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The application of X-ray absorption spectroscopy in archaeological conservation: Example of an artefact from Henry VIII warship, the *Mary Rose*

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ABSTRACT

We report a microfocus X-ray absorption (XAS) investigation of a thin film sample from an iron contaminated wooden arrow tip raised from the seabed with the *Mary Rose*. The XAS studies were combined with optical and scanning electron microscopy measurements. The arrow tip had been treated with polyethylene glycol (PEG) soon after it had been raised and stored in a controlled environment. The measurements revealed a significant concentration of iron sulfide nanoparticles. This indicates that in this sample there was a reduction of the oxidative effects of the normal ambient atmosphere that is usually seen in untreated timbers. The film was treated overnight with an aqueous solution of diethylenetriaminepentaacetic acid (DTPA), which is normally very effective in sequestering iron. This had little effect in terms of removing iron from the film and possible explanations are discussed.

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1. Introduction

X-ray absorption spectroscopy (XAS) is now a well-established tool for probing the local structure of materials. The pioneering work with this technique began roughly half a century ago and in the UK, one of the leading figures was Neville Greaves, to whom this volume is dedicated. In addition to his early studies of glass structure, he was responsible for the building of the first UK XAS beam line, station 7.1 at the Daresbury Synchrotron Radiation Source (SRS). For nearly two decades, Neville led XAS development at the SRS and played a major role in the establishing Daresbury as a leading international centre for synchrotron experiments [1]. Many of the UK users of the XAS technique owe their training, either directly or indirectly, to Neville. This is especially true for the authors of this contribution as they include ex-colleagues from the Daresbury SRS and long-term research collaborators. Since the early beginnings the technique has found applications over the whole scientific spectrum and is now widely used in archaeological, heritage and museum studies, the basis of this contribution. This article will begin with a brief overview of the application of XAS in this field and then focus on the conservation of waterlogged archaeological wood using our recent studies of the *Mary Rose*, a flagship of

Henry VIII that is now in a dedicated museum in Portsmouth Historic Dockyard [2]. The *Mary Rose* and the associated artefacts are a national treasure and represent a unique time capsule of life in Tudor England.

As the basics of XAS experiments and data analysis have been the subject of many books and reviews [3–9] only a brief overview is given below. The experiment involves measuring the X-ray absorption coefficient of a sample as the incident energy of the X-rays is scanned from high to low across the characteristic absorption edge leading to photoemission of a core electron (K or L shell) from atoms of a chosen element in the sample. As the X-ray energy moves across the absorption edge of the atom there is a sharp jump in the absorption coefficient followed by a series of oscillations. The spectrum is divided into two regions: the X-ray absorption near-edge structure (XANES) extending some 50 eV beyond the edge and the extended X-ray absorption fine structure (EXAFS) covering the oscillations at higher photon energies.

The oscillations in the EXAFS region arise from interference between the outgoing photoelectron wave and that part of itself which is backscattered from neighbouring atoms. Each shell of neighbouring atoms contributes a sine wave to the overall EXAFS. It is the quantitative analysis, performed with interactive computer programmes [10–14], of the frequency and amplitude of the oscillations that provide detailed information on the local structure around the target atom out to a distance of ~5 Å; namely the number ($\pm 20\%$), type (± 3 in Z, atomic number) and distance (± 0.01 Å) of surrounding atoms. Unlike diffraction

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methods it does not depend on long-range order and can be used to study local environments in liquids and both crystalline and amorphous solids. It is an element specific technique and can be sensitive to very low concentrations of the target element. However, there is one note of caution in that the commonly used XAS is an averaging technique, in that it probes the local environment of all the target atoms of the selected element illuminated by the incident X-ray beam on the sample.

In the XANES region the edge position is sensitive to the oxidation state of the target atom; the edge moves to higher energies in going to a higher oxidation state due to the increasing charge on the target atom. Hence the edge position can be used to determine the oxidation state of the target atom. The XANES region beyond the edge is complex as the photoelectron is moving slowly and interacting with the electrons of the neighbouring atoms. Progress is being made in quantitatively fitting this region by using density functional theory (DFT) calculations to evaluate the electronic density states of the system and predicting the transitions available to the photoelectron [13,14]. However, the most common approach is to compare the XANES with spectra of standards with known local geometry (i.e. square planar, tetrahedral, or octahedral, etc.) and use a 'fingerprint' approach.

