

Difference in radiocarbon ages of carbonized material from the inner and outer surfaces of pottery from a wetland archaeological site

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Abstract: AMS (Accelerator Mass Spectrometry) radiocarbon dates for eight potsherds from a single piece of pottery from a wetland archaeological site indicated that charred material from the inner pottery surfaces (5052 ± 12 BP; $N = 5$) is about 90 ^{14}C years older than that from the outer surfaces (4961 ± 22 BP; $N = 7$). We considered three possible causes of this difference: the old wood effect, reservoir effects, and diagenesis. We concluded that differences in the radiocarbon ages between materials from the inner and outer surfaces of the same pot were caused either by the freshwater reservoir effect or by diagenesis. Moreover, we found that the radiocarbon ages of carbonized material on outer surfaces (soot) of pottery from other wetland archaeological sites were the same as the ages of material on inner surfaces (charred food) of the same pot within error, suggesting absence of freshwater reservoir effect or diagenesis.

Keywords: radiocarbon dating, carbonized material adhering to pottery, freshwater reservoir effect, diagenesis, wetland archaeological site

1. Introduction

Charred material adhering to pottery has been used frequently for radiocarbon dating at archaeological sites. Carbonized materials from the inner and outer surfaces of pottery are different in origin, so caution is necessary in some cases when interpreting their ages. Materials adhering to outer surfaces of pottery consist mainly of soot derived from the firewood used as fuel, whereas materials adhering to inner surfaces of pottery are composed mainly of charred food residues. In this study we examined radiocarbon dates of materials from the inner and outer surfaces of potsherds from the Irienaiko

archaeological site, which is an Early Jomon site at Lake Biwa, Shiga Prefecture, Japan.¹⁾ In this study, we investigated the phenomenon of different radiocarbon ages observed on the inner and outer surfaces of potsherds from the Irienaiko site and from other Japanese wetland archaeological sites.

Most Japanese archaeologists consider the age of pottery recovered from archaeological sites in terms of typology. They use the stratigraphic order of appearance of pottery types to define a pottery-type series and then use the position of a potsherd within that series as a measure of its relative age. They estimate the ages of other archaeological remains from the same excavation layer by reference to the position in the pottery-type series of potsherds in that layer.

On the other hand, a research group at the National Museum of Japanese History (NMJH) has measured radiocarbon ages of carbonized material adhering to pottery to determine the absolute age (radiocarbon ages) of each pottery type in a pottery-type series, thus making it possible to estimate ages more accurately by reference to the ^{14}C calibrated age curve. They have found that the calibrated ages are generally in agreement with the chronological order estimated from the pottery-type series (Fig. 1),^{2)–4)}

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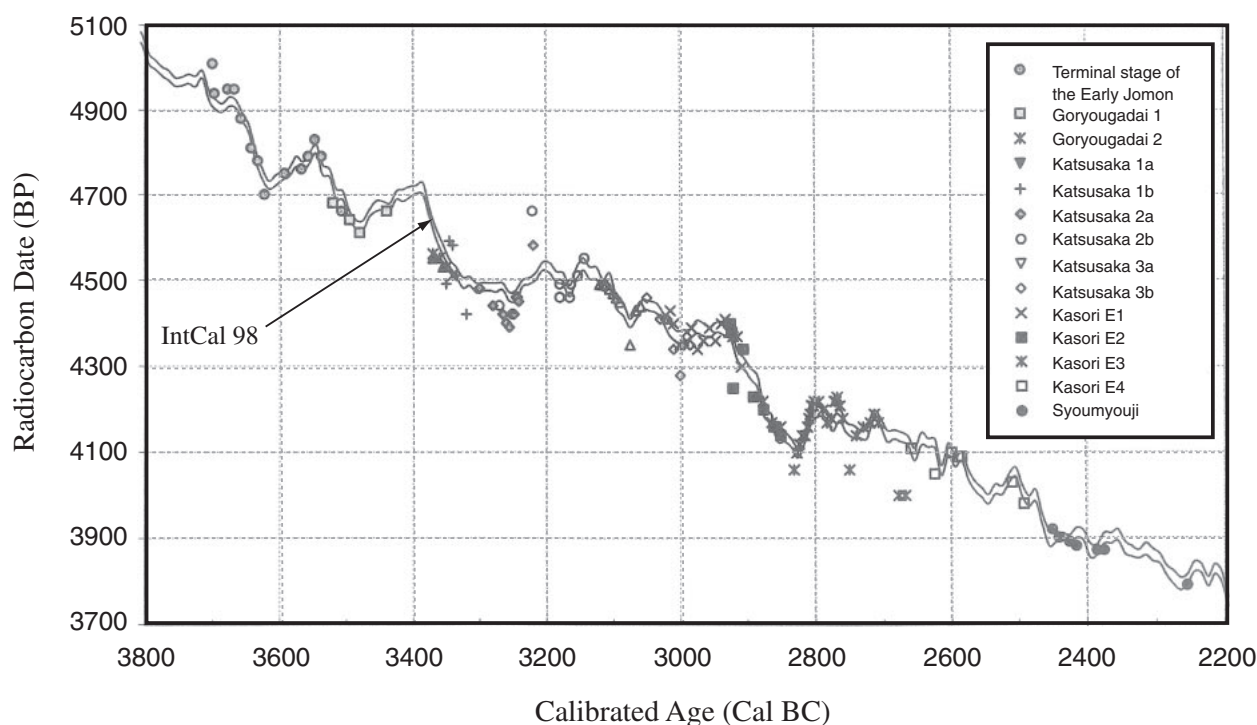


