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should be addressed to  
Y.F. (yvonne.fors@  
conservation.gu.se)

# Sulfur and iron accumulation in three marine-archaeological shipwrecks in the Baltic Sea: The Ghost, the Crown and the Sword

Yvonne Fors<sup>1</sup>, Håkan Grudd<sup>2</sup>, Anders Rindby<sup>3</sup>, Farideh Jalilehvand<sup>4</sup>, Magnus Sandström<sup>5</sup>, Ingemar Cato<sup>6</sup> & Lennart Bornmalm<sup>7</sup>

<sup>1</sup>Department of Conservation, University of Gothenburg, Sweden, <sup>2</sup>Bolin Centre for Climate Research, Department of Physical Geography and Quaternary Geology, Stockholm University, Sweden, <sup>3</sup>Cox Analytical Systems, Mölndal, Sweden, <sup>4</sup>Department of Chemistry, University of Calgary, Canada, <sup>5</sup>Department of Materials and Environmental Chemistry, Stockholm University, Sweden, <sup>6</sup>Department of Earth Sciences, University of Gothenburg, Sweden, and Geological Survey of Sweden, <sup>7</sup>Department of Earth Sciences and Department of Biology and Environmental Sciences, University of Gothenburg, Sweden.

**Sulfur and iron concentrations in wood from three 17<sup>th</sup> century shipwrecks in the Baltic Sea, the *Ghost wreck*, the *Crown* and the *Sword*, were obtained by X-ray fluorescence (XRF) scanning. In near anaerobic environments symbiotic microorganisms degrade waterlogged wood, reduce sulfate and promote accumulation of low-valent sulfur compounds, as previously found for the famous wrecks of the *Vasa* and *Mary Rose*. Sulfur K-edge X-ray absorption near-edge structure (XANES) analyses of Ghost wreck wood show that organic thiols and disulfides dominate, together with elemental sulfur probably generated by sulfur-oxidizing *Beggiatoa* bacteria. Iron sulfides were not detected, consistent with the relatively low iron concentration in the wood. In a museum climate with high atmospheric humidity oxidation processes, especially of iron sulfides formed in the presence of corroding iron, may induce post-conservation wood degradation. Subject to more general confirmation by further analyses no severe conservation concerns are expected for the Ghost wreck wood.**

**A**t seabed a vast cultural heritage rests in the form of marine-archaeological shipwrecks, in particular in the brackish waters of the Baltic Sea. However, the seabed environment may produce challenges for long-term preservation of recovered wood. Submerged wood provides habitats suitable for microbial communities and cycling processes<sup>1,2</sup>. Erosion bacteria are capable of degrading lignocellolytic material in low-oxygen environments<sup>3</sup> while scavenging sulfate reducing bacteria (SRB) metabolising organic debris and cellulose residuals, produce hydrogen sulfide. The HS<sup>-</sup> ions react in lignin-rich parts of the wood to form organic sulfur compounds, mainly thiols, or create with iron ions from corroding iron objects particles of iron sulfides in wood cavities<sup>4,5</sup>. Thus, microbial degradation of wood in shipwrecks resting within marine sediments in low oxygen conditions is usually accompanied with accumulation of sulfur and iron compounds<sup>6,7</sup>. When such wood is recovered from the seabed and brought into an aerobic environment of fluctuating humidity, primarily the unstable iron sulfides start to oxidize<sup>8,9</sup>. Acidic precipitates of iron(II) and iron(III) sulfates (melanterite, rozenite, jarosite) are often found on surfaces of marine-archaeological wood. Even in a stabilized museum climate especially iron catalyzed oxidation processes may result in high acidity, as for the famous wrecks of the warships *Vasa* (Sweden) and *Mary Rose* (UK), and the ill-fated *Batavia* (Australia) from the Dutch East India Company<sup>6,7,10,11</sup>, and eventually further degrade the wood structure.

The depth profiles of accumulated sulfur and iron often differ significantly, even through wood found in various environments in the same wreck site<sup>5</sup>. Previous analyses of shipwrecks from the Baltic Sea, the *Vasa*, the *Crown* and the *Riksnackeln*, generally showed high accumulation of sulfur and iron close to wood surfaces, while samples from the *Mary Rose* and some samples from the *Göta wreck* from the Swedish west coast, displayed more uniform distributions of these elements in the wood<sup>5,6</sup>.

