PREPARATION TECHNIQUES FOR RADIOCARBON DATING OF POTSHERDS

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ABSTRACT. Origins of carbon in potsherds are studied through field experiments which involve firing pots containing selected components and laboratory analyses. As temper seems to be the main source of carbon, radiocarbon dates may be too old if calcium carbonate is used. We can avoid the carbon from the clay by low-temperature burning of samples.

INTRODUCTION

Potsherds can be a complex radiocarbon dating material. In a previous paper (Gabasio & Evin, 1986), we reviewed the published studies dealing with radiocarbon dating of potsherds and analyzed most of the results obtained on scattered archaeologic samples. While most values generally agree with expected ages, some disagree widely without any apparent reason. Thus, such a dating material cannot be used with the same confidence as charcoal or bone (Evin, 1983). However, since the recent advances in accelerator mass spectrometry (AMS), dating potsherds becomes more attractive. Johnson *et al* (1986) succeeded in AMS dating carbonized organics isolated from potsherds. But, when these remains are not available, ceramics with homogeneous paste may be the only carbonaceous material at a site and the best remains of human activity.

The origin of carbon in potsherds is rather complex: the six most likely sources of carbon are:

1) carbon in the clay used by the potter
2) carbon from the temper added to the clay
3) carbon from the fuel of the kiln
4) carbon from resins or other substances applied on pots
5) carbon derived from the domestic use of the pot
6) carbon from geochemical contamination of the site.

Weight and relative age of each type of carbon have different effects on the ^{14}C determination of the total carbon of the samples. As for other dating material, potsherds may become reliable if a preparation technique can be devised to select the only source of carbon that yields ages contemporaneous with the firing of the pot. Carbon from fuel, domestic use (and perhaps temper, if vegetal matter is used) may yield reliable dates.

Two research procedures may be employed to establish a preparation technique: 1) analysis of many archaeological samples to classify all the aspects of ceramic components, or 2) the manufacture of vessels using selected components (clay, temper, fuel and humic matter). In order to avoid the destruction of artifacts that are difficult to find in well-defined contexts, we have chosen the latter. We preferred simulating Neolithic conditions because potsherds often are the only artifact found in sites from this period, which moreover, covers the range of the best relative precision of the ^{14}C dating method.

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We conducted field experiments and laboratory measurements for four years. Our results (Gabasio, 1987) suggest the preparation technique described below is suitable. Experiments are still in progress, as we have not yet solved all aspects of the problem.

FIELD EXPERIMENTS AND LABORATORY ANALYSES

The experiments were performed at Archeodrome, an open-air museum besides the Paris−Lyon highway. Pots were prepared with varying amounts of ingredients. First, an industrial clay without carbon was used, either pure, or after the addition of a small quantity (1 or 2%) of modern organic matter containing a measured amount of ^{14}C. Some samples were made from natural clay containing no carbon or some very old (0% ^{14}C modern) organic matter (Liassic clay). Various tempers were then selected with or without calcium carbonate – calcite and powdered shell or silicious sand and powdered bricks. Modern or old (ca 4000 BP) wood was used as fuel for filling two types of kilns. Such kilns were used (Andrieux & Arnal, 1986) for firing pots of homogeneous texture and dark color, like many prehistoric ceramics. The first kiln, constructed in the form of a clod, proved to be too oxidizing. The other pots were fired in a circle in meter-deep holes covered by an earthy cap with narrow blowholes (Fig 1). Thermometers set close to
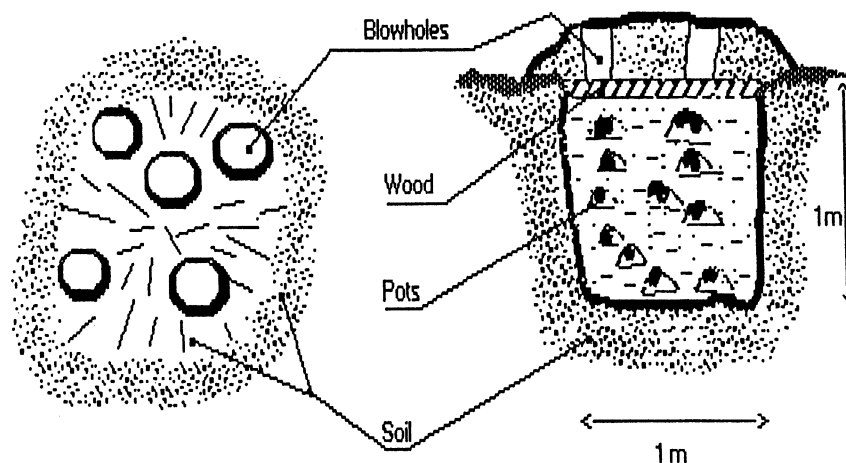

Fig 1, Top view (left) profile (right) yielding black pots under reducing conditions

the pot recorded the rising temperature, which was maintained at ca 600°C by alternately opening and closing the blowholes. The firing lasted, almost smothered, for 12 hours until all the pots were completely fired and dark-colored. Sections in the fired pots showed that carbon penetration inside the vessel structure was more-or-less even. After firing, the experimental pots looked like the coarse-grained potsherd often found at Neolithic sites.