Fig. 1. Relationships among radiocarbon ages, calibrated ages, and pottery-type classification of Middle Jomon pottery from the Kanto and Chubu regions (modified from Imamura *et al.*, 2001).²⁾

but they have reported that the time span represented by a particular type of earthenware vessel, which was previously thought to differ little among pottery types, varies from 20 to 80 years. Consequently, dating of material adhering to pottery has made it possible to evaluate the ages of archaeological material on a more detailed time scale than was possible using previous relative archaeological dating methods.³⁾ For example, the NHJH research group used this new technique to show that the real age of the beginning of the Yayoi period may be 500 years earlier than previously believed.^{5),6)} Similarly, based on the precedent study of a research group at Nagoya University,^{7),8)} our group has used this new approach to obtain a precise estimate of the age of appearance of the mounded tomb (Kofun) that differs from previous estimates made using conventional methods.⁹⁾

In view of these radiocarbon dating advances discussed above, ¹⁴C calibration curves and pottery-type series data, which together allow elucidation of Japanese history on a time scale of a few decades, it is very important not only to understand the cause of any difference in radiocarbon age between the inner and outer surfaces of the potsherds from the Irienaiko site but also to evaluate which radiocarbon age corresponds to the time that the food was cooked in

the pot. Moreover, similar age differences between the two sides of potsherds from other Japanese wetland archaeological sites also require explanation.

2. Samples and methodology

The Irienaiko archaeological site (35°18'45"N, 136°16'30"E; Fig. 2) is in the central part of Honshu, the main island of Japan. The site lies on a wetland on the eastern side of Lake Biwa that has been alternately inundated and exposed as the lake has expanded and contracted. The Irienaiko archaeological site was first occupied in the Jomon period, when a dry land surface became available along that part of the lakeshore.

We analyzed samples of charred material from the inner and outer surfaces of eight potsherds from a single "Kitashirakawa-kasou IIc type" pottery piece from the Early Jomon period.

Sample preparation were carried out at the Radiocarbon Dating Materials Laboratory, NMJH, and are summarized as follows.^{10),11)} The charred materials taken from the potsherds were mixed well and washed with an ultrasonic using acetone. The samples, then, were prepared by the acid-alkali-acid (AAA) treatment. Each sample was reacted 2 or 3 times with 1 N HCl, 1–2 times with 0.1 N NaOH, 4–5

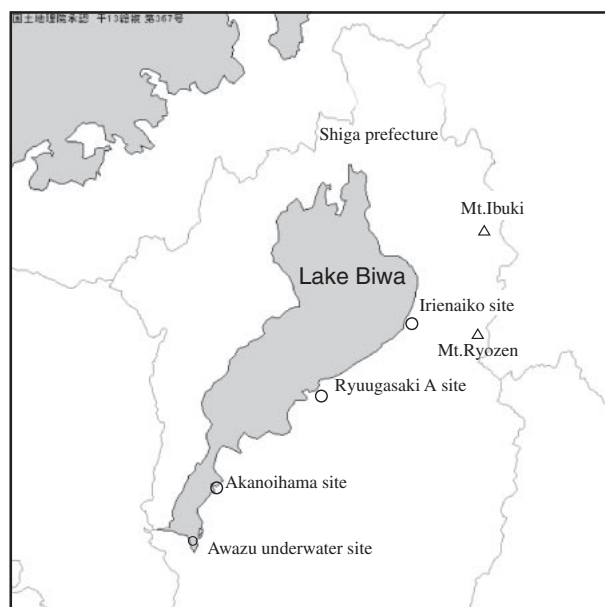


Fig. 2. Map showing the Irienaiko archaeological site near Lake Biwa in Shiga Prefecture, Japan.

times with 1 N NaOH, and 2 times with 1 N HCl for 1 h at 80 °C. The purified sample was then neutralized, washed with pure H₂O, filtered, and dried. The samples were then sent to Paleo Labo Inc., Gifu, Japan, where they were combusted with CuO at 850 °C for 3 h in a sealed quartz glass tube to produce CO₂ gas, which was then purified in liquid N₂ and EtOH-Liquid N₂ traps. The purified CO₂ gas was reduced to graphite with an iron powder catalyst. The graphite (plus iron powder) was then pressed into targets and analyzed at the Compact AMS facility of Paleo Labo Inc., Gunma, Japan.¹²⁾ For one sample (SGMB 4233b), CO₂ gas purification and reduction to graphite were done at NMJH and the AMS analysis at the Micro Analysis Laboratory Tandem accelerator (MALT) at the University of Tokyo.¹³⁾ Stable carbon and nitrogen isotope compositions of the carbonized material after AAA treatment were measured at SHOKO Co. Ltd., Saitama, Japan, with an elemental analyzer mass spectrometer equipped with a continuous flow system (EA1110 and a Thermo Electron Delta Plus Advantage). Carbon and nitrogen isotope results are reported in per mil notation relative to V-PDB for $\delta^{13}\text{C}$ and relative to air for $\delta^{15}\text{N}$.

3. Results and discussion

First, we considered the radiocarbon ages and the C and N chemistry (Table 1) of the charred

material, excluding analytical results for sample SGMB-4232b, as explained below.

The chemical composition of the material on the inner surfaces clearly differed from that of the material on the outer surfaces. The $\delta^{13}\text{C}$ values of the materials from the inner and outer surfaces were similar, but $\delta^{15}\text{N}$ values of the inner surface material were about half the magnitude of those of the outer surface material. Carbon contents of inner materials were about 10% lower than those of outer materials, and nitrogen contents of inner materials were about twice those of outer materials. Thus, C/N ratios of inner materials were about half those of outer materials, indicating that the inner surface materials probably originated either from some animal or plant foodstuffs such as yam and bean, cooked in the pot.

