How the world's most advanced analytical techniques are saving 'doomed' shipwrecks

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When wooden objects sink to the bottom of the sea, they are generally served an extended lifespan. On land, wooden artefacts such as shipwrecks may be destroyed through rotting, animals, or human action, but marine environments can prevent the biological, chemical, and mechanical changes that would cause an object to decay – preserving a rare time capsule to our past.

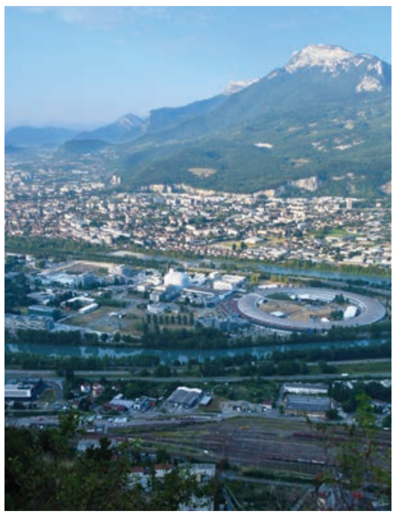
Drying process carried out inside the apparatus for large-scale lyophilisation procedure (Credit ARC-Nucleart) somewhere near top of page

However, when an ancient shipwreck is pulled from the water, the process of acidification can start and they can begin to crumble. In addition to structural changes from the drying of the wood – causing shrinking and cracking – iron present in features such as nails, combined with sulphur from bacteria, creates the compound 'iron sulphide'. This material, dormant under water, can develop into destructive sulphuric acid when met with oxygen above ground. This acidification 'infection' of the wood can spread and make the entire structure crumble within days, risking the loss of thousands of years of human history. One of the world's most famous shipwrecks, the 400-year old Vasa ship in Stockholm, was partially eaten by sulphuric acid in the early 2000s due to the ferociousness of the process.

Tackling the disease

New research from a consortium of scientists based at Institut Laue-Langevin (ILL), Grenoble (France) and University of L'Aquila (Italy) has explored the potential of an innovative new solution that uses nanoparticles in aqueous suspensions to tackle this 'disease' of archaeological wood.

Using neutron scattering to reveal the atomic structure deep inside materials alongside a variety of imaging techniques including microscopy and X-ray probing, the group showed how the nanoparticle suspension can be highly effective at neutralising the acid in the pores of the wood before it can cause further damage. Used in combination with a common technique of submerging the objects in polyethylene glycol (PEG) to replace the water in the structure, this approach has the potential to save precious relics from turning to dust.



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Further, the solution could be a transformative step in archaeology due to the considerable safety, sustainability and cost-effectiveness of the new nanoparticle approach. The solution uses water in the production and suspension of the nanoparticles, instead of alcohol. Given the size of many waterlogged wooden objects such as shipwrecks, immersing entire structures in a massive pool of alcohol represents a huge health and safety risk to archaeological researchers, as well as being an extremely expensive method. By proving that water is an effective way to deliver the nanoparticles to the artefact, the team has opened the doors to more affordable and sustainable restoration techniques that will not impact the health and working practices of cultural heritage professionals.

Exploration with neutrons

The study and characterization of a new nanoparticle suspension, especially one where the materials being treated are so delicate, rare, and precious to human history, is an essential step before any solution is applied. Ahead of testing the new solution on any archaeological wood samples, the treatment underwent extensive analysis, including small angle neutron scattering (SANS), to examine and compare the suspension of calcium- and magnesium-hydroxide nanoparticles in water.

SANS measurements were carried out at Institut Laue-Langevin (ILL), the world's flagship centre for neutron science, to study the particles directly in suspension in their solvent. To demonstrate the effectiveness of the nanoparticles in water, rather than alcohol, this technique was essential – it is uniquely capable of revealing the form of the nanoparticles without drying them, a process which may impact the shape or function of the active factors.

Using D11, an instrument designed for the study of chemistry, biology, solid state physics and materials science, a powerful beam of neutrons was directed at the suspension. The subsequent scattering of neutrons as a result of the atomic structure or magnetic properties in the material indicate the size and shape of the nanoparticles. This confirmed that the particles would be free to move into the wood and successfully deacidify.

co-author Ralf Schweins and Sylvain Prevost with D11

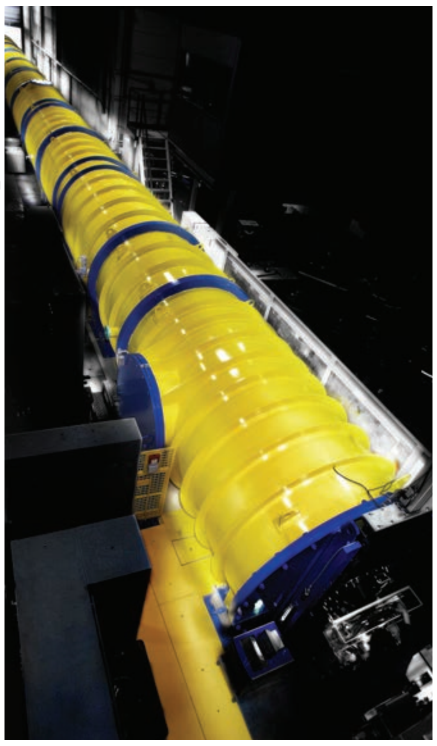
Neutrons are an important tool in cultural heritage studies, as they are non-destructive and can penetrate deep into solid or, uniquely, liquid materials to reveal what is happening at the atomic or molecular level. They can reveal metal manufacturing methods used on ancient swords, or improve the restoration processes used on centuries-old works of art.

