Radiocarbon dating of charcoal and bone collagen associated with early pottery at Yuchanyan Cave, Hunan Province, China

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Yuchanyan Cave in Daoxian County, Hunan Province (People's Republic of China), yielded fragmentary remains of 2 or more ceramic vessels, in addition to large amounts of ash, a rich animal bone assemblage, cobble and flake artifacts, bone tools, and shell tools. The artifacts indicate that the cave was a Late Paleolithic foragers' camp. Here we report on the radiocarbon ages of the sediments based on analyses of charcoal and bone collagen. The best-preserved charcoal and bone samples were identified by prescreening in the field and laboratory. The dates range from around 21,000 to 13,800 cal BP. We show that the age of the ancient pottery ranges between 18,300 and 15,430 cal BP. Charcoal and bone collagen samples located above and below one of the fragments produced dates of around 18,000. These ceramic potsherds therefore provide some of the earliest evidence for pottery making in China.

ancient ceramics | archaeology | ^{14}C | Yangzi River

Numerous caves in the vast karstic landscape of the southern area of the Yangzi River basin of China are known to have been inhabited by hunter-gatherer groups during the Late Pleistocene and early Holocene. The generally good preservation of the cave deposits and the presence of rich archaeological assemblages, including stone, bone, and shell tools, have led to a large number of excavations since the 1980s. While similarly well-preserved Late Pleistocene cave sites are found in other regions of the world, the cave sites in this region of South China (as well as several sites in neighboring Japan and the Russian Far East) are unique due to the presence of ceramic vessels in their otherwise Late Paleolithic assemblages. Among the well-known sites in China from this period are Xianrendong and Diaotonghuan in Jiangxi Province (1–4), Miaoyan in Guangxi Province (5, 6), and Yuchanyan in Hunan Province (7). Previous studies of these sites have produced dates for this pottery ranging ca. 16,000–10,000 cal BP (8–15), indicating that the world's first pottery was produced in East Asia. Many of these studies do not report a systematic analysis of the ages of the strata within the site, especially those containing the potsherds. Here we date the stratigraphic sequence deposited in Yuchanyan Cave, paying particular attention to the strata in close proximity to the potsherds.

Chinese Late Paleolithic sites such as Yuchanyan are rich in terrestrial and aquatic fauna, including deer, boar, birds, tortoises, fish, and various small mammals. Rice phytoliths and husks have been identified at Xianrendong, Diaotonghuan, and Yuchanyan, and several studies have attempted to differentiate wild and domestic species or to suggest an incipient stage of cultivation (4, 16, 17). Because of the presence of such plant remains and early pottery, these caves are often seen as the predecessors of the early Holocene open-air Neolithic villages found in the alluvial plain of the Yangzi River and its tributaries, such as the Pengtoushan and Bashidang sites, and other settlement sites of the Pengtoushan Culture (18, 19).

Paleoclimatic data for the region suggest similar trends to those reported globally (20). The last glacial maximum (LGM) ca. 23,000–18,000 cal BP led to lower temperatures and increased aridity, with average temperatures in the Yangzi basin ca. 4–5 °C cooler than today (21). Deciduous trees were increasingly replaced by grasses (22, 23). The Terminal Pleistocene warming was interrupted by the Younger Dryas ca. 13,000–11,500 cal BP. Although the Younger Dryas is seen in other regions as a generally cold and dry period, in South China the main effect of the Younger Dryas was probably the sudden onset of greater seasonality. Understanding the local impact of the Younger Dryas on the basin of the Yangzi River and in particular in the limestone region south of the main river channel is still not possible (20).

While there have been previous excavations of Late Pleistocene cave sites in the Yangzi Basin, the dating of these sites has been problematic. First, the complex deposition of interdigitating lenses of ashes, clays, and sometimes fine gravel requires systematic dating based on a series of radiocarbon determinations and this has been lacking. Secondly, accurate and precise radiocarbon dating of these sites in the past has proven to be difficult. While excavators of the cave sites have cited the cause as contamination from calcium carbonate in the karstic environment of the cave (2), this problem actually may be related to the presence of large amounts of calcite in the archaeological matrix of the caves. This can indirectly result in poor charcoal preservation (24). Here we apply a prescreening strategy for identifying the best-preserved bone collagen and charcoal samples. We then analyze 29 prescreened samples for radiocarbon contents. This results in a much clearer understanding of the chronology of Yuchanyan Cave and the age of the pottery found in this site, as compared to other Late Pleistocene caves in East Asia.

Excavations in Yuchanyan Cave. Yuchanyan Cave (25°30′ N, 111°30′ E) is located in Daoxian County, ca. 450 km south of the main course of the Yangzi River (Fig. 1 *Inset*). The cave is 12–15 m wide along its east-west axis and about 6–8 m wide from north to south.

