Dating the lost arrow shafts from Stellmoor (Schleswig-Holstein, Germany)

Datierung der verlorenen Pfeilschäfte aus Stellmoor (Schleswig-Holstein, Deutschland)

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Abstract - In 1935-36, at Stellmoor, near Hamburg, the archaeologist Alfred Rust recovered over 100 wooden arrow shafts and thousands of reindeer bones and antlers, from a gyttja layer attributed to the Younger Dryas. The arrow shafts were – and still are – the oldest direct evidence of bow-and-arrow hunting in the world. Rust described them in detail in his 1943 monograph on Stellmoor, but all the recorded wooden artefacts were lost in an air-raid in 1944. However, several small pieces of wood, resembling fragments of arrow shafts in the 1943 publication, were discovered in 2013 among Rust's personal effects. Two fragments were dated, to test their proposed attribution to Stellmoor. Both had clearly been treated with unknown compounds, which Rust may have applied in an early experiment in waterlogged wood conservation. Infrared spectroscopy and biomolecular analysis suggest that these consolidants consisted of plant oils mixed with rosin, which should be removed by solvent extraction. While solvent-extracted samples gave older radiocarbon ages than samples extracted by a normal acid-base-acid protocol, however, the results were still somewhat younger than expected, in one case significantly more recent. Extraction to α-cellulose finally yielded a date consistent with those of reindeer bones and antlers from Stellmoor.

Zusammenfassung - *In den Jahren 1935 und 1936 konnte der Archäologe Alfred Rust in Stellmoor bei Hamburg über 100 hölzerne Pfeilschäfte und Tausende von Rentierknochen und -geweihen aus einer Muddeschicht, die der Jüngeren Dryas zugeordnet wird, bergen. Bei den Pfeilschäften handelte – und handelt – es sich um den weltweit ältesten direkten Nachweis der Jagd mit Pfeil und Bogen. Rust beschrieb diese Pfeilschäfte detailliert in seiner 1943 erschienenen Monographie zu Stellmoor, aber alle erfassten Holzartefakte gingen bei einem Luftangriff 1944 verloren. Allerdings wurden 2013 mehrere kleine Holzstücke, die Bruchstücken der Pfeilschäfte aus der Publikation von 1943 ähneln, in Rusts persönlichem Nachlass entdeckt. Zwei Fragmente wurden datiert, um ihre vorgeschlagene Zugehörigkeit zum Fundplatz Stellmoor zu überprüfen. Beide waren eindeutig mit unbekannten Stoffen behandelt worden, die Rust in einem frühen Experiment zur Nassholzkonservierung verwendet haben könnte. Die Infrarotspektroskopie und molekularbiologische Analyse legen nahe, dass diese Festigungsmittel aus mit Rosin vermischten Pflanzenölen bestanden, die durch Lösungsmittelextraktion entfernt werden sollten. Auch wenn durch Lösungsmittel extrahierte Proben ältere Radiokarbonalter ergaben als Proben, die mittels eines gängigen Säure-Basis-Säure-Protokolls extrahiert worden waren, fielen ihre Ergebnisse immer noch etwas jünger aus als erwartet, in einem Fall sogar deutlich. Schließlich erbrachte die Extraktion von α-Zellulose ein Alter, das mit den an Rentierknochen und -geweih gewonnenen Daten aus Stellmoor übereinstimmt.*

Keywords - projectiles, Late Palaeolithic, wood conservation, radiocarbon, cellulose, biomolecular analysis
            Projektile, Spätpaläolithikum, Holzkonservierung, Radiokarbon, Zellulose, molekularbiologische Analyse

Introduction

In 1935-36, over 100 arrow shafts and foreshafts, made from pine wood, were recovered by Alfred Rust and his team from Lateglacial lake sediments at the foot of the Stellmoor hill, in the Ahrensburg tunnel valley, near Hamburg (Fig. 1; Rust 1943). This gyttja layer, which was attributed to the Younger Dryas on palynological grounds (Schütrumpf 1943), also yielded more than 17'000 mammal, bird and fish bones, as well as more than 5'000 reindeer antler remains (Kollau 1943; Krause & Kollau 1943; Bratlund 1996). Around 20 radiocarbon (^{14}C) results on bones or

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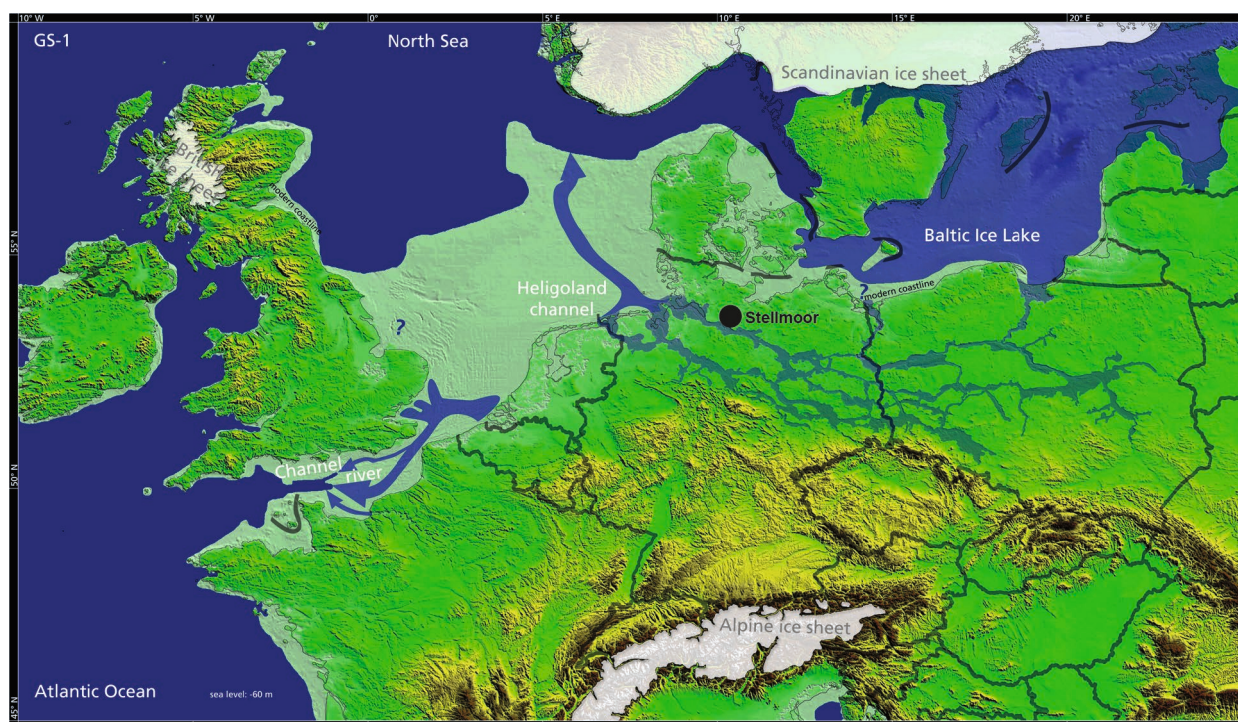
Fig. 1. Map of northern Europe during the Younger Dryas (c.12'000 cal BP), showing the location of Stellmoor (basic map RGZM, Grimm 2012, unpublished; compiled after Woldstedt 1956; Björck 1995; Konradi 2000; Boulton et al. 2001; Lundqvist & Wohlfarth 2001; Bourillet et al. 2003; Lericolais et al. 2003; Weaver et al. 2003; Clark et al. 2004; Ivy-Ochs et al. 2006; Gupta et al. 2007).

