

‘Stuck like glue’: assessing variability in hafting adhesives in the southern African Later Stone Age



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ABSTRACT

The characterisation of hafting adhesives, the glue of composite tools, by chemical analysis and microscopy provides a means by which we may evaluate these plastic components of technologies; reliable systems that have allowed members of our species to exist in dynamic environments and exploit a variety of resources. In southern Africa, the well-preserved assemblages of the Later Stone Age present a unique opportunity to evaluate the raw material sources of these adhesives. This thesis highlights the findings of the first multi-site study of hafting adhesives from the Holocene assemblages. The results a multi-method microscopic and chemical analysis suggest there is evidence to support variations in adhesive sources between ecological biomes and through time, with a dominance in compound adhesives found at the case study sites. The analyses of material from Sehonghong (Lesotho, Grassland) suggests a transition to the use of non-local adhesive materials among the last hunter-gatherer populations of the site. Evidence from Melkhoutboom in the Thicket Biome highlights the longstanding use of conifer pitch throughout the Holocene, while isolated hafted implements recovered from coastal caves further west along the southernmost coastline indicate a continued use of the same manufactured product into the Forest biome. From the Late Holocene assemblages at Boomplaas and Renbaan in the Fynbos, we see a diversification of resources; latex exudates from the *Euphorbia* and *Ammocharis* genus were identified at Boomplaas, while a hitherto unknown composite adhesive recipe composed predominantly of animal products and inorganic minerals was found at the Oliphant's River valley site of Renbaan. The current and novel adhesive recipes identified within these datasets highlights the inherent value of the adhesive components themselves and provides insight into the nature of these plastic technologies, the narrative of adhesive manufacture in southern Africa, and current archaeological discussion in this region.

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LIST OF ABBREVIATIONS

Abbreviation	Name	Abbreviation	Name
<i>Archaeological Terminology</i>		<i>Elemental symbols</i>	
BP	before present	Al	aluminium
MSA	Middle Stone Age	C	carbon
LSA	Later Stone Age	Ca	calcium
CCS	cryptocrystalline silicate	Cl	chlorine
BPA	Boomplaas	Fe	iron
MHB	Melkhoutboom	H	hydrogen
RB	Renbaan	K	potassium
RCC	Rose Cottage Cave	Mg	magnesium
SEH	Sehonghong	Mn	manganese
14C	radiocarbon	Na	sodium
<i>Instrumentation & Analytical Terminology</i>		O	oxygen
GC/MS	gas chromatography coupled mass spectrometry	P	phosphorus
py-GC/MS	pyrolysis - gas chromatography coupled mass spectrometry	S	sulfur
FTIR	Fourier transform infrared spectroscopy	Si	silicon
IR	infrared	Ti	titanium
SEM/EDS	scanning electron microscopy/ energy dispersive X-ray spectroscopy		
OLM	optical light microscopy		
XRF	X-ray fluorescence		
XRD	X-ray diffraction		
TIC	total ion current		
EIC	extracted ion chromatogram		
TMS	trimethylsilyl-		
DHA	dehydroabietic acid		

CHAPTER 1

INTRODUCTION

1.1. Research aims and rationale

The function and production of composite tool technologies has long occupied archaeological researchers (Rots, 2010). In-depth analysis of hafting adhesives has been used to investigate how members of the genus *Homo* existed within dynamic environments and exploited their resources with the flexibility to account for the variability in resource yield and composition (Wadley *et al.*, 2009; Lombard and Haidle, 2012). In southern Africa, analysts have so far largely focused on the identification and characterisation of hafting adhesives from the Middle Stone Age (MSA). Unsurprisingly, data from this time period have caught the attention of public media and high impact academic journals alike, contributing to the discovery of several ‘firsts’, particularly those behavioural proxies related to complex cognition (Wadley *et al.*, 2009; Wadley, 2010; Lombard and Haidle, 2012). This has, however, led to considerable neglect of the much better known Later Stone Age (LSA) (Wadley, 2014). Despite possessing examples of well-preserved adhesives from a number of sites (H. Deacon, 1967, 1984; Schweitzer and Wilson, 1982; Binneman and Mitchell, 1997; Jerardino, 2001; Wadley, 2005), only a handful of artefacts from LSA contexts have been studied (Walker, 1974; Villa *et al.*, 2012, d’Errico *et al.*, 2012; Charrié-Duhaut *et al.*, 2016) further creating a significant research bias, which this project attempts to address. In this thesis, I use microscopy and analytical techniques, including scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), gas chromatography coupled mass spectrometry (GC/MS) and Fourier transform infrared spectroscopy (FTIR), to assess the molecular composition of hafted technologies from stratified LSA sites located in a variety of geographies and ecologies across southern Africa. On a case by case basis, I attempt to

determine whether hafting adhesives were variable or stable, temporally and geographically, during the Holocene LSA. Following in the wake of the molecular characterisation studies of hafting adhesives previously conducted on materials from the MSA and early Later Stone Age (ELSA) (d'Errico *et al.*, 2012; Villa *et al.*, 2012; Charrié-Duhaut *et al.*, 2013), my study seeks to broaden our understanding of the origins and nature of hafting adhesives in the LSA, as well as the relationship between adhesive, stone tool manufacture processes, and the ecology of the surrounding region.

The LSA in southern Africa, dating from ~18 – 40 000 years ago (geography dependent) to within the last few hundred years spans both the late Pleistocene (up to ~11 500 years [Steele, 2007]) and the Holocene, and most recently has been broadly divided into six technocomplexes: early Later Stone Age (ELSA), Robberg, Oakhurst, Wilton, final Later Stone Age, and ceramic final Later Stone Age (Lombard *et al.*, 2012). These divisions are set against a climatic backdrop of cooler late Pleistocene (25-10, 000 years ago), the ameliorating conditions of the Pleistocene/Holocene boundary, and finally the regional climatic fluctuations of the Holocene (7-2,000 years ago) (Mitchell, 2002, 2013).

Of interest to this thesis are those sequences that appear 19-18,000 BP, after a downsizing of lithic assemblages occurred (Mitchell, 2002). First among these is the Robberg complex, also called the Late Pleistocene Microlithic to better account for the variability within it (J. Deacon, 1984; Orson, 2006). Appearing between 19–12,000 years ago (Mitchell, 2013), it is known for the systematic production of bladelets, as well as a suite of formal less standardised tools including scrapers and adzes (Mitchell, 2002). It has been suggested that these bladelets were hafted components of composite processing or hunting tools utilised by groups settled in the favourable refugia of the Last Glacial Maximum (Binneman, 1997; Mitchell, 2002, 2013). The Oakhurst, or Terminal Pleistocene/early Holocene non-microlithic (Lombard *et al.*, 2012), favoured the production of larger flakes and scrapers, and roughly dates to 12-8000 years ago (Mitchell, 2002). On a local scale, this assemblage apparently corresponds to changing hunting

patterns in regions like the southern Cape (J. Deacon, 1984). However, the reasoning for the abandonment of microlithic toolkits across southern Africa is still debated (Mitchell, 2013). Following this period of transition into the Holocene, we see the development of a second – and different - microlithic tradition, called the Wilton or Holocene Microlithic between 8-4000 years ago (Lombard *et al.*, 2012). This technological change resulted in highly standardised, formal tools, and different hafting methods, most likely resulting from a shift in dietary breadth caused by environmental instability during the Holocene (J. Deacon, 1984; Bousman, 2005). Continuing further into the Holocene, we see the development of the final Later Stone Age (Lombard *et al.*, 2012). This cultural sequence, between 4 000 BP to the 19th century, is characterised by an increasing variability in technology, including the post-classic Wilton and Smithfield regional variants (Bousman, 2005; Mitchell, 2009).

The presence or absence of hafting is largely based on the observed modifications of tools, and the corresponding macroscopic and microscopic damages that occur (Rots, 2010). These data lend evidence to support tool form and past hunting practices (Lombard and Pargeter, 2008; Yaroshevich *et al.* 2010). In exceptional circumstances, hafting may be identified from the presence of preserved residues deposited on the proximal end of a tool. The analysis of these trace remains presents a means of assessing the source of organic components of technologies that have long since degraded. Significant work has been conducted to determine the origins and taxonomic source of residues that are assumed to be derived from hafting, utilising microscopy in a variety of forms, as well as spectrophotometric methodologies. For example, heated birch bark has been identified from Middle Palaeolithic stone tools at Inden-Altdorf, Germany (125-115,000 BP; Pawlik and Thessen, 2011), and Campitello, Italy (Mazza *et al.*, 2006). A number of studies have also identified bitumen (tar) as a source of hafting adhesive from sites in Europe (Carciumaru *et al.*, 2010) and Syria (Boeda *et al.*, 2008; Hauck *et al.*, 2013 Monnier *et al.*, 2013), and in some instances has located the source of this natural product (Boeda *et al.*, 2008). These studies, in tandem with experimental and blind-test studies that support archaeological data

(Allain and Rigaud, 1982; Wadley *et al.*, 2009; Zipkin *et al.*, 2014), not only affirm the presence of tool hafting, but can to some extent describe the *chaîne opératoire* of the hafting process (Barham, 2013), placing emphasis on the adhesive component.

While Charrié-Duhaut *et al.* (2013: 3507) have argued that the outcome of chemical hafting adhesive studies was, at its core, driving discussions on “[the] technological and functional implications [of hafting] and, ultimately, on its transformation over time and variability in space”, this may not be an entirely valid assessment. I contend that, with the increasing tendency toward limited sample sizes in chemical adhesive studies and the ongoing practice of favouring the analysis of unique objects (Cârciumaru *et al.*, 2012; d’Errico *et al.*, 2012; Villa *et al.*, 2012; Charrié-Duhaut *et al.*, 2013, 2016; Hauck *et al.*, 2013; Monnier *et al.*, 2013; Matheson and McCollum, 2014), there may inadvertently be a limit on the degree of resolution on aspects of time and space that can be addressed, and that we are thus in danger of over-emphasising the contribution of these findings to larger debates.

Therefore, the goals of this research are:

- to design a methodology that emphasises the potential for variability of hafting adhesives, and characterises all organic and inorganic materials as best as possible;
- to apply this methodology to larger collections of material spanning multiple sites and cultural sequences;
- to contribute to compositional discussions on the manufacture of adhesives and an evaluation of resource acquisition during the LSA within the more constrained contexts of the archaeological case studies;
- to counter the existing bias in current southern African hafting research in favour of MSA and Pleistocene samples by focusing on those from Holocene LSA contexts.

1.2. Research hypotheses: an assessment of hafting adhesives in the southern African LSA

It was over half a century ago that J. Desmond Clark (1958: 151) postulated that hafting adhesives “...probably varied from region to region according to the natural products of each.” The ELSA studies at Border Cave by d’Errico *et al.* (2012) and Villa *et al.* (2012), as well as the Holocene study at Elands Bay Cave (Charrié-Duhaut *et al.*, 2016), are the bookends of a narrative with respect to both time and geography, yielding evidence as to the botanical sources of ‘mastic’ adhesives. We see continuity in the use of the conifer *Podocarpus* sp., as well as the appearance of other exudates from *Euphorbia* sp., not to mention various animal sources (d’Errico *et al.*, 2012). In accordance with the research aim above, and recognizing the limitations of small samples sizes, we may acknowledge that there may be dimensions of time and space present in the use of particular botanical genera as adhesives.

The prevalence of different exudate-producing plant species found in LSA contexts also brings into discussion the components of an adhesive ‘recipe’. Known LSA studies highlight two such recipes: a simple adhesive comprising only the plant exudate, and a composite adhesive containing other non-plant ingredients. Experimental testing of MSA analogues highlights the added stability resulting from the inclusion of loading agents (i.e. iron oxide, ochre) to a gum-based adhesive (Allain and Rigaud, 1986; Wadley, 2005; Wadley *et al.*, 2009; Zipkin *et al.*, 2014). Examples of adhesive mixtures, notably in the LSA, include evidence of fat, blood, and charcoal at Rose Cottage Cave (Wadley, 2005), vegetation in an exceptional mastic mount found at Steenbokfontein (Jerardino, 2001), and a beeswax and latex composite from a bound lump of material at Border Cave (d’Errico *et al.*, 2012). From these observations, Wadley’s (2010) assessment that adhesive recipes vary depending on the needs of an individual and the tools manufactured is well supported. However, due to the relatively recent arrival of molecular analysis of hafting trace at southern African sites, only rarely can a correlation be made between the composition of an adhesive, the purposeful selection of one exudate-producing species over

another, and the availability of exudate species within the area around the site at a given time. If we take into account the complexities of the ecology of the southern Africa, there is potential for variation from region to region just as Clark (1958) originally suggested. The intensity of research in the past on the LSA and its environmental setting offers a tangible opportunity to assess these technological strategies.

