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ORIGINAL ARTICLE

Prehistoric cereal foods from Greece and Bulgaria: investigation of starch microstructure in experimental and archaeological charred remains

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Abstract In order to investigate ancient cereal cooking practices, the microstructure of preserved starch in charred ground cereal remains recovered from prehistoric sites in Greece and Bulgaria has been analysed. A comparative modern set of cooked and subsequently charred cereals was produced. By scanning electron microscopy it is demonstrated that, under some conditions, distinctive cooked starch structure survives the charring process. Charring alone can occasionally produce morphological changes which typically occur during cooking. Despite this caveat, starch microstructure features which are indicative of heating in liquid, and which are visible in the experimental material, have been detected in the ancient charred cereal food remains. Although much more experimental investigation is required, it has been established that evidence for past food preparation survives in ancient charred starch microstructure.

Keywords Charred starch · Experimental archaeology · Bulgur · Ancient food processing · Scanning electron microscopy

Introduction

Transformation of cereal grain into easily cooked products such as cracked wheat, bulgur or flour has been common practice since ancient times. The most direct sources of evidence are the product remains, but they have rarely been recognised, still less investigated in detail.

Recent archaeobotanical work in southeastern Europe unearthed remains of ground cereals on two Greek Bronze Age sites, Mesimeriani Toumba and Archondiko (Valamoti 2002). Similar remains of ground cereals, found at the much earlier Neolithic site of Kapitan Dimitrievo in Bulgaria, have been published recently (Marinova 2006).

One technique to investigate ancient processed cereal foods is analysis of starch granule microstructure with scanning electron microscopy (Samuel 1996). The morphology of starch changes predictably according to the processing which it has undergone. Thus, detection of specific starch granule forms can be used to interpret ancient food preparation techniques. This type of study has focused on desiccated cereal foods, where preservation at the macroscopic and microstructural levels is often excellent.

If interpretation of ancient processing from starch microstructure is to be extended, understanding the effects of charring on processed cereals is crucial. If diagnostic starch structure can survive charring, this may open the

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door to interpretation of ancient cereal processing technologies wherever burnt cereal remains are preserved.

The objectives of this paper are threefold.

- To determine changes in cereal starchy endosperm microstructure caused by different processing methods
- To assess the effects of charring on starchy endosperm microstructure
- To begin to detect the nature of ancient cereal food processing from archaeobotanical remains

Materials and methods

Archaeological material

The Greek sites of Mesimeriani Toumba (Grammenos and Kotsos 2002) and Archondiko (Papaefthymiou-Papanthimou and Pilali-Papasteriou 1995; Papaefthymiou-Papanthimou et al. 2002) are dated to 2100–1900 cal B.C. which corresponds to the end of the early Bronze Age in northern Greece. The Bulgarian site of Kapitan Dimitrievo (Nikolov 2000; Marinova and Popova 2008) is dated to 5920–5730 cal B.C., corresponding to the Bulgarian early Neolithic (Fig. 1). All three sites are tells with burnt destruction phases and all archaeobotanical finds discussed were recovered from such levels. The Mesimeriani residues were a pure dense concentration associated with a pot in a room; the Archondiko find came from the interior of a post-framed house. Previous work suggests these deposits were ground prior to charring (Valamoti 2002). The Kapitan Dimitrievo find was in a whole storage vessel close to a hearth inside a house, together with other stored crops (Marinova 2006).

This material can be grouped into two categories.

1. Finely ground cereal grain—particles ranging from 0.5 to 2 mm. Fragments have shiny surfaces which may have been caused by boiling (Valamoti 2002). The material from Kapitan Dimitrievo in Bulgaria and from Mesimeriani in Greece falls into this category. The Mesimeriani finds contained a few securely identified einkorn fragments. Amongst the Kapitan Dimitrievo fragments, complete grains were identified as einkorn, emmer and barley. These whole grains may have been part of the ground cereal, or may have come from the storage of whole grain adjacent to this vessel.
2. Coarsely ground cereal grain—particles ranging from 1 to 2 mm. This material comes from Archondiko. The particles have matt surfaces and were found loose and in conglomerations. Most could not be identified; a few showed typical characteristics of barley. Their processing treatment in ancient times is unknown (Valamoti 2002). The ground grain may have formed lumps prior to charring but charring could have caused agglomeration.

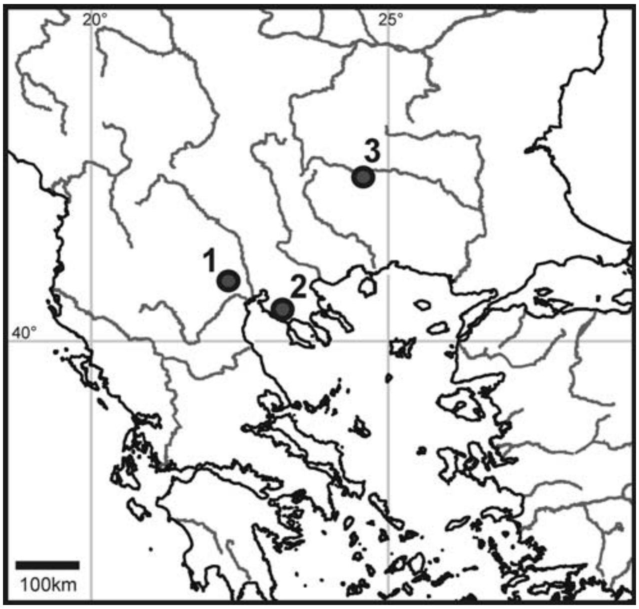


Fig. 1 Map of the study area and surrounding regions, showing the sites of *1*, Archondiko; *2*, Mesimeriani; *3*, Kapitan Dimitrievo

