The elemental chemistry of lithic microwear: an experiment

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Abstract

This paper examines the ability of elemental analysis to distinguish microwear traces on stone tools. Our research hypothesised that cleaning procedures of experimental specimens may have heavily influenced previous studies in this area. Experimental flakes are used and cleaned by two alternative methods before laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is applied to study use-wear chemistry. The results show that elementally recognisable traces remain on stone surfaces even with severe cleaning. Also studied were archaeological sickle blades from two sites in Northern England. The results were counter-intuitive demonstrating that experimentally validated models potentially require extensive modification and clarification before being applied to archaeological material. This research identifies methodological problems and errors concerning cleaning within previous experimental studies and highlights new directions for this quantitative analytic approach in microwear analysis.

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1. Introduction

In 1930, E. Cecil Curwen attempted to identify the cause for the polished surfaces observed on the edges of some ancient (Neolithic) serrated blades from various locations in Europe, the Near East and North Africa [13]. Aware that the principal hypothesis was that these tools were used for cutting corn, Curwen performed experiments with flints used as sickle blades. Upon examining the blades he observed that the band of surface polishing along the edge of the experimental sickle blades was much greater than that on the archaeological blades from Britain. Curwen thus concluded that these serrated blades were probably used for sawing wood rather than for reaping grain [13]. This conclusion was incorrect. It is likely that if Curwen had adequately cleaned his experimental specimens, he would have observed that the amount of surface polishing on the experimental blades was directly comparable to that on the archaeological blades.

Curwen was among the first to observe the microscopic characteristics of stone tools to infer use. Since the development of microwear analysis (following [30,38,46], many studies have examined new techniques to derive stone tool use from surface wear or residues. Analysts have experimented with interferometry [19], profilometry [43,44], digital recognition [22,48], computerised expert systems [18,23], residue analysis [6,27,42] and elemental characterisation [1,10—12,40,41]. The main impetus behind such studies is to provide a more objective means of wear identification and functional interpretation. Unfortunately, these techniques are yet to develop beyond the experimental stage except lithic residue analysis, which is being increasingly applied to assemblages, but continues to demonstrate difficulties [42].

Further to the problems of devising appropriate methods to bring greater objectivity to the functional and
diagenic analysis of stone tools, lithic microwear analysts have had considerable problems identifying the mechanisms of microwear formation [15,34; pp. 51–53, 47].

The aim of this study is to use elemental characterisation to examine the impact of intensive cleaning of lithic specimens and the survivability of specific chemical signatures. As such it highlights methodological problems and errors within elemental studies, examines the potential of the method to infer use on lithic artefacts, increases understanding of the mechanisms of wear formation, and highlights new directions for methodological investigations.

2. Background

From a modern analyst’s perspective there are two ways in which the function of an archaeological stone tool can be sought. Firstly, residues that remain on the surface such as blood and plant fibres can be identified, either chemically or morphologically; this is the field of residue analysis. Secondly, the microscopic features of wear produced by different materials can be characterised optically; this is microwear analysis. There is, however, some ambiguity regarding the formation processes of microwear and with the definition of the term ‘residue’. For the sake of clarity residue is defined here as non-parent material that is adhered to or incorporated on the surface of an object. From a tribological perspective (the field of engineering concerned with wear) residues can be considered as ‘wear debris’, adhering to the surface by cold-welds, in the case of adhesive wear, or by adsorption. Adsorption is defined as the atomic or molecular attachment to, usually a solid surface [35]. This can be either physical adsorption, which can be attributed to van der Waals forces, or ‘chemisorbtion’, which involves stronger forces of a chemical nature. Physical adsorption is highly reversible whilst chemisorbed material can only be removed under high energy circumstances.

Generally residue analysts have been concerned with macromolecular materials such as blood, lipids and plant remains, which can be removed from the surface of a tool. Other traces, those which are chemisorbed, have received little interest. These traces are resistant to heavy cleaning and are on a smaller scale consisting of molecules and individual elemental traces. Directly related to this are the mechanisms of wear formation which have been a central debate amongst microwear analysts (see [3,26,47]; for a summary see [15]).

