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COOKING IN PESTENACKER – EVIDENCE FROM ORGANIC RESIDUES IN VESSELS FROM ONE HOUSEHOLD IN A LATE NEOLITHIC WETLAND SETTLEMENT IN BAVARIA (3496-3410 BC)

The Late Neolithic wetland settlement of Pestenacker (Lkr. Landsberg am Lech / D) in southern Bavaria is well known for its extraordinary preservation of wooden house structures and thick cultural layers (Schönfeld 2009). The enclosed settlement was used only for a short period between 3496 and 3410 BC (Bauer 2009, 179-181). Since 2011, the location is part of the UNESCO World Heritage Project »Prehistoric Pile Dwellings around the Alps« and further excavations are no longer possible.

The ceramic assemblage excavated at Pestenacker was thoroughly studied for typo-chronological characteristics and for indications of trade and exchange (Limmer 2014). It shows a form spectrum comparable to the »Altheimer Group« as defined by J. Driehaus (1960). Although J. Driehaus proposed possible functions for the various pot types of Pestenacker, no study was ever undertaken to specifically address the actual Neolithic use of vessels from the Altheimer form groups. The ceramic assemblage of Pestenacker offers an optimal opportunity for such a study because many individual vessels could be restored, their dating is extremely precise, their find location within the house structures is known, and many organic surface residues are preserved.

In this paper, organic residue analysis was applied in order to identify the way a group of large vessels (»funnel pots« and »lug vessels«) from a single household was used. This study combines micro-botanical analysis of plant remains using scanning electron microscopy (SEM) with chemical analysis using Fourier-transform infrared spectroscopy (FTIR) and direct temperature-resolved mass spectrometry (DTMS). This combined approach has been proven effective in determining the original foods and non-foods prepared in Neolithic vessels from the Netherlands (see for more references Oudemans / Kubiak-Martens 2014; Raemaekers / Kubiak-Martens / Oudemans 2013; Kubiak-Martens / Brinkkemper / Oudemans 2015). This study aims to identify the original vessel contents of the large pots from Pestenacker and give a detailed insight in the nature of food and non-food preparation, the use of the larger pot types as well as identify activity areas within the household. This way the theories of the original excavators can be checked using independent evidence.

THE PESTENACKER SETTLEMENT

When in 1934 the Loosbach, a small brook near the village of Pestenacker, was straightened, workers came across the remains of a house belonging to the Late Neolithic Altheim Culture and dated to about 3800-3400/3300 BC (Reinecke 1935; Schönfeld 2009). Later excavations of the Bayerisches Landesamt für Denkmalpflege, funded by the Deutsche Forschungsgemeinschaft until 1993, uncovered an enclosed settlement (Schönfeld 2009) founded in the year 3495 BC (Bauer 2009).

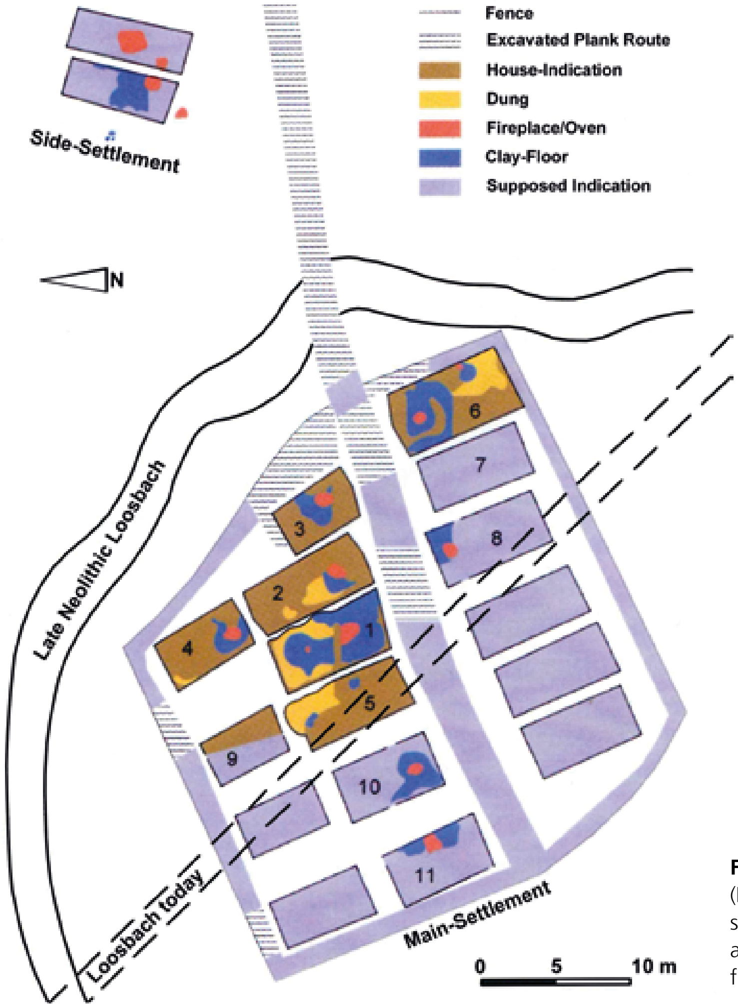

Fig. 1 Map of Late Neolithic Pestenacker (Lkr. Landsberg am Lech / D). Overview of the settlement of Pestenacker – main settlement (phase 1A) and side-settlement. – (After Schönfeld 2009, 137 fig. 1).

The main settlement consisted of 16 buildings (**fig. 1**). A plank route leads from the main settlement to a small group of houses, the so-called side-settlement. Of the buildings within the main enclosed settlement, House 1 had the most complete floor plan. According to G. Schönfeld House 1 was about 8 m × 3.90 m in size and was built in 3495 BC (phase 1A). After a fire in the year 3491 BC, it was rebuilt in the same position and in approximately identical construction (phase 1B/1C). On the southeastern side of the house, was a door leading into a 1 m wide corridor, which was separated from the main room by an internal partition (**fig. 2**). In all house phases, an oval oven stood in the main room. In the first phase of the building (phase 1A), there was one other room in the northern part of the house, which had a small fireplace. In the second phase of the building (phase 1B/1C), the northern room was divided into two smaller rooms. In the northwestern room, a fireplace was visible roughly at the same place as in the first house phase. In the northeastern room, a thick dung layer was found on a floor of birch slats. This room was probably equipped with a door leading into the rear courtyard. This evidence suggests that the northeastern room was used for seasonal housing of small livestock. The settlement was excavated in natural layers and finds were registered to the quarter square meter (Limmer 2009). For this reason, the stratigraphic position is known for almost every find, as is the position of the objects in the excavation area.

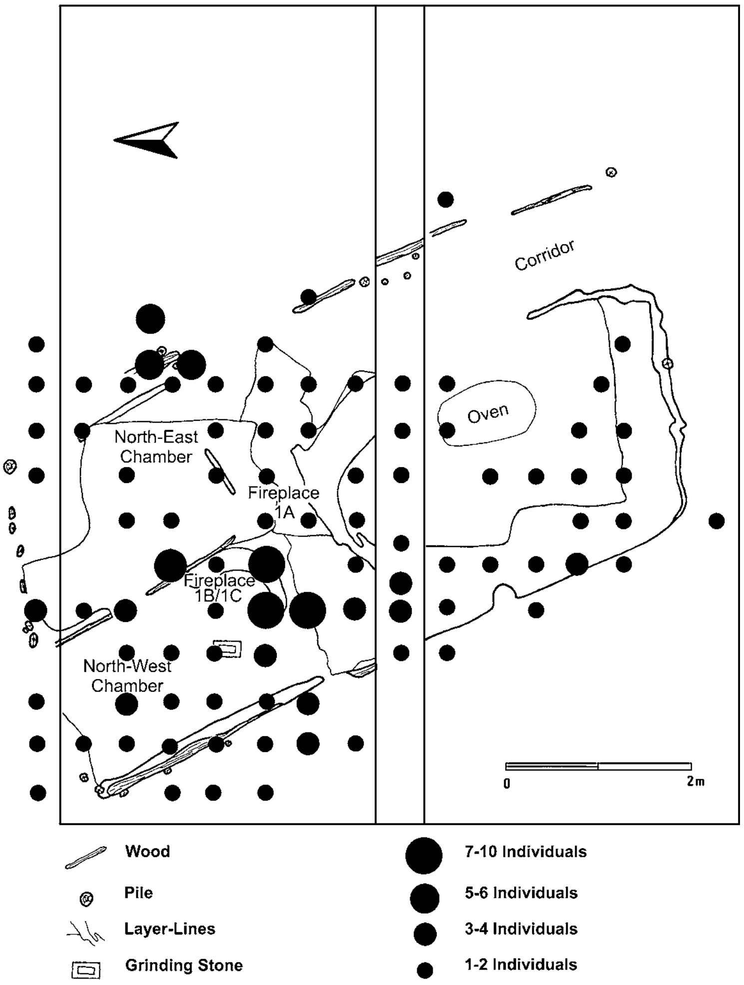

Fig. 2 Distribution of vessel units per quarter square meter in House 1 (n = 177). The sherds of each vessel unit are frequently highly shattered and spread over several square meters. The indicated vessel location was the quarter square meter in which most of the sherds of one individual were discovered. The edges of the excavation pit are indicated, and individuals shown outside the excavation pit were found in the profile of the pit. – (After Schönfeld 1991, 21 fig. 21).

PESTENACKER CERAMICS

The first comprehensive study of the Altheim ceramics was published by J. Driehaus (1960) and included the material found in Pestenacker in 1934. Typical characteristics of the Altheim ceramics are the arcaded rim and a slurry coating on the exterior surface of the vessel and are most frequently seen on funnel pots (**fig. 3**). Further common technological characteristics of the Altheim ceramics are coil technology, a grog temper and a lack of ornamentation (Driehaus 1960, 70-75; Petrasch 1985/1986). About the Pestenacker 1934 assemblage, J. Driehaus (1960, 36-37) reports the presence of various types of ceramic vessels. The funnel pots are the most common type of ceramics, followed by bowls, flasks with four handles, lug vessels, jugs, cups, conical bowls and steep-walled beakers (**fig. 3**). These observations can be largely confirmed by the analysis of the Pestenacker ceramic material currently in progress (Limmer in prep.). However, the ceramics from Pestenacker also show some affinity with the ceramic material of the Upper Swabian Pfyn-Altheim Group. This kind of Neolithic material is now referred to as »Lech Group« (Limmer 2010). This intermediate position also applies to other object groups as well as to aspects of settlements and plant cultivation (Hilbig/Neef 1991).

