Radiocarbon dating of charcoal from the Bianjiashan site in Hangzhao: new evidence for the lower age limit of the Liangzhu Culture

Xiaoyu Zhang[a,1], Dasong Huang[a], Han Deng[a], Colin Snape[b], Will Meredith[b], Ye Zhao[c], Yong Du[a], Xin Chen[a], Yongge Sun[a]

[a]Department of Earth Sciences, Zhejiang University, Hangzhou, 310027, China.
[b]Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK.
[c]Zhejiang Provincial institute of Cultural relics and Archaeology, Hangzhou, 310006, China.

Abstract

Located in the middle and lower reaches of the Yangtze River, the Liangzhu Culture was one of the most important Neolithic cultures at the dawn of Chinese civilization. However, uncertainty over the lower age limit ending the Liangzhu Culture has resulted in a lack of consensus in defining its timespan. In order to establish the lower age limit, a representative site of late Liangzhu Culture, the Bianjiashan wharf, located in Hangzhou City, Zhejiang Province, Eastern China, was selected for investigation. Wooden stakes in the wharf and charcoals in the sediment profile near to the wharf site were collected for ^{14}C AMS dating. To remove any contaminants, the charcoals were pre-treated by catalytic hydropyrolysis (HyPy) to isolate black carbon fractions (BC_{HyPy}).

The continuous charcoal age distribution along the vertical profile of the silt core suggests the continual occupation of the Bianjiashan Site and that the site was developed soon after the river formed. The end of river sedimentation indicates that the demise of the Bianjiashan Site occurred no later than Cal BC 2470 (95% probability). The mean age of the more recent calendar calibrated age range BC 2525 for the BC_{HyPy} residue

---

[1] Corresponding author. Tel.:+86-571-87951336;Fax:+86-571-87951336.

Email address: Zhang_xiaoyu@zju.edu.cn(Xiaoyu Zhang).

is consistent with earlier evidence. The wharf, as a typical structure of the late Liangzhu Culture, was established between Cal BC 2635 and 2890 (95% probability). The start of the river charcoal sedimentation was found to have a very similar overall age span and, therefore, the river existed at the Bianjiasha Site for no more than a maximum of just over 400 years, which is taken as the maximum period, it was occupied by the Liangzhu population. In comparison to the fresh charcoal samples, the BC_{HyPy} fractions and products were generally found to have similar probability age distributions. GC-MS analysis of the products (non-BC_{HyPy} fractions) released by HyPy indicated that the exogenous carbon from plants in the charcoal is present as both covalently bonded and adsorbed species, and was deposited at the same time as the charcoal, suggesting that the sediments have been preserved in a closed environment without disturbance as soon as the river ceased to exist. Thus, HyPy has confirms that there was no significant bias in the charcoal radiocarbon ages from more recent sedimentary organic matter.

Keywords: Late Liangzhu Culture; Bianjiashan Site; Black carbon; Hydropyrolysis; AMS dating

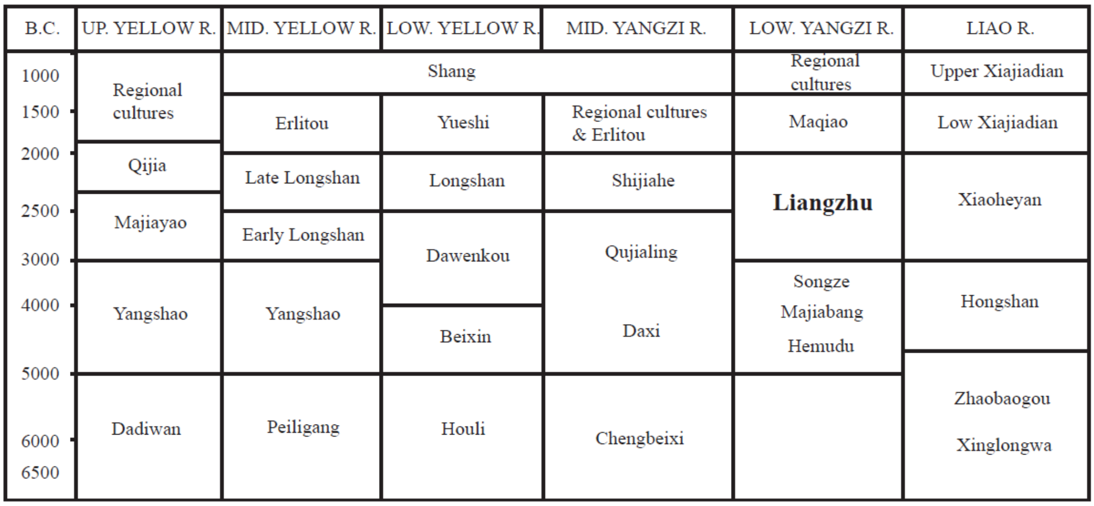
1. Introduction

Although it is believed domestically that China entered the ancient civilization era at about BC 3100, it is a controversial issue. The Liangzhu Culture, centered at Lake Tai along the middle and lower reaches of the Yangtze River, flourished at the dawn of Chinese civilization, and was one of the most notable late Neolithic cultures (Yang, 1991). Since it was discovered by Xingeng Shi in 1936, its significance has been widely debated as one of the earliest ancient Chinese civilizations. The Liangzhu Culture is named after the town near to the first discovered site in the Yuhang Division of Hangzhou City, Zhejiang Province, Eastern China. Dense villages, cemeteries and altars, together with a great deal of finely worked jade, engraved with symbols of birds, turtles and fish are the most characteristic aspects of the excavated articles (Shi, 1938).

The Liangzhu Culture lasted for over 1000 years (Table 1) and developed following the Dawenkou Culture but before the Longshan Culture (Du, 1992; Wu, 1989). These latter two cultures were distributed around the lower reaches of the Yellow River, and they constitute the core of the Southeast China cultural system. The Dawenkou Culture lasted for approximately 2000 years including early and late stages from BC 4300 to 2400, and the beginning of Liangzhu Culture coincided with the late stage of the Dawenkou Culture (Du, 1992; Wu, 1982). The Longshan Culture survived for only 600 years from BC 2600 to 2000, and began around the time of the late Liangzhu Culture (Wu, 1989).

As the core cultural system in southeastern China, the Liangzhu Culture also has a close relationship with the Maqiao Culture which has been confirmed to be the extended branch of the Liangzhu Culture at the south bank of Hangzhou Bay with a history of more than 700 years, but a gap of hundreds of years exists between the two cultures (Shao, 2006). Although the newly discovered Guangfulin Culture, which developed along the Song River in Shanghai links the Liangzhu and Maqiao Cultures, thus building a sequence of cultures (Table 1), there are still discontinuities in the age of the Cultures (Chen, 2007; Jiao, 2010; Zhou, 2007).

Table 1. Chronology of the major ancient Chinese cultures (Liu, 2003).



B.C.	UP. YELLOW R.	MID. YELLOW R.	LOW. YELLOW R.	MID. YANGZI R.	LOW. YANGZI R.	LIAO R.
1000	Regional cultures	Shang			Regional cultures	Upper Xiajiadian
1500		Erlitou	Yueshi	Regional cultures & Erlitou	Maqiao	Low Xiajiadian
2000	Qijia	Late Longshan	Longshan	Shijiahe	**Liangzhu**	Xiaoheyan
2500	Majiayao	Early Longshan	Dawenkou	Qujialing		
3000	Yangshao	Yangshao			Songze Majiabang Hemudu	Hongshan
4000			Beixin	Daxi		
5000	Dadiwan	Peiligang	Houli	Chengbeixi		Zhaobaogou Xinglongwa
6000						
6500						

The uncertainty over the actual lower age limit of Liangzhu Culture affects evaluation of the gap between the Liangzhu and Maqiao Cultures, further impeding the accurate reading of the upper limit of the latter. The accurate determination of the collapse of the Liangzhu Culture thus becomes a key point to resolve for improving our understanding of the origins of Chinese civilization.

