



Morphological, chemical and physical changes during charcoalfication of wood and its relevance to archaeological contexts

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ABSTRACT

Wood exposed to a heat source can be transformed into charcoal if subject to conditions of carbonisation (in the absence of air) or charring (in restricted air). Charcoal recovered from archaeological sites can yield fundamental information to our understanding of human economic and cultural development over time and (ecological) setting. This work describes the morphological (anatomy, degree of shrinkage), physical (reflectance) and chemical (elemental, molecular composition) properties of charcoal in relation to heat source and wood variables. In this study charcoal and charcoal fuel were experimentally produced whereby temperature (160–1200 °C), time of exposure (2–1440 min), heating rate (high and low) and wood type (angiosperm and conifer) were varied. The results show that charcoal, often described as an inert, black material, has different chemical and physical properties in relation to the investigated variables. By using these different properties it is possible to distinguish between the different types of fires (domestic and industrial) exploited by humans in the past. Morphological analyses and reflectance measurements are effective tools for this purpose and can be used in wood exposed to temperatures of 300 °C and above—temperatures which are relevant to archaeological research. Angiosperm and conifer wood react in different ways when exposed to heat and thus the taxonomic identity of archaeological material needs to be known. Chemical analyses can be used for wood exposed to temperatures below 400 °C whereas elemental analyses of the carbon content can be used for wood exposed to temperatures up to a maximum of 650 °C.

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1. Introduction

Wood has evolved over hundreds of millions of years to become arguably the most remarkable structural material on earth and for this reason has become an invaluable economic commodity for human society. The slow decomposition rate allows wood to remain in the soil for a number of years. However, over timescales of decades to millennia and, depending upon factors such as humidity, temperature, relative chemical composition and soil type (e.g. van der Wal et al., 2007), wood eventually succumbs to decomposition and is often lost from the historical record altogether. Nevertheless even though the archaeological record is relatively poor in wood *per se*, it contains a relatively rich record of charcoalfied material, including wood. Charcoalfied material is able to overcome both the physical and chemical decomposition associated with burial in the soil, and is thus the most common mode of survival of archaeological plant debris, whilst retaining the physical structure of the original material. Charcoal residue is therefore an

important source of information in helping our understanding of human economic and cultural developments over time. Although charcoalfied wood is often abundant in archaeological sites, little is known regarding the morphological, physical and chemical changes associated with the charcoalfication process of wood itself, even though such changes associated with carbonized fruits and seeds have been studied in detail (Braadbaart, 2004; Braadbaart et al., 2007, Braadbaart, 2008). Therefore we have undertaken a series of experiments aimed at increasing our knowledge regarding the changes associated with heating both wood and charcoal as a fuel, and thus being able to define the term charcoal in the archaeological context. Subsequently we explore the possibility of being able to retrieve information, additional to local vegetation composition and possible siccicultural practices for example, relevant to human activity in the past. A prerequisite to understanding the changes associated with charcoalfication is a basic understanding of the morphological, physical and chemical characteristics of modern wood. These characteristics are summarized below.

Wood can be subdivided into two main types depending upon its biological origin. Softwood, derived from conifers, is comprised predominantly of axial tracheids, which in turn is composed of

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25–35% lignin, 37–45% cellulose and 20–25% hemicellulose. Hardwood, derived from angiosperms, is morphologically more complex generally comprising up to five different axial elements including parenchyma, fibres and, most notably, vessels. The chemical composition of the elements in angiosperm wood also differs from that of conifer wood with generally a lower proportion of lignin (20–25%) occurring in angiosperm wood coupled with a higher hemicellulose content (20–35%) and similar proportions of cellulose (39–45%) (Sjöström, 1993; Blanchette, 2000). However, proportions can vary further, both within and between species, depending upon factors that can include mechanical (e.g. reaction wood) or ecological (e.g. arid habitat) stress, etc. (e.g. Meier, 1964; Malik et al., 2004).

Within the lignin fraction further differences exist between softwoods and hardwoods. Lignins are classified according to the relative amounts of guaiacyl (2-methoxyphenol), syringyl (2,6-dimethoxyphenol) and *p*-hydroxyphenyl monomers (Van der Hage et al., 1993). In general conifer lignin is composed primarily of guaiacyl monomers whereas angiosperm lignin is characterized by the presence of both guaiacyl and syringyl monomers.

Charcoal is considered to be an inert, black material, with morphological properties similar to that of modern wood, yet an exact definition is lacking (Connor et al., 1994; Antal et al., 1996; Kim and Hanna, 2006). Charcoal formation (charcoalification) occurs either by heating wood in a limited supply of air (oxygen) (i.e. charring), or in the absence of air (oxygen) (i.e. carbonization). In the literature these three terms have been used interchangeably and it is therefore necessary to clarify the distinction—the differences have been summarized in Fig. 1. Importantly the residues formed by these different heating processes can have different chemical and physical properties (Braadbaart, 2004).

On heating, wood constituents thermally decompose and volatiles are released. If air (oxygen) is present the volatiles can ignite and begin to burn producing the characteristic flame and giving the appearance of burning wood. In an abundant supply of air (oxygen) the wood will combust to form an ash end product, but under conditions of limited or no oxygen, charcoal will be formed (see Fig. 1).

The morphological, physical and chemical properties of charcoal can differ depending upon two main variables associated with the heating process (Braadbaart et al., 2007; Braadbaart, 2008): (1) heat source related variables, which include temperature, time of exposure and heating rate (°C/min); and (2) wood property variables, which include taxon, size, thermal conductivity and porosity—variables that can also change during the charcoalification process itself. With increasing temperature the initial changes to occur are: (1) morphological—the darkening of the wood which ultimately becomes black; (2) physical—considerable mass loss, shrinkage, and possible anatomical distortion, of the original material resulting from the formation and loss of many volatiles; and (3) chemical—the continuous and gradual conversion of the cellulose, hemicellulose and lignin to predominantly aromatic moieties, and thereby forming a new chemically-distinct, carbon-enriched end product (Shafizadeh, 1982; Boon et al., 1994; Braadbaart, 2004; Braadbaart et al., 2007).

With regard to the heating variables, human-related heating regimes can be divided into those that are domestic and those that are industrial. In the former, temperatures are usually relatively low and wood is used as the fuel. At the outset the heating rate of a domestic fire will be low, but later once the fire is established the heating rate of further wood fuel will increase. In this type of fire, wood is exposed to air and undergoes charring with the most likely end product being ash that is of little use to archaeologists. If this process is interrupted (e.g. dousing with water or not stoking the fire) then charring is often incomplete and charcoal can result.

Industrial processes required fires of much higher temperatures relative to their domestic counterpart. Required temperatures

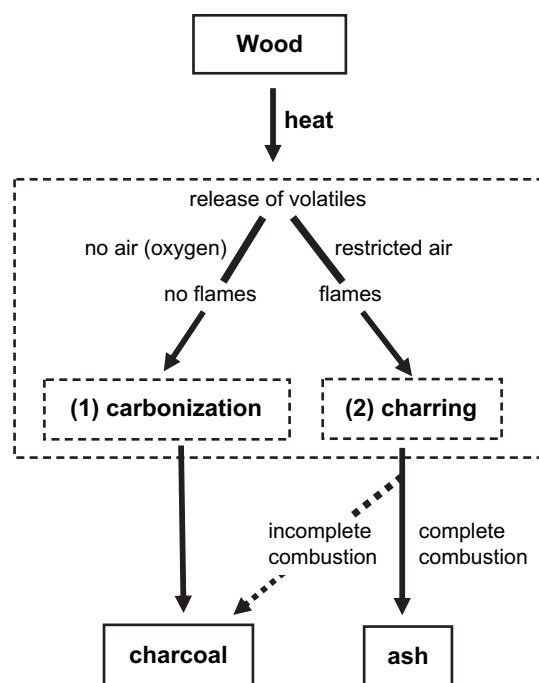


Fig. 1. Schematic diagram showing the main processes (dotted boxes) by which charcoal is produced from wood in archaeological contexts. On heating, volatiles are released and one of two processes can occur: (1) in the absence of air (oxygen) *carbonization* takes place at minimum temperatures $\sim 300^\circ\text{C}$. (2) If a limited supply of air (oxygen) is present, *charring* takes place with released volatiles igniting to produce flames (if there is a pilot heat source ignition occurs at $\sim 350^\circ\text{C}$, otherwise spontaneous ignition occurs at $\sim 600^\circ\text{C}$). At temperatures normally present in domestic fires, total combustion results in the formation of ash. If combustion is interrupted (e.g. dousing with water, fire left to extinguish or removal of material from the fire) the temperature will drop below $\sim 350^\circ\text{C}$, no further volatiles are released and the end product will be charcoal rather than ash. Together processes (1) and (2) can be termed *charcoalification*. Note that indicated temperatures depend upon length exposure and in archaeological situations length of exposure is taken as more than 15 min (see text for details).

ranged from 500 to 1200°C depending upon the purpose. When temperatures in excess of 900°C were required charcoal, with its higher calorific value, was the preferential fuel. In the presence of air (introduced via bellows for example), charcoal is capable of producing an intense heat about twice that of wood (Armstrong, 1978) and in this way a charcoal fuelled fire can attain temperatures of around 1300°C within 15 min. However, the charcoal fuel first had to be prepared in a separate industrial process where wood was heated, in the absence of air, to temperatures of $\sim 500^\circ\text{C}$ where it underwent carbonisation to form charcoal.

