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ORIGINS OF CARBON IN POTSHERDS

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INTRODUCTION

The general reliability of ^{14}C dating in archaeology induced us to try to extend the method to other datable materials that may be uncovered, even those which have till now been neglected or considered unreliable. Improvements in AMS techniques will also help us date very small samples or those with low carbon content. For these reasons we have undertaken a systematic study of the application of ^{14}C dating to potsherds which are usually abundant in prehistoric sites and often more representative of human activity than other materials such as charcoal (Evin, 1983).

Only a few attempts have been made to ^{14}C date potsherds. The first studies (Vogel & Waterbolk, 1963, 1967; Stuckenrath, 1963; Engstrand, 1965; Tauber, 1968) involved only isolated specimens from sites where comparison with other datable materials posed problems. There is generally good agreement between the dates derived from potsherds and those of other materials. Potsherd dates are often slightly older than other dates; only very rarely do potsherds yield a younger date. In a single case from the Palau site in the Philippines (De Atley, 1980), the dates appear totally erratic. In view of the overall reliability suggested by this comparison, potsherds would appear to be as useful a dating material as other more classical carbon sources. Until now, however, no systematic study of potsherds as a source for datable carbon has appeared. De Atley (1980) studied two series of samples from an archaeologic context but these were too complex for a meaningful analysis.

Our study considers possible sources of carbon in pottery samples, from manufacture to discovery. We also do some experimentation of relative importance to the ^{14}C date of these different carbonaceous materials. In the future we shall use samples from well-defined archaeologic contexts to verify the applicability of the technique.

TABLE 1
Carbon content of archaeologic potsherds

Sites	References	No. of samples	Carbon content (%C)
Chassey	Evin, Thévenot & Gabasio (1985)	10	3.00–4.00
Mauritania	Evin (1985)	11	0.20–2.00
Diverse French Neolithic sites		15	1.00–7.00

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CARBON CONTENT OF PREHISTORIC POTSHERDS

Total combustion and infra-red assay of CO_2 using 10mg samples of powdered potsherds are better adapted to estimating the overall carbon content of heterogeneous material such as pottery. We established carbon values for potsherds acid-treated from several archaeologic sites. Table 1 shows the value varies widely from 0.2% to 7%.

POSSIBLE ORIGINS OF CARBON IN POTTERY

The texture of potsherds from different sites varies widely from a homogeneous fine-grained matrix, which is generally poor in carbon and not useful for ^{14}C dating, to a coarse-grained or granular texture containing appreciable carbon. Fine-grained ceramics are typically products of later cultures and can be dated more easily by their style or decoration, whereas coarse-grained samples are typically protohistoric. These early samples vary in color from red-brown to black. They were fired in primitive kilns and typically contain enough carbon for ^{14}C dating. This carbon could stem from five sources:

1) *Carbon present in clay.* Some 50 to 70% of the weight of pottery is usually clay selected for its plastic properties, and may be derived from local clayey muds or from outcrops of pure clay in caves or quarries. Such clay contains a variable amount of organic matter of diverse ages. Quarried clays or marls may contain up to 20% organic matter, and yield an infinite age. Clays from muds which closely underlie surface vegetation, however, contain organic matter of which dates vary from a few thousand years to infinity. This intrinsic carbon in the clay may be of syngenetic or secondary origin, but it will always be older than the date of use by the potter and hence will tend to increase the apparent age of the potsherd by an unknown amount.

2) *Carbon from temper.* Another ca 20 to 50% of the mass of pottery comes from the temper which consists of sand, ground shells, vegetable matter, or other substances. In most cases, any carbonaceous material added in the temper will be essentially contemporary with the activity of the potter. Carbon from this source is thus generally useful for dating.

3) *Carbon from fuel in the kiln.* We already mentioned that the potsherds we are studying were fired in a very primitive kiln. The construction of the kiln will be considered in more detail below, but it is important to note that the pots and the fuel were in intimate contact. The vessels were fired at moderate temperature to avoid cracking and the hearth produced abundant smoke. Since the pottery was highly porous, it is reasonable to assume that smoke would permeate it and might be responsible for much of the carbon in the potsherd. Fuel would usually be wood or dry grass and thus essentially contemporaneous with the manufacture of the pot. Such carbon is perfectly suitable for dating purposes.

4) *Carbon derived from use of the pottery.* The fired pots were used for various purposes such as cooking or food storage. It is conceivable that organic material could be absorbed from the inside or the base of the pot. This material would yield a date corresponding to the time of its use.