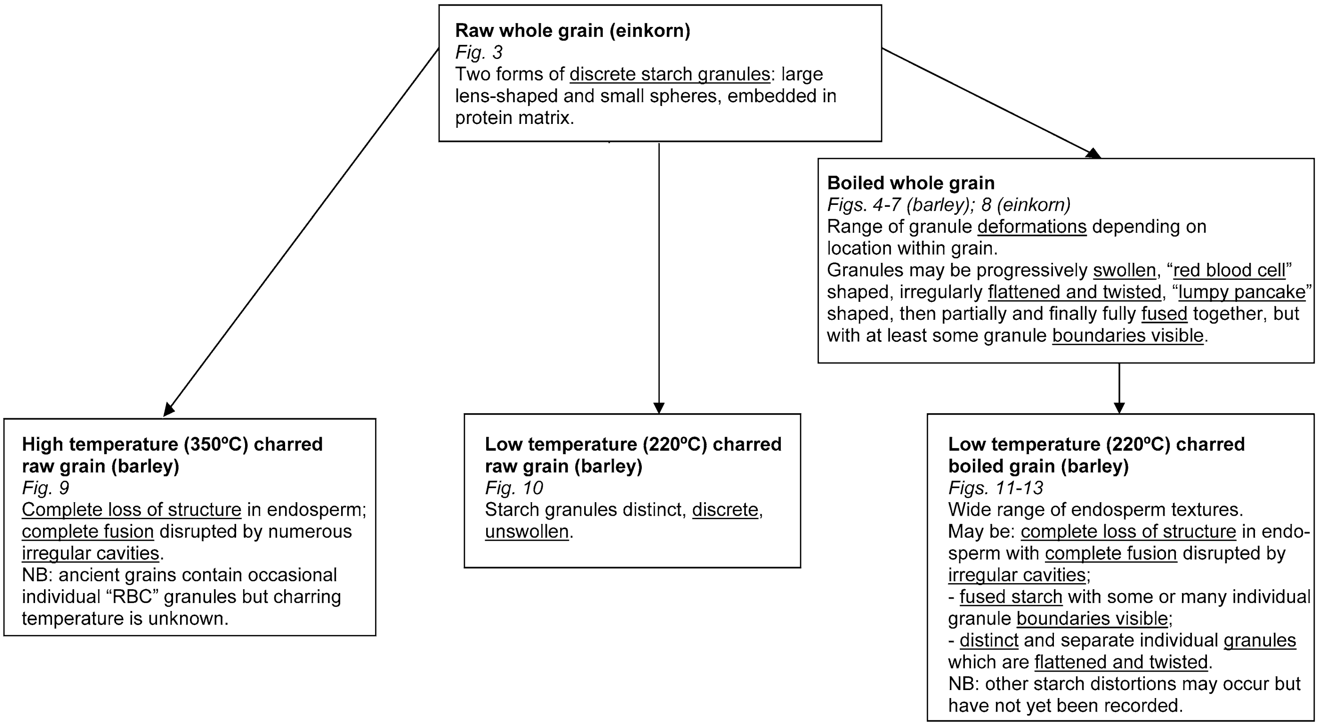
We also examined three charred whole, well preserved einkorn grains from Assiros in northern Greece, dating to the late Bronze Age (ca 1350 cal B.C.). These came from large quantities of spikelets in dedicated storerooms (Jones et al. 1986). It is unlikely that any post-harvest food processing was applied.

Experimental materials

Two modern cereal species were processed: einkorn and hulled barley. The barley comes from Gaziantep Province, Turkey. The einkorn was grown in the southern French Alps, and is a combination of landraces originally from Italy, Spain and the Near East.

Experimental cereal preparation

Starch microstructural changes caused by wetting and heating are already well established, but little work has focused on starch in cooked whole or fragmented grain. Some work has begun on non-cereal starch transformations (Wollstonecroft et al. 2008). Charring alterations have scarcely been studied. A series of ground cereal specimens with precisely controlled treatments were prepared. The specimens discussed in this paper demonstrate: (1) raw grain microstructure, (2) changes in whole grain microstructure caused by boiling, and (3) microstructural changes when raw or boiled grains are charred (Fig. 2).



Raw whole grain (einkorn)
Fig. 3
Two forms of discrete starch granules: large lens-shaped and small spheres, embedded in protein matrix.

Boiled whole grain
Figs. 4-7 (barley); 8 (einkorn)
Range of granule deformations depending on location within grain.
Granules may be progressively swollen, "red blood cell" shaped, irregularly flattened and twisted, "lumpy pancake" shaped, then partially and finally fully fused together, but with at least some granule boundaries visible.

High temperature (350°C) charred raw grain (barley)
Fig. 9
Complete loss of structure in endosperm; complete fusion disrupted by numerous irregular cavities.
NB: ancient grains contain occasional individual "RBC" granules but charring temperature is unknown.

Low temperature (220°C) charred raw grain (barley)
Fig. 10
Starch granules distinct, discrete, unswollen.

Low temperature (220°C) charred boiled grain (barley)
Figs. 11-13
Wide range of endosperm textures.
May be: complete loss of structure in endosperm with complete fusion disrupted by irregular cavities;
- fused starch with some or many individual granule boundaries visible;
- distinct and separate individual granules which are flattened and twisted.

NB: other starch distortions may occur but have not yet been recorded.

Fig. 2 Summary of experimental grain treatments, resulting starchy endosperm structure and illustrative figures

Dehulling

All grain was dehulled using a vertical type emery dehuller (Mer-ba Milling Co., Mersin, Turkey). The grain was then cleaned with an air channel and sieved to remove bran and flour particles.

Boiling

Six hundred millilitres of deionised water (pH 6.8) was heated to 97°C, and 200 g of grain was added. Barley was boiled for 35 min and einkorn for 30 min. The water was drained and the grain dried at 60°C with a tray dryer (Armfield Co., England). When the moisture content dropped to 13% (w.b.), drying was stopped (Bayram 2000).

Milling

The grain milling method was selected to ensure consistency, to control breakage, and to examine starchy endosperm. Samples were milled using a vertical disc mill (Cemotec, Foss Tecador, Germany) and sieved on a 0.5 mm sieve to remove finer particles and flour.

Charring

Charring was done in a reducing atmosphere for 8 h in a Naberthem N5/C20 oven. Specimens were loosely wrapped in aluminium foil, placed in sand-lined crucibles and the foil covered in sand. The oven temperature was set to rise by 50°C at 10 min intervals until 200°C. Five minutes after, when the temperature reached 220°C, it was kept stable for 8 h.

Two sets of charred material were produced. Previous experiments showed that lower charring temperatures cause much less distortion to cereal caryopses than higher temperatures (Valamoti 2002). Most charring was carried out at 220°C. Some experimental material was charred at 250°C, apart from a 45 min period which occurred at some point during the first two hours of heating, when the temperature rose to 350°C. Although this charring regime is somewhat problematic because it was not fully controlled, it provided comparative, more intensively charred material.

Scanning electron microscopy (SEM)

All samples were carbon coated to an average thickness of 200 Å, using a vacuum evaporator JEOL-4X. We used a JEOL JSM-840A scanning microscope and scanned at 21 kV. For reliability, different areas of several specimens from each sample were examined.

