

## Analyses of sulfur and iron in marine-archaeological wood

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Following the discovery of high acidity caused by oxidation of reduced sulfur compounds accumulated in the timbers of the Swedish 17<sup>th</sup> century warship *Vasa*, we have analysed cores from several shipwrecks worldwide with a variety of techniques. To obtain detailed profiles of how the total sulfur and iron concentrations vary with depth in the wood, line scans along the cores with an x-ray fluorescence technique is introduced, using condensed and focused high intensity x-rays and CCD detection of the excited x-ray fluorescence. At intervals along the cores sulfur K-edge X-ray near edge absorption spectroscopy (XANES) provides speciation of the sulfur compounds, while multielement analyses with x-ray photoelectron spectroscopy (ESCA) is used to follow the variation of sulfur in reduced and oxidised forms, the uniform penetration of borate, and the distribution of carbon in CH<sub>2</sub> and CO species as an indicator of cellulose degradation. Scanning electron microscopy (SEM), combined with energy dispersive x-ray spectroscopy (EDS), reveals the sulfur and iron distribution in the cell walls and in particles in the wood. The sulfur species originate from hydrogen sulfide, which is produced in anoxic conditions from sulfate ions in seawater by sulfate-reducing bacteria. The hydrogen sulfide probably reacts with active groups in lignin-rich parts of the wood forming organosulfur species, or with iron ions to iron sulfides and elemental sulfur. High accumulation of such reduced sulfur compounds in the wood seems to be coupled to the bacterial degradation of the cellulose, and may result in appreciable sulfur concentrations in waterlogged wood from shipwrecks. The iron and sulfur profiles sometimes follow each other for the *Vasa*, indicating formation of iron-sulfur compounds, but not for the *Mary Rose*. The *Bremen Cog*, which was preserved in river water, has low sulfur and iron concentration in samples from the hull timbers. Implications of the results for modified conservation procedures are discussed.

## Introduction

*The sulfur conservation problem.* Accumulation of sulfur in reduced forms in marine archaeological wood preserved in seawater is now being recognized as a major conservation concern. In 2001 we found that the extensive formation of sulfate salts on the surfaces of the *Vasa's* hull, in combination with high acidity, is caused by aerobic oxidation of large quantities of sulfur in reduced forms in the moist polyethylene glycol (PEG) treated wood.<sup>1,2</sup> The accumulated sulfur species originate from the sulfate ions in seawater, which are first converted to hydrogen sulfide by sulfate-reducing bacteria metabolising organic matter in insufficient oxygen supply. The dissolved hydrogen sulfide reacts with iron ions or with active groups in the organic material, and transforms in the wood to solid sulfur species. Unexpectedly, several tons of reduced sulfur species were found to have accumulated in the degraded outer layers of the *Vasa's* timbers during her 333 years on the seabed. After the salvage aerobic oxidation, probably catalysed by iron ions, produces sulfuric acid. Acid hydrolysis would eventually degrade the chain length of the cellulose polymers, catalytically and irreversibly. Sufficient chain length in the cellulose fibrils of the sound inner core of the hull timbers is necessary to maintain mechanical stability of the wood. In 2003 the concern for the consequences of the increasing acidity initiated the "Cure the *Vasa*" project, in which several international groups participate, coordinated by the National Maritime Museums of Sweden. The aim of the project is to neutralise the acid in the *Vasa's* wood, and to prevent further accumulation of acid by developing efficient methods to remove the sulfur and iron compounds or make them chemically inactive.<sup>3</sup>

*The iron conservation problems.* Iron is another, well-known conservation problem for wooden artefacts. Iron(II) ions from corroding iron will diffuse into the waterlogged wood, where they can react in different ways, e.g. forming iron(II) sulfides or iron pyrites,  $\text{FeS}_2$ , with the hydrogen sulfide produced in anoxic conditions. Tannin in the wood will also interact with iron ions, and forms when exposed to oxygen insoluble iron(III) tannates or pyrogallol complexes as in iron gall ink,<sup>4</sup> giving oak wood a characteristic dark "black oak" colour. Conservation problems can arise because mineral inclusions may block the wood microstructure for penetration of conservation liquid,<sup>5</sup> and also because iron sulfides are unstable in aerobic conditions. Iron(II) ions can act as a general catalyst for aerobic oxidation reactions, not only oxidation of reduced sulfur species to sulfates and acid, but also direct oxidative degradation of cellulose. Marine archaeological wood contains substances that can reduce iron(III) ions, e.g. degradation products from cellulose and, after heat treatment of PEG-impregnated wood surfaces, also formic acid. Thus, iron(II) ions are commonly found in rozenite ( $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ) or melanterite ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) salts on the surface of artefacts. When iron(II) ions are oxidized to iron(III) by oxygen, hydrogen peroxide forms as an intermediate in the stepwise radical reactions. In the Fenton reaction iron(II) ions react with hydrogen peroxide forming hydroxyl radicals ( $\text{HO}\cdot$ ),<sup>6</sup> which are strongly oxidising agents that readily can abstract e.g. hydrogen atoms from cellulose or hemicellulose. The cellulose polymer chain is then in chain reactions oxidised to smaller units, reducing the mechanical strength of the wood structure.<sup>7,8</sup>

Hence, in the presence of oxygen and some moisture, the redox couple  $\text{Fe}^{2+}/\text{Fe}^{3+}$  could catalyse the oxidation of organic materials, e.g. cellulose. Degradation of paper objects by iron-gall ink is a well-known example.<sup>4</sup> However, for waterlogged wood the oxidation of cellulose may be of less concern than the acid hydrolysis. The anti-oxidant lignin that is present in high concentration (*cf.* Figure 9) would react faster

with the produced radicals than cellulose, and most reduced sulfur compounds distributed in the wood would probably react even more rapidly. In this way the production of acid by oxidation of reduced sulfur compounds, as exemplified for elemental sulfur in reaction (1) below, becomes iron catalysed:



Iron metal in the wood would remain a concern also after conservation procedures, because it is now known that metallic iron (mild steel) corrodes rapidly in contact with PEG in moist wood,<sup>9</sup> thus providing a constant source of iron(II) ions. Thus, for a stable conservation of marine archaeological wood, it is desirable to remove the soluble iron species, or at least convert them into chemically inert compounds. For this purpose dedicated, very efficient iron(III) extraction agents are being tested. Bath treatments on planks from the *Vasa* show that the chelating agent EDMA (acronym for ethylenediimino-bis(2-hydroxy-4-methyl-phenyl)acetic acid), specially designed to form very stable water-soluble complexes with iron(III),<sup>10</sup> is capable of dissolving and extracting most iron corrosion products, even in alkaline solution with pH values up to 10-11.<sup>3,11</sup> The EDMA solution obtains a dark red colour of the [Fe(EDMA)]<sup>-</sup> complexes, and with a fresh solution this is a sensitive indicator to show when no more iron is extracted. The high solubility allows rinsing with water to clean the treated objects after the treatment. Such alkaline conditions will also inactivate iron(II) ions by oxidization to insoluble iron(III) (hydr)oxo compounds. However, prolonged exposure of the wood to solutions with pH values > 10 should be avoided due to the risk of alkaline hydrolysis of the cellulose.

Procedures to treat ink corrosion of paper by complexation of iron ions with phytates, i.e. salts of myo-inositol hexakis(dihydrogen phosphate), have been developed.<sup>12,13</sup> One requirement for paper conservation was the white colour of the insoluble iron(III)-phytate complexes. However, for the complexes to be stable, pH-values during and after a treatment should not be outside the pH-range 5.0 - 8.5.

### **How general is the sulfur accumulation problem?**

Questions raised e.g. by our investigations for the *Vasa* are:

- How general is the sulfur, or rather the acidity problem, for marine archaeological artefacts?
- What conservation treatment is needed for freshly salvaged shipwrecks and wooden artefacts to take care of sulfur and iron accumulation?
- What is the rate of further degradation of marine archaeological wood in an acidic and iron-containing matrix, and which treatments can be applied to already conserved museum artefacts?

