



	<p>Experiment title: Sulfur and iron distribution in marine-archaeological wood of historical ships and in plants</p>	<p>Experiment number: CH-1774</p>
<p>Beamline:</p>	<p>Date of experiment: from: 08 September 2004 to: 14 September 2004</p>	<p>Date of report: 2004-12-20</p>
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Report:

Introduction. Following the discovery of high acidity caused by oxidation of sulfur compounds accumulated in the timbers of the Swedish 17th century warship *Vasa*,¹⁻⁶ we analyzed several cores of marine archaeological wood by x-ray spectromicroscopy at the sulfur K-edge using the scanning x-ray microscope at beamline ID21, ESRF. The work in this project, see <http://www.fos.su.se/~magnuss/>, now is extended to cover the microscopic distribution and state of the sulfur in marine archaeological wood, i.e. where and in what form the sulfur is present in the wood, how the accumulation has occurred, and how general the problem is, especially for museum artefacts. The results will provide answers to how the accumulation has occurred, how stable the sulfur compounds are, and how accessible they are for treatment.

Spectromicroscopy of sulfur distributions. At beamline ID21 the sulfur distribution at energies corresponding to reduced and oxidised sulfur forms were mapped on thin slices of wood samples from the *Vasa*, and also on samples from the *Mary Rose*, Portsmouth, U.K., still under conservation treatment by spraying with polyethylene glycol solution. This was, as far as we know, the first time sulfur K-edge spectromicroscopy had been performed on wood, and the sample preparation turned out to be crucial. Very thin slices from the degraded wood, perpendicular to the cell structure with thickness of less than one cell, were required. The wet samples and sediments from the wreck sites were enclosed between layers of 4mm sulfur-free Ultralene film, to protect from the vacuum in the instrument. Scans were made of several slices of polyethylene treated core samples from the *Vasa* and the *Mary Rose*, obtained with an integration time of 600 ms on each pixel of size 0.5 μm , for 75x70 μm areas, at the maximum absorption energy 2473 eV of reduced sulfur, and at the sulfate energy 2483 eV. Finally, satisfying results could be obtained from core samples from the hull, also

from recently salvaged 16th century oak wood from the *Mary Rose* site, and sediment samples from the wreck site of the *Vasa*. The spectromicroscopy images show that the sulfur compounds can be divided into two categories; one constitutes particles of iron sulfide mostly present in cavities in the wood, the other organosulfur compounds principally in the middle lamella of the wood structure.

Oxidation products in the form of sulfate particles, probably gypsum and e.g. iron sulfates, are found mostly in the lumen of the wood structure. For the *Mary Rose* under conservation treatment, sulfide particles were found but little sulfate, probably because of the constant washing during the spray treatment with conservation liquid. Iron sulfides are fairly easily oxidized in humid conditions, and are likely to be the source of most of the acid present in the *Vasa*. For the ongoing conservation treatment of the *Mary Rose* and for additional conservation treatment of the *Vasa*, it is very important to assess how the acid from the iron sulfides can be neutralised, and how the remaining sulfur, present in organosulfur compounds in the wood, can be prevented to oxidize to form acid.

We also mapped the sulfur distribution of a transverse section in a pine needle with promising results. The scan showed high accumulation of oxidized sulfur closely below the surface of the needle.

XANES analyses of sulfur compounds. X-ray absorption near edge structure (XANES) features were recorded of spots in the spectromicroscopy images. These show the types of characteristic sulfur groups, and for the reduced forms the energies indicate thiols, disulfides, and possibly elemental sulfur. In the *Vasa* sediment sample, the solid reduced sulfur seems to be less oxidised (higher energy), and possibly contains more bacterially produced elemental sulfur.

Spectra of some representative points are shown in Figure 1. The lignin-rich parts, middle lamella and also the S₂-layers, contain high amount of reduced sulfur and little sulfate, with the peak energy at maximum slightly higher than that of pure cysteine, using the same calibration. Distinct grains are found that contain sulfur in the form of sulfate, probably gypsum.

