

Laboratory simulations of the transformation of peas as a result of heat treatment: changes of the physical and chemical properties

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Abstract

The residues of heated organic remains, usually called carbonized or charred remains, are ubiquitous in the archaeological record and are often used to interpret certain aspects of past ways of living. This study focuses on the physical and chemical alterations, both as a function of temperature and time that occur when the transformation of a polysaccharide-rich biomass is simulated in the laboratory. Peas (*Pisum sativum*) are heated at temperatures ranging from 130–700 °C under anoxic conditions and atmospheric pressure, during a maximum of 2 h. Changes in weight and the relative percentages of C, N, H and O are noted alongside modifications of the internal and external morphology. Vitrinite reflectance provides an elegant tool to determine the heating temperature of the residues. The kinetics that determine the changes and modifications are discussed. The resulting solid products of the heating process can be conveniently considered in five phases, which fit the physical and chemical properties. The simulation provides a rigorous basis for the study of the formation processes, as applied in the archaeology, after the so-called “carbonization” process.

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1. Introduction

The most common mode of survival of archaeological plant remains is a process generally referred to as charring or carbonization, because the majority of the archaeological finds are the charred remains of wood, fruits and seeds [41]. Not all parts of a plant will survive the carbonization process, but fruits and seeds carbonize well and are often still recognizable [6]. Generally they are morphologically well defined and thus samples of different batches can be compared while the natural variation in chemical composition is minimal. In particular, propagules of cereals, legumes, etc. are often found as carbonized entities in the archaeological record [3]. Previous studies on these kinds of fruits and seeds are usually restricted to the change of the dimensions

upon carbonization [5,29,35]. To date, only a few papers have addressed the change in the physical and chemical composition of fruits and seeds as a result of carbonization [19,23].

Carbonized fruits and seeds found in the archaeological record are the result of a series of processes called formation processes [32,33]. These processes include carbonization, deposition in the soil, post-depositional alteration, excavation and analysis. Apart from the fact that carbonization is the result of heating under anoxic circumstances it is still not fully understood when and where fruits and seeds become carbonized and to what extent subsequent transformations take place. This study reports on the laboratory simulations of the transformation of recent seeds and determines the resulting physical and chemical properties.

In the different fields of thermal conversion of organic material variations in terminology have come into common use. Terms like thermal decomposition, pyrolysis

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and carbonization are often used interchangeably [36]. In the context of the conversion of biomass, pyrolysis is described as thermal degradation, either in the complete absence of oxidizing agents, or with a limited supply. The pyrolysis technology has introduced terminology such as carbonization, conventional pyrolysis, fast and flash pyrolysis [11]. The temperature range in the case of carbonization is 300–500 °C with a residence time of hours or days. In the field of coal technology pyrolysis is generally defined as the thermal decomposition of coal in the absence of air. Carbonization is applied to the production of char or coke when coal is heated at temperatures in excess of 500 °C [36]. The term carbonization is also widely used in archaeology, but appears to refer to a black solid residue of biomass as the result of heat treatment, although the conditions under which the heat treatment took place are rarely mentioned. To date, no definitions exist for terms like char and charcoal, the solid products of conversion processes [13]. In light of these considerations the process of heating in the absence of oxygen in this paper will be called the heat treatment, and the resulting solid product, the residue.

Within the current project fruits or seeds of two species of plants are selected because of their occurrence in the archaeological record, their different chemical composition and because they include both mono- and dicotyledons. One dicotyledonous plant was chosen, namely the seeds of the pea (*Pisum sativum* L.), which contain mainly starch (56%, by weight) and protein (24%). The monocotyledonous plant, emmer wheat (*Triticum dicoccum* Schübl), was selected because of its high starch content (70%) [14]. In the current study the results of the heat treatment on peas are presented. The seeds are composed of a seed coat (testa) enveloping two cotyledons that constitute the major portion of the seed.

A number of parameters can be directly obtained from propagules found in the archaeological record and exposed to heat. These include size and shape, morphology and anatomy, physical and chemical properties. With this in mind the objective of this study is the assessment of the changes of the physical and chemical composition of the seeds of the pea that occur during heat treatment under anoxic conditions at atmospheric pressure. The seeds are heated at temperatures ranging from 130 to 700 °C. The total weight loss, the changes of the internal and external morphology, the chemical composition and the vitrinite reflectance of the seeds are studied. Hereby the physical and chemical properties of the solid residues of the seeds will be determined, as a function of heating temperature. The vitrinite reflectance measurements provide information pertaining the anatomy and the thermal history of the propagules ([44] and references cited therein). This means that a rigorous basis will be provided for studies regarding the effects of the formation processes on the solid residues as a function of the temperature after the “carbonization”

process, which is considered as the first of the formation processes.

2. Material and methods

2.1. Samples

Peas (*P. sativum*) were collected from the Centre for Genetic Resources, Wageningen, The Netherlands (CGN). Three Dutch varieties were selected: “Graauwe Erwt” (GE; CGN 10198), “Noord-Hollandse Rozijnerwt” (NHR; CGN 10293) and “Wijker Vale” (WV; CGN 10312). The flowers of these varieties are red and the outside colour of their seeds is generally brown and the surface is wrinkled. Based on these features they belong to the field pea (*P. sativum* ssp. *arvense*) [16]. The dimensions are roughly 8 × 5 × 3 mm and the average weight of a single pea is c. 400 mg. The three varieties were grown in the Hortus Botanicus of Leiden University and a new crop of peas was harvested at the end of the summer of 1999. About two months after harvesting, the peas were used for the carbonization experiments without any further pre-treatment. For most of the experiments variety GE was used.

A sample of peas from the archaeological record was made available by Prof. Dr C.C. Bakels from the faculty of Archaeology of Leiden University. This sample is referred to as H414 [4]. The peas were excavated from a site in a loess soil in Hienheim (Northern Bavaria, Germany) in pit 414. The age of the peas was determined by ¹⁴C as being 5100 years cal. BC.

