

Sulfur in the Timbers of Henry VIII's Warship *Mary Rose*: Synchrotrons Illuminate Conservation Concerns

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The *Mary Rose* was for 35 years a principal warship in Henry VIII's navy before she suddenly capsized and sank in 1545, maneuvering for battle with a French fleet outside Portsmouth, U.K. The starboard side of the wreck (Figure 1) was salvaged in 1982. Spray treatment with an aqueous solution of polyethylene glycol (PEG), to replace water and prevent cracking when drying the waterlogged wood, started in 1994 (Jones 2003). Recently, x-ray absorption near edge structure (XANES) spectroscopy was used at SSRL to show that about 2 tons of sulfur in reduced forms slowly are oxidizing to sulfuric acid in the almost intact hull of the 17th century Swedish warship *Vasa* (Sandström, *et al.*, 2002). The concern for this unique historical artifact has led to the international "Preserve the *Vasa*" project, started in late 2003. Methods are being developed to remove or stabilize the sulfur and iron compounds, and to neutralize the acid that may continue to form in marine archaeological wood after finishing the standard PEG conservation treatment. For a better understanding of the sulfur accumulation and acid-forming processes, investigations were also started of the *Mary Rose* timbers, which were preserved under somewhat different conditions (Jones 2003, Sandström *et al.*, 2005).

The total sulfur and iron concentrations were determined by x-ray photoelectron spectroscopy, high resolution x-ray fluorescence line scans and elemental analyses in several oak wood cores (0.4×15 cm) sampled from *Mary Rose* timbers (Sandström *et al.*, 2005). Along all cores the sulfur concentration fluctuates around 1 mass% S, indicating totally about two tons sulfur in the hull. This rather uniform sulfur distribution throughout the *Mary Rose* timbers differs from that in the



Figure 1. The starboard side of the *Mary Rose* (about 1/3 of the hull, ~280 tons oak timbers) is since 1994 being sprayed with an aqueous solution of PEG 200.

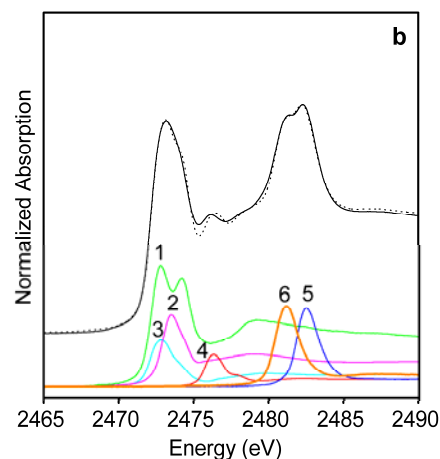


Figure 2. Sulfur K-edge XANES spectrum of *Mary Rose* oak core surface (0-3 mm). Standard spectra used for model fitting: **1** (solution), **1**⁻ (solid) disulfides R-SS-R (cystine with peaks at 2472.7 and 2474.4 eV) 45%; **2**: Thiols R-SH (cysteine, 2473.6 eV) 23%; **3**: Elemental sulfur (S₈ in xylene 2473.0 eV) 10%; **4**: Sulfoxide R(SO)R' (methionine sulfoxide, 2476.4 eV) 5%; **5**: Sulfonate R-SO₃⁻ (methyl sulfonate, 2481.2 eV) 10%; **6**: Sulfate SO₄²⁻ (sodium sulfate, 2482.6 eV) 7%.

Vasa, with high accumulation of sulfur and iron only in the surface layers (~1 cm), degraded by bacteria.

Sulfur K-edge XANES spectra, measured at the SSRL beamline 6-2, were used to determine *in situ* sulfur species with characteristic functional groups in segments along the cores. Principal component analyses indicated at least 6 significant sulfur components. Their relative amounts were evaluated by curve fitting with normalized XANES spectra of known "standard" compounds, mostly in solution (Figure 2).

In most cases several types of reduced species contribute to the major peak at 2473 eV: thiols (R-SH), disulfides (R-SS-R'), with a characteristic shoulder at 2474.4 eV, elemental sulfur (S₈), and occasionally also pyrite (FeS₂). Magazine stored timber and surface samples show minor amounts of sulfonates (R-SO₃⁻) and sulfate (SO₄²⁻), while hull timber under spray treatment has almost no sulfate. Sulfoxides R(SO)R', with a peak at about 2476 eV, can be discerned as a minor component, a few %, in all XANES spectra.

The near anoxic environment at or below the seafloor that slows down wood degradation, at the same time promotes the formation of the reduced sulfur compounds. Bacteria reduce sulfate ions in seawater to dissolved hydrogen sulfide, H₂S(aq), which penetrates and reacts to solid sulfur compounds within the waterlogged wood. The accumulated amount of sulfur depends on the state of wood degradation, the concentration of hydrogen sulfide and of iron ions, as shown by comparisons of the sulfur compounds in wood from shipwrecks preserved under different conditions (Sandström *et al.*, 2005). The XANES spectra show that two classes of compounds are formed: 1. *organosulfur* compounds (e.g. thiols, disulfides, sulfoxides), 2. *iron sulfides* (Fe_{1-x}S and pyrite FeS₂) and also elemental sulfur S₈. Iron sulfides may occur in large quantities in the wood when reactive iron corrosion products have been present providing iron(II) ions in excess. For the *Mary Rose*, the iron concentration in the wood fluctuates considerably.

