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Research Paper

"Nor ever lightning char thy grain"[1]: establishing archaeologically relevant charring conditions and their effect on glume wheat grain morphology

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Abstract Charring is the most ubiquitous form of preservation of plant material on archaeological sites, occurring wherever people use heat. The usefulness of preserved seeds for a range of analytical techniques is dependent on the conditions under which they were heated. In this study, we investigate the effect of experimental heating on two types of glume wheat grain (einkorn and emmer) under a range of conditions, with the intention of establishing the likely parameters for the generation of virtually undamaged, undistorted charred cereal grain on archaeological sites. The results show that grain morphology is very sensitive to the charring conditions, especially temperature, and that well preserved grains with little distortion are produced at relatively low temperatures (220–240°C). The implications of these findings for the study of grain morphology, biomolecules and chemical composition are assessed.

Keywords Archaeobotany, Charring, Glume wheat, Maillard reaction, Melanoidins, Dextrinisation

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Data availability The authors confirm that all data underlying the findings are fully available without restriction. All relevant data are contained within the paper.

Introduction

Archaeobotanical remains recovered from archaeological sites provide direct evidence of the plant resources available to past societies. The conventional starting point for interpretation of this material is morphological identification to the highest taxonomic level possible combined with numerical analysis of sample composition to provide information regarding the availability and frequency of plants. More recently, the potential of plant remains, primarily grain/seeds, to yield high-resolution chronologies through Accelerator Mass Spectrometry (AMS) dating, as well as stable isotopic and other biomolecular information, has expanded considerably: new avenues of research relate to crop husbandry (manuring – nitrogen isotopes, watering – carbon isotopes; e.g. Bogaard *et al.* 2014a; Wallace *et al.* in press), location (e.g. strontium and oxygen isotopes, and other trace elements; Bogaard *et al.* 2014a), and ancient DNA (aDNA) which, in addition to refining (genomic) identification, could indicate development and evolution of crop plants (Brown 1999; Bunning, Jones and Brown 2012; Heier, Evans and Montgomery 2009; Schlumbaum, Tensen and Jaenicke-Després 2008). Recently, morphometric studies using shape analysis techniques have shown potential to refine the identification of seeds (e.g. grapes, olives, date-palm and barley) even after heating, provided that distortion is not too extreme (Orru *et al.* 2013; Ros *et al.* 2014; Terral *et al.* 2004, 2010, 2012). Fundamental to these techniques based on the chemical or physical analysis of seeds or chaff items is the form and state of preservation of the plant material.

The aim of this paper is to establish the range of conditions under which cereal grains of the glume (or hulled) wheats, specifically einkorn (*Triticum monococcum* L.) and emmer (*Triticum dicoccum* (Schrank) Schübl.), are preserved by charring in a form that resembles that encountered archaeologically, and the impact of these conditions on grain morphology and chemistry. Charring is the most widespread form of preservation of plant remains associated with human activity on archaeological sites. The term

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'charred' refers to material that has been 'burnt to carbon, burnt black' ('charring' OED Online); 'charred' is preferred here to the term 'carbonised', which can also refer to material gradually reduced to carbon over geological timespans ('carbonised' OED Online). The glume wheats represent a major category of crop remains found on Old World archaeological sites. Previous work has shown that the effect of charring on cereal grain varies according to temperature, rate and duration of the heating period and the availability of oxygen (e.g. Boardman and Jones 1990; Braadbaart 2008; Wilson 1984; Yang *et al.* 2011). This work has, however, concentrated on charting the range of conditions under which cereal components survive rather than on identifying those particular conditions that yield relatively undistorted material identifiable to the highest taxonomic level and hence of particular interest for morphological, AMS dating, aDNA and stable isotope research. After reviewing existing literature, a set of experiments are described, which were designed to specify these charring conditions for einkorn and emmer grain, in order to assess implications for the survival of biological information.

Table 1 Cereal grain preservation and distortion scales as defined by Hubbard and al Azm (1990).

Class	
Preservation (1977)	
1	Perfect
2	Epidermis virtually intact; rhachillae, etc. observable
3	Epidermis incomplete; rhachillae, hairs, etc. occasionally preserved
4	Fragments of epidermis remaining; other features virtually unobservable
5	Identified by gross morphology only
6	"Clinkered" (mass of bubbled endosperm retaining the shape of the seed)
	Distortion (1977)
1	No noticeable distortion
2	Slight puffing of seeds noticeable
3	Clearly distorted
4	Gross distortion
5	Seeds fused together into a solid clump, facetted when free
	Distortion – modified (1986–8)
1	No noticeable distortion
2	Slight puffing of seeds noticeable
3	Clearly distorted
4	Gross distortion
5	Seeds fused together into a solid clump, facetted when free
6	Carbonised tarry material exuded from distal end of caryopses
7	Sides of the seed longitudinally wrinkled, partially collapsed and concave
8	Sprouting: as (7), but with the radical greatly elongated

Background

Though charred plant remains are ubiquitous on many archaeological sites, their frequency and state of preservation varies from low-density scatters of redeposited fragments identifiable only to broad taxonomic categories through to large concentrations of grain charred *in situ* and virtually unchanged from its original form. Hubbard and al Azm (1990) devised a system for classifying charred cereal grain based on scales of 'distortion' and 'preservation' (Table 1) that encompassed the range of conditions seen in archaeological material. The authors scored 'distortion' of grains due to charring (which they refer to as carbonisation) on a scale extending from 'no noticeable distortion' through to 'carbonised tarry material exuded from distal ends of caryopses'. The 'preservation' index, associated by the authors with mechanical disturbance resulting from burial and recovery, gave particular attention to the presence or absence of the seed coat (epidermis). This system attempted to distinguish between charring 'distortion' and post-charring 'preservation', but the two are linked, such that the poorest 'preservation' category ('clinkered') actually refers to charring-related distortion.

The processes by which grains became charred and preserved archaeologically are often difficult to establish for an individual sample, though contextual associations may point to a particular source of heat. On-site sources of heat have been categorised by various authors (e.g. van der Veen 2007) and include open fires or hearths (for heating, lighting and cooking), ovens (for food preparation, e.g. drying, parching, cooking and malting), kilns (for the manufacture of materials such as pottery, brick and glass), the use of fire for cleansing (e.g. of infested grain storage facilities), destruction of rubbish (including middens), and the accidental or deliberate burning of buildings or parts of buildings. The key factors affecting the condition of grain relate primarily to the heat generated, but other factors, such as oxygen availability and the directness of heat, also play a part. Charred plant remains are often found in secondary contexts, as for example, when ashes from domestic fires are disposed of as waste or used for a range of purposes (e.g. Hakbijl 2002).

Where grain concentrations are preserved in burnt buildings, e.g. at Late Bronze Age Assiros Toumba, Greece (Jones *et al.* 1986; Wardle 2009) and Neolithic Çatalhöyük, Turkey (Bogaard *et al.* 2009, 2014b), the cause of charring may be obvious but the conditions of heating can still vary considerably within a single room or building complex, even where they result from the same fire. At Assiros, for example, preservation within a single large burnt storeroom ranges from grains that have been totally reduced to ashes to those that are near 'pristine' in form (though not in colour), i.e. black, relatively undistorted externally, with only 'slight puffing' (Hubbard=2) and no sign of epidermal blisters. Glume lines – impressions left on the grain surface from the surrounding chaff – are visible, as is the epidermal cell pattern and in some cases the hairs at the apex of the grain. For such excellently preserved cases, the endosperm in cross-section has a structure resembling a dense network or reticulum of 'cells' with some filled areas (Fig. 1A). At Çatalhöyük, grain preservation is again variable, but a substantial proportion is well preserved both in storage contexts (e.g. small storerooms situated within individual houses are occasionally preserved when houses have burnt down) and rubbish dumps where spent fuel, frequently animal dung, is disposed of on a routine basis (Bogaard *et al.* 2014b). Figure 1 (2a–c) shows the external and internal features of emmer grain from one of these storage areas. Externally, preservation state is similar to that of the Assiros example, retaining features, such as the glume lines. Internally, the cell reticulum is also similar, though the walls of the cells seem to have retained more of the original cell contents. These differences in the internal and external structure of archaeological grains indicate that they were exposed to a range of heating conditions, and that within that range it is typically the less distorted material that can be usefully identified and analysed.