Abb. 1. *Karte Nordeuropas während der Jüngeren Dryas (ca. 12'000 cal BP), die die Lage von Stellmoor zeigt (Grundkarte RGZM, Grimm 2012, unpubliziert; zusammengestellt nach Woldstedt 1956; Björck 1995; Konradi 2000; Boulton et al. 2001; Lundqvist & Wohlfarth 2001; Bourillet et al. 2003; Lericolais et al. 2003; Weaver et al. 2003; Clark et al. 2004; Ivy-Ochs et al. 2006; Gupta et al. 2007).*

antlers of reindeer (*Rangifer tarandus*), bison (*Bison bonasus*) and horse (*Equus* sp.) date this assemblage to the second half of the Younger Dryas and the beginning of the Preboreal (Fischer & Tauber 1986; Lanting & van der Plicht 1996; Benecke 2004; Drucker et al. 2016; Drucker et al. in prep.), c. 12'200–11'400 calBP. The osseous and lithic artefacts found alongside the fauna in four distinct layers within the Younger Dryas gyttja comprise typical elements of the Ahrensburgian (Rust 1943), the last Palaeolithic tradition in the western part of the North European Plain and its adjacent upland zone (Taute 1968).

Their origin in the Late Palaeolithic makes the Stellmoor arrow shafts and foreshafts (Fig. 2) the world's oldest direct evidence of bow-and-arrow hunting. Different lithic projectile implements from the Upper Palaeolithic have been considered potential arrowheads (e.g. Junkmanns 2013 for Solutrean tanged points of the Parpalló type) but only provide indirect evidence. Actual examples of arrows and bows are attested from the Mesolithic onwards (e.g. Larsson 2009; Becker 1945). The Stellmoor projectiles are distinguished as arrows, rather than spears, by the presence of nocks (cf. Fig. 2: 5), slots into which the bow strings are laid, at their proximal ends (Junkmanns 2013). At the distal ends, Ahrensburgian lithic tanged points were frontally inserted into grooves, as illustrated by two foreshafts found with a lithic fragment still stuck in the groove (Fig. 2: 2; Rust 1943: pl. 92: 1;

pl. 93: 2). The characteristic element of the Stellmoor arrows is their composite shaft, consisting of a main shaft and a foreshaft jointed together (Becker 1945: 71; Rust 1962). Both the distal extremity of the main shaft and the proximal extremity of the foreshaft are notched in v-shape, in such a way that their tails fit into the notches of the other piece (Fig. 2: 4; Fig. 3). Foreshafts can serve various functions (cf. Pfeifer 2014); at Stellmoor, Rust (1962) considered that they were intended to save the main shaft in case the hit prey escaped.

The only other site where Rust excavated fragments of wooden arrow shafts is Hopfenbach-Aalfang (Rust 1958), situated about 4 km northeast of Stellmoor. However, the two artefacts recovered there lack the characteristic notches, as one was an apical fragment and the second an undefined fragment of 5 cm length.

