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Botanical analysis using SEM microscope

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Organic residue on early Neolithic pottery from Greven-Bockholt, Germany.
Botanical analysis using SEM microscope.

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1. Introduction

It is extremely challenging to determine actual prehistoric vessel use, to find out what food (or non-food) mixtures people prepared in ceramic vessels and what processing and cooking methods they used. The technique which combines botanical analysis with chemical residue analysis proved to be a successful approach in identifying original vessel contents. Each discipline uses its own highly sensitive method to identify information left in archaeological crusts.

Botanical analysis, using a scanning electron microscope (SEM), studies the anatomical features of very small fragments of plant tissues which occasionally survive the processes of food preparation, cooking and subsequent charring (e.g., fragments of cereal chaff, plant epidermis, leaf or stem tissue or starch grains). Under the SEM these tiny plant remains can be observed as being embedded in the matrix of cooked food. Not only plant components, but also meat and fish which were cooked in these prehistoric vessels, can be traced back with the help of a SEM microscope. The use of chemical analysis, such as direct temperature-resolved mass spectrometry (DTMS), makes it possible to chemically identify a broad range of organic compounds including lipids (common in fats and oils), plant waxes, terpenoids (major components of resins, pitches and tars), polysaccharides and oligosaccharides (components of sugars and starches) and protein fragments (components of meat, fish, milk products, and some seeds and nuts).

Such a combined SEM and DTMS analysis had been successfully applied earlier to a number of pottery assemblages from various archaeological sites in the Netherlands.[1]

For the Greven-Bockholt organic residue, the chemical direct temperature-resolved mass spectrometry (DTMS) analysis was carried out in the initial stage of the research. It was performed by Dr. Tania F.M. Oudemans of Kenaz Consult.[2] Now the botanical SEM analysis is added to the research strategy.

This report presents the results of the scanning electron microscope (SEM) analysis performed on the Greven-Bockholt residue. In this report, the results of the SEM analysis are also combined with the results of the earlier DTMS study making the reconstruction of the original vessel contents as complete as possible.

1.1 ORGANIC RESIDUE FROM GREVEN-BOCKHOLT

The organic residue from Greven-Bockholt was firmly encrusted on the interior surface of the pottery fragment (shard COC 2679) (see *fig. 1*), and, as such, it was considered to reflect the original content of the vessel and to represent the last, or

[1] e.g., Kubiak-Martens 2006; Oudemans & Kubiak-Martens 2012, 2013, 2014; Raemaekers et al. 2013; Kubiak-Martens et al. 2015

[2] T.F.M. Oudemans ''Residues on a Mesolithic antler axe and a possible Swifterbant shard from Greven-Bockholt'', *Kenaz Rapport* 32, April 2012.

one of the last, uses of the pot. A portion of the residue was AMS measured and gave a radiocarbon date of c. 4300 cal BC.[3] The shard is possibly associated with the Swifterbant Culture. The main aim of the SEM study was to trace back the food components that were cooked in the pot.

Figure 1 Ceramic shard, possibly associated with the Swifterbant Culture - find from the sand pit at Greven-Bockholt (courtesy of Mesolithic Research Unit, University of Köln)

2. Materials and method

2.1 SAMPLING THE ORGANIC RESIDUE FOR SEM STUDY

For reliability, two different areas of the residue were sampled for SEM analysis (see figs. 2 and 3). The small patches of organic residue were first detached from the potsherd and then mounted on SEM stubs using double-sided carbon tape strips. This part of the sampling procedure took place at BIAX *Consult'*s lab with the use of a Leica binocular microscope at 6-50x magnification. During the sampling process, the residue was described as ''medium crust, some approximately 1mm thick, brownish-black, solid to loose matrix''(see *table 1*).

[3] Info in T.F.M. Oudemans ''Residues on a Mesolithic Antler Axe and a possible Swifterbant shard from Greven-Bockholt'', *Kenaz Rapport* 32, April 2012.

Table 1 Overview of the SEM samples taken from the Greven-Bockholt shard

Sample Nr.	Object	Location of residue	Residue description	Fig. Nr.
SEM GB01	Shard COC 2679	Interior shard middle	Medium crust, brownish-black, solid to loose	2
SEM GB02	Shard COC 2679	Interior shard rim	Medium crust, brownish-black, solid to loose	3

Figure 2 Greven-Bockholt , shard COC 2679 showing organic reside encrusted on interior surface (middle). The white rectangle shows the location of residue sample SEM GB01. (The same area was sampled for DTMS analysis and referred to as GB03[4]). Foto: T.F.M. Oudemans.

