Institution: University of Kent		
Unit of Assessment: 8: Chemistry		
Title of case study: Mary Rose: Protecting Our Heritage through Chemistry		
Period when the underpinning research was undertaken: 2008-2018		
Details of staff conducting the underpinning research from the submitting unit:		
Name(s):	**Role(s) (e.g. job title):**	**Period(s) employed by submitting HEI:**
Professor Alan Chadwick	Professor of Chemistry Emeritus Professor of Chemistry	1970-2008 2009-present
Period when the claimed impact occurred: 2013-2020		
Is this case study continued from a case study submitted in 2014? No		

1. Summary of the impact (indicative maximum 100 words)

The Mary Rose Museum in Portsmouth's Historic Dockyard is one of the most celebrated heritage centres in the UK. Since the museum opened in 2013, scientists from the University of Kent and the Mary Rose Trust have used synchrotron-based approaches to annually monitor the ship's hull during a critical drying period. This has enabled chemical changes in the ship to be measured in real time, thus ensuring its integrity and informing conservation strategies. In 2016, a pioneering strontium carbonate nanoparticle procedure was developed to mitigate imminent and long-term threats of acid degradation, and this has been used to successfully treat some of the artefacts now on display in the museum. Preservation of the *Mary Rose* and the thousands of artefacts has been central to the museum's popularity, providing cultural, economic, and educational benefits. As a result, Kent's research is also being used to inform cultural heritage conservation projects internationally.

2. Underpinning research (indicative maximum 500 words)

The *Mary Rose* was King Henry VIII's flagship from 1512 until she sank in 1545. The ship remained relatively intact on the seabed, buried in silt, for nearly 400 years, before it was uncovered and raised in 1982. Following its removal from the sea, yellow salt precipitates started to appear on the ship's timbers. A similar problem was encountered with the *Vasa*, King Adolphus of Sweden's warship, which sank in 1628. The *Vasa*, whose oak beams were seemingly in excellent condition when first raised, dramatically deteriorated while housed in the Wasavarvet restoration facility (*Nature* 415: 893-897 [2002]). The problem, now commonly referred to as 'the sulfur problem', occurs when sulfur compounds in the timbers, which originate from bacterial processes whilst underwater, are oxidised to sulfuric acid on exposure to air. This acid attacks the cellulose within the beams, resulting in dramatic deterioration of the wood. Work on the *Vasa* has shown that the oxidation is catalysed by iron, which is prevalent across the ship in the form of bolts and other structural components, compounding the problem and accelerating the deterioration.

Since **2008**, Professor Chadwick's team from the School of Physical Sciences at Kent has conducted research with the Mary Rose Trust to understand the oxidation processes occurring in the ship **[R1, R2]**, to develop new chemical treatments that mitigate the 'sulfur problem' **[R2, R3, R4, R5]**, and to monitor the state of the ship through the use of synchrotron radiation studies to ensure its integrity **[R6]**.

Research into the 'sulfur problem' and the preservation of the *Mary Rose*

Published in **2008**, the Kent team's research reported on the analysis of core samples taken from untreated timbers of the *Mary Rose*. Synchrotron-based sulfur and iron K-edge X-ray absorption spectroscopy (XAS) of the cores revealed that sulfur oxidation was more prevalent at the surface than in the depth of the timbers, and that the 'sulfur problem' was worse the nearer the samples were taken from a piece of metal in the wood, particularly iron **[R1]**. Between **2009** and **2011**, the Kent team, funded by the Heritage Lottery Fund **[G1]**, investigated chemical treatments to solve the 'sulfur problem', including iron removal **[R2]** and nanoparticle de-acidification **[R3]**, and continued to work with synchrotron beamlines to characterise treatment effectiveness **[R2, R3]**.

When the *Mary Rose* was first raised, she was sprayed regularly with water to stop the hull from drying out and prevent microbial activity. In 1992, the conservation team stopped spraying with water and started spraying the ship with polyethylene glycol (PEG) to displace the water in the cellular structure of the wood to prevent shrinkage and collapse. In **2013**, the wood had become saturated with PEG and the process of drying the ship began. At this point, the Kent team and the Mary Rose Trust set up a programme of work with Diamond Light Source (the UK's national synchrotron facility) to take samples annually from the ship for analysis to monitor any changes in real time **[G2]**.