The charcoal remains found in archaeological sites can provide important information pertaining to not only local vegetation and sivilcultural practices but also temperature at which it was formed and thus fire type and human activity. It is the experimental formation of these charcoal remains that form the subject of this study. Charcoal derived from natural heat sources such as wild fires and hot pyroclastic flows in volcanic contexts are beyond the scope of this study.

In order to investigate more fully the influence of both heat source- and wood property related variables, a series of controlled experiments were undertaken to explore the chemical, physical and morphological properties of wood and whether such changes can be used to help interpret archaeological contexts. Angiosperm and conifer wood samples were heated using different regimes under experimental conditions. Previous studies (Braadbaart, 2004) have shown that experimental carbonization of fruits and seeds are similar to traditional methods for charcoal production

under less controlled conditions (e.g. an open fire). Open fire situations, simulating those found in archaeological contexts where conditions would have been less controlled, were also studied with both wood and charcoal being used as a fuel. This was undertaken to ensure that these controlled experimental procedures produced data for wood material that were comparable with data derived from archaeologically formed wood material, and in turn that general conclusions drawn from this study could be applied to archaeologically derived charcoal. Finally, the results from this study are applied to charcoal from archaeological sites with known contextual data to determine the feasibility of using the analytical approach to archaeological charcoal in this way.

2. Material

2.1. Modern samples

Wood of pine (*Pinus sylvestris*) and oak (*Quercus robur*) are often found in archaeological sites in Europe and therefore these taxa were selected for this study. In some experiments wood of yew (*Taxus baccata*), birch (*Betula pendula*), hornbeam (*Carpinus betulus*) and walnut (*Juglans regia*) were used as supplementary material and/or to verify the results obtained from the pine and oak samples, respectively. Wood samples of all taxa were taken from the trunks of trees, of similar age and with no evidence of damage or injury, originally growing in a forest along the North Sea coast in Heemstede, the Netherlands. From the heartwood, cubes measuring 20 × 5 × 5 mm were taken and left to dry for 1 month. For each experiment two such cubes were used to check for consistency in the results.

Charcoal fuel was obtained from a traditional charcoal kiln ('meiler') from Chr. Wagener, Netphen (Germany). For experiments in the laboratory where knowledge of the temperature was required, charcoal was made by heating oak wood in a preheated oven (to 450 °C) and allowed to cool to ambient temperature (~20 °C).

2.2. Archaeological samples

The archaeological material investigated includes charcoal samples recovered from archaeological excavations within the Netherlands, namely a hearth pit in Schipluiden (3600–3300 BC); a burnt grain silo in Maastricht (650 AD); a burnt wooden shed in Tiel (150–220 AD); a mesolithic tar production site near Hattummerbroek. In addition samples from a Medieval 'tandir' bread oven and two hearth pits from Girag Kasaman, Azerbaijan were also studied.

3. Methods

3.1. Experimental charcoal production

The procedure of Braadbaart (2004) was adopted to experimentally carbonize wood under controlled conditions. Wood samples were heated in a Carbolite tube oven (model MTF 12/38/250) at atmospheric pressure under a constant flow of nitrogen (150 ml/min) to ensure anoxic or reducing conditions. The samples were placed in an open Pyrex[®] vessel and inserted into a 30 cm long Pyrex tube (Ø 2.3 cm) at 18 cm from the inlet. To prevent melting, at temperatures >1000 °C a ceramic tube and vessel were used. Resultant gases and volatiles were vented and not investigated further. The influence of the heat source related variables namely temperature, heating rate and time of exposure were regulated as described below.

Wood samples were also heated in traditionally managed open industrial fires in the archaeological theme park Archeon (the

Netherlands) where temperatures were in excess of 600 °C. The charcoal end product was used for comparative purposes.

Samples of charcoal fuel were prepared experimentally in the laboratory by heating oak wood using the procedure outlined below. These samples were subsequently used to determine the effect of heating on charcoal fuel. In addition, charcoal fuel samples of oak, walnut and hornbeam, made in a traditional charcoal kiln (cf. Armstrong, 1978), were used for comparative purposes.

3.2. Time of exposure and mass loss

Initial experiments were undertaken on modern oak wood samples to determine an optimal time of exposure to heat taking into consideration the reasonable duration of fires in archaeological situations. To do this, oak samples were placed in the preheated oven and heated to 280, 310, 370, 440, 600 and 800 °C for time intervals ranging from 2 to 1440 min. Separate samples were used for each time interval. Mass loss for each sample was calculated from the difference between the mass of the cooled treated material and the untreated material and expressed as a percentage. These mass losses were plotted as a function of time on a logarithmic scale. The time beyond which no further sharp mass loss occurred, at temperatures relevant to this study (i.e. >300 °C), was taken as the point at which thermal conversion had been completed and therefore the optimum time of exposure (see Section 4 for details). The optimal time was taken as 60 min and was used for subsequent experimental procedures.

Further experiments investigating difference in mass loss between angiosperms and conifers were undertaken whereby samples were heated at the high heating rate to temperatures ranging from 160 °C to 1200 °C for 60 min (see Sections 3.3 and 3.4 for details). This was then repeated using the low heating rate (Section 3.3) for 60 min at 250, 280, 310, 370, 400, 440, 500, 600, 700 and 900 °C. The results from the two heating rates and different taxa were then compared.

3.3. Heating rate

Two heating protocols were investigated: (1) high heating rate (HHR) where wood samples were placed directly into a preheated oven and heated for 60 min, to simulate fuel being added to an existing fire; (2) low heating rate (LHR) where wood samples were placed into an oven at ambient temperature, heated to a pre-selected final temperature in 120 min and kept at this final temperature for 60 min, to simulate heating a starter fuel. Results from the two heating regimes were compared.

3.4. Temperature

For the modern wood samples a number of pre-selected final temperatures were investigated, namely 160, 220, 250, 280, 310, 320, 340, 370, 400, 440, 500, 600, 650, 700, 800, 900, 1000, 1100 and 1200 °C.

Laboratory-produced charcoal fuel was made by heating oak wood at the LHR to a final temperature of 450 °C and left for 60 min. Samples were allowed to cool and then reheated using the HHR to final temperatures of 800, 900, 1000, 1100 and 1200 °C for 60 min.

3.5. Morphological analyses

Charcoal samples made using the two different heating protocols and different final temperatures along with charcoal fuel heated to temperatures from 800 °C up to a maximum of 1200 °C, were prepared for microscopical study using standard techniques (Gale and Cutler, 2000). Anatomical structures were examined using epi-illumination under an Olympus BX41 microscope.

The degree of shrinkage can also be indicative of final temperature and has been used to help determine original seed size and artefacts (Braadbaart, 2008), or anatomical character(s) which in turn have helped reconstruct palaeoecology (although not without difficulty). Therefore degree of shrinkage was also investigated in the oak wood samples. The mean of 25 tangential diameters of the first formed, large early wood vessels of each oak charcoal sample prepared, using the two heating protocols and different final temperatures, were measured. Degree of shrinkage was expressed by plotting the mean diameter of the early wood vessels in each charcoal specimen as the percentage of the mean diameter of the early wood vessels in the unheated (fresh) oak wood sample against final temperature.

3.6. Physical analyses

The reflectance (% R_0) of charcoaled organic material provides information regarding the temperature at which the material became charcoaled (Braadbaart, 2004). Reflectance is defined as the percentage of vertically incident monochromatic light reflected from a highly polished surface of a sample calibrated against the light reflected from a standard of known reflectance. To determine relative reflectance and any taxonomic differences, the three planes of section (transverse, radial longitudinal and tangential longitudinal) were studied for each specimen of: (1) experimentally produced charcoal from oak, birch, pine and yew wood, heated at the HHR and a final temperature of 310–1200 °C; (2) charcoal fuel (oak wood), which was subsequently exposed to final temperatures ranging from 800–1200 °C; and (3) archaeological charcoal specimens.

