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Article

Quantitative studies on charcoalification: Physical and chemical changes of charring wood

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ABSTRACT

Charcoal is commonly preserved in both natural and artificial sediments, and is intensively used in paleontological, paleoenvironmental, and archaeological studies due to the abundant bio-information it contains. The biochemical properties of charcoal are also used for paleoclimatic reconstruction; however, the reliability of this approach has been challenged due to a lack of clarity on how physicochemical properties change during the charring process, as well as the temperatures required for charcoalification. To address this lack, in this study, Qinghai spruce and Chinese pine wood samples from the northeastern Tibetan Plateau were heated at different temperatures and for different lengths of time under restricted oxygen conditions. The reflectance; carbon, nitrogen, and oxygen content; and tracheid morphology were quantified before and after heating to assess changes related to the charring process. Archaeological charcoal remains were then evaluated to determine the charcoalification temperatures by comparing with the experimental results. The minimum temperature required for wood charcoalification was ~300 °C, while temperatures recorded by archaeological charcoal were concentrated at 400–500 °C. During the charring experiments, the tracheid cell walls gradually homogenized, and tracheid cell wall thickness and lumen area decreased by ~20%. On average, 50% mass losses were observed; the carbon and oxygen content (% wt.) approximately changed from 47% to 60% and 48% to 35% respectively, while the nitrogen content (% wt.) fluctuated around 0.2%. The reflectance increased slightly from 0% to 0.5%. We propose that the charcoalification of wood tissue refers to charring (in restricted air) and carbonization (in the almost absence of air) when the wood is exposed to a heat source, which then finally transforms into a black, inert solid. This quantitative study provided valuable data and a thorough assessment of the process of wood charcoalification, as well as accurately estimated the feasibility of using charcoal physicochemical properties in paleoclimatic research.

1. Introduction

Charcoal is a black, inert biological fossil formed during the incomplete combustion of wood, and is widely preserved in geological deposits and archaeological sites [1–3]. Charcoal contains not only anatomical and hence species information but also physical and chemical attributes representative of the environment at the time of its formation. The earliest charcoal findings can be traced back to 400 million years ago, after the establishment of plant life on land in the Silurian [4–5]. From this point onwards, charcoal is found in the strata on every continent [1,6-7]. Since charcoal (and associated anatomical information) can be completely preserved in sediments and rocks, it represents a direct record of early terrestrial plant evolution [4,8]. Charcoal can also record wildfires, which are suggestive of fluctuations in the atmospheric oxygen content, as well as paleoclimatic changes during the geological periods [5,9-11]. Owing to their often continuous sedimentary records and accurate dating, microcharcoals have been widely used to quantitatively characterize the paleoenvironment from about 25 Ma onwards [2,12-14]. Moreover, charcoal provides crucial clues to human and civilization evolution [3,15-16]. For example, archaeological charcoal remains from the Middle Pleistocene of *Homo erectus* (such as at Zhoukoudian) reveal vast amounts of charcoal that have pushed the history of fire use back to ~0.5 million years ago in China [17–18]. In samples dating from the Late Pleistocene, when charcoal became a common component of archaeological sites, charcoal sampling has frequently been used to identify species in studies of anthropological wood utilization strategies, vegetation history, and paleoclimatic events [19–23]. In summary, charcoal is now extensively used in paleontological, paleoenvironmental, and paleoanthropological studies [1-3, 4,7].

In addition to the abundant ecological information found in charcoal, biochemical attributes (such as carbon and nitrogen isotopes) can also be applied to reconstruct paleoclimatic changes. Tree-ring studies

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have revealed that carbon isotopes are fractionated by stomatal closing under drought conditions, while nitrogen isotopes are affected by both drought and soil fertility [24–26]. Combining abundant sediment charcoal samples with reliable radiocarbon dating can provide high-resolution climate records, compensating for the limited age of wood remains [27]. Several recent studies have used charcoal stable isotopes to reconstruct paleoenvironments and anthropogenic activities [28–29]. Unfortunately, the $\delta^{13}C$ and $\delta^{15}N$ biases caused by charcoalification (pyrolysis) remain disputed, preventing the broader application of isotopic analyses for charcoal remains [27,30]. Some studies have demonstrated no effects of the charcoalification process on $\delta^{13}C$ and $\delta^{15}N$, implying that isotopic measurements can be used for paleoenvironmental reconstruction [28-29, 31]. Nevertheless, other studies have suggested that high-temperature pyrolysis may significantly influence $\delta^{13}C$, and this shift in $\delta^{13}C$ values may challenge the reliability of paleoclimatic studies [27,30]. Due to this lack of clarity on how wood tissue physicochemical properties are affected by charring, as well as the temperatures required for charcoalification, it is difficult to accurately predict the usefulness of potential paleoenvironmental information in charcoal samples.

Based on wood morphology, reflectance, and spectral structure analyses, previous studies have investigated the formation of charcoal with a major focus on charring temperature. Braadbaart et al. [32] stated that archaeological charcoals were formed at temperatures that exceeded 350 °C for at least 15 min if subject to carbonization (in the absence of air) or alternatively charring (in restricted air). In Western Canada, charcoal reflectance values and FTIR (Fourier transform infrared spectroscopy) spectral characteristics suggest that most inertinite (a form of charcoal) is formed by wildfires at temperatures over 400 °C [33]. Other experiments have demonstrated that charcoalification occurs with pyrolysis and the formation of large polyaromatic sheets results in increasing reflectance; additionally, the temperature range of natural fires usually spans from 300 °C to 600 °C [32–34]. In exploring the charcoalification process, these studies have provided valuable information. However, few studies have analyzed multiple indicators, such as changes in reflectance, carbon and oxygen content, the microscopic morphology of cell tracheid, and mass losses, to quantitatively evaluate the charcoalification process; also, comparison with charcoal remains in the archeological site is lacking. Both approaches will be essential to precisely determine the temperatures needed for charcoalification.

Abundant charred remains of spruce (*Picea* A. Dietr.) and pine (*Pinus* Linn.) have been identified from prehistoric sites in the northeastern Tibetan Plateau (NETP) region. Two representative tree species for these genera, Qinghai spruce (*Picea crassifolia*) and Chinese pine (*Pinus tabulaeformis*) are widely distributed in the NETP. As such, this system provides a valuable opportunity to both quantitatively study physicochemical changes during experimental charring and then compare to archaeological charcoal remains [23]. In this study, a series of charcoalification simulation experiments were carried out by heating fresh spruce and pine samples at controlled temperatures for various time periods. Quantitative changes in the wood tissue morphology, color, microstructure, elemental content, and reflectance were investigated, as well as the relationships among these factors. In particular, the microstructural changes that occur during charring were quantitatively investigated for the first time by measuring the thickness of the tracheid cell wall and the lumen area. Additionally, archaeological charcoal remains were collected from the NETP, and key physicochemical factors were measured, with the goal of evaluating typical temperatures for anthropogenic combustion processes. Based on these experiments, this study sought to: (1) clarify the physical and chemical changes occurring during the charring and ashing processes; (2) identify the temperatures required for charcoalification; and (3) describe the formative processes for charcoal in sediments. Overall, this study improved our understanding of the wood charcoalification process and estimated the feasibility of utilizing charcoal physicochemical properties in paleoclimatic research.

2. Materials and methods

2.1. Fresh wood and archaeological charcoal sampling

Disks of fresh wood were collected from the trunks of dead trees on the Northeastern Tibetan Plateau for two tree species: Qinghai spruce (*Picea crassifolia*) and Chinese pine (*Pinus tabulaeformis*). Both species belong to the pine family (Pinaceae Lindl.) with similar physiological properties and anatomical structures [35]. Both also grow in the cold high-altitude zone and are widely distributed throughout the NETP. The wood tissue collected was dried to exclude complications from moisture disturbance. Charcoal fragments identified as spruce (*Picea A. Dietr.*) and pine (*Pinus Linn.*) were collected from three local archaeological sites [23]: Jianzui, Shuangerdongping, and Zongri. The distribution of collection sites for both fresh wood and archaeological charcoal samples is shown in Fig. S1.

