



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Prevention of sulfuric acid production in the timbers of Henry VIII's warship, the Mary Rose	<b>Experiment number:</b> EC-94
<b>Beamline:</b>	<b>Date of experiment:</b> from: 13 Dec 2006 to: 18 Dec 2006	<b>Date of report:</b> 11/5/07
<b>Shifts:</b>	<b>Local contact(s):</b> Muriel Salomen	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>Dr A.D.Smith – CCLRC Daresbury Laboratory</b> <b>Dr A.M.Jones – Mary Rose Trust, Portsmouth</b> <b>Dr T.Skinner – National Museums of Scotland, Edinburgh</b>		

## Report:

The aim of the experiment was to investigate the sulfur and iron speciation in waterlogged ships timbers from the Tudor warship, the *Mary Rose*, and to study the possible influence of iron chelating treatments.

These were our first experiments exploiting both S and Fe K-edges using ID21 and needed care in scheduling our measurements to allow for the extensive changeover time between these two edges. We also needed to consider how to best study before and after treatments, ideally this should be on the same specimen so that we were certain that any changes observed were due to the treatments and did not merely arise from natural variations in such a natural, heterogeneous material. In practice this proved more problematic than we had hoped for. Whilst it is practicable to keep the same sample mounted in the sample holder for the change from S to Fe edge, removing the thin fragment of sample to soak in the treatment solution and then successfully remount proved difficult. Additional uncertainties arising from this approach concern whether the soaking time available during the course of a single experiment is sufficient to allow any significant alteration. The types of measurement we collected here do however have the potential to show us how proposed treatment protocols interact with the iron and sulfur species contained within the wood cell structure. Our experiences in this run have proved useful in devising a revised future strategy to sample timbers at different stages of possible treatment protocols, whilst maintaining consistency of timber type and initial environment.

Nevertheless, we were successful in collecting both S and Fe K-edge valency information from the same area of several samples. We believe that this is the first time that this has been done for this type of problem and the first time that valence maps at the Fe K-edge have been collected. This is proving very insightful in understanding the interaction between iron and sulfur speciations in the wood timbers.

There is a wide energy shift at the sulfur K-edge separating the many possible sulfur valence states (from -2 to +6). At the Fe k-edge, there is less of a distinct resonant peak, but a clear shift is noticeable between Fe<sup>2+</sup> and Fe<sup>3+</sup> species. It is therefore possible to select a unique energy on the rising edge of the Fe<sup>2+</sup> K-edge, but which is still below the onset of the Fe<sup>3+</sup> edge, so that only the contribution from iron in the 2+ state is highlighted. This was then compared to a second map recorded well above the Fe K-edge which then shows both the Fe<sup>2+</sup> and the Fe<sup>3+</sup> contributions.

Figure 1 shows a series of valence state maps at sulfur and iron K-edges showing the distribution of key sulfur and iron phases within the wood cell structure. The sulfur maps show the presence of some reduced sulfur grains (2469.7eV) and a more widespread distribution of a slightly oxidised organo-sulfur component (2472.1eV). This latter species can be seen to reside primarily in the mid-lamella regions of the

wood between adjacent cells. This sulfur distribution compares well with that previously obtained by Sandström *et al* [1], although it should be noted that the energies we report here have been recalibrated to allow comparison with other SR experiments on bulk samples performed elsewhere. The bright sulfide grains seen at the sulfur K-edge correlate with an Fe<sup>2+</sup> species seen at 7120eV, this confirms the presence of a number of iron sulfide grains within the wood cells. The difference between the two iron maps shows that the Fe<sup>3+</sup> phase exists within the inner cell wall structure. A comparison with the organo-sulfur map shows that this iron is not well correlated with sulfur.

Figure 2 shows sample spectra obtained from various locations within the wood cell structure using the X-ray microscope. These show that the sulfide grains have a S K-edge maxima at 2469.5eV, which we interpret as having a sulfur valency equal to -1.3[2]. The corresponding Fe spectra show some similarity to that of pyrite or pyrrhotite, but with some noticeable differences. The valency is +2, however the presence of a strong pre-edge peak and shifts in the position of the major maxima and minima above the edge suggest a more complex species than a pure iron sulfide. We have yet to identify what this is.

