How X-rays are helping defeat the effects of micro-organisms in the preservation of *Mary Rose*

Alan V. Chadwick, Aaron Berko, Eleanor J. Schofield, A. Mark Jones, J. Frederick W. Mosselmans and Andrew D. Smith

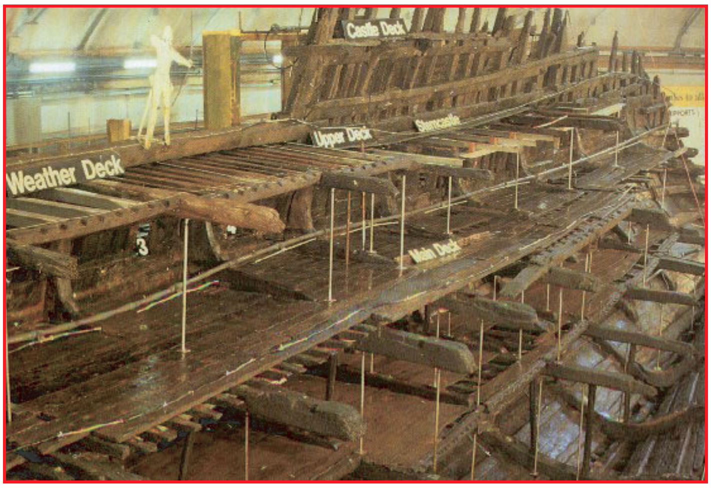
Abstract This article presents a brief overview of the role synchrotron-based X-ray techniques are playing in the preservation of the *Mary Rose*, a 16th century English warship. The particular problem facing the conservators is the effects of sulfuric acid in the wood formed from sulfur compounds which originate from microbial activity.

Keywords **Cultural heritage, wreck, micro-organisms, sulphur compounds, preservation, synchrotron radiation.**

Résumé **Comment les rayons X aident à lutter contre les effets des micro-organismes pour préserver le *Mary Rose***

Cet article montre le bénéfice de l'utilisation des rayonnements synchrotrons dans la préservation du *Marie Rose*, un navire de guerre anglais datant du XVIe siècle, notamment pour le problème particulier que sont pour le bois les effets des composés soufrés induits par des micro-organismes, problème auquel sont confrontés les conservateurs.

Mots-clés **Patrimoine culturel, épave, micro-organismes, composés soufrés, préservation, rayonnement synchrotron.**



The recovered hull of the *Mary Rose* on display in Portsmouth (England).
The model of the archer (on the weather deck) provides an impression of the ship's size.

The *Mary Rose* was the flagship of the English fleet and a favourite of King Henry VIII. In 1516, the year of her launch, she represented the state-of-the art in naval ships as she was fitted with gun-ports and newly developed heavy guns [1]. She was involved in wars with France, Scotland and Brittany and on 17th July 1545 she sank, losing some 500 men, in an engagement with the French invasion fleet in the estuary of the River Solent, just outside Portsmouth Harbour. The reason for the sinking is a mystery, although there is no evidence that it was due to French gun fire.

The wreck remained partially covered in silt on the sea-bed until it was re-discovered in 1971. The silt protected the timbers from wood-boring sea-life and the anoxic conditions prevented oxidation of the wood. In a complex engineering operation, the wreck was successfully raised in 1982 and moved to a preservation site in the Historic Dockyard at Portsmouth. Almost the whole starboard side of the original ship (length 32 m and breadth 12 m) with nearly half the decks,

A recovered Tudor knife handle.
The picture on the left shows mineral accretions due to the sulfur problem. The accretions are concentrated around the position of the steel blade, which has corroded away. The picture on the right is the same handle after treatment with an iron chelating agent.

cabins and ancillary structures were recovered. Along with the wreck, some 20,000 artefacts have also been recovered which represent a unique perspective of life at sea in Tudor England. The wreck is currently in the process of conservation, which involves spraying with aqueous solutions of polyethylene glycol, a waxy polymer, which impregnates the wood and provides mechanical integrity. The ship will then be dried and exhibited in a newly built museum in 2012. During the conservation, some of the timbers and wooden artefacts were found to develop surface discolouration and mineral deposits which were evidence of the "sulfur problem", a known effect in water-logged archaeological timbers.