4 T.F.M. Oudemans ''Residues on a Mesolithic Antler axe and a possible Swifterbant shard from Greven-Bockholt'', *Kenaz Rapport* 32, April 2012.

Figure 3 Greven-Bockholt , shard COC 2679 showing organic reside encrusted on interior surface. The white rectangle shows the location of residue sample SEM GB02. Foto: T.F.M. Oudemans.

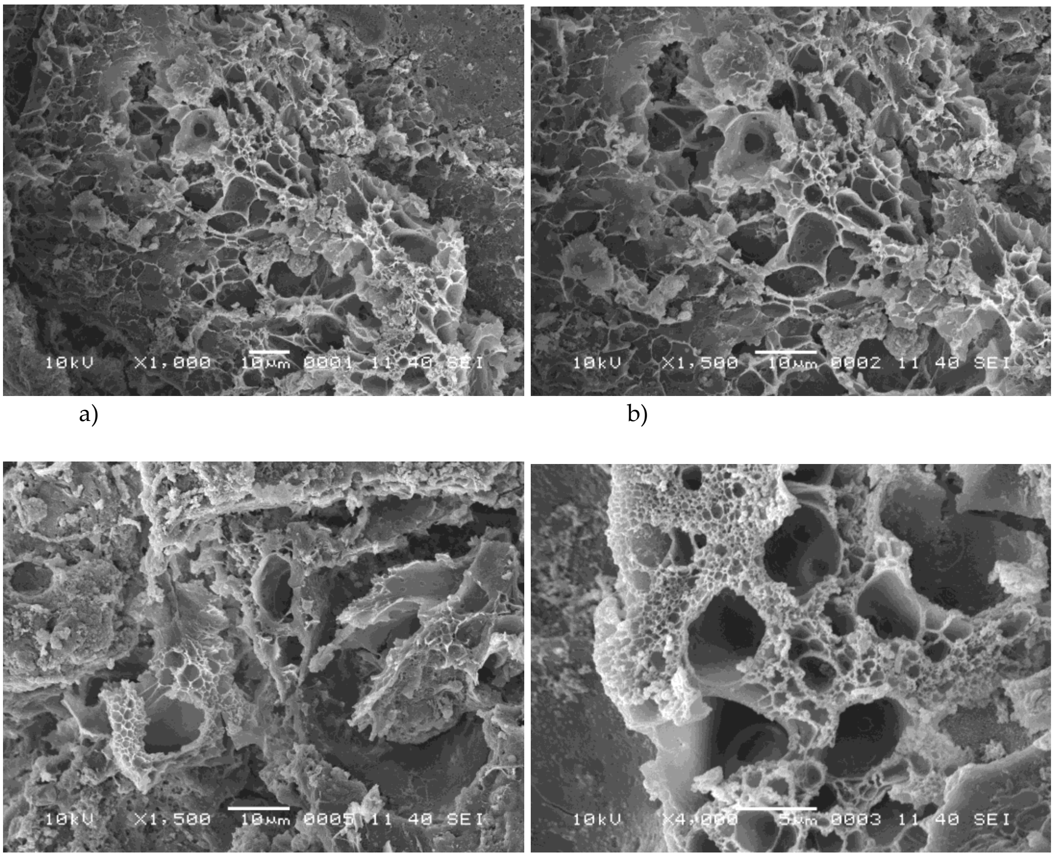
2.2 BOTANICAL STUDY WITH USE OF A SCANNING ELECTRON MICROSCOPE

The examination presented here was carried out at the SEM laboratory of the Naturalis Biodiversity Center in Leiden. At the Naturalis lab, the SEM stubs with the specimens of organic residue were platina-coated and examined using a JOEL JSM-6480L scanning electron microscope at magnifications of 700 to 4000x. For each residue sample (referred to as SEM GB01 and SEM GB02), two stubs with 1-4 residue pieces on each stub were examined under a SEM microscope.

3. Results and discussion

The results of the SEM analysis are presented in scanning micrographs in *Figures 4* through *6*). Under the SEM microscope, both residue samples (SEM GB01 and SEM GB02) show identical textures of the sample matrices, suggesting that both samples represent one cooking event. Characteristic of the residue matrix in both samples was its ''foamy or sponge-like'' texture. The matrix was made of small vesicles (air bubbles). They measured from approximately 10µm to micro-bubble sized just few microns (clearly visible in figs. 4d and 5a&5b). Even though the vesicles were of various sizes they created a rather homogenous pattern within the residue matrix.

