Implications of Chemical Deterioration on Mechanical Performance of Wood

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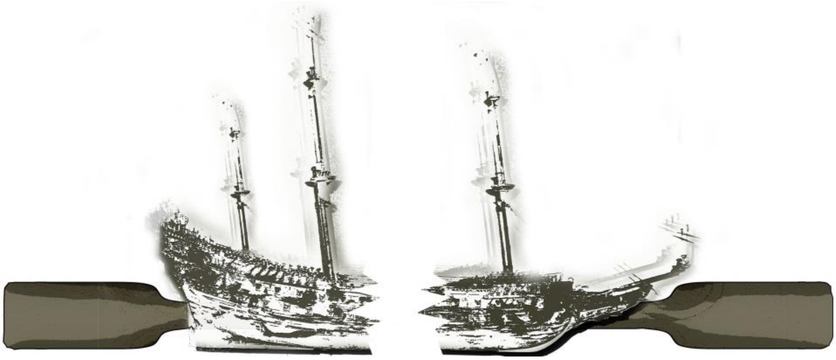

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Abstract

The oak wood of the 17th century warship *Vasa* has shown significant changes in the chemical and mechanical properties as compared to recent oak. The most important factors contributing to these changes are the incorporation of iron compounds during waterlogging and the uptake of polyethylene glycol (PEG) in the course of the preservation treatment. To investigate the effect of iron-dependent oxidative degradation reactions, samples of recent birch, pine and oak were impregnated with aqueous iron(II) chloride solution and thereafter exposed to air or pure oxygen at controlled relative humidity in long-term experiments, followed by tensile strength (TS) measurements. Iron-impregnated samples exposed to oxygen displayed significant effects already after one week and with a reduction in TS of ~50% after one year. Samples treated with additional PEG displayed less reduction in TS. The extent of oxidative degradation was monitored quantitatively following the O_2 consumption in closed vials with different relative humidity (RH), as a function of time. For oak, the initial O_2 consumption was high and declined with time. After 200 d, the accumulated O_2 consumption was 0.3-0.4 $\text{mmol}\cdot(\text{g wood})^{-1}$. The formation of carbon dioxide and oxalic acid was positively correlated with RH. Samples kept for 1500 d at RH55% had accumulated 0.044 $\text{mmol oxalic acid}\cdot(\text{g wood})^{-1}$, which equals the average oxalic acid content in the interior of *Vasa* oak. FT-IR analysis on iron(II) impregnated samples and on *Vasa* wood showed an increased signal intensity at 1710 cm^{-1}, assigned to carbonyl functions, in samples with reduced TS. The signal at 1710 cm^{-1} is not primarily related to oxalic acid. The results show that chemical changes and mechanical performance of iron contaminated wood are strongly correlated and that the state of degradation is observable using IR spectroscopy. Overall, the results confirm that iron compounds have a detrimental effect in wood and indicate that PEG might act as an antioxidant in oxidative degradation processes. Concerning the *Vasa*, it may be concluded that most degradation related to iron compounds and oxidative processes has taken place during the first period of conservation when the wood was exposed to oxygen in a still very humid state. Thus, the current rate of oxidative degradation under the present relatively dry museum conditions should be relatively low.

Keywords: Wood, iron(II), Fenton, tensile strength, oxalic acid, infrared spectroscopy, principal component analysis.

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Dedication

To all of my family and friends which believed in me.

“I am deathless; I am the eternal Lord.
For I have spread the seed of the Word”

Ferdowsi (فردوسی), 940-1020 CE

Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I NORBAKHSH, S., BJURHAGER, I. & ALMKVIST, G. 2013. Mimicking of the strength loss in the *Vasa*: model experiments with iron-impregnated recent oak. *Holzforschung,* 67**,** 707-714.

II NORBAKHSH, S., BJURHAGER, I. & ALMKVIST, G. 2014. Impact of iron compounds and oxygen on degradation of oak – modeling of the *Vasa* wood. (DOI: 10.1515/hf-2013-0197). *Holzforschung, (in press)*

III NORBAKHSH, S., ALMKVIST, G., PERSSON I. 2014. Tensile strength depletion of hard and soft wood by iron compounds (manuscript).

IV NORBAKHSH, S., BJURHAGER, I., ALMKVIST, G. 2014. FTIR analysis of chemically degraded wood **-** a comparison between recent oak and oak from the *Vasa* (manuscript).

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The contributions of Shahin Norbakhsh to the papers included in this thesis are as follows:

I Performing the chemical and mechanical experiments, calculations and writing the manuscript together with Ingela Bjurhager and Gunnar Almkvist.

II Participation in the planning of the project, doing most of the experiments and writing the manuscript together with Gunnar Almkvist.

III The planning of the project. All the experimental work and parts of the analysis and writing the manuscript.

IV The planning of the project together with Gunnar Almkvist. Experimental work and parts of the analysis and writing the manuscript together with Gunnar Almkvist.

Abbreviations

AAS	Atomic absorption spectrophotometry
AMMS	Anion micro membrane suppressor
AMW	Average molecular weight
CV	Cross validation
DTPA	Diethylene triamine pentaacetic acid
EDS	Energy dispersive X-ray spectroscopy
EGM	Environment gas monitor
EMC	Equilibrium moisture content
FTIR	Fourier transform infrared spectroscopy
$HO^{\bullet}$	Hydroxyl radical
LMW	Low molecular weight
MFA	Microfibril angle
nm	Nanometer
NMR	Nuclear magnetic resonance
PCA	Principal component analysis
PEG	Polyethylene glycol
ppm	Part per million
RH	Relative humidity
ROS	Reactive oxygen species
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
TS	Tensile strength

1 Introduction

1.1 Aim

The main topic of this thesis is the effects on wood caused by iron compounds in terms of chemical and mechanical changes. The investigations regarding the chemical deterioration started when salt precipitations were found on the surfaces of the Swedish warship *Vasa* – one of the largest conserved wooden maritime objects in the world. However, it is verified that the strength of the *Vasa* wood has reduced to more than half of that of recent oak (Bjurhager *et al.*, 2012). It is also affirmed that the presence of iron compounds in waterlogged archaeological wood is an issue of great importance for future conservation and stability. Iron compounds are abundant in the wood of the *Vasa* and it is spread throughout the cell walls of the wood (Almkvist & Persson, 2011). One hypothesis is that reactions catalyzed by iron compounds are the main cause of degradation of the wood. Iron compounds in *Vasa* occur partly as visible salt precipitation (e.g.natrojarosite, rozenite and melanterite) on the surfaces of the timber and loose wooden objects (Sandström *et al.*, 2002) and partly as integrated iron compounds which are present throughout the timber (Håfors, 2001).

It has been known since the end of 19th century that iron(II) can act catalytically with oxygen to create strong oxidative conditions which can effect organic material (Fenton, 1894). In Fenton type of reactions reactive hydroxyl radicals ($HO^{\bullet}$) are formed, which are able to attack organic substances and break C-C bonds which become smaller molecules by an oxidative reaction.

Analyses of *Vasa* wood indicate conditions favoring the action of oxidative reactions referred to 10 % content of water and accessible oxygen and iron. The *Vasa* wood is more acidic and the content of iron and sulfur is higher than recent wood. Besides these facts, the *Vasa* is treated with polyethylene glycol (PEG) during the conservation which also has affected the wood in different ways. In general, breaking of bonds of wood components would lead to loss in mechanical strength. One sensitive tool to measure wood degradation is tensile strength (TS). Basically, TS gives information regarding the degree of physical change of material which has been subjected to abnormalities. TS of wood is influenced by many factors such as the content of cellulose, the length and orientation of fibres in the cell walls (Fu & Lauke, 1996). Changes of these parameters will affect the average strength of the wood. Archaeological wood often behaves differently compared to recent wood. A model study of the *Vasa* wood regarding the impact of iron ions and oxygen on recent wood was performed. The changes that took place were similar to those observed in the *Vasa* wood which could give information about the degradation mechanisms involved. This is particularly important for large structures such as *Vasa* as well as any other large structures that contain curvatures which are often parallel to the longitudinal direction of the wood (*Figure 1*). Extended degradation with decrease in mechanical performance would eventually lead to rupture of the planks and beams.

Figure 1. Lower gun deck inside the Vasa shows some of the knees with obvious bends and curvatures. These huge logs are the supporting parts for shelf clamps and the frame mounted outside with iron bolts.

1.2 Salvation

As a matter of fact, the modern and scientific history of the ship began 50 years ago when it was brought to the surface after 333 years on the seabed in the Stockholm harbor. At the salvation of the *Vasa* the chemical conditions changed dramatically. As soon as the *Vasa* broke the water-line the conditions changed from anaerobic to aerobic, which probably started a number of chemical reactions. Relatively high concentrations of iron compounds in the wooden timbers of the ship and the change in oxygen concentration made oxidative chemical reactions suddenly possible. To prevent an immediate drying of the timber and crack formation the *Vasa* was sprayed by water with fire-hoses, and later a sprinkler system was adapted to keep the wood wet

(Håfors, 2010). Accumulated sediment on the surface of the wood was washed away. The wooden surface was revealed and it became unprotected against the surrounding air.

Figure 2. A picture when Vasa stood on the pontoon for restoration at Beckholmen (right). The spraying of PEG and borax started by the people inside and outside the ship by hand (left) (Photos: Swedish National Maritime Museum).

1.3 Conservation

It was important to choose a conservation agent which was available, easy to use, reversible, non-toxic and affordable. After preliminary experiments it was decided that polyethylene glycol (PEG) would be the best choice as a dimension stabilizing agent to protect the *Vasa* from cracks and dimension changes despite little was known about PEG in this kind of application at that time.

The treatment period after the salvage can be divided into three periods: the wet period, the drying period and the period on display in the new museum hall from 1990. During the wet period the ship was sprayed for almost 18 years with an aqueous solution of PEG and borax. Borax ($Na_2B_4O_7$)/boric acid (H_3BO_3) was added to prevent fungal growth. The hull was sprayed with PEG with an average molecular weight of 1500 $g \cdot mol^{-1}$ at the beginning followed by PEG 600 was added (1971) to prevent cracks and shrinkage more effectively (Håfors, 2001; Håfors, 1990). 1979-1990 the ship was left to dry to a mean water content of ca 10 % before it went to public display in 1990 in the present museum hall.

1.4 Brief historical dictum and present state

Every culture in the human world demands its own identification. In order to obtain these identifications, incidents and experiences during the course of history of that particular culture will build up the people's conception. During the 17th century, Sweden was one of the main actors in the thirty-year war in

Europe (1618-1648). King Gustavus Adolphus II was an excellent strategist and during his rule large parts of Scandinavia, parts of Russia, Poland and Germany were conquered. To maintain the ascendancy of the empire, the control of the Baltic Sea was of highest strategic importance (Glete, 2006). The success of this task depended on the latest war technology of those days. Five large and powerful warships were ordered by the king and the pearl of this armada would have been the *Vasa* (the king´s family name). The *Vasa*, unfortunately, wrecked at its maiden voyage in 1628. Almost all of the cannons were salvaged during the following decades. However, the remains of the ship fell in oblivion for centuries. During 1950s, she was discovered by Anders Franzén and the *Vasa* was salvaged in 1961.

After the salvage an extensive conservation work was at head. The ship was taken to a nearby dock at Beckholmen where a detailed archaeological examination was undertaken. In 1962, the *Vasa* was moved to another dock nearby there the conservation work was undertaken and in 1988 the *Vasa* was brought to its final destination at the present museum hall which still was incomplete at that time (*Figure 3*). The *Vasa* with its approximately 1000 tonnes is mounted on regular hard standings fit with wooden cubes. The climate conditions were unstable in the museum hall regarding temperature and humidity which led to a massive fluctuation. Considering the size and weight of the *Vasa*, probably significant amounts of water were transported in and out of the wood. However, after a very rainy summer in year 2000, it was decided to optimize the conditions in the museum hall. Today the climate in the museum is controlled and regulated to a relative humidity (RH) of 55 % and the temperature is kept at 19 °C. The lights are damped to avoid a photo-catalytic degradation.

Figure 3. The Vasa in its present display at the Vasa *museum. Relative humidity and temperature are regulated but the platform it stays on is still the same as during the conservation period (Photo: Swedish National Maritime Museum)*

2 Chemistry and mechanical strength

2.1 Wood

Wood probably is one of the most important materials in human history. It has been used as fuel or material for structures as houses, bridges, wagons etc. for very long time. 300 000 years old tools and weaponry made of wood have been found (Fengel & Wegener, 1984).

The cross-section of a tree stem is divided into different parts with specific task and properties. From the most inner part, the pith to most outer bark, heartwood, sapwood, cambium and phloem are lined up (*Figure 4*A). The heterogeneous chemical composition of wood is made up by four main components i.e. cellulose, hemicelluloses, lignin and extractives. The amount and type of every single component depend on species and geographical origin. Wood consists of two main groups, softwood (coniferous) and hardwood (deciduous). Wood from softwood trees have a more simple macro-structure than hardwoods by less number of cell types and combinations of them (Fengel & Wegener, 1984). The macro-morphology of wood consists of two major parts with different properties. The outer and inner parts are called sapwood (a mixture of dead and living cells) and heartwood (dead tissue, closer to the pith) respectively (Bowes, 2010). Heartwood is an important factor for mechanical stability of wood (Long *et al.*, 1981).