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ANTHROPOLOGY

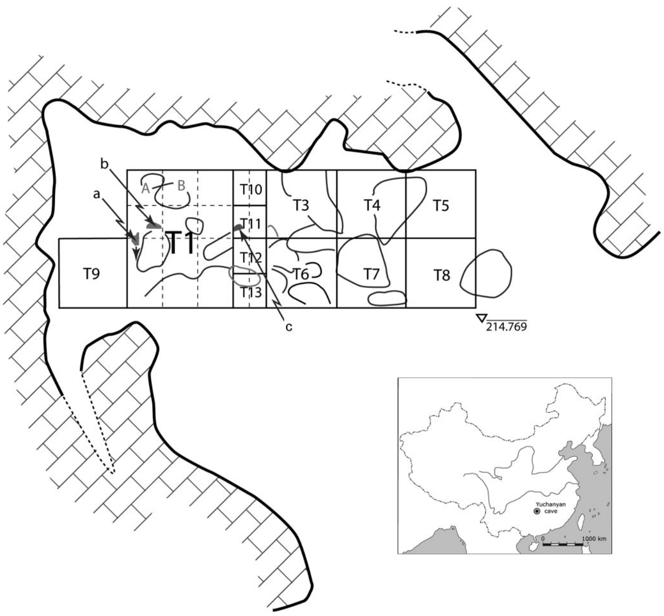

Fig. 1. Location of Yuchanyan Cave in China (*Inset*) and excavation grid showing locations of ceramics (arrows: *a*, location of potsherds found by J.Y.; *b* and *c*, locations of potsherds found in this study).

Fig. 2. Photograph of the section in square T11 showing the calcitic ash lenses and reddish clay-rich lenses. One of the ceramic sherds was found embedded in this sequence. Its location is marked with O. (Scale bar: 20 cm.)

The uppermost deposits were removed in historical time. The cave was first excavated in 1993 and 1995 by one of the authors (J.Y.), who uncovered 2 clusters of potsherds indicating the presence of 2 vessels (Fig. 1). A piece of charcoal closely associated with the potsherds was dated to 16,700–15,850 cal BP and organic residue from the ceramic to 17,750–16,900 cal BP (7, 16, 17, 25;) (Table 1). The pottery was coarsely made, with thick, uneven walls up to 2 cm thick, and was fired at low temperatures. Infrared spectra indicate that the firing temperature was between 400 and 500 °C, with kaolinite being a major clay component. Due to the crumbly state of the sherds, only one pot could be reconstructed. Its form features a round rim 31 cm in diameter and a pointed base—a type known in the Chinese literature as a *fu* cauldron. The vessel has a height of 29 cm. Both the interior and exterior surfaces were impressed, possibly with cordage (7).

The 1993 and 1995 excavations at Yuchanyan opened an area of 46 m^2, with an excavation grid subdivided into squares (Fig. 1). During the excavations in 2004–2005, we subdivided the large rectangular square T1 into 1 × 1 m squares and added, along the baulk between T1 and T3, four 1 × 1 m squares, T10-T13. These were subdivided into 4 quadrants of 50 × 50 cm (Fig. 1). We also excavated a one meter square in T4 and cleaned all of the sections to clarify the exposed stratigraphy. In addition to the radiocarbon dating reported here, we studied site formation processes using micromorphology and mineralogy. A taxonomic and taphonomic study of the fauna was also carried out (26). The small collection of lithic artifacts recovered was recently recorded and found to reflect the same tool categories, dominated by core-choppers and retouched flakes, known from the first excavations. A few bone and shell tools were reported previously (16).

Results

Cave Sediments. The bedrock of Yuchanyan Cave slopes steeply from the east, where it is about 2.0 m below datum, to the west, where it is 3.2 m below datum. The cave can be roughly subdivided into 3 main areas differentiated mainly by major rockfalls. The western area (mainly square T1) is composed of 2 major lithostratigraphic units: the uppermost intact unit is composed of approximately 80 cm of calcareous anthropogenic deposits resulting from numerous burning events. Specifically, they are stringers composed of white and light gray calcitic ash lenses that in some cases overlie discontinuous bands of red clay, which are approximately 1–3 cm thick by approximately 30–50 cm long. The many ashes and red bands are compact and massive, with millimeter-size aggregates of red clay (Figs. 2 and S1). Well-bedded lenses with varying white and red colored fine-grained sediments are separated by brown colored sediments. The major mineral components of these sediments are calcite, quartz, and clay. The central area (squares T3 and T4) contains brown colored sediments with fewer lenses. The sediments here are also composed mainly of calcite, quartz, and clay. The eastern part of the cave (square T5) contains massive brown sediments with almost no color differences, and stratification is not clearly visible. These sediments are also dominated by calcite, quartz, and clay. Micromorphological analyses of the sediments clearly show that the calcite is mainly composed of wood ash that has been weakly cemented. The ash is remarkably well-preserved, and in many samples, rectangular pseudomorphs of wood-derived calcium oxalate crystals can be observed. Furthermore, much of the red clay (Fig. S2) was purposefully brought into the cave, as there are no possible geological means for clay to accumulate as lenses within the cave. In fact, the massive lenses (e.g., the one shown in Fig. S1) are constructed surfaces and are

Table 1. Uncalibrated and calibrated radiocarbon dates of the samples analyzed after the excavations in 1993 and 1995 (7)

