Chemical analyses of extremely degraded wood using analytical pyrolysis and inductively coupled plasma atomic emission spectroscopy

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Abstract

Alum-treated archaeological woods from the Oseberg collection, excavated and treated in the early 1900s demonstrate an extreme deterioration, only discovered in the past decade. This research was aimed at understanding the characteristics of the naturally aged material through chemical analyses of both organic and inorganic components. Analytical pyrolysis-gas chromatography/mass spectrometry with *in situ* silylation using hexamethyldisilazane (Py(HMDS)-GC/MS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were used to investigate a set of samples of alum-treated archaeological wood and untreated archaeological wood. Sound woods of the same species were also analyzed in order to compare the results.

Results from Py(HMDS)-GC/MS analyses of alum-treated woods from Oseberg showed an extreme depletion of carbohydrates and a highly deteriorated lignin network. The majority of the lignin had undergone oxidation reactions, illustrated by high relative amounts of acidic pyrolysis products. In particular, p-hydroxy-benzoic acid was detected for the first time as degradation product of archaeological wood. In addition, it was possible to relate the degree of chemical degradation of the Oseberg woods to their visual condition (observed with the naked eye). Results from ICP-AES showed variable concentrations of aluminum and potassium from the alum treatment, as well as iron, copper, zinc and calcium. The extent of oxidation observed by Py(HMDS)-GC/MS appeared to correlate with relative amounts of iron and calcium in the samples, which may suggest that

degradation promoted by iron compounds is inhibited in the presence of calcium compounds.
The results obtained for a sample of archaeological wood treated with alum salts five years ago showed that chemical deterioration of lignin had already begun, mainly involving depolymerization reactions, though only a slight increase in oxidation was evident.

Keywords:
Py(HMDS)-GC/MS, ICP-AES, archaeological wood, alum-treated wood, Oseberg collection

Introduction

From the mid-1800s to the late 1950s, conservation by alum salts (aluminum potassium sulfate dodecahydrate) – with some variations – was a common method for treating highly deteriorated waterlogged archaeological wood. After this period it was gradually removed from the repertoire of conservation treatments and nowadays its consequences are not well understood [1].
At the Museum of Cultural History (KHM) of Oslo (Norway), a large portion of the Viking Age wooden objects from the Oseberg burial site were treated with alum salts in the early 1900s. The ship burial, dated to 834 AD, was made for two women of high standing [2]. The deceased were laid to rest in a grave chamber which had been decorated with sumptuous textiles and duvets of eiderdown. The chamber was surrounded by objects and sacrificed animals required in the afterlife. The mound was then sealed with approximately 5000 tons of turf and large stones.
The mound contained – in addition to the Oseberg ship and a number of metal artifacts and textiles – a collection of wooden objects such as a ceremonial wagon, three sleds, and animal head posts which lay together with cooking kits, weaving tools and looms, agricultural implements and ship gear. The contents of the grave provided archaeologists with insight into Viking Age burial rituals, the types of objects which were used as a part of everyday life, as well as Viking Age wood-working technology and wood-carving achievements [3]. Thus, this collection represents one of the richest, most complete collections of Viking Age wooden objects in the world. Many wooden objects bear intricate carvings, the prime signatures of this collection [3]. The find is exhibited at the Viking Ship Museum in Oslo, Norway, attracting over 400 000 visitors per year.

Over one hundred years after their original conservation, the alum-treated objects are in a precarious state of preservation. The wood is highly acidic (pH ≤ 2), and it is chemically and mechanically weakened. Surfaces are covered by numerous treatments and many objects are extensively reconstructed, some from thousands of fragments.

The seemingly well-preserved varnished surfaces of these objects mask a completely different situation within the wooden fabric. In many cases it is reduced to a powdery mass which is only visible in areas with new breaks. Although the mechanisms behind the observed deterioration are not elucidated, it has been found that they are directly related to the alum conservation treatment applied over 100 years ago, and the release of sulfuric acid during alum treatment is believed be a key factor [4].

However, the presence of metal ions in the Oseberg artefacts could also contribute to their degradation. There is some evidence that Al(III) can accelerate acid-catalysed hydrolysis of cellulose in paper [5, 6]. Furthermore, X-radiographs have illustrated that some of the brass and iron fittings have corroded, causing migration of ionic iron and copper compounds into the wood, which can promote wood degradation via radical Fenton reactions [7-10]. Other metal compounds can have also been absorbed into the objects over their long lifetime from sources such as the ground soil in which they were buried, and metal tanks used for their treatment and storage.

Problems with iron compounds and sulfuric acid in archaeological wood have been documented in well-known case studies on shipwrecks such as the Vasa, Mary Rose and Batavia [11, 12]. However, in these studies the presence of sulfuric acid potentially dangerous for wood preservation appears to result from oxidation of reduced sulfur compounds accumulated in the marine environment (anoxic water) in which the shipwrecks were found. This oxidation is thought to be catalyzed by the presence of iron species from sources such as corroded bolts [11, 13].

The case of the Oseberg artefacts is distinct from these studies in many respects, first and foremost that they were treated with alum, while the abovementioned shipwrecks were conserved with polyethylene glycol. Although the Oseberg collection was discovered under waterlogged conditions, it was not found in a marine environment, and the origin of sulfuric acid is from the sulfates introduced in the alum treatment, rather than oxidation of reduced sulfur species. Moreover, the extent of the degradation is particularly dramatic, and whether chemical influences other than sulfuric acid have played a significant role in this is not yet known. Thus the Oseberg case represents a unique example of deteriorated archaeological wood that requires further investigation

All signs point towards active deterioration; if it is not slowed down/halted the alum-treated finds will not be possible to salvage. The development of appropriate preservation strategies is therefore underway in the research project *Saving Oseberg*. This includes detailed chemical characterization of the wood in order to elucidate the extent and causes of the deterioration.

From a chemical point of view wood is mainly composed of cellulose, hemicelluloses and lignin, three inter-linked biopolymers. These inter-polymeric associations make wood challenging to analyze chemically [14]. This complexity is enhanced in archaeological wood, as degradation processes are influenced by both biologically- and/or chemically-related sources [13, 15]. Among the available analytical techniques used to investigate archaeological wood, such as classical wet chemical analysis, infrared spectroscopy and nuclear magnetic resonance spectroscopy (NMR) [16-23], Py-GC/MS has been proven to be a powerful tool, which can provide semi-quantitative estimations of wood components and give detailed information at a molecular level relatively rapidly; the method also requires a very small amount of sample (ca. 100 µg) [24, 25]. Py-GC/MS has been successfully applied to the evaluation of the state of degradation of archaeological wood [23, 26-30].

In this work we applied Py-GC/MS with *in situ* silylation using HMDS to investigate the organic components of a series of samples from the Oseberg collection and ICP-AES to obtain information on the inorganic elements. The research presented in this paper represents a starting point from which to better understand the chemical changes caused by the alum-treated wood from the Oseberg collection.

Materials and methods

The alum-treatment

The alum-treatment as it was used on the Oseberg finds involved heating a concentrated solution of alum salts to 90°C. The waterlogged wood fragments were immersed in the bath for an average of 24 hours. The concentration likely used was 2 parts alum to 1 part water by weight. More concentrated baths were also prepared, but the concentration was not specified in the excavation publication [3]. Sample Arch-aspen-alum was treated with alum in 2009 in a similar manner, that is by immersing it for 24 hours in a bath composed of 2:1 parts alum to water warmed to 90°C.

Samples

Wood species were identified by light microscopy. Fifteen samples were analyzed. Six archaeological wood samples from the Oseberg find treated with alum salts in the period 1905-12 were collected from six slices which originally fit together in a weaving loom and were named the ‘185-series’, the individual slices numbered from 185-1 to -6. This object had fallen apart into its six slices at some point before or after its treatment with alum and had an interesting variability in condition: slice 185-1 was in best visual condition while 185-6 was in worst condition. That is, there was increasing darkening and decreasing structural integrity from samples 185-1 to -6 (Figure 1). Microscopic examination established that the 185-series is a diffuse porous hardwood, most likely birch. The extreme degradation of wood did not allow identification to the species level.

Two non-alum-treated samples from Oseberg were also analyzed, one from Oseberg ship (oak) and the other from an animal head post nr.124 (maple).

Two archaeological aspen samples from the same branch excavated from the site Presterød, Tønsberg, Vestfold county in 2005 and dated to the Viking Age were also analyzed. One sample was treated with alum in 2009 and analyzed after 5 years, in order to evaluate the short-term effect of the alum-treatment on wood. The second aspen sample was untreated and only freeze dried.

Five sound wood samples - maple (*Acer* spp.), aspen (*Populus* spp.), birch (*Betula* spp.), alder (*Alnus* spp.) and oak (*Quercus* Spp.) were also analyzed as references. Alder was included as a second reference (in addition to sound birch) for the 185-series as microscopic identification of these samples was slightly uncertain. The samples are described in Table 1.

Figure 1. Alum-treated wood from Oseberg, 185-series (circled in photo above). Fragments originated from a loom. It shows a progressive worsening of condition from slice 1 to 5 (6 was mainly in powder form).

Table 1. Sample overview and description.