The application of XAS measurements to problems in archaeological, heritage and museum sciences has been the subject of several reviews [15–19]. There is an enormous breadth of problems to which the technique has been applied; ranging from the origin of Ancient Greek (5th century BCE) burial vessels [20], to the deterioration of medieval stained glass windows [21], to degradation of historic documents by iron gall ink [22] and to the origin of van Gogh's yellow paint [23]. Artefacts that have been a particular focus for XAS studies are waterlogged archaeological timbers, namely the historic ships the *Vasa* [24–31] and the *Mary Rose* [32–40]. It is this latter ship that has been of interest to the current group of authors with a special interest in the 'sulfur problem'.

The *Mary Rose* was the flagship of the English fleet and a favourite of King Henry VIII. In 1511, 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 [2]. She was involved in wars with France, Scotland and Brittany and on 19th 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 gunfire. The wreck remained partially covered in silt on the seabed 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, 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 was conserved, which involved spraying with aqueous solutions of polyethylene glycol (PEG), a waxy polymer, which impregnates the wood and provides mechanical integrity [41]. Since 2013, the ship has been exhibited in a purpose-built museum and currently is in a drying process.

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 waterlogged archaeological timbers. The sulfur problem was first observed [24,25] 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 microorganisms [25,32]. In the anoxic conditions of the seabed, the microorganisms 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, arrowheads, etc.) to form iron sulfides. It has been estimated that the *Vasa* and *Mary Rose* hulks each contain about 2 t 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 microorganisms will also produce sulfuric acid. The problem is exacerbated in iron rich regions as iron is believed to catalyse the production of sulfuric acid [26,33,42,43]. 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.

Since the early XANES experiments on the sulfur speciation in the *Vasa* [25] XAS measurements at both the S and Fe K-edges have played a key role in the study of water-logged wooden artefacts. In the case of the *Mary Rose* the measurements have been used to identify the iron and sulfur compounds in the timbers [32,33] and to determine the effectiveness of chemical treatments to remove iron [34,45] or the use of nanoparticles to neutralise sulfuric acid in the wood [35,37,38,40]. The technique has also been used to study bacteria that could be in the timbers [39] and in long-term monitoring of iron and sulfur compounds of the ship in the museum environment [44]. This contribution will discuss the results of a study of an arrow tip from the ship, which in contrast with most of our previous work, is for an artefact, which was preserved by PEG impregnation soon after it was raised from the seabed and then stored in a controlled humidity and temperature environment. Thus, it provides an interesting contrast with results from the timbers and the effectiveness of sequestering methods.

2. Experimental details

2.1. The artefact and treatment solution

The sample studied was a thin slice taken from the tip of an arrow. The arrow would originally have been sheathed by the iron arrowhead, which has been completely corroded during its exposure to seawater. This is expected to leave heavy iron deposits within the timber of the arrow tip. The remainder of the arrow shaft (unstudied here) is unlikely to have been exposed to iron corrosion products. It had been observed that the tip of the arrow was heavily stained with deposits, indicative of the presence of sulfur compounds. The arrow was subjected to normal timber conservation methods shortly after recovery from the seabed. These included treatment with polyethylene glycol, grades PEG400 and PEG4000, (where 400 and 4000 are the average molecular weights) before freeze-drying. After treatment the arrow tip was stored at a constant relative humidity (RH) and temperature of 55% and 20 °C, respectively.

The treatment solution tested was 0.1 M aqueous solution of diethylenetriaminepenta-acetic acid (DTPA), which was very effective in sequestering iron from samples of the *Mary Rose* timbers [34,45]. Laboratory tests [45] involving soaking timber samples in solutions of DTPA have already demonstrated its potential in this application with rapid (within minutes) changes to the colour of solution as iron products are removed from the wood.