Southern Africa has an extensive research history in the detection of hafting adhesives (Walker, 1974; Phillipson, 1976; Williamson, 1996, 1997; Gibson *et al.*, 2004; Wadley *et al.*, 2004; Lombard, 2005, 2006, 2008; Wadley *et al.*, 2008; d'Errico *et al.*, 2012; Villa *et al.*, 2012;; Charrié-Duhaut *et al.*, 2013, 2016; Soriano *et al.*, 2015). Unfortunately, Wadley's (2014) assessment that there is a disparity between research focused on the MSA versus the LSA rings equally true in microscopic and molecular residue studies of this material. Presently, there is a higher frequency of residue studies on hafting trace and a higher number of analysed specimens conducted on MSA material (Wadley *et al.*, 2004; Lombard, 2005, 2006, 2008; Charrié-Duhaut *et al.*, 2013) compared to overwhelmingly few from the LSA (Williamson 1997; d'Errico *et al.*, 2012, Villa *et al.* 2012; Charrié-Duhaut *et al.*, 2016). In the MSA, hafting trace is limited to studying projectile weaponry and cutting tools; the selection of flakes, segments, and points are recognised as providing further insight into not only hafting arrangements, but also hunting and butchery practices (Gibson *et al.*, 2004; Delagnes *et al.*, 2006; Lombard 2006, 2008; Charrié-Duhaut *et al.* 2013).

The LSA, by contrast, is well known as a source of excellent organic preservation (Wadley, 2014). Intensive excavation programmes have yielded material culture that exhibits a distinctive diversity that is presently not paralleled in the MSA (Mitchell, 2005). In the LSA, traces of hafting adhesive (called 'mastic' in much of the literature) have been visually identified on a greater range of tool typologies, including scrapers and adzes, as well as bladelets and segments (H. Deacon, 1967; Schweitzer and Wilson, 1982; Binneman and Mitchell, 1997). Other unique finds from this period have included large lumps of well-preserved mastic (H. Deacon, 1976; J. Deacon,

1984; Jerardino, 2001). Despite the number of LSA sites yielding plant exudate-based mastic artefacts, analysis conducted on material of this kind, beyond visual observation, is surprisingly rare. This harkens back to the point emphasised by Wadley (2014), who critiqued archaeologists' relative preoccupation with the 'firsts' of the MSA as a factor that now increasingly overshadows the LSA. It stands to reason that the relative diversity of unstudied artefact typologies containing evidence of hafting adhesive should provide an excellent starting point from which to broaden our understanding of the composition of hafting adhesives during the LSA and how this relates the tool function and the units of composite technology. In this manner, a focus on plastic technologies may be the impetus needed to develop new paradigms for the LSA and develop innovative research (Mitchell, 2005; Wadley 2014).

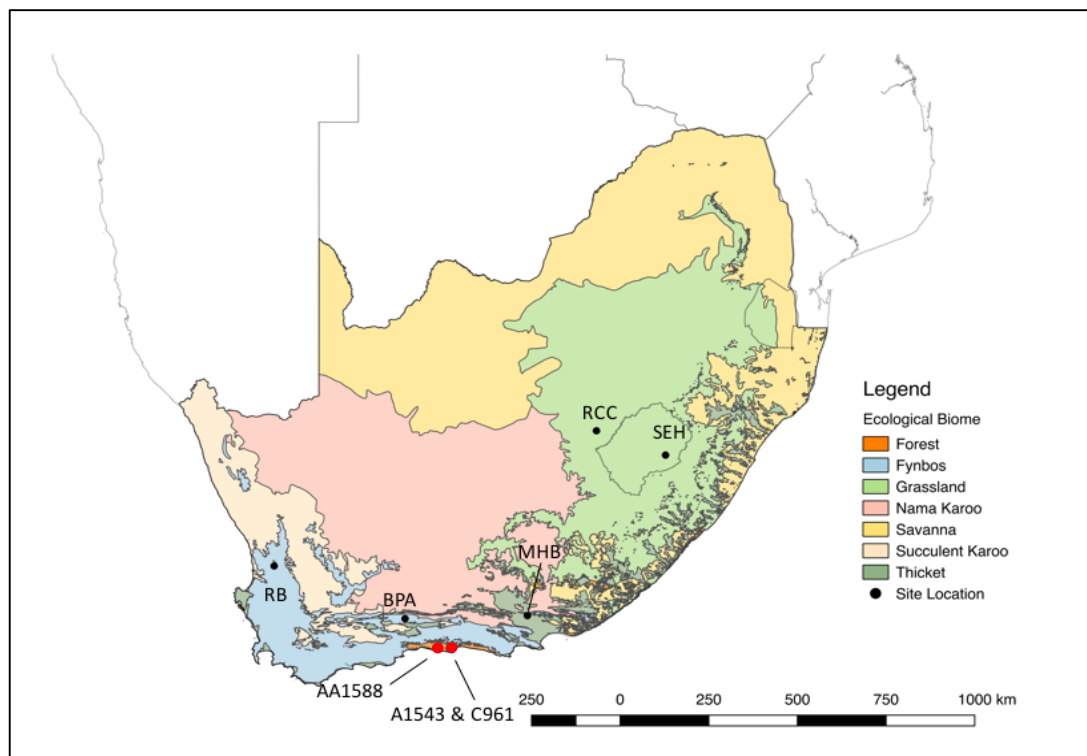


Figure 1.1. The archaeological case studies site locations set against the ecological biomes of southern Africa. Locations in red are approximate. Vegetation Map of South Africa, Swaziland, and Lesotho 2012 available from the Available from the Biodiversity GIS website bgis.sanbi.org, downloaded Dec 5, 2016. African countries layer by Esri.

Given the archaeological context and discussion of southern Africa in which these hafting adhesives are situated, which I highlighted above, I propose the following hypotheses to be tested in this doctoral research:

- 1) *Given the ecological mosaic of southern Africa's biomes, there will be variability in hafting adhesive formulae through time and across differing ecological spaces corresponding to differences in vegetation.*
- 2) *The geographic and temporal distance between molecular identifications of hafting adhesives in residues suggests continuity in the use of exudate-producing plant species as adhesives, despite the differences in technological industries and manufacturing processes. There will thus be similar continuity within LSA sites.*
- 3) *The prevalence of single component adhesives versus composite mixtures will be influenced by tool function, typology and the raw materials that make up a composite tool.*

The case studies presented herein (Figure 1.1) represent distinctive geographic and ecological circumstances, spanning the breadth of the southernmost coastline of South Africa, as well as the interior reaches of Free State (South Africa) and the highlands of Lesotho; the Fynbos, Forest, Thicket, and Grassland ecological biomes are all represented. The analyses conducted spans several Holocene technocomplexes and the tools selected include high-impact projectiles, high-impact non-projectiles, and low-impact tools. As such, while each case study is exemplified by its own unique circumstance, which may limit inter site discussion to a degree, I argue that these case studies provide the groundwork within these discrete ecological and LSA contexts for further work in the compositional study of the adhesives of multi-component tools.

1.3. Thesis structure

This thesis comprises eight chapters and three appendices. Beyond the Introduction included herein, Chapter 2 provides a brief review of tool hafting and how it may be identified in the archaeological record, with an emphasis on hafting adhesives. It then describes the methodologies used to identify the composition of hafting adhesives, highlighting analytical techniques and global case studies. Chapter 3 explores hafting adhesives in southern Africa, from the MSA through the recent historical and ethnographic records, placing emphasis on the known finds from all technocomplexes of the LSA. Chapter 4 presents the methods and materials associated with the analyses of hafting adhesives for this research, while Chapter 5 outlines the archaeological contexts of the specimens studied including the Thicket Biome site of Melkhoutboom, the Fynbos sites of Boomplaas and Renbaan Cave, the Grassland sites of Rose Cottage Cave and Sehonghong (Leosotho), and three museum specimens recovered from non-provenienced locations in the Fynbos and Forest Biomes. Chapter 6 presents the results of the analyses, with interpretive summaries provided for each site and museum implement. The main findings are then employed to address the research hypotheses, with a selection of adhesive resources expanded upon within each hypothetical discourse to highlight their relevance in archaeological discourse. In the final chapter of the thesis, I review the main contributions of this research to southern African archaeological study and the potential for further applications of chemical studies on this topic. Five appendices serve to complement the main text, with Appendix 1 having records of the material analysed from Chapter 6, Appendix 2 infrared spectroscopy data from the modern exudate references, Appendix 3 a selection of chromatography/ mass spectrometry data from modern reference collections used for comparative purposes, Appendix 4 a copy of the permit report discussing the results from Rose Cottage Cave, and Appendix 5 a selection of photographs of the analysed material and a collection of measurements and observations of two hafted implements housed at the Iziko Museum that were not accessible for sampling due to permit restrictions.

CHAPTER 2

BONDS AND BINDS: HAFTING ADHESIVES & THEIR CHARACTERISATION

Introduction

Analyses of hafting adhesives, the glue of composite technologies, using microscopy and analytical chemistry techniques, have been conducted on archaeological and historic objects worldwide (Regert *et al.*, 1998; Koller *et al.*, 2001; Gibson *et al.*, 2004; Mazza *et al.*, 2006; Galanidou, 2006; Helwig *et al.*, 2008; Shaham *et al.*, 2010; Pawlik and Thissen, 2011; Vahur *et al.*, 2011; Cărciumaru *et al.*, 2012; Villa *et al.*, 2012; Hauck *et al.*, 2013; Matheson and McCollum, 2014). The study of trace remains and micro-samples of whole objects allows microscopists and chemists to determine both the organic and inorganic components of adhesive recipes, expanding our impressions of past populations as competent engineers and chemists (Wadley *et al.*, 2009; Charrié-Duhaut *et al.*, 2013) with the flexibility to account for variability in resource yield, procurement strategies, and the composition of plant, animal, and mineral resources.

Before homing in on southern Africa, this chapter discusses the basic concepts of hafting and the role adhesives play in the process in our understanding of the manufacture of multi-component tools from a global perspective. Its aim is to highlight a feedback system that characterises adhesive research; the diverse nature of adhesives, in many cases identified through the end of a microscope lens, has created a diverse set of analytical applications to study their composition in detail.

Section 2.1. introduces the concept of hafting and provides a short discussion on how the identification and characterisation of hafting adhesives contributes to discussions of tool design and the adaptive strategies of past populations. In Section 2.2., I then first highlight the use of microscopic techniques as a starting point to begin the characterisation process of adhesives, before moving on in greater detail to the analytical techniques used to identify adhesive constituents, organic, inorganic, or both. Finally, section 2.3. provides concluding remarks on the chapter review.

2.1. The mechanics of hafting and adhesives: the components and their appearance in the archaeological record

Composite, multi-component tools comprise an insert with a working edge, a join or haft (which may include an adhesive and/or a binder), and handle (Zipkin *et al.*, 2014). Taken as a whole, the components are more than the sum of their parts and increase the reliability and productivity of task performance (Barham, 2010, 2013). The mechanics of combining each unit, however, are not the only aspect that requires consideration, as past populations would also have had to factor in the raw materials available for each component as well as the expertise required to accomplish such a task (Rots, 2016).

With composite technologies and hafting comes the question of purpose and function: what task does this tool need to perform? Hafts are, in their construction, the weakest point of a multi-component tool, and the types of hafting employed, the placement of the working edge, and the materials used to create a haft are dependent on the nature of the stresses that a tool will undergo over the course of its life. Barham (2010, 2013) highlights several haft types commonly identifiable in the prehistoric and ethnographic contexts (Figure 2.1 for an example from South Africa), each of which serves a functional purpose. Three haft types are described: 1) a handle is inserted into a

tool with a working edge ('female'); 2) a tool is inserted into the handle ('male'); and 3) a tool is placed and bound next to a handle ('juxtaposed') (Rots, 2008).

Rots (2016) proposes two categorical aspects to identify hafting in the archaeological record. They include those direct lines of evidence from one or a sub-set of a population, such as intact hafts (Clark, 1959; Rudner, 1979) and wear patterns (Rots, 2010; Yaroshevich *et al.*, 2013) on the one hand. On the other, there is the indirect evidence from whole assemblages, which includes morphological changes to lithic artefacts (Barham, 2010), tool formalisation, and microlithisation (Clarkson *et al.*, 2008).



Figure 2.1. An example of a 'male' hafted tool. C961, a hafted implement accessioned at the Albany Museum, South Africa. A quartz insert was hafting at an angle into the adhesive. It has since been lost. Photo taken by author.

By contrast, the binding and adhesive components (as well as the handles) are not so frequently observed in the archaeological record, due to the prominence of organic materials in these components. Our understanding of adhesive components and hafting orientation is limited to complete or nearly complete objects (Maloney *et al.*, 2015; Bisulca *et al.*, 2017) or traces preserved on the surface of a tool (Lombard, 2006). Barham (2013: 186) describes the adhesive components as bonding materials that are either "extremely strong and able to withstand large stresses ...or designed just to hold an object in place." Adhesives may be categorised as 'single component' adhesives, which have only one constituent (Mazza *et al.*, 2006; Baales *et al.*, 2017) or 'composite', which have multiple ingredients derived from several sources (Wadley *et al.*, 2009; d'Errico *et al.*, 2012). The main component can be made from plant (resins, gums, latexes, or

manufactured pitch) or animal (hide/bone glues, beeswax, and insect lac) materials (Regert, 2004; Barham, 2013; Bisulca *et al.*, 2017). Additional fillers like plant fibres, fats, waxes, sand, hair, or charcoal alter the flexibility and durability of the material. Indeed, the addition of loading agents into experimental adhesive mixtures has documented changes in stability and their ability to bear stress (Allain and Rigaud, 1986; Wadley *et al.*, 2009; Zipkin *et al.*, 2014; Kozowyk *et al.*, 2017a, 2017b). With the differential preservation of each of these materials due to variations in solubility (Langenheim, 2003) and interactions with the depositional environment (Langejans, 2011), it is not surprising that the narratives of adhesive use and identification are punctuated and increase in frequency as we approach recent times. Table 2.1 provides details of identified hafting adhesive composition by site and region.