All the recorded wooden artefacts from Alfred Rust's excavations in the Ahrensburg tunnel valley were lost in an air-raid at the *Museum vorgeschichtlicher Altertümer* in Kiel on 22nd May, 1944. On this subject, the archives of the Archaeological State Museum (ALM) now Archaeological Museum Schloss Gottorf in Schleswig contain a document (Ahrensburg 47) stating that, among others, wooden arrow shafts from Rust's excavation, which were stored in glass tubes, were destroyed. When his daughter Elke Rust handed over her father's artefact collection, personal effects and
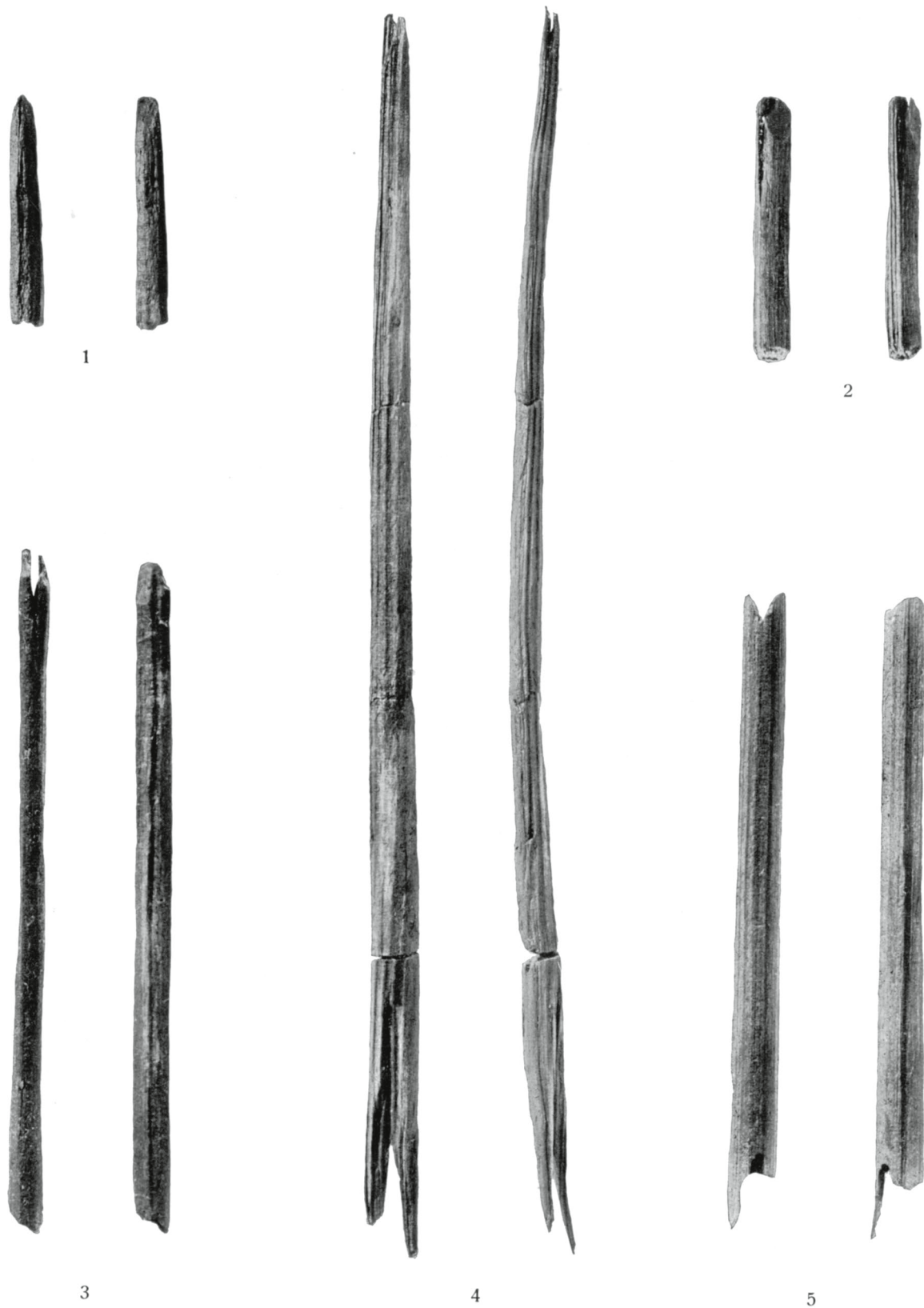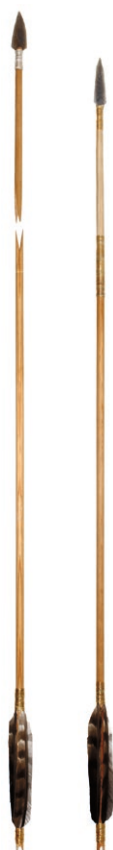
Fig. 2. Wooden arrow shaft elements from Stellmoor (Rust 1943: pl. 93).
Abb. 2. Hölzerne Pfeilschaftelemente aus Stellmoor (Rust 1943: Taf. 93).

Fig. 3. Modern reconstruction of Ahrensburgian arrow from Stellmoor (Harm Paulsen). Photograph: Stiftung Schleswig-Holsteinische Landesmuseen Schloss Gottorf.

Abb. 3. *Moderne Rekonstruktion eines Pfeils der Ahrensburger Kultur aus Stellmoor (Harm Paulsen). Foto: Stiftung Schleswig-Holsteinische Landesmuseen Schloss Gottorf.*

Fig. 4. Wooden artefacts from Rust's collection (left: Arrow 1; right: Arrow 2).

Abb. 4. *Holzartefakte aus Rusts Sammlung (links: Pfeil 1; rechts: Pfeil 2).*

archaeology-related documents to the ALM in 2013, Stone Age curator Sönke Hartz discovered 11 small pieces of wood in a cigarette box (Hartz et al. 2019). One of these, henceforward called Arrow 1, is reminiscent of the Stellmoor arrow elements because of the notch at one of its extremities (Fig. 4) as well as its shape and dimensions, and could be refitted to a second piece. Another element, called Arrow 2, also resembles them from a morpho-dimensional point of view.

Since these pieces were not labelled, could not be identified among the artefacts published in the Stellmoor monograph (Rust 1943) or appearing in unpublished photographs held by the ALM, and were incompatible with the two arrow shaft fragments from Hopfenbach-Aalfang (cf. above), one goal of our study was to establish whether or not they represent genuine artefacts. Therefore, Arrow 1 and 2 were sampled for dating, for comparison with ^{14}C ages of reindeer bone and antler from the surviving Stellmoor archive (Hartz et al. 2019). Judging from their shiny surfaces, both pieces had apparently been conserved with unknown organic compounds, which Rust may have applied experimentally. Moreover, an oily substance oozed out of Arrow 2 during sampling. Thus, the second goal of the study was to identify the consolidant used on both pieces.

Methods

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR is an almost non-destructive method of material analysis, which produces a spectrum based on the transmission (or reflection) of a focused infrared beam at different wavelengths. The spectrum obtained depends on the presence and abundance of different molecular bonds, which may interfere with the beam transmission at specific wavelengths. FTIR spectra therefore reflect a sample's molecular structure, and may be used to detect the presence of consolidants used to conserve archaeological artefacts. In theory such a consolidant may also be identified, if its FTIR spectrum is sufficiently distinct, and if the sample spectrum matches relevant reference spectra.