PKU lab number	Material dated	Layer	^{14}C age ± 1σ year BP	Calibrated age ± 1σ year BP	Calibrated age ± 2σ year BP
BA95058	Charcoal	T1, layer: 3E	13680 ± 270	16700–15850	17150–15450
BA95057a	Humic substances from potsherds	T1, layer: 3H	11970 ± 120	13970–13720	14150–13550
BA95057b	Potsherds residue	T1, layer: 3H	14390 ± 230	17750–16900	18050–16450

Table 2. Prescreening results for bones and charcoal from different excavation squares in the cave

	Bones		Charcoal	
Excavation square	No. of samples analyzed	No. of samples with pure collagen suitable for dating	No. of samples analyzed	No. of well preserved samples suitable for dating
T9	2	1	(4)	(2)
T1 Sub-squares D and E	6	2	12	10
T10				
T11	21	10	18	5
T12	11	8	8	6
T4	12	3	21	4
T5	12	2	12	6
Totals	64	26	75	33

virtually identical to similar features from the Paleoindian site of Dust Cave in Alabama (27). Infrared spectra of the red lenses show that some of them were exposed to temperatures between 400 and 500 °C based on the absence of absorption peaks around 3600 cm^{-1}. For kaolinite, one of the major clay components in these sediments, these peaks disappear when the clay is exposed to temperatures above 400 °C (28). Note, too, that the clay component extracted from white lenses also often showed these characteristics. Thus, the exposure to elevated temperatures was probably part of the normal use of fires and was not associated with the production of ceramics.

Prescreening of Bone and Charcoal Samples for Radiocarbon Analysis. The distribution of bones was more or less uniform in all areas of the cave. In contrast, the charcoal was much less abundant in the eastern T5 square, especially in the deeper part of the section. Of the samples collected from throughout the cave, about 35% of the bones and about 45% of the charcoal were suitable for dating. For both bone and charcoal, the proportions of dateable samples in squares T4 and T5 were much less than for the squares in the eastern parts of the cave. The preservation conditions are clearly much better in the western part of the cave. The results of the prescreening procedure are presented in Table 2.

Seventy-five charcoal samples were selected, prescreened, and pretreated. After the pretreatment, 21 samples were found to contain clay based on their infrared spectra (strong absorptions at 1033 cm^{-1} together with absorptions at 535 and 472 cm^{-1}). As clay is a potential carbon carrier and therefore a possible contaminant, these samples were excluded. Furthermore, an additional 8 samples dissolved completely during the procedure. The infrared spectra of the remaining samples showed only charcoal (peaks from 1718 to 1595 cm^{-1}) and thus could potentially be used for ^{14}C analysis. Twenty of these samples that contained relatively large amounts of material were also analyzed by Raman spectroscopy (29). The average fluorescence intensity after the first and last HCl steps decreased in all samples except for 4 (YAS 237d, 540, 559, and T1E 6), indicating that most of the humic acid was removed during the acid-alkali-acid (AAA) treatment. These 4 samples were also rejected.

Sixty-seven bones were analyzed from the different areas in the cave. All were treated with 1N HCl, and an acid insoluble fraction was identified in 43 samples. This fraction was then isolated, and 25 samples were shown to produce a pure collagen infrared spectrum. The weight percentage of insoluble collagen ranged from 0.02% to 1.6%. The infrared splitting factor (IRSF) values of 4 samples were within 2.6–2.9, i.e., the IRSF values of fresh bones (30), while most of the samples had an IRSF value between 2.9 and 3.3. In some of the collagen spectra, the presence of humic acid was detected; therefore, after whole pretreatment, the collagen was again characterized by infrared spectroscopy before target preparation for accelerator mass spectrometry (AMS) dating (31).

Radiocarbon Analysis. A total of 27 samples were analyzed for their ^{14}C contents. They were selected based on the quality of context and material preservation. Of these, 10 pretreated samples were separated into 2 parts and were prepared separately as duplicate analyses. Three samples (BA 95098, 95057a, 95057b) (12) were analyzed during the 1990s excavations when prescreening procedures were not used (Table 1). Table 3 lists the 40 radiocarbon dates according to excavation square, and within each square the samples are arranged according to increasing stratigraphic depth. The duplicate analyses are also listed. The uncalibrated and calibrated ages are shown. All of the radiocarbon dates were calibrated with OxCal 3.10 by Bronk-Ramsey (32, 33).

The reproducibility of the duplicate measurement analyses (Fig. 3) shows that the data distribution based on the analytical uncertainty follows a normal distribution. This result shows that there is no bias between the measurements, and that there is no consistent difference between charcoal and bone samples from the same depth or level.

Fig. 4 shows a plot of the calibrated ages obtained in each excavation square, and within each square the samples are arranged according to increasing depth. This shows that the upper part of each section contains sediments from around 14,600–13,800 cal BP. Older sediments were found close to the base of the sections in squares T1 D and E, as well as in squares T10–12. Most of these sediments are from around 18,000–16,400 cal BP. A major exception is a bone sample which was just above bedrock in T1 that gave an age of 21,000 cal BP. In square T9, near the western cave wall, the ages are similar and show no trend with depth.

Discussion

In each stratigraphic section from which samples were analyzed, the ages increase with increasing stratigraphic depth, with 2 exceptions. The dates show that the cave was occupied from around 18,000 to 14,000 cal BP (Table 3). There were some periods from which no dates were obtained. This may be due to the sample distribution or because during these periods very little sediment may have accumulated.

