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AMS ^{14}C DATING USING BLACK POTTERY AND FIBER POTTERY

Shozo Mihara[1,2] • Kazuo Miyamoto[3] • Hidefumi Ogawa[4] • Teiji Kurosaka[5] • Toshio Nakamura[6] • Hiroko Koike[1]

ABSTRACT. A technique of accelerator mass spectrometry (AMS) has made it possible to directly measure radiocarbon ages of pottery by isolating organic materials sealed in the pottery when the pottery was formed. We analyzed the carbon contents and ^{14}C ages for "black pottery" from the Philippines and "fiber pottery" from Japan using the relevant carbonaceous materials extracted from the pottery samples, i.e., adhered chaff or grass fibers that were incorporated in the pottery matrix, respectively. The carbon yield of the pottery sample varied largely depending on the pottery types, the preservation conditions, as well as the chemical pretreatment methods to purify carbonaceous materials for ^{14}C dating. We will discuss criteria for sample selection of well-preserved pottery, and a modified method, instead of the standard alkali treatment, to obtain sufficient material for precise ^{14}C dating.

INTRODUCTION

Radiocarbon ages for pottery have previously been measured on charcoal blocks and shell fragments existing in association with the pottery in the sedimentary layers (Kuzmin et al. 1997) or on carbonized materials such as soot and charred food residues on pottery surfaces (Nakamura and Iwahana 1990; Nakamura et al. 1990; Kolic 1995; Nakamura et al. 2001; Oda and Yamamoto 2001). However, there are 2 possibilities in ^{14}C age offsets for these sample types. First, soot extracted from exterior surfaces of the pottery may have been deposited during pottery firing using wood of unknown age, which could possibly introduce a ^{14}C reservoir effect. Secondly, carbonized materials on interior surfaces are usually from foods, and unless the types of foods that were processed in these vessels are known, they could introduce an offset such as a "marine reservoir effect" from cooking marine foods. In this study, instead of using soot or charred food residues, we have targeted short-lived organic materials, either sealed in the matrix of pots (grass) or deposited on the pot surface when they were fired (chaff). These types of organic temper are considered to be reliable materials for ^{14}C dating (Hedges et al. 1992).

We examined "black pottery" from the Philippines and "fiber pottery" from Japan, and extracted the respective carbon contents, using these to determine ^{14}C ages. Black pottery (Figure 1) is distributed from China to Southeast Asia, and is still produced today at San Nicolas, Northern Luzon, the Philippines. Raw pottery is fired in a pit in the ground using wood for fuel. After the pottery turns red, it is covered with a large amount of chaff (husks of rice or millet) which chars on the pottery surface to produce a black, carbon-adsorbed coloring. Pottery fragments containing the carbon that was transferred from chaff were selected for ^{14}C dating.

Black pottery samples came from excavations at the Lal-lo shell midden sites located in the lower basin of the Cagayan River, Northeast Luzon. In this area, the shell midden layer on the river terrace yielded black pottery assigned to the Iron Age in the Philippines, and the silt layers under the shell midden layer yielded the red pottery belonging to the Pre-Iron Age (Ogawa 2000).

[1]Graduate School of Social and Cultural Studies, Kyushu University, 4-2-1, Ropponmatsu, Chuo-ku, Fukuoka, Japan.
[2]Corresponding author. Email: cs200027@scs.kyushu-u.ac.jp.
[3]Faculty of Humanities, Kyushu University, 6-19-1, Hakozaki, Higashi-ku, Fukuoka, Japan.
[4]Dept. of Philippine Studies, Tokyo University of Foreign Studies, 3-11-1, Asahi-machi, Fuchu, Tokyo, Japan.
[5]Saitama Cultural Deposits Research Corporation, 4-4-1, Funakidai, Ohzato, Saitama, Japan.
[6]Dating and Materials Research Center, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8602 Japan.