The chemical composition of sample SGMB-4232b, which was from the outer surface, was similar to that of the other outer surface samples, but the radiocarbon age of this sample was similar to those of the inner surface samples.

The radiocarbon ages of the carbonized materials clearly differed between the inner and outer surfaces of the potsherds (Fig. 3). Material from the inner surface (mean age 5052 ± 12 BP; $N = 5$) was about 90 ¹⁴C years older than that from the outer surface (mean age 4961 ± 22 BP; $N = 7$). Only one pair of radiocarbon dates from the inner and outer surfaces of a single potsherd did not clearly show the 90 ¹⁴C age difference because the age difference was less than the radiocarbon measurement error of ± 25 –40.

We calibrated the radiocarbon data set given in Table 1 (Fig. 3) using the RHcal 3.2 program¹⁴⁾ based on IntCal09 data.¹⁵⁾ When sample SGMB-4232b is excluded, the calibrated dates of material from the inner surfaces are older than 3800 cal BC, whereas those of material from the outer surfaces are younger than 3800 cal BC (Fig. 4). These results strongly suggest that the carbonized materials from the inner and outer pottery surfaces are of different origin. Although sample SGMB-4232b was from the outer surface, both its calibrated and radiocarbon ages were similar to those of the inner surface sample. As we could not explain these age results for sample SGMB-4232b, we excluded them from further consideration.

We now consider three possible causes of the observed age differences of charred matter from the inner and outer potsherd surfaces: the old wood effect, reservoir effects, and diagenesis.

Table 1. Comparison of radiocarbon ages and the carbon and nitrogen chemistry of charred materials from the inner and outer surfaces of pottery sherds from the Irienaiko archaeological site.

Sample No.	Lab. No.	^{14}C age BP ($\pm 1\sigma$)	$\delta^{13}\text{C}$ ‰	$\delta^{15}\text{N}$ ‰	C %	N %	C/N ratio
<u>Inner surface</u>							
SGMB-4232a	PLD-5314	5055 ± 25	-26.9	7.5	56.3	6.2	9.1
SGMB-4233a	PLD-5316	5040 ± 25	-27.5	7.3	49.6	5.4	9.2
SGMB-4236a	PLD-5319	5065 ± 25	-27.1	5.9	57.3	6.1	9.4
SGMB-4238a	PLD-5322	5060 ± 25	-27.2	7.0	52.0	5.8	9.0
SGMB-4239a	PLD-5324	5040 ± 30	-26.8	5.8	54.8	6.2	8.8
Mean ($\pm 1\sigma$)		5052 ± 12	(N = 5)				
<u>Outer surface</u>							
<i>SGMB-4232b</i>	<i>PLD-5315</i>	<i>(5035 \pm 25)</i>	<i>-25.5</i>	<i>11.0</i>	<i>66.8</i>	<i>4.3</i>	<i>15.5</i>
SGMB-4233b	MTC-06987	4975 ± 35	—	—	—	—	—
SGMB-4234a	PLD-5317	4980 ± 25	-25.5	13.3	64.1	3.9	16.4
SGMB-4234b	PLD-5318	4955 ± 25	-25.6	13.6	65.6	3.7	17.7
SGMB-4236b	PLD-5320	4980 ± 25	-25.4	12.2	62.8	2.7	23.3
SGMB-4237b	PLD-5321	4920 ± 25	-25.5	11.7	66.2	3.9	17.0
SGMB-4238b	PLD-5323	4950 ± 30	-25.0	11.7	67.8	3.5	19.4
SGMB-4239b	PLD-5325	4970 ± 30	-25.9	11.8	62.5	3.5	17.9
Mean ($\pm 1\sigma$)		4961 ± 22	(N = 7)				

*SGMB-4232b was excluded from the statistical calculations.

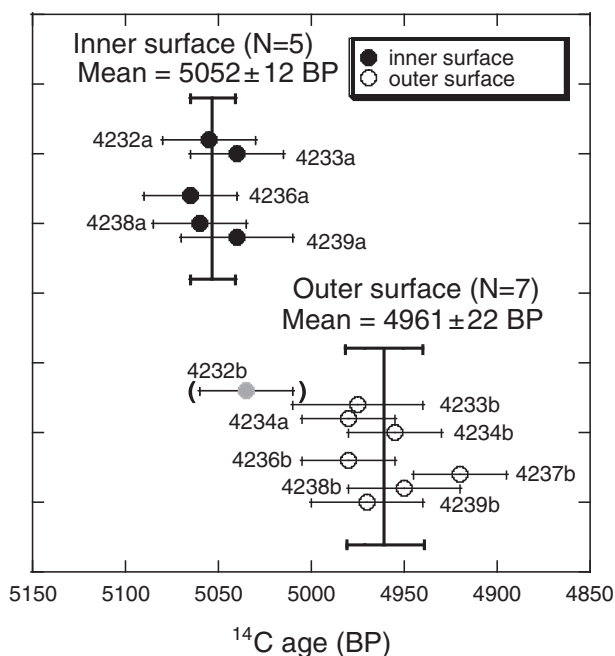


Fig. 3. Differences in radiocarbon ages of carbonized materials from the inner and outer surfaces of potsherds from the Irienaiko archaeological site. Sample SGMB 4232b was excluded from the statistical calculations.