Material was embedded in resin blocks and polished. Reflectance was measured under oil immersion at a wavelength of 546 nm using a Leitz motorized DMLA microscope equipped with an xyz-stage and a Basler video camera. For each specimen a total of 100 randomly performed reflectance readings were taken (to obtain a statistically acceptable population) and the mean reflectance of each specimen calculated. Preparation of polished blocks and reflectance measurements were performed in accordance with standard methods defined in ISO 7404, part 2 (1985) and ISO 7404, part 5 (1994).

This study was then extended to determine the influence of exposure time on reflectance values of oak and pine samples heated at the HHR for 15 min and 24 h at 370, 440, 600 and 800 °C and compared with the results obtained for heating at the final temperature (up to 1200 °C) for 60 min.

3.7. Chemical analyses

3.7.1. Elemental analyses

Differences in the elemental (carbon) composition of treated oak wood samples relative to untreated oak wood were investigated. Each specimen was ground to a fine powder and subjected to a carbon analysis using a Fisons Instruments NA 1500 series 2 NCS analyser. The temperature in the combustion reactor was maintained at 1020 °C. The combustion products were separated on a Porapak QS column with a length of 2 m. All values stated are based on singular measurements corrected for water and ash content. To calculate the carbon content as dry and ash free (daf), the water and ash content were determined on a Thermogravimetric Analyser TGA 2950 Hi-Res. The carrier gas was air and the heating rate was set at 25 °C/min, water content was determined at 105 °C and ash content at 960 °C.

3.7.2. Molecular analysis

Differences in molecular composition of heated wood samples relative to unheated wood were investigated using direct

temperature-resolved mass spectrometry (DTMS) with a JEOL SX-102A double focusing mass spectrometer (B/E) with a direct insertion probe equipped with a Pt/Rh (9/1) filament for analysis under electron impact (EI) conditions. Powdered samples of unheated and heated oak and pine wood were placed on the filament and inserted directly into the ion source of the mass spectrometer. Under EI conditions ions were generated by low voltage electron ionization (16 eV) in an ionization chamber kept at 180 °C and accelerated to 10 kV. The scan range was m/z 20–1000 with 1 s cycle time and mass resolution of 1000 and 3000. Data were acquired using a JEOL MP-7000 data system. Since previous measurements on residues of peas, wheat grains and sunflower achenes showed that the sampling and experimental variance was very small (Braadbaart, 2004), only single measurements were performed for each sample.

3.8. Archaeological simulation of fuel exposure to heat

Oak wood is known from archaeological settings to have been used as a fuel for domestic cooking fires (e.g. Gale and Cutler, 2000). Therefore oak wood and charcoal fuels were used to investigate the heating process in a traditional open fire. A fire was lit and left to burn for 1 h during which time the fire was stoked to simulate a cooking fire. After burning for one hour the heat at the centre of a cooking fire was determined by measuring the temperature of a piece of wood situated in the middle of the fire (800 °C) using a thermocouple. A piece of oak fuel wood was subsequently placed in the fire and once it had also reached 800 °C it was left for 15 min and subsequently removed. Reflectance was then measured using the procedure outlined above.

Three pieces of charcoal fuel produced in a traditional charcoal kiln were placed in a fire prepared for bronze smelting. Once they had reached the desired temperature of ~1200 °C they were left for a further 15 min before removal. Reflectance was then measured using the procedure outlined above. These samples were then used to compare results derived from the archaeological charcoal with the results from the controlled heating experiments.

4. Results

4.1. Time of exposure

The optimal time of exposure to ensure carbonization of the wood material was determined from the mass loss of oak samples heated using the HHR protocol at 280, 310, 370, 440, 600 and 800 °C plotted as a function of time (black squares, Fig. 2). At 280 and 310 °C no constant mass loss is reached even after 6 h (360 min). However samples heated at 370 and 440 °C, show an initial rapid mass loss followed by a considerably reduced mass loss after approximately 10 min. After 60 min heating to all temperatures above 310 °C, no further significant loss in mass occurred and therefore this time was taken to be the optimal time of exposure.

4.2. Mass loss

Difference in mass loss between taxa (pine versus oak) and heating regime (HHR versus LHR) at different temperatures is plotted in Fig. 3a,b. In all cases initial mass loss was rapid with ~60% of the mass being lost over the 220–310 °C temperature range (Fig. 3b). From 310 °C up to ~400 °C mass loss continued but at a lower rate which decreased still further from 400 °C to 1200 °C (Fig. 3a). At 1200 °C the total mass loss reached 75–85%, but does not become constant.

Taxonomic identity also incurs a difference in mass loss. In the temperature range 160–350 °C oak wood exhibits a greater mass

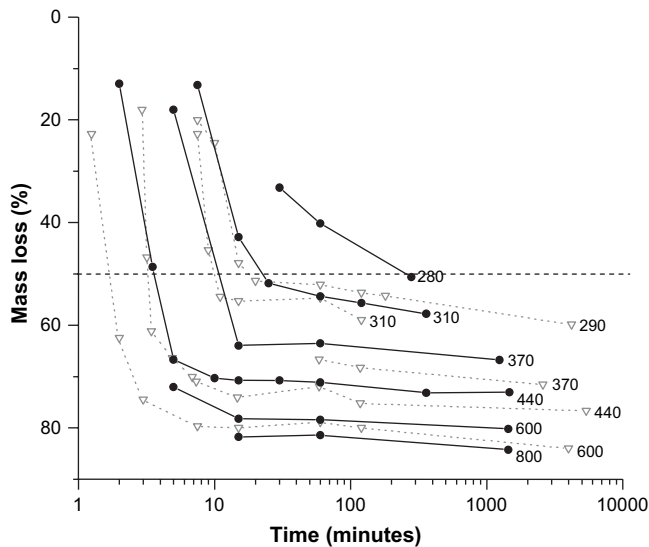


Fig. 2. Mass loss (%) of oak wood samples (black circles) heated at different temperatures (°C), expressed as a function of the time of exposure (minutes), is plotted on a logarithmic scale to determine the optimum time of exposure. Compare these data with those (open triangles) obtained from heating wheat grains (*Triticum dicoccum*) adapted from Braadbaart (2004; his figure 7.3) where similar mass losses were found. For dashed line see text.

loss compared with pine, whereas at temperatures >350 °C mass loss in pine wood was greater than that of oak wood (Fig. 3).

Heating protocol also affects mass loss. The mass loss in samples heated at a HHR is consistently 5–10% higher than those samples heated at a LHR.

4.3. Morphological analyses

4.3.1. Low heating rate

Up to temperatures of ~ 300 °C the wood characteristics change little from that of untreated wood (Table 1). The colour becomes increasingly dark but the texture and properties are essentially that of wood rather than charcoal. Between 310 and 370 °C the physical properties of the wood undergo a change from being essentially wood-like to becoming typically charcoal-like. This was accompanied by a more pronounced colour change (dark brown to black), ability to break the specimen by hand (not possible to possible), weight/mass change (becoming relatively light in weight), degree of reflectance under epi-illumination (non-reflective to reflective) and its friability (non-friable to friable). In the oak material this was also accompanied by an anatomical change whereby the characteristic multiseriate rays can appear ‘exploded’ as if a sudden release of pressure had occurred through this region of relatively weak tissue. This was not observed in the pine, probably due to the rays being only one cell wide. A further physical change occurs above 600 °C such that by 800 °C the anatomy can appear distorted, and increasingly so with increasing temperature. By 900 °C the charcoal has become powdery and fragments easily. By 1000 °C the anatomy is deformed and by 1200 °C the anatomy is no longer recognizable.

