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ESRF

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.

ESRF	**Experiment title:** THE STABILITY OF REDUCED SULFUR SPECIES IN WATERLOGGED ARCHAELOGICAL TIMBERS	**Experiment number**: **EC- 627**
Beamline: ID21	**Date of experiment**: from: 14/04/2010 to: 19/04/2010	**Date of report**: Jan 2011
Shifts: 15 shifts	**Local contact(s)**: Dr. Marine COTTE	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Prof. Alan Chadwick*, University of Kent

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Dr. Mark Jones*, The Mary Rose Trust

Report:

Aim of the experiment:

The aim of this proposal was to study the stability of reduced sulfur species in waterlogged archaeological wood. Characterising this is of crucial importance as these compounds have the capability to oxidise and form acidic substances which can destroy the wood. In this study we looked at timbers from Henry VIII's flagship the *Mary Rose*. The timbers were subjected to a vareity of conditions, such as increased oxygen levels, temperature and low concentration acidic solutions. The approach was to study wooden samples from the *Mary Rose* and monitor the sulfur compounds and wood components as a function of varied conditions such as acidity, increased oxygen levels and temperature.

Summary:

Due to the length of treatment times expected to be necessary to induce changes, samples were treated prior to arrival at the ESRF. This meant that consecutive slices of the same artefact had to be used as before and after samples. In a parallel study to this, the research team have been looking at sulfur speciation and distribution within some *Mary Rose* artefacts using sulfur k-edge x-ray absorption experiments at Stanford Synchrotron Radiation Laboratory Beamline 4-3. During July 2010, post experiements at ESRF in April 2010, we found some very shocking results. Heterogenity of these chemically complex archaeological materials has always been discussed and an issue but the lengthscale on which dramatic changes exist was unknown. We found that proportion changes of reduced to oxidised sulfur compounds could change from 1:3 to 3:1 respectively by moving as little as 1 mm in distance along the sample. From this information we had to come to the conclusion that information could not be extracted for treatments used on different slices of wood used as before and after scenarios. Unfortnately, this means that the data collected at ESRF can not answer

the questions we initially set out to answer. However, the time allocated was still extremely informative and key information was gained that is essential for the development of future experiments. It is clear that important data could be collected using these techniques once the problems highlighted have been addressed. We will use this report to demonstrated that whilst publishable data was not obtained, the time at ID21 significantly advanced our ability to use these techniques to get information in the future.

Experimental and results

SXM mapping and XANES:

Each sample was analysed using XANES on a bulk area of the sample to get an overall indication of the sulfur speciation. This was achieved by using an unfocused beam. From this we found that in the particular piece of *Mary Rose* timber that we were studying the majority of sulfur was reduced (shown by the peak at E = ~ 2473 eV in Figure 1) and little/no oxidised sulfur was present (would present itself by a peak at E = ~ 2482 eV in Figure 1). Following subjection to extreme environments, no significant change in the proportion of reduced to oxidised sulfur was observed. This would indicate that the treatments had little/no effect on the sulfur compounds and would suggest that longer/harsher treatments are required. To investigate this on a macro-scale, SXM images were taken on all samples at two energies. Firstly at 2483 eV to encompass all the sulfur present and then at 2475 eV. By taking this second map we are able to subtract the former from the latter and display a representation of the reduced to oxidised sulfur from the area scanned. This data for the *Mary Rose* untreated 'control' sample is shown in Figure 2. In accordance with the bulk XANES data, the majority of the sulfur is found to be reduced. Corresponding XANES data were collected at the points indicated within the SXM image to determine if any sulfur speciation variation existed. The XANES from points 1-5 shown in Figure 2 conclude that no variation was present in the different locations within the wood structure.

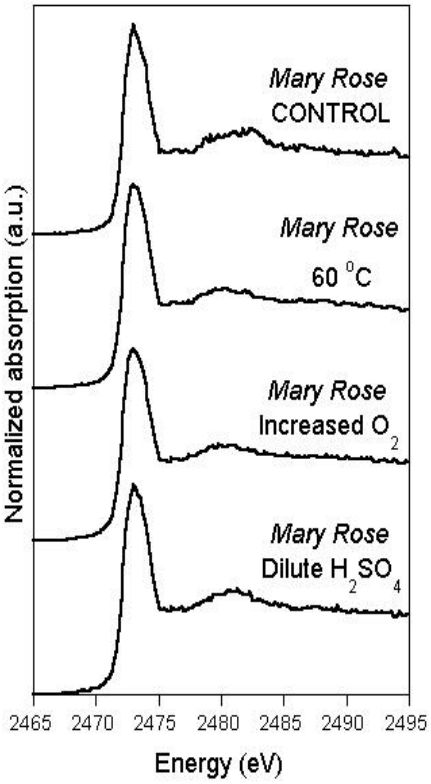

Figure 1: Bulk XANES of pre-treated and treated *Mary Rose* timbers

The same data was collected for the all the ttreated samples and the same data analysis completed. For each sample no variation in the suflur present was observed on a micro-scale and the majority of sulfur was in the reduced form. An example of this is shown in Figure 3 for *Mary Rose* timbers which were subjected to a dilute acidic solution.