Today in tribology, wear is seen as resulting from a complex amalgamation of a variety of different wear processes [29]. For simplicity, models of wear formation, as presented by lithic microwear analysts, can be put into two categories: those which support a purely abrasive process and those which suggest that although abrasion takes part, varying degrees of adhesive wear, atomic wear, diffusive wear and melt wear are responsible for the formation of microwear attributes (definitions of these terms can be found in [35]). The silica–gel theory, a very specific model of silica dissolution and particle integration [2,4], is an extreme example of the latter. Following work in the early 1990s it is seemed that microwear analysts would accept abrasive models [24]; but this debate has resurfaced following the results of elemental analyses.

The first application of elemental methods to study microwear was Andersen and Whitlow’s use of a variety of ion beam analysis (IBA) techniques [1]. They briefly mention how different use-polishes have different chemical profiles but mainly comment on the nature of polish formation, stating that their results show ‘strong evidence for the gel-formation hypothesis’.

Christensen’s research group, using proton induced X-ray emission spectroscopy (PIXE) and Rutherford backscattering (RBS), provide a study focusing on bone working [10] in which they concluded that the mechanism of polish formation is accounted for by the incorporation of mineral components of the worked matter, smoothing the roughness of the flint. A further study [11] found that wear produced by ivory can be distinguished from bone using microbeam PIXE and RBS. Their final study explored the mechanisms of wear formation further by implanting copper in the surface of flint flakes prior to use [12]. These studies, especially the latter, where implanted copper is not removed from the tool during use, conclude that wear formation mechanisms are predominantly adhesive.

Šmit et al. [40,41] provide a further two studies which essentially concur with the findings of the previous elemental studies. They studied the microdistribution and composition of wear using elemental mapping and show that elemental concentrations and their ratios can be applied to infer use on archaeological tools.

In contrast, important implications can be drawn from the studies of Jahren et al. [27] and Kamińska-Szymczak [28], which conducted a greater degree of cleaning than that of Christensen et al. [10–12] and Šmit et al. [40,41]. Jahren et al. [27] placed their experimental specimens in 35% hydrogen peroxide for 24 h, yet still observed bamboo fragments on tool surfaces using scanning electron microscopy (SEM). Kamińska-Szymczak [28] cleaned experimental tools using cold 6% HCl but her SEM figures show clear traces of physically adsorbed residue. Further to these, Shanks et al. [39] show that residue extraction from the surface and microcracks of a tool edge can only be achieved through harsh ultrasonic cleaning. As Jahren et al.’s and Kamińska-Szymczak’s cleaning methods left visible amounts of surface residue and
Shanks et al. identified the need for ultrasonic cleaning for residue extraction, it could be argued that physically adsorbed residue accounts for the results of Šmit et al. [40,41] and Christensen et al. [10,11], where cleaning methods were much less robust than in either of these cases. This hypothesis could also account for Christensen et al.’s [12] copper implantation experiment as the Cu could have been dislocated and mixed amongst residue remaining on the surface or lodged in microcracks.

These experimental chemical studies [10–12,28,40,41] have not reflected upon the implications of Curwen’s findings. As shown by Curwen’s study, cleaning and diagenic processes have always been an issue. Those studying microwear have tended to reduce chemical cleaning of surfaces from fear that they will alter wear traces on the stone tool surfaces or remove informative residues [15]. Those attempting to show that one can identify tool use through residue analyses do little cleaning of their experimental tools. If residues cannot survive most cleaning procedures, then how is it possible that they can survive for thousands of years in most burial environments? It is suggested that to be viable as a technique for reconstructing tool use, one must demonstrate that the survival of residue in some meaningful form on ancient archaeological specimens conforms to current diagenic and burial environment models of preservation.

Surface residue studies have also encountered problems similar to those in microwear studies where poor results from blind tests [17,31] and a general lack of confidence in the ability of immunological tests to perform in archaeological situations [8,20] have restricted growth in the field. One recent study demonstrates that microwear analysis and surface residue studies can be used well in conjunction [37] but, again, a recent blind test study [49] showed that after a month of burial 40% of the sample (n = 10) could not be identified correctly including one false positive result. These studies have grave implications on the long term survival of surface residues within a variety of different burial environments. On this basis elemental characterisation of chemisorbed traces may be highly beneficial to functional lithic studies as, theoretically, surface chemistry may be less susceptible to diagenic processes. Such signatures can thus survive for greater time scales than surface residues and be identified where post-depositional processes have confounded visual identification of microwear traces.