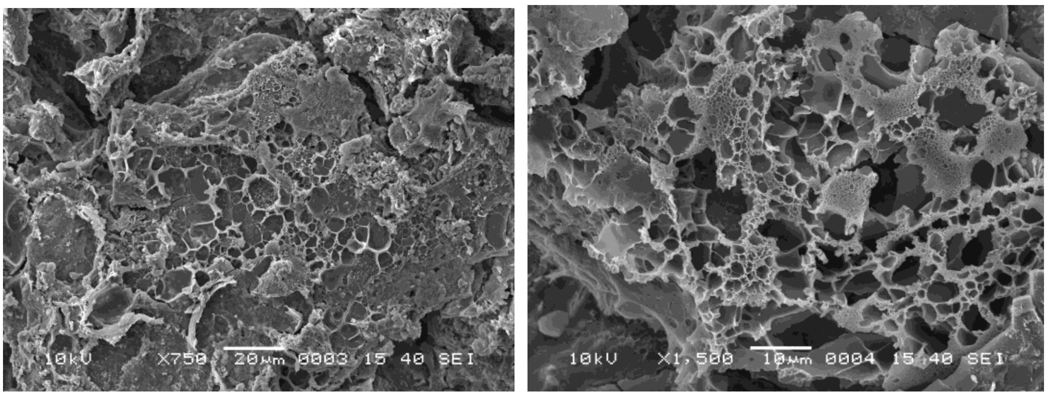
The residue did not contain any plant tissue such as cereal chaff, plant epidermis or parenchymatous tissue which are often observed in archaeological residues. It also did not contain any morphologically recognizable animal remains such as tiny bone fragments or fish scales.



a) b)

c) d)

Figure 4 SEM micrographs of organic residue from Greven-Bockhol (sample SEM GB01), showing vesicular residue matrix. Photos: L. Kubiak-Martens



a) b)

Figure 5 SEM micrographs of organic residue from Greven-Bockholt (sample SEM GB02), showing vesicular residue matrix. Photos: L. Kubiak-Martens

The only components of the Greven-Bockholt residue were the siliceous skeletons of diatoms detected in sample SEM GB02 (see fig. 7). The algae species that secretes these skeletons was identified as *Cocconeis placentula.* This diatom species is characteristic of fresh water environments and can live, for example, on the surface of reed stems.[5] The diatom skeletons were embedded in the residue matrix, suggesting that they belong to the original contents of the pot. The most plausible explanation for their presence in the studied residue is that they would have entered the pot together with a portion of water that was scooped out of a local water reservoir and then mixed with the rest of the pot contents.

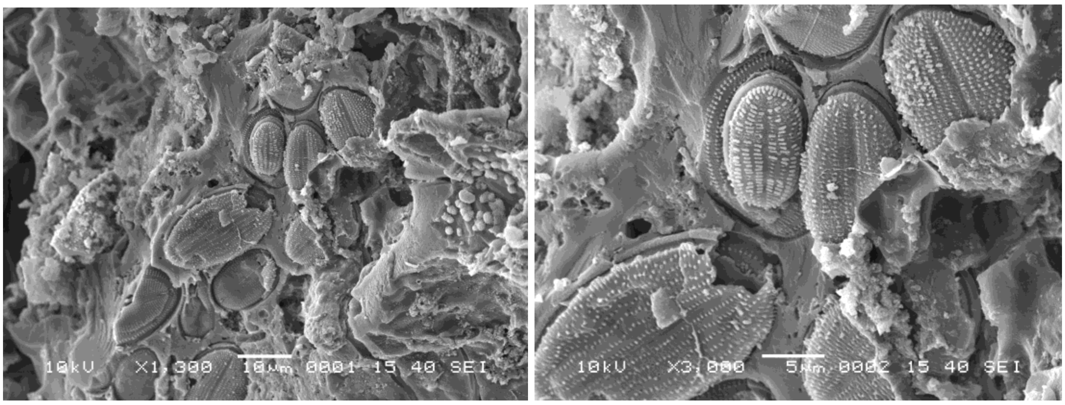


Figure 6 SEM micrographs of organic residue from Greven-Bockholt (SEM GB02), showing diatoms (*Cocconeis placentula*) embedded in residue matrix. Identification by Hein de Wolf (Palaeodiat Diatom Research, the Netherlands). Photos: L. Kubiak-Martens

The residue from Greven-Bockholt, with no plant food tissue or animal remains embedded within the matrix, is very different from many organic residues known to the author from the sites of the early Neolithic Swifterbant Culture in the Netherlands (including sites S3 and S25).[6] For example, organic residues from S3 - with SEM evidence for cooking cereal food - revealed rather solid matrices with emmer chaff embedded in their structures. In these cereal-based residues, the matrices are made of distorted starch granules which, through the process of cooking the grain and the subsequent charring, fused into consistently solid matter.