Note: Data analysis was completed using PyMCA, SixPack and SMAK.

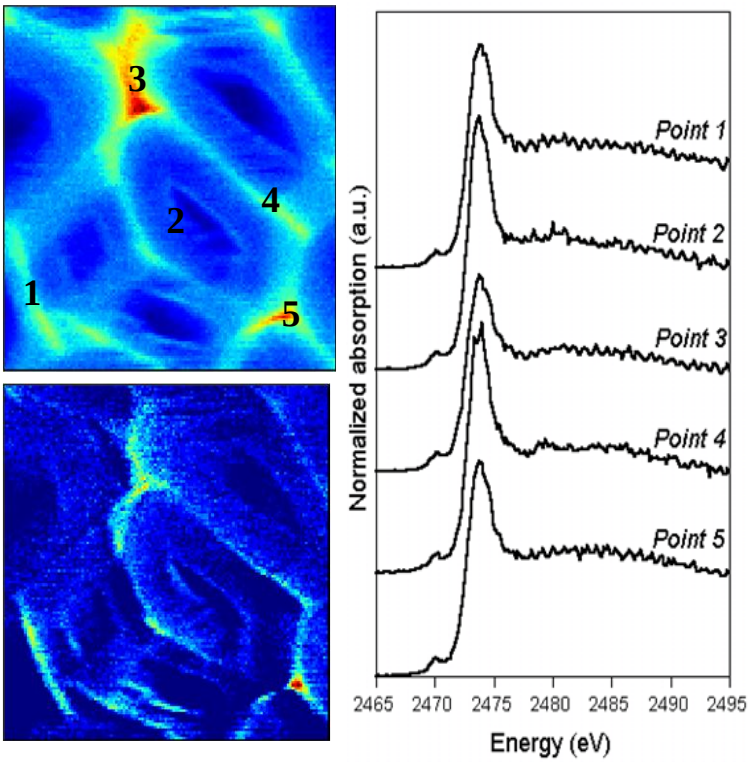

Figure 2: SXM image of reduced (top) and oxidised (bottom) sulfur and corresponding spot XANES analysis at locations indicated

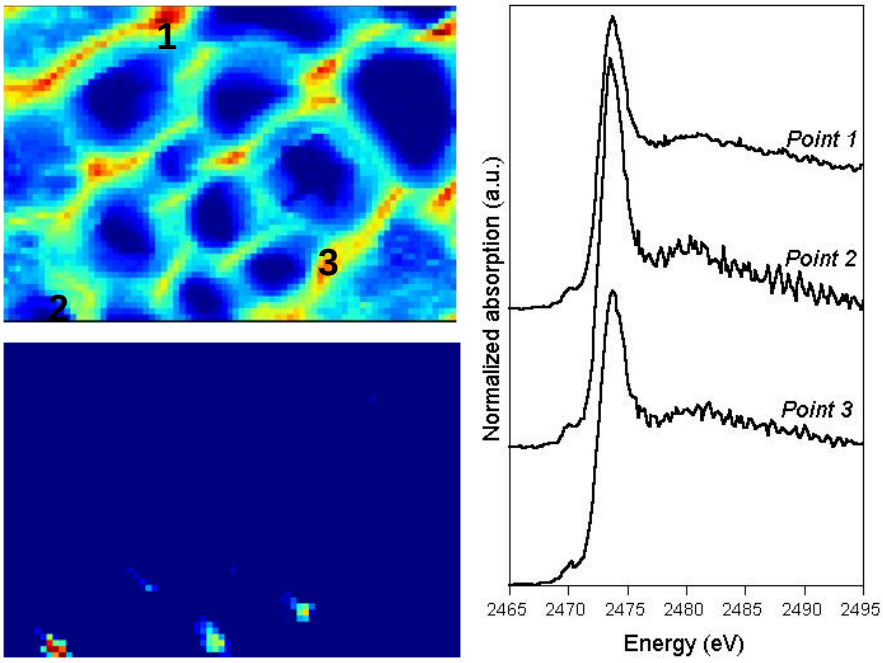

Figure 3: SXM image of reduced (top) and oxidised (bottom) sulfur and corresponding spot XANES analysis at locations indicated for *Mary Rose* wood treated with acidic solution

FT-IR mapping:

