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Determining Stone Tool Use: Chemical and Morphological Analyses of Residues on Experimentally Manufactured Stone Tools

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We report on experimental and chemical investigation of bamboo and bone residues on used and unused modern stone tools. Flakes used were manufactured from a chert nodule and employed in three ways: splitting of bamboo, scraping and splintering of bone; others were left unused. Specimens were examined using light microscopy, SEM, and EDS elemental analysis. Tools used to process bamboo and bone exhibited chemically and morphologically distinct bamboo and bone residues. Similarity in morphology between isolated bamboo mineral and residue on stone tools used to process bamboo indicates the bamboo mineral material adheres to tool surfaces. All residue morphologies persisted through a treatment designed to simulate diagenesis, suggesting that processing residues may persist on ancient tools. The elemental signatures of the residues were slightly altered by the diagenesis treatment, but remained distinctly different from one another. EDS elemental analysis and SEM examination, when used in conjunction with the chemical signature and morphology of suspected residue sources, has potential to yield definitive answers to questions of ancient tool use.

Keywords: STONE TOOLS, LITHICS, BAMBOO, PHYTOLITH, RESIDUE.

Introduction

Recent innovations in the analysis of stone tools have provided a means to determine past cultural practices. Much of the information has been gained by analysing tool morphology and microwear features (Keeley & Toth, 1981; Toth, 1985), and also from experimentally reproducing tool manufacturing and tool use (Toth, 1987; Toth & Woods, 1989). Some additional information has been gained through observations of the exposure of non-human primates to stone tool-making activities (Toth, 1993; Westergaard & Suomi, 1994), and chance encounters with peoples whose life strategies depend heavily on stone tools (Toth, Clark & Ligabue, 1992).

In addition to micro-erosional features on lithic surfaces, residues adhering to tool surfaces may provide insights into tool use and environmental conditions. This is particularly true if the residue is of an inorganic (i.e. mineral) rather than organic nature, since such material will persist longer in a greater variety of burial environments.

Plants and animals contain a variety of mineralogical components. Plants, particularly grasses (Yoshida, Ohnishini & Kitagishi, 1962; Jones, Milne & Sanders, 1966; Geis, 1978), are widely known to be silicified, and the mineralized fragments are commonly referred to as *opal phytoliths*. Animals also possess mineralized tissues, particularly the minerals apatite and carbonate in bones and teeth. When stone tools are used for the

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processing of plants and bones it is likely that this mineral component may adhere to the stone surfaces, and persist for some time during burial. Indeed, environments that favour the preservation of a stone tool also favour preservation of the mineral component of the residue on a stone tool.

Although numerous studies have investigated the morphology of tool residues (Briuer, 197; Shafer & Holloway, 1979; Anderson, 1980), chemical analysis of residues on stone tools has not been extensively explored, an exception being the analysis of blood residues on tools (Loy, 1983; Nelson, 1986; Gurfingel & Franklin, 1988; Loy & Wood, 1989; Kooyman, 1992, Loy & Hardy, 1992; Smith & Wilson, 1992). For this study, we have experimentally investigated the chemical and morphological nature of bamboo and bone residues on stone tools, and the likelihood that they might persist after burial.

The archaeological context of this work follows from field-work in 1990–1992 by a combined United States–China research team excavating earlier Pleistocene sediments with utilized stone tools and fossil fauna in the Nihewan Basin, Hebei Province in northern China. The palaeomagnetism of these beds is reversed, indicating an age of $\geq 1{\cdot}0$ million years. This work concerns the "Movius Line", or the imaginary geographical line drawn for the Lower Palaeolithic which divides Africa, the Near East and Western Europe with their developing handaxe technologies from Eastern Europe and South-eastern Asia where "chopping-tool" industries and use of casually retouched flakes were dominant. Several explanations exist for this discontinuity, including that the eastern regions were subject to chronological, geographical and other barriers, and also that there were differences in functional requirements between the separated peoples.

