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The Impact of Metal Corrosion Products on the Degradation of Waterlogged Wood Recovered from Historic Shipwreck Sites

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ABSTRACT

It is the chemistry and biology of a wreck site that are the determining factors in the extent of deterioration of wood recovered from shipwrecks. However, if these factors are similar, then it is the years of submersion, the species and the presence of metal corrosion products in the wood matrix that have the most effect on the durability of wooden ships' timbers. Samples of metal impregnated waterlogged wood recovered from historic shipwreck sites were analysed by Fourier transform infra-red (FT-IR) and ¹³C-NMR spectroscopic techniques. The effects of the incorporated corrosion products on the extent of wood degradation were studied.

INTRODUCTION

The destructive effects caused by actively corroding iron in contact with the wood is a well known phenomenon. Where metals are found in intimate contact or in close proximity to wooden artefacts their corrosion products will diffuse into and remain in the wood matrix [Mills Reid 1988]. The presence of these metal corrosion products in the wood has several effects. There will be an effect on the mechanical strength, the chemical stability of the wood structure and the rate of biological degradation. The precipitation of metal corrosion products will also replace water in the presumably swollen state of the timber and plug the voids in the internal wood structure providing stability to the wood cells by a bulking process. However, they can prevent penetration of consolidants into the interior cells and degrade cellulose by hydrolysis and metal catalysed auto-oxidation [Florian 1977; Florian et al. 1977; Grattan 1987; Grattan et al. 1980; Jespersen 1989; MacLeod 1987, 1990b; Mills Reid 1988; Muhlenthaler 1973; Savard et al. 1965; Watson 1985]. In addition, major post treatment changes can occur in conserved metal impregnated waterlogged wood [Jespersen 1989; MacLeod & Kenna 1991]. Therefore, many workers suggest that corrosion products and salts need to be removed from waterlogged wood before and during conservation [Blackshaw 1976; Grattan et al. 1980; Jespersen 1989; MacLeod 1987; 1990b; MacLeod et al. 1991; MacLeod & Kenna 1991; Watson 1985]. Consequently, there has been a long term need for understanding the mechanism of interaction of corrosion products with waterlogged wood so the most appropriate conservation treatments can be developed for metal impregnated waterlogged wooden artefacts. Therefore, it is important to characterise the mineralogy of the specific corrosion products incorporated in the wood and investigate the effect that these minerals can have on the *in-situ* degradation of the waterlogged wood structure.

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This research programme involved analysing ten metal impregnated wood samples recovered from four shipwreck sites and comparative unimpregnated sound wood samples of the same wood genus by FT-IR and solid state ^{13}C -NMR. Further investigation needs to be carried out on analysis of unimpregnated waterlogged wood from the same sites, however, owing to archaeological and budgetary constraints, the collection of these samples was not possible.

EXPERIMENTAL

Ten metal impregnated wood samples were obtained from wrecks of the *Vergulde Draeck* (1656), *Rapid* (1811), *Favourite* (1867) and the *Hadda* (1877). Following excavation, all samples were permitted to air dry with associated warping, shrinkage and collapse. Four samples of modern, undegraded hardwoods and two samples of softwoods were also collected for comparative analyses. The wood species of all waterlogged samples were identified by polishing the end-grains to a 1200 SiC grit finish and microtome sections were cut from the radial and tangential longitudinal surfaces. Slides of these latter two surfaces were prepared for examination by transmission microscopy.

The corrosion products in the outer and inner regions of the metal impregnated wood samples were analysed and characterised by scanning electron microscopy (SEM) and x-ray diffraction (XRD). Dry sample sections were firstly examined by SEM using a Jeol JSM-2 SEM with EDAX using the backscattered low vacuum mode in an environmental cell at the Mineral Processing laboratories of CSIRO in Perth. This mode of SEM operation requires no sample preparation [Robinson & Nickel 1979]. Prior to XRD analysis, CSIRO technicians prepared the samples using standard mineralogical techniques. The corrosion products were then analysed by XRD on a Philips 1140 x-ray diffractometer. The resolution of the complex mixtures of corrosion products was effected through a combination of comparisons with traces of standard spectra of phases identified by SEM and a search using the Hanawalt search manual. The corrosion products identified were given their mineralogical name when the XRD pattern was coincident with that reported in the JCPDS index for such compounds, otherwise the chemical name alone was reported.

Small sub-samples of wood were taken from the outer, aerobic surfaces, the middle and inner, low oxygenated regions of each bulk section and samples were also removed from the modern, undegraded wood sections. These samples were then analysed by FT-IR spectrophotometry at the Chemistry Centre of Western Australia using a FTS-40 Biorad-Digilab division single beam FT-IR spectrophotometer equipped with a mercury cadmium telluride detector. Analysis of the organic materials involved positioning a small sample between the two diamonds of a diamond anvil cell (DAC) (high pressure diamond optics). The DAC was mounted directly in the sample compartment and the spectrum recorded without the aid of beam condensing optics, ratioing against a stored background of the empty DAC. The spectra were manipulated utilising a Galactic Grams 386 program. Peak heights of the major diagnostic absorption bands were measured from a computer generated baseline between $1770\text{-}870\text{cm}^{-1}$ and these results assisted in measuring the degree of wood deterioration.

Approximately 300mg of the modern, undegraded wood and wood samples from the outer and inner regions of the metal impregnated samples were collected and finely ground with a ball mill for comparative purposes. These ground samples were then analysed by solid state ^{13}C -NMR spectroscopy with cross polarisation and magic angle spinning (CP/MAS)

on a Bruker CXP90 instrument operating at 22.5MHz for carbon at the University of Western Australia (UWA). A Doty probe with a double air bearing rotor was used. Recycle time was 1s. A 90° pulse of 4µs was used; contact time was 1ms and data was collected in 1K data points, zero filled to 4K and Fourier transformed with a line broadening factor of 50Hz to obtain the frequency domain spectrum.

RESULTS AND DISCUSSION

General

General information relating to the four wreck sites and some of the environmental parameters are outlined in Table 1. It can be seen from this tabulated data that the shipwreck sites have, generally, been subject to similar marine environments and water depths.

Table 1. Environmental parameters of the wreck sites.

Vessel	Date Lost	Years of Submersion	Mean Water Temperature ¹	Depth of Wreck (m)	Nature of Site
<i>Vergulde Draeck</i>	1656	326	21°C±4	8	aerobic
<i>Rapid</i>	1811	169	24°C±2	5	aerobic
<i>Favourite</i>	1867	117	24°C±2	6	aerobic
<i>Hadda</i>	1877	115	24°C±2	4	aerobic

¹ [MacLeod 1985]

The end-grains of six of the ten samples of metal impregnated waterlogged archaeological wood were examined by transmission microscopy, the wood species identified and the results are presented in Table 2. The other four wood samples were not identified as they were from the same wood samples that were previously identified.

Table 2. Wood identification of the metal impregnated waterlogged wood samples.

