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Oxidative degradation of archaeological wood and the effect of alum, iron and calcium salts

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Abstract

Oxygen consumption measurement was used to study potential oxidative degradation reactions occurring in wooden artefacts from the Viking age Oseberg collection in Norway. Model samples of fresh birch were impregnated with iron, calcium and alum salts to mimic concentrations of such compounds found in Oseberg artefacts and to assess their effect on oxygen consumption rates. The results showed that heated impregnation with alum salt ($KAl(SO_4)_2 \cdot 12H_2O$) significantly increased the rate of oxygen consumption, confirming a previously observed link between alum-treatment and wood oxidation. The presence of iron salts in alum-treated wood specimens, even at low concentrations, also substantially increased the oxidation rate. However, the mechanism by which this occurred appeared to be influenced by the alum-treatment. Samples treated with both iron and calcium salts were also studied, in order to investigate a proposed inhibition of iron-induced oxidation by calcium ions. However, these did not appear to consume oxygen at significantly different rates. In Oseberg samples, a large variation in oxygen consumption rates from 0.48 to an apparent $8.2 \mu g O_2 (g \text{ wood})^{-1} \text{ day}^{-1}$ was observed, and these values were consistently higher than those for reference fresh wood. The results demonstrated that oxygen consumption measurement is a viable method of evaluating chemical stability in this case, but is best applied to model samples with limited compositional variability.

Keywords: Oxygen consumption, Degradation, Waterlogged wood, Alum, Iron compounds, Oseberg

Introduction

Ongoing degradative processes are a well-documented problem in collections of waterlogged archaeological wood, as are the challenges associated with studying them [1–4]. As the processes are slow, the chemical changes they produce within a reasonable timeframe can be hard to detect, and some uncertainty arises when using destructive analysis of micro-samples due to the heterogeneity of the material. It can therefore be difficult to determine rates of degradation, which in turn limits measurement of the stabilisation effectiveness of conservation treatments.

Oxygen consumption measurement has been shown to be an effective means of monitoring real time chemical change in wooden objects related to degradation [5, 6]. In studies on Fe(II)-impregnated fresh oak used to model iron-catalysed processes occurring in the Swedish warship *Vasa*, oxygen consumption was linked to depolymerisation of cellulose, acidification and reduction in mechanical strength [7]. In waterlogged archaeological wood, it was shown that oxidative processes, probably autooxidation, were ongoing and measurable as oxygen consumption, despite conservation treatment [8, 9].

In the Norwegian Oseberg collection, one of the richest and most comprehensive collections of Viking Age wooden objects in the world, degradation has in fact been exacerbated by conservation with the historical alum-treatment [10–12]. The treatment, as it was used on the most degraded wood from the Oseberg finds, involved

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soaking the waterlogged fragments in hot (90 °C) concentrated solutions of alum for an average of 24 h, in order to prevent shrinkage during drying [13]. Available information specifies use of potassium alum ($KAl(SO_4)_2 \cdot 12H_2O$) [14], though a recent study suggests that this was often mixed with varying proportions of ammonium alum ($NH_4Al(SO_4)_2 \cdot 12H_2O$) [15]. The alum conservation method was widely used to treat waterlogged archaeological wood up until the 1950s, especially in Scandinavia [16–18], but is now obsolete. Studying issues in the Oseberg artefacts has required developing new knowledge about the chemical nature of alum-treated archaeological wood and its degradation processes, which is not only important when considering the future preservation of these finds, but also applicable to other alum-treated objects that may be present in collections worldwide. The deterioration in the alum-treated Oseberg artefacts is believed to be an active process, and while linked to acid formation due to alum-treatment, a lack of clear correlation between pH levels and degree of deterioration suggests that acid hydrolysis is not the only reaction at play [1]. We have not yet been able to obtain any realistic estimate of the present rate of degradation. However, the fact that alum-treatment appears to be related to extensive lignin oxidation, in addition to almost complete holo-cellulose depletion, indicates that the speed of the decay could be at least partially measured by oxygen consumption monitoring [19, 20]. Furthermore, it is known that iron ions can play a catalytic role in oxidative wood degradation [21, 22], an issue that has been discussed in several studies on archaeological wooden artefacts [23–27]. In studies on the alum-treated wood of the Oseberg collection, our group observed some evidence of potential relationships between iron and oxidation, but so far it is relatively weak [19, 20]. We noted a potential moderating effect of calcium on iron-promoted degradation in the same studies. The present work uses oxygen consumption measurement to investigate such oxidative processes in alum-treated and Oseberg wood. We herein describe studies of the rates of oxidation of model birch samples treated with combinations of iron, calcium and alum salts, in addition to various samples of alum-treated wood from the Oseberg collection and Oseberg ship oak (which is not alum-treated), in order to explore ongoing processes. We also aim to determine whether oxygen consumption monitoring is a viable tool for assessing degradation rates of alum-treated objects and/or evaluate the success of retreatments.

Materials and methods

Samples

A total of 44 wood samples used in the oxygen consumption experiments are summarised in Table 1. The first

nine sets are model samples from fresh birch rods that were cut into ca. $3 \times 1 \times 1$ cm³ pieces and treated in different ways. Potassium alum, iron(II) chloride tetrahydrate, calcium chloride and iron(II) sulfate tetrahydrate, purchased from Sigma-Aldrich, were used to treat these samples.