Sample	Description
185-1	Oseberg, from a part of a weaving loom. Alum-rich layer (from surface). Identified as most likely to be birch.
185-2	Oseberg. alum-rich layer. Fragment that fits to 185-1
185-3	Oseberg. alum-rich layer. Fragment that fits to 185-2
185-4	Oseberg. alum-rich layer. Fragment that fits to 185-3
185-5	Oseberg. alum-rich layer. Fragment that fits to 185-4
185-6	Oseberg. alum-rich layer. Fragment that fits to 185-5. Mainly in powder form.
Arch-aspen	Archaeological aspen. Untreated and freeze dried. Excavated from Presterød, Tønsberg, Vestfold county in 2005 and kept in a waterlogged state.
Arch-oak	Sample from the Oseberg ship, which was in very good condition upon excavation in 1904 such that it withstood air-drying (i.e. is untreated). From fragment 10.2.

Arch-maple	Archaeological maple from animal head post nr. 124 (Oseberg collection), which was in poor condition upon excavation in 1904. Was destroyed during storage in water, hence remained untreated; air dried.
Arch-aspen-alum	Archaeological aspen cut from the same fragment as Arch-aspen, treated with alum in July 2009;
Sound maple	*Acer* spp.
Sound birch	*Betula* spp.
Sound aspen	*Populus* spp.
Sound alder	*Alnus* spp.
Sound oak	*Quercus* Spp.

Py(HMDS)-GC/MS

Analytical pyrolysis was performed using 1,1,1,3,3,3-hexamethyldisilazane (HMDS, chemical purity 99.9%, Sigma Aldrich Inc., USA) as a silylation agent for the *in situ* thermally assisted derivatisation of pyrolysis products. The instrumentation consisted of a micro-furnace Multi-Shot Pyrolyzer EGA/Py-3030D (Frontier Lab) coupled to a gas chromatograph 6890 Agilent Technologies (USA) equipped with an HP-5MS fused silica capillary column (stationary phase 5% diphenyl e 95% dimethyl-polysiloxane, 30 m x 0.25 mm i.d., Hewlett Packard, USA) and with a deactivated silica pre-column (2 m x 0.32 mm i.d., Agilent J&W, USA). The GC was coupled with an Agilent 5973 Mass Selective Detector operating in electron impact mode (EI) at 70 eV. The pyrolysis temperature was 550 °C and interface temperature was 250 °C. Similar amounts (c. 100 µg) of sample and HMDS (5 µL) were inserted into the platinum cup. Chromatographic conditions were as follows: initial temperature 50 °C, 1min isothermal,10 °C min^{-1} to 100 °C, 2min isothermal, 4 °C min^{-1} to 190 °C, 1min isothermal,30 °C min^{-1} to 280 °C, 30min isothermal. Carrier gas: He (purity 99.995%), constant flow 1.0 ml min^{-1}. Before being analysed, all the samples were oven-dried for 24 h at 40-50 °C to remove all the residual water content. After instrumental analysis, the compounds were identified by comparing their mass spectra with spectra reported in the Wiley and NIST libraries or in the literature [31-37]. Samples were analyzed in triplicate. Peak areas were normalized with respect to the sum of the peak areas of all identified pyrolysis products for each sample, and the data were averaged and expressed as percentages. The % relative abundances of pyrolysis products from holocellulose and lignin were also summed separately, and their ratio (H/L) was calculated. The standard deviation associated with the H/L ratio for three replicates was also calculated.

ICP-AES

ICP-AES was applied to the samples from the 185 series, because they showed a high level of wood degradation. Sound birch wood was also analyzed to compare the results. The samples (ca 0.2 g) were dried at 105°C overnight, then weighed into digestion vessels to which 4 mL nitric acid (≥ 65% HNO_3), 1 mL hydrofluoric acid (50% HF), 1 mL hydrogen peroxide (30% H_2O_2) and 1 mL pure water were added. The samples were digested in a microwave (Anton Paar) at 200°C for 2 hours. After cooling to room temperature, ultra-pure water was added to the digested solutions to 50 mL. To avoid matrix effects, all standards were adapted to the acidity of the samples. If necessary, the samples were diluted.

An ICP-AES Ultima 2, Horiba Jobin Yvon instrument was used. Elements analyzed included Aluminum (Al), Calcium (Ca), Copper (Cu), Iron (Fe), Potassium (K), Magnesium (Mg), Manganese (Mn) and Zinc (Zn). The selection of these metals was based upon previous SEM-EDS analyses of ashed samples 185-1 and 185-6 (not shown). Nine replicates for each element were analyzed. Sulfur was not quantified. Table 2 shows the characteristic emission wavelengths used to quantify each element. Elemental concentration is given in µmol/100g.

Table 2. Characteristic emission wavelengths for ICP-AES quantification.

Element	λ (nm)
Al	396.15
Ca	393.37
Cu	224.70
Fe	259.94
K	769.90
Mg	279.55
Mn	257.61
Zn	213.86

Results and discussion

Py(HMDS)-GC/MS

A total of 114 pyrolysis products were identified and assigned to the wood components from which they originated (holocellulose, and the guaiacyl and syringyl components of lignin). Table 3 shows the % relative abundances calculated for each identified compound, the most abundant *m/z* peaks in the mass spectra and compound attribution to wood

components (H – holocellulose, L – lignin, S – syringyl-lignin, G – guaiacyl-lignin). At the end of Table 3, the H/L ratios are also presented, which have been shown to be good indicators reflecting degree of degradation of wood [26, 27]. Pyrolysis products # 1, 4 and 5 were not included in the calculations, as they may originate from both holocellulose and lignin [33, 38].

Figure 2 compares three chromatographic profiles: sound wood (sound aspen, Figure 2a), archaeological untreated wood (Arch-aspen, Figure 2b) and archaeological alum-treated wood naturally aged for over 100 years (185-6, Figure 2c). The most representative pyrolysis products are indicated by their compound number, given in Table 3.

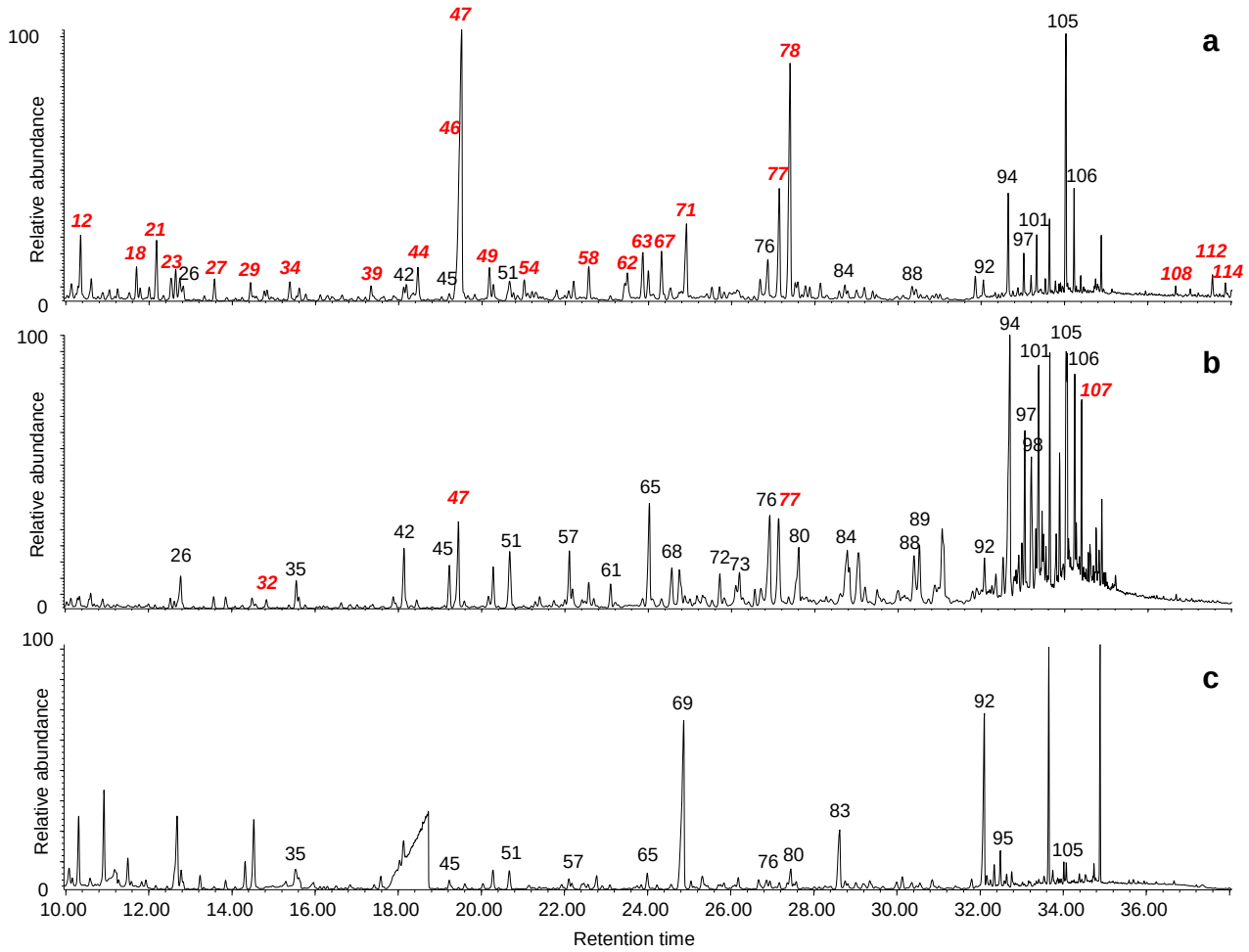

Figure 2. Py(HMDS)-GC/MS chromatographic profiles of **a)** sound aspen, **b)** arch-aspen, **c)** 185-6 samples. Numbers refer to Table 3. Holocellulose pyrolysis products are labelled in bolded, italicized, red script.

