

## Deterioration of the seventeenth-century warship *Vasa* by internal formation of sulphuric acid

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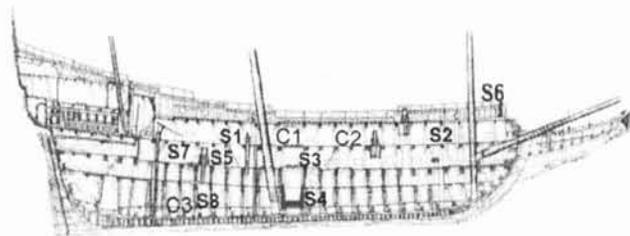
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The seventeenth-century Swedish warship, *Vasa*, was recovered in good condition after 333 years in the cold brackish water of Stockholm harbour. After extensive treatment to stabilize and dry the ship's timbers<sup>1</sup>, the ship has been on display in the Vasa Museum since 1990. However, high acidity and a rapid spread of sulphate salts were recently observed on many wooden surfaces<sup>2</sup>, which threaten the continued preservation of the *Vasa*. Here we show that, in addition to concentrations of sulphate mostly on the surface of oak beams, elemental sulphur has accumulated within the beams (0.2–4 per cent by mass), and also sulphur compounds of intermediate oxidation states exist. The overall quantity of elemental sulphur could produce up to 5,000 kg of sulphuric acid when fully oxidized. We suggest that the oxidation of the reduced sulphur—which probably originated from the penetration of hydrogen sulphide into the timbers as they were exposed to the anoxic water—is being catalysed by iron species released from the completely corroded original iron bolts, as well as from those inserted after salvage. Treatments to arrest acid wood hydrolysis of the *Vasa* and other wooden marine-archaeological artefacts should therefore focus on the removal of sulphur and iron compounds.

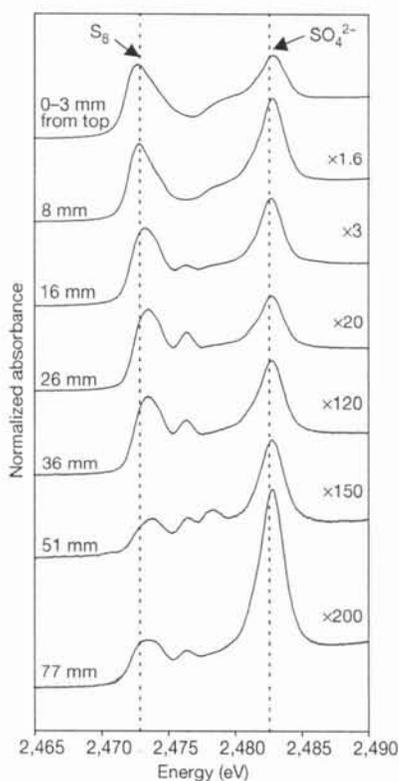
The *Vasa* sank in Stockholm harbour on her maiden voyage in 1628, and was salvaged in 1961. The massive oak beams were seemingly in good condition after 333 years at 32 m depth (see <http://www.vasamuseet.se/indexeng.html> and links therein). Marine burial occasionally deposits wooden objects in near anoxic environments that arrest natural decay. This favours sulphate-reducing bacteria producing hydrogen sulphide in an environment inhospitable to most wood-metabolizing microbes<sup>3</sup>. In such conditions slow biodegradation of waterlogged wood takes



**Figure 1** Outline of the hull of the *Vasa* with sample positions indicated. C1–C3, for cores; S1–S8, surface XRD samples. Dimensions: length 61 m (69 m including bowsprit), maximum width 11.7 m, stern castle 19.3 m high, displacement 1,210 tons.