Results and discussion

Individual units of starch may be referred to as starch grains and/or starch granules. To avoid confusion, here

Table 1 Features noted in the scanning electron micrographs, with their labels, descriptions, and the figures in which they appear

Label	Feature description	Figures
A	Large starch granule, raw form	3, 5, 10
B	Small starch granule, raw form	3, 7, 10
Cr	Crater on surface of charred endosperm matrix of unknown origin	19
Cu	Curved mark on starchy endosperm matrix, of unknown origin	16
D	Doughnut-shaped starch granule, probably a more extreme form of red blood cell-shaped granule	18
E	Boundary (edge) of starch granule, visible in continuous starchy matrix	8, 17
F	Fused matrix of charred starchy endosperm, without any distinguishing features	9, 11, 14
Fl	Somewhat flattened and thinned granule	10, 12
G	Angular-shaped starch granule, formed during heating when the starch is closely packed together and cannot expand evenly	8, 12, 13
H	Rough surface of charred matrix	(8), 13, 19
J	Thin projection spanning gap within the starchy endosperm, resembling charred protein (PSt) but of unknown composition	12
L	Lumpy pancake shaped starch granule	6, 7, 12, 18
M	Continuous starchy matrix in which some starch granule structure is still visible, formed by heating, charring, or both	6, 7, 8, 12, (13), (17)
N	Grain ventral furrow	4
P	Unmodified protein matrix	3
PBd	Tiny bead-like protein structure in uncooked grain charred at low temperature	10
PSt	String-like protein structure in uncooked grain charred at low temperature	10
R	Red blood cell (RBC) shaped starch granule: swollen compared to the original raw form, inner part thinned, outer perimeter thickened; may be not at all or somewhat twisted	5, 12, 15, 17, 18
Rm	Melted-looking, highly distorted form of red blood cell shape	15
S	Swollen starch granule	5, 12, 13
Sph	Swollen spherical starch granule	18
St	Starch granule, not further described	7, 17
T	Elongated, flattened and twisted starch granule, transitional between RBC and lumpy pancake forms, distinction between thin inner area and thickened perimeter is clear	5, 6, 7
U	Unidentified particulate matter on the surface of charred ancient specimens	16, 17, 18, 19
V	Cavity in charred fused starch matrix	9, 14, 15, 16
VLth	Large thin walled cavity	11
VSem	Small embedded cavity	11
VSth	Small thin walled cavity	11
W	Cell wall seen in cross-section	5, 10, 13
Wf	Cell wall fragment seen from side view rather than cross-section	10

Brackets indicate that the feature appears but is not labelled

"grain" always refers to a cereal caryopsis or caryopses. The term "granule" always refers to starch. Table 1 describes the microstructural features we have identified, not all of which are specified in the captions. Figure 2 summarises the changes in starchy endosperm microstructure observed in experimental material. We emphasise that our results are highly preliminary. We are aware that our modern material is limited (see also Wollstonecroft et al. 2008) and that different charring regimes may have great effects on endosperm microstructure.

Modern uncharred cereal starchy endosperm microstructure

Raw endosperm

Cereal caryopses are mostly composed of starchy endosperm. Figure 3 shows the typical starchy endosperm microstructure of a modern uncharred einkorn grain. Starch granules are discrete and well separated. The starchy endosperm structure of barley and all other wheat species is very similar.

Isolated starch cooked in water

Cooking can have a dramatic effect on starchy endosperm microstructure. Depending on the conditions to which the starch has been exposed, granules become progressively swollen, distorted, fused, or lose their structure entirely (Williams and Bowler 1982). Changes are dependent on both temperature and the amount of water available. A classic experiment examined how a starch system heated to 100°C contains granules which progressively fold, collapse and finally disintegrate as moisture content increases (Derby et al. 1975). Another classic study investigated starch in a moisture system of 35% water, and showed that at temperatures of 90°C, the lack of water meant that granules could only deform to a limited extent (Hoseney et al. 1977).

Starch in cooked whole grain

When whole grain is cooked, water must diffuse through the outer heated layer into the grain core (Bakshi and Singh 1980). Initially, water penetrates freely into the outer parts, and upon heating, the starch becomes swollen and twisted, and depending on the extent of cooking, can fuse. Depending on the length of cooking time, the amount of water at the grain centre is more limited. Because of this, even if the temperature reaches ambient cooking level, starch in the central grain core may be much less affected than that of the outer layers. As a result of these structural and moisture differences, the starch granule population within a single whole cooked cereal grain can be modified into distinctly different shapes. We demonstrate this with a whole barley grain from a batch which we boiled, then dried and milled (Fig. 4).

The grain centre is most protected from the effects of liquid and heat (Fig. 5). A few granules are hardly distorted from their raw structure or are only slightly swollen. Many granules are modified into a characteristic “red blood cell” (RBC) form. Intermediate between the core and outer starchy endosperm (Fig. 6), many granules are distinctly swollen, flattened and twisted, while some starch has fused. Starch closest to the surface of the grain is most extensively modified (Fig. 7). Several typical types of starch deformation occur, most notably a continuous matrix in which the boundaries of some or many of the original granules are still detectable.

Along the moisture and temperature gradients, from lowest at the grain core to maximum levels at the outer periphery, there is a progression in starch structure deformation. Because individual granules behave slightly differently in the same conditions, there can be considerable overlap in forms across the gradient. See Fig. 2 for a summary of granule deformation in boiled whole grain.

In contrast, little starch variation is detectable in an einkorn grain exposed to the same treatment as the barley

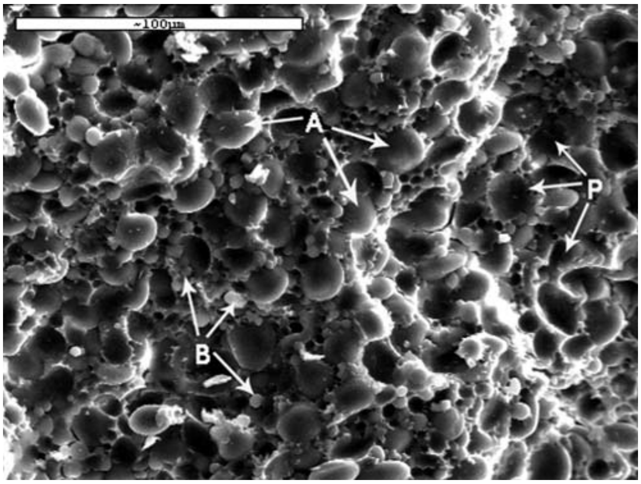


Fig. 3 Raw whole einkorn grain, uncharred core starchy endosperm. Two starch granule types: large disk-shaped (*A*); smaller, spherical (*B*), embedded in protein matrix (*P*)

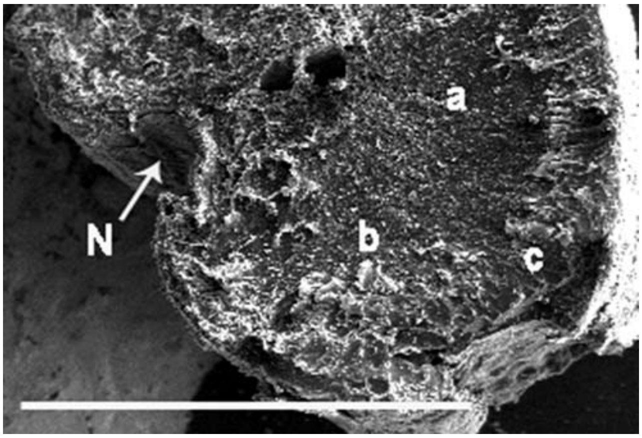


Fig. 4 Boiled whole barley grain, uncharred cross-section. Ventral furrow (N). “a”—position of Fig. 5; “b”—Fig. 6; “c”—Fig. 7. *Scale bar* 2 mm