From a qualitative point of view the chromatographic profile of sound aspen (Figure 2a) was dominated by holocellulose pyrolysis products and lignin monomers (# 94, 105). For

arch-aspen (Figure 2b) holocellulose pyrolysis products showed very low abundance, resulting in a relative increase of lignin pyrolysis products. For 185-6 (Figure 2c) holocellulose pyrolysis products were almost absent and lignin pyrolysis products containing acidic functionalities (#69, 83, 92) were the most abundant.

Table 3. Relative abundance (%) of pyrolysis products identified by Py(HMDS)-GC/MS. H=Holocellulose, L=Lignin, G=Guaiacyl lignin, S=Syringyl lignin.

	Compound	m/z	Origin	Alder	Aspen	Birch	Maple	Oak	Arch oak	Arch aspen	Arch maple	Arch aspen 2009	185-1	185-2	185-3	185-4	185-5	185-6
1	1,2-dihydroxyethane (2TMS)	73,103,147,191																
2	2-hydroxymethylfuran (TMS)	53, 73, 81, 111, 125, 142, 155, 170	H	0.30	0.37	0.30	0.41	0.42	0.23	0.02	0.07	-	-	-	-	-	-	-
3	phenol (TMS)	75, 151, 166	L	0.29	0.49	0.22	0.28	0.29	0.36	0.27	2.07	0.18	-	-	-	-	-	-
4	2-hydroxypropanoic acid (2TMS)	73, 117, 147, 190											-	-	-	-	-	-
5	2-hydroxyacetic acid (2TMS)	73, 147, 177, 205											-	-	-	-	-	-
6	1-hydroxy-1-cyclopenten-3-one (TMS)	53, 73, 81, 101, 111, 127, 155, 169	H	0.74	0.41	0.78	0.46	0.43	0.45	0.07	0.09	0.08	0.27	0.02	-	-	-	-
7	3-hydroxymethylfuran (TMS)	53, 75, 81, 111, 125, 142, 155, 170	H	0.12	0.10	0.10	0.16	0.07	0.07	0.01	0.00	0.01	0.04	-	-	-	-	-
8	o-cresol (TMS)	73, 91, 135, 149, 165, 180	L	0.11	0.12	0.07	0.12	0.09	0.10	0.14	0.35	0.21	-	0.74	0.66	0.66	0.84	0.47
9	2-furancarboxylic acid (TMS)	73, 95, 125, 169, 184	H	0.13	0.15	0.14	0.24	0.14	0.05	0.06	0.17	0.24	-	-	-	0.11	0.06	0.03
10	Unknown holocellulose I	73, 152, 167	H	0.40	0.23	0.40	0.32	0.92	0.66	0.19	2.56	7.66	5.75	3.89	4.01	0.40	0.56	0.82
11	m-cresol (TMS)	73, 91, 165, 180	L	-	0.05	0.03	0.30	0.78	0.03	-	-	0.08	0.08	-	-	0.26	0.05	-
12	2-hydroxy-1-cyclopenten-3-one (TMS)	53, 73, 81, 101, 111, 127, 155, 170	H	4.64	5.12	2.86	4.63	2.08	3.05	0.37	0.48	0.05	0.01	-	-	0.01	-	-
13	p-cresol (TMS)	73, 91, 165, 180	L	0.12	0.06	0.05	0.09	0.05	0.07	0.25	0.24	0.35	0.39	0.53	0.50	-	0.32	0.60
14	3-hydroxy-(2H)-pyran-2-one (TMS)	75, 95, 125, 151, 169, 184	H	0.02	0.09	0.03	0.04	0.07	0.01	-	0.01	-	-	-	-	-	-	-
15	Unknown holocellulose II	59, 73, 85, 101, 115, 131, 159	H	0.37	0.33	0.33	0.40	0.11	0.21	0.02	0.11	-	-	-	-	-	-	-
16	Unknown holocellulose III	59, 73, 85, 103, 115, 129, 145, 173, 188	H	0.40	0.37	0.43	0.26	0.16	0.22	0.09	0.20	-	-	-	-	-	-	-
17	*Z*-2,3-dihydroxy-cyclopent-2-enone (TMS)	59, 73, 115, 143, 171, 186	H	0.00	-	-	-	-	0.00	-	-	-	-	-	-	-	-	-
18	*E*-2,3-dihydroxy-cyclopent-2-enone (TMS)	75, 101, 143, 171, 186	H	0.84	0.34	1.22	0.38	0.49	0.68	0.03	0.07	0.01	-	-	-	-	0.00	-
19	1,2-dihydroxybenzene (TMS)	75, 91, 136, 151, 167, 182	G	0.04	0.01	-	-	-	-	-	-	-	-	-	-	-	-	-
20	3-hydroxy-(4H)-pyran-4-one (TMS)	75, 95, 139, 151, 169, 184	H	0.72	1.25	0.60	1.09	0.50	1.17	0.12	0.12	0.01	-	-	-	-	-	-
21	5-hydroxy-2H-pyran-4(3H)-one (TMS)	59, 75, 101, 129, 143, 171, 186	H	1.65	0.76	2.80	0.94	0.88	1.47	0.10	0.06	-	-	-	-	-	-	-
22	2-hydroxymethyl-3-methy-2-cyclopentenone (TMS)	73, 103, 129, 173, 183, 198	H	-	-	-	-	0.02	0.02	-	0.01	-	-	-	-	-	-	-
23	1-hydroxy-2-methyl-1- cyclopenten-3-one (TMS)	73, 97, 125, 139, 169, 184	H	0.72	0.72	0.82	0.45	0.46	0.60	0.55	0.38	0.21	-	-	-	-	0.06	0.02

	Compound	m/z	Origin	Alder	Aspen	Birch	Maple	Oak	Arch oak	Arch aspen	Arch maple	Arch aspen 2009	185-1	185-2	185-3	185-4	185-5	185-6
24	1-methy-2-hydroxy-1-cyclopenten-3-one (TMS)	73, 97, 125, 139, 169, 184	H	1.05	0.76	1.01	0.72	0.63	1.69	0.27	0.23	-	-	-	-	-	0.01	-
25	1,3-dihydroxyacetone (2TMS)	73, 103, 147, 189, 219	H	0.81	0.23	0.89	0.37	0.26	0.58	0.50	-	-	-	-	-	-	-	-
26	guaiacol (TMS)	73, 151, 166, 181, 196	G	0.34	0.22	0.12	0.37	0.19	0.22	1.25	2.11	2.17	2.26	3.21	3.54	1.56	2.12	1.77
27	Unknown holocelluloseI V	73, 217, 232	H	0.65	0.41	0.78	0.41	1.21	0.94	0.50	0.53	1.11	-	-	-	0.01	-	0.26
28	3-hydroxy-6-methyl-(2H)-pyran-2-one (TMS)	73, 109, 139, 168, 183, 198	H	0.01	0.05	0.01	0.05	0.02	0.02	-	-	-	-	-	-	-	-	-
29	Unknown holocellulose V	73, 101, 116, 131, 173	H	1.48	1.29	1.02	1.58	0.51	0.58	0.03	-	-	-	-	-	-	-	-
30	2-methyl-3-hydroxy-(4H)-pyran-4-one (TMS)	73, 101, 153, 183, 198	H	0.17	0.23	0.14	0.17	0.18	0.25	0.15	0.23	0.08	-	-	-	0.01	0.06	0.03
31	2-methyl-3-hydroxymethyl-2-cyclopentenone (TMS)	73, 103, 129, 173, 183, 198	H	0.11	0.11	0.11	0.10	0.06	0.08	-	0.01	-	-	-	-	-	-	-
32	2,3-dihydrofuran-2,3-diol (2TMS)	73, 147, 231, 246	H	0.49	0.32	0.24	0.16	0.38	0.60	0.41	0.27	0.16	-	-	-	-	-	-
33	2-furyl-hydroxymethylketone (TMS)	73, 81, 103, 125, 183, 198	H	0.04	0.07	-	0.05	0.07	0.01	-	-	-	-	-	-	-	-	-
34	5-hydroxymethyl-2-furaldehyde (TMS)	73, 81, 109, 111, 139, 169, 183, 198	H	0.61	0.66	0.92	0.47	0.85	0.44	0.14	0.57	0.35	-	-	-	-	0.01	-
35	4-methylguaiacol (TMS)	73, 149, 180, 195, 210	G	0.31	0.21	0.13	0.26	0.24	0.25	0.78	1.17	2.54	0.52	2.49	2.51	2.00	1.23	0.49
36	1,2-dihydroxybenzene (2TMS)	73, 151, 239, 254	G	0.93	0.97	0.57	1.32	0.57	1.07	0.47	1.39	1.44	5.14	4.18	4.40	1.69	1.38	0.70
37	2-hydroxymethyl-2,3-dihydropyran-4-one (TMS)	73, 142, 170, 185, 200	H	0.06	0.03	0.02	0.03	0.01	0.04	0.01	0.03	-	-	-	-	-	-	0.00
38	1,4:3,6-dianhydro-α-D-glucopyranose (TMS)	73, 103, 129, 155, 170, 171, 186	H	0.30	0.21	0.16	0.21	0.10	0.05	-	0.30	0.75	0.34	0.28	0.24	0.01	-	0.33
39	Z-2,3-dihydroxy-cyclopent-2-enone (2TMS)	73, 147, 230, 243, 258	H	0.51	0.33	0.63	0.29	0.43	0.48	0.09	0.01	-	-	-	-	-	-	-
40	4-methylcatechol (2TMS)	73,180, 253, 268	G	0.48	0.34	0.29	0.49	0.28	0.56	0.57	0.69	3.73	0.07	3.08	2.42	1.63	0.14	1.48
41	4-ethylguaiacol (TMS)	73, 149, 179, 194, 209, 224	G	0.05	0.02	0.02	0.05	0.03	0.04	0.14	0.15	0.08	-	0.07	0.13	0.09	-	0.02
42	syringol (TMS)	73, 153, 181, 196, 211, 226	S	0.73	0.64	0.52	1.11	0.51	0.48	2.95	1.77	2.87	3.55	5.57	6.08	4.31	2.20	2.79
43	1,4-dihydroxybenzene (2TMS)	73, 112, 239, 354	G	0.45	0.51	0.36	0.48	0.30	0.34	0.24	0.16	-	-	-	-	0.14	-	-
44	arabinofuranose (4TMS)	73, 147, 217, 230	H	0.94	1.05	1.96	1.10	1.41	2.90	0.45	0.52	1.62	0.31	0.16	0.65	0.33	0.01	-
45	4-vinylguaiacol (TMS)	73, 162, 177, 192, 207, 222	G	0.84	0.59	0.30	0.90	0.45	0.60	2.27	2.87	3.64	4.33	3.81	3.84	1.44	1.08	1.24
46	3-hydroxy-2-hydroxymethyl-2-cyclopentenone (2TMS)	73, 147, 257, 272	H	0.68	0.98	0.74	0.74	1.29	0.92	0.12	0.14	0.08	1.26	0.01	-	0.13	-	0.00
47	E-2,3-dihydroxy-cyclopent-2-enone (2TMS)	73, 147, 243, 258	H	19.95	25.38	20.20	18.22	14.31	19.21	5.11	2.95	1.80	0.67	-	0.02	0.01	0.04	-