The ceramics from Pestenacker are well preserved and between 300 and 400 vessel units (here called individuals) could be identified. Almost half of these individuals were found within House 1 or in the narrow alleyways directly around it. Due to the exceptional preservation and complete excavation of House 1, this

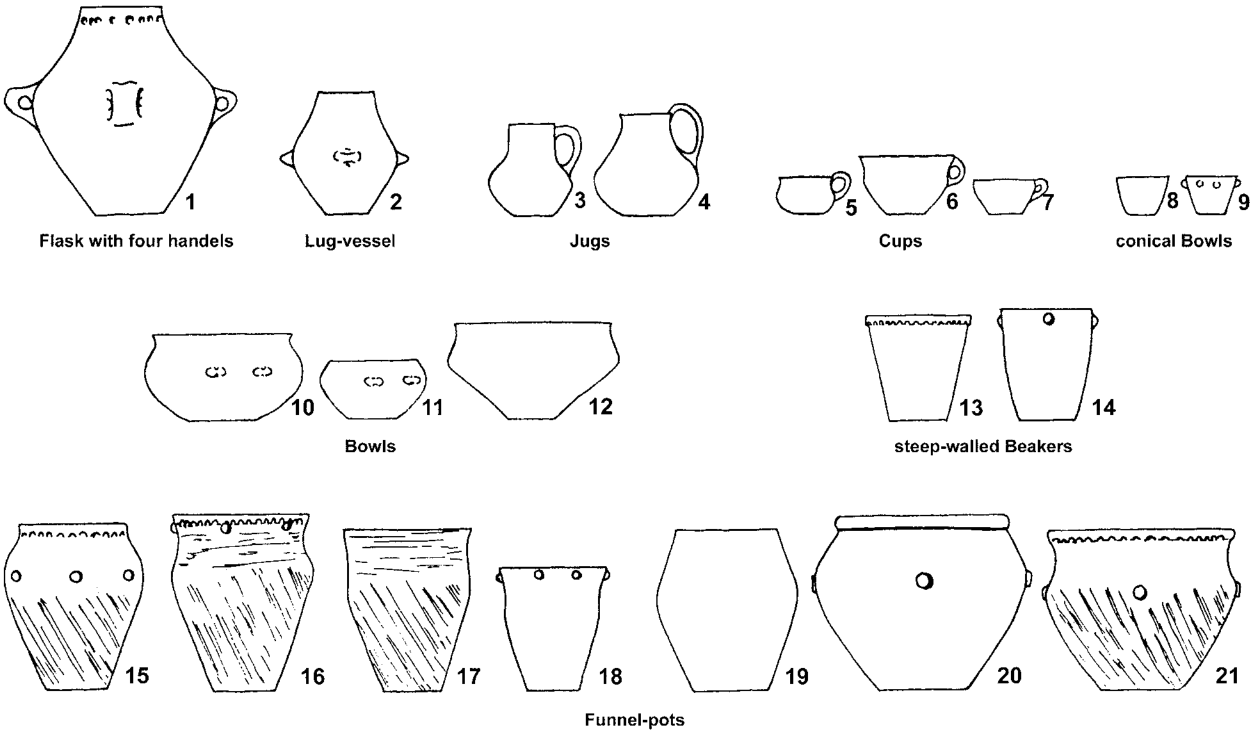

Fig. 3 Pestenacker (Lkr. Landsberg am Lech/D). Overview of the main vessel types. – (After Driehaus 1960, tab. 3).

sample no.	find context, house no.	vessel type	vessel no.	residue location	residue colour	residue thickness [mm]	SEM	FTIR	DTMS
PA01	H1	FP 15	G-235	upper wall	black	3	×	×	×
PA02	H4	FP 17	–	rim	black	1-2	×	×	×
PA03	H1	FP	G-120	rim	black	<1	×	×	×
PA04	side-settlement	FP	–	upper wall	black	1	×	×	×
PA05	H1	FP	–	wall	dark brown	3	×	×	×
PA06	H1	LV	G-270	bottom/ lower wall	dark brown	–	×	×	×
PA07	H1	FP 15	G-236	lower wall	dark drown	3	×	×	×
PA08	H1	FP	G-084	bottom/ lower wall	black	3	×	×	×
PA09	H1	FP/LV	G-222	–	black	1	×	×	–
PA10	H1	FP 20	G-170	wall	black	3	×	×	×
PA11	H2	?	–	wall	brown	4	×	×	×
PA12	H1	FP	G-167	bottom/ lower wall	black	2	×	×	–
PA13	–	–	–	–	transparent	<1	–	×	–

Tab. 1 Overview of the residue samples and analyses. The description includes the find context and house number, a description of the vessel including the vessel type (FP = funnel pot; LV = lug vessel) and vessel number and a description of the residue. The residue description contains information on the location of the residue on the vessel, residue colour and residue thickness.

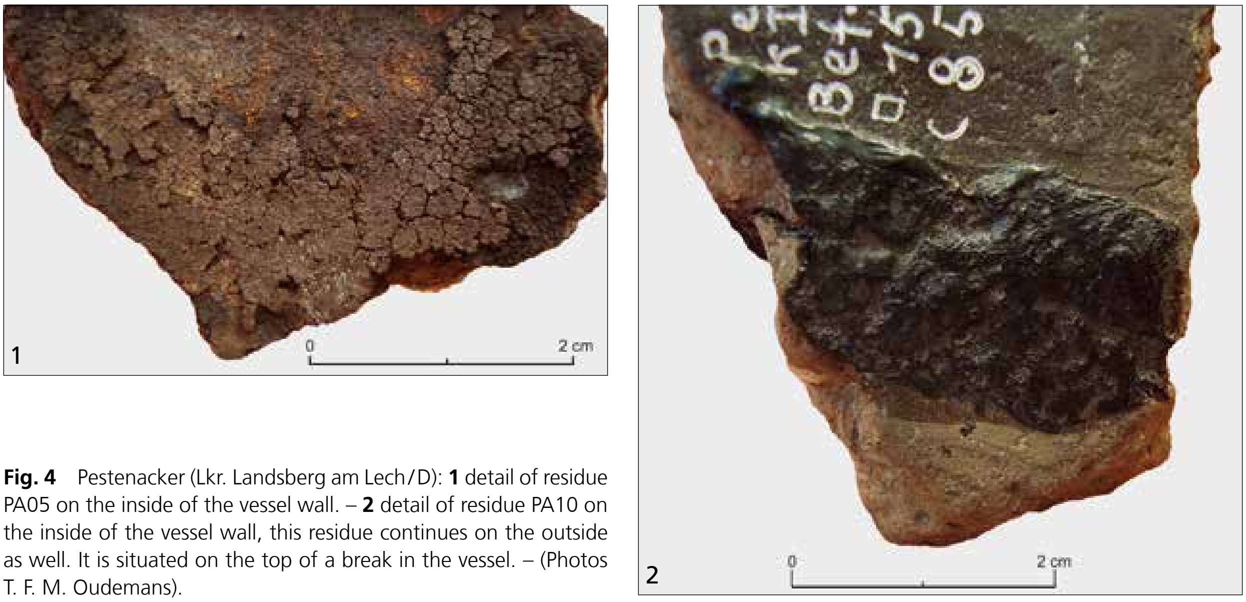

Fig. 4 Pestenacker (Lkr. Landsberg am Lech / D): **1** detail of residue PA05 on the inside of the vessel wall. – **2** detail of residue PA10 on the inside of the vessel wall, this residue continues on the outside as well. It is situated on the top of a break in the vessel. – (Photos T. F. M. Oudemans).

study focuses on the ceramics from this building (**tab. 1**). All stratigraphic layers of House 1 were summarized since no differences in the distribution of ceramic individuals could be seen. The mapping of the individuals in House 1 (**fig. 2**) shows that none was found in the corridor. In the main room, some sporadic vessels were scattered along the walls and around the oven. The main concentration of individuals occurs in the two rooms on the northern side of the house, especially near the fireplaces of phases 1A and 1B/1C. In phase 1B/1C, a grinding stone was found near the fireplace. In the original publication of Pestenacker, the northwestern room was assumed to be a kitchen (Schönfeld 1991).

ORGANIC RESIDUES

A total number of 177 individual vessel units, the majority of which were funnel pots, were found in House 1 (**fig. 2**). Many individuals (41) contained visible organic surface residues either on the exterior or on the interior vessel wall (see **fig. 4, 1-2**). The majority of the charred organic residues were found on funnel pots (27 individuals = 66 % of the residues). Two residues (5 %) were discovered on vessels that could be identified as either a lug vessel (G-270) or a funnel pot or a lug vessel (G-222). Of the remaining twelve residues, six were found on individuals of unknown vessel type, and the other six were distributed over other vessel types.

The material available for sampling consisted of groups of sherds belonging to the same individual. The sherds (sometimes originating from different quarter square meters) had been washed, dried, numbered and glued together to form individuals. A shiny transparent material could be detected on many fragments. It was assumed that this was a modern polymer applied for consolidation, and residues without such material were selected. Twelve residues were sampled and a sample of the transparent material was taken for comparison (**tab. 1**). The majority of the residues originated from House 1 and three residues were taken from vessels found in other locations (**tab. 1**).