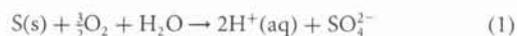
place mainly by heterotrophic 'erosion' bacteria<sup>4</sup>, leaving a weak water-filled skeleton of cell lamellae. Before the wood can be dried, the internal water must be replaced with a non-volatile material to prevent shrinkage of the artefact. The *Vasa* was the first major object for which aqueous solutions of polyethylene glycol (PEG),  $H(OCH_2CH_2)_nOH$  with  $10 < n < 90$ , was used. Intermittent spraying was applied for 17 years followed by nine years of slow drying before the ship was put on display in 1990 in the *Vasa* Museum, Stockholm<sup>1</sup>. PEG treatment is now commonly used for many ancient shipwrecks that have been salvaged, such as the *Skuldelev* Viking ships, the *Bremen Cog*, the *Mary Rose* (Portsmouth) and the *Batavia* (Western Australia). However, waterlogged wood may, even if PEG-treated, develop high acidity and salt formation, which if left unattended will damage the artefacts.

In July 2000, salt formation and pH values below 2 were observed inside the *Vasa* in numerous places; there are now more than 600. Using X-ray powder diffraction (XRD) we identified crystalline hydrated sulphates, most frequently gypsum,  $CaSO_4 \cdot 2H_2O$ , natrojarosite,  $NaFe_3(SO_4)_2(OH)_6$ , melanterite,  $FeSO_4 \cdot 7H_2O$ , and also elemental sulphur (brimstone  $S_8$ ) on the wooden surfaces<sup>2</sup>. Core samples were taken (Fig. 1), several at sample position C1 (surface pH about 3) and at C3 (visibly sound) by drilling ~10 cm into large (~40 × 40 cm) oak beams, and at C2 through a 70-mm oak plank 'armouring' the oak beams around the gun ports. The wood was soft and dark for the first few millimetres, but became harder and lighter with increasing depth. The sulphur K-edge XANES (X-ray absorption near-edge structure) spectra showed characteristic features that allow identification of the sulphur compounds (Fig. 2). The two major XANES peaks correspond to elemental sulphur (2473.0 eV), and sulphate ( $SO_4^{2-}/HSO_4^-$ ; 2482.6 eV). Although XRD spectra



**Figure 2** Sulphur K-edge XANES spectra from core C1a (oak from upper gun deck of the *Vasa*). The major peaks are from elemental sulphur (2,473.0 eV) and sulphate  $SO_4^{2-}$  (2,482.6 eV) with intermediate minor sulphur compounds in different oxidation states between 0 and +VI. The intensity factors between the normalized spectra are estimated from the elemental analyses (see Methods).

showed traces of pyrite,  $FeS_2$ , below the surface no disulphide features (2472.4 eV) were detected<sup>2</sup>. The XANES spectra show several intermediate oxidation states between 0 and +VI (Fig. 2), corresponding to a stepwise oxidation to sulphuric acid in the overall reaction:



We applied X-ray photoelectron spectroscopy (XPS), which allows quantitative determination of all significant elements except hydrogen (see Supplementary Information), to the samples. The sulphur 2p XPS spectrum of the neighbouring core C1b (Fig. 3) displays two peaks for sulphur, representing high and low oxidation states. The total sulphur, determined by elemental analyses on dried wood (see <http://www.mikrokemi.se>), is about 6 mass% within a surface layer of 1 cm, decreasing to a low level further inside (Fig. 4a). In core C2 through the plank the total sulphur is much lower but increases close to both surfaces (Fig. 4b). Core C3 exhibits intermediate sulphur concentrations. Elemental sulphur dominates, except on the outer exposed surfaces. The boron concentration is high (~0.3–1 mass%) at all depths (Fig. 3), indicating that boric acid—uncharged  $H_3BO_3(aq)$  that dominates below pH ~9, from the fungicidal boric acid/borax (7:3) mixture (1–4%) in the PEG spray-solutions<sup>1</sup>—efficiently penetrated the wood. Iron has its highest concentration in the surface layer and a low level (~0.1 atom%) deeper inside (Fig. 4).