	Compound	m/z	Origin	Alder	Aspen	Birch	Maple	Oak	Arch oak	Arch aspen	Arch maple	Arch aspen 2009	185-1	185-2	185-3	185-4	185-5	185-6
48	4-ethylcatechol (2TMS)	73, 147, 179, 231, 267, 282	G	0.05	0.05	0.04	0.11	0.03	0.02	0.08	0.09	0.03	0.03	0.19	0.06	0.06	0.01	-
49	3-hydroxy-2-(hydroxymethyl)cyclopenta-2,4-dienone	73, 147, 255, 270	H	1.20	0.94	1.39	0.70	1.93	1.35	0.59	1.07	0.71	-	-	-	-	-	-
50	eugenol (TMS)	73, 147, 179, 206, 221, 236	G	0.16	0.17	0.06	0.27	0.11	0.18	0.27	0.52	0.99	0.24	0.22	0.21	-	-	0.30
51	4-methylsyringol (TMS)	73, 167, 210, 225, 240	S	0.53	0.60	0.52	0.69	0.61	0.55	1.90	1.38	3.54	1.93	2.80	3.17	3.27	1.30	1.97
52	3-methoxy-1,2-benzenediol (2TMS)	73, 153, 254, 269, 284	S	0.36	0.34	0.15	0.84	0.10	0.44	1.32	0.74	1.67	1.44	3.17	3.26	1.45	1.34	0.92
53	3,5-dihydroxy-2-methyl-(4H)-pyran-4-one (2TMS)	73, 128, 147, 183, 271, 286	H	0.27	0.21	0.22	0.17	0.63	0.18	0.05	0.05	0.04	-	0.01	-	0.00	0.01	0.00
54	1,6-anydro-beta-D-glucopyranose (TMS at position 4)	73, 103, 117, 129, 145, 155, 171	H	0.21	0.09	0.29	0.08	0.19	-	-	-	-	-	-	-	-	-	-
55	1,6-anydro-beta-D-glucopyranose (TMS at position 2)	73, 101, 116, 129, 132, 145, 155, 171	H	0.17	0.06	0.17	0.22	0.34	-	-	-	-	-	-	-	-	-	-
56	*Z*-isoeugenol (TMS)	73, 179, 206, 221, 236	G	0.07	0.06	0.02	0.06	0.04	0.04	0.07	-	0.11	-	-	0.04	0.06	0.04	0.12
57	vanillin (TMS)	73, 194, 209, 224	G	0.59	0.37	0.28	0.46	0.27	0.39	2.16	2.10	0.92	-	0.15	-	0.74	1.37	0.86
58	1,2,3-trihydroxybenzene (3TMS)	73, 133, 147, 239, 327, 342	H	1.66	2.03	1.14	2.08	1.47	2.02	0.51	0.27	0.51	0.33	0.66	0.70	0.28	0.63	0.57
59	5-methyl-3-methoxy-1,2-benzenediol (2TMS)	73, 151, 210, 253, 268, 283, 298	S	-	0.14	0.93	0.18	0.07	0.78	0.82	0.74	2.16	0.53	0.81	1.45	0.79	0.74	0.81
60	4-ethylsyringol (TMS)	73, 191, 209, 224, 239, 254	S	0.05	0.07	0.05	0.07	0.08	0.07	0.30	0.16	0.24	0.08	-	0.07	0.11	0.05	0.08
61	*E*-isoeugenol (TMS)	73, 179, 206, 221, 236	G	0.54	0.54	0.19	0.62	0.33	0.68	1.12	2.07	2.89	2.33	1.08	1.08	0.83	0.39	0.69
62	1,4-anydro-D-galactopyranose (2TMS)	73, 101, 116, 129, 145, 155, 171, 217	H	0.61	0.70	1.20	0.47	2.36	0.86	-	0.10	-	-	0.08	0.29	-	-	-
63	1,6-anydro-D-galactopyranose (2TMS)	73, 101, 116, 129, 145, 161, 189, 204,	H	0.72	0.90	2.01	0.50	3.39	0.79	0.01	0.43	-	-	0.36	0.73	-	-	-
64	2-hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one (2TMS)	73, 129, 147, 155, 183, 273, 288	H	1.05	0.61	1.82	0.66	1.40	1.41	0.34	0.61	-	-	-	-	-	-	-
65	4-vinylsyringol (TMS)	73, 179, 222, 237, 252	S	1.47	1.64	1.15	2.33	1.28	1.41	5.47	4.09	6.93	6.57	5.25	5.11	2.06	1.10	2.27
66	1,4-anydro-D-glucopyranose (2TMS at position 2 and 4)	73, 101, 116, 129, 155, 191, 204, 217	H	0.03	0.16	-	1.81	-	-	-	-	-	-	-	-	-	-	-
67	1,2,4-trihydroxybenzene (3TMS)	73, 133, 147, 239, 327, 342	H	4.78	4.36	2.38	4.03	2.62	3.03	0.26	0.45	0.37	0.02	0.02	0.05	0.01	0.09	0.07
68	acetovanillone (TMS)	73, 193, 208, 223, 238	G	0.49	0.30	0.22	0.43	0.19	0.36	2.15	2.30	0.75	-	-	-	-	0.95	0.64
69	4-hydroxy benzoic acid (2TMS)	73, 147, 193, 223, 267, 282	L	-	2.64	-	-	-	-	-	3.69	-	36.67	36.47	36.06	44.63	24.58	37.29
70	propenyl-syringol (TMS)	73, 205, 236, 251, 266	S	0.20	1.60	0.16	0.24	0.17	0.31	0.70	0.74	0.74	0.42	0.87	0.38	0.58	-	-
71	1,6-anydro-beta-D-glucopyranose (2TMS at position 2 and 4)	73, 101, 116, 129, 155, 191, 204, 217	H	2.73	2.41	4.07	2.30	9.36	0.51	0.11	0.07	-	-	0.43	-	-	-	-