2.2. Charcoalification experiments in the laboratory

Fresh wood samples covering two wide rings were excised from the tree trunk disks (Fig. 1a). The mass of a typical sample was about 30 mg. The samples were randomly divided into eleven groups. After weighing, each group of samples was heated in a muffle furnace under limited oxygen conditions at one of the following temperatures: 150 °C, 200 °C, 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C, or 650 °C. For each temperature group, measurements were taken after one, two, and four hours of heating. While heating, wood tissue samples were wrapped in aluminum foil and covered in sand within a crucible to simulate oxygen-poor conditions. The heating rate in the furnace was 10 °C/min. After heating, the samples were cooled to room temperature and then weighed.

2.3. Photography and scanning electron microscopy

Prior to heating, the numbered fresh wood samples were first scanned and photographed along the boundary lines of the earlywood and latewood rings through an electron microscope. After heating in the muffle furnace, the residual material was photographed along the same boundary line; the same tracheid cells (before and after heating) were then matched according to their shape (Fig. 1b). For both before and after photographs, the thickness of the tracheid cell wall (which contains the intercellular components) and the lumen area were measured (Fig. 1c1). For homogenized tracheid cells (introduced in Section 3.2), which share a wall with an adjacent tracheid, the cell wall was measured and divided by two (Fig. 1c2). Tracheid cells in the latewood were relatively small and inflexible, making them easier to track. Therefore, five latewood tracheid cells were measured for each sample; since tracheid cells have four cell walls, the average of the four wall measurements was taken for each measured cell. For those samples where the tracheid cells were severely distorted after heating and could not be matched, latewood cells were randomly selected for measurement. The color and shape of heated samples were also photographed using a digital camera. The measurement software used was Image J. The scanning electron microscopy (SEM) was carried out in the Electron Microscopy Center at Lanzhou University, with a Thermo Fisher-Apreo SEM incorporated with an Energy Dispersive X-ray Analysis (EDX) system.

2.4. Elemental analysis

The samples were sectioned and ground into a fine powder, homogenized, and then weighed in small silver vessels. The sample vessels were inserted into an elemental analyzer (VARIO EL iii) and heated to high temperatures, whereupon the evolved carbon dioxide and nitrogen oxides were absorbed by an analytical column for measurement. For quality control purposes, one standard sample was analyzed for every nine test samples. The content analysis of C and N elements was conducted by

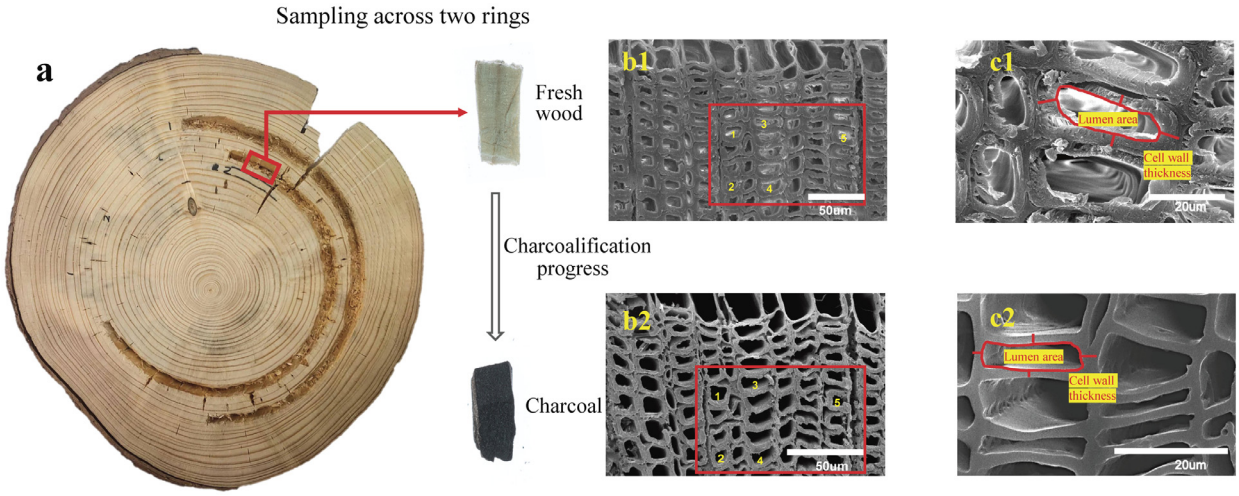

Fig. 1. Fresh wood samples were excised across two rings on the disk (a); the wood samples were photographed using a SEM before and after heating. Photographs of the same tracheid cells (matched by morphology) before and after heating (b1, b2). Five latewood tracheid cells were randomly selected and measured; representative photographs show example measurements of cell wall thickness and lumen area for fresh wood samples and those with homogenized walls, respectively (c1, c2).

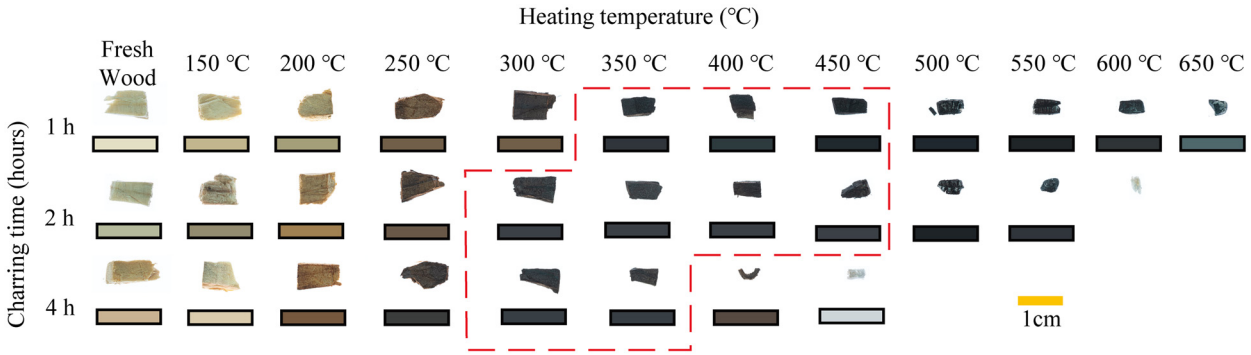

Fig. 2. Schematic of color and volume changes associated with temperature and heating time for Qinghai spruce. The section marked by a red box represents completely charred tissue (charcoal) with characteristic of black streaks. The left of the red box includes uncharred or slightly charred wood, while to the right shows samples that have been gradually ashed (from the surface to the whole sample).

the Elemental analyzer in the Testing Center of Lanzhou University. The oxygen content was measured by semi-quantitative analysis using EDX attached to the SEM. The compositional data were obtained at specific locations by selecting both points and areas of latewood on the samples via EDX. The analytical errors for the determination of the major elements were within 5%. The oxygen content was tested in the Electron Microscopy Center of Lanzhou University.

2.5. Reflectance analysis

Reflectance (%Ro) is defined as the percentage of vertically incident monochromatic light reflected from the highly polished surface of a sample, calibrated against the light reflected from a standard of known reflectance. Reflectance testing was performed in accordance with ISO 7404, Part 5 (1994) [36]. Samples were embedded in resin blocks and polished. Reflectance was measured in an oil immersion bath using a Nikon microscope. The instrument was calibrated against gadolinium gallium garnet (Ro = 1.72%) and sapphire (Ro = 0.59%). Thirty measurements were taken at random for each individual sample to calculate a mean random reflectance (Ro_{mean}) and standard deviation (SD). Reflectance testing was conducted at the Oil and Gas Research Center, Northwest Institute of Eco-Environment and Resources (Lanzhou), Chinese Academy of Science.

3. Results

3.1. Color changes and mass loss during the charring process

Fresh wood tissue was transformed to charcoal and eventually ash as the temperature and time increased under limited-oxygen conditions. The macroscopic criteria for identifying charcoal proposed by Scott [1] were used here, including black color and streaks; conchoidal fracturing; fragility; and bright silky luster. Both Qinghai spruce and Chinese pine samples showed identical color changes with heating. The lowest heat that produced charcoal was 300 °C when samples were heated for 4 h (Fig. 2). As charcoalification progressed, wood samples notably changed color from light yellow to brown and finally to black. The sample mass for both Qinghai spruce and Chinese pine gradually decreased until reaching 50% when charcoal was formed (Fig. 3). The rate of mass loss gradually increased over time and with temperature, reaching a maximum when close to charring. When charring conditions were attained, any residual material maintained the characteristic charcoal features, even if the temperature was increased; in this case, the sample mass continually decreased, but at a slower rate. As the temperature continued to increase, the charcoal surface began to burn and form white-colored ash. In the ashing stage, sample weight loss reached 80%, and the residual material continued to lose mass until almost 100% of the sample was eventually lost.

