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Introduction

1.1. Why review lithic residue analysis?

Over 40 different techniques have been applied to the study of residues on stone tools (listed in the Appendix). However, a recent review of technical advances has not been undertaken. To date, reviews of lithic residue analysis techniques have been incorporated into wider reviews about lithic usewear (Grace, 1996; Odell, 2004, 2001), or have been confined to one residue type, such as starch (Copeland and Hardy, 2018; Hall et al., 1989; Loy, 1994), or one technical approach, such as reflected visible light microscopy (Langejans and Lombard, 2015), and IR spectroscopy (Monnier, 2018). Although there are a number of publications that have included, to a greater or lesser extent, methods of lithic residue analysis (Barnard and Eerkens, 2007; Brown and Brown, 2011; Evershed, 2008; Evershed and Roffet-Salque, 2018; Haslam et al., 2009; Henry, 2020; Lemorini and Cesaro, 2014; Marreiros et al., 2015; Weiner, 2010), there are no current resources focused exclusively on the techniques for residue analysis on stone tools. Lithic residue analysis deserves its own review due to the vast and growing array of techniques available that may be baffling to anyone not involved in this area of research. Some basic guidance for the techniques used by residue analysts is needed. At the same time, expanding interest in the discipline calls for this diversity of techniques to be discussed in a cohesive treatment.

1.2. Who is this monograph for?

This work provides an up–to–date review and methods guide for the diverse approaches used in archaeological lithic residue analysis that will be useful for students entering this rapidly expanding area of research. This contribution will also further discussions and assist in clarifying best practice in residue analysis. Additionally, it will be a useful resource for any archaeologists who are considering incorporating lithic residue analysis in their projects or simply want to learn more about this area. Lithic residue analysis is a specialised subdiscipline in archaeology, and this monograph aims to make all the techniques used accessible in one place by offering a brief overview. Each technique is described in terms of how it works, what archaeological information has been gained from each technique, and any concerns and limitations. A transparent discussion of the type of interpretation achievable with each technique is also a major focus throughout, making the strengths and challenges of lithic residue research clear for non–experts.

This review and guide is limited to studies that investigated residues on handheld flaked and ground stone tools providing information relevant to understanding human behaviours in the past. Academic publications found in books and journals were reviewed, as were PhD theses. Grey literature such as government documents, unpublished or commercial archaeology reports, were not included. Overall, this work is organised according to each technique used on archaeological and/or modern lithic residues. The Appendix provides a list of lithic residue techniques, associated acronyms, the in situ or extraction requirement of each technique, the type of information gained about the residue from the technique, and references.

1.3. What types of archaeological residues can be found on stone tools?

A wide range of trace residues can be encountered on the surfaces of archaeological artefacts from their use on plant, animal, and mineral materials. Plant materials such as reeds and grasses may be cut and gathered for making mats and basketry using a stone tool, leaving durable silicified plant tissues behind on the edge of the tool surface. Animals may be butchered for meat, and their bones broken for marrow, potentially depositing a host of related residues such as fat, hair, muscle proteins, and tiny fragments of bone on stone tools. Minerals may be extracted from their geologic source by cutting and grinding with stone tools, also leaving traces behind. Some residues are first located with a microscope, and some residues are only revealed via molecular analysis. Examples of archaeologically significant residues that are microscopically visible include birch bark tar (Fig. 1.1), osseous tissues such as antler (Fig. 1.2), and red ochre (haematite) pigments (Fig. 1.3).

Additionally, some materials were intentionally applied to stone tools for technological or ritualistic purposes. For instance, one could enhance the functional performance of a multi–component tool by using adhesive glue to slot a stone blade into a wood haft. The hafting adhesive applied acts as a shock absorber that prevents the blade from shattering on impact, and residue analysts look for residue traces of this glue technology. Hafting residues occupy a major portion of all residue discoveries, due to the long–term chemical stability of lipids and hydrocarbons in sticky matrices. Another example of an intentionally applied material on stone tools might be pigment to imbue the tool with spiritual power, perhaps to improve hunting outcomes. These traces serve as important indicators of past human activities and give us intimate insight into peoples' lives.