	Compound	m/z	Origin	Alder	Aspen	Birch	Maple	Oak	Arch oak	Arch aspen	Arch maple	Arch aspen 2009	185-1	185-2	185-3	185-4	185-5	185-6
72	5-vinyl-3-methoxy-1,2-benzenediol (2TMS)	73, 147, 179, 222, 280, 295, 310	S	0.56	0.47	0.54	1.06	0.46	0.72	1.38	1.40	2.92	0.48	0.75	0.55	0.13	0.48	0.89
73	*Z*-propenylsyringol	73, 205, 236, 251, 266	S	0.11	0.13	0.04	0.23	0.17	0.10	0.79	0.18	0.34	-	-	-	-	-	-
74	1,4-anydro-D-galactopyranose (3TMS)	73, 129, 147, 157, 191, 204, 217, 243,	H	0.20	0.07	0.12	0.10	1.01	0.18	0.86	0.14	3.61	-	-	-	-	-	-
75	unknown lignin I	73, 147, 193, 239, 313, 401, 416	L	1.31	1.61	0.76	1.35	1.05	1.39	0.44	1.74	2.86	0.91	1.09	0.88	1.28	1.46	1.52
76	syringaldehyde (TMS)	73, 224, 239, 254	S	1.69	1.42	1.63	1.81	1.10	1.35	6.33	2.74	1.99	0.07	0.03	0.54	0.85	2.14	1.51
77	2,3,5-trihydroxy-4H-pyran-4-one (3TMS)	73, 133, 147, 239, 255, 270, 330, 345,	H	4.48	3.03	5.36	3.62	8.15	10.93	2.34	4.04	1.92	-	-	-	-	0.03	-
78	1,6-anydro-beta-D-glucopyranose (3TMS)	73, 103, 129, 147, 191, 204, 217, 243,	H	4.91	6.80	11.68	4.78	13.42	6.88	0.26	14.67	9.31	11.20	8.32	7.97	1.49	2.79	0.96
79	1,4-anhydro-D-glucopyranose (3TMS)	73, 103, 129, 147, 191, 204, 217, 243,	H	0.27	0.11	0.35	0.32	0.92	0.42	-	0.74	0.29	0.07	-	0.08	0.16	0.12	0.07
80	*E*-propenylsyringol (TMS)	73, 205, 236, 251, 266	S	0.75	1.08	0.51	1.23	0.75	1.61	2.50	2.63	5.63	3.85	2.85	1.70	1.34	0.59	0.97
81	unknown lignin II	73, 179, 217,342, 358, 415, 430	L	-	-	-	-	-	0.13	0.01	0.00	-	-	0.16	0.00	-	-	-
82	unknown lignin III	73, 147, 193, 239, 313, 401, 416	L	1.03	0.97	0.32	0.98	0.54	0.27	0.22	0.16	0.04	-	-	-	-	0.09	0.02
83	vanillic acid (2TMS)	73, 253, 282, 297, 312	G	0.48	0.17	0.13	0.32	0.14	0.30	0.52	3.64	1.25	1.30	1.30	1.49	8.05	15.96	11.81
84	acetosyringone (TMS)	73, 223, 238, 253, 268	S	0.55	0.47	0.48	0.62	0.35	0.65	2.94	2.30	1.15	0.40	0.54	0.36	1.05	0.65	0.75
85	5-propyl-3-methoxy-1,2-benzenediol (2TMS)	73, 147, 179, 209, 296, 311, 326	S	-	-	-	-	-	-	-	0.31	-	0.27	-	-	-	0.49	0.59
86	coumaryl alcohol (2 TMS)	73, 189, 205, 267, 279, 294	G	0.14	0.24	0.24	0.57	0.31	0.78	0.28	0.23	0.45	0.25	0.26	0.25	0.05	0.06	-
87	vanillylpropanol (2TMS)	73, 179, 206, 221, 236, 311, 326	G	0.12	0.02	0.06	0.09	0.20	0.14	0.29	-	1.08	0.11	0.11	-	-	-	-
88	*Z*-coniferyl alcohol (2 TMS)	73, 204, 252, 293, 309, 324	G	1.01	0.77	0.35	1.30	0.43	0.94	1.79	0.25	-	-	0.01	0.01	0.05	-	-
89	4-hydroxy-3,5-dimethoxy cinnamic acid methyl ester (TMS)	73, 147, 179, 222, 280, 295, 310	S	-	-	-	-	-	-	-	-	0.35	-	-	-	0.05	-	0.09
90	coniferylaldehyde (TMS)	73, 192, 220, 235, 250	G	0.57	0.41	0.23	0.48	0.18	0.19	1.61	0.04	-	-	-	-	-	-	-
91	trihydroxy cinnamic alcohol (3TMS)	73, 147, 210, 254, 368, 383, 398	S	0.07	0.09	0.03	0.07	0.14	0.08	0.20	0.21	0.37	0.04	0.03	0.01	0.05	-	0.11
92	syringic acid (2TMS)	73, 253, 297, 312, 327, 342	S	0.77	0.37	0.54	0.71	0.54	0.80	1.24	6.10	1.65	2.27	1.50	2.09	12.04	27.44	19.44
93	unknown lignin IV	73, 179, 209, 237, 280, 310, 325, 340	L	0.03	0.03	0.01	0.03	0.06	0.02	1.00	0.21	0.76	-	-	-	0.11	0.04	0.20
94	*E*-coniferyl alcohol(2 TMS)	73, 204, 235, 293, 309, 324	G	6.00	4.50	2.74	6.01	1.64	4.16	9.13	3.57	1.62	0.94	0.70	0.57	0.56	0.93	0.89
95	3,4-dihydroxy-5-methoxy benzoic acid (3TMS)	73, 137, 147, 223, 253, 297, 385, 400	S	0.07	0.06	0.06	0.12	0.07	0.19	0.38	0.97	0.29	0.13	0.28	0.26	1.16	1.81	1.56

	Compound	m/z	Origin	Alder	Aspen	Birch	Maple	Oak	Arch oak	Arch aspen	Arch maple	Arch aspen 2009	185-1	185-2	185-3	185-4	185-5	185-6
96	syringylpropanol (2TMS)	73, 210, 240, 341, 356	S	0.10	0.16	0.10	0.14	0.18	0.20	0.60	0.13	0.83	0.08	0.04	0.04	-	0.35	0.02
97	*Z*-sinapyl alcohol	73, 234, 323, 339, 354	S	0.93	0.65	0.98	1.36	0.85	1.11	3.58	0.70	0.31	0.63	0.06	0.10	0.06	-	-
98	unknown lignin V	73, 179, 209, 237, 280, 310, 325, 340	L	0.04	0.01	-	-	-	0.00	2.73	0.33	1.73	0.02	-	-	-	0.05	-
99	3,4-dihydroxy cinnamyl alcohol (3TMS)	73, 205, 293, 355, 382	G	0.64	0.39	0.39	0.91	0.27	0.61	0.37	0.17	0.01	0.01	-	0.04	0.03	0.04	0.01
100	trihydroxy cinnamic alcohol I (3TMS)	73, 147, 210, 254, 368, 383, 398	S	-	-	-	-	-	-	-	-	0.76	-	-	-	-	-	0.03
101	sinapylaldehyde (TMS)	73, 222, 250, 265, 280	S	1.52	1.25	1.38	1.66	0.70	0.57	5.59	0.05	0.07	-	-	-	-	-	-
102	trihydroxy cinnamic alcohol II (3TMS)	73, 147, 210, 254, 368, 383, 398	S	-	-	-	-	-	-	-	-	0.53	-	-	-	-	-	0.02
103	*Z*-2-methoxy-3,4-dihydroxy cinnamic alcohol (3TMS)	73, 235, 323, 385, 412	S	-	-	-	-	-	0.35	0.49	-	-	-	-	-	-	-	-
104	synapyl alcohol (TMS)	73, 234, 251, 267, 282	S	0.23	0.07	0.15	0.12	0.07	0.08	-	-	-	-	-	-	-	-	-
105	*E*-sinapyl alcohol (2TMS)	73, 234, 323, 339, 354	S	6.98	4.27	4.72	6.39	3.18	3.74	10.12	6.47	2.53	1.35	1.23	1.32	1.76	1.61	0.86
106	*E*-2-methoxy-3,4-dihydroxy cinnamic alcohol (3TMS)	73, 235, 323, 385, 412	S	1.25	0.79	1.53	2.31	0.74	1.31	2.14	0.31	0.07	0.05	0.04	0.08	0.08	0.11	0.03
107	unknown lignin VI	73, 147, 196, 253, 355, 370	L	-	-	-	-	-	0.53	2.70	0.60	0.71	-	-	-	-	-	-
108	unknown anhydrosugar I	73, 103, 117, 147, 177, 189, 303, 347	H	0.20	0.26	0.70	0.16	0.36	0.25	0.00	-	-	-	-	-	-	-	-
109	unknown anhydrosugar II	73, 103, 117, 129, 147, 204, 217, 361	H	0.20	0.26	0.30	0.26	0.29	0.17	-	0.02	-	-	-	-	-	-	-
110	unknown anhydrosugar III	73, 103, 117, 129, 147, 204, 217, 223,	H	0.07	0.09	0.11	0.09	0.10	0.07	-	0.06	0.51	-	0.10	-	0.01	-	-
111	unknown anhydrosugar IV	73, 103, 117, 129, 147, 204, 217, 243,	H	0.86	0.99	2.14	0.93	1.69	1.17	0.10	0.13	-	-	-	-	-	-	-
112	unknown anhydrosugar V	73, 103, 117, 129, 147, 190, 204, 221,	H	0.15	0.20	0.19	0.17	0.37	0.38	0.02	0.00	-	-	-	-	-	-	-
113	unknown anhydrosugar VI	73, 103, 117, 129, 147, 204, 217, 289,	H	0.10	0.12	0.13	0.08	0.12	0.04	-	0.03	0.01	-	-	-	-	-	-
114	unknown anhydrosugar VII	73, 103, 117, 129, 147, 204, 217, 289,	H	0.07	0.13	0.20	0.11	0.16	0.06	0.01	-	-	-	-	-	-	-	-
	Sum Holocellulose (% total sample)			63.87	66.86	75.61	58.09	78.78	68.39	14.89	32.99	31.46	20.26	14.34	14.75	2.97	4.46	3.16
	Sum Lignin (% total sample)			36.13	33.14	24.39	41.91	21.22	31.61	85.11	67.01	68.54	79.74	85.66	85.25	97.03	95.54	96.84
	H/L			1.77	2.02	3.13	1.39	3.72	2.17	0.18	0.49	0.46	0.26	0.17	0.17	0.03	0.05	0.03
	Standard deviation			0.04	0.04	0.39	0.12	0.21	0.15	0.02	0.02	0.05	0.09	0.03	0.02	0.00	0.01	0.01

The results showed that for sound woods the H/L ratios ranged from 3.72 to 1.39, depending on the wood genus (Table 3). For the untreated archaeological samples, Arch-oak from the Oseberg ship showed an H/L ratio 2.17. The comparison of this value with the H/L ratio obtained for sound oak wood (3.72) indicated a loss of holocellulose of around 10 %, suggesting a very good state of preservation. Arch-maple and Arch-aspen showed H/L ratios 0.49 and 0.18 respectively, which when compared to the values obtained for the corresponding sound woods (1.39 and 2.02 respectively), were indicative of an extensive loss of carbohydrates. The lower H/L ratios calculated for the archaeological untreated woods were in agreement with the majority of the observations that can be found in the literature, showing that reduction of carbohydrates - which have either leached into the soil or were fully metabolized by bacteria during burial - is one of the main consequences of the decay of archaeological wood [14, 27, 39-41]. Lignin generally undergoes relatively less deterioration during burial [21, 40, 42].