Sample	Wood Type
<i>Rapid</i> (RP1.1 and RP1.2)	<i>Quercus sp.</i> American white oak
<i>Rapid</i> (RP2.1 and RP2.2)	hard pine of the pitch pine type
<i>Hadda</i> (HA30056.TOP and HA30056.BOT)	<i>Quercus sp.</i> European white oak
<i>Hadda</i> (HA30057.TOP and HA30057.BOT)	<i>Fagus sp.</i> European beech
<i>Favourite</i> (FAV 3075)	<i>Ulmus sp.</i> Elm
<i>Vergulde Draeck</i> (GT 6154)	pine of the red deal type

Corrosion Products

The corrosion products impregnating the wood samples were analysed by SEM and XRD techniques. Samples of the corrosion products were collected from both the outer regions of the wood samples, which were fully exposed to the aerobic marine environment and the inner regions of the wood, which were in low oxygenated environments, in intimate contact with the residual metal.

The predominant corrosion product identified in the outer regions of the copper impregnated waterlogged wood samples was paratacamite ($\gamma\text{-Cu}_2(\text{OH})_3\text{Cl}$). This is one of the major copper corrosion products formed by the aerobic corrosion of copper alloy fastenings in intimate contact with wood. It is interesting to note that no atacamite was identified in the outer regions of the wood samples. Calcite and aragonite, different crystalline forms of calcium carbonate, were also identified in the outer regions of these wood samples. These minerals are very common in concretions and form the major component of the same. Calcium carbonates also line holes formed in wood by shipworms, such as *Teredo* worms, which are ubiquitous in our tropical to semi-tropical aerobic marine environments. In addition, the outer region of the beech sample recovered from the *Hadda* site contained hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$).

In the inner, low oxygenated regions of the wood samples the major copper corrosion products were copper sulphides, with chalcocite being the more common phase. The formation of these copper sulphides is common on copper alloys corroding under anaerobic conditions. In addition, anglesite (PbSO_4) was identified in the inner regions of the *Favourite* elm sample which was in intimate contact with a leaded bronze gudgeon. Anglesite is the most commonly found lead mineral on lead artefacts recovered from aerobic marine environments, however, this compound may also be formed in low oxygenated micro-environments [MacLeod & Wozniak 1996].

The major corrosion product identified in the outer, exposed areas of the iron impregnated wood sample was goethite. Iron oxyhydroxides are common iron minerals formed by the corrosion of iron in oxidising marine environments and are often found in wood which has been in close proximity to corroding iron. The fact no other forms of iron corrosion products were identified in this wood sample would be due to post aerial oxidation of iron minerals to goethite as the wood was exposed to the atmosphere on drying. There were no different corrosion products present in the inner regions of the iron impregnated wood sample.

In the outer zones of the metal impregnated timbers recovered from aerobic shipwreck sites, the characteristic metal corrosion products are fully oxidised metal hydroxy chlorides, oxy hydroxides and hydroxy carbonates. These minerals are typically formed by hydrolysis and precipitation in oxidising, alkaline marine environments. However, it is interesting to note that wood exposed to an aerobic marine environment is capable of supporting anaerobic micro-environments adjacent to the metal/wood interface, within the space of a few centimetres. Therefore, without characterisation of the major corrosion products present in the different regions of the wood, the sharp transition in aerobic to anaerobic micro-environments within the wood would be difficult to identify. As the timber is traversed from the outer to the inner zones, the changes in the local micro-environments would effect the biological and chemical degradation mechanisms occurring in the wood. Hence, the extent of wood degradation will not only be effected by the amount of waterlogging but by the ability of dissolved oxygen to penetrate the waterlogged wood.

Given the mineralogy of the major copper corrosion products identified in the copper impregnated wood samples and the general site parameters measured on these shipwreck sites (Table 1), it is possible to use standard thermodynamic functions and the relevant Pourbaix diagram (Figure 1) to estimate the range of pH and redox potential (E_h) represented by the corrosion product mixture. Estimation of the redox potential and pH

range that the iron impregnated wood sample had been subjected to on-site is difficult due to the post aerial oxidation of the iron corrosion products.

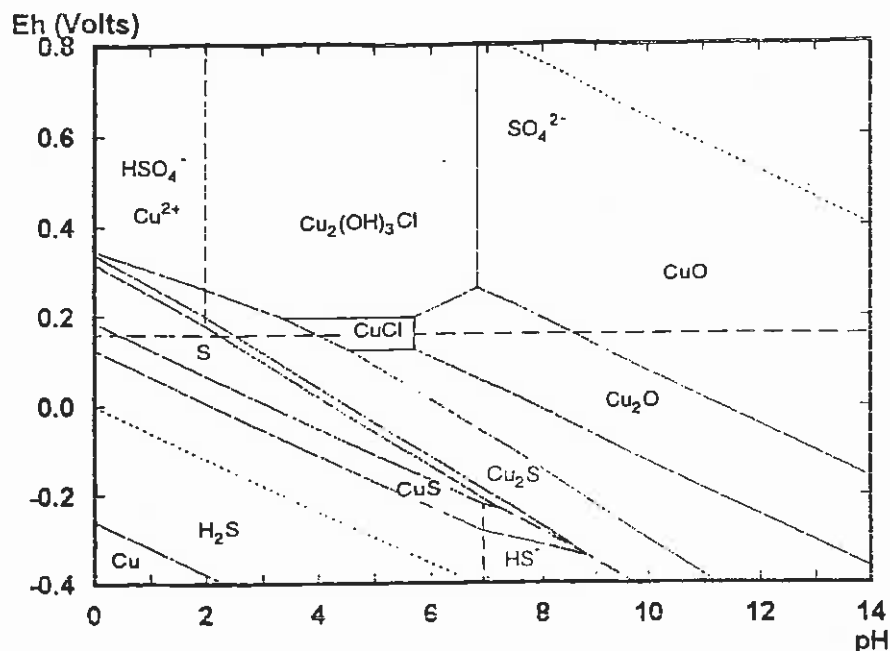


Figure 1. Pourbaix diagram for pure copper in anaerobic sea water containing 10^{-2} M additional S^{2-} at 25°C . Dissolved Cu at 10^{-6} M [HSC Chemistry for Windows 1993].

The redox potential for the wood is estimated to range from approximately +0.30V to -0.25V versus NHE for a pH range of about 5.7 to 7.5. The surface pH of some structural timbers measured on the *Hadda* site was about 8.1 and the pH of normal sea water on-site was 8.08. The most thermodynamically stable corrosion product at a redox potential of +0.3V and a pH of 8.1 is tenorite, CuO (Figure 1), however, there was no evidence of this mineral present in the outer regions of the wood. The absence of tenorite is due to the greater kinetic stability of $\text{Cu}_2(\text{OH})_3\text{Cl}$ and Cu_2O formation under these oxidising conditions in a marine environment. Only two examples of tenorite have been found on copper alloy objects recovered from marine environments and these artefacts were subjected to extremely high temperatures [MacLeod 1991].

The typical pH range, measured *in-situ* by MacLeod (1982b), from the inner to outer regions of aerobic and anaerobic concretions on copper surfaces was 6.0 to 8.2. The same author measured the surface pH of a copper bar surrounded by European white oak hull timbers and the value was 5.7. In another study, the surface pH of a copper alloy fastening on another similar aerobic shipwreck site was measured after the removal of the surrounding wood and the pH was 7.63 [Richards 1996]. Therefore, the calculated pH range that these copper impregnated wood samples have been subjected to is in good agreement with actual on-site measurements.