The present study concerns three historically significant 17<sup>th</sup> century shipwrecks from the Baltic Sea, the *Ghost wreck* (sw. *Spökskeppet*), the *Crown* (sw. *Kronan*) and the *Sword* (sw. *Svärdet*), of which at least one may become



salvaged in the near future. The *Ghost wreck* is a Dutch fluit, located 30 nautical miles east of the island of *Gotska Sandön* in the middle of the Baltic Sea, in upright position on a hard and mineralized seabed at 125 m depth<sup>12</sup>. The intact hull, dated to 1630–1650, is covered as well as the seabed with a white coating, characteristic for the sulfur-oxidizing bacteria *Beggiatoa spp* of the  $\gamma$ -proteobacteria clade. *Beggiatoa* are referred to as an indicator of strongly reduced (anoxic) seabed conditions, which generally occur in areas where a continuous accumulation of porous fine-grained organo- or hydrocarbon-rich sediments takes place<sup>13–15</sup> (Fig. 1). The royal warship *Crown* was lost after an explosion in battle 1676 outside the Swedish island of *Öland*. The remaining hull is immersed in soft anaerobic clay, covered with a few decimetres of sand at 26 m depth<sup>16</sup>. The warship *Sword* was ravaged by fire and wrecked in the same battle as the *Crown*. When relocated in 2011 at 90 m depth the hull was submerged rather deep into soft sediment, although with a large portion of the deck emerging over the seabed.

The total concentration profiles of S and Fe have been obtained by XRF scanning of samples of the waterlogged wood along a line from the outer to the inner wood (sub-)surface. The pattern and amount of the accumulated sulfur and iron compounds depend on the conditions at the wreck site, while for the conservation strategy also the sulfur speciation is important in order to assess the reactivity of the

sulfur compounds and possible development of sulfuric and other acids<sup>4,5</sup>. The sulfur K-edge XANES spectroscopic method allows, when utilizing the intense X-ray radiation from synchrotron sources<sup>17</sup>, such speciation analyses and has previously been used for several shipwrecks<sup>4,5,10,18</sup>, including samples from the *Crown*<sup>5</sup>. Analyses of the sulfur speciation in a wood sample from the *Ghost wreck* (*Spökskeppet*) are presented in the current study.

## Results

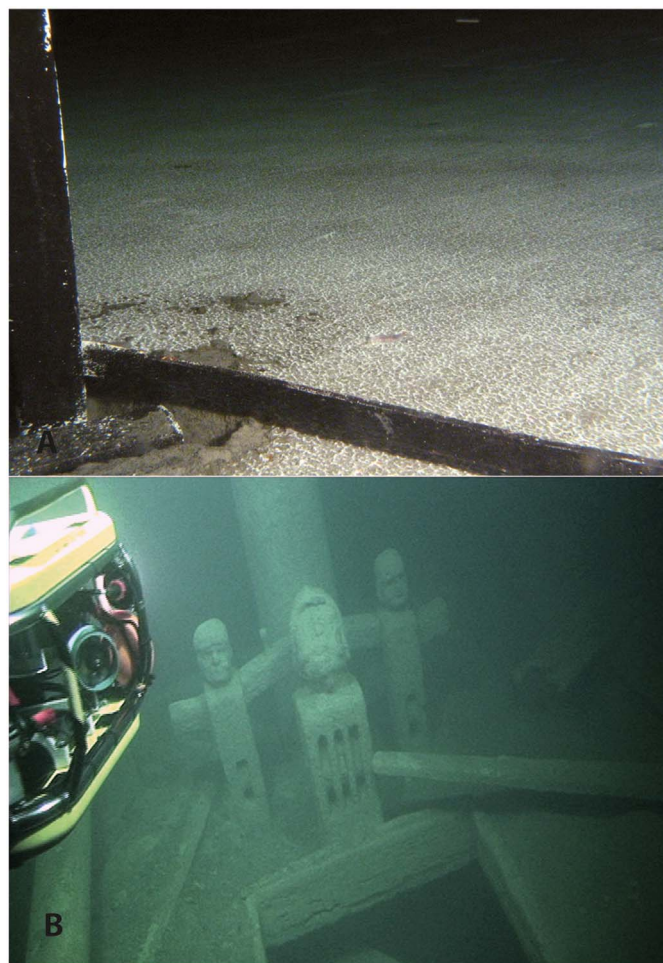
**XRF scanning results.** The sulfur and iron accumulation profiles into the wood of all three shipwrecks are similar to the interconnected sulfur and iron profiles in earlier analyses of waterlogged wood from the Baltic Sea, such as the *Vasa* and the *Riksnackeln*<sup>5,6</sup>. In general the highest concentrations are found in surfaces in one or both ends of the samples and in wood cracks (Figs. 2–4, Figs. S1–S4). The concentration of sulfur is higher than that of iron in all cases but one: the outer surface of sample *Sword* 1d (Fig. S3B). The iron concentration is generally quite low in the inner parts of the wood, usually below 0.2 mass% total Fe.