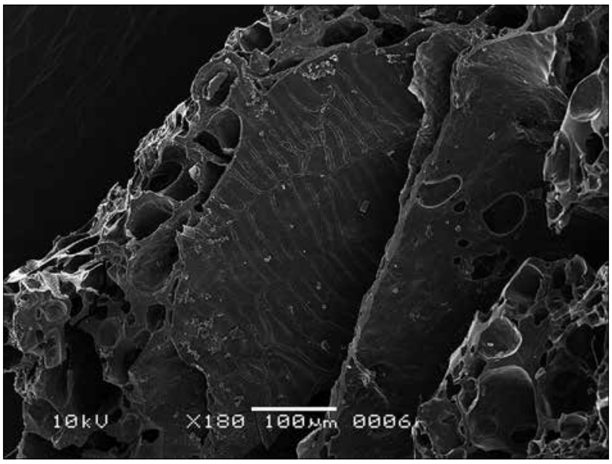

Fig. 5 Pestenacker (Lkr. Landsberg am Lech/D). SEM micrograph of transverse cell layer from emmer grain embedded in the residue matrix of PA01. – (Photo L. Kubiak-Martens).

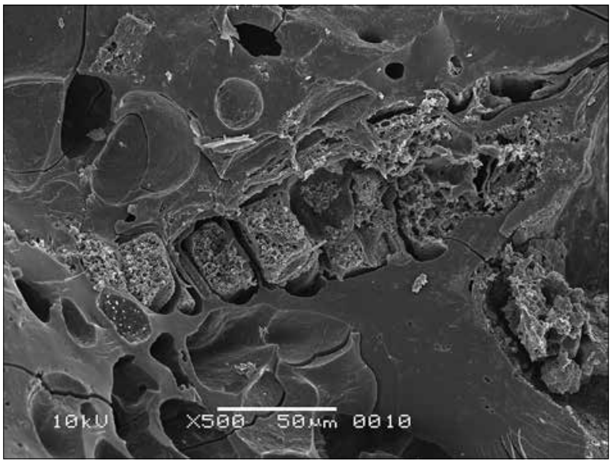

Fig. 6 Pestenacker (Lkr. Landsberg am Lech/D). SEM micrograph of a single-layered aleurone tissue (as to be seen in transverse section through the grain) of PA04, from emmer grain, embedded in residue matrix. – (Photo L. Kubiak-Martens).

MICRO-BOTANICAL RESIDUE ANALYSIS

Scanning electron microscopy (SEM) examination

Twelve residues were examined under an SEM microscope[1]. Specimens were first detached from the sherds, mounted on SEM stubs using carbon cement and subsequently platinum-coated and examined using a JOEL JSM-5300 SEM at magnifications of 80× to 1700×. For reliability, usually, three areas within each organic residue were sub-sampled and SEM-examined. SEM examination provides an opportunity to study both micro-morphological and anatomical features of very small fragments of plant tissue that have survived the process of food preparation and subsequent cooking and charring (e.g. fragments of cereal chaff, grain tissues, leaf or stem tissues, starch granules or particles of wood charcoal).

Results

The results of the SEM analyses are presented as scanning electron micrographs (**figs 5-10**) and summarized in the discussion (**tab. 4**). Six residues (50%) revealed information about plant food (PA01, PA04) and non-food components (PA08, PA10-PA12). The remaining six residues (PA02-PA03, PA05-PA07, PA09) revealed rather featureless matrices that provided no information about the original vessel contents. The six informative residues can be divided into Group A represented by residues with emmer grain tissue and Group B with residues containing wood charcoal.

Group A – residues with emmer grain tissue (PA01 and PA04)

Sample PA01 contained fragments of emmer bran (or pericarp tissue) embedded in the residue matrix. The identifications of the bran tissues were based on criteria established by U. Körber-Grohne and U. Piening (1980). The layers that were exposed in the matrix of sample PA01 are of the transverse cells (**fig. 5**). The

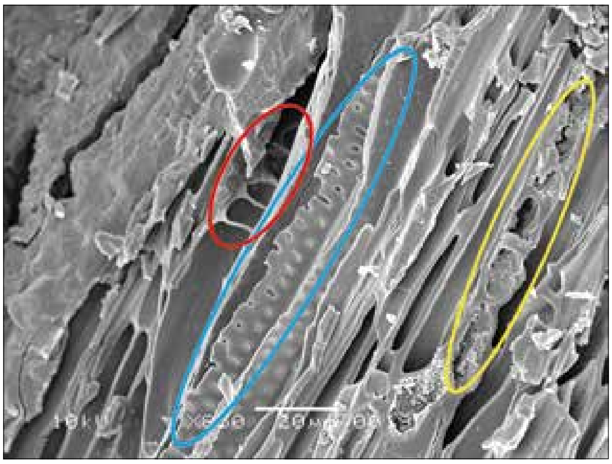

Fig. 7 Pestenacker (Lkr. Landsberg am Lech / D). SEM micrograph of hazel (*Corylus avellana*) wood charcoal embedded in the residue matrix of PA08 showing perforation plates (red circle), big pits in the vascular cells (blue circle) and a one-cell width wood ray (yellow circle). – (Photo L. Kubiak-Martens).

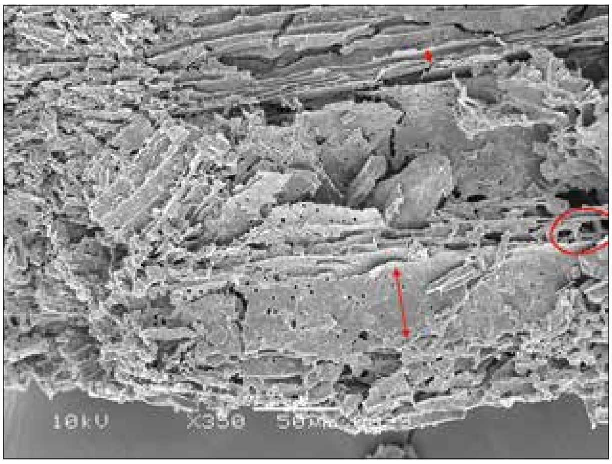

Fig. 8 Pestenacker (Lkr. Landsberg am Lech / D). SEM micrograph of sample PA11 showing deciduous wood structure in partly tangential section, with one-cell width wood rays marked with a red circle and vessels width and fibre width marked by red arrows. – (Photo L. Kubiak-Martens).

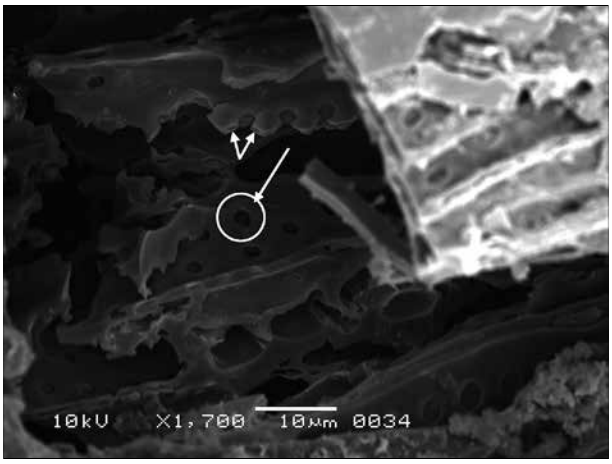

Fig. 9 Pestenacker (Lkr. Landsberg am Lech / D). SEM micrograph of wood charcoal embedded in the residue matrix of PA11, with pits in vascular cells, which are characteristic of coniferous wood (marked by a white circle and arrows). – (Photo L. Kubiak-Martens).

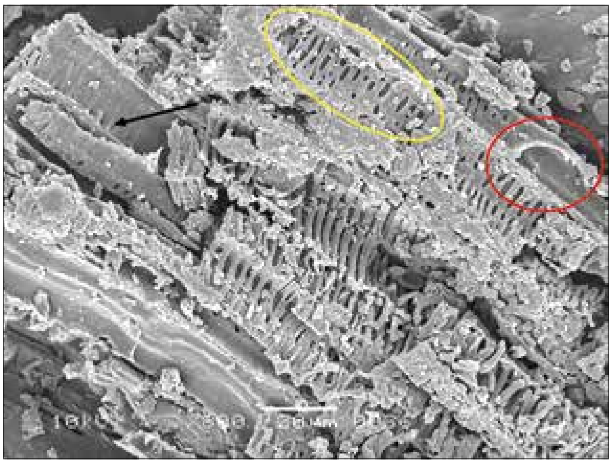

Fig. 10 Pestenacker (Lkr. Landsberg am Lech / D). SEM micrograph of fragment of deciduous wood structure embedded in the otherwise solid residue matrix of sample PA12. The photo shows a simple perforation plate (red circle), slightly oval pits originally situated in the same line but enlarged to broad pits over the full width of the vessel (yellow circle) and indications for spiral thickening in the wall of the vessel (black arrow). – (Photo L. Kubiak-Martens).

anatomy of the transverse cells and their size (80-100 µm long and 12-18 µm wide) in residue PA01 are characteristic of emmer grain (*Triticum dicoccon*). Although the anatomy of the transverse cells in emmer grain is similar to those of spelt (*Triticum spelta*), they are considerably longer in spelt (on average 155 µm) than in emmer.

Sample PA04 revealed fragments of an aleurone layer, which were embedded in an otherwise featureless matrix. The aleurone layer encloses the outer surface of the starchy endosperm in cereal grain. The aleurone cells store the grain's main protein content. The aleurone tissue preserved in PA04 was clearly single-layered (**fig. 6**). A single-layered aleurone tissue is characteristic for emmer grain and other wheat species, rye and oat. Barley meanwhile, is the only cereal with multiple aleurone layers and offers an unmistakable determination of fragmented barley grains in archaeological material (Körber-Grohne / Piening 1980). The anatomical features of transverse cells and the single-layered aleurone tissue indicate that the food cooked in this pot, at least partially derived from emmer grain.

Group B – residues containing wood charcoal (PA08, PA10-PA12)

In sample PA08 (**fig. 7**) small fragments of hazel (*Corylus avellana*) wood charcoal could be observed embedded in an otherwise featureless matrix. In some charcoal fragments, a small portion of a radial section of wood with a perforation plate was exposed (**fig. 7**, red circle). The scalariform perforations plate showed only four bars relatively far apart, which is characteristic for hazel wood (**fig. 7**, blue circle). The pits between the vascular cells were quite big, which also points to *Corylus avellana*. In addition, a typical hazel wood ray was also observed with a one-cell width and slightly heterogenic cells (**fig. 7**, yellow circle).