For the “Fe” samples, solutions of 0.1 M $FeCl_2$ in deionised water were made up with $CaCl_2$ added in the following Fe:Ca molar ratios: 1:0, 1:1, 1:2 (three samples each). Three birch pieces were immersed in each solution, with further three pieces immersed in deionised water as a control set. After one month immersion the wood pieces were removed and air-dried. For the “alum” samples, alum-treatment in the lab mimicked alum-treatment as it was used on the Oseberg finds, with a concentration of 2:1 parts potassium alum to water by weight and immersion time in the hot (ca. 90 °C) alum bath for 24 h before air-drying. Birch pieces to be treated with alum were waterlogged in deionised water prior to treatment. Potassium alum (40.0 g, 84.3 mmol) was mixed with 20 mL deionised water and heated in a water bath at 93 °C such that all alum dissolved to give ca. 40 mL of solution. Mixtures with 0.20, 2.00 and 20.00 mmol of $FeSO_4$ were also prepared, to give solutions with iron concentrations of ca. 0.005, 0.05 and 0.5 M (taking into account that potassium alum dissolves in its own crystal water on heating). Three waterlogged birch pieces were immersed in each solution, along with a control set in deionised water heated to the same temperature. The wood pieces were immersed in the hot solutions for 24 h, before removing, rinsing with cold water and allowing to air dry. Impregnation of iron and calcium species and alum throughout the wood was confirmed with scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) (see Additional file 1 for more details).

In order to assess model alum-treated samples of archaeological wood as well as fresh wood, four pieces of alum-treated archaeological birch from earlier experiments in 2012 were also included.

The remaining samples are fragments from the Oseberg collection. Two samples of oak from the Oseberg ship were included, along with corresponding fresh oak references, all untreated and with roughly the same regular dimensions of ca. $5.9 \times 0.8 \times 1.6$ cm³. The other samples are alum-treated fragments from unreconstructed parts of Oseberg objects including a loom (185), a simple sled (229) a baking trough (207) and a barrel or vat (210), with and without linseed oil, as described. The wood in these objects was too degraded to identify the genus.

Oxygen consumption experiments

All samples were pre-conditioned at $52\% \pm 2\%$ RH in a desiccator. The desiccator was not temperature

Table 1 Description and sizes of wood samples used in oxygen-consumption experiments

Sample name	Treatment/description	Vol. (cm ³)
Fe	0.1 M FeCl ₂ treated birch, 3 samples	3
Fe-Ca	0.1 M FeCl ₂ + 0.1 M CaCl ₂ treated birch, 3 samples	3
Fe-2Ca	0.1 M FeCl ₂ + 0.2 M CaCl ₂ treated birch, 3 samples	3
Ref-ambient	Untreated birch immersed in water, 3 samples	3
Alum	Alum treated birch, 3 samples	3
al-Fe0.005	Alum + 0.005 M FeSO ₄ treated birch, 3 samples	3
al-Fe0.05	Alum + 0.05 M FeSO ₄ treated birch, 3 samples	3
al-Fe0.5	Alum + 0.5 M FeSO ₄ treated birch, 3 samples	3
Ref-heated	Untreated birch heated in water (as in alum treatment), 3 samples	3
Arch12-frag1	Archaeological birch treated with alum in 2012	27
Arch12-frag2	Archaeological birch treated with alum in 2012	9
Arch9-1-frag1	Archaeological birch treated with alum in 2012	19
Arch9-1-frag2	Archaeological birch treated with alum in 2012	16
oseberg-d11	Untreated, archaeological oak from Oseberg ship (two pieces 1 and 2)	7
Fresh Oak	Untreated fresh oak (two pieces, 1 and 2)	8
185-2	Alum-treated arch. diffuse porous wood from Oseberg, no other additives	9
185-5	Alum-treated arch. diffuse porous wood from Oseberg, no other additives	11
229-5-AR	Alum-treated arch. diffuse porous wood from Oseberg, no other additives	3
207-frag1	Alum-treated arch. diffuse porous wood from Oseberg, linseed oil coated	12
207-frag2	Alum-treated arch. diffuse porous wood from Oseberg, linseed oil coated	4
207-frag3	Alum-treated arch. diffuse porous wood from Oseberg, linseed oil coated	2
210-frag3	Alum-treated arch. ring porous wood from Oseberg, linseed oil soaked	4
210-frag7	Alum-treated arch. ring porous wood from Oseberg, linseed oil soaked	5
210-frag8	Alum-treated arch. ring porous wood from Oseberg, linseed oil soaked	4

controlled (ambient temperature generally 21 to 25 °C). The samples were then sealed in oxygen-tight bags prepared using Escal film and equipped with a PreSens oxygen-sensitive spots, and oxygen levels measured as % oxygen saturation using a Fibox3 m, in accordance with published procedures [6, 9]. The rate of oxygen consumption was calculated in micrograms of oxygen per gram of wood per day as described therein, with modifications for salt content. For model wood samples impregnated with salts, the mass of the wood without salts was used in calculations. For alum-treated Oseberg samples, the mass of alum was estimated based on Al contents determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, reported herein or in [28]) and subtracted from the total sample mass to give an estimate of the wood mass. The internal volume of air in the wood was calculated by Eq. 1 to account for salt content:

