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DATING MATERIALS IN GOOD ARCHAEOLOGICAL CONTEXTS: THE NEXT CHALLENGE FOR RADIOCARBON ANALYSIS

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ABSTRACT. Radiocarbon dating has had an enormous impact on archaeology. Most of the dates are obtained using charred materials and, to a lesser extent, collagen from bones. The contexts in which charred materials and bones are found are often, however, not secure. There are 3 other datable materials that are usually in secure contexts: plaster/mortar, phytoliths, and the organic material in the ceramic of whole vessels. The plaster/mortar of walls and floors are often in very secure contexts. Phytoliths are abundant in archaeological sites and in some situations form well-defined surfaces. Whole vessels are usually found in secure contexts and their typologies are indicative of a specific period. Dating each of these materials has proved to be difficult, and solving these technical problems represents major future challenges for the ^{14}C community. The effective use of charcoal and bone collagen for dating can also be improved by paying careful attention to the micro-contexts in which they are found, such as in clusters or as part of well-defined features. Pre-screening to identify the best preserved material can also contribute to improving the accuracy of the dates obtained. A general objective should be to have an assessment of the quality of the material to be dated so that the potentially invaluable information from outliers can be exploited.

INTRODUCTION

Radiocarbon analysis is a powerful tool for obtaining absolute ages of past events recorded in the archaeological record. The quality of a ^{14}C date is a function of the degree of confidence in the archaeological context from which the sample is recovered, the demonstrated purity of the material to be analyzed (van Klinken 1999; Alon et al. 2002), and the known accuracy and precision of the analytical method (Scott 2003). All 3 parameters define the quality of the date. The first 2 parameters should, however, be assessed *independently* of the actual date obtained. In this way, the date obtained can be objectively evaluated. Unexpected results may provide invaluable archaeological information when problems of context and analytical procedures can be excluded. This information could lead to a revision of the chronology, but may also provide insights into the site structure and the site formation processes, such as disturbed contexts.

Most dates are based on the analysis of charred materials and, to a lesser extent, on the collagen preserved in bones. Unfortunately, both charred materials and bones are often not preserved in the locations where they were originally deposited, as they are susceptible to being moved by bioturbation. The contexts in which they are found, are therefore often not secure. In contrast, 3 materials exist that are often preserved in excellent contexts, and, in principle, can be dated. These are plaster/mortar, phytoliths, and the organic residues preserved inside ceramic walls. In practice, however, it has proved difficult to date all 3 of these materials. As a secure context is essential for ^{14}C dating, the next major challenges are to resolve these problems. There is, in addition, still much to do in terms of improving our ability to date bones and charcoal (Boaretto 2007). Here, I briefly review these aspects of ^{14}C dating.

WHAT ARE SECURE DATABLE CONTEXTS?

In the macroscopic context, visible architectural remains such as walls and floors almost always represent well-defined contexts. The datable material associated with walls and floors is plaster and mortar. Another datable material often present in archaeological sites is the organic matter occluded inside the silica of phytoliths (Figure 1) (Piperno and Stothert 2003; Piperno 2006). As phytoliths can form well-defined layers, these layers constitute a well-defined context (Shahack-Gross et al.

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2005; Albert et al. 2008). The layers may in some cases even be visible to the naked eye (Figure 2). In fact, such phytolith-rich layers have sometimes been mistaken for plaster floors. They, however, were not formed as well-defined surfaces, but they are the products of the decomposition of large amounts of organic material produced by plants (Albert and Weiner 2001). These accumulations of organic matter could have been food storage sites, thatched roofs, or most commonly, dung accumulations in animal enclosures. The end product after all the organic matter has been removed biologically is a layer of phytoliths that can range in thickness from millimeters to centimeters. These layers are generally well defined within the stratigraphy.

Figure 1 Micrograph of a phytolith assemblage extracted from a phytolith-rich layer from Tel Dor, Israel. Scale bar: 100 µm.

The organic matter adsorbed on the surfaces inside ceramic fragments is also, in principle, a potentially good context for dating, provided the fragments are from whole vessels (Stott et al. 2001). Individual sherds can be intrusive.

Bones or charred materials are usually not confined to a visible layer that can separate events that occurred before and after the formation of the layer. Bones and charred remains are often found randomly in many strata of a site. At a smaller scale, there are situations in which bones and charred materials can be in a good context, such as articulated skeletons, seeds in jars, or bones and charred materials clearly associated with a larger feature, such as an oven or a hearth. These, however, are often not common, and it is difficult to build a systematic chronology of a site based only on such contexts. In practice, bones and charred materials are collected from well-defined strata, and these are assumed to be *in situ*. Some rules of thumb can be applied, such as large bones are less likely to be intrusive, and clusters of charred seeds are less likely to be either intrusive or residual. For the latter situation, it is important to prove that the seeds are indeed charred, as it is common for ants, rodents, and other animals to transport these materials under ground.