Wood charcoal fragments can also be seen in the matrix of PA11. Some exposed partially preserved tangential sections, showing wood rays of one-cell width (**fig. 8**, red circle). The difference in width of the fibres in comparison with the vascular cells makes clear that it is a deciduous wood. The size difference of the vascular cells and the fibres, the size of the pits and the clustering of vascular cells all point to either alder (*Alnus*) or hazel (*Corylus avellana*) wood. In addition, fragments of coniferous wood were embedded in residue PA11. In one fragment, the pits in the vascular tissue looked like bordered pits with the aperture (the opening of the pit) smaller than the chamber of the pit (**fig. 9**, arrows and circle). This kind of pits is typical for coniferous wood.

Residue PA12 also revealed wood charcoal embedded in a rather solid matrix (**fig. 10**). Some anatomical characteristics could be observed, however, the material was not sufficiently preserved to provide proper identification. Under the SEM, simple perforation plates were observed (**fig. 10**, red circle). The slightly oval pits, originally situated in the same line, became one big broad pit over the full width of the vessels. There is also an indication for a spiral thickening in the wall of the vessels (**fig. 10**, black arrow). All these anatomical features suggest deciduous wood, however, it is not wood from *Alnus* or *Corylus avellana*.

The wood fragments found in the residue PA10 could not be identified.

Discussion of botanical results (including charcoal identification)

In cereal grain that was processed and subsequently cooked, various tissues would have been exposed and partially preserved, while the starchy endosperm would usually turn into an amorphous matrix through the process of cooking and heating (Valamoti et al. 2008). In the samples PA01 and PA04, the presence of emmer grain bran and aleurone tissues, respectively, could be shown. This suggests that the food prepared in these pots consisted (at least partially) of emmer grain. No individual starch grains survived the cooking process. The only SEM evidence of their earlier presence is a completely fused residue matrix. The appearance of emmer grain in these samples coincides with previous archaeobotanical analyses. Emmer grain is the most commonly found grain in Pestenacker (Neef 1990; Bittmann 2001).

The presence of wood charcoal in four residues and the absence of plant or animal components in these samples, suggests that these residues were not food but some other product. In three residues it was clearly charcoal of deciduous wood that could be identified, including hazel (PA08), a mixture of deciduous (either alder or hazel) and coniferous wood (PA11), and deciduous wood (other than alder or hazel) in sample PA12. No further determination of the wood fragments found in residue PA10 was possible.

CHEMICAL RESIDUE ANALYSIS

Chemical analysis using FTIR and DTMS

Small samples of complex solid organic materials are notoriously hard to identify using analytical chemistry. However, using a combination of attenuated total reflection – Fourier-transform infrared spectrometry (ATR-FTIR) and direct temperature-resolved mass spectrometry (DTMS), even extremely small samples (60 µg) of solid ancient organic materials can render a great deal of information.

FTIR is used as a rapid screening technique to study the overall chemical composition of the residues. FTIR gives information about the nature of the residues, their homogeneity and their state of preservation. The use of pyrolytic techniques such as DTMS makes it possible to characterise the complete organic composition of the material, including volatile, extractable compounds and non-extractable solid compounds. The DTMS results give information about a broad range of compounds such as lipids, waxes, terpenoids, saccharides, small peptides, and protein fragments, and a broad range of thermally stable more or less condensed, polymeric components (commonly called »charred«, or »carbonised«).

Prior to FTIR analysis c. 10 µg of sample is applied to the diamond window and flattened using the pressure arm of the ATR unit. FTIR analysis is performed in the ATR modus of Fourier-transform infrared spectrometer (Thermo Scientific Nicolet iS5). The spectral resolution is 4 cm^{-1} and the spectral range is 4000-550 cm^{-1}. A total of 64 scans is collected per measurement and analysed using OMNIS software[2].

Prior to DTMS analysis c. 50 µg of sample is suspended in 5 µl of methanol and homogenised. A small amount of the suspension is applied to the filament of the mass spectrometer, dried and subsequently analysed. DTMS is performed in a DSQ II Thermoelectron instrument. Source temperature is 250 °C, the temperature programs initial current is 0 mA (5 s) ramping to 1000 mA (with 10 mA/s) and held at 1000 mA for an additional 20 s. The following MS conditions were applied: the electron ionisation energy was 16 eV, the scanning range was m/z 20 – 1050 and the scanning speed was 5 scans per second. Data were collected and processed using Xcalibur software[3].

Results

FTIR characterisation of organic residues

Each sample was measured three or more times to estimate the internal homogeneity. Limited chemical variation was seen between multiple measurements. The results of the FTIR analyses are summarized (**tab. 3**) and discussed using the FTIR spectra (**fig. 11**). The identification is based on earlier FTIR work with heated and charred foodstuffs (Oudemans/Boon/Botto 2007) and references from the world of art conservation (Derrick/Stulik/Landry 1999). The archaeological residues can be divided into three groups based on their FTIR characteristics.

FTIR Group 1 contains charred materials with lipids and proteins (PA05-PA07 and PA09). The FTIR spectrum of exemplary sample PA06 shows aromatic characteristics typical for partially charred organic materials and indications for proteins and lipids (**fig. 11**). FTIR Group 2 contains more severely carbonised organic materials (PA01-PA04). The FTIR spectrum of exemplary sample PA03 is determined by few strong broad resonances, typical for highly thermally degraded organic materials and salts of fatty acids. FTIR Group 3 contains four residues that consist of birch bark tar (PA08 and PA10-PA12). The FTIR spectrum of PA11 shows many characteristics for a degraded triterpenoid resin.

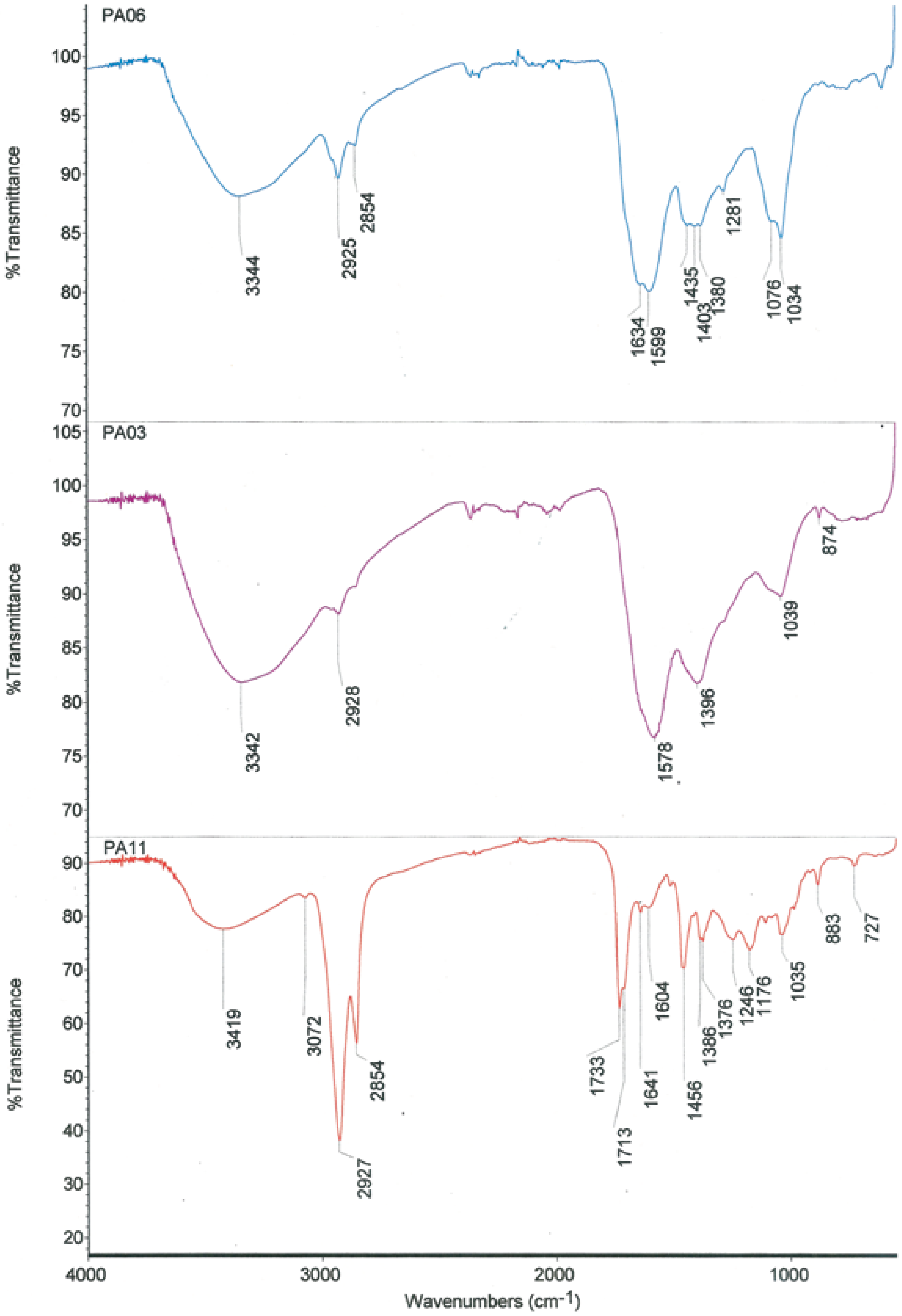

Fig. 11 Pestenacker (Lkr. Landsberg am Lech/D). FTIR spectra of residues representing FTIR Group 1 (PA06, top), FTIR Group 2 (PA03, middle) and FTIR Group 3 (PA11, bottom). – (Illustration T. F. M. Oudemans).