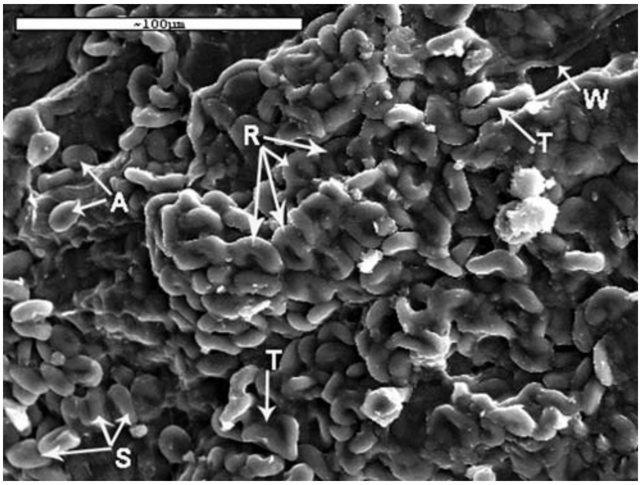


Fig. 5 Boiled whole barley grain. Close-up of starchy endosperm area a, Fig. 4 (*inner core*). Granule forms: undistorted large (*A*); somewhat swollen (*S*); "red blood cell" (*R*); twisted and elongated (*T*). Most granules retain individual boundaries, are little fused together

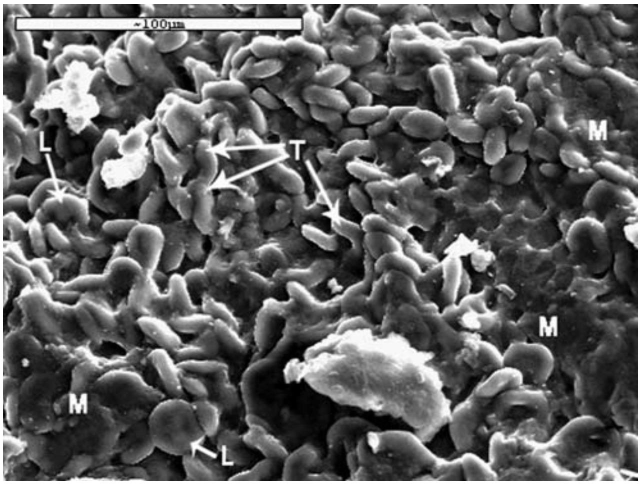


Fig. 6 Boiled whole barley grain. Close-up of starchy endosperm area b, Fig. 4 (*intermediate region*). Starch granule forms: elongated, flattened and twisted (*T*); "lumpy pancake" (*L*); more-or-less continuous matrix (*M*)

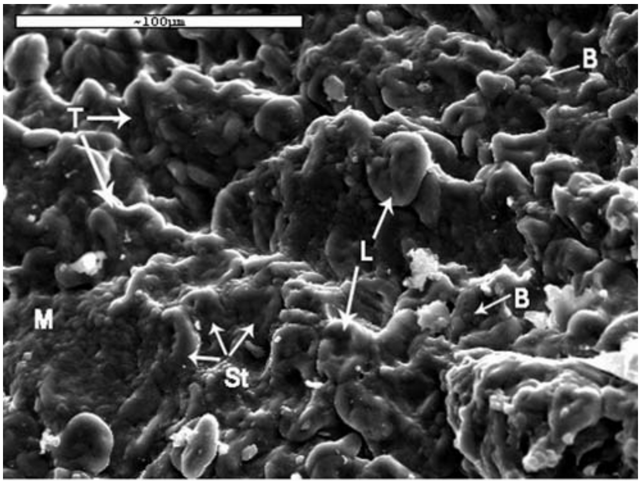


Fig. 7 Boiled whole barley grain. Close-up of starchy endosperm area c, Fig. 4 (*outer grain edge*). Starch granule forms: small (*B*)—least distorted; elongated and twisted (*T*); lumpy pancake (*L*). Distorted granules (*St*) fuse into continuous matrix (*M*)

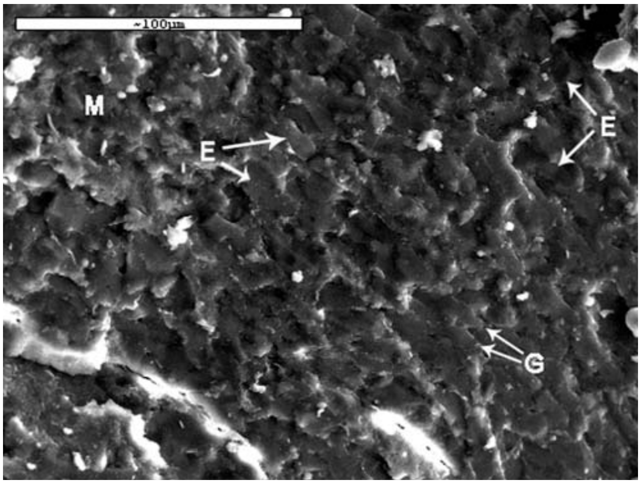


Fig. 8 Boiled whole einkorn grain, inner starchy endosperm. Compare to individual granules of raw grain (Fig. 2). Fused, more-or-less continuous matrix (*M*); boundaries between starch granules (*E*); angular granules (*G*)

(Fig. 8). The starch has fused into a glassy, more-or-less homogeneous matrix throughout the endosperm, in which boundaries of granules are visible in some areas. These differences relative to the cooked barley endosperm may partly be due to einkorn grain shape. Since it is thinner than barley, the inner core is closer to the grain surface. Heat and water may penetrate more quickly and evenly. A shorter cooking period for einkorn might cause deformations similar to those presented in Figs. 5, 6, 7. The differences may also be due to variations in water permeability of the bran, starch packing, the precise physicochemical nature of einkorn and barley starch, and the type and proportion of grain protein.

Modern charred cereal starchy endosperm microstructure: results

Raw grain charred at high temperatures

Braadbaart et al. (2004) and Braadbaart (2008) investigated effects of charring on cereal starchy endosperm over temperatures ranging from 190 to 600°C. Using SEM, they observed that starchy endosperm structure is drastically modified at temperatures of 270°C and over, with complete loss of granule structure. The endosperm is completely fused and disrupted by numerous irregular cavities. The precise temperature or temperature range at which this occurs has not yet been fully established and it may vary according to species. Braadbaart et al. (2004) call this highly modified material “converted endosperm”, a term which we also use. Figure 9 shows the endosperm structure of an unprocessed whole grain specimen which was charred up to 350°C. This confirms the structural modification findings of Braadbaart et al. (2004).

Raw grain charred at low temperatures

Experiments show that starch granule morphology can survive charring at low temperatures. Braadbaart and colleagues observed that starchy endosperm microstructure was unaffected at 235°C (Braadbaart et al. 2004). Our low temperatures of 220°C also mostly preserved raw grain starchy endosperm structure.