In addition, within these pH and redox potential ranges, Cu metal and Cu_2O are also thermodynamically stable. These minerals were not identified by the XRD analyses but were identified by visual inspection of the sectioned wood by transmission microscopy. As copper fastenings in wood corrode in an aerobic environment cuprous chloride complexes diffuse along the rays and through the cell walls towards the wood/sea water

interface. Cuprite is one of the major corrosion products precipitated as the $\text{CuCl}_x^{(1-x)-}$ species hydrolyse or oxidise in oxygenated sea water. Deposits of elemental copper have been formed amongst cuprite zones [MacLeod 1991]. One possible explanation is that some wood decomposition products are readily oxidised and react with either the Cu_2O or CuCl_2^- species to form deposits of elemental copper.

From the identification and characterisation of corrosion products present within waterlogged wood, it is possible to show that a wide range of micro-environments can exist within an artefact and this will have a marked effect on the corrosion of the metal and the degradation of the wood.

FT-IR Spectrophotometric Analyses

The FT-IR spectra of the metal impregnated and unimpregnated wood samples showed the same basic characteristics. The differences in the absorption peaks located in the $1750\text{-}850\text{cm}^{-1}$ ('fingerprint') region will aid identification of different wood species and assist in measuring the extent of wood deterioration. The North American white oak spectrum (Figure 2) will be used as an example to illustrate the major absorption bands corresponding to the carbohydrate and lignin fractions of the wood samples.

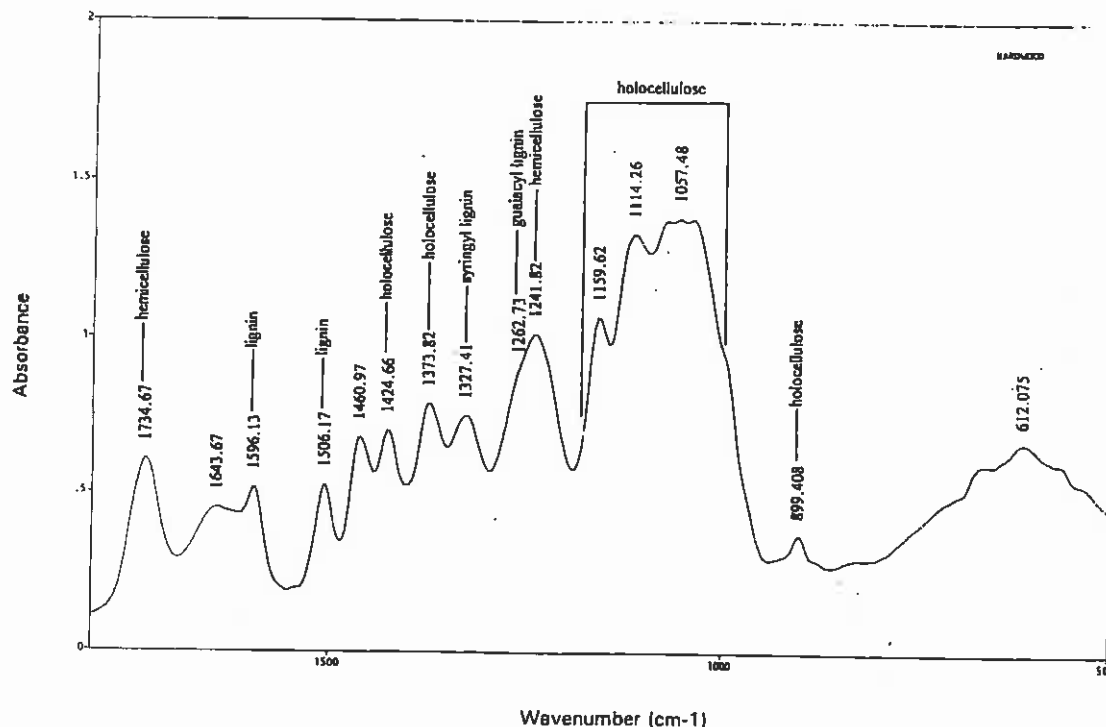


Figure 2. FT-IR spectrum ($1800\text{-}500\text{cm}^{-1}$) of modern, undegraded North American white oak (*Quercus alba* L.)

The absorptions in the $1000\text{ to }1200\text{cm}^{-1}$ region refer mainly to the carbohydrate part of the wood. For the purpose of this study, the bands near 1370cm^{-1} , 1160cm^{-1} and 896cm^{-1} were used to identify the holocellulose portion of the wood samples. The absorption bands at approximately 1740cm^{-1} and 1240cm^{-1} are characteristic of hemicellulose [Faix et al. 1991; Mikolajchuk et al. 1989; Pavlikova et al. 1993; Wang & Lin 1991; Wilson et al. 1993].

The bands in the 1200-1600cm⁻¹ part of the spectra arise primarily from lignin [Wilson et al. 1993]. The absorption around 1600cm⁻¹ can be easily impaired by water present in the sample and thus, the intensity of the lignin absorption band at 1510cm⁻¹ was used in the determination of the lignin content in wood [Kirolov & Mikolajchuk 1990; Wang & Lin 1991]. The bands at approximately 1260cm⁻¹ and 1330cm⁻¹ arise from guaiacyl and syringyl lignin units, respectively. Since softwoods contain only guaiacyl lignin units in the wood matrix and hardwoods contain both guaiacyl and syringyl lignin units, the intensities of both bands were used with the hardwood spectra.

On closer inspection of the FT-IR spectrum of the North American white oak (Figure 2), there is considerable overlap of the 1262cm⁻¹ band assigned to guaiacyl lignin and the hemicellulose peak at 1242cm⁻¹. Similarly, there is overlap between the syringyl lignin band at 1327cm⁻¹ and the 1324cm⁻¹ peak corresponding to holocellulose. The relatively recent computer driven FT-IR spectra manipulation technique of deconvolution could be used to separate these overlapping peaks into single bands, however this technique has not been applied to these analyses.

As waterlogged wood degrades, the carbohydrates are selectively removed while the lignin portion of the wood matrix is mostly retained. As a consequence, in FT-IR spectra, the intensities of the absorption bands associated with the carbohydrate portion decrease and the intensities of the lignin bands correspondingly increase. Since the FT-IR spectra of the copper impregnated waterlogged wood samples were similar, only representative spectra of wood recovered from the *Favourite* (FAV3075) and the *Rapid* (RP1.1) will be presented. The FT-IR spectra of the heavily iron impregnated wood recovered from the *Vergulde Draeck* (GT3154) will be presented for comparison.

The *Favourite* (1867) was supposedly of American provenance and the wood sample was identified as an elm (Table 2). The undegraded reference sample used for FT-IR comparison was European elm (*Ulmus procera* Salisb.) as an American elm was not available. The FT-IR spectra of the FAV3075 hardwood sample and the undegraded European elm are shown in Figure 3. The absolute peak heights of the major bands attributed to holocelluloses and lignin are presented in Table 3.

Table 3. Absolute peak heights of diagnostic absorption bands (cm⁻¹) from the FT-IR spectra of European elm and FAV3075.