At micro scale the wood cell walls are divided into three main layers, called S1, S2 and S3 (Wu *et al.*, 2009; Wimmer & Lucas, 1997). Approximately 80% of the wood cell wall consist of the S2 layer (Jager *et al.*, 2011) and an impact in this region would cause a significant change in mechanical performance. The so-called microfibril angles (MFA) is a term used to denote the angle between the orientation of cellulosic microfibrils in the S2 layer and the long axis of the cell (Barnett & Bonham, 2004). This angle is almost perpendicular to the fiber axis for S1 and S3 which results in large angles while the direction of micro-fibrils in the S2 layer is almost parallel to cellular axis and thereby a small MFA which seldom exceeds 30°, *Figure 4*B, (Bjurhager, 2011). These fibres contain mainly of cellulose, which is built up of D-anhydroglucopyranose (glucose) residual monomers polymerized by 1-4 β-glycosidic bonds (Henriksson & Lennholm, 2009; Fengel & Wegener, 1984). The high degree of polymerization (DP) of cellulose chains and the strong hydrogen bonds between the chains make this polymer crystalline. The structure of crystals are uniform which make them more resistance against chemical attacks than amorphous structures (disordered)(Harvey & Freedland, 1990). This property makes cellulose a very important component regarding the mechanical strength of wood.

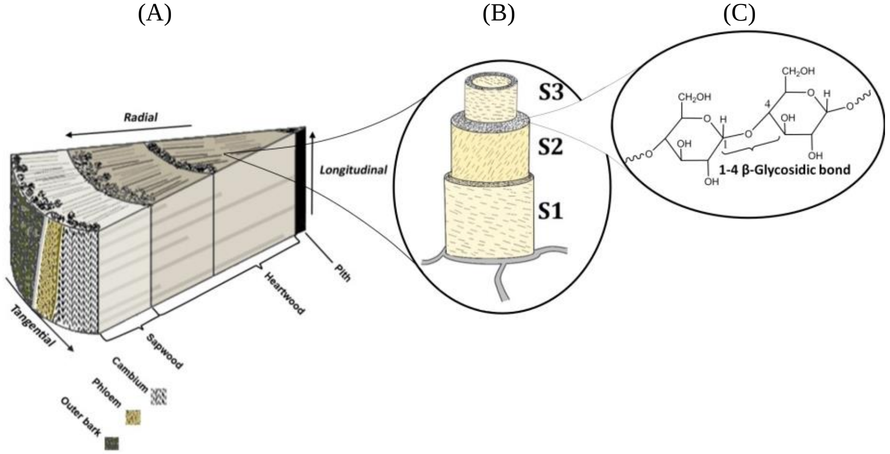

Figure 4. General illustration in macro-scale of a piece of wood trunk showing the structure. From the taper of the wooden sector at the radial direction pith, heartwood, sapwood, cambium, phloem and outer bark is revealed (A). The three main parts of wood cell walls S1, S2 and S3, are illustrated in (B).The 1-4 β-glycosidic bond between two glucose monomers shows the principle cellulose polymerization (C).

Two hardwood species, oak (*Quercus robur*) and birch (*Betula pendula*), and one softwood, pine (*Pinus sylvestris*) wood were used in this study. Heartwood from oak and pine has a darker tone in color and the threshold between heartwood and sapwood are more pronounced compared to birch. This is probably caused by the amount of extractives (extractable compounds) which increases during heartwood formation by the plant to protect itself against fungi. The darker color of heartwood is due to the formation of polyphenols (Jansson; *et al.*, 2009).

2.2 Iron

2.2.1 Iron chemistry

The most common oxidation state of iron found in nature is +II and +III as minerals e.g. hematite (Fe_2O_3), magnetite (Fe_3O_4) and pyrite (FeS_2) (Greenwood & Earnshaw, 1997) but it also rarely occurs as iron with an oxidation number of +IV (Schwertmann & Cornell, 2000). The corrosion of metallic iron under wet conditions is relatively fast as the oxides do not form any protective sheet to provide protection against further oxidation. Thereby metallic iron often fades away completely from its origin form.

In chemical contexts the oxidation of metallic iron to iron(III) proceeds in two steps. In the first step iron oxidizes to its +II oxidation state because it is favored thermodynamically. Thereafter further oxidation to iron(III) is possible when the conditions so allow. However, presence of iron in waterlogged archaeological wood has always been and still is a challenge for conservators to deal with.

2.2.2 Iron as a catalyst

Several studies have shown that iron(II) ions together with a peroxide may catalyze oxidative reactions (Mayer & Jarrell, 1996; Emery & Schroeder, 1974; Stumm & Lee, 1960; Bawn, 1953; Weiss, 1953). It is also established that wood deteriorating microorganisms such as brown-rot seem to utilize the catalyzing ability of iron to produce radicals for their purpose (Kerem *et al.*, 1999; Hyde & Wood, 1997; Wood, 1994; Schmidt, 1981). According to Neevel (1995) iron(II) in wood have two pathways for degradation of cellulose. Iron may catalyze the production of superoxide radicals ($O_2^{\bullet-}$) and further formation of organic radicals (Eq. 1; 2; 3 & 4) or, if hydrogen peroxide is available, through Fenton type of reactions to produce the highly reactive hydroxyl radical, $HO^{\bullet}$ (Eq. 5). These reactions are dependent on the availability of both iron(II) and oxygen.

$$Fe^{2+}(aq) + O_2(g) \rightarrow Fe^{3+}(aq) + O_2^{\bullet-}(aq) \qquad \text{(Eq. 1)}$$

$$Fe^{3+}(aq) + O_2^{\bullet-}(aq) + RH \rightarrow Fe^{2+}(aq) + HOO^{\bullet} + R^{\bullet} \qquad \text{(Eq. 2)}$$

$$R^{\bullet} + O_2(g) \rightarrow ROO^{\bullet} \qquad \text{(Eq. 3)}$$

$$ROO^{\bullet} + R'H \rightarrow ROOH + R'^{\bullet} \qquad \text{(Eq. 4)}$$

The overall Fenton reaction:

$$Fe^{2+}(aq) + H_2O_2(aq) + H^+(aq) \rightarrow Fe^{3+}(aq) + HO^{\bullet} + H_2O \qquad \text{(Eq. 5)}$$

It is known that iron has a deteriorating effect on wood (Marian & Wissing, 1960). Around nails and bolts used to keep wooden structures together, one might observe that wood often is affected and seems to be degraded (Baker, 1974). The wood is darker in color around the iron nails which is an indication of the complex of iron ions and tannic acid found in the wood.

2.2.3 Iron in *Vasa* wood

The *Vasa* was held together by iron bolts. These and other iron objects aboard were completely corroded during the time on the seabed. This is the source of the content of iron in the wooden hull of the *Vasa* found today. At micro-scale view of the *Vasa* wood, iron is distributed mostly in lumen and the cell walls as nano-precipitants (10-100 nm) (Almkvist & Persson, 2011). The oxidation reaction of iron depends on factors such as oxygen concentration, pH and temperature (Stumm & Lee, 1961). At the seabed, the oxygen concentration was very low – a condition that suddenly changed when the hull was brought to the surface (*Figure 5*). According to the descriptions above initially the metal objects oxidized into iron(II) ions (Eq. 6). Eventually hydrated iron(II) ions diffused into the timber whereas iron(II) sulfides, pyrite, FeS_2 and rust (iron(III) (hydro)oxides) remained in the surface region (Fors & Sandström, 2006).

$$2Fe_{(s)} + O_{2\,(g)} + H_2O \rightarrow 2Fe^{2+}(aq) + OH^{-}(aq) \qquad \text{(Eq. 6)}$$

$$2Fe^{2+}_{(aq)} + ½O_{2(g)} + 5H_2O \rightarrow 2Fe(OH)_{3(s)} + 4H^{+}_{(aq)} \qquad \text{(Eq. 7)}$$

According to Almkvist and Persson (2011) iron(III) compounds are dominating in the surface area while at larger depths a mixture of iron(III) and iron(II) is present. One explanation to the differences of iron oxidation state of in-/exterior part of the wood could depend on mobility of iron(II), iron(III) compounds and oxygen in wet wood. In other words, the wood was impregnated by iron(II) compounds in the beginning of its period of wreckage on the seabed. Furthermore, it is more difficult for air to diffuse into large beams of wood which limits the oxygen availability and thereby iron(II) has been preserved inside the wood until present days. Despite a rigorous control of the climate regulations, iron bolts (ca. 5500) used during the 1960's, to hold the ship assembled, are heavily corroded today and replacement program is in progress.

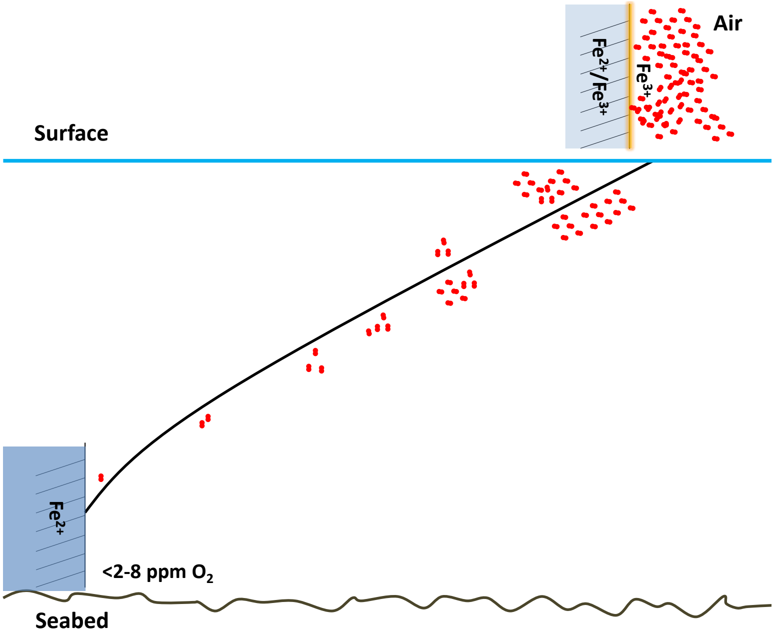

Figure 5. An illustration showing the oxygen content at depth of the Baltic Sea.

2.3 Polyethylene glycol (PEG)

2.3.1 Chemistry of PEG

PEG is a polymer made of several repeated monomers of ethylene oxide with hydroxyl groups at the ends. The mean number of monomeric units in the polymer is denoted "*n*". In the case of *Vasa*, PEG 600, 1500 and 4000 was used which give mean *n* values of 13, 34 and 90, respectively (*Figure 6*). It is important to stress that "n" is a mean number and that a technical product includes many different polymer lengths.

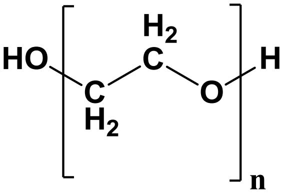

Figure 6. General chemical formula for polyethylene glycol.

The physical properties of PEG are dependent on the mean polymer chain length. The state of aggregation, viscosity and melting point are some of these parameters. It behaves as an oily liquid for average molecular weight (AMW) less than 600 while the aggregation state of PEG with higher AMW is solid at ambient room temperature with a waxy character. The hygroscopic property of PEG is negatively correlated to its AMW (Martelli & Laurindo, 2012) which was considered when PEG 4000 was used as the last treatment on the outermost surface of the *Vasa*.

PEG is soluble in both water and organic solvents (Roberts *et al.*, 2002), it is non-toxic and easy to work with. This has led to a vast usage of PEG in different disciplines. In conservation science one of the most important parameters which always must be considered is the reversibility of the material used to protect the objects. This was one of the most important properties of PEG as the conservation agent for the *Vasa*. However, in general terms, when introducing a substance into wood the complex structure and matrix of wood make the substance almost impossible to remove completely (Christensen *et al.*, 2012).

2.3.2 PEG degradation

PEG can be degraded to shorter chains by oxidative reactions. According to Han *et al.* (1995) PEG is susceptible to free radicals which results in depolymerization and a shortening of the polymer chain. One such oxidation reaction is described by Kerem *et al.* (1998). At conditions similar to those found in the *Vasa* wood i.e. high acidity and presence of iron and oxygen, PEG could undergo degradation which leads to low molecular organic molecules. By loss of a hydrogen atom from a carbon adjacent to an ether oxygen in the chain a highly reactive polymeric radical is formed. The PEG chain could undergo a so called hydrogen abstraction (Han *et al.*, 1995) and can be lost if the conditions are oxidative or induced to sufficiently high temperatures. The surrounding oxygen, iron and the acidic condition could then allow a so called β-scission to proceed (*Figure 7*). Most of the products formed were identified by Almkvist and Persson (2008c) with NMR and mass spectroscopy when PEG was treated with Fenton reagent´s. These end products were also found from degraded PEG of the *Vasa*. Moreover, PEG can experience photo-degradation, radiolytic degradation and persulfate-induced degradation (Mkhatresh & Heatley, 2004) which will not be discussed further here (Appendix 4).

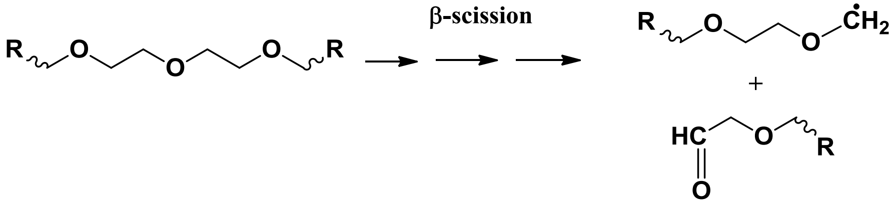

Figure 7. A possible degradation process is via β-scission or direct oxidation by oxygen of PEG chain (Kerem et al., 1998). The conditions are comparable to those in the Vasa wood (Almkvist & Persson, 2008c).