The sulfur problem

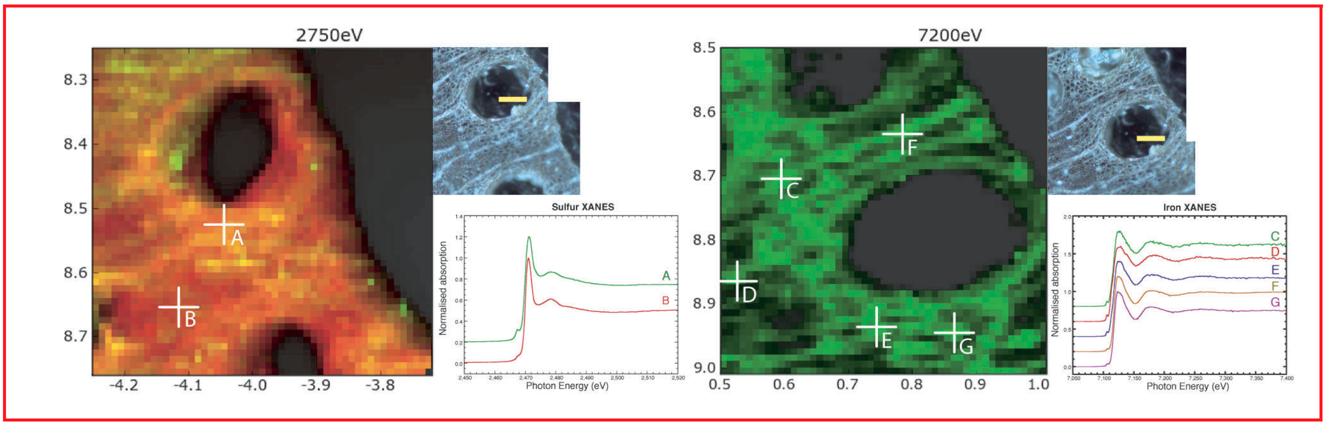
The sulfur problem was first observed on timbers of the *Vasa*, a 16th century Swedish warship raised from Stockholm Harbour and currently on display in a Stockholm museum. It results from the formation of sulfuric acid from reduced sulfur compounds in the timbers which then attacks the wood and can lead to mechanical breakdown. There are a range of reduced sulfur compounds in the timbers (elemental sulfur, thiols, cystine, cysteine, etc.) originating from the actions of micro-organisms. In the anoxic conditions of the sea-bed, the micro-organisms metabolise sulfur compounds in the polluted harbour waters to produce hydrogen sulfide which can react with organic matter. The hydrogen sulfide also reacts with corroding iron artefacts in the wreck (nails, bolts, knives, arrow heads, etc.) to form iron sulfides. It has been estimated that the *Mary Rose* hulk contains about two tonnes of sulfur in various forms. Once a wreck is raised the moist, oxygen-rich conditions of the atmosphere lead to the oxidation of the reduced sulfur compounds to form sulfuric acid. The reaction pathways are complex and can be both abiotic and biotic as sulfur-oxidising micro-organisms will also produce sulfuric acid. The problem is exacerbated in iron rich regions as iron is believed to catalyse the production of sulfuric acid. For the conservator the challenges are firstly to understand the underlying processes and secondly to develop a remediation strategy which has to provide long-term protection for the timbers.

The role of synchrotron techniques

Since the early 1990's, synchrotron based experiments have increasingly been used in the investigation of problems related to art, archaeology and cultural heritage [2]. The range of advanced synchrotron-based analytical techniques is playing a major role in combating the sulfur problem and we have been using them in studies of the *Mary Rose*. The work has involved experiments at a number of synchrotrons including Daresbury SRS, Diamond Light Source, ESRF, Swiss Light Source, Stanford Synchrotron Radiation Light Source and SOLEIL, using instruments that are optimised for specific techniques, *i.e.* microscopy, spectroscopy, X-ray fluorescence (XRF), diffraction, etc.