X-ray revelations

Several analytical techniques were then used to study the structure of nanoparticles and evidence of degradation in wood samples following the selection of preventative and curative treatments. The samples were taken from a 2,000 year-old Gallo-Roman barge at the Lugdunum museum (Lyon, France) on loan from ARC-Nucléart (Grenoble, France).

A number of these measurements involved the use of X-rays, taking place at the University of L'Aquila. X-rays are an excellent complementary tool to neutron scattering as while neutrons are exceptionally capable of identifying lighter elements – such as hydrogen – in the molecular structure of materials, X-rays can reveal with great resolution the mid- and heavier-weight elements in a sample.

In this case, X-ray fluorescence and X-ray powder diffraction were used to analyse the chemical composition of the acid precursors – the iron compounds that emerge from features such as nails and fasteners in the wood. X-ray diffraction measurements were also used to evaluate the structure, composition and crystallinity of the nanoparticles – using a X'PertPRO diffractometer – as well as their penetration inside the wood structure.



The small angle neutron scattering instrument D11 at ILL (copyright-Bernhard Lehn)

An array of microscopy

The selected wood samples were also analysed with a range of microscopy techniques, before and after the washing process as well as after the nanoparticle treatments. The morphological features were investigated by optical stereomicroscopy (SM, Stereozoom S8APO microscope) and Scanning Electron Microscopy (SEM) (SEM-BSE XL30CP). The SEM revealed the diffusion of iron and sulphur around the regions containing nails, that are the origin of the acidification 'disease'.

The morphology and size of the synthesized calcium hydroxide (CH) and magnesium hydroxide (MH) nanoparticles were investigated using both Transmission Electron Microscopy and Atomic Force Microscopy (with a Cypher Asylum Research microscope using the Partnership for Soft Condensed Matter platform). This revealed that the nanoparticles appear to be made up of hexagonal lamellas (typical of magnesium hydroxide) composed of self-assembling, ever smaller nanoparticles – the so called primary nanoparticles – with a size of 2-3 nm, a hexagonal shape and very thin, with a thickness less than 2 nm.

Excavation site in Lyon (Credit ARC-Nucleart)

Advancing the field

Having demonstrated that the new solution has both preventative and curative effects when it comes to preventing the destruction of wooden artefacts, the next steps for this research will involve studying the effects of the solution on a bigger sample. Ideally this would be a piece of wood that is comparable to the thickness of the wood used on a ship.

Understandably, only tiny samples of the Gallo-Roman barge were used in the experiments until we had proven its effectiveness. It is now vital to ensure the right penetration depth and dosage of the nanoparticles is achieved for scaling up the solution for large objects. The team wants to show to those working in restoration that the penetration of the nanoparticles is deep enough to cover the whole thickness of the wood used in the ship. This will ensure the treatment is proven to work in the exact conditions archaeologists and restorers experience on a daily basis.

Experimental Hall (Copyright Briq ecliptique)

Rescuing human history

The importance of advancing the techniques used in cultural heritage come into focus when you consider the richness of information that can be obtained about human history from objects such as shipwrecks.

The barge Lyon Saint George 4 used in the study was found in 2003 in the Saône, a river crossing Lyon, during the work on Saint George Park in the town. It was used some 2000 years ago as a barge to transport heavy and bulky loads along the river: loading heavy stones, wood, amphoras for wine, garum (a fermented fish sauce used as a condiment in the cuisines of Phoenicia and other ancient people) or olive oil.

The ship was abandoned with six other barges of the same type – dating from the 1st to 3rd century AD – in a location that acted as a sort of 'cemetery' of Roman boats: throughout this period of abandonment – until they became buried in the mud – the boats were alternately submerged or in the open air according to the level of the river and the seasons. We know that they were discarded because the boats were found empty without their load, so it was not an accident that caused them to sink. In addition, the large amount of iron salts resulting from the corrosion of the steel of the nails indicated that the barge remained for a long time in the open air and not only at the bottom of the water.

Indications of how ancient civilisations ate, travelled, traded and innovated are contained in the composition, building materials and chemical state of waterlogged wooden objects, so it is exciting to see the research methods in this field continue to advance through pioneering collaborations.

Views of a part of the gallo-roman barge floor (2th a.c) LSG$ from Lugdunum Museum in Lyon after its Poyethylene Glycol Freeze Dryin Treatment (Credit ARC-Nucleart)