ALKALINE EARTH CARBONATES FOR THE TREATMENT OF PROBLEMATIC SULFUR ASSOCIATED WITH MARINE ARCHAEOLOGICAL WOOD

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ABSTRACT

Wooden archeological artefacts excavated from marine sources contain problematic sulfur which can result in degradation. A treatment to safely neutralize sulfur using alkaline earth carbonates is tested on samples from the warship *The Mary Rose*. S K-edge X-ray absorption spectroscopy confirms the neutralization of acid already in the wood, by forming insoluble sulfates salts. The treatment also catalyzes the conversion of iron sulfides to soluble iron sulfates, thus removing the future source of this acid. Calcium carbonate is favored as it is non-toxic and economical. This treatment is relevant to all organic artefacts that are threatened by sulfur compounds.

KEYWORDS

X-ray Absorption Spectroscopy, S K-edge, The *Mary Rose*, Waterlogged Wood, Acid Degradation, Carbonate Neutralization Agent.

ABBREVIATIONS

X-ray Absorption Spectroscopy (XAS), X-ray Absorption Near Edge Structure (XANES), polyethylene glycol (PEG)

INTRODUCTION

A wide variety of organic archaeological artefacts are threatened by the formation of sulfuric acid, by oxidation of adventitious or endogenous low-valent sulfur compounds (Fors et al., 2012, Fors and Sandström, 2006, Frank et al., 2012, Sandström et al., 2002). In wooden artefacts, externally deposited metal sulfides and inherently present organic sulfur are oxidized by atmospheric oxygen in the presence of water and/or iron ions, ultimately forming sulfuric acid (Fors, 2008, Sandström et al., 2005, Wetherall et al., 2008). In paper, external sizing agents such as alum leads to acidification and the destructive hydrolysis of cellulose fibers (Zappalà et al., 1996). Although not sulfuric acid, acid degradation has also been observed in ancient texts and parchment (Bowden and Brimblecombe, 2003, Arčon et al., 2007). The mechanisms of acid formation have been investigated in studies of many archeological artefacts, laying the foundation for the development of a treatment plan based in applying chemical principles (Fors et al., 2012, Frank et al., 2012, Sandström et al., 2005, Sandström et al., 2002, Wetherall et al., 2008, Fors, 2014).

The *Mary Rose* is a sixteenth century Tudor warship that was excavated in 1982, near Portsmouth harbor, UK (Jones, 2003, Marsden, 2003, Rule, 1982). Over time, it has been treated with polyethylene glycol (PEG 200 to reinforce the cell walls and PEG 2000 to seal the surface) to maintain structural integrity and is currently being dried under environmentally controlled conditions. Other methods have been investigated for the stabilisation of waterlogged wood (Sandu, 2011). The 17th century warship, *Vasa*, was raised a decade previously to the *Mary Rose* and has undergone similar treatments for

mechanical stabilization (Håfors, 2001). The sulfur problem was first discovered on the dried timbers of the *Vasa* and subsequent investigations into the source of the sulfur (Fors and Sandström, 2006, Sandström, et al., 2002) instigated similar investigations into *Mary Rose* timbers (Sandström et al., 2005, Wetherall et al., 2008). In waterlogged wood such as the *Mary Rose* and *Vasa*, the iron sulfides (such a pyrite) responsible for acid formation are deposited by the action of sulfur reducing bacteria present in anoxic marine environments. Past studies on the *Mary Rose* have amply demonstrated that these iron sulfides are oxidatively transformed to sulfuric acid when exposed to water and oxygen (Sandström et al., 2002, Schofield et al., 2011).