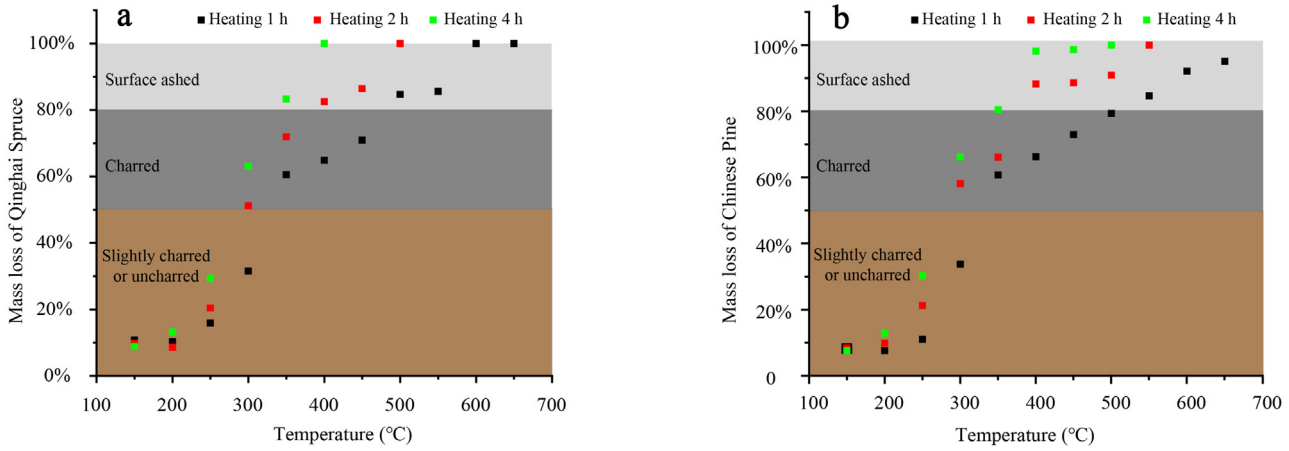

Fig. 3. Mass loss of Qinghai spruce (a) and Chinese pine (b) wood samples varied with heating temperature and heating time. According to the recognized standards for identifying charring, the graphs are divided into three parts: mass loss below 50% (slightly charred or uncharred wood), mass loss between 50%–80% (wood transformed into charcoal), and mass loss above 80% (charred wood surface became ashed).

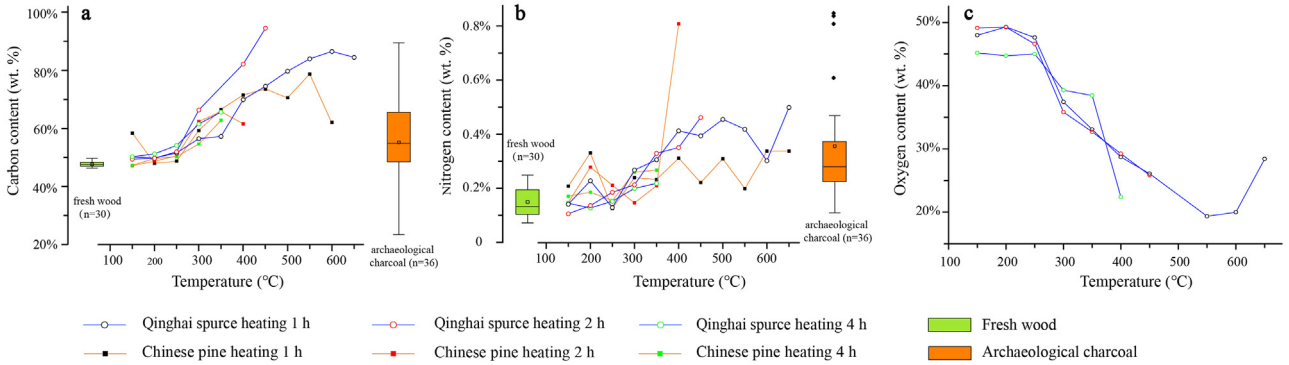

Fig. 4. Changes in carbon (a), nitrogen (b), and oxygen (c) content in heating experiment residues for Qinghai spruce and Chinese pine. The orange and green boxes in (a-b) represent archaeological charcoal and fresh wood samples, respectively.

3.2. Changes in carbon, nitrogen, and oxygen content

Carbon, oxygen, and nitrogen are the major elemental constituents of wood [37]. During charcoalification, these elements showed similar patterns for both Qinghai spruce and Chinese pine (Fig. 4). In the heating experiment, the temperature was positively correlated with the carbon content (Fig. 4a). The carbon content (% wt.) of fresh wood was 47.67% ± 0.85% (1σ, n = 30), whereas in charcoal, the carbon content could reach more than 60%. As the temperature rose, the carbon content also increased, even when ashing was underway. However, archaeological charcoals can exhibit a wide range of carbon contents ranging from 30% to 80%, values that differ from those measured in charcoalification experiments performed in the laboratory. In comparison, the nitrogen content (% wt.) of the wood samples changed less during charcoalification. The nitrogen content of both wood and charcoal samples was typically around 0.2% (Fig. 4b). As the temperature increased, there was a slight tendency for the nitrogen content to also increase; this increase ranged from 0.1% to 0.5%. The oxygen content (% wt.) decreased as temperature increased, completely opposite to the pattern for carbon (Fig. 4c). The oxygen content of the fresh wood samples was around 48%, gradually decreasing to about 35% as charcoal was formed. However, it should be noted that EDX measurements of oxygen content are only semi-quantitative.

3.3. Changes in wood microstructure

Besides clear macroscopic changes in the color and shape of the wood samples, microscopic changes in the cell structure also occurred. Qinghai spruce and Chinese pines have similar cross-sectional cell morphology, leading to nearly identical changes during charcoalification. Increases in temperature and heating duration resulted in tracheid cell homogenization, shrinkage, fracture, deformation, and ashing. Homogenization of the tracheid cells occurred with wood charcoalification, resulting in the “fusion” of adjacent cell walls and the disappearance of intercellular layers (Fig. 1c1 and c2). Homogenization occurred after heating for 2 h at 300 °C when the wood samples were charred or almost fully charred (Fig. 5b and S3). Rising temperatures after charcoalification further altered sample structure, distorting cell walls and forming many cracks (Fig. 5d). When the temperature reached 650 °C, the wood tissue was completely ashed, and the tracheid structure and morphological features almost disappeared; the whole area resembled a white snowflake (Fig. 5f). More details on the microscopic changes associated with higher temperatures and longer heating times are shown in Fig. S3.