The mineralogical and micromorphological analyses of the sediments both indicate that ash calcite was a major component of almost all samples, implying that they were produced mainly during periods of human occupations. Another unusual anthropogenic activity is evidenced by the clay-rich sediment formed into lenticular bands that must have been brought into the cave by humans and functioned as prepared surfaces (Fig. S2). The clay may have been red colored initially or became red due to heating. Infrared analysis shows that some of these sediments were heated to temperatures between 400 and 500 °C (28).

Snail shells found in the cave sediments were analyzed and almost all were found to be composed entirely of aragonite. As aragonite is less stable than calcite, its presence indicates that the preservation conditions were generally good for ash and bones (34). Calcite, however, buffers the ground water to above pH 8, and this is often not conducive to the preservation of charred materials. In fact, the prescreening showed that the charcoal was

Table 3. Uncalibrated and calibrated radiocarbon dates of all the samples analyzed

Weizmann Institute number	PKU lab number	Material dated	Location	^{14}C age ± 1σ year BP	Calibrated age ± 1σ year BP	Calibrated age ± 2σ year BP
RTT 3967	Average	Charcoal	T9, west section, 129 cm	12190 ± 85	14020–13850	14090–13790
RTT 3968				11970 ± 90		
				12089 ± 62		
RTT 3966		Charcoal	T9, west section, 135 cm	11975 ± 85	13940–13750	14030–13670
RTT 3969		Charcoal	T9, west section, 190 cm	12230 ± 85	14210–13960	14600–13800
RTB 5117	BA05429a	Bone	T9, west section, 191m	12100 ± 70	14210–13850	14650–13750
RTB 5117	BA05429b			12275 ± 50		
	Average			12188 ± 124		
RTT 3970		Charcoal	T9, west section, 194 cm	11865 ± 85	13820–13630	13920–13480
RTB 5208	BA05898–1	Bone	T10a, 3A, 195 cm	12440 ± 40	14490–14190	14750–14100
RTB 5208	BA05898–2			12350 ± 40		
	Average			12395 ± 28		
RTB 5113	BA05425a	Charcoal	T1, south, 198 cm	12290 ± 50	14180–14050	14250−13990
RTB 5113	BA05425b			12230 ± 50		
	Average			12260 ± 35		
RTB 5112	BA05424a	Charcoal	T1, south, 204 cm	12360 ± 50		14650–14050
RTB 5112	BA05424b			12345 ± 60	14380–14130	
	Average			12348 ± 33		
RTB 5205	BA05895–1	Charcoal	T11a, 3A IV, 217 cm	11670 ± 40		13620–13370
RTB 5205	BA05895–2			11600 ± 40		
	Average			11635 ± 28	13540–13410	
RTB 5206	BA05896–1	Charcoal	T10a, 3A, 219 cm	11860 ± 40	13780–13700	13820–13650
RTB 5206	BA05896–2			11870 ± 40		
	Average			11865 ± 28		
RTB 5207	BA05897–1	Charcoal	T1c, 3BIII, 228 cm	12020 ± 40	13930–13810	13980–13780
RTB 5207	BA05897–2			12020 ± 40		
	Average			12020 ± 28		
RTB 5209	BA05899	Bone	T10c, 3B III, 230 cm	12400 ± 40	14580 (6.7%) 14530	14800–14100
					14500 (61.5%) 14200	
RTB 5204	BA05894–1	Charcoal	T11a, 3C, 236 cm	12200 ± 40	14650–14000	14950–13850
RTB 5204	BA05894–2			12430 ± 40		
	Average			12315 ± 163		
RTB 5110	BA05422	Charcoal	T1D-c, layer: 3E, 251 cm	13890 ± 50	16760–16340	16950–16150
RTB 5107	BA05419a		T1E, layer: 3E, 251 cm	12835 ± 40	15250–15020	15400–14940
RTB 5107	BA05419b	Charcoal		12815 ± 60		
	Average			12829 ± 33		
RTB 5108	BA05420	Charcoal	T1E, layer: 3E 254 cm	11855 ± 50	13790–13670	13840–3580
RTB 5109	BA05421	Charcoal	T1A, layer: 3E, 255 cm	12735 ± 70	15170–14910	15350–14700
RTB 5114	BA05426	Bone	T1E, layer: 3E 253–258 cm	13425 ± 70	16140–15740	16400–15550
RTB 5465	BA06865	Bone	T11a, layer: 3FH, 252 cm	14695 ± 55	17990–17700	18050–17350
RTB 5463	BA06863	Charcoal	T11c, layer: 3H, 255 cm	14610 ± 55	17900–17510	18000–17150
RTB 5466	BA06866	Bone	T11c, layer: 3H, 257 cm	14835 ± 60	18500 (14.1%) 18350	18550–17750
					18200 (54.1%) 17850	
RTB 5464	BA06864	Charcoal	T11c, layer: 3H, 260 cm	14800 ± 55	18080–17800	18500–17650
RTB 5470	BA06867	Charcoal	T12a, layer: 3H, 260 cm	14795 ± 60	18500 (13.3%) 18420	18600–18000
					18390 (54.9%) 18100	
RTB 5115	BA05427	Bone	T1E, layer: 3I, 260–264 cm	17720 ± 90	21110–20700	21300–20550
RTB 5111	BA05423a	Charcoal	T5, east, 222 cm	12260 ± 60	14160–14040	14230–13980
RTB 5111	BA05423b			12235 ± 50		
	Average			12245 ± 38		
RTB 5116	BA05428	Bone	T5, east, 229 cm	12315 ± 60	14370–14070	14650–14000
RTB 5471	BA06868	Charcoal	T5, 305–314 cm	12825 ± 50	15250−15010	15420–14920