Monitoring experiments carried out between **2013** and **2018** analysed 14 well-defined cores of the ship's hull, chosen as being representative of major areas of the *Mary Rose*'s timber. Samples were initially collected during the PEG treatment and again in real time during the drying period, enabling the analysis of both drying time and depth into the wood. The cores were subjected to sulfur and iron K-edge XAS, using the synchrotron at the national facility and results were analysed by comparing the spectra with well-defined standards. During the initial phase of the study, it was shown that significant amounts of oxidised sulfur were appearing on surfaces where previously not observed. In **2016**, a procedure to mitigate this oxidation using strontium carbonate nanoparticles was introduced by the Kent team **[R4]**. Importantly, this study showed that PEG does not prevent the reactivity of the nanoparticles with the sulfur compounds present in the artefacts, and a surface brushing method was found to be successful in removing the oxidised sulfur **[R4]**. Initial monitoring results also indicated that oxidised sulfur was progressing into the depth of the timber core, and oxidised zinc was found in coexistence with oxidised sulfur and iron in highly degraded regions **[R6]**. Reduced sulfur based species, such as sulfur, cystine, and methionine, and iron compounds were found to be present within the timber core at all times.

The monitoring project has shown that the level of oxidised sulfur building within the ship has levelled out and stabilised, and is not an immediate threat to the ship's integrity, indicating that the conservation methods being applied are working successfully. A report on core samples taken from six locations across the hull during the PEG treatment and again five months into the drying phase, has been published **[R6]**. Future publications are in the pipeline and a short film describing the project has been produced by KMTV. The Kent team continues to evaluate the effectiveness of PEG in the conservation of the *Mary Rose* **[R5]**.

3. References to the research

[R1] Wetherall, K. M., Moss, R. M., Jones, A. M., Smith, A. D., Skinner, T., **Pickup, D. M., Goatham, S. W., Chadwick, A. V.**, and **Newport, R. J.** (**2008**). 'Sulfur and iron speciation in recently recovered timbers of the *Mary Rose* revealed via X-ray absorption spectroscopy'. *Journal of Archaeological Science* 35: 1317-1328. http://doi.org/10.1016/j.jas.2007.09.007

[R2] Berko, A., Smith, A. D., Jones, A. M., **Schofield, E. J.,** Mosselmans, J. F. W., and **Chadwick, A. V.** (**2009**). 'XAS studies of the effectiveness of iron chelating treatments of *Mary Rose* timbers'. *Journal of Physics Conference Series: 14th International Conference on X-ray Absorption Fine Structure (XAFSI 4)* 190: 012147. http://doi.org/10.1088/1742-6596/190/1/012147

[R3] Schofield, E. J., Sarangi, R., Mehta, A., Jones, A. M., Mosselmans, J. F. W., and **Chadwick, A. V**. (**2011**). 'Nanoparticle de-acidification of the *Mary Rose*'. *Materials Today* 14: 354-358.

https://doi.org/10.1016/S1369-7021(11)70166-3

[R4] Schofield, E. J., Sarangi, R., Mehta, A., Jones, A. M., Smith, A., Mosselmans, J. F. W., and **Chadwick, A. V.** (**2016**). 'Strontium carbonate nanoparticles for the surface treatment of problematic sulfur and iron in waterlogged archaeological wood'. *Journal of Cultural Heritage* 18: 306-312. http://doi.org/10.1016/j.culher.2015.07.013

[R5] Chadwick, A. V., Berko, A., Schofield, E. J., Smith, A. D., Mosselmans, J. F., Jones, A. M., and Cibin, G. (**2016**). 'The application of X-ray absorption spectroscopy in archaeological conservation: Example of an artefact from Henry VIII warship the *Mary Rose*'. *Journal of Non-Crystalline Solids* 451: 49-55. http://doi.org/10.1016/j.jnoncrysol.2016.05.020

[R6] Aluri, E. R., Reynaud, C., Bardas, H., Piva, E., Cibin, G., Mosselmans, J. F. W., **Chadwick, A. V.**, and **Schofield, E. J.** (**2020**). 'The Formation of Chemical Degraders during the Conservation of a Wooden Tudor Shipwreck'. *ChemPlusChem* 85: 1632-1638. http://doi.org/10.1002/cplu.202000160

Grants

[G1] Chadwick, A. V., and **Newport, R. J.** (**2008-11**). 'An investigation of remediation methods for the sulphur problem in *Mary Rose* timbers'. Heritage Lottery Fund grant administered by the Mary Rose Trust.

[G2] Chadwick, A. V. (**2013-18**). 'Monitoring Iron and Sulfur Speciation in *Mary Rose* Timbers in the Museum Environment'. Diamond Light Source grant (SP10104): 2 days of beamtime every 6 months.