3.1. Old wood effect. First, it is quite likely that the outer materials adhering to pottery were composed mainly of soot, derived from the firewood used as fuel. Thus, the radiocarbon ages of the charred material from the outer surface may not represent the real age of the pot. This might be the case, for example, if 500-year-old heartwood was used for fuel to heat the pottery vessel; in that case, the soot adhering to the outer surface would yield a radiocarbon age much older than the time at which the pot was used. This effect is known as the “old wood effect.” However, there is no evidence of the old wood effect in the radiocarbon data obtained at NMJH.^{6),16)}

The relationships between radiocarbon ages and $\delta^{13}\text{C}$ values of carbonized matter from the outer surfaces of Jomon and Yayoi pottery and the ^{14}C calibration curve from 3000 to 2000 BP are shown in Fig. 5.¹⁵⁾ The ^{14}C calibration curve (Fig. 5, right)¹⁶⁾ shows sudden changes in the concentration of ^{14}C in the atmosphere at about 800 BC and about 380 BC, corresponding to 2700–2600 BP and 2400–2300 BP, respectively. For these periods, the number of radiocarbon data points is low, so the gaps (blank areas) in the radiocarbon data are not unexpected. The atomic ratios (C/N) and the carbon and nitrogen stable

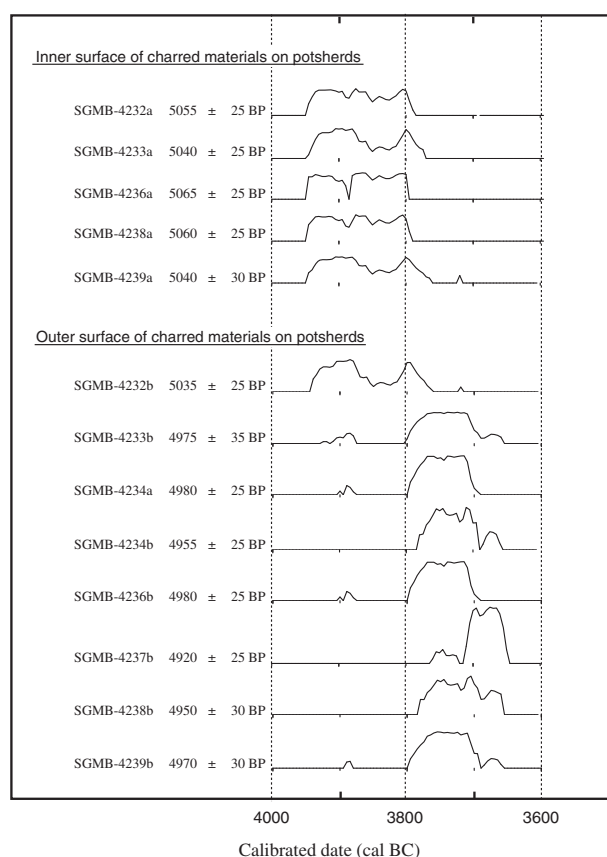


Fig. 4. Differences in the calibrated ages of carbonized material from the inner and outer surfaces of potsherds from the Irienaiko archaeological site.

isotopic composition ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) of the charred materials from the inner and outer surfaces of potsherds from the Jomon and Yayoi periods indicate that the material on the outer surfaces is of similar chemical composition in all areas of Japan except North Tohoku and Hokkaido.¹⁷⁾ This finding may suggest that dead tree branches were used for fuel during these periods. Moreover, wood samples from C_3 plants (*i.e.*, most trees) usually have $\delta^{13}\text{C}$ values of -25‰ to -27‰ (Fig. 5, left). Gaps in the radiocarbon data for materials on the outer surface of potsherds correspond to the jumps in the calibration curve at about 2650 BP and 2350 BP in the ^{14}C calibration curve (Fig. 5, right). These observations imply that the old wood effect had minimal impact on the radiocarbon dating results for carbonized material from the outer surfaces of potsherds.¹⁶⁾ In fact, the age difference we observed is the reverse of that which would be caused by the old wood effect.

3.2. Reservoir effects. It is well known that reservoir effects can cause radiocarbon ages determined from charred material on the inner surface of potsherds (food residues) to be several hundred years older than the real age of the pot.^{6),11)} For example, if charred residues of foods of marine origin cooked in the pottery vessel were left on the inner surface of the vessel, the dates obtained would show a marine reservoir effect. Because ^{14}C concentrations in surface waters of the northwestern Pacific are substantially depleted compared to those typical of surface waters