*The exception, the Bremen Cog.* Our analyses of samples from a number of historical shipwrecks reveal that accumulation of reduced sulfur compounds in concentrations up to several mass% is common in marine archaeological wood preserved in seawater. However, the *Bremen Cog* from 1380, preserved in river water, is an outstanding exception with very low sulfur concentration in samples from the hull timbers. The *Bremen Cog* was discovered during dredging operations of the river Weser in 1962 downstream Bremerhaven, Germany. Evidently, the cog drifted away during a storm from the shipyard where it was being built, and sunk before completion.<sup>14</sup> After the salvage, completed in 1965, a two-step PEG conservation treatment (PEG 200 followed by PEG 3000) took place from 1982 to 1999. The ship is reassembled and

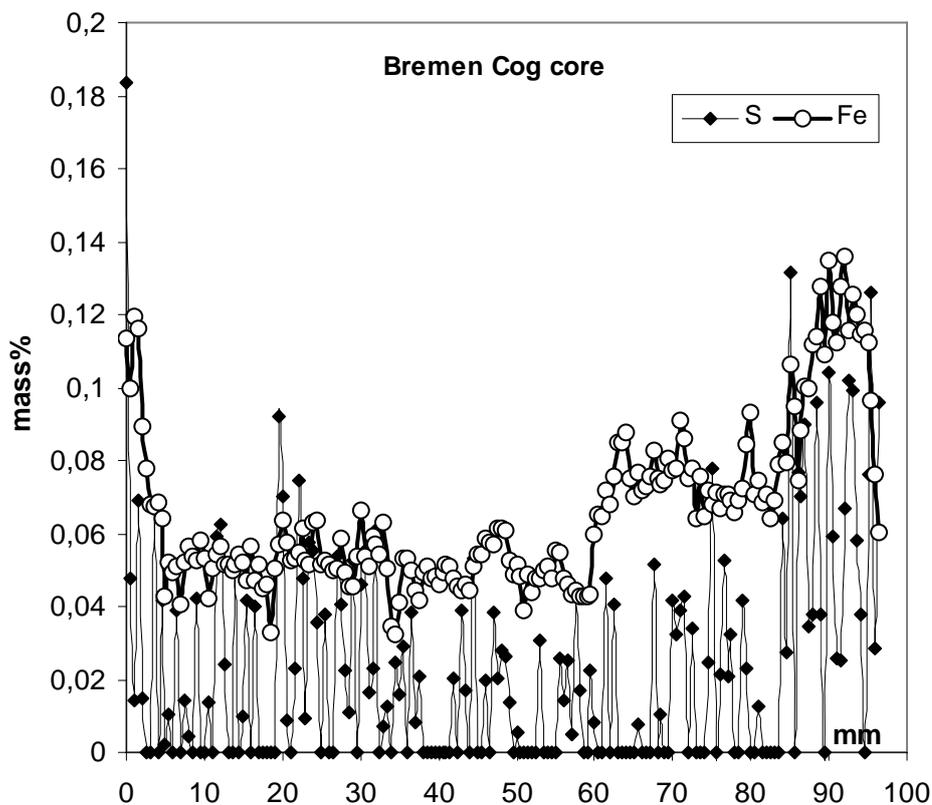
from May 2000 officially on public display in the Deutsches Schiffartsmuseum, Bremerhaven.<sup>15</sup>

Core samples from the hull of the *Bremen Cog* were taken from a rib on the starboard side, which was down into the mud, and through a plank from the port side, which was exposed longer and is the more degraded. An x-ray fluorescence (XRF) line scan (see Methods of analyses) of a 97 mm core from the port side is shown in Figure 1. The total sulfur and iron content is low, with less than 0.05 mass% in the inner parts, and slightly higher values ( $< 0.2$  mass%) at the surfaces. The XRF values are consistent with elemental analyses of the total sulfur in two other cores, also showing the highest values,  $\sim 0.15$  mass% sulfur, at the surfaces.

We collected sulfur K-edge XANES spectra in fluorescence mode at the beamline 6-2 of Stanford Synchrotron Radiation Laboratory (SSRL), of cores from the port and starboard sides of the *Bremen Cog*, with the samples in 1 atm helium atmosphere, as previously described (see Methods of analyses). The normalised XANES spectra of a core from the port side display two major peaks, which represent sulfur compounds with different characteristic groups are shown in Figure 2.

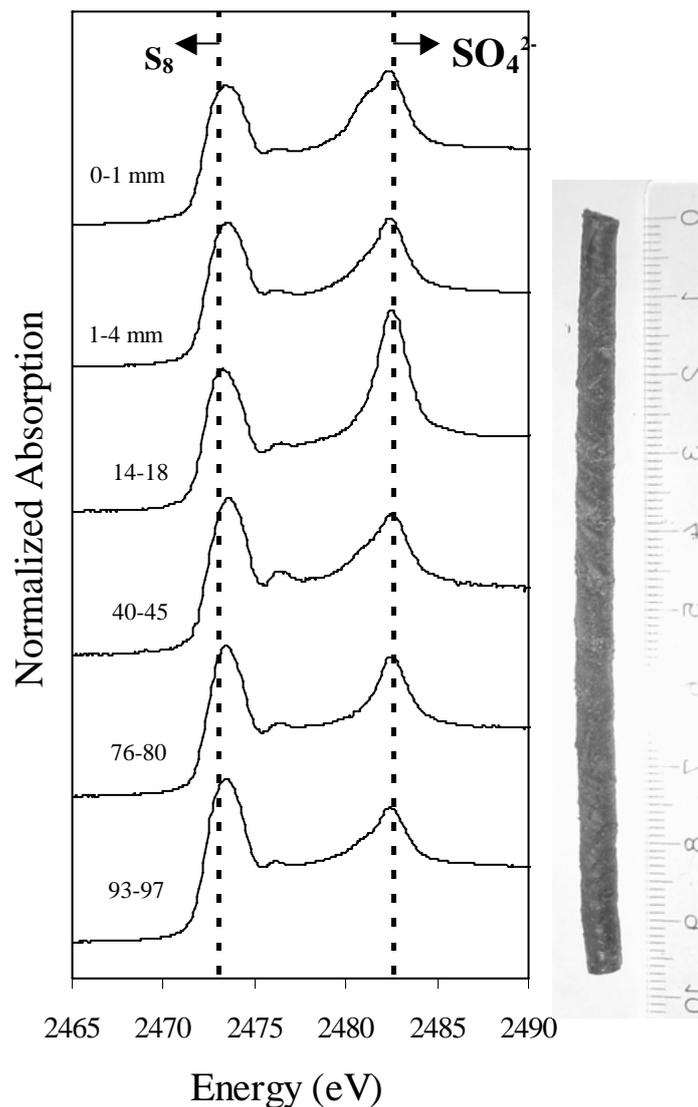
Detailed analyses show that the 2473 eV peak is composed of a mixture of overlapping peaks from elemental sulfur, thiols and disulfides, and that the reduced sulfur compounds dominate, see the example of fitting with standards in Figure 3. That result is typical, and also applies to the XANES spectra from the *Bremen Cog*.

The minor peak at 2476 eV corresponds to sulfoxides,  $R(SO)R'$ , the large peak at 2483 eV to oxidised sulfur compounds (oxidation number +6), mostly sulfates,  $SO_4^{2-}$ , with a shoulder at about 2481 eV from sulfonates  $RSO_3^-$ .