4. Details of the impact (indicative maximum 750 words)

Pioneering conservation technology to preserve underwater cultural heritage

1. *Measuring chemical changes in the* Mary Rose *in real time*

Chadwick has a longstanding relationship with the Mary Rose Trust, and has been exploring technologies to preserve the ship and her artefacts since 2008. His pioneering research, undertaken by Kent with the Mary Rose Trust and Diamond Light Source between **2013** and **2018**, enabled chemical changes in the ship to be measured in 'real time' for the first time **[a, b]**. At the outset of the study, the Kent team, the Mary Rose Trust, and Diamond Light Source had to design a robust chamber to collect XAS spectra for soft elements like sulfur. This was built at the Diamond Light Source, and thanks to its success is now being used as standard equipment on the beamline used in the project (B18). Principal Beamline Scientists at Diamond Light Source, Professors Giannantonio Cibin and Fred Mosselmans, confirm that 'The problem posed by the complexity and the nature of the [*Mary Rose*] material itself has helped us to provide new techniques, to be able to push […] our technology', and that the use of the new techniques 'has enabled the conservation tactics used on the *Mary Rose* to develop' **[b]**.

Under the research guidance of the Kent team, the oxidation processes within the *Mary Rose* timbers are now much better understood, particularly in the museum environment. These monitoring and evaluation experiments have informed conservation practice, including decisions made about the upgrade to the air-conditioning system in **2016**, which has provided a stable environment for the *Mary Rose* and all of its artefacts. Although further similar experiments and monitoring will be required in the future, the work has provided a platform for many years of conservation. Professor Eleanor Schofield, Head of Conservation and Collections Care at the Mary Rose Trust and an Honorary Professor at Kent, highlights the importance of the monitoring project to the preservation of the *Mary Rose*, stating it 'has confirmed during the final stages of drying the ship, that our conservation methods are working and has given us confidence that the environment surrounding the ship is correct' **[a]**.

2. *Eliminating acid degradation in wood and other materials*

Discoveries made during the monitoring research enabled the Kent team to develop a pioneering strontium carbonate nanoparticle treatment to eliminate imminent and long-term threats of acid degradation **[b]**. This treatment has already been used on artefacts now on display. Schofield confirms that 'Work completed at Kent, developing nanoparticle treatments for the conservation issues of marine archaeological wood, has been implemented in the museum. Specifically, artefacts set to go on display in the new museum in 2013 were treated to combat conservation issues, which left unresolved would have resulted in the items being unable to go on display. These included things like gun carriages, which are critical for the curational narrative of the museum' **[a]**. Having proved the chemistry, ways to apply the nanoparticles to the bulk of the ship are now being investigated **[b]**. Schofield confirms that 'Kent research and our collaboration with the Kent team has also facilitated the beginning of a pilot project at the Mary Rose Trust for conservators to investigate different application methods' **[a]**.

Kent's researchers, the Mary Rose Trust team, and Diamond Light Source are continuing to develop techniques to treat the artefacts, including the ship's bricks **[b]**. Schofield explains that 'The issues that we see with the salts in the wood we are starting to see in other materials and one of those is the bricks' **[b]**. The Kent team is currently working with the Mary Rose Trust team to understand what impurity phases are resulting in the degradation of the ship's bricks **[a, b]**. 'It is expected that this understanding can then be exploited to develop preservation techniques.' **[a]**

3. International impacts on cultural heritage conservation

Kent's research on nanoparticle de-acidification of waterlogged wood and the real-time monitoring of chemical degradation in the *Mary Rose* has also assisted other conservation projects around the world, including the preservation of wooden artefacts from the Norwegian Viking ship *Oseberg* **[c]** and timbers from the *Princess Carolina*, an eighteenth-century wooden merchant vessel excavated in the 1980s in Manhattan **[d]**. Dr Susan Braovac, Conservator on the Saving Oseberg Project (Norway), confirms that 'Research on archaeological materials is a relatively small field. Only a handful of institutions have research positions specializing in these materials', and she highlights that 'Research on the *Mary Rose* contributes to the knowledge-building that helps preservation specialists make the right decisions' **[c]**.

Kent's research is helping to improve understanding of the *Oseberg*'s wooden artefacts treated with alum salts. Braovac explains that even though the groups are working with different types of archaeological woods, they are dealing with similar types of chemical degradation (sulfates and iron) and confirms that the Kent team's work 'on deacidification of wood using nanoparticles (strontium carbonate) has inspired [her] own research on nanoparticle application to deacidify wood, albeit, a different type (calcium hydroxide)' **[c]**. Braovac also highlights the impact of Kent's real-time monitoring project and its findings: 'The publication on chemical degraders in the *Mary Rose* is […] relevant for my own understanding of the chemistry of alum-treated wood. We have […] observed similar elements [described in the Kent paper] (zinc) present in the wood. I had not previously read about zinc in archaeological wood outside of my own work' **[c]**.