no.	CC	sample		PA 01	PA 02	PA 03	PA 04	PA 05	PA 06	PA 07	PA 08	PA 09	PA 10	PA 11	PA 12	PA 13
		trans. bands	region [cm^{-1}]													
1		O-H (s), N-H (s)	3600-3200	++	++	++	++	++	++	++	+	++	+	+	+	+/–
2	Ar	C=H (s) vinyl	3100-3000	–	–	–	–	–	–	–	+/–	–	+	+	+	-
3	Al	C-H (s) -CH$_3$-	2962/2872	+	+/–	+	+/–	+/–	+	+	–	+	–	–	–	++
4	Al	C-H (s) -CH$_2$-	2925/2850	+	+/–	+	+	+/–	++	++	+++	++	+++	+++	+++	++
5	Lip	C=O (s) carb. a.	1730-1700	–	–	–	–	–	+/–	–	++	–	++	++	++	–
6	R	C=O (s) ester	1720-1690	–	–	–	–	–	–	–	++	–	+++	+++	+++	+
7	Pr	N=O and C=O (s) Amide I	1650 (1680-1630)	–	–	–	–	–	+	+	–	+/–	–	–	–	++
8	Al	C=C aliphatic	1640-1635	–	–	–	–	–	–	–	+/–	–	+	+	+	–
9	R	C=C conjugated	1615-1600	–	–	–	–	–	–	–	–	–	+	+	+	–
10	Lip	[O-C=O]- (s) salts of carb. a.	1600 (1610-1590)	++	++	++	++	+++	+/–	+	–	+/–	–	–	–	–
11	Ar	C-C (skel. vibr.)	1600-1585	++	++	++	++	+++	+++	+++	–	+++	–	–	–	–
12	Ar	Aryl-H	1580	+	+	+	+	+	–	+	–	+	–	–	–	–
13	Pr	C-H (s), N-H (b) Amide II	1550 (1565-1500)	–	–	–	–	–	–	–	–	–	–	–	–	–
14		C-O (asym. s)	1540	–	–	–	–	–	–	–	–	–	–	–	–	–
15	R	C=C	1513	–	–	–	–	–	–	–	+	–	+	+	+	–
16	Al	C-H (b)	1470-1440	+/–	+/–	+/–	–	+/–	+	+	++	+	++	++	++	+
17	Pr	C-H (b) Amide III	1450	–	–	–	–	–	–	–	–	–	–	–	–	–
18	Ar PS	C=C (skel. v)	1450 (1500-1400)	++		+/–	–	+	–	–	–	–	–	–	–	–
19	Ar	C=C (skel. v)	1425-1415	+/–	++	++	+	+	+	++	+	+	–	–	+/–	–
20		O-H (b) alcohol, phenol	1385 (1410-1260)	–	–	–	–	–	–	–	–	–	–	–	–	+
21	Lip	[O-C=O]- (s) salts of carb. a.	1400-1390	++	++	++	++	++	+/–	+/–	–	–	–	–	–	–
22	Al	C-H (b)	1375-1380	–	–	–	–	–	+	+	+	–	+	+	+	–
23		C-O-H (s)	1280-1275	–	+/–	–	–	–	+/–	+	–	–	–	–	–	++
24	Lip/R	C-O (s) carb. a.	1245	–	+	–	–	–	–	–	+	–	+	+	+	–
25	R	C-O-C ester	1160-1088	–	–	–	–	–	–	+/–	+	–	+	+	+	+
26	PS	C-O-C (skel. v)	1080	+/–	–	+	+	+/–	++	++	++	++	–	–	–	–
27	Si	Si-O-Si (asym. s)	1050 (1200-800)	–	–	–	–	–	–	–	+	–	–	–	–	–
28	PS	C-O (s) alcohol	1040-1035	+/–	+/–	+	+	+/–	++	++	++	++	+	+	+	+
29	CC	O-C-O (b) CaCO$_3$	878, 713	–	–	–	–	–	–	–	+/–	–	–	–	–	–
30	Ar/R	C=C vinyl	880-875	–	–	–	–	–	+/–	+/–	+	–	+	+	+	–
31	Si	Si-O quartz	777, 792	–	–	–	+/–	–	+/–	+	–	–	–	–	–	–
32		C-H$_2$ (b)	846	–	–	–	–	–	–	–	–	–	–	–	–	+++
32	Al	C-H (r) C4-C10	720-727	–	–	–	–	–	–	–	–	–	+	+	+	–

Tab. 2 FTIR results. Indicated are the relative intensities of different kinds of FTIR-transmission bands (s = stretching; b = bending; v = vibration; r = rocking; def. v = deformation vibration; skel. v = vibration in the ring structure; asym. s = asymmetric stretching) in four categories of intensity being: +/-: very low; +: normal; ++: high; +++: very high. Several compound classes (CC) for which the resonances are indicative (Lip = lipids; Al = aliphatics; Ar = aromatics; R = resinous materials; PS = polysaccharides; Si = silicates; Pr = proteinaceous).

sample no.	DTMS code	Sig	TIC max	lipids				Tr	proteins		polysac-charides		Con	origin
	092016			S FA	U FA	AG	S		PP	PC	PS	PSC		
PA01	19 16:37	L/M (33×)	0.96	–	–	–	–	–	–	–	–	–	Ph	modern contamination with plasticizers
PA02	20 12:41	M (65×)	1.05	+	+/–	+	+ AS	–	–	+	–	+	Ph	medium degraded lipids with charred proteins and polysaccharides
PA03	20 15:15	M (71×)	1.15	+	–	+	+ AS		–	+	+	+	Ph Hs	degraded lipid with charred proteins and polysaccharides; contamination with human skin fat
PA04	20 16:26	M (67×)	1.19	+	–	+	–	+	–	+	–	+	Ph	degraded lipid with charred proteins and polysaccharides; small amount of triterpenoids (possibly birch bark tar)
PA05	20 17:01	M (67×)	1.02	++	–	++	++ AS	–	–	–	+/–	+/–	Ph PA	degraded lipids and few charred PS, no proteins
PA06	21 10:57	H (709×)	1.01	++	+++	+++	+ A	–	–	++	–	–	NC	well-preserved lipids and proteins of animal origin; possibly milk or dairy product
PA07	21 12:38	H (300×)	0.70 0.96	+/–	–	+/–	+/– A	+	–	–	–	–	Ph NC	modern contamination with plasticizers and nitrocellulose
PA08	21 14:09	H (252×)	1.13	+	–	–	–	+++	–	–	–	–	–	BBT with some fatty acids
PA09	21 15:12	L/M (38×)	1.04	++	++	+++	+/– A	–	–	++	–	–	–	well-preserved lipids and proteins of animal origin; possibly milk or dairy product
PA10	–	–	–	–	–	–	–	–	–	–	–	–	–	–
PA11	21 15:37	H (377×)	1.05	–	–	–	–	+++	–	–	–	–	K	birch bark tar
PA12	–	–	–	–	–	–	–	–	–	–	–	–	–	–
PA13	21 16:59	M (45×)	0.75	–	–	–	–	–	–	–	–	–	Ph NC	modern polymer nitrocellulose

Tab. 3 DTMS results. Indicated are the presence or absense of different groups of chemical components. – Sig = the signal intensity of the TIC where H = high (more then 100 × the background value), M = medium (100-40 × the background value), L/M = low to medium (40-20 × the background value) and L = low (less then 20 × the background value); TIC max = time (in minutes) for the maximum of the total ion current; SFA = saturated fatty acids; UFA = unsaturated fatty acids; AG = acylglycerides; S = sterols (where P = plant; A = animal; AS = alkylated steradienes); Tr = tritepenes; PS = intact polysaccharides; PSC = carbonised polysaccharides; PP = intact proteins and peptides; PC = protein char and amino acids; Con = markers for contaminants (Ph = Phthalates; AK = Alkylphenols; K = Potassium; Hs = Human skin fat; PA = Polyaromatics; NC = Nitrocellulose).

The transparent modern material PA13 was identified using FTIR as cellulose nitrate (Kovalenko et al. 1994). The material is one of a number of adhesives and lacquers based on cellulose nitrate (e. g. Duosan, Agateen lacquer, Collodion, Duco Cement or ordinary nail polish), many of which were commonly used for the consolidation of archaeological objects and ceramics. The FTIR spectra of samples PA06 and PA07 showed some contamination with this compound (peaks at 1647 and 1280 cm^{-1} are unusually increased). Apart from these minimal contaminations, no other samples were affected.

DTMS characterisation of organic residues

Ten archaeological residues were analysed and the results are presented in mass spectra (**figs 12-14**) and summarized in **table 3**. Individual compound identification is based on earlier work with heated reference materials (for a complete list of references see also Oudemans/Boon 1991 and Oudemans/Eijkel/Boon