The samples are ordered by stratigraphic depth. The results from the western section (T9, T1, T10-T12) are followed by those from the eastern section (T5). Note that there is a distance of about 5 m between the two areas in the cave.

generally poorly preserved, especially in the eastern part of the cave, which today, at least, is much wetter than the western part (24). We also note that less than half the bones contained acid insoluble collagen. This, too, points to relatively poor preservation conditions for organic matter. Bearing this in mind, we assume that the consistent dates obtained can be attributed to the rigorous prescreening procedures. We did not analyze the radiocarbon contents of any of the samples that were rejected during the prescreening.

The distribution of the dates in the 70–80 cm of the upper part of the ash and red clay deposits reflect a more or less undisturbed accumulation as the series of radiocarbon dates demonstrate an increasingly older age with depth (Fig. 4). This is less clear in the area where most of the potsherds were found in Square T1.

During the 2004 excavation, a sherd was found in sublayer 3E at 255 cm below datum and some 40–50 cm from where the original cluster of reconstructable potsherds were uncovered during the previous excavations. The location is shown in Fig. 1 (arrow *b*). The deposits in T1 between the large boulder and the northern section slope toward the northern wall of the cave and, in addition, were somewhat disturbed. We note that the 2 samples (RTT 5110 and RTT 5108) that are clearly out of the overall stratigraphic order are from this location.

The calibrated ages for sediments associated with the cluster of the pottery in T1 are from 16,950 to 13,580 cal BP with 2 SD

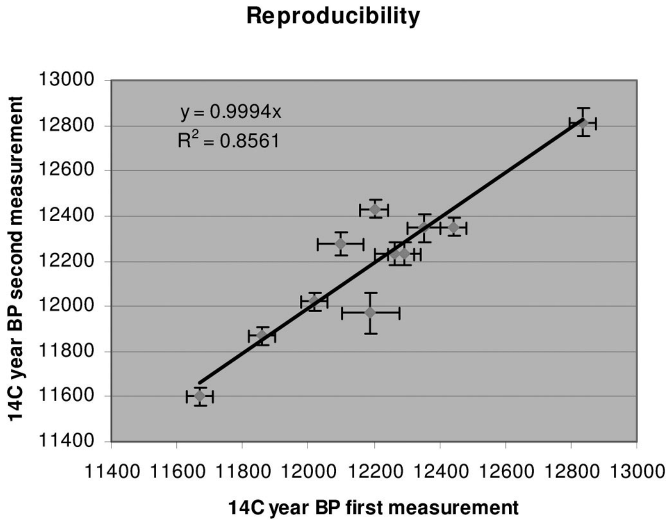

Fig. 3. Plot of the duplicate measurements showing the distribution of the data and the analytical reproducibility. The linear interpolation line with the intercept = 0 and the correlation coefficient are shown in the plot. The data are reported in Table 2.

(RTB 5110, 5107, 5108, 5109, and 5114) (Table 3). The sherd that was found in Square T11 is underlain and overlain by sediments that date between 18,600 and 17,150 cal BP with 2 SD (RTB 5465, 5463, 5466, 5464, and 5470). We note that a charcoal fragment from sublayer 3E that was located just above the cluster of sherds during the previous excavation was dated to 13,680 ± 70, or 16,700–15,850 cal BP (7) (BA95058) (Table 1). A fragment

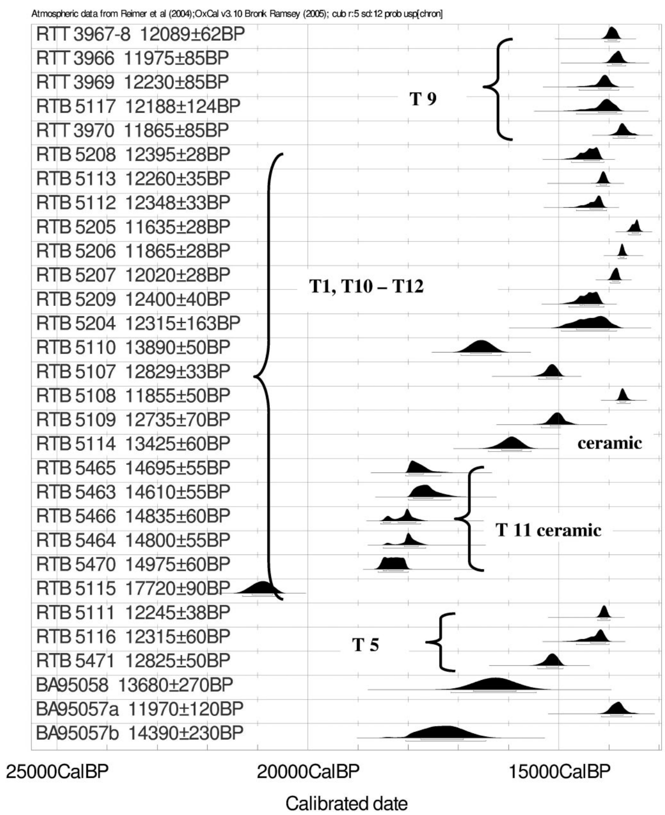

Fig. 4. Age distribution of the samples analyzed from Yuchanyan Cave. The samples are ordered according to stratigraphic depth following Table 3.