The combination of X-ray analyses (XANES, XPS and XRD) reveals oxidizable elemental sulphur beneath every surface of the *Vasa*, which has a surface area of about 14,000 m<sup>2</sup> (ref. 5). The first centimetre (density ~0.9 kg dm<sup>-3</sup>, ~30 mass% PEG)<sup>1</sup> of core C1 contains about 3 mass% elemental sulphur, equivalent to 0.5 mol dm<sup>-3</sup> sulphuric acid when oxidized. For core C2 (~0.2 mass% S) the potential acid concentration is about 0.03 mol dm<sup>-3</sup>. For the *Vasa*, with 1,210 tons displacement, the total potential yield of sulphuric acid from the oxidizable sulphur is estimated to be at least 5,000 kg.

The sulphate present indicates that a large amount of sulphur has already been oxidized. The acid produced probably consumed the large amounts of borax added to keep the pH of the re-circulated preservation-spray solution up at about 7 (ref. 1). A final surface treatment of the *Vasa* was made with long chain PEG (relative molecular mass  $M_r$  4,000)<sup>1</sup>. The surplus was melted off, forming a wax-like layer. However, PEG 4,000 was not applied inside the hold, which now has large acidic areas. Current neutralization treatment with wet carbonate/bicarbonate poultices temporarily raises the surface pH from 1–2 to about 6, but in a few months the pH reverts back to low values.

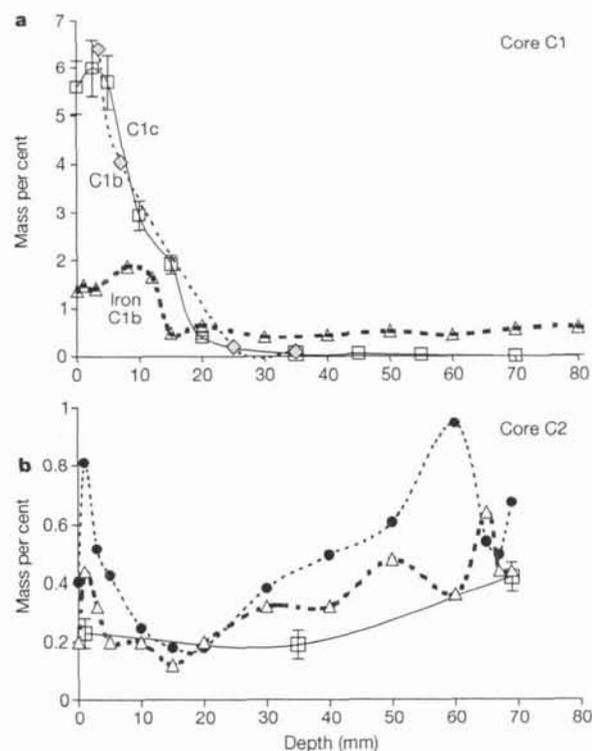
We wondered what was the origin of the high sulphur content. In the past, the sewage from the city of Stockholm resulted in anoxic bottom waters with bacterial reduction of sulphate to hydrogen sulphide,  $H_2S$ . In 1943 analyses showed 7 mg  $H_2S$  per litre in the *Vasa* locale<sup>1</sup>. The large quantities of elemental sulphur in the wood must have accumulated from pre-salvage oxidation of penetrating  $H_2S(aq)$ . Recently, we analysed fresh cores from the submerged wreck of the warship *Kronan*, which sank in battle in 1676 outside Öland in the Baltic (see <http://www.kalmarlansmuseum.se/kronan/english/index.html>), and found large amounts of elemental sulphur but little sulphate. Cores from the *Batavia* contained mostly elemental sulphur together with sulphate, but also iron sulphides in iron-rich environments. This is consistent with the redox conditions shown in Fig. 5 (ref. 6), even though the oxidation mechanism of  $H_2S$  to elemental sulphur, bacterial or chemical, is still unknown.