5) *Secondary carbon contamination.* Once embedded in its archaeologic

context, the potsherd is subjected to the same influences as any fossil material. It is affected by geochemical processes of its environment and may accumulate organic matter derived from the soil (humic material, rootlets, etc). All these organic elements, the mean age of which is a function of the turnover time of organic matter in the particular context, are younger than the potsherd.

It is difficult to estimate the influence of this contaminating matter on the date of any given sample, but treatment with sodium hydroxide or pyrophosphate will probably eliminate most of this secondary carbon from potsherds (as it does for other samples) (Gilet-Blein, Marien & Evin, 1980).

Of these 5 sources of carbon in potsherds, three: 2), 3), and 4) derive from contemporary carbon and should yield satisfactory dates; two will give false dates: 1) too old, 5) too young.

FIELD EXPERIMENT

We prepared pottery under simulated primitive conditions and varied some of the parameters described above. We then compared the ^{14}C dates of several series of experimental pots. We chose this approach both because of the difficulty of obtaining enough well-characterized archaeologic material for a meaningful study, and because multiple unknown variables that could render archaeologic analysis unreliable. Nevertheless, we hope to complete our study with suitable prehistoric samples.

We produced ca 100 pots from a standard mold, using clay from four sources with different carbon content mixed with powdered brick or pure calcite as temper. Up to 10% additional organic matter (horse dung and plants fermented 1 year) was also added (Table 2).

Kilns. Simulated Neolithic kilns were constructed at the Archeodrome, an open-air museum situated beside the Paris-Lyon highway near Beaune (Beaune-Tailly Service Area), as described by Arnal (1976). A circular flat-bottomed pit, 2m in diameter and 20 to 30cm deep, was filled with freshly made pots, and wood and dry grass were used as fuel (Fig 1). The size of the aeration holes at the base and top of the kiln are crucial in determining the heat of the fire. Our experiments were carried out under oxidizing conditions with a strong draught and produced generally light-colored pottery.

TABLE 2
Composition of experimental pots

Clay (50–80%)		Temper (20 or 40%)	Added organic matter (0.1 or 10%)
Industrial (red)	Pure clay of known composition—0.1% C	Calcite or powdered brick	+
Enriched (red)	Industrial clay with added organic matter equilibrated for a year before use—2.6%C	Calcite or powdered brick	−
Liasic (yellow)	Natural clay—1.9%C	Calcite	+
Cave (red)	Natural clay—1.8%C	Calcite	+

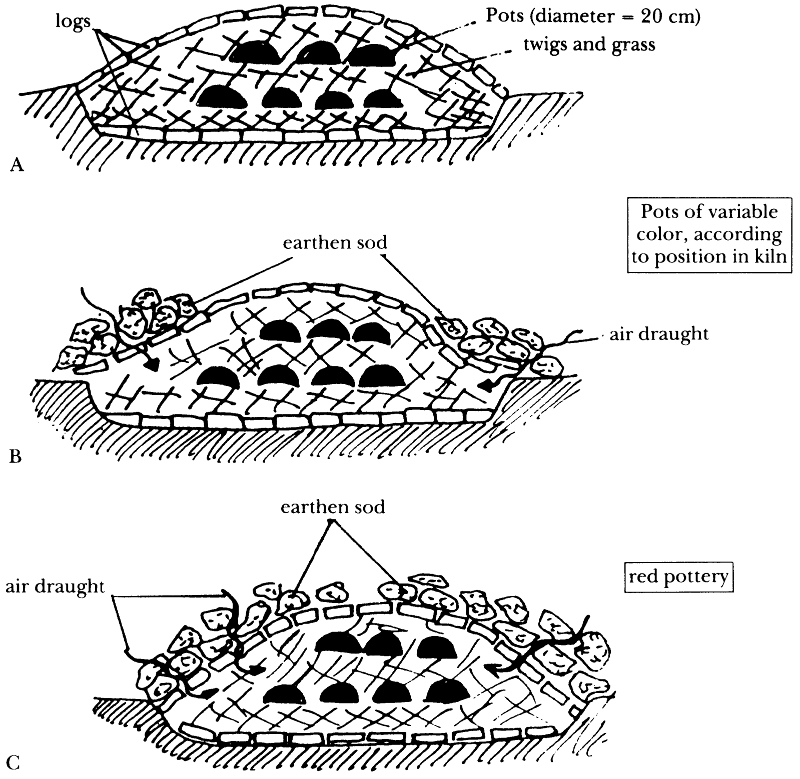

Fig 1. Construction of oxidizing kilns—A and B mildly oxidizing, C highly oxidizing

In the four kilns constructed, temperatures attained some 600°C or 800°C at least in some areas. Experiments under reducing conditions will be performed at a later date. Construction of such kilns presents some practical difficulties but the general plan is shown in Figure 2.