2.2. XAS measurements

The timber section was placed in a small cell machined from polycarbonate and covered with a thin Kapton window. The cell was fitted with small feed throughs which could be used to introduce treatment solutions and then flush the sample afterwards. It also allowed the section to be kept in a moist environment during measurement to avoid it drying out and curling. It should be noted that during the in-situ treatment process and whilst in transport between the X-ray spectroscopy

instrument and the SEM that the rather fragile thin section did distort slightly. Specifically, a break seen running diagonally through some of the SEM and optical images opened up and some material was lost. This makes direct visual comparison with exactly defined locations before and after treatment difficult. Fig. 1 shows a photograph of the in-situ sample cell mounted on the I18 beamline.

The fluorescence mode XAS and X-ray fluorescence (XRF) measurements were performed on the microfocus beam line, I18, at the Diamond Light Source [46]. This electron synchrotron operates at energy 3 GeV and a normal beam current of 300 mA. The energy range of I18 is 2.05 to 20.5 keV and the beam size can be as small as $2 \times 2 \mu\text{m}$; in the current work, the footprint was $2 \times 4 \mu\text{m}$. Data for XRF and spectroscopy measurements at both iron and sulfur edges were collected using a 4-element Vortex™ detector.

Data were collected in one of two modes, initially raster scans were made across the sample with the microfocussed X-ray beam in a series of predefined steps while collecting the X-ray fluorescence (XRF) emission from the sample. This gave a map of the distribution of the element of interest. As the beamline is tunable in energy, it was possible to set the incident photon energy to preferentially excite certain valence states. This was used to highlight areas of Fe^{2+} in contrast to Fe^{3+} . The second mode of operation was to use the XRF maps to determine selected points from which to collect XAS spectroscopy data, mainly XANES, which provides rich information on the chemical state, especially the valence state, of the element of interest at that point.

2.3. Scanning electron microscopy measurements

Scanning electron microscopy (SEM) images were collected for the thin section after XAS measurements using a Hitachi TM3000 tabletop microscope.

3. Results and discussion

3.1. Microscopy

Figs. 2 and 3 show optical and SEM micrographs, respectively, of the arrow tip section after the X-ray measurements. Close inspection of the optical image shows the gunmetal grey colouration of pyrite clusters along with a few small patches of an orange coloured iron corrosion phase. The SEM image also shows large clusters of pyrite nanoparticles, these can be seen to be collecting particularly on the walls of the larger vessels in this section. There is no evidence of the cellular voids being filled with PEG, although it should be noted that core sections of oak,

Fig. 1. Thin timber section mounted in the polycarbonate in-situ treatment cell (white circular object) and mounted on the I18 beamline. X-rays come from the right and the photograph taken from the position of the X-ray fluorescence detector used to collect the spectroscopy data.

Fig. 2. Optical micrograph of the thin section. Iron corrosion products typically have an orange colour and whilst frequently seen in some sections of timber collected from the vicinity of iron fittings, are only seen in moderation in this section (circled).

taken from the ship's hull only shows PEG filling cell voids if there is an open pathway (e.g. a crack) into the body of the timber through which the PEG can flow in sufficient quantities to fill the cells completely.

3.2. Iron K-edge XAS

XAS Fe K-edge spectra of a variety of iron compounds are shown in Fig. 4. This shows a shift towards higher energy of the absorption edge (the steep rising edge in the absorption spectrum) with increasing valency. Iron metal (Fe^0) has the lowest energy edge with an absorption edge, defined as the maximum in the gradient of the rising edge, of 7114.6 eV. The Fe^{2+} species, such as wüstite (FeO) and the iron sulfides, pyrite (FeS_2) and marcasite (FeS_2) have a leading edge at about 7120.8 eV, whilst the Fe^{3+} oxides (hematite (Fe_2O_3), goethite ($\text{FeO} \cdot \text{OH}$)) have edges at approximately 7129.0 eV. Magnetite (Fe_3O_4) has mixed $\text{Fe}^{2+};^{3+}$ valency, the Fe^{3+} dominates the edge, but a lower energy shoulder can be seen due to the Fe^{2+} contribution. Key features to note are the peak of the Fe^{2+} resonance, which is marked with an A in Fig. 4 at 7120 eV, this contrasts with the Fe^{3+} feature marked with a B (7134.2 eV to 7137.0 eV). It can be seen that the various model Fe^{3+} oxide species show distinctly different features on this peak; these arise because the model compounds are of well-defined oxide species with specific local atomic structures. Iron oxides species seen in the *Mary Rose* timbers do not usually show this degree of fine structure [33], suggesting that they are less well formed than model compounds. This peak does not coincide with the broader hump seen at around 7140 eV (C) in the two iron sulfide spectra.