The volume of charred wood decreased continuously both at the macro- and microscale as the temperature increased. In the heating experiment, microstructure shifts were quantified by tracing the same tracheid cells before and after heating, as well as measuring any changes in lumen area or cell wall thickness. For both the tracheid wall thickness and lumen area, the ratio of values before-to-after heating was negatively correlated with temperature (Fig. 6a). However, the correlation was weaker for lumen area versus tracheid wall thickness, and also nonlinear (Fig. 6b). Both measures were reduced by about 20% after charcoalification, and further reduced by 60% (cell wall thickness) and 40% (lumen area) when the sample surfaces ashed. Due to the severe damage to the wood structure at high temperatures (500–650 °C), most of the

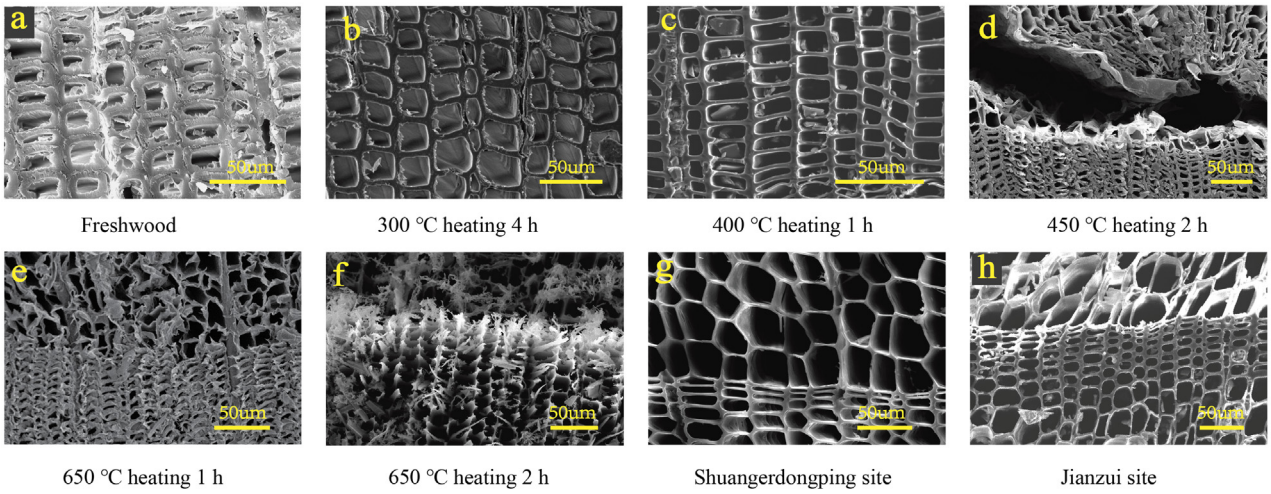

Fig. 5. Microstructure of cross-sectional photos of charcoal and fresh wood samples. Cross-sectional features were identical for Qinghai spruce and Chinese pine. Microscopic photos of fresh wood samples (a); microscopic structure of charred wood residues under different temperatures and heating times (b-f); microscopic structure of charcoal fragments unearthed from archaeological sites (g-h).

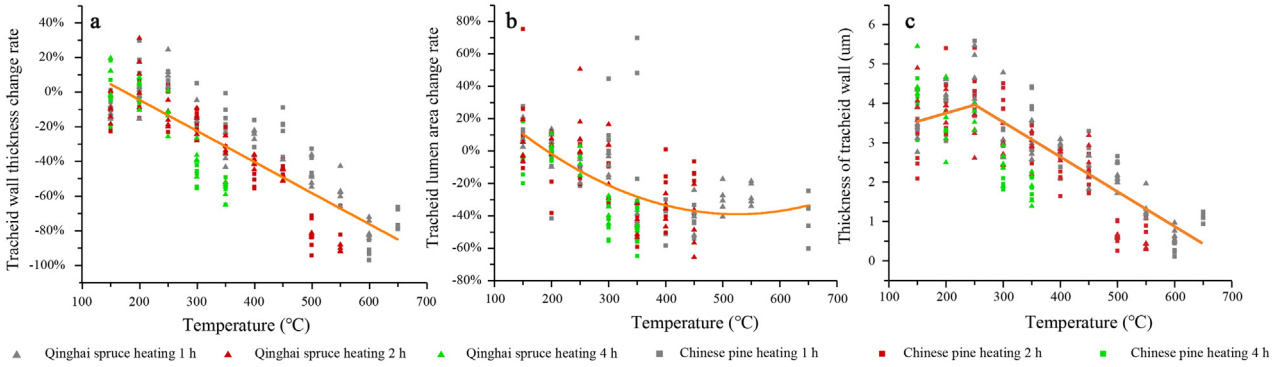

Fig. 6. Quantitative study of tracheid cell morphology in Qinghai spruce and Chinese pine. The vertical axis in (a, b) represents the rate of change in latewood tracheid cell walls and lumen area, respectively, before and after heating; the vertical axis in (c) shows the absolute change in tracheid wall thickness. Part of the data displayed in (a) is from unmatched tracheid cells in the following treatments: 500 °C, and 550 °C with 2 h of heating; 600 °C with 1 h heating. Unmatched cells were used because at high temperatures, few tracheid cells could be matched due to severe deformation.

photographed tracheid cells could not be matched after heating. Therefore, some tracheid cells were randomly selected for measurement post-heating. The thicknesses of these "surviving" tracheid walls conformed to the expected negative linear relationship (based on matched comparisons), but the pattern for the lumen area was inconsistent with the trend observed for the matched tracheid cells. Therefore, only thickness measurements for unmatched tracheid cells are displayed in Fig. 6a. Finally, the absolute width of the tracheid cell walls was also correlated with temperature (Fig. 6c).

3.4. Changes in charcoal reflectance during charcoalification

Reflectance values for charred Qinghai spruce samples were obtained for a series of temperatures between 150–650 °C. The results of this reflectance experiment (for both charred spruce samples and archaeological charcoals) are shown in the Supplementary Materials (Fig. S2 and Table S1). Reflectance values for both the experimental charcoals and the archaeological charcoals varied from 0.1% to 2.2%, with standard deviations less than 0.35. Below 250 °C, the wood sample reflectance was close to zero; however, the reflectance increased to 0.8% once samples were completely transformed into charcoal (Fig. 7). After reaching active charcoalification conditions, reflectance values continued to increase with the increasing temperature (Fig. 7).

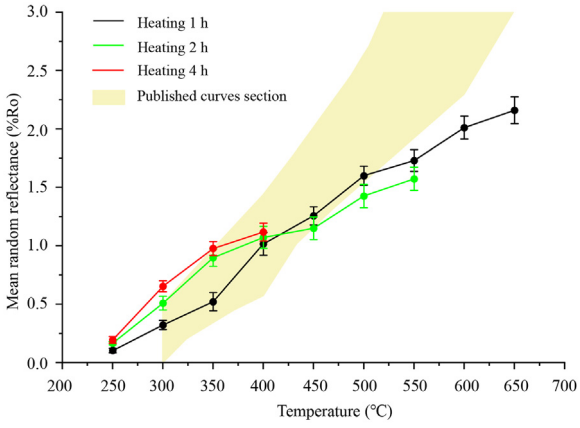

Fig. 7. The relationship between reflectance and heating temperature for charred Qinghai spruce wood samples, with separate curves based on heating duration. The yellow area represents the combination of four published calibration curves [32,34,40,48].

In addition, the reflectance was affected by heating duration. When the temperature was lower than 400 °C, extending the heating time promoted an increase in reflectance. However, when the temperature

exceeded 400 °C, temperature became the dominant factor controlling reflectance and heating duration had only a minimal effect. Furthermore, wood tissue reflectance was positively correlated with temperature, even when the wood surface was converted to ash. Archaeological charcoal samples collected from the NETP were randomly selected to measure reflectance. Reflectance ranged between 0.8% and 2.4%; looking at the data overlap for all three sites (87% of the total), reflectance ranged between 0.8% and 1.6% (Fig. S2 and Table S1). The standard deviations for most test results (83%) were less than 0.35; cases with higher standard deviations may have been caused by uneven heating of the test samples.

4. Discussion

4.1. Physicochemical properties in wood tissues during charcoalification

Under oxygen-deficient conditions, high temperatures resulted in charring and then ashing of wood samples. Several key factors were comprehensively analyzed to explore these two processes. The physicochemical properties changes were nearly identical for both Qinghai spruce and Chinese pine. Previous studies have classified the products of combustion continuum into the following categories: slightly charred biomass, char, charcoal, soot, and graphitic black carbon [38–39]. The heating experiment results mostly agreed with this classification, except that furnace charring did not produce graphitic black carbon and soot, but rather ash and ashed charcoal. Therefore, the transformation of wood via heating might be divided into three phases: slightly charring, charring, and ashing. Sample physicochemical changes during heating are displayed in Fig. 8. During the heating process, sample mass loss, reflectance, and carbon content increased steadily, but reflectance did not change much at low temperatures (< 250 °C). At the same time, the oxygen content, tracheid cell wall thickness, and lumen area generally decreased, although the cell wall thickness and lumen area both increased slightly at lower temperatures (< 250 °C). This indicated tracheid cells experienced an expansion and widening process at the beginning of heating, which was also confirmed by the change rate of tracheid cell thickness being greater than zero (Fig. 6a). The most noticeable aspects of charcoalification and ashing were changes in sample color and streaking, which allowed clear identification of heating phases. As the temperature increased, the sample microstructure also became homogenized, fractured, and distorted.