Whilst similarities exist between the timbers of the *Vasa* and *Mary Rose*, environmental conditions during burial, storage conditions post-excavation and conservation treatments used can significantly alter the current state of the wood. Therefore threat levels associated to chemical processes can vary. In particular, there are significant differences between the sulfur distributions; sulfur within *Vasa timbers* is concentrated at the surface, while in the *Mary Rose* the problematic sulfur is distributed evenly throughout the wood (Sandström et al., 2005). Over recent years *Vasa* research has focused on other acid sources within the wood, produced from mechanisms such as PEG and holocellulose degradation, driven by the presence of iron (Almkvist and Persson, 2006). These acids are deemed a more significant threat to *Vasa* wood, than those produced via sulfur compounds as they are evenly distributed deep into the timbers. The presence of these acids in *Mary Rose* wood is currently under investigation. Regardless, the presence of sulfur through the *Mary Rose*

timbers makes production of acid from this source a serious threat, which must be addressed (see Figure 1B for the extent of damage on a wooden wheel artefact).

Understanding the sulfur chemistry in the wood is therefore key to developing treatment and conservation methods. To achieve this, a synchrotron based sulfur K-edge X-ray absorption spectroscopy (XAS) methodology has been developed as a powerful tool to follow the oxidation of exogenous low-valent sulfur compounds through intermediate chemical states to sulfuric acid (Sandström et al., 2002, Fors and Sandström, 2006). This technique is especially powerful for its applicability to inhomogeneous systems, a category to which most cultural heritage artefacts belong. The composition and variability in sulfur species is obtained by utilizing a carefully selected library of standard sulfur K-edge XAS spectra of model compounds, followed by a linear combination analysis (LCA) of the S K-edge XAS from the artefact. The wide use of this method has resulted in general understanding of the transformation of sulfur to acid in recovered wooden artefacts (Fors and Sandström, 2006, Frank et al., 2012, Sandström et al., 2002, Schofield et al., 2011).

An effective plan should address neutralization of immediate acid and resolve the source of slow acid formation. Previous treatments have used aqueous solutions of NaHCO_3 and soda (Fors and Sandström, 2006). This treatment however removed the surface PEG and resulted only in a temporary increase in pH. Treatments using $\text{Ca}(\text{OH})_2$ nanoparticles have also been proposed (Giorgi et al., 2005). Both these treatments generate alkaline conditions that can be harmful for archaeological wood. Treatments with NH_3 gas have also been performed (Fors and Richards, 2010), but some degradation of hemicellulose (wood constituent) has

been observed and gas treatments are susceptible to desorption. Additionally, gaseous reagents are not practical treatment agents for many conservation scenarios. Derivatives of ethylene diamine tetraacetic acid (EDTA) have shown promising results to sequester Fe^{3+} from timbers of the *Vasa* (Sandström et al., 2003, Almkvist and Persson, 2006, Berko et al., 2009). However this is a costly and time-consuming process which is not always possible on artefacts that have already been treated for consolidation. Given the precedence with the artefacts and other ships, acid degradation will be a major challenge in the future and will become widespread if unchecked (Sandström et al., 2005, Schofield et al., 2011).

It is also important to note that conservators and scientists are dealing with varying scenarios where an acid treatment is required, (1) when first excavated (wet), (2) during a conservation plan (wet) and (3) after the initial conservation is complete (dry) These scenarios require different approaches in terms of the treatment application method, as penetration and reaction rates may vary due to an altered state of the wood.

Here, a mild chemical treatment plan is described based on aqueous suspensions of alkaline earth carbonate, and applied to dried and PEG treated wooden artefacts from the *Mary Rose* (conservation scenario 3 listed above). The efficacy of the treatment has been followed using S K-edge XAS spectroscopy. Three alkaline earth carbonates (Sr, Ba and Ca) have been evaluated for their ability to neutralize the endogenous acid produced from sulfur compounds present in the wood.

MATERIALS AND METHODS

Preparation of wood samples

The *Mary Rose* arrow shaft fragment samples for treatment were obtained from the *Mary Rose* Trust, Portsmouth, UK. Arrow shaft specimen (approximately 6 cm long and 0.7 cm in diameter), previously treated with 70% polyethylene glycol (PEG) 6000 and air-dried, was cut in half along the shaft and then into 1.5 cm sections. The wood of the arrow shaft artefact was soft, porous, and externally uniform in color and texture (Figure 1).