Fig. 5 shows a selection of Fe K-edge spectra taken of the conserved arrow tip, but prior to treatment with DTPA. This shows a significant fraction of pyrite like structures, particularly at point (1) which gives a spectrum very similar to the model compound iron sulfide data of Fig. 4, although locations (4) to (7) also show a feature at about 7120 eV (A) which is related to the sulfide Fe^{2+} signature seen in Fig. 4. Measurements from (6) and (7) show maxima at 7133 eV, which corresponds more to an Fe^{3+} oxide and occurs at a slightly lower energy than the maxima seen at (1), (4) and (5), suggesting that spectra from these latter locations is dominated by sulfide content, whereas (6) and (7) represent a more mixed environment of iron sulfide and oxide. Spectra from locations (2) and (3) do not show any sulfide like structures and appear more oxide like, although of different types. Spectrum (2) has a maximum at 7133 eV and is predominately Fe^{3+} , whereas spectrum (3) has a maximum at 7127 eV (D) which implies a Fe^{2+} valency. Comparing the XRF map area with the optical images of

Fig. 3. SEM images of thin section of arrow tip from the *Mary Rose*. (a) low magnification image of section. The white areas are clusterings of pyrite nanoparticles, shown in detail in (b) a high magnification close up showing pyrite nanoparticles lining the walls of a vessel.

Figs. 2 and 5 and the SEM of Fig. 3, shows that the sample contains some areas with heavy concentrations of pyrite nanoparticles. Near the edges of the sample, a higher proportion of iron oxide is seen.

Diethylenetriaminepentaacetic acid (DTPA) is a chelating agent and is currently being tested as a potential treatment for waterlogged archaeological timbers due to its ability to sequester iron. Laboratory tests [45] involving soaking timber samples in solutions of DTPA have already demonstrated its potential to be effective in this application with rapid (within minutes) changes to the colour of solution as iron products are removed from timber that has been in contact with iron corrosion. Soaking the thin section in a solution of 0.1 M DTPA overnight did not induce significant change in the iron content of the sample, neither did there appear to be significant uptake of iron by the solution; it remained clear. Treatment of a PEG treated core sample from the ship's hull timbers produced a similar, unchanging response. In contrast, other timber samples from the *Mary Rose* produced strong and rapid changes, indicating that DTPA is normally effective in removing iron from waterlogged archaeological marine timbers. The lack of reaction of the current sample may be due to a protective coating of PEG. Although the

micrographs of the sample showed no evidence of PEG in the wood cells, the surface could still be covered with a thin layer of PEG.

Fig. 6 shows Fe K-edge spectra taken after the DTPA treatment from a range of locations, in approximately the same area as before. An attempt was made to correlate the areas studied with those seen in the SEM, bearing in mind the slight changes in topography due to sample movement between the two measurements. The iron fluorescence signal is approximately unchanged, indicating that the DTPA has not been effective in removing iron from this sample (removal rates of between 40% and >99% are observed in non-PEG treated samples [34, 45]). With the exception of location (6) (which appears to be an Fe^{3+} oxide) the spectra all show close similarities to that of the iron sulfide model compounds.

3.3. Sulfur K-edge XAS

Switching the beamline to operate at the sulfur K-edge allowed data to be collected on the sulfur speciation within the section, however due to the complexities in changing the beamline operation, it was only possible to measure the sulfur after the treatment with DTPA. Fig. 7 shows spectra collected from 6 locations within a map area of $300\ \mu\text{m} \times 200\ \mu\text{m}$. Two maps were collected, at incident photon energies of 2469.5 eV, 2473 eV and 2482 eV. These correspond to the sulfide, organo-sulfur/elemental sulfur and sulfate resonances respectively and in principle allow strong variations in these chemical species to be distinguished [32]. Due to the ability of the beamline to transmit higher order radiation, it proved possible to map for sulfur and iron content at the same time. In these maps the sulfur concentration is coloured red, whilst the iron content is green (as in the other XRF maps presented here).