Two types of experiment have been carried out to assess the nature of charring conditions on archaeological sites. First, laboratory-based studies of seeds have been conducted under controlled conditions in laboratory ovens (e.g. Boardman and Jones 1990; Braadbaart 2008; Braadbaart *et al.* 2004b,c, 2005; Hopf 1955; Märkle and Rösch 2008; Milić *et al.* 1975; Stewart and Robertson 1971; Wilson 1984). The range of variables tested, including temperature (100–750°C), heating duration (10 minutes to 8 hours), oxygen availability (zero to atmospheric), rate of temperature rise (2–200°C $minutes^{-1}$) and the type and form of plant material tested (cereals, pulses, oil plants, etc.; grains and chaff) are shown in Table 2 and Fig. 2. Broadly, the conclusions of previous work are that the temperature to which archaeological charred crop grains were exposed was at least 250°C, with preservation much more likely above 300°C, for a period of <2 hours under low-oxygen conditions.

The second type of experiment simulated potential archaeological charring conditions first by burning grain in reconstructed hearths (Guarino and Sciarrillo 2004; Gustafsson 2000; Sievers and Wadley 2008) and second by burning down a building (Gustafsson 2000) containing grain, and recording the temperatures and charring survival of grain. Also of note are experiments by Werts and Jahren (2007), wherein the temperature in soil below campfires was recorded, and Braadbaart *et al.* (2012) in which the heating properties of wood, peat and cow-dung fuel were assessed; although this work did not examine the impact of fire on grain or other plant remains, the temperatures recorded for the different fuels and the range of temperatures seen

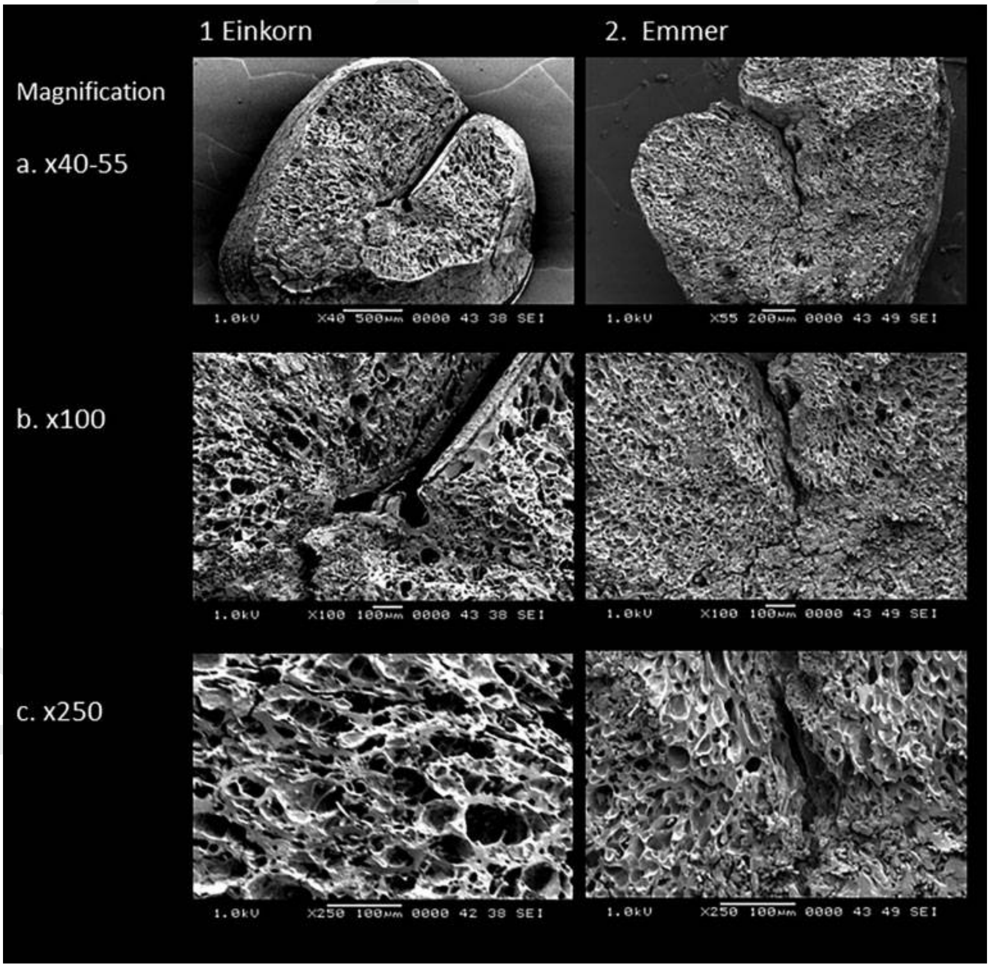

Figure 1 Cross section of archaeologically charred einkorn (1) and emmer grain (2) at low power, medium power and high power.

Table 2 Summary of previous archaeological experimental heating work on cereals and pulses.

Taxa and [plant parts]	Temperatures		Durations	Oxygen availability	Heating rates	Notes	Reference
Triticum monococcum	250°C		30 minutes	High: open to air	*Unspecified*	Plant material dried before charring	(Boardman and Jones 1990)
	300°C		1 hour	Low: covered crucibles			
T. dicoccum	350°C		3				
T. spelta [seeds, straw nodes, glume bases, whole spikelets]	400°C		5				
	450°C						
T. aestivum [seeds, straw nodes, rachis]	500°C						
Hordeum vulgare var. *hexastichum* (hulled) [seeds, straw nodes]	550°C						
Pisum sativum subsp. *arvense* (3 var.) [seeds]	130°C	310°C	Up to 2 *unspecified intervals*	Low: N atmosphere	Slow: 2°C minutes^{-1}		(Braadbaart *et al.* 2004b)
	160°C	340°C			Rapid: 200°C minutes^{-1}		
	190°C	370°C					
	220°C	400°C					
	235°C	440°C					
	250°C	500°C					
	270°C	600°C					
	290°C	700°C					
Triticum dicoccum (7 var.) [seeds]	130°C	310°C	7.5–280 minutes *unspecified intervals*	Low: N atmosphere	Slow: 2°C minutes^{-1}		(Braadbaart *et al.* 2004c)
	160°C	340°C					
	190°C	370°C					
	220°C	400°C					
	235°C	440°C					
	250°C	500°C					
	270°C	600°C					
	290°C	700°C					
Triticum dicoccum (7 var.)	130°C	310°C	2 hours (*Triticum* spp.)	Low: N atmosphere	Slow: 2°C minutes^{-1}		(Braadbaart *et al.* 2005)
	160°C	340°C					
	190°C	370°C					
	220°C	400°C					
	235°C	440°C	1 hour (*Pisum* sp.)				
T. aestivum (4 var.)	250°C	500°C					
T. durum (3 var.)	270°C	600°C					