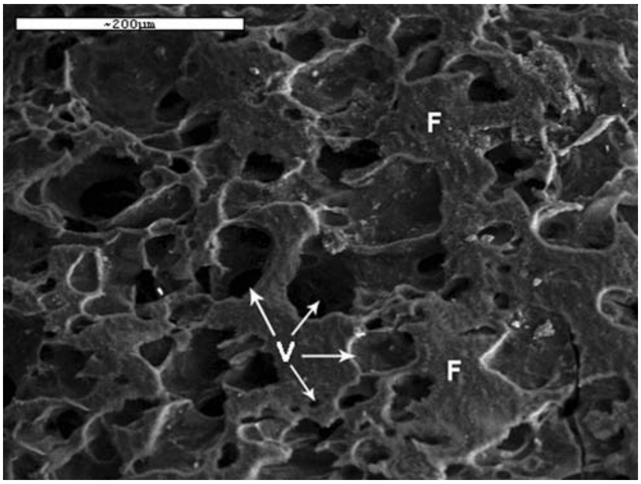


Fig. 9 High temperature (350°C) charred raw barley grain, core starchy endosperm. Completely fused endosperm (*F*); small and large cavities (*V*). *Scale bar* 200 μm

Unprocessed charred barley endosperm (Fig. 10) resembles that of uncharred starchy endosperm (Fig. 3). Importantly, isolated starch granules in the low temperature charred grain show some signs of distortion, with the beginnings of flattening and thinning into the RBC shape typical of starch partially deformed by heating in water. This evidence indicates that some unprocessed starch can be distorted by the charring process alone into forms which typically derive from processing at normal cooking temperatures.

Cooked grain charred at low temperatures

Unlike the raw grain, low temperature charring caused pronounced and complex changes in the experimentally cooked grain. A wide range of microstructure was produced, and it is only possible to present a selection of examples, demonstrated by whole barley boiled in water, dried, milled and then charred at 220°C (Figs. 11, 12, 13).

In some areas, the starchy endosperm has fused and developed cavities—there are no features resembling starch granules (Fig. 11). The material looks similar to the converted endosperm seen in uncooked grain charred at high temperature (Fig. 9). Another fragment shows a marked contrast (Fig. 12), in which the starch appears mostly unaffected by charring and resembles some areas of cooked, uncharred grain endosperm (Figs. 6, 8). A further fragment contains unruptured cell walls enclosing fused starch (Fig. 13). There are no separate granules, but distorted granules and granule boundaries are visible within

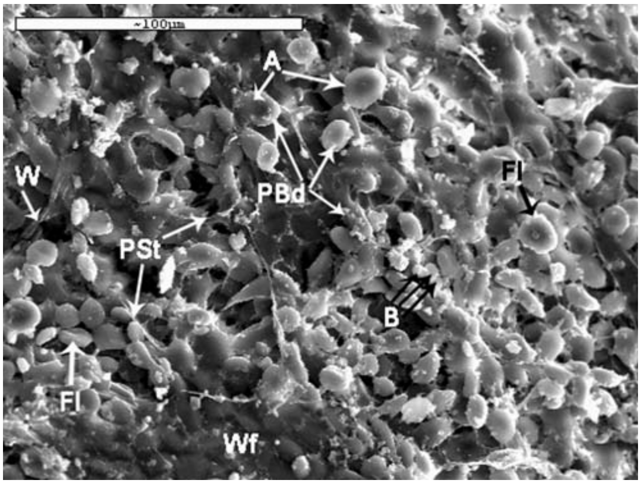


Fig. 10 Low temperature (220°C) charred raw barley grain, inner starchy endosperm. Starch granule shapes: undistorted large (*A*); undistorted small (*B*); flattened and thinned (*Fl*)

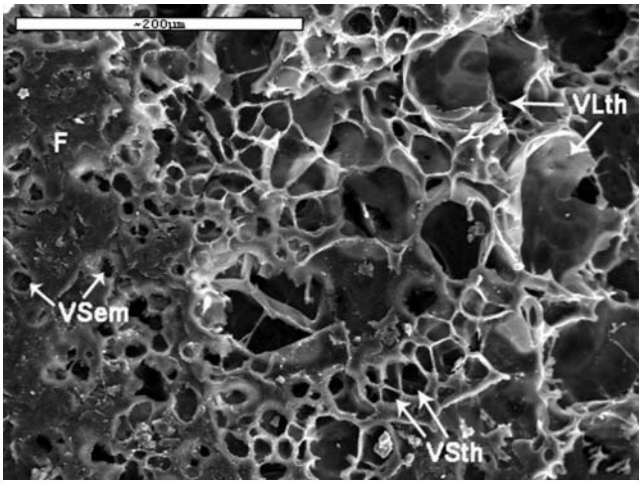


Fig. 11 Low temperature (220°C) charred boiled barley grain, inner starchy endosperm. Fully fused starchy endosperm with no granule structure (*F*). Matrix cavity types: small and thin walled (*VSth*); large and thin walled (*VLth*); small and deeply embedded (*VSem*). *Scale bar* 200 μm

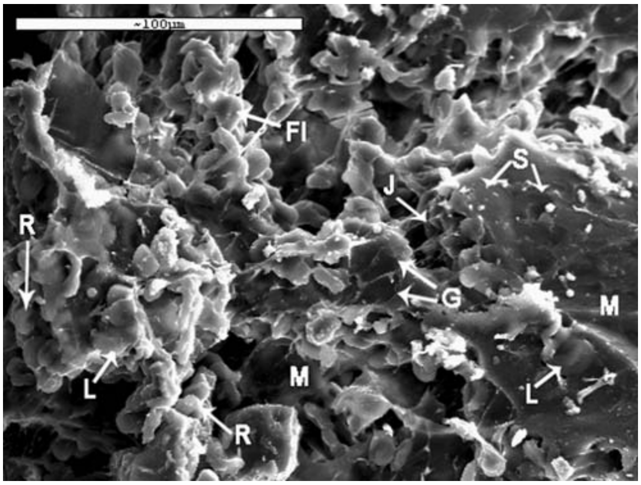


Fig. 12 Low temperature (220°C) charred boiled barley grain, inner starchy endosperm. Starch granules forms: flattened (*Fl*); red blood cell forms (*R*); lumpy pancakes (*L*). Matrix features: continuous matrix (*M*); edges of swollen (*S*) and angular (*G*) starch granules

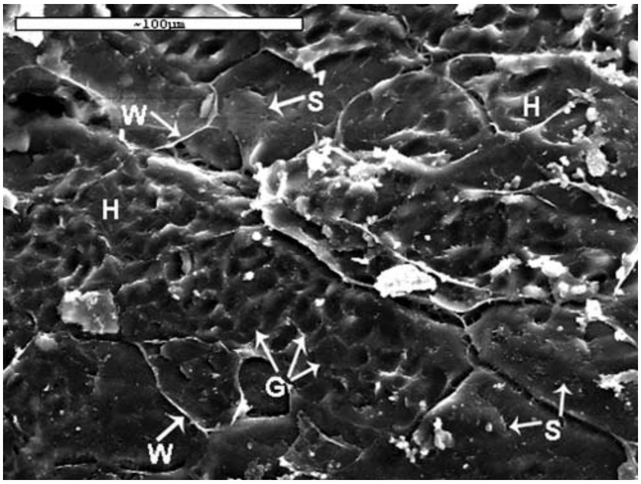


Fig. 13 Low temperature (220°C) charred boiled barley grain, inner starchy endosperm. Cell walls (*W*) separate the glassy starch matrix. Granule forms: swollen (*S*); angular (*G*)

the fused matrix. This structure most resembles our experimental well-cooked einkorn (Fig. 8).