2.3.3 PEG in the *Vasa* wood

Waterlogged wood artifacts should be kept wet until conservation, since uncontrolled drying can lead to irreversible cellular collapse (Smith, 2003). PEG was used as a replacement of the water in the wood to stabilize the microstructure of the wood due PEGs many physical and chemical properties (Hoffmann *et al.*, 2004; Seborg & Inverari.Rb, 1962).

PEG is not uniformly distributed in the wood. At sites where the wood was less microbially degraded PEG penetrated only a few centimeters from the surface, see *Figure 8*, whereas at sites with a higher level of degradation, PEG have diffused effectively (Håfors, 2001) due to increased porosity and void volumes. Analyses of PEG show often a mixture of PEG with different AMW (Almkvist & Persson, 2008c). The oxidative conditions in the *Vasa* probably have degraded PEG. If the degradation of PEG is severe enough and low molecular weight (LMW) PEG (<600) is formed it will become liquid (Mortensen *et al.*, 2007) which is more hygroscopic (Martelli & Laurindo, 2012) leading to increase mobility. However, one theory is that the wood could act as a chromatographic packing material, which separate molecules with different molecular weights. If this is the case in principle the formed LMW PEG could penetrate deeper into the wood.

Figure 8. The distinct borderline where PEG has slowed down diffusion into the wood (arrows) is obvious shown from a core sample from Vasa (65701).

2.4 Acids in waterlogged wood of *Vasa*

The pH of aqueous extracts from milled wood in this context was informative. Previous studies showed that aqueous extracts from *Vasa*, often from degraded sites, showing a drop in pH by 2 units relative to recent oak wood (Almkvist & Persson, 2008a). Aqueous extracts from untreated oak, birch and pine wood have, at standard conditions, pH around 4-5 (Fengel & Wegener, 1984) where oak is one the most acidic among them. The acidity of oak is probably attributed by the relatively high concentrations of acetic and formic acid. The origin of acetic acid is due to hydrolysis of acetyl ester functional groups of hemicelluloses while the origin of formic acid is still unknown (Gibson & Watt, 2010). Generally hardwood is slightly more acidic than softwood due to more occurring acetyl ester groups on their hemicellulose.

Chromatographic analyses of aqueous extracts from the *Vasa* wood show significant amounts of oxalic acid. Oxalic acid is a weak acid with dissociation constants of $pK_{a1} = 1.25$ and $pK_{a2} = 3.81$ (David R. Lide, 2005). Thus, the low pH values for these samples are most probably caused by high concentrations of oxalic acid. Approximately 55 µmol oxalic acid·(g dry wood)$^{-1}$ was found in the interior parts of the wood from sites with severe chemical degradation (Almkvist & Persson, 2008a). Usually oxalic acid is associated to wood degrading microorganisms utilizing it to deteriorate the wood components in chemical attacks (Kaneko *et al.*, 2005; Hyde & Wood, 1997; Micales, 1994; Green *et al.*, 1991; Schmidt, 1981), but this can hardly be the case of *Vasa* wood. The latter statement refers to the establishment that the microorganism degradation activity of the *Vasa* during the time on the seabed, when oxygen was restricted (Blanchette *et al.*, 1990), was primarily from the erosion bacteria (EB). These bacteria consume the wood components at a rather slow rate of the wood components. Furthermore, the *Vasa* wood was mostly affected in the outer centimeters by erosion bacteria (Björdal *et al.*, 2000).

Oxalic acid form fairly strong complex with iron(III). This property affects the oxidative reactions caused by the presence of iron depending on the oxalic acid concentration (Zuo & Hoigne, 1992). According to Tanaka *et al.* (1994) the catalytic activity of iron is regulated by the concentration of oxalic acid and at a certain range this activity is highly promoted. This thesis will discuss the formation of oxalic acid in recent wood impregnated with iron(II) chloride.

2.5 Tensile strength (TS)

Tensile strength is the measure of a material's mechanical resistance against a known external force pulling it apart. The dimensions of a specimen, deformation and load, are parameters which are important in order to describe the mechanical properties of that particular material (Bjurhager, 2011). TS (σ) is calculated by the ratio of force (F) per area (A) affected by the force. The results are obtained by plotting tensile stress (σ) as a function of strain (ε). The experiment provides several kinds of information. At the start the material is elastic which means as long as the function is linear, a reversible deformation is possible (*Figure 9*A). The latter statement follows Hooke´s law which could be described as "An Ideal material will behave reversibly in its shape (elasticity) as long as the applied force on to that material is limited, and the extended distance of the material is proportional to that force". This parameter is the slope of the linear relationship in the beginning of the force applied and it is called Young´s modulus (*E*). Young´s modulus provides information about the materials resistance against applied force. At a certain point created by a continuation of the force the material will undergo an irreversible deformation which at last will break apart (*Figure 9*B). In principle the general illustration in *Figure 9* can be solved by the simple linear relation $\sigma = E \cdot \varepsilon$.

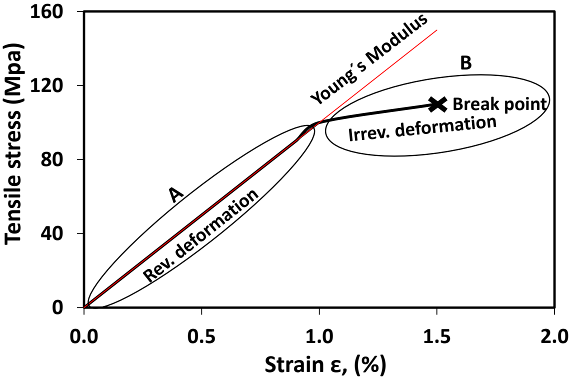

Figure 9. An example of a chart showing the tensile stress σ as a function of strain ε.

TS of wood attributes mainly from cellulosic fibres in the cell walls of the wood (Fengel & Wegener, 1984). The mechanical properties of wood are related to the orientation of the fibers, fiber length and the matrix system of cellulose polymers in the secondary cell walls (Fu & Lauke, 1996). The TS is often low when significant damages on cellulose microfibrils in S2 layers of the cell walls are present (Rowell, 1990). The MFA of the fibers is an important factor and in principle describes the elasticity of a material subjected to force given as Young´s modulus (Eder *et al.*, 2013).

Regarding the *Vasa* wood, an issue is the addition of PEG and the effects it has on mechanical strength. This has been studied by compressive tests on *Vasa* wood (Ljungdahl & Berglund, 2007) and longitudinal TS test on both *Vasa* wood and recent oak (Bjurhager *et al.*, 2010). It was shown that the compressive strength in the radial direction of *Vasa* wood is on average reduced by 50 % compared to recent oak wood (Ljungdahl & Berglund, 2007). However, no change in longitudinal TS was obtained from PEG impregnated recent oak. Although the overall TS of the *Vasa* wood had reduced heavily it was shown that the TS is more reduced toward the interior where no/low content of PEG is present (Bjurhager *et al.*, 2012).

3 Materials and methods

3.1 Sample preparation

3.1.1 Solid samples

The samples were prepared from tree logs of European oak (*Quercus robur*), birch (*Betula pendula*) and pine (*Pinus sylvestris*). The planks were obtained from commercial workshops. Both heartwood and sapwood from pine were chosen. The wood types used were sound and without any visual knots with normal annual rings. The wooden planks were divided into different sections in longitudinal direction (e.g. A, B, C,…). From every section blocks with a size of 200 x 20 x 15 mm in the longitudinal, tangential and radial direction, respectively, were sawed out in such a way that the same annual rings were represented in both sides. It is important that each sample should have the same property all over because wood is a heterogeneous material. Furthermore, studies have shown that micro-fibril angles (MFA) decreases in the wood cell wall for the cells closer to the pit (Barnett & Bonham, 2004; Lichtenegger *et al.*, 1999). To summarize, the samples have been made of three sections, one section in each end for grip and a mid-section for measurement of TS. Each block produced five samples where three, randomly chosen, were used for treatment with iron(II) chloride and the other two were used as their corresponding references (paper I).

Figure 10. The untreated "dog bone" shape made of oak.

Pieces of the size 50 x 15 x 4 mm in longitudinal, radial and tangential direction, respectively, from each wood type i.e. oak, birch and pine (both heart- and sapwood) from the same logs as the "dog bone" samples were treated with iron(II) chloride (section 3.1.2). One group of samples treated in this way contained only oak wood was conditioned at different RH and used to measure oxygen consumption. Group of samples made of pine, birch and oak were conditioned at RH 55% and thereafter the change of oxygen concentration was measured. It shall be emphasized that the procedures were performed in anaerobic conditions.

3.1.2 Impregnation of solid samples

Solutions of iron(II) chloride were prepared from deionized water and degassed by nitrogen to remove dissolved oxygen before use. The samples were immersed in the solution and a mild vacuum (200 mbar) was introduced to allow better penetration. This procedure was repeated five times. After impregnation the samples were dried at predetermined RH until the change in weight per day was stabilized. According to Simpson (1998) EMC of wood is different depending on the pathway to reach the preferred RH. The EMC of wood is higher when wood lose water and vice versa. *Figure 11* illustrates this effect by displaying the EMC as a function of RH. However, it must be stressed that all the conditioning processes in this study were performed equally. Moreover, a group of oak samples were post-treated in a solution of aqueous PEG with AMW of 600 (Aldrich) with a concentration of 30 % (w/v).

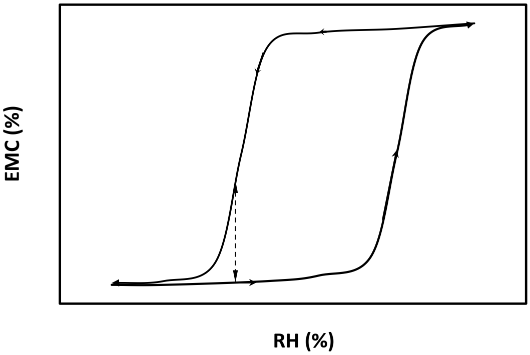

Figure 11. A general illustration showing the hysteresis effect. The crosshatched double arrow show different EMC for the same value of RH.

3.1.3 Extraction of wood powder

Oak wood was ball milled and sieved to 60 mesh (250 µm). The powder was Soxhlet extracted in a series of solvents at different steps to rinse and dissolve the extractives. The powder was rinsed with three solvent mixtures, acetone/water 7:3 v/v, toluene/ethanol 2:1 v/v and isopropanol/NaOH (Lindfors *et al.*, 2008). The residual sample was dried until the weight difference per day stabilized. The extract from oak powder after the last step in the extraction procedure had a high pH compared to aqueous extract from fresh oak. The wood powder was stirred in a buffer of acetic acid/acetate buffer at pH ~ 4 for two days to stabilize the pH. Samples from each extraction step were impregnated with iron(II) chloride as described above.

3.2 Analyses

3.2.1 pH measurement and ion exchange chromatography

Milled wood samples were soaked in deionized water. The suspension was sonicated and pH was measured with micro combination electrode (Hamilton Spintrode) immersed directly in the suspension before separation. The extracts were separated from the solid parts by centrifugation (3000 rpm, 5 min) and filtration. The low molecular organic acids were determined with Dionex (ICS-90 and ICS 2000) ion chromatograph assembled with ionpac AG14A-5µm guard column (3x30mm), ionpac AS14A-5µm column (3x150 mm) and anion micro membrane suppressor 4mm AMMS 300. The aqueous extracts were eluted with a mixture of sodium carbonate (8 mM) and sodium hydrogencarbonate (1 mM) by a rate of 0.5 $ml \cdot min^{-1}$. The extracts were analyzed by Innventia AB, Stockholm, Sweden and Department of Soil and Environment, Swedish University of Agricultural Sciences, Uppsala (both laboratories are accredited).

3.2.2 Flame atomic absorption spectrophotometry

In order to measure the total concentration of iron in the wood it was necessary to dissolve the wood. To achieve this, the impregnated wood was fragmented and boiled in nitric acid (65 %, analytical grade, Merck) until it was completely dissolved. The remaining solution was diluted quantitatively and iron was measured by flame atomic absorption spectrophotometry.

The sample solution was aspired into flames and the element of interest (iron) was atomized at high temperature (2000-3000 K). The excited atoms of iron absorb light at a well-defined wavelength (248.3 nm). The burner head had a length of 10 cm. Beer-Lambert´s law was obeyed and thereby a direct proportionality between concentration and absorbance was established.

3.2.3 Tensile test

Part of this testing was performed with an Instron universal testing instrument 5566 and part on a Shimatzu Autograph AGS-X tensile instrument. Both were equipped with a load cell of 10 kN and set to a pulling rate of 1 $mm \cdot min^{-1}$. A video extensometer registered and measured the strain of the sample. Prior to the testing, the mid-sections sizes of every sample were measured with a digital Vernier caliper. The samples were pulled apart until breakage. The force used to break the wooden “dog bones” was registered (*Figure 12*).

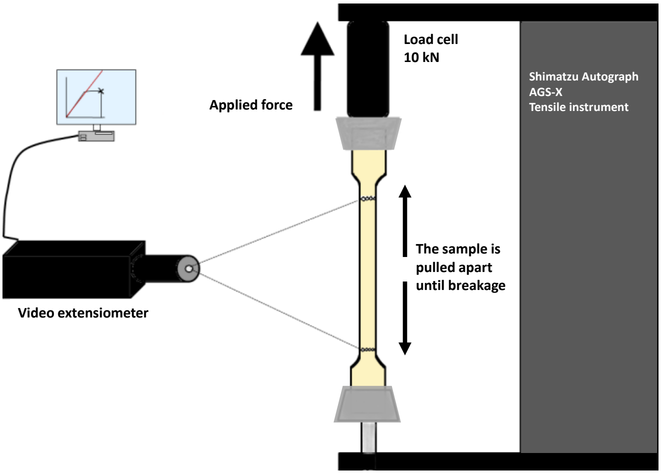

Figure 12. An image of Shimatzu autograph AGS-X showing the assembly of the “dog bone” shaped samples. The video extensometer measures the change of distance between the marks when the sample is exposed to applied force.