Table 2. *Continued*

Taxa and [plant parts]	Temperatures	Durations	Oxygen availability	Heating rates	Notes	Reference
Pisum sativum	290°C 700°C					
Triticum dicoccum	310°C	1 hour	Low: N atmosphere	Slow: 1–5°C minutes^{-1}		(Braadbaart 2008)
T. aestivum [seeds]	440°C			Rapid: pre-heated oven		
	600°C					
Hordeum vulgare	200°C	45 minutes	High: open to air	Slow: 2 hour temperature ramp	Dried for 24 hours at 60 C prior to charring	(Ferrio *et al.* 2004)
Triticum aestivum seed	250°C		Low: buried in sand			
	300°C					
Panicum miliaceum	180°C to 750°C *unspecified intervals*	1 hour	**High**: open to air	**Slow**: 20–40 minutes heat ramp	Seeds not dried prior to charring	(Markle and Rosch (2008))
Setaria italica		2	**Low**: in crucible covered with aluminium foil			
Linum usitatissimum		3				
Papaver somniferum		4				
Cannabis sativa seeds/fruits						
Hordeum vulgare seed	250°C	10–50 minutes (at 10 minutes intervals)	*Unspecified*	*Unspecified*	Plant material roasted rather than charred	(Milić *et al.* 1975)
Hordeum distichon and H. vulgare Triticum monococcum, T. dicoccum and T. aestivum [seed]	Unspecified	10 minutes	*Open*	*Unspecified*	Seeds heated on asbestos pad after drying to 11 or 15% moisture	(Stewart and Robertson 1971)
Allium cepa	250°C	30 minutes	High: open to air	Rapid: pre-heated oven	Plant material either dry (dried in desiccator) or wet (36 hour soak in chilled water) before charring	(Wilson 1984)
Pastinaca sativa						
Petroselinum crispum						
Portulaca oleracea						
Atriplex hortensis	350°C					
Thymus sp.						
Salvia officinalis		16	Low: buried in soil			
Lens culinaris						
Pisum sativum	550°C					
Linum usitatissimum						
Plantago major						
Brassica oleracea [seeds]						

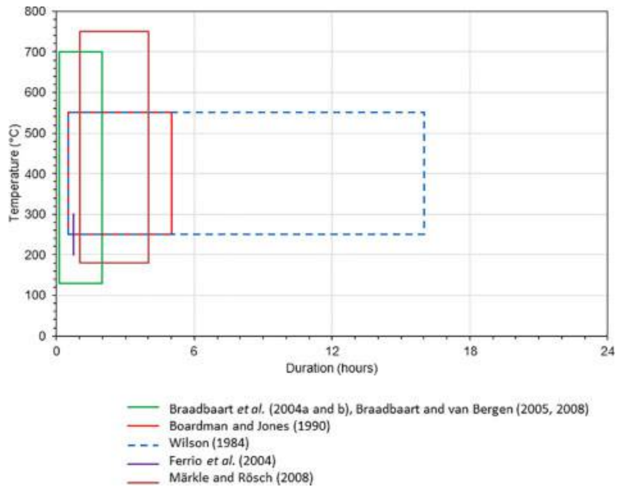

Figure 2 A summary of time and duration of heating explored in previous studies of the effect of heating on crops.

within and below the fires are of relevance here. This work demonstrates that a range of fuel types produce fires that are capable of reaching temperatures in excess of 600°C (e.g. Braadbaart *et al.* 2012: 838; Guarino and Sciarrillo 2004: 67–8; Sievers and Wadley 2008: 2915), the temperature found to reduce many types of plant material to ashes. Sievers and Wadley showed that a fire allowed to burn itself out maintained a temperature of around 600°C in the centre for some 3 hours, before steadily declining to air temperature over a further 3 hours (2008: 2915, Fig. 5). Braadbaart *et al.* (2012) recorded substantial temperature differences across the area covered by a fire, ranging from 800°C in the centre to 400°C at the edge, suggesting that plant material will be exposed to less extreme temperatures at increasing distance from the centre. Recording of the temperatures occurring in the soil beneath the fire demonstrated that the temperature drops rapidly below the surface; 5 cm beneath a 600°C fire, the temperature was just 328°C (Sievers and Wadley 2008: 2914). Similarly, Guarino and Sciarrillo recorded a maximum temperature of 400°C 30 cm below a 750°C fire (2004: 68, Fig. 9), while Werts and Jahren measured temperatures of <300°C just 3–4 cm below a 700°C fire (2007: 853). In addition to the effects of varying the heating regime, changes in seed morphology also resulted from differences within and between species due to factors such as seed structure, moisture content and chemical composition (e.g. fats, oils, lipids, sugars and starch) (Guarino and Sciarrillo 2004; Gustafsson 2000).

Recognition of 'charring'

Boardman and Jones (1990) used external seed colour to estimate the extent of charring, with cereal grains becoming progressively darker from brown to black with increasing temperature. Braadbaart and colleagues recorded colour change during heating in emmer grain (Braadbaart *et al.* 2004c) and peas (Braadbaart and van Bergen 2005). The inside of emmer grains darkened at a slower rate than the outside, and seeds were blackened throughout after charring at 270°C for 1 hour, the outer grain surface becoming black at 290°C (Braadbaart *et al.* 2004c). In pea, these stages are reached at 220 and 270°C, respectively (Braadbaart *et al.* 2004b). However, colour has not always been shown to relate to the extent of charring; for example, Märkle and Rösch (2008) question the value of colour as a diagnostic criterion due to variation between species. They found that the seed surface of broomcorn and foxtail millet remained dark-brown even under temperatures high enough to blacken the interior of the grain, whereas flax and poppy seeds turned black despite clearly being in a state that would not survive archaeologically, as they remained soft and oily.

An additional criterion for identifying relevant 'charring' conditions is that seeds should become sufficiently transformed chemically to survive archaeologically, such that they are inert and relatively unaffected by biological attack by micro-/macro-organisms (see Märkle and Rösch 2008 for further bibliography). Braadbaart and colleagues highlight the replacement of polysaccharides and proteins by aromatic compounds, and predict that the survival of emmer, peas and sunflower is greatest at temperatures above 310°C; at temperatures below 250°C, they argue, the presence of sugars and proteins, albeit dehydrated, indicates that microbial degradation may occur (Braadbaart *et al.* 2004a, 2007).

Examination of the published photographs of material produced by the laboratory-based experiments carried out by Braadbaart and colleagues (Braadbaart 2008; Braadbaart *et al.* 2005) suggests that the charred grain is typically 'clearly' or 'grossly' distorted (3 or 4 on the Hubbard and al Azm scale) and is usually shorter and rounder than the uncharred grain, often with substantial areas of blistering on the grain surface. This suggests that much of the material previously reported upon has been exposed to more extreme conditions than the well preserved and relatively undistorted grain (1–2 on the Hubbard and al Azm scale; 'no noticeable distortion' 'slight puffing of seeds') of the sort routinely encountered archaeologically. For example, emmer grains heated to 250°C are described as 'swollen'; at 270°C 'protrusions' (exudation of grain contents) appear and increase to a maximum level at 290°C, while 'vesicles' (where the pericarp rises away from endosperm) appear at 340°C (Braadbaart *et al.* 2004c).

Physical and chemical properties of cereal grain and the effect of heating

Establishing the changes in chemical composition and physical structure of the grain as a direct result of charring provides insight to the conditions required to preserve the grain, such as the temperature needed to destroy organic components or convert them to stable compounds.

The wheat grain consists of a central core of endosperm surrounded by the bran. The endosperm is made up of relatively large, thin-walled cells full of starch grains in a matrix of protein, primarily gluten. The outer bran consists of seven layers in total, generally summarised as the aleurone layer, testa and pericarp (Percival 1921). The outer testa or seed coat often behaves like a single layer and does not reliably survive archaeologically. The elemental composition of the grain reflects these morphological observations and is typically c.40% carbon, c.1.5% nitrogen and c.7% hydrogen in fresh grain (Fraser *et al.* 2013; Styring *et al.* 2013).