Elsa Sangouard, Senior Conservator at the Mariners' Museum (USA), describes the Kent's team's research on the application of nanoparticles to archaeological wood as 'critical work that has led the way in improving, diversifying, and strengthening the conservation of such cultural heritage for present and future generations. Today, this research is providing a foundation for the work we, and other conservation laboratories around the world, are conducting.' A preservation project at the Mariners' Museum has carried out tests on previously treated acidified waterlogged wood from the *Princess Carolina*, using an approach similar to that reported by the Kent team. Sangouard states that 'Initial test trials have begun […]. If they are conclusive, we may apply nano-calcium carbonate particles, one of the products investigated by Schofield et al., on a large-scale to the re-treatment of timbers from the Princess Carolina' **[d]**.

Overall, the Kent team's research into the preservation of the *Mary Rose* and her artefacts since 2008 has had a significant impact on cultural heritage research and has been widely cited by the conservation community. The *Mary Rose* website **[f]** provides a list of published papers from research projects that have focused on the ship and her artefacts, including the six articles cited here **[R1-R6]** that describe key work carried out by the Kent team. Other projects that have cited the work of the Kent team in their research publications include the conservation of sculptures and decorative artefacts from the *Vasa*, Norwegian Viking age wooden objects (from the *Oseberg*), a Bronze Age logboat (the *Hanson*) from Derby, a Gallo-Roman wreck (the *Lyon Saint-Georges 4*) in France, Baroque retables and altarpieces from Portugal, and a Polish medieval bridge and other artefacts **[e]**.

Cultural, Economic, and Educational Benefits

Housed in its own purpose built museum, the restored *Mary Rose* is the central attraction in Portsmouth's Historic Dockyard, one of the most important and visited heritage sites in the UK. The museum employs 11 front-of-house staff directly involved with the upkeep and operations of the museum as well as two academic researchers and two conservators **[a]**. Schofield, Head of Conservation and Collections Care at the Mary Rose Trust, explains that 'The concept of the museum is to provide an immersive experience for the visitors showing them, through the objects, day-to-day life on board the *Mary Rose*', and confirms that 'Having the artefacts with the ship enables us to display everything in context which allows us to tell the story of the people that worked on board more effectively' **[a]**. The Trust has an extensive website describing the extraordinary history of the ship, including large sections on the conservation process and research projects, which reference the Kent team's research **[f]**. The website also states that there are now 19,000 artefacts in the collection, with 5,000 of the preserved items now being on display in the museum **[f]**.

Preserving and presenting the thousands of artefacts in a pristine condition has been central to the museum's popularity **[b]**. This is acknowledged by Jane Singh, Visit Portsmouth Tourism and Marketing Manager at Portsmouth City Council, who states: 'The conservation of the *Mary Rose* and the role played by the University of Kent in this work has been essential in ensuring the ship and related artefacts can be successfully conserved and remain on view in the museum. […] As the only ship of her kind on display in the world, along with the thousands of original objects found with her, the *Mary Rose* offers a unique insight into Tudor England' **[g]**. Josephine Payter-Harris, Guest Experience Manager at the Mary Rose Trust, also highlights the impact that Kent's research has had on the museum experience: 'Without all of the conservation work these artefacts wouldn't be here on display and it's something that people find absolutely fascinating that these are real artefacts […] that were under the water for all that time' **[b]**.

There is a growing focus at the museum on highlighting the various processes involved in the conservation, with a view to including more of this information in outreach projects **[b, f]**. Singh, from Portsmouth City Council, confirms that 'The *Mary Rose* also has a huge part to play in the cultural offer for both local residents and visitors and offers, in more usual times, a range of events and educational activities that complement the museum visit' **[g]**. Schofield states that between **2014** and **2019** the museum received on average 300 school visits and over 255,000 individual visitors annually (the museum was temporarily closed in 2020 in line with government COVID-19 regulations) **[a]**. Portsmouth City Council highlights the economic importance of the *Mary Rose* to Portsmouth, where it is regarded as its top attraction and a key driver for visitors, and the role it plays in generating income from tourism in excess of £610 million, supporting around 12,700 jobs (Portsmouth, Economic Impact of Tourism estimates, 2015, Tourism South East) **[g]**.

5. Sources to corroborate the impact (indicative maximum of 10 references)

[a] Testimonial: Head of Conservation and Collections Care, the Mary Rose Trust (UK).

[b] KMTV short film: *Mary Rose: A Chemical Conundrum*.
https://research.kent.ac.uk/impact-mary-rose-heritage-chadwick/

[c] Testimonial: Conservator, Saving Oseberg, Museum of Cultural History (Norway).

[d] Testimonial: Senior Conservator, the Mariners' Museum and Park (USA).

[e] Report detailing research publications from other conservation projects that cite Kent research.

[f] Mary Rose Trust website, with referenes to the Kent team's research.

[g] Testimonial: Visit Portsmouth Tourism and Marketing Manager, Portsmouth City Council (UK).