Wood Sample	hemicellulose		holocellulose			lignin		
	1740	1240	1370	1160	896	1510	1330	1260
European elm	0.20	0.40	0.33	0.51	0.06	0.16	0.29	0.40
FAV3075								
inner	0.10	0.78	0.95	1.10	0.18	0.59	1.00	0.72
mid	0.09	0.41	0.42	0.69	0.07	0.31	0.45	0.38
outer	0.04	0.22	0.21	0.36	0.05	0.17	0.24	0.20

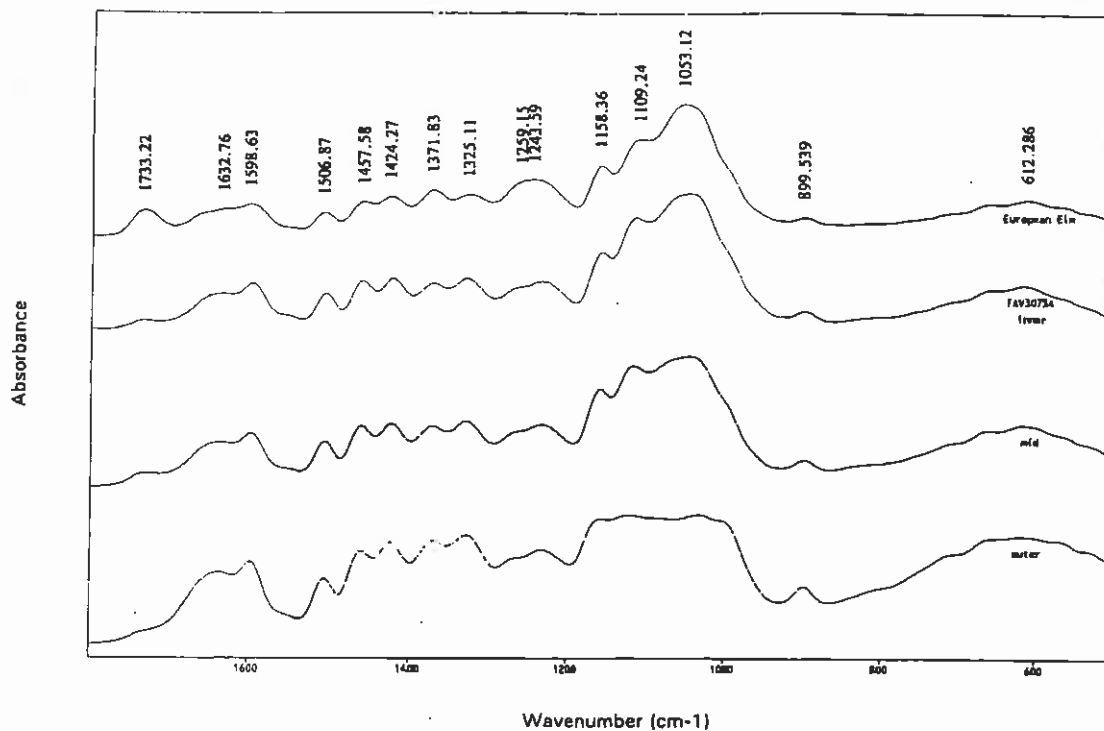


Figure 3. FT-IR spectra of copper impregnated waterlogged wood (FAV3075) recovered from the *Favourite* wreck site and modern undegraded European elm.

There has been an overall decrease in the intensities of the peaks assigned to the polysaccharides, while the peak heights of the lignin bands have remained stable or increased. Hence, the ratio of lignin to holocellulose has increased, indicating degradation of the carbohydrates, especially the hemicelluloses and selective preservation of the lignin in the wood matrix. On further inspection of Figure 3, the intensities of the holocellulose, hemicellulose and lignin bands decreased from the inner to the outer region of the waterlogged wood sample. This trend implies that the extent of deterioration of these wood chemicals increases as the wood is traversed towards the outer regions.

The waterlogged wood sample (RP1.1) recovered from the *Rapid*, an American China trader, was identified as an American white oak. Consequently, the undegraded wood sample used in the FT-IR comparison was North American white oak (*Quercus alba* L.).

In comparing the FT-IR spectra (Figure 4) and the peak heights of the major bands (Table 4), the *Rapid* samples have higher lignin to carbohydrate ratios than the undegraded wood sample. This indicates that the holocellulose fraction of the wood matrix has been preferentially degraded with respect to the lignin portion. The major hemicellulose absorption bands at 1735cm^{-1} for the waterlogged samples are almost entirely non-existent indicating that there has been considerable destruction and dissolution of the polyoses in these samples.

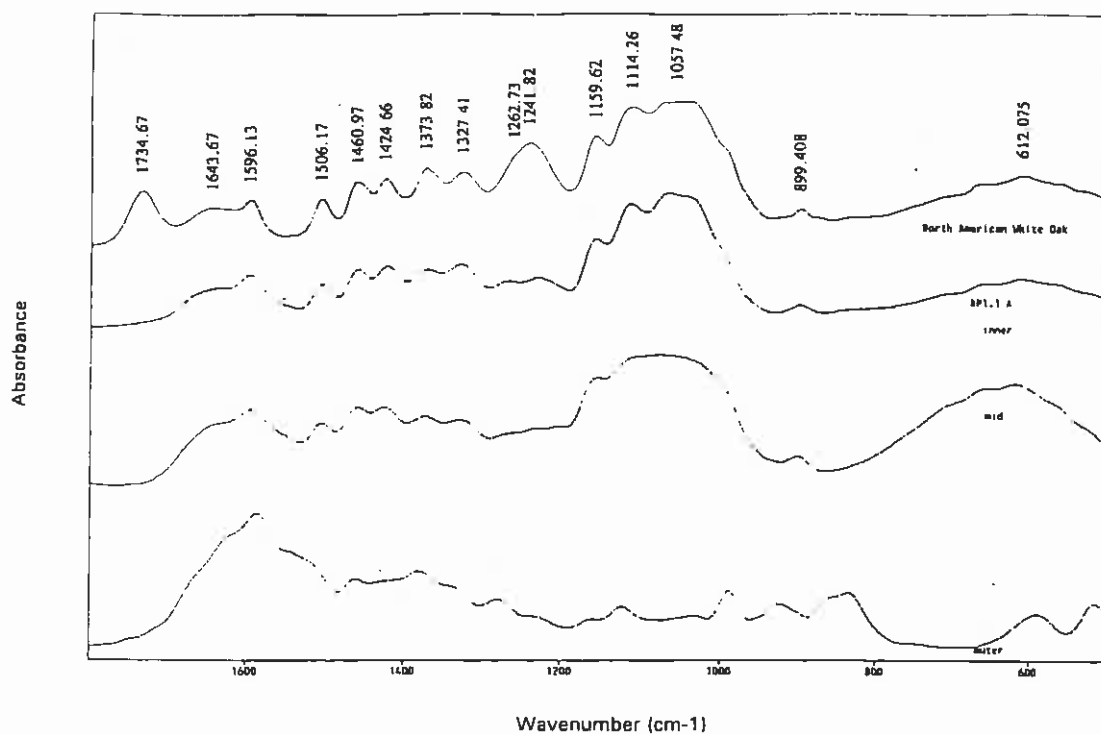


Figure 4. FT-IR spectra of copper impregnated waterlogged wood (RP1.1) recovered from the *Rapid* wreck site and modern, undegraded North American white oak.

