RÖMISCH-GERMANISCHE KOMMISSION
DES DEUTSCHEN ARCHÄOLOGISCHEN INSTITUTS

BERICHT DER RÖMISCH-GERMANISCHEN KOMMISSION

BAND 97
2016

PDF-Dokument des gedruckten Beitrags

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Shields and hide – On the use of hide in Germanic shields of the Iron Age and Viking Age

SCHRIFTLEITUNG FRANKFURT A. M. PALMENGARTENSTRASSE 10–12

GEBR. MANN VERLAG · BERLIN

MIT 132 TEXTABBILDUNGEN, 27 TABELLEN, 2 ANHÄNGEN
UND DIGITALEN SUPPLEMENTEN

Die wissenschaftlichen Beiträge im Bericht der Römisch-Germanischen Kommission
unterliegen dem peer-review-Verfahren durch auswärtige Gutachterinnen und Gutachter.

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Tous les textes présentés à la revue «Bericht der Römisch-Germanischen Kommission»
sont soumis à des rapporteurs externes à la RGK.

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ISBN 978-3-7861-2840-3
ISSN 0341-9312

Verlag: Gebr. Mann Verlag, Berlin – www.reimer-mann-verlag.de
Verantwortlicher Redakteur: David Wigg-Wolf, Römisch-Germanische Kommission
Graphische Betreuung: Kirstine Ruppel, Römisch-Germanische Kommission
Formalredaktion: Susanne Biegert
Satz und Druck: LINDEN SOFT Verlag e.K., Aichwald
Printed in Germany

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Die Zusammenfassungen wurden von Sandy Hämmerle und Isabel Aitken (Summaries) und Yves Gautier (Résumés) übersetzt.

Shields and hide

On the use of hide in Germanic shields of the Iron Age and Viking Age

By Rolf Fabricius Warming, René Larsen, Dorte V. P. Sommer, Luise Ørsted Brandt and Xenia Pauli Jensen

Keywords: *Shields / Hide / Leather / Germanic / Viking Age / Iron Age / Weaponry / Combat / ZooMS / Microanalyses*
Schlagwörter: *Schilde / Haut / Leder / germanisch / Wikingerzeit / Eisenzeit / Waffen / Kampf / ZooMS / Mikroanalysen*
Mots-clés: *boucliers / peaux / cuir / germanique / époque viking / âge du Fer / armement / combat / ZooMS / microanalyses*

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Introduction

Amongst the array of armaments contained in the archaeological record of Northern Europe, the shield merits special attention, presenting itself as a particularly instructive topic for Iron Age and Viking Age warfare studies. It was not only an integral component of combat but constituted the largest singular piece of equipment carried by the warriors of the age, dictating – or at least greatly influencing – the nature of combat and the applied fighting tactics of the carrier. However, to attain any such understanding of martial practices, it is first necessary to outline the shield construction as an extrasomatic technology in detail as well as the nature of the many raw materials of which it is often composed (see Mauss 1992; Horn 2013, 100).

An unparalleled amount of well-preserved shield material for constructional analyses has survived from the Iron Age and Viking Age in Northern Europe, owing to the region's long-lasting weapon deposits and weaponry burial practices. The different find contexts and excellent preservation conditions, especially those of the sacrificial bogs of the Scandinavian Iron Age, have produced a vast archaeological record of thousands of shield components of both an organic and metallic nature, dating from between c. 350 BC and AD 1000. Although these finds have provided an invaluable understanding of the general composition of Germanic shields, it is evident that several constructional aspects warrant further examination for a fuller understanding.

One intricate but essential feature of Germanic shields which has hitherto remained obscure despite the many well-preserved shield finds is the nature of the hide products used for reinforcing the shield board and its rim. These thin organic layers have seemingly perished in the vast majority of archaeological finds, including the otherwise well-preserved shields from the weapon deposits of the Iron Age. The hide components are for the most part only identifiable through:

1. distinctive discolourations on the shield board,
2. the now-unoccupied space between the metallic shield rim fittings and the shield board or
3. rows of perforations along its rim (not to be mistaken for the perforations deriving from rim fittings).

Only in exceptional cases have such organic materials survived, most often in relatively small and mineralised fragments. These are typically identified through ocular inspection, aided either by optical microscopy or scanning electron microscopy (SEM). Skin-like structures can sometimes be observed in cross-sections, even in mineralised remains (e. g. Cameron / Edwards 2004). It is important to note that shield finds with surviving hide elements are in accordance with the other archaeological shield finds in their construction, suggesting that the scarcity of surviving hide material is owed to preservation conditions. There is, in other words, little to suggest that shields with hide elements belong to

Fig. 1. Distribution map of the Scandinavian and Baltic sites mentioned in the text. Red stars mark the sites with analysed shield facing, black dots mark comparative finds (illustration: the authors).

a separate category of shields and it must therefore be assumed that the vast majority of shields were equipped with hide elements.

While it is generally accepted that hide was used in the construction of most South Scandinavian shields, it is less clear what animal species were preferred and, especially, how these hide products were processed. This is partly due to a previously widespread tendency of disregarding the fundamental differences between various hide products – such as tanned leather, rawhide, parchment, vellum and alike – which have traditionally all been grouped together as "leather" or "hide" when discussed in an archaeological context (Harris 2014, 9 ff.; Hodges 1995, 151). However, as noted by Harris (2014, 9): "For those without a specialist interest in leather it is easy to overlook the variability of products among this group of materials and to lose sight of the specific reasons behind the choice of leather in particular situations and according to different cultural and temporal contexts." These considerations and factors obviously have significant implications for the construction of shields, especially in terms of durability, but remain largely uninvestigated.

In this paper, we present the results of an interdisciplinary study of the choice and use of hide reinforcements in a selection of South Scandinavian shields based on multiple microanalyses of archaeological samples. The aims of the microanalyses were to identify animal species, potential tanning processes and the state of condition, including specific deterioration features linked to the hide processing. The analyses centre around three archaeological finds of shields from the Scandinavian region *(fig. 1)*: Borremose (mid-4th century BC),

Baunegård (grave 11, 2nd half of the 3rd century AD) and Birka (grave Bj 850, 10th century AD). For comparison and further contextualization, we have also included microanalyses conducted on an additional set of samples stemming from a shield facing from Latvia (9th century AD) which is of Curonian origin and thus falls outside the category of Germanic shields (defined below). The dating of the shield finds discussed in the following pages therefore range from c. 350 BC to c. AD 1000.

Germanic shields

To appreciate the role of hide elements in shields and the significance of the results attained in this study, it is first necessary to outline the general construction of the shield types represented by the archaeological finds as well as the find circumstances themselves. The prehistoric shields analysed in this study can be broadly classified as oblong shields and round shields, these being the two main shield types that were predominant amongst the Germanic peoples in the period 350 BC–AD 1000. The term "Germanic", which is often reserved for North European peoples of the Roman Iron Age, is used in this context to stress the continuation of traditions, most notably the *Germanic flat round shield tradition* (defined below). North European shields dated to the Pre-Roman Iron Age and Viking Age are therefore also referred to as Germanic shields in this study.

Oblong shields

The oblong shield was a common shield type during the Iron Age, being in widespread use across Europe and, to a lesser extent, the Middle East from the 8th century BC to the 1st century AD (Stary 1981, 287; Travis / Travis 2015, 33 ff.). Although sometimes erroneously referred to as "Celtic shields", such shields were not exclusively used by Celtic peoples; however, much of their widespread use and uniform features can be attributed to influence from the Celts (Gunby 2000, 362 ff.). Shields belonging to this type typically feature a flat (or nearly flat) oblong shield board, horizontal handle and spindle-shaped or round boss from which a vertical spine *(spina)* sometimes extends in both directions. The shields are generally oblong or elongated but appear in different shapes, such as oval, rectangular, hexagonal, barrel-shaped, etc. All surviving shield boards consist of single layers of flat wooden planks, with the exception of a single shield from Chertsey (U. K.), which was made entirely of bronze (Stead 1987), and another from the Fayum (Egypt) which was curved and constructed out of birch plywood (Kimmig 1940, 106–111). Despite certain shared features, however, it is evident that oblong shields not only greatly vary in terms of shape and size but also in the extent of applied metal components, owing either to metal poverty or changing fashions (Stary 1981; Kaul 2003, 172; Travis / Travis 2015, 37).

Surviving oblong shields of the Barbaricum lie within this broader typology and date to between the 4th century BC and 1st century AD. The oldest fully preserved Germanic shields of this type are those belonging to the weapon deposit at Hjortspring (Denmark) dating to c. 350 BC *(fig. 2a)*. At least 64 shields have been identified from this deposit along with further fragments, producing a probable total number of about 80 shields (Rosenberg 1937, 48 ff.; Kaul 2003, 152). Even though the average length of the shields is 70–75 cm with a breadth of 45 cm, the length and breadth of the shields vary between 61–102 cm and 29–52 cm, respectively. The shields are thickest in the centre (c. 1.8–1.0 cm) and become gradually thinner with a thickness of c. 0.6–0.3 cm at the rim. They show a large degree of variability in shape and construction: some shields are oblong in shape while others are more rectangular or square with rounded edges (Rosenberg 1937, 48;

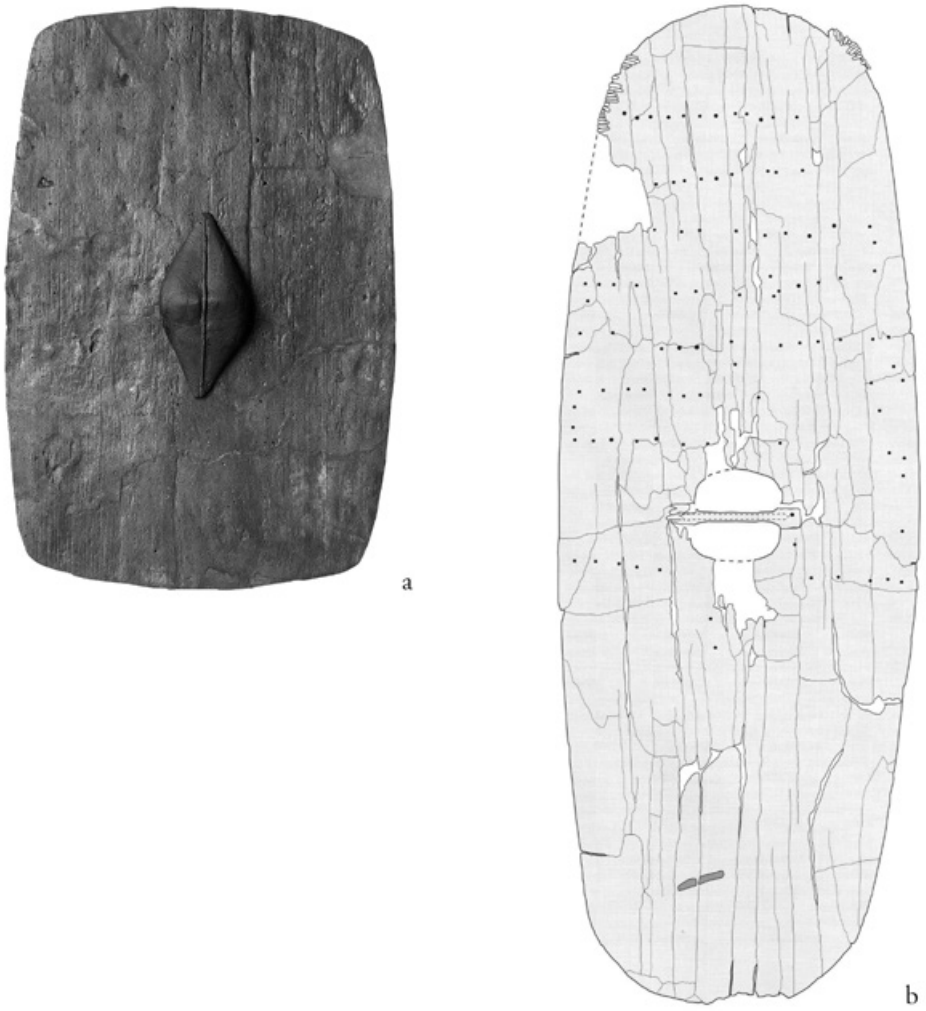

Fig. 2. Germanic oval shields from (a) Hjortspring and (b) Vædebro / Alken Enge, Denmark (after Rosenberg 1937 Fig. 32a; Ilkjær 2001 Abb. 319).

Ilkjær 2001, 356; Kaul 2003, 152 f.). Most of these are constructed out of a single piece of timber, but some consist of a single layer of two or, more rarely, three wooden boards joined together by resin or tongue-and-groove joints (Rosenberg 1937, 48 ff.; Kaul 2003, 152). The majority of the shields are made of light and soft wood like alder *(alnus)*, linden *(tilia)* and birch *(betula)*; a minority are made of hardwood, such as oak *(quercus)* (Rosenberg 1937, 49; Ilkjær 2001, 355 f.). The shields host an oval hole in the centre of the board and are equipped with a horizontal grip which is fastened to each side of the hole with tenon joints. The centre holes were originally covered with separate spindle-shaped bosses of wood with short spina, apart from one case in which both the shield board and boss were made from a single piece of timber. The shields are completely devoid of metal fittings but were most likely covered with hide for reinforcement. No traces of hide have hitherto been identified on the Hjortspring shields but indirect evidence can be observed on the edges of several shield boards, judging from the many rows of delicate grooves around the edge. These seem have been applied to the edge to make it more suitable for accommodating

some sort of stitching, such as that which can be observed on the shield from Clonoura (Ireland), a contemporary shield very similar to those from Hjortspring (Cunliffe 1997). The hide cover from Borremose, which has been included in this study and discussed in detail below, stems from a shield not unlike those from Clonoura and Hjortspring and, like the latter, is also dated to c. 350 BC.

A later Germanic variant of the oblong shield stems from Vædebro / Alken Enge (Denmark) dating to the 1st century BC *(fig. 2b)*. The shield was found almost complete with the shield board and handle in situ but the boss missing. The shield board is nearly oval in shape and made of a single board of alder *(alnus)*. The height and width of the shield is 105.5 cm and 38.5 cm, respectively. It is 0.5 cm thick at its rim (measurement taken 1 cm from the edge) and 0.5–6 cm at the centre hole, although the latter was probably thicker originally (Kaul 2003, 171 f.; Ilkjær 2001, 356). Like the later shields from Illerup Ådal (see below), the shield board hosts a D-shaped or figure eight-shaped aperture, in the middle of which a wooden handle and handle fitting of iron has been fastened. One half of the aperture is larger than the other, indicating how the shield would have been held. The upper half of the shield board is further equipped with two segments of edge reinforcements of organic material (probably wickerwork) and rows of drilled perforations which are not known from other surviving shields (Kaul 2003, 171 f.; Ilkjær 2001, 356). The exact function of the perforations is unclear but their placement on the upper half of the shield, which is most liable to be attacked, may indicate that the perforations are to be associated with a potential facing of organic material which once reinforced the shield board. No organic material was found in the drilled holes during conservation but possible traces of red paint were observed upon inspection.

A variant of the oblong shield with metal rim fittings and metal shield boss dates to the Early Roman Iron Age. They are difficult to identify in the often badly preserved grave finds and in only one instance has it been possible to ascribe shield fittings from a weapon deposit to an oblong shield, namely at Vimose (Denmark) (Pauli Jensen 2008, 212). Two rich grave finds from Kastrup, Denmark, and Hunn, Norway, contain rectangularly-shaped oval shields with metal fittings. The shield find from the central grave at Kastrup was only recently identified as an oval shield (Leen Jensen 2006; Leen Jensen, personal comment). Both graves can be dated in the early phase B2, i. e. late 1st century AD. (Leen Jensen 2006; Resi 1986, 70 f.). The dimensions of the Kastrup shield or Vimose shield can unfortunately not be determined, but the good preservation of the shield from Hunn F.19 allows the height and width to be estimated as 105 cm and 51 cm, respectively. The Hunn shield is constructed with shield boards made from linden *(tilia)* and equipped with an iron boss as well as rim fittings and grip fittings of copper-alloy (Resi 1986, 71).

Round shields

Large wooden round shields with circular bosses and more-or-less flat shield boards is another widespread type of shield construction in Europe, being predominant amongst Germanic peoples from the Roman Iron Age until the Viking Age. In comparison to oblong shields, round shields generally have a more complex construction, consisting of more numerous planks as well as other organic layers and fittings. The distinction between late oblong shields and early round shields is not always clear, particularly since some exhibit transitional features. Later oblong shields – such as the shield from Hunn mentioned above – are equipped with circular bosses (Kaul 2003, 172; Travis / Travis 2015, 8) and, more significantly, can have a broad oval shape and be slightly convex, for example the 'Amazon shield' from *Dura Europos* (Syria, c. AD 256) (James 2004, 159 ff.). The shields

Fig. 3. The wooden board and handle of a Viking Age shield found at Trelleborg, Denmark (photo: R. Warming, Society for Combat Archaeology).

from *Dura Europos* and Illerup Ådal (Denmark, early 3rd century AD) suggest that the round shields with circular or nearly circular shield boards become prominent after the early or mid-3rd century.

Whilst often studied independently of each other, the Germanic round shields of the Roman Iron Age (c. AD 1–375), Germanic Iron Age (c. AD 375–800) and Viking Age (c. AD 800–1050) can be subsumed under one and the same tradition, namely the *Germanic flat round shield tradition* (Warming 2016). The tradition arguably continues into the High Middle Ages and finally merges with the sword and buckler tradition (Warming 2016, 83 ff.). Shields belonging to the *Germanic flat round shield tradition* can generally be characterised by a number of shared features. In general, Germanic flat round shields of the Iron Age and Viking Age consisted of a single layer of about 5–8 relatively thin wooden planks (max. c. 1 cm) that had been butted together, forming a roughly flat and round shield board with a diameter of c. 80 cm or more *(fig. 3)*. The vast majority of shield boards from the weapon deposits of the Roman Iron Age (c. AD 1–375) are made from alder *(alnus)*, a wood type which was common at the time, resistant to moisture and not easily deformed (Ilkjær 2001, 347 f.; Malmros 2012, 76). Wood determination of the shields showed very close growth rings, indicating that the alder had probably been cultivated or pollarded. Shields of the Viking Age seems to primarily have been constructed from coniferous softwood, such as Scots pine *(pinus sylvestris)* as is the case with the shield board from Trelleborg (Bonde / Bartholin / Thun 2013, 222 ff.). Shield boards from

Nydam (from late Roman to early Germanic Iron Age) show very clear marks of being planed across the joints of the shield boards (Malmros 2012, 77), meaning that the shield boards were butted together before the surface was tapered and made smooth.

The centre holes of round shields are covered with a round boss of metal or wood. These can be of rather complex types in the Iron Age: At times, they are equipped with protruding spikes and other apices, but simpler hemispherical shield bosses are also present in both the Roman and Germanic Iron Age (Zieling 1989; Ilkjær 2001, 273 ff.; Nørgård Jørgensen 1999, 77 ff.). In the Viking Age, the bosses are typically simpler in shape, being more-or-less hemispherical (Rygh 1885, 30 fig. 562–565).

The rim of round shields could be additionally reinforced with metal fittings, offering structural support to the construction. Metal fittings are numerous on the flat round shields of the Roman Iron Age where they are especially used as ornamentation and for repairs (Ilkjær 2001, 339 ff. 360 f.). Metal fittings also appear on round shields of Viking Age, although generally taking on a simpler appearance, such as iron or copper-alloy clamps, for example Birka grave Bj 850 (*fig. 10*; see Arbman 1943, 323 ff.). Round shields were further reinforced by a handle of either organic or metallic material, or a composite, which was adjacently fastened across centre hole with iron nails. While typical handles are relatively short in the Roman and early Germanic Iron Age – such as at Vimose, Illerup and Nydam (see Ilkjær 2001, 313 ff.) – and only cover the central hole of the shield board, it is evident that medium length handles become more numerous in the late Germanic Iron Age, for example the shield handles from Valsgärde 7, Sutton Hoo mound 1, etc. (for finds, see Arwidsson 1977; Bruce-Mitford 1978). Medium length handles continue to be used in the Viking Age (e. g. the shield handle from Trelleborg and the handle fittings from Rends), but long handles seem to have been more prevalent, spanning across or nearly across the entire diameter of the shield, for example shields from Birka grave Bj 736, Gokstad, etc. (for finds, see Brøndsted 1936 no. 65; Pedersen 2014, 99; Arbman 1943, 259 ff.; Nicolaysen 1882 pl. VIII). The central section (the grip) could be shaped differently from the rest of the handle and equipped with bindings of textile or hide in order to facilitate a better grip, such as on the shield grips from Boss Hall (U. K.) from the 6th century AD (Cameron / Edwards 2004, 3).

Shield facings of hide and other organic material on Germanic shield boards

While this paper seeks to contribute with new knowledge regarding the use of hide products in Germanic shields, a valuable body of information can be gained from past historical, archaeological and experimental research. Having treated the topic only sporadically thus far, this section rehearses some of the main observations regarding hide products in shields based on existing data.