Clay. We examined the behavior of the carbon in different clays by infra-red analysis of the four clays used for the manufacture of our pots before and after baking at 800°C in an electric furnace. The results (Table 3) show that, as expected, the amount of residual carbon depends not only on the length of the heat treatment and the amount of oxygen but also on the type of clay. This suggests that the amount of original bound carbon in the clays of ancient potsherds will influence their dating.

Temper. For the experimental pots, we compared the carbon contents before and after firing (Table 4). The initial value is the amount of the carbon content of the different ingredients. Powdered brick is not a carbonaceous material and pure calcite is removed by acid treatment. Therefore, these tempers will not influence the observed date.

The addition of up to 10% of organic matter to the temper did not influence the carbon content of the pot after firing. This suggests that the secondary organic material added in this way is nearly completely consumed, and will have little influence on the observed date.

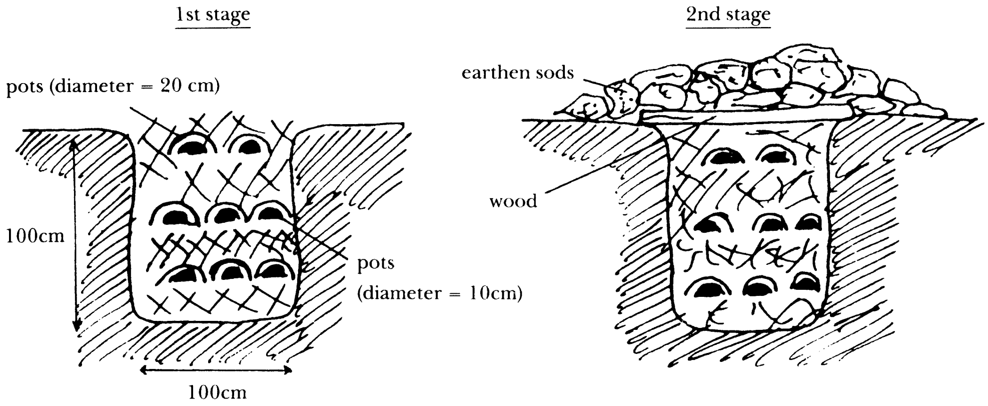

Fig 2. Construction of reducing kilns

Pots. Most of the pots were adequately fired after three hours. They were hard and generally uncracked, and, as expected, light in color. A few pots broke during firing, but, as they were wrapped in wire mesh before being placed in the kiln, the fragments could be recovered for study. The weight of the fired pots was ca 1.1kg, corresponding to an ignition loss of ca 10%. Color was strongly influenced by factors such as their position in the kiln, air draughts, and closeness to flames or fuel. These differences in color, and the frequent blackened patches, especially on pots from the bottom of the kilns, strongly suggest that the third source of carbon (from the fuel) is of some importance. It may be expected that this will hold still more true when we can carry out experiments in a reducing kiln.

VARIATIONS WITHIN A POT

The color of the pots varies considerably in cross-section and among pots. In general, the central section is blackest, but in some cases, the whole section may be uniformly black or light colored.

We used microprobe electron microscopy to establish whether the dark coloration was really associated with a higher carbon content. Difficulties were encountered due to the heterogeneous granular nature of the

TABLE 3
Behavior of carbon in clay samples in baking

Clay	% carbon in clay			
	Industrial	Enriched	Liasic	Cave
Raw clay	0.1	2.6	1.9	1.8
Acid-treated raw clay	0.1	2.3	1.0	0.6
Baked 90 min at 800 °C reduced air	0.1	1.0	0.4	0.6
Baked 210 min at 800°C reduced air	0.1	—	0.1	0.1
Baked 90 min at 800°C in open tube	0.1	0.1	0.1	0.6
Baked 210 min at 800°C in open tube	—	—	0.2	0.1