Table 4. Absolute peak heights of diagnostic absorption bands (cm^{-1}) from the FT-IR spectra of North American white oak and RP1.1.

Wood Sample	hemicellulose		holocellulose			lignin		
	1740	1220	1370	1160	896	1510	1330	1260
American white oak	0.42	0.78	0.57	0.82	0.10	0.32	0.52	0.75
RP1.1								
inner	0.04	0.44	0.55	0.85	0.07	0.42	0.60	0.41
mid	0.00	0.17	0.21	0.34	0.05	0.20	0.20	0.15
outer	0.04	0.01	0.30	0.00	0.00	0.00	0.22	0.11

The lignin to holocellulose ratios increased from the inner to the outer regions of the *Rapid* wood samples indicating the extent of carbohydrate deterioration increases as the outer surfaces are approached. The outer surface of RP1.1 is extensively degraded denoted by very few carbohydrate bands remaining in this FT-IR trace. Furthermore, the large decrease in the intensities of the bands at 1506, 1327 and 1261 cm^{-1} verifies significant deterioration of the lignin matrix in the outer RP1.1 sample.

The *Vergulde Draeck* wood sample was identified as a pine of the red deal type (Table 2) and a sample of European redwood (*Pinus sylvestris* L.) was used as the undegraded comparative sample.

The iron impregnated waterlogged wood spectra show a great decrease in the intensity of the band at about 1740 cm^{-1} (Figure 5, Table 5) indicating an extensive loss in hemicellulose content. Generally, the ratios of lignin to holocellulose for the inner and

mid sections of the waterlogged wood samples have increased indicating selective degradation of the holocellulose fraction and subsequent preservation of the lignin portion of the wood matrix. On the other hand, the intensities of the carbohydrate absorption bands in the 1000-1200 cm^{-1} region for the outer surface of GT6154 are severely decreased indicating extensive degradation and removal of the polysaccharides in this area. There has also been some modification and deterioration of the lignin matrix supported by the loss of the major peaks at 1509 cm^{-1} and 1268 cm^{-1} . Therefore, this iron impregnated waterlogged wood sample possesses a particularly degraded outer layer and the extent of wood deterioration decreases towards the inner surfaces.

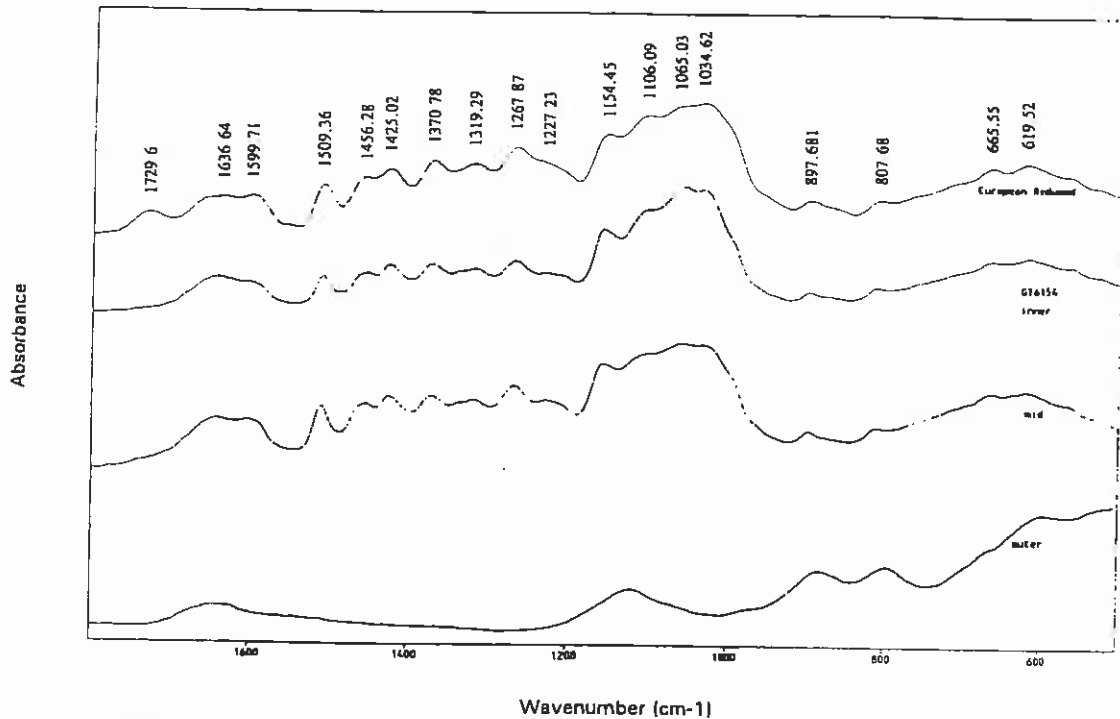


Figure 5. FT-IR spectra of iron impregnated waterlogged wood (GT6154) recovered from the *Vergulde Draeck* wreck site and modern, undegraded European redwood.

Table 5. Absolute peak heights of diagnostic absorption bands (cm^{-1}) from the FT-IR spectra of European redwood and GT6154.

Wood Sample	hemicellulose		holocellulose			lignin	
	1740	1220	1370	1160	896	1510	1260
European redwood	0.13	0.42	0.42	0.56	0.09	0.28	0.49
GT6154							
inner	0.02	0.24	0.30	0.53	0.06	0.23	0.32
mid	0.04	0.31	0.35	0.51	0.06	0.32	0.40
outer	0.00	0.00	0.00	0.00	0.00	0.00	0.00

From the results obtained from the FT-IR spectra, it appears that there has been significant selective degradation of the metal impregnated waterlogged wood samples in comparison to the modern, undegraded wood samples. The extent of degradation is greater in the outer surfaces of the waterlogged wood samples than in the inner regions and the major wood polymers effected are the carbohydrates, especially the hemicellulose

fraction. There was also some small loss of lignin character in the outer regions of the metal impregnated wood samples.

¹³C-NMR Spectroscopic Analyses

A typical solid state ¹³C-NMR spectrum of wood is shown in Figure 6. The sample is an undegraded hardwood, North American white oak.