4.3.2. High heating rate

As with the LHR, up to temperatures of ~ 300 °C the characters of both oak and pine wood changed little from that of untreated wood (Table 1). Although the colour became increasingly dark again the texture and properties are essentially that of wood rather than charcoal. The exception to this generalisation is oak wood at temperatures above 250 °C where the sample became

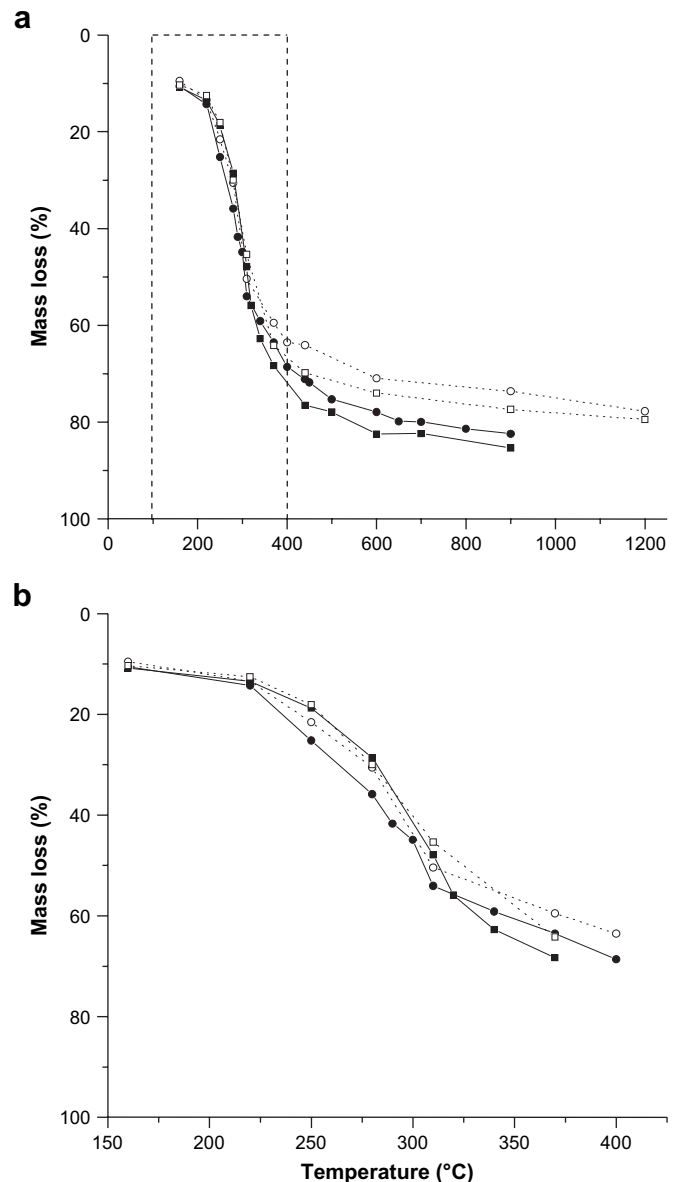


Fig. 3. Mass loss (%) oak (circles) and pine (squares) experimentally heated for 60 min plotted as a function of the temperature (°C). Solid symbols represent samples heated at a high heating rate (HHR) and open symbols represent samples heated at a low heating rate (LHR). (a) full temperature range from 160–1200 °C; (b) enlargement of the temperature range 160–400 °C (dotted box in (a)) over which the most rapid mass loss occurs.

easier to break by hand. This was not observed in pine probably due to the absence of the multiseriate (sometimes aggregated) rays, and thus lines of weakness, along which fracturing was able to occur in oak. Between 310 and 370 °C the physical properties of the wood underwent a change from being essentially wood-like to becoming typically charcoal-like. This was accompanied by a colour change, albeit not as pronounced as in the LHR (dark brown to black), ability to break it by hand (not possible to possible), weight/mass change (becoming relatively light), degree of reflectance under epi-illumination (non-reflective to reflective) and its friability (non-friable to friable). Moreover the ‘exploded’ rays in the oak sample were also observed at this temperature. By 800 °C the anatomy of both the oak and the pine had become distorted and by 900 °C the texture was distinctly powdery. By 1000 °C the anatomy was deformed and by 1200 °C the anatomy was no longer recognizable.

Table 1 Summary of the morphological changes that occur when conifer (pine) and angiosperm (oak) wood underwent experimental carbonization to form charcoal when exposed to different final temperatures for 60 min

	Temp., °C											
	160	220	250	280	310	370	440	600	800	900	1000	1200
<i>Pinus</i>												
Colour	Yellow	Dark yellow	Mid-brown	Dark brown	Very dark brown	Black-brown Charcoal	Black	Black	Powdery charcoal, often with white tinge	Black	Powdery charcoal, often with white tinge	Black
Physical appearance	Wood	Wood	Wood	Wood	Wood	Charcoal	Charcoal	Charcoal	Fragments easily, light in weight	Powdery charcoal, often with white tinge	Fragments easily, light in weight	Powdery charcoal, often with white tinge
Ability to fracture by hand	No	No	No	No	No	Intact	Intact	Intact	Fragments easily, light in weight	Can be distorted and/or fused in part	Fragments easily, light in weight	Fragments easily, light in weight
Anatomy	Intact	Intact	Intact	Intact	Intact	Intact	Intact	Intact	Can be distorted	Can be distorted and/or fused in part	Deformed and/or fused in part	Deformed and/or fused in part
Reflective	No	No	No	No	No	Good	Good	Good	Can be distorted	Very good	Deformed and/or fused in part	Deformed and/or fused in part
Friable	No	No	No	No	No	Yes	Yes	Yes	Can be distorted	Very good	Deformed and/or fused in part	Deformed and/or fused in part
<i>Quercus</i>												
Colour	Yellow	Dark yellow*	Mid-brown	Dark brown	Very dark brown	Black-brown	Black	Black	Black	Black	Black	Black
Texture	Wood	Wood	Wood	Wood	Wood	Charcoal	Charcoal	Charcoal	Powdery charcoal	Powdery charcoal	Powdery charcoal	Powdery charcoal
Ability to fracture by hand	No	No	No	No	No	Fractures relatively easily but not by hand	Fractures relatively easily but not by hand	Fractures relatively easily but not by hand	Fragments easily, light in weight	Fragments easily, light in weight	Fragments easily, light in weight	Fragments easily, light in weight
Anatomy	Intact	Intact	Intact	Intact	Intact	Intact	Intact	Intact	Can be distorted	Can be distorted and/or fused in part	Deformed and/or fused in part	Deformed and/or fused in part
Reflective	No	No	No	No	No	Good	Good	Good	Can be distorted	Very good	Deformed and/or fused in part	Deformed and/or fused in part
Friable	No	No	No	No	No	Yes	Yes	Yes	Can be distorted	Very good	Deformed and/or fused in part	Deformed and/or fused in part

Different heating rate (HHR versus LHR) resulted in no distinct morphological differences other than that asterisked. *At the HHR the colour appears dark yellow. Table should be read left to right with morphological change from the previous state noted at the relevant temperature.

4.3.3. Fuel charcoal prepared at 450 °C

The wood samples that were heated to 450 °C and then allowed to cool before heating to a range of temperatures between 800 and 1200 °C all retained the anatomy of charcoal heated to around 450 °C regardless of the final temperature to which it was exposed. They were black in colour, obviously charcoal but fractured easily by hand yet were not powdery or excessively friable. The anatomy was intact and reflectance was relatively high.

The glassy or vitrified charcoal as for example described by Marguerie and Hunot (2007) were not found in the charcoal produced under the present experimental conditions. However, a glassy product with chemical composition of tar (Braadbaart, unpublished data), with no morphological structure, similar to that described by Marguerie and Hunot (2007) was formed along side the charcoal specimens.

4.3.4. Degree of shrinkage

The results (Fig. 4) indicate that initial shrinkage was more pronounced when heated at the HHR relative to the LHR. However, at temperatures above 370 °C the relative shrinkage was similar for both heating regimes. For wood specimens initially heated to 450 °C to form charcoal, then reheated to a final temperatures above 800 °C the shrinkage was similar to that observed by the wood heated directly to that final temperature using, in particular, the low heating rate. Vessel diameter of specimens subjected to the HHR to final temperatures above 900 °C could not be used due to the extensive anatomical disruption (Table 1).

4.4. Physical analysis

Reflectance measurements were taken from oak, birch, pine and yew samples heated at final temperatures ranging up to 1200 °C (Fig. 5) and on samples of (oak) charcoal fuel material.

From Fig. 5 it can be seen that reflectance measurements taken from oak samples are consistently greater than the pine samples over the whole range of investigated temperatures. This

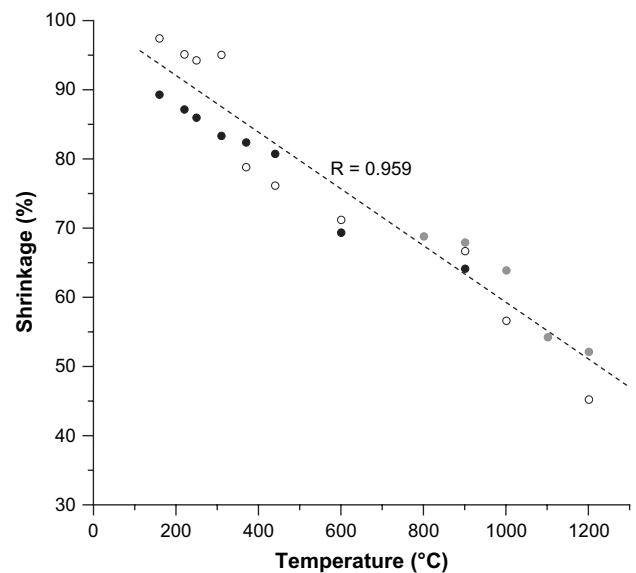


Fig. 4. Graph illustrating the relationship between the degree of shrinkage in early wood vessels of oak samples ($R = 0.959$) heated using the two different heating regimes (HHR, solid circles, $R = 0.980$; LHR, open circles, $R = 0.966$; fuel wood, grey circles, $R = 0.958$) and different final temperatures expressed as a percentage of the diameter of untreated oak wood.