The profiles of the outer wood surfaces of the *Ghost wreck* samples coated with *Beggiatoa spp* show distinct peaks reaching up to 1.8 mass% total sulfur (Figs. 2 and S1, left) whereas the inner (sub)surface toward the seabed displays broader peaks of lower sulfur concentration, e.g. in *Ghost* 1a (Fig. 2A, right). Within the wood the sulfur concentration appears fairly uniform; ~0.5 mass% in *Ghost* 1 (Fig. 2), and ~0.2 mass% S in *Ghost* 2a (Fig. S1A). The iron and sulfur profiles seem fairly interrelated throughout, except at the inner surface of sample *Ghost* 1a (Fig. 2A). The iron concentration that generally is low in the inner parts of the wood; <0.02 mass% total Fe in *Ghost* 1, reaches 0.5 mass% total Fe close to the outer *Beggiatoa*-covered surface in *Ghost* 2a (Fig. 2, Fig. S1A). The larger iron peaks are slightly shifted relative to the sulfur peaks in the outer surface of sample *Ghost* 2a (Fig. 2B) and at both surfaces in 1b (Fig. S1A). In sample *Ghost* 2a the pattern of repeating broad iron peaks (~0.2 mass% Fe) possibly is connected to density variations in the annual rings (Fig. 2B).

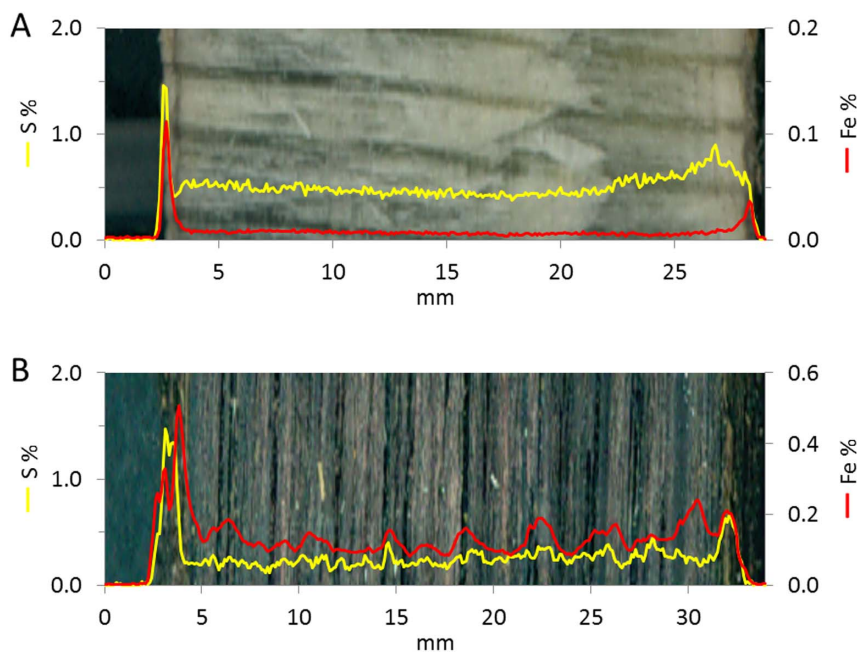
For the *Crown*, the more aerobic samples *Crown* 2a and 2b show higher accumulation of sulfur (but not iron) at the surfaces than the anaerobically preserved wood of samples *Crown* 1a and 1b (Figs. 3 and S2). The sulfur concentration of the *Crown* samples extends up to 4 mass% S with 0.5 mass% Fe in the outer surface of the sample *Crown* 2b (Fig. S2B). A distinct peak a few mm underneath the subsurface (S: 0.9%, Fe: 0.2%) in the sample *Crown* 1b may indicate an iron sulfide particle (Fig. 3A). The differences in sulfur and iron accumulation at the surfaces in samples *Crown* 2a and *Crown* 2b from the same part of the object, demonstrate the inhomogeneity of the accumulation (Figs. 3B, S2B).