There are currently 52 reported dating data sets, although 30 of these, derived from thermo-luminescence have large inaccuracies (Song, 1999). An age range spanning from BC 3835 to 2050 obtained by the remaining 22 radiocarbon derived dates has been widely accepted (Luan, 1992). From different interpretations accompanied with cultural comparisons, three periods have been identified as the lower age limit of the Liangzhu Culture ranging from BC 2050 to 2550. The youngest date, BC 2050, was proposed in the early 1990s and was supported by two pieces of wood and bone buried in a late Liangzhu tomb, which suggested that there was continuity between the Liangzhu and the following Maqiao Cultures (BC 1950, Chen, 1989). This viewpoint has now been discounted due to a lack of evidence from both dating data and cultural elements (Shuo, 2000; Song, 1999; Wang, 2004). A proposed lower age of BC 2250 was suggested by Xia (1977) and reiterated by Huang (1992). Both of these authors suggested that Liangzhu Culture is in the same period as the middle and late stages of the Dawenkou Culture. Therefore, the ^{14}C date of BC 2340 from the upper layer of the Lujiakou site, Shandong Province, marking the lowest age of Dawenkou Culture, can be a reference for the Liangzhu Culture lower age limit. Zhang (1995) and Ruan (1997) suggested that the lower limit of Liangzhu Culture should be BC 2550 and also indicated that the Liangzhu Culture again has the same age span with middle and late stage of the Dawenkou Culture. They also suggested that the recent discovery of a Guangfulin site as a separate culture entity between the Liangzhu and Maqiao Cultures in the Taihu Basin is contrary to the date of BC 2050. The date of BC 2550 is also supported by probability statistics from the 22 dating data sets which belong to different stages of the Liangzhu Culture, with the date of the most frequent occurrence assigned to the corresponding stages, although it lacks some credibility due to the over simplifications involved. Moreover, as the lower age limit is a timespan rather than a single date, It is beneficial to have a consistent series of ^{14}C data (Xia, 1977).

To try and obtain a precise age of late Liangzhu Culture, 37 samples were collected from the sediment in the ash pit of the Bianjiashan Site for ^{14}C dating. However, the samples were disproportional with respect to the different stages of the Bianjiashan Site with only one sample from the latest stage, while the samples are also believed to be disturbed. The study indicated a time span from BC 2900 to 2500 when the ash pit was used, suggesting that the lower age limit of Liangzhu Culture should be later than BC 2500 (Zhejiang Provincial institute of Cultural relics and Archaeology, 2014).

BC is a ubiquitous material which can be used for ^{14}C dating and is derived largely from the incomplete combustion of fossil fuels and biomass (Goldberg, 1985). It is understood to represent a broad continuum, from partially charred plant material that still retains its physical structure, to char, charcoal, soot and ultimately graphite, reflecting different precursors and formation processes (Watson et al., 2005). Global biomass burning generates an estimated 40-250 million tons of BC per year (Kuhlbusch and Crutzen, 1996), part of which is preserved for millennia in soils and sediments. In essence, BC is a carbon sink with long half-lives of 5-7 ky, dependent on environmental conditions (Preston and Schmidt, 2006). The chemical and thermal stability of BC is evident from its aromatic structure and physical protection, binding with minerals and other organic compounds (Forbes et al., 2006). However, in sedimentary environments, BC can absorb and potentially covalently bind with younger or older exogenous carbon which can cause inaccuracies in ^{14}C dating.

Catalytic hydropyrolysis (HyPy) is pyrolysis assisted by high hydrogen pressure (>10 MPa) with a dispersed sulphided molybdenum (Mo) catalyst to separate labile and refractory carbonaceous components has emerged as a new tool for isolating and quantifying BC (Ascough et al., 2009). The ability of HyPy to purify BC is of considerable significance both for age measurement and tracing studies. It has been used in analysis of terrestrial kerogens getting overall 100% conversions of thermally labile material (Roberts et al., 1995). Also, HyPy is capable of providing detailed molecular distributions of non-BC contaminations (Meredith et al., 2013). The ability of HyPy for isolation and quantification of BC was demonstrated by using 12 reference materials employed in the International BC Ring Trial (Hammes et al., 2007), with the carbonaceous fraction found to be stable under HyPy conditions termed BC_{HyPy} and is thought to be composed of peri-condensed aromatic clusters with >7 rings (Meredith et al., 2012). Thus far, the applicability of HyPy for ^{14}C measurement has been investigated for ancient charcoals with geological and archaeological significance (Ascough et al., 2009; Ascough et al., 2010; Bird et al., 2014).

Accelerator Mass Spectrometry (AMS) is a sensitive dating method directly measuring ^{14}C where even trace amounts of contaminants can affect the results. As many different types of compounds can be present as contaminants in charcoal, a number of pre-treatment regimes have been developed. Among these, the sequential acid-base-acid (ABA) extraction and the modified acid-base-oxidation-stepped combustion (ABOX-SC) are the most popular charcoal pre-treatments used. However, the ABA technique can hardly remove all of the contaminating carbon and the ABOX-SC method inevitably causes large losses of sample material. Furthermore, it is impractical to analyze the chemical composition of the removed contaminants for both these methods (Bird and Gröcke, 1997).

In this study, to establish the lower age limit of the Liangzhu Culture and to further demonstrate the efficacy of HyPy for pretreatment of charcoals, charcoal samples were recovered from a continuous river sedimentary profile at the Bianjiashan wharf. These have provided a series of radiocarbon dates to determine the demise of the Bianjiashan Site, and so provide evidence for the possible date of the end of the Liangzhu Culture. Any labile organic matter present and the non-BC_{HyPy} fraction of charcoal comprising relatively small aromatic structures that are released by HyPy were recovered and characterized by GC-MS to identify their potential source. In addition, dates of the original charcoals and the BC_{HyPy} fractions are compared to assess the extent of the degree of contamination. Two pieces of wooden stakes were also selected for ^{14}C dating to substantiate the reliability of dating data from charcoals. As these samples would contain no carbonaceous that would be stable under HyPy conditions, they were instead cleaned up with a standard “acid-alkali-acid” (AAA) procedure.

2. Materials and methods

2.1. Site description and sampling

The Bianjiashan site, located southeast of Pingyao town, Yuhang division, Hangzhou City is a typical late Liangzhu site. The main part of the site is an east-to-west elongated mound about 1 km in length, 30 to 50 m in width(Fig. 1a) and 1 to 2 m in height, surrounded by wetlands, farmlands and bamboo forest . The site was under a humid subtropical monsoon climate, with an annual precipitation of 1200-1500 mm and annual temperature of 16°C during the late Liangzhu Culture. The landform evolved from lacustrine facies to river alluvial facies from the early to late Liangzhu Culture (Yoshikazu et al., 2007). The wharf located at the south of the site comprised an orderly arrangement of wooden stakes, excavated during 2003-2006, is the most typical example reconstructing the context of ancient waterway transportation and water-based lifestyle of the Liangzhu population (Zhao, 2012).

The development of the Bianjiashan Site is clear in that the oldest tombs, from the first stage of development, appeared at the middle and north of the site in the early period of the middle Liangzhu Culture. Two large ash pits were excavated during the middle Liangzhu Culture, belonging to the second and third stages of the Bianjiashan Site, respectively. The wharf was finally established as the fourth stage, representing the late period of late Liangzhu Culture. Overlying the Bianjiashan Site is a 0-60 cm thick layer of pure bluish yellow silt (Fig. 1b), which is thought to be contemporaneous with the demise of Liangzhu Culture, although no dating work has been undertaken on it.

In this study, the fragments of charcoals, which were discovered distributing along the natural sedimentary profile in the ancient river around the wharf, were collected to provide a means of determining the age of demise of Bianjiashan Site, and hence evidence of the lower age limit of late Liangzhu Culture. The charcoals are granular and were found distributing continuously along the profile. They were only observed in water area around the wharf and dwelling site, and were believed to have direct relationship with charcoals found in the ash pit and yards of the dwelling site (Zhao, 2007; Zhejiang Provincial institute of Cultural relics and Archaeology, 2014).

The sedimentary profile is shown in Fig. 2. Large pieces of black charcoal, numbered #1 to #14 were obtained from the black clay layer, located at depths of 220 to 305 cm. Visible impurities were removed in the laboratory, with only the charcoal fragments retained and crushed into a fine powder. In addition two pieces of wooden stakes (#084 and #120) were selected and ground into powder for ^{14}C dating.