Modern charred cereal starchy endosperm microstructure: discussion

The starchy endosperm of raw grain charred at low temperatures mostly contains undistorted starch granules and a modified protein matrix. Some granules have become distorted. More research is needed to determine how common distorted starch granules are, and the extent to which their structure changes. Our limited evidence suggests that low temperature starch granule distortion may be restricted and rare. In contrast, granules distorted by processing conditions generally occur in clusters or as part of a continuum of modified starch structure. When these distorted granules are preserved by charring, the grouping or continuum seems to be retained (Figs. 12, 13). Before modified starch can be used to interpret cereal processing, many micrographs need to be studied from a given grain assemblage, and the overall pattern of starch modification needs to be taken into account.

Low temperature charring can cause complete loss of starchy endosperm microstructure, but our pilot experiments demonstrate that diagnostic starch structure often survives. For example, the rounded granules in the charred uncooked grain (Fig. 10) resemble the large and small granules of uncharred and uncooked starchy endosperm (Fig. 3). The RBC and lumpy pancake distortions found in uncharred cooked endosperm (Figs. 5, 6, 7) are also found in some regions of the same experimentally prepared but charred grain (Fig. 12).

Low temperature charring may cause changes not seen in the uncharred processed grain, exaggerating starch deformation. For example, our cooked charred barley (Fig. 13) contained well-fused starch which was not observed in the same uncharred batch (Fig. 7). The well-fused charred barley starch visible in Fig. 13 does occur in uncharred cooked einkorn (Fig. 8).

Variations amongst individual cereal grains may also be responsible for the differences in starch microstructure of our cooked uncharred and charred barley samples. The even nature of granule swelling and lack of cavities in the charred matrix (Fig. 13) suggest that the microstructure changes are mainly due to the previous processing sequence, rather than being entirely due to charring. To date, we have not seen misleading patterns of starch structure in experimentally charred grains, but further comparison of deformation by charring and by processing is needed.

Charred starchy endosperm from ancient whole grains

Most of the ancient charred starchy endosperm of the Assiros einkorn matches the structure of modern typical converted endosperm (Fig. 14, compare with Fig. 9). In the apex of one grain, however, we detected a different type of structure. This area contains a feature which appears to be a RBC-shaped starch granule, and a few highly distorted, almost melted-looking RBC shapes (Fig. 15). Single or occasional finds of RBC-type or other distorted starch granules in ancient charred cereal remains cannot be taken to indicate that the fragments had been processed. The Assiros RBC-type starch granules were found within starchy endosperm which was apparently in the process of transformation into converted endosperm. This example demonstrates the need for considerable caution and the

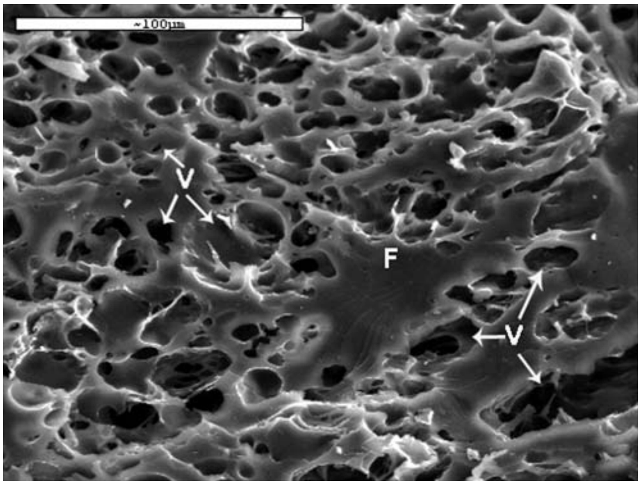


Fig. 14 Ancient raw charred einkorn grain from Assiros, inner starchy endosperm. Highly fused matrix with no surviving starch structure: *F*; numerous irregular cavities: *V*

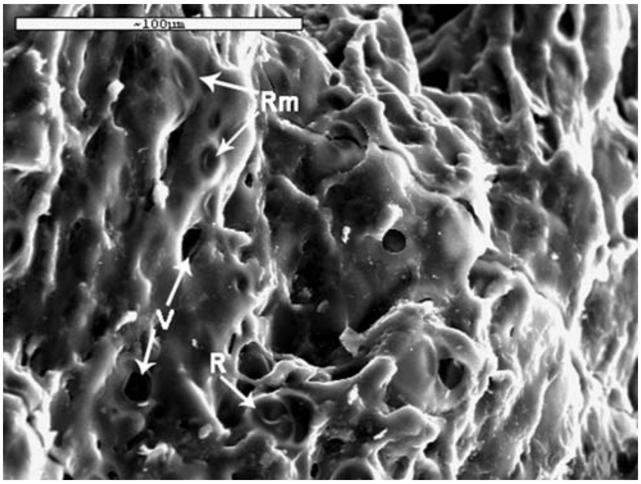


Fig. 15 Ancient raw charred einkorn grain, from Assiros: starchy endosperm in grain apex. Converted endosperm cavities: *V*. Granule forms: "red blood cell" (*R*), possible highly distorted RBC (*Rm)*

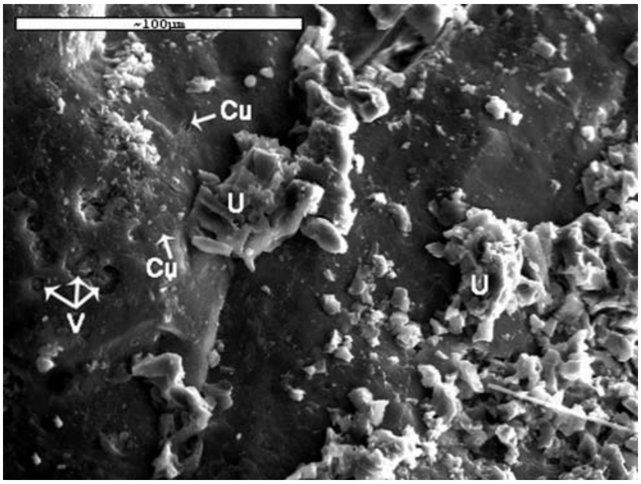


Fig. 16 Ancient charred processed einkorn grain fragment from Mesimeriani, typical endosperm microstructure. Cavities (*V*) are small and shallow. Fine particulate matter: *U*