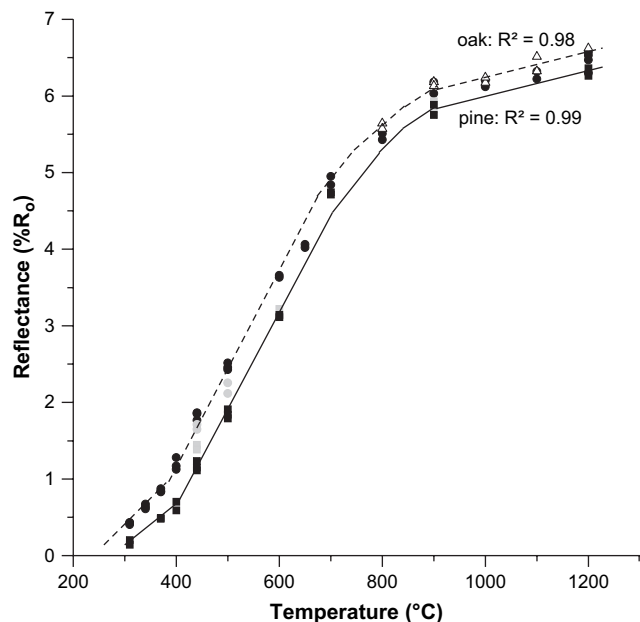


Fig. 5. Mean reflectance measurements ($\%R_0$) taken from wood samples experimentally heated, using the HHR, for 60 min as a function of the final temperature ($^{\circ}\text{C}$). Solid circles, oak; grey circles, birch; solid squares, pine; grey squares, yew; up-triangles, charcoal fuel sample.

taxonomic difference in reflectance is slightly greater in lower temperature range (up to 500°C) but decreases at temperatures above 600°C . To verify this difference, samples of a second angiosperm (birch) and conifer (yew) sample was heated using the same protocol to final temperatures of 440 , 600 and 900°C . Reflectance measurements of these samples again showed that conifer woods have a lower reflectance value than angiosperm material when exposed to the same final temperature. Moreover, at temperatures $>800^{\circ}\text{C}$ these differences are also reduced.

Using the HHR regime, modern oak and pine wood samples heated to 310°C had reflectance measurements for 0.40 and 0.20 , respectively. Reflectance values steadily increase to $\sim 6.5\%R_0$ at 1200°C . However the increase in reflectance of material subject to temperatures above 400°C is more rapid per increase in temperature when compared with the reflectance of material subject to temperatures lower than 400°C . This relatively rapid increase in reflectance remains rapid up to 700°C . Above 700°C the rate of increase of the reflectance decreases and then decreases still further at temperatures above 900°C .

Reflectance measurements on charcoal fuel samples heated to temperatures $>800^{\circ}\text{C}$ at the HHR showed similar results to those obtained from the oak and birch material heated at the HHR to equivalent final temperatures.

Using the LHR regime no difference was observed between pine samples subject to the two heating regimes and heated to equivalent final temperatures (data not shown). This corresponds with earlier observations on wheat grains subject to similar heating conditions (Braadbaart, 2008).

The effect of time of exposure on reflectance of samples of oak and pine can be seen in Fig. 6. Reflectance increases not only as a function of temperature (which was to be expected) but also as a function of time, with the shorter time of exposure to a given temperature resulting in a lower reflectance. However, at lower temperatures (370 and 440°C) the influence of time is relatively less than at higher temperatures (500 – 800°C). At temperatures above 900°C , the influence of time of exposure again decreases.

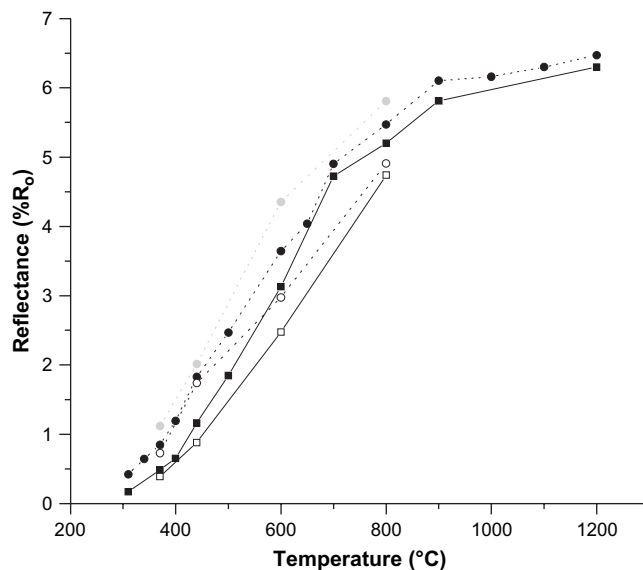


Fig. 6. Mean reflectance measurements ($\%R_0$) taken from oak and pine wood samples experimentally heated, using the HHR, for 15, 60 and 1440 min, plotted as a function of the final temperature ($^{\circ}\text{C}$). Reflectance is seen to increase as a function of time exposed to a particular temperature as well as the temperature itself with the greatest increase falling in the temperature range of 440 – 800°C . Symbols as in Fig. 5.

4.5. Chemical analysis

4.5.1. Elemental analysis

The elemental analysis of the untreated oak wood sample shows a carbon content of $50.1\text{ wt}\%$, daf (Fig. 7). The carbon content of the wood up to a temperature of 220°C remains relatively stable. As oak wood is heated to temperatures above 220°C the carbon content increases sharply rising from $\sim 51\text{ wt}\%$, daf at 220°C to

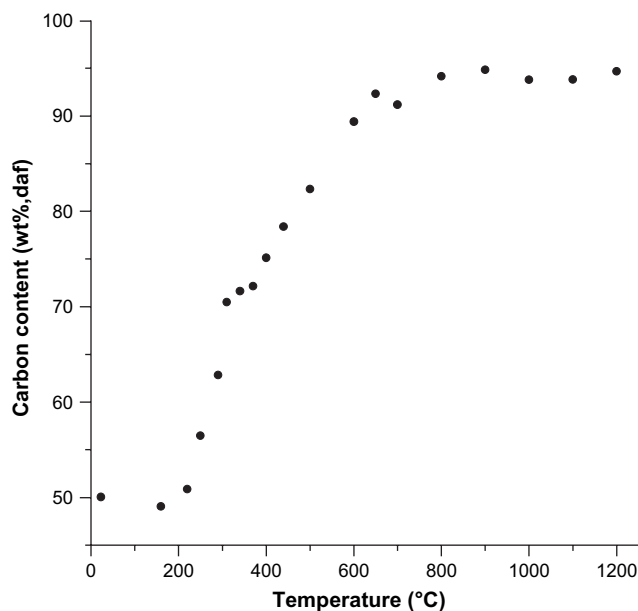


Fig. 7. Results of the elemental analyses of the carbon content ($\text{wt}\%$, daf) of oak wood samples: untreated and subject to the HHR as a function of the temperature ($^{\circ}\text{C}$). Note the rapid increase in carbon content between 220°C and 650°C with a subsequent levelling off at temperatures $>650^{\circ}\text{C}$. Note the slight (unexplainable) decrease in carbon content at 160°C which was also found in peas and sunflower achenes and seeds subjected to the same experimental protocol (Braadbaart, 2004, figure 2.5; Braadbaart et al., 2007, figure 4).

70.5 wt%, daf at 310 °C and then steadily up to ~94 wt%, daf at 650 °C. At temperatures from 650 to 1200 °C the carbon content remains relatively constant.

4.5.2. Molecular analysis

Cellulose, hemicellulose and lignin are structural biopolymers of wood. During thermal decomposition (DTMS-EI) each polymer system generates its own chemical moieties with a characteristic mass distribution and appearance temperature. Together the presence of these different biopolymers results in a relatively complex pyrolysate. Thermal decomposition of these biomolecules as a function of the temperature has been discussed extensively in earlier studies (Braadbaart, 2004; Poole et al., 2002; Braadbaart et al., 2007) and thus thermal decomposition of wood will only be summarized here. The chemical composition of untreated oak and pine differ and therefore the results are presented separately.