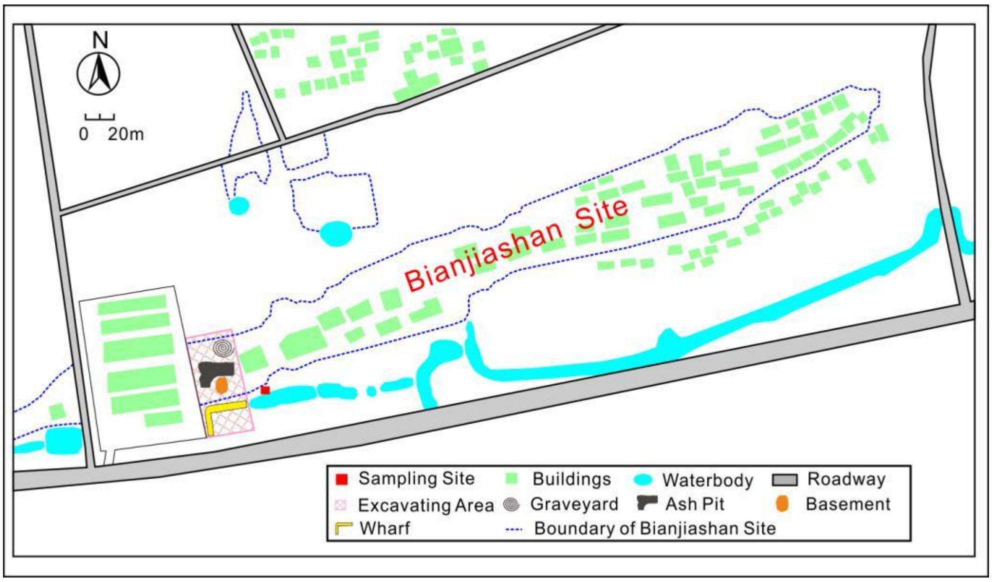


Fig. 1a. Distribution of the Bianjiashan site.

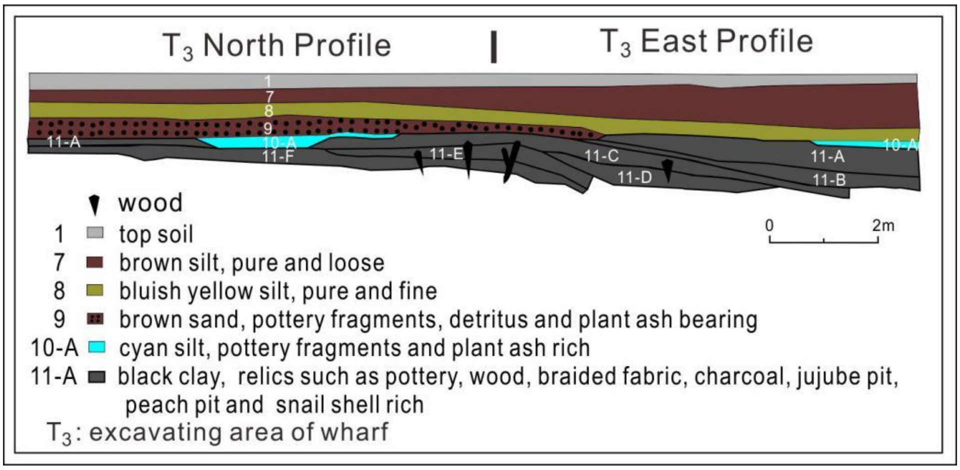


Fig. 1b. Sediment strata of the north and east profile of the wharf site.

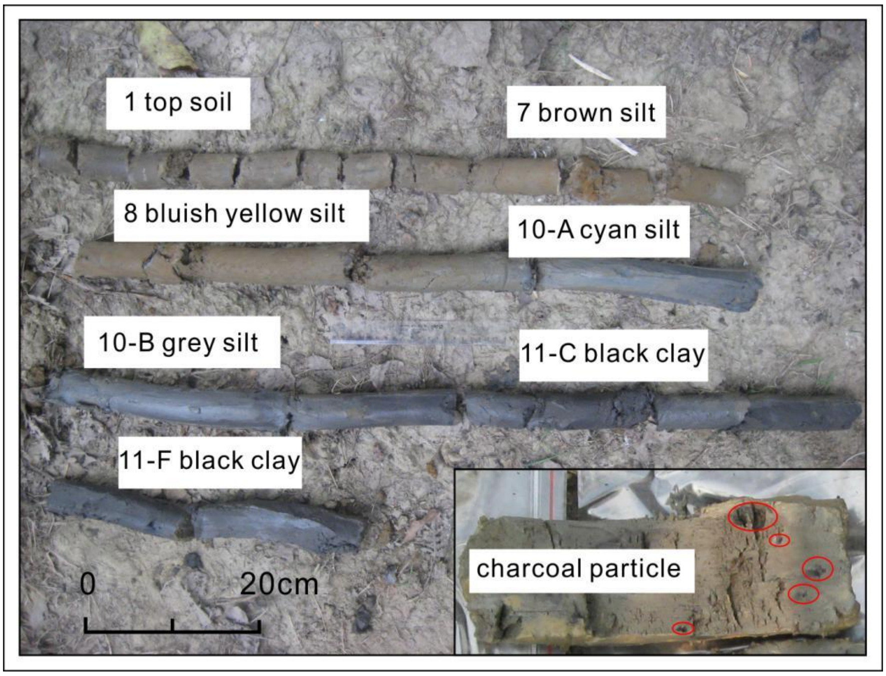


Fig. 2. Photograph showing the silt core from the sedimentary profile and the charcoal particles noted by red circles.

2.2. Elemental analysis, sample selection and BC quantification

The carbon contents and atomic H/C ratios of the 14 original charcoal samples were measured in duplicate using a Thermo Scientific 1112 Flash EA. Samples #1, #2, #5, #6, #10, #11, #13, #14 were selected due to their relatively high carbon contents for BC_{HyPy} determination. The BC_{HyPy} content of each charcoal was calculated by comparing the organic carbon (OC) present in the catalyst loaded samples prior to HyPy, with those of their HyPy residues as described by Meredith et al (2012).

The BC_{HyPy} fractions recovered from charcoal samples #1, #6, #10, #13 with high BC_{HyPy} contents were submitted for dating. The dates obtained from these fractions could then be compared to ^{14}C AMS dates of the fresh, acid washed charcoals to assess the efficacy of the HyPy technique for clean-up prior to radiocarbon dating.

2.3. Hydropyrolysis pre-treatment

The HyPy operating conditions for isolating the BC_{HyPy} fractions of the charcoal was based on previous work on carbonaceous material (Ascough et al., 2009; Meredith et al., 2012). In this study, 595°C was selected as the final hold temperature, as it is the maximum safe operating temperature of the HyPy system and to ensure maximum conversion of non-BC_{HyPy} components (Meredith et al., 2012). When used for BC isolation, a HyPy temperature of 550°C is known to discriminate against the portion of the BC continuum that is composed of aromatic structures with a relatively low degree of condensation (that is with an average cluster size of <7 aromatic rings) (Meredith et al., 2012). Together with a potential further loss of carbon due to the onset of hydrogasification to yield methane (Li et al., 1996), increasing the temperature to 595°C may increase the underestimation of BC in these samples. However as this study required the BC_{HyPy} fraction to be isolated primarily for dating rather than accurate quantification purposes, it was deemed essential to remove all traces of non-BC material to prevent erroneous dates (Bird et al., 2014), and so the highest possible temperature was used.

The silica to be used for trapping the non-BC_{HyPy} fraction was firstly extracted with *n*-hexane and then dichloromethane: methanol (v:v 93:7). The pre-extracted silica was then heated in a muffle furnace at 500°C for 5 hours to remove any solvent residues. To remove trace carbon contamination it was then baked at 1000°C for 15 minutes in a UIC Inc. Coulometrics instrument, with the CO_2 evolved measured to ensure that the silica was carbon free at the end of the procedure. The cleaned silica was transferred to pre-cleaned vials and stored in desiccator.

HyPy was performed using the procedures described in detail by Ascough et al (2009) and Meredith et al (2012), the apparatus being shown in Fig. 3. In brief, aliquots of each sample (100 mg) were firstly loaded with Mo catalyst (10 mg) using an aqueous solution of ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$], and placed with shortened borosilicate pipette ends (20 mm long) plugged at each end with pre-cleaned quartz and silver wool, with only the silver wool being in direct contact with the sample. The samples were pyrolysed with resistive heating from 50°C to 250°C at 300°C min^{-1}, then from 250°C to 595°C at 8°C min^{-1}, finally held for 2 mins under a hydrogen pressure of 150 bar. A hydrogen sweep gas flow is 5 L min^{-1} ensured that the products were quickly removed from the reactor for subsequent trapping on dry ice cooled silica (Meredith et al., 2004).