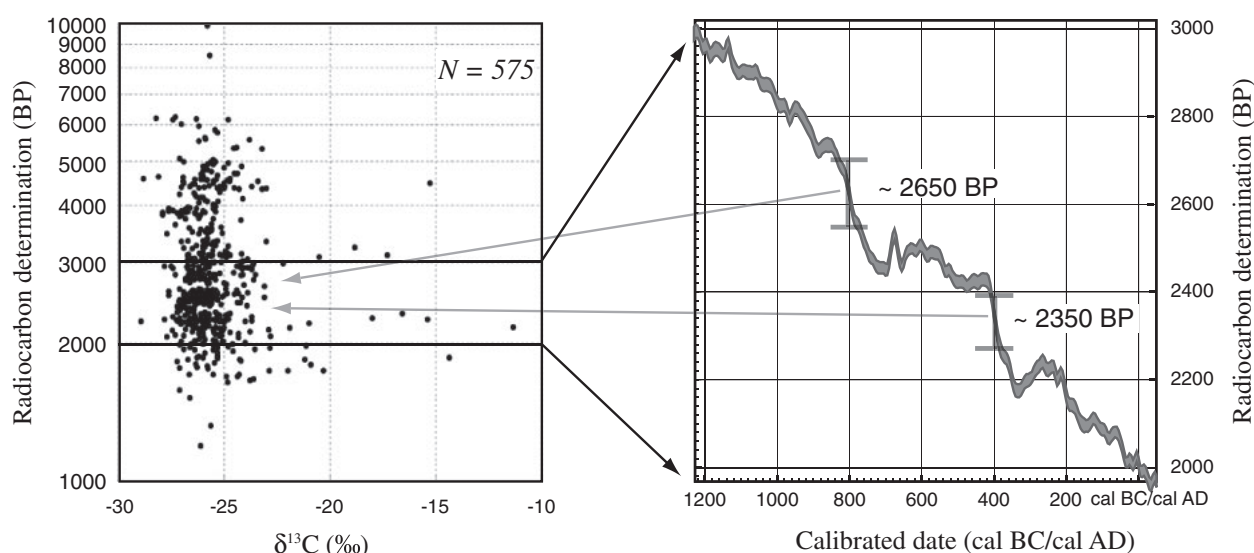


Fig. 5. Relationship between radiocarbon ages and $\delta^{13}\text{C}$ values of carbonized materials from the outer surfaces of potsherds, and the ^{14}C calibration curve from 3000 to 2000 BP (modified from Imamura and Sakamoto, 2008).¹⁶⁾

worldwide,^{18),19)} charred residues of marine food from the northwestern Pacific found on the inner surfaces of pottery yield radiocarbon ages that are older than the real age. Stable carbon isotope ratios ($\delta^{13}\text{C}$) can be used to determine whether the charred material is of oceanic origin because $\delta^{13}\text{C}$ values of marine organisms typically range from -21‰ to -23‰ . The $\delta^{13}\text{C}$ values of the charred materials from the inner pottery surfaces of this study, however, were less than -26‰ , a value which is typical of material of terrestrial origin. Therefore, the marine reservoir effect can be ruled out as a cause of the radiocarbon age differences that we observed.

A great deal of organic matter flows into Lake Biwa, and very old radiocarbon ages can result from the retention of old carbon in peat layers formed from plants such as the ditch reeds that grow along the lakeshore. Radiocarbon ages may also be affected by a freshwater reservoir effect. At Lake Biwa, a reservoir effect can result from the inflow of aged subsurface waters containing dissolved old carbon from the carbonate rocks of Mt. Ibuki and Mt. Ryozen (Fig. 2). For example, sediment samples from 3–4 cm below the lake floor in Lake Biwa collected in November 1984 (sediments at this depth have a ^{210}Pb age of about 1950 AD and thus were unaffected by atmospheric nuclear tests) showed $\Delta^{14}\text{C}$ values of -250‰ to -230‰ , corresponding to a radiocarbon age of 2200–2400 BP.²⁰⁾

Nakamura *et al.*²¹⁾ measured radiocarbon ages of wood, mammalian bone, and fossil shells (*Corbicula sandai*) collected from a single layer of a shell mound at the Awazu underwater archaeological site at the southern end of Lake Biwa (Fig. 2). They found that the ^{14}C dates were systematically different among the three types of samples: fossil shells showed the oldest ages (about 4900 BP), mammalian bones the youngest ages (about 4300 BP), and the wood sample ages were in between (about 4600 BP). Minami and Nakamura²²⁾ remeasured the radiocarbon ages of the mammalian bone collagens from this site after first decalcifying and hydrolyzing the bone samples, and then extracting amino acids from the acid-insoluble residues and purifying them using XAD-2 resin. After this treatment, the remeasured radiocarbon ages of the bone collagen were close to those of the wood samples, suggesting that the radiocarbon ages initially obtained for the mammalian bone samples had been affected after burial by younger carbon (such as fulvic acid).

Assuming that the radiocarbon dates of the wood samples are consistent with their archaeological

context, then those of the fossil *Corbicula sandai* may have been affected by old carbon in Lake Biwa. *Corbicula sandai* inhabit areas of a few meters water depth and use dissolved calcium and inorganic carbon in the lake water to grow their calcium carbonate shells. Therefore, the radiocarbon age of the carbonate of their shells very likely reflects that of the dissolved inorganic carbon in the lake water. The difference in the radiocarbon ages between the fossil shells and the wood samples suggests that the freshwater reservoir effect manifested in the Middle Jomon period at Lake Biwa. Because the present-day average residence time of Lake Biwa water is less than a decade, its direct influence on the reservoir effect is small, which suggests that old carbon has been supplied into Lake Biwa.

If the food residues on the inner potsherd surfaces included freshwater fish and mollusks affected by the freshwater reservoir effect, then the carbonized material on the inner surfaces of potsherds would be expected to yield older ages than that on the outer surfaces.²³⁾

3.3. Diagenesis. It is possible that secondary matter such as soil contaminated the samples and caused the radiocarbon age of the material on the inner surfaces of the potsherds to be older. The soot coating the outer potsherd surfaces consisted mainly of completely carbonized material that originated from the wood burnt as fuel, whereas the charred food residues on the inner potsherd surfaces were produced by the complete evaporation of the cooking water in the pot.