TABLE 4
Variation in carbon content of experimental pots

				After acid-treatment		
Composition				% carbon before firing	% carbon after firing	
Clay	Temper (%)		Organic matter (%)		Light zone	Dark zone
Industrial clay	Calcite	20	0	0.1	0.1	0.1
			1	0.4	0.1	
			10	2.6	0.2	0.2
		40	0	0.1	0.1	
			1	0.4	0.5	
			10	3.4	0.2	
	Powdered brick	20	0	0.1	0.1	
			1	0.3		
			10	2.0	0.3	
		40	0	0.1		
			1	0.3	3ppm	
			10	2.0	0.2	
Enriched clay	Calcite	20	0	2.3	0.1	
		40	0	2.3	0.3	
	Powdered brick	20	0	1.8	0.4	0.5
		40	0	1.4	0.2	0.5
Liasic	Calcite	20	0	1.0	0.1	
		20	1	1.1		
			10	3.3	0.3	0.5
		40	0	1.0	2.8 (?)	
			1	1.3	0.1	0.2
			10	4.1		

specimens and the ultra-fine resolution of the microprobe, but the results confirm a strong association of carbonaceous material with the dark areas.

We realized the controlled combustion of three different colored samples from a single pot. The carbon content of the samples was first determined by infra-red analysis, then the samples were baked at ca 500°C, at 600°C and finally, burned in oxygen at 1000°C. The CO_2 collected after combustion at 1000°C (Table 5) indicates that the blackest sample lost most of its carbon in baking, but that the lighter colored samples retained appreciable amounts of carbon until combustion at 1000°C, suggesting a closer association with the clay matrix.

CARBON CONTENT OF POTS

The carbon content of different pots was measured after acid-treatment in an infra-red analyzer, by total combustion of a 10mg sample at 1000°C and the released CO_2 assayed by an infra-red absorption spectrometer. The overall carbon content of our pots fired under oxidizing conditions was lower than that of black archaeologic specimens, generally ca 0.3% with a maximum of 1.7%.

^{14}C ANALYSIS

We have limited our present study to determinations on three samples to which no secondary organic material had been added. When pots fired

TABLE 5
Carbon distribution in different zones of a pot

Sample color	% carbon	% carbon after baking at:		
		430°C	550°C	600°C
Black	1.7 acid-treated		0.1	0.2
Brown	1.9 non-acid-treated	2.0		1.5
Brick	0.3 acid-treated			0.3

under reducing conditions are available, we will extend these observations to other samples. The three specimens varied considerably in color (and in carbon content derived from the fuel in the kiln), but their intrinsic carbon content was simply that of the clay used in manufacture. Ashes were collected from the kiln ash which reflects the bomb-testing activity of the 1970s. However, the lower the carbon content of the sample (Table 6), the lower the ^{14}C activity. This suggests that an appreciable fraction of ancient "dead" carbon from the clays used remains in the fired pot.

TABLE 6
^{14}C activity of experimental pots

Composition	Color	Carbon yield (%)	^{14}C activity (% NBS oxalic acid)
Industrial clay—60%, 0.1% C Powdered brick—40%	Brown with blackened zones	0.3%	Ly-3468: 86.4 ± 2.6
Carbon-enriched clay—60%, 2.3% C Powdered brick—40%	Red to black	0.2%	Ly-3466: 94.0 ± 2.0
Liasic clay 80%, 1% C	Black with brownish zones	0.8%	Ly-3467: 105.8 ± 1.1
Charcoal from kiln			Ly-3506: 135.0 ± 3.0

CONCLUSION

The relatively high values of carbon content obtained from blackened samples, together with ^{14}C dates suggest that fuel is indeed the major source of carbon in these samples. However, the above observations indicate that the intrinsic carbon from the clays remains present in the pot even after firing at over 600°C, while the carbon added in the temper disappears almost completely under these conditions. This suggests that we might be able, by controlled combustion, to separate the carbon derived from the fuel which is useful for dating, from the intrinsic carbon of the clay, which is not. Our field experiments indicate that carbon acquired during firing may outweigh all other carbon sources in potsherds, and thus, even in the absence of precise methods for the estimation of the intrinsic carbon content of the clay, dating may be possible on very black potsherds. Moreover, certain archaeologic contexts may allow us to determine the precise origin of the clay used, when its carbon content can be measured. We believe that the carbonaceous material in potsherds produced under reducing conditions will be so preponderantly that of the fuel that dating might be possible with only calculated estimates of the carbon content of the clay.

The results shown here lead us to believe that potsherds may be considered as an adequate material for ^{14}C dating, at least when the obviously preferable samples such as bones of large pieces of charcoal are absent. We trust that comparative studies with improved techniques of thermoluminescence dating and the future availability of sensitive AMS methods for ^{14}C dating will lead to development of accurate dates of potsherds, which are so closely related with human activity in prehistory.

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