Carbonate treatment

The BaCO_3 , SrCO_3 and CaCO_3 tested were ground using an agate mortar and pestle for several minutes to reduce agglomerations. The reagents were then prepared for treatment by suspension in water, which was sonicated immediately prior to use. The saturated solution was applied to the samples using a brush applicator. The method was applied every two hours over eight hours each day for 4 days prior to the XAS measurements. A total of four samples were prepared; one untreated for control purposes, and three samples treated with the aqueous carbonate suspension via brush application.

Sulfur K-edge X-ray Absorption

S K-edge XAS data were collected on the 20-pole 2T wiggler unfocussed beamline 4-3 under standard ring operating conditions of 3 GeV and ~300 mA ring current. A Si(111)

double crystal monochromator was used for energy selection. Upstream optics include a Ni-coated vertically collimating and harmonic rejection mirror. Room temperature measurements were obtained in fluorescence mode using a Lytle detector and a 4-element Vortex detector. A 2 mm x 8 mm beam was used for the measurements. Specimens were attached to a sample paddle using an Al-spacer and S-free Kapton tape and were measured under He gas. Energy calibration was achieved using the first peak of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ fixed at 2472.02 eV, which was run at intervals between sample scans.

The program SIXpack was used for data processing and analysis (Webb, 2005). A second-order polynomial was fit to the pre-edge region and subtracted from the entire spectrum as background. The data were normalized by fitting a polynomial to the post-edge and fixing the flat post-edge region at unit intensity. Least squared fitting was performed on the S K-edge XAS data of the treated and untreated arrow shaft artefact using a library of sulfur XAS spectra of standard model compounds using SIXpack. Model compounds BaSO_4 and CaSO_4 were measured as described above. To avoid self-absorption, the BaSO_4 and CaSO_4 samples were prepared as a dilute liquid mull by grinding with mineral oil, which was spread on the sulfur free Kapton tape as a thin layer. The standard data files were processed using the same protocol as the *Mary Rose* dataset to minimize normalization and background subtraction related errors.

The goodness of fit was determined by reduced chi-squared error, eq. 1.

$$\chi_{red}^2 = \frac{\chi^2}{\nu} = \frac{1}{\nu} \sum_{i=1}^N \frac{(y_f - y_i)^2}{\sigma_i^2} \quad (1)$$

where, y_f is the theoretical value from fit, y_i is the observed value from data, N is the number of data points, v is the degrees of freedom and σ^2 is the variance. Both the error value and a visual impression of the fit were taken into consideration, when determining the goodness of fit.

The systematic error of the fit and the error in each component were determined using methods previously established (Frank et al., 2012) using S K-edge XAS, eq. 2

$$d_{sys} = \sqrt{(1 - S)^2} \quad (2)$$

where d_{sys} is the systematic error and S is the sum of the fractions of the components in the fit prior to normalization. The error of each component can then be derived from this value by using the relative error.

RESULTS

The normalized S K-edge XAS spectrum for the untreated *Mary Rose* sample is presented in Figure 2A. The spectrum consists of several rich transitions between 2470 and 2510 eV. To lower energy (between 2470 to 2485 eV), are the dipole allowed transitions from the S 1s level to bound molecular levels containing S 3p character (Glaser et al., 2000, Sarangi et al., 2008). To higher energy (between 2485 and 2510 eV) are multiple scattering features that arise due to the local repeating structure around the absorbing S atom (*vide infra*). A visual inspection of the low energy region shows two sets of features, with respective peak maxima at ~2473 eV and ~2482 eV. The feature at ~2473 eV is representative of low-

valent sulfur compounds, such as sulfides, elemental sulfur, thiols and thioethers (oxidation state between -2 to 0). The intense feature at ~2482 eV is representative of high-valent sulfur compounds, in particular sulfates and sulfate esters (oxidation state +6). This distribution is in agreement with previous reports of sulfur present in the wood of recovered marine artefacts (Sandström et al., 2005, Schofield et al., 2011).