2.2. Heat treatment

For each experiment ten intact peas were placed into an open glass vessel and inserted in a 30 cm long glass tube (Ø 2.3 cm) at c. 18 cm from the inlet. The tube was inserted in a pre-heated Carbolite tube oven (model MTF 12/38/250) and subsequently heated at one of the following temperatures: 130, 160, 190, 220, 235, 250, 270, 290, 310, 340, 370, 400, 440, 500, 600 or 700 °C under a constant flow (150 ml min⁻¹) of N₂ at atmospheric pressure. During the experiment the heating rate of the oven was set at 2 °C min⁻¹. In an additional experiment at 340 °C the heating rate of the oven was increased to 200 °C min⁻¹. The glass vessel with the peas was weighed before and after heating, in order to determine the percentage weight loss. In the initial experiments the samples were heated as a function of time at 190, 235, 250, 290, 340 and 600 °C for a period of up to 120 min required to determine the optimal heating time. Based on these initial experiments, peas used for the subsequent analyses were heated for 60 min. Gases and volatiles were vented and not investigated further.

To determine the variations between internal and external temperatures experiments were undertaken with

one pea in the glass vessel. A hole (\varnothing 0.3 mm) was drilled in the pea and a “K” type thermocouple was inserted in the middle of the pea. Just beside the pea a similar type of thermocouple was placed to monitor the temperature of the carrier gas. The exposed wires were insulated with glass fibre. The thermocouples were connected to a two-channel writer (Kipp en Zonen, model BD41) and the temperatures were recorded continuously versus time. The thermocouples were calibrated with a pyrometer. Similar experiments were carried out with ten peas in the glass vessel where only one of the peas in the middle was equipped with a thermocouple.

2.3. Microscopy

Visual changes in the external gross morphology of complete peas were studied using a Zeiss Axioskop incident light microscope. The internal morphology was examined on polished resin-embedded cut specimens using a Zeiss Axioskop reflected light microscope.

2.4. Chemical analyses

For the chemical analyses the testa was removed and only the cotyledons, which constitute the bulk of the peas, were ground and used. CH analyses were performed using a LECO CHN-1000 analyser. The furnace temperature was set at 1050 °C. S analyses were executed using a LECO SC-144DR. Additional C and N analyses were executed on a NA 1500 series 2 NCS analyser from Fisons Instruments. 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 at least two measurements corrected for H₂O and ash content, which were determined on the Thermo-gravimetric Analyser TGA 2950 Hi-Res. The carrier gas was air and the heating rate was set at 25 °C min⁻¹, water content was determined at 105 °C and ash content at 950 °C.

2.5. Mineral content

Five peas were ground using a Tungsten-carbide mill in an automated grinding and pressing machine (Herzog HSM-HTP). The ground sample was pressed with wax into tablets, on which XRF-analyses were performed. The tablets were analysed for major and trace elements by X-ray microscopy, using an ARL9400 spectrometer with a Rh tube, with full matrix correction for major elements and Compton scatter method for trace elements.

2.6. Vitrinite reflectance measurements

Entire specimens of peas were heated for 60 min at oven temperatures ranging from 250 to 700 °C. The

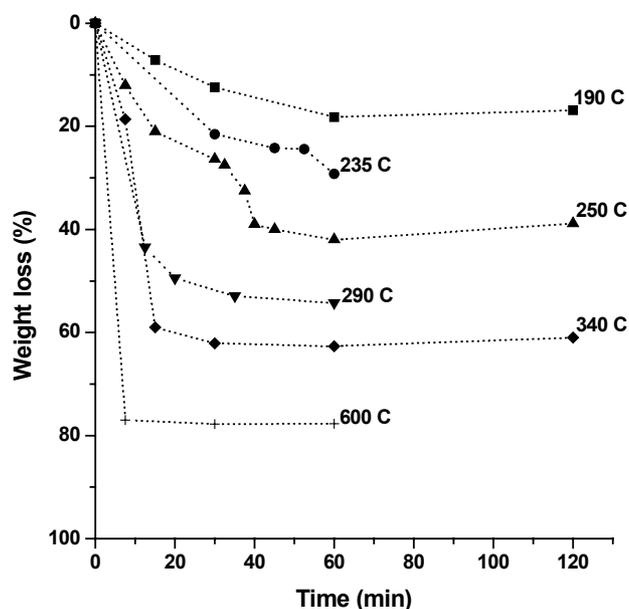


Fig. 1. Weight loss during heat treatment of 10 peas (*P. sativum* var. Graauwe erwt) with N₂ as carrier gas. Weight loss (%) vs. time (min) at oven temperatures of 190, 235, 250, 290, 340 and 600 °C.

residues were embedded in resin blocks and polished. Mean maximum vitrinite reflectance measurements (%*R*_{max}) were carried out under oil immersion at a wavelength of 546 nm using a Leitz MPV II microscope system. One hundred reflectance measurements were made on each specimen. Preparation of polished blocks and reflectance measurements were carried out according to standard methods defined in ISO 7404, part 2 [21] and ISO 7404, part 5 [22].

3. Results

3.1. Heat treatment

3.1.1. Heat treatment at a constant temperature vs. time

The weight loss of ten peas was determined at different times (*t* in min) at the various constant oven temperatures (*T*_{oven} in °C). The conditions of the experiments did not allow for continuous measurement of the total weight loss. Therefore a separate experiment was needed for each measurement. The results show that for each *T*_{oven} the total weight loss reaches a constant level after a certain time and the higher the temperature the shorter the time after which the weight loss remains constant (Fig. 1). The rate of weight loss changes according to *T*_{oven}. At *T*_{oven}=250 °C (and probably also at *T*_{oven}=235 °C) two events of weight loss can be recognized, one until c. 15 min with a weight loss of c. 20% and a second one starting after c. 25 min and leading to a further weight reduction of 20%.

To obtain additional insight into these phenomena subsequent experiments were executed with a single pea in the glass vessel to measure the temperature as a

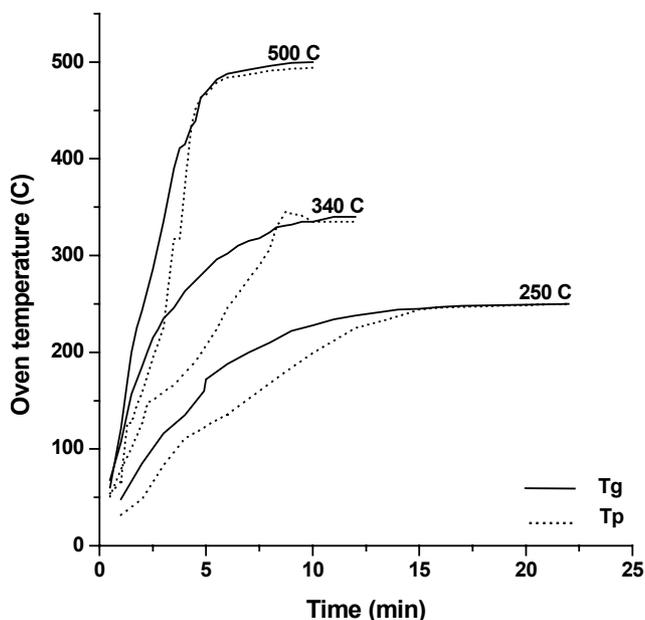


Fig. 2. Experiment with one pea (*P. sativum* var. Graauwe Erwt) showing the occurrence of endotherm and exotherm reactions. Internal temperature T_p ($^{\circ}\text{C}$) and external temperature T_g ($^{\circ}\text{C}$) vs. time at oven temperatures of 250, 340 and 500 $^{\circ}\text{C}$.