The archaeological aspen sample treated with alum in 2009 showed an H/L ratio significantly higher (0.46) than the untreated Arch-aspen. This is counter-intuitive as infrared analyses in a previous study showed that the alum-treatment caused immediate deterioration of the carbohydrate moiety [4]. One possible reason for higher holocellulose values in the alum-treated sample may be related to natural variability: the untreated and the alum-treated Arch-aspen samples were cut from different parts of one branch, which may represent slightly different chemical compositions. Another hypothesis is that the alum-treatment initiated chemical alterations in the lignin structure (as explained further in this section) such that cleavage of some lignin-carbohydrates bonds occurred, which in turn may result in a greater availability of carbohydrates to undergo pyrolytic reactions and thus increasing their abundance in the sample.

The Oseberg samples from the 185-series generally showed a very low H/L ratio which decreased from 185-1 to -6, reaching values around 0 for samples 185-4,5,6. This was indicative of an almost complete loss of the polysaccharide component in these samples. As illustrated above, the H/L ratio can be a good indicator for comparing the general state of preservation of moderately deteriorated archaeological woods relative to their sound counterparts [26, 27]. However, the H/L ratio failed to reflect the visual and chemical variation in the states of preservation of the highly deteriorated archaeological samples.

In the 185-series, the general low amount of polysaccharide components coupled with an extensive deteriorated lignin network contributed to H/L values which are unexpectedly similar, despite the differences in their structural integrities.

Indeed, a closer look at the lignin pyrolysis products showed significant differences in the chromatographic profiles. Lignin-derived compounds were sorted into seven categories according to their structures and functional groups: monomers (coniferyl and sinapyl alcohols), long chain compounds (guaiacyl and syringyl units with modified C3 alkyl chains), short chain compounds (guaiacyl and syringyl units with up to C2 alkyl chains), carbonyl compounds (compounds containing aldehyde and ketone functionalities), carboxyl compounds (acids and esters), demethylated / demethoxylated compounds (guaiacyl and syringyl units in which the methoxy groups on the aromatic rings had undergone alteration), others (phenol, cresols and unidentified lignin pyrolysis products) [43]. Peak areas from lignin pyrolysis products from each category were expressed as percentages relative to the sum of all lignin pyrolysis products. Figure 3 shows the distribution of lignin pyrolysis products for all analyzed samples.

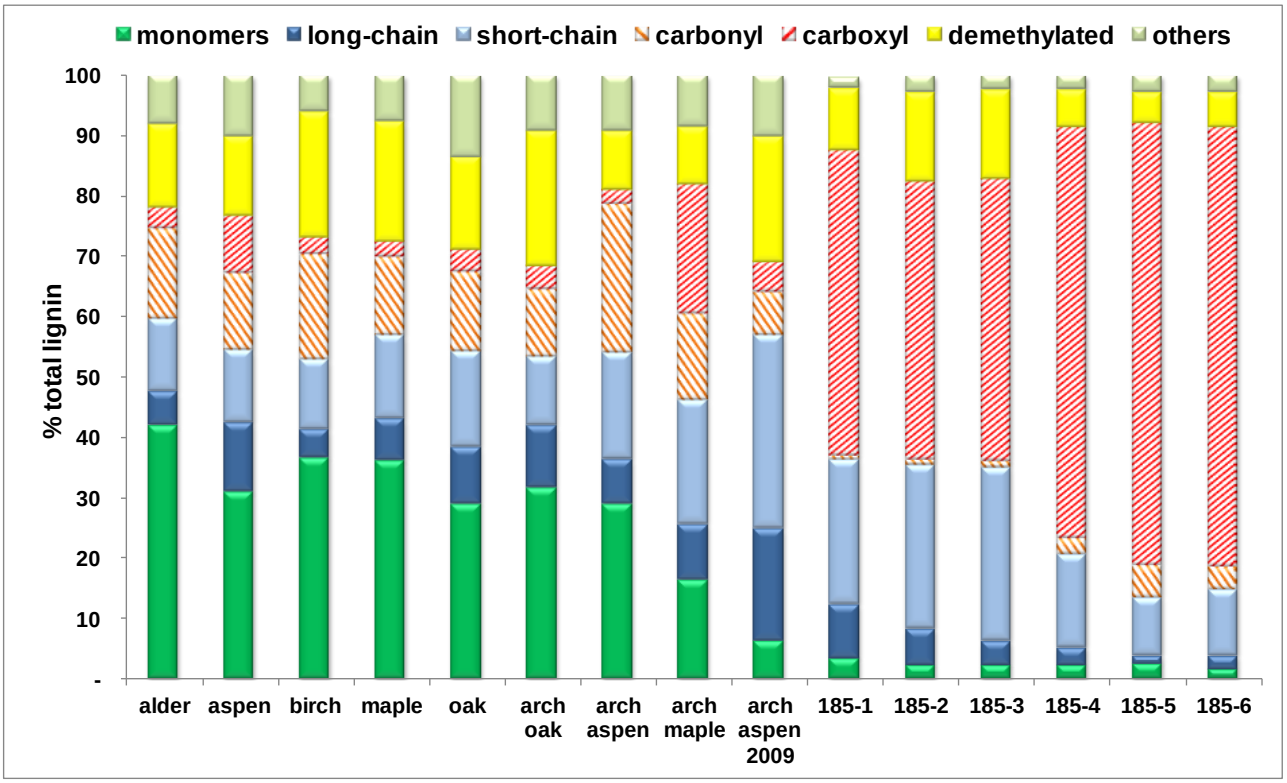

Figure 3. Distribution of lignin pyrolysis products in the samples analyzed.

For the sound woods only slight differences were apparent in lignin makeup, which were genus-related. Generally under the analytical conditions used, monomers constituted 30-40 % of all the lignin pyrolysis products, long chain compounds 5-10 %, short chain compounds 10-15 %, carbonyl compounds ca. 15 %, carboxyl compounds 3-5 % and demethylated compounds 15-20 %.

For the untreated archaeological woods, Arch-oak (from the Oseberg ship) showed a distribution of lignin pyrolysis products almost identical to that obtained for sound oak, confirming the relatively good chemical state of preservation of this sample. This is also reflected in its physical condition, which retains a high structural integrity despite the fact that it possesses only ≈30% of its bending strength relative to sound oak [44]. Arch-maple from Oseberg showed a decrease in monomers and an increase in short chain and acidic compounds relative to sound maple. This indicated that lignin degradation processes, such as depolymerisation and oxidation occurred in this sample to a moderate extent [43]. The observed deterioration is likely due to a combination of degradation initiated during burial and that occurring post-excavation from natural aging. Arch-aspen did not show great differences in lignin distribution with respect to sound aspen, except for a slight increase in carbonyl compounds.

On the other hand, Arch-aspen treated with alum in 2009 showed significant differences in lignin composition. In particular, monomers were drastically reduced with a relative increase in both modified long-chain and short chain pyrolysis products. Thus after five years, the alum treatment led to significant chemical alterations of lignin, but did not involve extensive oxidation. The low extent of lignin oxidation generally implies little colour change (darkening) making Arch-aspen-alum visually similar to its untreated counterpart, Arch-aspen; it is however more brittle due to the alum-treatment.

For the Oseberg samples treated with alum in the early 1900s, differences relative to sound birch and alder were remarkable: the relative amount of carboxyl compounds highly increased. In fact the chromatographic profiles showed that generally vanillic acid, syringic acid and p-hydroxybenzoic acid were the most abundant pyrolysis products (Figure 2c). Lignin monomers had very low abundance, while the remaining lignin pyrolysis products were mainly composed of short chain compounds. Degradation of lignin in archaeological wood can be accompanied by oxidation with a consequent increase in carbonyl and carboxyl functionalities [26, 45, 46], but an increase to such extent has never been previously observed in archaeological wood. Additionally, p-hydroxy benzoic acid has not been previously reported as a lignin break-down product in naturally aged archaeological samples analyzed using this method [21, 26-28, 47]. P-hydroxybenzoic acid is reported to be a characteristic component of aspen lignin, which forms some terminal ester and ether linkages with the macromolecule [48, 49]. In fact a low abundance was detected in sound aspen wood (Table 3), likely originating from the cleavage of these ester and ether bonds under pyrolytic conditions. This compound was not detected among the pyrolysis products

of other sound woods. The presence of p-hydroxybenzoic acid is often detected in lignin extracted in industrial processes (acidolysis, hydrolysis, etc.) with the aim to separate it from the holocellulose fraction [50-52]. In these processes lignin is often exposed to oxidizing conditions which promote the formation of significant amounts of carbonyl and carboxyl compounds, such as vanillin, syringaldehyde, vanillic acid and syringic acid [53, 54]. Thus these results suggested that the archaeological woods from the alum-treated Oseberg samples were exposed to extreme oxidizing conditions and the particular formation of p-hydroxybenzoic acid was likely a result of several reactions, including β-O-4'-cleavage, demethoxylation and side-chain cleavage coupled with oxidation.
In addition, a trend was observed within the 185-series, where the relative amount of acid pyrolysis products in samples 185-1, -2, -3 was comparable, whereas it was significantly higher in samples 185-4, -5, -6, thus highlighting an increase in oxidation from sample 185-1 to sample 185-6. This agrees with the visual state of preservation of these samples, where 185-1, -2, -3 are generally lighter in colour and the wood fabric possesses greater structural integrity than samples 185-4, -5, -6 (Figure 1).