Recently, questions have been raised as to what types of residues can be identified using visual microscopic

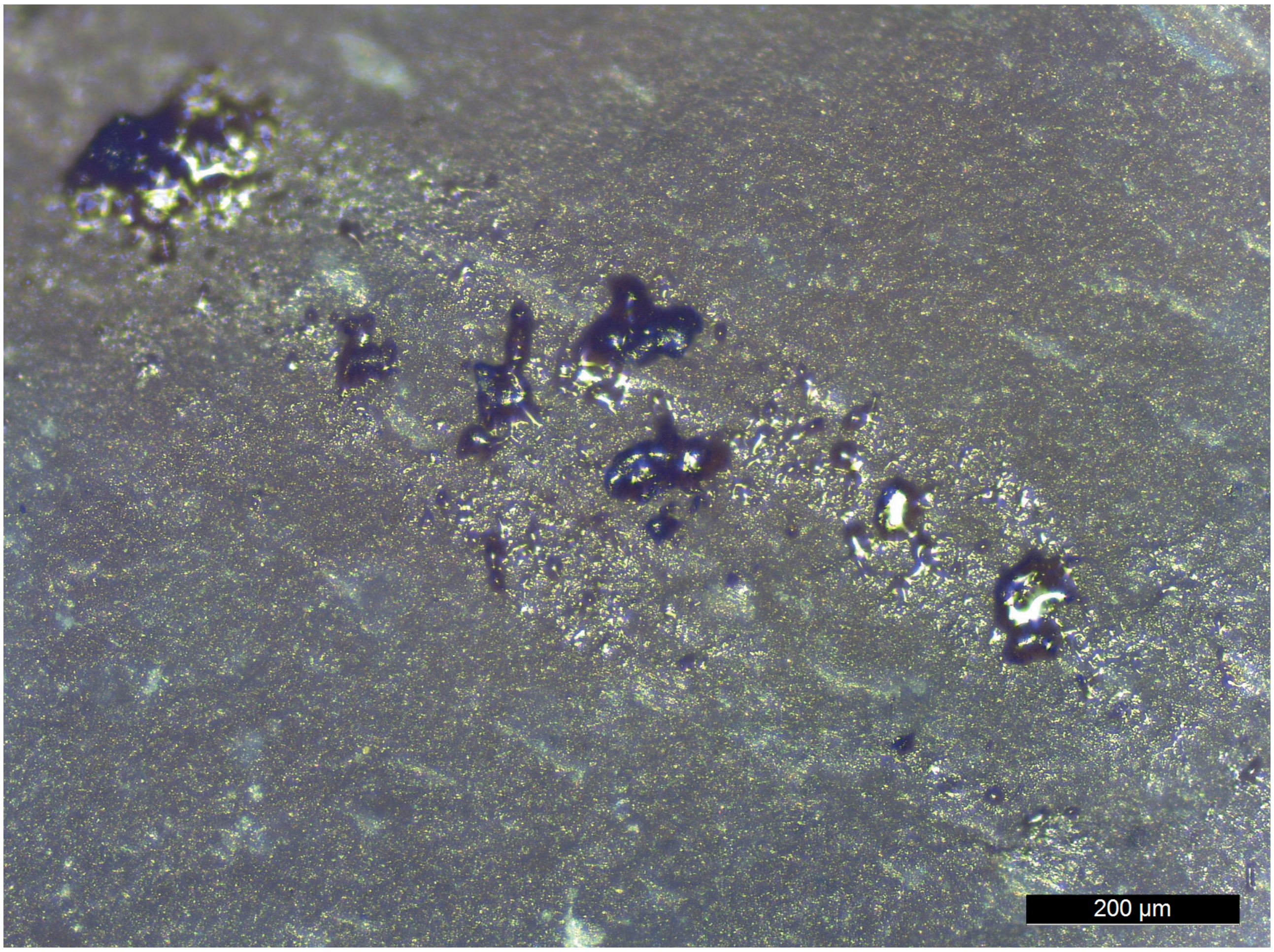

Fig. 1.1. Modern birch bark tar on a flint tool, reflected VLM. This birch bark tar residue was later extracted for gas chromatography–mass spectrometry (GC-MS) to provide a chemical comparative reference for archaeological residues with a similar microscopic appearance (reported in Croft et al. 2018b).