$$V_{int} = V_{smp} - \frac{m_{smp}}{1 + F} \left(\frac{1}{\rho_{wood}} + \frac{F}{\rho_{H_2O}} \right) - \frac{m_{salt}}{\rho_{salt}} \quad (1)$$

where V_{smp} is the volume of the sample, m_{smp} is the mass of the sample without salts, m_{salt} is the mass of the salts estimated from ICP data or mass differences before and

after impregnation, ρ_{H_2O} is the density of water, ρ_{salt} is the density of the salt as given in [29] or an approximate average in the case of mixtures, ρ_{wood} is the cell wall density (1.5 g/cm³) and F is the fraction of water in wood relative to dry weight at 50% RH (0.09) as given in [30].

Volumes of the wood samples, given in Table 1, were either calculated from measured dimensions in regularly shaped samples, or by measuring their buoyancy (weight of displaced fluid) in water (samples kept dry using parafilm or plastic bags) if irregularly shaped. Volumes of the sealed Escal bags were also determined using buoyancy.

The oxygen consumption of the samples was monitored at ambient temperature for up to 443 days. Measurements of reference bags containing potassium alum and only air were also performed.

ICP-OES

Samples from the following fragments were analysed by ICP-OES: 185-2, 185-5, 207-frag3 (inner core and outer surface samples) and 210-frag3 (surface). Samples 210-C, D are surface samples from a separate fragment from object 210, and 210-E is a core sample from the same fragment. A separate sample of fresh birch was also analysed as a reference. ICP-OES analyses were performed

using a Thermo Scientific iCAP 6300 Dual View ICP-OES with a CETAC ASX-260 autosampler. Three replicates were analysed per sample. After incineration of the samples in a muffle furnace (550 °C), treatment of the resulting ashes with aqua regia, filtration, and dilution with 2% (w/w) nitric acid in ultrapure water, the concentrations of Al, Ca, Fe and K were measured. Such a sample treatment method was developed along with previous studies of complex organic-inorganic materials [31, 32].

The spectral lines used and the plasma view mode for element quantification were as follows: Al, 308.215 nm (axial); Ca, 317.993 nm (axial); Fe, 259.940 nm (axial); K, 769.896 nm (radial). These were chosen after an appropriate method development for this matrix and were the most accurate ones. The operating conditions of the instrument are reported in Table 2.

The main analytical figures of merit of the developed ICP-OES method for the measurements carried out for this study are reported in Additional file 1.

Statistical analysis

Statistical tests were used to evaluate the significance of the difference between mean oxygen consumption rates of the model fresh birch samples. One-way analysis of variance (ANOVA) and independent *t*-tests (two-tailed, equal variance) were applied at a significance level of 0.05 using SPSS software (v. 25.0). ANOVA was used to

determine if there were significant differences in oxygen consumption rates of iron treated samples due to different calcium concentrations, (i.e. between means of the Fe, Fe-Ca and Fe-2Ca samples), and oxygen consumption rates of alum-treated samples due to different iron concentrations (i.e. between means of the alum, al-Fe0.005, al-Fe0.05 and al-Fe0.5 samples). In the case of ANOVA finding overall significance, this was followed by a Tukey post hoc test to determine which means were different. Independent *t*-tests were used to determine the significance of differences between the Fe samples or alum samples and the respective control set (ref-ambient or ref-heated). Effect sizes were calculated to help assess if differences were large enough to have a practical value, and were measured using Hedges' *g*, due to the small number of samples [33]. Guidelines for its interpretation are similar to those associated with Cohen's *D*, for which values of 0.8 can be considered large [34] and greater than 2 can be considered huge [35].

Results and discussion

Fresh birch samples with iron(II) and calcium salts

Figure 1 shows the results of the sets of model samples investigating the effects of iron and calcium ions. The Fe:Ca molar ratios reflected those observed in the previously investigated Oseberg samples [19, 20] and the ICP-OES results of samples analysed for this work (Table 3), which were all generally between 1:0 and 1:2. Amounts of iron absorbed by the model samples were somewhat higher than the quantities found in the Oseberg samples: the mass difference of the samples treated with FeCl₂ before and after treatment reflect an Fe content in the model samples of ca. 68 mmol/100 g wood, compared to ca. 0.1 to 3.5 mmol/100 g in the Oseberg samples. This was deemed acceptable in order to increase the rate of iron-promoted degradation and thereby our chances of obtaining rate information within a reasonable time-frame. Indeed, even with these concentrations, it took 443 days for the oxygen saturation to drop below 10% for all these iron-treated model samples. Figure 1a shows that the slopes of the curves decrease with decreasing oxygen concentration in all treated samples. Linear curves were obtained for (O₂ sat %)^{1/2} vs. time, and the equivalent plots against time with O₂ sat %, its natural logarithm or inverse were not linear. The integrated rate laws therefore reflect non-integer (pseudo-half) order reactions, and preclude zero, first or second order reactions. This suggests complex but similar reaction kinetics in these samples. As discussed previously, the reaction kinetics of oxygen consumption in wood samples are probably complicated by diffusion effects, and by the presence in the sample of possible oxygen consuming species other than wood [7, 9]. However, we note here that the Fe(II)