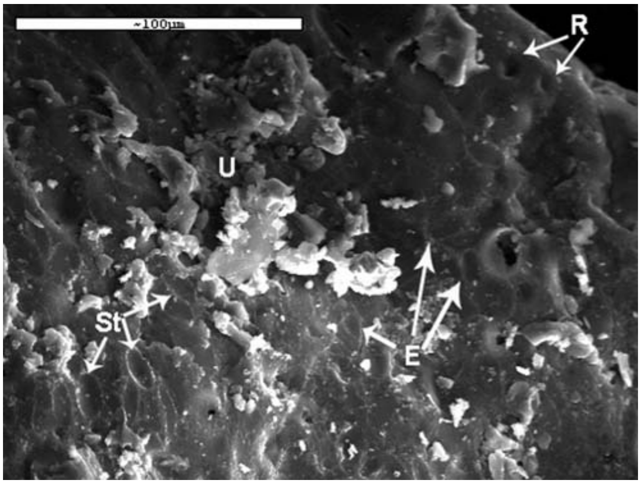


Fig. 17 Ancient charred processed grain fragment from Mesimeriani, inner starchy endosperm. The dense matrix contains granule boundaries (*E*) and packed starch granules (*St*). "Red blood cell" shapes: *R*

analysis of multiple views and specimens when attempting to interpret ancient charred material.

The study of a much wider range of ancient raw cereal grains would be valuable. A stumbling block is the difficulty in determining original charring temperatures but techniques such as those used by Braadbaart et al. (2004) may be applicable.

Ancient charred cereal food remains: evidence for ancient processing techniques

Mesimeriani

Previous work suggests that the small fragments with shiny surfaces derive from bulgur (Valamoti 2002). Their microstructure is heterogeneous. Figure 16 shows the typical appearance of the Mesimeriani starchy endosperm. Few diagnostic features survive. The starchy endosperm of other fragments (not shown) is full of cavities and the matrix has no distinguishing features. This is similar to the typical converted endosperm shown in Figs. 9, 14.

Some structures, however, are indicative of starch (Fig. 17). The most convincing evidence is regions of tightly packed, perhaps somewhat swollen granules with clearly visible edges. On their own, the swollen RBC forms also seen in Fig. 17 would not be sufficient evidence for processed starch. As demonstrated, unprocessed charred grains can contain such structures (Figs. 10, 15). The RBC forms of the Mesimeriani material are closely associated with densely packed starch in a solid matrix and without irregular cavities. This bears little resemblance to the structure of converted endosperm or badly distorted, perhaps not fully converted endosperm (Fig. 15). Nor does it resemble the endosperm of low temperature charred raw grain with the majority of starch granules more-or-less undistorted (Fig. 10).

Where distinguishable starch granules survive in these ancient fragments, they resemble the packed starch granule microstructure seen in experimental boiled barley which was charred after drying and milling (Fig. 13). This supports the original interpretation of the Mesimeriani grain fragments as the remains of bulgur.

Kapitan Dimitrievo

The cereal fragments from Kapitan Dimitrievo resemble those from Mesimeriani. The microstructure of the particles is complex and only one example is shown here. Many have the same type of smooth glassy matrix exhibited by the Mesimeriani fragments and shown in Fig. 16, but the cavities are somewhat larger and there are more of them. The surfaces are covered with particulate matter.

In one region, numerous starch granules are markedly swollen (Fig. 18). They measure approximately 50 µm in diameter compared with the more usual 20–25 µm diameter of unmodified large starch granules. We have not recorded such marked swelling in our experimentally prepared cereals, but highly swollen granules are well known to form under some heating conditions in the presence of moisture (Derby et al. 1975; Rockland et al. 1977). Some granules have a doughnut rather than a RBC shape, which may be partly due to the harsh effects of charring. The thinner interior of the doughnut-shaped granules may have ruptured because they were more susceptible to damage.

These structures are indicative of deformation due to cooking conditions. They compare well with the microstructure of modern cooked barley (Fig. 6), but the ancient starch granules are much more swollen. The clarity of the starch granule structure, and the lack of large irregular cavities within an undifferentiated matrix, makes it unlikely that these patterns are wholly charring artefacts.

Overall, the type of Kapitan Dimitrievo starch forms, and the resemblance of many surfaces to the Mesimeriani smooth glassy matrix, suggests these residues were derived from cooking cereal grain in water. The wider range of starch forms, however, may indicate that the ancient cooking process was uneven, perhaps because the heating technology available to the inhabitants of Kapitan Dimitrievo was not efficient. It is possible that the markedly swollen granules were caused by gradual heating. If this scenario is correct, it fits well with the much earlier date of Kapitan Dimitrievo.

Archondiko

Earlier study of the larger, matt cereal remains from Archondiko was inconclusive. The microstructure is equally enigmatic. No clear starch structure seems to be preserved (Fig. 19). The matrix structure, largely unmarked by cavities, suggests that these fragments are not composed of converted endosperm. We do not have matching structures within the experimental comparanda analysed so far.

On present evidence, the Archondiko remains may derive from processing techniques which we have yet to investigate. Their conglomerate nature, compared to the Mesimeriani and Kapitan Dimitrievo individual grain fragments, also implies a different type of foodstuff. The apparently good preservation of the starchy endosperm,

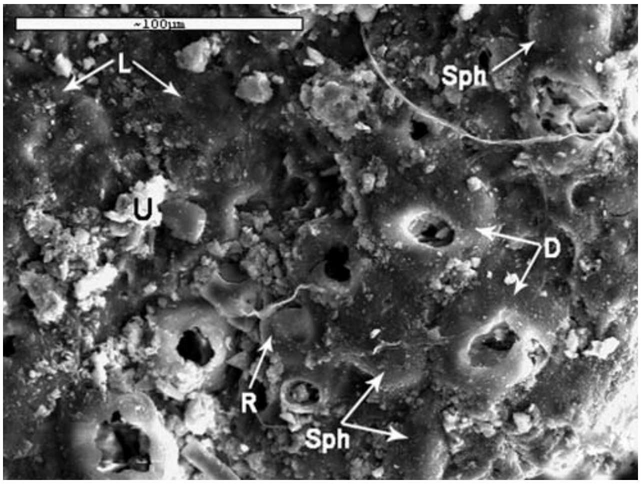


Fig. 18 Ancient charred processed grain fragment from Kapitan Dimitrievo. Starch forms: spherical (*Sph*), “red blood cell” (*R*), doughnut-shaped (*D*), lumpy pancake (*L*)