The present aerobic sulphur oxidation (equation (1)) is probably chemically controlled because the boric acid suppresses microbial activity. Strict regulation of the relative humidity (about 55%) and low temperature (<20 °C) in the museum hall will slow down the process somewhat<sup>7</sup>, mainly by decreasing water and

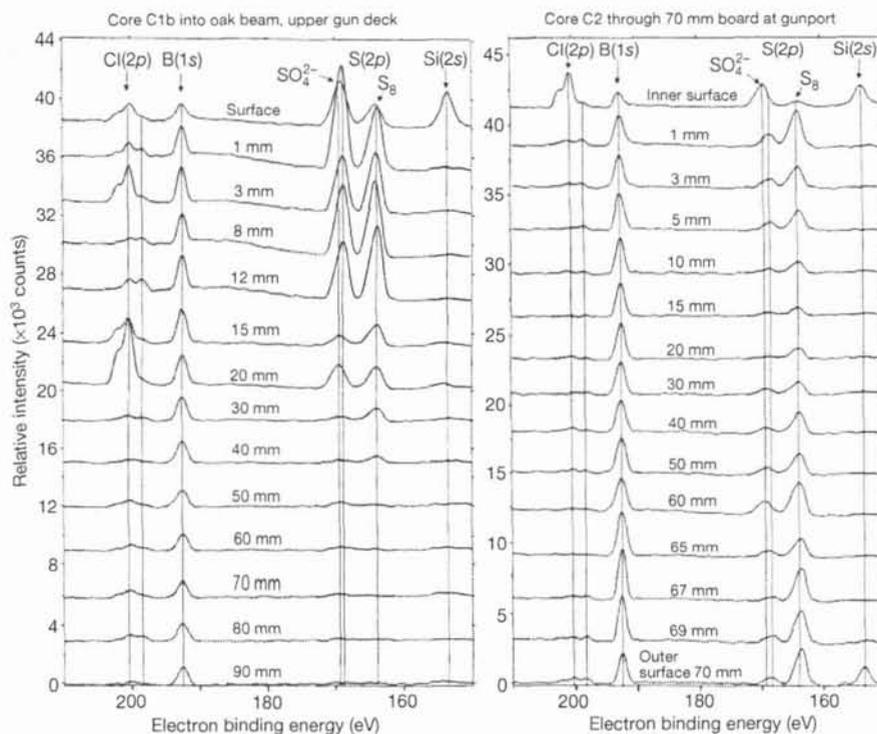
oxygen migration in the wood. The transformation of elemental sulphur or sulphides to solid hydrated sulphate salts leads to substantial volume expansion<sup>7</sup>. If such crystallization takes place inside the wood structure, mechanical damage may result<sup>7</sup>. Equilibrium calculations show that precipitation of natrojarosite can occur in a wide pH range from a solution containing iron(III), sodium and sulphate (Fig. 5)<sup>2</sup>. In the *Vasa*, the moderate calcium and iron concentrations are highest close to the surface, consistent with the surface formation of the low-solubility gypsum and natrojarosite salts.

Iron species increase the reaction rate for oxidation of sulphur<sup>8,9</sup>, and catalyse the oxidative degradation of cellulose<sup>10</sup>, and probably of polyethylene glycol, giving, for example, formic acid<sup>11</sup>. Metallic iron corrodes rapidly in PEG solutions and metal ions coordinate the ether oxygens and hydroxy groups of the PEG polymers<sup>12-14</sup>. Many of the roughly 8,500 iron bolts, inserted to hold the hull together instead of the completely corroded original bolts of the *Vasa*<sup>1,5</sup>, now show severe corrosion and provide a new iron source in the PEG-treated wood. Replacement bolts of inert material, followed by sequestration of iron species in the wood, are required. Selection of a stable chelating agent that can make iron(III) complexes electrochemically inert and extractable even in alkaline aqueous solution<sup>15</sup>, needs further investigation<sup>2</sup>.

The experimental use of PEG and borates in the conservation treatment of the *Vasa*<sup>1</sup> seems to have been successful, but has not amended the problems caused by the sulphur and iron contaminations. The increasing acidity shows continuing sulphur oxidation. The most immediate threat is acid-catalysed hydrolysis of the cellulose which would reduce the stability of the wood<sup>16</sup>. Repeated neutralization treatments are necessary, although the many hidden surfaces of the large intact structure of the *Vasa* cause severe problems, and it is important to slow down the production of the acid.