The samples *Sword* 1a–1d (Figs. 4, S3) also exemplify the inhomogeneous accumulation. In *Sword* 1a and 1b the S and Fe concentrations are consistently lower than in *Sword* 1c and 1d, which originate from the opposite side of the same beam (see Table 1). Both surfaces of samples 1a and 1b show high accumulation of total S and Fe but only the outer surface of sample 1c and 1d. The sulfur concentration is also significantly higher in sample *Sword* 2b than in the neighboring sample *Sword* 2a (Fig. S4). The sulfur and iron accumulation profiles are interrelated throughout the wood, although with a small shift between the peaks in the outer surface of samples *Sword* 1a, 2a and 2b (Fig. 4A and Fig. S4). Again the concentrations are highest at the surfaces and in wood cracks (>8 mass% S and 2.8 mass% Fe in sample *Sword* 1c (Fig. 4B).

**XANES analyses of the *Ghost wreck* samples.** The sulfur K-edge XANES spectra of sample *Ghost* 2c display two major composite peaks at about 2482 and 2473 eV (Figure 5), corresponding to several high- and low-valent sulfur functional groups, respectively<sup>11</sup>. By fitting the normalized experimental spectra with linear combinations of normalized S K-edge XANES spectra of standard



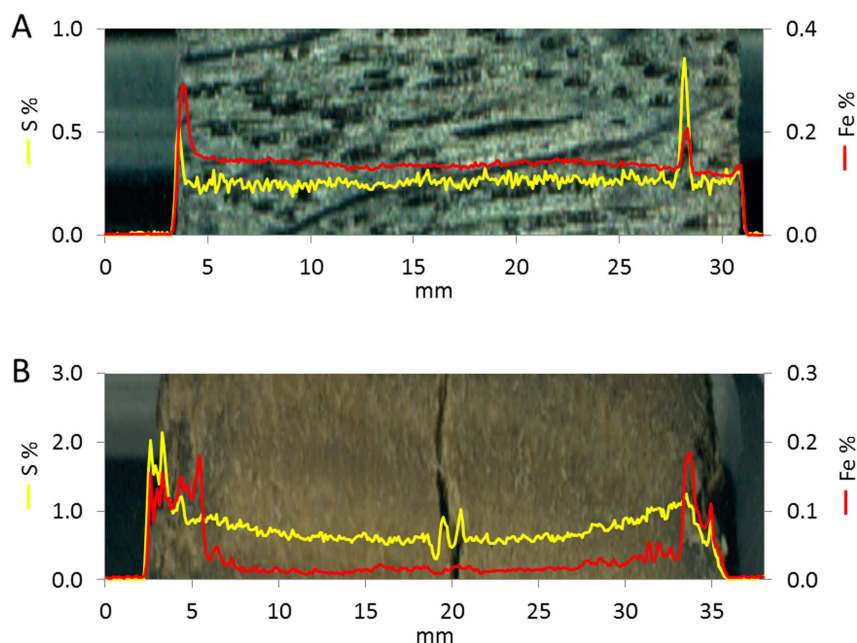
**Figure 1** | Characteristic “white net” of the bacteria *Beggiatoa spp* distributed over the seabed in the Baltic Sea. Photo A: Geological Survey of Sweden©. (A) The sulfur-oxidizing bacteria *Beggiatoa* is an indicator of strongly reduced (anoxic) seabed conditions in this accumulation area of fine-grained sediment (clay) in the central Baltic Sea. Photo B: Deep Sea Productions©. (B) The upper deck of the *Ghost wreck* (dated to 1630–1650) covered with a white coating.