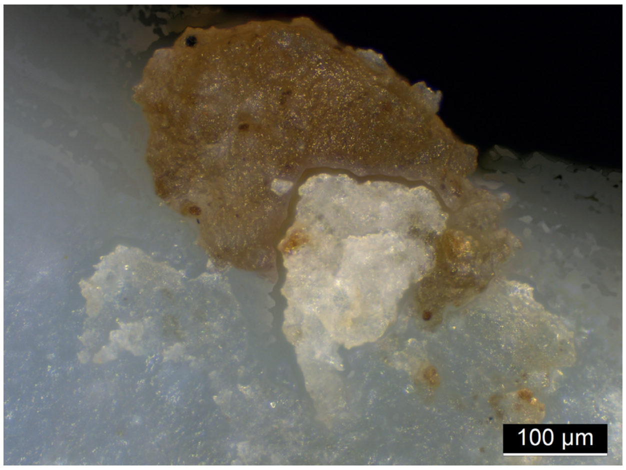

Fig. 1.2. Residues of modern deer antler present on an experimental flint tool, reflected VLM.

methods. Experimental research has shown that even modern residues that have not been subject to degradation processes such as the examples above can be difficult to interpret visually because their morphology can be ambiguous (Croft et al., 2016; Kozowyk et al., 2020; Monnier et al., 2012). Additionally, there are often multiple natural and anthropogenic residue sources that have a similar appearance, which can mislead or confound identification (Croft et al., 2018a). Many microscopic trace residues are not immediately identifiable by visual observation alone, resulting in a push within lithic residue studies to rely more heavily on chemical analytical characterisation techniques.

1.4. Brief history

Lithic residue analysis is a developing subdiscipline in archaeology. Its older counterpart, microscopic usewear analysis, evolved in the 1960s with the PhD work of Sergei Semenov (translated into English 1964, published in Russian 1957). An interest in lithic usewear spawned the subsequent development of residue research, with Frederick Briuer (1976) publishing the first study on prehistoric stone tool residues, in conjunction with usewear analysis. Briuer (1976) examined residues both in situ with light microscopy and conducted extractions and application of indicator stains from a sample of 37 Arizonan lithics from rock shelters and open–air sites. An impressive range of plant micro–remains were identified morphologically: starch granules, stellate hairs, pollen, calcium oxalate crystals, raphides, cell walls (lignified,