The carbon content of all the fired pots was analyzed in the laboratory using several techniques. The best results were obtained by an infrared analyzer or by collecting CO_2 from total combustion in an O_2 flow. The ^{14}C content was measured only by liquid scintillation counting which involved the preparation of large amounts of samples (ca 1kg).

We chose the components of the pots and the fuel wood to answer three questions:

1) What happens to the organic matter of the clay during firing?

2) Does the total quantity of carbonaceous elements of the temper (carbonates or vegetal matter) remain in the pots?

3) How much carbon from the wood gets incorporated into the structure of the pots?

THE THREE MOST PROBABLE SOURCES OF CARBON

Of the most likely sources of carbon in potsherds mentioned above, items 4), 5) and 6) can be discarded. Carbon from resins and domestic use are rather rare, and occur in relatively small amounts. Carbon from soil contamination has to be eliminated in pretreatment which also eliminates all carbonate fraction. Thus, three most probable sources of carbon remain.

1. Carbon from Clay

Ancient potters surely did not get their clay very far from their settlements. They could find suitable material from outcroppings of clay sediments upon which vegetation and humic matter became part of the soil profile. Jambu and Dupuis (1975) studied the carbon release of humic matter fired under controlled conditions. They demonstrated that almost everything is destroyed at a rather low temperature (ca 400°C) under oxidizing conditions. The firing of clays in an electric oven gave the same result, when done directly in an O_2 flow. But if the clays were first heated under reducing conditions (at 500°C, in an N_2 flow) they later released only half their carbon at 400°C and could be burned completely only at 500°C (Table 1). This means that the previous heating under reducing conditions strongly binds the carbon molecules with the fired clay or pyrolyzes the organic matter in short-chain hydrocarbons which are more resistant to oxidation. Thus, even though black potsherds have a higher carbon content, it may be possible to avoid burning the carbon from the clay.

TABLE 1

Carbon extraction of clays in an electric oven

	Carbon content (%)			
Temperature	0°C	510°C	400°C	700°C
Gas flow		N_2	O_2	O
1st experiment	2.6		0.2	0.1
2nd experiment	2.6	1.3	0.5	0.1

2. Carbon from Temper

Temper, which may be sand, ground bricks, shells or calcite, or organic matter, makes up 20–40% of a clay vessel. It is used in ceramic manufacture to prevent cracking during firing. With the same proportion of pure sand and calcium carbonate with or without 10% of organic matter, our pots contained 0–10% of carbon in their temper. Table 2 compares these values with the remaining carbon, after decarbonation, in pots fired in oxidizing and reducing conditions. We first observed that, in oxidizing conditions, the carbon from the temper disappears almost completely, whatever the temper material. Only very little remained when old organic matter was used. Thus, even if a great deal of vegetal temper can be seen on red archaeologic potsherds, they are not suitable for dating, as the carbon from that temper must have disappeared in the kiln.

Table 2 shows that the range of carbon content (also measured after removing all carbonate fraction) of fired pots in reducing conditions is very wide, 0.4–4.5%. But we assume that 0.4% comes from the kiln fuel, as this value was obtained from 0% of carbon from the temper and the clay. Thus, comparisons between values obtained with $CaCO_3$ and sand tempers, with or without organic matter, obviously show large differences. Even at quite low temperatures (ca 400–600°C), an interference occurs with the carbon from the calcium carbonate of the temper. Such a phenomenon, which is a source of carbon in the fired pot, is not understood completely. It has been

TABLE 2

Carbon content of fired pots in relation to the carbon content
of their components

Maximum carbon content (%) of components					Carbon content (%) of fired pots	
Clay	CaCO₃	Sand	Org matter	Total	Oxidizing kiln	Reducing kiln
0	2			2	0.2	1.5
0	2		5	7	0.1	1.2
0	4			4		3.5
0	4		5	9		5.0
0		0		0	0.2	0.4
0		0	5	5		0.9
1	2			3	0.6	1.6
1	2		5	8		4.5
1	4		5	10		3.4
1		0		1		2.5
1		0	5	6		2.2
2	2			4	0.4	1.4
2	4			6		2.6
2		0		2	0.3	1.7

partly studied in the last field experiments (summer 1988) using two types of calcareous temper (modern oyster shells and old calcite). Comparison among Ly-4538, -4663 and -4664 with -4662 (granitic sand temper) shows that pots with calcium carbonate temper have the highest carbon content and that old calcite yields the lowest ^{14}C content. This source of carbon in the fired pots may be the primary reason for the disagreement in some ^{14}C dates of potsherds.