After salvage, with access of atmospheric oxygen to the moist wood, acid-producing oxidation of the reduced sulfur compounds becomes a conservation concern, especially in the presence of catalytically active iron(II) ions. To determine the distribution of the reactive sulfur species we examined thin wood slices, cut perpendicular to the cell walls, by scanning x-ray absorption spectro-microscopy (SXM) at beamline ID21 of the European Synchrotron Radiation Facility (ESRF). Raster scanning of the samples was performed in the focused

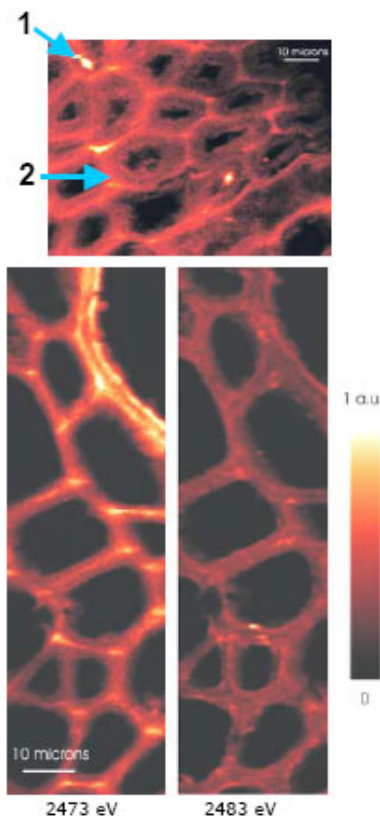


Figure 3. Scanning x-ray micro-spectroscopy (SXM) images of *Mary Rose* wood to map reduced and oxidized sulfur species over a sample area at high spatial resolution, ~0.5 μm, and spectral resolution, 0.5 eV, (brighter color → higher concentration): (top) oak core at 2473 eV, sampled from hull timber under spray treatment. Micro-XANES curves (not shown) indicate that the bright spot **1** is a pyrrhotite (Fe_{1-x}S) particle, and spot **2** corresponds to thiols in the middle lamella.

(lower) Freshly salvaged oak wood from the *Mary Rose* after 459 years on the seafloor. The left SXM image at 2473 eV, displays two distinct layers of thiols in the lignin-rich cell wall of a vessel (top right corner), where liquids are transported in oak wood; the dark patches surrounded by cell walls are the lumina. The 2483 eV SXM image to the right shows a few bright sulfate particles and a diffuse sulfate background from seawater in the waterlogged wood.

beam at energies of characteristic sulfur XANES resonances, ca. 2473 and 2483 eV, to map the distribution of reduced and oxidized sulfur species, respectively.

The SXM images reveal high concentrations of *organosulfur* species in lignin-rich parts of the wood structure, especially in the middle lamella holding the cells together (Figure 3 (*lower*), at 2473 eV). Freshly salvaged oak wood from the *Mary Rose* wreck site displayed reduced sulfur (thiols) in a distinct double layer in the walls of a vessel, which is a lignin reinforced channel for water transport, although how the lignin is distributed is not known. The high concentration of organosulfur in lignin-rich parts indicates direct reaction of the hydrogen sulfide (or HS⁻ ions) with active sites in lignin. This resembles the formation of organosulfur species in humic matter, which may partly be composed of lignin. Cross-linking of thiols via S-S bonds has been proposed to build macromolecular structures, which may have geochemical importance for the stabilization of organic matter in anoxic marine sediments and subsequently for the presence of sulfur in fossil fuels (Vairavamurthy *et al.*, 1997).

Focused micro-XANES spectra occasionally show *iron sulfides* in particles (Fe_{1-x}S, 0 < x < 0.1, with peak energy ~2471 eV), and deconvoluted SSRL XANES spectra sometimes reveal pyrite FeS₂. Microcrystalline iron sulfides are known to be unstable towards oxidation in a humid environment, and are probably the primary source of the acid that forms in the moist wood of the shipwrecks. About 2 tons of sulfuric acid is estimated to have accumulated in the *Vasa*'s PEG impregnated hull after the spray treatment was stopped in 1979 (Sandström *et al.*, 2003).

In the "Preserve the *Vasa*" project, tests are being carried out to remove iron or in other ways slow down oxidation processes of the sulfur compounds. Specially tailored derivatives of the well-known chelate EDTA, which form water-soluble complexes with particularly strong bonds to iron(III), are being tested for iron extraction. The spraying washes out the acid produced in the hull timbers of the *Mary Rose*, and the rate of acid production is carefully monitored to assess a suitable end point of the current spray treatment. After the strongly acid-forming iron sulfides are exhausted, antioxidants could be added to stabilize the lignin-bonded organosulfur compounds and also to prevent PEG degradation. For the *Vasa* a new wet spray treatment would be stressful for the degraded wood. Neutralizing the accumulated acid with an ammonia gas treatment, followed by storage in stable and low (~55%) relative humidity, may be sufficient to hold back the effects of acid-forming oxidation processes. Monitoring the progress of the ongoing work at synchrotron facilities, as well as analyses of new marine-archaeological artefacts will have important influence on the direction of future conservation efforts.

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