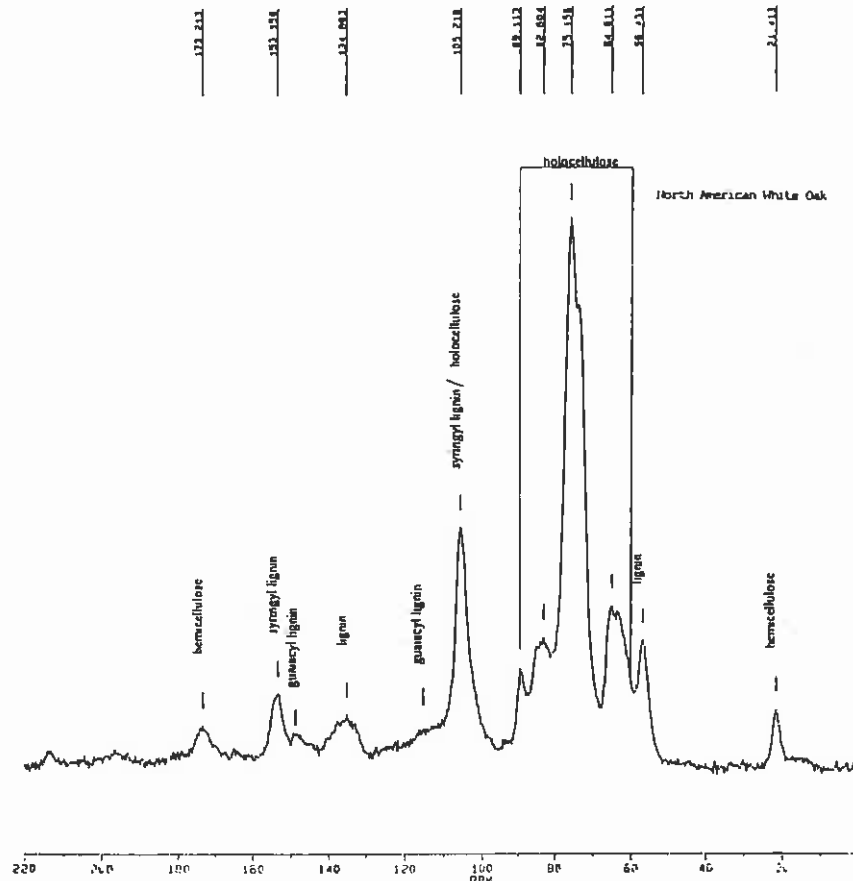


Figure 6. ¹³C-NMR spectrum of modern, undegraded North American white oak.

The bands associated with lignin are usually much less intense than those bands assigned to the carbohydrate part of the undegraded woods. The broader phenoxy signal located in the 155-148ppm range arises from lignin. With a hardwood (Figure 6), the signal can usually be divided into two resonances at approximately 154 and 148ppm, which are not clearly resolved. These resonances represent the C₃ and C₅ aryl oxygen carbons of etherified syringyl units and the C₃ and C₄ carbons of etherified guaiacyl units, respectively [Attalla et al. 1988; Hatcher 1987; Leary & Newman 1992; Wilson et al. 1993]. Other resonances from lignin in wood can be assigned as follows. The resonance at or about 136ppm is due to the non-protonated, carbon substituted aromatic carbons in syringyl units and/or guaiacyl groups [Attalla et al. 1988; Hatcher 1987; Kolodziejewski et al. 1982; Wilson et al. 1993]. The very broad and relatively undefined resonance at 115ppm arises from guaiacyl lignin. The resonance at 105ppm may arise from syringyl units, holocellulose and tannins. Another characteristic peak for lignin in ¹³C-NMR

spectra is at about 56ppm. This peak is assigned to methoxyl carbons. Hardwoods usually show greater relative contributions from methoxyl than softwoods [Attalla et al. 1988; Hatcher 1987, 1988; Hatcher et al. 1989; Kolodziejewski et al. 1982; Newman 1992a; Newman & Hemmingson 1990; Wilson et al. 1983, 1987, 1993].

Aliphatic C-O carbons, other than methoxyl, in lignin usually show peaks at 60, 74 and 84ppm. However, these are masked, to a large extent, by peaks for carbohydrates that resonate in the 65-89ppm region of the spectra [Attalla et al. 1988; Hatcher 1987, 1988; Kolodziejewski et al. 1982; Newman 1992a; Taylor et al. 1983; Wilson et al. 1983, 1993]. The peaks at 174 and 22ppm in the hardwood spectrum represent the acetate and methyl functional groups of hemicellulose, respectively. The resonance at 22ppm can sometimes be hidden by peaks in the 0-50ppm range attributed to unsubstituted sp^3 carbons, generally arising from paraffinic carbons in resins and waxes [Attalla et al. 1988; Hatcher 1987].

The main differences between ^{13}C -NMR spectra of recent undeteriorated wood and degraded waterlogged wood are the higher relative intensities of lignin derived peaks at about 56, 115, 134 and 150ppm for degraded wood due to the selective preservation of lignin. In the 60-90ppm range of the spectra, cellulose and lignin peaks overlap but overall the intensities of these peaks will decrease with increasing degradation due to the deterioration of holocelluloses in the wood. Since the ^{13}C -NMR spectra of the copper impregnated wood samples were all similar, only one example of a ^{13}C -NMR obtained from a copper impregnated waterlogged wood sample and the comparative modern undegraded wood sample is shown in Figure 7.

The ^{13}C -NMR spectroscopic analysis of the iron impregnated waterlogged wood sample (GT6154) could not be carried out because iron corrosion products are highly paramagnetic and strongly interfere with this spectral technique. Absolute peak heights (mm) of the major resonance bands for lignin (154, 136, 56ppm) and holocellulose (75ppm) were measured directly from the spectra and used to calculate lignin to holocellulose ratios. The resonance band at 75ppm was used in the calculations of the lignin to holocellulose ratios as the intensity remained relatively constant for the copper impregnated waterlogged wood samples. These ratios assisted in determining the extent of wood degradation and are presented in Table 6 and shown graphically in Figure 8.

The bands situated at 21 and 173ppm, corresponding to hemicellulose carbons, were almost non-existent in any of the waterlogged wood spectra, indicating extensive degradation of the polyose fraction of the copper impregnated waterlogged wood. The different ratios of lignin to holocellulose for the undegraded European white oak and the sample from the inner regions of HA30056.BOT were virtually the same. This is an indication that the wood in the inner region of the sample was relatively undegraded. On the other hand, the increase in the ratio of lignin to holocellulose for the outer sample denotes deterioration of the polysaccharide fraction and selective preservation of the lignin. Lignin is renowned for being quite stable to chemical and biological degradation in marine environments.

