absorption and reduced scattering coefficients were retrieved by fitting the data to an analytical solution of the Radiative Transport Theory in the Diffusion Approximation, applying the Extrapolated Boundary Conditions for an infinite homogeneous slab [1]. The theoretical curve was previously convoluted with the instrumental response function (IRF) and then a Levenberg-Marquard algorithm was applied to fit the experimental data. To overcome variations in the observed absorption due to the swelling or shrinking of wood, a parabolic normalization procedure based on the absorption spectrum of the sample was employed after the optical parameters were obtained [2].

RESULTS

In figure 2 we report the absorption spectra for the samples of pine and oak both for the par-and per configuration. As can be seen, the oak spectrum in the region below 900 nm is much higher with respect to the pine spectrum due to the strong presence of extractives which are dominant in hardwood species. This strong absorption also affects

the signal level: for this reason, for wavelength shorter than 800 nm we could not recover the absorption coefficient with the available optical power. For both samples, bands are attributed to cellulose (around 920 nm) and to the combined effect of water and cellulose around 970 nm. The rapid increase of the absorption below 850 nm can be attributed to lignin and extractives.

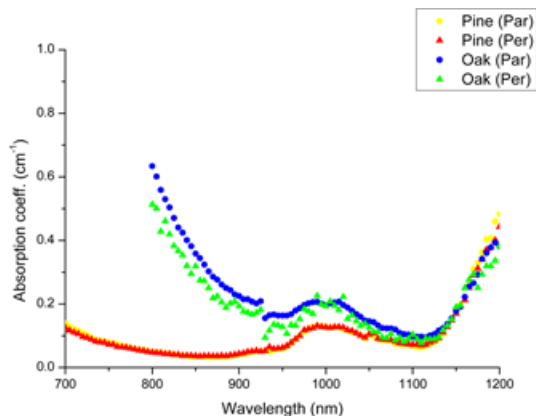


Fig.2 Absorption spectrum of pine and oak measured in the par- and per-configuration.

The reduced scattering coefficient is reported in Figure 3 for pine and oak both for the par-and per- configuration. Due to the strong effect of wood anisotropy, the scattering coefficients measured in the two configurations are very different: in the par-configuration, when the light is able to follow the path of the wood vessels, the scattering is lower than in the case found in per-configuration when light is propagating perpendicular to the vessels. In all the cases the scattering spectra is characterized by a flat behaviour. Finally, measurements have been carried out on artificially degraded wooden samples, where a structured modification took place, revealing changes of the scattering spectra.

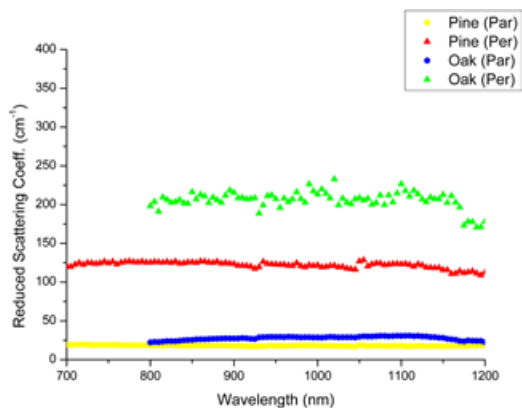


Fig.3 Scattering spectrum of pine and oak measured in the par- and per-configuration.

Figure 4 shows the absorption spectra of the sample used for the evaluation of the dynamic change in moisture content (MC) at various stages during the drying process. The spectra have been normalized to compensate for the shrinking of the sample. As can be observed, there is a correlation between the decrease in the MC and the reduction in absorption coefficient for wavelength greater than 900 nm. Even small differences (less than 1%) in MC lead to discernible changes in absorption spectra of the wood sample.

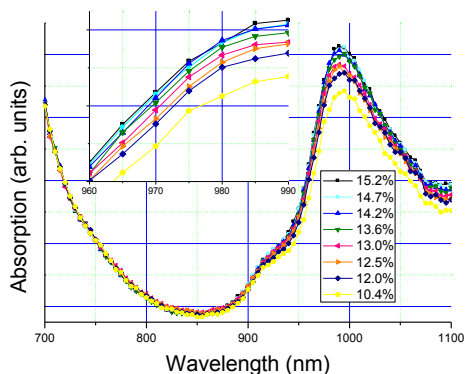


Fig. 4 Parabolic normalized absorption spectrum obtained for a wooden sample monitored during the drying process (RH from 84% to 10%). (Inset) A zoom of the wavelength range 960-990 nm is shown.