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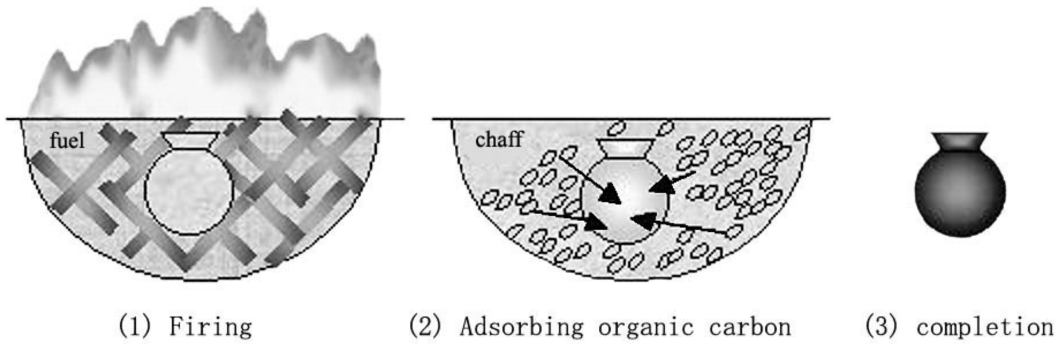
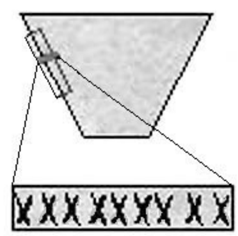


Figure 1 Fired pottery (1) in China and Philippines adsorbs carbon from organic materials such as chaff (2) and is stained black (3). This method was evident in San Nicolas in the Philippines where the black pots are now made.

The fiber pottery samples were collected from the Myouonji cave site, Saitama prefecture, Japan. Fiber pottery (Figure 2) is a class of Jomon pottery that contains charred fibers within the pot matrix. The fiber pottery was produced during the Earliest and Early Jomon periods, and was distributed mainly in central Japan. To make fiber pottery, grasses such as *Gramineae*, which are rich in silica, were mixed into the clay in order to strengthen the pottery matrix. After firing, charred grass fibers remain in the pottery, and it is possible to isolate these residues for AMS dating (Kuzmin et al. 2001). Fiber pottery has previously been analyzed by Yoshida et al. (forthcoming) and is known to give reasonable ages for selected carbonaceous materials after an acid-alkali-acid (AAA) treatment.

Figure 2 Fiber pottery contains charred fibers within the pot matrix.



MATERIALS AND METHODS

The pottery samples used here are the following: a) modern black pottery shards that were obtained at San Nicolas for a check on our carbon extraction methods and a reliability test of dating this type of sample; b) Philippine Black Pottery I, which was excavated from a cultural layer between the Red Pottery II and Black Pottery II; and c) Japanese Jomon pottery in 4 styles: 1) Todo-Kasou, 2) an unidentified type of pottery decorated with incised lines, 3) Sekiyama, and 4) Kurohama.

Surface dirt was removed from all pottery samples with a dental disk. Powder samples were then taken from the cleaned pottery sherds and were chemically treated by AAA to remove acid and alkali soluble materials, such as humic acids and fulvic acids which may have been incorporated from burial soil. The AAA treatment consisted of successive cleaning by 0.1N HCl at 80 °C, 0.1N NaOH at 80 °C, and again by 0.1N HCl at 80 °C. The residues were rinsed to neutral and dried.

After being chemically treated, the charred materials were analyzed for carbon content and $\delta^{13}C$ using an automated nitrogen and carbon analysis mass spectrometer (ANCA-MS, Europa Scientific Ltd). Analyses were done on 2 sets of 10-mg fractions from each pottery sample, and the average was calculated.

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For AMS analysis, samples of the pretreated charred material containing about 2 mg of carbon were combusted at 850 °C for 4 hr in evacuated and sealed Vycor tubes together with CuO and Ag. The CO_2 was then purified cryogenically (using normal-pentane slush at –130 °C and ethanol slush at –90 °C) on a vacuum line. The purified CO_2 samples were then reduced to graphite (Kitagawa et al. 1993). The graphite samples were measured against a standard (NBS-II) using the Tandetron AMS (Model-4130 AMS, HVEE) at Nagoya University (Nakamura et al. 2000). We corrected for carbon isotopic fractionation using the $\delta^{13}C$ values provided by the AMS.

RESULTS

Significant differences were observed in carbon content among all samples (0.21% to 0.77%; Table 1). The carbon contents of the Philippine Black pottery samples were 0.51% in the modern sample, and from 0.23% to 0.45% in the archaeological samples. In fiber pottery of the Japanese Jomon period, carbon contents were 0.39% and 0.21% for 2 badly preserved samples, and from 0.33% to 0.77% for the better preserved samples (Table 1). Pottery matrix including charred carbon was lower for the badly preserved samples and yielded a lower carbon content. It is not easy to explain the large variation of extracted carbon, which may be due to chemical pretreatment procedures. The concentration of NaOH in the standard AAA procedure may cause a varying loss of organic carbon. In addition, the large variation in extracted carbon yields may also depend upon the preservation condition of the material and the amount of material used for treatment.