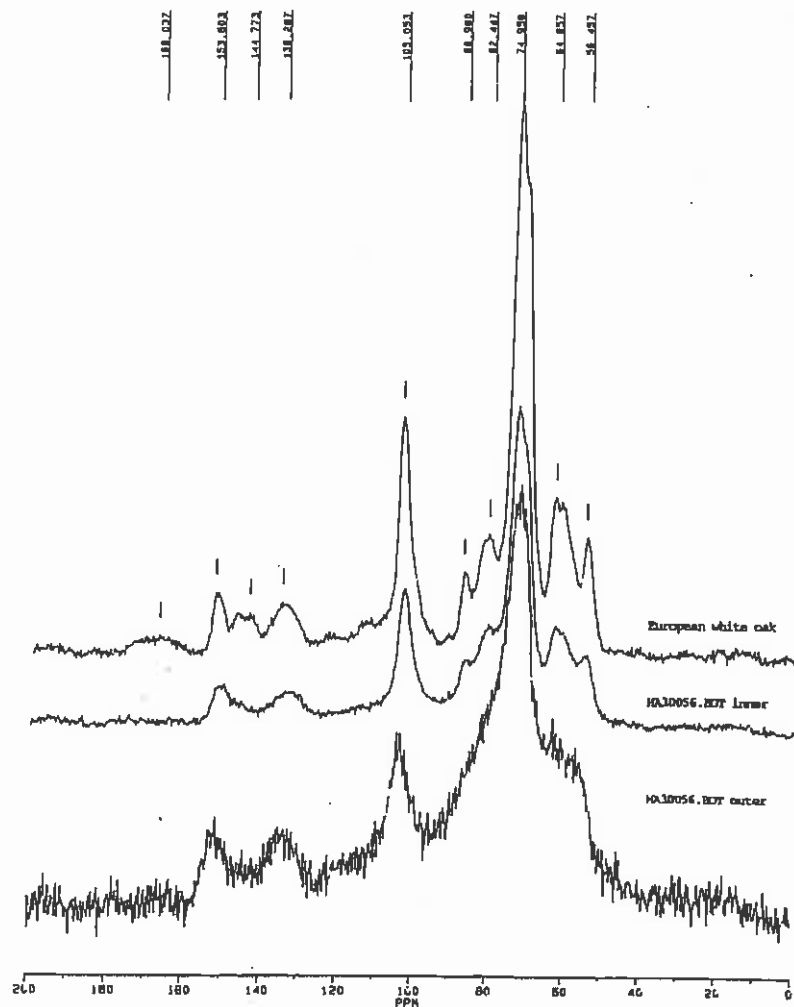


Figure 7. ^{13}C -NMR spectra of the inner and outer regions of the copper impregnated waterlogged wood sample (HA30056.BOT) and modern, undegraded European oak.

Table 6. The ratio of the peak heights (mm) of major lignin resonance bands relative to the holocellulose peak height at 75ppm for HA30056.BOT, FAV3075, RP1.1 and their comparative undegraded wood samples calculated from the ^{13}C -NMR spectra.

Wood Sample	Lignin Resonance Bands (ppm)		
	154 syringyl lignin	136 lignin	56 methoxyl
European white oak	0.11	0.10	0.22
HA30056.BOT inner	0.12	0.10	0.22
outer	0.17	0.18	0.37
European elm	0.14	0.11	0.25
FAV3075 inner	0.11	0.09	0.20
outer	0.19	0.19	0.30
American white oak	0.13	0.10	0.23
RP1.1 inner	0.11	0.12	0.21
outer	0.17	0.17	0.25

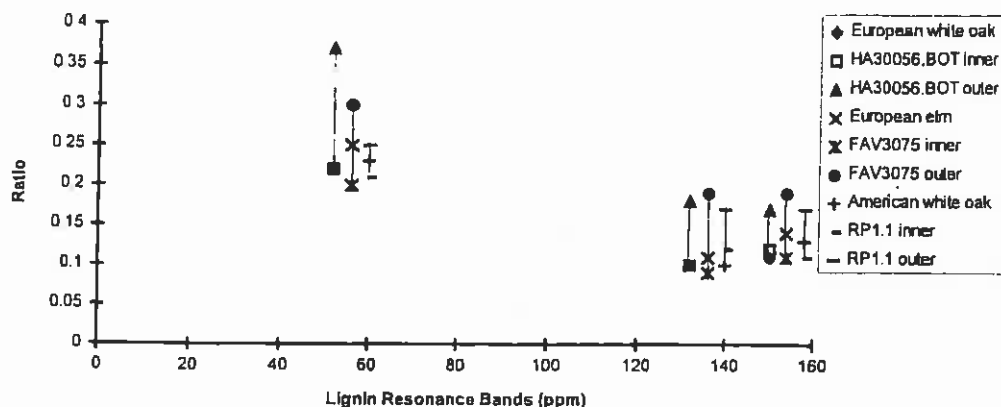


Figure 8. Graphical representation of the lignin to holocellulose ratios presented in Table 6.

The ratios of lignin to holocellulose for the outer regions of the FAV3075 waterlogged wood sample increased denoting degradation of the cellulose and hemicelluloses. The extent of deterioration is greater in the outer surfaces than in the inner regions. The relatively small decrease in lignin to holocellulose ratios for the inner section may suggest some small degree of degradation of the polysaccharide fraction with a slight decrease in lignin character.

The increases in the lignin to holocellulose ratios for the outer sample from RP1.1 represents more extensive degradation of the polysaccharides and selective preservation and concentration of the lignin fraction in comparison to the inner section. The *Rapid* sample showed a very small loss of lignin character, namely syringyl units which are not as stable to chemical and biological degradation as guaiacyl lignin units. There was also a corresponding decrease in the methoxyl content of the lignin because of the predominance of syringyl units in these hardwood samples.

From the results of the lignin to holocellulose ratios calculated from the ^{13}C -NMR spectra, it appears that the *Hadda* copper impregnated wood is generally more degraded than the wood recovered from the *Favourite* and *Rapid* sites. Furthermore, the *Rapid* samples seem slightly less deteriorated than the *Favourite* wood.

CONCLUSIONS

Due to the natural heterogeneity of the wood samples and the often uneven impregnation of corrosion products, some discrepancies will appear in the spectroscopic traces of some of the samples that will not fit in with general degradation patterns, however, there are still some clear trends emerging from the data. Other causes for deviations relate to small differences in micro-environments on and between wreck sites and the method of sampling for these analytical techniques. The FT-IR spectra represent very small, discrete areas of a wood sample and this particular type of sampling procedure may not be representative of the entire wood sample. Alternatively, the ^{13}C -NMR traces tend to present an average measure of the extent of degradation of the wood samples as this technique utilises greater quantities of the wood. However, because of the larger amounts needed for analysis, discrete regions would be difficult to collect on smaller samples, hence providing wood deterioration information on larger areas which may be misleading.

Large concentrations of corrosion products cause line broadening and noisy NMR spectra which makes accurate measurements of resonance peak heights difficult. In addition, large concentrations of iron corrosion products interfere with the NMR analysis technique.

It is important to note that the difference between biological and chemical degradation of waterlogged wood is not easy to differentiate with FT-IR and ^{13}C -NMR spectroscopic techniques. SEM and high resolution optical microscopy of thin sections of samples recovered from the outer, middle and inner regions of the waterlogged wood may provide additional information regarding the extent of bacterial and fungal attack.

Despite the discrepancies, some conclusions can still be drawn from these preliminary analyses. The FT-IR and ^{13}C -NMR analyses showed that these samples of metal impregnated waterlogged wood had been degraded, to some extent, when compared to the reference samples of the same wood genus. In these waterlogged wood samples, the carbohydrates were degraded in preference to the lignin and the hemicellulose fractions were more degraded than the cellulose portion. These results support the fact that wood polysaccharides are chemically and biologically degraded in preference to lignin and hemicelluloses undergo hydrolysis and oxidation faster than cellulose in wood tissues.

In addition, the extent of degradation of these waterlogged wood samples was greater in the outer, more exposed surfaces than in the inner regions. This degradation trend can be simply explained by the increase in physical degradation, such as water and sand blasting, biological deterioration and the rate of chemical reactions that occur on the outer surfaces due to the exposure to the open, oxygenated marine environment. Lignin is relatively stable and resistant to hydrolysis, however, aerobic bacteria and soft rot caused by certain marine fungi may cause modifications in lignin structure and some slight loss of lignin components may occur.