function of time inside and outside of the pea using thermocouples. Fig. 2 reveals that in the first part of the curves the external temperature, T_g ($^{\circ}\text{C}$), is greater than the internal temperature, T_p ($^{\circ}\text{C}$), of the peas, which indicates a competition between the heat necessary to increase the temperature of the pea and the heat necessary for the reactions. Initially this positive thermal lag ($T_g - T_p > 0$) is simply the temperature gradient required to affect the heat transfer from the oven to the N_2 -gas and to the pea, which has a poor thermal conductivity. This initial period is followed by a short period where T_p remains almost constant. The result is an increase of the thermal lag. After this stage T_p increases again, the thermal lag gets smaller as a function of time and eventually $T_p = T_g$. At $T_{\text{oven}} = 250$ $^{\circ}\text{C}$ T_p reaches T_g after 15 min and with increasing T_{oven} the necessary time decreases; at $T_{\text{oven}} = 500$ $^{\circ}\text{C}$ this is 4.3 min (Fig. 2).

However, from $T_{\text{oven}} = 290$ $^{\circ}\text{C}$ the $T_p = T_g$ phase is followed by a negative thermal lag and from then on $T_g - T_p < 0$. The curve, with strictly a positive thermal lag (Fig. 2, curves marked 250 $^{\circ}\text{C}$), changes into a curve consisting of a positive, followed by a negative, thermal lag [1], as shown in Fig. 2 with the curves marked as 340 and 500 $^{\circ}\text{C}$. At all oven temperatures T_g becomes constant upon reaching the predefined temperature of the oven. Some minutes later T_p remains also constant, but about 2 $^{\circ}\text{C}$ lower than T_g . The positive thermal lag is evidence of an endothermic or heat demanding reaction, which is present in all experiments. From $T_{\text{oven}} = 270$ $^{\circ}\text{C}$ the positive thermal lag is followed by a

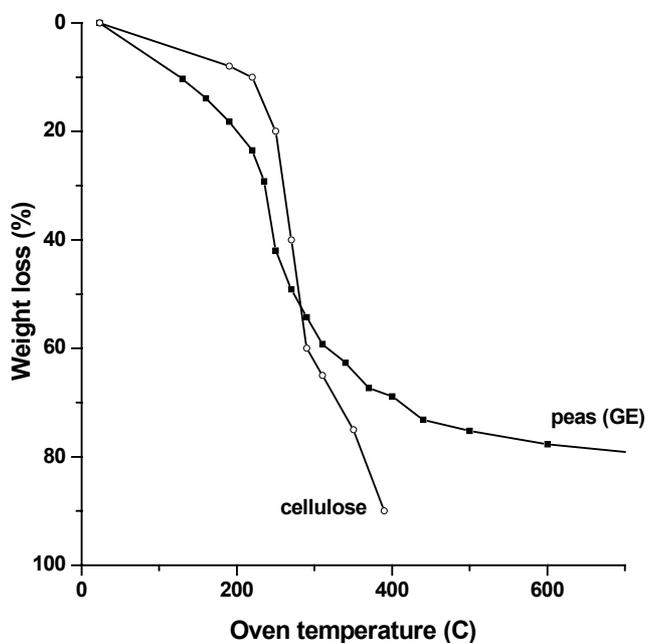


Fig. 3. (a) Weight loss of 10 heated peas in the absence of oxygen (*P. sativum* var. Graauwe erwt) vs. various oven temperatures ($^{\circ}\text{C}$) heated for 60 min. (b) Microcrystalline cellulose heated for 2.5 hrs based on data by Pastorova et al. [27].

negative thermal lag, which is a signature of an exothermic or heat liberating reaction [26].

For the regular experiments 10 peas were used in the glass vessel. Thus to allow an appropriate comparison 9 peas were added to the one pea equipped with a thermocouple. The results show a delay in reaching the final temperatures of T_g and T_p on the order of 4 min in the case of $T_{\text{oven}} = 250$ $^{\circ}\text{C}$ and 3 min at $T_{\text{oven}} = 340$ $^{\circ}\text{C}$. The shape of the curves did not change.

The influence of the heating rate of the oven on the results was measured by increasing the rate from 2 to 200 $^{\circ}\text{C min}^{-1}$ at $T_{\text{oven}} = 340$ $^{\circ}\text{C}$. The curve of T_g did not change, but the curve for T_p did result in a smaller thermal lag, both for the endotherm and the exotherm phase. In the endotherm phase the lag was reduced by half to 40 $^{\circ}\text{C}$.

3.1.2. Heat treatment for 60 min at constant temperature

The results as presented in Fig. 1 reveal that for all T_{oven} the total weight loss after 60 min becomes stable. A series of experiments was executed between $T_{\text{oven}} = 130$ $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$ and the weight loss determined. The results for a typical pea are presented in Fig. 3. The strongest weight loss is found in the range of $T_{\text{oven}} = 220$ $^{\circ}\text{C}$ up to $T_{\text{oven}} = 270$ $^{\circ}\text{C}$. From temperatures $T_{\text{oven}} = 270$ $^{\circ}\text{C}$ upwards the increase of the rate of weight loss slowly decreases until the total weight loss reaches a value of almost 80% at $T_{\text{oven}} = 700$ $^{\circ}\text{C}$. For comparative reasons the weight loss of carbonized microcrystalline

cellulose after Pastorova et al. [27] is also shown, as the experimental conditions are almost identical. From $T_{\text{oven}} > 270$ °C the peas show less total weight loss compared with cellulose.