3.2.4 Non-invasive quantitative O_2 and CO_2 measurement

Oxygen

In order to have control of the initial and final quantity of O_2, pieces of iron(II) impregnated wood were incubated in vials equipped with special sensors. A smaller vial filled with saturated salt solution was placed adjacent to the samples to keep the desired relative humidity (Rockland, 1960). The partial oxygen pressure in the headspace was regularly measured. The sensors were excited at a wavelength (λ) in the range of blue light. The active element in the sensors is made of a ruthenium(II)-polypyridyl complex integrated in polymer films. The excitation and decay time (τ) of the luminophores are detected by an optical oxygen meter Fibox3 from PreSens precision sensing GmbH (Matthiesen & Wonsyld, 2010). The Fibox3 uses dynamic (collisional) fluorescence quenching based on the Stern-Volmer equation (Demas *et al.*, 1995; Klimant & Wolfbeis, 1995; Carraway *et al.*, 1991). This means that the decay time of the fluorescence is directly proportional to the oxygen pressure. Thus, it can be recalculated to oxygen concentration (Klimant *et al.*, 1995). The measuring range is 0-200 ppm with an accuracy of ±2 ppm. The methodology has been utilized to measure O_2 concentrations *in situ* or incubated archaeological wood (Matthiesen & Wonsyld, 2010).

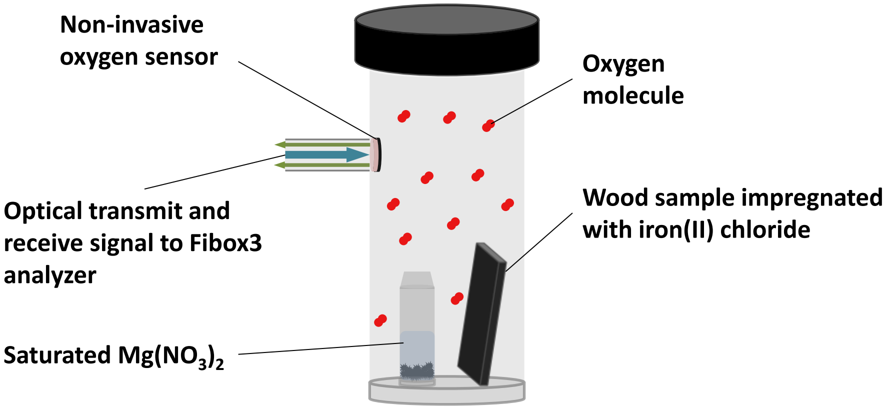

Figure 13. An illustration of the reaction vials prepared for O_2 monitoring.

Vasa samples

Seven core samples from different location of the *Vasa* were collected manually with a sampling drill. These sites were at places where earlier samplings have been made. The length (L) and diameter (Ø) of the samples were in the ranges 35-85 mm and 5 mm respectively. The cylindrical wooden samples were wrapped in plastic foil and dark sample tubes for transport. To avoid void volumes as much as possible NMR tubes (6.5-pp-7; Wilmad-labglass), fit the sample size, were used. The tubes were equipped with O_2-sensors and samples. To protect the samples from surrounding air the tubes were filled with paraffin wax. The samples were divided to an outer (A) and inner (B) part.

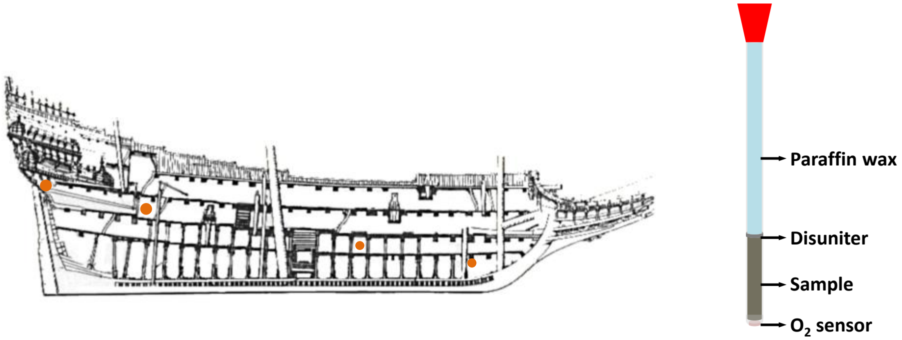

Figure 14. Sampling sites at the Vasa and measuring tube.

3.2.5 Carbon dioxide

The concentration of CO_2 in the head-space of the samples was analyzed by careful opening of the vial in a 500 ml glass container connected to an environmental gas monitor (EGM-4) based on non-dispersive infrared light (www.ppsystems.com). The samples remained for two hours until equilibrium. CO_2 was measured by directing the gas in the jar into the instrument.

3.2.6 Nuclear magnetic resonance (NMR)

The concentration of low molecular acids and soluble carbohydrates in aqueous extracts was determined by NMR. Milled wood was soaked in D_2O. The extract was separated by centrifugation. A 30 mM Trimethylsilyl propanoic acid (TMS-P) solution was added to the extract. The samples were analyzed with Bruker Avance III 600 MHz instrument at 303.15 K. The integration of peaks where used to quantify the acids and carbohydrates.

3.2.7 Fourier Transform InfraRed (FTIR)

Core samples from different location of *Vasa* were received. These samples were previously studied and were properly characterized by the mean of acid, iron and sulfur content, holocellulosic AMW distribution and pH (Bjurhager *et al.*, 2012)(Innventia AB) (Appendix 2). Sample 65695 was obtained from a large beam in the cargo hold of the ship adjacent to an iron bolt, 60 mm. Sample 65698 was collected from the middle part of the ship in the orlop deck, 53 mm, and the last sample 65701 was drilled manually from the port side in the back of the ship, 80 mm. The samples were divided depending on coloration and chemical characters. 1 mm sheet from different positions on the core were epilated with a scalpel. The samples were milled and placed in a desiccator which was evacuated for two days in order to remove water.

Four additional samples in the form of “dog bones” used for TS tests by Bjurhager *et al.* (2012) sawed from a large block of oak received from the orlop deck of the ship. This block had gone through the same conservation treatment as the rest of the ship (PEG, drying and relative humidity at 55% etc.). Samples were taken by cutting a piece at the breakage edge. The same preparations were performed as mentioned above.

Iron(II) chloride impregnated fresh oak used to determine the TS in the previous study (paper I) was subjected to sampling with a scalpel. In order to remove water more efficiently some of the samples were incubated together with D_2O. Ground dry samples and potassium bromide (KBr) in the ratio of 1:100 were mixed and exposed to a pressure of 10 ton for four minutes in order to prepare a KBr tablet (*Figure 15*).

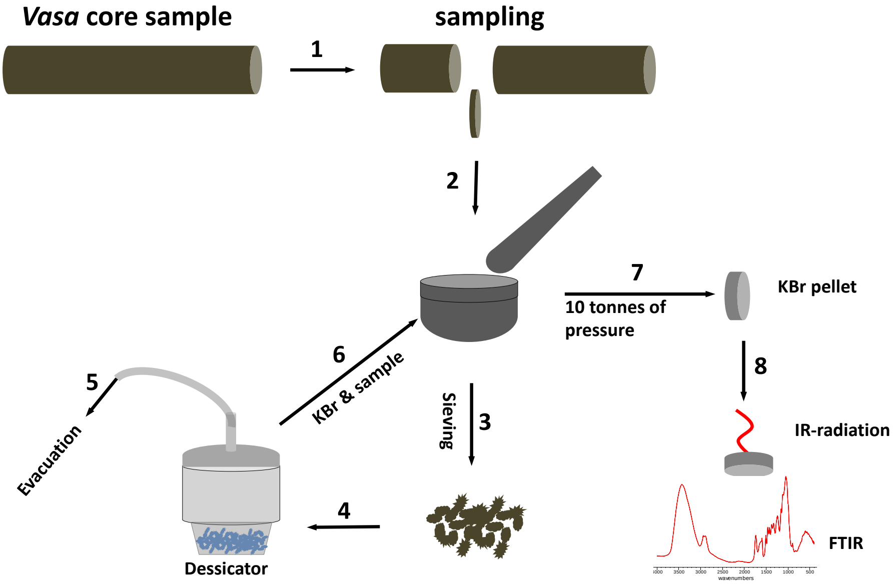

Figure 15. An illustration of sample preparation of Vasa core samples for FTIR analysis. The length and depth of sampling of the cylindrical sample were determined and denoted as surface and inner part.

Data analysis

All collected spectra were baseline corrected by a spline function using five predetermined points (paper IV). A normalization of the peaks was performed such that all spectra were fixed at 1507 cm^{-1}. The deconvolution of the spectra was calculated by the use of the Fityk® software (Wojdyr, 2010) utilizing a Gaussian function for the shape and area of the peaks. A Levenberg-Marquadt algorithm was used for the final fit of the curves of interest. The width and position of Gaussian peaks were locked to maintain the same data treatment function for all spectra.

The obtained data from peak areas and other corresponding parameters such as pH, TS, AMW, iron content etc. were input to the computer programming SIMCA-P 12.0® for multivariate data analysis.

4 Results and discussion

4.1 Iron in fresh wood

In order to mimic the *Vasa* wood in terms of iron content, impregnation tests were performed. The total content of iron in oak treated in aqueous solution with different iron(II) concentrations was analyzed by atomic absorption spectrophotometry.

Table 1. The total iron content (mg·g^{-1}) in dissolved wood after impregnation in aqueous iron(II) chloride solution at different concentrations.

Species	$FeCl_2$ (aq) (mM)		
	50	100	500
Oak	2.8 (-)	5.7 (1.0)	13.8 (-)
Birch	3.1 (0.7)	3.9 (0.4)	13.7 (0.7)
Pine- heartwood	3.2 (0.7)	4.8 (1.2)	18.8 (2.4)
Pine- sapwood	2.6 (0.7)	5.1 (0.4)	24.6 (2.7)

The values in parentheses are standard deviations.

It was found that wood impregnated with an 100 mM aqueous iron(II) chloride solution gave concentrations near the levels found in *Vasa* wood, ca. 5 mg·g^{-1}, (Almkvist & Persson, 2008a). It was not only the total content of iron in the wood which was the issue in this study, it was also a matter of penetration and accumulation pattern of iron in the cell walls. The impregnated wood was subjected to scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) which confirmed the presence of iron in the samples (paper I). Analyses of different parts of iron(II) impregnated wood by AAS (paper III) show that iron was distributed homogeneously throughout the samples. Only oak showed a significant difference between outer and inner parts in terms of iron concentration. The cellular deposits of iron in the cell walls shows close similarity to the *Vasa* wood (Almkvist & Persson, 2011).

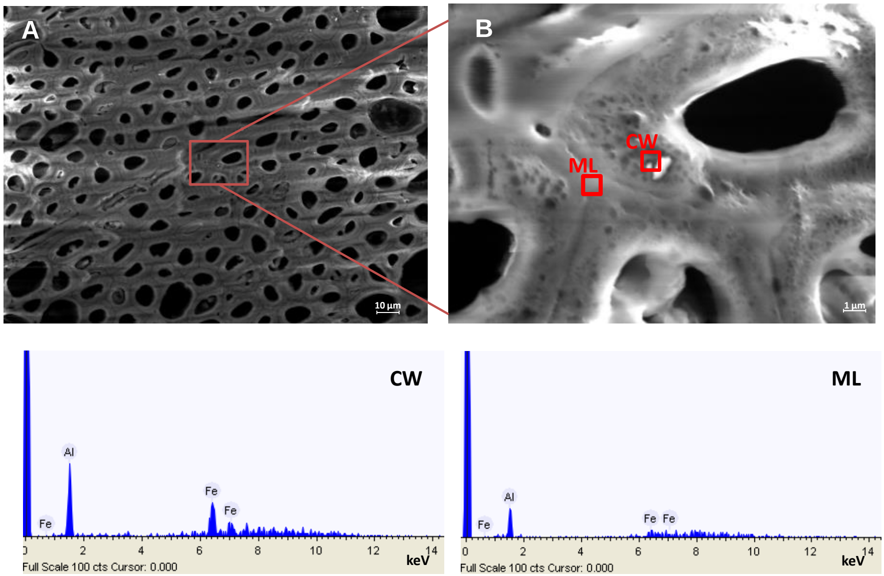

Figure 16. SEM images of iron(II) impregnated oak at 1000 (A) and 10000 times (B) enlargement. EDS spectra (below) show a higher content of iron in the cell wall (CW) compared to the middle lamella (ML).

4.2 Tensile tests

Mechanical properties of wood may change when exposed to different conditions. A previous study of oak wood from the *Vasa* showed that TS decreased more than 50 % compared to fresh oak wood (Bjurhager *et al.*, 2012). According to Bjurhager (2011) both recent and *Vasa* oak display a linear relationship between axial TS (σ) and strain (ε) (reversible deformation) followed by negligible plasticity. Similar results were obtained in this study. The values from untreated samples were used as references and regarded as normal. The average for 148 oak references had the following mechanical parameters, TS = 110±14 MPa, Young´s modulus (E) = 13±2 GPa and strain = 0.9±0.1 %. These values indicate that the wood used for mechanical tests was in good condition and proper to use.