Firstly, it should be noted that hide has long been recognised as a suitable material for shield constructions in Northern Europe, being used in a variety of ways across the centuries. Some earlier prehistoric shields have been totally or primarily constructed from boiled leather *(cuir bouilli)*, such as the Bronze Age shield from Clonbrin (Ireland) (Coles 1962, 175). Wooden moulds for such shields are known from Churchfield and Kilmahamogue (Ireland) suggesting it was a common shield construction method (Jope 1951). In contrast to these 'hide shields', however, the Germanic shield types incorporate relatively thin hide products as a method by which to reinforce the wooden shield board and its edge, being no less important for the functionality of the shield (see below). Despite different uses in prehistoric shield constructions, hide seems to have been an important consideration in all cases.

Although evidence for hide products rarely survive archaeologically, it is reasonable to assume that most shields have been reinforced with hide products[1]. This can be gained from both indirect evidence – such as the space between metal fittings and the shield board – as well as fragments of hide which have survived on the shield board. In such cases, only vague traces remain. On some of the shield boards from the Illerup A deposit, for example, only patches of some greasy layer of organic material could be identified (Ilkjær 2001, 361). The widespread use of hide on shields is also attested by the microscopic analyses conducted on Anglo-Saxon shield fittings, concluding that at least 107 out of 148 analysed shields were equipped with hide of one form or another (Watson 1994, 41). Adding to this, there are several instances in historical sources where hide is mentioned in association with shields. In *Waltharius* – a 9th or 10th century AD Latin poem which is probably Frankish in origin – a shield is said to have hide over it *(pellis superaddita)* that keeps it together even after the wooden parts (boards?) have been broken (Magoun / Smyser 1950; Härke 1992, 51). Several other sources specifying the animal species of the hide (discussed below) provide us with a similar image of shield constructions. There are thus sufficient indications for assuming that hide was widely applied to shields, despite the relative scarcity of well-preserved finds.

Going further, North European shield types show a clear tendency of being covered with hide on both the front and back, forming a composite sandwich-like construction. Turning to Anglo-Saxon shields, which slightly deviate from the shield types discussed here (but on which more data is available), hide was identified on both sides of the shield board in nearly all cases where it had survived (Watson 1994, 38; see also Watson 2002, 4 ff.). Interestingly, Watson (2002, 4) reports a great variation between hide thicknesses (less than 1 to nearly 4 mm) on the shields from Edix Hill (late 5th to early 7th century AD) while Cameron / Edwards (2004, 2 f.) report thicknesses between 1 mm and 1.5 mm on the shields from Boss Hall (6th century AD); most Anglo-Saxon shield facings, however, seem to be between 1–2 mm thick (E. Cameron, personal comment). In many cases, the front and back hide facings of Anglo-Saxon shields appear to have had different thicknesses (Watson 2002, 4 f.; Cameron / Edwards 2004, 2 f.). Some shields from Boss Hall, for example, had an outer face with thickness of 1.5 mm while the inner facing measured 1 mm (Watson 2002, 3).

Differences in thicknesses between the front and back hide facings have not been observed on the shields examined in the current investigation but they do share the same characteristic laminated construction. Both the shields from Baunegård grave 11 *(fig. 4)* and Birka (Bj 850) are reinforced with a thin layer of hide on each side of the shield board place (c. 1 mm thick). The shield board from Bj 850, moreover, had also been reinforced with a thicker rim of hide (c. 2 mm) which had been folded over the edge. Three copper-alloy clamps served as placeholders for the hide rim. In the case of Baunegård, the shield board had been equipped with continuous copper-alloy fittings along its edge. Similarly, the round shield from Tira was also reinforced with a hide facing on both the back and front but was additionally reinforced with a layer of grass or bast fibres between the front hide facing and the shield board (Warming / Zeiere in prep.). Unfortunately, no shield board was found in conjunction with the shield cover from Borremose; however, if we accept the complete shield from Clonoura (Cunliffe 1997) as being representative for such a shield, it can be assumed that the Borremose shield would have been of a similar composite

[1] Ilkjær (2001, 361) and Becker (2010, 105) both suggest a rim and facing of gut but there is as yet no substantial evidence for this hypothesis.

Fig. 4. The rim of the shield from Baunegård (c. 350 AD) showing the composite structure of the shield with a layer of hide on each side of the shield board (photo: J. Nyborg Andreassen, Society for Combat Archaeology).

construction with hide on both sides. Accordingly, the composite hide-wood-hide shield construction appears to have been common, although appearing in different variations during the Iron Age and Viking Age.

The facings of some shield boards appear to have been further reinforced or fitted out with other layers of organic material. An analysis of the shield remains from Tranmer House (U. K.) indicated that some shields (graves 868 and 909) have a calcite-, lumino-silicate- and beeswax-containing layer between their zoomorphic / disc mounts and the front board cover (Bullock et al. 2011, 19). The layer has been interpreted as either an adhesive, a packing material or a preparation layer for a painted surface extending over the entire board. A similar reported case is the 7th century Alemannic shield from grave 28 at Oberflacht (Wylie 1855, 137): "On the left were the remains of an oval wooden shield, covered with some white material, and this again with leather, two feet and a half long, and one foot and a half broad." Given the early date of excavation and the placement of the collapsed shield board in the grave (leaning against the side of the coffin), it is worth noting in this place that the reported shape and dimensions of the shield may be incorrect. The shield has unfortunately not survived for further study (K. G. Kokkotidis, personal comment). Based on the above description, the "white material" could be interpreted as some sort of adhesive but could simultaneously have served as a packing material. Further miscellaneous details regarding methods of facing shield boards can be gained from the well-preserved Roman finds from *Dura Europos* (Syria) where remains of up to 22 shields boards dating to c. AD 265 were found (Travis / Travis 2015, 63 ff.; James 2004, 159 ff.). It has been observed that several of the broad oval shield boards from this site were covered with hide on both sides. Between the board and the hide was "a thick layer of glue, into which was laid a pale, fibrous material, aligned roughly across the grain of the planks" (James 2004, 162). The exact nature of the fibre is not yet known. It is most likely vegetable in

nature but could also consist of shredded tendon. Another method of facing observed on the shields from *Dura* did not involve hide covers but consisted of a layer of fibres in a glue matrix (as described above), which had subsequently been coated with a white plaster-like substance, identified as gesso. A variant of this method has also been observed, where a layer of fabric had been glued to the surface and then coated with gesso (James 2004, 162). While parallels in construction methods certainly can be drawn between the shield from Tira and those from *Dura* described above, especially those representing the first method, there is little evidence to suggest that such methods were widespread amongst Germanic shield construction practices. On the whole, the Germanic shield construction practices seem to have favoured the composite hide-wood-hide method, as exemplified by the shields from Baunegård and Birka. The rare finds discussed above do, nonetheless, illuminate the complex use of organic materials in shield constructions and the various methods by which shields could possibly be strengthened, even though such evidence may not always survive archaeologically.

Archaeological experimentation has concluded that even the simplest application of hide will provide a functional advantage in combat, regardless of whether the facings are of a tanned or untanned nature. During the 1980s and 1990s, a number of experiments were carried out on replicas of shields of the type represented by the 3rd century shield from Baunegård. Two independent experiments were set up by the archaeologists O. Nielsen and H. Paulsen with the aim of exploring the efficiency of arrows on shields, using replicas of different types of arrowheads found in the weapon deposits from the Late Roman Iron Age (Nielsen 1991; Paulsen 1998; Pauli Jensen 2009). The arrows had a devastating effect on both shields with no leather coating and the shields with soft leather coating. The shields collapsed almost instantly regardless of the shooting range (Nielsen 1991 fig. 10; Paulsen 1998, 422 ff.). Consequently, it became evident that some sort of facing or coating was necessary in order to have a fully functioning shield.

New experiments were therefore undertaken following an analysis of the shields from the early 3rd century weapon deposit of Illerup Ådal where a greasy layer of organic material and traces of red paint had been observed. Examinations also showed that there was no room for thick leather coating between the shield boards and the metal fittings (Ilkjær 2001, 361). Consequently, L. Møller Andersen suggested that the shield boards were laminated with a thin layer of leather or parchment covering the paint. In 1998, a shield was constructed with eight shield boards held together by hide glue and planed down to a thickness of 10 mm in the middle and 5 mm near the rim. Subsequently, a layer of parchment of pigskin was attached to both the front and the rear of the shield and riveted to the rim. The shooting experiments clearly showed that this method was far more efficient than the previously mentioned experiments (Ilkjær 2001, 361 f.). More recent experimentations with Viking Age shield replicas against sword cuts confirm the necessity for hide facings and rim, also in the context of close-quarter fighting (Warming 2018).

The experiments emphasise the need for a fully functional shield in combative contexts and for the *Germanic round shield tradition* this included a hide facing. However, we cannot discard the possibility that some shields deposited in burials were made exclusively for the burial ceremony and consequently did not need the extra durability.

The question of animal species and tanning processes

As mentioned, the exact nature of hide products for shield facings and rims remain unclear. While this project is the first specialised study aiming to identify hide elements of prehistoric shield constructions by microanalyses, a number of isolated analyses have

previously been carried out on archaeological shield finds by use of relatively subjective measures. These approaches, however, have thus far not been able to provide any positive identification of hide product types.

One such case is the analysis of the hide facing of shield I from Valsgärde grave 8 (Sweden) from c. AD 625–650 which was identified as tanned leather. The argument rests on an ocular inspection which concludes that no traces of hair or fur was observable on the surviving fragments (Arwidsson 1954, 54). The explanation provided is questionable as the absence of hairs could also be attributed to unhairing processes (e. g. scraping) which are undertaken in conjunction with the production of untanned hide production (see section "Hide, skin, parchment and leather" below).

The hide facing of the shield from Sutton Hoo mound I (U. K), dated to early 7th century AD, has also been identified as vegetable tanned leather based on an ocular inspection. Here, according to R. L. Sykes, the colour seemed to indicate the presence of tannins (Bruce-Mitford 1978, 28 f.). Unfortunately, no supportive evidence for this claim is included in the publication. Moreover, as Bruce-Mitford himself notes, the traces of tanning may be derived from the surrounding environment, specifically the oak hull of the ship (Bruce-Mitford 1978, 28 f.). As such, it is evident that questions regarding the type of hide used in shield constructions have generally eluded archaeological research in the past.

One possible exception which has been able to illuminate some aspects of how hides were prepared before they were applied to shields is the study done on a hide facing from the cemetery of Butler's field (U. K.), dated to the mid- or late 5th century to the 7th century (Boyle et al. 1998; Cameron 1991). Having observed twisted or contracted fibre bundles in some samples from grave 149, Cameron concluded that the hide had possibly been treated with heat before having been applied to the shield (Cameron 1991, 31–32). She notes that such change occurs when collagen is heated above its shrinkage temperature, this being at 65 °C in its raw state and 70–80 °C after vegetable tanning (ibid.). While it is thus possible that this is a case of *cuir bouilli*, it remains uncertain whether the hide facing had been tanned or untanned without additional data.

Similarly, the question of which animal species have been used in the construction of Germanic shields has not been systematically explored either, owing mostly to the scarcity of sufficiently preserved hide specimens. With the exception of the shield facing from Sutton Hoo, which was identified by ocular inspection as cattle hide (Bruce-Mitford 1978, 28 f.), it is evident that scholars have instead predominantly relied on historical sources for understanding the choice of animal species in shield constructions. Several contemporary writers deal with this subject. Clause 15 of the Anglo-Saxon *Laws of Athelstan* (AD 926–930) specifies that "no shieldmaker is to put any sheepskin on a shield" (Härke 1992, 51). While the clause does not offer any insight into the nature of the hide product type, it demonstrates that active measures were taken to control the choice of animal species for use in shield constructions. Concurrently, the very stipulation of this law indicates that it was intended to address a real concern about sheepskin being used for shields. These concerns are in all likelihood based on considerations regarding the strength of the hide, given the relative pliability and thinness of hide products made from sheep species. The notions that hide elements in shield constructions have been selected on the basis of their strength and thickness is likewise reflected in *Waltharius*. In lines 773–780, the poet refers to a shield covered with bull's hide, which is meaningful as relatively durable and thick hide elements can be produced from cattle. Although not a Germanic shield, it is interesting to note that Polybius reports that the Roman *scutum* was also covered with cattle hide in the form of calfskin (Polybius 6.23). Another non-Germanic shield type, the Byzantine *Peltai*, was supposedly sheepskin or goatskin-covered (Grotowski 2010, 211; see also 216

note 343). Notwithstanding these historical details and parallel shields, it remains unclear whether cattle were the preferred animal species for hide components in Germanic shield constructions and whether other animal species were considered equally suitable.

Identifications of other objects of leather from Iron and Viking Age Europe can possibly offer an indication of the range of animal species available for hide products. Leather finds from North-western Germany dating to the 1st century BC to the 4th century AD have primarily been determined as cattle and goat, although sheep and a few objects of horse and deer have also been identified by microscopy (Gräf 2015, 38). While cattle skin seems to have been preferred for shoes, the picture seems more diffuse with regards to other object types. Skin garments are common amongst the finds from the Danish peat bogs dating from 500 BC to AD 400, but also hats, belts, shoes and bags occur (Mannering et al. 2012, 105–114). Not many of these finds have been species identified; however, eleven elements of skin garments were identified as sheep, goat and cattle by a proteomics approach (Brandt et al. 2014). In Viking Age Haithabu, cattle and goatskin also make up the majority of the identified leather material, whereas a minority was identified as sheep or deer (Groenman-Van Waateringe 1984, 13). The leather from 9th–11th century York was dominated by cattle, while sheep and goatskin was present in small quantities (Mould et al. 2003, 3265). Such finds indicate that domesticated species, cattle, sheep and goat, were most commonly used for leather, whereas deer and horse were utilised to a minor degree.

Of these, sheep and cattle can be considered particularly suitable as shield facings. Their general availability and the overall dimensions of the skins would conceivably have rendered them favourable for shield constructions which had large surface areas to be covered. If the hide elements were not large enough, they would need to be stitched together in segments. This seems to have been the case with the shield found at Tira, Latvia, where two hide segments had been securely stitched to the shield board on each side (four segments in total). Similar perforations for such stitching were also identified on several shields from Gokstad in conjunction with this project, giving reasons to critically question previous ceremonial interpretations of the shields (Warming in prep.).

Colour

In contrast to the vibrant colours of Greek vases and Roman mosaics, the Scandinavian material from bogs and burials seem both brown and dull when they emerge from the soil. At the outset, this also seems to be the image conveyed by the Germanic shield material. The vast majority of shield finds stands in stark contrast to the well-preserved Roman shields from *Dura Europos* (Syria) from the 3rd century AD, which are adorned with vibrant colours and intricate geometric designs (James 2004, 176 ff.). It is nonetheless plausible to assume that the brown and dull appearance of much of the Germanic shield material is owing to preservation conditions.

In Scandinavia, traces of colour have been identified on more than 25 shields from weapon deposits and burials of the Roman Iron Age alone (Capelle 1986; Zieling 1989, 339 ff.; Lund Hansen forthcoming), suggesting that the majority of the shields were originally painted or decorated in some other way. Normally, only traces of colour have been preserved, wherefore it has not been possible to gain much knowledge of the patterns used. A fortunate example, however, came to light in the excavation of Nydam bog (Denmark) in 1997 *(fig. 5)*. One of the many round shields recovered from Nydam showed evidence of having been decorated with red and blue colour, forming patterned bands along the rim of the shield (Rieck et al. 1999, 21). Traces of red and blue colour have also been identified

Fig. 5. Detail of shield board from Nydam bog, Denmark, with red and black colour (Photo: Per Poulsen, National Museum of Denmark).

on a shield from the late Roman Iron Age burial at Gommern (Germany). These colours were analysed and identified as cinnabar and Egyptian blue (Becker 2010, 177).

Considering the relative frequency by which red and blue paint appears on Scandinavian round shields, it is not surprising that traces of red colour have been identified on one of the shields included in this current study. The red colour on the shield from Baunegård grave 11 was already mentioned by the excavator in the late 19th century (Vedel 1886, 123; 354 f.) and has in connection with the present study been identified as cinnabar *(app. 2)*. In the Iron Age, cinnabar or vermilion was imported from the Roman Empire (most likely from Almadén in Spain), as the mineral does not occur naturally in Northern Europe (Riederer 1987, 150).

Coloured shields of Germanic tribes of the Iron Age are also mentioned in contemporary historical sources. Tacitus (Germ. 6.2–6.3), writing around AD 98, describes how the shields of Germanic tribes are "marked with very choice colours." Besides being practical for identifying troops and tribes in battles, Tacitus also notes elsewhere (Germ. 43.5) how coloured shields of Germanic tribes were employed in a more tactical sense: "The Harii, besides being superior in strength to the tribes just enumerated, savage as they are, make the most of their natural ferocity by the help of art and opportunity. Their shields are black, their bodies dyed. They choose dark nights for battle, and, by the dread and gloomy aspect of their death-like host, strike terror into the foe, who can never confront their strange and almost infernal appearance. For in all battles it is the eye which is first vanquished." According to Plutarch (late 1st century AD), moreover, the Cimbri carried "gleaming white shields" (Mar. 25).

There is ample historical and archaeological evidence for a continued use of coloured round shields in the Viking Age. Especially white and red colouration are mentioned in association with shields in the historical sources. In *Eiríks saga rauða* (ch. 10–11), white shields appear to be used to indicate peace while red shields signal hostility (Sephton 1880, 28–29). Interestingly, analyses conducted on a Viking Age shield board found at Trelleborg (Denmark) indicate that the shield had been coloured white and red (Dobat 2013, 163 ff.). Another significant find is the 64 black and yellow round shields from the

Gokstad ship burial, which had been fixed to the side of the ship in alternating colours (Nicolaysen 1882). It is not within the scope of this paper to treat all the various colours which can be found in both archaeological and literary sources; however, the above will suffice to illustrate the long-lasting colourful appearance of these defensive weapons from the Iron Age onwards.

Selection of find contexts and dating

The selection of finds included in this study comprise both oblong shields and round shields, dating to between c. 350 BC and AD 950. It is important to note the chronological and regional differences between the shields. The find situations and contexts are also different (see *fig. 1*).

The oldest shield in the analysis was found in Borremose in northern Jutland near the city of Aars. The site is especially known for its fortified village and the bog bodies from the Pre-Roman Iron Age (Martens 1994; id. 2010). However, the peat digging in 1948 also revealed the remains of a hide shield or a hide covering for a (rounded rectangular) oval shield. The shield has a round hole in the centre, making room for the grip and shield boss that protected the hand. Curved ornaments have been identified around the centre hole (Kaul 1988, 39; Martens 1994, 268). The shield has been ^{14}C-dated to around 350 BC and constitutes the oldest specimen of our inquiry *(fig. 6)*.

Another shield included in the present study is one stemming from the Baunegård cemetery, which is situated in the southern part of Bornholm in the Baltic Sea on a sandy plateau between to barrows approx. 2 km from the sea. The site was excavated in the late 19th century and partially published by the county governor and archaeologist E. Vedel (Vedel 1886, 354 f.). Even though a few scholars had subsequently mentioned the site, the grave field remained unpublished in full until 1989 (Foss 1989). Vedel identified 20 burials, both cremation and inhumation graves. Grave 11 is an inhumation grave richly furnished with weapons (double-edged sword, spear, javelin, shield boards with shield fittings of copper-alloy and iron), an awl, an ornamented jug, a golden finger ring (Beckmann VII,39) and a rare find of a partly preserved leather belt with copper-alloy fittings *(fig. 7)*.

Documented details from the excavation, the remaining shield boards and the rim fittings, clearly identify the shield as a round shield. Amongst Vedel's descriptive details of the find, it is noted that thin leather was discovered between the copper-alloy rim fitting and the shield board, and that one side of it was coloured bright red (Vedel 1886, 355). The grave goods place the grave firmly in phase C2 of the Late Roman Iron Age, that is in the second half of the 3rd century AD (Foss 1989, 135 ff.).

Both the wood fragments and red colouration on the hide have been analysed in conjunction with this project. The wooden samples, which were analysed by N. Bjerregaard Pedersen, were unfortunately too deteriorated to identify an exact species, but it was concluded that the wood stemmed from hardwood, possibly common hazel *(corylus avellana) (app. 1)*. The red colour has been identified by J. van Lanschot as cinnabar *(app. 2)*.

The shield from the Tira bog in Rucava (Latvia) near the Baltic Sea represents yet another find type, namely a deposit with a variety of different objects *(fig. 8)*. The find was recovered in 1936 during peat cutting and includes a flat wooden round shield and a convex round shield plus a number of other objects (probably wrapped in a cloak). Only a single shield plank of the convex round shield was uncovered, constituting the only surviving archaeological evidence of a wooden shield board of this type (Warming / Zeiere in prep.). The find has been dated to the first half of the 9th century AD based on associated artefacts (Urtans 1964; Bliujiene 2010). However, a ^{14}C-dating undertaken by Aarhus

Fig. 6. The hide cover from Borremose displayed at Vesthimmerlands Museum (photo: S. Friis).

AMS Center as part of this investigation indicates a likely dating of 875–985 calAD *(app. 3)*. Given the general challenges with typological dating and the possibility for intergenerational artefacts (heirlooms), it seems reasonable to date the shield to c. AD 875. The flat round shield find consists of a wooden shield board (c. 86.3 cm in diameter in its current condition), two layers of hide (front and back), a layer of grass (or possibly bast fibre), a wooden handle and a wooden boss made of birch knot. The wood species of the shield board has been analysed by N. Bjerregaard Pedersen in conjunction with this project and been determined to be coniferous softwood, either European spruce *(picea abies)* or larch *(larix) (app. 1)*.