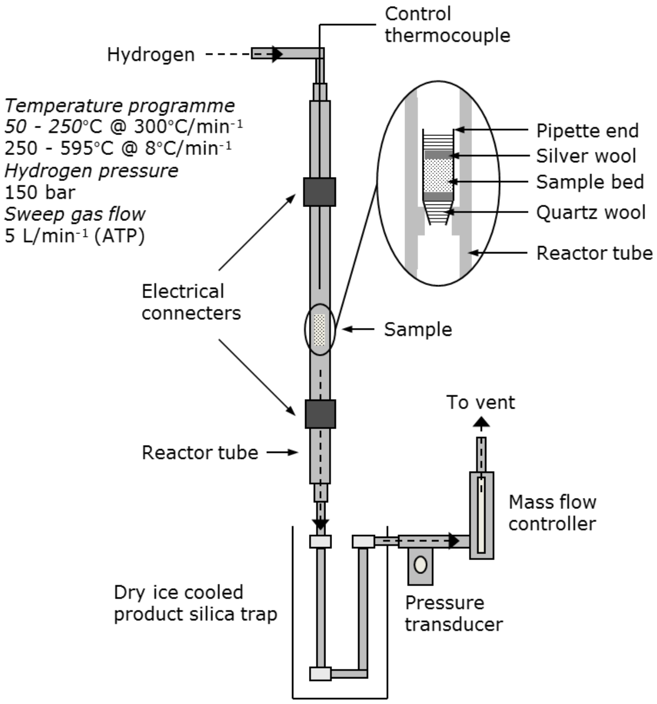


Fig. 3. Schematic diagram of the HyPy apparatus (adapted from Meredith et al., 2012).

2.4. Gas chromatography-mass spectrometry (GC-MS)

Gas chromatography-mass spectrometry (GC-MS) was used to characterize the aliphatic and aromatic compounds recovered from the non-BC_{HyPy} fractions, as well the composition of the whole DCM extract.

The non-BC$_{HyPy}$ fraction of each sample were desorbed from the trap silica with 10 ml aliquots of *n*-hexane and *n*-hexane:DCM (60:40 ratio), with the two fractions then combined. DCM extractions were performed on 50 mg aliquots of the charcoal samples #2 and #11 by ultrasonic extraction (3 x 5 ml DCM for 5 mins each). The recovered fractions were then evaporated to 1ml under a stream of nitrogen at room temperature prior to analysis. GC-MS analyses in full scan mode (*m/z* 50-450) were performed on a Varian CP-3800 gas chromatograph, interfaced to a Varian 1200 mass spectrometer (EI mode, 70 eV). Separation was achieved on a VF-1MS fused silica capillary column (50 m × 0.25 mm i.d., 0.25 um thickness), with helium as the carrier gas, and an oven programme of 50°C (hold for 2 min) to 300°C (hold for 33 min) at 5°C min^{-1}. The abundance of the individual *n*-alkanes and isoprenoids were quantified from the *m/z* 57 mass chromatograms, and for the PAHs the mass chromatograms of the molecular ion of each compound was used, following the addition of 1-1 binapthyl (Acros Organics) as an internal standard, assuming a response factor for each compound of 1.

2.5. ^{14}C pre-treatment and AMS dating

AMS ^{14}C dating was conducted by Beta Analytic Inc. The samples analysed were of four types: (A) original charcoal samples #1, #6, #10, #13; (B) BC$_{HyPy}$ fractions isolated from samples #1, #6, #10, #13; (C) the non-BC$_{HyPy}$ fraction recovered from sample #13; (D) samples of the wooden stakes #084 and #120. Standard "acid-alkali-acid" (AAA) was applied on the two pieces of wooden stakes (type D), 0.1N HCl acid washes were applied at 70 °C for 1 hours and repeated as necessary to ensure the absence of any carbonate. After rinsing to neutral, dilute sodium hydroxide solution was used repeatedly until all the humic acids were e removed. After rinsing to neutral, a final acid wash was applied to ensure the absence of atmospheric contamination from the alkali. During this process all roots and organic debris were eliminated. The samples were dried and microscopically examined for cleanliness, uniformity and where applicable appropriately sub-sampled for the measurements. The charcoal samples (types A, B, C) that were available in small quantities were subject to only the initial acid treatment to remove carbonate, since the alkali treatment would have dissolved the entire sample. Single AMS measurements were carried out on all the samples.

The measured radiocarbon ages were corrected for isotopic fractionation using the ^{13}C values, following by calendar calibration to the final calendar years. The parameters used for the corrections have been obtained through precise analyses of hundreds of samples taken from known-age tree rings of oak, sequoia, and fire up to *ca*. 12000 BP. The Pretoria Calibration Procedure program has been chosen for these calendar calibrations. It uses splines through the tree-ring data as calibration curves, which eliminates a large part of the statistical scatter of the actual data points. The spline calibration allows adjustment of the average curve by a quantified closeness-of-fit parameter to the measured data points. The calibration database used was INTCAL13 (Reimer, et al., 2013). One sigma (68% probability) and two sigma statistics (95% probability) were represented on the calibration curve and both probabilities are reported.

3. Results and discussion

3.1. Elemental and BC_{HyPy} contents

Elemental compositions of the fresh charcoals and their counterpart BC_{HyPy} residues and the BC_{HyPy} contents of the charcoals are listed in Table 2; all the values listed are means of duplicate determinations. The carbon contents of BC_{HyPy} residues are consistently higher than those of the untreated charcoals, with the carbon contents of the charcoals ranging from 19% to 47% and the BC_{HyPy} residues from 21.5% to 64.5%. The carbon contents of the charcoals generally decrease with increasing depth (2) which may indicate degradation of the original charcoal, especially that composed of relatively small aromatic clusters after deposition (Hockaday et al., 2006; Jaffé et al., 2013).

The atomic H/C ratios of the charcoals prior to HyPy and the resultant BC_{HyPy} fractions are presented in Fig. 4. Most of the fresh charcoals have relatively low atomic H/C ratios (all below 1.0) and they generally fall in a relatively narrow range of 0.20 to 0.37 (except #10, #13 and #14), which indicated that they were composed of extremely large PAH clusters. As with the previous studies on charcoals and other BC-rich materials (e.g. biochars and soot) by Ascough et al (2010) and Meredith et al (2012), the atomic H/C ratios of the BC_{HyPy} fractions isolated from these charcoals all fall in a very narrow range between 0.2 and 0.4. This is consistent with the inferred composition of BC_{HyPy} identified by Meredith et al (2012) of a structure of >7 peri-condensed rings. The highly aromatic nature of the fresh charcoals, and their uniformly high BC_{HyPy} contents (all >68%, 3 charcoals >90%) are consistent with a high combustion temperature of formation (McBeath et al., 2011).

Table2. Elemental compositions of charcoals before and after HyPy and their BC_{HyPy} contents.

Sample	Untreated material		BC_{HyPy} residue		BC/OC (%)
(#)	C (%)	H (%)	C (%)	H (%)	+/- 2%*
1	46.8	1.4	64.5	1.7	97
2	20.2	0.5	23.6	0.6	89
5	33.1	0.8	36.2	1.0	78
6	32.1	0.8	38.2	0.7	102
10	27.9	1.5	38.6	1.1	95
11	33.3	1.1	31.2	0.9	68
13	19.0	1.4	24.3	0.7	75
14	19.8	0.9	21.5	0.6	81

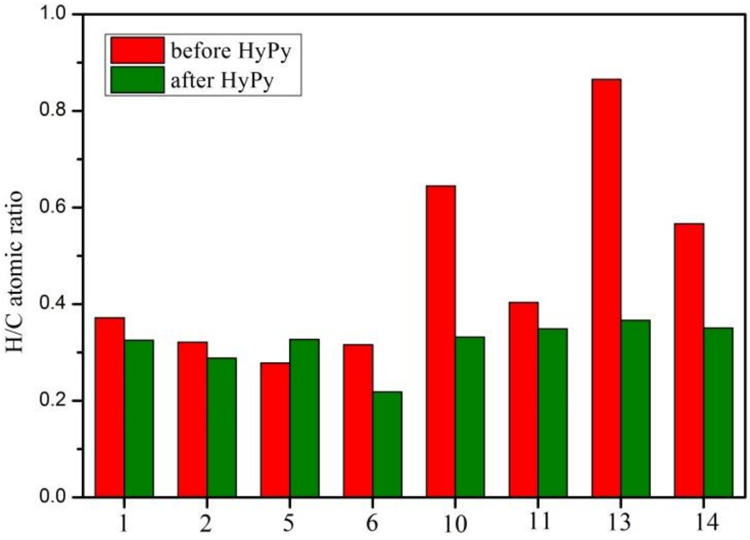


Fig. 4. Atomic H/C ratios of the initial charcoals and the BC_{HyPy} residues.