of the pot that was dated earlier produced a date of 14,390 ± 230 calibrated as 18,050–15,450 cal BP with 2 SD (BA95057b) (Table 1). Bearing in mind that all of the samples dated were from a 10 cm thick sediment sequence that was rather disturbed, we conclude that the lower limit for the age of the ceramics is around 15,000 cal BP. The upper limit is based on the fragment found in square T11 that is more firmly dated to 18,300 cal BP.

Dates as early as 17,000 to 16,000 cal BP have been conjectured for the earliest pottery in East Asia, such as at the Xianrendong and Diaotonghuan sites in Jiangxi Province, but these could not be confirmed due to ambiguities in the stratigraphic sequences of these sites (8, 20). Our work in dating Yuchanyan Cave differs from previously dated early pottery sites in China in that it is based on high-precision dating the entire sequence of the deposits, and by doing this with small sampling intervals of only a few centimeters in the areas close to where potsherds were excavated. The results obtained allow us to securely date the pottery in Yuchanyan Cave to as early as 18,300 to 17,500 cal BP (1 SD). These dates precede by a thousand ^{14}C years the earliest date of the Incipient Jomon (NUTA-6510 13,780 ± 170 ^{14}C year BP) (35) 16,700–16,100 ± 1 SD and 17,050–15,850 cal BP 2 SD) pottery in the Japanese archipelago (8, 36, 37). This supports the proposal made in the past that pottery making by foragers began in south China.

Materials and Methods

Prescreening in the Field. In the field, samples from well-defined contexts (for example ash lenses) were collected with the associated sediments. All charcoal pieces were collected separately, placed in aluminum foil, and dried before closing. For the bones, preliminary tests were conducted on-site by dissolving a small bone fragment in 1N HCl and then determining if a light insoluble fraction was preserved. The light insoluble fraction indicates, but does not prove, that insoluble collagen is preserved. As only about half the bones did have an insoluble fraction, we collected many more samples for an extensive prescreening in the laboratory.

Prescreening in the Laboratory. All of the samples that were selected in the field based on context and size for radiocarbon dating were subjected to further prescreening procedures to determine the state of preservation and their suitability for dating based on the quality parameters (defined in ref. 31).

Sixty-four bones from squares T1, T4, T5, T9, T11, T12, T14, and T15 were initially checked in the laboratory for mineral crystallinity based on their splitting factor (38). The splitting factors ranged from 2.6 to 3.0, which is close to the value of 2.7 ± 0.2 for modern bone (30). Only one sample had a splitting factor as high as 4. The HCl insoluble fraction was then quantitatively extracted and used to determine if any collagen was present based on infrared spectroscopy. The FTIR spectra of the 1N HCl insoluble fractions indicated that 23 samples showed good preservation of collagen as indicated by the 1645, 1545, and 1450 cm^{-1} Amide I and II and proline peaks respectively. In some of the collagen spectra the presence of collagen and/or humic acid was detected. Therefore after the entire pretreatment procedure, the collagen was again characterized by infrared spectroscopy to ensure that it was pure (31) before target preparation for AMS dating.

Many charcoal samples were collected and prescreened in the laboratory before and after acid and alkali treatment using Raman microspectroscopy to assess humic acid contamination (29, 31) removal, infrared spectroscopy to assess clay contamination (31) and loss of weight. The latter proves to be a good indicator of charcoal preservation (24) and in practice determines the yield of clean charcoal and hence whether or not the sample can be dated. Only samples that were well-preserved and free of detectable contaminants were dated.

Bone and Charcoal Pretreatment for Radiocarbon. Sample pretreatment for bone and charcoal was performed at the Weizmann Institute according to the procedure presented in ref. 31. The cleaning procedure for the collagen samples chosen for dating was based on the AAA technique (39). The bone (2 to 4 g) was ground to powder and homogenized. Ten to 20 ml of 1N HCl were added and after 30 min the sample was centrifuged for 3 min at 3000 rpm. The supernatant was removed and the pellet was washed with distilled water (DW) to pH 7. The pellet was re-suspended in 7 ml of 0.1% NaOH for 15 min and centrifuged again for 7 min at 3000 rpm. The supernatant was removed and the pellet was washed with DW to pH 7. The atmospheric CO_2 adsorbed during the alkali treatment was removed by adding 7 ml of 1N HCl for 30 min and washing the pellet until the supernatant reached pH 3. A few milliliters of solution were left over the pellet.