The S K-edge XAS data for the untreated *Mary Rose* arrow shaft sample is qualitatively similar to data from other artefacts and core samples from the *Mary Rose*. However, the intensity ratios indicated quantitative differences in the type and amount of various sulfur species. The S K-edge XAS spectra for the untreated *Mary Rose* were subjected to least-squares fitting analysis using a library of standards used in previous studies on the *Mary Rose* (Schofield et al., 2011). This library was supplemented with data on additional standards, which were deemed necessary during the course of the fit, but no standard was used without adequate justification for its presence. At the end a sub-library of ten standards were used to fit the *Mary Rose* data. The low-valent standards included cysteine, methionine, elemental sulfur, cystine and pyrite (FeS_2) and the high valent standards included anhydrous ferrous sulfate, natrojarosite [$\text{Na}(\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6)$], and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)(ESRF). Two intermediate oxidation state standards, methionine sulfoxide and cysteine sulfonate were also included, which are common oxidation products of methionine and cysteine (Conte and Carroll, 2012, Stadtman et al., 2005). The compounds were statistically prevalent and visually noticeable in the *Mary Rose* XAS spectrum, as seen by the peak at 2476 eV (methionine sulfoxide) and the asymmetry of the sulfate peak (lower energy shoulder due to the presence of cysteine sulfonate). Importantly, all standards

used here have been previously reported in marine and lacustrine archaeological wood artefacts.

The high-energy, multiple scattering region of the S K-edge XAS spectrum is typically omitted from least-squares fitting analysis. As such, the spectral features in this region are represented by the sulfate standard chosen for the analysis. Recently, we showed that this region holds valuable information about the sulfate counterion, which leads to a unique spectral shape for a particular salt (Schofield et al., 2011). This spectral shape arises due to strong contribution of long-range multiple scattering effects near the post-edge region, where the photoelectron wavelength is long and the cross-section is high (Benfatto and Della Longa, 2001). Thus, the multiple-scattering feature resulting from Na^+ , K^+ , Ca^{2+} , Ba^{2+} , Sr^{2+} , Fe^{2+} , and Fe^{3+} sulfates are uniquely different and the least squares fitting method can accurately distinguish between these counterions, provided fits are performed over the adequate energy region. Therefore, the least squares fit were performed from 2460 to 2510 eV, which covers well beyond the entire sulfur K-edge XANES region.

The least squares fitting results for the untreated *Mary Rose* arrow shaft sample are presented in Figure 2A and Table 1. The fit reveals that the sample consists of exogenous sulfide in the form of pyrite, endogenous low-valent sulfur such as cysteine/methionine and cysteine, endogenous oxidized sulfonates and sulfoxides and a significant fraction of sulfates. A majority of the sulfate is in the form of gypsum, while a minority is as anhydrous ferrous sulfate or natrojarosite, which are both iron sulfates. These iron sulfates likely form when iron from structural fittings (e.g., nails) dissolve in water and becomes

incorporated into the surrounding wood. They can also be formed by the oxidation of low valent iron sulfides (pyrite) present on the wood surface.