Non-exposed samples showed no significant reduction in TS but as soon as the wooden samples were exposed to oxygen the deterioration started. The results showed a fast reduction of longitudinal TS at the beginning of the exposure, Table 2. Time of exposure and concentration of oxygen are important factors for the deterioration of impregnated wood. Basically, as long as there are organic substances in sufficiently close to iron and oxygen, the oxidative reactions would continue. In pure oxygen the rate of degradation is higher and the deterioration processes behave exponentially as a function of time. After one month and one year the longitudinal TS reduced to 17 and 35, % respectively, for samples exposed to air (Table 2). It should be emphasized that these samples were preconditioned in pure N_2 for one week. The values for samples with no preconditioning in N_2 during the wet period the reduction of TS became 3 and 1.5 times greater after one week and one month respectively (Table 2 & Table 5). This means that presence of water during the initial exposure to oxygen decreases the deterioration processes significantly. In pure oxygen the samples display a more accelerated degradation.

Table 2. Results from the TS test on oak samples with different pre-treatments in terms of oxygen exposure.

Pretreatment Wetting, drying, oxygen and $FeCl_2$	Exposure Pure N_2	 Air	 Pure O_2	Relative change, TS %	Significance level
Water (refs untreated)	-	Week	-	-1	NO
dry samples	-	-	Year	-7	NO
$FeCl_2$ (Direct tensile tests)	-	-	-	6	NO
$FeCl_2$ (refs untreated)	Week	-	-	-7	NO
$FeCl_2$ (refs untreated)	Week	Week	-	-6	NO
$FeCl_2$ (refs untreated)	Week	Month	-	-17	<0.1%
$FeCl_2$ (refs untreated)	Week	Year	-	-35	<0.1%
$FeCl_2$ (refs untreated)	-	-	Week	-19	NO
$FeCl_2$ (refs untreated)	-	-	Month	-30	<5%
$FeCl_2$ (refs untreated)	Week	-	Year	-50	<0.1%

References are untreated

The rate of degradation is important when it comes to preservation of wooden artifacts. One issue to understand is the present rate of degradation of *Vasa* wood. However, iron(II) impregnated fresh oak show a 50 % reduction of axial TS after exposure to pure O_2 for one year. It seems that the rate of TS reduction is strongly dependent on time and oxygen concentration. The reduction of TS was relatively fast in the beginning but declined exponentially with time. This becomes more clear when TS is plotted as a function of logarithmic exposure time (*Figure 17*). This plot shows a linear relationship between exposure time and relative change in TS. For comparison, the TS data from the *Vasa* is added in the chart (paper I). It shows that the mechanical decline is not as severe as the model experiments. This result is probably because of the extreme conditions recent wood went through and the oxygen availability was definite. The large beams in the *Vasa* containing high concentration of PEG in the surfaces might limit the diffusion of oxygen into the wood. As the chart shows the concentration of oxygen at the initial time determines the course and rate of mechanical degradation. Thereby the amount of oxygen in the wood of *Vasa* might not have reached the levels as high as the model samples. However, the exponential relationship of deterioration to time strongly suggests that the present degradation rate in the *Vasa* wood may indeed be very slow.

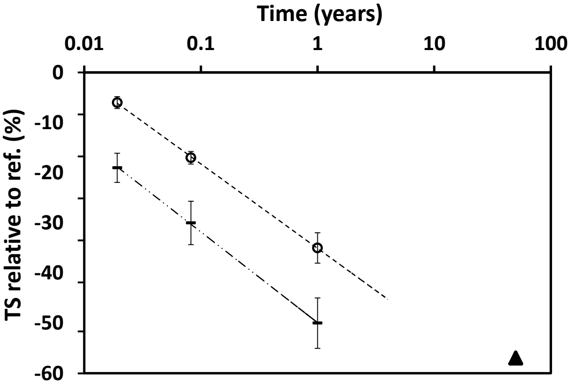

Figure 17. Relative change in TS as a function of time for iron(II) impregnated oak exposed to air (○) and pure oxygen (-). The triangle (▲) denotes the TS of Vasa oak after 50 years in air (Bjurhager et al., 2012).

The longitudinal TS of iron(II) impregnated oak show clearly the impact on wood when both iron and oxygen are present. Many artifacts within and around the ship were made of other species than oak. Theoretically any wood species should act similar to oak wood regarding oxidative degradation. Generally speaking as it was mentioned in section 2.1, the cellulose in common wood species such as pine and birch function similarly as in oak wood, although there are differences in their arrangement, orientation and their relative amounts.

The mechanical parameters for untreated birch and pine used as references behave similar to oak with a slightly higher tensile stress, Young´s modulus and strain (paper III). The average mechanical TS for birch had the highest values among the wood species studied (Appendix 1). This might be caused by the MFA of the birch. It has been shown that Young´s modulus increases when MFA of the cell walls decreases (Eder *et al.*, 2013). A comparison of the two hardwoods, oak and birch, shows somewhat different Young´s modulus. Birch wood gave a Young´s modulus value of ca. 13 GPa whereas this parameter for oak wood was 16 GPa. However, the relative TS of birch and pine treated with iron(II) chloride and air exposure for one month show similar degradation as oak in this study, Table 3.

Table 3. The result of TS for iron(II) impregnated birch and pine wood after one month in air.

wood-type	TS [%]	Significance level
Birch	-17	< 1%
Pine-heartwood	-16	< 1%
Pine-sapwood	-15	< 1%

4.2.1 Post-treatment by PEG

One important result in this study is the TS of samples post-treated with PEG. Bjurhager *et al.* (2010) showed that TS from fresh oak wood impregnated with PEG 600 was not affected in the longitudinal direction and in fact it increased in one case. However, no iron was present in those samples. With the gained experiences from the results concerning iron(II) and O_2 what would the effect be if PEG was added to oak wood pretreated with iron(II)?

The results of the longitudinal TS of samples treated with iron(II) and PEG 600 after 30 days of air exposure showed **no** reduction (Table 4). This result is good news for the *Vasa*. This result strongly indicates that PEG as conservation agent for *Vasa* was a fortunate decision regarding the longitudinal strength even though compressive tests showed a 50 % reduction in the transverse direction compared to recent oak (Ljungdahl & Berglund, 2007). Therefore, PEG might quench the radicals and thereby protect the cellulose from depolymerization. A previous study (Almkvist & Persson, 2008b) showed that low molecular PEG was found in *Vasa* wood sites with low pH and high content of iron. The diffusion of PEG has been limited in the wood of the *Vasa* (Håfors, 2001) and tensile tests from PEG rich outer parts towards low PEG content inner parts indicate a correlation to the average longitudinal TS (Bjurhager *et al.*, 2012). Another cause could be that PEG limits the diffusion of oxygen into the wood. According to Mexal *et al.* (1975) the mass transport of oxygen in the medium of PEG decreases with increasing concentration and AMW. This is rather important in this study because the rate of degradation is dependent on the concentration, the diffusion and mass transport of oxygen molecules.

Table 4. Iron(II) impregnated and PEG 600 treated oak showing the effect on tensile strength.

Pretreatment oak wood	**Time in Air**	**Relative change, TS %**	**Significance level**
$FeCl_2$ + PEG 600	Month	-4	NO
$FeCl_2$ + PEG 600*	Month	29	<0.1%

*References treated in $FeCl_2$ solution

4.2.2 The effect of RH

The samples conditioned at RH 98 % without any pre-treatment in N_2 resulted to a TS reduction of 18 % after one month compared to the references. The result can be compared to samples conditioned at RH 55 % for the same period of time. The TS for samples at RH 55% show a reduction of 27 % in air (Table 5). The difference between these samples is the amount of water in the wood. It seems that water is a hampering factor in the degradation process.

Table 5. TS of iron(II) impregnated oak exposed in the air during one week and one month at RH 55 % and 98 %.

Pretreatment oak wood	**Time in Air**	**Relative change, TS %**	**Significance level**
$FeCl_2$; RH 55%	Week	-18	<1%
$FeCl_2$; RH 55%	Month	-27	<0.1%
$FeCl_2$; RH 98%	Month	-18	<0.1%

4.3 Chemical implications

4.3.1 Oxygen consumption

The reduced strength of iron(II) impregnated wood is exclusively caused by the presence of oxygen indicating that the degradation is mostly due to oxidative reactions. A direct monitoring of oxygen uptake by impregnated wood was, therefore, performed. The results show that iron(II) impregnated wood consumed more oxygen than untreated ones. Among the wood species oak consumed more oxygen than the others with a consumption of approximately 500 µmol $O_2 \cdot (\text{g dry wood})^{-1}$ during one year. The O_2 consumption rate declined exponentially as a function of time (*Figure 18*A). After 30 days birch and pine had consumed approximately 40-50 µmol $O_2 \cdot (\text{g dry wood})^{-1}$ while, for oak wood, this value was ~120 µmol $O_2 \cdot (\text{g dry wood})^{-1}$ (*Figure 18*B). The different oxygen consumption of the wood species studied suggests that the overall chemical degradation is different although the reduction of TS is comparable. Oxygen consumed by oak may also be oxidations of other non-stabilizing components which are absent in e.g. birch and pine wood.

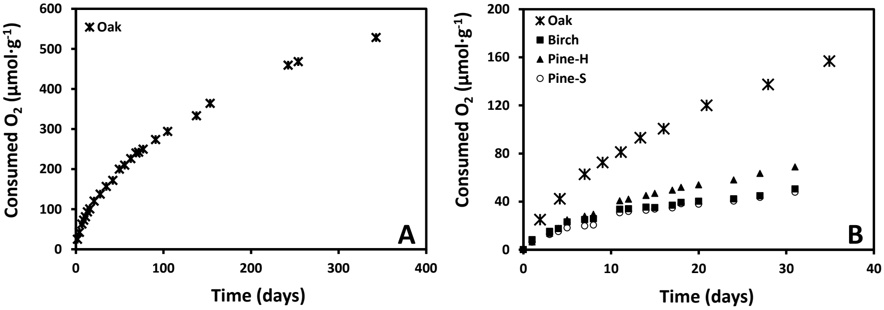

Figure 18. Consumed O_2 from iron(II) impregnated and incubated (A) oak during 1 year and (B) oak, birch and pine during 30 days.

Matthiesen and Wonsyld (2010) emphasized that one of the drawbacks of non-invasive oxygen technique is that the measurements are static and it is impossible to have a wet-dry cycle. To overcome this problem O_2 consumption of several impregnated oak wood samples with different RH were monitored. It showed that, after 30 days, samples in dry condition (RH 43 %) consumed most oxygen. However, after 200 days the total amount of consumed oxygen was highest from samples treated at RH 75 % (Table 6). These results imply that, in long term perspective, conditions at lower RH (≤55 %) are less deteriorating for oak when iron and oxygen are present.

Table 6. The cumulative O_2 consumption by iron(II) impregnated oak conditioned in different RH shows the values after 30, 80 and 200 days.

	O_2 consumption (µmol·g^{-1})					
RH (%)	30 days	(SD)	80 days	(SD)	200 days	(SD)
43	94	4.3	141	18.5	262	33.4
55	89	6.0	133	6.2	267	-
75	82	2.9	200	14.7	397	18.0
85	80	5.1	193	28.8	394	40.8
98	69	4.0	138	8.8	319	13.8
100	69	5.2	150	8.5	370	10.9
43_{ref}	7	3.4	-	-	-	-
98_{ref}	15	4.7	28	6.6	34	-

At the start when O_2 is introduced the interaction between iron and O_2 is faster in dry wood. However, in wet conditions perhaps accumulated water in the void volumes may dissolve O_2 and limit the availability of O_2. One might keep in mind that the RH adjustments for these samples started from wet condition and the samples were dried until stabilized weight at satisfied RH (see section 3.1.2). This pathway was deliberately chosen because of the history of the *Vasa* where the wood went from wet to dry conditions.

4.3.2 *Vasa* wood

Four samples from the *Vasa* showed much higher oxygen consumption than other samples. After 35 days, all available O_2 in the sample tubes were consumed. A rate of 0.15 $\mu mol \cdot g^{-1} \cdot day^{-1}$ O_2 was measured from the sample 65875A (0-27 mm) which is the sample with the highest oxygen consumption (*Figure 19*). A comparison to adjacent samples (65361; 65518 and 65702) characterized earlier (Bjurhager *et al.*, 2012; Almkvist & Persson, 2008a) showed that neither pH (~4) nor the content of acids (<2 $mg \cdot g^{-1}$) can explain the high consumption of O_2. However, the total iron content is extreme (50 $mg \cdot g^{-1}$) which might explain the high oxygen consumption rate in this sample. The results urge to complementary chemical analyzes to explain the high consumption of O_2.

Next the sample, 65873 A & B, 25 and 11 mm from the surface, respectively, are compared to sample 65007. An increasing gradient of iron content toward the depth and decreasing concentration of PEG in this region may be the cause for high O_2 consumption. This sample behaves similar to those of model experiments. Finally, the sample 65876B which probably contained high concentrations of both iron and low molecular acids as mentioned previously consume O_2 at levels as 65873 A & B. The comparable and corresponding sample to 65876B is 65003, and it contained high concentrations of iron (4.2 $mg \cdot g^{-1}$) and oxalic acid (61 $\mu mol \cdot g^{-1}$). All analytical values and site pictures for the samples are given in Appendix 2&3.