A final specimen analysed in this study stems from the cemetery of Birka in Lake Mälaren near Stockholm, Sweden (artefact id: SHM 1323609). It was excavated in the late

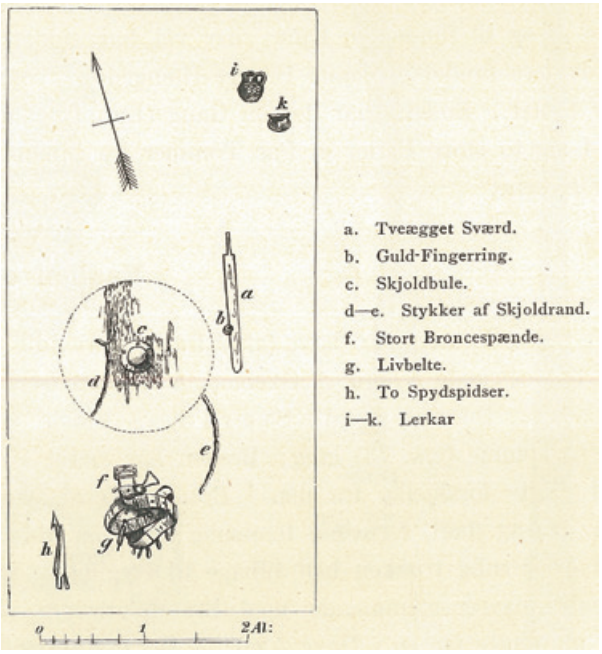

Fig. 7. The excavator's drawing of Baunegård grave 11 containing the round shield (after Vedel 1886 fig. 262).

Fig. 8. The round shield from Tira (photo: E. Āboliņš, National History Museum of Latvia).

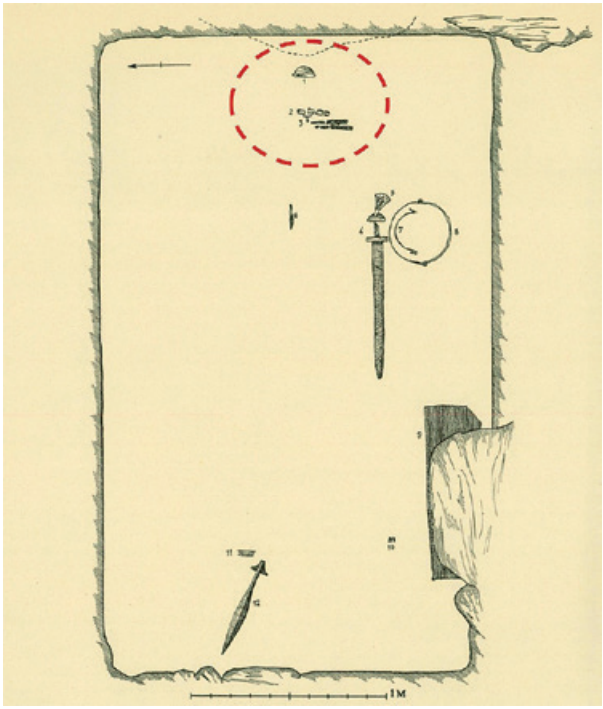

Fig. 9. The excavator's drawing of Birka chamber grave Bj 850 containing the round shield. Artefacts associated with the shield (a boss and handle of iron; a handle terminal and three shield rim fittings of copper-alloy) are indicated in red (after Arbman 1943, 324).

Fig. 10. Shield rim from Birka bj 850 (photo: R. Warming, Society for Combat Archaeology).

19th century by H. Stolpe and published by H. Arbman (Arbman 1940; id. 1943). Grave Bj 850 was a chamber grave comprising weaponry (sword, spear, arrowheads and shield fittings of iron and copper-alloy), vessels of glass and ceramics, fittings for a wooden bucket

and a chest, and personal equipment (beads, knives etc.) dating to the 10th century AD *(figs 9–10)*. Fittings of copper alloy were found along the shield rim: "Reste der Schildbekleidung, nämlich eine dünne Lederschicht, die wahrscheinlich den ganzen Schild bedeckt hat, und eine aus Kernleder, die um den Rand gebogen war" (Arbman 1943, 325; id. 1940 Taf. 18). The shield board was 0.4 cm thick at the rim (excluding the hide and copper-alloy fitting) with a noticeable tapering occurring c. 2 cm from the edge (though only on one side of the shield board). According to a notation attached to the artefacts, the wood has been determined to be spruce *(picea sp.)*. The organic parts of the rim – i. e. the wooden shield board and hide rim, but not the copper-alloy fitting – has a total thickness of c. 0.7 cm.

These four shields are the focus of the two following sets of nature science analysis: the identification of animal species and the identification of processing of the skin.

Identification of animal species with ZooMS: methods and results

To understand the defensive capabilities of the shields and how they would have functioned in combat, it is important to understand the properties of their hide facings. Two primary factors which must be considered in this respect are the animal species and, if treated, the treatment process the hide has gone through (Harris 2014, 10). This section will therefore investigate the animal species of the hide from the shields included in this study after having explored the characteristics of hides from different animal species and possible methods for distinguishing them. Section 4 will further explore their possible treatments.

The skins of different animal species have distinctive structures in terms of their total thickness, the dimensions of their fibre bundles and the relative thicknesses of the different layers of the skin (Haines 2006, 12; see *fig. 13*). Furthermore, skin properties also vary with age, breed, nutrition and between different body parts (Haines 2006). Normally, the dermis of calf and goat has a denser and firmer fibre structure with relatively thicker fibres than that of wool sheep which produces relatively more hair and fat (lanolin) and less collagen fibres (Reed 1972, 41 ff.). The latter results in a more empty and flexible material when tanned into a leather. Moreover, the wool sheep has "pockets" of fat deposits in the layer between the grain and corium which may cause the grain to be loosened (BLMRA 1957, 36). This is seen as wrinkles on the surface of the leather and may ultimately result in a complete splitting of the grain and corium. Skin from adult cattle has similar properties to calf skin but is thicker.

Traditionally, dehaired animal skin has been species identified by microscopy of the empty hair follicles of its grain surface which form specific patterns between species (grain patterns) (Haines 1981; Larsen et al. 2009, 78 ff.). The method is informative in that it can potentially distinguish variations within species (e. g. between sheep breeds with varying coats) and the age of the animal given the identifiable differences in grain patterns, for example between adult cattle and calf (Reed 1972; Larsen et al. 2009, 79). Yet, grain pattern analysis is not straightforward when analysing archaeological skin samples that may suffer from wear and degradation that result in partial or a complete lack of grain surface patterns (Larsen et al. 2009, 87). Such analyses will also be challenging in the case of small samples where only small parts of a pattern can be seen. A further complication is that reference collections used for comparison of skin surfaces are almost exclusively composed of modern skins which may not resemble skins of prehistoric animals. Previous research has demonstrated such difficulties of morphological identifications when compared to species identification by proteomics (Brandt et al. 2014).

Sample No.	(P1)	α2(I) 988 –1000 (A)	α2(I) 494–508 (B)	α2(I) 512–529 (C)	(P2)	α2(I) 803–826 (D)	α1(I) 602–634 (F)	α2(I) 767–799 (G)	ZooMS ID
Borremose	1105,6	1192,7 +1208,7	1427,7	1580,8	1648,8	2131,1	2853,4	3017,5 +3033,5	Cattle
Tira S2	1105,6	1192,7 +1208,7?	1427,7	–	1648,8	2131,1	2853,4?	3017,5? +3033,5	Cattle
Tira S5	1105,6	1192,7 +1208,7	1427,7	–	1648,8	2131,1	2853,4	3017,5 +3033,5	Cattle
Bj 850 facing	1105,6	–	1427,7	–	1648,8	2131,1	2883,4?	3033,5	Deer* / sheep?
Bj 850 rim	1105,6	–	1427,7	–	1648,8?	2131,1	2853,4	3033,5	Cattle
Baunegård	1105,6	–	1427,7	1580,8	1648,8	2131,1	2853,4	–	Cattle

Tab. 1. ZooMS identifications of the six analysed samples. '?' signifies peaks of low intensity, or low signal to noise threshold. * red or fallow deer or elk.

During the last decades, identification methods based on both ancient DNA and proteins have been applied to archaeological skin materials. A particular promising approach is ZooMS; short for Zooarchaeology by Mass Spectrometry. ZooMS is a species identification method based on specific signatures (markers) of the protein collagen (Buckley et al. 2009)[2]. Collagen is the predominant protein in tissues such as bone, antler, and skin, and has been documented in several archaeological skin materials (Kirby et al. 2013; Brandt et al. 2014; Toniolo et al. 2012; Fiddyment et al. 2015). ZooMS utilises small differences in collagen sequences between animal species as fingerprints for species identification. During sample preparation, collagen is digested by the enzyme trypsin that cuts collagen into shorter protein chains of amino acids – peptides (see *fig. 11*). Because trypsin always cleaves at the amino acids, arginine and lysine, the resulting peptides will have predictable lengths. Small differences between the amino acid compositions between species will, moreover, result in differing masses of peptides or markers which are subsequently measured in a MALDI-ToF mass spectrometer (Matrix-Assisted Laser Desorption / Ionization Time of Flight). The measurements will result in spectra of the detected masses with the mass at the x axis and the intensity at the y axis. Intensive markers will appear as "peaks". Spectra are manually investigated using mMass (Strohalm et al. 2008). The markers can then be compared to a list of masses of known animal species, from which the animal species of the sample can be inferred.

The reference databases of collagen markers have developed and currently include a wide range of domesticated and wild mammals (Buckley et al. 2009; Welker et al. 2016),

[2] The method has also been developed for keratin (Hollemeyer / Altmeyer / Heinzle 2002; 2007; 2008; Hollemeyer et al. 2012; Solazzo et al. 2013; 2014; Solazzo 2017).

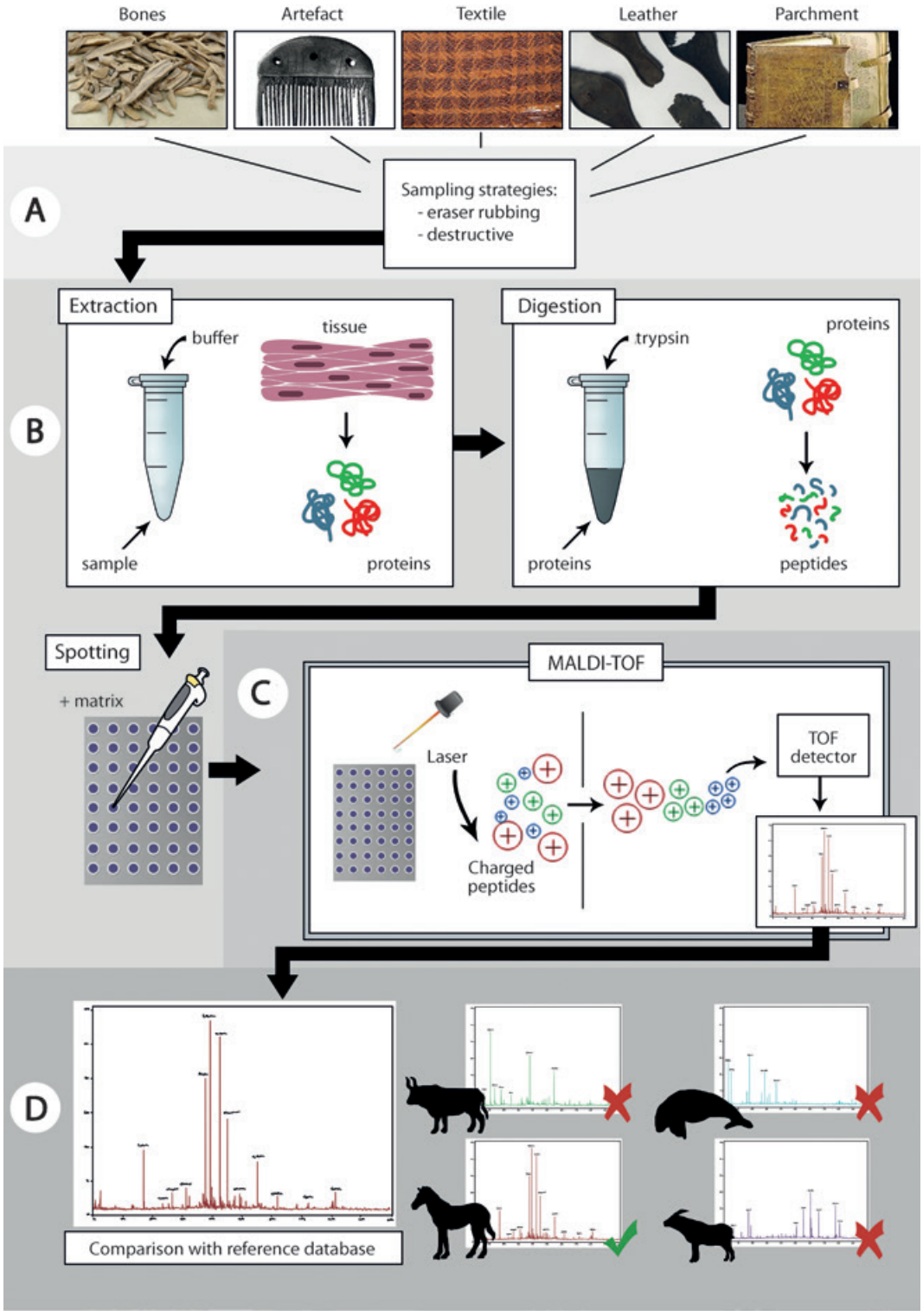

Fig. 11. Workflow in ZooMS analysis (illustration: the authors).

marine mammals (Buckley et al. 2014) and fish (Richter et al. 2011) and is constantly expanding. More markers recognised on the spectra increases the chances of specific identification. Ideally, the combination of markers will represent masses that are diagnostic for only a single species. However, some species are so closely related that they share all markers and it will therefore not be possible to distinguish them (Buckley / Larkin / Collins 2011; Coutu / Whitelaw / Le Roux 2016).

ZooMS is advantageous in that it only uses small amounts of sample material, which is ideal for cultural heritage material of high value, and the procedure is fast and cheap. Moreover, proteins have over the past years been demonstrated to survive further back in time than DNA and proteins have been recovered in environments from which DNA could not be amplified (e. g. Demarchi et al. 2016; Welker et al. 2015; Brandt et al. 2014). ZooMS is therefore ideal for identifying species of precious skin materials from degrading environments.

Materials: sampling for ZooMS

Samples of a size between 2–4 × 2–4 mm were taken for ZooMS from the hide from Baunegård, Birka, Borremose and Tira. From Birka, a sample was taken from hide, originating both from the rim and the facing. From Tira, a sample was taken from both the small segment of the outer facing (S2) and the larger segment of the inner facing (S5).

Method: preparing and analysing the samples by ZooMS

The samples were prepared with reference to previously published ZooMS protocols for skin (Fiddyment et al. 2015; Kirby et al. 2013) but with a modification for archaeological skin (Ebsen et al. 2019).

One microliter of the eluted peptides was spotted onto a Bruker steel plate and mixed with 1 µL of α-cyano-4-hydroxycinnamic acid matrix solution (1 % in 50 % ACN/0.1 % TFA) and allowed to air dry. All samples were spotted in triplicate. Mass spectra were calibrated against a reference standard containing six specific peptides spotted on reference spots on the plate.

Samples were analysed using a MALDI-TOF instrument in reflector mode. Mass spectra were acquired over the m/z range 800–4000. Spectral analysis was performed using the open-source cross-platform software mMass (www.mmass.org) (Strohalm et al. 2008). The three spectra generated for each sample were averaged and the average spectrum was manually inspected for the presence of peptides markers designated A–G (Buckley et al. 2009) and P1 and P2 (Buckley et al. 2014). Taxonomic identifications were assigned by comparison of peptide markers with a list of markers for potential domesticated and wild mammals (Buckley et al. 2009).

Results of the species analyses

The ZooMS analysis provided species identification as cattle for five out of six samples based on the presence of unambiguous markers that in combination are unique to this species only. For Borremose (see *fig. 12*), Tira S5, Bj 850 rim and Baunegård the identification was reached by the markers 1105,6; 1427,7 and 2131,1 in combination with 2853,4 (with one or more supporting markers for the first three samples, particularly 1192,7; 1208,7; 3017,5 and 3033,5). For Tira S2, the identification was made by the presence of markers 1192,7 and 3033,5 (ruling out muskox). One sample, the Bj 850 facing, was identified

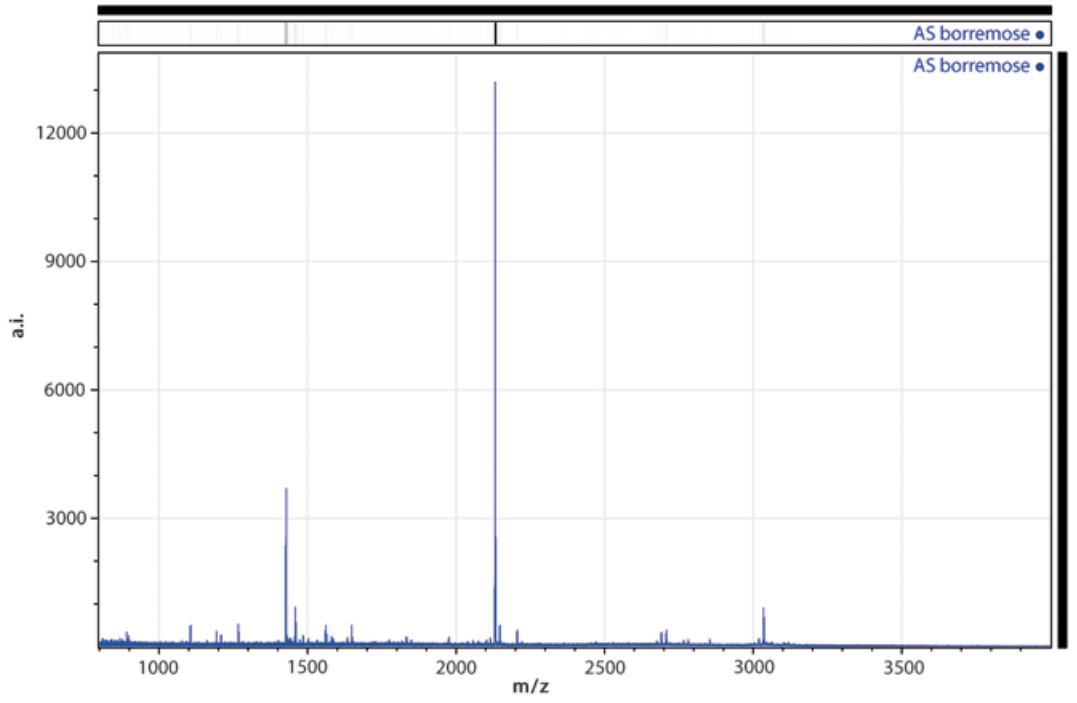

Fig. 12. MALDI ToF spectrum of Borremose with markers identifying the sample to cattle (illustration: the authors).

as belonging to the families of bovids and cervids based on the markers 1105,6, 1427,7, 1648,8, 2131,1 and 3033,5. Whereas a marker of lower intensity and lower signal to noise threshold marked with '?', 2883,4, could point to an identification to either to sheep, red or fallow deer or elk (Buckley et al. 2009) (ruling out African species and muskox).

Hide products / Microanalysis: materials, methods and results

Multiple microanalyses have previously been used in the study of the deterioration and conservation of historical leather (STEP 1993; ENVIRONMENT 1996; Larsen 2000; id. 2008) and more recently in the study of historical parchment (MAP 2002; IDAP 2007; Možir et al. 2014; Mühlen Axelsson 2014; Sommer et al. 2017; Bell et al. 2018; Kern et al. 2018). The aims of the present multiple microanalyses were to clarify if the hide or skin material used for the shields were untanned or vegetable tanned as well as to identify potential types of tannins and tanning processes. This also includes the determination of the state of condition of the samples and their fibre structure as the specific deterioration features, fibre morphology and shrinkage behaviour during heating in water differs for vegetable tanned and untanned materials.

The clarification of whether the hide or skin material was tanned or untanned may contribute important information regarding the durability and function of the shields. In addition, the determination of the state of condition of the samples is important in relation to future conservation of the shields or fragments of these.

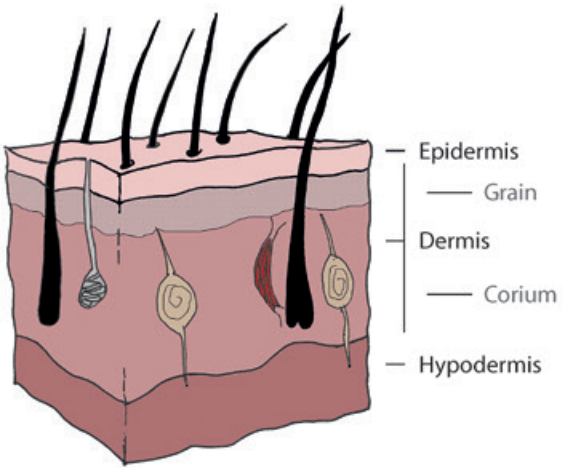

Fig. 13. Skin cross section showing the different skin layers (Illustration: the authors).