Table 2 Operating conditions and types of instrument parts employed for ICP-OES analyses

Operating condition/ Instrument part	Value/Type
Effective focal length	383 nm
Spectral range	166847 nm
Detector	CID86 chip (charge injection device)
RF generator	27.12 MHz solid state
Plasma viewing	Dual
Plasma and shear gas	Argon
Nebulizer	Burgener MiraMist High Solids Nebulizer (0.4-2.0 mL/min)
Spray chamber	Glass cyclone
Plasma torch	Enhanced matrix tolerance (EMT) semi-demountable
RF power	1150 W
Pump rate	50 rpm
Auxiliary gas flow	0.5 L/min
Nebulizing gas flow	0.5 L/min
Maximum integration time for low WL range	15 s (both axial and radial)
Maximum integration time for high WL range	10 s (axial) and 5 s (radial)
Flush time	45 s

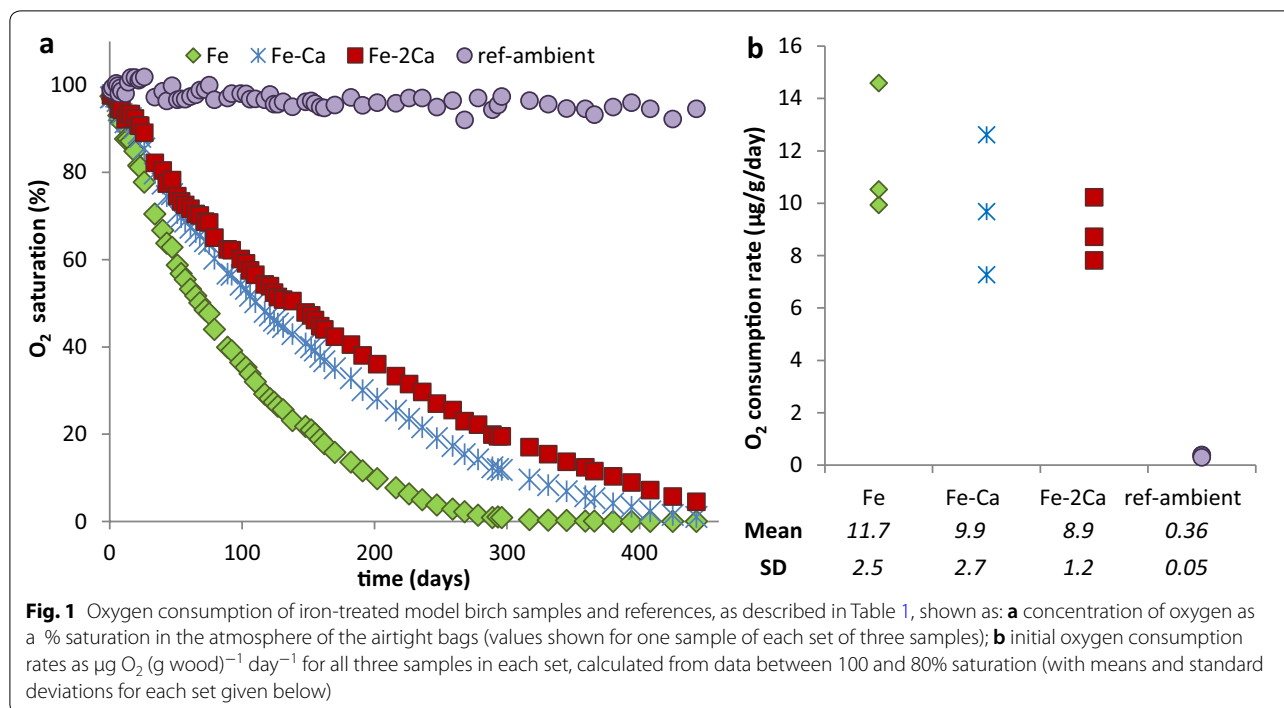


Table 3 ICP-OES results from Oseberg wood samples in mmol/100 g

	Al	Ca	Fe	K
Fresh Birch	< LOD	0.590 (4)	0.0107 (1)	1.0*
185-2	163 (1)	0.623 (9)	0.40 (1)	169 (1)
185-5	207 (1)	0.739 (6)	0.632 (0)	233 (1)
195C	94.7 (4)	0.261*	25.1 (2)	103 (2)
207-outer	175 (0)	2.38 (1)	1.35 (0)	19.5 (1)
207-inner	182 (1)	0.446 (1)	0.39 (2)	19.5 (2)
210-C	129.5 (2)	4.13 (2)	1.76 (0)	25.8 (6)
210-D	158 (1)	1.85 (1)	2.456 (8)	24.7 (8)
210-E	36.5 (2)	0.304 (2)	1.847 (8)	6.5 (6)
210-frag-3-surf	111.8 (2)	2.725 (8)	3.462 (6)	19.3 (4)
229-1B-AP ^a	195	0.6	0.7	168
229-1B-AR ^a	198	1.0	2.4	183
229-1C-AP ^a	25	3.3	1.1	64
229-1C-AR ^a	180	1.4	2.9	184
229-1D-AP ¹	17	2.5	1.2	54
229-1D-AR ^a	105	3.5	2.7	142
229-5-AP ^a	68	2.4	1.1	83
229-5-AR ^a	153	2.1	3.5	189
Oseberg ship (oak) ^b	-	11.18 (0)	27.14 (3)	-