The earliest surviving evidence of the adhesive component of a hafting join appears in Eurasia during the Middle Palaeolithic (Mazza *et al.*, 2006). Though cited by many as the oldest find at 200,000 BP (Wragg Sykes, 2015), the stratigraphic integrity and lithic technology associated with the Campitello (Italy) find make it difficult to attribute it to an absolute date range as many have done. With a more cautious position in mind, the best evidence for the appearance of hafting adhesive comes from the site of Inden-Altdorf, Germany, where birch bark pitch (or tar) was found on lithics dating to 125,000 BP. The earliest identification of adhesive joins in Africa then appears at Diepkloof rock shelter, South Africa, by 105,000 BP in the form of *Podocarpus* sp. resin. It is interesting to note in the case of composite adhesives that the oldest cases of joins have a predominant content of organic material, with the inorganic constituents less well represented.

A list-based approach of dates, sites, and adhesive recipes is all well and good for the sake of highlighting adhesive breadth and variability. However, these case by case studies also have the capacity to inform wider archaeological debates. In a broader sense, the identification of the composition of adhesives presents an opportunity to shift focus towards the roles that the organic components of tools may play in current discussions of hunter-gatherer adaptive strategies,

economic costs and benefits, as well as tool design. Bousman (1993) notes that archaeologists are handicapped by differential preservation of organic materials when attempting to address the underlying causes for technological variability, however recent developments in archaeological science open up the possibility of applying a cost-benefit approach (Hiscock, 2006; Ferris, 2015; Garvey, 2015) to the organic constituents of technologies.

While current literature models the economic risk associated with lithic procurement and tool manufacture (Bousman, 2005; Hiscock, 2006; MacKay and Marwick, 2011), it is rare that this assessment is addressed from the perspective of the procurement and manufacture of the hafting adhesive itself. The identification of the constituents of hafting adhesives provides a means of re-evaluating tools and their raw materials as a strategy for buffering environmental risk. The identification of adhesive composition, particularly when complemented by experimental recreations of adhesive recipes (Groom *et al.*, 2013; Kozowyk *et al.*, 2017a), can highlight the nuances associated with the procurement of resources and the manufacture of these materials. From this we may begin to acknowledge, as Charrié-Duhaut and colleagues (2013) note, that these products require sustained multi-level operations; these components of tools are high value commodities in their own right and more than a step of a flow diagram in the *chaîne opératoire* of a composite implement.

Table 2.1. A list of archaeological sites with hafting adhesives (and available dates in the format they were published), alongside comments on the adhesive material identified and the analytical technique applied to determine the composition.

Region	Site	Published Date	Adhesive Identified	Analytical Technique	Reference
Africa	Knysna, South Africa	N/A	Unidentified	Paper chromatography; FTIR	Walker, 1974
	Makwe, Zambia	1730 ± 80 BP (SR-207) - 970 ± 70 BP (SR-206)	Plant exudate	FTIR	Phillipson, 1976
	Eland's Bay Cave, South Africa	~8000 BP or 3000 BP	"Resin"	Paper chromatography; FTIR	Walker, 1974
	Eland's Bay Cave, South Africa	~8000 BP or 3000 BP	<i>Heeria sp.</i> resin; <i>Podocarpus sp.</i> resin and quartz sand	GC/MS; FTIR	Charrie-Duhaut <i>et al.</i> , 2016
	Border Cave, South Africa	43-42,500 BP	<i>Podocarpus sp.</i> pitch; <i>Euphorbia sp.</i> latex, beeswax, proteinaceous material	py-GC/MS; GC/MS; radiocarbon dating	d'Errico <i>et al.</i> , 2012; Villa <i>et al.</i> , 2012
	Diepkloof, South Africa	60 – 55,000 BP	<i>Podocarpus sp.</i> pitch, with quartz and possible bone sherds	GC/MS; SEM	Charrie-Duhaut <i>et al.</i> , 2013
	Sibudu Cave, South Africa	77-59,000 BP	Conifer resin, likely <i>Podocarpus sp.</i>	GC/MS	Soriano <i>et al.</i> , 2015
Eurasia	CH3 and CH4, France	5120-5020 BP & 4990 - 4900 BP	Birch bark tar; beech, oak, alder tar; animal fat; bitumen	GC/MS	Regert <i>et al.</i> , 1998
	Tyrolean Alps (Ötzi the Iceman)	5200 BP	Birch bark tar	GC/MS	Sauter <i>et al.</i> , 2000
	Mondsee, Austria	5750 - 4750 BP	Birch bark tar	GC/MS	Hayek <i>et al.</i> , 1991
	Waldbillig-"Karelsle", Luxemburg	Middle Neolithic	Birch bark tar	GC/MS	Regert, 2004

Thatcham III, United Kingdom	9200 ± 90 BP	Radiocarbon date only	Radiocarbon dating	Hedges <i>et al.</i> , 1994
Star Carr, United Kingdom	9300-8500 calBP	Pine resin	GC/MS	Croft <i>et al.</i> , 2018
Star Carr, United Kingdom	9350 ± 90BP (OxA-2343)	Birch bark tar	Radiocarbon dating; GC/MS	Hedges <i>et al.</i> , 1994; Aveling and Heron, 1998
Friesack, Germany	9640 ± 60 BP (OZQ694-U1) & 9250 - 9000 BP (anticipated)	Organics, with possible bitumen	SEM/EDS; GC/MS; radiocarbon dating	Yates <i>et al.</i> , 2015
Pulli, Estonia	10,650 – 10,500 calBP	Birch bark tar mixed with fat and conifer resin	FTIR	Vahur <i>et al.</i> , 2011
Gesher, Israel	10,950 BP	Mud plaster and plant fibres	FTIR; XRD; SEM/EDS	Shaham <i>et al.</i> , 2010
Wessling, Germany	11,500 BP	Inorganics, manganese-based	SEM/EDS; GC/MS; radiocarbon dating	Yates <i>et al.</i> , 2015
Bergkamen, Germany	14,220 – 11,550 calBP	Beeswax	GC/MS; FTIR	Baales <i>et al.</i> , 2017
Ohalo II, Israel	23,000 BP	Carbonaceous material and calcareous deposits	FTIR; SEM/EDS	Yaroshevich <i>et al.</i> , 2013
Kastritsa, Greece	23,880 ± 100 BP (B-131046) – 15,930 ± 130 BP (B-143304)	Organics, unidentified source	IR; py-GC/MS	Galanidou, 2006
Gura Cheii-Rasnov, Romania	30,450 ± 300 BP - >22,160 ± 90 (GrN-14,621)	Bitumen	GC/MS; FTIR; XRD/XRF; ICP-AES	Carciumaru <i>et al.</i> , 2012
Cueva Morin, Spain	36,590 ± 1100 BP (GifA-96263) – 23,640 ± 190 BP (Poz-66758)	Resin with ochre and burned bone	FTIR Raman SEM/EDS	Bradtmoeller <i>et al.</i> , 2016
Les Vachon, France	38-29,000 BP	Birch bark tar	SEM/EDS	Dinnis <i>et al.</i> , 2009
Umm el Tlel, Syria	40,000 BP	Bitumen	GC/MS	Boeda <i>et al.</i> , 1996

	Konigsau, Germany	48,400 ± 3700 BP (OxA-7125) – 43,800 ± 2100 BP (OxA-7124)	Birch bark tar	GC/MS; radiocarbon dating	Grunberg, 2002
	Umm el Tlel, Syria	70,000 BP	Bitumen	GC/MS	Boeda <i>et al.</i> , 2008
	Hummal, Syria	80-50,000 BP	Bitumen	GC/MS, carbon isotopes; SEM/EDS, Raman, FTIR	Hauck <i>et al.</i> , 2013; Monnier <i>et al.</i> , 2013
	Inden-Altdorf, Germany	128-115,000 BP	Birch bark tar	SEM/EDS	Pawik and Thissen, 2011
	Campitello Quarry, Italy	>187,000 BP	Birch bark tar	GC/MS	Mazza <i>et al.</i> , 2006
North America	Multiple sites, Arizona, United States	1605 - 550 BP	Insect lac and diterpenoid exudate	GC/MS	Bisulca <i>et al.</i> , 2017
	Newberry Cave, United States	3730 - 2970 BP	Lac insect resins	GC; GC/MS	Stacey <i>et al.</i> , 1998
	Multiple ice patch sites, Yukon, Canada	8103 - 170 BP	Spruce resins, some had additions of ochre and animal fat	GC/MS FTIR Raman SEM/EDS	Helwig <i>et al.</i> , 2008; Helwig <i>et al.</i> , 2014
	Hoyt Site, United States	11,500 – 11,000 BP	'Amber-like' material and charcoal	SEM; XRD; Solubility tests	Tankersley 1994; Beck, 1996
Oceania	Yelgun, Australia	Late Holocene (anticipated age)	Organics, unknown source and <i>Xanthorrea</i> sp. resin	SEM/EDS; GC/MS; radiocarbon dating	Yates <i>et al.</i> , 2015
	Graman, Australia	2200-2000 BP	Resins, possible <i>Xanthorrea australis</i>	Paper chromatography	Boot, 1993
	Carpenter's Gap, Australia	3160-2954 BP	Resin, source unknown	Radiocarbon dating	Maloney <i>et al.</i> , 2015

2.2. Characterising sticky things: applications of microscopy and analytical chemistry in the analysis of hafting adhesives

Pollard and Heron (1996:2) emphasise the fundamental relationship in archaeology between “residues, artefacts...and human behaviour” with archaeological science now providing a means of elucidating aspects of human activity that, in the past, were merely speculative. The molecular analysis of the trace remains (residues) associated with archaeological materials offers a means of recreating and understanding the world in which past societies lived, the resources they exploited, and other aspects of sociocultural behaviour (Haslam, 2006).

Hafting adhesives have been identified in the archaeological record using a multitude of techniques, sourced from differing types of instrumentation. The potential for the presence of both organic and inorganic ingredients places these materials in a unique situation of often requiring multiple types of analyses conducted on one sample to reliably identify all constituents present. This multi-method framework is well-established in the literature, having gained popularity in the identification of the constituents of heritage objects for museum studies and conservation efforts (i.e. Corbeil *et al.*, 2004; Andreotti *et al.*, 2006; Helwig *et al.*, 2014).

For hafting adhesives specifically, techniques may be divided based on their applicability for identifying a sample’s composition. Primary methods, i.e. those directly providing compositional information include Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS), gas chromatography – mass spectrometry in various forms (GC/MS), with additional techniques including Raman spectroscopy, X-ray diffraction (XRD), and X-ray fluorescence (XRF), as well as older techniques such as paper chromatography and solubility testing. Secondary techniques, notably radiocarbon dating, are those that do not contribute to sample characterisation and would in fact directly benefit from the application of primary

techniques before such work is undertaken. Table 2.1 highlights the techniques utilised to identify the constituents of adhesives on a case study basis.

2.2.1. Microscopy: techniques for screening and identifying residues

The analysis of hafting adhesive remains has been compounded into traceology studies. A novel term, traceology (Fullagar and Matheson, 2013) serves to describe the study of use-wear on the edges and the surface of an artefact, alongside the study of residual trace, i.e. the materials that are transferred to and adhere to an artefact as the result of its manufacture and use (Fullagar, 2006). Both types of analysis conjoined with extensive reference collections provide a means of reconstructing tool function with what little evidence remains (Anderson, 1980; Fullagar *et al.*, 1996; Rots and Williamson, 2004; Rots, 2010; Monnier *et al.*, 2012; Borel *et al.*, 2013).

The identification of hafting in the archaeological record places a greater emphasis on the analysis of working edges to confirm the presence of multi-component technologies and ascertain the finer points of tool manufacture. These are based on two functional implications: the effects of the hafting process on the proximal portions of tool opposite the working edge (i.e. polish, striations, rounding [Rots, 2010,2016]), or tasks the tool is performing (i.e. impact fractures of projectiles [Lombard and Pargeter, 2008; Yaroshevich *et al.*, 2013]). Residue analysis, by contrast, focuses on the trace material that has become preferentially concentrated along portions of a tool as the result of the hafting process, including the adhesive itself and evidence of the handle (Lombard, 2008; Cooper and Nugent, 2009; Langejans and Lombard, 2015).

The bulk of microscopy-based hafting adhesive studies has been conducted on South African collections (Williamson, 1996, 1997; Gibson *et al.*, 2004; Wadley *et al.*, 2004, 2009; Lombard 2005, 2006, 2008; Delagnes *et al.*, 2006), and as such are discussed in further detail in Chapter 2. The systematic approach employed by Lombard and colleagues (2006, 2008) plotted the distribution and qualitatively characterised residues on a comparatively large sample size with reference collections

and blind-test studies. This body of work may arguably be considered among the most comprehensive and prolific programmes on archaeological residues, with the analysis of hafting adhesives one of its focal points.

Recent publications in residue analysis especially have highlighted several methodological complications that have proven to be problematic when interpreting the sources of trace remains. Monnier *et al.* (2012) and Croft *et al.* (2016) have both critiqued residue analysis by microscopy, acknowledging that amorphous residues can be difficult to identify and that there is a lack of transparency in the studies presented for peer-review. Croft *et al.* (2018), highlight several points associated with issues in confirming the authenticity and sources of residues, which were first brought to light over a decade ago (Haslam, 2006; Langejans, 2009). A glaringly obvious statement put forward by the authors noted that “residues may be identified incorrectly due to insufficient information” (Croft *et al.*, 2018:430). In an aim to rectify this, the movement to combine microscopy with more objective identifications from analytical methods has added robustness to datasets.