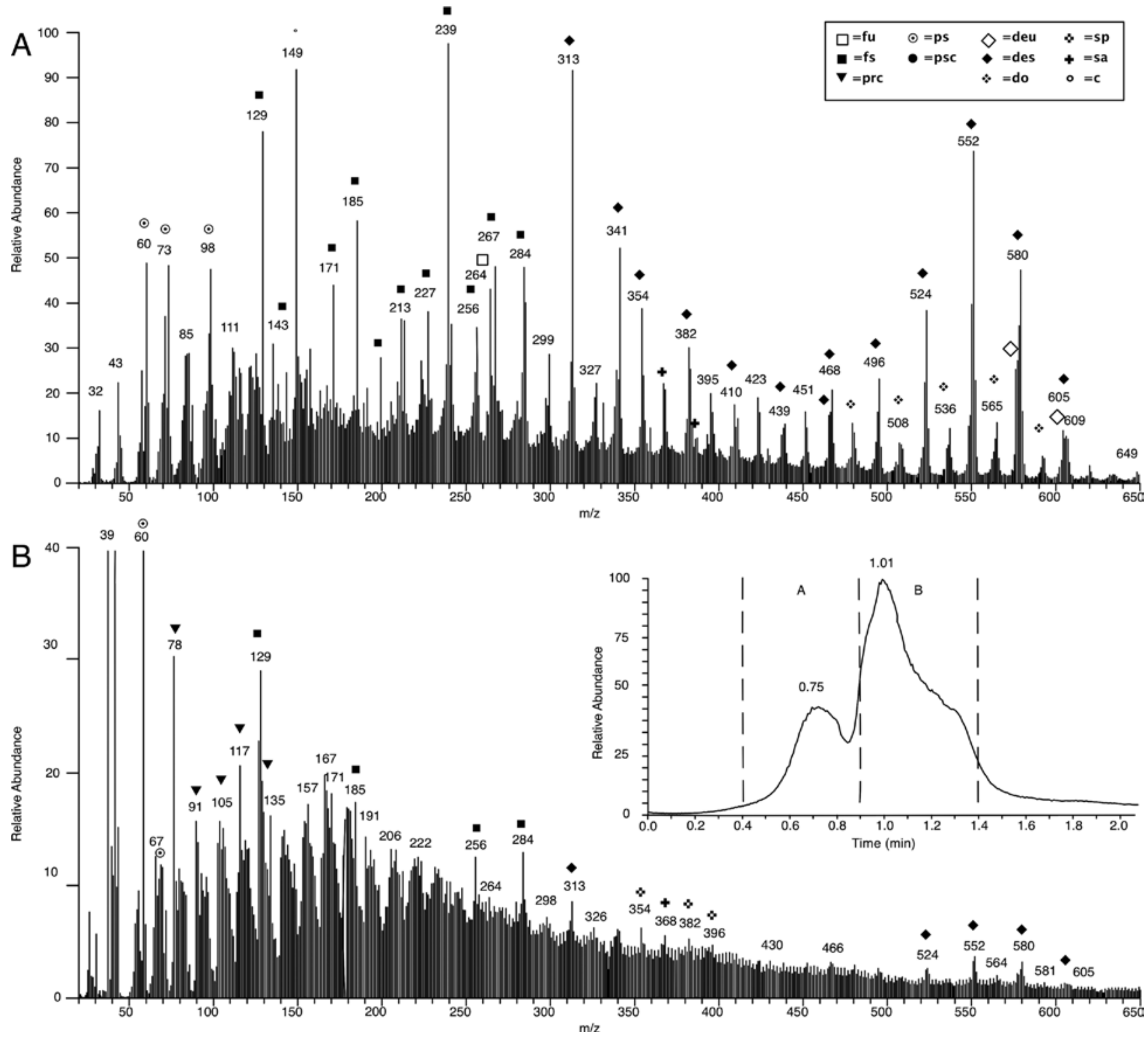

Fig. 12 Pestenacker (Lkr. Landsberg am Lech / D). DTMS results of residue PA06: The TIC (small inset) shows two peaks: a minor peak in the evaporation phase (area A, at 0.75 minutes) and a major peak in the pyrolysis phase (area B, at 1.01 minutes). – **A** The total mass spectrum of the desorption phase A. – **B** The total mass spectrum of the pyrolysis phases B. Markers for component classes are indicated with symbols: fu = fatty acids unsaturated; fs = fatty acids saturated; prc = charred proteins; ps = polysaccharides; psc = charred polysaccharides; deu = even numbered unsaturated diacylglycerols; des = even numbered saturated diacylglycerols; do = odd numbered diacylglycerols; sp = non-specific sterols; sa = cholesterol; c = contaminant. – (Illustration T. F. M. Oudemans).

2007). Eight samples rendered significant information and two samples (PA01 and PA07) only contained modern plasticizers (phthalates). The eight archaeological residues could be divided into three groups based on their chemical characteristics. Each group is discussed in detail based on the DTMS results of one exemplary residue.

DTMS Group 1: Residues with charred proteins and well-preserved lipids (PA05, PA06, PA09)

The total ion current (TIC) of residue PA06 (**tab. 3; fig. 12**) shows a material with a high organic content consisting of a mixed polymeric fraction with a medium degree of condensation and a large number of volatile compounds. The desorption phase, area A, shows markers for saturated and unsaturated free fatty

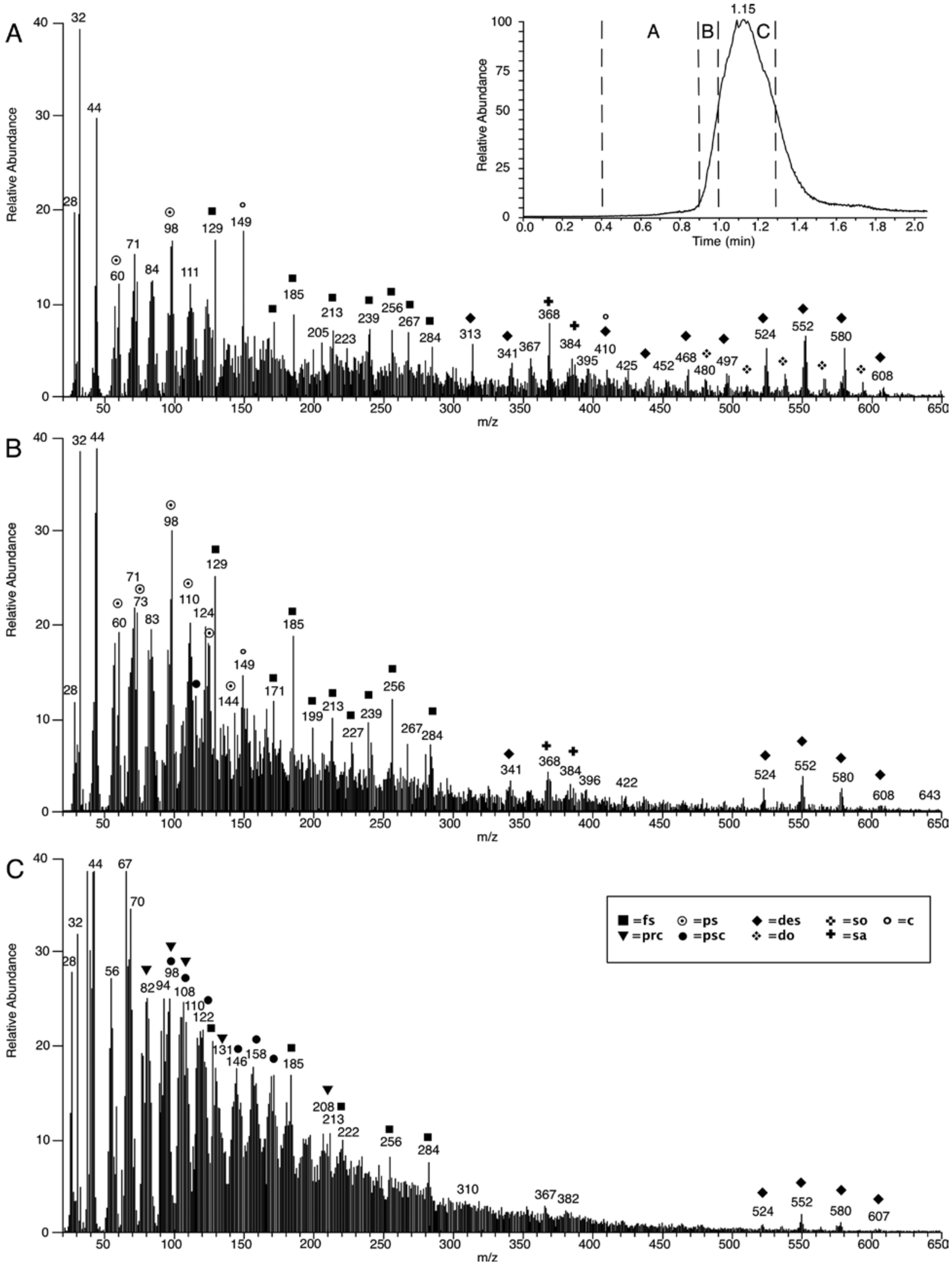

Fig. 13 Pestenacker (Lkr. Landsberg am Lech / D). DTMS results of residue PA03: The TIC (small inset) shows one major peak in the pyrolysis phase (at 1.15 minutes). – **A** The mass spectrum of the desorption phase A. – **B** The mass spectrum of the early pyrolysis phase B. – **C** The mass spectrum of the later pyrolysis phase C. Markers for component classes are indicated with symbols: fs = fatty acids saturated; prc = charred proteins; ps = polysaccharides; psc = charred polysaccharides; des = even numbered saturated diacylglycerols; do = odd numbered diacylglycerols; so = non-specific sterols; sa = cholesterol; c = contaminant. – (Illustration T. F. M. Oudemans).

acids as well as intact acylglycerols (including odd diacylglycerols). Triacylglycerols are not visible in this residue. A minimal amount of cholesterol is detected. The pyrolysis phase, area B, still shows some lipids. Markers for mildly heated polysaccharides such as alkylated furans (Pastorova et al. 1994) cannot be seen in any significant quantity. Their absence indicates a lack of sugars or starches in this residue. Because the lipid spectrum indicated low thermal degradation, the polysaccharides would still be preserved. The pyrolysis phase also shows markers for amino acids and thermally degraded proteins. The mild heating conditions have preserved some of the proteinaceous nature of the original material. The presence of markers for condensed aromatics (naphthalenes, phenanthrenes) suggests contamination with minor amounts of smoke condensates from a wood fire (not indicated in **fig. 12**).

One of the other residues in this group PA05 lacks cholesterol, but some markers for thermally degraded sterols are visible in the form of alkylated steradienes.

DTMS Group 2: Severely carbonized mixed foodstuff (PA02-PA04)

The total ion current (TIC) of residue PA03 (**tab. 3; fig. 13**) shows a material with a medium-high organic content consisting of a mixed polymeric fraction with a high degree of condensation and a small number of volatile compounds. The desorption phase, area A, shows various lipids in combination with markers for polysaccharides and some contaminating compounds. Small amounts of saturated free fatty acids and intact acylglycerols (including odd-numbered diacylglycerols), cholesterol in combination with squalene (*m/z* 410) and some contaminating plasticizers (phthalates) are detected. Triacylglycerols are not visible in this residue. Markers for mildly heated polysaccharides such as alkylated furans (Pastorova et al. 1994) can be observed in the early pyrolysis phase, area B, indicating the presence of sugars or starches in the residue. The later pyrolysis phase, area C, shows residual lipids indicating that the lipids were either encapsulated in the charred matrix or chemically bound to it. The mass spectrum is dominated by a large number of markers for a highly thermally resistant polymeric matrix formed from proteins and polysaccharides.

In another residue from this group, PA04 some additional triterpenoid compounds can be detected, most likely originating from a minor amount of bitch bark tar in the sample.