The experiments were executed at a constant flow of N_2 (150 ml min^{-1}). This means that vapours will be removed from the reaction site. To investigate the relation of weight loss versus flow, experiments were carried out with 150 and 0 ml min^{-1} flow. At $T_{\text{oven}} = 250$ °C for 60 min the total weight loss was, respectively 42.8 and 43.6 ; at $T_{\text{oven}} = 340$ °C for 30 min 63.4 and 62.9% . Under the present experimental conditions the weight loss appears independent of flow rate.

3.2. Morphology and anatomy

3.2.1. Description of the untreated mature pea (*P. sativum*)

The outside of the Graauwe Erwt is wrinkled and the colour is light reddish-brown with ochre patches. The seed coat or testa is composed of 2 layers. The outside layer is called the epidermis and the inside layer the hypodermis [30,45]. Elongated cells with thickened walls and a well-defined cuticle characterize the epidermis. These cells are called the palisade or Malpighian cells. The much-discussed light line of this tissue layer is observed near the apical ends of the cells. The hypodermis is composed of specialized, so-called, hourglass cells [7,17]. The chemical composition of the testa is mainly cellulose and pectin [37].

The hypodermis is followed by loosely organized parenchyma and the endosperm. However, these tissues are ill defined or lacking when the seed is approaching maturity. Inside the seed coat two cotyledons with the storage parenchyma cells are observed. These cells contain large starch grains, numerous protein bodies and small deposits of fats [2,38]. However, the bulk of the pea is composed of starch grains. The cell walls consist mainly of non-starchy polysaccharides, which account for 80% of the walls [2].

3.2.2. External changes caused by heat treatment

The external changes of the peas treated by heat were examined by light microscopy (Tables 1 and 2). Table 1 shows the changes of the peas heated at $T_{\text{oven}} = 250$ °C as a function of time. The outside colour changes from light reddish-brown with ochre patches into black after 22.5 min of heating. The first cracks in the testa appear after 7.5 min in 20% of the peas. However, even after 120 min not all 10 peas have cracks. Table 2 shows the changes during heating for 60 min at $T_{\text{oven}} = 130$ °C until 700 °C. At $T_{\text{oven}} = 220$ °C the external colour has changed into black and the first cracks in the testa appear in 40% of the peas. At $T_{\text{oven}} = 310$ °C all peas have cracks in the testa. The cotyledons start having the cracks at $T_{\text{oven}} = 270$ °C and in all peas heated to 370 °C and higher. It is noteworthy that the surface of the testa

becomes strongly crackled at $T_{\text{oven}} = 310$ °C and this feature disappears again at $T_{\text{oven}} = 400$ °C. At all temperatures the testa is still present, except at places where cracks have developed. Some curling occurs at the edges of the cracks.

3.2.3. Internal changes due to heat treatment

The colour of the cotyledons changes from white through yellow into black at $T_{\text{oven}} = 270$ °C. Polished surfaces revealed a drastic change in the internal structure. In Fig. 4a an example is shown of the internal structure of an untreated pea showing its distinct cells. These cells are filled with a nucleus, cytoplasm, starch grains and protein bodies [2]. The greater proportion consists of starch grains with a 5 to 10 times larger diameter than the protein bodies [43]. This situation does not change until $T_{\text{oven}} = 190$ °C (Fig. 4b and c). From then on the distinct cell structure slowly disappears. At $T_{\text{oven}} = 270$ °C (Fig. 4d) there is no cell structure as such present, but one can still see some faint former cell boundaries. These are completely absent at $T_{\text{oven}} = 310$ °C (Fig. 4e). A grey matrix is visible in which light grey patches can be distinguished. These patches must have been the original starch grains, which have been converted into new thermostable entities. The patches are larger than the original grains, but from the results at $T_{\text{oven}} = 270$ °C and $T_{\text{oven}} = 290$ °C (not shown) it appears as if the grains have “fused”. Another phenomenon is the formation of cavities between the cells and later in the grey matrix. Between $T_{\text{oven}} = 310$ and 440 °C the light grey patches become increasingly faint, but never disappear. The quantity and size of the holes increase until they constitute about 50% of the total volume. From $T_{\text{oven}} = 440$ °C (not shown) a new feature becomes visible. The quantity and size of the holes increase dramatically to about 80% of the total volume. Fig. 4f is an example of this stage at $T_{\text{oven}} = 600$ °C. Around the holes a matrix is visible in which patches can be seen that must have been the original starch grains. Streamline features are visible as if the mass has been pushed aside.

3.3. Chemical analyses and mineral composition

Chemical analyses reveal an increase in the relative percentage of carbon and a decrease of hydrogen (Fig. 5). The major changes occur between $T_{\text{oven}} = 220$ and 270 °C. Carbon increases from c. 45% (daf) to c. 87% (daf); hydrogen decreases from c. 7% (daf) to c. 1.5% (daf). Oxygen (by difference) decreases from c. 40% (daf) to c. 6% (daf). Nitrogen shows a strong variation between c. 2% (daf) and c. 7% (daf). Sulphur (not shown) varies from 0.38% (daf) of the untreated pea to 0.27% (daf) at $T_{\text{oven}} = 700$ °C. To study the natural variation of C and N in ten peas both parameters were measured and the results are shown in Table 3. The

Table 1
Colour and morphology changes in *P. sativum* var. GE heated at $T_{\text{oven}}=250$ °C for the given time (min) with N_2 as carrier gas

Heating time (min)	Outside colour (testa)	Inside colour cotyledon	Cracks in testa (%)	Length cracks in testa (mm)	Testa crackled	Testa curled at cracks (%)	Cracks in cotyledon (%)	Colour tarry liquid in outlet tube
Untreated	lrd+op ^a	white	0	0	no	0	0	–
7,5	rd+op ^b	yellow	20	3	no	0	0	clear
15	drb+dbp ^c	brown–yellow	60	3–8	no	0	0	clear
22,5	black	brown	70	3–8	no	0	0	clear
30	black	brown	60	3–8	no	0	0	light yellow
37,5	black	brown	80	3–8	no	0	0	light yellow
45	black	dark brown	80	3–8	no	0	0	yellow
60	black	brown–black	80	3–8	no	0	0	yellow–brown
120	black	brown–black	80	3–8	no	0	0	yellow–brown

^alrd+op=light reddish brown+oker patches.

^brd+op=red–brown+oker patches.

^cdrb+dbp=dark red–brown+dark brown patches.