Figure 2B shows the normalized S K-edge XAS data of the *Mary Rose* samples treated with aqueous suspensions of the neutralizing agents BaCO_3 , SrCO_3 and CaCO_3 . Figure 2B shows that all the treated samples have similar sulfur species in the low- and high-energy region, but the sulfur speciation in the multiple scattering region varies dramatically. This indicates the presence of alkaline earth metal sulfates formed due to the treatment process. Least squares fitting analysis (fits shown in Figure 3) was performed on all datasets using the same standards as used for the untreated *Mary Rose* sample, with one exception. In each sample, a standard of the corresponding alkaline earth metal sulfate was included. The results are presented in Table 1 and reveal qualitatively similar results with each reagent. First, no pyrite is observed in any of the treated samples, whereas the untreated sample required the inclusion of a pyrite component to achieve an acceptable fit. Second, some of the other reduced sulfur species such as cysteine and methionine are oxidized to cystine and cysteic acid and methionine sulfoxide, respectively. Finally, as visually indicated, the corresponding alkaline earth metal sulfate is present in significant quantities (Table 1).

ANALYSIS

Previous studies of *Mary Rose* core samples and artefacts amply demonstrate the inhomogeneity in the relative composition of sulfur species. Not only does the composition change with depth (as the O_2 exposure decreases), but a wide variability is observed in the

reduced to oxidized sulfur ratio between two closely associated regions in some artefacts. Least-squared fitting results show not only that there is a significantly larger amount of oxidized sulfur in the arrow shaft samples, but also that the predominant sulfate component found in the previous study was natrojarosite whereas the predominant sulfate component in the arrow shaft samples is gypsum. This difference can be attributed to the disparate micro-environments (such as the presence of catalytically active metal ions) the artefacts were subjected to whilst submerged.

A close inspection of Figure 3 shows that the relative intensities of the sulfate and reduced sulfur peaks vary between the arrow shaft samples prepared for the S K-edge measurements. Given the compositional variability in the *Mary Rose* artefacts discussed above, it is important to show that the treatment-induced modifications including removal of pyrite, decrease of low-valent sulfur, and formation of corresponding alkaline earth metal sulfate in arrow shaft samples were not an artefact of sample variability. To achieve this, post S K-edge XAS measurement, the previously untreated standard sample (from Figure 2A) was treated with the aqueous CaCO_3 suspension following standard protocol. The S K-edge XAS spectra for this untreated and subsequently treated sample are presented in Figure 4 and the expanded low-valent sulfur region is shown in the inset. The inset reveals that the leading edge of the untreated data shifts to higher energy post treatment. This is consistent with a diminished pyrite fraction, since pyrite contributes strongly in that region. Least-squares fitting results confirmed this assessment: all the pyrite was removed upon treatment while the CaSO_4 XAS was required to obtain a good fit. These results confirm that removal of pyrite, the decrease of low-valent sulfur and appearance of alkaline

earth metal sulfates observed in the XAS of the treated samples is the result of neutralization treatment and cannot be attributed to sample variability.

The alkaline earth carbonates were chosen as they are mild bases and the sulfate neutralization products are of low solubility. Carbonates have been shown to react with problematic sulfur associated with archaeological wood in previous studies (Schofield et al., 2011). This treatment can both neutralize acid from sulfur compounds and immobilize sulfate to prevent re-acidification. Note that the treatments used a concentrated solution/suspension of reagents for optimum results in a short amount of time. The amount of reagent used in the treatment protocol might be impractical in a museum environment. Nonetheless, the principle with a lower concentration of reagent would remain the same, and deacidification would be achieved, albeit at a slower rate.

Low-valent mineralized sulfur species, such as pyrite (FeS_2), can form detrimental acids in archaeological artefacts (Fors, 2008, Fors et al., 2012, Fors and Sandström, 2006). Pyrite is deposited onto the surface by anaerobic bacteria, which metabolize sulfur, and diffuse into the wood. These bacteria sequester sulfur compounds from the surrounding sea-water reducing them into low-valent sulfur. This reactive, low-valent sulfur can then combine with the relatively high concentrations of iron present in the water, which accumulates from the rusting and dissociation of various metal artefacts on the *Mary Rose*, forming FeS_2 (pyrite) (Passier et al., 1999). Underwater and under anoxic conditions, the FeS_2 particles stay dormant. As soon as the wet artefact is exposed to oxygen, the slow chemical

transformation of pyrite to FeSO_4 and H^+ begins, slowly acidifying and degrading the wood structure (see reactions below) (Jerz and Rimstidt, 2004).

