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Organic Residues on 3000-Year-Old Potsherds from Natunuku, Fiji

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ABSTRACT

Organic remains are not normally found during archaeological excavation other than under exceptional conditions of cold, aridity or waterlogging. Archaeological evidence for the plants in possible use in prehistory is therefore difficult to obtain. Chemical analyses have been investigated to establish whether this could be a useful tool for adding to knowledge of the food plants in use by ancient man.

Results from chromatographic techniques have proved particularly encouraging, as specific lipid and fatty acid patterns have been obtained which allow for some reasonable deductions as to the possible plant source. High levels of lauric and oleic acids, for example, indicated the possible use of a member of the Lauraceae group such as cinnamon, while a particularly high level of myristic acid could suggest the presence of a member of the Myristicacae family.

Keywords: CHEMICAL ANALYSIS, POTTERY RESIDUES, ORGANIC REMAINS, FIJI.

As part of a long term study of organic residues, a detailed examination of twelve samples from Site VL1/1 at Natunuku in Fiji was undertaken for Dr Foss Leach at the University of Otago. Site VL1/1 is an archaeological site in a sandy bay on the north coast of Viti Levu, Fiji. Excavations in 1967 recovered Lapita pottery and other artefacts. Charcoal from the base of the deposit was dated to 1290 +100 b.c. (Mead *et al.* 1975:44).

Two of the samples examined were carbonised residues and the remainder were potsherds. In addition, five soil/sand samples associated with five of the potsherds were examined in order to assess the degree of exchange. It was hoped that the study would give information concerning diet.

The analysis of organic residues found either on or trapped within the ceramic matrices of potsherds can give useful information about vessel usage (Evans and Biek 1976). The major problems in such studies are firstly, the completeness of extraction and subsequent identification of the organic compounds present; secondly, ascertaining whether there has been any substantial exchange of organic substances between the sherd and the surrounding soil; and thirdly, the shortage of data on the decomposition processes involved when food traces, etc., have been buried for substantial periods of time.

The first of these problems, completeness of extraction, can be satisfactorily overcome by using a range of solvents of varying polarities, starting with a non polar solvent such as hexane. In this way not only is extraction practically complete but also each solvent extracts a particular group of compounds. For instance, hexane tends to extract lipids and consequent identification is thus simplified. The identification of the components of a particular extract is a somewhat complex task but recent advances in instrumentation, especially in the field of chromatography, have somewhat simplified the exercise (Condanin *et al.* 1976). The major problem in this area is the small amounts of many of the components and consequently one can sometimes only suggest a general origin for a particular residue.

The second problem, exchange, appears not to be as serious as was at first feared. A recent study of medieval pot sherds from Exeter (Allan 1980) has shown that contamination by ground organic substances is minimal, as several samples contained no detectable material. However, exchange may be a factor of ground conditions and consequently in this type of study, analyses of soil samples are a useful adjunct to those of the sherds.

Our experience has indicated that the third problem, decomposition, is also less serious than was first supposed. In the case of charred residues it appears that the very act of carbonisation produces vesicles within which some of the original material, often only slightly degraded by heat, becomes trapped within a tough, inert wall of carbon. It is consequently protected from further degradation and can remain unchanged until the char is crushed for analysis. Similarly, when the organic material penetrates the ceramic matrix, it is also protected, as the external faces of the pot become sealed, either by decomposition or by other processes that show little penetration.

The two residues were examined under the scanning electron microscope. Neither contained recognisable debris and both exhibited the usual vesicular structure associated with charred residues. Both samples clearly consisted of a series of layers. It is probable that the uneven surface of the pot made it difficult to remove all the burnt material after a particular cooking session and consequently, the burnt area would act as a centre for later burning, thus the layering effect would be produced. The crude residues were examined by infra red spectroscopy and the spectra obtained suggested the presence of complex organic mixtures.

Samples of all the potsherds were freed from surface debris, then crushed and passed through a 100 mesh sieve. Approximately 2 grams of the fine material was then extracted in a soxhlet apparatus with the following series of solvents:– hexane, chloroform, 2-propanol and water. This group of solvents is employed because they not only extract specific groups of material but also are suitable for subsequent analysis by High Performance Liquid Chromatography (HPLC).

The two residues and the soil samples were similarly crushed and subjected to the same procedure. In the case of the residues, the sample size was approximately 200 mg.

The various extracts were examined by Thin Layer Chromatography (TLC). Examination of the hexane extracts gave recognisable triglyceride patterns for the two residues and sherds P1 and P4.

By comparison with standard substances, sherd P1 and residue R1 appeared to contain a triglyceride pattern similar to palm type oil, residue R2 to contain a mixture of fish and palm type oil and sherd P4, a pattern similar to coconut oil.

Further data were obtained by hydrolysing the triglyceride extracts and converting the fatty acids obtained into methyl esters for examination by Gas Liquid Chromatography (GLC) and into naphtacyl esters for examination by HPLC. The results showed that both residues and all the sherds contained fatty acids (Table 1). Levels in sherds P5 and P7-9, however, were barely traceable.