CONCLUSIONS

In conclusion, TRS can be used to record the absorption and scattering spectrum of wood and has the advantage of being able to probe the bulk properties of the material. Analysis has demonstrated that TRS can be usefully employed to assess the chemical components of wood (related to absorption spectrum), and to assess the dynamic changes in moisture content. Moreover, the scattering spectrum provides information on the structure of the wooden sample. With advances in instrumentation, TRS can be designed to be a fully portable and compact technique, whenever laboratory studies have identified the key parameters and defined the operating conditions. It is hoped that it will be possible to extend the technique to the monitoring of other samples of archeological and conserved wood and to investigate changes which occur with degradation of wooden samples.

We are currently working on the possibility to integrate the TRS with other optical techniques in order to increase the information content. In particular, we are focusing on the integration of TRS with GASMAS (Gas in Scattering Media Absorption Spectroscopy) [3,4]. In particular TRS measurements are useful for GASMAS to assess the photon pathlength and therefore to improve the quantitative analysis. Conversely, GASMAS provides insight on the porosity of the medium, and the identification of gas species inside the sample. In particular, an integrated TRS-GASMAS instrument can be foreseen to be employed on the field for wood characterization.

ACKNOWLEDGMENTS

The present project is supported by the “Ministero dell’Istruzione dell’Università e della Ricerca of the Republic of Italy” and by the Swedish Research Council under the “Executive Programme for Scientific and Technological Cooperation between Italy and Sweden”. We would also like to thank the Vasa Museum for providing nice samples of the warship Vasa and Riksäpplet.

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31.

POSTER: LONG TERM BEHAVIOUR OF STABILISATION METHODS USED FOR LARGE WATERLOGGED WOODEN OBJECTS

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The currently most popular stabilisation methods for large waterlogged wooden objects - such as ships and timbers which can not fit into a freeze-drying chamber - were compared with regard to their stabilisation efficiency, the appearance of the treated wood, the technical and financial requirements of the process, the necessary attendance and skill of personnel by Hoffmann (2007).

Most published results of conservation methods are based on the evaluation directly after finishing conservation treatment. In general, published long term measurements or evaluations of treated archaeological wooden objects are surprisingly rare. Due to the fact that conservation should preserve cultural heritage for present and future generations the possible long term influence of the conservation treatments to the objects should be of interest. Therefore, here a visual and dimensional evaluation of the same samples used by Hoffmann (2007) will be summarized 6 years after conservation. Samples were of pine, beach and oak wood treated with four different conservation methods; PEG 3000, Sucrose, Lactose combined with Trehalose and Kauramin.

Hoffmann, P., 2007; On the efficiency of stabilisation methods for large waterlogged wooden objects, and on how to choose a method, In: Proceedings of the 10th ICOM Group on Wet Organic Archaeological Materials Conference, S.323-350, ISBN 978-90-5799-139-4

32.

POSTER: THE INTERACTION OF IRON AND OXYGEN ON OAK WOOD – DETERMINATION OF DEGREE OF DETERIORATION OF IRON IMPREGNATED FRESH OAK WOOD BY TENSILE STRENGTH AND CHEMICAL ANALYSES AND COMPARISON WITH VASA WOOD

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Wood degradation in the warship Vasa has been studied systematically regarding the chemical and physical properties as function of time. The aim of this study is to investigate the chemical reasons to the deterioration of the wood, irrespective whether it is a Fenton-type reaction or acidic hydrolysis. Furthermore, it is still a question whether the deterioration reactions still go on or if they did stop soon after the ship was salvaged. In this work fresh oak wood was treated with iron solutions and different degree of oxygen exposure. Several series of fresh oak wood were cut in a “dog bone” shape, and stored in aqueous solutions containing iron(II) or iron(III). These samples were exposed to different concentrations of oxygen. An Instron universal testing machine was used for axial (i.e. parallel to the fibers) tensile testing and the tensile strength required to break the wood was registered. The changes from untreated reference samples and those exposed to iron and oxygen show distinguishable differences in tensile strength. Variation of time and concentration of oxygen exposure showed that the deterioration of the wood takes place at the initial stages of the exposure. It was shown that the exposure of pure oxygen increases the deterioration rate of this process. However, the scavenging effect did decline after about 14 days. Extraction with water of ground samples indicated an increase in the production of low-molecular organic acids in the wood tissue and a decrease in pH to approximately 2 was observed. The properties of holo-cellulose are also affected and size exclusion chromatography (SEC) showed significant decrease in the degree of polymerization of the carbohydrates compared to untreated samples. Presence of iron

