Powerful X-ray technique finds new degradation-inducing materials in British shipwreck

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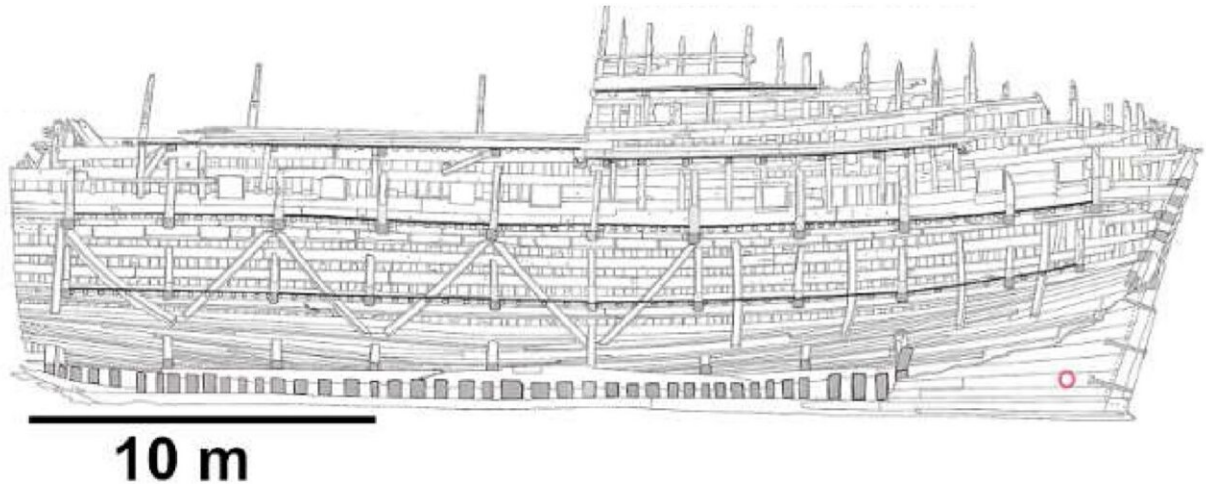

Drawing of the Mary Rose. Credit: Jensen et al./*Matter*

In 1545, King Henry VIII's favorite ship, the Mary Rose, capsized and sank in the Battle of the Solent defending England and Portsmouth from a French invasion fleet. The wreck remained on the seabed until 1982 when it was salvaged in a widely viewed televised event. Now, it is a time capsule for 16th century Tudor society, and conservators are working to preserve it for future generations. In research published in the journal *Matter* on October 27, scientists use X-ray analysis to identify previously undetected products in the wood—nanoparticles

originating from underwater bacterial activity.

"It is remarkable that this technique at the ESRF allows us not only to image and locate these nanoparticles in Mary Rose wood, but also to evaluate their structure. This is the first time zinc sulfide nanostructures—the bacterial byproducts—have been observed in Mary Rose wood," says senior author Serena Cussen, head of the Department of Materials Science and Engineering at the University of Sheffield, UK.

As Eleanor Schofield, co-author on this work and deputy chief executive at the Mary Rose Trust explains, "Centuries spent under the seabed saw the uptake of harmful iron and sulfur species by the Mary Rose hull, which were produced through degradation of metal fixtures and artifacts and anaerobic sulfur-reducing bacteria, respectively."

To compensate for degradation of the wood and loss of material, conservators impregnated the Mary Rose with a polymer called poly-ethylene glycol (PEG). This prevents shrinkage upon drying and gives the ship mechanical stability so it can be displayed for the public. In the final stage of active conservation, the Mary Rose was dried, and this exposure to oxygen has led to the formation of acidic species which can create even more damage to the wood.

"Up to now, it has not been possible to obtain quantitative structural information about the nature of these potentially harmful species residing within Mary Rose wood," says Cussen. "This is because it is really challenging to assess the range of materials present within archaeological samples, which can include amorphous, nanostructured, and polycrystalline materials."

When characterizing precious cultural artifacts like the Mary Rose, it is important to use a method that does not damage the material. Cussen and her colleagues used a technique at the ESRF called X-ray computed

tomography to provide detailed structural information about the wide range of materials present in the Mary Rose hull without destroying the sample.

The researchers mapped out where compounds were lodged in the material by combining X-ray computed tomography with pair distribution function analysis (ctPDF). Using these two methods together allows them to determine the distance between the PEG and the nanoparticle products and therefore assess where potential threats lie within the wood.

"What our results have done is alert conservators to these previously unknown deposits and expand the study of degradation-inducing materials. Knowing the structure of these potentially harmful species also allows us to design targeted treatments for their future removal," says Cussen. In collaboration with the Mary Rose Trust, her team is also developing a series of magnetic nanoparticle-based treatments to target and remove these harmful deposits within artifacts.

More information: Serena A. Cussen, Location and characterization of heterogeneous phases within Mary Rose wood, *Matter* (2021). DOI: 10.1016/j.matt.2021.09.026.
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