Roasting coffee beans and cereal grains

The roasting of coffee or coffee substitutes, including cereal grains, provides useful information for understanding the effect of heat on wheat grain. Coffee bean composition is broadly similar to that of cereals, though there is a higher percentage of lipids, and chlorogenic acid is also present. Coffee beans are typically roasted at 200–240°C in open, aerobic conditions for periods of c.3–12 minutes (Illy 2002). During roasting, the beans pass through two 'cracking' stages of extreme morphological change (marked by audible 'cracks') at c.190 and 224°C, which are thought to be caused by processes of dehydration and pyrolysis, respectively. The onset of pyrolysis, causing the release of bound water and carbon dioxide, continues for up to c.17.5 minutes and results in a reduction in grain mass (Rodrigues 2003). Changes in bean shape and colour occur within seconds of the roasting temperature being reached (Fischer and Cammenga 2001), producing a wide range of surface colours from dark brown to black depending on the precise temperature and duration of roasting. Mass lost decreases consistently with both temperature and time and, after the roasting period, averages 17.6% (Bekedam *et al.* 2008; Geiger *et al.* 2005; Redgwell *et al.* 2002), exceeding the typical water content estimates for green coffee beans, and presumably reflecting the release of volatiles. Polysaccharides within the beans are degraded as the cells expand under pressure from the release of steam and carbon dioxide (Redgwell *et al.* 2002); at 240°C, a 35–40% decrease in polysaccharides can be seen after 7–8.5 minutes (Bekedam *et al.* 2008; Geiger *et al.* 2005; Redgwell *et al.* 2002).

Investigation of the Maillard reactions taking place in coffee during roasting suggests that the reactions are initiated rapidly, with melanoidins increasing four-fold after even the shortest duration roast (Bekedam *et al.* 2008; Geiger *et al.* 2005; Redgwell *et al.* 2002). The nature of the melanoidins produced varies considerably in terms of molecular weight, with high molecular weight (HMW) melanoidins increasing seven-fold to make up 37% of melanoidins in the material heated for the longest time. This may be of relevance to survival of charred grains in soil, as the higher molecular weight polymers are most resistant to microbial attack (Moreira *et al.* 2012).

Dry roasting of barley grain causes initiation of Maillard reactions and dextrinisation processes within 10 minutes, resulting in loss of water, starch and α-amino nitrogen (Milić 1975, see Table 1), increases in melanoidins, dextrin, total sugars and reducing sugars, and a decrease in starch content. These trends continue for the duration of roasting.). Grain mass decreases rapidly, with c.13% lost within 12 minutes (Geiger *et al.* 2005) compared with the 17.5% lost after 1 hour as recorded by Braadbaart *et al.* (2004c) for emmer grains heated at 220°C. Pazola and Cieslak (1979) record a very rapid decrease in barley starch levels from c.45 to 10% of the dry weight between 30 and 60 minutes. Part of the explanation for the disappearance of starch is its conversion to dextrin, which occurs when starch is heated under low moisture conditions (Pazola and Cieslak 1979). Dextrins are often brown and contribute to the change in colour observed in the grain. Caramelisation, which occurs in sugar-rich grains (e.g. cereals) at temperatures above 110°C, also causes discolouration and darkening (Ajandouz *et al.* 2001).

A recent study by Styring *et al.* (2013) investigated changes occurring in einkorn grains heated to 230°C for 2–24 hours using elemental analysis, spectroscopy, and gas chromatography of amino acids. This study showed that mass loss continues, though at a slower rate, until it reaches 38% after 24 hours. The major elemental loss is in oxygen, especially between 2 and 4 hours (47.4–30.8% lost). In contrast, percentages of carbon (41.5 to 62.9%) and nitrogen (2.9 to 4.3%) increase substantially (Styring *et al.* 2013, Table 7). After 24 hours, the authors' observations suggest that the starch had mostly reacted with the cereal protein, leaving only alkyls and aromatic carbon.

Methods

The experiments described here were intended to investigate the relationship between temperature and duration of heating on cereal grains commonly occurring on archaeological sites across Europe and western Asia. Other variables tested include reduction of the air available during grain exposure to heat. Two species of glume wheat commonly found at a wide range of archaeological sites were selected for the experiments, an unimproved land race of einkorn (Haute Provence, France); and emmer (UK).

Experimental conditions

Air-dried grain samples were placed in the centre of a pre-heated high precision oven accurate to ±2°C. Low

Table 3 Comparison of the major chemical components of cereal grains.

	Wheat (%)	Barley (%)	Rye (%)	Oats (%)
Water	13.1	9.4	10.6	8.2
Protein	12.6	12.5	10.3	16.9
Lipids	1.5	2.3	1.6	6.9
Carbohydrates	71.2	73.5	75.9	66.3

Source: http://ndb.nal.usda.gov/ndb/foods oxygen conditions were achieved by tightly wrapping grains in aluminium foil and placing them in the middle of a 250 ml Pyrex beaker full of sand. Thus, air availability was substantially reduced but air was not completely excluded from the sample, mimicking likely archaeological charring in which at least some air would have been available. Medium oxygen levels were achieved by wrapping the material in aluminium foil and placing each packet in an open crucible. Finally, in order to assess the effects of charring under conditions of plentiful air, a replicate of each batch was placed in an open crucible. The temperature in the crucibles and beakers was monitored using thermocouples connected to a digital thermal recorder. Beakers/crucibles were removed from the oven after the selected time period and allowed to cool at room temperature. The continuous record of temperatures provided by the thermocouples showed that the temperatures in the oven varied little through the duration of the experiment. To investigate further the differences visible in the cut sections of heated grains, cross-sections were examined using a Scanning Electron Microscope (SEM).

After cooling, the grain was examined under a low-power stereoscopic microscope (×7 to ×45 magnification). Grains from each sample were cut transversally so that the effect of charring on the internal parts of the grain could be assessed. Five variables were recorded on a 1–4 or 5 point scale, where 1=the appearance of the unheated material (see Table 4 for a list of the recording scales for the variables).

The five variables are as follows:

1. Colour – the colour of the cut section's surface was recorded. Archaeological grains are usually completely black, though occasionally there may be a hint of dark-brown colour, typically in the outer epidermal layers.
2. Distortion – the average level of distortion of the grains in a sample was scored on a modified scale based on the scale of the Hubbard and al Azm (1990), from 1 (=no noticeable distortion) to 4 (=gross distortion). The final point on this scale equates to level 6 on the Hubbard and al Azm scale; level 5 on their scale (seeds fused into a solid lump) was not relevant in our experiments. The best preserved/least distorted archaeological material would have a score of 1, indicating that the grain has undergone minimal morphological change, usually in the form of a slight shortening and rounding.
3. Blisters – the presence of blisters on the surface of the grain. Generally absent in undistorted archaeological material.
4. Lines – the presence of 'lines' (linear indentations) running at right angles to the long axis of the grain that sometimes appear during heating.
5. Shininess – while uncharred glume wheat grains have a dull or matt surface, charring causes increasing shininess.

Experiment 1 – einkorn

Einkorn grains were heated in batches of 5–10, at temperatures from 100 to 600°C for 1 to 120 hours and under low to high oxygen availability to establish the broad parameters of preservation (Table 5). For each set of experimental conditions, grains were heated both within the spikelet and after the glumes had been removed.

Experiment 2 – emmer

In order to explore the effects of charring on another cereal type, and to test and refine the results of the first experiment, another set of experiments was carried out using emmer. Free grains (not enclosed within the spikelet) were heated under low oxygen conditions. A narrower range of temperatures and durations was chosen to cover key stages established in the einkorn experiment: a low temperature (200°C) where the grain is never fully blackened; a medium temperature (230°C) associated with only slight distortion and hence approximating well preserved archaeological grain; and a high temperature (260°C) where grain is 'clearly distorted', for durations of 3, 6 and 9 hours. Prior to heating, grains were photographed, weighed and measured (length, breadth and thickness). They were then wrapped and charred individually in order to facilitate one-to-one comparison of pre- and post-charring dimensions compared to the less specific information recorded in the first (einkorn) experiment. All measurements were repeated after charring, and the percentage change recorded. A minimum of nine grains was charred for each combination of durations and temperatures.