ICP-AES

It is clear from the Py(HMDS)-GC/MS data that 185-series represents an unusually extreme example of wood degradation. In order to obtain a more complete picture, ICP-AES analyses were performed to investigate the inorganic components of the wood. The concentrations of various inorganic elements found in the 185-series are summarised in Table 4. Analysis of fresh birch is included for comparison.

Table 4. Concentration of elements analyzed by ICP-AES in µmol/100g.

	µmol/100g							
	Al	**K**	**Ca**	**Fe**	**Cu**	**Zn**	**Mn**	**Mg**
185-1	25.41 ±1.42	185.42 ± 7.06	0.06 ± 0.02	0.13 ± 0.00	0.21 ± 0.00	1.07 ± 0.01	≤ 0.022 ± 0.00	0.00 ± 0.00
185-2	23.57 ± 0.21	164.41 ± 7.28	0.16 ± 0.01	0.11 ± 0.00	0.20 ± 0.00	0.88 ± 0.02	≤0.019 ± 0.00	0.00 ± 0.00
185-3	23.64 ± 0.31	195.42 ± 7.52	0.39 ± 0.01	0.43 ± 0.01	0.66 ± 0.00	3.82 ± 0.09	≤ 0.035 ± 0.00	0.00 ± 0.00
185-4	21.32 ± 0.31	198.91 ± 8.14	0.43 ± 0.02	0.60 ± 0.01	0.96 ± 0.01	0.67 ± 0.03	≤ 0.047 ± 0.00	0.00 ± 0.00
185-5	38.33 ± 0.07	184.01 ± 5.62	0.00 ± 0.00	0.47 ± 0.02	0.56 ± 0.00	1.59 ± 0.02	≤ 0.016 ± 0.00	0.00 ± 0.00
185-6	31.20 ± 0.02	152.96 ± 4.21	0.00 ± 0.00	0.59 ± 0.01	0.63 ± 0.01	3.21 ± 0.04	≤ 0.021 ± 0.00	0.00 ± 0.00

Fresh birch	-	-	0.97 ± 0.02	0.00 ± 0.00	0.00 ± 0.00	0.04 ± 0.01	≤ 0.071 ± 0.00	0.58 ± 0.02

High levels of Al and K are of course due to the alum treatment, while the presence of iron and copper may be due to proximity to corroding brass and iron pieces, either in the object itself or in the soil in which it was buried. Copper vats were also used during alum treatment. Significant levels of zinc are probably due to wet storage of the objects in zinc vats prior to conservation.

The potassium levels were consistently higher than the aluminium levels in all samples (Figure 4), with K:Al ratios varying from approximately 5:1 to 9:1, despite the fact that these elements have a 1:1 ratio in alum ($KAl(SO_4)_2.12H_2O$). This could be due to precipitation of insoluble monomeric and polymeric aluminium-hydroxide containing compounds in the treatment baths, as these are known to form in aqueous solution as a result of hydrolysis of hexa-aquo aluminium(III) species [55]. Such precipitates have been observed during heating of alum solutions, and were shown to contain alunite ($KAl_3(SO_4)_2(OH)_6$) by means of X-ray diffraction measurements, though other amorphous compounds may have also been present [4].

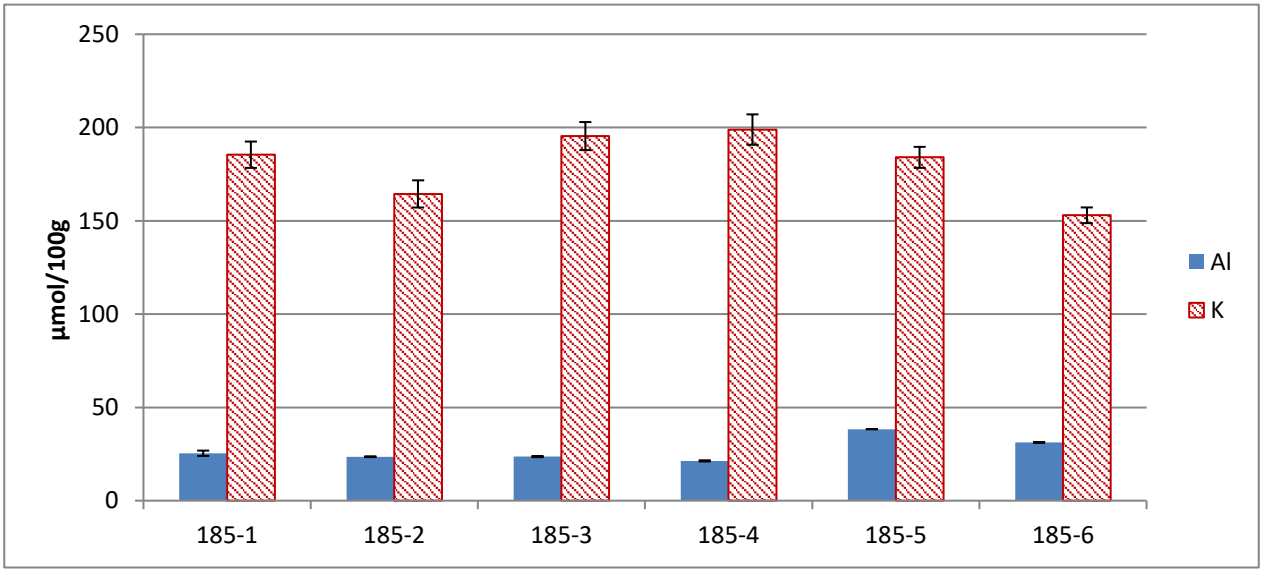

Figure 4. Al and K concentrations in the 185-series.

The variation between the K/Al ratios did not obviously correlate with the degree of degradation of the fragments. However, the Al content partially correlated with poor condition, as assessed by the sum of acid pyrolysis products (Figure 5). This could suggest some relationship between degradation and Al content. One possible explanation is that the aluminium was initially present as an alum salt deposit, which decomposed over

time to produce sulfuric acid that diffused into the local wood environment. Alternatively, it is possible that Al(III) itself could have a detrimental effect on the wood, as there is some literature suggesting that Al(III) can accelerate degradation of cellulose in paper [5, 6],. Further investigations would be useful to test these hypotheses.

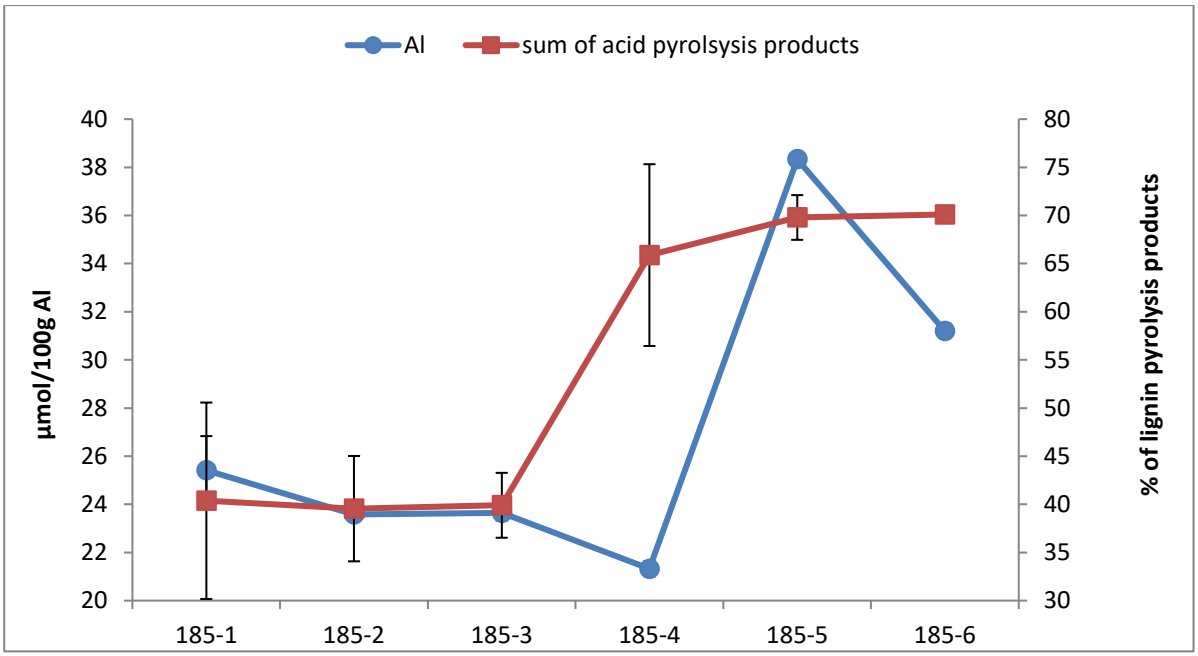

Figure 5. Comparison of the sum of acid lignin pyrolysis products to Al content in 185-series.