Based on the changes described above, the transformation from wood to charcoal likely requires heating at 300 °C for 4 h minimum; when temperatures were > 300 °C, charcoalification required less time. The proposed minimum temperature for charcoal formation (300–350 °C) is consistent with studies of other species, such as *Pinus sylvestris* [32,34], *Rhizophora apiculata* [34], and *Quercus robur* [32,40]. In these studies, similar changes were observed during charcoalification, such as color darkening, ~50% mass losses [32], reflectance increases (up to 0.5%) [32,34,40], and carbon contents (wt.%) exceeding 60% [32,34]. As seen here, there was little variation among species, likely because pine and spruce had similar chemistries; however, species differing in wood density may be predicted to show variable charcoalification processes [32,37]. In addition, limiting oxygen affected charcoal properties when temperatures exceed the charring temperature, and further resulted in ashing at > 500 % in this experiment [32,34,40]. In summary, differences in charcoal properties among studies were driven by species identity and oxygen availability (during heating); however, these effects only influenced the degree of charring, and not the overall trends.

4.2. Pyrolytic explanation of wood charring

Wood charcoalification produced complex changes in sample chemical composition; demonstrating these changes has provided insight into the thermal degradation of wood during charcoalification. The main components of wood include cellulose, hemicellulose, and lignin. As a key structural component, cellulose accounts for more than 50% of wood mass and contributes most to wood thermal degradation [37]. During the charcoalification process, fresh wood first gives off water vapor, desiccating until temperatures reach slightly above 100 °C. Hemicellulose is unstable and begins to depolymerize at 130 °C, releasing small amounts of volatile components such as carbon monoxide, carbon dioxide, acetic acid, and methanol. Cellulose begins to decompose at 250 °C, and this decomposition dominates charcoalification at higher temperatures. At temperatures above 300 °C, charcoal is produced and tar is driven off such that the fixed carbon content of the charcoal increases. When the temperature increases above 400 °C, the cellulose loses about 91% of its initial mass, converting into a large volume of volatiles and charred solids [41–42].

In summary, the charcoalification of wood tissues represents a process of thermal degradation. Polysaccharides and lignin gradually dissipate during the process and are replaced by aromatic compounds which release volatile gases [33–34]. The limited oxygen available during charcoalification accelerates the mass loss of any residual matter. Changes in sample chemical composition during charcoalification also explain observed changes in color, mass loss, elemental content, and reflectance. The degradation of wood tissue, along with the release of volatile components, leads to mass loss. During the process of thermal degradation, the formation of organized polycondensation aromatic hydrocarbons results in an increase in reflectance [32,34]. Furthermore, the formation of aromatic hydrocarbons is also accompanied by deoxygenation and dehydrogenation, resulting in overall carbon enrichment [34]. Color changes in heated pine and spruce wood samples are due to the production of colored extracts during thermal degradation [43]. The homogenization of cell walls associated with tissue microstructure was caused by cellulose melting in the initial stages of pyrolysis.

4.3. Reinterpretation of the natural charcoal formation process

The formation of charcoal in nature requires a complex burning process. Many factors may impact the charcoalification process, such as temperature, the duration of heating, oxygen availability, the rate of heating/cooling, the shape/size of the wood specimen, the woody plant species, and the moisture content. It is hard to completely replicate this process via laboratory simulation experiments; however, credible equivalent conditions for wood charring may be recreated. Therefore, it is critical to eliminate any minor factors in the experimental design. Clearly, temperature is a key factor in wood charcoalification, and the duration of heating also affects the results, especially for temperatures < 400 °C. Here, the experimental design controlled temperature and time in a carefully designed heating regime, while fixing extraneous factors (*i.e.*, oxygen availability, the rate of heating/cooling, the shape/size of the specimen, and the wood moisture content). Based on the results of these charcoalification experiments, a new model to explain natural charcoal formation is presented in this study.

The charcoalification process essentially represents a thermal degradation process, consisting of a series of chemical reactions which feature both endothermic and/or exothermic side reactions; these side reactions are in turn controlled by a complex of environmental factors. Charcoalification can be broadly described in terms of the extent of carbonization and charring, according to the oxygen availability and whether a flame is produced [32]. Carbonization may take place with no flaming when oxygen is almost absent; this is seen in some specific natural processes, including the formation of charcoal by molten rock in volcanoes [44–45] and as a result of underground forest fires [1,6], and in the anthropogenic-production of charcoal, such as that recovered from archaeological kilns [40]. These carbonization processes (which occur in the near absence of oxygen) show similar trajectories to those observed in the experiments undertaken here. When heating at temperatures above 300 °C, thermal decomposition of wood tissues occurs and pyrolytic volatiles are released; charcoal is then generated after prolonged heating. Charcoal is more commonly produced by char-

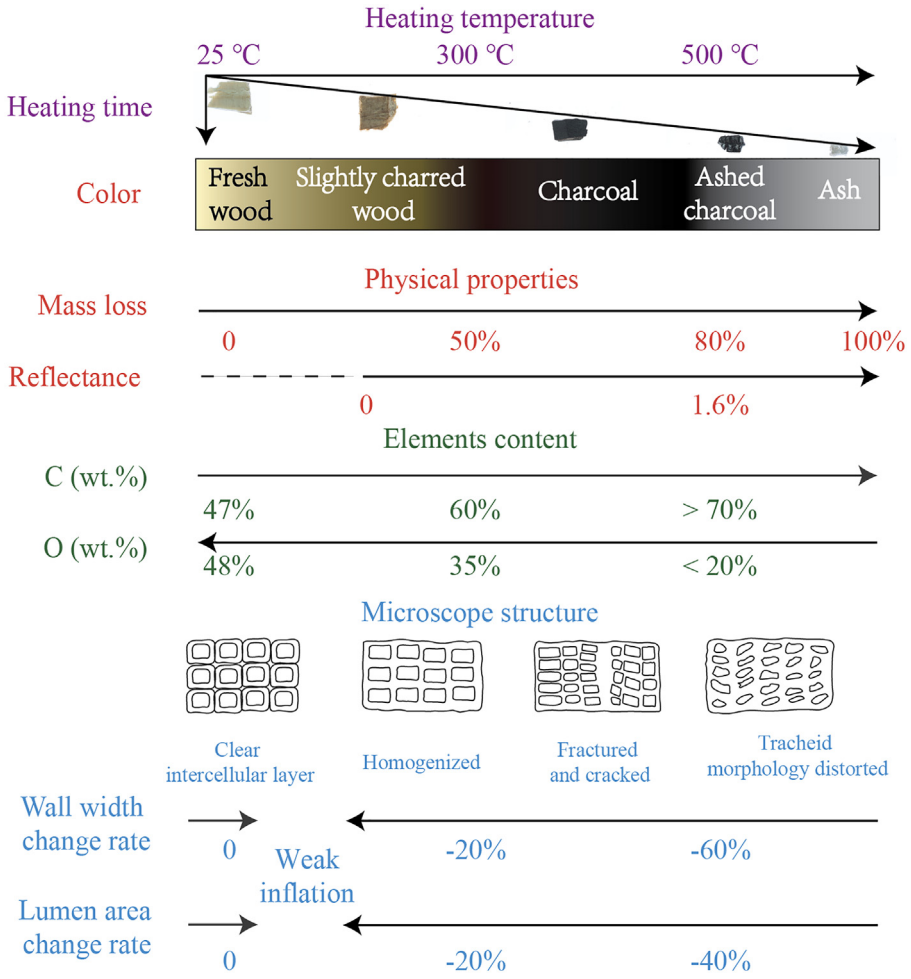

Fig. 8. Alterations in various wood physical and chemical factors over the course of the heating experiment, as well as the relationships among the various factors.