Results

Experiment 1 – einkorn

Figure 3 shows einkorn grain heated from 100 to 400°C in lateral view and cross-section while Table 5 records the colour of the cross-section of grain. As the grains were

Table 4 Scales used to record changes in grain appearance after charring. Shaded conditions indicate the characteristics of well-preserved archaeological grain.

Class	Colour	Distortion	Blisters	Lines	Shininess
1	Light brown	None	None	None	Dull
2	Brown	Low	Low	Some/faint	Mid/dull
3	Dark brown	Medium	Medium	Medium	Mid
4	Dark brown/black	High	High	High	Mid/shiny
5	Black	Extreme	Extreme	Extreme	Shiny

Table 5 Recorded colour of einkorn grains in cross-section after charring at various temperatures, durations and levels of oxygen availability. 1 = light brown, 2 = brown, 3 = dark brown, 4 = dark brown/black, 5 = black. Dash indicates conditions tested but colour not recorded.

Oxygen	Temperature [°C]	Time [hours] 1	2	4	8	24	48	72	96	120
High oxygen availability	200				3	4	4	4	4	4
	210	1	2	3	4	5	4	5		
	220		4	4	5					
	230		4	5						
	240	4	5							
	250	5	5							
Low oxygen availability	200				2	3	3	3	3	3
	210		1	2	3	4	3	4	4	4
	220		3	3	4	4	4	4	4	4
	230		3	4	5					
	240	3	4	4	5					
	250	5								

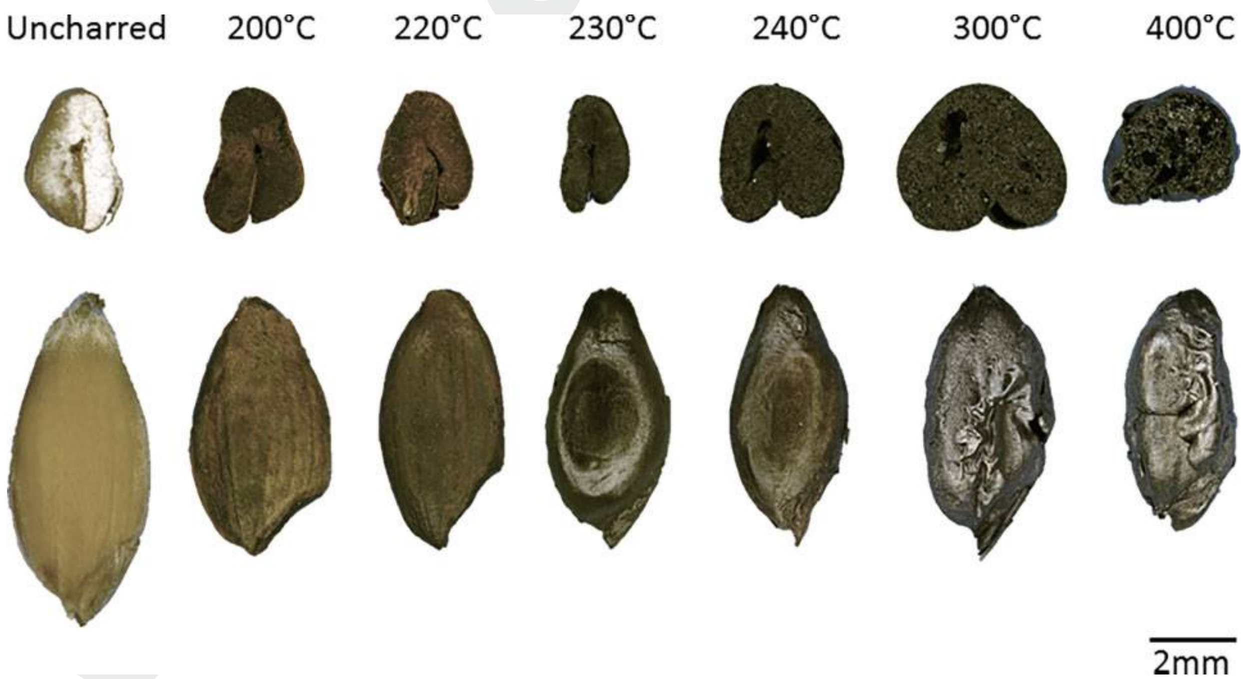

Figure 3 Low power microscopy of modern einkorn grains heated between 100 and 400°C, cross section (top row) and whole grain (bottom row).

'clearly distorted' or reduced to ash above 400°C, results above this temperature are not shown. There was also very little difference between grains charred within and without the spikelet under the same charring conditions. Where differences were noted, these were minor and inconsistent, and are not discussed further.

100–210°C

At the lower end of the temperature range, the grain is little altered in shape with a slight reduction in length and increase in breadth and thickness, and the glume lines, though still visible, are reduced in prominence. In cross-section, the grain is more rounded with thin fissures appearing within the grain. Externally, grain colour darkens, with some areas of darker brown, while internally the grain does not blacken even after 120 hours.

210–240°C

>At these temperatures, einkorn grain broadly matches the gross morphology observed in well preserved, little distorted archaeological material (Hubbard = 1–2) (Fig. 3). The lowest temperature to produce consistent charring and blackening in cut sections within 24 hours was 210°C, and under these conditions, the grain shows very slight shape change from the uncharred form. Increasing the temperature to 220 and 230°C reduces the time required for full blackening to 8 and 4 hours, respectively, while the level of distortion increases (Hubbard = 2) due to the grain rounding off. At 240°C, the time required for full blackening is reduced to 2 hours, but grain shape change is more marked, with the grain rounding substantially at all time intervals. There is also an increased tendency for blisters to develop on the surface of the grain, and faint 'lines' (linear indentations) to appear at right angles to long axis of grain (which does not occur at higher temperatures or on grains enclosed within the spikelet).

250–300°C

At 250°C, the grain becomes clearly distorted (Hubbard = 3) showing marked signs of morphological alteration (bulges or blisters on the surface as well as substantial rounding), though the grains are still recognisable as einkorn. Above 250°C, the grain is blackened even at the shortest duration tested (1 hour) and is also 'grossly distorted' (Hubbard = 4), to the point where identification to species becomes difficult.

Above 300°C

At 300°C, the grain is substantially shorter and rounder and there are several surface blisters and occasional exudations. The cross-section of the grain shows that the roundness is caused by a combination of factors: blistering resulting from the pericarp separating from the seed endosperm or aleurone layer, a change in the shape of the endosperm, and the appearance of cavities within the grain. Between 300 and 500°C, the grain becomes increasingly 'damaged' by surface blistering and shrinkage or crumpling of the inner endosperm core; at 500°C, the grain starts to break up and at 600°C is reduced to ash.

Cellular changes

Figure 4 shows the cut surface of the grain at a range of different heating conditions. The unheated grain at low magnification has a homogeneous appearance with no fissures; at higher magnification, small linear filled cells are visible. Heating at 200°C causes the emergence of large fissures across the surface; the individual endosperm cells are filled and appear to have wavy cell walls. At 220°C, the fissures occupy less of the cut surface and there is a more open network of empty starch 'cells' as well as areas resembling those seen at 200°C. At 240°C, the fissures have disappeared and there is a more open network of relatively large 'cells' lacking any contents.

Experiment 2 – emmer

200°C

Grain colour in emmer darkens progressively over time but does not become black in either cross-section or surface appearance even after 9 hours of heating; the change in grain morphology is small (Hubbard = 0–1) (Fig. 5). The most striking features in cross-section are a series of large internal shrinkage fissures, not visible in einkorn, extending across half or two-thirds of the grain at all heating durations, though they are most pronounced at 3 hours (Fig. 6). On average, there is a 15% loss of grain mass at this temperature with a slight increase in mass loss with time (1% for each extra 3 hour period) (Table 6). These levels of mass loss match those noted in previous experiments (e.g. Braadbaart *et al.* 2004c; Geiger *et al.* 2005) during the early stages of heating, which are equated to loss of free-moisture present in the grain.