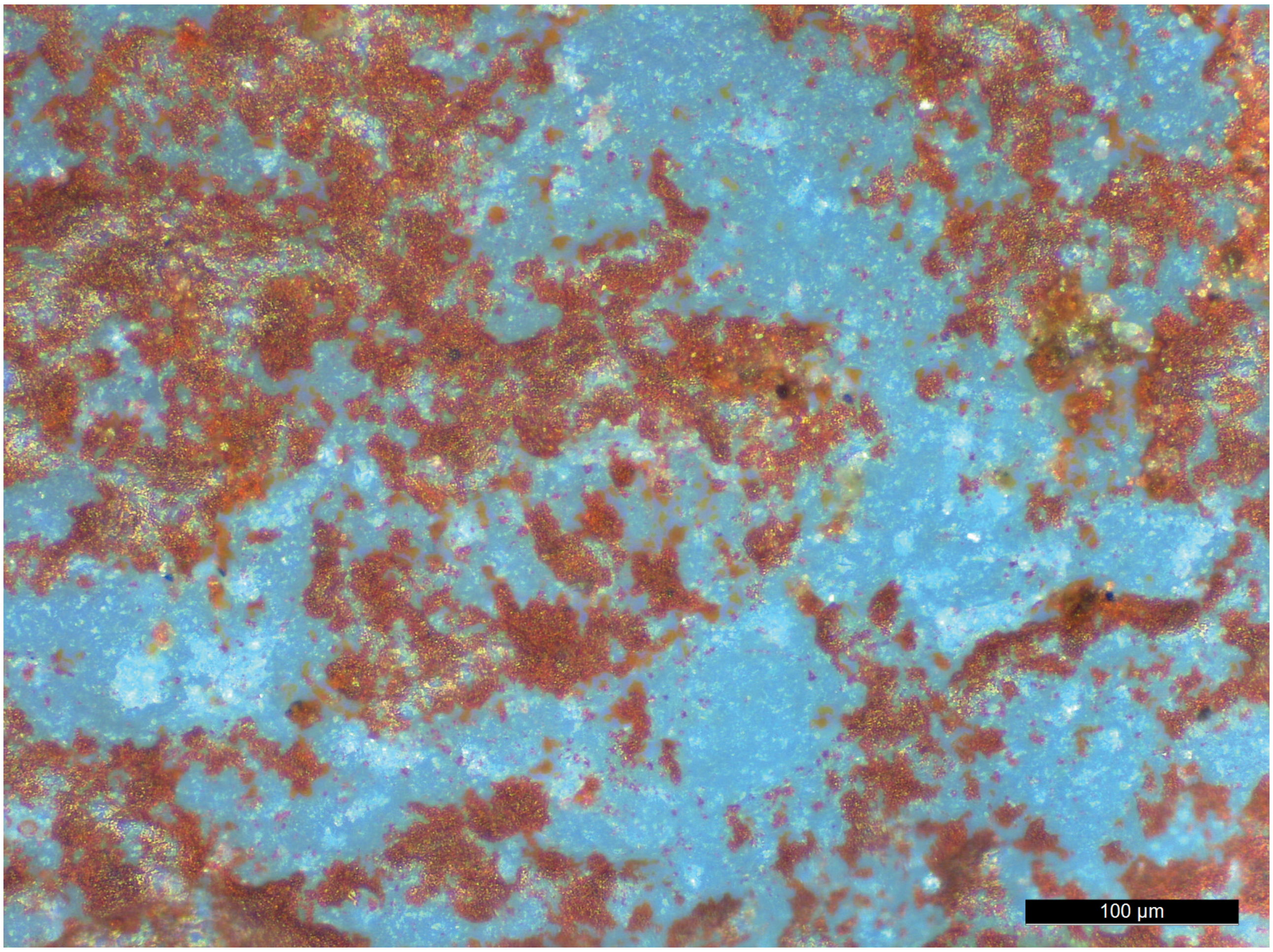

Fig. 1.3. Modern powdered haematite applied to a flint flake, reflected VLM. The haematite residue was part of an experiment to test the extent of visual residue preservation in different burial conditions. Sourced from Croft et al. 2016, *Internet Archaeology,* https://doi.org/10.11141/ia.42.5, licensed under CC-BY 3.0.

suberised, and cutinised), cell lumen, tracheids, fibre tips, spiral vessels, and hair vessels (trichomes). Even at this nascent stage of residue analysis development, Briuer designed his study to exclude natural phenomenon as causal factors for the presence of the residues on the tools. Briuer selected 20 random rocks and botanical remains near the archaeological sites and tested them with the same stains used to test the archaeological residues. The off–site items had no residues similar to those found on the archaeological tools. Briuer (1976) also attempted chemical characterisation of two extracted residue samples with mass spectrographic analysis, which returned no clear results due to the complexity of compounds present. Briuer's study showed lithic residues could be used as a means to understand the function of artefacts, and thus the activities, of past peoples.

Shafer and Holloway (1979) followed Briuer and conducted a functional analysis of 25 Archaic chert flakes from Hinds Cave, Texas, using residue analysis together with usewear. Shafer and Holloway drew comparisons between modern replica tools used for various tasks, using experimental archaeology to better understand the archaeological record. The study determined that most of the stone tools examined were multipurpose, and usewear patterns were often not distinct or attributable to specific uses. The finding that hunter–gatherer stone tools were often multipurpose was an important insight from residue analysis. It made clear that archaeologists should not uncritically impose functional categories on stone tools based on gross morphology or assume there exists 'one tool for one task'.

Like several analysts studying usewear in the later 70's and early 80's (Kamminga, 1979; Keeley, 1980; Keeley and Newcomer, 1977; Vaughan, 1985), Anderson–Gerfaud examined stone tool polishes. Polish is considered the microscopically observed reflective areas of wear on the stone tool with a dissolved or 'melted' appearance that can result from working plant and animal tissues. Anderson–Gerfaud (1980) analysed the inorganic mineral component of the residues trapped within polishes, using experimental residues for comparison. Anderson–Gerfaud (1980) described residues both morphologically with an optical reflected visible light microscope and elementally with a scanning electron microscope (SEM) with energy dispersive X–ray spectroscopy (EDS). This work showed that micro–remains (such as calcium oxalate crystals, silica phytoliths, and small bone and antler pieces), could become trapped within the mineralised matrix of polishes.