The ^{14}C ages obtained for the different types of pottery appear to confirm the reliability of chaff residues as a target material for dating. Chronologically, both black pottery and red pottery appears to have changed from a decorated type (I) to a non-decorated type (II). The calibrated calendar age of the Black Pottery II phase is already known to be from 1800 cal BP to 1000 cal BP, and that of the Red Pottery II phase is older than 3000 cal BP (Mihara et al. 2002). Samples in this study are of the decorated type (I) and belong to the cultural layer between the Red Pottery II and Black Pottery II.

^{14}C ages for the 2 Black Pottery I samples are 2170 ± 30 BP and 2290 ± 30 BP (2310–2095 cal BP and 2350–2180 cal BP; Figure 3). For the Japanese fiber pottery samples, the Todo-Kasou style pottery was dated to 8660 ± 45 BP (9770–9535 cal BP). The unidentified pottery type was dated to 7855 ± 45 BP (8780–8540 cal BP), the Sekiyama type to 7220 ± 40 BP (8110–7940 cal BP), and the Kurohama type to 7540 ± 45 BP and 6540 ± 45 BP (8405–8205 and 7560–7330 cal BP) (Figure 4).

DISCUSSION

This is the first report applying AMS to directly dating the Black Pottery I phase; no other ^{14}C ages have been published for this phase. The possibility of using AMS to date these black pottery samples should enable researchers to establish a more detailed chronology.

Two ^{14}C ages for Black Pottery I samples, a decorated type, are consistent with the archaeological interpretation that Black pottery I belongs to the cultural phase between Red Pottery II and Black Pottery II.

The variation in carbon recovery for both black pottery and fiber pottery samples suggests that there is a possibility for improvements in carbon yield, and in particular, the alkali treatment method, perhaps in the concentrations of NaOH solution. The alkali treatment at lower concentrations than 0.1N, possibly 0.05N, may preserve more residual organic carbon in the sample, and a higher carbon recovery would also provide greater amounts of material for ^{14}C dating.

Table 1 Carbon contents and ^{14}C ages for pottery samples.

Sample nr	Sample	Site	Type	Preservation state	Carbon content (%)	$\delta^{13}C$ (‰)	Size of graphite	Conventional ^{14}C age (BP)	Calibrated ^{14}C age (cal BP)	(%)[a]	Lab # (NUTA2-)
01PO18	black pottery	San Nicoras, Philippines	—	hard	0.51	—	—	modern	1990s		—
01PO13	black pottery	Bangag I, Philippine	Black Pottery I	hard	0.31	—	1.77 mg	2170 ± 30	2310–2220 2185–2095	45 46	5367
01PO14	black pottery	Bangag I, Philippines	Black Pottery I	hard	0.23	—	1.30 mg	2290 ± 30	2350–2300 2245–2180	60 37	5368
01PO21	fiber pottery	Myouonji Cave, Japan	Tado kasou	fragile	0.39	–26.2	0.95 mg	8660 ± 45	9770–9535	100	5983
01PO25	fiber pottery	Myouonji Cave, Japan	unidentified[b]	hard	0.33	–24.7	1.03 mg	7855 ± 45	8900–8830 8780–8540	6 89	5991
01PO27	fiber pottery	Myouonji Cave, Japan	Sekiyama	hard	0.36	–23.9	1.37 mg	7220 ± 40	8110–8075 8065–7940	19 76	5992
01PO28	fiber pottery	Myouonji Cave, Japan	Kurohama	fragile	0.21	–23.2	1.02 mg	7540 ± 40	8405–8290 8260–8205	81 19	5984
01PO29	fiber pottery	Myouonji Cave, Japan	Kurohama	hard	0.77	–24.3	1.11 mg	6540 ± 40	7560–7535 7510–7415 7395–7370 7350–7330	11 77 7 5	5985

[a]Percentage of main peak in the probability distribution of calibrated age.
[b]An unidentified pottery type decorated with incised lines.