Results also shown from fresh birch reference and previously reported values from samples from object 229 and the Oseberg ship. When available, the uncertainty is given in parenthesis as standard deviation. The * indicates that the value in the diluted solution was below the limit of quantification of the method, but above the limit of detection (LOD)

^a From results described in [20]

^b From results described in [12]

quantities added to the wood samples are quite small relative to the rates of oxygen consumption observed in the iron-treated samples (Fig. 1b). At the lowest average rate of $8.9 \mu\text{g O}_2 (\text{g wood})^{-1} \text{day}^{-1}$, over the course of 30 days, 1 g of sample would consume 0.27 mg of oxygen, corresponding to 8.5 mmol. We can, therefore, reason that the oxidation of Fe(II), which would be at most 0.08 mmol, is not a significant contributor to this oxygen consumption.

Comparing the oxygen consumption rates shown in Fig. 1b, which were calculated based on linear regression analysis of the first part of the oxygen curve (100 to 80% saturation), we can clearly see that the Fe samples consume oxygen more rapidly than the waterlogged reference pieces ($p=0.001$, $g = 5$), as was anticipated. However, the effect of calcium is less apparent; although the average rate of oxygen consumption appears to drop as the calcium concentration increases, the differences are small relative to the standard deviations. Statistical analysis did not find significant differences between the Fe, Fe-Ca and Fe-2Ca samples. Therefore, although a potential trend is observed, a modulating effect of calcium on iron-promoted oxidation cannot be confirmed by these results. While this does not necessarily prove no effect, especially given the small number of samples in this study, we can suggest from this that the presence of calcium salts probably does not have a practically significant effect on oxidation rate, relative to the sizeable increase due to Fe(II) treatment.

Fresh birch samples treated with alum and iron(II)

Sets of model samples treated with both alum and iron were investigated to ascertain whether there was a relationship between iron and oxygen consumption rate of wood samples when alum was present. The iron concentrations used in the treatment solutions were chosen such that they reflected the range observed in Oseberg artefacts, relative to alum. The quantities of iron found by ICP analyses in the unreconstructed alum-treated objects previously described [19, 20] were fairly low. However, for this work we also performed ICP-OES on additional samples, to gain a more accurate idea of iron and alum levels in diverse Oseberg objects, results of which are shown in Table 3. Here, a sample from near a corroding iron rod (195C) measured an iron level as high as 25 mmol/100 g, which is approximately 25% of the content of alum ions (Al, K).

Figure 2 shows the oxygen consumption rates of the model alum-treated fresh birch pieces, treated with iron in four different concentrations ranging between 0 and 25% of the alum concentration in the hot solutions (ca. 2.1 M). The results show an increase in average oxygen consumption rate with each increase in iron concentration during treatment ($p=0.04, 0.04, <0.001$ and $g=2, 3, 14$ for increases in Fe concentration from 0 to 0.005, 0.005 to 0.05, 0.05 to 0.5 M, respectively). Compared to the rate of the alum samples without iron, the rate of consumption of the al-Fe0.005 samples is about double,

while those of al-Fe0.05 and al-Fe0.5 are about four and fifteen times higher, respectively. This suggests that even the lowest concentrations of iron observed in Oseberg artefacts could have led to an increase in oxidation rate.

Furthermore, the samples that were only alum-treated consumed oxygen significantly faster than the reference samples ($p < 0.001, g = 8$), at about four times the rate. This supports our previous observations of a relationship between alum-treatment and wood oxidation [19, 20], and implies it is at least partially independent of iron content. At first glance, this increase in oxygen consumption rate may appear to be modest relative to the difference between the Fe and ref-ambient sets shown above in Fig. 1. However, we note here that we cannot meaningfully compare the oxygen consumption rates of the alum-treated and iron-treated samples as a measure of overall degradation rate, due to the different mechanisms by which alum and iron induce degradation in wood. Iron-induced degradation is believed to first proceed via a radical oxidation pathway, and organic acids formed as a result can further promote such reactions as well as acid hydrolysis [25, 36, 37]. The mechanism of alum-induced wood degradation, while poorly understood, is thought to involve acid hydrolysis from the outset, caused by sulfuric acid introduced during alum-treatment [11], which is potentially accompanied by non-redox reactions catalysed by aluminium ions [1, 19]. It is clear that oxidative