230°C

The grain is consistently black in cross-section for all three durations, though the outermost seed coat, the pericarp, always has a faint dark-brown hue. The cross-section also shows that the large internal fissures seen in the grain heated to 200°C are reduced in number and size through time. A number of small surface blisters are also present. Morphologically, the percentage change in grain dimensions is more than double that seen at 200°C (Table 6) making the grain more rounded than the original, albeit with the major diagnostic features retained (Hubbard = 1). In cross-section, the rounding of the grain can be seen to have arisen in part from the pericarp lifting away from the testa. The average loss of mass is greater at 230°C than at 200°C, and there is a marked increase in mass loss between 3 and 6 hours, with only a slight further increase between 6 and 9 hours (Table 6).

260°C

The cross-section of the grain charred at 260°C shows considerable consistency in colour, surface texture and morphology across all heating durations. The grain is uniformly black inside and out, without internal fissures, and has a generally more rounded appearance than at 230°C. Under a low-power microscope, the cut surface of the sectioned grain, consisting primarily of the endosperm, appears homogeneous, resembling a series of similarly sized 'beads'. Grain shape is considerably more distorted than at 230°C, most noticeably in grain thickness (Table 6). In contrast to the grain heated at 230°C, there are fewer surface blisters; instead the grain's roundness seems to be the result of the swelling of individual endosperm cells. There is another substantial increase in the average loss of mass (c.50%) but again little change across the durations tested.

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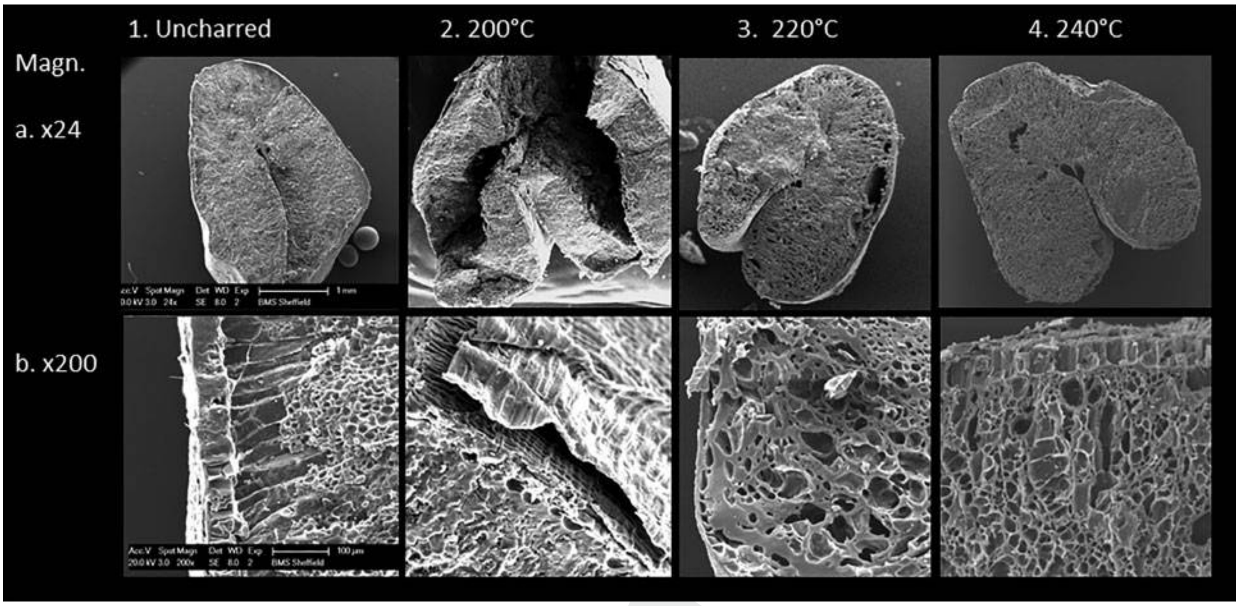

Figure 4 SEM images of modern einkorn grains unheated (1) or heated to 200°C (2), 220°C (3), and 240°C (3) for 4 hours. Grain cross-section, (a) low power (top row), (b) high power (bottom row).

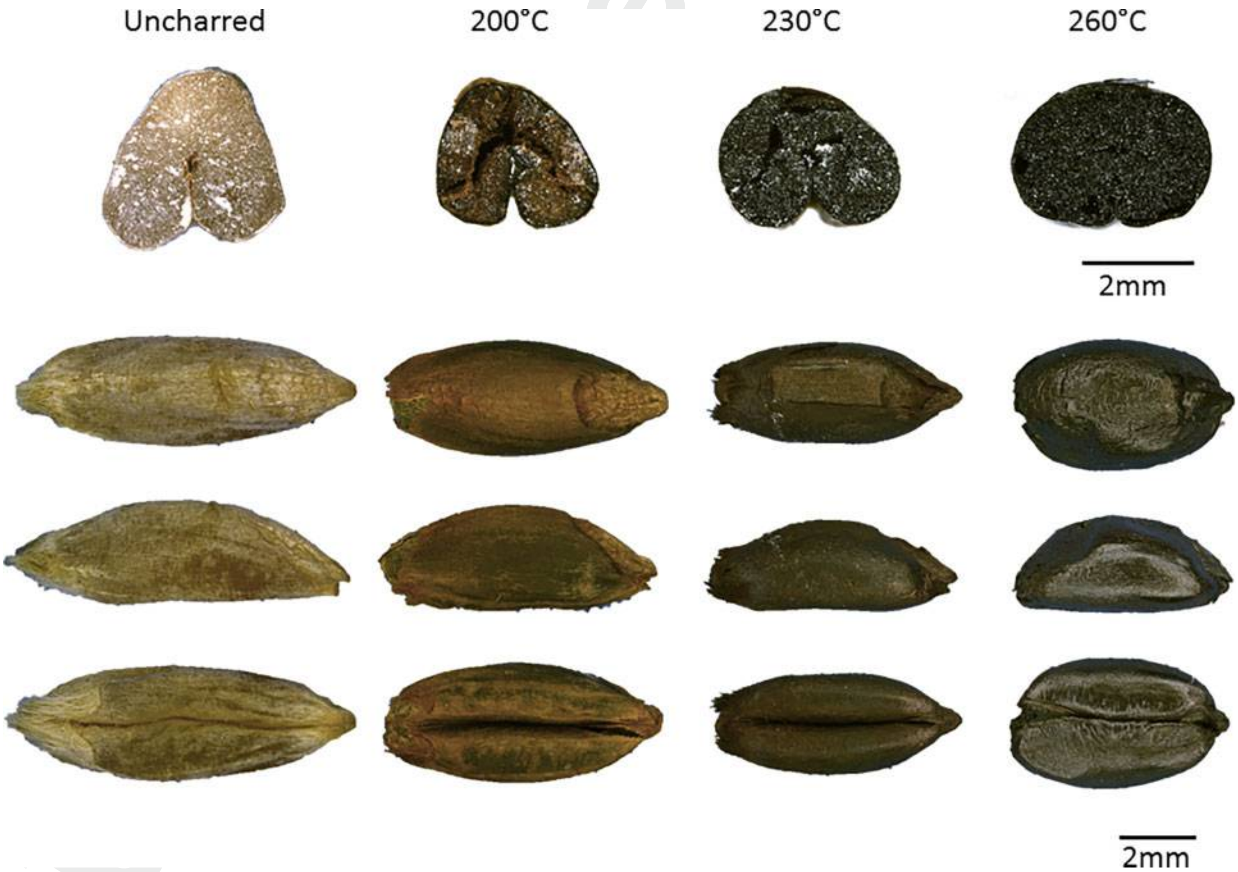

Figure 5 Modern emmer grain before and after charring at 200/230/260°C.