Figure 2 Photograph of a phytolith-rich layer about a centimeter thick from the Iron Age strata of Tel Dor, Israel. Scale bar is 20 cm.

The current state-of-the-art is that the materials that can be dated with confidence, namely bone collagen and charred materials, are the ones that often are not in the best contexts. The materials that are in good contexts and, in principle, can be dated, such as plaster/mortar, phytoliths, and organic residues in ceramics, cannot yet be dated with confidence. It is therefore a worthwhile challenge to solve these technical problems.

THE STATE-OF-THE-ART

Lime Plaster and/or Mortar has been studied as a possible dating substrate for more than 20 yr (Van Strydonck et al. 1986, 1989, 1992; Ambers 1987). The problems are well known. The component that is datable is the calcite produced from the reaction between calcium hydroxide and atmospheric carbon dioxide. This calcite is, however, inherently unstable both because it is relatively disordered at the atomic level (Chu et al. 2008) and the crystals are small. Furthermore, this binder calcite is often associated with larger fragments of limestone that are deliberately added or were only partially burnt during the production of the calcium oxide (Van Strydonck et al. 1986). This calcite does not record the age of the lime plaster. There have been several attempts to quantify the relative proportions of binder and limestone aggregates in order to “correct” the date obtained (Heinemeier et al. 1997; Lindroos et al. 2007). The more difficult problem is knowing whether or not the binder calcite has recrystallized and has lost its original ^{14}C signal. It has been proposed to use the ratio of 2 peaks in the infrared spectrum of calcite, ν_2 and ν_4, 875 cm^{-1} and 713 cm^{-1}, respectively, to track this diagenetic change (Chu et al. 2008).

Phytoliths are composed of the mineral silica (also known as opal) and a few weight percent of organic material (Piperno 2006). The organic materials should maintain the original ^{14}C signal at the time it was formed. In fact, the signal should be very reliable bearing in mind that the organic material is totally isolated from the surroundings. Phytolith dating started in the 1990s (Mulholland and Prior 1993). Few dates from organic materials from phytoliths have been published (Piperno and Stothert 2003). Several other laboratories, including my own, have been trying to date phytolith organic material, but with little success. Either the dates are too young or too old. We suspect that the siliceous surfaces of the phytoliths somehow strongly bind carbon dioxide. A complex procedure for extracting protein intrinsic to diatom frustules has been presented (Hatté et al. 2008). This method might provide some new methodological directions for phytolith dating as well.

Organic residues inside ceramics have been extracted and analyzed for their ^{14}C contents (Stott et al. 2001). This study showed that this approach is feasible, but technically challenging. Furthermore, some inconsistencies were noted between the ^{14}C contents of different molecules extracted from the same vessel. This indicates that this sample was contaminated to some extent. The advantage of using the residues from whole vessels is that the context is secure.

DATING OF BONES AND CHARRED MATERIALS

It is helpful to differentiate macro-context from micro-context in relation to ^{14}C dating of bones and charred materials. The macro-context refers to the archaeological context visible to the naked eye and how well characterized this stratum is in the site. The micro-context refers to the local environment in which the sample to be dated is located.

The first step is to only consider samples from strata whose macro-contexts are well defined and secure. Architectural remains, installations, and *in situ* ceramics are examples of such contexts. Ceramic assemblages, and in particular complete ceramic vessels, are important for defining good contexts. Seeds found inside a silo or a vessel can be considered as excellent contexts for ^{14}C samples. Only after strata with secure archaeological contexts have been identified should the question of which materials are better suited for dating be addressed. This will avoid the temptation to date the ideal sample type even though the context is questionable.

The next step is to consider the micro-context. Within a stratum, there may be regions where micro-context is more secure than in other locations due, for example, to absence of bioturbation or human intervention. Burrowing activities of various animals can move artifacts around. If this has occurred, then the samples are regarded as being intrusive. If this possibility has not been excluded, such samples should not be analyzed. A more difficult situation is, for example, to associate scattered charred seeds found on or in a floor to an *in situ* vessel partially embedded within the same floor. These may or may not be contemporaneous, as the floor sequence may not be complete and/or the seeds may belong to an earlier floor. Thus, obtaining information on the floor formation processes is important.