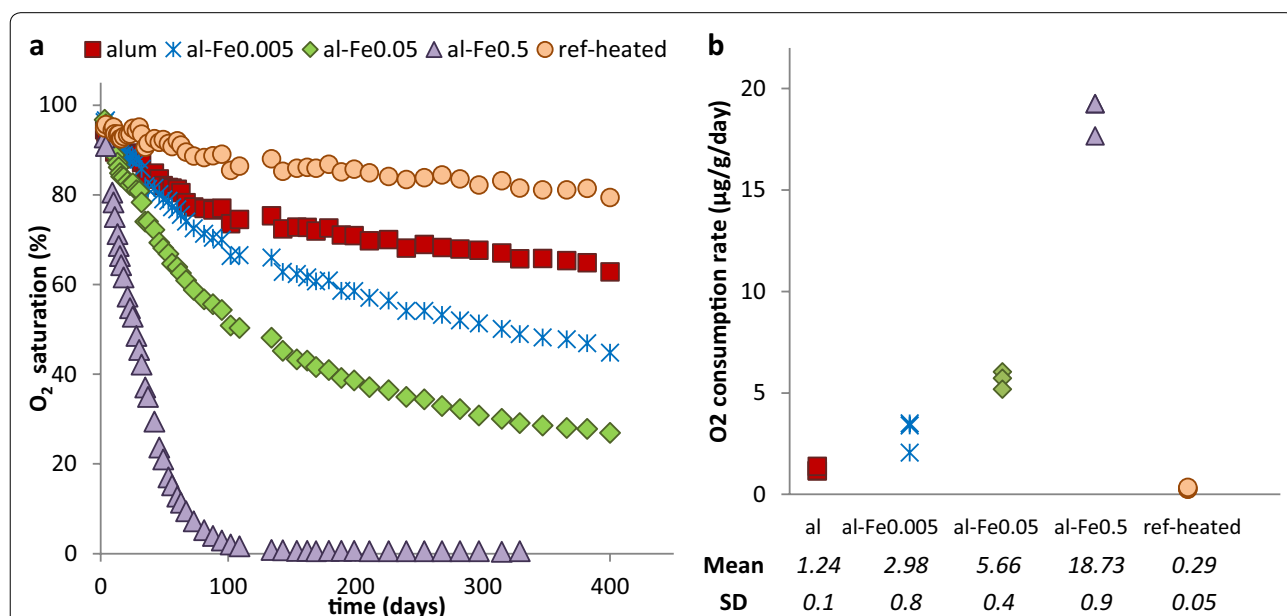


Fig. 2 Oxygen consumption of alum-treated model birch samples and references, as described in Table 1, shown as: **a** concentration of oxygen as a % saturation in the atmosphere of the airtight bags (values shown for one sample of each set of three samples); **b** initial oxygen consumption rates as $\mu\text{g O}_2 (\text{g wood})^{-1} \text{day}^{-1}$ for all three samples in each set, calculated from data between 100 and 80% saturation (with means and standard deviations for each set given below)

processes are also accelerated by alum-treatment, whether as a result of changes caused by these non-redox reactions or by some other mechanism, but the role of alum is presumably indirect, in contrast to the case with iron.

The reaction kinetics for these sets of model birch samples appear to differ from those of the iron-calcium sets, as they do not give linear plots for $(O_2 \text{ sat } \%)^{1/2}$ vs. time. Rather, a more linear relationship is generally observed between $\ln(O_2 \text{ sat } \%)$ vs. time, at least for the al-Fe0.5 samples, which would suggest pseudo-first order rate equation. We would not expect the alum salt itself in these samples to consume oxygen, as confirmed by the reference sample of pure alum, which gave a $\mu\text{g } O_2/\text{day}$ value comparable to the reference bag containing only air (0.24 and 0.25 $\mu\text{g}/\text{day}$, respectively). The difference in the shapes of the curves of the alum-treated birch pieces compared to the non-alum-treated birch pieces could therefore suggest different mechanisms of wood oxidation. This may therefore indicate that, although the presence of iron salts in alum-treated wood seems to increase the oxidation rate manyfold, the fact that the

wood has undergone alum-treatment defines the overall mechanism.

Archaeological samples

The results of the archaeological samples are shown in Fig. 3. As mentioned above, pure alum salt does not consume oxygen on its own, so the given values are calculated based on wood mass without alum salt. We can immediately see that the oxygen consumption rates of the samples of alum-treated Oseberg artefacts are extremely variable, ranging from 0.48 to 8.2 $\mu\text{g}/\text{g}/\text{day}$. As a result, statistically significant differences between object/treatment groups cannot be observed from this data, though we can speculate on potential causes of the variability and possible trends. We note that these samples were all of different shapes and sizes, with volumes ranging from ca. 2 cm^3 to 12 cm^3 . However, the Arch12 and Arch9-1 samples, which are recently alum-treated archaeological birch, vary between volumes of ca. 9 cm^3 and 27 cm^3 , and display much less variation. The variability is therefore probably largely due to the inhomogeneity of the alum-treated Oseberg artefacts in terms of salt content and degree of wood degradation,