Table 2
Colour and morphology changes in *P. sativum* var. GE heated for 60 min at the given oven temperature (T_{oven}) with N_2 as carrier gas

T_{oven} ($^{\circ}\text{C}$)	Outside colour (testa)	Inside colour (cotyledon) colour	Cracks in testa (%)	Length of cracks in testa (mm)	Testa surface crackled	Testa curled at cracks (%)	Cracks in cotyledon (%)	Colour tarry liquid in outlet tube
Untreated	lrb+op ^a	white	0	–	no	0	0	–
130	lrb+op ^a	light yellow	0	–	no	0	0	clear
160	rb+lrbp ^b	brown–yellow	0	–	no	0	0	clear
190	drb+rpb ^c	light brown	0	–	no	0	0	clear
220	black	brown	40	3–8	no	0	0	light yellow
235	black	dark brown	40	3–8	no	0	0	yellow
250	black	brown–black	80	3–8	no	0	0	yellow–brown
270	black	black	80	3–8	no	0	10	yellow–brown
290	black	black	90	3–8	no	0	0	brown
310	black	black	100	3–8	strong	60	50	brown
340	black	black	100	3–8	medium	10	80	brown
370	black	black	100	3–8	weak	20	100	brown
400	black	black	100	3–8	no	80	100	brown
440	black	black	100	3–8	no	100	100	brown
500	black	black	100	8	no	100	100	brown
600	black	black	100	8	no	100	100	brown
700	black	black	100	8	no	100	100	brown

^alrb+op=light reddish brown+oker patches.

^brb+lrbp=red–brown+light red–brown patches.

^cdrb+rpb=dark red–brown+red–brown patches.

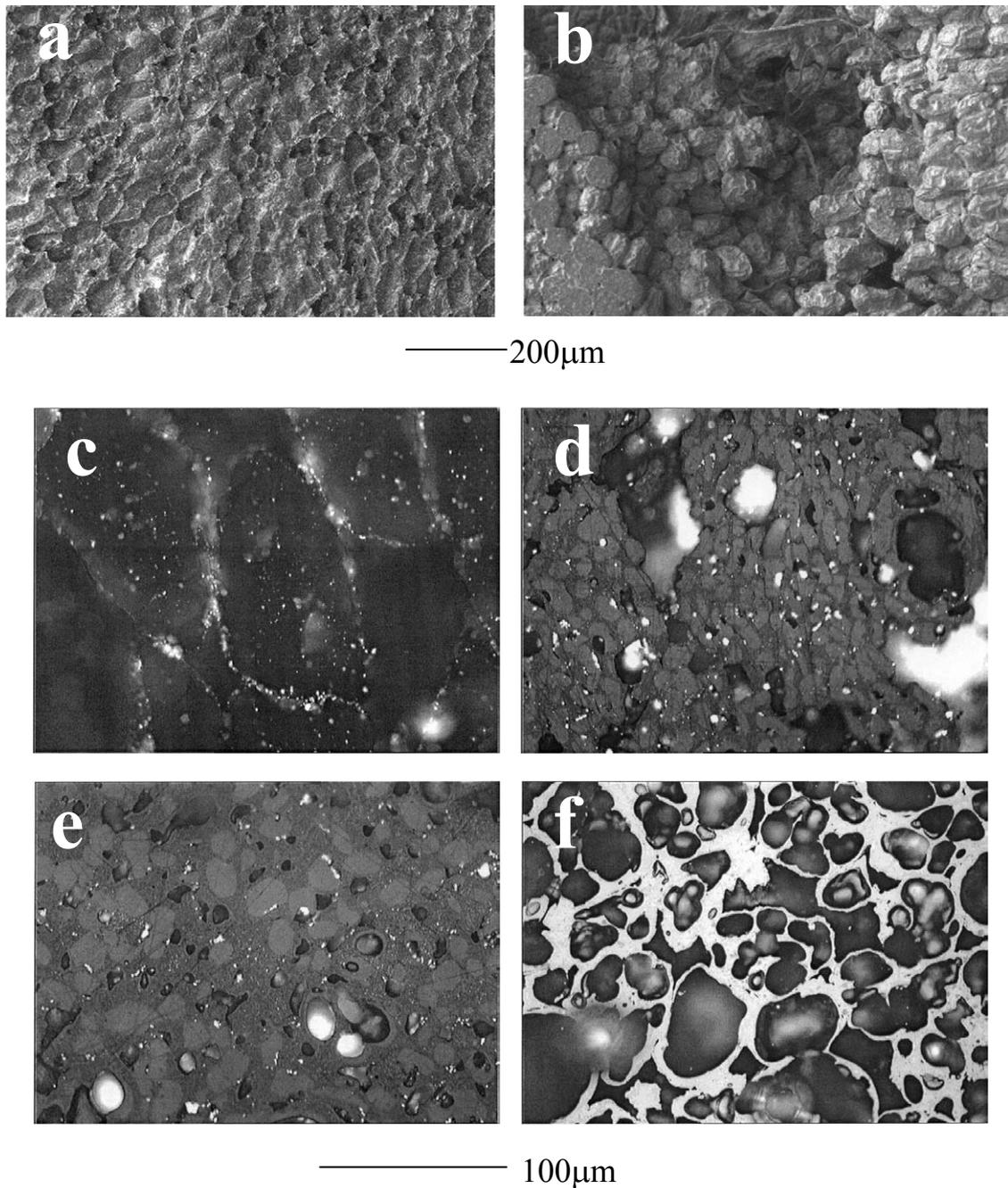


Fig. 4. The internal structure of heated peas (*P. sativum* var. Graauwe erw) with N_2 as carrier gas at various oven temperatures (T_{oven}). SEM photomicrographs: a. Untreated pea, b. $T_{oven}=190$ °C. Reflected-light photomicrographs: c. $T_{oven}=190$ °C, d. $T_{oven}=270$ °C, e. $T_{oven}=310$ °C and f. $T_{oven}=600$ °C.

value of C is sufficiently constant and will not influence the results of the chemical analyses in relation to the heat treatment. This is not the case for the values of N. Plotting the atomic ratio H/C against O/C in a van Krevelen diagram (Fig. 6) reveals a large decrease in the H/C and O/C ratios from the untreated pea to $T_{oven}=250$ °C [40]. The mineral content in peas is shown in Table 4.