Charred food residues on the inner surfaces of potsherds may have been less carbonized than the soot coating the outer potsherd surfaces because the food in the pots was not directly exposed to the fire and may not have been evenly burnt. At the end of its useful life, the pottery was likely thrown away and it remained in the soil for several thousand years. Decomposition and assimilation by soil microbes would have had a much greater effect on the less-carbonized material on the inner surfaces of potsherds than on the more-carbonized material on the outer surfaces. For the same reason, the carbonized material on the inner surfaces would be more vulnerable to soil diagenesis.²⁴⁾

The difference in the radiocarbon ages of charred material between the inner and outer potsherd surfaces thus may reflect the influence of humic acids (which are older), which characteristically occur in the soils at the wetland archaeological site at Lake Biwa.

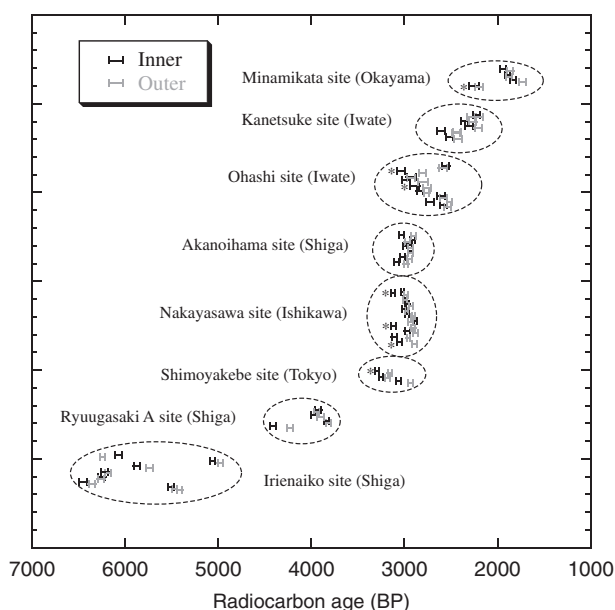


Fig. 6. Radiocarbon ages of carbonized material from the inner and outer surfaces of individual potsherds from several wetland archaeological sites. Samples marked with an asterisk ($\delta^{13}\text{C} > -25\text{‰}$) may have been affected by the marine reservoir effect. Error bar indicates $\pm\sigma$.

3.4. Radiocarbon dating at other Japanese wetland archaeological sites. The Irienaiko archaeological site is in a wetlands environment. In this section, we discuss differences in radiocarbon ages of charred materials between the inner and outer surfaces for samples excavated from other Japanese archaeological sites located in wetland environments.

Two studies have determined radiocarbon ages of charred material adhering to Early Jomon to Middle Yayoi pottery excavated from wetland archaeological sites in Japan (Fig. 6).^{25),26)} Although some of the radiocarbon ages determined by these studies may have been influenced by the marine reservoir effect, in most cases, the inner surface samples showed older radiocarbon ages than the outer surface samples.

Considering only the potsherds of these studies that were unaffected by the marine reservoir effect (42 of 49), we calibrated the ages of 10 potsherds that showed an age difference of more than 100 ^{14}C years between ages determined on materials from their inner and outer surfaces (Fig. 7). The age of the inner surface material of another pair of samples, THHS 69a and b, excavated from the Shimoyakebe site and belonging to “Angyo 3c type” pottery was also more than 100 ^{14}C years older than that of the outer material. However, the ages of the TTHS 69a and b

samples are not in harmony with the pottery typology of other Angyo 3 type series examples excavated from the same site.²⁹⁾ Therefore, we excluded samples TTHS 69a and b from this discussion.

We evaluated which carbonized material, that adhering to the inner or that adhering to the outer surfaces of potsherds, gave the more reliable radiocarbon age by comparing the calibrated ages of the materials from the inner and outer surfaces of the potsherds with the lifetime of their pottery type in the pottery-type series (Fig. 7). The lifetime of a particular pottery type of the pottery-type series is defined as the period during which earthenware vessels of the same pottery type were used continuously, and before the following pottery type begins to be used. We compare the measured radiocarbon ages of charred materials adhering to potsherds with the order of a particular pottery type of pottery-type series and locate a pottery group of multiple dates in ^{14}C calibration curve. By doing so, we are able to construct the detailed absolute lifetime of a particular pottery type of the pottery-type series so far.

For example, samples IWM-4a and c (Fig. 7.3) were excavated from Kanetsuki site (Iwate Prefecture) and belong to the Obora A'-Sunazawa pottery type, the lifetime of which was from the terminal stage of the Final Jomon period to the beginning of the Early Yayoi period (Fig. 7.3). The probability that the calibrated age of IWM-4c (the sample from the inner surface; Fig. 7.3) corresponds to the real (calendar) age within the dates spanned by the curve infilled with gray is 95.4%. Compiled calibrated ages for this pottery type, on the other hand, indicate that its lifetime was 500–350 BC (shown by the hatched area of Fig. 7.3).^{4),28)} In contrast, the calibrated age range of IWM-4a (carbonized material adhering to the outer surface of the pottery) overlaps with the hatched area indicating the lifetime of the pottery type. Therefore, the radiocarbon age of the charred material from the outer surface of the pottery is estimated to correspond to the right age (the time when food was cooked in the pot).

The radiocarbon ages of the charred materials from the outer surfaces of some other potsherds (Figs. 7.4, .5, .7, and .8) were similarly estimated to indicate the right ages of the pottery. The lifetime of the pottery type of one sherd (shown in Fig. 7.1) is uncertain, but it probably spanned at least the period the vertical dash lines shown by the doubleheaded arrow. The radiocarbon age of the charred matter from the outer surface of this sherd was therefore also estimated to correspond to the actual age of the pot.