ring wood tissue under limited oxygen conditions. Typically, charring progresses in tandem with combustion [1,6]. Incomplete combustion, or combustion interrupted by temperature or air reductions, leads to the production of large amounts of charcoal, as seen in nature. Three key elements are required to sustain combustion: fuel, an ignition source, and oxygen. Ignition requires a heat source like lightning, a volcanic eruption, spontaneous combustion, or human activity. The atmospheric oxygen content affects the lowest possible burning temperature and the combustion frequency [7]. Wood combustion is a complex oxidation reaction and consists of four steps: water evaporation (drying), pyrolysis of the wood tissue, combustion and gasification, and gas-phase reactions [44]. A schematic for charcoal formation during wood combustion is given in Fig. 9. Under normal oxygen conditions (*i.e.*, an atmospheric oxygen content of 21%), when the surrounding temperature is higher than 225 °C, the surface of the wood tissue breaks down rapidly and releases both volatile and combustible components. These released gases will flame with oxygen when heating exceeds 300 °C, resulting in ignition [46–47]. At the moment of ignition, the emitted heat penetrates the wood tissue. This results in immediate pyrolysis of the surface molecules, which then release volatiles. The pyrolysis zone quickly expands as heat transfers throughout the specimen. Surface combustion begins when the flammable volatiles mix with the air and achieve a critical proportion. At the same time, the surface of the wood becomes ashed and the charring zone below expands; these processes continue as temperatures exceed 350 °C, the point at which cracking also occurs. These cracks create a channel for inner pyrolysis products (see Fig. S3), leading to the escape of pyrolysis volatiles. Upon encountering oxygen molecules, these volatiles contribute to additional exothermic combustion (with flaming), and the cycle of internal charring and surface ashing continues. When the volatiles have burnt off, any residual solids smolder until extinguished. If the reaction is stopped because of sudden cooling and/or a shortage of oxygen [7], then charcoal remains; otherwise, the wood tissue is completely combusted and turns to ash. The charcoal produced may be transported, buried in sediments, and preserved as charcoal fossils or remains.

4.4. Reconstruction of temperatures for charcoal production and validation of archaeological charcoal

This and other studies have illustrated the strong positive correlation between reflectance and temperature; as such, reflectance may serve as an index for temperature, allowing the reconstruction of temperatures in ancient fires [32,34,40,48]. In addition, the homogenization of the tracheid wall may be used to identify charcoals, as well as cases where fire temperatures exceeded 325 °C (the lowest temperature needed for homogenization in previous studies) [1,6]. Here, homogenization of the tracheid cell wall occurred when wood tissues were exposed to temperatures of 300 °C for 2 h, at which point the wood was nearly or already transformed into charcoal (Fig. S4). Therefore, homogenization can aid in the identification of charcoal and reveal fire temperatures above 300 °C.

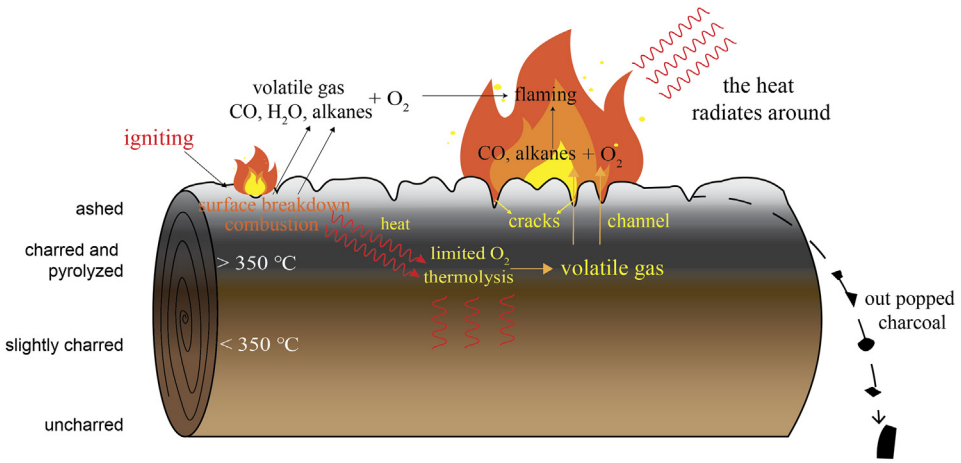

Fig. 9. Schematic diagram of charcoal formation during natural wood combustion.

Reflectance calibration curves have been described for different experimental conditions and tree species [48]. In this work, a new calibration curve was delineated for Qinghai spruce. Compared to previously described curves, the slope for this curve was less steep, as illustrated in Fig. 7. This may be a result of both the simulated oxygen conditions and the species used. As outlined in Fig. 7, the four previously published curves were derived from a model carbonization experiment conducted in the absence of oxygen [32,34,40,48]. However, this study simulated the charring process in a limited oxygen environment, which is more realistic and akin to natural combustion processes. In addition, this study used different charcoal forms for study, including experiential charcoal produced by heating fresh Qinghai spruce at different temperatures and charred spruce samples from archaeological sites (for comparison). In the experiments, we found that the absolute thickness of the tracheid wall of latewood had the potential to indicate the temperature during the charcoal formation, as shown in Fig. 6c. Therefore, both reflectance and cell wall thickness were used to determine the formation temperature for charcoal; these results are displayed in a two-dimensional contour plot (Fig. 10). Assuming the formation of archaeological charcoal is related to historical fire usage, normal ("daily life") circumstances would typically not allow for prolonged periods of wood burning. The contour plot was therefore based on the use of reflectance data and latewood cell wall widths for samples heated under restricted oxygen conditions for 1 h.

The reflectance and thickness of spruce latewood cell walls collected from three archaeological sites (Jianzui, Shuangerdongping, and Zongri) were mapped on the contour plot. The temperature ranges for charcoal formation were inferred to be: 350–500 °C for the Zongri site; 400–550 °C for the Shuangerdongping site; and 350–700 °C for the Jianzui site (Fig. 10). Thus, charcoal production temperatures varied among sites, and even within each site. Collectively, archaeological charcoal formation temperatures ranged between 350 °C and 700 °C. Importantly, all three sites appear to have produced charcoal under overlapping temperatures of 400–500 °C, which represent the typical temperatures for natural fires [40]. This temperature range is also representative of typical fires used by ancient humans. Such temperatures can meet basic needs for cooking, lighting, and heating [32].

The distribution of reflectance data for the archaeological charcoals was consistent with that for the experimental data; however, the predicted thickness of the latewood tracheal cell walls did not conform to the expected range (based on experimental data). This mismatch could be related to differences in material type (*e.g.*, samples collected from different tree parts) or alterations to charcoal properties during burial. The experimental wood disks were taken from tree trunks, but the archaeological charcoal samples were likely produced by the burning of branches. In addition, the archaeological charcoal would also be affected by compaction and burial, which may result in tracheid deformation [3]. These factors could result in the observed deviations in reconstructed temperatures. Therefore, compared to the reflectance data, cell wall thickness less accurately records the temperatures associated with archaeological charcoal formation, and at best may serve only as an auxiliary indicator.

4.5. Assessing charcoal fossil characteristics from a multidisciplinary perspective

Although the accuracy of environmental information obtained from charcoal fossils has been of concern for several disciplines, this situation may shift with a better understanding of charcoalification and depositional processes. Sedimentological studies have shown that charcoal can be readily fragmented and transported by both wind and water; burial may slightly impact charcoal properties, but these changes can be reverted with chemical treatment [1,3,6]. Therefore, the climatic signals recorded in charred wood may be applied for paleoclimatic reconstruction if charring effect can also be quantified. Dendroclimatology studies have used wood $\delta^{13}C$ values as a reliable record for reconstruction of past climatic and environmental conditions [24–25]. The present work provides reasonable temperature ranges for both experimental charcoal and archaeological charcoal. Within this temperature range, the $\delta^{13}C$ bias can be used to determine if isotopic trends related to the paleoenvironment have been preserved. Building on previous studies, this work also delivered the following key data on the charcoalification process. As the temperature increased, wood samples transformed into black-colored charcoal, and tracheid cell walls homogenized at temperatures of at least 300 °C. Compared to fresh wood samples, heated samples showed reductions in cell wall thickness and lumen area of about 20%, as well as a 50% mass loss. The carbon content increased from 47% to 60%, while the oxygen content decreased from 48% to 35%; the nitrogen content fluctuated around 0.2%. The reflectance values increased roughly from zero to 0.5%. Finally, the thermal degradation of cellulose, lignin, hemicellulose, and other polymers resulted in the reduction of oxygen groups, an increase in aromatic compounds, and a greater organization of the molecular structure.

