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

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Sulfur and iron concentrations in wood from three 17th 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 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. Erosion bacteria are capable of degrading lignocellolytic material in low-oxygen environments while scavenging sulfate reducing bacteria (SRB) metabolising organic debris and cellulose residuals, produce hydrogen sulfide. The HS⁻ 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. 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. 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. 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, 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 sites. Previous analyses of shipwrecks from the Baltic Sea, the Vasa, the Crown and the Riksnynckeln, 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.

The present study concerns three historically significant 17th 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^{12}. 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 γ-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^{13–15} (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^{16}. 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^{4,5}. The sulfur K-edge XANES spectroscopic method allows, when utilizing the intense X-ray radiation from synchrotron sources^{17}, such speciation analyses and has previously been used for several shipwrecks^{4,5,18,19}, including samples from the Crown^{17}. 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 Riksnyckeln^{4,5}. 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^{17}. By fitting the normalized experimental spectra with linear combinations of normalized S K-edge XANES spectra of standard

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**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.
compounds representing different sulfur functional groups (Figure 6), the relative amount of such species can be obtained (Table 2)\(^1\). The intensity of a high-valent sulfur feature generally is 3–4 times stronger than for the low-valent ones\(^1\), 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, \(S_\text{e}\) (∼22%) was also found (Table 2), while no contribution of the standard spectrum of pyrite could be included in the fitted model.

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.

Figure 3 | XRF-scans of the Crown samples 1b (A) & 2a (B). The sulfur and ion 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).
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, was found mainly at the surface. A few atom% S occurs as organosulfur compounds with an intermediate oxidation state (~2476 eV). The sulfoxide model compound does not give a perfect fit and also trimethylsulfonium has been proposed as a possible additional minor functional group.

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, who conclude that the error limits in a determination will probably never be better than about ±10%.

**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    |

**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. Submerged wood provides ecosystems of high microbial diversity, connected to the successive degradation of the wood. 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. 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
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 Riksnyckeln. 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. 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 (~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 cycling and related biochemical activity. 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 (~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.

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.

**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. 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 Walsch Dendrocut 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 Kα X-rays (1.5420 Å) in a high intensity 2 × 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
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 2 at beamline 4-3, Stanford Synchrotron Radiation Lightsource, SSRL. The characteristics of the refurbished beamline and procedures at measurement were as described elsewhere (18). 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 (Na2S2O3•5H2O) to 2472.02 eV (19). For each sample three scans were collected and averaged. The spectra were normalized using the WinXAS program (20).

The DAFFIT 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 (21-01-2014) at http://www-srsl.sacl.stanford.edu/exafspak.html) (21). The following standard compounds were used in the fitting, see Figure 6: (1) elemental sulfur S (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 RS(OMe)2 model, (5) methanesulfonic acid CH3SO2H as model for RO>S (67 mM solution at pH 1.8), (6) sodium sulfate (55 mM solution), (7) myo-inositol-hexasulfate as sulfate-ester R-OSO32− model (25 mM solution). Those model spectra were measured at beamline 6-2 at SSRL, as previously described (22).

| Component | Surface: 0–1 mm (‰) | Interior: 11–12 mm (‰) |
|-----------|---------------------|-------------------------|
| S (1)     | 0                   | 23                      |
| R-SH (2)  | 24                  | 43                      |
| R-S-S-R (3) | 37                | 18                      |
| R2S2-O (4) | 7                  | 4                       |
| RSO32− (5) | 9                  | 4                       |
| SO42− (6) | 12                  | 9                       |
| R-OSO32− (7) | 11             | –                       |

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

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**Additional information**

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