Gelatinization was achieved by heating the pellet in acid solution pH 3 to 70 °C for 20 h (40). The solution was then filtered through a polyethylene filter (Eezi-filter™) and then by superfiltration (Vivaspin 20). The filtrate was lyophilized (Heto LyoLab 3000) to produce pure dry collagen (41). The quality of the collagen was checked again using infrared spectroscopy.

Charcoal Purification. The cleaning procedure was based on the AAA procedure (39), except that after each step the pellets were dried at 60 °C, weighed, and a few milligrams were taken for infrared and Raman analyses. The alkaline step was repeated between 2 to 3 times depending on the solution color. In the last step after adding the 1N HCl, the solution was placed on a hot plate and heated slowly to 80 °C for an hour, centrifuged, and the pellet was washed with DW to pH 7 and dried at 60 °C.

Monitoring the removal of humic acids from the charcoal samples by Raman spectroscopy is based on the fact that humic acids tend to fluoresce strongly (42). Measurements were made using a Raman Imaging Microscope (Renishaw) through a 50× lens. The excitation at 632 nm was produced by a 25 mw He/Ne laser. Each homogenized sample was measured 10 times at different places, and the spectra were averaged. The spectral resolution was 4 cm^{-1} and the range analyzed was1200–2000 cm^{-1}. For details of the method see ref. 29.

Bone and charcoal samples indicated the highest preservation and provided enough material for the AMS measurement.

Target Preparation and ^{14}C Measurement. The carbon content of the samples was analyzed by Elemental Analyzer-ELEMENTAR, vario EL. Samples were weighed according to their carbon contents and sealed with copper oxide and silver in quartz tubes under vacuum system. The combustion temperature was 850 °C. The CO_2 from the tubes was purified and transferred into the gas container separately. The reduction from CO_2 to graphite was performed with H_2/Fe in a new vacuum line. The new system has 2 graphitization lines, each line has 10 reactors. Fe catalyst is cleaned and activated under 450 °C with O_2 and H_2 separately before reduction (43). The graphite was formed at 540 °C. Magnesium perchlorate is used to trap water (44), and it was replaced for every new sample.

The AMS radiocarbon measurements were carried out on a NEC 1.5SDH-1 0.5MV Pelletron with 40-sample MC-SNICS ion source. The accuracy of this system is better than 0.4% and the machine background is lower than 0.03pMC.