The following proxy study tests the ability of elemental techniques to identify traces of use on tools whose edges have been cleaned by two different processes in an attempt to answer questions about microwear formation mechanisms and an attempt to develop residue and microwear studies in a new direction.

3. Proxy study

3.1. Method

Fifteen freshly knapped flint flakes (Brandon flint) were randomly assigned to three groups. Five were used for 50 min to cut moist hay (Graminae sp.); another five flakes were used for 50 min to whittle soaked post-vellvet antler (Cervus elaphus). The remaining flakes were assigned to an ‘unused’ category (control). All flakes were further assigned, within groups, to two different cleaning methods, two to a ‘mild’ treatment and the remainder to a ‘harsh’ treatment.

‘Mild cleaning’ entailed soaking in water, soft brushing in soapy water, and rinsing with acetone. This represents a somewhat stronger cleaning method than those used in Christensen et al. [10–12] and Šmit et al. [40,41]. The harsh cleaning treatment comprised the mild process with an additional step: 10 min of ultrasonic in 5% ammonium hydroxide (NH₄OH), prior to the acetone rinse. This was derived through combining techniques used in microwear analysis [5,15] and those used for the extraction of residues from stone tools [39]. This treatment was not designed to replicate diagenesis or burial, but to maximise the removal of residue whilst preserving the surface of the tools.

Following cleaning, flakes were analysed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). LA-ICP-MS is a minimally destructive microprobe technique that can focus at specific areas on a sample and detect elemental concentrations at the ppm level [25,33,36]. The instrument used was a PlasmaQuad 3 coupled from a MicroProbe II Nd:YAG ultraviolet (200 nm) laser ablation system. Sampling was performed with a computer-controlled video imaging system consisting of digital mapping of ablation paths across polished areas of each tool which are then followed by the laser during analysis. The path shown in Fig. 1 took...
about 4 min to ablate and was typical of the sampling strategy adopted. The laser was used at 4 mJ (100% energy) and ablated at a speed of 30 μm/s, with the spot size set at 50 μm in diameter and 5 μm deep. Laser sampling liberates a dense aerosol made up of particles that are often variable in size. As the mass spectrometer sweeps the element range, this variability can lead to degradation in the precision of results. To reduce this effect three linked analytical runs are made in each sampled area. After ablation has started the ICP-MS carries out a survey run consisting of 20 sweeps of the mass range, dwelling on each mass peak for 1000 μs. Three analytic runs are then made, each lasting approximately 60 s. Each run consists of 60 sweeps of the mass range, measuring each specified mass for 10,000 μs and used a peak jumping system to study the specified isotopes only, thus reducing polyatomic and isobaric interference problems. The device was calibrated using the National Institute of Standards and Technology’s SRM611 and SRM613 glass standards. Because these are glass and not flint, some calibration issues, associated with matrix matching, can arise from the use of these standards. Glass standards are well tested, however, and are the closest to flint; calibration issues that may occur were not considered sufficient to impinge on the overall outcome of this analysis.

Two elements, phosphorus and manganese, were included in the LA-ICP-MS analysis. These were selected based on the composition of each of the three materials (flint, hay and antler), and the subsequent study of the biochemistry of these elements in each of the use materials. Phosphorus was selected as a potential marker of antler produced wear because of its high concentrations in antler, associated amongst other things with hydroxylapatite (Ca₁₀(PO₄)₆(OH)₂), a main structural constituent of osseous matter [9,45]. Other elements constituting antler were considered to be either less diagnostic, such as sulphur, or more susceptible to modification during post-depositional processes, such as sodium and calcium [7, pp. 84–87]. Manganese was selected because it is present in plants as an essential trace element [14] associated with photosynthesis and often concentrated in cell vacuoles [21]. Elements suitable for identifying grasses, amongst which was potassium, were either thought to be present in too low abundance or to be diagenetically unstable. Manganese was seen as a compromise between those which are stable and those which were present in too low abundance for this study.

The concentrations of these two elements in the three materials lead to the formation of an initial predictive model. Given that tools were unused or used on grasses or antler, then an enhancement of manganese in areas at the edge of a tool could be used to suggest that the tool was used to work grasses while an enhancement of phosphorus would be indicative of use on antler. The experimental program was used to test the basis of this model and to evaluate the behaviour of these elements under differing cleaning techniques.