seems to be an important factor for the degradation and reduction in tensile strength of the wood. This is unfortunately a significant problem as iron compounds are common in Vasa wood. The results from this study show that these deterioration reactions seem to be limited in time and take mainly place soon after exposure to oxygen. Deterioration reactions are also dependent on several other parameters such as temperature, humidity, diffusion rate of oxygen and transport properties of water in the wood. As soon as the Vasa was exposed to oxygen it is believed that these deterioration reactions started in the surface area, while it took longer time at larger depths due to the slow diffusion of oxygen into the wood. The uniform presence of iron compounds in Vasa wood makes the presence of oxygen and low pH the determining factors for these deterioration reactions.

Keywords: the warship Vasa; Fenton-type reactions; oak wood; tensile strength; acid hydrolysis.

33.

POSTER: NON-INVASIVE OPTICAL DIAGNOSIS OF GASES IN WOOD

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ABSTRACT

The GASMAS (Gas in Scattering Media Absorption Spectroscopy) technique is applied to study various wood samples. The molecular gases oxygen and water vapour, located in the pores of the strongly scattering wood material, are detected using laser spectroscopy in the near-infrared spectral region. Diffusion properties of wood pre-treated in pure oxygen environments are studied and discussed. The goal of the project is to gain increased knowledge on gases and gas diffusion in archeological wood.

INTRODUCTION

Thorough chemical and physical characterization is of great importance to understand the phenomena behind degradation processes of wood. In turn, understanding of these degradation processes is essential for the preservation and consolidation of archeological wooden objects. Methods based on optical radiation are promising as “bulk” techniques, in order to characterize the structure and chemical composition of wooden objects at

a macroscopic scale. As is common for most optical approaches, such methods have significant potential advantages, e.g., non-invasiveness and non-destructiveness, and the possibility for a robust instrument compatible with field applications. The handling can also be kept simple and without risk for the operator. The non-invasiveness and non-destructiveness of the technique are of great importance when studying valuable archeological artifacts.

In this paper we present a comparatively new optical technique meant to complement bulk material investigations with information about gas composition and gas transport processes in wood.

We use a technique known as GASMAS (Gas in Scattering Media Absorption Spectroscopy) [1], a non-intrusive optical spectroscopic technique based on light in the visible/NIR region.

The fundamental principle of GASMAS is the essential difference between absorption of light by free atoms or molecules, and by perturbed ones in solid and liquid phases. When atoms and molecules are held together in a solid or liquid, their energy levels form bands, resulting in broad-band absorption features. Atoms and molecules in gas phase, however, exhibit sharp transitions. By choosing the proper light source, matching the wavelength of an absorption line of the specific gas of interest, it is possible to monitor the gas even in a surrounding of absorbing and scattering solids (the mean light losses in the bulk material is typically many orders of magnitude greater than the absorption by the gas). This approach can be used to measure the concentration of a gas of interest (e.g. oxygen and water vapour). It can also be used to give insight into the porosity of the medium [2, 3].

In this work GASMAS is applied for the analysis of both softwood and hardwood samples. This is achieved by placing a light source on one side of the sample and a detector on the other side (transmission geometry). When the light passes through the sample it travels partly through the pores and will thus experience the spectrally sharp gas absorption. Light leaving the sample will carry this information to the detector.