This combined approach has certainly been the case in the study of hafting adhesives (Helwig *et al.*, 2008, 2014; Monnier *et al.*, 2013; Croft *et al.*, 2018) with microscopy providing a starting point to identification by delivering an assessment of the adhesive sample *in situ*. These multi-method studies will likely continue to play a significant role in how methodological programmes are developed, with analytical techniques allowing for a rigorous evaluation of the research hypotheses generated by microscopists.

2.2.2. Analytical analyses: primary characterisation of organic and inorganics

2.2.2.1. Fourier transform infrared spectroscopy (FTIR)

FTIR is considered by many as a natural starting point for analytical analyses due to its ability to characterise both the organic and inorganic constituents of materials from artistic, archaeological, and historic contexts (Adler, 1996; Castro *et al.*, 2007; Guiliano *et al.*, 2007; Mizzoni and Cesaro,

2007). Its function is based on the ability of the functional groups of a material type (natural oils, resins, and waxes; inorganic minerals; synthetics) to absorb infrared radiation (Vahur *et al.*, 2011), particularly within the mid-IR range ($4000\text{--}400\text{ cm}^{-1}$). The resulting spectra produced by a sample can be compared to known references and characterised based on peak location, band intensity, and functional group assignment. As long as due consideration is paid to band overlap and peak shifting when mixtures are present, as highlighted by Prinsloo *et al.* (2014) and Monnier *et al.* (2017), identification of the source is possible. Depending on instrumentation set-up, the procedure is rapid, and either non-invasive (direct from specimen surface) or non-destructive (sampled material), requiring small amounts of material to produce reliable results (Figure 2.2).



Figure 2.2. Left: A micro-sample of red ochre for analysis by FTIR, with a No. 4 scalpel blade (137mm edge) for comparison. Right: Cary 640 FTIR with ATR accessory use at the Research Laboratory for Archaeology and the History of Art, Oxford. Photos taken by author.

This method has been employed as both a component and as the main means of analysis of hafting adhesives in both archaeological contexts and ethnographic case studies (Matheson and McCollum, 2014; Bisulca *et al.*, 2017). Helwig *et al.* (2014) utilised FTIR to complement GC/MS, Raman, and SEM/EDS results of red-coloured adhesives obtained from projectiles recovered from a receding ice patch in the Yukon Territory, Canada, radiocarbon dated to between 8103 and 170 BP. Similarly, Charrie-Duhaut *et al.* (2016) employed this method as means of initially characterising the organic functional groups present in mastic objects and a sample of sealant acquired from

Holocene layers at Eland's Bay Cave, South Africa. In all but one identified study (Vahur *et al.* 2011), FTIR was a component of a multi-method approach, providing results that could be confirmed with other types of analyses (Shaham *et al.*, 2010; Monnier *et al.*, 2013; Bradtmoller *et al.*, 2016). The analysis of composite adhesives from a lump of black material and a flint insert from an early Mesolithic site called Pulli in Estonia, remains the only single method IR study identified to date (Vahur *et al.*, 2011). Despite the potential limitations in this approach on its own, the authors stipulated a preference for a non-invasive method of analysis and chose a single means of data acquisition.

2.2.2.2. Gas Chromatography coupled Mass Spectrometry (GC/MS)

Gas chromatography coupled mass spectrometry (GC/MS) is the most frequently used instrumentation methodology for identifying adhesive composition and was described in the literature by the early 1990s (Hayek *et al.*, 1991). The instrumentation set up involves a chromatography component, whereby volatilised molecules are separated by size as they travel through a capillary column. The separated components then move on to the mass spectrometer detector, where they are ionised (by electron ionisation or less commonly, by chemical ionisation); ionised compounds then travel to the mass analyser where they are separated by various mass related properties before entering the detector where data output occurs. Additional GC/MS configurations that include a pyrolysis (heating of a sample) stage before a sample enters the GC have also been employed (d'Errico *et al.*, 2012; Villa *et al.*, 2012).

The ability of GC/MS to identify the organic constituents of a sample when compared to known reference biomarkers (Evershed, 2008) means that this method can be used on its own or as part of a suite of techniques, particularly when the analysis of inorganic components is required. This flexibility in method use is demonstrated in the adhesive studies listed in Table 2.1. It also highlights this technique's ability to identify a multitude of adhesive sources including plant exudates such as conifer resins (Helwig *et al.*, 2008; Villa *et al.*, 2012; Croft *et al.*, 2018), latexes (d'Errico *et al.*, 2012),

and manufactured pitch (Sauter *et al.* 2000), animal-derived beeswax (Baales *et al.*, 2017) and insect lac (Bisulca *et al.*, 2017), and the mineral-based hydrocarbon bitumen (Carciumaru *et al.*, 2012). Depending on the extraction and analysis protocols, the breadth of identifiable compounds can also be broadened to include proteinaceous material (d'Errico *et al.*, 2012).

A notable GC/MS method combination in adhesive analysis includes a pairing with radiocarbon dating. As discussed in further detail below, combining a primary analysis technique to identify the composition of the adhesive with a secondary technique to provide additional non-compositional information about the material, and by extension any objects with which a specimen is associated, highlights a dynamic system where each method can add value. Publications by Villa *et al.* (2012), d'Errico *et al.* (2012), and especially Yates *et al.* (2015) exemplify this multi-method approach.

2.2.2.3. Scanning electron microscopy/ energy-dispersive X-ray spectroscopy (SEM/EDS)

SEM/EDS analysis is the second-most frequent technique employed in assessing the composition of hafting adhesives (Shahem *et al.*, 2010; Monnier *et al.*, 2013), and the most commonly used of the elemental characterisation techniques. This is likely due to their combining of two distinct instrumentation components: a scanning electron microscope for imaging and an energy-dispersive X-ray spectroscope to assess elemental composition (quantitatively or qualitatively). The technique is non-invasive and non-destructive; depending on the type of system available, an entire object can be placed inside a SEM.

Elemental composition of material can serve to identify whether a specimen contains organic or inorganic components. The presence of carbon confirms the presence of organic constituents, supporting other forms of analyses including FTIR, and GC/MS; other elements may be attributed inorganic minerals (Shaham *et al.* 2010; Charrie-Duhaut *et al.*, 2013) or the inorganic components of complex structures (i.e porphyrin structures in bitumen; Carciumaru *et al.*, 2012) identified through

other analyses. As an example, the SEM analysis of a Late Howiesons Poort quartz flake from Diepkloof in South Africa containing adhesive residues served to provide additional information as to additives present in the trace, identifying bone fragments and quartz grains that were likely purposefully included (Charrie-Duhaut *et al.* 2013).

2.2.2.4. Additional methods

Several methods are grouped together in this sub-section. Their grouping does not preclude their utility or importance, rather they are clustered here as they are among the methods that were not utilised in this research and are also not frequently applied to adhesive materials. Included herein are: Raman spectroscopy and X-ray-based techniques including X-ray diffraction (XRD) and X-ray fluorescence (XRF), as well as older techniques such as paper chromatography and solubility testing.

Raman Spectroscopy

Raman spectroscopy is another form of vibrational spectroscopy akin to FTIR analysis (Monnier *et al.* 2017). It is among the most non-invasive of the analytical techniques, and has been employed in the analysis of inorganic pigments in numerous types of cultural material including, rock art (Prinsloo *et al.*, 2013), wall paintings, ceramic, and illuminated manuscripts (Madariaga, 2015); as well as its more recently in the analysis of organic pigments and colorants (Centeno *et al.*, 2006; Ropret *et al.*, 2008). In the analysis of hafting adhesives, Raman spectroscopy has been employed in three studies (Monnier *et al.* 2013; Helwig *et al.*, 2014; Bradtmoller *et al.*, 2016) and has been met with mixed success depending on whether the analyses focused on organic or inorganic materials. Bradtmoller *et al.* (2016) have highlighted the difficulty in acquiring results from residues *in situ* on Gravettian and Aurignacian stone tools due to intense fluorescent background masking bands, which may have been caused by a combination of silica oxides of the stone tools and the organic residues themselves. Similar difficulties may have resulted in the comparatively few Raman analyses highlighted in the study of bitumen adhesives from Hummal, Syria (Monnier *et al.*, 2013). Overall,

Raman analysis serves to support results obtained from other analytical techniques (i.e. SEM/EDS and FTIR in the case of the Monnier *et al.* [2013] study).

X-ray methods: X-ray Diffraction (XRD) and X-ray Fluorescence (XRF)

X-ray diffraction (XRD) and X-ray fluorescence (XRF) are two analytical methods that are commonly used in the characterisation of inorganic materials from cultural heritage contexts (Artioli and Angelini, 2010). XRD allows for the identification of inorganic materials based on their mineral structure, using minute amounts of sample for the analysis, and can distinguish between various compound phases with identical chemical formulae. As this method has progressed its instrumentation has moved into the study of micro-samples (Hradil *et al.*, 2016), as well as non-invasive, portable applications (Getty Conservation Institute, 2009). XRF provides an assessment of the elemental composition of an object as this type of instrumentation has been reduced in size to be portable it is a non-invasive means to begin the characterisation process of an object while it is still on display.

Three adhesive studies were found to have utilised XRD in their suite of analyses (Tankersley, 1994; Shaham *et al.*, 2010; Carciumaru *et al.*, 2012). The earliest study (Tankersley, 1994) applied this technique to prove the absence of inorganic minerals in an adhesive sample from a Clovis point from the Hoyt Site, United States, alongside presumptive tests. The more recent studies, by contrast, used this technique to complement other confirmatory methods. Shaham *et al.*'s (2010) multi-method study of a flint crescent identified an inorganic red-coloured plaster adhesive with plant fibres added as for friction. Carciumaru *et al.* (2012) included XRD and XRF (the only study in this set to do so) to support the findings by organic analysis to confirm the presence of a bituminous adhesive applied to Middle and Upper Palaeolithic tools at the site of Rashov in Romania.

Solubility tests & paper chromatography

Due to the changing ethics of sampling cultural heritage material for the purposes of characterisation, it may be argued that the application of solubility tests and paper chromatography has largely fallen out of favour to the lack of specificity in its results output compared to other routinely applied methods. Solubility tests, however, still play a major role in conservation to identify non-original layers, design cleaning systems, and consolidate material with protocol development still discussed in this field (Burke, 1984; Barros Garcia, 2014).

Paper chromatography appeared as a method in the mid-1970s (Walker, 1974) and again in the early 1990s (Boot, 1993). Both studies were viewed by the authors as producing decidedly mixed results, despite have comparative references to which they compared their archaeological samples. Walker's (1974) analysis of adhesives from Eland's Bay Cave and the hafted implement AA1588 from Knysna, both in South Africa, could not successfully identify the adhesive source, although the author noted that in the case of the Eland's Bay specimen the material was resinous in origin. A study of resins from stone tools from Graman, Australia, by Boot (1993) was able to identify resin from *Xanthorrhoea australis* as the likely candidate as a hafting adhesive. However, four samples failed because they were not composed of resin (blood and plant gum were the hypothesised sources) and could not be tested by this method. Solubility tests were carried out in one study (Tankersley, 1994), the results of which were heavily contested due to the author's ambiguous and interchangeable use of nomenclature. Beck (1996) in his critique highlights that with the methods applied, particularly the use of solubility testing to ascertain the source of the organic materials, the author was unable to distinguish between amber, resin, pitch, or bitumen as being the source of the material. Both methods highlighted here also required large amounts of sample and are completely destructive; Walker (1974) describes ~100mg of sample taken for analysis, while Boot (1993) omits this point entirely.

2.2.3. Secondary analytical analyses: a note on radiocarbon dating

Although small quantities (in milligrams) of adhesive material are commonly worked with for analysis, a measure of the radioactive carbon (^{14}C) from an adhesive sample is possible, with five published instances obtained from adhesives sourced from the United Kingdom, South Africa, Germany, and Australia. The earliest are dates obtained from the eighteenth date list of the Oxford Radiocarbon Accelerator Unit, and included Mesolithic dates associated with either lumps of adhesive or adhesive trace on tools from three sites (Hedges *et al.*, 1994), with the date from the Thatcham II adhesive the only one directly associated with a tool. At Border Cave, South Africa, *Podocarpus* sp. pitch on a microlith, and a *Euphorbia* sp. and beeswax mixture described as a hafting adhesive, were directly dated and found to be consistent with other early Later Stone Age dates from the site (Chapter 2; d'Errico *et al.*, 2012; Villa *et al.*, 2012). A study by Maloney *et al.* (2015) describes the dating of the hafting adhesive (described as a mixture of resin and plant fibres) from a point recovered from Carpenters Gap 1, Western Australia, highlighting the potential of this application for elucidating the times of technological change when compared to radiocarbon dates from the same archaeological context. In developing a viable methodology for radiocarbon dating residues from stone tools after use-wear and residue analysis, Yates *et al.* (2015) described the dates from Yelgun, Australia, and Friesack and Wesseling, Germany. In doing so, they highlight the potential issues that may arise over the course of radiocarbon dating an adhesive sample.