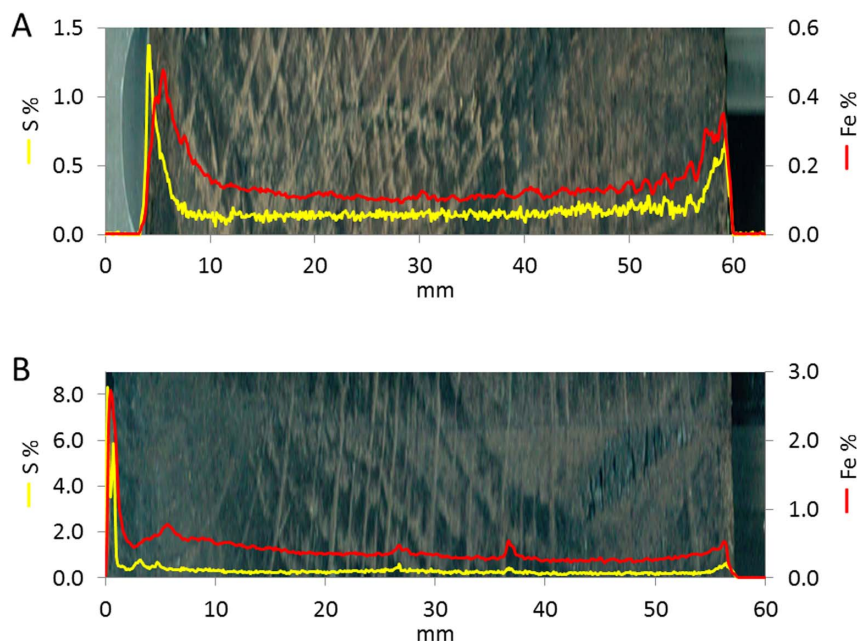
**Figure 2** | XRF-scans of the Ghost wreck samples 1a (A) & 2a (B). The wood was scanned from the outer surface (left) to the inner subsurface (right) along a line in the middle of each sample. Iron and sulfur show fairly interrelated profiles throughout the wood (note the different concentration scales), except at the inner surface of sample Ghost 1a (A) and 2a (B). A region of broader sulfur peaks appears close to the inner surface (right) of sample Ghost 1a, which should be compared to the much sharper sulfur peak in the outer surface (left in figure A) coated with *Beggiatoa spp* (also Fig. S1). (B) A repeating pattern of broad iron peaks occurs in Ghost 2a.

compounds representing different sulfur functional groups (Figure 6), the relative amount of such species can be obtained (Table 2)<sup>17</sup>. The intensity of a high-valent sulfur feature generally is 3–4 times stronger than for the low-valent ones<sup>17</sup>, which were found to dominate both at the outer surface, 0–1 mm (~61%) and inside the wood at 11–12 mm (~84%). At the surface the relative amount of sulfur was

~24% as thiols (R-SH) and ~37% as disulfides (-S-S-), the first oxidation product. Within the wood thiols are dominating (~44%) with just ~18% as disulfides. A significant amount of elemental sulfur, S<sub>8</sub> (~22%) was also found (Table 2), while no contribution of the standard spectrum of pyrite could be included in the fitted model.



**Figure 3** | XRF-scans of the Crown samples 1b (A) & 2a (B). The sulfur and iron concentration profiles are to some extent interrelated for both samples from the *Crown*, although with higher sulfur concentration than iron (note the different concentration scales), especially close to the surfaces with up to 4 mass% total sulfur and 0.5 mass% total Fe in sample Crown 2b (Fig. S2B). The distinct peak beneath the subsurface (A, right) of the sample Crown 1b indicates an iron-sulfide particle. The sample Crown 1 found in anaerobic clay at the wreck site show consistently lower sulfur concentrations than the more aerobic samples from Crown 2 (Fig. S2).



**Figure 4** | XRF-scans of the Sword samples 1a (A) & 1c (B). High sulfur and iron concentrations (note the different concentration scales) are found at the outer surface of sample Sword 1c (B, left side); see also Fig. S3B with >8 mass% S and 3.8 mass% Fe in sample 1d.

High-valent sulfur is as expected present in higher concentration close to the surface of the wood (~25%) than in the interior (~13%). Sulfate is the most frequent form, with relative amounts of 12 and 9%, respectively (Table 2). Some amount of organosulfonate  $R-SO_3^-$ , which is a typical autoxidation end product of thiols<sup>18</sup>, was found mainly at the surface. A few atom% S occurs as organosulfur compounds with an intermediate oxidation state (~2476 eV). The sulf-oxide model compound does not give a perfect fit and also trimethylsulfonium has been proposed as a possible additional minor functional group<sup>18</sup>.

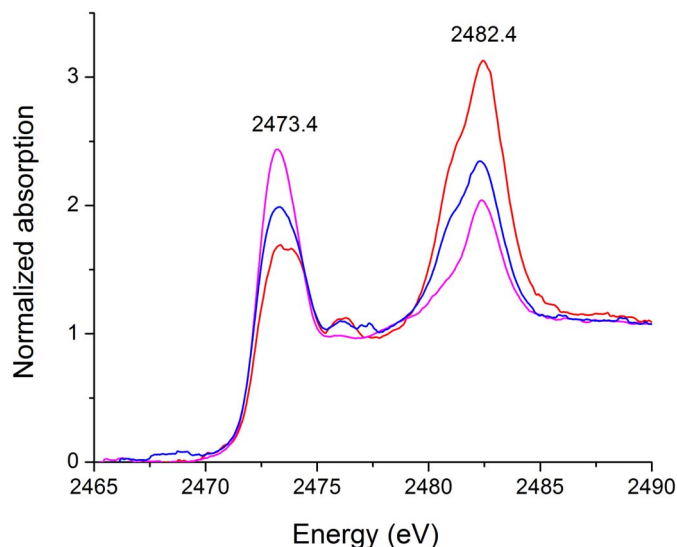
It should be noted that the characteristic spectral features of a covalently bound functional sulfur group are to some extent modified by its surrounding and external interactions. Archaeological wood provides a large number of microenvironments, which make it difficult to distinguish e.g. between sulfate esters vs. combinations of sulfates and organic sulfonates, and also influence the spectra of disulfides. The normalization and fitting procedures and their influence on the errors in the XANES analyses of functional sulfur groups in a natural sample have been discussed by Frank and coworkers<sup>18</sup>, who conclude that the error limits in a determination will probably never be better than about  $\pm 10\%$ .

