Abstract. The oxidation of sulfur in marine archaeological timbers under museum storage conditions is a recently identified problem, particularly for major artefacts such as historic ships excavated from the seabed. Recent work on the Vasa has stressed the role of iron in catalysing the oxidative degradation of the wood cellulose and the polyethylene glycols used to restore mechanical integrity to the timbers. In developing new treatment protocols for the long term preservation of Henry VIII of England’s flagship, the Mary Rose, we are investigating the potential of chelating agents to neutralise and remove the iron products from the ships timbers. We have explored the use of aqueous solutions of chelating agents of calcium phytate, ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) and ammonium citrate to extract the iron compounds. All of these solutions exhibit some level of iron removal; however the key is to find the most effective concentration at pH of around 7 of the reagent solution, to minimise the treatment time and find the most cost-effective treatment for the whole of the Mary Rose hull. Fe K-edge XAFS data from samples of Mary Rose timbers, before and after treatment by the chelating agents mentioned has been collected. The data collected provide valuable insights into the effectiveness of the treatment solutions.
Sulfur deposits have been discovered in timber artefacts from the *Mary Rose*, a flagship of Henry VIII which sank whilst engaging the French fleet a few miles off the Portsmouth harbour in 1545. It remained buried under water for 437 years until it was raised on October 11, 1982.

Large numbers of sulfur compounds exist naturally in the sea at different oxidation states and include hydrogen sulfide (H\textsubscript{2}S), pyrite (FeS\textsubscript{2}), sulfates (SO\textsubscript{4}\textsuperscript{2-}), sulfur dioxide (SO\textsubscript{2}) and elemental sulfur (S) \[1\]. Under anaerobic conditions sulfur reducing bacteria of the genus *Desulfovibrio* and *Desulfotomaculum* can turn reducible sulfur species into hydrogen sulfide by utilising them as terminal electron acceptors in their respiratory processes. In the process these sulfur containing ions are reduced to hydrogen sulfide. A simplified overall reaction is given below \[2\].

\[
2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-
\]

In the above reaction, CH\textsubscript{2}O represents organic matter, *i.e.* cellulose. In anaerobic conditions the stable forms of freely occurring sulfur species are elemental sulfur, hydrogen sulfur and where there is iron present, iron sulfide. These sulfur species can accumulate in the wood over time and once exposed to oxygen, rapidly oxidise to sulfates and eventually sulfuric acid. This process is thought to be catalysed by the presence of iron \[3\]. Iron readily binds with sulfur to form iron sulfide and can be oxidized in humid conditions to form iron sulfate and sulfuric acid \[4\].

\[2 \text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{FeSO}_4 + \text{H}_2\text{SO}_4\]

Analyses show the presence of various iron species present in *Mary Rose* timbers from corroding iron bolts and fastenings used in timber ship building. It is believed that the iron (II) sulfide species is primarily responsible for the production of sulfuric acid \[5\]. Iron (II) can also catalyze the breakdown of cellulose via a series of Pseudo-Fenton oxidation processes.

\[
\begin{align*}
\text{Fe}^{2+} + \text{O}_2 + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \text{HOO}^– \\
\text{Fe}^{3+} + \text{HOO}^– + \text{H}^+ & \rightarrow \text{H}_2\text{O}_2 \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^– \\
\text{OH}^– + \text{Cellulose} & \rightarrow \text{depolymerisation}
\end{align*}
\]

The use of calcium phytate as a chelating agent in treatment of cellulose based manuscripts written with iron gall ink is now established \[6\]. This makes calcium phytate along with DTPA (due its low toxicity and strong iron chelating properties) favoured chelators in this project.

### 2. Experimental

Two pieces of recently recovered timber (MR03-T0022 and MRT04) from the *Mary Rose* were cut into 6cm long sections. EXAFS was collected at the Fe K-edge from these before and after one month’s treatment with a variety of chelating agents. Additionally a third piece (MR03-0074) which was very heavily discoloured with orange iron corrosion products was also measured and treated. These have been labeled in the figures with a sample reference number: (1) MR03-T0022, treated with 0.1M calcium phytate; (2) MR03-T0022, treated with 0.1M DTPA; (3) MR03-T0022, treated with 0.1M EDTA; (4) MR03-T0022, treated with 0.05M EDTA; (5) MR03-T0022, untreated only; (6) MRT04, treated with 0.05M calcium phytate; (7) MRT04, treated with 0.1M ammonium citrate; (8) MR03-0074 treated with 0.05M DTPA. The wood samples had been kept in a moist condition since excavation and were measured in air and hydrated, wrapping them in thin polymer sheet to prevent drying.