The XRF maps suggest that there is little sulfide present in the imaged area, this is confirmed by the spectra collected from 6 locations across the mapped area and shown in Fig. 7. The presence of sulfide (S^{2-}) would be evident by a peak at approximately 2469 eV in the sulfur XANES. The six spectra show a variety of other features; spectra [1,2, 6] show a peak centred at 2471.8 eV (X in Fig. 7), corresponding to elemental sulfur (S^0), whereas spectra [3,4,5] show an absorption edge shifted to slightly higher energy. This suggests a slightly oxidised form of sulfur, such as an organo-sulfur species. Additionally, spectra [4,5] show a peak at 2482 eV (Y) which is related to sulfate (S^{6+}), although the percentage of sulfate is small. The iron concentration in the mapped

Fig. 4. Fe K-edge spectra of iron standards. Designations A, B and C are discussed in the text.

Fig. 5. Fe K-edge spectra from seven locations within the section of the arrow tip, taken before treatment with DTPA. Top left, an XRF map collected at a photon energy of 7300 eV of the iron content in an area $275 \mu\text{m} \times 350 \mu\text{m}$, marked with the locations from which the individual spectra were collected. Lower left; the corresponding area on an optical micrograph. Areas of high pyrite concentration, as seen in the SEM image of Fig. 3, are highlighted in yellow. Designations A, B, C and D are discussed in the text.

area is largely confined to two areas and it is possible that the region of the section that was studied at the S K-edge does not correspond to that measured at the iron edge. The SEM (Fig. 3) does show that the pyrite contamination only occurs in certain locations within the arrow tip and it is possible that the area selected for sulfur K-edge analysis did not correspond well to the previously selected region.

4. Conclusions

The current study used a powerful combination of microfocus XAS, optical and scanning electron microscopies to study a thin section of an artefact from the *Mary Rose*; namely a PEG-treated, iron contaminated wooden arrow tip. The study involved an investigation of the nature

of the iron and sulfur compounds in the wood and the effectiveness of a chelating agent, DTPA, in removing iron from the wood. The significant findings of the study were the observation from both the XAS and microscopy measurements of a prevalence of clusters of iron sulfide nanoparticles in the wood and the lack of reactivity of the sample with DTPA. This contrasts with previous studies of timber samples from the *Mary Rose* [32,34,45]. A possible explanation of both findings lies in the nature of the conservation treatment applied to the arrow tip.

A key feature of the conservation treatment of the arrow tip was the long term storage conditions of RH at 55% and a temperature of 20°C . These conditions would reduce the rate of oxidation of sulfur compounds. It is interesting to note that the climate conditions of the *Vasa* museum have been upgraded to stabilise the ship [41,42]. Similarly,

Fig. 6. Fe K-edge spectra from six locations within the section of the arrow tip, taken after treatment with DTPA. Top left; an XRF map collected at a photon energy of 7300 eV of the iron content in an area $300 \mu\text{m} \times 300 \mu\text{m}$, marked with the locations from which the individual spectra were collected. Lower left; the corresponding area on an SEM micrograph.

Fig. 7. S K-edge spectra from six locations within the section of the arrow tip, taken after treatment with DTPA. Left top, left middle, left bottom: XRF maps collected at photon energies of 2469.5 eV, 2473.0 eV and 2482 eV, respectively, in an area $300\ \mu\text{m} \times 200\ \mu\text{m}$, marked with the locations from which the individual spectra were collected. In the maps, red indicates the relative sulfur content, green is the iron content. Designations X and Y are discussed in the text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the climate control in the *Mary Rose* museum has been designed to have tight control of the RH and temperature. The current studies indicate that these controls should have long-term beneficial effects.

The lack of reactivity of the iron compounds in the sample was at first surprising even though the contact time was relatively long. It seems that it is unlikely that it is a PEG coating that is protecting the sample as current studies indicate that DTPA is effective on some PEG treated *Mary Rose* artefacts [47]. An explanation may be found in the high iron sulfide and low sulfate contents found in the arrow tip. Iron sulfides have a low solubility in water [48], which would lead to a slower reaction with DTPA.

Overall, the current study emphasises the role of the conservation treatment and climate control in mitigating the sulfur problem.

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