Hide, skin, leather and parchment

Leather and parchment are mainly produced from mammalian hide of larger animals (e. g. cows) and skin from smaller animals, such as calf, goat, sheep and other smaller species (in the following we are using only the term skin, see also *fig. 13*). The part of the skin used is the dermis where the main constituents are the fibrous proteins collagen I and III (Epstein / Munderloh 1978; Henkel / Glanville 1982; Ramshaw 1986; Keene et al. 1987; Lovell et al. 1987; Fleischmajer et al. 1990a; Fleischmajer et al. 1990b; Herfeld 1990; Sommer / Larsen 2016). The molecules of these collagens consist of three left screwed helical peptide chains with short non-helical terminal peptides which are right-handed super coiled and staggered laterally in a micro fibril believed to be overall left-handed. The micro fibrils are believed to be further associated into fibrils, continuing the super coiling alternately left and right-handed, following the mechanical principles of rope-building forming a three-dimensional flexible fibre network. In leather, the supercoiling is easily recognizable at the fibre level under the microscope (Herfeld 1990; Kennedy / Wess 2003; Wess 2005; Bozec et al. 2007; Mühlen Axelsson et al. 2012).

Dehairing the skin

In early leather and parchment production, the dehairing process (removal of the epidermis) and removal of the hypodermis was performed by simple scraping with sharp scrapers or knives (Pedersen 1935, 17 ff.; Reed 1972, 51 ff.; 88 ff.). Later, a dehairing method known as "sweating" was introduced and has been used till rather late in history (Pedersen 1935, 27 f.; 273; Reed 1972, 95 f.; 37 f.; Zissel 1989, 62; Goffer 2007, 330 f.). During "sweating", the skins are placed lying or buried in the ground for a few days or weeks until a partial putrefaction has loosened the epidermis to an extent that makes it possible to remove it with hair and hair roots using a blunt scraper (Pedersen 1935, 37 f. 111).

Fig. 14. From the Parchment Maker, 1568: 'The Parchment Maker places sheep and goat skins in lime, washes them, stretches them on the frame and scrapes them; the ears and paws are boiled into glue.' Poem by Hans Sachs, woodcut by Jost Amman, 1568 (La Lande 1763).

Sweating is a controlled putrefactive process that loosens the epidermis without damaging it (Pedersen 1935, 27 f.; Goffer 2007, 330 f.). Other methods include placing the skins in urine for a few days (Pedersen 1935, 26; 28; Reed 1972, 90 ff.), pouring the hides with ash or bathing them in an aqueous ash suspension (Pedersen 1935, 29) or using a bath of weak acidic solutions of leaves or other parts of plants which accelerated the loosening of the epidermis (Reed 1972, 90 ff.). The latter may be the precursor for tanning performed in aqueous extracts of tannins. The method of bathing the skins in calcium hydroxide solutions (liming) as part of the dehairing process in European leather and parchment production was probably not common before the production of parchment was introduced around the 8th century (Reed 1972, 132 ff.), probably even much later in Northern Europe and Scandinavia where acid dehairing was still taking place around the 19th century (Reed 1972, 136 f.). A woodcut illustrating the process can be seen in *figure 14*.

Production of leather by tanning

Through history, the most common way to tan the dehaired skin into leather has been by treatment in an aqueous extract of crushed plant material in the form of leaves, bark, fruits, roots or other parts of the plant (Gräf 2015, 39–40; 47). According to Reed (1972, 86–87), later texts written by Greek and Roman authors – such as Herodotus, Dioscorides and

Pliny – as well as Rabbinical literature produced by Jewish scribes state that the method was already well established in Egypt by 1600 BC. Similar evidence for sophisticated early leather production is also available from Babylonian and Assyrian sources (Reed 1972, 87 f.). Moreover, Reed cites a text found at Carchemish covering the period 1000 to 600 BC (Reed 1972, 88): "Six shekels of Alum;... minea of oak-galls; ⅓ ka of fat, ⅓ mina and 2 shekels of myrrh for the tanning have been delivered… to the leather worker". See also Gräf (2015, 40–50).

In the earliest form for leather production in Northern Europe and Scandinavia, the skins were probably placed in a hole in the ground or in a vessel in layers with the plant material between each skin so that the moisture from the skins and from the surroundings could extract the tannins from the plant material, after which it was slowly absorbed into the skin (Gräf 2015, 47–48).

The tanning components of the very complex extract of plant material, which also contain carbohydrates, inorganic salts, organic acids, proteins and starch etc., consist of polyphenols compounds (Faber 1985, 44). Based on their structural characteristics, it is possible to divide the tannins into four major groups: gallotannins, ellagitannins, complex tannins, and anthocyanidins (condensed tannins) (Khanbabaee / van Ree 2001, 643)[3]. In addition, a fifth group of tannins, phlorotannins, can be added to the family. However, neither phlorotannins nor the complex tannins are important for leather tanning (Falcão / Araújo 2018, 1084).

Moreover, in the classical definition, the gallotannins and ellagitannins are classified together as hydrolysable tannins (Khanbabaee / van Ree 2001, 642). This classification, which is the most widespread in areas of the leather technology and conservation, is also used in this study. According to Falcão / Araújo (2018, 1084) hydrolysable tannins can be defined as: "a monosaccharide core, usually glucose, esterified with gallic acid, forming the gallotannins, or with hexahydrodiphenoic acid, the precursor of ellagic acid, and gallic acid, forming the ellagitannins. Upon heating in acidic aqueous medium, they hydrolyse to yield gallic and ellagic acid. Thermal decomposition produces pyrogallol which has given rise to the former name of these classes of compounds".

Condensed tannins have a flavonoid origin. They are oligo- or polymeric proanthocyanidins where the phenolic hydroxyls are totally or partially esterified with gallic acid. In Northern and Western Europe and Russia, barks from indigenous plants were used, including *Alnus glutinosa* (alder), *Betula alba* (birch), *Larix spp.* (larch), *Picea abies* (spruce), *Pinus cembra* (pine), *Quercus robur* (oak), *Salix fragilis* (crack willow) and *Salix caprea* (goat willow) (Falcão / Araújo 2018, 1081 ff.). More details on the description of these tannin source can be found in Faber 1985 and Howes 1953.

The chemical interactions between the vegetable tannins and the collagen consist mainly of hydrogen bonds between the tannin phenol groups and the peptide carbonyl oxygen, the peptide amino hydrogen and polar groups in the side chains of the collagen. In

[3] The four tannin groups are defined as (Khanbabaee / van Ree 2001, 643): (1) Gallotannins are all those tannins in which galloyl units or their meta-depsidic derivatives are bound to diverse polyol-, catechin-, or triterpenoid units. (2) Ellagitannins are those tannins in which at least two galloyl units are C–C coupled to each other, and do not contain a glycosidically linked catechin unit. (3) Complex tannins are tannins in which a catechin unit is bound glycosidically to a gallotannin or an ellagitannin unit. (4) Condensed tannins are all oligomeric and polymeric proanthocyanidins formed by linkage of C-4 of one catechin with C-8 or C-6 of the next monomeric catechin.

addition, covalent bonds formed by condensation of the tannins with reactive sites in the side chains of the collagen are also believed to exist (Lollar 1978, 201 ff.; Faber 1985; Schlottau 1993, 67–85; Brown / Shelly 2011). The tanning process results in a flexible product due to the high angle three-dimensional fibre network where the fibrils and fibres are isolated by the tannins and thus are relative free to move.

Other methods, which may have been used are tanning with for example brain, fat, oil, smoke and alum (Faber 1985, 184; 193; Gräf 2015, 40; 44; 47), or combinations of these with vegetable tannins (Gräf 2015, 41; Reed 1972, 88). These are methods which normally produce flexible leathers and skins. However, the tanning compounds are difficult to detect in archaeological materials. Moreover, alum is mentioned rather late in Nordic tanning history and is not a very realistic candidate in the production of weapon shields. In addition, alum is relatively easily washed out from the skin if buried in soil and the aluminium compounds, which are naturally present there, can be absorbed into the skin, thus giving a false indication of this type of tanning.

Parchment and skin

Parchment is normally not tanned. However, the earliest sources describing the production of parchment are the same as referred to for leather. The wet skin was stretched in a frame and scraped with a knife until the wanted uniform thickness was obtained (Reed 1972, 118 ff.). The process was repeated several times until the three-dimensional fibre network was stretched into an almost two-dimensional layered structure, leaving a relative hard inflexible material which is more difficult to cut than the flexible leather, but easier to split in layers (ibid. 120 ff.). The use of vegetable tannins in parchment production is normally none or kept to a minimum (ibid. 122). When used, it may have been applied to the surface of the finished parchment for decorative purposes or to promote the dehairing process. The earliest known written description of use of lime in the parchment production in Europe is found in the Lucca Manuscript (Codex 490, Bib. Cap. Lucca), which is assumed to originate from the 8th century (Reed 1972, 133). The treatment in the lime bath could last for days or weeks and eased the dehairing process and is still used in modern leather and parchment production in a modified quicker process lasting 24 hours. However, it is doubtful if treatment in lime of untanned skins has been used in the production of Germanic shields, given that the earliest written sources of its use only refers to the production of parchment for writing purposes, as mentioned above. Dehairing based on liming in Northern European leather production did not become common before around the 19th century (Reed 1972, 136 f.; Pedersen 1935, 26 ff.; 90 ff.). It is more likely that the dehairing has been performed by sweating or simply scraping the skins in stressed condition as it was done among Native Americans in Northern America (Pedersen 1935, 25).

The quality of skin products and leather

It is important to note that the quality of all types of skin products is strongly dependent on the growth of collagen fibres, production of fat etc., which, again, is dependent on the type of diet, diseases, the age of the animal and the season of slaughtering (BLMRA 1957; Roddy 1978). Alterations in these factors may result in great variations in the quality of the leather or skin product. Last, but not least, the quality of the leather is also strongly dependent of the quality of its production, including the methods and length of the production processes, the quality of raw materials (e. g. tannins) and the time of year of production as well as the skills of the producer (BLMRA 1957; Kanagy 1978; Roddy 1978).

In addition, failures like splitting, which, as outlined above, may occur in the case of leather from wool sheep skin (BLMRA 1957, 36), may also appear if the skin has not been completely tanned and is left with an inner core of raw untanned skin (Gräf 2015, 44; Pedersen 1935, 277) or due to hydrolysis resulting in lack of cohesion between the grain layer and the underlying corium fibres (Roddy 1978, 32). On the other hand, splitting has not been observed in parchment produced from wool sheep, possibly owing to the stretching which brings the collagen fibres closely together in the layerwise two-dimensional structure and thus closes the holes after the fat deposits. However, loose grain and grain splitting may occur in untanned material if this has only been stretched slightly, leaving a more open three-dimensional fibre structure.

Vegetable tanned leather, untanned skin and parchment from other types of animals like hair sheep, deer and pigs, normally provide products with a quality close to that of calf and goat.

In general, due to the isolation of the collagen fibres, vegetable tanned leather is relatively soft and flexible compared to untanned materials, which normally become stiff and inflexible if not softened. The leather could, for example, be treated with lipids in the form of oil or fat that isolates the fibres and, in case of lipids rich in polyunsaturated fatty acids, gives rise to a proper fat or oil tanning of the collagen. Moreover, vegetable tanned leather is resistant to water and can regain its flexibility by handling after drying. Both vegetable tanned leather and untanned skins are soft and flexible in wet condition and can easily be stretched around a wooden shield; both may harden and shrink to their original size after drying. However, the hardening of the untanned material is normally greater and the physical forces that it exerts on the wooden structure of the shields will be greater. A layer of hide on each side of the wooden shield board can to some extent counter such forces, thereby minimising the risk of the shield becoming deformed (see section "Shield Facings of Hide and Other Organic Material on Germanic Shield Boards"). The grain side of the vegetable tanned leather is normally relatively soft due to the high angle of the thin collagen fibres in this part of the skin and therefore easier to cut with sharp weapons. Due to the lower angle of the dense collagen structure of untanned skin, the grain surface becomes harder and more difficult to cut with sharp weapons.

Materials: sampling for microanalyses

Samples of the size between 3 × 4 and 10 × 13 mm were taken from Baunegård, Birka, Borremose and Tira for visual analyses, of these sub-samples of a length of around 1–2 mm and a width of 1–2 mm were taken for microanalyses. For comparison with the shield leathers/skins, a selection of reference materials was used *(tab. 2)*.

The leathers from the 1930s are unique as they were part of a long-term storage trials of leathers of known tannage prepared for the trial (Innes 1931; Taylor 1971; STEP 1993, 11; ENVIRONMENT 1997, 8). The leathers were divided in two parts and bound on books placed in the British Museum Library, the present British Museum (B and BL) in London (polluted environment) and the National Library of Wales (W) in Aberystwyth (clean environment), respectively. The twin leathers of the books have been analysed from time to time over the years (STEP 1993, 11) and more detailed analysis of the leather from selected books have provided valuable information on the difference in deterioration patterns due to the difference in storage environment and tannin types (STEP 1993; ENVIRONMENT 1997; Larsen 2000; id. 2008).

Sample name(s)	Provenience
11H	A so-called Russian leather c. 1600 covering on a Royal chest used by James II (STEP 1994, 13; 22) by analysis considered to be tanned with a condensed tannin (STEP 1994, 94).
BO, WO	Two leathers from 1930s tanned with oak bark analysed to contain pure condensed tannins (STEP 1994, 25; 95).
BL7	One leather from the 1930s traditional oak tanned – probably tanned with bark from a young tree (ENVIRONMENT 1997, 9; 41; Howes 1952, 86; Aaby 1946, 71–72).
BS, WS	Two leathers from the 1930s tanned with sumac, that is pure hydrolysable tannins (STEP 1993, 177,185; STEP 1994, 25).
Collagen type I	modern fibrous collagen type I made from calf hide (Sigma product)
P061_new_	modern calf parchment (bought from Pergamena, USA)
Gelatin	modern gelatin (commercial household gelatin)

Tab. 2. List of reference materials for the microanalysis.

Microanalytical methods: describing and identifying the skin materials

To achieve maximum information on the composition and the related condition of the samples, multiple micro-analyses were performed according to Sommer et al. 2017. The identity and condition of the samples were described by microscopy, fibre assessment, micro-chemical spot test, measurement of the hydrothermal stability by the micro hot table method (MHT) and attenuated total reflectance – Fourier transformed infrared spectroscopy (ATR-FTIR).

Visual examinations

Each sample and subsample was visually examined by the naked eye and under an optical microscope (OM) with reflected visible light, using magnifications from ×10 to ×40. Heavily deteriorated historical vegetable tanned leathers are characterised by severe disintegration of the fibre structure, which in the worst case turns to powder. Although in some cases brittle, the pronounced powdering that characterises vegetable tanned leather is normally not observed for other leather types or parchment. This indicates that the powdering phenomena is due to the relatively large vegetable tannin molecules filling the fibre network and which, through condensation and establishment of strong tannin-collagen bonds, may stiffen, thus making the fibres brittle and easily breakable. The gradual disintegration or powdering of the leather is observable in a small sample of fibres scraped off with the tip of a scalpel. The fibres from vegetable tanned leathers can be categorised into five progressive states of powdering due to chemical breakdown (ENVIRONMENT 1997, 113 f.):

1. Very coherent
2. Coherent and slightly powdery
3. Equal part coherent and powdery
4. Slightly coherent and powdery
5. Completely powdery

Fibre assessment

The method is based on the observation of the morphology of separated fibres in full hydrated condition. The subsamples of corium fibres were prepared in water and observed by optical microscope in visible transmitted light for the recording of the morphological characteristics according to Mühlen Axelsson 2014, Mühlen Axelsson et al. 2012 and 2017 and Sommer et al. 2016.

The intact fibre is characterised by helical twists appearing regularly in the firm structure (IDAP 2007, 17–21). Eight different morphologies have been distinguished for degraded parchment fibres at microscopic level:

1. frayed – fibrils sticking out from the fibre like threads from a frayed rope
2. split – fibrils in the fibre are visible like in a rewound rope
3. flat – appearance like flat bands
4. cracked – appears normally like flat bands with cracks across the length of the fibre
5. pearls on a string – structured with swollen and twisted areas
6. bundles – of small fibre fragments sticking together
7. gel-like – normally single fragments or bundles of small sticky fragments
8. dissolved – fibres and fragments that dissolve (gelatinise) by contact with water.

One fibre may display more than one of these morphological characteristics including intact areas along its length. The different morphologies along all single fibres (in a digital image) were determined and measured, and a degradation level of the length of the fibres was calculated in percent.

Hydrothermal stability

Measurement of the hydrothermal stability is used to describe the state of deterioration of leather and parchment fibres. When progressively heated in water, the bonds keeping the collagen structure together will be broken, leading to the evolution of random coil disordered structures over a defined temperature interval. The process is called thermal denaturation, and this process can be seen as a shrinkage motion of the fibres when observed through a stereomicroscope. Collagen shrinkage activity associated with thermal denaturation is described by a sequence of temperature intervals: no activity – A1 – B1 – C – B2 – A2 – complete shrinkage. The intervals A1 and A2 denote distinct shrinkage activity in individual fibres. Intervals B1 and B2 are defined by shrinkage activity in one fibre (occasionally more) immediately followed by shrinkage activity in another fibre. Interval C is the main shrinkage interval, where at least two fibres show shrinkage activity simultaneously and continuously. The starting temperature of the C interval is defined as the shrinkage temperature, Ts. Tfirst is the temperature at which the very first motion is observed and Tlast defines the temperature of the very last observed motion. While the shrinkage activity of collagen fibres from new leather and parchment runs through all these intervals, not all intervals may be observed for historical samples.

Raw fresh skin has a Ts of around 67 °C and the Ts of vegetable tanned skin may range between 70 and 90 °C depending on the type of vegetable tannin and the quality of performance of the tanning. Deteriorated leather and parchment have lower Ts, sometimes even as low as room temperature (Larsen 2000; IDAP 2000, 70; Bell et al. 2018). However, archaeological leathers often show a relatively high Ts, above 60 °C, despite the leathers having a low physical strength. The high Ts is usually explained by an absorption of minerals and other tanning materials from the soil into the skin structure

		Untanned		Vegetable tanned	
	Category	Tfirst (°C)	Ts (°C)	Tfirst (°C)	Ts (°C)
Undamaged	1	> 45	> 50	> 45	> 70
Slightly damaged	2	> 40 ≤ 45	> 45 ≤ 50	> 40 ≤ 45	> 55 ≤ 70
Damaged	3	> 35 ≤ 40	> 40 ≤ 45	> 30 ≤ 40	> 40 ≤ 55
Heavily damaged	4	≤ 35	≤ 40	≤ 30	≤ 40

Tab. 3. Damage categories for untanned skin and vegetable tanned leather based on average temperature intervals.

(Chahine / Vilmont 1987; Larsen / Vest 1991; Chahine / Rottier 1997; Sommer et al. 2013).

Two sub samples, each placed in a cavity of a microscope slide, were soaked in demineralised water and carefully separated using fine preparation needles. When the fibres were fully soaked, the cavity was filled with demineralised water and its content secured under a cover glass. The microscope slide was inserted into the micro hot table (Mettler FP82 Hot Stage, Mettler Toledo) and heated by 2 °C / minute starting from 25 °C continuing to 100 °C after the last observed motion in a fibre. The heating rate was controlled by a FP90 Central Processor (Mettler Toledo) (Sommer et al. 2017; Sommer / Larsen 2017). The accuracy of measurement of the Ts is ± 2 °C.

The results are evaluated with respect to damage categories. The damage categories are based on the Tfirst and Ts values. For untanned materials a description of damage categories can be found in IDAP 2007 (69–72) and Badea et al. 2015. As the damage categories for vegetable tanned leather till now have been defined by five categories (Larsen et al. 2011), these have now been transformed into four categories *(tab. 3)* to be comparable to that defined for parchment (IDAP 2007, 69–72). It should be noted that the categorization is made on a rough estimation and in some cases the observed Tfirst and Ts may fall into two different categories. In such cases, the rounded average of the two categories is used.

Micro-chemical spot-tests

Spot tests can be a useful tool in the identification of the tannin type in vegetable-tanned leather. The present spot tests are based on visual assessment of a colour difference between a reference and a reacted sample.

The ferric spot test indicates the presence of vegetable tannins, and the test is based on the principle that the phenolic-based vegetable tannins react with iron-salts forming a dark black / grey reaction product. This reaction has been known for decades and has amongst others been exploited in the manufacture of ink (van Driel-Murray 2002; Poulsen 2002; Falcão / Araújo 2011). However, the test is only indicative as the iron-salts react with any phenolic compounds present.

Two small samples of leather fibres were placed in each end of a microscope slide, each covered with a drop of demineralised water and a cover glass. One drop of 2 % ferric chloride w/v in water was placed at an edge of one of the cover glasses. A filter paper was held to the opposite edge of the cover glass to draw the ferric chloride under the cover glass and in contact with the leather fibres. A positive reaction was visualised by the colour difference between the two samples.