The ''foamy'' or spongy Greven-Bockholt residue is very different. The only interpretation we could think of here was that there must have been some kind of liquid used which, when heated, would have formed this kind of ''foamy'', ''light'' residue matrix.

Because the chemical analysis suggested ''proteineceous fatty animal material, possibly a milk product''[7], the author of this report carried out an experimental charring of cow milk from a local dairy farm. The main goal of this experiment was to be able to compare the matrices of the archaeological (possibly milk) residue with the experimentally-charred cow milk residue. In this experiment, the cow milk went through the process of cooking - and subsequent burning –

[5] Identification by Hein de Wolf from Palaeodiat Diatom Research, the Netherland.
[6] Raemaekers et al. 2013; S25 unpublished data (work in progress)
[7] T.F.M. Oudemans ''Residues on a Mesolithic Antler Axe and a possible Swifterbant shard from Greven-Bockholt'', *Kenaz Rapport* 32, April 2012.

until the point at which it formed a charred layer on the bottom of a pot. The residue was later studied under a SEM microscope. The results are presented as SEM images in figure 7 (a-c).

Under the SEM microscope, the matrix of the experimentally-charred milk revealed a rather porous texture, with many small air bubbles incorporated in the matrix. This vesicular appearance resembles the pattern observed in the Greven-Bockholt residue. However, despite the similarity between both the archaeological matrix and the matrix of the experimentally-charred milk, it remains difficult to clearly define the original contents of the Greven-Bockholt pot. At the same time, however, the SEM and DTMS analyses do not contradict one another.