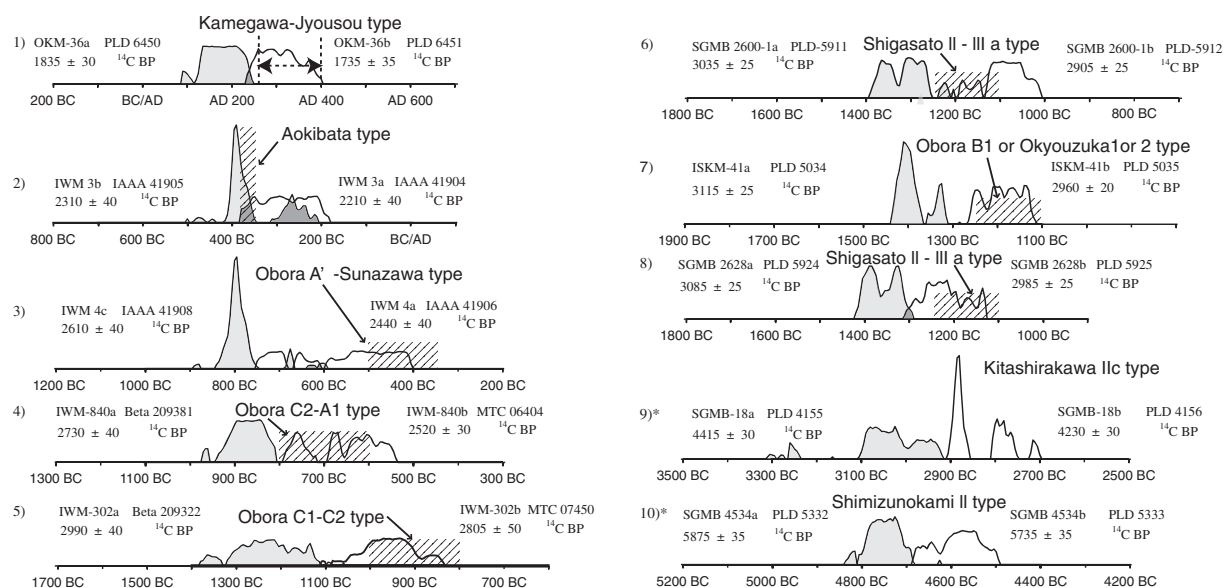


Fig. 7. Radiocarbon age differences of carbonized matter from the inner and outer surfaces of individual potsherds from several wetland archaeological sites. The panels are arranged in increasing order of the calibrated radiocarbon ages. Inner surface samples with $\delta^{13}\text{C}$ values $> -25\text{‰}$ have been excluded to eliminate the marine reservoir effect. The horizontal axis means calibrated age (BC or AD). The curves show the probability distributions of the calibrated dates (2σ : 95.4%). The areas under the curves of samples from the outer surfaces of potsherds are filled with white and those of samples from the inner surfaces are filled with gray. Dark gray indicates cases where the calibrated ^{14}C ages of the inner and outer surface samples overlap. Hatching (panels 2–8) shows the lifetime of the pottery type of the earthenware vessel of which the sherds were a part. The lifetime of the pottery type shown in panel 1 probably lies between the vertical dashed lines.^{27),28)} 1) Kamiifuku site, Okayama Prefecture (middle portion of the Early Kofun period); 2) Kanetsuki site, Iwate Prefecture (beginning of the Early Yayoi period); 3) Kanetsuki site, Iwate Prefecture (from the terminal stage of the Final Jomon period to the beginning of the Early Yayoi period); 4) and 5) Ohashi site, Iwate Prefecture (Final Jomon period); 6) Akanoihamasite, Shiga Prefecture (beginning of the Final Jomon period); 7) Nakayasawa site, Ishikawa Prefecture (beginning of the Final Jomon period); 8) Akanoihamasite, Shiga Prefecture (beginning of the Final Jomon period); 9) Ryuugasaki A site, Shiga Prefecture (Middle Jomon period); 10) Irienaiko site, Shiga Prefecture (Early Jomon period). *There is a clear difference in the calibrated ages of charred materials between the inner and outer surfaces of the Kitashirakawa IIc type (panel 9) and Shimizunokami II type (panel 10) potsherds, but a detailed pottery-type series for the Early to Middle Jomon period, similar to that for the Late to Final Jomon period, has not yet been established. Moreover, very few reliable calibrated age data for carbonized materials adhering to pottery of these pottery types are available. Therefore, the data are insufficient with which to judge which materials, those from the inner or the outer side, show the right age.

This method could not always be used to reveal the right age. In the case of the potsherd shown in Fig. 7.2, the lifetime of its pottery type is 380–350 BC. This time period corresponds to the period of overlap between the calibrated ages of the carbonized materials from the inner and outer surfaces of the potsherd. In this case, therefore, we estimated the age of the charred material on the inner surface of the potsherd to be the same as that of the outer material and considered both ages to be the right age. The lifetime of the pottery type of the samples shown in Fig. 7.6, on the other hand, overlaps the time spans of the calibrated ages of both the inner and outer materials from a single potsherd. As a result, whether the charred material from the inner or outer surface shows the right age cannot be determined using only these data. Finally,

in the case of the sherds shown in Figs. 7.9 (Kitashirakawa IIc type) and 7.10 (Shimizunokami II type), there is a clear difference in the calibrated ages between charred materials from the inner and outer surfaces of the potsherd, but a detailed pottery-type series similar to that for the Late to Final Jomon period has not yet been established for the Early to Middle Jomon period and few reliable calibrated age data for carbonized materials adhering to pottery of these pottery-types are available. Therefore, we do not have sufficient information for judging whether the inner or outer material shows the right age, and we exclude these samples from further discussion. To summarize, at wetland archaeological sites in Japan, the radiocarbon age of the carbonized materials from the outer surface of a potsherd generally shows the actual age of the pot.