Data were collected on station 16.5 at the Daresbury SRS using a Si220 monochromator and 30-element SSD fluorescence detector and measurements were made at room temperature. Where possible the intensity of the incident beam and the detection geometry were kept constant to allow a quantitative comparison of the Fe content from the edge step. Data analysis used Excalib and Exspline for calibration, summing and background subtraction, whilst Excurv98 was used for *ab initio* calculation of the phase-shift corrections and for curve-fitting analysis of EXAFS data \[7\]. Between 4 and 8 scans were collected for each sample. Edge calibration was done with reference to an iron foil transmission measurement.
3. Results

Figure 1 shows the Fe K-edge XANES and EXAFS data collected from the 8 wood samples prior to treatment, whilst Figure 2 shows the corresponding data after treatment for 1 month. All the XANES spectra show a weak, single peaked, pre-edge feature (A) which can be related to a slightly distorted octahedral symmetry around the central iron atom. This octahedral geometry is seen in the EXAFS as producing a primary oscillation corresponding to an Fe-O shell at about 2 Å. This shell can be split into 2 subshells, each of 3 oxygens and with bond lengths of 1.934 Å – 1.979 Å and 2.007 Å – 2.092 Å, with errors of ±0.02 Å for each shell fitted. The expected octahedral symmetry from the pre-edge feature was used to scale the EXAFS to take account of self-absorption effects in the measurements.

The edge position for most of the samples lies in the range 7124.1 eV – 7125.8 eV, which equates to an Fe$^{3+}$ valency. The exceptions to this are the untreated samples (1), (6), (7) and both treated and untreated sample (8). These have edges in the range 7120.3 eV – 7122.7 eV which is closer to an Fe$^{2+}$ state. Similar shifts in position are seen in the pre-edge feature. The EXAFS of these samples is also different and shows a peak in the transform at a bond length of ~3 Å. This can be fitted by reference to model compound data for goethite (FeOOH – sample (9) in Figure 2), which has a Fe-Fe shell at 3.04 Å and also an additional one at 3.40 Å, although pure goethite is Fe$^{3+}$. These samples exhibited heavy orange discoloration from iron corrosion products, particularly sample (8). This Fe–Fe shell was reduced after treatment with calcium phytate, but not obviously by ammonium citrate or DTPA. It did not appear to be present in the samples for treatment with EDTA. Sample (8) shows the least alteration after soaking in 0.05 M DTPA, with approximately 50% reduction in iron content whereas other less contaminated samples had relative iron removal of up to approximately 90%. However, the heavy initial contamination indicates that a longer treatment time might be necessary in this case.

Two of the samples treated with DTPA and ammonium citrate show additional features in the EXAFS and both exhibit a pronounced feature at the absorption edge (C). Without a good a priori model to fit to the EXAFS, an understanding of the chemical structure responsible remains uncertain. However, it does suggest an Fe-O shell at approximately 2.86 Å with a further shell at 4.26 Å. Refinement gives a slight preference for this to be an Fe-O shell of high occupancy (9±3) rather than an Fe-Fe shell of lower occupancy (1.5±0.8). There is a suggestion that this structure is also present in...
the treated (3) and (4) and untreated (4) and (5) samples, indicating that it may be a second iron speciation within untreated timber and that the effect of the DTPA and ammonium citrate has been to preferentially remove other iron chemicals. These samples also show a broadening of the principle XANES line with a post-edge ‘shoulder’ at (C).

Figure 2 : Fe K-edge XANES and EXAFS of the same samples as shown in Figure 1 after treatment by a number of different chelating agents. Dashed line at 7125eV indicates the position of the Fe$^{3+}$ edge. Sample (9) is model compound goethite data. Solid lines are experimental data with the EXAFS modelling shown dashed.

Samples treated with calcium phytate ((1) and (6)) show the least structure, with only the primary Fe-O octahedra present in the EXAFS, they also exhibit a distinct feature (B) in the XANES.

Untreated timbers from the Mary Rose contain iron of Fe$^{2+}$ and Fe$^{3+}$ oxidation states depending on their location and iron corrosion content. Due to variations in initial iron speciation in different timbers, direct comparison between different chelating agents is not straightforward. However, removal rates of between 50% and 90% are observed depending on initial levels of iron content and all chelating agents leave predominately Fe$^{3+}$. Timbers containing appreciable iron corrosion show the most obvious alteration to iron chemical speciation, with the loss of the Fe–Fe bond at ~3Å.

The authors acknowledge the assistance of Mr. Robert Bilsborrow in help with the experiments.

References
[1] Greenwood N, Earnshaw A 1997 “Chemistry of the elements” [Butterworth Heinemann, Oxford] 2nd ed, 15 647.
[2] Pallud C and Van Cappellen P 2006. Geochim. et Cosmochim. Acta, 70 (5), 1148
[3] Lowson R T 1982. Chem. Rev. 82 461.
[4] Moses C O, Nordstrom D K, Herman J S. and Mills A L 1987. Geochim. Cosmochim. Acta, 51 1561.
[5] Sandstrom M, Jalilehvand F, Damien E, Fors Y, Gelius U, Jones M and Salome’ M 2005 Proc. Nat. Acad. Sci. U. S. A. 102 14165.
[6] Selih, V.D., Strlic, M., Kolar, J., Pihlar, B., 2007 Pol. Degrad.Stab., 92 1471
[7] Binsted N, Campbell J W, Gurman S J, Stephenson P C, SERC Daresbury Program Library, Daresbury Laboratory, Warrington, Cheshire WA4 4AD, UK, 1992.