3.2. ^{14}C dating

Charcoal #1 was collected from the top of the silt core. Both the BP and calibrated ages from the original fresh charcoal with standard Beta pretreatment and from BC_{HyPy} residue are similar (Table 3 and Figure 5) and also confirm that this charcoal has the youngest age in the vertical sedimentary profile. The ^{14}C ages are older for the BC_{HyPy} residue but only just outside the experimental error for the BP ages which suggests there could be minor contamination of charcoal #1 by more recent carbon.

Table 3. Details of the samples collected from Bianjiashan Wharf.

Sample (#)	Material	Depth (cm)	Pre-treatment	Sub-samples	Laboratory number	Conventional radiocarbon age	Calendar calibrated age (INTCAL13 database used)	
							(95% probability)	(68% probability)
1	Charcoal	220-225	Acid wash	Fresh	Beta-358047	3960±30 BP	Cal BC 2565 to 2520	Cal BC 2485 to 2465
							Cal BC 2495 to 2455	
							Cal BC 2415 to 2410	
				HyPy product	n.m.	n.m.	n.m.	n.m.
				HyPy residue	Beta-358048	4020±30 BP	Cal BC 2615 to 2605	Cal BC 2575 to 2485
							Cal BC 2580 to 2470	
6	Charcoal	245-250	Acid wash	Fresh	Beta-358049	4160±30 BP	Cal BC 2880 to 2830	Cal BC 2875 to 2835
							Cal BC 2820 to 2625	Cal BC 2815 to 2675
				HyPy product	n.m.	n.m.	n.m.	n.m.
				HyPy residue	Beta-358050	4150±30 BP	Cal BC 2875 to 2620	Cal BC 2870 to 2835
								Cal BC 2815 to 2800
								Cal BC 2780 to 2665
7	Charcoal	250-255	None	Fresh	n.m.	n.m.	n.m.	n.m.
				HyPy product	n.m.	n.m.	n.m.	n.m.
				HyPy residue	n.m.	n.m.	n.m.	n.m.
8	Charcoal	260-265	None	Fresh	n.m.	n.m.	n.m.	n.m.
9	Charcoal	265-270	None	Fresh	n.m.	n.m.	n.m.	n.m.
10	Charcoal	270-275	Acid wash	Fresh	Beta-358044	4150±30 BP	Cal BC 2875 to 2620	Cal BC 2870 to 2835
								Cal BC 2815 to 2800
								Cal BC 2780 to 2665
				HyPy product	n.m.	n.m.	n.m.	n.m.
				HyPy residue	Beta-358045	4110±30 BP	Cal BC 2865 to 2805	Cal BC 2850 to 2810
							Cal BC 2760 to 2575	Cal BC 2745 to 2725
								Cal BC 2695 to 2615
								Cal BC 2605 to 2580

11	Charcoal	280-285	Acid wash	Fresh	n.m.	n.m.	n.m.	n.m.
				HyPy product	n.m.	n.m.	n.m.	n.m.
				HyPy residue	n.m.	n.m.	n.m.	n.m.
12	Charcoal	290-295	None	Fresh	n.m.	n.m.	n.m.	n.m.
13	Charcoal	295-300	Acid wash	Fresh	Beta-358041	4230±30 BP	Cal BC 2900 to 2865	Cal BC 2890 to 2875
							Cal BC 2805 to 2760	
				HyPy product	Beta-358043	4160±30 BP	Cal BC 2880 to 2830	Cal BC 2875 to 2835
							Cal BC 2820 to 2625	Cal BC 2815 to 2675
				HyPy residue	Beta-358042	4160±30 BP	Cal BC 2880 to 2830	Cal BC 2875 to 2835
							Cal BC 2820 to 2625	Cal BC 2815 to 2675
14	Charcoal	300-305	None	Fresh	n.m.	n.m.	n.m.	n.m.
				HyPy product	n.m.	n.m.	n.m.	n.m.
				HyPy residue	n.m.	n.m.	n.m.	n.m.
84	Wood	-	Acid-alkali-acid	Fresh	Beta-358039	4200±30 BP	Cal BC 2890 to 2850	Cal BC 2880 to 2865
							Cal BC 2810 to 2745	Cal BC 2805 to 2760
							Cal BC 2725 to 2695	
120	Wood	-	Acid-alkali-acid	Fresh	Beta-358040	4170±30 BP	Cal BC 2880 to 2830	Cal BC 2875 to 2850
							Cal BC 2820 to 2660	Cal BC 2810 to 2745
							Cal BC 2650 to 2635	Cal BC 2725 to 2695

n.m. – not measured

Assuming that the age of charcoal #1 represents the time when the ancient river dried up and the civilization was in decline, it can be deduced that the collapse of the Bianjiashan site should not be considered to have begun earlier than Cal BC 2580 to 2470 (95% probability), the date obtained from BC_{HyPy} residue which is considered to be a more reliable indicator than the original charcoal giving the latest possible age range as Cal BC 2415 to 2410 (95% probability). Thus, the BC_{HyPy} residue gives the last possible date as being 60 years older than the original charcoal. It was suggested that the lifespan of the Bianjiashan Site ash pit is from BC 3150 to 2550 (Zhejiang Provincial institute of Cultural relics and Archaeology, 2014) where the relics were from late period of middle Liangzhu Culture to early period of late Liangzhu Culture. The estimate of no later than BC 2550 for the lower age limit of Liangzhu Culture (Zhejiang Provincial institute of Cultural relics and Archaeology, 2014) is consistent with the mean age of the more recent calendar calibrated age range BC 2525 for the BC_{HyPy} residue (Table 3).

Charcoals #6 and #10 are from the middle of black clay layer, with sample #6 collected from 245-250 cm depth and sample #10 being collected only 15 cm deeper than sample #6. The BP and calibrated ages ranges for the original charcoals and BC_{HyPy} residues are very similar for these charcoals (Table 3 and Figure 5)with the latter spanning BC 2880 to 2575 (95% probability, the mean being BC 2730) and demonstrate that the middle layer of the silt core is older than the overlying sedimentary strata. Clearly, within experimental error, charcoals #6 and #10 have the same age with no bias being observed between the original charcoals and the BC_{HyPy} residues, suggesting that contamination is minimal.

Charcoal #13 was collected at a depth of 295-300 cm, near to bottom of the black clay layer, suggesting the habitation began a little later than after sedimentation commenced. The calibrated age for the original charcoal and BC_{HyPy} residue give a probability distribution from Cal BC2900 to 2830 and Cal BC2820 to 2625 with 95% probability (Table 3 and Figure 5), suggesting that the timespan for the river being established and occupation of the site by the Liangzhu population. Given that the Bianjiasha Site began during the late period of the middle Liangzhu Culture (Zhejiang Provincial institute of Cultural relics and Archaeology, 2014), an age of Cal BC2900 to 2865 appears reasonable for charcoal #13.

Charcoal #13 is the only sample for which the HyPy product i.e. the non-BC_{HyPy} fraction was dated, this being Cal BC 2880 to 2830 or Cal BC 2820 to 2625. This date, derived for the labile components which HyPy was able to remove, indicates the exogenous carbonaceous material is derived from the same period as the charcoal.

The two pieces of wooden stakes have basically consistent age distributions, with sample #120 has a younger lower limit of Cal BC 2650 to 2635 than that of sample #084, Cal BC 2725 to 2695. The wharf was established in the later stages of the Bianjiashan site (Zhao, 2007) and was then extended and repaired, the overall lower limit of Cal BC 2725 to 2635 for the wooden stake 084 should be the time at which the wharf was established.