One provocative explanation includes the favoured use of bamboo as a raw material. Bamboo was and is plentiful in these regions and contains up to 70% pure silica by weight (Jones, Milne & Sanders, 1966), giving crude tools fashioned from splitting bamboo glass-like sharpness. Under this hypothesis, stone tools take on a secondary role, their main purpose being the initial processing of bamboo. Within this context, an analysis of tool residue that indicates bamboo processing might contribute critical support to this hypothesis. We embarked upon the work described here in order to learn if it is reasonable to expect bamboo to persist as tool residue, and whether it is distinguishable from other basic types of residue, such as bone.

Morphological Method

Tool flakes were manufactured from chert rock experimentally and then pounded into bamboo (*Bambusa indigena*) growing at the north China field site. Once settled into the bamboo, the chert was further struck in order to wedge through the bamboo and thus break the bamboo culm at the wedge point. It is likely that *Bambusa indigena* or some species of *Bambusa* was available to prehistoric occupants of the site. After longitudinal splitting operations were performed on the broken bamboo using the same chert flake, concentration of residue was obvious along the tool edge that had impacted the bamboo. A second chert flake was used to scrape and splinter *Odocoileus virginianus* (white-tailed deer) bone that had been commercially purchased as venison meat. This bone was uncooked and received no pretreatment, except minimal defleshing with fingers in order to expose the bone surface. It is likely that prehistoric occupants of the north China site had access to some species of deer, probably of the genus *Cervus*. All tool surfaces were examined by light microscopy. A third chert flake was left unused. Tools were then rinsed with water and prepared for examination under the Scanning Electron Microscope (SEM). Tools were first fractured with a larger piece of hand-held chert in order to create SEM chamber-sized fragments. Fragments bearing residue were identified under the light microscope, and then mounted on aluminium stubs and coated with Au according to standard SEM techniques. Fragments bearing residue were also soaked in 35% H_2O_2 for 24 h at room temperature to simulate the effects of diagenesis or burial. After soaking in peroxide, the specimen was rinsed in de-ionized water, and then mounted and coated in Au according to standard SEM techniques, which were performed to look for changes in the residue resulting from the H_2O_2 treatment.

The H_2O_2 treatment acts to remove any oxidizable organics; preferential removal of oxidizable organic components is a commonly observed attribute of aerated burial environments.

Approximately 1 g portions of the bamboo and bone used in the processing experiments were soaked in 35% H_2O_2 for 24 h at room temperature to remove organic matter and expose mineral components. The mineral residue was then rinsed in de-ionized water, mounted, coated in Au, and examined using SEM. Another portion of the bamboo was digested using the method described by Geis (1978) which involves digestion in H_2SO_4 followed by oxidation with H_2O_2. The resulting mineral material was examined under light microscope, filtered through a glass filter (fibre diameter = 1 μm), mounted, coated in Au, and examined using SEM.

All SEM work was done on a IDIS-microscope (stage 2) at 10 kV. Magnification levels ranged from 93 to × 3900, with most features showing best resolution at about × 200.

The entire experiment was repeated twice through in order to ensure reproducibility. Identical results were achieved by repeating the experiment.

Chemical Method

SEM equipped with energy dispersive spectroscopic (EDS) abilities was used to assess the presence of elements with atomic mass greater than 12 [g mol^{-1}] in some samples. In using EDS, a 1 μm^2 area of the specimen is focused upon using SEM with voltage set at 10–20 kV and a detector is activated to sense element specific dispersion between the energies of 0·0 and 0·010 keV. If the peak dispersion detected at a certain energy exceeds the given peak area for the detection limit, EDS identifies the element specific to that energy as present. In this way, EDS analysis provides a *qualitative* chemical analysis of elements present in a sample. It is important to remember that EDS only senses dispersion by the surface of what is being analysed. For this reason, we expect the EDS spectrum of residue analysed on a stone tool to be the spectrum of the residue only, not residue spectrum + tool spectrum. Standard preparation technique employed on all samples analysed by EDS includes rinsing in de-ionized water, mounting, carbon coating to ensure necessary conduction and X-ray penetration; it is this coating process that renders the technique useless for determination of carbon (atomic mass = 12 g mol^{-1}) and lighter elements.