Bones: Pre-Screening and Quality Control

Bones are potentially excellent ^{14}C samples provided that they still contain preserved collagen protein (Hedges 2002). There are many other proteins in bone besides collagen (Lowenstam and Weiner 1989), and they tend to be more stable or better protected by the mineral phase, and thus can be found in bones in which the collagen has degraded. These proteins, however, for reasons unknown, do not provide reliable dates. The collagen in bones can be regarded as short-lived, even if the animal from which the bone was derived lived for a long time. The reason is that bones continually undergo remodeling, and thus the collagen in any given mature bone can be between a few years old and at most around 30 yr old (Price et al. 2002).

A good indication that the bone may contain collagen can be obtained in the field by dissolving a small amount of bone in acid and by visual inspection, determine if an insoluble organic suspension remains. This is often collagen. This, however, needs to be proved in the laboratory. I often use this assay in the field.

There are a few "rules-of-thumb" that can be taken into account in the field in order to increase the chance that the bone samples collected will be suitable for ^{14}C dating. The presence of high concentrations of clay in the sediments minimizes water throughput, and this in turn may result in better bone preservation. Bones that are not brittle when fractured may have preserved collagen.

If collagen is preserved, more tests need to be undertaken in order to determine whether or not the collagen is contaminated with other organic material. The C/N ratio is widely used, as collagen has a ratio quite different from most other forms of organic material, or even proteins (DeNiro 1985). Another approach is to obtain an infrared spectrum (DeNiro and Weiner 1988). As collagen *in vivo* has no associated polysaccharides, the infrared spectrum readily detects the presence of additional organic materials as they usually have a strong absorption peak in a region where collagen hardly absorbs. After minerals and contaminating organic materials have been removed by dissolving the collagen and filtering, it is advisable to recheck whether indeed the final collagen sample is free of mineral and/or humic substances contamination (Yizhaq et al. 2005; Gianfrate et al. 2007).

CHARRED ORGANIC MATERIALS

It is often assumed that charcoal and other charred organic materials are inert because they are not degraded by microbes. However, it has been demonstrated that this is not the case (Bird et al. 2002); these materials undergo oxidation and change from being hydrophobic when initially produced to being hydrophilic after oxidation. The main change chemically is the introduction of charged carboxylate groups (Cohen-Ofri et al. 2006).

In a study of charcoal structure and preservation, Cohen-Ofri et al. (2006) used a variety of different methods to characterize fossil charcoal. None of these, however, appeared to be useful for assessing the state of preservation of the charred materials that are most suitable for dating. Such charred materials should be stable enough to withstand the very harsh treatments involving alkali, acid, and wet oxidation (Bird et al. 1999) that are commonly applied for removing the contamination. We have found that to date the most practical approach is to monitor the weight loss of the sample after each acid and alkali treatment (Rebollo et al. 2008). This can be considerable for poorly preserved samples. The samples that lose the least weight are regarded as being better preserved and, hence, more likely to be free of contamination after the AAA treatment. The AAA procedure itself could be tailored to the state of preservation of the sample (Boaretto 2007).

Another problem with major losses in weight is that this tends to increase the relative proportion of clay in the sample. As clay can also contain associated organic matter of a different age, this can alter the date obtained. This was demonstrated during the dating of the site of Motza in Israel (Yizhaq et al. 2005). The presence of remaining contamination after each stage of the AAA treatment can be determined by the fluorescence signal using micro-Raman spectroscopy (Alon et al. 2002). This can also be used to differentiate the purest samples for dating.

For charred materials, as in the case of bone, there are also a few "rules-of-thumb" that can be taken into account in the field in order to increase the chances of collecting the best preserved charcoal. We have noted in Kebara Cave, Israel, that charcoal is preserved in parts of the cave where ash calcite and bones are absent (Rebollo et al. 2008). Rebollo et al. (2008) suggested that this is due to a lowering of the pH in this region that not only caused the bones and ash to dissolve, but also removed metals such as iron and manganese that were bound to the charcoal. These metals are known to be able to catalyze the oxidation of charred materials. Thus, the charred materials present in contexts where calcite is absent in the sediments may be better preserved.

INTEGRATING ALL THE DATA

The key to being able to analyze the whole set of dates obtained is to not have included from the outset any samples that have unacceptable uncertainties. In this way, the data set is of uniform quality, and can be analyzed as a whole. This analysis, be it by inspection or by mathematical modeling, will define the resolution of the data, and will identify any outliers or misfits. The latter can be excluded and the resolution can be redefined provided the criteria used are applied consistently (Boaretto et al. 2005; Sharon et al. 2007). On the other hand, it may well be that the outliers actually highlight previously unconsidered scenarios, which may now be taken into account. This is, in essence, the scientific method.

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