The soil/sand extracts contained some fatty acids as well, but at barely detectable levels (less than 5 percent of those from the other samples excluding sherds P5 and P7-9). The possibility of contamination must therefore be considered. However, experience suggests that as the fatty acid concentrations in the residues were not higher than those in the pots (excluding P5) it seems unlikely that ground contamination has occurred to any extent in most cases, particularly as one would have expected the absorbing properties of the carbonised surfaces to take up

TABLE 1
APPROXIMATE PERCENTAGES OF COMPONENT ACIDS

Results shown are based on both GL and HPL Chromatographic data

Sample	Lauric	Myristic	Palmitic	Stearic	Oleic	Linoleic	Palmitoleic	Other
P1	70	T	8	2	20	–	–	–
P3	30	22	20	T	25	2	–	1
P4	40	20	15	T	10	5	–	10
P6	T	75	14	1	10	–	–	–
P10	–	T	35	1	40	2	8	14
R2	–	2	40	3	30	4	13	8
R1	5	3	33	3	46	7	–	3
P5								
P7-P9	–	T	T	–	T	–	–	–
Soil								

Levels were too low for quantification on Sherds P5, P7-9 and all soil samples.
– = Not detected T = Trace <1%

substantially higher amounts. It seems more reasonable to assume that vegetable debris, possibly from food preparation or even natural causes, has been "dumped" on the soil and consequently contaminated it. This problem does indicate the need to take special note of sample environments and local vegetation when sherds and soil are being selected for any study, particularly of this type.

The fatty acid distribution patterns obtained for the four samples that gave identifiable TL chromatograms were in good agreement with the TLC evidence. However, sherd P1 showed unexpected levels of lauric and oleic acids, which could indicate the use of a member of the Lauraceae family, possibly a species of Cinnamomum. Sherds P2 and P6 gave interesting results, as both contained high levels of myristic acid (80 percent or more) accompanied by low levels of palmitic and oleic acids. Such results suggest the use of a member of the Myristicacae family.

The fatty acid pattern obtained for P3 was similar to that of a member of the palm family. The oleic acid level (approximately 25 percent) is somewhat high for coconut or palm kernel oil and is more in keeping with the levels found associated with the betel nut (a related family). However, the acid levels are not constant but depend on the nature of the soil, processing, etc. What does seem certain is that the source is not a true palm oil but a product of seed fat.

Of the remaining potsherds, P10 gave a similar result but additionally contained palmitoleic acid, a fish acid, much weaker than that obtained for the associated residue R2. Sherds P5 and P7-9 gave low levels of palmitic, myristic and oleic acids only.

All the soil/sand samples also contained only myristic and palmitic acids but at barely detectable levels. In this latter case, therefore, ground contamination is a possibility.

The chloroform extracts yielded traces of the substances already detected in the hexane extracts but sherd P1 also contained traces of wood tar. As this sherd comes from a different location from the remaining samples, it may well show a change of vessel usage or cooking process. At this stage of the investigation, it remains an interesting enigma.

The absence of wood resins from the other samples supports a genuine food utilisation origin for the organic materials. If the substances extracted had originated from fire (for example, resins distilling out of the wood during the burning process), then one would expect wood resins to be present in some quantity.

The propanol and water extracts were examined by TLC for such materials as carbohydrates, and by electrophoresis for proteins. The only positive results obtained were for the sherds P10 and P6 which contained traces of sucrose. No additional substances were detected by either GLC or HPLC. Hydrolysis of the extracts with 6M hydrochloric acid for 24 hours gave no amino acids except slight traces in P10 and its associated residue R2. One must conclude that either the proteins have been totally degraded (unlikely since sucrose was detected), or the pots were never generally used for meat cooking (except possibly for fish in sherd P10).

The residues and all the aqueous extracts were tested for a range of inorganic ions. All samples gave (not unexpectedly) positive chloride and carbonate results. The absence of phosphates from the samples gives further support for the vegetarian nature of the pot contents.

Finally, the elemental composition of the samples was determined by emission spectroscopy. All samples were found to contain the following "soil" elements: calcium, aluminium, magnesium, silicon, iron, titanium, copper, manganese, nickel, sodium, potassium and phosphorous. However, both residues and all the sherd samples, except P1, also gave chromium and lead at levels around to 1 to 2 parts per million. The absence of these from the soil samples suggests that either the pottery was made at some other site or, at some stage, a plant containing traces of these elements was employed or cooked in the pots. Further investigation into this matter is being undertaken. Again it is interesting to note that sherd P1 is the odd one out.

It is hoped that this preliminary report has shown the potential contribution that the study of organic remains in or on potsherds can make to identifying pottery usage. It must be stressed that this is an interim report and that several of the conclusions are tentative and will be subject to further investigation.

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