The purpose of invoking EDS technique was to compare elemental compositions of processed substrates, resulting tool residues, and resulting tool residues after subjection to the H_2O_2 treatment. Substrates were analysed in pure form, while residues and treated residues were analysed on the tool surface, residue removal and isolation is not necessary for this procedure. Preliminary investigations revealed that pure substrate yielded the same EDS spectrum as residue on tools after being used to process the substrate. Tool specimens analysed with SEM/EDS were all experimentally manufactured according to the process described previously. An unused chert tool, an approximately 1 g sample of the processed bone, and an approximately 1 g sample of the processed bamboo were considered the "pure" substrates, and were prepared according to standard techniques and then subjected to EDS analysis. For comparison with the untreated substrates, an unused chert tool, a tool used to process bone, and a tool used to process bamboo were all soaked in 35% H_2O_2 for 24 h at room temperature to simulate the effects of diagenesis or burial, and then prepared according to standard techniques and subjected to EDS analysis.

Results of the Morphological Analyses

Observed by light microscope, the unused tool exhibited a uniformly rough surface with no outstanding features. Small dark discolorations were metallic mineral impurities found in the chert. The SEM image of the unused tool specimen (Figure 1) revealed the rough, porous aspect of the unused tool surface.

Bamboo mineral material isolated according to the method described by Geis (1978) appeared to have two morphologies under the microscope: small, indistinct particles, and bundles of prismatic structures (Figure 2). Light microscopy and SEM of bamboo residue on stone tools also exhibited two distinct morphologies: smooth, waxy surfaces, and bundles of prismatic structures (Figure 3). Focusing through the field of magnification revealed that these residue features are raised relative to the residue-free tool surface, indicating that they represent mass added to the stone tool during processing.

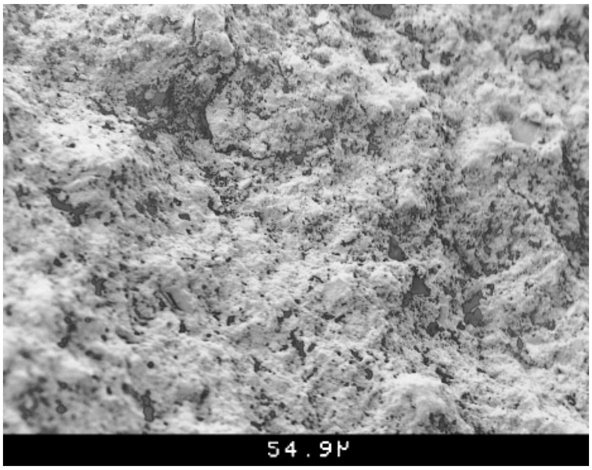

Figure 1. SEM image of unused tool surface. Bar represents 54·9 μm.

Figure 2. SEM image of isolated bamboo mineral material. The bamboo mineral has been mounted on glass filter with fibres of approximately 1 μm in diameter: the filter appears as the threaded matrix of the image. The bar represents 44·2 μm.

After soaking in 35% H_2O_2 for 24 h at room temperature, bamboo residue could be located on the stone tools that had been used to split and pound bamboo (Figure 4). The bundles of prismatic structure persisted extremely well through the H_2O_2 treatment; in fact, bamboo features on the tool identified before the treatment were recognizable after the treatment.