Although some of the core samples from *Vasa* consume oxygen at a higher rate than others they consumed far less oxygen than the model samples. A comparison of the values in Table 6 and *Figure 19* show that the oxygen consumption of *Vasa* wood samples is only 10 % of those of iron(II) impregnated recent oak. The oxygen consumption of the model samples is decreasing with time. This indicates that *Vasa* wood after ca. 50 years in air has already passed the period of high oxygen consumption which probably peaked soon after the salvage.

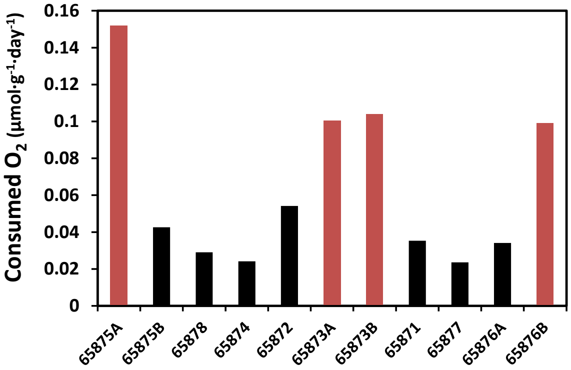

Figure 19. Consumed O_2 from core samples obtained from different sites of Vasa.

4.3.3 CO_2 emission

At the end of every observation of O_2 measurements the amount of CO_2 evolved was analyzed. The emitted CO_2 from oak after 30 days is significant at all RH levels studied. However, after 200 days exposure in air, there is an obvious increase in CO_2 emission with increasing RH (Table 7). A low RH (43 %) hardly any CO_2 was detected although the amount consumed O_2 under dry condition during the first month was higher than under wet conditions, Table 6.

Table 7. The absolute value of emitted CO_2 at 30 and 200 days treated in varies RH.

	CO_2 (µmol·g^{-1})	
RH (%)	**30 days**	**200 days**
43	4 (3)	6 (4)
55	26 (6)	77 (-)
Untreated (55)	3	3
75	25 (7)	98 (8)
85	31 (3)	120 (6)
98	37 (8)	238 (39)
100	29 (10)	233 (35)

The molar ratio of emitted CO_2 and consumed O_2 after 30 and 200 days are shown in *Figure 20*. They indicate that under wet conditions most of the consumed oxygen, ~70-80 %, is converted to CO_2 (RH 98 & 100%). CO_2 is kind of indicator toward a complete oxidation process of organic materials. These results imply that the oxidation of organic components is promoted when water is abundant.

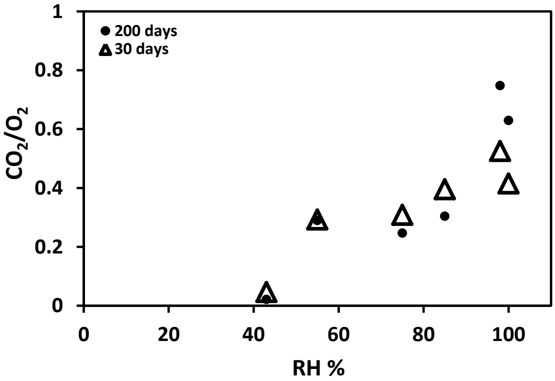

Figure 20. The molar ratio between emitted CO_2 and O_2 for iron(II) impregnated oak conditioned in a RH range between 43 % and 100 %.

The total emitted CO_2 for iron(II) impregnated birch and pine at RH 55% after one month is approximately ⅓ of that of oak. One explanation might be that oak contains more wood extractives and these are prone to oxidize and form CO_2 in an oxidative environment. A comparison between the hardwoods, oak and birch, shows that the consumption of oxygen and formation of CO_2 is higher for oak in both cases although the amount of iron(II) in the woods is similar (Table 8).

Table 8. The molar concentration of CO_2 formed after 30 days and corresponding total iron concentration in different wood species.

	CO_2 ($\mu mol \cdot g^{-1}$)	$iron_{tot}$ ($mg \cdot g^{-1}$)
Birch	8 (1)	3.1 (< 0.05)
Ref.	4	
$Pine_{Heartwood}$	7 (< 1)	5.2 (< 0.05)
Ref.	4	
$Pine_{Sapwood}$	10 (< 1)	5.4 (<0.05)
Ref.	6	

4.3.4 Acid formation

An observation of the total amount of low molecular organic acids shows that the concentration of all acids analyzed in this study have increased significantly where acetic and oxalic acid are the dominating ones. Time in air and the presence of iron(II) are probably two of the factors which contribute most to the acid formation. Formic and oxalic acid seems to increase faster in wet conditions while acetic and glycolic acids are not affected by the variation in RH during 200 days of air exposure.

Table 9. Amount of low molecular organic acids and soluble carbohydrates from iron(II) impregnated oak for different RH after 200 and 1500 days in the air. The values are obtained by quantitative ^{1}HNMR and IEC.

RH / time (% - Days)	Acetic acid	Formic acid	Glycolic acid	Oxalic acid	soluble carbohydrate	pH
	µmol·g^{-1}				mg·g^{-1}	
55%-1500	94 (1)	6 (0.9)	7 (1)	44 (1)	80 (9)	2.4
43%-200	56 (2)	2 (0.3)	3 (0.5)	12 (1)	30 (1)	2.5
55%-200	86 (15)	2 (0.2)	4 (2)	12 (2)	34 (4)	2.4
75%-200	105 (4)	2 (0.1)	2 (0.2)	13 (0.3)	41 (9)	2.6
85%-200	65 (14)	2 (0.3)	2 (1)	13 (0.6)	28 (1)	2.6
98%-200	51 (18)	4 (1)	2 (1)	22 (2)	26 (6)	2.6
100%-200	60 (25)	5 (1)	3 (1)	15 (4)	22 (3)	3.1
Recent oak*	2	0.1	n.a.	0.2	0.9	3.9

*The values are brought from Almkvist and Persson (2008a)

Oxalic acid is probably the main substance contributing to the low pH observed in aqueous extracts of *Vasa* wood. This was illustrated in previous studies by Bjurhager *et al.* (2012) which showed clearly that analysis from different depths in wood from the *Vasa* has a negative correlation with the concentration of oxalic acid and pH.

The pH values for all wood samples impregnated with iron(II) chloride decreased after 30 days in the air and it was kept during the rest of the experiment time. This result is in accordance with the content of oxalic acid analyzed. The total content of oxalic acid is dependent on time of exposure in air. Oxalic acid seems to be formed as soon as oxygen is available. The formation rate of oxalic acid compared to the rates of oxygen consumption and TS reduction, indicate that oxalic acid is an end product formed in a secondary reaction.

The amount of oxalic acid formed in oak is twice the amount formed in birch and pine after 200 days. The pH of all the iron(II) impregnated samples decreased by 1-2 pH units. The results show that the formation of oxalic acid in birch and pine increased more between 30 and 200 days compared to oak although the total amounts are lower for birch and pine, Table 10. However, the presence of iron(II) compounds seems to promote the formation of oxalic acid and drop in pH. The amount of oxalic acid in pine sapwood is higher than the corresponding heartwood. This could depend on different composition of sap- and heartwood. Pine heartwood contains aromatic compounds of different stilbenes such as pinosylvin, which is a phenolic fungicide found only in the heartwood of pine (Jansson; *et al.*, 2009; Fengel & Wegener, 1984). According to Rossi *et al.* (2013) stilbenes could partly act as natural hydroxyl radical scavengers and thereby limit the deterioration process and the corresponding end products.

Table 10. The content of oxalic acid from iron(II) impregnated wood after exposure to air during 30 and 200 days.

Wood-type	Time in air (days)	Oxalic acid ($\mu mol \cdot g^{-1}$)	pH
Oak			
Ref.	30	2	3.7
Iron(II)	30	4 (< 0.1)	2.5
Iron(II)	200	14 (-)	2.4
Iron(II)	500	26 (0.6)	2.5
Iron(II)	1500	44 (1.2)	2.5
Birch			
Ref.	30	< 0.1	4.5
Iron(II)	30	1 (< 0.5)	2.5
Iron(II)	200	6 (< 0.5)	2.6
Pine-heartwood			
Ref.	30	< 0.1	4.6
Iron(II)	30	0.5 (< 0.5)	2.5
Iron(II)	200	4 (< 0.5)	2.7
Pine-sapwood			
Ref.	30	0.1	4.2
Iron(II)	30	1 (< 0.5)	2.5
Iron(II)	200	7 (< 0.1)	2.6

A long term study of the release of oxalic acid in impregnated oak wood treated at two different RH, 55 and 98 %, showed that the total amount of oxalic acid is raised to levels equal to those found in *Vasa* wood. 44.5 $\mu mol \cdot g^{-1}$ oxalic acid was obtained for samples treated at RH 55 % which is comparable to degraded core samples from the *Vasa* (50 $\mu mol \cdot g^{-1}$) (paper II). The same amount of oxalic acid was formed in oak samples treated at RH 98 % after only 1.5 years. This result shows that wet conditions promote the formation of oxalic acid. This indicates that the oxalic acid found in *Vasa* wood may have formed during the wet period immediately after the ship was salvaged. With an uncontrolled climate and iron(II) and oxygen available the formation of oxalic acid was unavoidable.

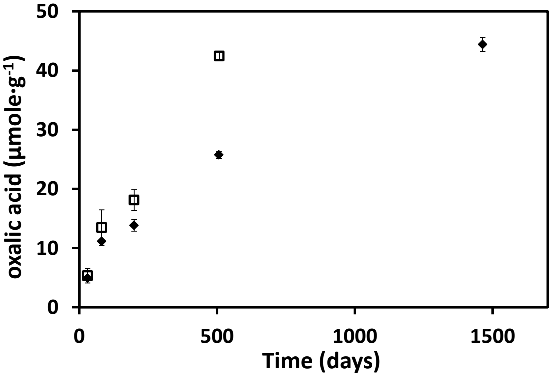

Figure 21. Molar concentration of oxalic acid as a function of time for iron(II) impregnated oak samples at RH 55 % (◆) and 98 % (☐).

According to Varela and Tien (2003) and Shimada *et al.* (1997) oxalic acid in an oxidative environment oxidizes to CO_2 by scavenging the reactive radical electron from e.g. a hydroxyl radical and thereby two CO_2 and a superoxide radical is formed which could reduce iron(III) to iron(II) to close the catalytic circle.

$$(COO)_2^{2-} + HO^{\bullet} + O_2 \rightarrow 2CO_2 + O_2^{\bullet -} \qquad \text{(Eq. 9)}$$

The concentration of formed oxalic acid and CO_2 in iron(II) impregnated wood seems to be positively correlated (*Figure 22*). Stoichiometrically, all formed CO_2 does not come from oxalic acid and this indicates that other components might oxidize in a similar way. Hydroxyl radicals are very reactive and if they are formed, bonds will probably be broken not only in oxalic acid but also in other organic substances. Another observation is the relationship between extractives, oxalic acid and CO_2. It is obvious that the presence of extractives affect the formation of oxalic acid and thereby the formation of CO_2. However, recent oak impregnated with iron(II) produced most oxalic acid after 30 days. Oak pretreated with acetone (step 1) and impregnated with iron(II) display a lower concentration of oxalic acid nonetheless somewhat higher CO_2. Further solvent treatments of oak shows that as the concentration of extractives reduces the formation of oxalic acid and CO_2 becomes closer to the levels of birch and pine.

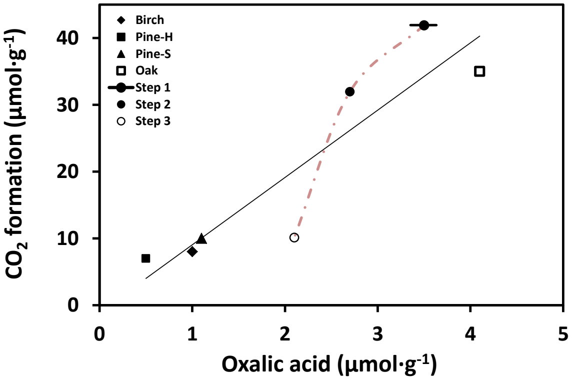

Figure 22. The relationship between CO_2 and oxalic acid for different wood types after 30 days of air exposure. Result from Soxhlet extracted and iron(II) chloride treated oak are inserted.. Step 1, 2, 3 denotes oak extracted with acetone/water 7:3, Toluene/ethanol 2:1 and 2-propanol/1% NaOH respectively.

4.4 Carbohydrates

Analysis of iron(II) impregnated oak showed an increase of soluble carbohydrates by 90 times after 1500 days in air compared to recent oak (Table 9). This result implies that wood polymers have broken up into smaller ones, more hydrophilic and water soluble substances as end products of degradation reactions from wood components are formed. Previous studies (Bjurhager *et al.*, 2012; Almkvist & Persson, 2008c; Lindfors *et al.*, 2008) showed, through size exclusion chromatography (SEC) on *Vasa* wood, that the average molecular weight (AMW) distribution of holocellulose is significantly shifted toward more LMW peaks. Similar deteriorations are obtained for iron(II) impregnated oak exposed to air (paper I). These results strongly suggest that the degradation mechanisms occurred in the presence of iron(II) in the *Vasa* which are similar to model experiments in this study.