Maloney *et al.*'s (2015) case study – and indeed the earliest work by Hedges *et al.* (1994) – differs in methodological approach from those described by d'Errico *et al.* (2012), Villa *et al.* (2012), and Yates *et al.* (2015) in that they combined both adhesive characterisation by GC/MS and radiocarbon dating of the adhesive material. Yates *et al.* (2015) emphasised the need to have a critical understanding, prior to submission for radiocarbon dating, of the potential sources of contamination that can be introduced as well as the nature of the carbon source of the adhesive itself. In the case of the analysed materials in their study, modern contamination by plasticisers (phthalates) and an

addition of bitumen to an adhesive mixture from the material from Germany were identified as being likely culprits in distorting the age ranges, adding old carbon to the measurements (Yates *et al.*, 2015).

The arguments put forward by Yates *et al.* (2015) suggest that there is a threshold for the inclusion of mixtures of organics in samples destined for radiocarbon dating, particularly given the nature of adhesive mixtures and the inclusion of other material from other components of the tool or its use. However, the development of single-compound dating techniques that extract a compound of interest and measure the radiocarbon from that single constituent, have enabled the dating of lipid residues from ceramics (Evershed *et al.*, 2008; Craig *et al.*, 2011) and the isolation of hydroxyproline from bone collagen to improve radiocarbon date ranges (Deviese *et al.*, 2018). Given the breadth of markers available from organic adhesives (beeswax, plant resins, etc.) and significant work conducted in understanding compound modifications for several biomarker classes (Regert *et al.*, 2001; Evershed, 2008; Colombini and Modugno, 2009), efforts to move radiocarbon research in this direction would likely be welcomed provided they fit within the constraints of sample quantity and sampling ethics.

2.3. Concluding remarks

The review of hafting in this chapter was necessarily brief and broad for the sake of the topics discussed throughout this thesis. I acknowledge that there are other published works that describe in detail the cognitive revolution that was hafting (Barham, 2013). Studies associated with the microscopic and molecular analysis of hafting adhesives have sought to contribute to ongoing debates in 'origins' studies, especially those firsts related to composite technologies and hunter-gatherer toolkits (Wadley *et al.*, 2009; Wadley, 2014). Although focused on just a few sites, they have nonetheless enhanced our understanding of early human cognitive capabilities (Wadley, 2010).

Those topics related to material 'firsts', however, are not the focus of this research, with the review in Chapter 3 grounded in the archaeological record of the southern African Later Stone Age

supporting this stance. This chapter instead emphasises breadth in different aspects, namely in hafting adhesive types, which in turn reflects the methodological breadth applied to their study. Further to this, a review of the application of both microscopy and analytical techniques serves to underscore a shift toward the multi-method analysis of hafting adhesives, as is presently the case in compositional study of heritage objects for conservation.

CHAPTER 3

HAFTING ADHESIVES IN SOUTHERN AFRICA: A REVIEW

Introduction

Archaeology, history, and ethnography make plain that southern Africa has an extensive history of the use of adhesives as components of composite technologies. The terms *cement*, *gum-cement*, and *mastic* used to describe these adhesives are found in seminal works describing the southern African archaeological record (Peringuey, 1911; Hewitt, 1912a; Goodwin, 1928, 1929; Clark, 1959). While few efforts were made to ascertain the sources of the adhesive at the time, the choice of nomenclature employed by early archaeological specialists is suggestive. The use of the term *mastic* is traditionally applied in a classical sense to describe the resin of the *Pistacia* sp. tree, used throughout the Mediterranean and well-known in the Greek, Roman, and Ancient Egyptian worlds (Charrié-Duhaut *et al.*, 2007). However, the term also has a long association with descriptions of hafting adhesives in southern Africa. The addition of *gum* as a qualitative descriptor of cements implies that botanical sources for components of these adhesives may have been hypothesised from an early date.

In this chapter, I discuss the basis of our understanding of hafting adhesive use and their identifiable ingredients, focusing first on the historical and ethnographic literature of the 19th through to the 21st centuries followed by the Middle Stone Age (MSA) research programmes led by Lyn Wadley, Marlize Lombard, and others, and finally the breadth of adhesive finds of the Later Stone Age (LSA) and the few chemistry-based studies centred around objects of this time period. In doing so, I wish to draw attention to the value of LSA finds as an untapped resource in the

narrative of adhesive use in southern Africa based on their prevalence, geographic distribution, and breadth of find typologies. The LSA has been neglected in recent archaeological studies in southern Africa, in favour of research on the ‘behavioural’ firsts of our species widely documented in the MSA (Wadley, 2014). A total of 148 LSA sites and non- provenienced locations were assessed for the prevalence of adhesive find descriptions in published literature. Finds were collated into a synthesis of identified finds to date in southern Africa (including LSA sites in South Africa, Lesotho, Zimbabwe, Namibia, and Zambia) to highlight the breadth of adhesives described in archaeological contexts throughout this time period. Alongside emphasising the value of LSA assemblages in discussions of the production and use of adhesive in composite technologies, I highlight a discontinuity between the ethnographic and historic records and the archaeological record. This is best explained by the temporal, geographic, and cultural divide among sources, and, it may be argued, renders temporally recent adhesive compositional evidence unsuitable as analogues for LSA and MSA findings. The available literature on adhesive composition is mainly centred in the Middle Stone Age or sourced from historic and recent ethnographic records. Nevertheless, we may consider these disparate sources as bookends of an extensive narrative of use and manufacture of hafting adhesives, provided that their contextual histories and interpretational limitations are acknowledged.



Figure 3.1. Examples of hafted composite tools from southern Africa. Left: An arrow with mastic mount and missing quartz inserts, from the Pitt Rivers Museum collections (Oxford, United Kingdom). Right: A1543, an adze mounted in mastic, and a rhinoceros horn handle acquired by the Albany Museum in 1908. Photos reproduced with the permission of the Pitt Rivers Museum, Oxford and the Albany Museum, Grahamstown (South Africa). Photos taken by the author.

3.1. Historic and ethnographic records: regional adhesives

Table 3.1 provides a review of the available ethnographic and historic literature that highlights the sources of adhesives throughout southern Africa. Available historic sources from this period cover literature that dates from the beginning of European colonial presence, beginning with the Dutch settlement in South Africa in 1653 and extending to up to around 50 years ago. Ethnographic literature comprises both old (i.e. Stow, 1905; the Bleek/Lloyd notebooks, <http://lloydbleekcollection.cs.uct.ac.za/>) and new sources (Bosc-Zanardo *et al.*, 2008; Wadley *et al.*, 2015). I outline the adhesives identified in the historic and ethnographic literature of this region, highlighting both the benefits and caveats of the utilisation of sources of this kind for its application to archaeology.

Table 3.1. A summary of botanical details of adhesives utilised in southern Africa. This is an edited and expanded version of the list provided by Walker (1974). It includes further species identified in ethnographic literature or described historic records, as well as the removal of plant genera that are found outside the region of interest. The degree of taxonomic specificity is variable.

Family ¹	Name ¹	Details of Use	Region or Culture Utilising Source	References
Amaryllidaceae	<i>Ammodorus coranica</i> (Ker Gawl.)	Pot sealant	Lesotho	Walker, 1974; Wadley <i>et al.</i> 2015
	<i>A. coranica</i>	Adhesive in projectile making	Ju/'hoan San, Botswana	Wadley <i>et al.</i> , 2015
	<i>Brunsvigia radulosa</i> (Herb.)	Pot sealant	Lesotho	Walker, 1974
	<i>Hypoxis</i> sp. (L.)	Hafting adzes and spears	Xhosa	McLaren, 1918
Anacardiaceae	<i>Ozoroa paniculosa</i> (Sond.) R Fern. & A Fern.	"Closing holes and cracks of domestic utensil" (1962:44)	Zulu	Watt and Breyer-Brandwijk. 1962, under <i>Heeria paniculosa</i>
	<i>O. schinzii</i> (Engl.) R.Fern. & A.Fern.	Composite adhesive with charcoal additive	Ju/'hoan San, Botswana	Wadley <i>et al.</i> , 2015
	<i>Protorhus longiflora</i> (Bernh. Ex C. Krauss)	"Fix assegai blades in the handle" (1962:49)	Zulu	Watt and Breyer-Brandwijk, 1962

	<i>Sorendeia</i> sp.	Caulking boats and general adhesive (1962:56)	Mozambique	Watt and Breyer-Brandwijk, 1962
Apocynaceae	<i>Diplorhynchus condylocarpon</i> (Mull. Arg)	Bird-lime	Southern Zimbabwe	Watt and Breyer-Brandwijk, 1962
		Projectile fletching	Luvala of Zambia and Angola	Watt and Breyer-Brandwijk, 1962
Asparagaceae	<i>Asparagus exuvialis</i> Baker	Adhesive used in poison preparation	Ju/'hoan San in Botswana	Wadley <i>et al.</i> , 2015
Asteraceae	<i>Othonna arbuscula</i>	Hafting adhesives	Western Cape	Smith, 1966
Burseraceae	<i>Commiphora</i> sp. Jacq.	Hafting	Mid-Zambezi region	Walker, 1974
Celastraceae	<i>Pterocelastrus</i> sp.	Hafting adzes and spears	Xhosa	McLaren, 1918
	<i>Pterocelastrus tricuspidatus</i> Loes. & <i>P. variabilis</i> N.E.Br.	Hafting and mending pots	Xhosa, Southwestern Cape to Eastern Cape	Walker, 1974 (referenced personal communications); Clark, 1958
Combretaceae	<i>Terminalia sericea</i> Burch. ex DC.	Adhesive in projectile making	Ju/'hoan San in Botswana	Wadley <i>et al.</i> , 2015
Compositae	<i>Euryops</i> sp. (Cass.)	Resin substitute	Northern Cape between Roggeveld and the Cape Colony Borders	Burchell, 1822: 259 as 'harpuisbos'
Euphorbiaceae	<i>Euphorbia clavarioides</i> (Boiss.)	Glue and bird-lime	Sotho, Lesotho	Walker, 1974
	<i>E. grandidens</i> (Haw.)	Caulking boats and general adhesive (1962:406)	Mozambique	Watt and Breyer-Brandwijk, 1962
	<i>E. triangularis</i> (Desf.)	Hafting spearheads	Xhosa	Walker, 1974
	<i>Euphorbia</i> sp.	Arrow fletching, mixture with red clay; Component of poison	Namaqualand San	Atherstone's accounts transcribed in Webley, 1994
	<i>Euphorbia</i> sp. (possible)	Adhesive substance used in arrow making, summarised in translations as 'milky juice from a pumpkin-like poisonous plant'	/Xam San	Bleek/Lloyd Notebooks (L.LVIII.1. 6088-6091 ²)

	<i>Euphorbia</i> sp.	Adhesive component of poison		H. Deacon and J. Deacon, 1999
Fabaceae	<i>Acacia mellifera</i> (M. Vahl) Benth.	Adhesive used in poison preparation	Ju/'hoan San in Botswana	Wadley <i>et al.</i> , 2015
	<i>A. nilotica</i> (L.) Wild. Ex. Delile	Edible gum, adhesive, source of lac	KwaZulu-Natal	Watt and Breyer-Brandwijk 1962
	<i>Acacia</i> sp.	Adhesive in projectile making	/Xam San	H. Deacon and J. Deacon, 1999, based on Bleek and Lloyd records
Geraniaceae	<i>Pelargonium</i> sp. L'Her.	Hafting adhesive in projectile making	San hunter-gatherers, Bushmanland	Dunn, 1879; Clark, 1975; Bosc-Zanardo <i>et al.</i> , 2008
Hyacinthaceae	<i>Scilla rigidifolia</i> Baker	Hafting	Zulu	Clark, 1958
Malvaceae	<i>Hermannia geniculata</i> Eckl. & Zeyh.	"Cement for repairing broken clay pots" (1962:1014)	Southern Sotho	Watt and Breyer-Brandwijk, 1962
	<i>Malva parviflora</i> L.	"Repairing broken earthenware pots" (1962:740)	Southern Sotho (plant not native to Lesotho)	Watt and Breyer-Brandwijk, 1962
Rubiaceae	<i>Gardenia imperialis</i> K. Schum.	Fixing pots	Northern Zambia	Walker, 1974

¹ Botanical nomenclature has been updated following the JSTOR Global plant database, <http://plants.jstor.org/>, and thus may not reflect the taxonomic designations described in some of the references.

² The citation system for the Bleek/Lloyd notebooks: for Bleek's (WB) notebooks, reading right to left has the initials 'WB' followed by a roman numeral to indicate the notebook number, followed page numbers; for Lloyd's (LL) notebooks, again reading from right to left use has the initials 'LL', followed by the roman numeral to refer to the informant, then a notebook number in normal script, followed by page numbers. See: <http://lloydbleekcollection.cs.uct.ac.za>.

The 19th- century descriptions of hafting adhesives are lacking detail beyond a brief assessment of their appearance or basic nomenclature. Dale (1870), in highlighting the manufacture of an arrow acquired by Palgrave in the lower Orange River region, only notes that crystal quartz inserts were embedded into "a fine cement, apparently of clay" (365-66) at the arrow's tip. Dunn (1879: 34) describes a similar arrow construction where two stone fragments "are cemented to the arrow tip" and records the use of *Pelargonium* sp. as an arrow adhesive. The arrows made in 1878 for Wilhelm Bleek by a /Xam informant, which then came to be housed in the University of Cape Town

collections according to Goodwin's 1945 publication (Rudner, 1979) held stone inserts "set in wax" (1979: 5). Another set of arrows made for Bleek in the 1860s, sent to the University Museum Oxford and now making up part of the Pitt Rivers Museum collections (Figure 3.1, left), were attributed to the same /Xam informants by Clark (1975). The accession details of these specimens notes that the arrows were manufactured with chert microliths set in mastic (JC 1 8 2003, objects.prm.ox.ac.uk).