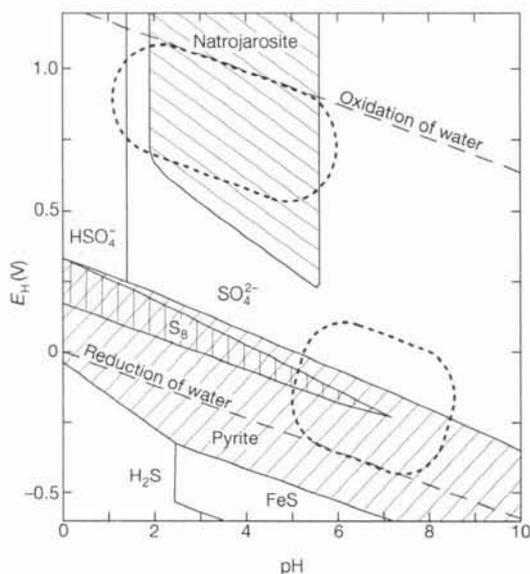


**Figure 4** Depth profiles of total sulphur and iron in cores for oak beams of the *Vasa*. **a**, Cores C1 (80 mm into oak beam). Elemental analyses of total sulphur in core C1b (squares) and C1c (diamonds); XPS analysis of iron (C1b, triangles). **b**, Core C2 (through 70-mm board). Total sulphur from elemental analysis (squares) and XPS (dots), and iron from XPS (triangles) analyses.



**Figure 3** XPS spectra of oak-wood cores C1b and C2 from the *Vasa*. The binding energies in the energy range 150–210 eV of element-specific photoelectrons are shown. Two well-resolved peaks of the sulphur 2p photoelectrons correspond to reduced (at 164 eV)

and oxidized (at 169 eV) sulphur. Boron is abundant at all depths, and silicon and chlorine occur at the surfaces (it seems that core C1b cuts through a crack at 20 mm depth).



**Figure 5** Redox (Pourbaix) diagram  $E_H = f(\text{pH})$  showing predominant sulphur-containing species in equilibrium with iron and sodium ions in aqueous solution (calculated for  $[\text{Fe}^{3+}] = 0.05 \text{ M}$ ,  $[\text{Na}^+] = 0.4 \text{ M}$ ,  $[\text{SO}_4^{2-}] = 0.35 \text{ M}$ ). The calculations performed using *MEDUSA* and *HYDRA* with equilibrium constants and standard electrode potentials at 25 °C include approximate corrections for activity factor variations<sup>25</sup>. The dashed lines enclose the water stability range<sup>6</sup>. Conditions at sea-bottom where sulphate-reducing bacteria are active in a near-anoxic environment are represented by the lower area enclosed with a dotted line, where pyrite ( $\text{FeS}_2$ , right-diagonal hatched area) and elemental sulphur ( $\text{S}_8$ , vertically hatched area) can coexist. Natrojarosite ( $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ , left-diagonal hatched area) can precipitate in the current oxidizing museum atmosphere (upper area within dotted line) if formation of the more stable iron oxide hydroxides (for example, goethite  $\text{FeOOH}$ ) is suppressed. The effective oxygen activity from  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$  corresponds to the redox potential  $E_H = 1.23 - 0.059(\text{pH} - 1/4\log P_{\text{O}_2})$ <sup>6</sup>.