4.5.2.1. Oak. The EI spectrum of the untreated sample has an ion distribution that represents the characteristic mass peaks of polysaccharides and lignin (Fig. 8a). Mass peaks m/z 43, 57, 60, 73, 98, 126 and 144 are derived from hexosesugars (cellulose) and m/z 85 and 114 from pentosesugars (hemicelluloses) (Pouwels et al., 1989; Boon et al., 1994; Braadbaart, 2004). The main lignin markers in this spectrum are the monomeric guaiacyl units m/z 124, 137, 150, 151, 178, 180 and the syringyl units m/z 154, 167, 180, 194, 208, 210 (Van der Hage et al., 1993). The major mass peaks are assigned to coniferyl alcohol (m/z 180) and sinapyl alcohol (m/z 210). In the higher mass region, several lignin markers are visible. Mass peak m/z 272

is a well-known product of lignin pyrolysis with several plausible structures (Evans et al., 1986).

The samples heated at 160 and 220 °C have an identical mass distribution to the sample of untreated oak. At 250 °C masses m/z 110, 124, 138, 140, 154 and 168 (alkyldihydroxybenzenes or alkylmethoxyphenols or trimethoxybenzenes) become more apparent and are indicative of the presence of masses related to the thermal degradation of lignin (Klap et al., 1996). A relative increase of the aforementioned ions continues at 280, 290 and 300 °C. At 310 °C the intensity of the polysaccharide markers has decreased substantially (Fig. 8b) and at 340 °C these markers are no longer apparent in the spectrum and only thermal degradation products of lignin are observed (not shown).

At 340 and 370 °C the spectra (not shown) present clusters of three mass peaks with (CH₂) mass increments such as m/z 146, 147, 148, 160, 161, 162, etc. that correspond to a homologous series of condensed aromatic compounds and mass peaks related to alkylated phenols and benzenes such as m/z 91, 92, 94, 107, 108 and 122 with a relatively low intensity. These mass peaks are typical products resulting from the thermal degradation of polysaccharides and lignin (Boon, 1992; Braadbaart et al., 2007). Finally, at temperatures above 400 °C, the material is characterized by a very low amount of pyrolysis products. The spectra show ions m/z 28 (CO) and 44 (CO₂) derived from O-containing polyaromatics. Also m/z 78 (benzene) is present indicative of a highly condensed material.

4.5.2.2. Pine. Untreated pine wood is characterized by the presence of the above mentioned characteristic polysaccharide and lignin markers, but only monomeric guaiacyl units (m/z 124, 137, 151, 178 and 180) are observed (Fig. 9a). In conifer wood m/z 272 is usually higher in abundance when compared with angiosperm wood (Evans et al., 1986). The higher mass range is characterized by masses m/z 239, 285, 300 and 302, which are indicative of the presence of pine resin (Colombini et al., 2005). Masses m/z 256 and 284 are attributed to fatty acids.

The mass distribution of the samples heated at 160, 220 and 250 °C remain unchanged relative to the untreated sample. Above 250 °C the presence of masses m/z 110, 124 and 138 (dihydroxybenzenes or alkylated methoxyphenols) indicate the presence of thermally degraded lignin (Klap et al., 1996). At 310 (Fig. 9b) and 320 °C the polysaccharide and lignin (guaiacyl) pyrolysis products remain abundant (in contrast to oak), which is also true for mass peaks m/z 91, 92, 94 and 107. The masses m/z 284, 298, 312 and 326, with a relative high intensity can be attributed to fatty acids.

From 340 °C the polysaccharide and lignin markers are no longer observed. The spectrum is characterized by the presence of mass peaks m/z 110, 124 and 138, and m/z 91, 92, 94 and 107. As with the oak material, at temperatures above 440 °C, the pine wood is characterized by a very low amount of pyrolysis products and ions m/z 28 (CO) and 44 (CO₂) and m/z 78 (benzene).

4.6. Archaeological simulation of fuel wood exposure to heat

The piece of oak wood fuel placed in an established cooking fire and left for 15 min, once the wood had reached a temperature of 800 °C, had a reflectance value of 5.21%R₀ (Table 2). One of the three pieces of charcoal fuel from the charcoal kiln introduced to an established fire and left for 15 min at a temperature of 1100 °C had reflectance value of 5.95%R₀. The other two pieces, exposed to a temperature of 1200 °C for 15 min had an average reflectance values of 6.21%R₀ (Table 2).

5. Discussion

Charcoal is a term that is frequently encountered in the literature, yet there is no standard definition for this residue. Therefore

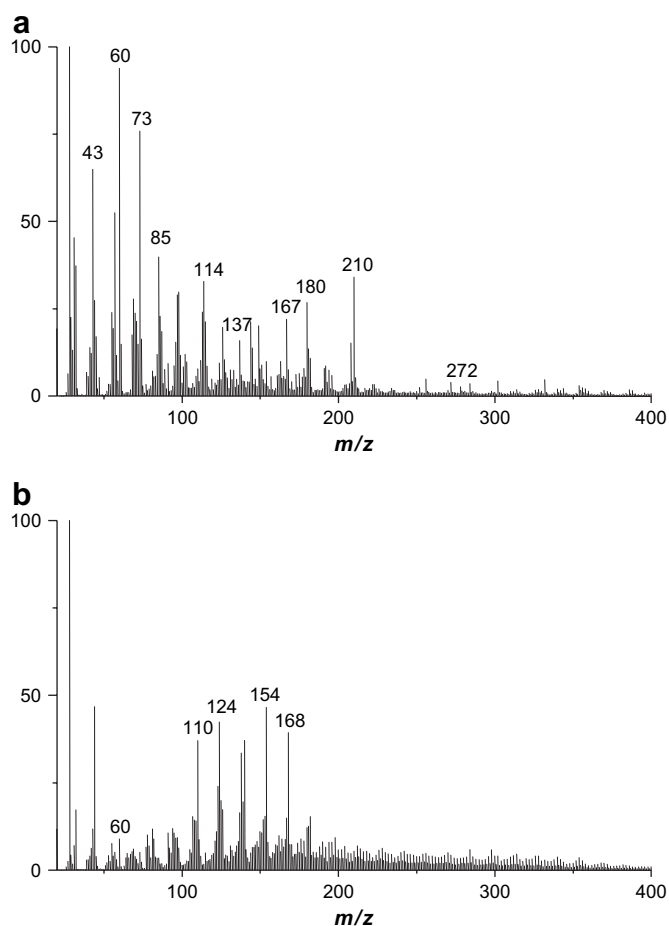


Fig. 8. DTMS-EI mass spectra of oak wood. (a) untreated; (b) heated in the absence of air at 310 °C for 60 min.

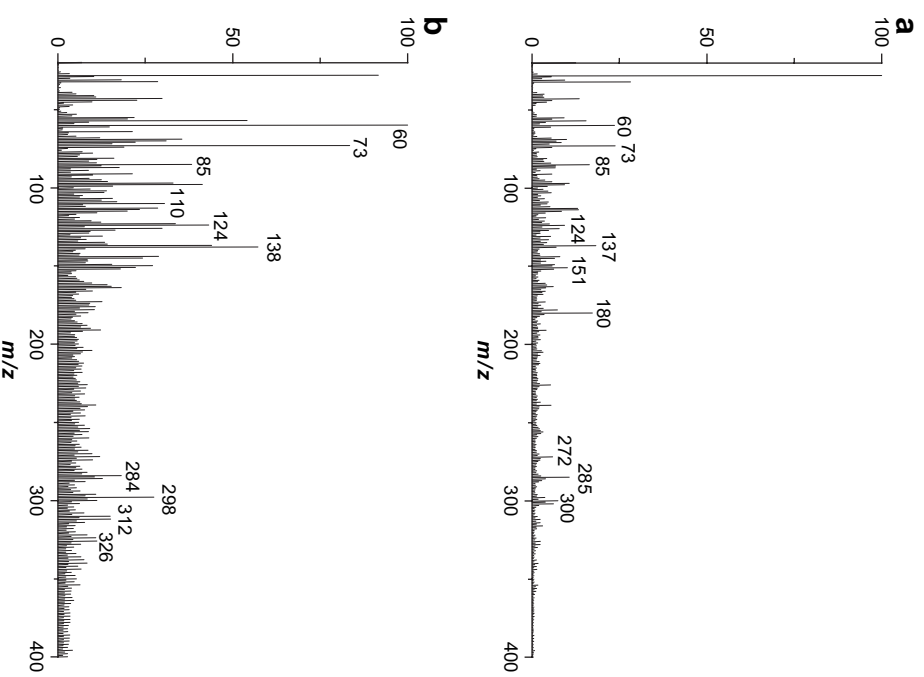


Fig. 9. DTMS-El mass spectra of pine wood. (a) untreated; (b) heated in the absence of air at 310 °C for 60 min.

the aim of this research was to determine how the processes associated with charcoalification affect the morphological, physical and chemical characters of the original wood to (1) define archaeological charcoal, and (2) determine how the properties of archaeological charcoal can be used to reveal more detail regarding possible human activities in the past.