4.5 Changes in FTIR spectra

The FTIR spectra from iron(II) impregnated oak wood, *Vasa* wood and untreated oak wood were collected. The IR absorption bands for all of the samples show general wavenumbers typically for oak wood. However, at a further close examination of the spectrum it was obvious that *Vasa* wood differed significantly. Bands in the region 1800-900 cm^{-1} containing absorption bands from single wood components C-C, C-H and C-O stretching and bending were changed. At 1736 cm^{-1} corresponding to the characteristic band for unconjugated carbonyl (C=O) stretching attached to xylan seems to both changing in intensity and shifting towards lower wavenumbers (Emandi *et al.*, 2011; Colom *et al.*, 2003). Spectra of the samples 65695, 65698 and 65701 taken 30-50 mm from the nearest surface indicate several differences to spectra from recent oak (*Figure 23*). These differences are (i) at 1738-1700 cm^{-1} underlying bands result in band broadening (ii) the band at 1620 cm^{-1} has increased in intensity (iii) a new band at 1398 cm^{-1} has raised and (iv) the broad band at 1240 cm^{-1} has to some extent split.

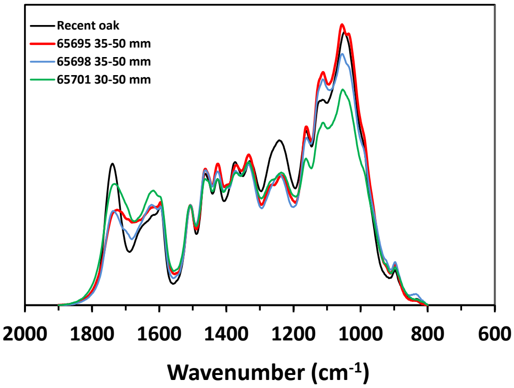

Figure 23. Spectrum of three Vasa samples combined with recent oak. The spectrums are data treated by baseline correction and normalization at 1507 cm^{-1}.

Spectra from surface region of these samples contained extensive amount of PEG which made the bands originating from wood component impossible to evaluate. The bands from PEG not only overlaps the absorption bands from wood, but also make the powder samples impossible to dry probably due to PEGs hygroscopic properties. According to Lappi *et al.* (2004) H_2O has a strong band at 1638 cm^{-1} and can be observed as a broad band in the spectra from samples with additional PEG (*Figure 24* D).

This method could possibly be utilized to make a gradient of the PEG from outer parts to inner parts. FTIR analysis is fairly sensitive to the presence of free water which must be removed from the samples as much as possible. This is especially important for this study where the changes at the range 1750-1600 cm^{-1} are often the case. Moreover, a describable way to recognize the absorption bands is to analyze the individual components of wood (*Figure 24*).

To interpret the spectra from *Vasa* oak and model samples comparable multivariate data analysis was applied. Secondary derivative function was used to the normalized and baseline corrected data to spectra in order to determine and pinpoint underlying peaks. The data were brought to Fityk programming for deconvolution of the peaks and thereby peak properties such as peak area, height and shifts were determined. Recent oak was used as a standard for fitting. 23 Gaussian peaks in the range 1800-1200 cm^{-1} provided the best fit with satisfactory statistical features.

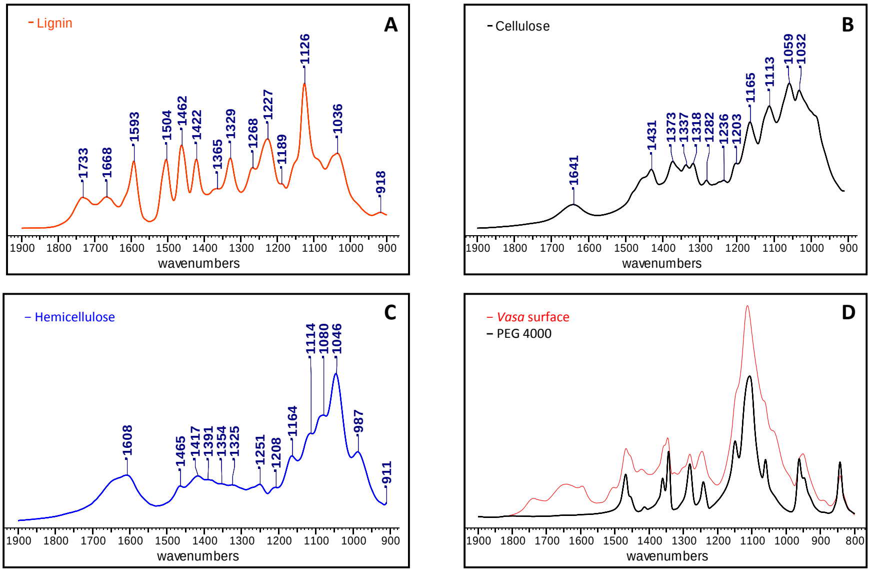

Figure 24. FTIR spectra of lignin (A), crystalline cellulose (B) and xylan (C) yielded conventionally from birch, FTIR spectrums of surface area of Vasa wood and pure PEG 4000 (D).

Principal component analysis (PCA) was used to classify and discriminate occurred FTIR data from wood samples. This method help to create a regression model which could be used to predict the conditions of the wood (Eriksson *et al.*, 2001). However, the PCA of data from TS and corresponding FTIR data provided four PCs for best prediction (*Figure 27*). The cross validation (CV) of these data suggests that the four components explain 85 % (0.85) of the model by the cumulative R-square (R^2). The Score plot of the first and second principal component show a clear separation between the *Vasa* samples and model oak. A line through the origin of the corresponding loading plot towards the point of TS was drawn. The positions of the points occurred from different bands in perpendicular relation to this line determine the correlation relationship to the TS. However, the bands 1742 and 1710 cm^{-1} strongly correlates the peak areas against reduced TS (*Figure 25*). The negatively correlated peak area of 1710 cm^{-1} to TS gives an indication that when carbonyl-and carboxylic groups expand it leads to reduced strength of wood (paper IV). The band 1742 cm^{-1} is positively correlated to TS. Furthermore, the position of these two bands together with nearby bands in the loading plot determined the grouping in the score plot.

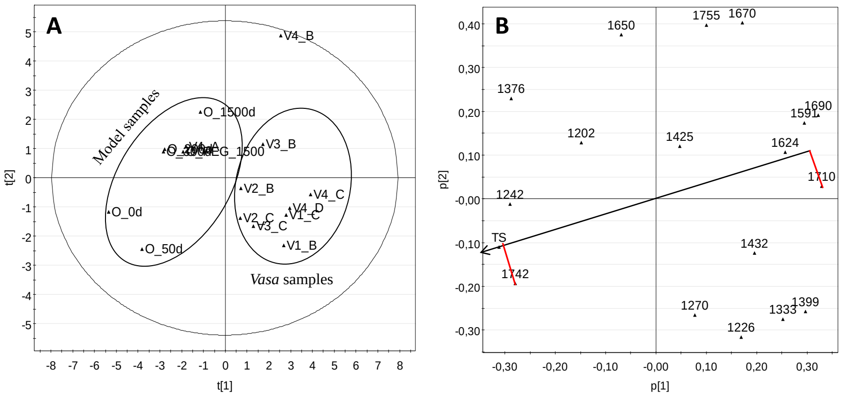

Figure 25. PCA score plot shows the separation of *Vasa* and model samples (A). The corresponding loading plot (B) shows that the bands at 1742 cm^{-1} and 1710 cm^{-1} are most correlated to Tensile strength.

Another overview of the score plot contained only the first PC, provided interesting and clearer information. The alignment of the *Vasa* and model samples suggest a gradient of degradation caused by exposure time (*Figure 26*).

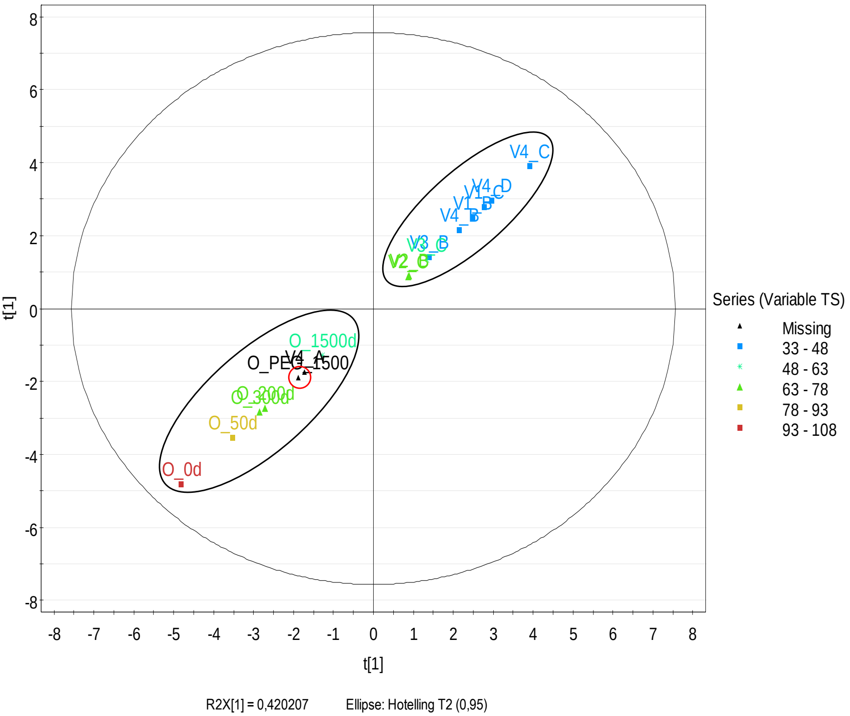

Figure 26. The score plot for the first PC of modelled (O_#days) and Vasa samples (V#) data set regarding tensile strength.

Iron(II) impregnated recent oak (O_#d) show that with time in air the wood properties approach those of the *Vasa* samples. O_0d is the sample with no exposure in oxygen. The position of this point in the score plot is clearly separated from those exposed to air and *Vasa* samples. This means that oxygen plays a central role in deterioration reactions of wood shown in previous sections, and PCA analysis of FTIR data seems to be an excellent complementary method. The samples V4_A and O_peg_1500 (red ring, *Figure 26*) position in the score plot are close to each other. The TS values for these two samples were missing but it shows that they are comparable by the information obtained by FTIR. This is an indication that the deteriorations of PEG treated wood has similar behavior. It also indicates that *Vasa* samples, rich in PEG, are less deteriorated. According to the score plot, *Vasa* sample V4_C is the most degraded among the samples used in this study.

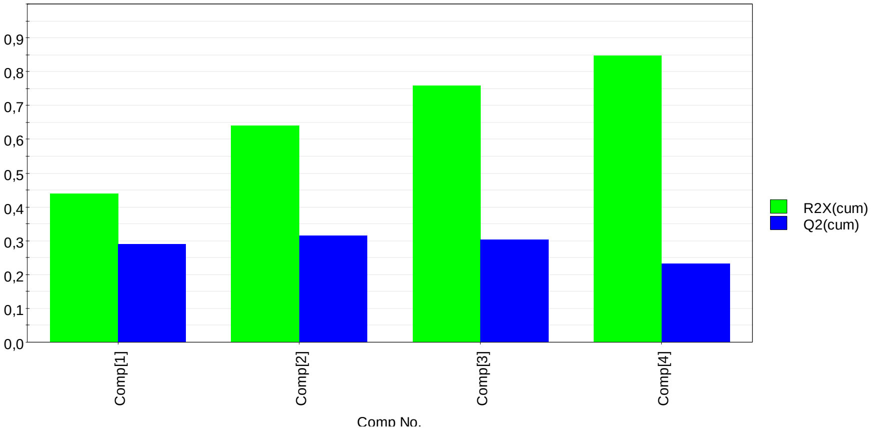

Figure 27. *The plot shows the overall R^2- and Q^2 statistics as a function of model complexity. PC1, PC2, PC3 and PC4 explain up to 80 % correlation.*

This model includes a relative low number of samples but it shows clearly the differences and similarities of *Vasa* wood and impregnated recent oak. However, these results urge to improve the response from this powerful statistical tool by a total mapping of the *Vasa*. A more reliable prediction model may open many possibilities such as lower amount of sample is needed for analysis. Furthermore, FTIR spectroscopy is convenient and relatively fast compared to many traditional chemical methods.

5 Conclusion

Reduction in tensile strength was observed for all the wood species when they were impregnated with iron(II) chloride and exposed to oxygen. The results showed a fast degradation rate immediately after the introduction of oxygen. It was also shown that the initial degradation rate is dependent on oxygen concentration and it increases with increasing oxygen concentration. The degradation of *Vasa* wood caused by iron catalyzed oxidative processes has their major impact when oxygen is present. This suggests that degradation activity in the *Vasa* wood today is much lower compared to the time when oxygen started to diffuse into the wood after the salvation.

The addition of PEG seems to inhibit the oxidative reactions catalyzed by iron. This is in accordance with the previous studies on *Vasa* wood (Bjurhager *et al.*, 2012). No reduction of TS was obtained for fresh oak impregnated with iron(II) and PEG. A hypothesis is that the ability of PEG to scavenge the radicals formed e.g. from Fenton type of reactions, might protect the cellulose involved in the longitudinal strength of wood.

As expected the results from direct oxygen measurement followed the same trends as the results from the TS measurements. Oxygen is the promoting substance and its presence is as necessary as iron(II) will create a condition where reactive oxygen species (ROS) are formed. ROS such as $HO^{\bullet}$ are very reactive and probably have a major role in the depolymerization of organic components in wood including reduced mechanical strength and formation of low molecular organic acids. The fast oxygen consumption from iron(II) impregnated wood at the initial stages strengthened the suggested oxidation reactions in the wood. Although different wood species act differently regarding consumption of oxygen, they all reduced similarly regarding the mechanical strength after a predetermined time of exposure (one month). The corresponding CO_2 produced from these experiments was less than the consumed oxygen which showed that all oxygen is not converted to CO_2.