DTMS Group 3: Birch bark tar (PA08, PA11)

The total ion current (TIC) of PA11 (**fig. 14**) shows a material with a high organic content consisting of a medium complex polymeric fraction with a relatively high degree of condensation and a large number of volatile compounds.

Both the desorption phase, area A, and the pyrolysis phase, area B, show a combination of markers typical for a natural pentacyclic triterpenoid resin. There is a minor shift in intensities between the various markers over time, but the spectra for the desorption and the pyrolysis phase are very similar. The highest peaks belong to fragment ions for pentacyclic triterpenoids (methyl moronate and methyl oleonate). The second group of masses belongs to indicative molecular ions of triterpenoids from the lupane family, such as botulin, lupenone, allobetul-2-ene and lupeol and their fragment ions lupeol, lupenone and botulin.

Discussion of the chemical evidence

The organic residues from Pestenacker are relatively high in organic content (**tab. 3**). The excellent preservation of other organic materials in Pestenacker agrees with these findings. Several studies on residues from the Dutch late Neolithic have shown similar well-preserved residues (Oudemans/Boon 2007; Oudemans/Kubiak-Martens 2014; Raemaekers/Kubiak-Martens/Oudemans 2013). No indications for post-de-

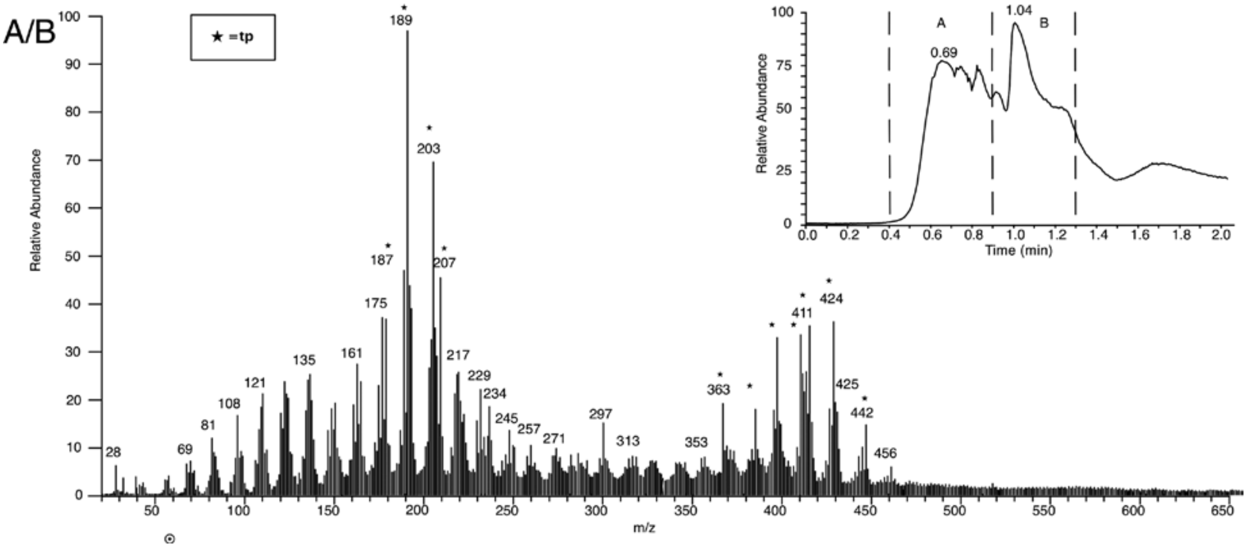

Fig. 14 Pestenacker (Lkr. Landsberg am Lech/D). DTMS results of residue PA11: **A** The TIC of residue PA11 shows several peaks. – **B** The total DTMS spectrum for the evaporation phase and the pyrolysis phase (areas A and B, 0.4-1.3 minutes). – Markers for component classes are indicated with symbols: tp = molecular ions of triterpenoids and fragment ions for pentacyclic triterpenoids. – (Illustration T. F. M. Oudemans).

positional contamination with soils or plant debris could be detected, and the residues are therefore assumed to be the remainder of one of the last use phases of the vessels. The possible origin of the various residues is summarized in **table 4** and discussed below.

The residues from the Groups 1 and 2 were the remainders of food preparation processes. The residues from Group 1 (PA05-PA06 and PA09) are a combination of mildly heated proteins and abundant well-preserved lipids. Polysaccharide markers could not be identified. An animal origin of the lipids can be positively identified (except for PA05 due to the lack of indicative sterols). In addition, the presence of short chain lengths in the acyllipids, in combination with odd-numbered diacyllipids, suggests ruminant milk fats (e.g. cattle, goats or sheep) as origin. The presence of charred proteins seems to confirm this origin.

The residues from Group 2 (PA02-PA04) suffered a higher degree of thermal degradation and thus rendered less information about the original vessel content. The residues are severely carbonized mixed foodstuffs consisting of polysaccharides and proteins and a small number of degraded fats. A minor amount of lipids shows significant thermal or biological degradation such as saturation and hydrolysis. The lipids are partly originating from contamination with human skin fat (probably a post-excavation contamination). Lipid markers for relatively short chain lengths, in combination with odd diacylglycerols, suggest an origin of ruminant milk fats (e.g. cattle, goats or sheep), although a meat origin cannot be excluded. These residues were the remainder of a starch-rich food with some proteins (possibly from milk), and could, for instance, be formed from burning a porridge made from grain with some milk or meat mixed in. The residues must have been exposed to temperatures over 250°C for several hours. This may be the result of food preparation in prehistoric times. However, the thermal exposure suggested above is not habitually reached during normal cooking processes. The thermal degradation can be the result of post-depositional heating (when sherds lay in or near a fireplace) or in the case of Pestenacker may well have been caused during the fire in the settlement.

sample no.	FTIR	DTMS	plants and charcoal	original material
PA01	highly carbonised: few lipids	modern contamination	emmer grain (transverse cells)	food with emmer
PA02	highly carbonised: few lipids	severely carbonised polysaccharides, proteins and a few fats	unidentifiable featureless matrix	severely charred mixed starch-rich foodstuff
PA03	highly carbonised: few lipids	severely carbonised polysaccharides, proteins and a few fats	unidentifiable featureless matrix (with pattern of rounded vessels)	severely charred mixed starch-rich foodstuff
PA04	highly carbonised: few lipids	severely carbonised polysaccharides, proteins and a few fats plus some triterpenoids	emmer (aleurone layer)	severely charred mixed starch-rich foodstuff with emmer; also a small amount of triterpenoid resin (possibly birch bark tar)
PA05	highly carbonised: few lipids	well-preserved lipids with charred proteins, few polysaccharides, degraded sterols	unidentifiable matrix with long tubes?	mildly heated mixture of lipids and proteins; possibly milk or dairy product
PA06	char: lipids and proteins	well-preserved lipids with charred proteins, few polysaccharides, degraded sterols, and minimal soot contamination	unidentifiable matrix with long tubes?	mildly heated mixture of lipids and proteins; possibly milk or dairy product
PA07	char: lipids and proteins	modern contamination	featureless matrix (rather solid)	unknown
PA08	birch bark tar	birch bark tar plus lipids	fragments of hazel (*Corylus*) and coniferous wood charcoal	birch bark tar mixed with some lipids and charcoal fragments (hazel and coniferous wood)
PA09	char: lipids and proteins	well-preserved lipids with charred proteins, few polysaccharides, degraded sterols	unidentifiable featureless matrix (with pattern of rounded vessels)	mildly heated mixture of lipids and proteins; possibly milk or a dairy product
PA10	birch bark tar	–	fragments of unidentifiable wood charcoal	birch bark tar (with charcoal fragments)
PA11	birch bark tar	birch bark tar	fragments of deciduous wood charcoal, most likely alder (*Alnus*) or hazel (*Corylus*)	birch bark tar with charcoal fragments (deciduous wood)
PA12	birch bark tar	–	fragments of deciduous wood charcoal, other taxon then alder or hazel	birch bark tar with charcoal fragments (deciduous wood)

Tab. 4 Summary of results. The botanical and chemical evidence and possible origin of the various residues.

The residues from Group 3 (PA08, PA10-PA12) show degraded triterpenoid resins. The degradation is most likely the result of thermal degradation of birch bark during dry distillation as used in the production of tar (Kurzweil/Todtenhaupt 1991). The pure birch bark tars (PA10-PA12) were applied onto cracks in vessels probably in order to repair them. Although it is not clear if cooking could still be performed in repaired vessels, they were obviously worth repairing. Such tar application could be seen frequently on vessels from House 1. Similar applications of birch bark tar to cracks in pottery have been identified in other archaeological contexts (e.g. Charters et al. 1993). Residue PA08 is a birch bark tar mixed with lipids that may have been produced intentionally to make the tar more pliable for functions such as hafting material, paint or waterproofing material on pots, medicine, or fuel on torches (for more references see Pollard/Heron/Armitage 2017). However, the residue could also be the result of further use of the same vessel after a repair with tar.