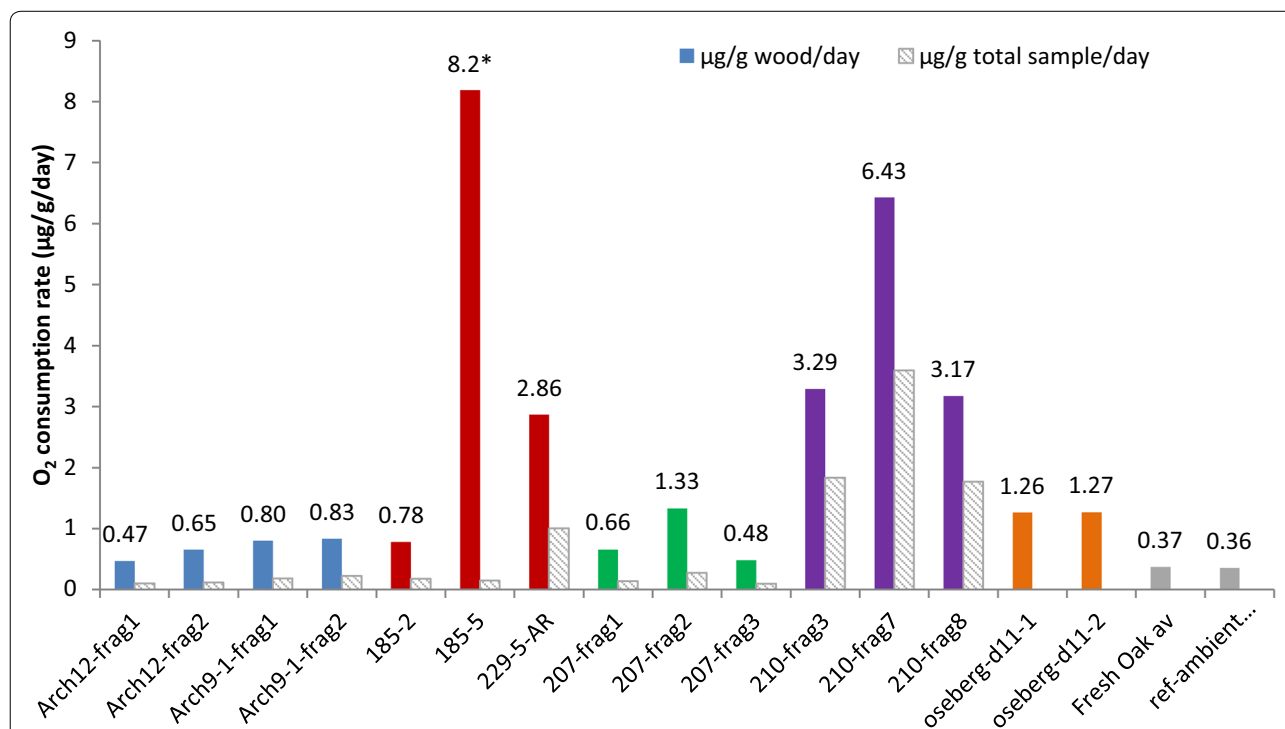


Fig. 3 Initial oxygen consumption rates of archaeological wood samples as $\mu\text{g } O_2 (\text{g wood})^{-1} \text{ day}^{-1}$, calculated from data between 100 and 80% oxygen saturation, shown with average values calculated for fresh oak and fresh birch (ref-ambient) references. Different colours designate different groups of samples based on object number/treatment type: recently alum-treated (blue); Oseberg, alum-treated only (red); Oseberg alum-treated and linseed oil coated (green); Oseberg alum-treated and linseed oil soaked (purple); Oseberg ship, not alum-treated (orange); fresh wood references (grey). For alum-treated samples, values in $\mu\text{g } O_2 (\text{g total sample})^{-1} \text{ day}^{-1}$ are also shown, where the total sample mass is the mass of wood plus alum. The * indicates that the value calculated for 185-5 is somewhat tentative due to a very low wood content in this fragment

which has been noted previously [19, 20, 28]. As we did not wish to destroy whole fragments, extracting and weighing their salt contents was not possible. The wood mass was therefore estimated based on alum contents calculated from ICP-OES data. A drawback to this solution is that inhomogeneity in alum content could skew the calculated rate, especially as this accounts for a large proportion of the total mass of the fragment. This can be visualised by comparing the oxygen consumption rate in $\mu\text{g O}_2 (\text{g wood})^{-1} \text{day}^{-1}$ to rates in $\mu\text{g O}_2 (\text{g total sample})^{-1} \text{day}^{-1}$, where the total sample includes the mass of alum, as shown for the alum-treated samples.

Fragment 185-5, for example, has the highest alum content, which apparently accounts for some 98% of its mass (supported by masses measured before and after aqueous extraction of samples from similar fragments [15]). As a result, the low wood content might contribute to inaccuracy of the calculated rate, and the seemingly high value should be interpreted with caution. This value contributes to an apparently large variation in oxygen consumption rates of the 185 and 229 samples in particular, which are grouped together as they are similar in terms of their treatment and state of degradation. They were all treated only with alum, were extremely visibly degraded and powdery, and previously reported analytical pyrolysis showed almost complete holocellulose depletion and extensive lignin oxidation [19, 20]. Fragments 185-2 and 185-5 were initially selected for this analysis based on observations that the lignin fraction of the latter was significantly more oxidised than the former, and, indeed, its calculated oxygen consumption rate is also much higher. However, this correlation could be somewhat dubious, given how similar these samples are in the context of all the samples analysed, along with the aforementioned tentativeness of the value calculated for 185-5.