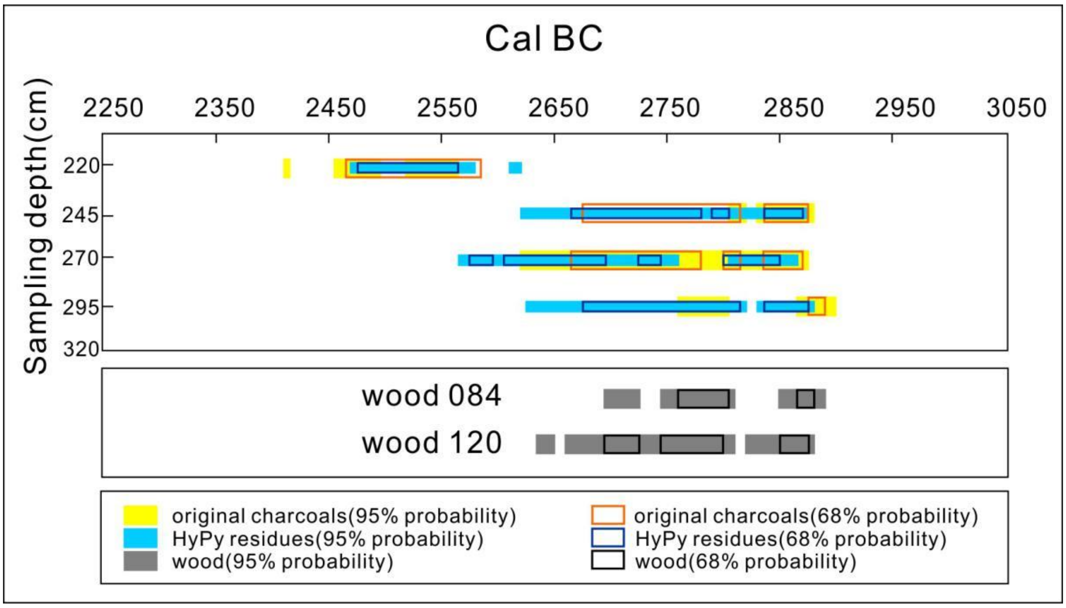


Fig. 5. Variation in the calibrated ^{14}C dates for the original charcoals and the HyPy residues with depth.

3.3. Origin of the carbonaceous impurities

Both the HyPy products (non-BC$_{HyPy}$ fraction) and DCM extracts were analyzed by GC-MS, with examples for samples #2, #11, #13 being presented in Fig. 6 and Fig. 7. The DCM extracts were dominated by *n*-alkanes (highlighted in the *m/z* 57 mass chromatograms) in the range from nC$_{12}$ to nC$_{18}$, with no significant odd/even preference. The isoprenoids, pristine and phytane derived from chlorophyll are also major constituents of the impurities.

The HyPy products of the thermally labile non-BC$_{HyPy}$ fraction of the charcoals are dominated by polycyclic aromatic hydrocarbons (PAHs) ranging from naphthalene to coronene, with pyrene being the most abundant. These PAH, that were released and trapped following HyPy treatment, may well, together with the remainder of the charcoal have had a pyrogenic origin, and so should be considered as part of the BC continuum. Their presence in the non-BC_{HyPy} fraction will be due to their greater volatility relative to the larger more condensed and refractory aromatic domains which form the BC_{HyPy} (Meredith et al., 2013).

Phenol and a series of alkylphenols (cresols, xylenols and propylphenol) are also abundant in the HyPy product of charcoal #13. These are typical pyrolysis products of lignin and may also derive from carbohydrate and proteinaceous precursors (Tsuge and Matsubara, 1985) suggesting a plant origin. The strong intensity signals of these small aromatic clusters are consistent with the relatively high H/C atomic ratio and low BC_{HyPy} content of this sample before HyPy, indicating impurities from terrestrial plants in the charcoal.

In addition, *n*-alkanes dominated by C_{24} and C_{26} are also present in the non-BC_{HyPy} fraction from sample #13. The even numbered distribution of these compounds suggests a probable source from biolipids, with these even numbered longer chained ($>C_{24}$) lipids known to be a component of both microbial biomass and the epicuticular waxes of land plants (Rieley et al., 1991). Such lipids are known to be hydrogenated under HyPy conditions to form the corresponding even-numbered *n*-alkanes (Meredith et al., 2006; Sephton et al., 2005). In contrast, the diversity of alkylphenols and *n*-alkanes in charcoal #11 is relatively limited, and reflected by the low H/C atomic ratio of the charcoal prior to HyPy.

The above analysis suggests that the carbonaceous impurities adsorbed by the charcoal are the degradation products of plant in the same period. The same age span of the HyPy residue and liquid product indicate that there is no obvious disturbance after precipitation. The sediments are reserved well as whole after the river cease development, no modern manmade contaminants are observed.

The distinct differences between the charcoal DCM extractable oil and the HyPy products suggest that DCM can only remove much of the adsorbed alkanes which would result in BC contents being overestimated, , whereas HyPy is capable of isolating combined covalent bonding carbons, thus significantly improving dating accuracy if the samples are contaminated with carbonaceous materials.

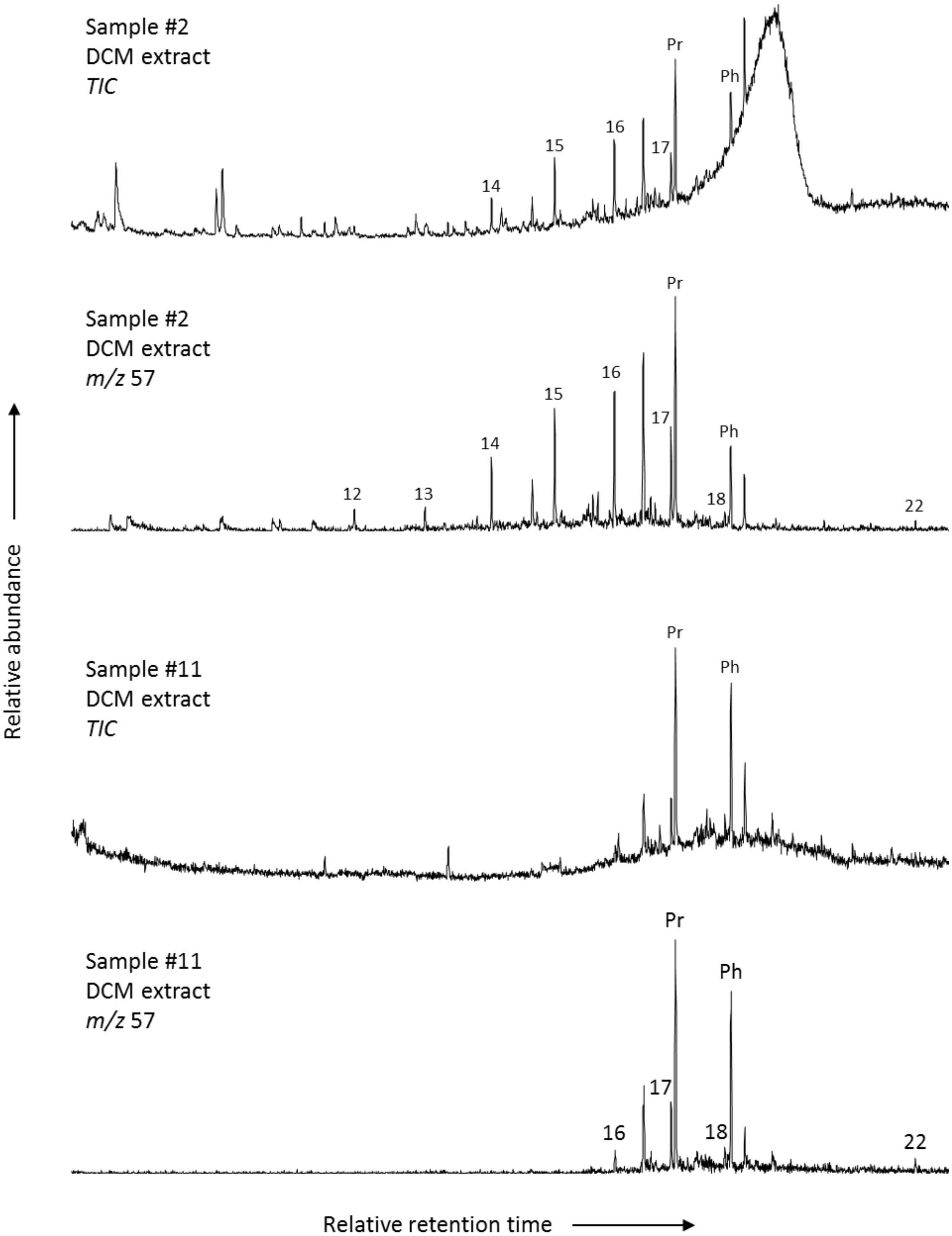


Fig. 6. Total ion chromatograms *(TIC)* and *m/z* 57 mass chromatograms of the DCM extract of samples #2 and #11. Numbers refer to chain length of *n*-alkanes; Pr - Pristane; Ph - Phytane.