EXPERIMENTAL SETUP

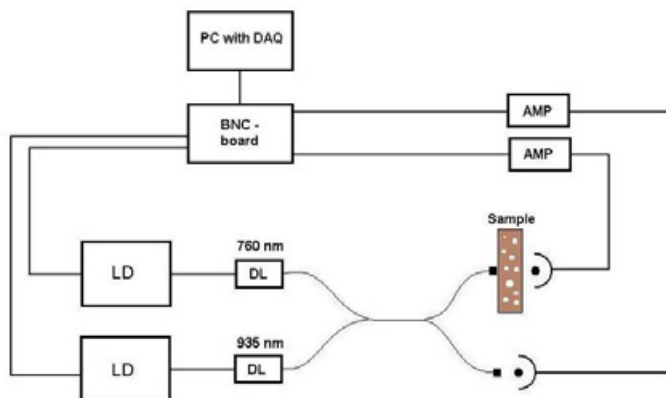


Figure 1: Schematic of the GASMAS setup with two diode lasers operating at 760 nm and 935 nm, respectively.

The instrument used for GASMAS measurements is seen in the schematic Figure 1. The equipment is described in detail in Ref. [4]. Two diode lasers (DL) (Nanoplus, DFB single mode lasers) are used by the instrument, with wavelengths of 760 nm and 935 nm, respectively. The wavelengths and intensities of the lasers are controlled with laser drivers (LD) (Melles Griot, Model O6DLD103 and Thorlabs, Model ITC 502 for oxygen and water vapour, respectively). The results presented in this work pertain to the monitoring of only the change in oxygen concentration and the wavelength used for studying oxygen is 760 nm.

The light from the lasers is coupled via optical fibers that join into a common fiber carrying light of both wavelengths. The light is once again split with a beamsplitter into two new fiber arms. The splitting gives 10 percent of the light in one fiber and 90 percent in the other one. The fiber containing 10 percent of the light is then coupled to a photodiode (S3590, Hamamatsu); this part of the instrument is called the reference arm. The other fiber, containing 90 percent of the light, is coupled to a probe where the light is eventually emitted. This probe is placed close to the sample under investigation and on the other side of the sample a photodiode detector (S3204, Hamamatsu) is placed; this is called the sample arm of the instrument. In the case of very low light transmission through the sample a photomultiplier tube can instead be used in the sample arm.

The detectors generate currents that are amplified (AMP) and converted into voltages by amplifiers (FEMTO, Model DLPCA-200). On these amplifiers the gain (unit Volts/Ampere) can be adjusted from 103 to 109 in steps of one order of magnitude. The voltages generated by the amplifiers are coupled into a BNC board (BNC-2110, National Instruments) which is connected to a DAQ-card (PCI-6120, National Instruments) placed in a PC. The data acquisition (DAQ) card records the voltages and transfer them into digital values that can be analyzed by software (in this case LabView, National Instruments).

Instead of using expensive and bulky lock in amplifiers, the DAQ card is used as a source for modulation voltage which is sent to the laser drivers through the BNC-board. To be able to achieve as high resolution in the modulation voltage as possible a down converter is connected between the BNC-board and the laser drivers. This allows the whole output voltage scan from the DAQ-card to be used while maintaining the desired wavelength modulation.

MEASUREMENTS AND RESULTS

Dynamic processes related to gas diffusion in wood were investigated. Different types of wood with varying thicknesses were of interest. Norway spruce, Balsa, Pine, Oak and also an oak sample from the Swedish warship Riksäpplet were studied. All samples were placed individually in a transparent plastic bag that was flushed with oxygen before any measurements were performed. After approximately 24 hours enclosed in the plastic bag the sample was placed in the instrument, still inside the bag as shown in Figure 2. The measurement was started as the bag was cut open and the sample was re-exposed to ambient air.

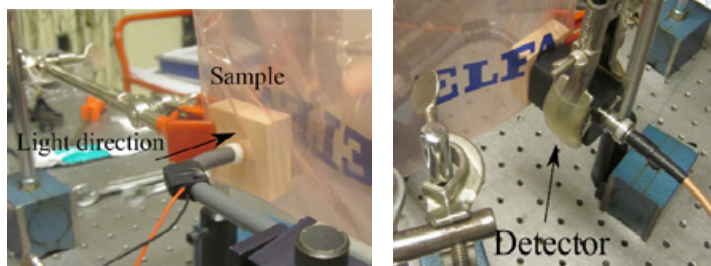


Figure 2: A Norway spruce sample placed in the GASMAS instrument. Left: injection side, Right: detection side.