The inner surfaces would be expected to be the least degraded, as the lower oxygen environment would retard biological and chemical attack and physical deterioration will be minimised because of the protection provided by the outer layers of wood to excessive water movement. However, under low oxygenated conditions some bacteria are capable of degrading wood, albeit much slowly, where marine fungi and wood borers are completely excluded because of the limited oxygen supply. The presence of copper sulphides in the inner regions will not retard biodeterioration but the formation of acidic hydrogen ions from copper sulphide precipitation may cause some acidic hydrolysis of the polysaccharides.

The extent of degradation of the outer and middle surfaces of the waterlogged wood, heavily impregnated with copper corrosion products, is relatively small and this would be due to the precipitation of these minerals in these areas which are biologically toxic and protect the wood from further aerobic biodeterioration. This observation is supported by the fact that the outer region of the RP1.1 sample, which was only lightly impregnated with copper minerals and submerged for about the same period of time as the other copper impregnated samples, was extensively degraded. The outer surface of the iron impregnated sample was heavily degraded as the wood had been exposed to the open, aerobic marine environment for about 326 years prior to excavation and the presence of high concentrations of iron corrosion products will tend to increase biodeterioration and chemical degradation of the wood tissue.

All wreck sites had similar general site conditions and the metal impregnated waterlogged wood samples were subjected to very similar micro-environments. Therefore, the differences in the extents of degradation would be primarily due to the time of submergence, the wood species and the type of metal corrosion products incorporated in the wood structure.

The iron impregnated *Vergulde Draeck* sample was the most degraded and had been exposed to the marine environment for 326 years. The *Rapid* copper impregnated wood was the next most degraded and had been immersed for approximately 169 years, while the copper impregnated *Hadda* and *Favourite* samples were only slightly degraded being submerged for about 116 years. The results show that the longer the wood is exposed to aerobic marine conditions the greater the extent of wood degradation.

In the light of the above discussion it is clear that from a combination of SEM, XRD, FT-IR and solid state ¹³C-NMR spectroscopy it is possible to obtain detailed information regarding the chemical micro-environment of waterlogged wood recovered from shipwreck environments and qualitatively determine extents of degradation. From this information the most appropriate, cost effective conservation treatment can be applied to the wooden artefact.

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Jacqui Watson: I just wanted to say that the other study that I actually am involved in, besides waterlogged wood, is identifying organic materials that have been preserved by contact with metal corrosion products. So mine are really fairly well gone. I was interested to see that you have said that the iron does, definitely, dissolve the lignin because, by coincidence, in a lot of my wood preserved by iron corrosion products the middle lamella has been etched away to reveal all the lovely interior pit detail in iron corrosion products and sometimes some residues of the cell wall. I probably had extreme examples of what you are seeing just at the starting point of in your waterlogged wood.

Ian MacLeod: Yes, one of the beauties of degradation is that it just shows up so much more. It is a bit like looking at the pigs. You saw that half-degraded pig and then the x-ray. It is so much easier to find out what a pig is like on the inside with all the flesh is off. And so it is with the degradation of the timber. I think you can learn much more about your partly degraded timber from where the metal ions have had a pronounced effect on the cell wall and the structure. Then maybe this helps to explain other phenomena where you don't have such massive amounts of corrosion products which basically slow down the biodeterioration. You will notice from that slide which shows the nature of the wood deposit around the boat that it is only where the copper corrosion have diffused out along the wood grain that the marine organisms have come along and gone chomp, chomp, chomp and then stopped. It is great for stopping gross degradation.

Jim Spriggs: I am most impressed with your NMR spectra. You were able to actually pick out all the various types of cellulose, the lignin peaks and so on. The results that Ian Panter showed us a slide of yesterday are of NMR work that we have done on terrestrial wood at Durham University. The people operating the NMR equipment there were unhappy about identifying those peaks as to exactly what they were because of the overlap of many of the lignin species with cellulose species. So there is confusion. That was one comment I wanted to make. Also while I am on the mike could you at the same time say what levels of iron in your wood you would expect to start interfering with the NMR spectra? All this marine wood is essentially contaminated with iron. It has got to be hasn't it?

Ian MacLeod: In terms of the level of iron in the material from the [Fouchault de Bracque], when you ash it, it has about 48 % wt of iron in it. Massive. You can get away with a reasonable amount of iron. I mean you can have it coloured. You can if you find there is too much broadening of the peaks just give it a rinse. Just give the ground up wood a little, quick rinse in neutral ammonium citrate or something to just get out some of the bulk iron. You would still be able to pick up the real wood chemistry without it being changed significantly. Those assignments of the peaks have been done by a friend of Ian Godfrey. They did an NMR study on some ancient, degraded woods that were dug up in Botany Bay and someone found out they were 95,000 years old. In fact the NMR was the only way in which they were able to identify, for example, what the basic type of wood was. The wood structure was so collapsed and so degraded that they used the NMR and the presence of the different ratios of the different types of lignins as the method of identification. It is a really rather exciting thing. These spectra are just raw. They are straight off the spectrometer. Because all the data is captured electronically you can then put that through a deconvolution programme and get a much clearer view of where you have your over-lapping holocellulose and some of your lignins, in that middle band. You would be able to get deconvolution of that and then get much more quantitative data. The reason

why I found it so exciting was that finally we are able to pick up differences between the inside, the outside and the middle of your timber. We all know that not only is every piece of wood a mixture of degradation but also across the diffusion interface between a metal object and the wood around it there is a huge difference in chemical and physical environment.

Anthony Crawshaw: It is about 7 or 8 years since I have worked in NMR but it was certainly the case then that different carbon peaks of a molecule were affected to a different extent and were broadened to a different extent by the same amount of para-magnetic impurity. So you may get some peaks of the material broadening to the point of being indistinguishable while others are still present. Also, you could not generally use the peak height as a good measure of the amount of carbon remaining because of the differential broadening. If you are going to use this technique I would like to see it validated by taking blocks off new, undegraded wood, soaking them in known concentrations of, say, iron salts and showing that the broadening did not remove the peaks specifically. I feel the presence or absence of peaks cannot necessarily be used as proof of presence or absence of the wood components.

Ian MacLeod: As with all techniques there is a huge range of variables and, of course, we went and showed our best examples. Like all good scientists we tend to put a bias on the ones which, at least, are interpretable. You tend to get other non-interpretable materials. We were fortunate that the nature of the samples we were looking at were reasonably homogeneous in terms of a subset. We were able to get a reasonable comparison because all those ones you saw were impregnated with copper corrosion products either from pure copper, a bronze or a brass. So because of the similarity of the samples you were able to draw conclusions that otherwise, if you were looking at a range from a bigger subset, you might not be able to. But I take your point.

Haydn Sutcliffe: It is widely known, chemically, that when an organic compound is co-ordinated to a metal ion then the properties of that compound can change considerably. It may become more reactive or in some cases it may become less reactive. It may be with the wood in this case that the metal ions are accelerating the decomposition. The same thing would apply to NMR. What the last speaker said is certainly very true about the peak broadening due to para-magnetic elements being present but also the peak absorption frequencies would change relative to an un-co-ordinated lignin site which would shift it in the spectrum. So as the gentleman just said it is very important to do some experiments with lignins.

Ian MacLeod: These observations are preliminary results.