Walker (1974) produced the only compilation to date of adhesives for comparison to archaeological collections. The taxa reviewed were not only used for hafting adhesives, but were also employed as pot sealants, bird-lime and caulk for boats. This extensive list, including references from eastern and central Africa, was derived from a number of sources: publications of expeditions within southern Africa (Burchell, 1822, 1824; Dunn, 1879); botanical literature (Watt and Breyer-Brandwijk, 1962; Smith, 1966); and personal communications from archaeologists and museum curators of the time including J. D. Clark, E. M. Shaw, and ethnologist E. H. Bigalke. Additives, including charcoal and beeswax, were described by several authors (Walker, 1974; Wadley *et al.*, 2015). This compilation, edited and expanded upon in Table 3.1, emphasises the breadth of species that may be employed for their adhesive qualities.

The relative lack of specificity of identifications of adhesive-producing plants alongside an inherent bias ascribed to historic authors in their observations is notably problematic in this compilation. Where specific botanical taxa are described (i.e. Watt and Breyer-Brandwijk 1962), other motives like medicinal enquiry were the primary aim of the authors in the compilation of such information. In other instances, early records of adhesives discuss genera or plant families that were components of the manufacture process, but, in many instances the exact taxa were not specific (Webley, 1994) and may have been biased by the author's limited knowledge of botany. Other cases are generic descriptions which may be lost in translation; the /Xam informant |han=kass'o (Klein Jantje), for example, described the milky juice from a pumpkin-like poisonous plant (LL.VIII.1.6088-6091) used in arrow manufacture, but ascribing this plant to *Euphorbia* sp. (as

proposed in Table 3.1) is speculative based on the visual characteristics of the latex exuding from plants of this genus.

Within these sources there is also a relative preoccupation with projectile weaponry, and the components of those projectiles (i.e. species of reed, manufacture of points, poisons etc.). This may be an artefact of the historic persona of the San and how these populations were viewed in the past; Bosc-Zanardo *et al.* (2008) describe the bow and arrow set being an iconic cultural marker for this population by those who viewed it with fear and thus a source of preoccupation. It may be argued therefore that within historical ethnographies, and historic observations, we are lacking a complete view of the breadth of resources utilised as adhesives. A publication by Wadley and colleagues (2015) is a marked contrast, as they record no fewer than five species associated with an adhesive production event by informants of Ju/'hoan San of Nyae Nyae, Namibia (added to poisons or used in the manufacture of the projectile), describing where the plants were acquired and how they were processed. This research certainly highlights the gaps in older records, bringing to light questions that perhaps went previously unasked.

In returning to how these historic and ethnographic sources may link to archaeological contexts, some species are frequently highlighted as 'best suited' candidates for archaeological adhesives. Indeed, Clark (1958), Walker (1974), and Shaw's (Clark, 1958) preoccupation with *Pterocelastrus* sp. resin as an adhesive is the most notable within the context of archaeological literature. The fixation on this genus is likely due to its documented use by the Xhosa (McLaren, 1918) and by hunter-gatherer groups in the Cape (Clark, 1958). However, it was not identifiable in any archaeological specimens analysed at the height of its candidacy (Walker, 1974).

This raises questions yet again as to whether historic and ethnographic records are suitable for the task of providing archaeological analogues. I put forward two limitations for consideration based on the compilations of Table 3.1. The first is that these records are representative of groups that exist within similar environments to archaeological populations, but are culturally distinct from

their past counterparts. Differences in material culture may consequently result in the use of different resources for manufacturing adhesive materials. The second point may be considered the inverse of the first; the available records of adhesive use among hunter-gatherer populations in southern Africa are based in relatively arid environments, differing significantly from the majority of adhesive finds in archaeological contexts from the Fynbos, Grasslands, and Thicket Biomes. Bosc-Zanardo and colleagues (2008) highlight these points in their attempt at a combined ethno-archaeological approach to southern African San hunting gear. They stipulate that comparisons between archaeological, ethnographic, and historic sources are problematic as none of these sources occupy the same time and space. Ethnographic examples of arrows are centered on the populations of the Kalahari Desert, while historic records are focused around groups in the environs of the Cape of Good Hope and the southernmost coastline of South Africa. The separation by time and distance that was noted for hunting gear rings equally true for hafting adhesive and is an illustration of a wider dysfunction (see: Pargeter *et al.*, 2016 for wider discussion).

These limitations raise the question: how, then, should these records be treated? I suggest that we can treat them for what they are - lists of species describing the diversity of plant taxa that has been exploited by past and present-day populations across a range of geographies and environments. Indeed, Table 3.1 highlights that adhesives may be obtained from various types of flora, be they succulents, shrubs, or trees, processed or freshly extracted materials. Wadley *et al.* (2015) succinctly describe this point, in that adhesive recipes from ethnographic sources (and by extension historic ones as well) are not necessarily analogous to archaeological recipes, but *can* provide models for how they were manufactured and how their ingredients were acquired.

3.2. Middle Stone Age adhesives

As a contrast to the previous section, the extensive research conducted on Middle Stone Age (MSA) adhesives not only provides the foundation for classifying the organic and inorganic ingredients of hafting adhesives in southern Africa, but also represents a starting point for understanding the functional abilities of these recipes by experimental means. In this section, I highlight these MSA research programmes and their contributions to an archaeological narrative. Table 3.2 describes the instances where hafting has been identified and whether the nature of the adhesive could be elucidated.

The narrative of hafting in southern Africa begins with evidence of hafted spear tips from the earliest MSA layers at Kathu Pan 1, South Africa, approximately 500,000 BP (Wilkins *et al.*, 2012). While the presence of modifications along the base of some of the stone points from this site is consistent with their hafting to create a composite tool, there are no indications of the nature of this haft. The identification of adhesives, and the beginnings of the attribution of trace remains to specific ingredient sources, begins instead with the transition into the MSA (<300,000 BP to >20,000 BP) with the proliferation of large-scale, systematic use-trace studies (including use-wear, micro-fracture analysis, and residue analysis) to contribute to the discussions of behavioural modernity and complex cognition in humans (Wadley *et al.*, 2009; Wadley, 2010).

Table 3.2 A summary of MSA adhesive finds in southern Africa, including the cultural association, the type of finds and the type of techniques employed to identify the adhesive.

Site	Associated Technocomplex and Date (BP)	Find Type & Means of Identification	Reference
Apollo 11 Cave, Namibia	Late MSA, 27-25,000	Visual description of extent of adhesive trace	Wendt, 1972
Blombos Cave, South Africa ¹	MSA , >40,000BP	Hafted bone points	Henshilwood and Sealy, 1997
Die Kelders, South Africa ^{1,2}	MSA, not specified	Ochre stained artefact described, the nature of staining not specified in publication	Thackeray, 2000; Wadley <i>et al.</i> , 2015
Diepkloof, South Africa	Late Howiesons Poort, 60-56,000BP	Chemical analysis. Trace on stone flake. <i>Podocarpus elongatus</i> pitch, with possible bone and quartz additives	Charrié-Duhaut <i>et al.</i> , 2013
Kathu Pan 1, South Africa	Early MSA, 500,000 BP	Hafting of points identified by diagnostic impact fractures	Wilkins <i>et al.</i> , 2012
Rose Cottage Cave, South Africa	Howieson's Poort, 66 – 58,000 BP	Microscopic residue analysis. Trace on backed tools described as combination of ochre and plant exudates	Williamson, 1997; Gibson <i>et al.</i> , 2004
Sibudu Cave, South Africa	Still Bay – Late Howison's Poort, 71-38,000 BP	Microscopic residue analysis. Trace on backed tools described as combination of ochre and plant exudates Chemical analysis. Identification of conifer resin (possible Podocarpaceae family), and unknown lipid	Lombard, 2005
Umhlatuzana, South Africa	Howieson's Poort, 66 – 58,000 BP	Microscopic residue analysis. Trace on backed tools described as combination of ochre and plant exudates, and plant exudates by themselves	Lombard, 2007

¹ The means by which hafting at Blombos Cave and Die Kelders was identified was not evident in the original publications.

² Wadley *et al* (2015) stipulate that ochre staining noted at Die Kelders implies the presence of hafting in the review. However, the original publication by Thackeray (2000) does not make this assessment.

The methodological design of these studies was centred on the systematic exploration of the surface of the tool and the statistical quantification of residue types based on spatial distribution and comparison to blind-test studies (Lombard and Wadley, 2007). These micro-detection methods were the basis of a research platform designed to explore cognitive and sociocultural behaviour,

focusing on the Still Bay (77-70,000 BP), Howiesons Poort (66-58,000 BP), and Sibudu (58-45,000 BP) technocomplexes (nomenclature as described by Lombard *et al.* 2012) at Sibudu (Lombard, 2005, 2006a, 2006b, 2008), Umhlatuzana (Lombard, 2007; Lombard and Wadley, 2009), and Rose Cottage Cave (Williamson, 1997; Gibson *et al.*, 2004). Results from this work have identified a predominance of two residue types concentrated along the proximal or backed edges: black residues (hypothesised to be derived from plant gums or resins) and ochres (see: Gibson *et al.*, 2004; Lombard 2005, 2006a, 2006b, 2007 for detailed distributions). These two residues were thus attributed to tool hafting and adhesive remains (Lombard, 2006a, 2006b). This research programme, particularly those studies at Sibudu spanning the largest number of technocomplexes of the MSA, have provided the foundation for our understanding of hafting arrangement and tool function during this period, paying particular attention to hunting weaponry and cutting tools, but have also begun the process of characterising the adhesives from these archaeological contexts.

When the subject of ochres and inorganic additives was tabled in the publication of the aforementioned MSA studies, it inevitably became an intensely discussed topic owing to its implications in the study of symbolic behaviour, human cognitive development, and behavioural variability. From a purely mechanical perspective, loading agents improve the malleability of an adhesive and aid in the steadfastness of the join between two components (Zipkin *et al.*, 2014). Experimental studies have been employed to assess the adhesive-making process and the effectiveness of these composite recipes from either a functional or a materials science perspective (Allain and Rigaud, 1986; Wadley *et al.*, 2004, 2009; Wadley, 2005; Hodgskiss, 2006; Zipkin *et al.*, 2014). Studies by Wadley *et al.* (2009) and Hodgskiss (2006) identified the particle size of loading agents as critical to the success or failure of a compound adhesive in functional testing. Indeed, sand additive adhesives were among the most successful adhesive type and their inclusion was described by Hodgskiss (2006:114) as being “important in the success of any adhesives, including ochre adhesive.” Zipkin’s (2014) evaluation of loading agents and adhesive joins develops from Wadley and Hodgskiss’ findings, highlighting that surface roughness (of the tool raw material) more

strongly influences the effectiveness of an adhesive and the toughness of the join bond. Lombard's (2007) archaeological study of segments from Umhlatuzana briefly addresses the influence of raw materials on adhesive recipes in her observation of the absence of ochre residue on the quartzitic material used to make them.

The introduction of molecular techniques to the analysis of organic archaeological materials is relatively recent compared to other geographic regions and fields of archaeological study (i.e. d'Errico *et al.*, 2012; Villa *et al.*, 2012; Charrié-Duhaut *et al.*, 2013). This is perhaps a product of the relative success of microscopy studies in South Africa and a preference for more conservative approaches of residue analysis. The morphological approach favoured in the studies I have cited earlier in this section require residues to remain *in situ*, which maintains the contextual integrity of the trace (Loy, 1993; Langejans, 2011; Bradfield, 2014) but can reduce the relative specificity of the identification in some contexts. Such limits include attempts to identify the sources of amorphous residue types, and Soriano *et al.* (2015) point out that optical light microscopy cannot distinguish between sources that are visually similar, yet chemically distinctive (i.e. plant exudate types such as saccharide-based gum versus terpenoid-containing resins). Applying chemistry-based techniques to Howieson's Poort material has thus served to complement large-scale research programmes, providing a chemical specificity that was originally lacking in the identification of organic trace in this region.

The studies from Diepkloof (Charrié-Duhaut *et al.* 2013), and Rose Cottage Cave and Sibudu (Soriano *et al.* 2015) are two such cases. Charrié-Duhaut *et al.* (2013) analysed a single quartz flake from the Late Howieson's Poort (~60 – 56,000 BP) assemblages at Diepkloof in the Western Cape. Analysis by GC/MS and SEM identified an oxidised pitch derived from *Podocarpus elongatus* (yellowwood) as the most likely source of the adhesive, with bone fragments and quartz grains as possible additives. Three segments from Sibudu (KwaZulu-Natal) and one from Rose Cottage (Free State) also underwent chromatographic analysis, with only of the two pieces from Sibudu

producing organic markers consistent with a conifer resin and an unknown lipid material. The series of abietane and pimerane diterpenoids identified in the sampled material were interpreted as likely being derived from members of the Podocarpaceae family (Soriano *et al.*, 2015).