5.1. Mass loss, temperature and time of exposure

Although temperature is well known to be an influential factor for wood conversion to charcoal, little consideration has been given to the length of time of exposure to a heat source in relation to charcoal formation. Mass loss is a direct means by which the effects of time of exposure can be monitored. Samples heated to increasing final temperatures attain equal mass losses at decreasing times of exposure (see horizontal dashed line depicting equal mass loss in Fig. 2). The results found for the wood samples studied here are similar to the findings of experiments performed on wheat grains (Bradshaart, 2004) whereby mass loss in the wheat grains exhibited the same behaviour as the charcoal albeit at somewhat higher temperatures and over a shorter time scale when compared with lower temperatures (Fig. 2). These earlier studies on wheat grains showed that the residues with equal mass loss also have identical chemical structure and composition thus the amount of energy (in this case heat) to convert the constituent biomolecules, cellulose, hemicellulose and lignin, into new compounds is identical for samples with equal mass loss. Therefore after a constant exposure

Table 2

Temperatures at which charcoal was formed inferred from reflectance measurements, and temperature ranges (estimated) as determined using morphology when material was available

Location	Identification number	Taxonomic status	Context	Final temperature (°C)	Length of exposure	Reflectance (%R ₀)	Standard deviation	Estimated temperatures (°C)	
								Derived from %R ₀ values ^a	Derived from morphology
<i>A. Archaeologically simulated charcoal samples</i>									
Germany	MC1	<i>Carpinus</i> (A)	Charcoal prod.	500	Days	2.55	0.072	510	>440 < 800
Germany	MC2	<i>Quercus</i> (A)	Charcoal prod.	500	Days	4.13	0.094	580	>440 < 800
Germany	MC3	<i>Juglans</i> (A)	Charcoal prod.	500	Days	3.84	0.227	560	>440 < 800
Archeon (NL)	MC2	<i>Quercus</i> (A)	Bronze melting	1200	30 min	6.13	0.267	1100	>900
Archeon (NL)	MC3	<i>Quercus</i> (A)	Bronze melting	1200	30 min	6.23	0.214	1100	>900
Archeon (NL)	Ar1	<i>Pinus</i> (C)	Bronze melting	1200	30 min	6.41	0.243	1250	-
Archeon (NL)	Ar2	<i>Pinus</i> (C)	Iron ore smelting	1200	24 h	5.51	0.236	860	-
Archeon (NL)	Ar3	<i>Quercus</i> (A)	Domestic fire	Up to 800	15 min+	5.21	0.232	750	-
<i>B. Archaeological samples</i>									
Schippluiden	8941	<i>Prunus</i> (A)	Hearth pit	800	15 min+	1.0–1.5	0.227	380–420	>400 < 800
Maastricht	1–55,8	<i>Quercus</i> (A)	Grain silo	Not known	Not known	0.47–0.60	0.076	320–340	>400 < 800
Tiel	22	<i>Quercus</i> (A)	Burnt shed	Not known	Not known	1.15	0.136	390	>400 < 800
Hattummerbroek	5843–1	<i>Pinus</i> (C)	Tar prod.	500	15 min+	0.98	0.091	440	>400 < 800
Hattummerbroek	5630–3	<i>Pinus</i> (C)	Tar prod. ^b	500	15 min+	0.89	0.98	440	>400 < 800
Hattummerbroek	4547–4	<i>Pinus</i> (C)	Tar prod.	500	15 min+	1.16	0.162	450	-
Azerbaijan	S1	<i>Quercus</i> (A)	Hearth pit	800	15 min+	1.1	0.120	390	>400 < 800
Azerbaijan	S2	<i>Ulmus</i> (A)	Tandir	Not known	Not known	0.51	0.071	310	>400 < 800
Azerbaijan	S3	<i>Ulmus</i> (A)	Hearth pit	800	15 min+	1.27	0.165	400	-

^a Temperatures derived from the calibration curve for angiosperm and conifer wood accordingly, (A) angiosperm, (C) conifer.

^b This sample yielded material characterized by intact anatomy associated with the glassy, tar material similar to that described by Marguerie and Hunot (2007).

time (60 min) morphological, chemical and physical changes in charcoal at different final temperatures were compared.

In addition to final temperature and exposure time, heating rate also contributed to *when* such changes occurred. This is important as it might help determine whether the wood was used as a starter fuel (LHR) or simply fed to an already established fire (HHR). These findings are similar to those of Braadbaart (2008) when wheat grains were subject to the same experimental conditions. This rapid mass loss is tentatively attributed to the violent reactions that take place with a sudden injection of energy associated with the HHR resulting in more material being lost to the external environment. The morphologically denser structure of the conifer wood would explain why an apparent increased amount of energy is required to break down conifer wood—volatile products released will be relatively more mass loss constrained when compared with the more open structure of the angiosperm wood.

5.2. Morphological changes

An important aspect to archaeological charcoal studies is its morphology (colour, anatomy and texture). Residues are generally labelled 'charcoal' if they are dark brown-black with a relatively light texture and can be fractured by hand. However, the degree of change may provide further information regarding temperature and thus fire type and usage.

At temperatures of $\sim 350^\circ\text{C}$, regardless of heating regime, the predominantly wood like residue becomes a predominantly charcoal like residue. This infers stability in chemical and physical properties associated with a greater resistance to decomposition after deposition into the soil. Therefore the archaeological record is less likely to preserve evidence of wood heated at temperatures below 350°C and a charcoal residue is indicative of fires attaining temperatures of $\sim 350^\circ\text{C}$ and above.

At temperatures from 350 to $\sim 800^\circ\text{C}$ a charcoal residue is characteristically black in colour, can be easily fractured to reveal a well preserved anatomical structure that can be easily seen under epi-illumination. However at temperatures above 800°C , although the outward appearance is that of charcoal, the residue has become powdery in nature and the anatomy often distorted. At temperatures above 1000°C the anatomy is always distorted or deformed often appearing as if it has become fused prior to solidification. This type of charcoal residue is often termed 'poorly preserved' when in fact it is indicative of very high temperatures and thus possibly of industrial, as opposed to domestic, fires.

In this study 15% shrinkage had occurred at 350°C whereas at 800°C , 35% shrinkage had occurred. Little difference is seen between degree of shrinkage and heating regime although shrinkage is initially (up to $\sim 800^\circ\text{C}$) greater with the HHR regime compared with the LHR regime. Charcoal fuel also shrinks in similar fashion to that of wood fuel. However, without knowledge of parameters derived from the original wood, degree of shrinkage is of little use to the archaeologist in determining temperature and thus fire type.

5.3. Physical changes

It has been noted that under epi-illumination increasing temperature results in an increased reflectance. This change in reflectance is related to a change in molecular arrangement. Above $\sim 280^\circ\text{C}$ there is a gradual increase in the formation of multi-ring (3–5) aromatic structural units which causes an increase in reflectance (Carr and Williamson, 1989; Braadbaart, 2004). At about 440°C condensation reactions take place accompanied by further molecular reorganization and the formation of large polyaromatic sheets which serve to increase reflectance still further (see below). From around 800°C the change in molecular structure becomes less drastic and this is reflected in the reflectance values increasing

less steeply. This reflectance with increasing temperature can be quantified using the reflectance of known standards. From this purpose a calibration curve (Fig. 5) was established such that the final temperature to which charcoal residue was heated can be obtained. Note that this curve was prepared using a time of exposure of 60 min and different exposure times result in different mass losses (Fig. 2). Thus (estimated) time of exposure has to be taken into consideration when determining temperature from reflectance.

Although heating regime (HHR versus LHR) produces no difference in reflectance values at a given temperature (and thus no change in the shape of the plot; Fig. 5), time of exposure and taxonomic identity do. An increased time of exposure results in an increased reflectance at any particular temperature (Fig. 6). This difference is most obvious in the temperature range 500 – 800°C when the gradient of the curve is at its steepest. When reflectance values are $<1\%R_0$, the difference in temperature attained after 15 min and 24 h of heating is in the order of $\pm 15^\circ\text{C}$. This is also the case with reflectance values greater than $5.5\%R_0$. In the mid range, between reflectance values of 1.5 and $5.5\%R_0$, the errors in temperature estimates can be as great as $\pm 75^\circ\text{C}$ ($\%R_0 = 4$).