Cellular changes

At 200°C, the individual endosperm cells are no longer discernible; instead the cut surface resembles a smooth and relatively homogeneous 'paste' (Fig. 7Ai–ii). At 230°C, there is a more open network of empty starch 'cells' (Fig. 7Bi–ii) as well as areas resembling those seen at 200°C. Heating at 260°C produces an open network of relatively large 'cells' lacking any contents with no areas of smooth, homogeneous paste remaining (Fig. 7Ci–ii).

These observations are similar to the changes in micromorphology noted for emmer by

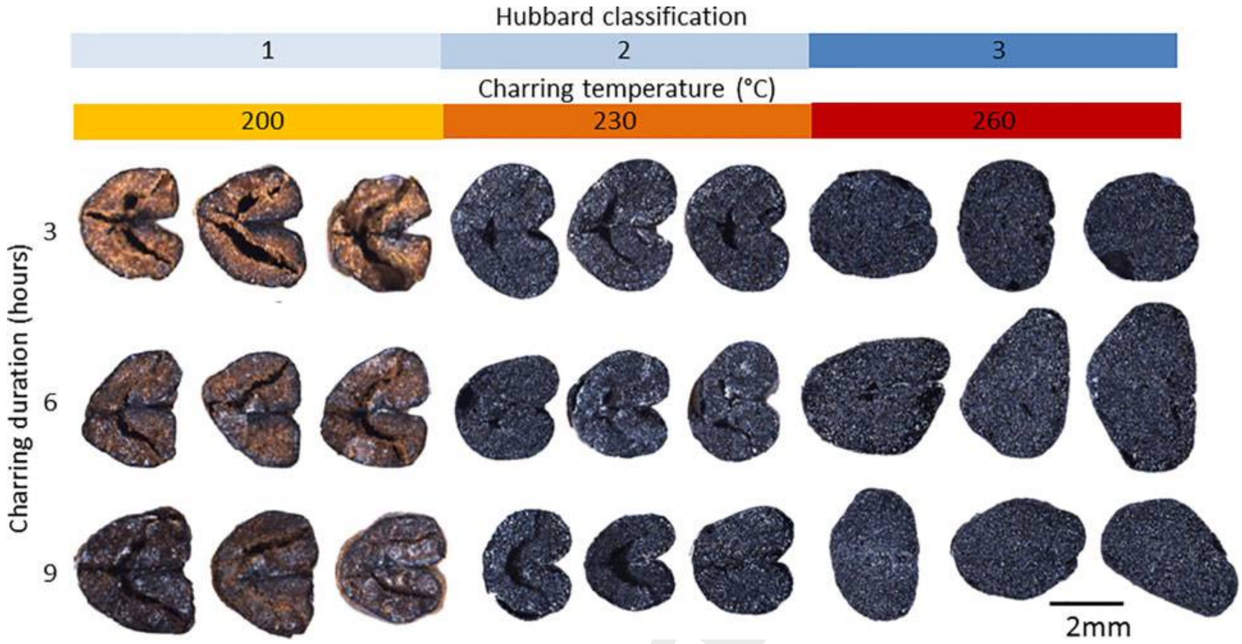

Figure 6 Cross sections of modern emmer grain heated at 200, 230 and 260°C for 3, 6 or 9 hours. Low power microscopy – magnification.

Table 6 Changes is emmer grain dimensions and mass under different heating regimes.

	Temperature	200°C	230°C	260°C
		% change		
Grain size	Breadth	7.3	14	18.9
	Thickness	0.1	4.2	14
	Length	−4.4	−9.2	−12.2
Grain mass	After 3 hours	14.2	27.4	48.2
	After 6 hours	15.5	40.2	50.1
	After 9 hours	16.5	43.1	52.3
	Average	15	30	50

Braadbaart *et al.* (2004c) with the appearance of 'cavities'; critically, however, they occur at lower temperatures in our experiments for emmer (230°C) and einkorn (240°C) compared with that of 270°C recorded in emmer by Braadbaart *et al.* (2004c).

Discussion

Einkorn and emmer grains heated at temperatures above 240°C become increasingly distorted and more difficult to identify. At temperatures of 220–240°C for periods of 2 or 3 hours in low oxygen conditions, the grains resemble well preserved, relatively undistorted archaeological grains internally and externally in terms of colour and gross morphology. Prolonged heating – up to 24 hours – has little additional visible impact on the grain. Although grain response to heating was broadly similar between the two glume wheats tested, there were sufficient differences to suggest that the work should be repeated for the range of major crop types recovered archaeologically, since the morphology and chemical composition of each species vary.

Grains exposed to temperatures of 220–240°C have been through a series of chemical changes, and it remains to be considered whether such a heating regime sufficiently transforms cereal grains to allow them to survive archaeologically, a question posed by Braadbaart *et al.* (2004c), in their study of emmer grain. These authors note that experimental charring of emmer for 120 minutes up to 250°C results in brown-black grain that is still rich in dehydrated polysaccharides and proteins, and reason that such material 'may be microbially degraded similar to the degradation of untreated wheat grains' (Braadbaart *et al.* 2004c). They argue furthermore that grain charred at temperatures above 310°C would 'have a better chance to survive the degradation processes and thus may be found in the archaeological record' (Braadbaart *et al.* 2004c). To assess the extent of this transformation and its implications for archaeological preservation, the major physical and chemical processes known to occur in cereal grains heated to relatively low temperatures are outlined below.

Grain morphology

Examination of the internal structure of glume wheat grain and the changes induced by heating has been crucial in understanding how grain morphology is affected. The initial development of fissures that may equate to the first 'cracking' process noted in coffee occurs in both species at c.200°C, and the fissures disappear between 230 and 260°C. These fissures account for much of the early change in gross morphology before they are subsumed by the expanding endosperm cells that eventually produce the final rounded grain shape.

The current study of einkorn and emmer emphasises the sensitivity of cereal grain morphology to relatively small changes in temperature between 200

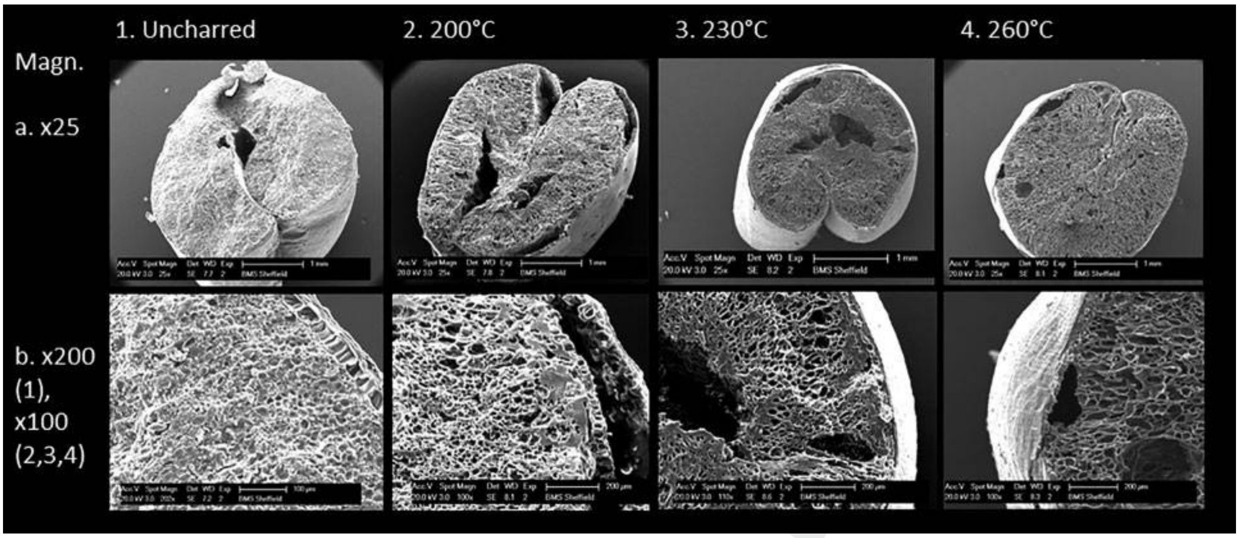

Figure 7 SEM images of modern emmer grains unheated (1) or heated to 200°C (2), 230°C (3) and 260°C (4) for 6 hours. Grain cross-section, (A) low power (top row), (B) high power (bottom row).

and 260°C, whereas the duration of heating has comparatively little effect on morphology. Grain shape (length, breadth and thickness) follows a relatively predictable path as temperature increases up to 260°C, with length decreasing and breadth and thickness increasing more or less proportionally. Above 260°C, and certainly at the higher temperatures that Braadbaart *et al.* (2004c) consider to be archaeologically relevant (>300°C), distortion of overall grain morphology and other signs of heating such as surface blistering or endosperm exudation are marked, and species-level identification criteria tend to be lost.