The acid formation in these samples is another proof of oxidative reactions and the similarities to *Vasa* are unequivocal. It was established that substances found in the *Vasa* wood in significant amounts, could also be found to the same degree in model experiments. One of the important substances was oxalic acid having strong acidic properties. The formation rate of oxalic acid was not as fast as the oxygen consumption and reduction of tensile strength. Oxalic acid found in the *Vasa* wood is probably a result of the oxidation reactions which took place immediately after the introduction of air but it might have been formed during the drying time and further on.

The comparison of *Vasa* wood and modeled oak by FTIR showed that this method could be an informative and affordable way to determine the condition of wood. The prediction model suggest that iron(II) impregnated oak becomes more similar to *Vasa* wood the longer they are stored in oxygen. The multivariate model could be used to characterize the wood by only using FTIR analysis which demands very small quantities of sample (<5 mg). However, further development of this model is needed for more reliable predictions.

It is recommended that the relative humidity should be kept as it is today at 55 %. Although the reduced TS was lower for comparable samples conditioned at RH 98 %, however, both consumed O_2 and formation of acids were significantly higher than those at RH 55 %.

6 Recommendations for future findings

As ending words, I would like to suggest some procedures if possible when new archaeological waterlogged wooden object are discovered. In some cases it is better to leave the artifact alone in its burial site. However, many times due to political, financial, public interest, etc. artifacts have to be salvaged.

If possible an artifact should be incubated already in the water near the burial site. On the surface the incubator should be evacuated with an inert gas such as N_2 or Ar. The pressure should be kept as the ambient pressure (1 atm.). This procedure is recommended to protect the artifact against air.

A characterization of the object is needed to determine the abnormal elementary contaminations. If the concentration of iron is sufficiently high it must be removed or at least quantitatively decreased. This can be done by strong complex agents. Diethylene triamine pentaacetic acid (DTPA, used on *Vasa* artifacts) is one of the common iron complex agent. After the treatment of iron chelating agent the content of iron is probably lowered significantly to levels where the harmful effects are controlled. The artifacts could now be out in the open air for further treatment. Usually freeze drying followed by treatment with PEG is the common procedure nowadays. If possible, even this procedure should be performed under oxygen free conditions. This would optimize the treatment for any effect of iron and oxygen to the artifact.

Hopefully this work would contribute to a better understanding of the processes which could emerge when iron is present in wood.

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Appendix 1.

The relative tensile strengths are calculated via:

$$\text{TS }\% = \frac{\sigma_{samle} - \sigma_{Ref}}{\sigma_{Ref}} \times 100$$

Tensile strength, Young's modulus and strain to fracture

#	Pre-Treatment				Tensile strength $\boldsymbol{\sigma}$ (stdev) [Mpa]	Tensile stiffness Young's mod. E (stdev) [Gpa]	Strain to fracture $\boldsymbol{\varepsilon}$ (stdev) [%]	Number of samples
Effects wetting, drying, oxygen and Fe(II) chloride on oak wood		**N_2**	**Air**	**O_2**				
A1	-	-	-	year	100 (8)	14.0 (1.3)	0.74 (0.05)	7
	reference	-	-	year	107 (14)	13.6 (1.5)	0.79 (0.08)	6
A2	Water	-	Week	-	127 (19)	13.4 (1.5)	1.01 (0.16)	7
	reference	-	Week	-	128 (27)	13.0 (2.0)	0.95 (0.10)	6
B1	$FeCl_2$ (aq)	-	-	-	82 (18)	8.7 (1.2)	1.14 (0.09)	7
	reference	-	-	-	77 (15)	8.9 (1.9)	1.07 (0.20)	6
B2	$FeCl_2$ (aq)	-	Week	-	97 (19)	13.4 (1.5)	0.83 (0.11)	24
	Water (ref.)		Week	-	118 (29)	13.0 (2.0)	0.99 (0.16)	16

Tensile strength, Young's modulus and strain to fracture

#	Pre-Treatment				Tensile strength σ (stdev) [Mpa]	Tensile stiffness Young's mod. E (stdev) [Gpa]	Strain to fracture ε (stdev) [%]	Number of samples
Effects wetting, drying, oxygen and Fe(II) chloride on oak wood		**N_2**	**Air**	**O_2**				
B3	$FeCl_2$ (aq)	-	Month	-	93 (16)	12.7 (2.6)	0.78 (0.09)	24
	Water (ref.)	-	Month	-	127 (23)	14.2 (3.2)	1.00 (0.14)	16
B4	$FeCl_2$ (aq)	-	-	Week	76 (20)	11.5 (3.8)	0.67 (0.10)	7
	Water (ref.)	-	-	Week	94 (16)	11.8 (2.0)	0.84 (0.08)	6
B5	$FeCl_2$ (aq)	-	-	Month	57 (12)	11.2 (2.6)	0.61 (0.07)	7
	Water (ref.)	-	-	Month	81 (17)	9.6 (2.4)	0.89 (0.13)	6
B6	$FeCl_2$ (aq)	Week	-	-	114 (16)	13.8 (0.7)	0.83 (0.07)	7
	Water (ref.)	Week	-	-	122 (15)	14.5 (1.6)	0.86 (0.07)	6
B7	$FeCl_2$ (aq)	Week	Week	-	87 (16)	11.5 (2.0)	0.73 (0.09)	7
	Water (ref.)	Week	Week	-	93 (25)	11.8 (3.2)	0.83 (0.13)	6
B8	$FeCl_2$ (aq)	Week	Month	-	96 (8)	16.1 (1.3)	0.65 (0.07)	7
	Water (ref.)	Week	Month	-	115 (5)	15.6 (1.3)	0.80 (0.11)	6
B9	$FeCl_2$ (aq)	Week	Year	-	83 (13)	14.2 (2.4)	0.48 (0.10)	7
	Water (ref.)	Week	Year	-	128 (12)	16.8 (2.0)	0.92 (0.16)	6
B10	$FeCl_2$ (aq)	Week	-	Year	60 (6)	14.9 (1.5)	0.44 (0.08)	7
	Water (ref.)	Week	-	Year	118 (20)	15.4 (3.0)	0.80 (0.11)	6

Tensile strength, Young's modulus and strain to fracture

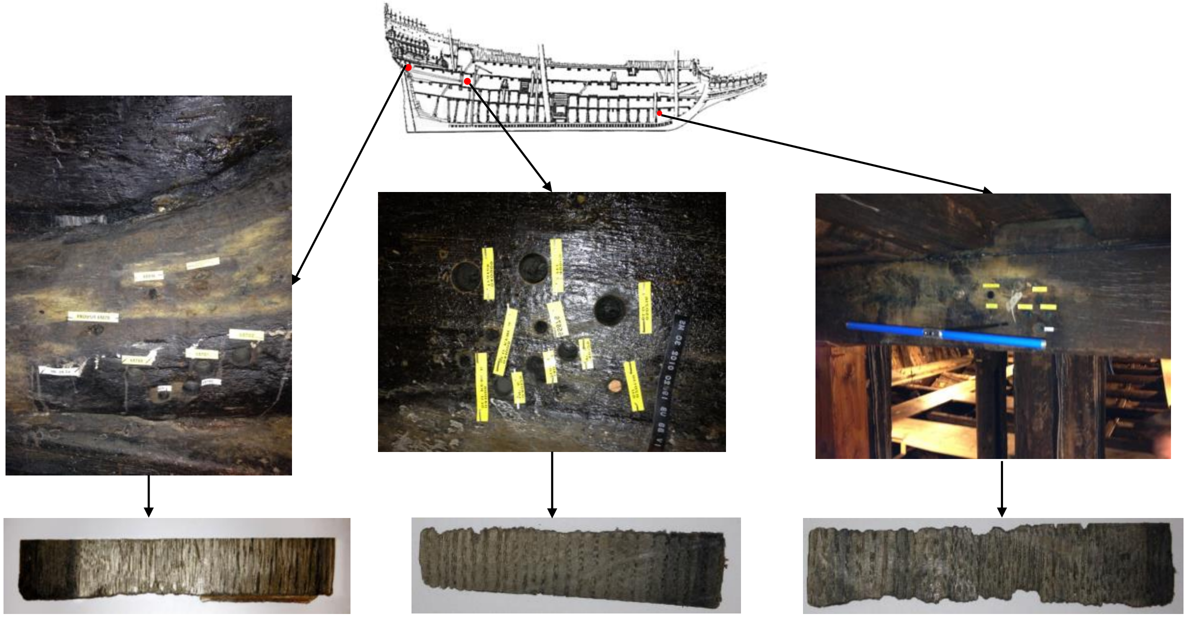
#	Pre-Treatment				Tensile strength σ (stdev) [Mpa]	Tensile stiffness Young's mod. E (stdev) [Gpa]	Strain to fracture ε (stdev) [%]	Number of samples
		N_2	Air	O_2				
Effects of RH								
C1	$FeCl_2$ (aq); RH 98%	-	Month	-	86 (13)	11.3 (2.3)	0.87 (0.13)	32
	Water (ref.); RH 98%	-	Month	-	106 (13)	12.3 (2.7)	1.02 (0.09)	8
Effects of additional compounds								
D1	Solvent-treated + FeCl2 (aq)	-	Month	-	101 (18)	12.5 (2.9)	0.88 (0.19)	25
	Water (ref.)	-	Month	-	118 (31)	12.6 (1.6)	1.00 (0.22)	15
D2	$FeCl_2$ (aq) + PEG 600	-	Month	-	119 (17)	13.5 (1.3)	0.95 (0.17)	7
	Water (ref.)	-	Month	-	124 (18)	15.0 (0.7)	0.83 (0.08)	6
D3	$FeCl_2$ (aq) + PEG 600	-	Month	-	92 (26)	11.5 (1.8)	0.86 (0.13)	24
	$FeCl_2$ (aq) (ref.)	-	Month	-	71 (17)	11.8 (1.8)	0.61 (0.12)	16
D4	Cysteine + $FeCl_2$ (aq)	-	week	-	71 (12)	8.8 (1.8)	0.71 (0.23)	7
	Water (ref.)	-	week	-	87 (8)	10.5 (1.2)	0.87 (0.08)	6
D5	Cysteine + $FeCl_2$ (aq)	-	Month	-	85 (22)	13.3 (2.1)	0.67 (0.15)	24
	$FeCl_2$ (aq) (ref.)	-	Month	-	84 (26)	13.2 (3.2)	0.63 (0.16)	17
Effects of heating								
E1	$FeCl_2$ (aq) + heat 55°C	-	Month	-	56 (20)	18.5 (3.4)	0.32 (0.16)	7
	Water (ref.)	-	Month	-	142 (19)	16.7 (1.0)	0.82 (0.15)	6
E2	$FeCl_2$ (aq)+ cysteine + heat 55°C	-	Month	-	55 (7)	14.3 (1.4)	0.41 (0.09)	7
	Water (ref.)	-	Month	-	102 (18)	13.4 (1.7)	0.84 (0.11)	6

Tensile strength, Young's modulus and strain to fracture

#	Pre-Treatment				Tensile strength σ (stdev) [Mpa]	Tensile stiffness Young's mod. E (stdev) [Gpa]	Strain to fracture ε (stdev) [%]	Number of samples
Effects of heating								
		N_2	**Air**	**O_2**				
E3	$FeCl_2$ (aq)+ PEG 600 + heat 55°C	-	Month	-	75 (13)	15.5 (2.0)	0.50 (0.09)	7
	Water (ref.)	-	Month	-	112 (34)	15.0 (0.7)	0.72 (0.13)	6
Other wood types								
	Birch							
F1	$FeCl_2$ (aq)	-	Month	-	122 (22)	10.3 (2.0)	1.2 (0.3)	26
	Water (ref.)	-	Month	-	146 (27)	10.2 (1.6)	1.4 (0.2)	20
	Pine-Heartwood							
F2	$FeCl_2$ (aq)	-	Month	-	100 (23)	7.6 (2.2)	1.5 (0.9)	27
	Water (ref.)	-	Month	-	121 (20)	13.9 (3.9)	1.0 (0.3	18
	Pine-sapwood							
F3	$FeCl_2$ (aq)	-	Month	-	98 (20)	7.7 (2.6)	1.5 (0.8)	27
	Water (ref.)	-	Month	-	116 (22)	8.6 (1.2)	1.4 (0.3)	18

Appendix 2

Sampling sites at *Vasa*



Appendix 3

The values are brought here from previous studies for comparison (Bjurhager *et al.*, 2012; Almkvist & Persson, 2008a)

Sample ID	Corresponding samples	Depth from nearest surface (mm)	PEG (%)	pH	Acetic acid	Formic acid	Oxalic acid	Fe	S
							$(mg \cdot g^{-1})$		
65873A & B	65007	7.5	21	5.1	0.3	0.3	n.a.	1.9	2.4
	65007	18	3	4.2	3	0.4	n.a.	3.2	1.3
65875A	65361	3	59	4	0.2	0.3	n.a.	50.3	10.5
	65361	16	50	4.4	0.4	0.7	n.a.	17	16
	65518	5	61	3.8	0.9	0.8	0.8	17	16
	65702	7.5	55	4.9	2	1.8	0.4	19.8	13.8
	65702	32	34	3.6	10.2	2.4	2.6	2.7	2.3
65876B	65003	40	32	3.4	2.4	4.8	n.a.	n.a.	n.a.
	65003	60	19	3.3	2.7	4.3	5.5	4.2	0.4

Appendix 4

Different degradation pathways of polyethylene glycol according to Mkhatresh and Heatley (2004) , Kerem *et al.* (1998) and Han *et al.* (1995).