The oily substance from Arrow 2 was therefore analysed by FTIR, at the Leibniz-Labor für Altersbestimmung und Isotopenforschung, Christian-Albrechts-Universität zu Kiel, using an ATR (attenuated total reflectance) Nicolet 380 Spectrometer equipped with a diamond crystal. A fine shaving of untreated wood from each artefact was analysed by the same method. Some laboratory extracts were also analysed by FTIR, to monitor the removal of consolidants. Sample spectra were compared visually and statistically to libraries of reference spectra.

Gas Chromatography-Mass Spectrometry (GC-MS)

To confirm the proposed identification of the oily compound, a wood sample of Arrow 1 was ultrasonicated for 30 min at 40°C in a 2:1 v/v dichloromethane-methanol mix. The solution was decanted and dried. GC-MS analysis was carried out at the University of Bradford, United Kingdom, on an Agilent 7890A series GC attached to an Agilent 5975C Inert XL mass selective detector.

A known amount of an internal standard (C34 n-alkane) was added to each GC-MS sample before analysis to allow quantification. The samples were derivatised by adding 30 µl BSTFA to each sample and heating in a closed vial at 60°C for 30 minutes. After cooling the excess BSTFA was evaporated off under a stream of dry nitrogen with gentle heating (40°C). The samples were dissolved in dichloromethane for GC-MS analysis.

For GC-MS analysis the splitless injector and interface were maintained at 300°C and 280°C, respectively. Helium was used as the carrier gas at constant inlet pressure. The column was inserted directly into the ion source of the mass spectrometer. The ionisation energy was 70eV and spectra were obtained by scanning between m/z 50 and 800. All samples were analysed using an Agilent DB5-ms-UI 30 m x 2.5 mm x 2.5 µm column. The oven temperature was programmed to be isothermal at 50°C for 2 minutes, followed by a rise of 10°C per minute up to 350°C and an isothermal hold for 10 minutes. Compounds were identified by comparison with the National Institute of Standards and Technology (NIST) library of mass spectral data and published data.

Radiocarbon Dating

Archaeological samples require laboratory pretreatment in order to separate their original organic components from contaminating substances (both natural sources of organic and inorganic carbon in the burial environment, and artificial sources, such as deliberately applied consolidants). For wood samples, after microscopic examination and manual removal of visible rootlets, a series of chemical reagents is applied in order to dissolve natural contaminants, which are then removed by rinsing repeatedly in distilled water, until only a clean insoluble residue is left; this 'extract' is converted to carbon dioxide by combustion and reduced to pure carbon in graphite form for the ^{14}C measurement.

Natural contaminants tend to be water-soluble in either strongly acidic or strongly alkaline conditions, so most laboratories employ an acid-base-acid protocol: an acid solution to dissolve carbonates present in mineral inclusions or precipitated from groundwater, followed by an alkaline solution to release secondary organic compounds (humics) derived from the breakdown of soil organic matter, and another acid treatment to dissolve any secondary carbonate which may have precipitated in the alkaline

conditions. As oils and waxes are insoluble in water over a wide pH range, however, they must be dissolved using non-polar organic solvents. A sequence of different solvents, of steadily increasing polarity, is required to remove both the contaminating lipid compounds and the organic solvents themselves.

At the Leibniz laboratory in Kiel, therefore, a 10–20 mg wood sample of each object was initially extracted using a 'Soxhlet' apparatus, which washes the samples with a sequence of hot tetrahydrofuran, chloroform, petroleum-ether, acetone, methanol and water (each 3x), to remove oils and waxes (Bruhn et al. 2001). The cleaned samples were then given normal acid-base-acid (A-B-A) pretreatment (with 1 % HCl, 1 % NaOH, each at 60°C, and again 1 % HCl); the insoluble residue was combusted, graphitised and dated. Two graphite targets were made from different aliquots of the Arrow 1 extract, and dated separately by accelerator mass spectrometry (AMS) to confirm the reliability of the combustion, graphitisation and measurement steps.

As both results were significantly later than expected (cf. below), new samples of both objects were processed in Kiel, by carrying out the entire Soxhlet process three times before acid-base-acid extraction. For comparison, additional samples were dated after simple acid-base-acid pretreatment without any solvent cleaning, Arrow 2 in Kiel and Arrow 1 at the Aarhus AMS Centre, Aarhus University, Denmark. The Aarhus acid-base-acid protocol differed only in the pretreatment temperature, which was 80°C instead of 60°C. As the results remained perplexing, both arrows were sampled a fourth time, for AMS dating of a specific fraction of wood, α-cellulose. 80–100 mg of finely shredded wood was soaked overnight, ultrasonicated in hot acidified bleach (5 h, 70°C, with 200–250 mg $NaClO_2$ and 136–170 µL 100 % CH_3COOH added hourly), then ultrasonicated in hot alkali solutions (10 % NaOH, 1 h, 70°C, and then 17 % NaOH, 1 h, 70°C), and finally acidified (1 % HCl, 2 h, 20°C), rinsed repeatedly, and freeze-dried. The Arrow 2 sample dissolved totally during the bleaching process, but Arrow 1 gave 0.91 mg of cellulose, which was sufficient for dating. For quality control, known-age and background wood samples were extracted to α-cellulose and dated concurrently with the arrow samples.