Light microscopy and SEM analysis of the bone residue resulting from processing by stone tools exhibited an amorphous greasy appearance, that lacked

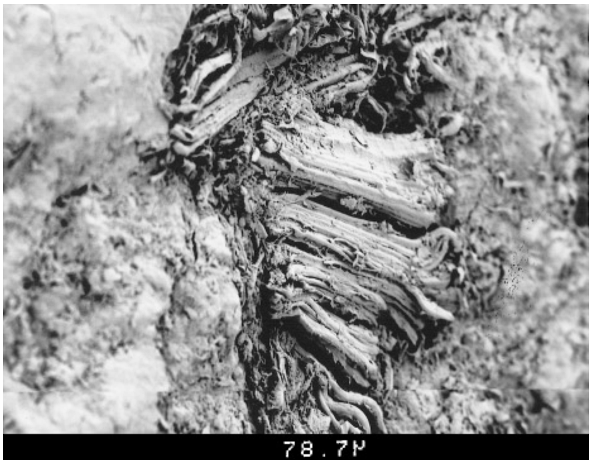

Figure 3. SEM image of bundle of prismatic structures in residue on stone tool after processing of bamboo. Bar represents 78·7 µm.

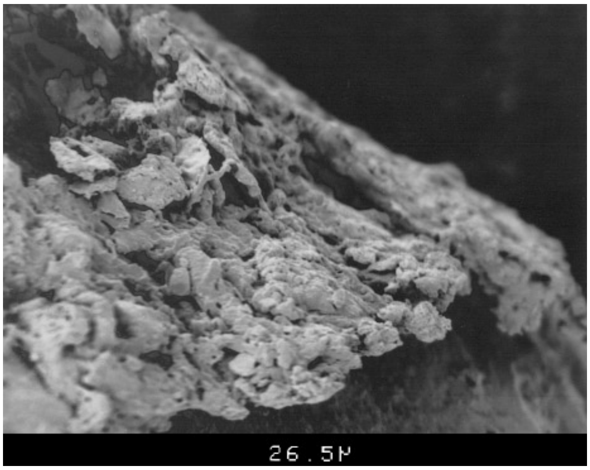

Figure 5. High magnification SEM image of residue on stone tool after processing bone. Bar represents 26·5 µm.

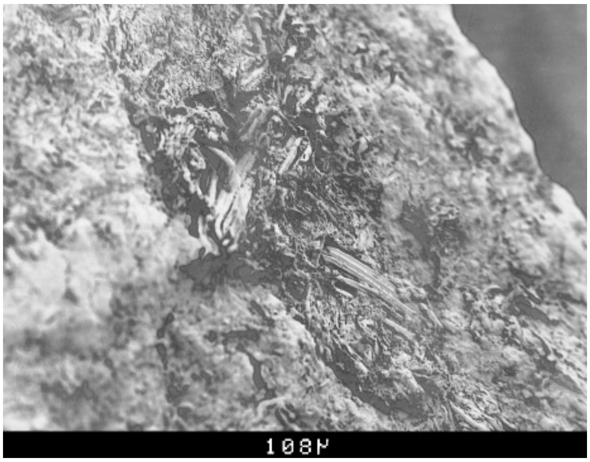

Figure 4. SEM image bundle of prismatic structures in residue persisting through H_2O_2 treatment on stone tool used to process bamboo. Bar represents 108 µm.

characteristic structure even at high magnification (Figure 5). Field-of-focus manipulations did reveal the residue to be raised relative to the tool surface, indicating that the residue did represent mass transferred to the tool as the result of bone processing. Light microscopy revealed that bone residue was noticeably reduced on the surface of the tool after the H_2O_2 treatment, but SEM analysis did not reveal significant morphological changes in the post-H_2O_2 bone residue as a result of the treatment.

Results of the Chemical Analyses

Results of SEM/EDS analyses are presented in Table 1. A representative EDS spectrum is presented in Figure 6.