Due to chemical and anatomical differences, taxonomic identity affects the reflectance at a given temperature. Reflectance of pine wood charcoal is consistently lower than that of oak wood charcoal. These results were confirmed by repeating the experiments with birch and yew. Therefore in order to use reflectance values to determine temperature from archaeological charcoal, knowledge of the taxonomic identity and an informed estimate of time of exposure based on contextual data are fundamental prerequisites.

5.4. Chemical changes

From elemental analysis of oak wood the increase in carbon content with increasing temperature correlates to the change in reflectance. Noteworthy is that at temperatures above $\sim 650^\circ\text{C}$ the carbon content levels off at about 95% daf (Fig. 7), which is at more or less the same temperature at which the reflectance also levels off (Fig. 5). Therefore carbon content of archaeological material in the range of 55–90% daf can only be used by archaeologists to indirectly determine temperature up to $\sim 650^\circ\text{C}$.

The change in molecular composition with temperature is more complex since the taxonomic identity of the initial wood affects the resultant composition. For both conifers and angiosperms, DTMS-EI spectra of samples heated to 250°C are similar to untreated wood with an essentially carbohydrate–lignin dominated structure with both polysaccharide and lignin markers still present even though dehydration reactions have changed the chemical composition. This gradual change continues at temperatures $>250^\circ\text{C}$ where the polysaccharide and lignin markers gradually disappear and are replaced by thermal degradation products of these biomolecules. Above 300°C ($\sim 310^\circ\text{C}$ for oak wood and $\sim 340^\circ\text{C}$ for pine wood) polysaccharide and lignin markers are lost with angiosperm wood producing more aromatic compounds relative to conifer wood at any given temperature. At 400°C only aromatic moieties are present in both conifers and angiosperms. At temperatures above 400°C the gradual change from the carbohydrate–lignin dominated structure to new, chemically distinct material with a highly carbon enriched character characterized by DTMS spectra showing masses representing CO, CO₂ and benzene, has been completed. Therefore temperature related changes cannot be determined from samples heated to above $\sim 400^\circ\text{C}$. The slower chemical change in conifer wood during the charcoalification process co-occurs with changes seen in the morphology and reflectance values as discussed above. Therefore it appears that more thermal energy is needed to convert conifer wood into charcoal when compared with oak wood. This observation is most probably related to the

morphological/anatomical composition of the conifer wood. The denser structure of conifer wood could significantly impact (i.e. reduce) the release of volatile products, i.e. cannot be released or undergo fast secondary condensation reactions. This would lead to the apparent slower chemical changes. This might also explain the observation by Fengel and Wegener (1984) that above 340 °C, heating pine wood produced more wood tar than oak wood, which in turn contributed to a higher mass loss and less charcoal residue for pine wood.

5.5. Application to charcoal recovered from archaeological contexts and simulated situations

In light of the results obtained from these studies on experimentally produced charcoal, the techniques were first applied to archaeologically simulated material to calibrate the experimental results, and then the analyses described here were applied to charcoal from known archaeological contexts to evaluate feasibility. Some methods (chemical analyses) were not applied as they do not provide any additional insight to that already available from morphological and physical analyses. Since an indication of exposure time and taxonomic identity is required for further charcoal residue studies, identifications were carried out and exposure times estimated for the archaeological samples that were made available for this study. Estimations of time of exposure can be gained from the contextual data.

In general, residues from three different heating regimes are frequently encountered in the archaeological record. Domestic fires, for heating and cooking, use wood as a fuel, which undergoes charring in the presence of air. Much of the fuel succumbs to complete combustion to form ash at temperatures that can reach 800 °C. This ash is subsequently lost from the archaeological record. However, charcoal residues from such a context will not be the fuel that reached these high temperatures but rather the fuel that was either added towards the end of the life of the fire, or had been removed from the fire either directly by human intervention, or indirectly by falling out of, or on to the edge of, the fire. In these situations temperatures falling to below 350 °C coupled with no further volatile-release result in an interruption of the carbonization process as the fire becomes extinguished. Time of exposure will be relatively short (>15 min but less than 30 min). Such pieces of wood will usually record temperatures of 300–400 °C. Higher temperatures will be recorded if the exposure time is short (i.e. 10–15 min).

Charcoal fuel and tar production exploits the process of charring where air (oxygen) is excluded from the heating process to ensure a good quality product with a high calorific value. Clay, turf or other similar material would have covered the kiln or pit to ensure anoxic conditions and thus prevent combustion, which would inevitably occur if oxygen comes into contact with wood heated to between 450 and 500 °C. The time of exposure for charcoal formation in this way would be relatively long, at least 24 h (Armstrong, 1978).

Industrial fires, in contrast to their domestic counterparts, require temperatures in excess of 600 °C. For firing pottery, wood can be used as the fuel to reach the required temperature of 600–900 °C (Livingstone, 2001). For fires requiring temperatures ~800 °C and above, the higher calorific value of charcoal as a fuel had to be exploited. Such fires, with temperatures reaching 1300 °C, would have been used for smelting ore or melting metals, for example. Air is introduced to the fire to ensure high temperatures are reached and maintained, and again charring takes place. As with a domestic fire, the charcoal residue will be derived from fuel added towards the end of the life of the fire or pieces that had been removed from the fire. The exposure time of this charcoal residue will also have been short but will record much higher temperatures.

The details of charcoal produced in simulated archaeological setting have been given in Table 2A and those of archaeological charcoal from known contextual settings in Table 2B. Using morphological changes of archaeologically simulated material of known taxonomic identity at heated to known temperatures for given lengths of time (Table 1), derived final temperature values can be inferred by the %R₀ values from the calibration curve given in Figs. 5 and 6. When these estimated temperatures are compared with the known final temperatures, the derived temperatures were in general agreement with the actual temperatures at which they were produced in all cases.

Even though some derived temperatures deviated from the actual temperatures they were in good agreement with the range of temperature found in a particular fire type (i.e. domestic versus industrial). When the final temperatures of the archaeological samples are determined using %R₀ values (Table 2B) and the curves in Figs. 5 and 6, there is once again good agreement between the estimated temperature and the contextual information. One example illustrating the importance of taxonomic identity is the reflectance measured on charcoal samples from four beams, situated in close proximity to one another (<5 m), recovered from Herculaneum (Italy) (unpublished data). Reflectance measurements from the three angiosperm beams were higher than that measured on the one conifer beam. From the calibration curve (Fig. 5) the conclusions regarding exposure temperature drawn from the conifer wood would have been ~100 °C lower than those estimated for the angiosperm material had taxonomic identity not been taken into consideration.

6. Conclusions

Based on the results of this study it is concluded that:

- Archaeological charcoal can be defined as an inert, black material heated to temperatures exceeding 350 °C for at least 15 min either by (1) carbonization in the absence of air (oxygen), or (2) incomplete (interrupted) charring in the presence of a restricted supply of air (oxygen).
- Charcoal residue formation is related to not only temperature but also length of exposure to the heat source and the associated heating rate.
- Morphological analyses of archaeological charcoal can provide additional information relating to final temperature and in turn further understanding of the type of fire in which it was formed (i.e. industrial or domestic), and by inference human activities at that site.
- Physical analyses (reflectance) can also provide additional information relating to final temperature and by inference human activities at that site. A recommended minimum size of ~3 mm² in transverse section of the charcoal specimen should be used, which would allow identification of anatomical preservation as well as taxonomic identity (conifer or angiosperm).
- Chemical (molecular, DTMS-EI, and elemental, i.e. carbon) analyses were undertaken to determine whether additional information, to that which could be derived from morphological and physical analyses, could be obtained. No additional information could be obtained for archaeological charcoal samples heated to temperatures in excess of ~400 °C for DTMS-EI and 650 °C for elemental analysis. Below these temperatures (and especially below 300 °C) the time of exposure plays an important role in interpreting the data. For archaeological samples, time of exposure is not known and thus prevents the use such data to draw any meaningful conclusions.
- Differences in the morphology of wood appear to impact the physical and chemical changes. The denser conifer wood

requires relatively greater energy input in order to undergo similar chemical and physical alteration when compared with angiosperm wood. This is due to mass loss constraints.

- Conclusions derived from morphological and physical analyses have to be used together with the archaeological contextual data wherever possible.

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