A key piece of information in understanding the processes underlying the sulfur problem is the speciation of iron and sulfur in the timbers. X-ray absorption spectroscopy (XAS) has been pivotal in yielding these data. In XAS the absorption of X-rays by a sample is measured as the incident beam energy is scanned across the absorption edge, *i.e.* the energy for photoemission of a core (K or L shell) electron for an atom in the sample, and is characteristic for each element. The XAS region is usually considered in two regions. The extended X-ray absorption fine structure (EXAFS) extends some hundreds of eV beyond the edge and contains oscillations due to the interference effects created by the out-going photoelectron wave and that part of the wave which is back-scattered by surrounding atoms. The frequency and magnitude of the oscillations provide detailed information on the local structure around the atom, *i.e.* the distance and nature of the local coordinating atoms. The X-ray absorption near edge structure (XANES) is the region at the edge and extending out a few tens of eV beyond the edge. The edge position is dependent on the formal charge on the atom and the spectral features just beyond the edge depend on the local electronic structure around the atom. The XANES spectra for sulfur compounds show a range of edge shifts (changing linearly as the oxidation state moves from -2 to +6) and are rich in features.

Thus the sulfur species have been identified and quantified in both freshly raised timbers and timbers exposed to the normal atmosphere for many years, providing some insights into the oxidation processes. Similar information on the iron compounds has been gained from iron XANES experiments. Simple sulfur K-edge XANES experiments on cores taken from the timbers have shown that sulfate formation occurs at the surface of the timbers. Utilising XAS within synchrotron X-ray microprobe experiments have been crucial in locating and correlating the various iron and sulfur compounds and their spatial distribution in the wood structure with micron resolution.



Synchrotron micro XRF maps of a section of *Mary Rose* timber of sulfur (left) and iron (right) along with the corresponding optical micrographs (the scale bar is 100 micron).

The insets are the corresponding XANES plots from selected locations. The iron spectra are indicative of iron oxide. The sulfur spectra are indicative of the organosulfur compound in the mid-lamella regions. The maps were collected at the Diamond Light Source.

For example, the organic sulfur compounds are found predominantly in the mid-lamella regions, the Fe(II) sulfide (pyrite) is in the form of grains (their identity confirmed by EXAFS) on the inner cell walls and Fe(III) has been found within the cell walls but not correlated with sulfur. This information gives clues as to the nature of the oxidation mechanisms.

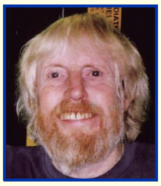
Future prospects

Currently our work is focussing on possible methodologies to remediate the sulfur problem, in which the removal or passivation of iron species is crucial. The removal of the organic sulfur compounds is not considered feasible as it would involve solvents that would damage the wood. We have been assessing the effectiveness of a range of iron chelating agents, antioxidants and surface barriers. Several common chelating agents are effective in iron removal, however there are questions to be resolved concerning efficiency, cost and time. XAS measurements are being used to monitor the effect on the speciation and location of the iron compounds that are removed from the timbers. Future work is planned to study the kinetics of the removal process in detail by using quick XAS measurements, where the spectra are collected on a time scale of seconds, compared to ~ 30 minutes for conventional XAS. Other areas that we are exploring are the activity of sulfur oxidising microbes, which are large enough to resolve in synchrotron microfocus experiments. The interest here is the location and biochemical activity of these organisms as they provide another route to sulfuric acid in the timbers. Thus synchrotron investigations will continue to play an important role in this battle to conserve this unique historic artefact.

References

[1] The detailed history of the *Mary Rose* project and information on visiting the museum can be found at www.maryrose.org.

[2] The interested reader can find more details in : *Physical Techniques in the Study of Art, Archaeology and Cultural Heritage, vol. 2*, D. Creagh, D. Bradley (eds), Elsevier, **2007**, chapt. 1 and 2; *Heritage Microbiology and Science*, E. May, A.M. Jones, J. Mitchell (eds), Royal Society of Chemistry, **2008**, p. 128-143; Cotte M., Susini J., Janssens D.J., Synchrotron-based X-ray absorption spectroscopy for art conservation: looking back and looking forward, *Accounts of Chemical Research*, **2010**, *43*, p. 705.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