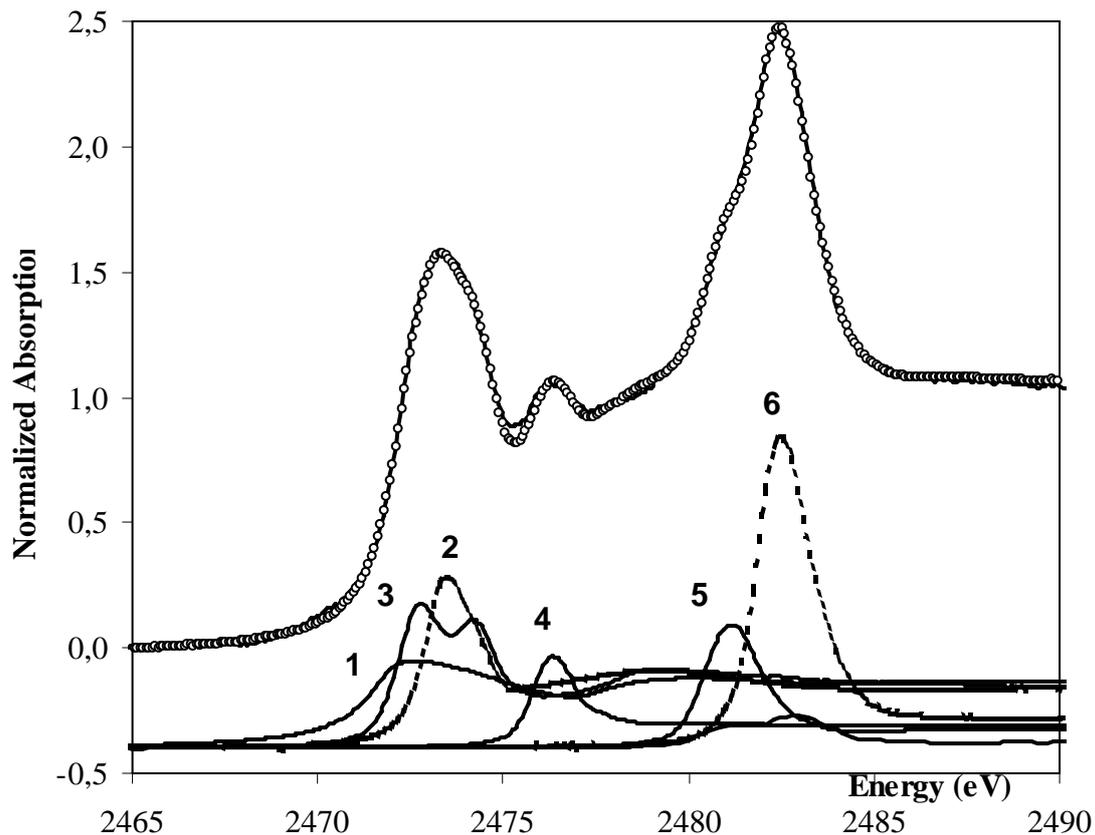


**Figure 1.** X-ray fluorescence (XRF) line scan of a 97 mm core from the port side of the *Bremen Cog*, showing with 0.5 mm resolution profiles the amounts of total sulfur (line with diamonds) and iron (solid line with open rings). The sulfur concentration is very low in the interior, but increases to 0.18 mass% at the outer surface.

The reason why such a small amount of sulfur had accumulated in the timbers of the *Bremen Cog* is probably because of the low sulfate concentration in river water, and consequently the low production of hydrogen sulfide in anaerobic conditions. However, Dr. Per Hoffman, responsible for the treatment of the *Bremen Cog*, reported that aluminium sulfate was added as flocculant to facilitate removal of bacteria and algae from the liquid in the conservation tank. After some time, silvery bubbles with a foul smell started to pass by the windows of the tank, and black patches appeared on the wood surfaces! The water had become oxygen free so that sulfate-reducing bacteria could start to form hydrogen sulfide from the added sulfate, which then was replaced by aluminium chloride.<sup>16</sup>



**Figure 2.** Normalized sulfur K-edge XANES spectra of samples along a 97 mm core through a plank from the port side of the *Bremen Cog*. The vertical dashed lines indicate the peak energies for elemental sulfur ( $S_8$ ) and sulfate ( $SO_4^{2-}$ ) at 2473 and 2483 eV, respectively.



**Figure 3.** a) XANES spectrum (solid line, upper figure) of untreated *Vasa* oak kept in cold storage under water after salvage. The open rings (upper figure) show the fit of a linear combination of standard spectra (see Methods of analyses). The standards used for the fitting, shown separately below, are: 1. Elemental sulfur  $S_8$  28%; 2. Thiols R-SH (as cysteine) 23%; 3. Disulfides R-S-S-R (as cystine) 23%; 4. Sulfoxide  $R_2(S=O)$  7%; 5. Sulfonate  $R-SO_3^-$  7%; 6. Sulfate  $SO_4^{2-}$  15%. The total sulfur concentration for this sample at 41-44 mm depth is  $\sim 0.1$  mass% S. The sulfur concentration at the surface of the oak beam (lower picture) is about 2 mass% S.

### **Sulfur speciation and distribution in shipwrecks.**

The sulfur speciation for the *Bremen Cog* resembles that found for other shipwrecks, even though the samples from shipwrecks preserved in seawater often contain much higher sulfur concentrations. In Figure 3 an example of a XANES analysis is given for untreated oak from the *Vasa*, by fitting with a linear combination of spectra of standards (see Methods of analyses). The fitting procedure reveals that the 2473 eV peak is typically composed of overlapping peaks from elemental sulfur, thiols and di- (or poly-) sulfides, and that the reduced sulfur compounds dominate over the oxidized in the samples. The minor peak at 2476 eV corresponds to sulfoxides,  $R(SO)R'$ , the peak at 2483 eV to oxidised sulfur compounds (oxidation number +6), which mostly are sulfates,  $SO_4^{2-}$ , with a shoulder at about 2481 eV from sulfonates  $RSO_3^-$ . Note the much higher intensity of oxidised forms than the reduced at the same concentration.<sup>1</sup>

The concentration and the distribution of sulfur compounds vary greatly between different shipwrecks. A special feature for the *Vasa* seems to be that most of the sulfur resides within the first 1-2 centimetres beneath the surface of the wood (*cf.* Figure 4). Total sulfur and iron concentrations over 10 mass% have been found in that layer, but are much lower, typically 0.1 – 0.2 mass%, further inside the wood. This suggests that the penetration and accumulation of sulfur and iron is coupled to the bacterial degradation of the cellulose in the surface layer. Also, the variations in the iron and sulfur profiles often closely match for the *Vasa*, implicating reaction between penetrating iron(II) and hydrogen sulfide when submerged.

*Acid in the wood.* The accumulated reduced sulfur species are not in themselves detrimental to the stability of the wood; rather such effects are a consequence of the aerobic oxidation processes releasing sulphuric acid, see reaction (1). During the *Vasa's* 17-year spray treatment period, unexpected amounts of acid were washed out.<sup>17</sup> The conservation liquid was then continuously neutralized by adding borax,  $Na_2B_4O_7 \cdot 10H_2O$ . We estimated that about  $\frac{1}{4}$  of the total accumulated reduced sulfur was removed in this way.<sup>3</sup>

The concentration profile of total sulfur is much more uniform throughout the wood for cores from the *Mary Rose* (Figure 5). The sulfuric acid washed out of the *Mary Rose* hull timbers has so far, during 10 years of spray treatment, required 2500 kg added sodium bicarbonate ( $NaHCO_3$ ) to keep the pH of the recycled conservation liquid at about 7.6. This corresponds to neutralisation of about 1.5 tons sulfuric acid, and is estimated to be less than  $\frac{1}{3}$  of the total sulfur amount.<sup>18</sup> Evidently; the accumulated sulfur could be a conservation concern also for the *Mary Rose*.