The objective was to study the gas transport through the wood samples and to determine how gas transport may change for different types of wood. Two samples of Norway spruce, two samples of Balsa and one Oak sample were placed in bags with pure oxygen (oxygen was continuously flushed into the bags to assure a slight over pressure). Both the Norway spruce and Balsa samples were of two different thicknesses, 15 mm and 7 mm while the Oak sample was of thickness 7 mm. The measurement series were run for no longer than 25 hours per sample.

The result of the diffusion experiments can be seen in Figure 3. The diffusion curves have been fitted with a sum of two exponentials. The figure shows that the gas transport is governed by both short and long time constants. In Norway spruce the gas transport is at first very rapid after which a much slower gas transport process takes place. The Balsa wood has a slower gas transport during the initial phase as compared to Norway spruce and is then followed by even slower gas diffusion. The Oak sample shows similar behavior as the spruce sample in having a very rapid first time constant. However, a puzzling behavior is observed during the early stages, approximately around 20-40 min into the measurement- the oxygen signal drops down and then swings back up before finding its equilibrium value. The three Oak curves in Figure 3 are all measurements of the same sample. The same phenomenon is reproduced for all of the measurements on the Oak sample with variations of the effect. Figure 4 displays this unexpected result better.

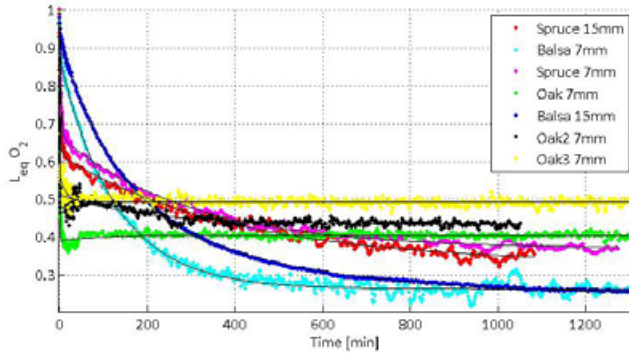


Figure 3: Diffusion of oxygen from samples of spruce, balsa and oak with different thicknesses. The mean equivalent path length is normalized to the maximum value for each sample. The reason to why the equilibrium values differ slightly for the same Oak sample is due to the penetration of oxygen into the sample differed slightly between the measurements.

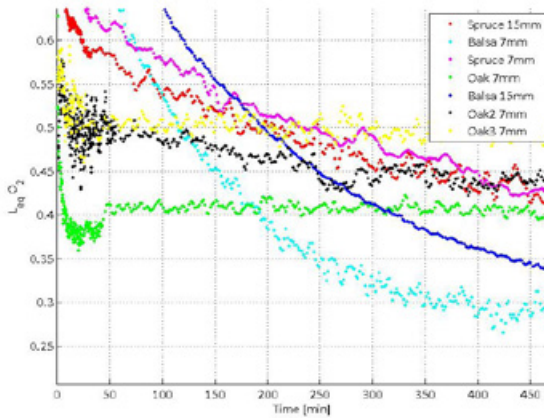


Figure 4: A closer look at oxygen signal for the oak sample around 20-40 min. We also notice the extremely fast decay in the beginning for the oak samples.

Further, another measurement series was done with the same procedure as previously, in regard to the pre-treatment in pure oxygen environment. The samples investigated were two pieces of pine wood and a sample of spruce wood. The diffusion curves are presented in Figure 5 and Figure 6. The very rapid initial gas transport for pine wood is captured in Figure 6.

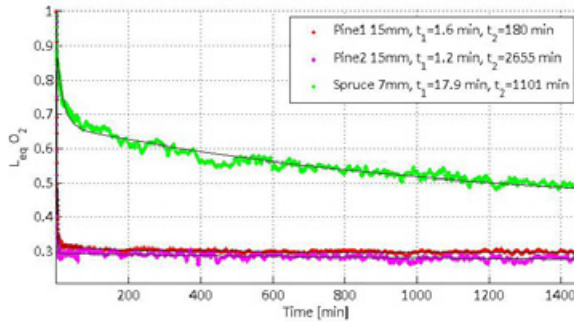


Figure 5: Diffusion of oxygen on samples of Pine and Spruce. The mean equivalent path length is normalized to the maximum value for each sample.