Results

FTIR Spectroscopy

FTIR spectroscopy of the oily substance extracted by pressing Arrow 2 (Fig. 5) gave possible matches with abietic acid (FDM Comprehensive Organics library, reference 2638; © 2004, Fiveash Data Management, Inc.), a major component of rosin (distilled pine resin), and ricinoleic acid (FDM FTIR Spectra of Surfactants, reference 0199; © 2004, Fiveash Data Management, Inc.), the main constituent of castor oil. FTIR of wood
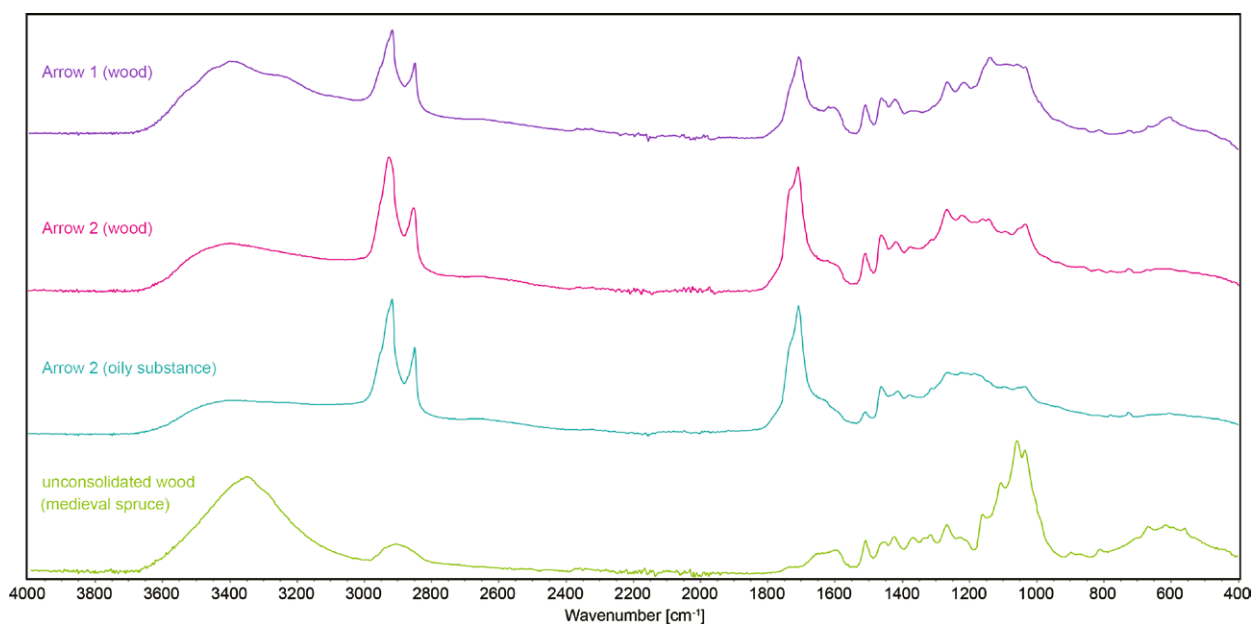
Fig. 5. ATR-FTIR spectra of wood from Arrows 1 and 2 before pretreatment (top), compared to spectra of the oily substance in Arrow 2 and unconsolidated archaeological spruce wood (bottom). Prominent peaks in the spectrum of the oily substance, at 2'918, 2'850 and 1'710 cm-1, dominate the spectra of both arrows, but are absent in the uncontaminated wood spectrum.

Abb. 5. *ATR-FTIR-Spektren des Holzes von Pfeil 1 und Pfeil 2 vor der Vorbehandlung (oben), im Vergleich zu den Spektren der öligen Substanz in Pfeil 2 und nicht verfestigten archäologischen Fichtenholzes (unten). Markante Höchstwerte im Spektrum der öligen Substanz, bei 2'918, 2'850 und 1'710 cm-1, dominieren die Spektren beider Pfeile, fehlen jedoch im nicht verunreinigten Holzspektrum.*

shavings suggested that a similar mixture was applied to both artefacts. Both wood sample spectra included sharp peaks at 2'918, 2'850 and 1'710 cm^{-1}, absent in FTIR spectra of unconsolidated wood but coinciding with peaks in the spectrum of the oily substance. The Arrow 1 spectrum also had a minor peak at 1'140 cm^{-1} that is difficult to attribute to either the wood itself, or to the oily substance squeezed out of Arrow 2.

Spectra of dated extracts (discussed below) suggest that normal acid-base-acid pretreatment did not completely remove the oily substance, whereas the spectrum of the cellulose extract from Arrow 1 is almost identical to that of cellulose extracted from an unconsolidated timber, and does not show any evidence of contamination (Fig. 6).

GC-MS
The Arrow 1 extract was dominated by saturated fatty acids ($C_{16:0}$, hexadecanoic acid; $C_{18:0}$, octadecanoic acid) (Fig. 7: 6, 8). Unsaturated $C_{18:1}$ octadecenoic fatty acid was present but less abundant (Fig. 7: 7). Oxidation products of unsaturated fatty acids (dicarboxylic acids, oxofatty acids and a dihydroxyfatty acid (Fig. 7: 2, 3, 5, 9, 11, 12)) were also present, but there was no evidence of polyunsaturated fatty acids. The very low abundance of any acids with chain length $<C_{16:0}$ and the absence of odd-carbon number fatty acids points to a plant oil rather than animal fat. Ricinoleic (12-hydroxyoctadecenoic acid) was not detected. The FTIR spectra of fatty acids are very similar and the detection of a dihydroxyfatty acid in the sample may have resulted in a composite spectrum similar to

ricinoleic acid. The oil is highly hydrolysed, with only traces of monoacylglycerols. Only traces of molecules with an abietane carbon skeleton (dehydroabietic acid and 7-oxodehydroabietic acid (Fig. 7: 10, 13) were seen. The minor resin (*Pinaceae* sp.) component could derive from naturally-occurring diterpenoids from the pine wood shaft.