The sulfur species in the mid-lamella regions has a maximum at 2472.0eV, equivalent to a sulfur valency of +0.2. The Fe K-edge spectra in the inner cell walls matches well to the key features in goethite. From this we can conclude that the wood cells can contain a number of iron sulfide grains, but that the majority of the iron species is contained within the cell walls, probably in a hydroxylated iron oxide form with the majority of the sulfur bound in a slightly oxidised form and largely within the mid-lamella.

As a result of the experiment in this beamtime, we have been successful in understanding more of the role that iron apparently plays in the oxidation of sulfur in marine archaeological timbers. Our measurements on proposed treatment protocols were less fruitful, but provided valuable insights into improvements in our experimental methods for future studies on this aspect. Some of the results we have obtained are being combined with other data in a paper we are currently submitting to J.Arch.Sci. [3].

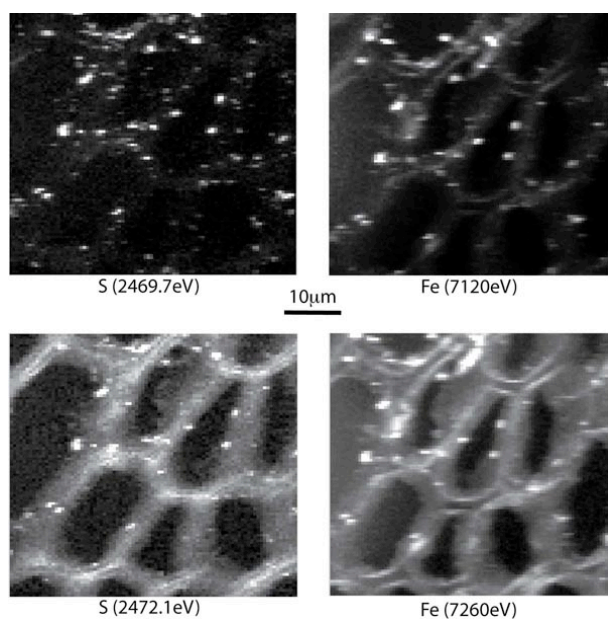


Figure 0 : Valence state maps at the S and Fe K-edges of a wood section from the proximity of a nail hole.

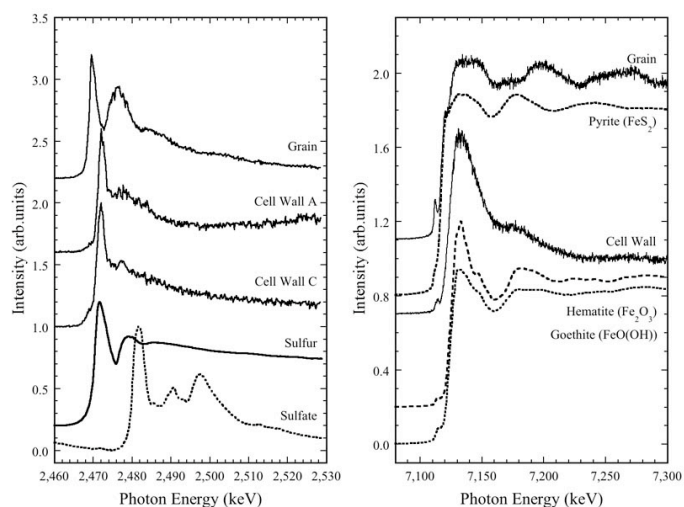


Figure 2 : Sulfur and iron K-edge XANES obtained from several typical locations in the wood cell structure, combined with reference spectra.

## References

- [1] M.Sandström, F.Jalilehvand, E.Damian, Y.Fors, U.Gelius, M.Jones, M.Salome. (2005) "Sulfur accumulation in the timbers of King Henry VIII's warship Mary Rose: A pathway in the sulfur cycle of conservation concern" *PNAS*.**102** pp.14165–14170
- [2] J.Pietzel, J.Thieme, U.Neuhausler, J.Susini, I.Kogel-Knabner (2003) "Speciation of sulphur in soils and soil particles by X-ray spectromicroscopy. *Eur.J.Soil.Sci.* **54** pp.423–433.
- [3] K.M.Wetherall, R.M.Moss, A.M.Jones, A.D.Smith, T. Skinner, D.M.Pickup, S.W.Goatham, A.V.Chadwick, R.J.Newport. (2007) "Sulfur and iron speciation in recently recovered timbers of the Mary Rose revealed via X-ray absorption spectroscopy" *J.Arch.Sci.* (submitted)