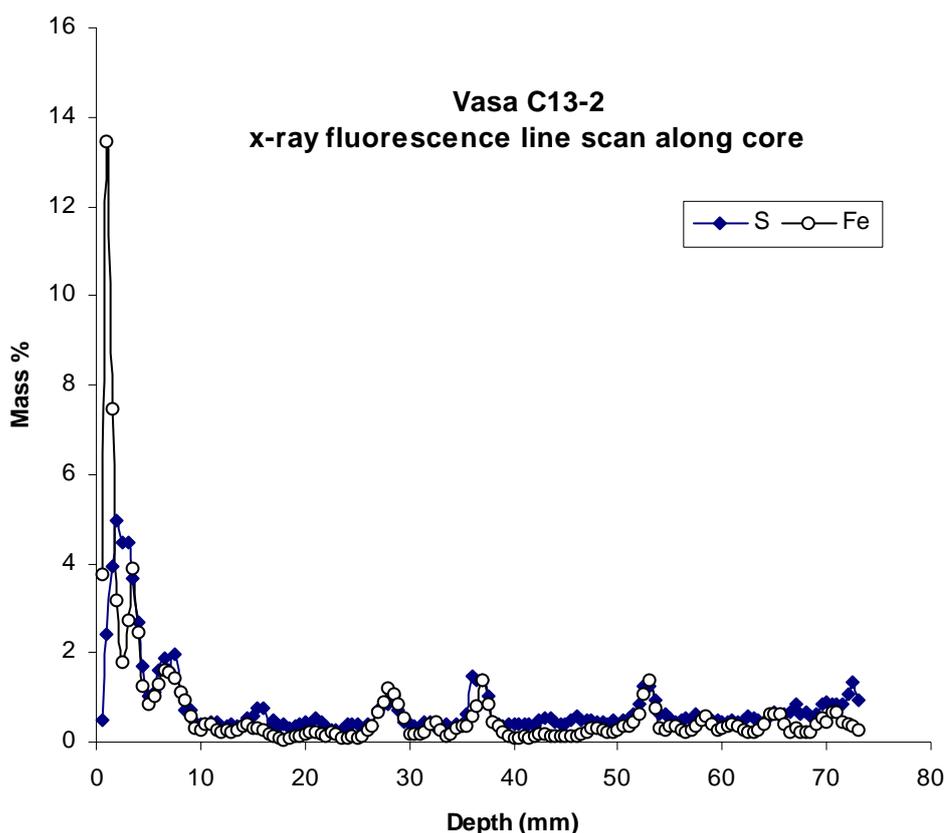
As discussed above, long-term exposure of the wood to high acidity is detrimental, because of catalytic hydrolysis of the cellulose. The acid forming in the wood is washed out and neutralised during spray or bath treatment, but when significant amounts of reduced sulfur compounds remain after the PEG conservation treatment, high concentrations of acid could gradually build up, as for the *Vasa*. In such a case, firstly the acid should be neutralised. For preventing more acid to form, we need to find out whether removal of the iron compounds, and reducing variations in and decreasing humidity and temperature, to reduce diffusion of oxygen and water into the wood, would be sufficient measures to enable a stable long-term preservation. If not, active removal of the reduced sulfur forms would eventually become necessary.

*Connecting speciation to treatment.* For developing adequate treatments to remove the reduced sulfur, knowledge of the chemical and physical state of the compounds is important, as well as the degree of degradation of the wood. The chemical properties

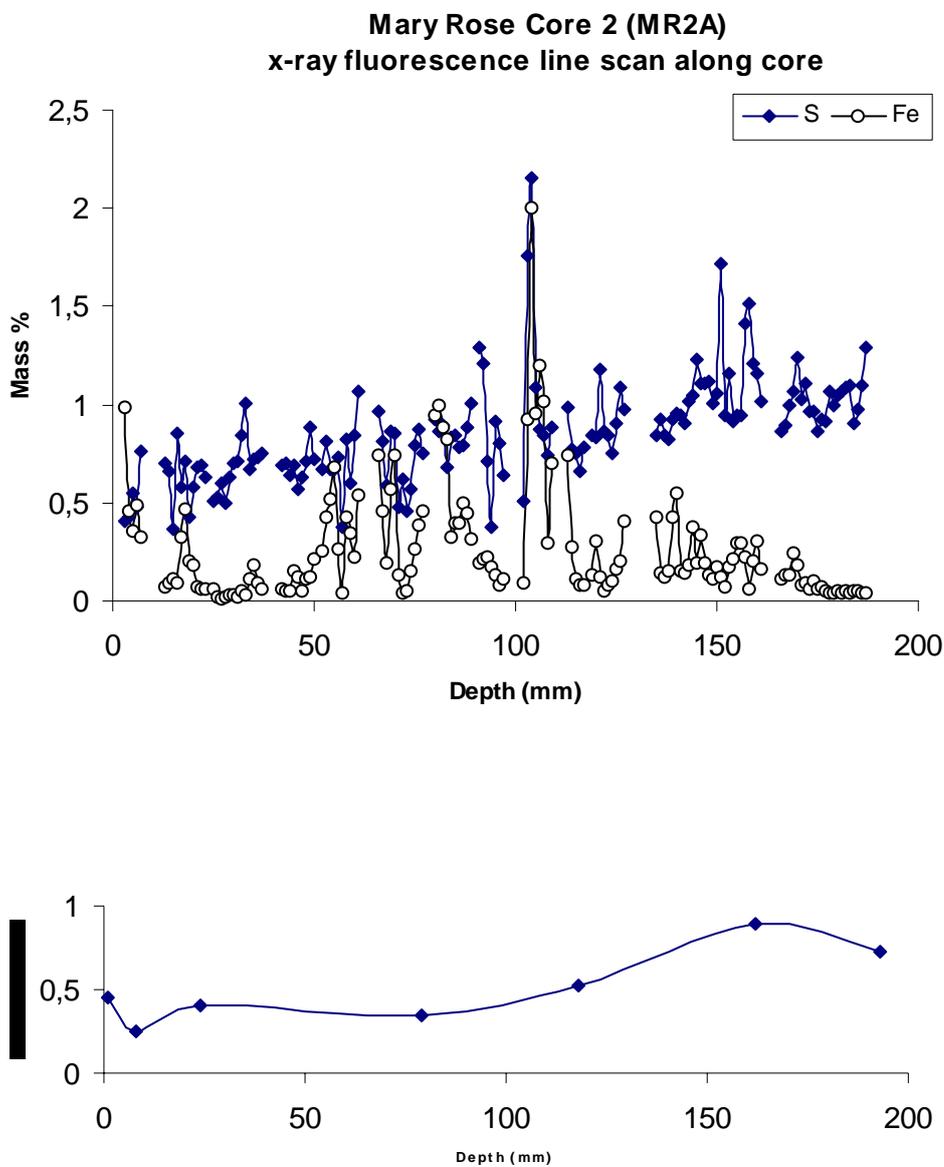
of the sulfur compounds depend on their speciation. However, it can be quite difficult to analyse or even to identify the separate sulfur species *in situ* for this “spectroscopically silent” element with its complex redox chemistry. Stable sulfur compounds in nature occur usually in the formal oxidation states: -2, -1, 0, +2, +4 and +6. Mild oxidants can readily convert thiols, R-SH, into disulfides, R-S-S-R, with the formal oxidation state -1. Stronger oxidants, such as  $\text{Fe}^{3+}$ , e.g. in the corrosion product  $\text{FeO}(\text{OH})$ , will readily react with  $\text{H}_2\text{S}$  if moisture is present. Primary reaction products are then iron sulfides, e.g.  $\text{Fe}_{1-x}\text{S}$ ,  $\text{FeS}_2$  (pyrite), and elemental sulfur.

Thus, the speciation will be decisive for what type of treatment that would be the most efficient, e.g. when considering some of the following treatments:

- Speed up the oxidation of reduced sulfur under controlled conditions, chemically or bacterially, to sulfate and sulfuric acid, which can be neutralised.
- Remove catalysts to reduce the rate of oxidation, by solubilizing iron compounds with chelates, or bind iron ions in inert complexes with e.g. EDMA.
- Enclose the sulfur in the wood, e.g. with a surface coating that reduces the rate of oxygen diffusion and possibly contains a neutralizing base reservoir.
- Extract elemental sulfur with some agent, e.g. a microemulsion, or remove sulfur solubilized from iron-sulfides dissolved with the EDMA chelate



**Figure 4.** X-ray fluorescence line scan (*cf.* Methods of analyses and Ref. 19) along a core through an oak plank (ceiling) from the cabin in the *Vasa*. The sulfur and iron profiles show high accumulation in the degraded part of the wood at the outer surface, and also increase at cracks and hidden surfaces.