Radiocarbon Dating
Both arrows gave progressively older ^{14}C ages with increasingly aggressive pretreatment protocols (Fig. 8). Simple acid-base-acid extraction produced insoluble residues weighing 44 % (Arrow 1) and 48 % (Arrow 2) of the starting weight; coincidentally, these extracts gave identical ages, of 8'555 ± 40 BP and 8'555 ± 40 BP respectively. A single Soxhlet extraction cycle prior to acid-base-acid extraction produced extracts of 25 % (Arrow 1) and 15 % (Arrow 2) of the starting weight, with ^{14}C ages of 9'260 ± 35 BP (weighted mean of results from two targets) and 9'800 ± 50 BP respectively. Triple Soxhlet pretreatment before acid-base-acid extraction led to yields of 24 % (Arrow 1) and 21 % (Arrow 2), with ^{14}C ages of 9'365 ± 45 BP and 9'915 ± 45 BP respectively. Lastly, the α-cellulose extract from Arrow 1, only 0.9 % of the starting weight, produced a ^{14}C age of 10'050 ± 90 BP. Known-age wood samples processed to α-cellulose concurrently gave acceptable ^{14}C ages.
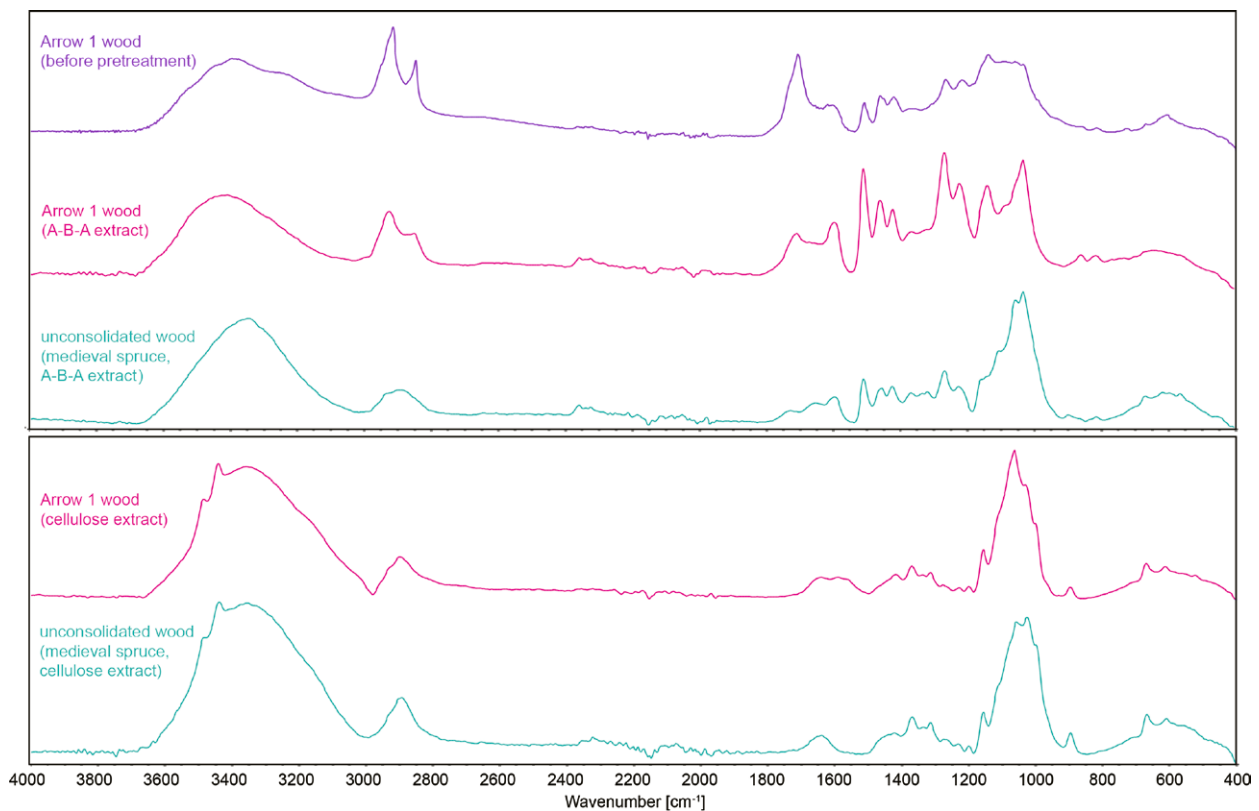
Fig. 6. Above: ATR-FTIR spectra of wood from Arrow 1 before pretreatment (top), after normal acid-base-acid pretreatment (middle), compared to unconsolidated archaeological spruce wood after acid-base-acid pretreatment (bottom). Peaks attributed to the consolidant, at 2'918, 2'850 and 1'710 cm-1, and perhaps 1'140 cm-1, are still visible in the Arrow 1 extract, but not in equivalent extract of uncontaminated wood. Below: ATR-FTIR spectra of α-cellulose extracts of Arrow 1 (top) and unconsolidated archaeological spruce (bottom), showing no significant differences which might be attributed to conservation treatments.

Abb. 6. Oberes Bild: ATR-FTIR-Spektren des Holzes von Pfeil 1 vor der Vorbehandlung (oben), nach der normalen Säure-Lauge-Säure-Vorbehandlung (Mitte), im Vergleich zu nicht verfestigtem archäologischen Fichtenholz nach Säure-Lauge-Säure-Vorbehandlung (unten). Höchstwerte, die dem Verfestigungsmittel zugeordnet werden, bei 2'918, 2'850 und 1'710 cm-1, und vielleicht 1'140 cm-1, sind noch sichtbar im Extrakt aus Pfeil 1, aber nicht im vergleichbaren Extrakt aus nicht verunreinigtem Holz. Unteres Bild: ATR-FTIR-Spektren des α-Zellulose-Extrakts von Pfeil 1 (oben) und von nicht verfestigtem archäologischen Fichtenholz (unten), die keine signifikanten, möglicherweise Konservierungsbehandlungen zuzuschreibenden Unterschiede zeigen.