It was considered that the variability in the state of preservation of the 185-series might also be related to other inorganic elements. We note that Zn was the most abundant element detected after K and Al. However, to our knowledge there is no literature suggesting a role of Zn in wood degradation, and no notable connection between Zn and the extent of degradation was found for these samples.

However, though the concentrations of iron and copper were low relative to Al, K and even Zn, the fact that they can act as catalysts in Fenton degradation of wood [11, 13] means that small amounts can still be quite harmful. Iron-catalysed degradation tends to be efficient under acidic conditions, while copper-catalysed Fenton processes are inhibited in the presence of oxygen at acidic pH [56]. Thus we might expect iron species to be more detrimental to these acidic wood samples than copper species. Accordingly, it appeared to be the iron concentration that correlated more closely with the condition of the fragments. Figure 6 compares plots of the iron content in the 185-series to the sum of acidic pyrolysis

products. The Pearson's correlation coefficient *r* between iron concentration and the percentage sum of acid pyrolysis products was 0.81.

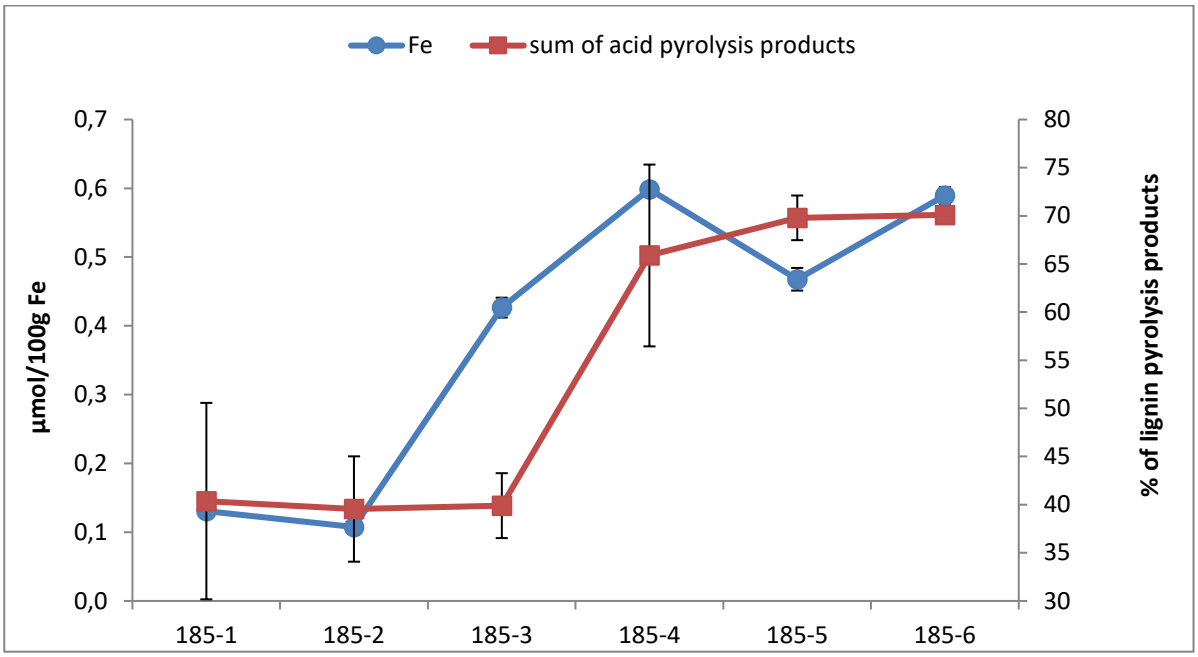

Figure 6. Comparison of sum of acid lignin pyrolysis products to Fe content in 185-series.

However, it was interesting to note that, for the fragments that had higher iron levels, those with significant levels of calcium were less degraded than those without, which might suggest inhibition of iron-catalysed degradation in the presence of calcium. Such observations have been reported previously by Schilling [57], who noted an inhibiting effect of calcium salts on brown rot fungal degradation of wood. This was proposed to be due to the calcium ion reacting with species that assist the supply of Fe(III) for Fenton chemistry, thereby indirectly limiting its availability. Figure 7 shows a plot of iron concentrations in the 185-series after subtracting calcium concentrations, to illustrate this trend. The Pearson's correlation coefficient *r* between the difference of iron and calcium concentrations and the percentage sum of acidic pyrolysis products was 0.88, thus proving an increase in correlation between Py and ICP results when both iron and calcium were considered.

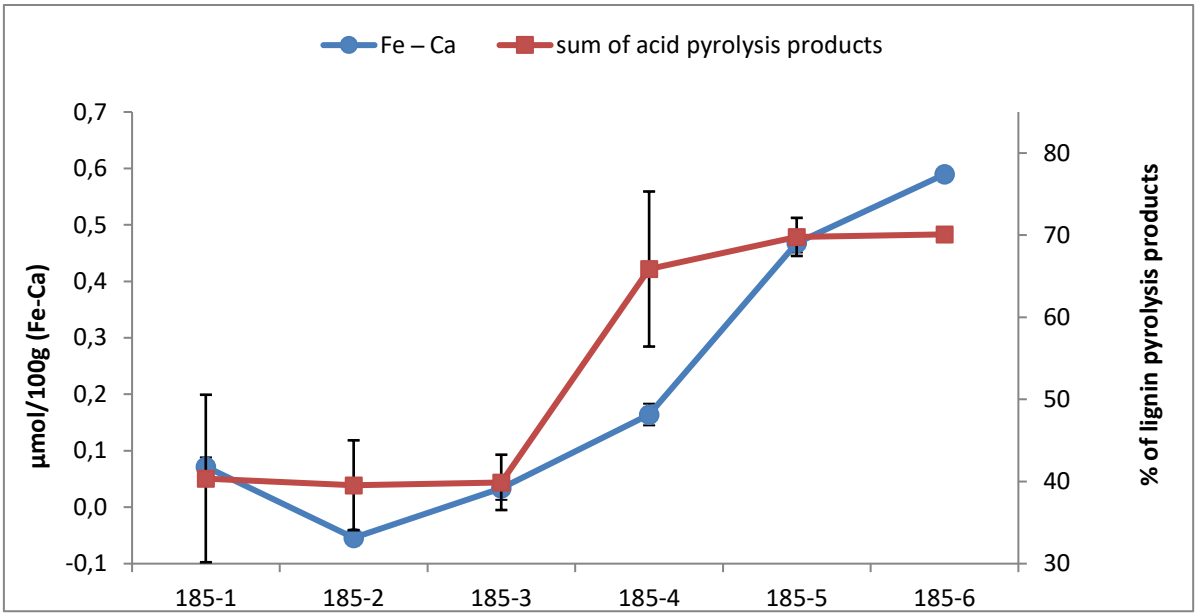

Figure 7. Comparison of sum of acid lignin pyrolysis products to Fe content minus Ca content in 185-series.

Conclusions

Py-GC/MS with *in situ* silylation was applied to archaeological wood samples from the Oseberg find, in order to provide information about wood degradation. ICP-AES was also applied on a series of alum-treated samples to investigate the inorganic content and to look for correlations between the presence of specific elements and wood deterioration. The results showed that the observed deterioration in alum-treated woods (185 series) was directly linked to the alum-treatment itself, thus confirming the previous hypothesis [4]. In fact, the comparison between archaeological alum-treated woods, archaeological untreated woods and sound woods showed a drastic degradation of alum-treated woods. In particular, over 100 years after treatment with alum, an extreme depletion of holocellulose and a highly deteriorated and oxidized lignin fraction were observed. Significant levels of p-hydroxy benzoic acid were identified. It was the first time that this compound was detected in archaeological wood. Its presence provided concrete evidence that alum-treated wood creates an oxidizing atmosphere.

It was also found that chemical deterioration was related to an increase in darkening (likely due to increased oxidation of the lignin polymer) and a decrease in structural integrity.

A simulation of alum treatment was also performed and after five years, Py(HMDS)-GC/MS showed that lignin was significantly depleted in monomeric residues, suggesting that acid from the alum-treatment initiated deterioration. Nevertheless, significant oxidation of lignin was not observed, nor darkening of wood. Relationships between selected

inorganic elements and extent of acidic lignin breakdown products identified by pyrolysis were observed. In particular, there was partial correlation between Al content and the total amount of acid pyrolysis products from lignin, which could suggest a relationship between degradation and either alum decomposition or Al(III) ions. However, a convincing relationship between iron content and degradation was observed. The correlation increased when the difference between concentrations of iron and calcium were considered, suggesting that calcium compounds could modulate iron-promoted degradation.

Thus, experimental results have shown that the combination of Py(HMDS)-GC/MS and ICP-AES provided increased insight into potential deterioration reactions, occurring in a complex material as alum-treated archaeological wood. A link between chemical state of preservation and visual condition of wood was also found and this will aid conservators in further work in classifying the other objects in the Oseberg collection. However, more work is planned in order to go deeper into the degradation mechanisms with the final aim to find a suitable conservation strategy for these precious objects.

Acknowledgements

The authors are grateful for the financial support from the Norwegian Ministry of Education and University of Oslo, which fund the Saving Oseberg project. We also thank Andrea Jung, from the Leibniz Institute for New Materials, Saarbrücken, Germany for undertaking ICP-AES analyses.

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