The sulphur problem seems to be general for marine-archaeological wooden artefacts recovered from near-anoxic conditions. For objects *in situ*, special attention should be given to oxidizable sulphur. Conservation procedures should be developed that will oxidize or remove the sulphur without degrading the cellulose<sup>16</sup>, together with rendering transition-metal ions such as iron or copper catalytically inactive. □

## Methods

### XANES measurements

Sulphur K-edge X-ray absorption spectra were collected in fluorescence mode on wiggler beamline 6-2 at the Stanford Synchrotron Radiation Laboratory (SSRL) under dedicated conditions of 3.0 GeV and 75–99 mA of current. The X-ray energy was varied using a Si(111) double-crystal monochromator and a nickel-coated mirror to reject higher-order harmonics. The beam-path and sample chamber were in helium atmosphere. The samples, stored and handled in inert atmosphere in a glove box, were filed to fine particles and mounted as a thin layer on a sulphur-free tape covered by a 6 µm polypropylene film. The emitted X-ray fluorescence, proportional to the X-ray absorption in the sample, was measured at 90° using a nitrogen-filled Lytle detector<sup>17</sup>. The energy scale was calibrated against the first peak position of sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , set to 2,472.0 eV (ref. 18). The energy of the sulphur K-edge, that is, for releasing a core electron from the 1s orbital, is sensitive to the oxidation state, shifting 13 eV from sulphides to sulphate<sup>19</sup>. The near-edge features are also sensitive to the chemical environment of the absorbing sulphur atom, but self-absorption effects must be considered, especially in solids<sup>20</sup>. The intensity of the XANES features is not only affected by the sulphur concentration but also by the symmetry-dependent (1s → valence orbital) transition probability for each sulphur component in a sample<sup>19,21,22</sup>. Thus, the XANES intensity maximum of elemental sulphur is almost a factor of 3 less than that of sulphate. Comparisons of the spectra and their second derivatives with those from standard compounds can reveal the relative amount of characteristic sulphur groups in a given sample<sup>19</sup>. For instance, the pH at various depths of the cores can be estimated from the  $\text{SO}_4^{2-}/\text{HSO}_4^-$  ratio of the sulphate peak. Preliminary fits

to the surface XANES spectrum of core C3 indicate an  $\text{SO}_4^{2-}/\text{HSO}_4^-$  ratio consistent with the pH of ~2 (ref. 2), measured with pH paper (Merck). The XANES spectra presented in Fig. 2 have been normalized to a unit absorption edge step<sup>19</sup>, which means that for comparing intensities from different samples a concentration factor obtained for the elemental analysis must be applied.

### XPS measurements

Thin oak wood slices were taken at various depths along the core, mounted and transferred in vacuum into the sample chamber of a Scienta ESCA 300 instrument<sup>24</sup>. High-intensity monochromated Al K<sub>α</sub> X-ray radiation (1,487 eV) was used to excite photoelectrons from the core shells of all elements in the sample. The kinetic energy of the photoelectrons was measured to obtain the binding energy of the core electrons. The following elements were found to be present in significant amounts in the oak rod: B, C, N, O, Na, S, Si, Cl, Ca, Fe; and the elements Li, P, K and Mn were below the XPS detection limit. Pumping for several hours was required to reduce the vapour pressure, which was about  $1 \times 10^{-6}$  Pa when starting the measurements, and often at  $4 \times 10^{-7}$  Pa at the end of the analyses. The low pressure reduces the concentration of volatile compounds in the samples, for example water. The intensity is proportional to the atomic concentration of each element and the sulphur 2p photoelectrons allowed quantitative analyses of fair accuracy. The photoelectrons are strongly absorbed by the sample itself, and only the surface layer (<100 Å) contributes to the signal. This means that surface contamination can easily affect the results. Comparison with the elemental analysis reveals some discrepancy; for example, the sulphur concentration by XPS at 3-mm depth for core C1b seems to be too low (see Supplementary Information). This may be due to partial vaporization (vapour pressure about  $5 \times 10^{-4}$  Pa at 25 °C of crystalline sulphur). However, the simultaneous carbon and oxygen variation indicate that smearing of the surface in the PEG-rich surface layer may influence the low sulphur value. Radiation damage of the sample is also possible, and after long exposure a small reduction of the sulphate signal and a corresponding increase of the signal for elemental sulphur was observed.

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**Supplementary Information** accompanies the paper on *Nature's* website (<http://www.nature.com>).

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