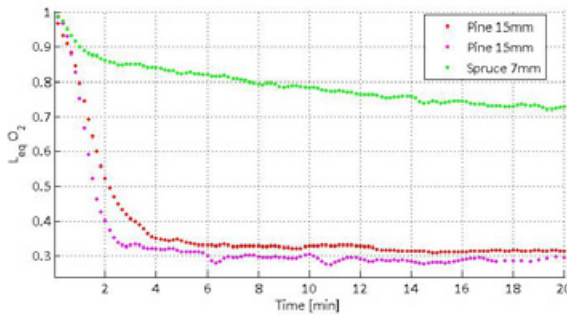


Figure 6: The first 20 minutes of the diffusion of oxygen through samples of Pine and Spruce.

In contrast to spruce the gas transport is very rapid for the pine wood samples. Most of the gas was probably located in the coarser or more open parts of the samples which diffuse rapidly as soon as the samples are re-exposed to ambient air.

In Figure 7 the diffusion curve for an oak sample of the warship Riksäpplet is presented. The first time constant is very short and is most similar to that observed in pine wood. Due to the fact that the light transmission was low the signal was noisy, therefore longer averaging times were needed. That is the reason to why there are fewer data points and more uncertainty than in previous measurements. The initial under shoot of the curve that was observed for the previously mentioned oak samples, can again be sensed, however, the noise level of the curve prevents us from drawing too much conclusions on this.

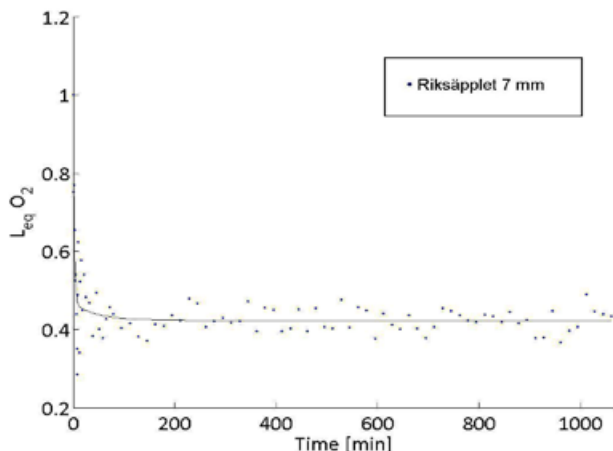


Figure 7: Diffusion curve of oxygen on an archeological oak sample from the warship Riksäpplet. The sample has been exposed to a pure oxygen environment before the measurement.

DISCUSSION AND CONCLUSIONS

The GASMAS technique can be used for analyzing gas diffusion properties of wood samples. For some samples it has been shown that the gas transport is very rapid and occurs during the first couple of minutes while for other samples it is a much slower process. The reasons are not fully understood but it seems relate to how coarse or open the structure of the material is, which will affect how quickly the gas can diffuse. The slower processes are probably a product of when the gas has to penetrate the cell walls. Cracks in the sample should also affect the rate at which the gas is transported in the sample.

Future work will focus on more diffusion measurements on archeological wood, both untreated and PEG treated samples, e.g. from the Swedish warship Vasa. We will work on improving measurement sensitivity and on exploring other wavelength regions where the bulk absorption might be lower. Then some suitable tracer gas with proper absorption properties would be sought to mimic the transport of normal air. Further measurements on the Oak samples comparable to those shown in Figures 3 and 4 will be carried out in order to further investigate the unexpected features observed. Comparison with the physiologically inert gas nitrogen will also be pursued. Improving the understanding of what affects the diffusion properties is essential. Interdisciplinary collaboration with experts in different fields is crucial for a full understanding of gas exchange in wood of different types and different pre-history. The use of the GASMAS technique as a valuable tool for improved characterization of archeological wood is the final goal of the project

The GASMAS setup will be integrated with another optical technique, Time-Resolved Diffuse Optical Spectroscopy (TRS). This technique can provide information on the wood in terms of solid composition, structure, light depth penetration and temporal changes [5]. TRS and GASMAS can together provide a more complete picture of the wood material, yet with no great added complexity for a potential integrated instrument.