The two alternative hypotheses were tested by this experiment. If after harsh cleaning, a chemical difference remained between the chemistry of used and unused tools then the experiment would further support an adhesive model. On the other hand, no significant chemical differences would be suggestive that the abrasive hypothesis was sufficient to explain our results. Fig. 2 illustrates the two generalised wear formation models and the implications of each model on residue and surface chemistry survival through the two stages of cleaning.

3.2. Results

Single-factor analysis of variance (ANOVA) was applied to evaluate experimental data. This technique is appropriate for testing the equality of several means [32: p. 64] and was used with a confidence coefficient of
0.95. The results of mildly cleaned specimens (Fig. 3a) indicate distinct variation with significant differences in elemental concentration between the two use categories and the control (phosphorus: \( F = 87.5, \ p < 0.0001 \); manganese: \( F = 81.7, \ p < 0.0001 \)). This pattern is very clear; it fits the predicted model and demonstrates that material is deposited from both antler and hay during use. The composition of use material can be predicted based on the elemental chemistry of the materials, supporting previous claims that have been made using different analytical methods [10–12,40,41].

The effect of harsh cleaning can be seen in Figs. 3b and 4. Although patterning can still be seen, the concentrations of manganese and phosphorus on the tools’ surfaces are generally lower and have greater sample variance. Statistically, concentrations of phosphorus are significantly higher (\( F = 40.2, \ p < 0.0001 \)) on edges of those flakes used to work antler. There was no significant difference between the concentrations of manganese (\( F = 2.49, \ p > 0.098 \)). Fig. 3b shows all data from each analytic run individually. Two data points (ringed) are extreme outliers and probably result from the combined effect of ablated particle variation and isotope scanning. When these are removed from the ANOVA and the sample means are used, the phosphorus result gains strength (\( F = 41.84, \ p < 0.0001 \)) and the manganese result becomes significant (\( F = 4.39, \ p < 0.047 \)). Fig. 4 shows these data as sample means, where the three runs from the same area of each tool edge are combined. This limits the variability caused by laser sampling. The graminae utilised edge that is similar in composition to the controls represents a sample where the ablation track was not placed sufficiently close to the edge of the piece.

4. Archaeological application

Four archaeological samples (Fig. 5) were analysed in the same manner as the experimental tools. Two of these tools, BLF.FEY and BLF.GIF, are from Lismore fields, Derbyshire. Each of these exhibits sickle gloss and was interpreted, with high confidence, by traditional
microwear analysis as being used to cut soft plant material [16]. The other tools, HC2.371.FB and HC2.141.SC+, were collected on the Lincolnshire Wolds and graciously provided by William Bee for this analysis. These are both serrated blades exhibiting sickle gloss along at least one edge. These were also interpreted by microwear analysis as being used to work soft plant material.

Analysis was carried out at two locations on the archaeological samples. The first was a region on the dorsal surface, carefully selected to be away from any areas exhibiting use-wear. The second location was along an edge in areas where microwear analysis detected surface polishing. Given that both areas on the same tool are likely to have undergone the same post-depositional processes, this technique provides a background chemistry specific to each artefact and burial environment, thus foregoing the requirement of knowing the geology for each type of flint studied.

4.1 Results

BLF.FEY was significantly enhanced in phosphorus at the working edge relative to its dorsal surface $(T = 3.06, p < 0.02)$ but shows no significant difference in the concentration of manganese $(T = 0.79, p > 0.4)$. BLF.GIF was significantly enhanced in phosphorus at the working edge relative to its dorsal surface $(T = 1.87, p < 0.05)$ but shows no significant difference in the concentration of manganese $(T = 0.53, p > 0.4)$.

HC2.371.FB was significantly enhanced in phosphorus at the working edge relative to its dorsal surface $(T = 6.69, p < 0.001)$ but shows no significant difference in the concentration of manganese $(T = 0.63, p > 0.5)$. HC2.141.SC+ showed no significant difference in the concentrations of phosphorus or manganese between the surface and the working edge.

5. Discussion

The experimental stage of this project has highlighted a number of important issues. Chemical analysis of the mildly cleaned tools produces distinctively different results to the tools treated by harsh cleaning. Whilst the control concentrations remain equal the mildly treated samples show considerably higher concentrations of the two elements studied when compared to harshly cleaned samples. Given the experimental design and control, this difference can only be accounted for by the limited removal of surface residues through mild cleaning treatment. The harsh cleaning treatment effectively removes these residues.