3. Carbon from Kiln Wood

The background of ca 0.4% of carbon indicated in Table 2 suggests that carbon from fuel may have a major effect when the total carbon content of the fired pots is low. During firing, we observed that red pots, in oxidizing conditions, quickly turn black as soon as the fire shifts down. But the change from red to dark color may be due to the oxidation state of the iron oxides and numerous analyses of total carbon prove that, even with a very dark color up to the inner portion of the potsherd fragments, carbon content remains low. To reproduce this and try to quantify the influence of black smoke in reducing conditions, kilns were filled with modern or old wood in order to fire pots with the same components, and their ^{14}C activity was measured. Table 3 shows that ^{14}C activity in wood does not greatly modify the ^{14}C activity of total carbon in the fired pot which depends, above all, on the activity of its components. We conclude that even dark-colored potsherds get most of their carbon from the clay or the temper and not from the fire.

SELECTION OF RELIABLE CARBON

Carbon fractions from various sources do not have the same chemical composition and they are more-or-less tightly bound in structure. Some carbon (from clay) may occur in very complex molecules; others (from kiln smoke) are probably amorphous. Experiments carried out on clays and ceramics (Johnson *et al*, 1988) showed the complexity of the carbon loss in firing according to the temperature. We also burned samples under controlled conditions, and separated carbon fractions by placing ground potsherds in an electric oven under an O_2 flow at several temperatures. The thermogravimetric curves of the loss of weight (Fig 2) look like the curve of the loss of carbon obtained by Johnson *et al* (1988, Fig 1). Both figures show that the extraction of carbon occurred in several steps. Such irregularity is obviously linked to the presence of several forms of carbon.

^{14}C measurements on successively extracted fractions of archaeologic samples (Table 4) show two types of results. The first result shows about the same value for all fractions and so we may be sure that no old carbon has been extracted. The second result shows a lower value for the fraction of the highest temperature, and from this we assume that carbon from the clay was extracted in the last burning phase.

Previous analyses (Gabasio, 1987) suggest that carbon from smoke does not burn at low temperatures. Thus, the carbon that is first released may come only from the temper if we assume that the carbon from the soil was previously eliminated by appropriate chemical pretreatment. Later releases

TABLE 3
^{14}C activity of pots fired with old or modern wood

Material	Components C content (%)	Components Assumed age of C	^{14}C activity (% modern) Kiln wood	^{14}C activity (% modern) Fired pots
Clay 0% C CaCO$_3$ Sand	0.6	?	60.8±0.9 (Ly–3769)	Ly–3927: 55.5±1.6
Clay 0% C Org matter CaCO$_3$	2.0	Modern	60.9±0.9	–3926: 97.9±1.1
Liassic clay Sand	0.6	Old	60.8±0.9	–3987: 33.8±1.2
Liassic clay Org matter CaCO$_3$	2.3	Old and Modern	60.8±0.9	–3925: 56.6±0.8
Clay 0% C Bricks	0.3	?	135.0±3.0 (Ly–3506)	–3468: 86.4±2.6
Clay 0% C Org matter	0.2	Modern	135.0±3.0	–3466: 94.0±2.0
Liassic clay CaCO$_3$	0.8	Old	135.0±3.0	–3467:105.8±1.7
Liassic clay Sand	0.7	Old	141.3±1.6 (Ly–3768)	–3923: 72.9±1.0
Liassic clay Org matter CaCO$_3$	1.5	Old and Modern	141.3±1.6	–3924:103.7±1.6
Clay 0% C Org matter	0.4	Modern	141.3±1.6	–4091:113.3±3.0
Clay 0% C Org matter	0.5	Modern	141.3±1.6	–4090:115.2±2.9
Clay 0% C Org matter	0.6	Modern	141.3±1.6	–4092:107.6±2.4
Clay 0% C Org matter	0.8	Modern	141.3±1.6	–4093:111.5±3.3
Clay 0% C CaCO$_3$	ca 4	Old	135.0±3.0	–4538: 63.9±2.9
Clay 0% C CaCO$_3$	ca 3	Old	ca 125	–4663: 84.6±1.5
Clay 0% C Oyster shell	ca 4	Modern	ca 125	–4664:114.1±2.7
Clay 0% C Granitic sand	0		ca 125	–4662:113.2±2.0