ACKNOWLEDGEMENTS

The authors are grateful to Märta Lewander and Tomas Svensson for valuable contributions in techniques development. The present project is supported by the “Ministero dell’Istruzione dell’Università e della Ricerca of Republic of Italy” and by the Swedish Research Council under the “Executive Programme for Scientific and Technological Cooperation between Italy and Sweden”. We would also like to thank the Vasa Museum for providing nice samples of the warship Vasa and Riksäpplet.

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34.

POSTER: USING A REFRACTOMETER TO TRACK PEG TREATMENTS IN WATERLOGGED TIMBERS

Marie Jordan

*Conservator at Newport Medieval Ship Project, with contributions from Erica McCarthy, Project Officer,
and Morwenna Perrott, Project Assistant*

Monitoring the concentration of PEG solutions for conservation at the Newport Ship is crucial to the effective treatment of the timbers. Using a refractometer to measure PEG concentrations enables conservation staff to monitor PEG concentrations and detect deviations. The causes of one discovered anomaly are still under investigation, but it is hoped that further monitoring with the refractometer and testing of possible solutions will rectify problems with PEG concentrations.

35.

POSTER: KAURAMIN TESTS FOR YENIKAPI 12 SHIPWRECK HULL

Namık Kılıç

Istanbul University Department of Conservation of Marine Archaeological Objects

Began in 2004 November, salvage excavations at İstanbul's Yenikapı district where a Byzantine harbour, Portus Theodosiacus was once situated, yielded 36 medieval shipwrecks. The conservation of 28 of those shipwrecks has been undertaken by Istanbul University's Department of Conservation of Marine Archaeological Objects. This poster presentation covers kauramin tests for the upcoming conservation procedure of Yenikapı (YK) 12 shipwreck's hull remains which subject to my MA dissertation. Tests were carried out on dislocated waterlogged wood fragments found at Yenikapı site which have similar characteristics with YK 12 timbers. Prior to the kauramin treatment, Umax ratios of samples which are between %280 - %650 were determined.

Kauramin is a melamine formaldehyde based resin produced by BASF company. Various concentrations of kauramin have been used for the conservation of waterlogged wood. Kauramin solution usually contains additives such as trietanolamine, triethyleneglycol, urea and glyceroldiacetate in order to provide required properties. Different ratios of concentrations and additives were tested separately to gain most proper post-treatment conditions of samples. For instance, samples which have Umax ratio of %600 were both impregnated with %40 and %25 kauramin concentrations. It was seen that transversal cracks and dimensional changes are minimum on samples treated with %40 concentration of kauramin. Same test was applied on samples having Umax ratio below % 280. However, it was observed that the high concentration of kauramin solution did not cause remarkable changes on samples in this case. Besides, the penetration of kauramin solution on oak samples having Umax ratio below %200 in particular, was very slow and numerous cracks were detected on those samples. The overall results of research will be evaluated in detail by this poster presentation.

36.

POSTER: THE VASA WARSHIP: LIGNIN CHARACTERIZATION BY MEANS OF THIOACIDOLYSIS AND CP/MAS ^{13}C NMR.

Teresia Sandberg

KTH Royal Institute of Technology, Department of Fibre and Polymer Technology

A great interest has been revealed for the chemical processes taking place in Vasa wood, and several research disciplines are involved in the examination. Today it is known that the polysaccharides in the wood, namely cellulose and hemicelluloses, are severely degraded. However, not much effort has been put on examining the conditions of lignin, which is the focus of this study. Lignin is a three dimensional network incorporating the cell wall and giving it strength and rigidity. By means of thioacidolysis, a wet chemical degradative method, and solid state NMR spectroscopy, the condition of the lignin polymer in Vasa wood was evaluated. The guaiacyl and syringyl lignin monomers from the thioacidolysis reaction were analysed with gas chromatography – mass spectrometry. CP/MAS ^{13}C NMR was performed directly on the wood samples. The results revealed no discernible effect of oxidative degradative reactions on the lignin polymer in Vasa wood.



SHIPWRECKS 2011

The chemical and biological aspects of preservation techniques and degradation processes of waterlogged wooden shipwrecks is the subject of current intense research in several countries. This international conference was organized in order to report and discuss the present knowledge in this important field of cultural heritage preservation.