Glume wheat grain colour and chemistry

Comparison with previous work on roasting coffee beans and barley grains (reviewed above) shows that chemical processes affecting grain colour, namely dextrinisation and Maillard reactions, are initiated after a few minutes' exposure to these temperatures and proceed rapidly, with much of the original polysaccharide content of the grain having been degraded after a couple of hours. As noted above, once the Maillard reactions have begun, conversion of sugars to melanoidins can continue even after the temperature drops; thus grain is likely to become increasingly dark through time, even in the absence of prolonged exposure to these temperatures. It is plausible that even grain not fully blackened during heating will become fully black and resistant to decay over time. It should also be noted that grain blackening is most rapid under conditions of low oxygen availability, and occurs at lower temperatures than under conditions of plentiful air availability. Once the grain is black, the components subject to biological attack are judged sufficiently transformed to be likely to survive burial in soil.

In this study, heating at 220°C produced fully blackened einkorn grains after 8 hours, at 230°C after 4 hours, and at 240°C after 2 hours. In emmer, full blackening occurs after 3 hours at 230°C. In Braadbaart *et al.*'s (2004c), experiment emmer was not fully blackened at 250°C. This contrast with our results may be due to the different conditions in the two experiments. In our experiments, grains were charred in closed conditions, whereas in Braadbaart *et al.*'s experiments, grains were charred in open conditions with a constant flow of nitrogen (2004c). The reasons for these differences are not fully understood, but are consistent with coloured volatiles released by heating being trapped within the aluminium foil wrapping, increasing grain discolouration.

Implications of these results for the analysis and interpretation of charred archaeological grain

The surface condition and overall morphology of charred archaeological grain may be used, to some extent, to estimate the temperature to which the grain has been exposed. Further experimental work will doubtless improve and refine this ability but, on the basis of current knowledge, it is possible to make some tentative suggestions on the charring temperatures associated with observable grain characteristics. Glume wheat grain charred at 220–240°C shows very slight change in shape from the uncharred state in the lower part of the temperature range, becoming shorter and more rounded in cross-section in the upper part of the range, with a tendency to form small blisters on the surface. Slight fissuring is still visible in cross-section. At 240–260°C, grain is clearly distorted, with bulging or blistering on the surface and substantial rounding in cross section. Internal fissures are likely to have disappeared. At temperatures above 260°C, grain shows gross distortion, becoming irregularly shaped, with severe surface blistering or crumpling of the endosperm, and occasional endosperm exudations. The features of the grain characterising these temperature bands can now be used to evaluate the grain's usefulness for different types of analyses.

Glume wheat grain charred at temperatures up to c.260°C may be suitable for morphologically based analysis, such as taxonomic identification and, at least for temperatures up to c.240°C, for assessment of changes in seed form through space and time [e.g. changes in seed size during domestication, Fuller 2007; Fuller, Asouti and Purugganan 2012]. Archaeological grain charred at temperatures greater that 260°C is not suitable for morphological work, and even determination to species or genus may not be possible. The identification of charring temperature is also useful for determining the likelihood of differential survival of grain, chaff and straw. Experimental charring by Boardman and Jones (1990) indicated that both grain and chaff survive charring well at c.250–350°C in high oxygen conditions, and at c.250–400°C in low oxygen conditions. The greatest limitation imposed by charring temperature on the interpretive usefulness of charred grain is probably in the area of biomolecular and elemental analysis. Experimental work has shown that, in the temperature range of 200–260°C, the effect of charring on stable isotope ratios is small but variable (e.g. Fraser *et al.* 2013; Heaton *et al.* 2009; Kanstrup *et al.* 2012; Nitsch, Charles and Bogaard 2015), though Nitsch *et al.* (2015) predict that isotopic values would diverge more at higher temperatures as they do for charcoal (Hall *et al.* 2007; Turney *et al.* 2006). Similarly, early experimental work indicated that no DNA could be detected in grain heated to temperatures of 225°C or above for more than 2–4 hours (Threadgold and Brown 2003, Fig. 3). Nevertheless, fragmented DNA has been extracted from charred cereal grains (including emmer, spelt, bread wheat and rice) at several archaeological sites of different dates and locations (see for example, Allaby, Jones and Brown 1994; Brown *et al.* 1998; Bunning *et al.* 2012; Castillo *et al.* 2015; Schlumbaum and Jacomet 1998).

Charring temperatures will of course vary depending on the context of burning. For example, open fires might be expected to generate temperatures well above 260°C that would completely destroy or cause gross distortion to any grain accidentally exposed directly to the fire. Lower temperatures might be encountered, however, in the cinders below the flames, generating charred grain with lower levels of distortion and less surface damage. Ovens for drying, parching or roasting grain are designed to produce relatively low temperatures whereas kilns for the firing of ceramics or glass require temperatures well above those used in our experiments. Relatively undistorted charred grain might therefore be expected only inside low temperature ovens (or in the 'rake out' from such ovens) when grain has been left in the oven too long and become accidentally charred (see for example, Monk and Kelleher 2005; van der Veen 1989). Dung cakes used to fuel ovens may also contain cereal grain incorporated into the cakes with chaff or straw. Seeds embedded in the dung are not directly exposed to the high temperatures within the fuel chamber, and are regularly recovered from charred livestock dung (Wallace and Charles 2013). The destruction of buildings by fire often produces a wide range of charring conditions, which may include conditions conducive to the generation of virtually undamaged, undistorted cereal grains, especially in the low oxygen conditions within ceramic vessels and other storage containers. For example, at Neolithic Catalhoyuk (Turkey) (Bogaard *et al.* 2009, 2014b) and Bronze Age Assiros Toumba (Greece) (Jones *et al.* 1986), grain within a single room has been found in states ranging from light brown partially charred material (presumably exposed to temperatures below 220°C) through relatively undistorted charred grain (likely to have been charred at c.220–240°C), to phytolith-rich ashes (resulting from exposure to temperatures well above 260°C).

Conclusions

The results of this study show that there is a clear and direct relationship between glume wheat grain morphology and the temperature to which grains have been exposed, whereas duration of heat exposure has only a limited impact on grain morphology. Comparison of the internal structure of archaeological grain at the cell level with experimentally charred grain provides a means for refining observations based on gross morphological features. The experimental heating temperatures that produce the closest morphological match to well preserved/low distortion charred glume wheat grain found on many archaeological sites lie between c.220 and 240°C.

These morphological results are of considerable significance for archaeobotanical research because heating indicators, including gross morphology, surface appearance, and internal grain structure where it can be observed, can be used to estimate the temperature at which archaeological grain was charred. This in turn allows us:

1. to approximate changes in grain dimensions, which is important for taxonomic identification and morphometric analysis
2. to estimate the likely extent of differential destruction of chaff expected at high temperatures, and so determine the accuracy with which we can use the relative frequency of grain and chaff fragments to infer crop processing activities
3. to predict charring-induced changes in stable isotope ratios and the likelihood of aDNA survival.

Conflicts of Interest

The authors declare that they have no conflict of interest.

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