The application of such techniques is clearly a promising prospect in elucidating botanical sources and identifying organic and inorganic additives. However, in strictly numerical terms, analyses have only been conducted so far on five specimens from three sites spread across South Africa, with only three producing sufficient organic markers for interpretation. Due caution is thus required as these small sample sizes sourced from sites that are not geographically constrained limit the conclusions that can be drawn on the application of adhesives and the longevity of manufacture techniques.

Despite the potential interpretational limitations, these MSA datasets can provide a starting point in testing the functionality and effectiveness of adhesive recipes. In taking a note from recent Neanderthal adhesive studies (Koller *et al.*, 2001; Grünberg, 2002; Pawlik and Thissen, 2011) and subsequent experimentation work (Schenck and Groom, 2016; Kozowyk *et al.*, 2017a, 2017b), the utilisation of archaeological evidence of adhesive resources can provide a suitable methodological framework to test production methods, the material properties of adhesives, and their functionality as components of composite tools. At present, southern African experimental studies fall short of their European counterparts and lack an assessment of adhesive components identified in archaeological contexts, instead preferring ethnographic analogies. Evidence of such preference is highlighted by the fixation on gum exudates as the main constituents of adhesives made for experimental purposes (Wadley *et al.*, 2004, 2009; Wadley, 2005; Hodgskiss, 2006; Zipkin *et al.*, 2014) despite the absence of this ingredient in archaeological contexts and the identification of resinous exudates instead (Charrié-Duhaut *et al.*, 2013; Soriano *et al.*, 2015). Future research, taking into consideration archaeological datasets and implementing said findings into actualistic

studies, would no doubt make a significant contribution to adhesive and composite tool construction models in southern Africa.

3.3. Later Stone Age adhesives

The transition to the Later Stone Age brings with it a greater frequency and range of tool types bearing trace or large components of hafting adhesives, with a total of thirty-nine sites or geographic locations identified, spanning the whole Later Stone Age (LSA) (~18, 000 BP to within the last few hundred years). Within this section, I describe these finds, first highlighting the earliest specimens acquired during the beginnings of archaeological research in South Africa, followed by a review of the LSA finds from South Africa, Lesotho, Zambia, Namibia, and Zimbabwe. I have divided the sites by geological time period (i.e. late Pleistocene, Holocene, late Holocene etc.) to account for differences in assemblage nomenclature between countries and between generations of archaeologists, though any technocomplex with which adhesives are associated is noted. The nomenclature and date ranges include those discussed in primary site publications, as well as site compilations (such as Lombard *et al.*, [2012]) and nomenclature reviews (Orton, 2014). I end this section with a brief discussion assessing the trends noted from this synthesis and from chemical studies conducted on the archaeological adhesives.

Three main find types are described in the literature. The most commonly identified category are traces of hafting adhesives or *mastic* on stone, bone, and wooden artefacts. The function of these components included high impact projectiles (i.e. stone segments or bone points), high impact non-projectiles (adzes), and low impact tools (i.e. scrapers, borers, blades/bladelets, etc.).

3.3.1. Early collection acquisitions of hafted implements

Among the first finds identified as having hafting adhesives were a series of complete or relatively complete implements collected from cave burials from the late 19th up to the first half of the 20th centuries (Peringuey, 1911; Hewitt, 1912a; Goodwin, 1928, 1929; Clark, 1959; H. Deacon,

1966). It is important to discuss these finds within the context of southern African archaeology and this hafting adhesive study more specifically for two reasons. Firstly, the archaeological context of this material is often dubious at best. The specimens were sourced from cave burials, and all are lacking archaeological or geographic provenience, either because of a lack of skeletal material from the recovery site or to dissuade other interested parties. The only exception is C961 from the Albany Museum, which was described as found in association with "...sherds typical of Cape coastal pottery" (H. Deacon, 1966: 89) and it is thus likely to have been produced during the ceramic final LSA (< 2000 BP, Lombard *et al.*, 2012).

The earliest of these finds were the handle and adhesive components of a tool sourced from a cave near the mouth of the Touw River in the Western Cape (~33° 59' 39.64 S, 22° 35' 53"E) by a Mr Dumbleton, and originally published in the Cape Town Diocesan College and School Magazine in 1892 (Peringuey, 1911). It was accessioned in the South African Museum (SAM) as SAM AA5355, where it remains today (see: Appendix V). Other such objects were soon to follow, including SAM AA1588 (from a cave near Kynsna [Goodwin, 1928], 34°2'8"S, 23°2'56"E), and SAM AA7433 (collected by F. Malan from the Porterville area and acquired by the museum in 1943[?], based on museum records). The Albany Museum of Grahamstown (Eastern Cape, SA) holds further specimens: A1543 (Figure 3.1, right) and C961 (both from caves near Plettenberg Bay (Hewitt, 1912, 1922; Deacon 1966), 34°3'0"S, 23° 21' 59.76"E), plus a lump of resin on a haft recovered from Woest Hill (accession details and archaeological context were unknown (Hewitt, 1922; Walker, 1974), 33° 20' 36.51"S, 26° 33' 36"E). Walker (1974) also describes an adze mounted in adhesive and a lump of adhesive with a haft impression (collected from unknown sources) which were donated by a Mr Marais in 1963 to the University of Cape Town's Department of Archaeology. They were described as being recovered from burial contexts, but specific cultural affiliations are lacking.

Thus, this early period of archaeological enquiry and excavation has produced an interesting dichotomy for those engaging with these objects in the present. On the one hand, it was

responsible for the recovery of the greatest number of complete composite tools within southern Africa, but on the other hand has resulted in these finds being completely detached from the archaeological record. Despite this, by including specimens of this kind in this study and attempting to ascertain their composition, we may begin the process of contextually adding to these object narratives. In doing so, we may be able to re-engaged with the LSA cultural assemblages from which they were removed.

3.3.2. Pleistocene to early Holocene assemblages

Three main technocomplexes span this period: the Early LSA (eLSA) (40 -18,000 BP), the Robberg or the late Pleistocene microlithic (18-12,000 BP, or 19-9,500 BP), and the Oakhurst or late Pleistocene/Early Holocene non-microlithic (12-7,000 BP). However, across its long time scale, only five sites have produced adhesive finds (Figure 3.2), all in current Grassland or Fynbos Biomes (Lombard *et al.*, 2012; Table 3.3).

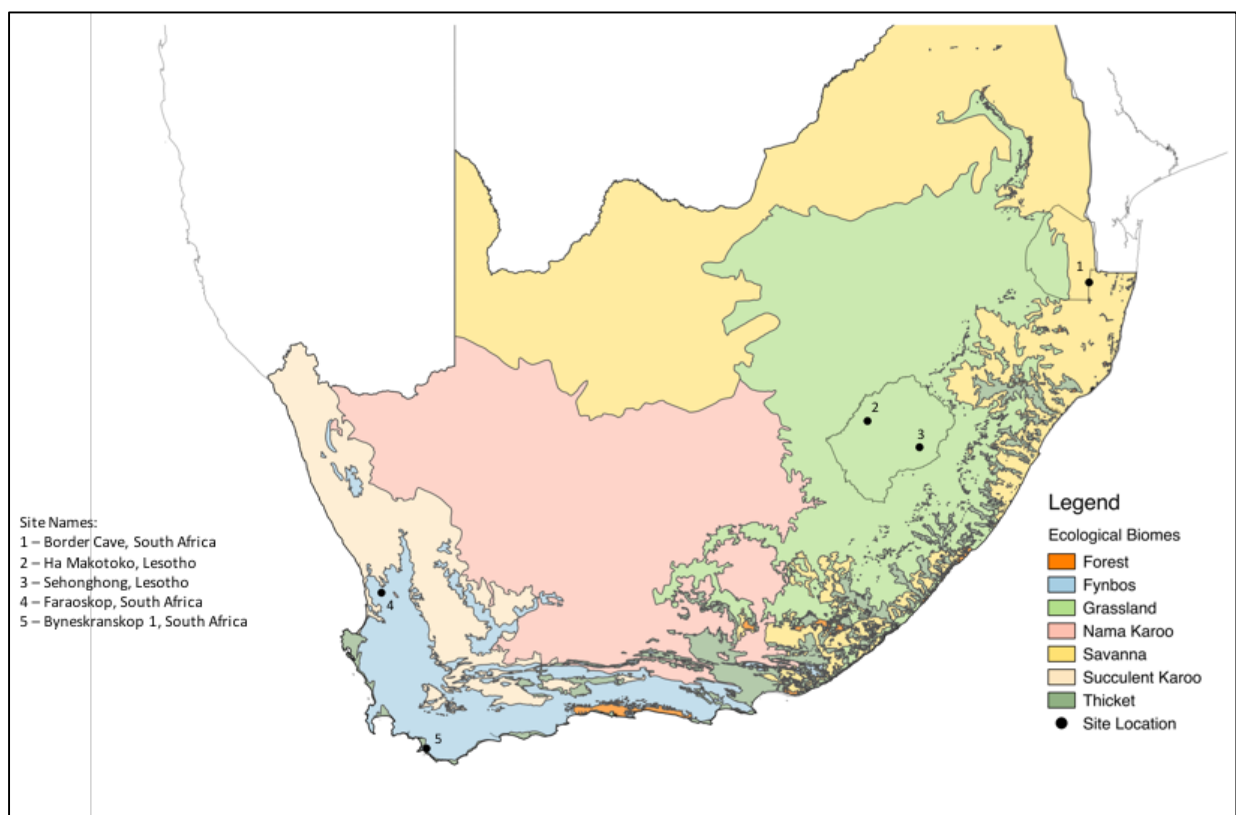


Figure 3.2. Pleistocene and early Holocene site assemblages with identified adhesive finds, highlighted by ecological biome. Vegetation Map of South Africa, Swaziland, and Lesotho 2012 available from the Available from the Biodiversity GIS website bgis.sanbi.org, downloaded Dec 5, 2016. African countries layer by Esri.

Table 3.3. Details of Pleistocene and early Holocene site assemblages with adhesive finds, corresponding to the site location points in Figure 3.2.

Site Names	Find Description	Associated Dates	References
1 – Border Cave, South Africa	Trace on four stone tools, and a lump of adhesives	41-39,000 cal BP (OxA-W-2455.52, OxA-X-2418-47)	d'Errico <i>et al.</i> , 2012; Villa <i>et al.</i> , 2012
2 – Ha Makotoko, Lesotho	Trace on a CCS flake	8370 ± 80 BP (Pta-5191)	Mitchell, 1993
3 – Sehonghong, Lesotho	Trace on CCS and quartzite bladelets	Series of dates ranging between 12,960 ± 55 BP (OxA-32922) and 11,090 ± 230 BP (Pta-1905)	Mitchell, 1995; Pargeter <i>et al.</i> , 2017
4 – Faraoskop, South Africa	Silcrete adzes and silcrete and quartz scrapers	11,550 ± 20 BP (Pta-4817)	Manhire, 1993
5 – Byneskranskop 1, South Africa	Trace on backed scrapers, a quartz borer and segments	9760 ± 55 BP (Pta-1587) and 6540 ± 55 BP (Pta-1905)	Schweitzer and Wilson, 1982; Loftus <i>et al.</i> , 2016

The oldest evidence of hafting adhesives in the LSA was identified at Border Cave, in KwaZulu-Natal, with dates ranging between approximately 41 and 39,000 calBP (d'Errico *et al.*, 2012; Villa *et al.*, 2012). Four microliths, including a portion of a bladelet, a flake or bladelet fragment, a scaled piece, and debris from bipolar knapping were all found to have trace or large fragments adhering to their surfaces, as indications of lateral hafting (Villa *et al.*, 2012). A lump of organic material wrapped in vegetable twine was also recovered and described by d'Errico and colleagues (2012:13218) as “certainly used for hafting purposes.” Chemical analysis was conducted on these organic materials followed by radiocarbon dating.

Two sites with Robberg assemblages were documented as having adhesive trace: Sehonghong in Lesotho and Faraoskop in South Africa's Western Cape Province. Trace on crypto-crystalline silicate (CCS) and non-CCS bladelets, in particular, was identified in the Robberg layers CLBRF, RBL, RF, and BARF at Sehonghong (Binneman and Mitchell, 1997; see Chapter 5), with dates ranging

between $12,960 \pm 55$ BP (OxA-32922) in RBL and $11,090 \pm 230$ BP (Pta-1905) (Pta-6065) in BARF (Mitchell, 1995; Pargeter *et al.*, 2017). Use-wear analysis by Binneman (Binneman and Mitchell, 1997) on a selection of bladelets from these layers indicated that they had likely been hafted parallel to the shaft of the tool. The authors postulated that the wear on the bladelets suggests that these pieces were components of knives used for processing plant material, among other things. The bladelets were multi-functional, also serving as components of projectiles. My own visit to the University of Cape Town's Department of Archaeology in May/June of 2016 identified trace on silcrete and quartz adzes and scrapers from the ABS layer at Faraoskop dating to $11\,550 \pm 20$ BP (Pta-4817) (Manhire, 1993).

Evidence of adhesives during the Oakhurst period was found at two sites. A CCS flake stained with ochre and adhesive was identified at Ha Makotoko in Lesotho, with an associated date from this layer (GWA) of 8370 ± 80 BP (Pta-5191) (Mitchell 1993). Schweitzer and Wilson (1982) also noted the presence of 'mastic' trace on a quartz borer from Layer 13 and a backed scraper from Layer 10, as well as an increasing frequency of segments with adhesives from Layer 12 onwards, at Byneskranskop 1 on South Africa's southernmost coastline. The associated or adjacent layers from which this material is sourced date to 9760 ± 55 BP (Pta-1587) in Layer 14, 7750 ± 90 BP (Pta-2347) in Layer 12 and 6540 ± 55 BP (Pta-1905) in Layer 10, all attributed to Oakhurst cultural assemblages (Loftus *et al.*, 2016).