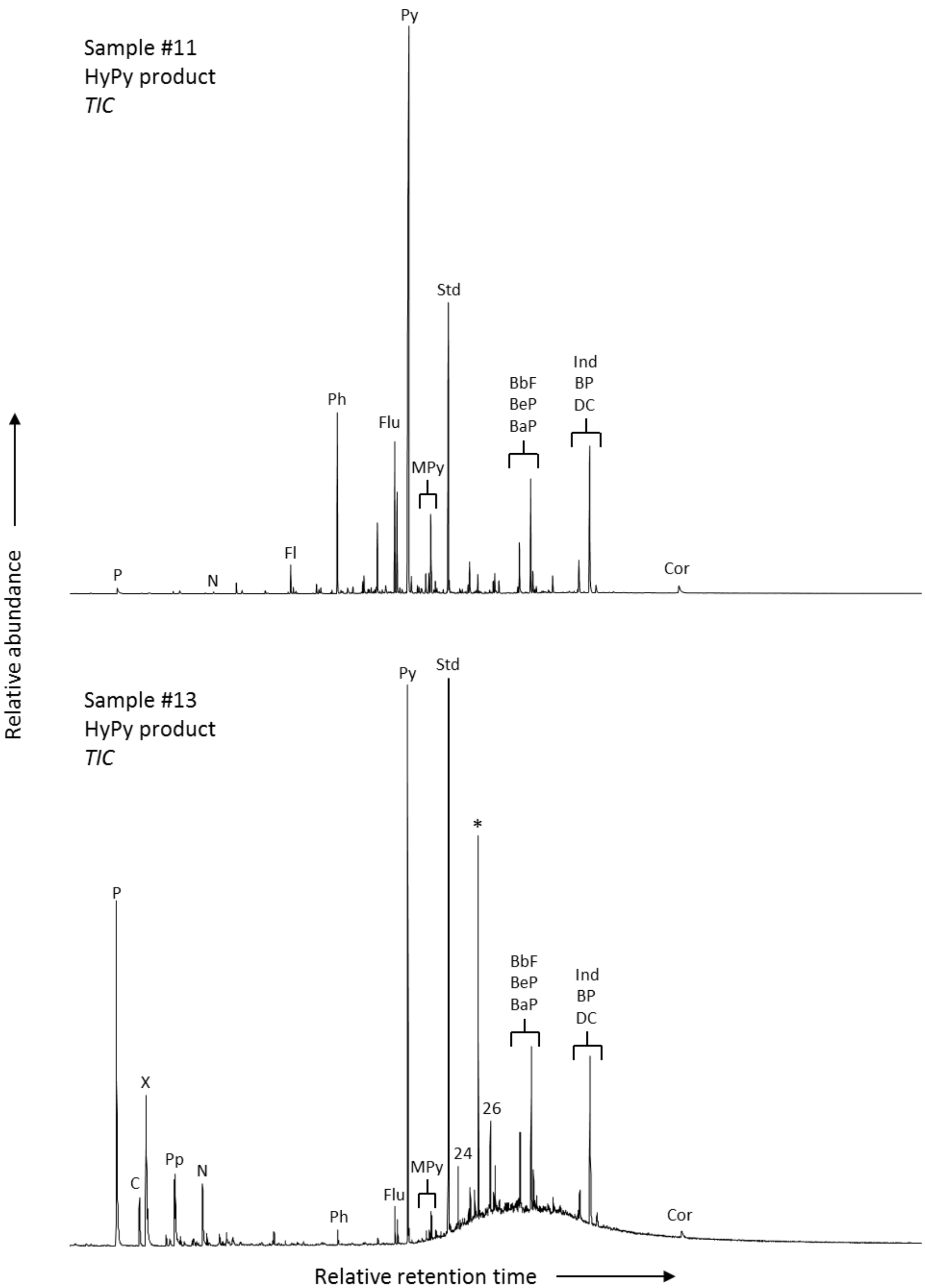


Fig. 7. Total ion chromatograms *(TIC)* of the HyPy products from samples #11 and #13. Numbers refer to chain length of *n*-alkanes; P - Phenol; C - Cresol; X - Xylenol; Pp - Polyphenol; N - Naphthalene; Fl - Fluorene; Ph - Phenanthrene; Flu - Fluoranthene; Py - Pyrene, Std - Standard; MPy - Methylpyrene; BbF - Benzo(b)fluoranthene; BeP - Benzo(e)pyrene; BaP - Benzo(a)pyrene; Ind - Indeno(1,2,3-cd)pyrene; BP - Benzo(g,h,i)perylene; DC - Dibenzo[def(mno)]chrysene; Cor – Coronene; * - Contaminant.

4. Conclusions

The Bianjiashan Site represents the latest stage of Liangzhu Culture (Zhao, 2007). The time of the the existence of the river, the sediment sequence of charcoals and establishing the wharf not only provides clues of the development of the Bianjiashan Site, but also give strong insights into the lower age limit of late Liangzhu Culture. From this study we can state the following conclusions:

1. The dating results obtained from BC residues #1, #6, #10 and #13 compose a continuum representing the evolution of the river and also continuous habitation. The dating data combined with previous results give a possible time span of the Bianjiashan Site from Cal BC2900 to 2865 (95% probability) to Cal BC 2580 to 2470 (95% probability). Thus, activity at this site continued for no more than about 400 years.

2. The end of river sedimentation suggests the termination of the Bianjiashan Site. The latest this could be is Cal BC 2470 and the mean age of the more recent calendar calibrated age range of BC 2525 for the BC_{HyPy} residue is consistent with earlier evidence.

3. The wharf was established between Cal BC 2635 and 2890 (95% probability) with the age span being similar to that for the start of the river charcoal sedimentation.

4. The HyPy product of charcoal # 13 has the same age distribution as the original charcoal and the BC_{HyPy} residue, which indicates that the exogenous carbon in the charcoal is from the same period. GC-MS indicated that the charcoal contamination arose mostly from plant constituents giving rise to phenols and n-alkanes in the non-BC_{HyPy} products cleaved from the charcoal. Therefore, HyPy has confirmed that there is no contamination of the charcoal from more recent plant material has occurred,

5. The impurities in the charcoal from degradation of plants in the same period suggests stable geological and geomorphic environment without climatic extremes during this period.

Acknowledgements

Funding for this research was provided by Natural and Science Foundation of Zhejiang Province, China (No. 506205) and the UK Natural Environmental Research Council (Grant No. NE/F0174456/1). The authors would like to thank the staff of Beta Analytic Inc. for the ^{14}C analyses.

References

Ascough, P., Bird, M., Brock, F., Higham, T., Meredith, W., Snape, C., Vane, C.H., 2009. Hydropyrolysis as a new tool for radiocarbon pre-treatment and the quantification of black carbon. Quaternary Geochronology 4, 140-147.

Ascough, P., Bird, M., Meredith, W., Wood, R., Snape, C., Brock, F., Higham, T., Large, D., Apperley, D., 2010. Hydropyrolysis: implications for radiocarbon pretreatment and characterization of black carbon. Radiocarbon 52, 1336-1350.

Bird, M.I., Gröcke, D.R., 1997. Determination of the abundance and carbon isotope composition of elemental carbon in sediments. Geochimica et Cosmochimica Acta 61, 3413-3423.

Bird, M.I., Levchenko, V., Ascough, P.L., Meredith, W., Wurster, C.M., Williams, A., Tilston, E.L., Snape, C.E., Apperley, D.C., 2014. The efficiency of charcoal decontamination for radiocarbon dating by three pre-treatments–ABOX, ABA and hypy. Quaternary Geochronology 22, 25-32.

Chen, J., 2007. A preliminary study on Guangfulin Culture. Relics From South 53-63 (In Chinese).

Du, J., 1992. Questions about Dawenkou Culture and Liangzhu Culture. Archaeological 10, 915-922 (In Chinese).