## Discussion

Analyses especially of the sulfur and iron distribution and chemical form in wood samples prior to a conceivable excavation of marine-archaeological shipwrecks are valuable for evaluating the prerequisites for continued long-term preservation *in situ* or in a museum environment. The accumulation of sulfur compounds in waterlogged archaeological wood is connected to microbial activity. The cycling of sulfur is required for the symbiotic biogeochemical interactions associated with microbial decay of waterlogged wood, in which consortia of marine bacteria including sulfate reducing bacteria (SRB) appear strongly environment-adaptive<sup>2,20,21</sup>. Submerged wood provides ecosystems of high microbial diversity, connected to the successive degradation of the wood<sup>13,14,22</sup>. It has been proposed that aerobic or fluctuating oxygen conditions promote sulfur accumulation by providing a wider range of symbiotic microorganisms than in an anaerobic environment<sup>1</sup>. Hence, the local environment and especially the availability of oxygen affects the microbial activity, which is generally higher at a surface that can be identified as exposed to water or the water-sediment interface. XRF scanning profiles frequently reveal significantly higher sulfur concentration close to the surfaces than inside the wood. Wood samples through an object that

**Table 1** | The analysed shipwreck wood samples in the study

Shipwreck	Sample name	Sampling details	Analyses
Crown	Crown 1a	oak deck plank, buried in clay (rel. anaerobic)	XRF
	Crown 1b	sample located next to 1a	XRF
	Crown 2a	oak piece found on top of seabed (rel. aerobic)	XRF
	Crown 2b	sample located next to 2a	XRF
Sword	Sword 1a	oak, prob. piece of planking found close to bow	XRF
	Sword 1b	sample located next to 1a	XRF
	Sword 1c	sample cut from opposite side (width-wise)	XRF
	Sword 1d	sample located next to 1c	XRF
	Sword 2a	oak piece from hull, found behind ship	XRF
	Sword 2b	sample cut from opposite side (width-wise)	XRF
Ghost wreck	Ghost 1a	sample found on mineralised seabed close to wreck	XRF
	Ghost 1b	sample located next to 1a	XRF
	Ghost 2a	sawed deck plank, a–c cut from freshly sawed end	XRF
	Ghost 2b	sample located next to 2a	XRF
	Ghost 2c	sample located next to 2b	XANES