must be very strong since the pottery is usually very porous and absorbs large amounts of humic matter. For example, a sample from the Fort Harrouard Bronze Age site yielded dates of 2200 and 3500 BP after the basic extraction at pH 11 and 13, and another sample from Le Bas des Touches Gallo-Roman site yielded 1100 and 2300 BP before and after basic pretreatment.
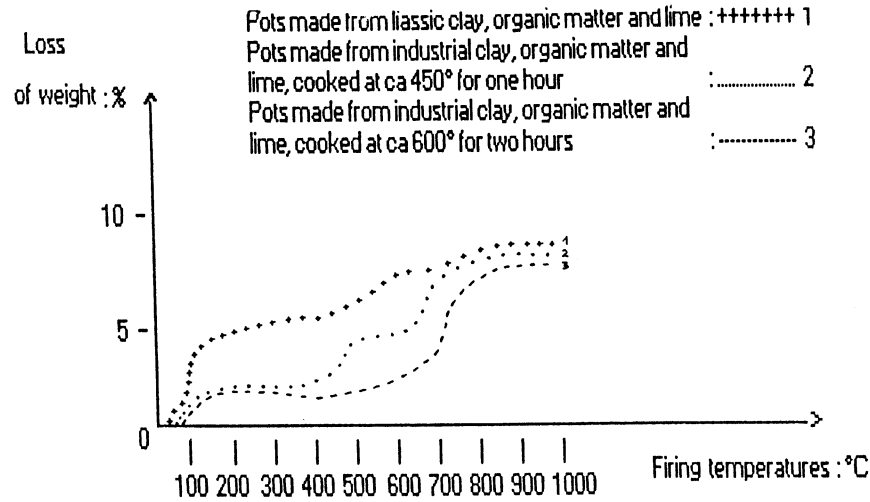
Fig 2. Thermogravimetric curves of experimental pots

TABLE 4

[14]C activity of experimental or archaeologic potsherds at different temperatures

Source of sample	Carbon content (%)	Expected age	Firing temp (°C)	Sample no.	Carbon content in % or BP age
Archeodrome	2.2	Modern	500–600	Ly–3826:	80.1±1.4
Archeodrome	2.2	Modern	350–400	–3924:	103.7±1.6
Archeodrome	2.2	Modern	200–250	–3984:	91.5±1.5
Mauritania					
Trig-Areicha	0.6	Iron Age	700	–4056:	2660±130
Trig-Areicha	0.6	Iron Age	400	–4055:	2780±160
Trig-Areicha	0.6	Iron Age	200	–4054:	2700±170
Taif-Oujaf	0.8	Iron Age	700	–4058:	2190±150
Taif-Oujaf	0.8	Iron Age	400	–4057:	2220±160
Hong-Kong					
Site HK94-P1	1.3	Early Neolithic	400	–4071:	7180±600
Site HK94-P1	1.3	Early Neolithic	300	–4070:	5560±400
Site HK94-P1	1.3	Early Neolithic	200	–4069:	5980±400
Tai Kai Wan	1.2	Early Neolithic	400	–4152:	9660±190
Tai Kai Wan	1.2	Early Neolithic	200	–4151:	7160±140
France					
Le Bas-des-Touches	?	Gallo-Roman	400–460	–4520:	9040±430
Le Bas-des-Touches	?	Gallo-Roman	300–340	–4519:	1970± 60
Le Bas-des-Touches	?	Gallo-Roman	280–300	–4518:	2460±210
Le Bas-des-Touches	?	Gallo-Roman	200–240	–4517:	2610±170

CONCLUSION: PROPOSED PREPARATION PROCEDURE FOR DATING POTSHERDS

Field experiments and laboratory measurements of potsherd samples lead us to propose the following procedure for reliable ^{14}C dating of archaeologic potsherds:

1) First choose the blackest pottery.
2) Discard pottery with calcareous temper.
3) Conventional acid-base acid pretreatment must be done until all humic fractions are extracted.
4) The powdered sample must be burned at the lowest temperature possible for the required amount of CO_2 for the ^{14}C measurement.
5) One or two ^{14}C measurements should be made on the CO_2 fraction extracted at a higher temperature to test that no old carbon has been extracted from the clay in the first fraction.

Such a laboratory procedure, which involves the loss of most of the carbon from samples containing not more than 5%, may be done only on very large samples, if the traditional method of counting ^{14}C radioactivity is used. AMS dating, however, permits the selection of 1 or 2 potsherds for careful pretreatment and selective burning.

We hope that, in the near future, many archaeologic sites without other dating materials will be dated in this way. This technique should present interesting comparisons between thermoluminescence and ^{14}C dating and provide a reliable method for both.

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