**Figure 5.** (*upper*) X-ray fluorescence line scan with 0.5 mm resolution along an oak core from the *Mary Rose* hull timbers (under spray treatment with PEG 200 aqueous solution), showing total sulfur and iron in mass% (*cf.* Ref. 19). The gaps in the lines are due to missing pieces of the core lost in previous elemental analyses. XANES measurements show that almost all sulfur is in reduced forms.

(*lower*) Elemental analyses of total sulfur by combustion and gas chromatography (*cf.* Methods of analyses and Ref. 20). Both types of analyses show a fairly uniform concentration profile for the accumulated sulfur throughout the core.

The physical properties of the sulfur compounds are also important. There has been a long debate about the composition and surface properties of bacterially produced globules of elemental sulfur, which are proposed to have unexpected densities and hydrophilic properties.<sup>21</sup>

Other relevant questions to be answered before devising treatments for sulfur incorporated in the wood are then:

- Is elemental sulfur present as small particles in the wood, as could be expected if bacterial processes convert hydrogen sulfide?
- Would the PEG used to impregnate the wood dissolve some sulfur compounds, e.g. elemental sulfur?
- Are significant amounts of the sulfur bound in organosulfur compounds, such as thiols (e.g. cysteine residues in peptides), or in iron sulfide or pyrite particles?

Organosulfur compounds, occurring as precursors to the sulfur species found in oil and coal bearing sediments, are proposed to form by direct reaction of hydrogen sulfide with active groups in the organic material, without bacterial involvement.<sup>22-25</sup>

To find out how the distribution of total iron and sulfur is connected in wood samples, we used scanning electron microscopy with x-ray fluorescence (EDS) detection. The pictures in Figure 6 are from a sample of the Burgzand Noord 3 wreck site in the Waddensea, the Netherlands, which is likely of an East India Company (VOC) vessel ('De Rob') that sank in 1640. The X-ray fluorescence shows that the particle in the lower picture has a ratio Fe:S = 1:2, as in pyrite, while the lignin-rich middle lamella in the upper picture show low Fe content but high in sulfur, which is consistent with organosulfur compounds such as thiols.

### Methods of analyses

Efficient methods of analysing and monitoring the sulfur and iron removal are obviously essential when judging the need for treatment, and when devising the most efficient, cost-effective, long-lasting and least damaging conservation methods for marine archaeological artefacts. For that purpose we analyse cores sampled from hull timbers by several methods: x-ray fluorescence (XRF),<sup>19</sup> x-ray photoelectron spectroscopy (XPS),<sup>26</sup> x-ray absorption spectroscopy (XANES),<sup>27,28</sup> scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS), and elemental analyses.<sup>20</sup> Descriptions of the methods with examples follow below.

*Sulfur speciation by XANES measurements.* X-ray absorption spectroscopy is the only technique able to provide detailed information on the speciation of sulfur compounds in natural samples. For good quality spectra the very intense and highly tuned x-ray beam from a synchrotron is required in a dedicated and optimised beamline, which at present is available in very few places worldwide; one is beamline 6-2, SSRL, Stanford, U.S.A.<sup>28</sup> Sulfur K-edge x-ray absorption near-edge structure (XANES) spectra are obtained by varying the x-ray energy and measuring the absorption in the sample over the absorption edge, which is the energy needed to eject a photoelectron.

The XANES features in the pre-edge part of the spectra correspond to electron transitions from the sulfur 1s atomic orbital to molecular orbitals with some sulfur 3p character. Covalent bonding and interatomic interactions with the specific sulfur group may significantly affect the energy of the electronic states and change the symmetry-dependent transition probabilities. Thus the shape, intensity and position of the peaks in the sulfur K-edge XANES spectra can be used to identify characteristic sulfur groups in the sample. The position of the sulfur K-edge, i.e. the binding energy of a S<sub>1s</sub>

electron, shifts about 13 eV from sulfides(-II) to sulfate(VI), but the correlation with the formal integer oxidation number can, especially for organosulfur species, differ with up to one unit.<sup>24,25</sup>

In our measurements the energy scale was set by assigning the first peak position of sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , to 2472.0 eV.<sup>28</sup> Also, we perform theoretical computations of spectra by means of the DeMon StoBe program, using transition potential DFT Kohn-Sham's delta DFT calculations, to identify sulfur species and evaluate the influence of chemical interactions.<sup>29</sup>

The spectra can be recorded of samples in any aggregation state, even for amorphous solids and solutions at low concentrations. The sensitivity is quite high (about 0.01 mass% S) and several different, mostly reduced, sulfur forms are clearly revealed also for the cores for the *Bremen Cog* cores with sulfur concentrations below 0.02 mass% inside the wood (Figure 2). A great advantage for natural samples is that the sulfur K-edge measurements can be performed in atmospheric helium pressure, avoiding vacuum. For wooden core samples sections of a few mm along the cores were filed or chopped in inert atmosphere to particles, mounted as a thin layer on sulfur-free tape and covered by 4- $\mu\text{m}$  polypropylene film.

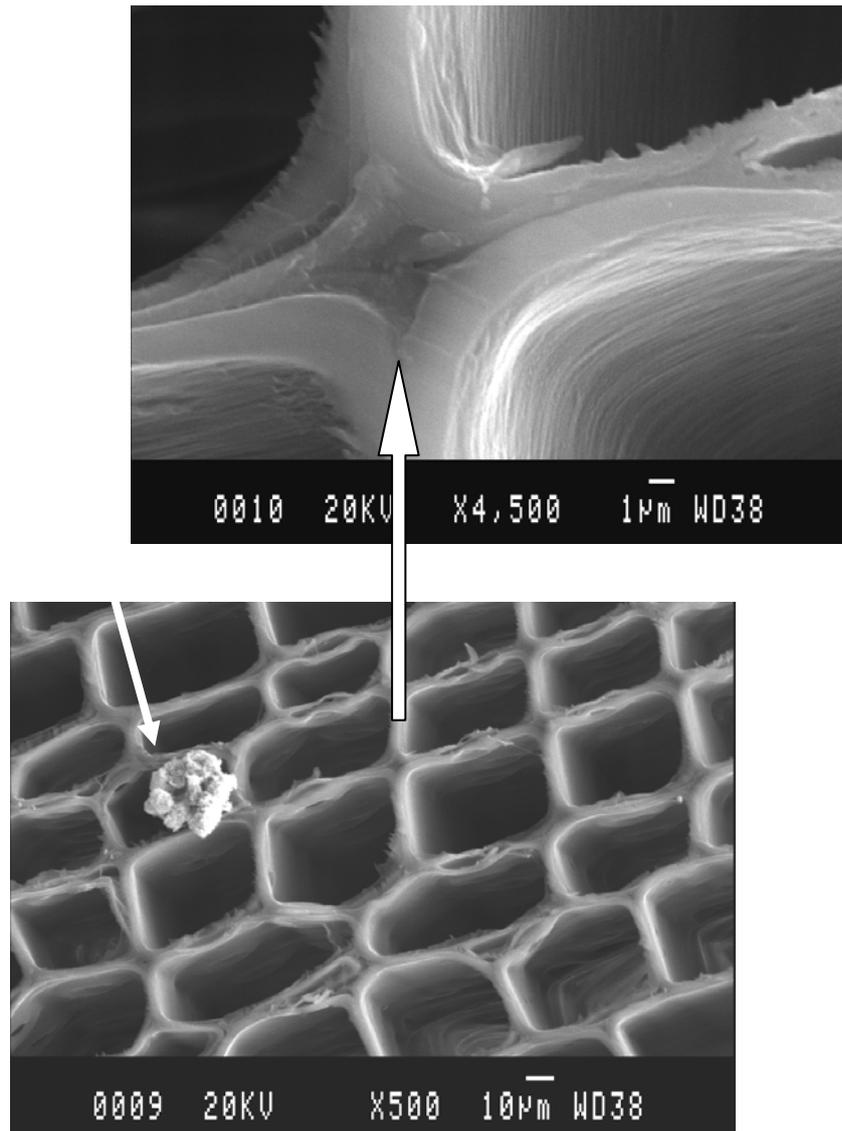
The analysis of the relative amounts of sulfur compounds in a sample with a mixture of characteristic sulfur functional groups, e.g. thiols, sulfoxides, polysulfides, sulfates, by linear combinations of XANES K-edge spectra of standard compounds (*cf.* Figure 3), requires a library of carefully selected spectra from known sulfur compounds in appropriate conditions. The absorption features are often sharper for solutions, because of self-absorption of x-rays or chemical interactions in solid compounds, as for particles of elemental sulfur.<sup>21</sup> Also, the spectral intensities of the oxidized forms are generally much higher than for reduced, because of the increasing number of 3p vacancies, e.g., the sulfate features are about 3 times more intense than those for elemental sulfur.