These results shed light on the charcoalification process, as well as the characteristics of experimental charcoal. However, among disciplines, the relevant characteristics of charcoal in sediments may vary. Paleontology and geostratigraphy deal with plant evolutionary and environmental changes on geological time scales. Charcoal fossils record ancient paleofires, as well as information on terrestrial plant communities in various pre-Quaternary geological periods [1,2,6]. Charcoal fossils are mainly preserved in sedimentary strata and occasionally found in volcanic rock, which may be characterized by fragmentation but owned

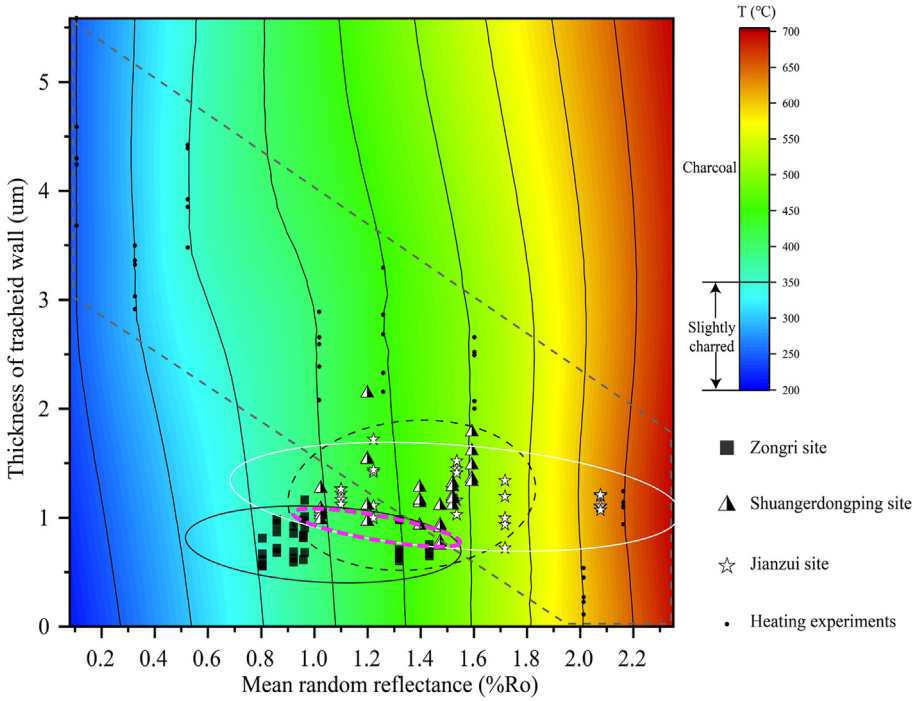

Fig. 10. Two-dimensional contour plot for latewood cell wall thickness and reflectance in Qinghai spruce. Red indicates high temperatures, while blue indicates low temperatures. The black dots represent experimental residues heated for one hour at rising temperatures; the rate of change boundaries are delineated with two black dotted lines. The ovals represent 90% confidence interval (CI). The black squares, checkered triangles, and white stars represent the three sample sites for archaeological charcoal. The magenta circle shows the area of overlap in charcoal formation temperatures for all three archaeological sites.

the microscopic structure. Coal mine geology defines charcoal (fusain) from the perspective of coalification. As a result of pyrolysis, combusted wood components are inert, with high carbon and low hydrogen content; inert fusains show high reflectance values (associated with wildfires), and cannot be gelificated or completely decayed during coalification [45,49]. Fusain can be distinguished from coal based on its physical properties, including the preserved micro-anatomical structure, silky luster, fragility, and lack of mineralization or coalification. Beginning 25 Ma, charcoal was increasingly preserved in often continuous natural sediments. Geographical research typically subdivides charcoal into two categories: macrocharcoal and microcharcoal. Macrocharcoal features a preserved, identifiable anatomical structure that records information on ancient vegetation and fire events. Microcharcoal aspects including morphology, size, and concentration provide regional fire information, as well as some data on plant community composition. Microcharcoal should be distinguished from black carbon, which is smaller and has no distinct morphological characteristics [12–13]. Archaeological charcoal refers to the charred wood residues left by ancient humans after the deliberate burning of wood; however, it is distinguished from carbonized seeds, which are difficult to preserve in rocks, but are common remains in archaeological sites [3].

By reviewing the various definitions of charcoal from the perspectives of the above disciplines, and combining it with the new knowledge from charcoalification experiments, the general characteristics of charcoal may be summarized as follows. Charcoal is produced by the fire-related thermal degradation of plant tissues, and results in black inert solids that are readily preserved in both strata and rocks; in macrocharcoals, anatomical structures can be preserved.

5. Conclusion

Charring is a common global phenomenon that occurs with fire events in natural environments. In this study, simulation experiments were carried out to quantitatively study this process using multiple approaches. Wood samples from Qinghai spruce and Chinese pine were charred at a range of temperatures (150–650 °C); charcoalification was found to occur at ~300 °C, as determined by the darkening color of the wood samples and tracheid cell wall homogenization. At temperatures >500 °C, the charcoal produced continues to ash, owing to limited oxygen availability. This study also recorded quantitative changes in sample physicochemical properties, including color darkening, increased reflectance, decreased tracheid cell wall thickness and lumen area, mass loss, oxygen dissipation, carbon enrichment, and nitrogen content fluctuation.

Based on these experimental results, charcoal formation was discussed in detail for both natural and anthropological settings. Charcoal is commonly produced by charring during combustion with flame (when air is restricted), but may occasionally be produced by carbonization (in the near absence of air with no flame) under particular conditions. Once produced, charcoal can be transported and often preserved in sediments or rocks as a black, fragile inert solid with defined anatomical structure. The temperatures associated with human-related fires were determined by measuring the reflectance and latewood tracheid cell wall thickness of archaeological charcoal remains. Data suggests that the charcoal formation temperatures were concentrated around 400–500 °C, within the range of normal household fires. These experimental results provide a reliable quantitative reference for the charcoalification process, as well as a key temperature reference for climate signal biases in stable isotopes (that occur during charcoalification). Further stable isotopic analyses of charcoals should be carried out in the future to facilitate their use in paleoenvironmental studies.

Declaration of competing interest

The authors declare that they have no conflicts of interest in this work.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fmre.2022.05.014.