Discussion

The pattern of ^{14}C results suggests that both arrows were heavily contaminated with predominantly modern carbon, and therefore that all the results may be regarded as minimum ages for the arrows themselves. The alternative interpretation, that laboratory pretreatment itself contaminated the samples with ^{14}C-free carbon, is contradicted by the acceptable results obtained on samples of more recent known-age wood. For both arrows, the large differences between results following the acid-base-acid protocol only and after solvent extraction imply that the younger contaminant was lipid-based, as indicated by FTIR. Triple-Soxhlet pretreatment produced insignificantly older ^{14}C ages than a single cycle of solvent extraction (Arrow 1: 105 ± 57 ^{14}C yrs older; Arrow 2: 115 ± 64 ^{14}C yrs older); thus it appears that most or all of the oily substance was removed during the first Soxhlet cycle. The fact that the ^{14}C age difference between the A-B-A-only extract and the triple-Soxhlet extract was much greater in Arrow 2

(Arrow 1: 805 ± 60 ^{14}C yrs; Arrow 2: 1'360 ± 60 ^{14}C yrs) could simply imply that Arrow 2 was more heavily contaminated, but with the same substance as Arrow 1. However, as the Arrow 1 α-cellulose extract gave a significantly older result than its triple-Soxhlet extract (difference 685 ± 101 ^{14}C yrs), but was insignificantly older than the Arrow 2 triple-Soxhlet extract (difference 135 ± 101 ^{14}C yrs), it seems more likely that Arrow 1 was conserved with a different and less soluble formulation than Arrow 2. Rosin and plant oils should both be soluble in several of the solvents used, but the long-term solubility of mixtures is unclear. Other factors which might have affected the results of each pretreatment protocol, such as the condition of each object at the time of excavation, or the time elapsed between excavation and consolidation, can never be known.

It cannot be assumed that the two arrows are really of the same date, and even if their provenance was known securely, there is a significant range of ^{14}C ages on reindeer bones and antlers from the Ahrensburgian layer at Stellmoor (c. 9'800–10'300 BP). Both arrows now appear to date within this range (Fig. 9), which
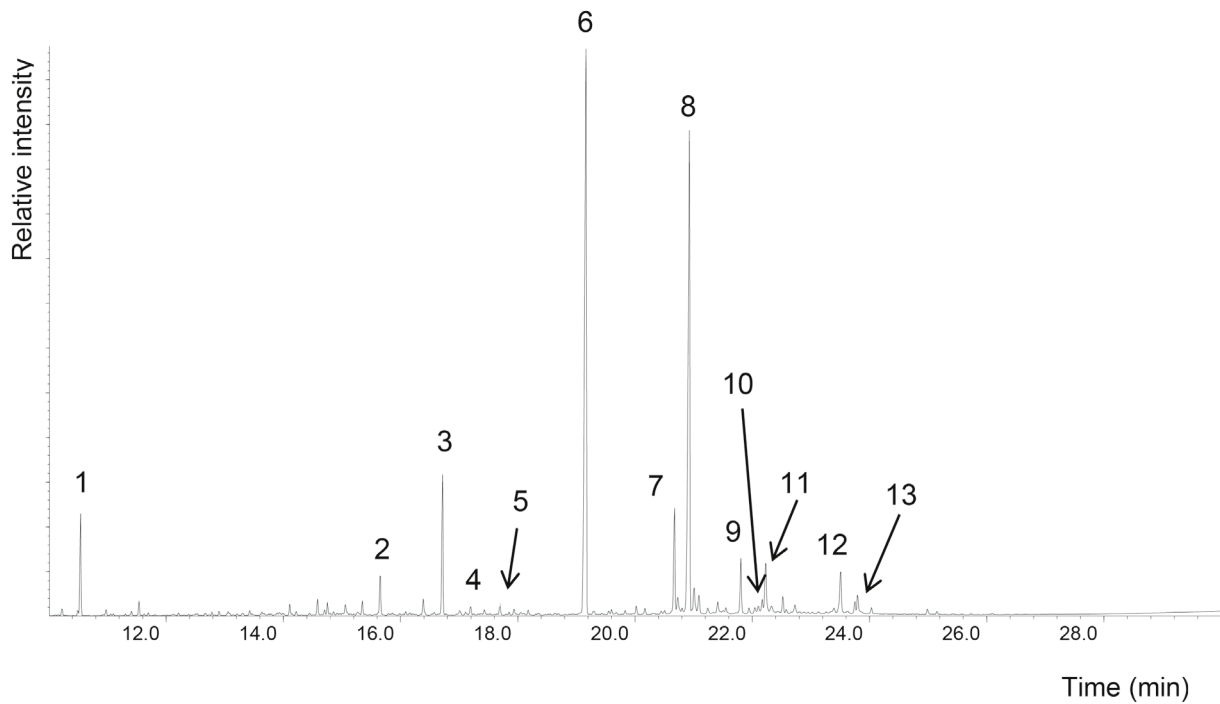
Fig. 7. Partial TIC (total ion current) chromatogram obtained by GC-MS analysis of the solvent-extracted sample from Arrow 1. Peak identities: 1 - glycerol (TMS ether); 2 - $C_{8:0}$ dicarboxylic acid (TMS ester) = Suberic acid (TMS ester); 3 - $C_{9:0}$ dicarboxylic acid (TMS ester) = Azelaic acid (TMS ester); 4 - $C_{14:0}$; 5 - $C_{10:0}$ dicarboxylic acid (TMS ester) = Sebacic acid (TMS ester); 6 - $C_{16:0}$ (TMS ester); 7 - $C_{18:1}$ (TMS ester); 8 - $C_{18:0}$ (TMS ester); 9 - probable oxofatty acid (TMS ester); 10 - dehydroabietic acid (TMS ester); 11 - probable oxofatty acid (TMS ester); 12 - 9,10-dihydroxyoctadecanoic acid (TMS derivative); 13 - 7-oxodehydroabietic acid (TMS ester).