3.4. Vitrinite reflectance measurements

The vitrinite reflectance measured on the “starch” grains of the heated peas is presented in Fig. 7. Only from $T_{oven}=270$ °C a true vitrinite reflectance could be measured. Two series of measurements were carried out. The reflectance of the lowest rank of vitrinites rises slowly from $T_{oven}=270$ °C to 400 °C. Thereafter it rises

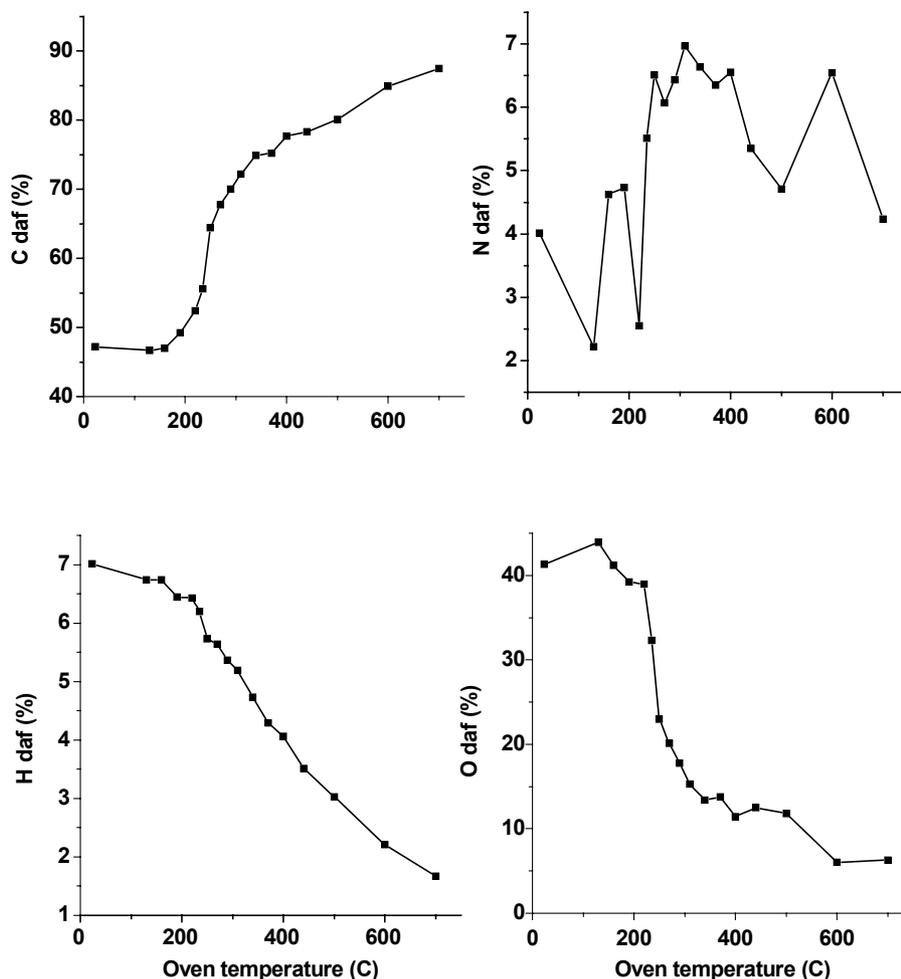


Fig. 5. Chemical analyses data of heated peas (*P. sativum* var. Graauwe erwt) with N_2 as carrier gas at various oven temperatures ($^{\circ}C$).

Table 3
Weight % of C and N in ten different seeds from five plants of *P. sativum* var. RE

	1	2	3	4	5	6	7	8	9	10
C(%)	40.15	41.27	41.09	41.10	40.60	41.20	40.90	40.99	40.48	40.38
N(%)	3.35	3.68	4.87	5.07	2.70	3.78	3.85	4.50	2.79	3.78

more rapidly to the last measured reflectance at $T_{\text{oven}}=700$ $^{\circ}C$. The S.D. of the measurements increases from 0.03 at $T_{\text{oven}}=270$ $^{\circ}C$ to 0.12 at $T_{\text{oven}}=600$ $^{\circ}C$ and reached at $T_{\text{oven}}=700$ $^{\circ}C$ a value of 0.23.

3.5. Archaeological peas (H414)

Chemical analyses and reflectance measurements were carried out on two different archaeological peas from the same sample. The results of the chemical analyses are: C=68.2% (daf), H=5.3% (daf) and N=6.5% (daf). The internal structure (not shown) does not show cell structures. A light matrix is observed with small

“fused” grains and c. 20% of the mass consists of holes. The reflectance measurements of the grains gave a value of 1.13 for $\%R_{\text{max}}$.

4. Discussion

This study determined the influence of heat treatment at different heating temperatures on the seeds of *P. sativum*. These seeds contain a mixture of polysaccharides, protein, fat and minor amounts of inorganic compounds naturally present. Starch represents the bulk of the material [15]. Each compound will carbonize or degrade at different rates and by different pathways, depending on the used apparatus and the set of experimental conditions. Heat treatment of organic material always results in 3 products: gas, liquid and a solid; the latter being the focus of this study. The measured physical properties of the pea (the solid) change with increasing heating temperatures. The changes that occur correspond to several phases that will be discussed below.

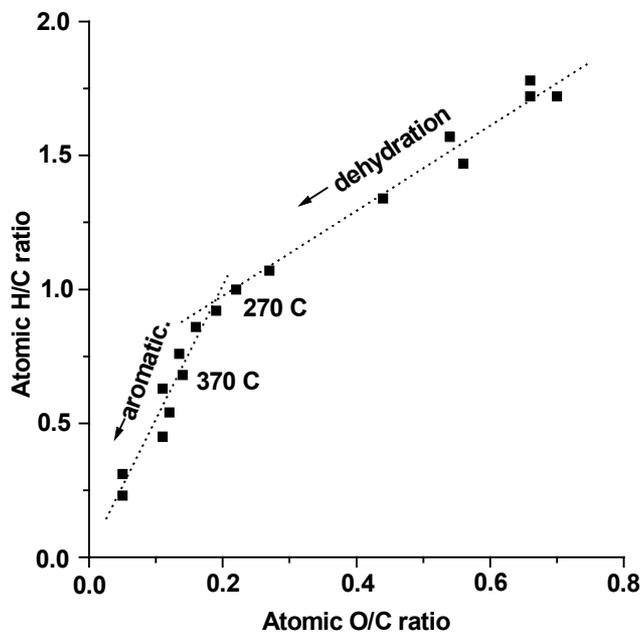


Fig. 6. van Krevelen diagram for heated peas (*P. sativum* var. Graauwe erwt) with N_2 as carrier gas.