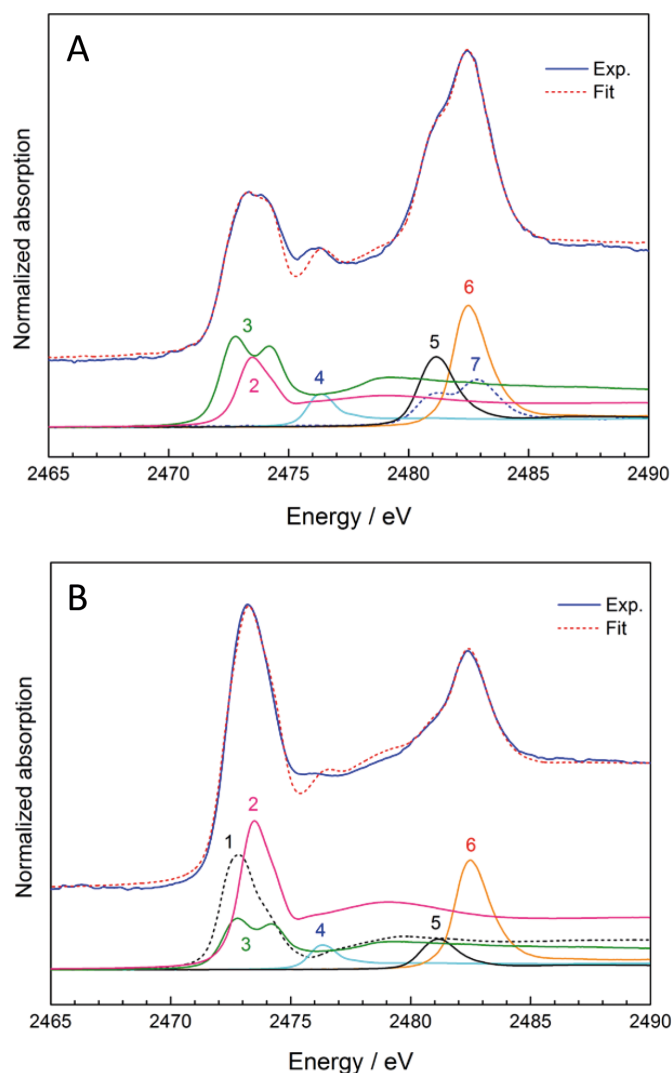


**Figure 5 | XANES spectra for Ghost 2c samples.** The spectral features show that the relative amount of oxidized sulfur compounds ( $\sim 2482$  eV) is higher in the outer surface 1: 0–1 mm (red) than in the subsurface 2: 31–32 mm (blue). The sample from the interior of the wood: 11–12 mm (magenta) is dominated by low-valent sulfur compounds ( $\sim 2473$  eV), generally with 3–4 times lower intensity than the high-valent ones.

show high sulfur concentration at both sides would thus indicate that both surfaces have been exposed to partly aerobic conditions at some time on the seabed. The XRF concentration profiles of sulfur and iron are mostly interrelated, often with sulfur higher than iron especially at high sulfur concentration, indicating an initial formation of iron sulfides as also in previously analyzed samples from the *Vasa* and the *Riksnymekeln*<sup>4,5</sup>. Further investigations of the connection of the sulfur cycle to the circulation of other redox element are needed in order to better understand the degradation and accumulation of natural compounds in waterlogged archaeological wood in different wreck site conditions.

In the Ghost wreck site the presence of *Beggiatoa* indicates sulfur cycling and related biochemical activity<sup>14</sup>. Sulfur speciation by S K-edge XANES analyses of a wood sample from the *Ghost wreck* shows that low-valent sulfur compounds such as thiols, disulfides and elemental sulfur dominate, which is consistent with the low iron concentrations found by XRF. In sample Ghost 2a the pattern of repeating broad iron peaks ( $\sim 0.2$  mass% Fe) may reflect different diffusion rates of iron(II) ions due to the density variations reflected in the annual rings (Fig. 2B). Assuming that the samples are representative for the entire shipwreck the low content of iron compounds, and in particular iron sulfides as indicated from the sulfur and iron accumulation patterns, is beneficial for its future preservation after salvage, with low risk for excessive acid formation from oxidative processes with iron ions as inherent catalysts<sup>4,10,11,19</sup>.

The samples of the *Crown* are, together with the XANES analyses reported in Ref. 5, of similar character as that from the *Ghost wreck* but with somewhat higher iron concentrations close to the surfaces and also with an indication of iron sulfide. In contrast the samples of the *Sword* display significantly higher and interrelated sulfur and iron XRF concentration profiles. However, the sulfur and iron distribution profiles can differ significantly even in neighbouring samples in objects from the same wreck. Further analyses in particular of wood close to corroded iron objects are required prior to salvage for a more general assessment of the sulfur and iron accumulation in order to design conservation programs to minimise future oxidative and acid-producing processes. The biological and chemical wood degradation should also be evaluated to estimate the mechanical strength of the hull of the *Ghost wreck*.



**Figure 6 | Model fitting of XANES spectra.** Fitting of standard XANES spectra (numbers in Table 2) for Ghost 2c wood samples; (A) surface (0–1 mm), (B) interior (11–12 mm).

## Methods

**The wood samples.** The samples Ghost 1 and Ghost 2 (Table 1) are from two planks found on the seabed close to the *Ghost wreck* (Fig. 1B). The samples from the *Crown* in the present study were collected from a piece of wood found on top of the seabed (Crown 2), which was exposed to fluctuating aerobic conditions, and a sample collected from wood within the anaerobic clay (Crown 1). The two oak wood samples from the *Sword* are from a piece of planking found close to the bow (Sword 1) and a piece of inside timber (Sword 2), found partly covered by sediments on the seabed behind the wreck. The fact that both oak wood pieces were partly burnt strongly suggests that they originate from the *Sword*. Dendrochronology shows that sample Sword 2 originates from a tree felled during the winter 1672–1673 and Sword 1 sometime after 1631 (provenience uncertain).