The vanillin spot test identifies condensed tannins by reaction between the hydroxide groups of the tannins and acidified vanillin (4-hydroxy-3-methoxybenzaldehyde) yielding a red reaction product (Deshpande et al. 1986). Two small samples of leather fibres were placed in each end of a microscope slide. One drop of 4 % vanillin w/v in 99 % ethanol was added to one of the samples. When the vanillin had fully soaked the sample, excess solution was removed, and a drop of 4M HCl added to both samples. The hypochlorous acid will initiate the reaction between tannin and vanillin. For new leather the colour of the reaction product is a bluish-red, but for deteriorated leather the colour may be red-brown. Condensed tannins can, in contact with hypochlorous acid, undergo a condensation that also results in the formation of a red colour. Whether the vanillin test is positive then depends on a visual difference between the colours of the reference sample and the sample subjected to vanillin (Poulsen 2002).

ATR-FTIR (attenuated total reflectance – Fourier transformed infrared spectroscopy)

As described in Sommer et al. 2017, ATR-FTIR spectra of both sides of the samples or the sub samples was recorded using a PerkinElmer Spectrum One FTIR-spectrometer. Spectra were recorded in the range 4000–600 cm^{-1} at spectral resolution of 4 cm^{-1} and with an average of 4 scans. The number of scans was chosen as some of the samples were very fragile and did not tolerate pressure from the crystal for prolonged time. Tests with higher numbers of scans on reference material did not result in significantly improved spectra.

In order to identify the presence of vegetable tannins in the internal of the sample, an additional spectrum of the inner core of a subsample from Baunegård was recorded. Spectra of reference samples from the British long-term storage oak bark tanned leathers (BO, WO; BL7), a sumac tanned (WS/BS) and the 1600 C leather (11H) as well as new calf collagen type I, gelatin and parchment were recorded. The resulting data was compared with data published by Falcão / Araújo 2013. In order to deconvolute overlapping bands, second derivative of the spectra scan data was calculated (Odlyha et al. 2009; Baldassaarre et al. 2015; Vichi et al. 2018).

Results and discussions

Visual examination of dry samples

Figure 15 shows the samples and fibres used in the visual examinations and *table 4* shows the results. The sample of Baunegård split in layers like parchment, and the appearance of its dry fibres and those of the Tira samples resemble fibres of deteriorated historical parchment. The fibres of the Birka and Borremose samples, however, resemble those of heavily deteriorated historical vegetable tanned leather in damage category 5.

Borremose 1 had a partly visible grain with a few remaining hair holes of relatively the same size originating from primary holes only. The hair holes are linearly oriented in groups of 3 to 5 holes placed in the grooves of the grain and a few bigger holes placed on grain tops forming the typical grain pattern of cattle. Taking the thickness of the leather into consideration, the most likely source would be calf.

Of the Tira samples, only S3 seems to have a fully preserved grain. It was covered with a black tar-like substance; however, light-coloured fibres could be seen below. Remains of the wood from the original shield construction covered the flesh side. The grain on samples S1, S2, S4, S5 and S6 was only partly preserved. In all cases, including S3, it is difficult to judge the condition of the grain due to the tar-like substance and the conservation

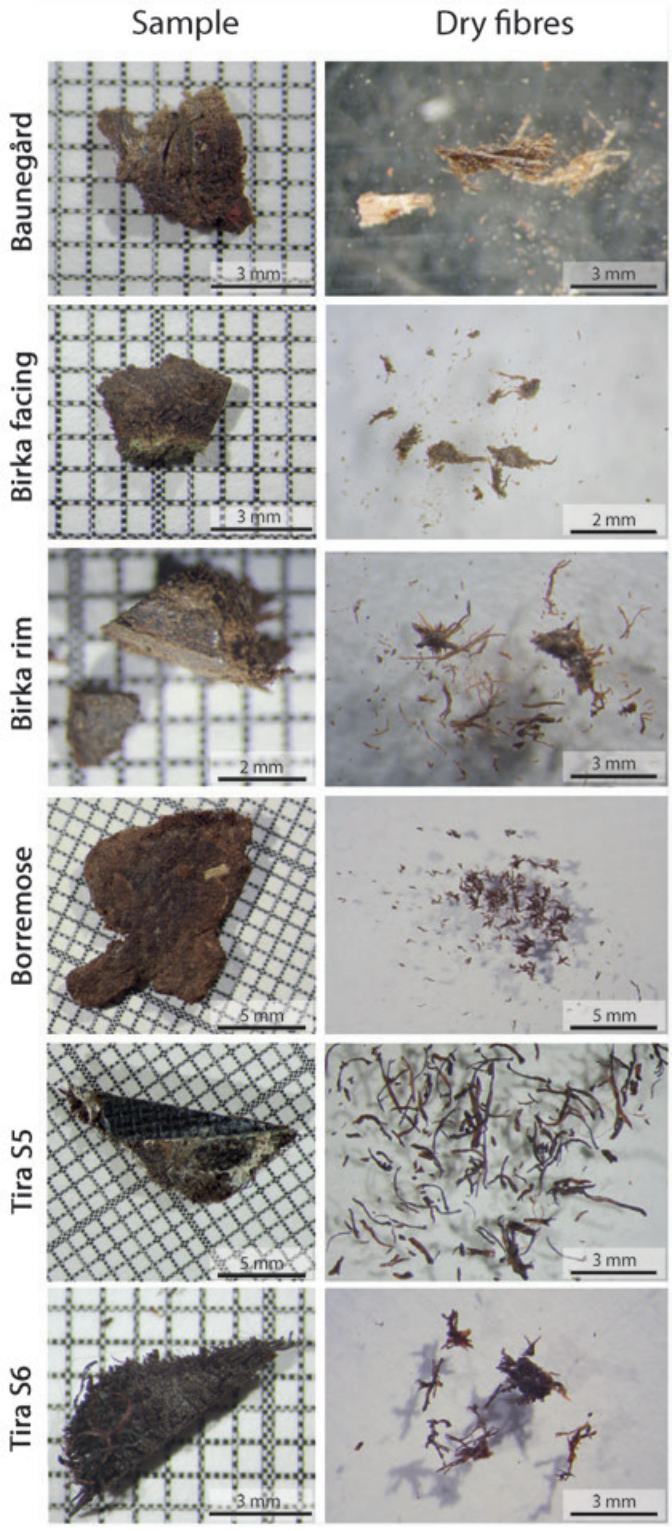

Fig. 15. The dry samples and fibres used in the visual examination (see comments in *table 4*; illustration: the authors).

Sample	Whole sample	Fibres and (damage category)
Baunegård 1	The sample measured about 4 × 4.5 mm with traces of red pigment on the surface. Appeared stiff/hard by handling. Two-dimensional structure of overlapping "flat" fibres was observable in the microscope. Thickness of measurable fibres around 0.03–0.10 mm.	The fibre structure split into horizontal layers like parchment by the subsampling. By division of the samples into loose fibres these split into small fragments of bundled fibres like observed for deteriorated historical parchments. (*)
Birka facing	The sample measured about 3 × 4 mm. Part of the surface was coloured green with copper probably from the bronze rim fitting. Felt stiff and very brittle by handling. The fibre structure appeared three dimensional "leather like". Not possible to measure fibre thickness.	The sample split into very small powder like fragments. (5)
Birka rim	The sample measured about 3 × 4 mm. Stiff and very brittle. The grain cracked easily. The fibre structure appeared three dimensional "leather like". Thickness of measurable fibres around 0.03–0.05 mm.	The sample split easily into small pin like fibre fragments very similar to fibre samples of the severely degraded historical leather sample 11H. (5)
Borremose 1	The sample measured about 10 × 13 mm and had a partly visible grain with a few remaining hair holes. Parts of the grain surface are dark or black coloured appearing like a burn or heat damage. The sample is in general brittle and very little coherent. Falls apart by slight pressure.	The fibres are largely incoherent and easy to separate. (5)
Tira 5	The sample measured about 4 × 10 mm. The grain layer seemed only partly preserved and the modern textile, of which the synthetic substance covered part of the flesh side. The synthetic substance also covered the remaining part of the flesh side and seemed to be present also underneath the textile. This indicates that the substance is a modern synthetic glue.	The fibres appeared sticky and relative thick ranging from. The dry fibres were difficult to separate and isolate because of their tackiness, but the isolated fibre fragments appears light coloured, thin and "parchment like". They seem very fragmented and kept together by the tar and modern conservation substance. (*)
Tira 6	The sample measured about 3 × 6 mm. Only little of the grain covered with tar is left and the corium fibres were visible where the grain has fallen of. The synthetic conservation glue covered part of the surface of the flesh side. These were relative thick ranging from about 0.02–0,25 mm.	Compared to S5, the sample feels less tacky and it was relatively easier to sample fibres, which came off completely incoherent indicating a strong physical deterioration of the fibre structure. Like the S5, the fibres appears light coloured underneath the tar, fragmented and mainly thin "parchment like". (*)

Tab. 4. Results of the visual examination of dry samples.

(*) Damage not categorised as the appearance of the dry fibres is not similar to vegetable tanned leather fibres.

treatments. Sample S1 has a white partly transparent coating of a modern probably synthetic substance on the flesh side. A modern textile (originating from the recent conservation treatment) covers the surface of the flesh side of S2. The fibres on sample S3 adhered tightly together due to the black substance on the surface. The Tira 5 and 6 subsamples were selected for fibre assessment, as their fibres were less covered by the tar-like substance and their morphological features appeared most evident.

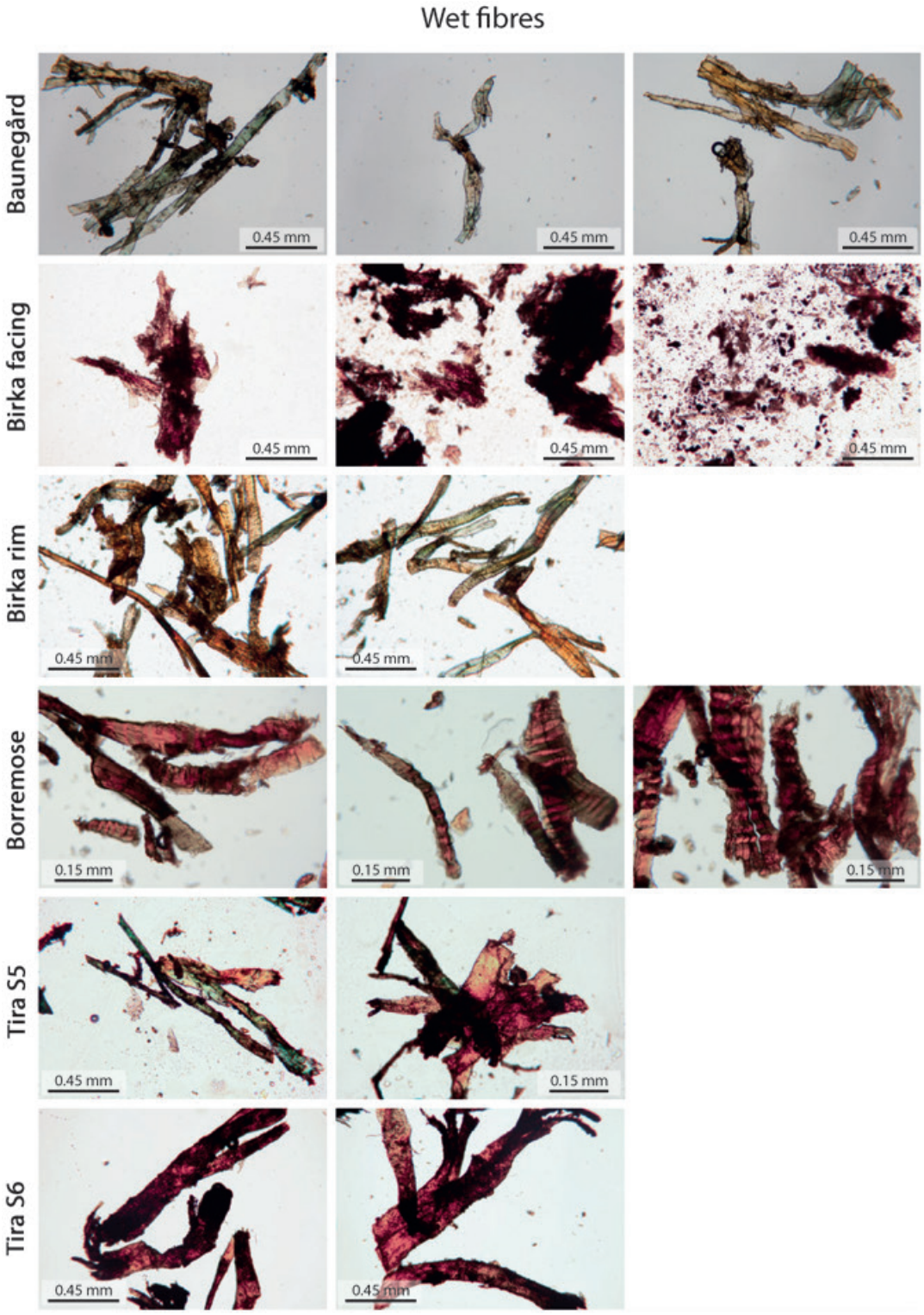

Fig. 16. Representative micro photos of the assessed fibres (see comments in *table 5*; illustration: the authors).

	Fibre morphologies	% Damage and (damage category)
Baunegård 1	Bundles of fibre fragments with fraying and cracks and some pearls on a string structure resembling heavily damaged parchment.	> 99 (4)
Birka facing	Separates into gel-like bundles that are impossible to further separate into individual fibres.	100 See "Damage category fibres" in *table 10*.
Birka rim	Cracked and frayed fragments of a dense leather like structure and some in the pearls on a string structures. Also a few fragments with the visible split into minor fibres, typical for leather and a single fragment partially with an intact structure.	See "Damage category fibres" in *table 10*.
Borremose 1	Heavily swollen and deform fragments with clearly visible cross striations. Most of them with the split into bundles of thinner fibres typical for leather. Some frayed fragments and a few deformed pearls on string and butterfly structures.	
Tira 5	Majority of fragments in the form of "pearls on a string", "butterflies", "bundles". Some of these with an intact fibre structure. In addition, several minor fragment parts.	≈ 98 (4)
Tira 6	Mainly small fragments like those seen forming bundles. They are characterised by fraying and splits. In addition, a few fragments with a deformed "butterfly" structure and some with part of the fibre structure intact.	≈ 99 (4)

Tab. 5. Assessment of fibres in water.

Fibre assessment

The results of the fibre assessment are given in *table 5*, while *figure 16* shows representative micro photos of the assessed fibres.

The morphology and condition of the almost colourless fibres in the sample of Baunegård 1 resembles very much a heavily damaged parchment. With respect to Birka rim, the fibres have a dense leather like structure and some fibres and a few fragments have split into minor fibres, typical for deteriorated vegetable tanned leather like 11H. However, the Birka facing is in a far worse condition appearing as gel-like fragments with almost no fibre structure left.

By adding water, the fibres of Borremose 1 reacted slightly hydrophobic, laying on the water surface and only slowly absorbed the water. The hydrophobic behaviour could be due to the presence of a hydrophobic conservation compound. Moreover, a major part of the fibres appeared as heavily swollen and deformed fragments with clearly visible cross striations after they had become completely hydrated. The type of swollen morphology has been observed previously in samples of historical vegetable tanned leathers after wetting and drying in a conservation experiment (Svendsen 2007).

Probably due to the tar and the conservation compound, the fibres of Tira 5 reacted hydrophobically on addition of water. However, especially the fragment bundles appear similar to those found in heavily deteriorated historical parchments, indicating an initial gelatinisation of the fibres. The fibres of Tira 6 reacted slightly hydrophobically in the water. The fact that the observed small fragments characterised by fraying and splits are

	Tfirst	Start B1	Start C (Ts)	Start B2	Start A2	Tlast	Damage category
Baunegård 1	27.4	29.5	31.5	47.1	51.4	59.5	4
Baunegård 2	37	39.6	40.1	50.4	53.2	69.9	3
Birka rim	26.2	28.4	36.9	–	44	75	4
Birka facing	26.6	31.8	32.9	44.7	46	55.6	4
Borremose 1	28.1	43.8	–	–	–	50,6	4
Borremose 2	32.1	43.1	47.2	60	61	69.2	3
Borremose 3	33.4	46	51.1	70	71.8	72.2	3
Borremose 4	33.4	48.1	50.8	59.5	61.1	67.8	3
Tira 3*	37.7	52.7	55	–	68.8	71.2	2
Tira 5	51.1	54.4	55.3	–	–	61.7	1
Tira 6	31.5	36	40.8	68.8	69.6	77.6	3

Tab. 6. Start temperatures (°C) of the five shrinkage intervals together with Tlast for the measured samples. The shrinkage temperature = Start C.

*Tira 3 was included as it was easier to extract the tar-like substance by washing in water and acetone from this compared to Tira 5 and 6, which remained slightly hydrophobic.

isolated (and not clustered in bundles) indicates that cross-links have been formed in the collagen and collagen fragments during the degradation. By continuing degradation this may lead to transformation of fibres into hard pin-like fragments rather than gelatinisation.

Hydrothermal stability

Table 6 and *figure 17* show the results of the measurement of hydrothermal stability. In general, the samples represent a relative great variation in deterioration as seen from the observed Tfirst, Ts and length of the shrinkage intervals *(fig. 17)* and thus confirm the results of the visual examination of the dry and wet fibres. Moreover, the results reflect the evolution of deterioration as expressed in their hydrothermal activity.

Good quality skin or leather has a high Tfirst, Ts and short shrinkage intervals with high activity in the shrinkage movements. In the initial phase of deterioration, the Tf and Ts decreases and the shrinkage intervals increases, reflecting the heterogeneity of the stability of the collagen fibres and molecules and the shrinkage activity will fall. This pattern continues until the distribution of the deterioration covers a greater part of the collagen structure after which the Tfirst and Ts continues to decrease but the shrinkage intervals decreases reflecting the more homogeneous distribution of damage. In the end phase of the deterioration, one or more of the shrinkage intervals may no longer be observed and finally the Ts may reach a temperature even below room temperature and the shrinkage activity becomes very low. In some cases, especially with parchment, the deteriorated collagen may have transformed into gelatin and may dissolve completely or partly by the heating or even by the first contact with water at room temperature (MAP 2002, 59–60).

In other cases, Tlast may be rather high even in deteriorated leathers and skin. This may be due to fragmentation of the collagen leaving the hydrophobic parts of the molecules,

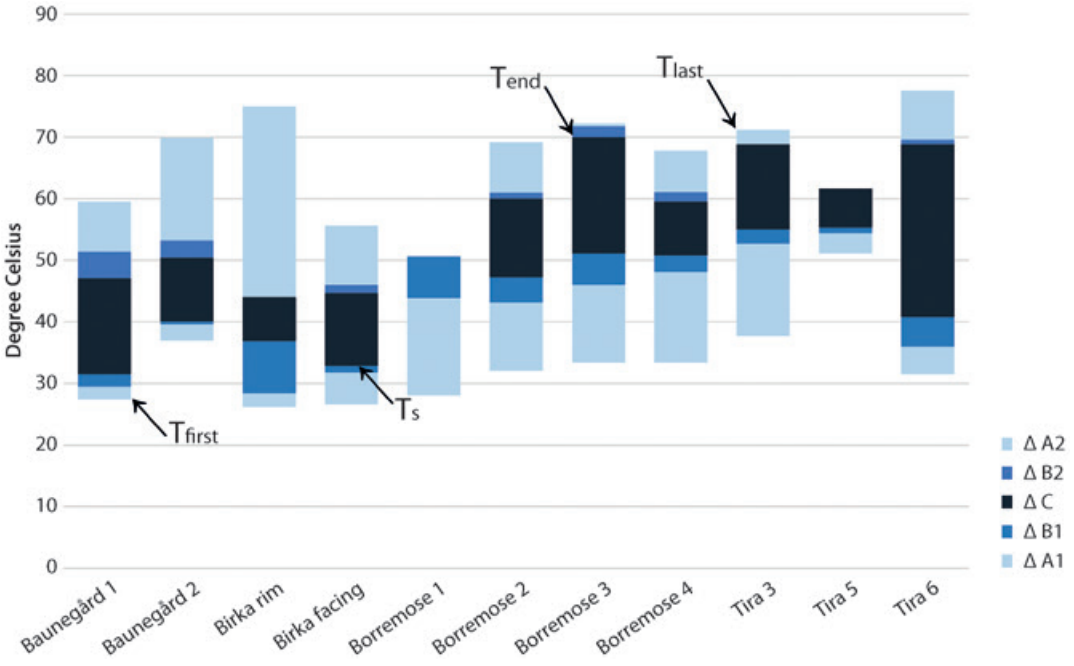

Fig. 17. Shrinkage intervals of the respective samples (illustration: the authors).

having a higher hydrothermal stability than the hydrophilic parts destroyed by the deterioration. Moreover, oxidative processes may also lead to the formation of covalent crosslinks between some of the collagen molecules and fragments, leading to a higher hydrothermal stability of these. Finally, tannage by iron from the soil may tan the collagen, causing an increase in the hydrothermal stability (Chahine / Vilmont 1987; Larsen / Vest 1991; Chahine / Rottier 1997). However, none of the samples have a hydrothermal stability indicating an iron tannage.