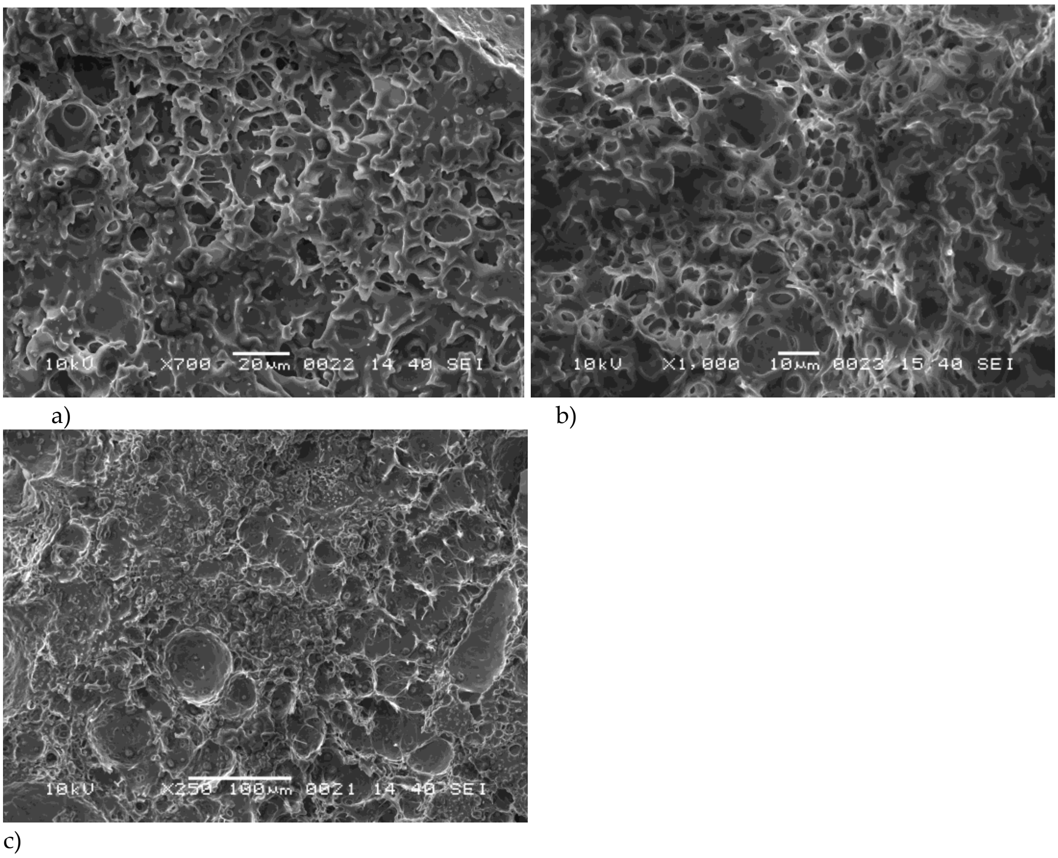


Figure 7 SEM micrographs of experimentally-charred cow milk, showing vesicular residue matrix. Photos: L. Kubiak-Martens.

4. Conclusions

The Greven-Bockholt residue most likely represents a burnt liquid. Even though the residue matrix shows similarities with experimentally-charred cow milk, and the DTMS analysis indicated 'possibly a milk product,' it is for further research (particularly additional lipid analyses) to confirm whether or not the Greven-Bockholt crust represents early evidence for heating milk or milk product in a ceramic vessel. Even though there is, as yet, no evidence associated with the Swifterbant Culture of the use of or processing of milk of domestic ruminants, the evidence is well documented for other early Neolithic cultures in temperate Europe. Perhaps one of the best examples is the study of lipids preserved in organic residues encrusted in the *Linearbandkeramik* vessels from the region of Kuyavia in north-central Poland.[8] That study provided direct evidence for early milk processing (between approximately 5400 and 4800 cal. BC.) in Neolithic Europe, and suggested that the use of milk and milk products might have been an older tradition than previously realized.

References

Kubiak-Martens, L., 2006: Roots, tubers and processed plant food in the local diet. In: L.P. Louwe Kooijmans & P.F.B Jongste (eds) Schipluiden, a Neolithic settlement on the Dutch North Sea Coast c. 3500 cal BC. *Analecta Praehistorica Leidensia* 37/38, Leiden University, 339-352.

Kubiak-Martens, L., O. Brinkkemper, T.F.M. Oudemans 2015, What's for dinner? Processed food in the coastal area of the northern Netherlands in the Late Neolithic, *Vegetation History and Archaeobotany*, vol 24: 47-62.

Oudemans, T.F.M. & L. Kubiak-Martens 2012, Botanical and chemical characterisation of charred organic residues found in ceramics. In: B.I. Smit, O. Brinkkemper, J.P. Kleine, G.C.G.M. Lauwerier & E.M. Theunissen (eds), 'A Kaleidoscope of Gathering at Keinsmerbrug (the Netherlands). Late Neolithic Behavioural Variability in a dynamic Landscape'. *Nederlandse Archeologische Rapporten,* vol 43: 107-130.

Oudemans, T.F.M. & L. Kubiak-Martens 2013, Broad-Spectrum Cooking - Botanical and chemical characterisation of charred organic residues found in Late Neolithic Pottery from Mienakker. In: J.P. Kleijne, O. Brinkkemper, R.C.G.M. Lauwerier, B.I. Smit & E.M. Theunissen (eds), 'A Matter of Life and Death at Mienakker (the Netherlands) - Late Neolithic Behavioural Variability in a Dynamic Landscape'. *Nederlandse Archeologische Rapporten*, vol 45, pp. 119-146.

Oudemans, T.F. M. & L. Kubiak-Martens 2014, Mixed food dishes in Corded Ware ceramics. Botanical and chemical study of charred organic residues. In: E.M. Theunissen, O. Brinkkemper, R.C.G.M. Lauwerier, B.I. Smit & I.M.M. van der Jagt (eds), 'A Mosaic of Habitation at Zeewijk (the Netherlands). Late Neolithic Behavioural Variability in a Dynamic Landscape' *Nederlandse Archeologische Rapporten*, vol 47, pp. 143-162.

Raemaekers, D.C.M., L. Kubiak-Martens & T.F.M. Oudemans 2013, New food in old pots - charred organic residues in Early Neolithic ceramic vessels from

[8] Salque et al. 2012.

Swifterbant, the Netherlands (4300-4000 cal. BC). *Archaeologisches Korrespondenzblatt*, vol 43(3), 315-334.

Salque, M., M.I. Bogucki, J. Pyze, I. Sobkowiak-Tabaka, R. Grygiel, M. Szmyt, R.P. Evershed 2012, Earliest evidence for cheese making in the sixth millennium BC in northern Europe*, Nature 1, Research Letter* doi:10.1038/nature11698