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1. MacNeish RS, Libby JG (1995) *Origins of Rice Agriculture: The Preliminary Report of the Sino-American Jiangxi (PRC) Project SAJOR*. (Univ of Texas, El Paso, TX).
2. MacNeish RS, Cunnar G, Zhao Z, Libby JGA (1998) *Second Annual Report of the Sino-American Jiangxi (PRC) Project SAJOR.*
3. Zhang C (2000) in *Daozuo, Taoqi he Dushi de Qiyuan (The Origins of Rice Agriculture, Pottery and Cities)*, eds Yan W, Yasuda Y (Cultural Relics Publishing House, Beijing), pp. 43–49 (in Chinese).
4. Zhao Z (1998) The middle Yangtze in China is one place where rice was domesticated: Phytolith evidence from Diaotunghuan Cave, Northern Jiangxi. *Antiquity* 36:885–897.
5. Institute of Archaeology (CASS), Guangxi Archaeological Team, Zengpiyan Museum, Guilin Archaeological Team (2003) *Guilin Zengpiyan (The Zengpiyan Cave in Guilin)*, ed Xianguo F (Cultural Relics Publishing House, Beijing) (Chinese with English summary).
6. Yan W (1996) Sekai saiko no doki to inasaku no kigen (The world's earliest pottery and the origins of rice agriculture). *Kikan Kōkogaku* 56:18–21 (in Japanese).
7. Yuan J (2002) Rice and pottery 10,000 years BP at Yuchanyan, Dao County, Hunan Province. *The Origins of Pottery and Agriculture*, ed Yasuda Y (Roli Books, New Delhi), pp 157–166.
8. Kuzmin YV (2006) Chronology of the earliest pottery in East Asia: Progress and pitfalls. *Antiquity* 80:362–371.
9. Lu TL (2006) The occurrence of cereal cultivation in China. *Asian Perspect* 45:129–158.
10. Wu X, Zhao C (2003) Chronology of transition from Paleolithic to Neolithic in China. *The Review of Archaeology* 24, pp 15–20.
11. Yuan S, et al. (1982) The reliability of the radiocarbon ages with the samples from the limestone region and the problem of the radiocarbon dates at Zengpiyan Site. *Acta Archaeologia Sinica* 65:243–250 (in Chinese).
12. Yuan S, et al. (1997) in *Application of Accelerators in Research Industry*, eds Duggan JL, Morgan IL (New York), Vol 392, pp. 803–806.
13. Yuan S, et al. (1995) 14C AMS dating the transition from the Paleolithic to the Neolithic in South China. *Radiocarbon* 37:245.
14. Zhang C (2002) The discovery of early pottery in China. *Documenta Praehistorica* 29:29–35.
15. Zhao C, Wu X (2000) The dating of Chinese early pottery and a discussion of some related problems. *Documenta Praehistorica* 27:233–240.
16. Yuan J (2000) in *Dao zuo tao qi he du shi de qi yuan (The Origins of Rice Agriculture, Pottery and Cities)*, eds Yan W, Yoshinori Y (Cultural Relics Publishing House, Beijing), pp. 31–42 (in Chinese).
17. Zhang W, Yuan J (1998) A preliminary study of ancient excavated rice from Yuchanyan site, Dao County, Hunan Province, P.R. China. *Acta Agronomica Sinica* 24:416–420.
18. Pei A (1998) Notes on new advancements and revelations in the agricultural archaeology of early rice domestication in the Dongting Lake region. *Antiquity* 72:878–885.
19. Hunan Institute of Archaeology (2006) *Hunan Institute of Archaeology and Cultural Relics 2006*. (Science Press, Beijing).
20. Cohen DJ (1998) The origins of domesticated cereals and the Pleistocene-Holocene transition in East Asia. *The Review of Archaeology* 19:22–29.
21. Lu TL (1999) *The Transition from Foraging to Farming and the Origin of Agriculture in China*. (Hadrian Books, Oxford).
22. Lu H, et al. (2000) Variability of East Asian winter monsoon in Quaternary climatic extremes in North China. *Quaternary Research* 54:321–327.
23. Ren G, Beug H-J (2002) Mapping Holocene pollen data and vegetation of China. *Quat Sci Rev* 21:1395–1422.
24. Rebollo NR, et al. (2008) Structural characterization of charcoal exposed to high and low pH: Implications for 14C sample preparation and charcoal preservation. *Radiocarbon* 50:289–307.
25. Yuan J (1996) Yuchanyan huo shui dao qi yuan xin wu zheng (New evidence for the origin of the rice cultivation). *Zhongguo wen wu bao* 8 (in Chinese), p 1.
26. Prendergast ME, Yuan J, Bar-Yosef O (2007) Resource intensification in the Late Upper Paleolithic: A view from southern China. *J Archaeol Sci* 36: 1027–1037.
27. Sherwood SC, Chapman J (2005) The identification and potential significance of Early Holocene prepared clay surfaces: Examples from Dust Cave and Icehouse Bottom. *Southeastern Archaeology* 24:70–82.
28. Berna F, et al. (2007) Sediments exposed to high temperatures: Reconstructing pyrotechnological processes in Late Bronze and Iron Age Strata at Tel Dor (Israel). *J Archaeol Sci* 34:358–373.
29. Alon D, et al. (2002) The use of Raman spectroscopy to monitor the removal of humic substances from charcoal: Quality control for ^{14}C dating of charcoal. *Radiocarbon* 44:1–11.
30. Ziv V, Weiner S (1994) Bone crystal sizes: A comparison of transmission electron microscopic and X-ray diffraction line width broadening techniques. *Connect Tissue Res* 30:165–175.
31. Yizhaq M, et al. (2005) Quality controlled radiocarbon dating of bones and charcoal from the early Pre-Pottery Neolithic B (PPNB) of Motza (Israel). *Radiocarbon* 47:193–206.
32. Bronk-Ramsey C (1995) Radiocarbon calibration and analysis of stratigraphy: The OxCal Program. *Radiocarbon* 37:425–430.
33. Bronk-Ramsey C (2001) Development of the radiocarbon program OxCal. *Radiocarbon* 43:355–363.
34. Weiner S, et al. (2007) in *Kebara Cave Mt Carmel, Israel. The Middle and Upper Paleolithic Archaeology.* eds Bar-Yosef O, Meignen, L (Peabody Museum of Archaeology and Ethnology, Cambridge, MA.), Part I, pp. 131–146.
35. Nakamura T, Taniguchi Y, Tsuji S, Oda H (2001) Radiocarbon dating of charred residues on the earliest pottery in Japan. *Radiocarbon* 43:1129–1138.
36. Keally CT, Taniguchi Y, Kuzmin YV (2003) Understanding the beginnings of pottery technology in Japan and neighboring East Asia. *The Review of Archaeology* 24:3–14.
37. Pearson R (2005) The social context of early pottery in the Lingnan region of south China. *Antiquity* 79:819–828.
38. Weiner S, Bar-Yosef O (1990) States of preservation of bones from prehistoric sites in the Near East: A survey. *J Archaeol Sci* 17:187–196.
39. de Vries HL, Barendsen GW (1954) Measurements of age by the carbon 14 technique. *Nature* 174:1138–1141.
40. Law IA, Hedges REM (1989) A semi-automated bone pretreatment of older and contaminated samples. *Radiocarbon* 31:247–253.
41. Brown TA, Nelson DE, Vogel JS, Southon JR (1988) Improved collagen extraction by modified Longin method. *Radiocarbon* 30:1–7.
42. Yang Y, Wang T (1997) Fourier transform Raman spectroscopy characterization of humic substances. *Vib Spectrosc* 14:105–112.
43. Nadeau MI, et al. (1997) The Leibniz-Labor AMS facility at the Christian-Albrechts University, Kiel, Germany. *Nucl Instrum Meth Phys Res Sect B* 123:22–30.
44. Santos GM, et al. (2004) Magnesium perchlorate as an alternative water trap in AMS graphite sample preparation: A report on sample preparation at the KCCAMS Facility at the University of California, Irvine. *Radiocarbon* 46:165–173.