The FeSO_4 is eventually oxidized to $\text{Fe}_2(\text{SO}_4)_3$. Other low-valent sulfur species that are inherently present in wood (such as cysteine and methionine) can be oxidized to higher valent forms (cystine and methionine sulfoxide) in the presence of Fe^{3+} ions (abundant in some artefacts) (Jameson et al., 1988, El-Brashy and Al-Ghannam, 1995). Subsequently, cysteine bound to the wood matrix can be oxidized to its higher valent sulfonic acid, analogous to cysteic acid, (Bagiyan et al., 2003) which is a potent acid and can also lead to degradation of the wood structure. The degradation of wood fibers (cellulose) (Sandu, 2003) can be catalyzed by the presence of iron ions via the formation of hydroxyl radicals (Lindfors et al., 2008).

As shown in Table 1, least-squares fitting results of the control sample from the *Mary Rose* reveal the presence of pyrite. S K-edge XAS data of the treated samples reveal the absence of pyrite following treatment with any of the reagents and using either method. Thus, the problem of pyrite is successfully resolved using the tested reagents. The least-squares fitting analysis shows that pyrite is oxidized to iron sulfate, the latter of which subsequently forms insoluble alkaline earth metal sulfates. It is important to note here that the alkaline

earth carbonates are themselves not oxidizing agents, but enhance the slow air oxidation of pyrite. Interestingly, although pyrite oxidation is a slow surface phenomenon, (Rimstidt and Vaughan, 2003, Chandra and Gerson, 2010) the treatment on the *Mary Rose* artefact resulted in the removal of quantifiable pyrite within four days. This indicates that the wood-deposited pyrite was most likely morphologically different from geological pyrite consistent with the pyrite nanoparticles shown in earlier studies (Wetherall et al., 2008, Sandström et al., 2005). A porous morphology and smaller particle size would result in much faster oxidation than geological pyrite. This, coupled with the mild basicity of the reagents accelerated the air oxidation of pyrite. Loss of pyrite is concomitant with an increase in total sulfate and formation of alkaline earth metal sulfates. In the case of BaCO_3 and SrCO_3 treatments, the endogenous gypsum is converted to BaSO_4 and SrSO_4 , respectively, consistent with the lower solubility of BaSO_4 and SrSO_4 . However the solubility of gypsum and CaSO_4 are similar (~ 0.205 g/100 g H_2O), which results in an equilibrium mixture of gypsum and CaSO_4 in the CaCO_3 treated wood (Table 1). The amount of cysteine sulfonate increases in the treated samples. This is possibly due to the oxidation of cysteine in the presence of free Fe^{3+} , resulting from the oxidation of pyrite mentioned above.

These results show that the carbonate salts are successful in dissociating, neutralizing acid and oxidizing pyrite to neutral, insoluble sulfate salts. It is important to note that the solubility of the carbonates used for the treatment is very low (ppm level in water) and the acid present on the wood surface reacts with the suspended carbonate particles (mediated

by the presence of water). The accelerated air oxidation of pyrite generates further acid, consuming the basic carbonate salts and driving the neutralization.

DISCUSSION

S K-edge XAS was used to study acid-neutralization treatment of wooden artefacts from the *Mary Rose*. Three alkaline earth metal carbonates were tested for their acid-neutralization potency; BaCO_3 , CaCO_3 and SrCO_3 . Interestingly, these reagents also have a far-reaching impact. They accelerate the air oxidation of the dangerous pyrite, which poses a sustained threat to the wooden artefacts as it slowly gets oxidized converting to sulfates and free acid. This reaction can proceed long after an acid neutralization treatment has been performed. Fast oxidation of pyrite to free sulfates and iron oxides has been observed in coal desulfurization, for which NaOH has been used as a base to accelerate pyrite surface oxidation (Masciantonio, 1965). In the case of archaeological artefacts, the accelerated oxidation of pyrite to Fe^{2+} , SO_4^{2-} and H^+ , solubilizes pyrite and removes this slow acid producer. The carbonate reagent can then neutralize the acid generated in the process.