We excluded from this discussion, however, cases in which the difference in radiocarbon age between materials from the inner and outer surfaces of a single potsherd were less than 100 ^{14}C years, because in such cases, the age difference was not statistically significant, despite calibrated radiocarbon ages being available for materials from both surfaces.

The archaeological sites in Shiga Prefecture at Akanoihamma, Ryuugasaki A, and Irienaiko are near the eastern shore of Lake Biwa and the dating result may therefore have been affected by the limestone rocks from Mt. Ibuki and Mt. Ryozen, as previously discussed (see also Fig. 2). Further, the Kanetsuki and Ohashi sites in Iwate Prefecture are near the Kitakami River, one branch of which flows from a region of limestone rocks.³⁰⁾ Therefore, it is possible that samples from these sites have also been affected by the freshwater reservoir effect. The other potsherds discussed (Fig. 7) are all from wetland sites, so they are likely to have been affected by diagenesis, which can lead to contamination by older organic matter from the wetland environment.

3.5. The importance of wetland sites for preservation of organic material. Taking into consideration the error inherent in radiocarbon dating (normally 25–40 ^{14}C years), the difference in the ages of carbonized materials from the potsherds we studied is small. However, when the radiocarbon age differences between the inner and outer surfaces of particular potsherds are statistically significant, then it is reasonable to infer that the ages of the carbon in the materials adhering to the inner and outer surfaces of the potsherds are different.

Nonetheless, it is only rarely that we can analyze carbonized material from both the inner and outer surfaces of the same potsherd because the food residue and soot adhering to the inner and outer surfaces, respectively, of particular potsherds must be preserved after burial for several thousand years in the soil before we are able to compare their radiocarbon ages.

Because of the particularly acidic soil environments in Japan, organic archaeological remains rarely survive, but when they do, it is usually in anoxic environments such as those at wetland and lowland sites. Because these environments, especially wetlands, usually contain a great deal of old organic matter, the less-carbonized material adhering to the inner surfaces of potsherds is more likely to be affected by secondary contamination (diagenesis) than the material (soot) on the outer surfaces, and dates determined from the inner residues thus tend

to be older than those determined from the outer residues. Moreover, at wetland archaeological sites close to lakes and marshes in which old organic matter is recirculated, or close to rivers flowing through limestone, the freshwater reservoir effect is likely to be observed.

In contrast, in upland areas, any carbonized material that originally adhered to pottery is less likely to survive. At sites in such areas, there are few radiocarbon dates from charred material from both the inner and outer surfaces of the same potsherds.^{25),26)} Moreover, the soil environment of upland sites is likely to be devoid of old carbon; instead, when radiocarbon ages of charred material on potsherds from such sites can be determined, the samples are more likely to have been affected by younger carbon. At such archaeological sites, it is likely that little difference would be observed between the ages of residues from the inner and outer surfaces of a particular potsherd. Therefore, most data showing radiocarbon age differences between the inner and outer surfaces on the same potsherds are from wetland archaeological sites at which older radiocarbon ages on residues from the inner surfaces of potsherds would be expected.

We conclude that the observed age differences in the inner and outer surface materials in potsherds at Irienaiko and other wetlands sites are dependent on local geomorphological and geological effects, such as the freshwater reservoir effect and diagenesis.

4. Conclusions

We attribute the difference in the radiocarbon ages of carbonized residues between the inner and outer surfaces of potsherds excavated from the Irienaiko archaeological site in wetlands near Lake Biwa either to the freshwater reservoir effect, arising from the food residues (fish and mollusks living at Lake Biwa) cooked in pottery, or to diagenesis, whereby old carbon such as that in humic acid has contaminated the charred food residues on the inner surfaces of the potsherds. By comparing pottery-type series information with radiocarbon ages of residues from the inner and outer surfaces of potsherds at other Japanese wetland archaeological sites, we inferred that the radiocarbon ages of the carbonized materials from the outer surfaces of pottery corresponded to the time when the foods were cooked in the pot, at least for pots from wetland archaeological sites. We also concluded that the radiocarbon ages of materials from the inner surfaces of pottery are the same as those of the outer materials, within error,

unless the materials have been greatly affected by the reservoir effect or by diagenesis. Before the advent of high-precision AMS radiocarbon dating, which has a resolution of ± 25 ^{14}C years, age differences of around 90 ^{14}C years such as those used in this study could not be resolved. The availability of AMS radiocarbon dating has only recently made it possible to resolve differences of this scale.

Future studies should examine the cause of differences in radiocarbon ages of charred materials from the inner and outer surfaces of pottery from upland archaeological sites. In addition, similar differences for pottery from wetland and lowland sites that were occupied before the Late Jomon period should be investigated. At present, accurate pottery-type series information and radiocarbon ages of pottery residues that can be used to estimate the lifetime of the pottery type to which an earthenware vessel belongs are lacking for these earlier periods.

Further information about the origins of the carbonized materials from the inner and outer surfaces of pottery may eventually make it possible to reconstruct paleodiets, that is, what the ancient peoples cooked in the pots for eating. Moreover, reevaluation of Lake Biwa itself as well as of the wetland environments around Lake Biwa from the viewpoint of the multiple carbon sources causing the radiocarbon age differences between materials from the inner and outer surfaces of pottery by an approach such as that used by this study may elucidate aspects of the carbon cycle at Lake Biwa during the middle to late Holocene.

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