This study contributed to the debate about the origin of polish on stone tool surfaces. Anderson–Gerfaud's (1980) findings suggested microwear polish is mainly added to the tool surface from the worked material as a deposit. However, Anderson–Gerfaud (1980) also concluded the dissolution of the stone itself imparts a smaller amount of silica to the formation of polish. Anderson–Gerfaud (1980) proposed the silica gel theory to explain that flint dissolution was playing a part in polish formation. Silica gel theory proposes that during working of water–containing materials, the flint surface is hydrated, causing the flint surface to become an amorphous silica gel layer. This amorphous silica gel also acts as a matrix that entraps particle residues from the worked material. In this way, Anderson–Gerfaud (1980) proposed a combination of factors to account for stone tool polish, the formation of 'amorphous silica gel' being caused by dissolution of the flint itself with the addition of residues trapped in the silica gel. The underlying mechanisms of polish formation on stone tools are problematically still nebulous and lack agreement in current usewear literature (Dubreuil and Savage, 2014, p. 148; Ollé and Vergès, 2014, p. 69; Stemp et al., 2015, p. 2; Werner, 2018, p. 597). More basic research is needed to resolve how and why polish develops on stone tools.

Archaeological residue studies gained momentum in the 1980s. A report in *Science* identifying bloods of several animal species on archaeological stone tools using haemoglobin crystallisation by Loy (1983) drew much attention and spawned further identifications of blood (Coughlin and Claassen, 1982; Fullagar, 1986; Loy, 1985a, 1985b; Loy and Nelson, 1986; Newman and Julig, 1989; Richards, 1989). This initial optimism faded, as blood preservation and methods of identification were questioned and essentially discredited (Fiedel, 1996). Interest in starch residues on tools from food plants also grew in 1980s and into the 1990s, with work being centred in Australia and Oceania (Barton et al., 1998; Fullagar, 1989, 1988, 1986; Fullagar et al., 1996; Hall et al., 1989; Loy et al., 1992). Starch granules were identified both in situ on the stone surface and within extracted residues, using light microscopy and cross polarising filters. Sometimes different stains were also applied to extracted starch granules to visually highlight their presence. Early chemical characterisation of what were often referred to as 'mastics' on stone tools had also begun.

The past ten years have seen lithic residue analysis enjoy increasing research interest – signalled by a rise in publication frequency and the diversity of techniques employed, as well as the formation of the Association of Archaeological Wear and Residue Analysts (AWRANA) in 2012. Two publications dedicated to stone tool usewear and residues also mark this growth: 'An Integration of the Use–Wear and Residue Analysis for the Identification of the Function of Archaeological Stone Tools' (2014), edited by Lemorini and Cesaro, and the book 'Use–wear and Residue Analysis in Archaeology', edited by Marreiros, Bao, and Bicho (2015). Both works are part of a trend indicating that usewear, and particularly residue analysis, are moving in a direction towards the incorporation of ever more sophisticated chemical and elemental analyses, such as Fourier transform infrared microspectroscopy (FTIRM), Raman microspectroscopy, X–ray fluorescence spectroscopy (XRF), SEM–EDS, and gas chromatography–mass spectrometry (GC–MS). Lithic residue analysis has arguably entered a new stage of development, and what is bringing it together is a decidedly heavier reliance on scientific verification. More robust conclusions are being drawn from the residues found on stone tools due to the use of objective data and greater scrutiny of results.

However, currently there is no standard or accepted protocol followed by lithic residue analysts collectively. Unlike more established areas of archaeological science, such as isotope analysis, lipid residue analysis on pottery, or palaeoenvironmental reconstruction based on biological indicators (e.g. macrobotanical remains, palynology, gastropods, chironomids, etc.), lithic residue analysis has yet to formulate a sequence of methodological steps and standard practices in order to generate reliable conclusions.