Discussion

Both bone residue and bamboo residue are raised relative to the stone surface of the tool, and residues exhibit a distinctly different surface appearance from that of the unused stone tool. The similarity in morphology between the isolated bamboo mineral material and bundles of prismatic structures in the residue on stone tools that have been used to process bamboo indicates that bamboo mineral material has been transferred to the stone tool during processing. This residue is equivalent to “sickle sheen” or “gloss” first recognized in the 1930s as the result of processing plant materials. Our observations of the residue concur with the suggestion that the gloss forms as a result of the fusion of plant mineral (opal) to the surface of the tool (Witthoft, 1967). The evidence that these prismatic bundle structures persist through a treatment designed to simulate diagenesis encourages hope that plant fibre-residue features could persist on ancient stone tools.

Residue on tools used to scrape and splinter bone exhibits a morphology that is distinctly different from that of the bamboo residue. Although both bone and bamboo residue are raised relative to the stone tool surface, the residues differ distinctly in their structure; bone residue is amorphous and greasy while bamboo residue contains strikingly prismatic, fibrous structures. Both bone and bamboo residues persist through a treatment designed to simulate diagenesis, although the treatment significantly reduces the amount of residue adhering to a stone tool that has been used for bone processing.

The results of EDS analyses indicate that the elemental signatures of compared substrate are different and that these distinctions persist through the H_2O_2 treatment. The elemental signatures evidenced by EDS faithfully reflect the composition of the substrate: chert (SiO_2), bone (apatite $Ca_{10}(OH)_2(PO_4)_6$, and calcite $CaCO_3$), and plant mineral ($SiO_2{\cdot}H_2O$ plus occluded organics). All elements persist in their signature through the H_2O_2 treatment, with the notable exception of potassium, and in the case of bamboo,

Table 1. Results of SEM/EDS analyses

Element	Al	Si	P	S	K	Ca	Fe
Atomic mass (approximate) (g mol^{-1})	27	28	31	32	39	40	56
Unused chert tool		x					
Unused chert tool after H_2O_2		x					
Bone			x		x	x	
Processed bone after H_2O_2			x			x	
Bamboo	x	x			x		x
Processed bamboo after H_2O_2	x	x		x			

"x" indicates that the designated element was present in the sample specified.

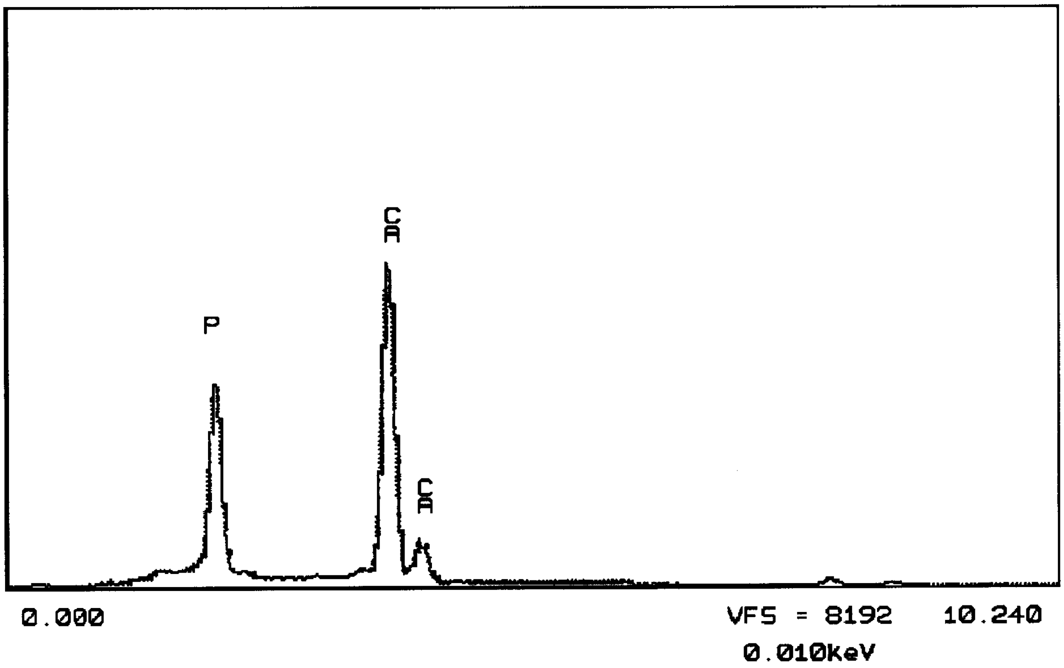

Figure 6. A representative EDS spectrum. This spectrum describes the elemental chemistry of the residue persisting on a stone tool after processing bone, and after the H_2O_2 treatment.