All wood samples were kept in sealed plastic bags after salvage and stored in freezer until sampling. No conservation agent applied. Wood slices (not burnt parts) were cut from the recovered wood samples by knife and from hard wood pieces with a Walesch Dendrocot twin blade electric saw. The samples were cut independent of the wood fiber orientation to show the penetration profile of sulfur and iron in the wood from the outermost surface (exposed to water or sediment) to the inner subsurface. For XRF scanning the wood slices were positioned on a frame.

**XRF scanning.** Concentration profiles of a range of elements in the wood samples, including sulfur and iron, were obtained by means of an Itrax Multiscanner (<http://coxsys.se>) at the Department of Physical Geography and Quaternary Geology, Stockholm University. A conventional X-ray aggregate equipped with a special collimator utilizing total reflection provided focused Cr  $K_{\alpha}$  X-rays (1.5420 Å) in a high intensity  $2 \times 0.05$  mm beam. The element specific X-ray fluorescence was excited along a line from the outer to the inner surface in the mid-section of the sample, and recorded with 0.05 mm resolution by means of an energy dispersive



**Table 2 | Relative amounts of sulfur in functional groups in the Ghost wreck wood by S K-edge XANES fitting\***

Component	Surface: 0–1 mm (%S)	Interior: 11–12 mm (%S)
S <sub>8</sub> (1)	0	23
R-SH (2)	24	43
R-S-S-R (3)	37	18
R <sub>2</sub> S=O (4)	7	4
RSO <sub>3</sub> <sup>-</sup> (5)	9	4
SO <sub>4</sub> <sup>2-</sup> (6)	12	9
R-OSO <sub>3</sub> <sup>-</sup> (7)	11	-

\*The numbers in brackets represent the functional groups of the standard compounds (see Method section) in Fig. 6.

solid-state X-ray detector, from left to right in the images in Figs. 3–5 and Figs. S1–S4. The analytical information depth in the wood was about 1 mm. Quantitative calibration was achieved by analysing standard reference material 1547 from NIST (National Institute of Standards and Technology).

**Sulfur K-edge XANES spectroscopy.** Sulfur K-edge XANES spectra were collected in fluorescence mode from the wood sample Ghost 2c at beamline 4–3, Stanford Synchrotron Radiation Lightsource, SSRL. The characteristics of the refurbished beamline and procedures at measurement were as described elsewhere<sup>18</sup>. The wood was filed in open air to powder, which was spread in a thin layer on sulfur-free Mylar tape in an Al-frame and covered by 6 μm polypropylene film. The X-ray energy of each spectrum was externally calibrated by assigning the first peak of sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O) to 2472.02 eV<sup>23</sup>. For each sample three scans were collected and averaged. The spectra were normalized using the WinXAS program<sup>24</sup>.

The DATFIT program from the EXAFSPAK suite was used for fitting the normalized experimental spectra with a linear combination of normalized S K-edge XANES spectra of standard compounds (EXAFSPAK can be downloaded (22-01-2014) at <http://www-ssrl.slac.stanford.edu/exafspak.html>)<sup>25</sup>. The following standard compounds were used in the fitting, see Figure 6: (1) elemental sulfur S<sub>8</sub> (52 mM solution in *p*-xylene), (2) cysteine as model for thiols R-SH (100 mM solution at pH 7.1), (3) cystine as model for disulfides -S-S- (saturated solution at pH 7.1), (4) solid methionine sulfoxide as R(SO)R' model, (5) methanesulfonic acid CH<sub>3</sub>SO<sub>3</sub>H as model for RSO<sub>3</sub><sup>-</sup> (67 mM solution at pH 1.8), (6) sodium sulfate (55 mM solution), (7) *myo*-inositol-hexasulfate as sulfate-ester R-OSO<sub>3</sub><sup>-</sup> model (25 mM solution). Those model spectra were measured at beamline 6-2 at SSRL, as previously described<sup>15,18</sup>.

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## Author contributions

H.G. carried out the XRF analyses, while A.R. modified the software, did technical development and validation. M.S. performed the XANES experiment at the SSRL. The normalisation and fitting of the XANES spectra was performed by F.J. Geochemical information were provided by I.C. and L.B. The project manager Y.F. collected and prepared the wood samples, interpreted the overall data, and wrote the main part of the manuscript with contributions from the co-authors.

## Additional information

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