We note that the oxygen consumption rates from object 207 are, on average, lower than those of 185 and 229 samples, and these samples appear to be less degraded, both visually and by analytical pyrolysis [38], which revealed a less oxidised lignin fraction in the former, and could support a trend between extent of wood oxidation and the current oxygen consumption rate. Though we note that there are also notable differences in the inorganic content of these samples, with 207 containing mostly ammonium alum and 185 and 229 containing mostly potassium alum [15] and minor amounts of the acid salt KHSO_4 [20], we would not expect these salts to contribute to the oxygen consumption beyond their influence on wood degradation mechanisms.

The 210 fragments, in which the alum content was estimated to be less than half the total sample mass, appear to consume oxygen fastest overall. However, as shown in

Table 3, iron levels found by ICP-OES in samples from object 210 (1.8 to 3.5 mmol/100 g) were comparable to those in object 207 (0.4 to 1.4 mmol/100 g) and 229 (0.7 to 3.5 mmol/100 g). We note that the type of wood in these samples is different to the other alum-treated Oseberg samples (ring porous rather than diffuse porous), but suggest that the higher oxygen consumption rate may be due to oxidation of linseed oil, with which they are thoroughly soaked. Linseed oil is known to undergo progressive oxidation over time [39], and we have also previously observed oxidation of linseed oil in alum-treated Oseberg artefacts [38]. Overall, the alum-treated samples appear to consume oxygen faster than the fresh wood references. The Oseberg ship samples (oak), which were not alum-treated, also appear to consume oxygen notably faster than the fresh wood references. This may be due to the high levels of iron due to corroding iron rivets; ICP-OES measured 27 mmol/100 g in a ship sample taken near a rivet (Table 3).

In general, we can hypothesise reasons for the different oxidation rates of these archaeological samples, since information about the chemical composition is available for either the specific samples or the objects from which they came. If we were to attempt to use oxygen consumption measurement to assess rates in the wider collection, the values would be difficult to interpret without such supplementary data. Furthermore, oxygen consumption rates cannot be construed as absolute rates of wood degradation, and we observe that comparison between objects is impeded by compositional variability, such as contents of alum, iron and linseed oil. Oxidation is indeed occurring and is measurable, as has been observed previously for conserved archaeological wood [9], but how quickly this will result in a concerning loss of structural integrity is uncertain. In previous studies, oxygen-consumption rates in wood samples have been connected to loss of mechanical strength in model wood samples [7], but in the case of inhomogeneous artefacts the relationships would be less straightforward. As for most evaluation parameters, comparing oxygen consumption rates in relation to certain variables is more meaningful when we have similar samples, such as in the model experiments. The use of oxygen consumption rates could therefore be of use as an evaluation parameter in tests of retreatment methods for alum-treated objects, in which samples have been selected for meaningful comparison.

Conclusions

Oxygen consumption measurement was used as a tool to study potential oxidative degradation reactions occurring in alum-treated wood and the Oseberg collection. Studies of model birch pieces treated with alum confirmed that alum-treatment results in a significant increase

in oxidation rate. Indeed, impregnation with iron and alum salts, both separately and in combination, significantly increased the rate of oxygen consumption. In samples treated with both alum and iron, even the lowest concentration of iron salt (0.005 M) resulted in a substantial increase in oxygen consumption rate relative to alum-treatment alone, suggesting that even the lowest iron concentrations observed in alum-treated Oseberg artefacts could have led to an increase in oxidation rate. Furthermore, the reaction kinetics inferred by the shapes of the oxygen consumption curves may suggest that the mechanism of iron-induced degradation is influenced by the alum-treatment. In contrast, investigation of previously proposed inhibition of iron-induced oxidation by calcium ions did not confirm any significant effect.

In archaeological samples, differences in rates were more difficult to explain, especially in alum-treated Oseberg samples, presumably due to their variable composition.

However, since in all cases the oxidation rates were measurable and higher than for reference fresh wood, the results are a promising indicator that oxygen consumption measurement could be a viable method of evaluating chemical stability of alum-treated test samples before and after re-treatment.

Supplementary information

Supplementary information accompanies this paper at <https://doi.org/10.1186/s40494-020-00377-0>.

Additional file 1. Supplementary information with details of SEM-EDS of salt-impregnated wood pieces, standard and reference ICP-OES solutions and analytical figures of merit of the ICP-OES method.

Abbreviations

ICP-OES: Inductively coupled plasma-optical emission spectroscopy; SEM-EDS: Scanning electron microscopy-energy dispersive X-ray spectroscopy.

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Authors' contributions

CM, MM and SB conceived, designed and set up oxygen consumption experiments. CM prepared the model fresh birch samples and CM and SB selected archaeological samples. CM collected and interpreted the oxygen consumption data, with help and input from MM and SB. FC and SM developed the ICP-OES method, performed ICP-OES experiments, and analysed their data. CM wrote the manuscript, which was reviewed and edited by all other authors. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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