Table 4

Mineral content in peas (*P. sativum*) var. GE

SiO ₂	<10 w%
Al ₂ O ₃	2.20 w%
TiO ₂	0.131 w%
Fe ₂ O ₃	<1 w%
MnO	<1 w%
CaO	0.05 w%
MgO	0.02 w%
Na ₂ O	0.35 w%
K ₂ O	2.99 w%
P ₂ O ₅	1.624 w%
Cu	<10 ppm
Pb	45 ppm
Zn	43 ppm
Sr	26 ppm
Ba	723 ppm
Rb	49 ppm
Zr	157 ppm

The decomposition of starch can be compared with that of cellulose, because the chemical composition and structure can be considered identical for the purpose of this study (cf. [39]). Heat treatment of cellulose is widely reported and numerous papers have dealt in detail with this issue. (For a review see e.g. [1].)

A reaction model for solid phase heat treatment is shown in Scheme 1 and is usually described as two parallel reactions preceded by an initiation step, also called the Broido–Shafizadeh model [10,12]. At lower temperatures and heating rates, the path for solids and gases is preferred, but at higher temperatures and heating rates the path of the tarry volatiles will be followed.

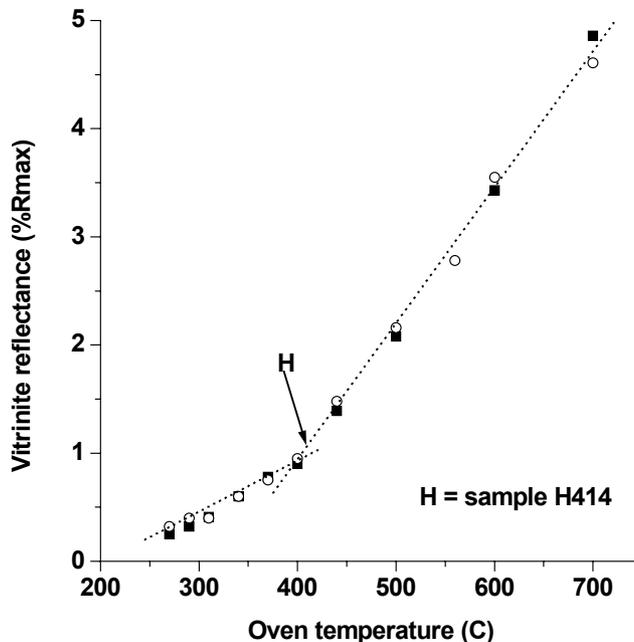
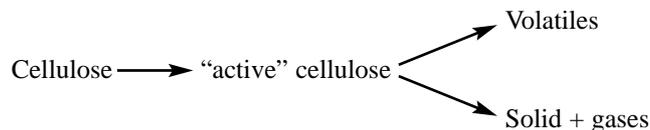


Fig. 7. Vitrinite reflectance measurements of heated peas (*P. sativum* var. Graauwe erwt) with N_2 as carrier gas vs. the oven temperature ($^{\circ}C$).



Scheme 1. The Broido–Shafizadeh model (1979) for the “carbonization” of cellulose.

The heat treatment of protein and the influence of starch and protein on each other through non-enzymatic browning (NEB) or Maillard reactions is a fairly unknown area of investigation as far as the solid residue is concerned [20,28]. In a separate paper dealing with the change of the molecular properties of heated peas this feature will be discussed further [9].

The results of the heat treatment of peas at $T_{\text{oven}} = 250$ $^{\circ}C$ is summarized in Fig. 8 and shows both the weight loss (%) as the internal and external temperature ($^{\circ}C$) as a function of the time. The weight loss has two phases with a first phase up to about 20 min and a weight loss of 22%. The thermal lag representing an endothermic reaction is almost completed in this phase. The colour of the inside of the pea has changed from white through yellow into brown and the colour of liquid condensate in the outlet tube is still clear (Table 1). The latter implies that only water has evaporated in this phase. As the amount of free water amounts to c. 11% the other part of the weight loss must be explained by other sources. The change of the colour into brown is most likely the result of NEB reactions,

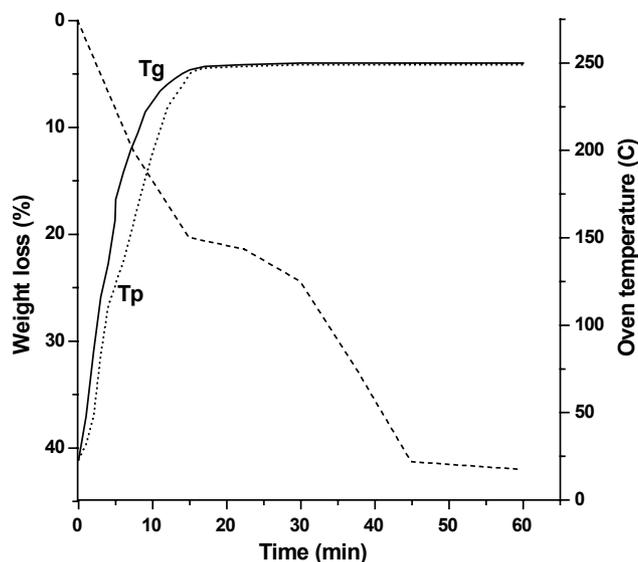


Fig. 8. Weight loss (%) of 10 peas heated at an oven temperature of 250 °C (*P. sativum* var. Graauwe erwt) with N₂ as carrier gas vs. time (min) as ---, the internal temperature T_p (°C) of one pea vs. time (min) and the external temperature T_g (°C) next to the pea vs. time (min).

which are accompanied by the release of water [24]. The samples consist of more than one component and each component does not decompose independently from the others, as is assumed in the case of ligno-cellulose material [34].

After 20 min the total weight loss remains almost constant for 10 min, thereupon increases again with 20% to reach its final value of 42% at 45 min, then remains constant. This last stage of weight loss is accompanied by a colouring of the condensate in the outlet tube from clear to yellow, indicating that in addition to water other compounds are volatilized. Fig. 6 shows that at $T_{\text{oven}}=250$ °C the main reaction is dehydration, so the bulk of the volatiles will be water. After 25 min the sample has reached the predefined oven temperature and hardly any heat is necessary to keep the sample at 250 °C. All the available heat can be used for the volatilization and no thermal lag is visible.