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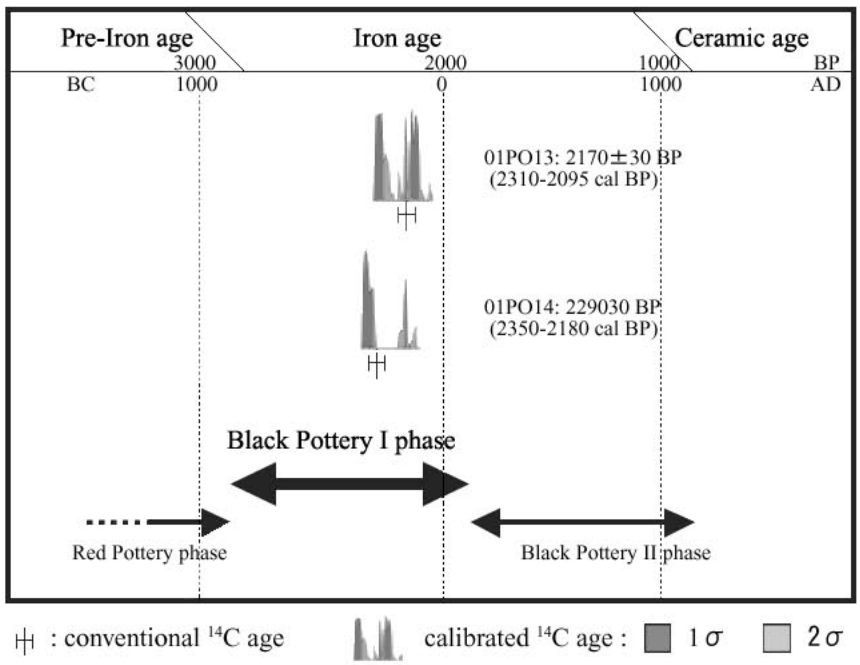

Figure 3 ^{14}C ages for the Black Pottery I from Lal-lo shell midden sites, the Philippines. The ages of the Red Pottery II phase and Black Pottery II phase were analyzed from bone and charcoal samples (Mihara et al. 2002).

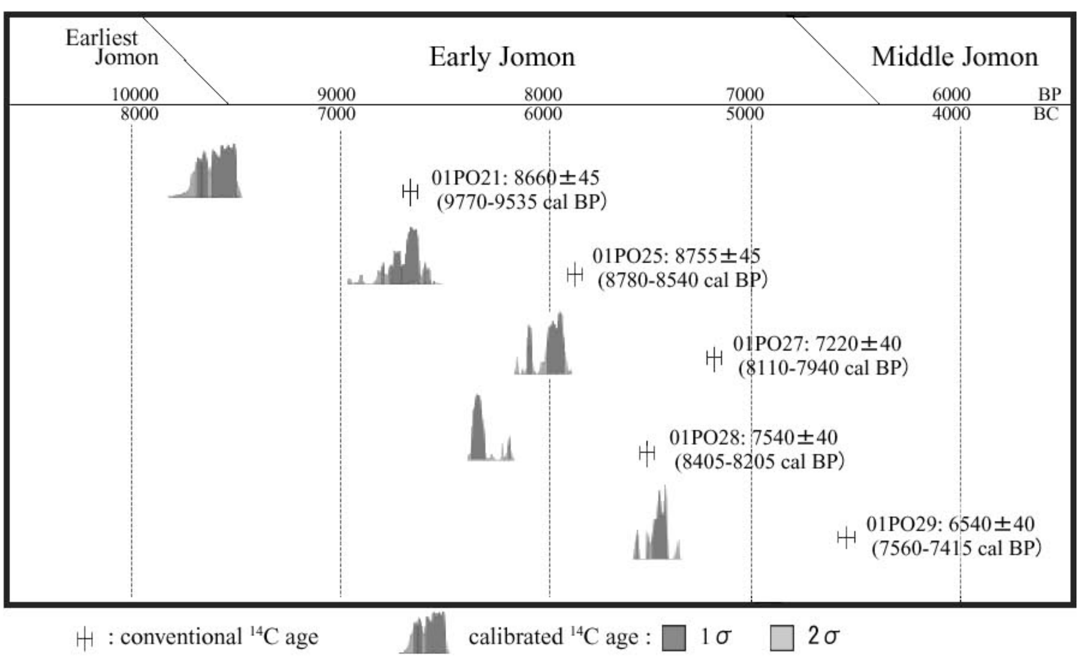

Figure 4 ^{14}C ages for fiber pottery in Myouonji Cave site, Japan, during the Jomon period

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^{14}C ages for the Japanese fiber pottery samples fluctuated largely. One of the fiber pottery samples (01PO28) belonging to the Kurohama style was older than the sample from the Sekiyama style which appeared before the Kurohama type. The anomalous date was for the Kurohama sample which was badly preserved and showed the lowest carbon content at 0.21%. The source of an older carbon contaminant which might have caused the ^{14}C age offset has not been identified.

We are now applying this method for analyzing black pottery from China, which is thought to be the origin for black pottery in Southeast Asia. We will also extend our research using this method to other black pottery samples and fiber pottery samples.

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