Summary. The results were very promising, and the technique is clearly capable of providing the answers hoped for. More time is needed for systematic investigations of the state and location of the organosulfur, and the identification of the characteristic sulfur groups in the marine archaeological wood. Many different iron sulfides are also possible, and are of special interest for the formation of acid at oxidation. The studies should also include the response of the various sulfur compounds to exposure to humid air and conservation liquids, and scans of the iron edge. The sediment samples provide important information on bacterial activity. The samples from plants and needles should be extended to reveal the accumulation and distribution of the excess sulfur in exposed plants.

References

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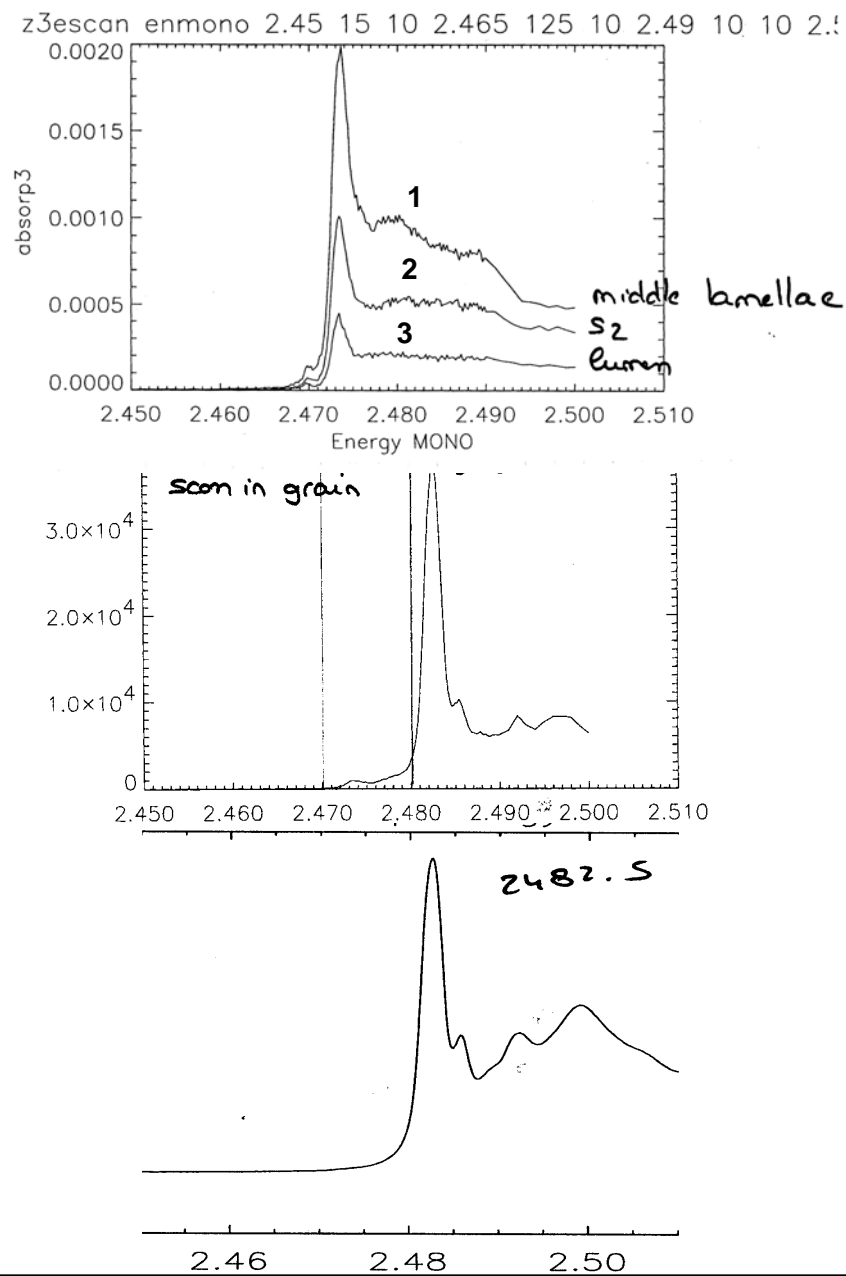


Figure 1. (upper) XANES spectra of points in the images of a core from the *Vasa*, showing reduced sulfur in the middle lamella and S₂ layer; the energy corresponds to thiols. (middle) XANES of grain shows a XANES spectrum similar to that of gypsum (lower) Standard spectrum of gypsum CaSO₄·2H₂O (main peak at 2482.5 eV).