The implications of this result fall into two categories: one could expect that even harsher cleaning might remove all chemical traces; thereby supporting the abrasive model of wear. Alternatively, if harsh treatment was successful in its goal, these results illustrate the validity of a model of microwear formation incorporating adhesion or chemical dissolution. Unfortunately, it is becoming increasingly clear that identifying the precise model of wear is hard to achieve experimentally or theoretically. The harsh treatment used in these experiments was designed to remove all surface residues so one might favor a model of wear formation which incorporates both adhesive and abrasive forms of wear; however, one cannot assume that it was successful. Regardless of this moot situation, as a chemical signature is identifiable despite rigorous cleaning, these results identify that elemental analysis may have potential as a characterising technique.

As mentioned above, the mild cleaning treatment used here was harsher than cleaning methods in previous elemental studies [10–12,40,41]. Given the findings of this study one can conclude that surface residues were probably still present during analysis in these previous studies. The presence of residues on the tool surface confounds the ability to study actual surface composition and consequently wear formation mechanisms. Therefore, these results concur with the supposition that
previous studies, using limited cleaning methods, have restricted value in terms of understanding wear processes or the elemental characterisation of microwear itself.

The archaeological results interestingly contrast with the findings of our experimental study. In the experimental study it was seen that manganese showed enhancement where tools had been used to work grasses. Phosphorus on the other hand was raised to a significant degree after mild cleaning but only slightly after harsh cleaning. On the other hand phosphorus was significantly enhanced when tools were used to work antler. Based on this one would expect that analysis of the archaeological sickle tools would demonstrate a similar trend. However, analysis of these shows no enhancement of manganese and, for the most part, significantly higher levels of phosphorus. If the archaeological tools were not obviously sickle blades then these results might have led the authors to suggest their use to be of osseous in nature. Thus the experimentally verified predictive model failed for these archaeological tools.

Aside from use related chemical modification, it is unlikely that the slightly elevated potassium concentrations result from other processes such as retouch or hafting using antler or bone. Only one tool (BLF.GIF) had retouch that could have been pressure flaked using antler (the serrated edges of two tools were probably produced with the edge of another flint flake). As use is seen on both sides of two of these tools (Fig. 5), it is thought that they may have been turned around in their haft which could leave wear traces along one edge. Not surprisingly, microwear analysis found no evidence that antler was used as a haft for any of these tools, however, it is not impossible that traces related to hafting or residues from mastic might have influenced the wear chemistry. Further experimental work is needed.

The results of the archaeological tool analysis were not entirely unexpected. Manganese, although one of the only reliable markers of grass cutting, has a lower ionic potential than phosphorus and therefore might be considered to be diagenically less stable. Other burial environment interactions could also be a factor in this situation and a greater understanding of each tool’s burial environment would be needed to discuss this point. The significant levels of phosphorus in the archaeological sickle gloss are also not entirely unexpected. The results of the experimental work above show that phosphorus was raised to a significant degree after mild cleaning but only slightly after harsh cleaning. Given that the archaeological sickle blades were clearly used for a much greater period of time than the experimental tools one could expect a greater enhancement of transferred elements. This enhancement would only be very small and this is indeed the case for the archaeological tools. As with manganese one can also consider that other factors in the burial environment play a role in this process.

Analysis of the archaeological results has shown that the application of a simple, experimentally validated, predictive model cannot be made without further consideration of how the surface of a used tool might interact with its burial environment. Interactions between tool surfaces and burial environments clearly occur and further work to understand these processes is required to disentangle the complexities of microwear chemistry.

6. Conclusion

This research has identified that previous experimental studies did not fully anticipate the effect of limited cleaning strategies for studying wear formation processes. This also limited the accuracy of findings reported in these studies for the use of chemical analysis to infer use on stone tools. This study has shown that, under aggressive cleaning, elemental analysis of experimentally produced stone tool microwear can differentiate tool use. These results highlight the potential of the technique for differentiating tool use when surface residue has been destroyed or modified by the burial environment. These chemical differences are quite subtle and LA-ICP-MS has proved highly suitable for such analysis. The study of the archaeological samples has highlighted the need for a better understanding of biogeochemical interactions between the tool surface and the burial environment before the full potential of this technique is to be realised.

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