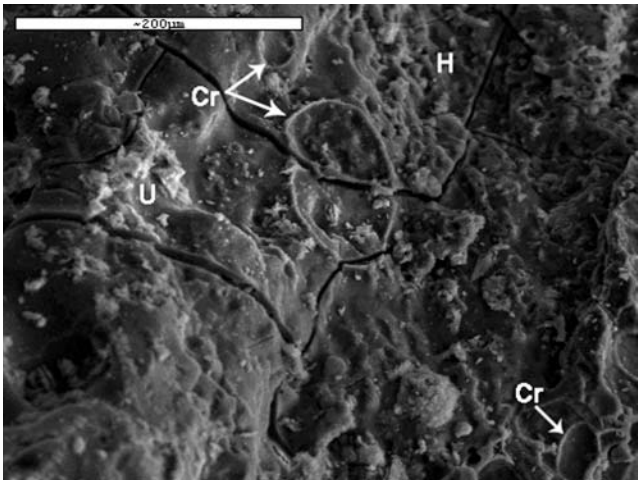


Fig. 19 Ancient charred processed grain fragment from Archondiko, typical microstructure. *Scale bar* 200 µm

suggesting low temperature charring, is an indication that the lumps were formed prior to charring, but more experimental work is needed for confirmation. It is possible that these cereal-based remains were mixed with other ingredients. In this case, very different microstructure might be generated as a result of both preparation and charring. Chemical analysis could prove especially valuable to understand these remains.

Conclusions

We have shown that morphologically recognisable starch granules can in some cases survive the charring process and are detectable in some ancient residues. On present evidence, we think that both high temperature charring and destructive low temperature charring of starchy endosperm produce a matrix which can be reliably distinguished from low temperature charred starchy endosperm transformed primarily by ancient processing techniques.

We suggest that preservation of starch granules in some ancient charred remains occurs at least in part because this material was charred at sufficiently low temperatures to preserve the original microstructure. On the basis of work by Braadbaart et al. (2004) and Braadbaart (2008), this suggests temperatures lower than 270°C, and possibly considerably lower. This could be explored further with the type of chemical characterisation undertaken by Braadbaart et al. (2004). Microstructure varies from fragment to fragment, as if the charring microclimate were very specific; therefore residues analysed for chemical composition would have to be selected individually. There is no doubt that a range of chemical analytical techniques would be invaluable to help understand the taphonomic processes undergone by these ancient food remains.

The application of SEM to modern experimental and ancient charred cereal foods looks promising for the interpretation of ancient cooking, but this paper marks the very early stages of research. It remains to be seen if good starch preservation occurs in charred material recovered from contexts other than burnt destruction levels. There may be a range of charred cereal remains which is suitable for such analysis. We hope that the development of this technique will allow researchers to explore more widely, and in greater detail, the ancient processing techniques used to convert raw grain into edible foodstuffs.

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References

Bakshi AS, Singh RP (1980) Kinetics of water diffusion and starch gelatinization during rice parboiling. J Food Sci 45:1387–1392

Bayram M (2000) Bulgur around the world. Cereal Foods World 45:80–82

Braadbaart F, Van der Horst J, Boon JJ, Van Bergen PF (2004) Laboratory simulations of the transformation of emmer wheat as a result of heating. J Therm Anal Calorim 77:957–973

Braadbaart F (2008) Carbonisation and morphological changes in modern dehusked and husked *Triticum dicoccum* and *Triticum aestivum* grains. Veget Hist Archaeobot 17:155–166

Derby RI, Miller BS, Miller BF, Trimbo HB (1975) Visual observation of wheat-starch gelatinization in limited water systems. Cereal Chem 52:702–713

Grammenos D, Kotsos S (2002) Α*νασκαφή στην* Π*ροϊστορική* Θ*έση* 'Μ*εσημεριανή* Τ*οὐμπα*' Τ*ριλόφου* Θ*εσσαλονίκης* [Excavations at the Prehistoric site "Mesimeriani Toumba" Trilofou Thessalonikis, in Greek]. Archaeological Institute, Thessaloniki

Hoseney RC, Atwell WA, Lineback DR (1977) SEM of starch isolated from baked products. Cereal Foods World 22:56–60

Jones G, Wardle K, Halstead P, Wardle D (1986) Crop storage at Assiros. Sci Am 254:96–103

Marinova E (2006) Vergleichende paläoethnobotanische Untersuchung zur Vegetationsgeschichte und zur Entwicklung der prähistorischen Landnutzung in Bulgarien. Dissertation Bot 401 Cramer, Berlin

Marinova E, Popova Z (2008) Chick pea (*Cicer arietinum*) in the Neolithic and Chalcolithic of Bulgaria: implications for cultural contacts with the neighbouring regions? Veget Hist Archaeobot. doi:10.1007/s00334-008-0159-5

Nikolov V (2000) Kapitan Dimitrievo Tell sequence and cultural characteristics (Brief report in the light of the sounding excavations in 1998–1999). In: Nikolova L (ed) Technology, style and society: contributions to the innovations between the Alps and the Black Sea in prehistory. British Archaeological Reports (BAR International Series 854). Archaeopress, Oxford, pp 51–63

Papaefthymiou-Papanthimou A, Pilali-Papasteriou A (1995) Α*νασκαφή στο* Α*ρχοντικό* Γ*ιαννιτσών* [Excavations at Archondiko Giannitson, in Greek]. Archaeologiko Ergo sti Makedonia kai ti Thraki 6:151–156

Papaefthymiou-Papanthimou A, Pilali-Papasteriou A, Basogianni D, Papadopoulou E, Tsagaraki E, Fappas I (2002) Α*ρχοντικό* 2000. Τ*υπολογική παρουσίαση και ερμηνευτικά προβλήματα των πηλόκτιστων κατασκευών* [Archondiko 2000. Typological presentation and interpretive problems concerning the clay structures]. Archaeologiko Ergo sti Makedonia kai ti Thraki 14:421–433

Rockland LB, Jones FT, Hahn DM (1977) Light and scanning electron microscope studies on dry beans: extracellular gelatinization of lima bean starch in water and a mixed salt solution. J Food Sci 42(1212):1204–1207

Samuel D (1996) Investigation of ancient Egyptian baking and brewing methods by correlative microscopy. Science 273:488–490

Valamoti SM (2002) Food remains from Bronze Age Archondiko and Mesimeriani Toumba in northern Greece? Veget Hist Archaeobot 11:17–22

Williams MR, Bowler P (1982) Starch gelatinization—a morphological study of Triticeae and other starches. Starch-Starcke 34:221–223

Wollstonecroft MM, Ellis PR, Hillman GC, Fuller DQ (2008) Advances in plant food processing in the Near Eastern Epipalaeolithic and implications for improved edibility and nutrient bioaccessibility: an experimental assessment of *Bolboschoenus maritimus* (L.) Palla (sea club-rush). Veget Hist Archaeobot. doi: 10.1007/s00334-008-0162-x