The long C and B2 shrinkage intervals of the two Baunegård samples reflect a large spread in the deterioration degree and stability of the fibre mass. The difference in hydrothermal stability between the two samples reflects the relative great difference in the degree of deterioration of these. This is not unusual and heterogeneity in the damage condition may vary a lot even within a small area of an object (Nielsen 2007). Interestingly, like damaged parchment, a greater proportion of the fibres transform into pearl on string structures during the shrinkage process indicating that the fibres are untanned. Thus, the shrinkage behaviour supports the results of the analysis of the dry and wet fibres. On the basis of this, the Baunegård samples can be assigned to damage category 3 (damaged: Tfirst = 37 °C and Ts = 40.1 °C) and 4 (heavily damaged: Tfirst = 27.4 °C and Ts = 31.5 °C). It should be remarked that the Ts of new parchment and untanned dehaired skins lies between 50 °C and 60 °C.

Similarly, the long intervals in the case of the two Birka samples also reflect heterogeneity in fibre stability. Furthermore, the difference in Ts between Birka rim (36.9 °C) and Birka facing (32.9 °C) corresponds well to the observation made by the assessment of the dry and wet fibres showing that the latter is the most damaged. This also includes the similarity to the historical leather reference 11H. The Ts of 11H was measured to 32.6 °C (ENVIRONMENT 1996, 183) and the shrinkage behaviour of the two Birka samples

	Baunegård	Birka rim	Birka facing	Borremose	Tira
Potential veg. tannins	no	yes	yes	yes	no
Condensed tannins	no	?	?	?	no

Tab. 7. Results of the microchemical spottest.

are very similar to that observed by 11H. That is a very low shrinkage activity with slow shrinkage movements and relatively small reductions in the size of the shrunken fragments. However, although the Ts of Birka facing and 11H are almost exactly the same, the physical conditions of the former are worse as some of its fragments dissolved during heating. This may reflect the different deterioration histories as burial in the soil may have caused a greater proportion of hydrolysis of Birka, whereas 11H (in addition to hydrolysis) also suffered from oxidative breakdown (Larsen 2000, 87). With Tfirsts below 30 °C and Ts below 40 °C, both Birka samples falls within damage category 4 (heavily damaged) for vegetable tanned leathers.

The shrinkage behaviour of the Borremose samples also resembles that of deteriorated historical vegetable tanned leathers confirming the characteristics observed by the assessment of the dry and wet fibres. Moreover, they represent a range of deterioration states. Borremose 1 has the lowest hydrothermal stability and shrinkage activity with no observable C interval and Ts thus belonging to damage category 4 (heavily damaged). Borremose 2, 3 and 4 can be assigned to damage category 3 (damaged).

The difference in Ts between Tira 6 (40.8 °C) on the one side and Tira 3 (55 °C) and Tira 5 (55.3 °C) on the other, is substantial. This could be explained by the remains of the tar-like substance and conservation compounds on the fibres Tira 3 and Tira 5, which may cause the Ts to rise. The shrinkage behaviour and Ts of Tira 6 are consistent with the fact that fibres of this appeared untanned after washing.

The hydrophobic behaviour of the Tira sample, which may be due to the tar-like substance, indicates that the skin-cover of the shield may have been water repellent and hardened as known from historical fire buckets made of leather. Assuming the skin is untanned, the Tfirst (31.5 °C) and Ts (40.8 °C) of Tira 6 place it in a damage category 3 (damaged) close to a category 4 (heavily damaged).

Micro-chemical spot tests

The results of the microchemical spot tests are summarised in *table 7*. The samples from Baunegård and Tira did not show a positive reaction with ferric chloride, therefore they are not considered as vegetable tanned. Indication of a vegetable tannage was found in the samples from Birka and Borremose, as these samples did yield a positive reaction with ferric chloride. It was not possible to clarify whether the Birka and Borremose samples were tanned with hydrolysable or condensed tannins, as the colour of the reference and the reaction samples all turned into an insignificant orange-brown hue.

ATR-FTIR (attenuated total reflectance – Fourier transformed infrared spectroscopy)

Table 8 shows the wave numbers of marker bands of the Baunegård and Tira samples and, for comparison, the marker bands of collagen type I, gelatin and parchment reference samples as well as the literature values from Boyatzis et al. 2016.

Boyatzis et al. 2016 Collagen	Boyatzis et al. 2016 Parchment	Collagen I	New parchment P061	Gelatin	Baunegård surface	Baunegård inner core	Tira S2 washed
3315 s, br	3302	3305 m, br	3292 s, br	3294 m, br	3293 s, br	3290 s, br	3289 s, br
3072 m–w, br	3072	3076 w, br	3073 w, br	3072 w, br	3073 w, br	3073 w, br	3073 w, br
2958	2926	2931 w, br	2926	2928 w	2928 w	2931	2931 m
1640 s	1644	1631 vs	1631 vs	1630 vs	1631 vs	1632 vs	1632 vs
1545 s	1538	1548 vs	1538 s	1538 s	1535 vs	1536 s	1523 s
1454 m–w	1448	1452 m	1448 s	1450 ms	1449 s	1449 ms	1449 s
1405 w	1408	1405 m	1405 m	1403 m	1402 m	1406 m	1406 m
1340 w	1334	1339 w	1335 m	1335 m	1334 m	1336 m	1335 m
1241 m–w	1230	1238 m	1235 s	1237 s	1233 s	1235 s	1233 s
1082, 1032	1084, 1031	1082, 1032	1081, 1031	1081, 1032	1080, 1031	1081, 1031	1082,1031

Tab. 8. Wave numbers in cm^{-1} of ATR-FTIR vibrational marker bands for Baunegård, Tira, collagen I, parchment samples and reference values from the literature.

vs: very strong; s: strong; m: medium; w: weak; sh: shoulder; br: broad

Figure 18 shows the spectra and their second derivatives of the Baunegård and Tira samples with the reference collagen type I and new parchment samples. It should be noticed that the spectrum of gelatin is very similar to these.

The convincing match between the spectra of the archaeological samples and the reference samples confirms that no tannins are present in the former. Especially, the spectra of the inner core of Baunegård and the new parchment are almost identical. The higher intensity of the bands in 1230–1030 cm^{-1} region is most likely due to the tar-like substance and the modern conservation compound. The difference in the wavelength and intensity of marker bands of the references and the literature value are probably due to differences in the sample materials *(tab. 8)*. In general, the small differences in band position and intensity between the spectra of the archaeological samples may be attributed to differences in the state of deterioration of the collagen. Thus, the changes in band profile are more distinct for gelatin than for parchment which is in accordance with the fact that the gelatin is chemically more modified during its production.

Moreover, we can confirm that spectra from the grain and flesh side may vary as shown by Odlyha et al. (2009, 143), but even if only the flesh side remains after shaving, differences in deterioration and contamination of the two sides may result in variations of the spectra of the two sides.

The deterioration of the collagen is characterised by a decrease of the strong amide II band around 1540 cm^{-1} together with an increase of the band at around 1230 cm^{-1} originating from among others Amide III (Boyatzis et al. 2016). In addition, deterioration causes decrease of the band at 1630 cm^{-1} (Odlyha et al. 2009), disappearance of other as well as appearance of new bands from the modified collagen and other substances present in the material.

In our case, a decrease of the band at around 1538 cm^{-1} is seen for gelatin and parchment compared to collagen. However, the increase of the band around 1238 cm^{-1} is

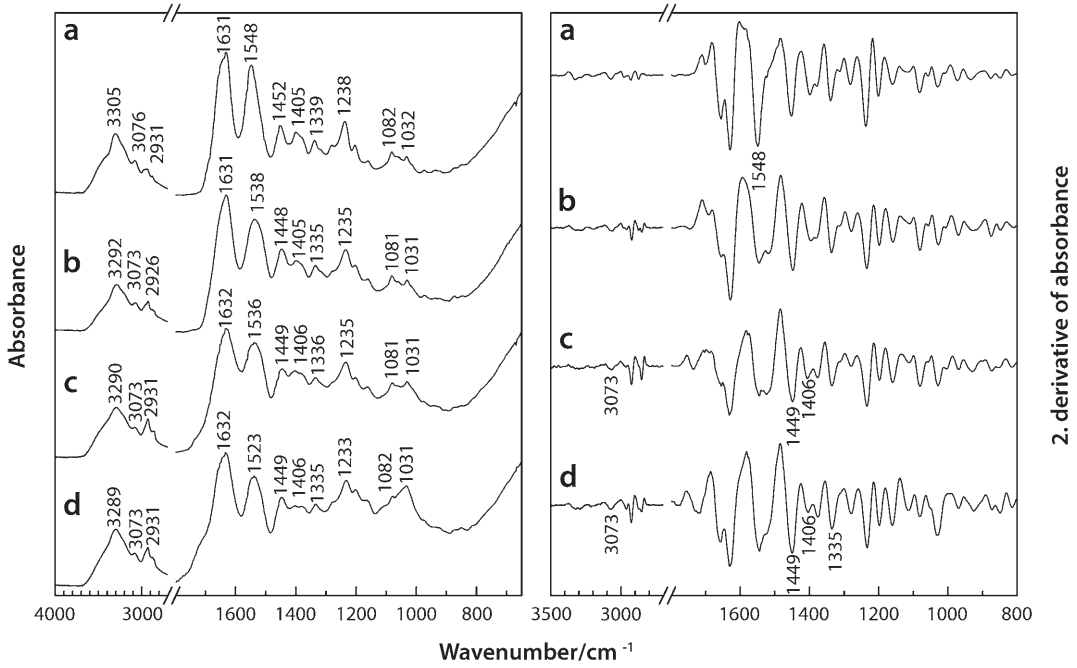

Fig. 18. ATR-FTIR absorbance spectra and the second derivatives of these of: (a) collagen I; (b) new parchment P061; (c) Baunegård inner core and (d) Tira 2 washed (illustration: K. Pilkjær Simonsen).

greater for collagen. On the other hand, the decrease of the band around 1538 cm^{-1} and increase of the band 1238 cm^{-1} is seen for the Birka and Tira 2 samples, respectively. In addition, a decrease of the bands around 1447 cm^{-1} and 1402 cm^{-1} is also seen for these.

According to Vichi et al. (2018), a downshift in the amide I band in the region 1645–1638 cm^{-1} was "assigned to the preserved collagen; when detected between 1637 and 1630 cm^{-1}, it was attributed to the unfolding of the helices and, when below 1630 cm^{-1}, it was assigned to gelatin. When gelatin was evident in the spectra, a shoulder at about 1655 cm^{-1} appeared, possibly resulting from remaining α-helix chains." However, the shoulder at about 1655 cm^{-1} is present in all the samples including the collagen and parchment samples (see the second order derivatives in *fig. 18*). Therefore, it may be questioned whether this band represents the presence of gelatin only and / or if it may be attributed to other structural phenomena like disordered collagen fragments?

Also, according to Vichi et al. (2018), the amide II band (in our case the band between 1548 and 1538 cm^{-1}) in the gelatin spectrum appeared upshifted, possibly as a consequence of hydration. However, this is not the case in the spectrum of the reference gelatin.

Boyatzis et al. (2016) have observed that bands at around 1616 and 1508 cm^{-1} reflect changes in amide I and II bands in accelerated aged parchment samples. They found that amide I bands showed "a decrease in the intensity of the helical components at ~1655 cm^{-1} with increasing ageing times and a relative increase in the contribution of random coils (around 1630 cm^{-1})." Moreover, by deconvolution and peak fitting of the spectral region including amide I and II peaks, they "uncovered two main components centred at ~1658 and ~1629 cm^{-1} corresponding to the helical and random (or uncoiled) components, respectively." Regarding the bands around 1616 and 1508 cm^{-1}, these are seen in the Baunegård and Tira spectra (second order derivatives in *tab. 8*) but possible contaminations from

Falcão / Araújo 2013*	BO	WO	BL7	BS	WS	11H	Birka Rim	Birka Facing	Borre-mose
Tannin compounds									
1612–1611 m–vs	1616 vs	1609 s	1608 m	1608 s	1607 s	a)	a)	a)	a)
1518–1514 w–m	1524 ms	1521 m	a)	1509 w	1510 w	1523 m	1514 s	1513 s	1518 m
1448–1447 m–s	1444 ms	1448 ms	1447 m	1448 s	1448 s	1450 s	1447 m	1447 m	1454 m
1207–1203 (mw-vs)	1196 vs	1189 vs	1199 ms	1204 vs	1290 vs	1202 s	1198 mw	1203 mw	1200 m
1040–1032 m-vs	1039 vs	1035 vs	1025 vs	1028 vs	1028 vs	1033 vs	1031 m	1030 vs	1035 vs
Condensed tannins									
1287–1283 m	1286 s, sh	1287 s				1280 m	a)	a)	1280 m
1157 w						1163 m	1159 mw	1159 ms	1166 m
1114 w-m						1118 m	1112 m	1113 s	1118 m
979–976 w		973 w				974 w	a)		972 m
842						a)	a)	a)	841
Hydrolysable tannins									
1708–1704 m–s		1705 w	1705 w		a)				1710 m
1326–1319 m-s			1325 mw						1325 m
Gallotannins									
1097–1092 mw–m				1089 m	1087 m	a)	a)	a)	a)
874–870 w	871 m	870 w	870 w	869 w	869 mw	874 w	875 w	871 w	874 w
765–760 w–m	767 m	762 w	761 m	758 m	758 m	754 wm	754 mw		

Tab. 9. Wave numbers in cm^{-1} of ATR-FTIR vibrational marker bands for vegetable tannins in Birka and Borremose samples and historical leather references (band intensity).

vs: very strong; s: strong; m: medium; w: weak; sh: shoulder; a): possible overlapped or shift in band location.

* Spectral vibrational intervals of marker bands of extracts from six 18th and 19th century leathers.

substances originating from the soil and conservation makes it difficult to conclude anything with certainty.

On the other hand, there are clear differences in the intensities of the bands around 1655 and 1630 cm^{-1} (see second derivatives in *tab. 8*). Odlyha et al. (2009, 145) calculated the ratio of absorbances at around 1660 and 1630 cm^{-1} and found that these provided sufficient variation to estimate a rank of damage of the parchment samples and showed a relation between the calculated ratios and the measured Ts of the samples. In the present case, a significant decrease in the band around 1655 cm^{-1} relative to the 1630 cm^{-1} band is seen for the gelatin and parchment reference samples compared to the collagen reference sample (*tab. 8* second derivatives). A similar decrease is seen in the spectra of the Baunegård samples.

Figure 19 shows spectra and second order derivatives of the reference samples BO, WO, BL7 and 11H, and *figure 20* the spectra and their second derivatives of 11H, Birka facing, Birka rim, BL7 and Borremose. *Table 9* shows the wave numbers of marker bands the same

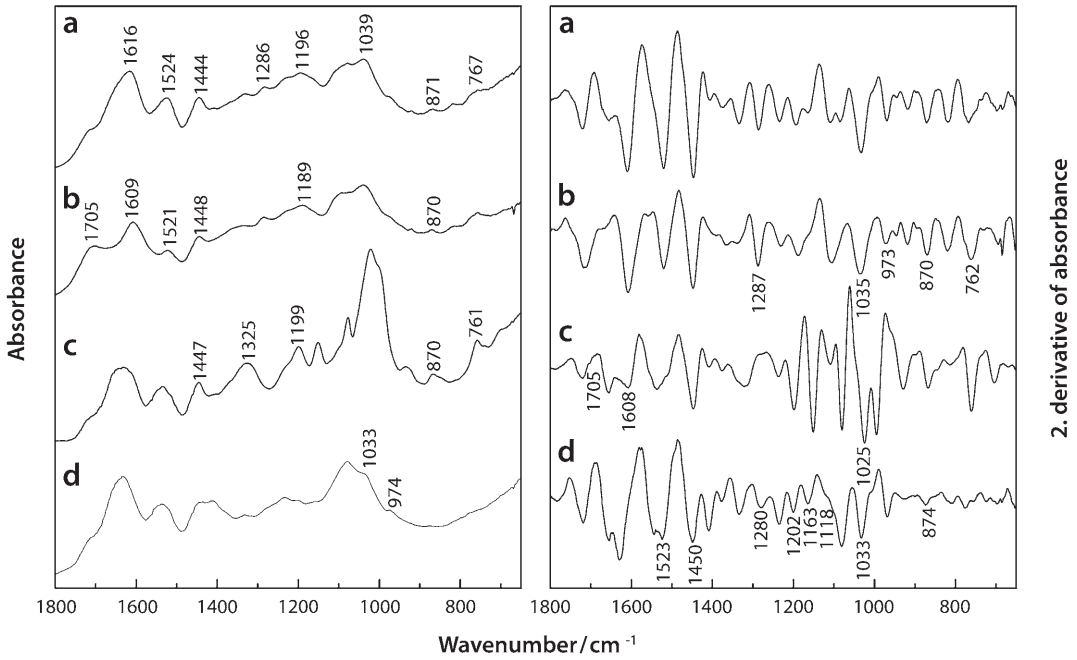

Fig. 19. ATR-FTIR absorbance spectra and their second order derivatives of the historical reference leathers: (a) BO;(b) WO; (c) BL7 and (d) 11H (illustration: K. Pilkjær Simonsen).

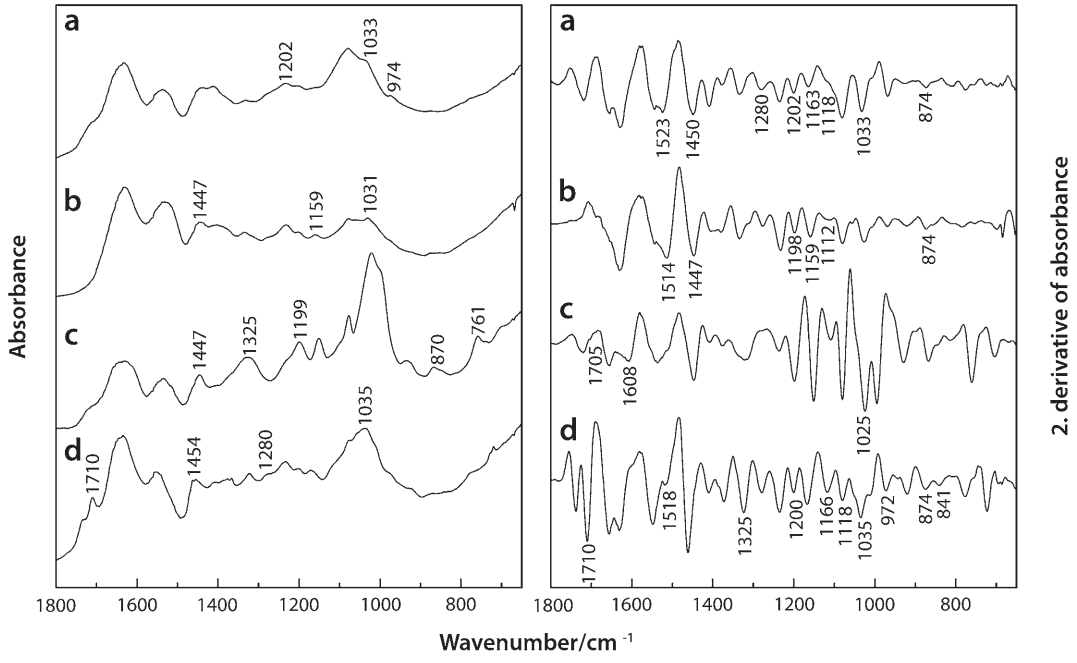

Fig. 20. ATR-FTIR absorbance spectra and their second order derivatives of: (a) 11H; (b) Birka rim; (c) BL7 and (d) Borremose (illustration: K. Pilkjær Simonsen).

as well as of BS and WS and the literature values of tannin extracts from historical leathers published by Falcão / Araújo 2013.

It should be noted that spectra obtained from extracts provide more detailed information on the tannin structure as they are not influenced by the collagen spectrum. However, all the archaeological samples were too small for extraction and all samples are therefore analysed by ATR-FTIR to ensure the comparability.

As expected, the presence of tannins has a great influence on the band profile. The spectra of leathers containing hydrolysable tannins are characterised by spectra with many distinct bands, whereas leathers containing condensed tannins are characterised by a greater degree of band overlapping. Spectra obtained from leathers containing a mixture of the two types are intermediates between these. Therefore, the spectrum profile may give the first hint concerning the main type of tannin present in the leather.

Compared to the spectra in *figure 18*, the spectra of the archaeological and the reference samples show several bands of high intensity overlapping with the collagen amide I bands at around 1655 cm^{-1} and 1630 cm^{-1} and amide II bands at 1544 cm^{-1} as well as with the collagen bands at 1080 cm^{-1} and 1030 cm^{-1} *(figs. 19–20)*. However, the overlapped bands were successfully revealed by the second order derivative calculation. The higher intensity of the overlapping bands is most likely due to a high content of tannins. The deviations in the location of the bands can be explained by deterioration, as mentioned above, as well as differences in the types of tannins.

Missing bands that are markers for tannins may be due to overlapping with other bands as mentioned by Falcão / Araújo 2013, which reports this for both new and historical leathers. Although several marker bands are missing *(tab. 9)*, the three oak bark tanned reference leathers seem mainly to contain hydrolysable tannins and probably a minor content of condensed tannins: Northern European oaks normally contain hydrolysable ellagitannins as the major part as well as condensed tannins (Howes 1953, 86; Falcão / Araújo 2018, 1087). The missing marker bands may be the result of the deteriorative chemical modification of the tannins. The shrinkage temperatures of the twin leathers BO (39.8 °C) and WO (62.9 °C) are rather low (STEP 1993, 161) compared to that of BL7 (65.7 °C) (ENVIRONMENT 1997, 160). The latter was stored in British Library together with BO, and comparison of the spectrum band profiles of these two strongly indicates that BL7 contains a higher amount of hydrolysable tannins and thus represents a more durable and higher quality leather.