iron. Our results indicate that K and Fe may be susceptible to removal by diagenesis and burial. The appearance of sulphur in the bamboo residue only *after* the H_2O_2 treatment is intriguing, and we can offer no absolute explanation. It may be that the composition of the residue is slightly inhomogenous with respect to trace elements, and that the several analyses we did on the H_2O_2-treated bamboo residue were done in a location with detectable S content.

Implications of the Study

SEM morphological studies in conjunction with EDS analysis have been successfully used to distinguish basic types of tool residue. Both the morphology and the elemental signature of the residue have been shown to be specific to the processed substrate, and to persist through a treatment designed to simulate diagenesis. Application of these techniques to questions concerning the use-interpretation of ancient stone tools will be most powerful when complemented with a comparison study of suspected residue sources or source proxies. In expanding the application, we wish to note that there are many types of elemental analyses available to the scientist, from monolayer ionization to quantitative elemental "mapping". The type of elemental analysis performed could be specifically chosen to accommodate samples that cannot be destroyed or altered. The particular SEM and EDS methods employed in this study required the destruction of samples: firstly the tools were broken into small pieces in order to accommodate the small size of the SEM sample chamber; and secondly, the tools were coated in Au for SEM analysis, and in carbon for EDS analysis. Many of the features we found useful for characterization in these residues were visible at magnifications of about

× 200—a power easily obtained using a standard light microscope. Light microscopy carries the disadvantage of not being able to provide focus on multiple sample planes—whereas SEM can—but light microscopy does not necessitate sample destruction. In practice, light microscopy might be used to look at a suite of tools from a site, in order to choose artefacts suitable for sacrificing to residue identification.

With respect to collection of artefacts slated for residue analysis and identification, we recommend as little excess handling as possible. Dry methods only should be employed in cleaning samples, such as "cleaning" with compressed air. Any abrasion of residues such as brushing and scrubbing should be avoided, as should extremes in temperature. A note of caution is appropriate here; this study has not presumed to characterize diagnostically the plant residue of bamboo species, only to differentiate bamboo residue from residue acquired as the result of bone processing. Before an identification of bamboo residue can be made, further work is required comparing residues acquired from bamboo to those acquired from other grasses and reedy plant families, such as *Typha*.

Once the nature of tool residue is determined, a wealth of other analyses may be employed according to one's interests. It has been suggested that the stage in the life cycle of the plant processed can be determined from the morphology of sickle sheen produced (Bettison, 1985). Also, the mineral components of both plant silica and bone occlude organic compounds and therefore may be appropriate for ^{14}C dating (Wilding, 1967; Mulholland & Prior, 1993). Some work has been done using the carbon stable isotope composition of phytolith-occluded organic carbon to determine the C_3/C_4 photosynthetic pathway of the plant species of origin (Kelly, 1991). If actual phytoliths can be observed in the plant residue, it may be possible to utilize the extensive work that has been done to link the morphology of the phytolith to the plant species of origin (Calderon & Soderstrom, 1973; Terrell & Wergin, 1981; Kondo & Sase, 1986; Piperno, 1988).

The first step of all these possibilities is to locate and identify the nature of stone tool residue, using the methods we describe here. Once the residue source is known, the archaeologist is led into considering the context of the implied tool use. Beyond this, the residue itself may be further explored, and may lead to discoveries of the time, the environment and the life strategy of the ancient tool manufacturer.

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