Forbes, M., Raison, R., Skjemstad, J., 2006. Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. Science of the Total Environment 370, 190-206.

Goldberg, E.D., 1985. Black carbon in the environment: properties and distribution. Environmental Science and Technology (USA).

Hammes, K., Schmidt, M.W.I., Smernik, R.J., Currie, L.A., Ball, W.P., Nguyen, T.H., Louchouarn, P., Houel, S., Gustafsson, Ö., Elmquist, M., Cornelissen, G., Skjemstad, J. O., Masiello, C.A., Song, J., Peng, P., Mitra, S., Dunn, J. C., Hatcher, P.G., Hockaday, W.C., Smith, D.M., Christoph Hartkopf-Fröder, M., Axel Böhmer, M., Lüer, B., Huebert, B.J., Amelung, G.W., Brodowski, S., Huang, L., Zhang, W., Gschwend, P.M., Flores-Cervantes, X., Largeau, C., Rouzaud, J.-N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F.J., Gonzalez-Perez, J. A., De La Rosa, J.M., Manning, D.A.C., López-Capél, E., Ding, L., 2007. Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. Global Biogeochemical Cycles 21, GB301610.1029/2006GB002914.

Hockaday, W.C., Grannas, A.M., Kim, S., Hatcher, P.G., 2006. Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil. Organic Geochemistry 37, 501-510.

Huang, X., 1992. The stages of Liangzhu Culture. The Shanghai Museum Journal Paper, 370-388 (In Chinese).

Jaffé, R., Ding, Y., Niggemann, J., Vähätalo, A.V., Stubbins, A., Spencer, R.G., Campbell, J., Dittmar, T., 2013. Global charcoal mobilization from soils via dissolution and riverine transport to the oceans. Science 340, 345-347.

Jiao, T., 2010. The origin of Maqiao Culture. South Cultural Relics, 70-75 (In Chinese).

Kuhlbusch, T.A., Crutzen, P.J., 1996. Black carbon, the global carbon cycle, and atmospheric carbon dioxide. Biomass burning and global change 1, 160-169.

Li, B., Mitchell, S.C., Snape, C.E., 1996. Effect of heating rate on normal and catalytic fixed-bed hydropyrolysis of coals. Fuel 75, 1393-1396.

Liu, L., 2003. " The products of minds as well as of hands": Production of prestige goods in the Neolithic and early state periods of China. Asian Perspectives 42, 1-40.

Luan, F., 1992. The age and stages of Liangzhu Culture. The Central Plains Cultural Relics 3, 79-86 (In Chinese).

Luan, F., 1997. The relationship between Dawenkou culture and Songze, Liangzhu Culture, The ninth annual meeting on Chinese archaeology, Cultural Relics Press, Beijing ,China (In Chinese).

McBeath, A.V., Smernik, R.J., Schneider, M.P., Schmidt, M.W., Plant, E.L., 2011. Determination of the aromaticity and the degree of aromatic condensation of a thermosequence of wood charcoal using NMR. Organic Geochemistry 42, 1194-1202.

Meredith, W., Ascough, P., Bird, M., Large, D., Snape, C., Song, J., Sun, Y., Tilston, E., 2013. Direct evidence from hydropyrolysis for the retention of long alkyl moieties in black carbon fractions isolated by acidified dichromate oxidation. Journal of Analytical and Applied Pyrolysis 103, 232-239.

Meredith, W., Ascough, P., Bird, M., Large, D., Snape, C., Sun, Y., Tilston, E., 2012. Assessment of hydropyrolysis as a method for the quantification of black carbon using standard reference materials. Geochimica et Cosmochimica Acta 97, 131-147.

Meredith, W., Russell, C.A., Cooper, M., E Snape, C., Love, G.D., Fabbri, D., Vane, C.H., 2004. Trapping hydropyrolysates on silica and their subsequent thermal desorption to facilitate rapid fingerprinting by GC–MS. Organic Geochemistry 35, 73-89.

Meredith, W., Sun, C.-G., Snape, C.E., Sephton, M.A., Love, G.D., 2006. The use of model compounds to investigate the release of covalently bound biomarkers via hydropyrolysis. Organic Geochemistry 37, 1705-1714.

Preston, C., Schmidt, M., 2006. Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. Biogeosciences 3, 397-420.

Reimer, P.J., Bard, E., Bayliss, A., Beck, J.W., Blackwell, P.G., Ramsey, C.B., Buck, C.E., Cheng, H., Edwards, R.L., Friedrich, M., Grootes, P.M., Guilderson, T.P., Haflidason, H., Hajdas, I., Hatté, C., Heaton, T.J., Hoffmann, D.L., Hogg, A.G., Hughen, K.A., Kaiser, K.F., Kromer, B., Manning, S.W., Niu, M., Reimer, R.W., Richards, D.A., Scott, E.M., Southon, J.R., Staff, R.A., Turney, C.S.M., Plicht, Jvd, 2013. IntCal13 and Marine13 radiocarbon age calibration curves 0-50,000 years cal BP. Radiocarbon 55(4):1869-1887.

Rieley, G., Collier, R.J., Jones, D.M., Eglinton, G., Eakin, P.A., Fallick, A.E., 1991. Sources of sedimentary lipids deduced from stable carbon-isotope analyses of individual compounds.

Roberts, M., Snape, C., Mitchell, S., 1995. Hydropyrolysis: fundamentals, two-stage processing and PDU operation, Composition, Geochemistry and Conversion of Oil Shales. Springer, pp. 277-293.

Sephton, M.A., Meredith, W., Sun, C.G., Snape, C.E., 2005. Hydropyrolysis as a preparative method for the compound-specific carbon isotope analysis of fatty acids. Rapid Communications in Mass Spectrometry 19, 323-325.

Shao, Y., 2006. The phenomenon of cultural fault and the end-result of Liangzhu Culture during 4000 years before present. People Press, Beijing, China (In Chinese).

Shi, X., 1938. Liangzhu - a preliminary report of black pottery cultural site in Yuhang Division. Cultural Relics Press, Beijing, China (In Chinese).

Shuo, Z., 2000. The preliminary study on Liangzhu Culture. Archaeological Journal Paper, 421-450 (In Chinese).

Song, J., 1999. The rise and fall of Liangzhu Culture. Liangzhu culture research-memory of Liangzhu Culture founding 60, 86-103(In Chinese).

Tsuge, S., Matsubara, H., 1985. High-resolution pyrolysis-gas chromatography of proteins and related materials. Journal of Analytical and Applied Pyrolysis 8, 49-64.

Wang, M., 2004. The Academic symposium on civilized process in the Changjiang River downstream. Calligraphy and Painting Press, Shanghai, China (In Chinese).

Watson, J.G., Chow, J.C., Chen, L.W.A., 2005. Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons. Aerosol Air Qual. Res 5, 65-102.

Wu, R., 1982. The age and stages of Dawenkou Culture. Archaeological Journal Paper 3, 261-282 (In Chinese).

Wu, S., 1989. The relationship between the Liangzhu Culture and Longshan Culture. Culture From Southeast 6, 73-77 (In Chinese).

Xia, N., 1977. C14 dating and prehistoric archaeology in China. Archaeology 4, 217-229 (In Chinese).

Yang, J., 1991. Theory of Liangzhu Culture stage. Culture From Southeast 6, 121-129 (In Chinese).

Yoshikazu, N., Zhao, Y., Xinsheng, J., Yihong, L., 2007. Molluscan remains from the Liangzhu archaeological sites of Zhejiang Province, China. Memoir of the Fukui Prefectural Dinosaur Museum 6, 45-55.

Zhang, Z., 1995. The era and the social stage of Liangzhu culture- an example of 5000 years ago Chinese into civilization. Cultural relic 5, 47-58 (In Chinese).

Zhao, Y., 2007. Destruction of ancient country and capital, Introducation of Liangzhu Sites, series of Liangzhu Culture researches, editor in chief, Binhuo Zhang, Zhejiang Photographic Press, Hangzhou, China (In Chinese).

Zhao, Y., 2012. The preliminary theory of wooden remains. Relics From South 4, 74-83 (In Chinese).

Zhejiang Provincial institute of Cultural relics and Archaeology, 2014. Bianjiashan Site, the sixth part report of Liangzhu Culture sites, Culture Relics Press, Beijing, China (In Chinese).

Zhou, L., 2007. The Liangzhu cultural relics in Guangfulin site. Relics From South, 44-52 (In Chinese).