Abb. 7. Partielles TIC-Chromatogramm (Gesamtionenstrom) der GC-MS-Analyse der mit Lösungsmittel extrahierten Probe: 1 - Glycerin (TMS-Ether); 2- $C_{8:0}$-Dicarbonsäure (TMS-Ester) = Suberinsäure (TMS ester); 3- $C_{9:0}$-Dicarbonsäure (Bis-TMS-Ester) = Azelainsäure (TMS ester); 4 - $C_{14:0}$; 5- $C_{10:0}$-Dicarbonsäure (TMS-Ester) = Sebacinsäure (TMS ester); 6 - $C_{16:0}$ (TMS-Ester); 7 -$C_{18:1}$ (TMS-Ester); 8 - $C_{18:0}$ (TMS-Ester); 9 - wahrscheinliche Oxofettsäure (TMS-Ester); 10 - Dehydroabietinsäure (TMS-Ester); 11 - wahrscheinliche Oxofettsäure (TMS-Ester); 12 - 9,10-Dihydroxyoctadecansäure (TMS-Derivat); 13 - 7-Oxodehydroabietinsäure (TMS-Ester).

suggests that their attribution to Stellmoor is probably correct, and that their oldest ^{14}C results (Arrow 1: KIA-49753, 10'050 ± 90 BP; Arrow 2: KIA-49754, 9'915 ± 45 BP) must be close to the true ^{14}C ages of the wooden shafts. Unfortunately, we do not have an FTIR spectrum from Arrow 2 after triple-Soxhlet extraction, but in any case the FTIR detection limit for the oily substance has not been established. The Arrow 1 α-cellulose FTIR spectrum has a minor peak at c. 1'600 cm^{-1} not seen in the α-cellulose spectrum from

unconsolidated timber (Fig. 6), but this peak, which is difficult to distinguish in the spectra of the oily substance or the consolidated wood, is not necessarily associated with a consolidant. As the unconsolidated wood spectrum (Fig. 5) has a small peak in the same position, it may be from incomplete degradation of the lignin or holo-cellulose components of the wood, which would not affect the ^{14}C age.

Therefore there is little doubt that the arrows are associated with the Ahrensburgian phase of the Final

Object	Extraction	δ^{13}C(‰)	F^{14}C	Conventional Age
Arrow 1 (wood splinter (*Pinus* sp.) with notch)	AAR-19534: A-B-A, 44% yield	-27.56 ± 0.66	0.3447 ± 0.0018	8'555 ± 40 BP
	KIA-49753: Sox+A-B-A, 25% yield	-25.91 ± 0.36	0.3145 ± 0.0018	9'290 ± 45 BP
		-25.95 ± 0.38	0.3169 ± 0.0017	9'230 ± 45 BP
	KIA-49753: 3x Sox+A-B-A, 24% yield	-25.77 ± 0.28	0.3117 ± 0.0017	9'365 ± 45 BP
	KIA-49753: α-cellulose, 0.91% yield	-25.63 ± 0.81	0.2862 ± 0.0032	10'050 ± 90 BP
Arrow 2 (wood splinter (*Pinus* sp.))	KIA-49754: A-B-A, 48% yield	-25.15 ± 0.20	0.3447 ± 0.0017	8'555 ± 40 BP
	KIA-49754: Sox+A-B-A, 15% yield	-27.42 ± 0.22	0.2953 ± 0.0016	9'800 ± 45 BP
	KIA-49754: 3x Sox+A-B-A, 21% yield	-26.04 ± 0.31	0.2910 ± 0.0017	9'915 ± 45 BP
	KIA-49754: α-cellulose, 0% yield			

Fig. 8. List of radiocarbon measurements carried out on Arrow 1 and Arrow 2.
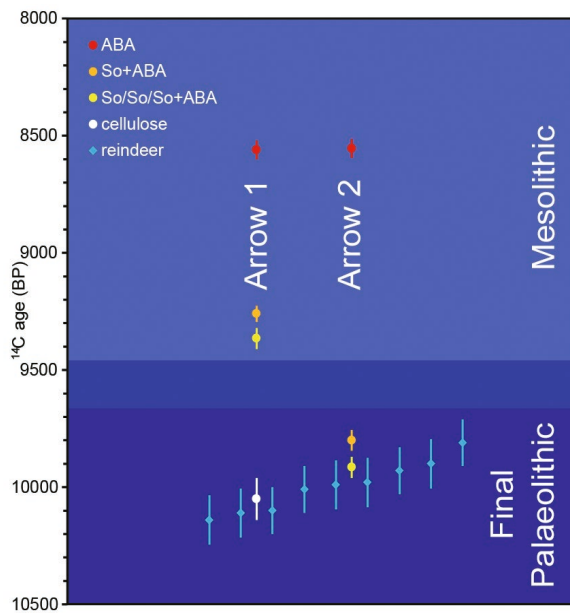*Abb. 8. Liste der an Pfeil 1 und Pfeil 2 durchgeführten Radiokarbonmessungen.*

Fig. 9. Radiocarbon ages of reindeer remains from the Ahrensburgian layer at Stellmoor (Fischer & Tauber 1986) and of various extracts of Arrows 1 and 2.

Abb. 9. *Radiokarbonalter von Rentierresten aus der Ahrensburger Kulturschicht in Stellmoor (Fischer & Tauber 1986) und diverser Extrakte von Pfeil 1 und 2.*

Palaeolithic, and are not Mesolithic in date. If these results are calibrated, using OxCal v4 and the IntCal13 calibration data (Bronk Ramsey 2009; Reimer et al. 2013), Arrow 1 falls on a plateau in calibration curve, giving a potential date anywhere in the range 11'970–11'260 calBP (95 % probability), which spans the Younger Dryas-Preboreal transition (c. 11'650 calBP). Arrow 2 appears to date to the Preboreal (11'610–11'220 calBP, 95 % probability), but even a small increase in its ¹⁴C age would put this sample on the same calibration plateau as Arrow 1. Even with its Preboreal date, however, Arrow 2 is potentially from the Ahrensburgian layer at Stellmoor. The possibility that the arrows were made experimentally by Rust, using old wood from the excavation, cannot be completely ruled out, and strictly speaking, the lack of diagnostic features on Arrow 2 means that its function is uncertain, but we are confident that Arrow 1 is currently the world's oldest directly-dated arrow.

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