The heat treatment for 60 min at the different oven temperatures can be conveniently considered in phases as described below:

Phase 1. From the untreated pea until $T_{\text{oven}}=220$ °C the colour of the liquid in the outlet tube remains colourless, the inside colour of the pea changes into light brown and the weight loss is 22% (Table 1 and Fig. 3). This is similar to the first 20 min as shown in Table 2 and Fig. 8. Phase 1 is therefore characterized by NEB reactions and dehydration.

Phase 2. At $T_{\text{oven}}=220$ °C the colour of the condensate turns into yellow and both the rate of the weight

loss and the relative %C increases strongly until $T_{\text{oven}}=270$ °C. The relative %H and %O start to decline from $T_{\text{oven}}=220$ °C. According to the van Krevelen diagram (Fig. 6) dehydration is the main process accompanied by the loss of a minor amount of other volatiles. Until $T_{\text{oven}}=270$ °C only endothermic reactions are present, the distinct cell structure of the pea is still recognizable but the pea has become black.

Phase 3. From $T_{\text{oven}}=270$ °C the following changes occur: (i) the rate of weight loss and the rate of increase of %C are reducing (Figs. 3 and 5); (ii) both endothermic and exothermic reactions are occurring (Fig. 2) and (iii) the cell structure starts to disappear. The van Krevelen diagram (Fig. 6) shows dehydration and aromatization as the main processes. The exotherm is the result of secondary reactions between converting solids and hot vapours traversing the pea on their way to the external environment. It confirms the results of the experiments that the flow of the carrier gas did not affect the weight loss. This process will result in an increase of the amount of converted solids and thus in a decrease of the rate of weight loss and the destruction of the cell structure. The total weight loss curve of the peas starts to deviate at $T_{\text{oven}}=270$ °C from the one of microcrystalline cellulose with a higher production of converted solids (Fig. 3). In comparison with cellulose, a pea has a more confined structure and will keep the volatile matter inside for further condensation [8]. Another reason to be considered for a higher production of converted solids is the catalytic action of inorganic ions naturally present in peas [31]. For the presence of inorganic ions in the peas used in the present study see Table 4. The possible role of water vapours is unknown [1].

Phase 4. From $T_{\text{oven}}=310$ °C the distinct cell structure is no longer present, instead a grey matrix with light grey patches and the beginning of the formation of holes is observed (Fig. 4e). The “fused” patches are the primary conversion product of the original starch grains and the matrix is the result of secondary reactions. Other features are the cracking of the surface of the testa, the cracks in the cotyledons and a further decrease of the rate of weight loss.

Phase 5. A new phase starts in the range of $T_{\text{oven}}=400$ to 440 °C. The rate of heating of the pea, necessary to reach the preset oven temperature, has increased from c. 10 °C min⁻¹ at $T_{\text{oven}}=250$ °C through c. 100 °C min⁻¹ at $T_{\text{oven}}=500$ °C to c. 200 °C min⁻¹ at $T_{\text{oven}}=700$ °C. The reaction rate has become high resulting in a larger endothermic reaction (Fig. 2) and violent reactions are observed. The reactions took place so fast with large amounts of vapours driven off rapidly causing the matrix and grains to be pushed outwards (Fig. 4f). The heat demand has increased dramatically and heat transfer issues are evident enhancing the thermal lag. The total weight loss is high in a relatively short time. The endotherm is still followed by an exotherm, however

smaller than at $T_{\text{oven}}=340$ °C. This would point to the presence of secondary reactions, but on the other hand the vapours appear to be blown out of the pea (Fig. 4f) and the residence time of the vapours in the pea has become so short that gas-solid (secondary) reactions are hardly possible. Also the grey matrix of the previous phase is no longer present. As the total weight loss hardly increases anymore from $T_{\text{oven}}=440$ °C no secondary reactions occur and other chemical reactions must be the cause for the exotherm [42]. In this phase mainly volatilization reactions occur as well as primary reactions that convert starch into the new thermo stable product [8]. From $T_{\text{oven}}=400$ °C the maximum vitrinite reflectance ($\%R_{\text{max}}$) shows a rise that continues until $T_{\text{oven}}=700$ °C (Fig. 7). The rise has been attributed to a progressive ordering of the molecular systems that comprise the converted solids of the pea [18,25].

5. Implications for the peas from the archaeological record

The results of the chemical analyses and the reflectance measurements of the peas from the archaeological record (H414) are compared with the results of the heat treatment of recent peas in the laboratory. The %C (daf) of 68 corresponds to a heating temperature of c. 280 °C and the %H (daf) of 5.3 to c. 320 °C, while the $\%R_{\text{max}}$ shows that the pea from H414 is heated at c. 410 °C (Fig. 7). The results are encouraging considering that %C and %H are measured once on one ancient pea only and the $\%R_{\text{max}}$ on another ancient pea, moreover the morphology and the chemical composition of ancient peas is not fully known. Also, it is uncertain whether 7000 years being buried in the soil affects the physical and chemical properties of heated peas.

6. Conclusions

Upon heating under controlled anoxic conditions the physical and chemical composition of the seeds of *P. sativum* (peas) change as a function of time and temperature. In spite of the complexities related to the multi-phase, multi-component aspects, the heat treatment of recent peas in a range of temperatures from 130–700 °C, after 60 min of heating under a flow of N_2 gas and atmospheric pressure, can be considered in five phases based on the physical and chemical properties. This implies that changes of the various properties occur at the same characteristic temperatures of 220, 270, 310 and 440 °C. The C content increases with increasing temperatures and eventually a strongly C-enriched product is formed, which will affect the molecular composition. The weight loss reaches c. 70% at 400 °C and results in a decrease of the dimensions of the seeds. These features suggest that the general term, carbonization, only means that the residues have been exposed to

heat. The physical and chemical properties depend on the temperature, which is probably also true for the molecular composition and the dimensions. For studies regarding the effects of the formation processes on the residues the heating temperature has to be known. In particular the vitrinite reflectance measurements provide a fast and reliable tool for determining the temperature to which the specimens have been exposed to.

The seeds of peas are still recognizable even after heating at 700 °C for 1 h. At all temperatures the testa remains almost intact and sticks to the cotyledons.

The simulations in the laboratory provide a rigorous basis for studies regarding the effects of the formation processes subsequent to the so-called “carbonization” process on the residues and can be described in the five phases. However, additional insights are needed to evaluate the changes of the molecular and dimensional properties as a function of the temperature.

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