As expected, the spectra of the two twin sumac tanned leathers are characteristic for pure hydrolysable tannins of the gallo type. In general, due to the different storage conditions leading to different rate and type of breakdown, there are substantial variations in the intensity, overlap and locations of the bands of BO, WO, BL7, BS and WS.

With respect to 11H, this leather has the characteristic marker bands for condensed tannins, but also two bands representing gallo tannins. However, this may be either due to traces of these tannin compounds in the plant source or gallo compounds formed by the deterioration of the tannins as reflected in the spectrum in *figure 19,d*. Moreover, sample 11H is defined as a Russian leather (STEP 1994, 13), a leather type which is tanned with birch bark containing condensed tannins (Falcão / Araújo 2018, 1086). Thus, the spectra of the reference leathers show that it is possible to determine the main types of vegetable tannins in leather by ATR-FTIR, but variations in the changes of the molecular structures of the collagen and tannin due to deterioration under different storage conditions make it difficult if not impossible to make a more specific determination of the tannin source.

As seen in *table 9*, the spectra of the two Birka samples contain marker bands representing condensed tannins and maybe breakdown products in the form of gallotannins. The

two samples are most probably tanned with the same type of tannins and the few deviations between them are most likely due to difference in their state of deterioration. Apart from the small variations in band intensity (especially the high intensity of the bands around 1080 cm^{-1} and 1030 cm^{-1} in the 11H spectrum), the spectrum of the Birka rim is very similar that of 11H. The spectrum of the Birka facing reflects a higher degree of deterioration compared to the Birka rim. However, due to the masking of several of the collagen bands from the bands of the tannins and their breakdown products etc., it is not possible to uncover further useful information on the degradation state of the collagen of the samples.

Despite the clear sign of deterioration in the spectra of the Borremose samples, these have several distinct sharp marker bands characteristic of hydrolysable tannins. The presence of the bands at 1710 cm^{-1} and 1325 cm^{-1} show the presence of a relatively high content of hydrolysable tannin of the gallo type, but they also contain marker bands for condensed tannins. Similar to Birka, the relatively high intensity of the bands in the overlap zones indicates a high content of tannins.

Both Birka samples contain condensed tannins and a minor amount of gallotannins or similar phenolic glycosides as seen in birch *(betula)* (Falcão / Araújo 2018, 1086). Other possible sources may be larch *(larix)* (Zhang et al. 2017; Bianchi et al. 2015; Bianchi 2016), pine *(pinus)* (Bianchi et al. 2015; Bianchi 2016), spruce *(picea)* (Bianchi et al. 2015; Bianchi 2016; Imran 2017) and willow *(salix)* (Janceva et al. 2011).

The Borremose samples are clearly tanned with a mixture of condensed tannins and probably hydrolysable gallotannins, the source of which could be oak (compare with the marker bands of sample BL7). According to Howes (1953, 86), oak bark tannins are a mixture of hydrolysable gallotannins and condensed tannins with the latter as the major constituent, but newer analysis shows ellagitannins as the major hydrolysable tannin source in most of the different species of oak bark analysed (Falcão / Araújo 2018, 1087). However, it should be taken into consideration that the tannin chemistry of bark is very complex, and it varies with the seasons of the year and the part of the bark (inner or outer) from which it is extracted. In a review of changes in the tannin content in oak leaves throughout a growing season Howes (1953, 82–86) mentions that while the content of hydrolysable tannins remained approximately constant, the condensed tannins (proanthocyanidins) did not appear until late May. Similar seasonal variations probably take place in the bark structures of the tree. It should also be taken into consideration that the amount of tannins extracted by the ancient tanning methods was probably low compared to the effective modern methods. The ancient methods were probably depending on a slow extraction during the tanning process which was carried out with little or no movement of the skins. This process may have extracted mainly the more extractable compounds like gallotannins and lower molecular size ellagitannins from the plant material. Furthermore, according to Khanbabaee / van Ree (2001, 645), gallotannins "are key intermediates in the biosynthesis of nearly all hydrolysable plant polyphenols". In addition, compared to the outer bark, the inner bark contains a higher amount of extractable gallotannins and could represent a possible source in case of the Birka sample.

Finally, the fact that no presence of tannins is found in the spectra of the Baunegård and Tira samples as well as that the high intensity of the marker bands of vegetable tannins in the spectra of the Birka and Borremose samples are comparable to those of the leather reference samples, strongly indicates that the latter represents leathers produced by a deliberate tanning process. In this connection, it is interesting to consider the low content of tannins present in hide materials buried in bogs like the Grauballe Man *(fig. 21)*, who was "re-tanned" with oak bark in order to get the whole skin structure completely tanned

Fig. 21. The Grauballe Man displayed in the Moesgaard Museum, Denmark (photo: R. N. Johansen, Foto/medie Moesgaard Museum).

(Asingh / Lynnerup 2007, 39–43). Together with the results of our analysis, this indicates that untanned skin may not be transformed into full tanned leather under archaeological burial conditions.

Overall discussion of the results of the multiple microanalysis

Altogether, complementary observations and results of the micro analyses have made it possible to distinguish convincingly between tanned and untanned archaeological skin samples as well as to identify the main types of vegetable tannins present in the tanned samples.

The observed parchment layer like fibre structure, fibre morphology, the negative ferri test, and the behaviour of the fibres during shrinkage in water strongly indicate that the two Baunegård and the Tira samples must be untanned. Moreover, the ATR-FTIR spectra of these samples match convincingly those of the collagen I, gelatin and parchment references and show no sign of vegetable tannins. In addition, the Baunegård samples can be characterised as parchment produced by stretching the wet de-haired skin until the fibres are brought into a low angle forming a layered structure, which by drying becomes stiff and inflexible.

The more three-dimensional fibre structure observed in the Tira samples is probably caused by greater thickness of the skin, which may have made it more difficult to stretch into the more layerwise two-dimensional structure that defines a parchment. The hydrophobic character of the fibres due to the tar-like substance on their surface indicates that the skin may have been produced to be water repellent.

The morphology, shrinkage behaviour, positive ferri test and condition of the fibres of the two Birka and the Borremose sample are in accordance with the ATR-FTIR spectra

showing the presence of tannins. Moreover, the fibre morphology, shrinkage characteristics and the ATR-FTIR spectra of the Birka samples are very similar to that of reference sample 11H. All three samples contain condensed tannins and maybe a minor amount of gallotannins or breakdown products in the form of gallic acid products originating from the breakdown of the former. The ATR-FTIR spectrum of the Borremose sample clearly shows that it contains a mixture of both condensed and hydrolysable gallotannins. The Birka facing is in a significant worse condition than the Birka rim as seen by its lower hydrothermal stability, the greater amount of damaged fibres and the ATR-FTIR spectrum. The reason for this could be the presence of copper ions from the metallic rim. Copper ions catalyse oxidation, and the Birka facing has been more exposed to light and other damaging factors from the surrounding environment than the rim sample, which had been covered underneath the bronze rim.

Influence of sample condition and conservation on the analyses

The state of deterioration and conservation treatments may have great impact on the possibility to perform and the outcome of the analysis. Thus, it may influence the possibility to judge the condition of the surface and fibres as in the case of the Tira samples due to the tar-like substance and the later applied conservation treatments. In addition, the tar-like substance made it difficult to separate the fibres for fibre assessment and the measurement of hydrothermal stability. Moreover, Borremose 1 and the Tira samples reacted slightly hydrophobically, probably due to the presence of a hydrophobic conservation compound and the tar-like substance in the case of the Tira sample. This may lead to the measurement of a higher hydrothermal stability in case the fibres are not completely soaked in water before performing the measurement. In addition, the heavily swollen and deformed appearance with clearly visible cross striations of the hydrated Borremose fibre fragments indicates that the sample has been dried out after the excavation and then soaked again later in connection with the subsequent conservation treatment.

Probably due to the chemical deterioration of the tannins, it was not possible to clarify whether the Birka and Borremose samples were tanned with hydrolysable or condensed tannins by the Vanilin spot test. As for deteriorated historical leather, the test seems unsuitable for analysis of archaeological leather.

The variations in the changes of the molecular structures of the collagen and tannin due to differences in breakdown mechanisms under different storage conditions makes it only possible to determine the main types of vegetable tannins in leather by ATR-FTIR. The presence of conservation compounds may further complicate the tannin identification as well as these may have an undesirable influence the collagen spectrum of untanned skins as in the case of the Tira samples.

The state of collagen preservation determines the chances of obtaining diagnostic collagen peptide markers and therefore also the possibility for obtaining a species identification. Treatment with PEG can, depending on its molecular weight, appear on and interfere with diagnostic markers on ZooMS spectra, and make it difficult to separate real peaks from PEG. This was, however, not the case here, where missing markers either did not appear or had too low signal-to-noise (S/N) ratios to acknowledge them with confidence.

Therefore, in order to maximise benefit from analysis, we recommend that sampling is done immediately after the excavation before any preservation and to keep the samples wet and cold to avoid further chemical and biological degradation until the analyses can be carried out.

Animal identification and tanning processes: summary and discussion

The main results and observations regarding animal species and potential tanning processes have been summarised in *table 10* based on the analyses conducted in this study. The reader is referred to the relevant sections ("Identification of animal species with ZooMS: Methods and Results" and "Hide Products/Microanalysis: Materials, Methods and Results", respectively) for explanations as to how these conclusions were derived.

All samples of hide, except the facing from Birka (Bj 850), indicated that the hide had been taken from cattle, showing evidence of both untanned and tanned facings. This fits well with cattle being amongst the dominant species for leather in Northern Europe in the Iron and Viking Age as well as with its suitable properties. The shield facings stemming from Baunegård and Tira were seemingly untanned. Microscopic analyses suggest that the rawhide products had been produced by stretching, giving a parchment-like fibre structure. On the other hand, the hide of the shields from Borremose and Birka (Bj 850) appear to have been tanned and can therefore be classified as leather. The leather from Borremose had possibly been tanned with oak bark tannins and some of the grain surface, moreover, showed indications of having been subjected to burn or heat damage. This could be interpreted as a case of *cuir bouilli,* but the current data is admittedly inconclusive. The samples from Bj 850 (facing and rim) may have been tanned with birch, larch, pine, spruce or willow. In contrast to all other samples, however, the facing of the shield from Bj 850 appears to have been made of sheep or deerskin. Although ZooMS analyses do not provide a clear identification, the skin was most probably made from sheep, given the suitability of such skins (broad and thin) as well as general availability of this animal (see section "The Question of Animal Species and Tanning Processes"). This variability in skin products, even within the same shield construction, reflect a high level of consideration regarding the choice and use of skins in shields.

The sample size of this study is admittedly much too small and dispersed to conclude anything definite regarding chronological or regional variations in shield construction practices. The conclusions drawn from these analyses are nonetheless revealing when considering the general properties of the hide products mentioned above and when held up against historical sources.

The aforementioned findings regarding animal species are paralleled by the insights gained from historical sources about shield constructions of the Iron Age and Viking Age. Most interestingly, the results described above are in accordance with the historical sources (mentioned in section "The Question of Animal Species and Tanning Processes") which give the impression that cattle hide was commonly used in shield constructions. The possibility of the facing from Bj 850 being sheep skin is also significant in relation to the historical sources in that such skins were used to cover Byzantine *peltai* shields and, more importantly, stipulated against in Anglo-Saxon law (see section "The Question of Animal Species and Tanning Processes"). As noted, the more-or-less contemporary Anglo-Saxon *Laws of Athelstan* (clause 15) stipulates that shield makers should not make use of sheepskin for their shields (Härke 1992, 51), probably owing to the relative weakness of hides made from sheep species. The discrepancy between this source and our results concerning the shield from Birka may hint at regional variations in shield technology practices, being particularly interesting when considering the amount of Scandinavian influence in Britain at this time.

Turning to the question of hide products, it is evident that tanned and untanned hides have different properties, being significant in relation to shield constructions in a variety of ways. Untanned cattle hide is typically stiff and provides the shield with a hard surface

Shield	Date	ZooMS ID	Tanned?	Observations
Borremose	c. 350 BC	Cattle	Yes	Possibly tanned with oak bark tannins. Black coloured parts of the grain surface may be due to a burn or heat damage.
Baunegård	c. 250–300 AD	Cattle	No	Produced by stretching: parchment-like. Traces of cinnabar.
Tira	c. 850 AD	Cattle	No	May have been produced to be hard and water resistant. Parchment-like.
Bj 850, facing	c. 900–1000 AD	Deer* / sheep?	Yes	Possibly tanned with birch, larch, pine, spruce or willow.
Bj 850, rim	c. 900–1000 AD	Cattle	Yes	Possibly tanned with birch, larch, pine, spruce or willow. Dense leather structure.

Tab. 10. Table of Summary: Evaluation of animal species and treatment of hide.
'?' signifies peaks of low intensity, or low signal to noise threshold; *red or fallow deer or elk.

which is more difficult to penetrate than a surface of tanned hide that has not been made stiff by, for example, heat treatment or a surface treatment of pitch or tar. The dense leather structure of the rim from the shield of Bj 850, however, must nevertheless have been deemed suitable for reinforcing the edge of the shield. It is possible that a relatively soft shield rim was preferred. In particular, it is worth noting that there is a combative advantage in having a shield into which the opponent's weapon could become stuck. While untanned hide is typically stronger, such a facing will make the shield more vulnerable to moisture and be more prone to change in its dimensions when wet; however, this can be avoided by treating the hide with pitch or tar. The parchment of the shield from Tira appears to have been treated in such a fashion, judging from the tar like substance found on the samples which indicate that the skin may have been made water repellent. This would have prevented, or at least limited, moisture from reaching the wooden shield board and the vegetable layer (of grass or bast fibres) below the hide facing. Untanned hide can also be treated with fat or oils, through which it can attain some of the same properties as vegetable tanned hide, i. e. making it softer, more flexible and more resistant to moisture, but simultaneously less resistant to cuts and stabs. Given the above, there can be little doubt that the different hide products would have significantly contributed to the shield constructions examined in this study, although in a variety of ways.

Conclusion

As witnessed, this investigation is composed of several different studies, each of which has been able to illuminate different aspects of the nature of hide products in Germanic shields and prehistoric shield constructions in general. Despite a good understanding of other prehistoric shield components and the widespread consensus concerning the important role of hide in shields, it is evident that the nature of such hide products has eluded research in the past. Being the first specialised investigation into this subject, this project is an initial answer to the call for more data regarding hide products in Germanic shield constructions and thus also a more complete understanding of such shields.

By adopting and developing a new set of methodologies for determining the nature of such hide products, this project has yielded novel information regarding both animal species and the treatment of the hide, including tanning processes. To investigate such intricate details, a variety of microanalyses were conducted on hide samples collected from a selection of Germanic shield finds (from Denmark and Sweden) and, for comparison, one Curonian (from Latvia), dating to c. 350 BC–AD 1000. Modern conservation compounds like synthetic glue or other polymers may influence the material analysis of archaeological samples, especially in cases where these are difficult to extract. Notwithstanding such challenges, the results reveal which type of hide product was used for each shield – i. e. tanned (leather) or untanned (rawhide / parchment) – and from which animal species the hide originated. Out of our samples, both tanned leather and parchment seems to have been applied to the shields, stemming mostly from cattle, although one shield facing possibly stems from deer / sheep; interestingly, the rim from the same shield is of cattle hide. Cattle and calf skin are dense, firm skins and, with the age of the animal, the skin grows thick. Vegetable tanned leather is relatively soft and flexible compared to untanned materials, which normally becomes stiff and inflexible if not softened. However, if treated with lipids in the form of oil or fat, untanned hide can obtain flexibility. Both vegetable tanned leather and untanned hide or skins are soft and flexible in wet condition and can easily be stretched around a wooden shield; both may harden and shrink to their original size after drying. An important result of the study is the fact that the tanning processes were deliberate and that the natural environment is not sufficient for a thorough tanning of the skin, as previously seen by the only partially tanned Grauballe Man. Already in the early Iron Age, skilled craftsmen had been involved in weapon production.

The sample size of this study is admittedly far too small to conclude anything definite with regards to chronological or regional variations in shield construction practices; however, the value of the methods and results presented in these pages are nonetheless evident. In particular, the data presented in this paper offer a much clearer understanding of the use of hide components in shields and shield constructions in general. Accordingly, it is now possible to build satisfactory authentic replicas of both Iron Age and Viking Age shields with references to actual finds. This calls for a re-evaluation of previous experimental trials with replica shields but also for entirely new archaeological experiments about how shields were constructed and their use in combat. Such experiments, in turn, are liable to contribute to our current understanding of the hide components and shields examined in the course of this project.

Ultimately, we hope that the current investigation will provide a frame of reference for future studies and evoke a fresh interest into hide products in Germanic shields and prehistoric shields in general. This not only entails applying the methodology to other shield finds where hide has already been identified, but also a re-examination of shields for traces of hide and other organic material, even though such fragments may not be immediately discernible. The importance of re-evaluating old shield finds became especially evident in the course of this project when indirect traces of hide were observed on some of the shields from Hjortspring (c. 350 BC), a significant detail which has escaped observation since 1921! Rather than being a definite work on hide components in shields, therefore, the issues and materials discussed in this paper should instead be regarded as an attempt at bringing attention to the significance of this topic and providing a basis for future research projects.

Acknowledgements

We thank the Carlsberg Foundation (grant CF15-0573) and the Danish National Research Foundations Grant DNRF119 (Centre of Excellence for Urban Network Evolutions) for supporting our research. A special thanks to the following museums for granting us permission to obtain samples from the archaeological shield finds in their collection: National Museum of Denmark, Swedish History Museum, Vesthimmerlands Museum and the National History Museum of Latvia. Furthermore, we like to thank former associate professor at School of Conservation, Copenhagen, Henriette van Lanschot Jettie, for her optical microscopical and SEM-EDS analysis of pigments, associate professor, PhD, Nanna Bjerregaard Pedersen, School of Conservation, Copenhagen, for her identification of wood and associate professor, PhD, Kim Pilkjær Simonsen, School of Conservation, Copenhagen, for his help with the ATR-FTIR spectra figures.

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Shields and hide. On the use of hide in Germanic shields of the Iron Age and Viking Age

Summary · Zusammenfassung · Resumé

SUMMARY · Hide has long been recognised as an essential component of shield constructions of the Iron Age and Viking Age in Northern Europe. Despite many well-preserved shields finds, however, several fundamental questions regarding the nature of such hide products have hitherto gone unanswered. How was the hide treated before having been applied to the shield and what animal species were chosen for the material? Both factors are essential to consider when interpreting prehistoric shields and their durability as well as combative techniques and tactics.

The project presented in this paper has sought to illuminate these factors by conducting multiple microanalyses and ZooMS analyses of hide samples from four well-preserved Iron Age and Viking Age shield finds. The study has yielded novel information regarding shield constructions in Northern Europe and is the first to successfully determine the nature of hide products in such shields. When coupled with past research, the results thus provide an unparalleled and more-or-less complete understanding of the investigated shield constructions. All in all, the new methodologies and findings presented in this paper not only stimulate central discussions of weaponry technologies and warfare practices in Northern Europe; they also allow for a range of future investigations, particularly in the fields of archaeological science and experimental archaeology.

ZUSAMMENFASSUNG · Tierhäute gelten seit langem als wesentliche Elemente in der Herstellung von eisen- und wikingerzeitlichen Schilden Nordeuropas. Trotz vieler gut erhaltener Funde blieben diverse grundsätzliche Fragen bezüglich der Beschaffenheit dieser Produkte bisher jedoch weitgehend unbeantwortet. Wie wurden beispielsweise die Tierhäute behandelt bevor sie auf die Schilde aufgezogen wurden und welche Tierarten wurden bevorzugt? Beide Aspekte sind sehr wichtige Faktoren in der Interpretation prähistorischer Schilde und deren Widerstandsfähigkeit sowie der damit verbundenen Kampftechniken und taktischen Überlegungen.

Das Ziel des in diesem Beitrag vorgestellten Projekts war es, diesen Fragestellungen mittels Mikro- sowie sogenannten ZooMS-Analysen an Tierhautproben von vier gut erhaltenen eisen- bzw. wikingerzeitlichen Schildfunden nachzugehen. Die Untersuchung brachte neue Erkenntnisse zur Schildkonstruktion in Nordeuropa. Zudem ist es nun zum ersten Mal gelungen, die Beschaffenheit der Tierhautprodukte solcher Schildfunde genauer zu ermitteln. Im Zusammenspiel mit früheren Untersuchungen bieten die Resultate einen bisher unerreichten und praktisch vollständigen Erkenntnisstand zur Konstruktion der untersuchten Schilde. Alles in allem haben die in diesem Beitrag präsentierten neuen Methoden und Erkenntnisse nicht nur wichtige Diskussionen zur Waffentechnologie und zu den Kriegspraktiken Nordeuropas angeregt, sondern auch den Weg für eine Vielfalt an weiteren Untersuchungen, vor allem in den Bereichen der naturwissenschaftlichen und experimentellen Archäologie, geebnet. (S. H.)