The data evaluation is often difficult for natural samples with several overlapping reduced forms, and we use Principal Component Analysis (PCA), as well as second derivatives of the spectra, to evaluate the number of species present. We estimate at least  $\pm 10\%$  error limit in the relative amounts reported of the characteristic sulfur groups in the samples.

With a scanning microprobe, as in beamline ID21, European Synchrotron Radiation Facility, Grenoble, x-ray absorption spectroscopy can also be used to map in high resolution the distribution of sulfur in different oxidation states over a surface.

*X-ray fluorescence analyses of total iron and sulfur.* A dedicated wood core scanner developed by Cox Analytical Systems (Itrax Wood Scanner),<sup>19</sup> was used to obtain quantitative concentration profiles for the total concentration of S, K, Ca, Cr and Fe by means of automatic XRF line scans along the cores. X-ray fluorescence was excited by means of  $\text{Cu K}_\alpha$  x-rays (1.5420 Å) from a conventional x-ray aggregate with a special collimator utilizing total reflection to obtain a condensed high intensity parallel beam with a diameter of ca 300  $\mu\text{m}$  and an analytical depth of about 0.1 mm into the wood. An energy dispersive solid-state x-ray detector detected the element specific x-ray fluorescence, with 0.5 mm between the scan points. Intensity calibration was performed on pellets with known concentration of iron sulfate and iron oxide mixed into a matrix of oak wood and PEG. The sensitivity covers the range from about 0.02 mass% to 20 mass% (*cf.* Figures 1 and 4). Repeated line scans indicated the accuracy to be within  $\pm 10\%$ .

The high resolution obtained with this method provides very useful information when judging the feasibility and efficiency of iron extraction procedures. For the *Vasa*, the iron content inside the wood was documented by elemental analyses of core samples during the conservation procedure, and reported as the ratio: iron to dry fiber weight, varying from below 0.1% to 1.5%.<sup>17</sup> The XRF line scans reveals that the iron profile can reach much higher values close to surfaces and cracks in the *Vasa's* wood, e.g. 13 mass% in Figure 4 without correction for the PEG content. The large differences between the sulfur and iron XRF profiles obtained for timbers of the *Bremen Cog*, the *Vasa* and the *Mary Rose* (cf. Figures 2, 4 and 5) indicate that different methods should be considered in the conservation treatment.



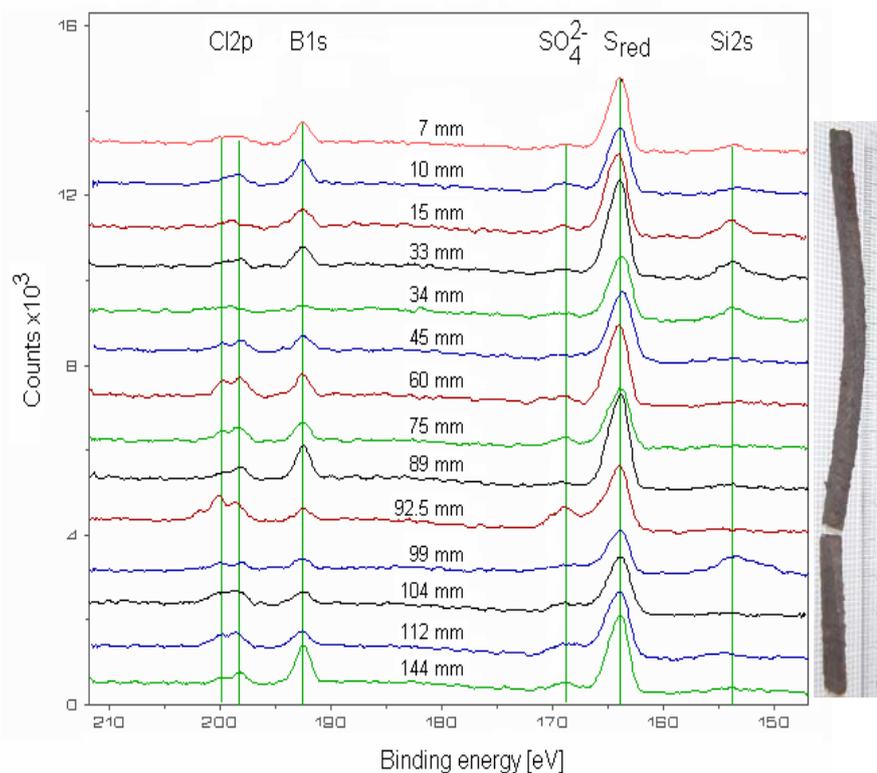
**Figure 6.** (*lower*) SEM picture of transverse section through marine archaeological wood, with partially degraded S2 layers, from the Burgzand Noord (BZN) wreck site 3, in the Waddensea, the Netherlands, with the wreck resting at a depth of 6 to 9 meters at high tide (see [www.bacpoles.nl](http://www.bacpoles.nl); sampling sites, No. 13). X-ray fluorescence (EDS) showed the ratio 1:2 of iron and sulfur for the particle (probably pyrite  $\text{FeS}_2$ ) located on top of the honeycomb-like structure of cell walls. (*upper*) X-ray fluorescence (EDS) showed high sulfur content but very little iron in the lignin-rich middle lamella (samples prepared by Prof. Thomas Nilsson).

*Electron microscopy.* Scanning electron microscopy (SEM) with energy dispersive (EDS) detection of the x-ray fluorescence provides microanalytic information about the sulfur and iron ratio and distribution in the cell walls, and in particles with a resolution of about 1  $\mu\text{m}$ . Quantitative measurements relative to other elements are possible from sodium to heavier elements. We have used a JEOL 820 SEM, equipped with a LINK AN10000 EDS microanalysis system. Slices of core samples were sputtered with a thin graphite layer and mounted on sulfur-free tape. A low-grade vacuum is maintained during the measurements. The information is useful for judging if the sulfur distribution on a microscopic scale is primarily in particles of iron-sulfur compounds or in organosulfur compound bound in lignin-rich parts. Also, the results indicate if iron occurs as oxide or sulfide particles (see Figure 6).

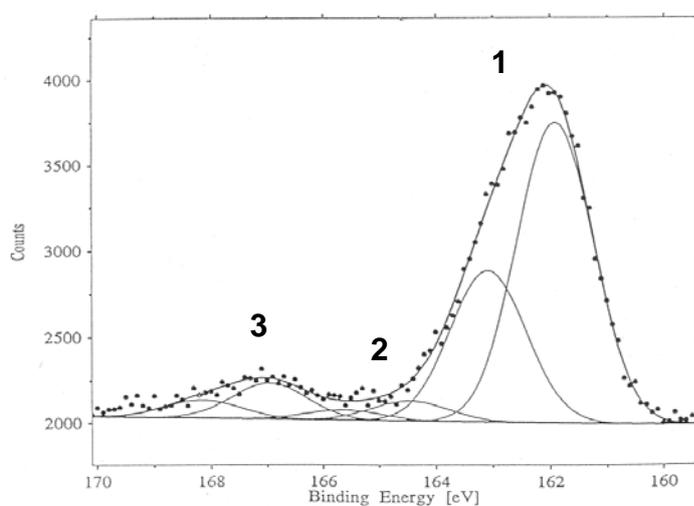
*Elemental analyses.* Mikrokemi AB, Uppsala, Sweden,<sup>20</sup> performed total sulfur analyses (see Figure 5). The sample (a few mg) is weighed in a tin-capsule. When oxygen is injected the temperature momentarily rises to about 1800 °C when the tin metal oxidizes. The combustion gases CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>x</sub>, SO<sub>2</sub> och SO<sub>3</sub> are led into a reduction chamber where SO<sub>3</sub> is reduced to SO<sub>2</sub>. The amount of SO<sub>2</sub> is then determined by gas chromatography. This type of analysis as described above requires total sulfur concentrations above about 0.1 mass% for good accuracy, is destructive and can only provide sulfur profiles with low resolution.