BaCO_3 and SrCO_3 are more toxic than CaCO_3 (although the final sulfate products are less soluble as they do not react to readily produce the toxic cations) and BaCO_3 can be harmful to human health. In a practical conservation scenario, the extra precaution and screening required for BaCO_3 handling and treatment would make it less ideal as a treatment agent. Thus, CaCO_3 is the ideal reagent for treatment, not only because of its cost effectiveness, but also for its low environmental impact.

In the artefacts used within this study the penetrated depth is unknown. Monitoring penetration and reaction rates as a function of depth of treatments in important archaeological artefacts where destruction of the item is not possible is challenging. Added to the challenge is the difficulty in obtaining a control sample due to the variation of the wood properties and contents on a micro level. This study shows that this treatment can currently be used as a reactive measure to identified problems. Applying the treatment in a preventative capacity will take further investigations, potentially on simulated samples to ensure consistency.

Although the methodology developed here may be used for various threatened artefacts, it would be judicious to apply the treatment plan after proper research on the system, the extent of acid damage and the proportion of the damage attributed to sulfur acid. It is important to note that unless mechanically removed (by washing, etc), this treatment deposits a thin layer of neutral sulfate salt on the surface, which may or may not be problematic for silk or paper artefacts.

CONCLUSIONS

The treatment developed and tested in this study is applicable not only to the artefacts found within the *Mary Rose* or to other waterlogged wood artefacts, but to the overarching problem of sulfur acid degradation of natural heritage artefacts worldwide. Such degradation has been observed in wood, silk, rubber and paper objects, causing widespread

changes in color, texture or overall integrity. Where possible, an aqueous solution of CaCO_3 would lead to very little stress of the artefact material and upon drying will cause minimal or no observable alteration to the artefact, making it ideal for a wide range of applications.

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FIGURE CAPTIONS

Figure 1. (A) The *Mary Rose*. (B) A wooden artefact from the *Mary Rose*. The regions labeled a and b and surrounding areas show visible damage due to formation of the yellowish precipitate. (C) Arrow shaft specimen (6 cm x 0.7 cm, approx.) from the *Mary Rose*. (D) Arrow shaft samples (1.5 cm x 0.7 cm, approx.) mounted on S K-edge XAS measurement paddles: left - untreated, middle - SrCO_3 aqueous treatment and right- CaCO_3 aqueous treatment. The samples show no change in color or texture post treatment.

Figure 2. (A) S K-edge XAS spectrum of untreated arrow shaft (light blue). The LCA fit of the untreated *Mary Rose* sample (dashed black). The inset details the component used in the LCA fit. (B) A comparison of the S K-edge XAS spectra of the aqueous treatments of the arrow shaft. Untreated (light blue), BaCO_3 (red), SrCO_3 (purple) and CaCO_3 (green). The inset shows expanded post-edge region demonstrating the rich spectral shape.

Figure 3. S K-edge XAS data and their corresponding LCA fits for the three aqueous treatments. Data (solid line), Fit (dashed line) Top: BaCO_3 treatment. Middle: SrCO_3 treatment. Bottom: CaCO_3 treatment. The inset details the component used in the LCA fit.

Figure 4. Comparison of control *Mary Rose* sample before and after treatment with aqueous CaCO_3 . Left inset highlights the difference in the expanded reduced sulfur region. Right inset details the LCA fit components of the aqueous CaCO_3 treatment.

Table 1. Least Squares Fitting Data for S k-edge XANES of *Mary Rose* samples

Figure 1

Figure 2

Figure 3

Figure 4