FT-IR maps were collected for the *Mary Rose* control sample, Fresh oak and the treated *Mary Rose* samples. Again bulk data was first analysed to become familar with analysing techniques and distinguish base characteristics of the samples. This was essential as the technique was new to the experimental team. The bulk FT-IR spectra can be seen in Figure 4 with the predominant peaks for wood structures labelled. A well established methodology for determining wood degradation is via analysing the ratio of lignin to cellulose. Cellulose is lost as wood degrades and therefore a corresponding increase in the lignin:cellulouse/hemi-cellulose is observed.
This pattern was observed when comparing *Mary Rose* oak to fresh oak as shown in Table 1, which shows the lignin as a ratio of each of the cellulose/hemicellulose peaks shown in Figure 4. In each case an increase is observed for the archaeological wood. However, when subjected to the treatments, the ratios's did not become larger as may have been expected. There are a few possible explanations for this. First of all, it may be that such a significant amount of cellulose was lost that the treatments started to attack the lignin. More likely, as it was not the exact same samples treated, they were degraded to

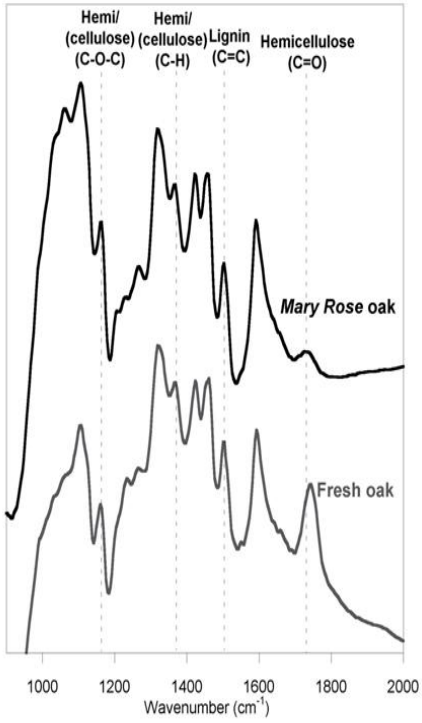

Figure 4: Bulk FT-IR spectra of *Mary rose* oak versus Fresh oak

Sample	I_{1505}/I_{1738}	I_{1505}/I_{1375}	I_{1505}/I_{1158}
Fresh Oak	0.378	2.129	1.101
Mary Rose	2.854	2.827	1.118
MR exposed to acidic solution	2.448	2.25	1.014
MR held at 60 °C	1.820	2.457	0.835
MR exposed to 75 % relative humidity	2.021	2.219	0.833
MR exposed to increased O_2 concentration	2.124	1.862	1.075

Table 1: Ratio's of lignin:cellulose/hemicellulose

varying amounts before treatment commenced.
As well as bulk measurements, FT-IR maps were collected on all of the samples. An example of this is shown in Figure 5 which shows the optical image of the area studied, and then the map of the lignin contribution and the cellulose contribution.

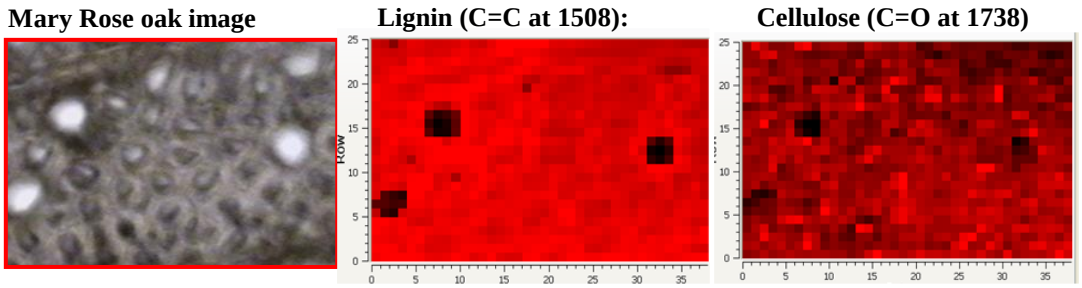

Figure 5: Optical image of *Mary Rose* oak with corresponding FT-IR image of lignin and cellulose

It is well known that the lignin is rich between the cell walls. As expected we see that the lignin contribution is much stronger than cellulose, indicating that this wood is degraded. However we are unable to clearly correlate the lignin location to the wood structure.

Implications for future work:

The main problem encountered was the realisation post-experiment that the sulfur distribution within the archaeological wood varied drastically on a micro-scale. This has not previously been documented and is currently the focus of a publication from the team which has been submitted to the Journal of Archaelogical Science for consideration. Also, it is possible that the treatments used were not harsh enough or left for long enough to invoke a change.

To combat this, future experiments (both SXM and FT-IR) would initially be carried out on Fresh oak impregnanted with sulfur compounds (a technique we are currently successfully using for other experiments). Therefore artificial ageing can be carried out on controlled samples which can be easily used as before and after scenarios, allowing long treatment times prior to arrival at the beamline. Determining the rate of sulfur/wood deterioriation will be an essential base for progressing to work on the archaeological wood. From this information we could develop harsher treatments which would allow us to treat the same archaeological wooden sample at the beamline (using the information gained from the fresh oak). Adopting this revised strategy, in light of the information gained during our previous beamtime, would allow us to start to answer our initial research question.