*Multielement x-ray photoelectron spectroscopy (ESCA).* XPS measurements, or Electron Spectroscopy for Chemical Analyses, can provide quantitative analyses of all major elements in the surface of the samples, except hydrogen. A Scienta ESCA-300 instrument at Department of Physics, Uppsala University was used to obtain the binding energy of core shell photoelectrons, excited from all elements in the surface layer (<100 Å) of the sample by means of high intensity monochromatic Al K $\alpha$  x-ray radiation (1487 eV), by measuring the kinetic energy of the photoelectrons in high vacuum (pressure below 1·10<sup>-6</sup> Pa).<sup>26</sup> The element specific photoelectron intensity is proportional to the atomic concentration of each element in the surface layer. Thin wood slices are cut at various depths along the core, mounted and transferred in vacuum into the analysis chamber of the Scienta ESCA-300 instrument. The extreme surface sensitivity requires careful sample handling to avoid contamination, and for PEG rich samples smearing may affect the quantitative results. To prevent uncontrolled charging of the electrically insulating samples the surface potential of the sample is kept constant by an excess current of low energy electrons (1 eV) supplied by a Scienta flood-gun. Only after an extended long exposure the signal for the oxidised sulfur showed a small reduction, indicating that radiation damage was negligible during the normal XPS measurements.

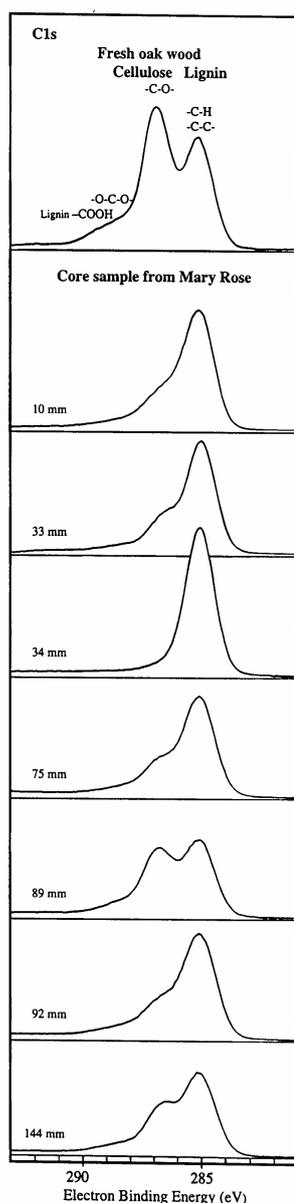
The ESCA measurements allow the amount of oxidised and reduced sulfur to be determined, even though with lower energy resolution than in the XANES analyses. Three different types of sulfur species can be considered in a least squares fitting procedure. Each sulfur component in the fitting is represented by two Gaussian peaks, corresponding to emission of photoelectrons from the sulfur 2p<sub>1/2</sub> and 2p<sub>3/2</sub> states with relative intensity 1:2, spin-orbit split by 1.18 eV, and with the same full width at half maximum, see Figure 8.



**Figure 7.** XPS spectra of an oak-wood core from the *Mary Rose* at increasing depth through a plank and into a hull timber, stored in magazine after treatment with a 5% borax solution. The vertical lines mark binding energies in the energy range 150-210 eV of element-specific photoelectrons for Cl (2p), B (1s), S (2p) and Si (2s). Two sulfur peaks correspond to reduced (~162 eV) and oxidized (~167 eV) sulfur forms, with the reduced forms dominating in rather uniform concentration along the core. At the hidden surface at 92.5 mm the sulfate concentration increases. The borate peaks demonstrate the efficient penetration of boric acid ( $\text{H}_3\text{BO}_3$ ) throughout the core.



**Figure 8.** Curve fitting of XPS spectra from 144 mm depth of the core in Figure 7 of the *Mary Rose*. Three sulfur species were considered, each represented by two peaks corresponding to photoelectrons from the sulfur  $2p_{1/2}$  and  $2p_{3/2}$  states with relative intensity 1:2: 1: 0.70 mass% reduced sulfur, 2: 0.03 mass% sulfoxide  $\text{R}_2\text{SO}$ , 3: 0.07 mass% sulfate  $\text{SO}_4^{2-}$ .



**Figure 9.** Large variations occur with depth in the two main  $C_{1s}$  peaks at 285.0 and 286.5 eV in a core from the *Mary Rose* (not PEG treated, see Figure 7). The peaks mainly correspond to carbon in lignin ( $CH_2$ ) and cellulose (C-O), respectively. The irregular variations with depth indicate that pockets of highly degraded cellulose occur all through the timbers.

For wood not treated with PEG, the variations in carbon and oxygen concentrations measured along the core can be used to estimate the ratio of cellulose+hemicellulose to lignin. Figure 9 shows measurements along a core from a hull timber of the *Mary Rose*. The relative size of the two  $C_{1s}$  peaks at 285.0 and 286.5 eV, which mainly correspond to  $CH_2$  (lignin) and C-O (cellulose) groups, respectively, is correlated to the degree of degradation of the wood. Bacteria normally degrade the cellulose, while the lignin-rich middle lamella remains.

### Concluding remarks

Combinations of a number of spectroscopic and analytical techniques are used to elucidate the chemistry in the complex systems created when wooden shipwrecks have been exposed for centuries to very different marine environments. Sulfur and iron accumulation in the wood are often found to be potential problems for stable conservation. However, the amount, distribution and chemical activity are different in every case, and analyses are needed to judge the type and extent of treatment that is needed. The examples from some combined studies from ongoing investigations shown above allow some conclusions to be drawn.

For the *Bremen Cog*, preserved in river water, it is evident that the concentrations found for the total sulfur in the interior of the hull timbers are close to those occurring in fresh wood, and would not in this case cause detrimental acid concentrations. It is possible that the increase in sulfur concentration at the surface is due to the period when hydrogen sulfide was produced from added sulfate in the conservation tank.<sup>16</sup>

For other shipwrecks from seawater, generally with much higher sulfur concentration, aerobic oxidation of the sulfur compounds has been found to cause high acidity in the wood, as for the *Vasa*. XANES speciation of the reduced sulfur compounds often shows, beside elemental sulfur appreciable amounts bound in thiols and di- or polysulfides. SEM measurements, combined with EDS microanalyses, indicate high sulfur content in the lignin-rich middle lamella of marine archaeological wood, consistent with direct reaction between hydrogen sulfide and active groups in the organic material, forming e.g. thiols.<sup>24,25</sup> For such organosulfur species, sulfur removal by chemical extraction would not be possible without serious damage to the wood structure.

The sulfur and iron distributions in the *Vasa* seem to be quite special, with high accumulation in the bacterially degraded part of the wood. The sulfur is concentrated to the surface layer (< 1 - 2 cm), and is probably to some extent bound in iron compounds. Preliminary iron extraction tests with the chelate EDTA in bath treatment on planks from the *Vasa* show efficient removal of iron in alkaline solution, and it is possible (not yet verified) that also the sulfur is to some extent solubilized and washed out. The iron extraction is in the first place intended to remove the catalyst for the sulfur oxidation to acid, but also to reduce the detrimental effects of the iron itself.

The sulfur distribution in cores from the *Mary Rose* is much more uniform, and less coupled to the iron content than for the *Vasa*. ESCA studies of the amount of carbon atoms in different groups indicate cellulose degradation (Figure 9), probably by bacteria,<sup>5,30</sup> in pockets throughout the wood for the *Mary Rose*. Such an extensive cellulose degradation deep into the wood is probably connected to the higher and more uniform sulfur concentration inside the wood below the surface layer of the *Mary Rose* than of the *Vasa*, cf. Figures 4 and 5.