RÉSUMÉ · La peau passa longtemps pour une composante essentielle des boucliers de l'âge du Fer et de l'époque des Vikings en Europe septentrionale. Cependant, malgré le nombre de boucliers en bon état de conservation, certaines questions fondamentales concernant la nature de ces peaux sont restées sans réponse. Comment fut traitée la peau avant d'être tendue sur le bouclier et sur quelle espèce animale fut-elle prélevée? Ces deux

facteurs jouent un rôle essentiel dans l'interprétation des boucliers préhistoriques, de leur résistance, ainsi que des techniques et tactiques de combat.

Le projet présenté ici s'est efforcé d'élucider ces facteurs en menant plusieurs microanalyses et analyses ZooMS d'échantillons de peaux provenant de boucliers bien conservés de l'âge du Fer et de l'époque des Vikings. Cette étude a livré de nouvelles informations sur les techniques de construction de boucliers en Europe du Nord et détermine pour la première fois la nature des peaux utilisées. Les résultats, combinés aux recherches précédentes, permettent ainsi une compréhension inégalée et plus ou moins totale des techniques de construction des boucliers étudiés. En somme, les nouvelles méthodologies et découvertes présentées dans cet article non seulement stimulent des discussions essentielles sur les technologies de l'armement et les pratiques guerrières en Europe septentrionale, mais ouvrent également la voie à de nouvelles recherches, particulièrement dans les domaines de l'archéométrie et de l'archéologie expérimentale. (Y. G.)

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Appendix 1. Dendroanalyses of the shields from Baunegård, Denmark, and Tira, Latvia (N. Bjerregaard Pedersen)

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Vedidentifikation

af Nanna Bjerregaard Pedersen

Vedbestemmelse af prøverne:
Tira S8, Tira S9, Tira s 11 og Baunegård (Foto 4, rød)

Metode:
De fire træprøver blev opfugtet med vand og tynde snit (20-30 µm), i de tre karakteristiske retninger: tvær-, tangentiel- og radialsnit, blev skåret med barberblad. Snittene blev placeret på objektglas, indlejret i vand og dække med et dækglas. Snittene blev observeret i gennemlysmikroskop. Vedbestemmelse foretages ved hjælp af Schweingruber (1990), Anagnost et al. (1994) og Hather (2000).

Resultater:
Tira S8
Tværsnit viser ensartet mønster af trakeider karakteristisk for nåletræ, samt harpikskanaler, hvor epitelcellerne ikke er bevaret. Meget nedbrudt nåletræ med mange svampehyfer tilstede i veddet. Det er ikke muligt at vurdere om overgangen fra vårved til høstved er abrupt eller gradvis.
I længdesnit (radial og tangentiel) ses marvstråle trakeider og udelukkende solitære ringporer, men ingen spiralfortykkelse. I krydsfeltet ses små picioide eller taxidoide porer. Pga. den høje nedbrydningsgrad er det ikke muligt at bestemme typen af krydsfeltsporer.
Konklusion: Veddet er nåletræ, enten *Picea abies* (rødgran) eller *Larix* (lærk)

Tira S9
Tværsnit viser ensartet mønster af trakeider karakteristisk for nåletræ. Meget nedbrudt nåletræ med mange svampehyfer tilstede i veddet. Det var ikke muligt at erkende harpikskanaler eller at vurdere om overgangen fra vårved til høstved er abrupt eller gradvis.
I længdesnit (radial og tangentiel) ses marvstråle trakeider og adskillige serate ringporer, men ingen spiralfortykkelse. I krydsfeltet ses små picioide eller taxidoide porer. Pga. den høje nedbrydningsgrad er det ikke muligt at bestemme typen af krydsfeltsporer.
Konklusion: Veddet er nåletræ, enten *Larix* (lærk) eller *Picea abies* (rødgran)

Tira S11
Ekstremt nedbrudt prøve. Fornemmer cellevægge og en længderetning, mange hyfer både i længderetningen og på tværs fra celle til celle. Tegn på ringporer, men usikkert.
Konklusion: Sandsynligvis nåletræ

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Baunegård, foto 4 rød
Ekstremt nedbrudt prøve. Løvtræ med karceller med stigeperforation, få stiger med stor afsted som i eksempelvis *Corylus avellana* (hassel)
Konklusion: Løvtræ

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Appendix 2. Colour and SEM analyses

Jettie van Lanschot

Optical microscopy

Three small samples (Baunegård-a and -b and Borremose) had traces of pigment. They were documented using optical microscopy (OM, Leica DM4M) with reflected visible light and dark field.

Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX)

A Hitachi S-3400N SEM equipped with a Bruker detection system was used to obtain elemental information. The analyses were performed under low vacuum, 25 Pa, on uncoated samples. Spectra and elemental maps were recorded using 20-kV voltage, 50-µA probe current and 10-mm working distance. The EDX system, QUANTAX 200, was equipped with two 30 mm^2 SDD X-ray detectors (XFlash® 6| 30 Silicon Drift Detector) which gives a better analytical geometry for rough surfaces. Semi quantitative EDX was performed with the internal references included in the Bruker Quantax software

Results

Optical microscopy

Baunegård-a and Baunegård-b clearly showed traces of red pigment, either in a layered structure or as particles in the archaeological matrix *(fig. 22)*. Borremose showed some very faint blue particles but no traces of red pigment. The sample consisted mostly of soil *(fig. 23)*.

SEM-EDX

For Baunegård-a and Baunegård-b several points were chosen on the highlights of the backscatter picture for the detection of elements. The spectra showed the elements semi-quantitatively. The BSE picture *(fig. 24)* contains elemental information, as different elements are displayed as varying grayscales. The heavier the element the more signal it emits, producing the highlighted areas on the picture. The picture therefore shows the distribution of the pigment as highlighted areas. The points marked on the picture were analysed with EDX.

The Borremose sample showed rather poor spectra with elements at rather low levels. The mapping technique was used to detect any local concentrations which could imply the presence of a pigment. This was not the case.

The results of all analysis on the three samples are resumed in *table 11*.

Discussion

The analysis of the Baunegård-a and Baunegård-b samples showed that they were inhomogeneous. However, when the ratio between mercury (Hg) and sulfur (S) is calculated stoichiometrically in each analysis, it is evident that the mercury and sulfur atoms are

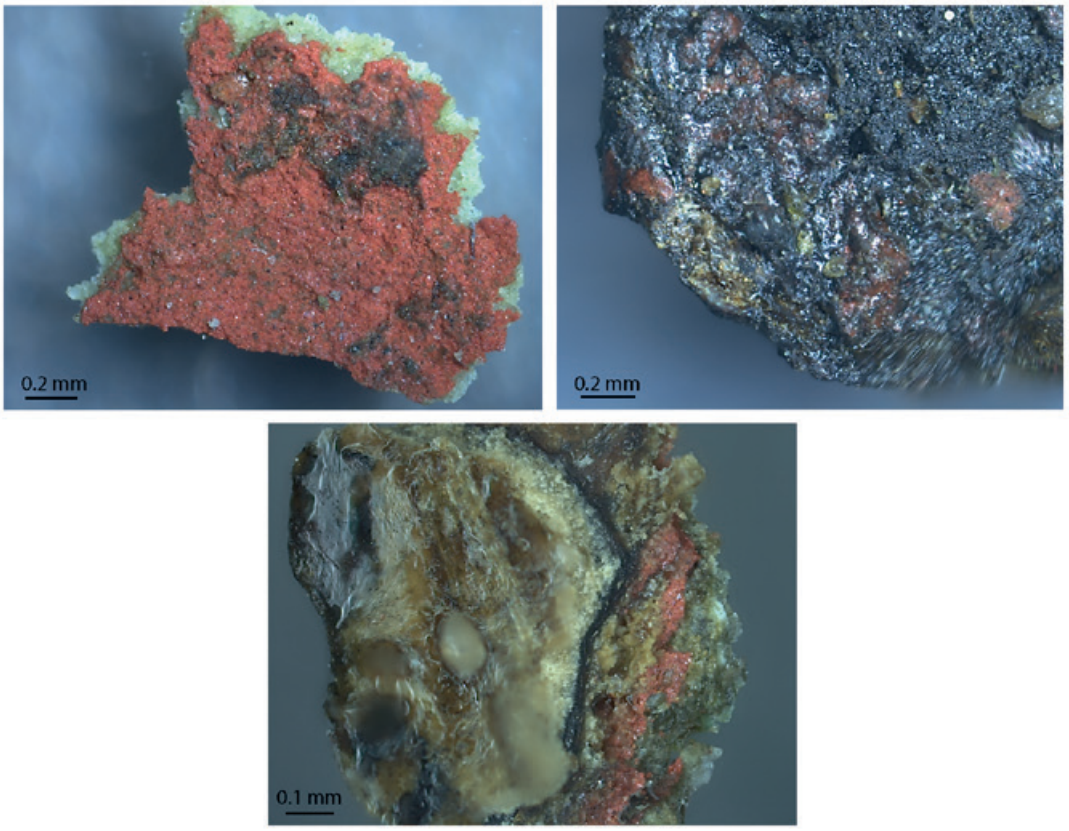

Fig. 22a–c. Baunegård-a and Baunegård-b clearly showed traces of red pigment, either in a layered structure or as particles in the archaeological matrix. Dark-field microscopy.

equivalent. The pigment is cinnabar/vermilion (HgS), which is consistent with the colour observed under the optical microscope.

Baunegård-b contained copper (Cu) and tin (Sn) situated on the same spot. Tin is the alloying element in bronze and the elements found could derive from the metallic rim of the shield or another artefact found near the sample.

All the samples were covered or mixed with sandy soil, and O and Si are the main components found in silica.

The elements at trace levels can be explained as elements normally found in soil or in the mineral cinnabar. Cinnabar can contain impurities from other minerals such as calcite, quartz, and pyrite, i. e. containing Ca, Si and Fe (Frost et al. 2002; Nöller 2015).

The faint blue colour spots on the Borremose sample were analysed using the map technology and several single spot analyses. We looked for vivianite and Egyptian blue. The former is found very seldom and the latter more often until AD 350–400 (Klindt-Jensen 1959; Christensen & Bregnhøj 2018). The presence of vivianite ([Fe]3[PO4]2.8H2O) could not be confirmed due to the lack of phosphorus concentrated in the specific areas where blue particles were observed. Iron was spread homogenously throughout the sample and probably originates from iron occurring naturally in soil or from iron corrosion products.

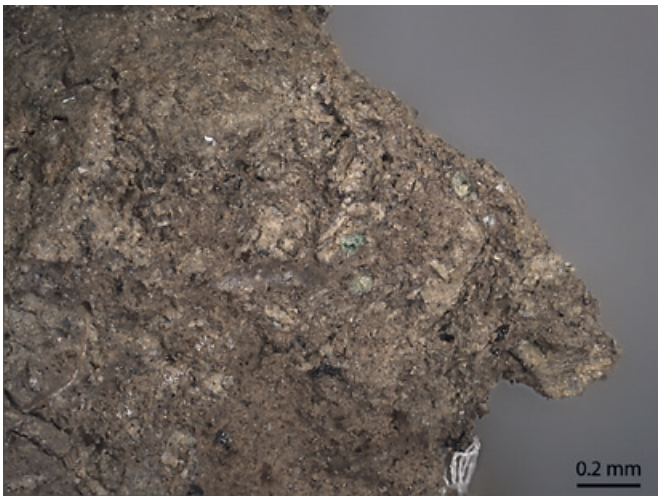

Fig. 23. Borremose. The sample mostly showed soil. Some very faint blue spots are hardly discernible.

Sample	Elements	Trace elements
Baunegård-a	O, S, Si, Cu, Hg	(Al), (Ca), (Fe)
Baunegård-b	O, S, Cu, Sn, Hg	(Al), (Si), (P), (Ca), (Fe)
Borremose	O, Si, Cu, Fe, Al	(P), (S), (K), (Ca)

Tab. 11. The elements in italics elements are present in relatively high levels. Elements in parentheses are present at trace levels (< 2 weight percent, normalized). At least three analysis were performed on each sample.

Egyptian blue (CaCuSi4O10), which is a very stable pigment can be excluded as a possibility as the stoichiometrical ratio between calcium (Ca) and copper (Cu) is wrong. Furthermore, Egyptian blue does not fade easily like vivianite (Christensen / Bregnhøj 2018).

Synthesis

It is not the scope of this article to distinguish between the synthetic HgS, called vermilion, or the mineral cinnabar, HgS, but it is known that cinnabar has been synthesized since antiquity as described by Theophrastus of Eresus (BC 371–286) and Vitruvius in the first century BC. The latter described making of vermilion by simply crushing cinnabar, followed by washing and heating until a bright colour occurred (Gettens et al. 1993; Siddall 2018). Nor did we analyse for any binding media, if any were left, which could consist of at least one organic compound, as this requires other techniques such as gas chromatograph by mass spectrometry (GC-MS) for identification (Siddall 2018).

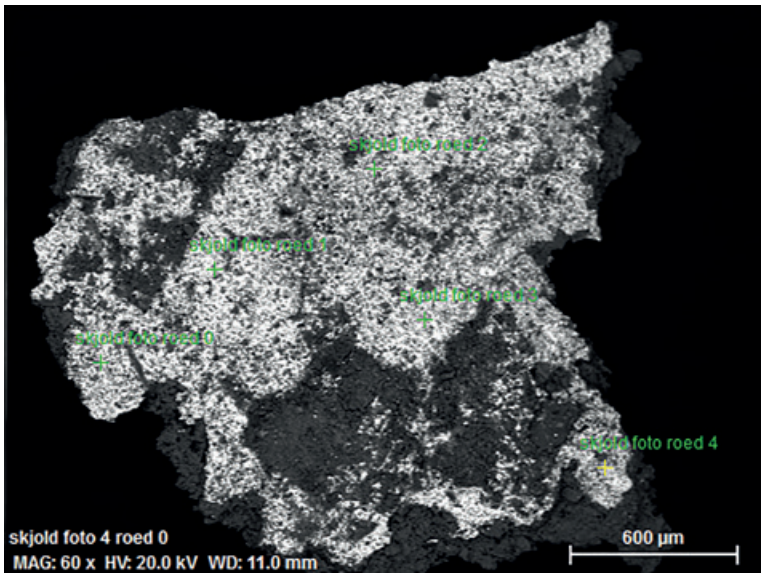

Fig. 24. Backscatter (BSE) picture of Baunegård-a. The BSE picture contains elemental information, as different elements are displayed as varying grayscales. The heavier the element the more signal it emits, i. e. highlighted areas on the picture. The picture therefore shows the distribution of the pigment as highlighted areas. The points marked on the picture were analysed with EDX.

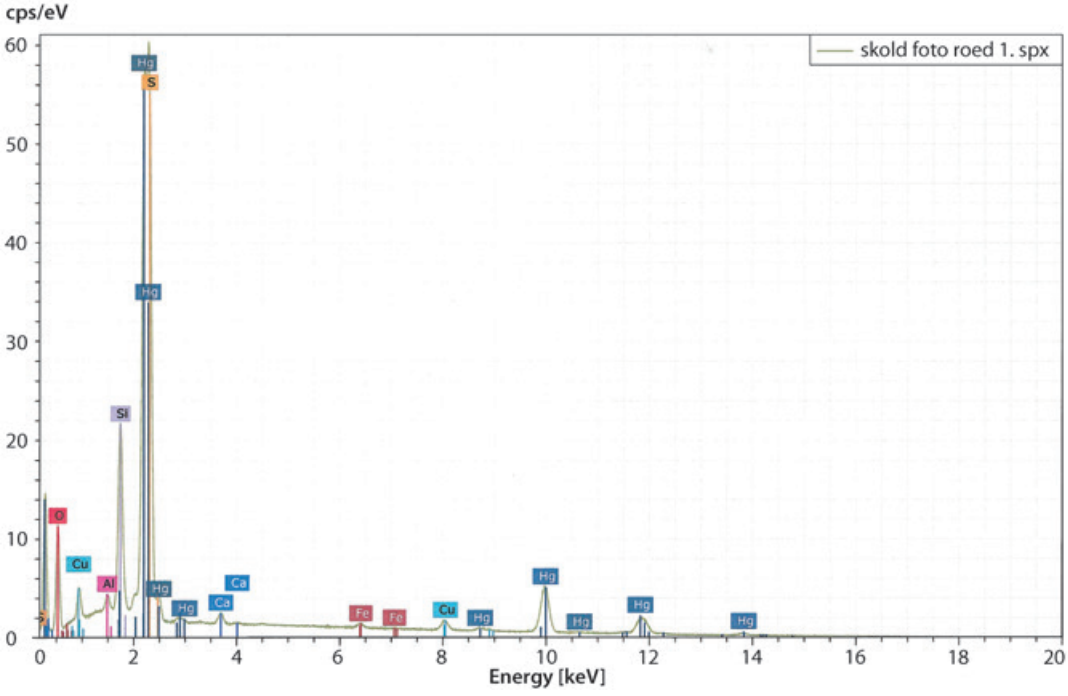

Fig 25. The spectrum from Baunegård-a, point skjold foto roed 1 (EDX analysis). The analysis shows the presence of cinnoba containing some trace elements deriving from the mineral or/and the surrounding soil.

In Europe cinnabar (HgS) is found as a bright red mineral which is locally abundant in Almadén, Spain, and several other regions, including notably several sources in Central Europe. Especially for the Iberian Peninsula, localities from the Neolithic onwards have been reported for the abundant exploitation of cinnabar as a medicine, a preservative, and as a red pigment for body paint and ceramics (Martín-Gil et al. 1995; Emslie et al. 2015). In Central Europe it is reported from 6th-millenium BC Vinca sites both on painted objects and in pots (Gajić-Kvaščev et al. 2012).

In Denmark pigments have mainly been analysed on archaeological finds from the Viking Age and later but have also been identified on earlier finds. Vermilion is reported as a red pigment on the shields from Illerup Ådal (Jensen 2003) while Egyptian blue on shields has been demonstrated from Roman Iron Age until AD 350 on several finds in and outside Denmark (Klindt-Jensen 1959; Rosenqvist 1959; Capelle 1986; Becker et al. 2010). Pigments have also been identified on the Viking Age shield board from Trelleborg, where traces of red iron oxides and lead carbonate were detected in very small amounts (Christensen 2013). The famous Hørning plank, dated to about AD 1060, also indicated that vermilion had been used as a red pigment (Christensen 2006).

In general, the analysis of pigments has posed some difficulties both because the samples often have undergone a conservation treatment, and because the sample materials are extremely small.

Vivianite is not a stable pigment and is easily converted into another compound. Vivianite has only been detected in a very few places on walls and wood in early Medieval times (Christensen 2018). The easy degradation of the blue pigment vivianite has made it even more difficult to detect (Christensen 2018).

However, the detection of vermilion in Baunegård a and b leaves little doubt, while the Borremose sample does not contain any, or too little pigment to make a proper analysis.

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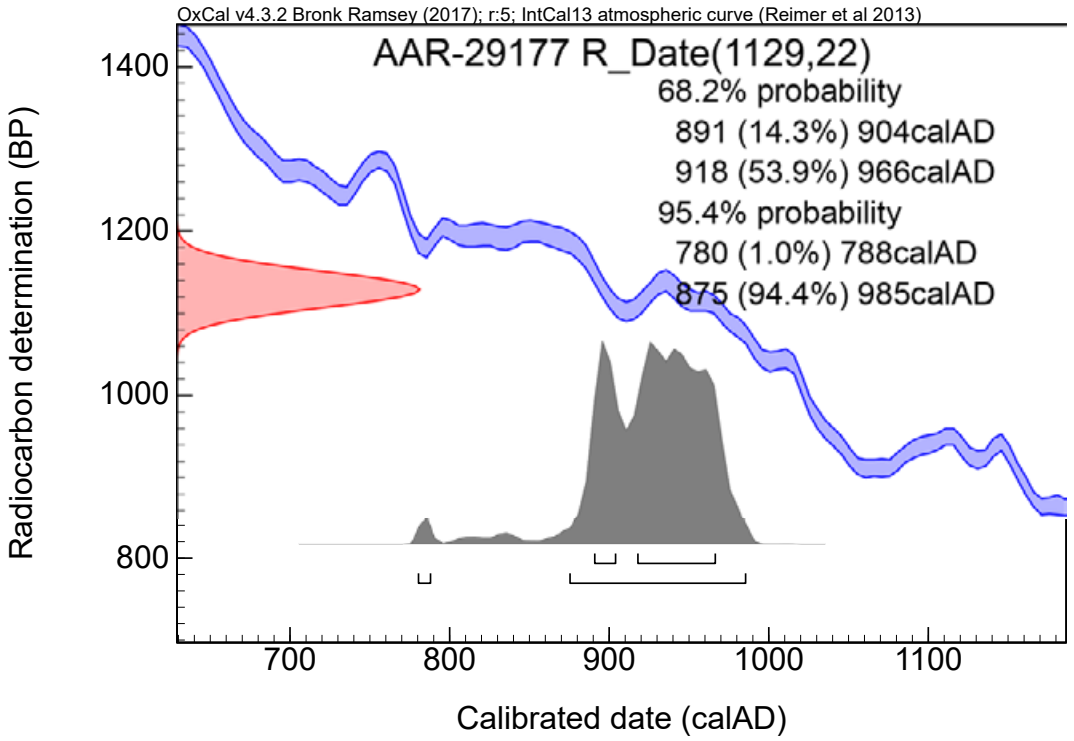
Appendix 3. ^{14}C Analyses of Tira (Aarhus AMS Center)



App. 3. ^{14}C Analyses of Tira (Aarhus AMS Center).