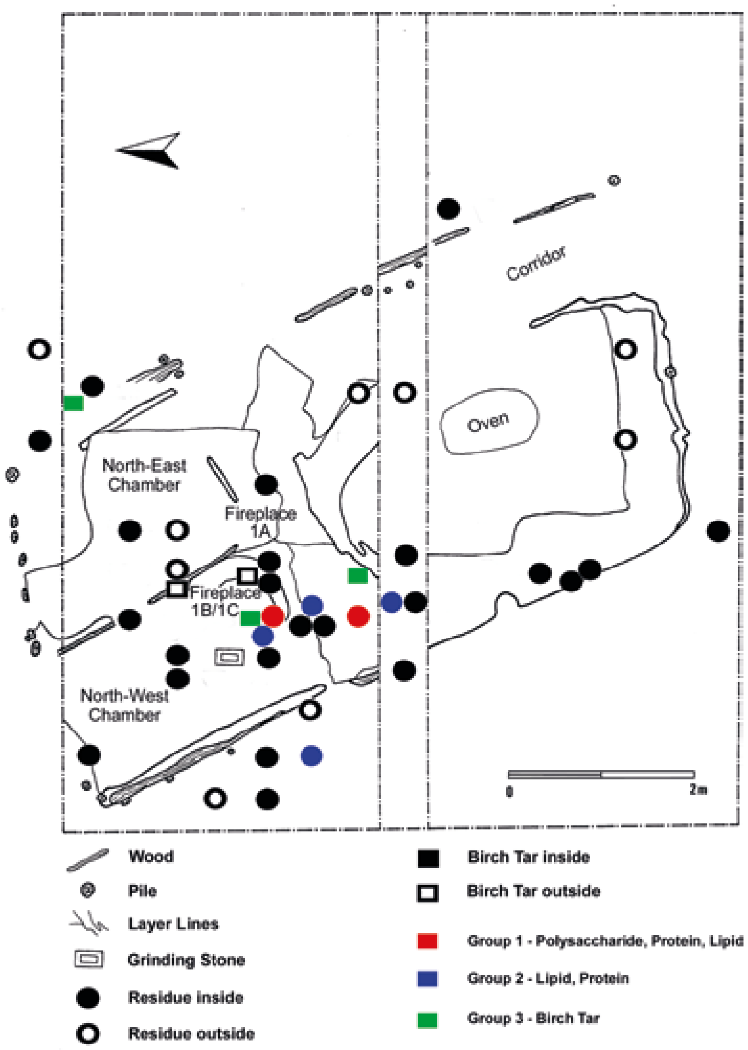

Fig. 15 Pestenacker (Lkr. Landsberg am Lech/D). Distribution of vessel units with residues or birch tar in House 1 (n = 41). – (After Schönfeld 1991, 21 fig. 21).

DISCUSSION OF VESSEL USE AND ACTIVITY AREAS IN HOUSE 1

When the chemical and micro-botanical evidence of the twelve studied residues (**tab. 4**) is projected on the vessel type (**tab. 1**), it is significant to notice that there is a certain correlation between pot type and vessel use. Residues from Group 1 (PA06 and PA09) contained lipids and proteins. The original material was possibly milk or a dairy product. Sample PA06 was taken from a lug vessel and PA09 from a vessel that was either a lug vessel or a funnel pot. The results suggest that lug vessels were used for heating, processing and storing of milk or liquid dairy products.

The funnel pots were used for food preparation processes. This agrees with the earlier proposition that funnel pots with arcaded rims were used as cooking pots (Driehaus 1960, 20. 71). However, it has become clear that funnel pots were used for two different kinds of food preparation. Five residues suggesting cooking starch-rich foods (PA01-PA05) were found on funnel pots, and it is, therefore, clear that these pots were used for cooking such meals (two of the four contained direct evidence of emmer grain). Sample PA05 is a residue of heating or processing of milk or milk products and is also found on a funnel pot. All residues of birch bark tar were discovered on funnel pots suggesting that preparing or repairing these vessels with tar was not uncommon.

When the distribution of all (41) individual vessels with residues is combined with the botanical and chemical evidence, a clear picture arises of where certain tasks were performed within House 1 (**fig. 15**). These results confirm many of the suggested activity areas proposed by G. Schönfeld (1991, 48) based on the spread of context, finds, and bones.

However, the independent scientific evidence presented here, adds more detail to what kind of activities were performed and in what kind of vessels.

The corridor of House 1 does not contain any vessels with residues. In the front room on the southern side of the house, only eight vessels with residues could be observed. Four residues were situated on the outside of vessels and are most likely soot deposits. On the western side of this room, a collection of three individuals with residues on the interior of the vessel were found. No birch bark tar was discovered in any vessel in this room. Obviously, this room was not primarily used for cooking food. The presence of an oven suggests room heating, and the independent evidence found here, confirms G. Schönfeld's earlier theories that this room was most likely a living and/or sleeping space that was kept clean.

Most of the vessels with residues on the inside originated from the northwestern room. Seven residues from the area around the fireplace were analysed. Four residues originated from heating or cooking of food; one could not be identified and two were birch bark tars on broken vessels (**tabs 1. 4**). The residues belonged to both food preparation processes, both cooking of starch-rich foods and dairy products. This means that the rearward room was indeed used as a place where both daily mixed foods (containing grain or other starches) were prepared, as well as milk or liquid milk products were processed. These two tasks obviously did not need exclusive activity areas. Two birch bark tars repair patches (PA10 and PA12) on two funnel pots were also located in this room. The find location suggests that the vessels still had a function in the activity area where food was cooked and heated. It is unclear whether the vessels could still be used as cooking pots after a repair was undertaken, or they obtained a secondary function (e. g. as storage vessel).

CONCLUSIONS

Organic residue analysis combining micro-botanical methods (using SEM) and chemical methods (ATR-FTIR and DTMS) resulted in the identification of vessel use of funnel pots and lug vessels originating from the Late Neolithic (3496-3410 BC) wetland settlement in Pestenacker in Bavaria (Germany).

The detailed identification of a series of residues from similar vessels resulted in the definition of different vessel uses for lug vessels and funnel pots. Lug vessels contained mildly charred residues with lots of lipids and charred proteins probably originating from ruminant milk or milk products. The results suggest that lug vessels were used for heating, processing and storing of milk or liquid dairy products. Funnel pots, however, most commonly contained severely charred mixed foodstuffs including polysaccharides and proteins and few or no lipids, probably originating from cooking starch-rich cereal porridge with some milk or meat addition. In several cases, funnel pots were repaired using birch bark tar. It is clear that repairing funnel pots was a common phenomenon, indicating that the value of the vessels was high enough to repair them. It is unclear what use the vessels had after they were repaired (cooking or another function).

The study of the distribution of the vessels with residues inside House 1, made it possible to identify two clear activity areas in the building. A living/sleeping area could be identified and a cooking area could be defined with two different kinds of residues representing two different tasks. These independent conclusions are completely in agreement with the earlier proposed activity areas and add detailed information to the exact use of funnel pots and lug vessels within one Neolithic household.

Notes

1) The examinations were carried out at the SEM laboratory at the Naturalis Biodiversity Center in Leiden.

2) ATR-FTIR measurements were done at the Kenaz Consult Laboratory in Berlin.

3) DTMS measurements were done at the analytical laboratory of the Schweizerische Institut für Kunstwissenschaft (SIK-ISEA) in Zurich.

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Zusammenfassung / Summary / Résumé

Kochen in spätneolithischen Töpfen – Ergebnisse einer Analyse organischer Rückstände aus Gefäßen eines Hauses der Feuchtbodensiedlung Pestenacker in Bayern (3496-3410 v. Chr.)

Der vorliegende Beitrag beschäftigt sich mit organischen Anhaftungen aus der jungneolithischen Feuchtbodensiedlung Pestenacker, wobei Trichtertöpfe und Ösenflaschen aus Haus 1 betrachtet wurden. Die Anhaftungen wurden auf botanische Makroreste, chemische Rückstände sowie deren Verteilung innerhalb des Gebäudes hin untersucht. Die Ergebnisse liefern Hinweise auf die Gefäßnutzung sowie auf verschiedene Tätigkeitsbereiche im Haus. Es konnten drei unterschiedliche Gruppen von Rückständen identifiziert werden. Die Ösenflaschen enthielten leicht verkohlte Rückstände, wohl Milch oder Milchprodukte von Wiederkäuern, die Trichtertöpfe ein stark verkohltes Gemisch. Dabei handelt es sich um einen stärkehaltigen Brei – teils mit Emmer – versetzt mit etwas Milch oder Fleisch. Daneben wurde Birkenrindenteer für mehrere Gefäßreparaturen beobachtet. Die Verteilung der unterschiedlichen Anhaftungen in Haus 1 bestätigt zwei Aktivitätszonen: ein Wohn-Schlafbereich sowie ein Kochbereich.

Cooking in Pestenacker – Evidence from Organic Residues in Vessels from one Household in a Late Neolithic Wetland Settlement in Bavaria (3496-3410 BC)

The combined botanical and chemical study of a series of organic residue on funnel pots and lug vessels excavated in one household in the late Neolithic wetland settlement of Pestenacker, resulted in the identification of how the vessels were used, and in the determination of different activity areas within the building of House 1. Three groups of residues could be identified. Lug vessels contained mildly charred residues, possibly originating from ruminant milk or milk products. Funnel pots contained severely charred mixed foodstuffs sometimes including emmer, possibly originating from a porridge rich in starch with some added dairy or meat. In several cases funnel pots were repaired using birch bark tar. The study of the distribution of the vessels with residues inside House 1, made it possible to identify a living / sleeping area and a cooking area each with different kinds of residues representing different tasks.

Cuisiner dans des pots du Néolithique final – résultats d'une analyse des résidus organiques des récipients d'une maison palafittique de Pestenacker en Bavière (3496-3410 BC)
Ce chapitre traite des résidus organiques des palafittes de Pestenacker au Néolithique tardif, où l'on a examiné des pots en forme d'entonnoir et des bouteilles de la Maison 1. Les caramels ont été examinées pour y déceler la présence de macro résidus botaniques, de résidus chimiques ainsi que pour étudier leur répartition dans le bâtiment. Les résultats fournissent des informations sur l'utilisation des vases et sur les différents domaines d'activité de la maison. Trois groupes différents de résidus ont pu être identifiés. Les bouteilles contenaient des résidus légèrement calcinés, probablement du lait ou des produits laitiers de ruminants, les pots en forme d'entonnoir contiennent un mélange fortement calciné. Il s'agit d'une bouillie – en partie avec de l'amidonnier – mélangée à du lait ou de la viande. De plus, du goudron d'écorce de bouleau a été observé pour plusieurs réparations de pots. La répartition des différents caramels dans la Maison 1 confirme deux zones d'activité: une zone de vie / de couchage et une zone cuisine. Traduction: L. Bernard

Schlüsselwörter / Keywords / Mots clés

Bayern / Neolithikum / Ernährung / Gefäßgebrauch / Analysen organischer Rückstände / Mikrobotanik
Bavaria / Neolithic / diet / vessel use / organic residue analysis / microbotany
Bavière / Néolithique / alimentation / utilisation des céramiques / analyses de caramels organiques / microbotanique

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