One generally feasible way to remove reduced sulfur species bound in the wood seems to be controlled oxidation to sulfates and acid, which can be washed away and neutralized, during a prolonged PEG conservation procedure. Elevated temperature (< 40 °C) of the conservation liquid would speed up the chemical oxidation process, but sufficient removal of sulfur would still require an expensive prolonged spray or bath treatment, and higher temperature would promote unwanted bacterial and microbial growth, which has to be controlled. Another, probably more efficient way of treatment could be to use carefully selected and tested bacterial strains, to selectively oxidise the reduced sulfur compounds.

Further studies are in progress, and it is anticipated that the “Cure the *Vasa* project” will lead to improved methods and procedures to take care of the unwanted effects of sulfur and iron compounds accumulated in the timbers of shipwrecks. For shipwrecks still resting on the seabed, it is recommended to test samples for sulfur and iron content, to assess if problems similar to those for the *Vasa* might arise after salvage. It may be better for the time being to leave the hull timbers of wrecks buried in the seabed, while modified conservation methods are being developed and tested.

### **Acknowledgements**

This work would not have been possible without the great interest shown by marine archaeological conservators worldwide and the encouragement by the support from many coworkers in the project. The first part of this work was supported by grants from The Knut and Alice Wallenberg Foundation, Sweden, and The Natural Sciences and Engineering Research Council of Canada (NSERC), and later performed within the National Maritime Museums of Sweden research project “Cure the *Vasa*” sponsored by The Bank of Sweden Tercentenary Foundation, The Swedish National Heritage Board, The Swedish Foundation for Strategic Research (SSF), The Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS), and The Swedish Agency for Innovation Systems (Vinnova). We gratefully acknowledge the beamtime for XANES measurements assigned at Stanford Synchrotron Radiation Laboratory, SSRL, operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences (DOE-BER).

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## Paper 13 Discussion, Magnus Sandström

**Hans Huisman:** The origin of the sulphur in the wood; you describe a process where iron and hydrogen sulphur react to elemental sulphur, but I can't see how that could happen? Because you're missing some electrons. You will have to oxidise something to do that. I would suggest that it is more likely that iron has reacted with sulphate – maybe in a phase when the harbour was not as dirty as you describe it now – to form the elemental sulphur.

**Magnus Sandström:** Iron II and Hydrogen Sulphide react with each other. It's a very, very long reaction.

**Hans Huisman:** You have to start out with elementary Iron, because if you have Iron II and Hydrogen Sulphide you would form Pyrite.

**Magnus Sandström:** Iron II is formed in the wood because we are oxidising base. As long as we have metallic iron .... We don't form very much Iron III. Iron II is then the mediate oxidising product. Also the lignin in itself is also a reducing agent so we reduce back Iron III to Iron II. So you have Iron II present in the wood. I mean this is a fact. We can see from the salts that we have lots of Iron II. One of the most common reactions in nature – in any anaerobic condition - you have hydrogen sulphide, you have bacteria and when you have Iron ions present hydrate is forming. It's probably one of the most common reactions on earth. It's very difficult to make in the laboratory – nature has no problems to make hydrate a million of times and Iron then reacts with hydrogen sulphate. It forms hydrate iron sulphate and also elemental sulphur and these are the main products. That's sort of a fact of nature. Actually I have tried to make some redox diagrams in this little book that is available if someone's interested. It's much chemistry in shipwrecks.

**Jim Spriggs:** The samples that you analysed so far were all from marine environment, right? Is there any reason why you should not get high levels of sulphur and iron in fresh water wood and would you expect the chemistry to be similar or different in terms of the sulphur problem?

**Magnus Sandström:** I can see that if only the sulphur comes from the sound irons in the water and these are converted by bacteria to hydrogen sulphate - normally that is happening on every seabed/sea bottom. That's the sulphur cycle in nature. In the fresh water you have very low sulphate concentrations. The sulphate concentration is much higher in seawater, so it's actually the availability of sulphate/iron that make the hydrogen sulphate level lower in the seabed. Also if you have water that flows around the ship – we see much higher sulphur level in the exposed parts of Vasa than in the keel that was down in the clay – probably because of the flow of hydrogen sulphide containing water– or maybe the nutrients from the bacteria – that somehow in the clay we don't get that much sulphur in the wood. We need to know more about this – we don't know really.

**Jim Spriggs:** Yes, I have just the feeling that if you look for sulphur in fresh water wood you might find it. We have samples from a bronze age dug out boat from the river Trent Valley, which is fresh water, which actually has quite considerable contents of sulphur. We're mystified as well as to where the sulphur comes from. Something to do with the burial medium, the mud at the bottom of the channel where this thing was buried, maybe?

**Magnus Sandström:** In bones, in whatever wood, you find also in archaeological wood hydrate. It's very common. Elemental sulphur as well, so yes, as long as you get sulphate, iron, bacteria, you have this product.

**Anton Weavers:** A very nice talk, very interesting. I think there are many problems to solve. At the end you said that when you store the wood you would have to keep the temperature and the humidity low, constant and low. It's not easy to do – both of them together. Then you need a very big plant to control. When you had to make the choice – the temperature low or the humidity low, what would you choose?

**Magnus Sandström:** The humidity.

**Anton Weavers:** The humidity. The temperature may be high and it's not a big problem, but humidity should be low.

**Magnus Sandström:** We have seen dry oak pieces of "Viksnycken". Anders Frantzen took them up. We have analysed them for sulphur because we thought they should contain sulphur, but there were hardly any sign of sulphur. They did not have PEG. They were dry, so nothing happened to them. So I think that has something to do with the problem – low humidity. And PEG attracts humidity into the wood. I think the combination of humidity and PEG - this is the problem. When we have the sulphur the PEG helps to promote the reaction.

**Anton Weavers:** Yes the PEG also contains a certain amount of water. It takes up the water and then you have a certain amount of water in the wood and it stays there.

**Khôi Tran:** In your talk did you mention different contents of sulphur in the wood – the 3, 4, 5 to 6% of sulphur in the wood. What is the lower limit of sulphur, which could be most dangerous for the long-term conservation of wood?

**Magnus Sandström:** I would take the German Cog as a good example. When we analysed the wood it showed that the level inside the wood was quite even about 0.3 -0.4% - which is close to the natural level that you have of sulphur in wood – bound as derivatives and also as sulphate of course. But if it is bound as organic sulphur you may get 400 ppm but it is not a problem, I would say.

**Khôi Tran:** But I wonder about the long term - the long-term behaviour?

**Magnus Sandström:** One cannot really hope to bring down the sulphur level in this marine archaeological wood – that would be difficult. Perhaps we can contain and slow down a little. Now and then we treat by neutralisation of acid – because acid is a problem. So when acid has formed you can neutralise. Then we can keep the deterioration under control. This is the key. We don't know how fast the wood is deteriorating by the acid, so it is not the sulphur really that is the problem. The iron is as much a problem as the sulphur because it can oxidise the wood by itself. It oxidises everything that is available. When you have Iron II in humid environments it oxidises cellulose, sulphur, lignin, whatever. Cellulose is the worst thing it can do. Sulphur gives acid. It also does the same job in a different way. There are two factors: iron and sulphur or acid, if you have got that.

**Khôi Tran:** If you get to the wet state in archaeological artefacts – if you find sulphur in objects – do you have to extract or eliminate totally the sulphur in your wood or not?

**Magnus Sandström:** Contain it in a good way. We don't know really what is the best thing to do – with the Vasa for example. We don't make a treatment that is more deteriorating than the acid. Maybe we can contain the problem in a different way and we do have the iron problem that we don't really know what to do with.

**Khôi Tran:** And a last question about the Australian shipwreck presented by Vicky Richards yesterday – have you made some measurements in this shipwreck?

**Magnus Sandström:** Yes, I have analysed for Iron and sulphur and that result express the sulphur and iron results from the Batavia shipwreck; there is not much left.