References

[1] A.C. Scott, Charcoal recognition, taphonomy and uses in palaeoenvironmental analysis, Palaeogeogr. Palaeoclim. Palaeoecol. 291 (2010) 11–39.
[2] A.C. Scott, F. Damblon, Charcoal: Taphonomy and significance in geology, botany and archaeology, Palaeogeogr. Palaeoclim. Palaeoecol. 291 (2010) 1–10.
[3] I. Théry-Parisot, L. Chabal, J. Chrzavzez, Anthracology and taphonomy, from wood gathering to charcoal analysis. A review of the taphonomic processes modifying charcoal assemblages, in archaeological contexts, Palaeogeogr. Palaeoclim. Palaeoecol. 291 (2010) 142–153.
[4] I.J. Glasspool, D. Edwards, L. Axe, Charcoal in the Silurian as evidence of the earliest wildfire, Geology 32 (2004) 381–383.
[5] C.H. Wellman, P.L. Osterloff, U. Mohiuddin, Fragments of the earliest land plants, Nature 425 (2003) 282–285.
[6] A.C. Scott, The pre-quaternary history of fire, Palaeogeogr. Palaeoclim. Palaeoecol. 164 (2000) 281–329.
[7] T. He, B.B. Lamont, Baptism by fire: The pivotal role of ancient conflagrations in evolution of the earth's flora, Natl. Sci. Rev. 5 (2018) 237–254.
[8] C.M. Belcher, L. Mander, G. Rein, et al., Increased fire activity at the triassic/jurassic boundary in Greenland due to climate-driven floral change, Nat. Geosci. 3 (2010) 426–429.
[9] I.J. Glasspool, A.C. Scott, Phanerozoic atmospheric oxygen concentrations reconstructed from sedimentary charcoal, Nat. Geosci. 3 (2010) 627–630.
[10] C.M. Belcher, J.C. MCElwain, Limits for combustion in low O_2 redefine paleoatmospheric predictions for the Mesozoic, Science 321 (2008) 1197–1200.
[11] A. Jasper, M. Guerra-Sommer, A.M. Hamad, et al., The burning of Gondwana: Permian fires on the southern continent-a palaeobotanical approach, Gondwana. Res. 24 (2013) 148–160.
[12] W.A. Patterson, K.J. Edwards, D.J. Maguire, Microscopic charcoal as a fossil indicator of fire, Quat. Sci. Rev. 6 (1987) 3–23.
[13] W.J. Bond, Fires in the Cenozoic: A late flowering of flammable ecosystems, Front. Plant Sci. 5 (2015) 00749.
[14] Y. Miao, F. Wu, S. Warny, et al., Miocene fire intensification linked to continuous aridification on the Tibetan Plateau, Geology 47 (2019) 303–307.
[15] S. Wang, A brief history of wood analysis at archaeological sites (in Chinese), Cultural Relics in Southern China (2011) 156–162.
[16] X. Gao, Fire for hominin survivals in prehistory (in Chinese), Acta Anthropol. Sinica 39 (2020) 333–348.
[17] X. Gao, S. Zhang, Y Zhang, et al., New evidences of in-situ using fire by the peking Man at Zhoukoudian locality1: Research history, controversy and new development (in Chinese), Acta Anthropol. Sinica 35 (2016) 481–492.
[18] X. Wu, Y. Li, W. Liu, The study of paleolithic fire relics (in Chinese), Archaeology 6 (2010) 537–545.
[19] E. Asouti, K. Ceren, Holocene semi-arid oak woodlands in the Irano-anatolian region of southwest asia: Natural or anthropogenic? Quat. Sci. Rev. 90 (2014) 158–182.
[20] H. Shen, X. Wu, Z. Tang, et al., Wood usage and fire veneration in the Pamir, Xinjiang, 2500 cal. yr BP, PLoS ONE 10 (2015) e0134847.
[21] S. Wang, H. Yue, Z Yue, High resolution reconstruction of ecological environment in Yinshang period (in Chinese), Cultural Relics in Southern China (2016) 148–157.
[22] L. O'Donnell, Woodland dynamics and use during the bronze age: New evidence from Irish archaeological charcoal, Holocene 27 (2017) 1078–1091.
[23] F. Liu, M. Ma, G. Li, et al., Prehistoric firewood gathering on the northeast Tibetan plateau: Environmental and cultural determinism, Veget. Hist. Archaeobot. (2021).
[24] MC. Danny, J.L Neil, Stable isotopes in tree rings, Quat. Sci. Rev. 23 (2004) 771–801.
[25] A. Gessler, J.P. Ferrio, R. Hommel, et al., Stable isotopes in tree rings: Towards a mechanistic understanding of isotope fractionation and mixing processes from the leaves to the wood, Tree Physiol 34 (2014) 796–818.
[26] A.K. Styring, A.M. Diop, A. Bogaard, et al., Nitrogen isotope values of Pennisetum glaucum (pearl millet) grains: Towards a reconstruction of past cultivation conditions in the Sahel, West Africa, Veget. Hist. Archaeobot. 28 (2019) 663–678.
[27] B. Audiarda, T. Blascob, B. Brossier, $\delta^{13}C$ referential in three Pinus species for a first archaeological application to Paleolithic contexts: "Between intra- and inter-individual variation and carbonization effect, J. Archaeol. Sci. Rep. 20 (2018) 775–783.
[28] J.P. Ferrio, J.L. Araus, R. Buxo, et al., Water management practices and climate in ancient agriculture: Inference from the stable isotope composition of archaebotanical remains, Veget. Hist. Archaeobot. 14 (2005) 510–517.
[29] J.L. Araus, J.P. Ferrio, J. Voltas, et al., Agronomic conditions and crop evolution in ancient near East agriculture, Nat. Commun. 5 (2014) 3953.
[30] P.L. Ascough, M.I. Bird, P. Wormald, et al., Influence of production variables and starting material on charcoal stable isotopic and molecular characteristics, Geochimica et Cosmochimica Acta 72 (2008) 6090–6102.
[31] R.A. Fraser, A. Bogaard, M. Charles, et al., Assessing natural variation and the effects of charring, burial and pre-treatment on the stable carbon and nitrogen isotope values of archaeobotanical cereals and pulses, J. Archaeol. Sci. 40 (2013) 4754–4766.
[32] F. Braadbaart, I. Poole, Morphological, chemical and physical changes during charcoalification of wood and its relevance to archaeological contexts, J. Archaeol. Sci. 35 (2008) 2434–2445.
[33] Y. Guo, R.M. Bustin, FTIR spectroscopy and reflectance of modern charcoals and fungal decayed woods: Implications for studies of inertinite in coals, Int. J. Coal Geol. 37 (1998) 29–53.
[34] P.L. Ascough, M.I. Bird, A.C. Scott, et al., Charcoal reflectance measurements: Implications for structural characterization and assessment of diagenetic alteration, J. Archaeol. Sci. 37 (2010) 1590–1599.
[35] X. Jiang, Y Cheng, Y Yin, et al., Atlas of gymnosperms woods of China (in Chinese), first ed., Science Press, Beijing, 2010.
[36] ISO 7404 part 5, 1994. International standard. Methods for the petrographic analysis of bituminous coal and anthracite. Part 5: Method of determining microscopically the reflectance of vitrinite, no. ISO 7404-5: 1994 (E). https://www.iso.org/standard/42832.html
[37] Y. Xu, Wood science (in Chinese), second ed., China Forestry Publishing House, Beijing, 2019.
[38] C.A. Masiello, New directions in black carbon organic geochemistry, Marin. Chem. 92 (2004) 201–213.
[39] J.I. Hedges, G. Eglinton, P.G. Hatcher, et al., The molecularly-uncharacterized component of nonliving organic matter in natural environments, Org. Geochem. 31 (2000) 945–958.
[40] L.C. Mcparland, M.E. Collinson, A.C. Scott, et al., The use of reflectance values for the interpretation of natural and anthropogenic charcoal assemblages, Archaeol. Anthropol. Sci. 1 (2009) 249–261.
[41] S. Wang, Q. Liu, Z. Luo, et al., Mechanism study on cellulose pyrolysis using thermogravimetric analysis coupled with infrared spectroscopy, Front. Energy. 1 (2007) 413–419.
[42] Q. Liu, S. Wang, K. Wang, et al., Pyrolysis of wood species based on the compositional analysis, Korean J. Chem. Eng. 26 (2009) 548–553.
[43] M. Sehlstedt-Persson, Colour responses to heat-treatment of extractives and sap from pine and spruce, in: 8th International IUFRO Wood Drying Conference, 2003, pp. 459–464. http://urn.kb.se/resolve.
[44] A.C. Scott, I.J. Glasspool, Charcoal reflectance as a proxy for the emplacement temperature of pyroclastic flow deposits, Geology 33 (2005) 589–592.
[45] A.C. Scott, I.J. Glasspool, Observations and experiments on the origin and formation of inertinite group macerals, Int. J. Coal Geol. 70 (2007) 53–66.
[46] C.K. Chen, Combustion science (in Chinese), first ed., China Machine Press, Beijing, 2013.
[47] L. Yang, Z. Guo, J. Ji, et al., Experimental study on spontaneous ignition of wood exposed to variable heat flux, J. Fire Sci. 23 (2005) 405–416.
[48] R. Veal, L. O'Donnell, L. McParland, Reflectance-current state of research and future directions for archaeological charcoal; results from a pilot study on irish bronze age cremation charcoals, J. Archaeol. Sci. 75 (2016) 72–81.
[49] Z. Li, Coal geology (in Chinese), first ed., Geological Publishing House, Beijing, 2005.



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