Overall, adhesive finds from the Pleistocene into the early Holocene are relatively few. The pieces with evidence of adhesives, particularly those from the microlithic assemblages of the eLSA and Robberg, demonstrate the multi-functionalism of the lithic components, and likely indicate that pieces (i.e. bladelets, flakes etc.) may have held several functions in composite technology (Binneman and Mitchell, 1997). However, the relatively few instances of such finds over such a breadth of time, one of known environmental fluctuation, inhibits our understanding of the extent

of functionality of the technologies and how such materials were adapted to each environmental episode.

3.3.3. The mid-Holocene assemblages

With the transition to the Wilton or Holocene microlithic assemblages (8-4 000 BP), there is an increase in the visibility of adhesive within archaeological sites, including trace on tools, lumps of material, and complete composite tools. Indeed, they are numerous enough in this period that they are divided into the aforementioned categories within this section. A similar increase in ecological diversity was identified for the distribution of sites. By the mid-Holocene, adhesive finds survive in sites located in the present-day *Zambian Woodlands*; the *Zimbabwean Savanna*, and the *Nama Karoo*, *Fynbos*, *Thicket*, *Grassland*, and *Forest Biomes* of southern Africa. Figure 3.3 and the corresponding Table 3.4 highlight these finds.

Trace material, and in some instances large amounts of adhesives adhered to tool surfaces, was identified on a variety of tool categories. Low-impact tools (i.e. scrapers, borers, bladelets and blades) were identified as having the highest prevalence adhesive trace, based on a site count. The bladelet from *Rose Cottage Cave* (Table 2.4) was included within this section grouping based on a use-trace study by Williamson (1996), whose results suggest that the bladelets were likely inserts for tools used to process plant material, not unlike the *Robberg* bladelets from *Sehonghong* (Binneman and Mitchell 1997). Overall, however, the most abundant tool type represented in this grouping were scrapers. They were found at: *Melkhoutboom Cave*, *Andriesgrond*, and *Renbaan Cave* in South Africa; *Sehonghong* in Lesotho; and *Apollo 11 Cave* in Namibia. High-impact projectiles (including points and segments) were identified at *Buzz Shelter*, *Byneskranskop 1*, *Nelson's Bay Cave*, and *Melkhoutboom* in South Africa. Further afield, an impressive collection of segments and backed microliths were recovered from two *Zambian* sites, *Makwe* and *Kalemba*. These specimens were attributed to the *Makwe Industry*, which was contemporaneous with the southern African Wilton period. Indeed, Phillipson (1976) draws on South African Wilton specimens

(especially Deacon 1969) as comparisons for hafting orientation among the Zambian collections. Some sites, by contrast, including Wilton Large Rock Shelter and Makwe (to some extent) are not specific in the range of tool types having adhesive trace.

A lump of amorphous material on a stick, described as adhesive was identified by H. Deacon (1976) at Melkhoutboom Cave. This find is likely representative of a means of adhesive storage, prior to its application to a tool, and is not unlike the organic lumps from Border Cave (Table 3.3) and Boomplaas (Table 3.5 and discussed in the next section). Other lumps of adhesive that were likely components of composites have been described at Cyrene, Zimbabwe, by the Rev. Paterson (Anon, 1949), as well as Oakhurst (Goodwin, 1937) and Eland's Bay Cave (Charrié-Duhaut *et al.*, 2016) in South Africa, with all finds bearing impressions of the organic or stone components they once held.

Finally, a complete hafted tool was also recovered from Eland's Bay Cave; an adhesive handle with a backed quartz microlith insert. Charrié-Duhaut *et al.* (2016) describe this tool as being held with a 'pencil grip', with one side of the insert fixed in the adhesive and the other remaining open and pressed against the thumb to allow for the insert to be changed as needed. Unfortunately, the precise age of this specimen is difficult to establish since while it is described as coming from the JOFR unit, the fill of a sleeping hollow dating to 3750 BP, the hollowing out of this area resulted in the unconverging of an earlier burial dating to 8000 BP. It is therefore "plausible but not demonstrable that the two artefacts are contemporary [to the human burial]" (Charrié-Duhaut *et al.*, 2016: 287), although, it is equally plausible that the specimens belong to the later occupants. As such, Eland's Bay has been included in both my mid-Holocene and late Holocene reviews.

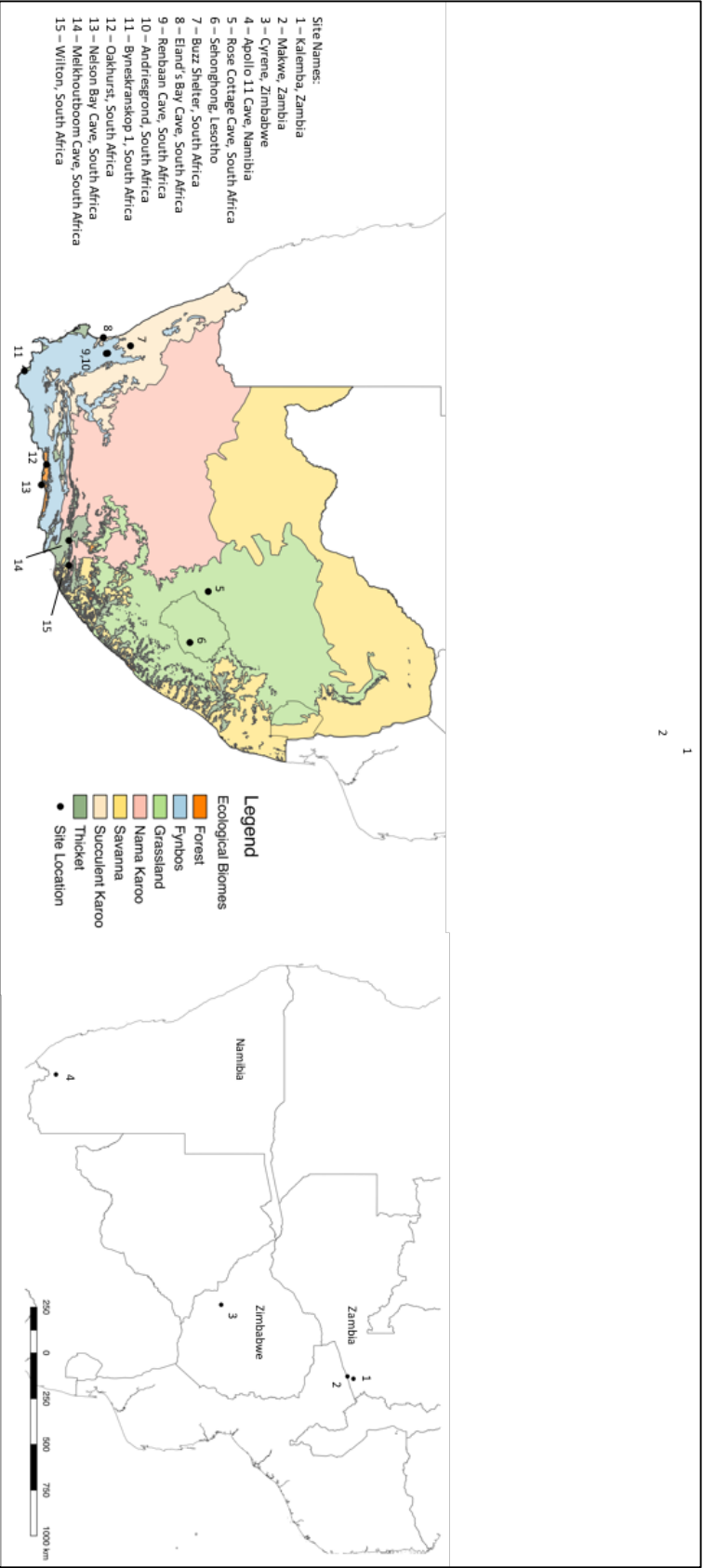


Figure 3.3. Mid-Holocene sites with identified adhesive finds. The ecological Biomes of southern Africa are highlighted, as this region is the focus of the study. Vegetation Map of South Africa, Swaziland, and Lesotho 2012 available from the Available from the Biodiversity GIS website bgis.sanbi.org, downloaded Dec 5, 2016. African countries layer by Esri.

Table 3.4. Details of mid-Holocene sites with adhesive finds, corresponding to site location points in Figure 3.3.

Site Names	Biome Type	Find Description	Associated Dates	References
1 – Kalembe, Zambia	Woodland	Six segments with trace	One layer, dates between 5040 ± 110 (N-1386) and 4480 ± 90 (N-1387)	Phillipson, 1976
2 – Makwe, Zambia	Woodland	Fifty-two tools with trace, especially on backed microliths	Multiple layers, dates ranging between 5010 ± 90 (SR-204) and 4380 ± 130 (GN-903)	Phillipson, 1976
3 – Cyrene, Zimbabwe	Savanna	Adhesive lump with handle impression	Historic mention, no associated dates	Anon, 1949
4 – Apollo 11 Cave, Namibia	Nama Karoo	Trace on stone tools, primarily small scrapers	One layer, dates between 9120 ± 90 (KN-610) and 6030 ± 65 BP (KN-609)	Wendt, 1972
5 – Rose Cottage Cave, South Africa	Grassland	CCS bladelet	From Pt layer, dated to 5970 ± 70 BP (Pta-5934)	Williamson, 1996
6 – Sehonghong, Lesotho	Grassland	Trace on a backed flake and scrapers, CCS and non-CCS	Blade from the ALP layer, with a series of dates with mean value of 7150 BP, and scrapers from the GWA layer, with a date of 5950 ± 70 BP (Pta-6154)	Mitchell, 1996
7 – Buzz Shelter, South Africa	Nama Karoo	Trace of adhesive and ochre on a CCS, backed point, Layer 4 (TU2) and a lump of resin in Layer 5 (TU2)	Dates obtained Layer 6, 5452 ± 54 BP (AA89912), and Layer 4, 4551 ± 54 BP (AA89911)	Orton <i>et al.</i> , 2011
8 – Eland's Bay Cave, South Africa	Fynbos	Adhesive handle, complete tool (adhesive with backed quartz microlith insert)	Two adhesives are either associated with a burial (8000 BP) or a later excavation that occurred at 3750BP	Charrié-Duhaut <i>et al.</i> , 2016
9 – Renbaan Cave, South Africa	Fynbos	Trace on silcrete scrapers and adzes, three total from Basal Unit	Date from Basal Unit, 5430 ± 70 BP (Pta-3760)	Kaplan, 1987
10 – Andriesgrond, South Africa ¹	Fynbos	Trace on silcrete scrapers from Layers 4 and 9	Dates from overlaying vegetation patch 4 - 3000BP. ¹⁴ C dates obtained from other organics in these layers were thought to be intrusive. Lithic assemblage classified as mid-Holocene	Anderson, 1991
11 – Byneskranskop 1, South Africa	Fynbos	Trace on segments (53 in total) but one one highlighted from layer 7, made of silcrete	Nearest dates from Layer 9 (below) 6370 ± 90 BP (UW-409) and 6100 ± 140 BP (Pta-1772) and Layer 5 (above) 3900 ± 60 BP (Pta-1571)	Schweitzer and Wilson, 1982

12 – Oakhurst, South Africa	Forest	Lump of adhesive bearing the impression of a flake and an oval bored stone with fragments of the same material	No associated dates. Described from burial Via, attributed to 'Early Wilton' based on lithics associated with the remains	Goodwin, 1937
13 – Nelson Bay Cave, South Africa	Forest	Trace on both sides of one chalcedony segment	Wilton layers span between 9080 ± 185 BP (UW-179) and 4860 ± 65 BP (UW-217)	J. Deacon, 1984; Inskeep and Avery 1987; Loftus <i>et al.</i> 2016
14 – Melkhoutboom Cave, South Africa	Thicket	Trace on chalcedony scrapers, segments, and borers from layers M, W, and MB	Dates obtained from WBM (below M) at 7300 ± 80 BP (UW-234), W at 6930 ± 65 (Pta-668), and MB 5900 ± 90 (Pta-680)	H. Deacon, 1976
15 – Wilton, South Africa	Thicket	Trace on stone tools.	No associated dates.	Hewitt, 1921; H. Deacon, 1963

¹Andriesgrond: Material from this site is included as a possible with the other Wilton site assemblages. Trace adhesives were identified on tools from Units 4 and 9. Anderson (1991) notes, however, that while these layers are likely contemporaneous, the associated dates are problematic as C14 results were acquired from tortoise shell bone. Dates from a vegetation patch in Unit 7 dates between 4000-3000 BP, indicating that the layers below are older than this. Based on the analysis of the lithic assemblages in these layers, Anderson (1991) attributes the cultural material to the mid-Holocene.

3.3.4. Late Holocene assemblages: final LSA and ceramic final LSA

The prevalence of finds increases yet again in the late Holocene, with a total of 21 sites known from the Zambian Woodlands, the Namib Desert and Nama Karoo Biomes of Namibia, and the Grassland, Thicket, Forest, and Fynbos Biomes of southernmost Africa. The increase in the number and diversity of finds warrants dividing by type namely projectiles (complete tools and trace), high-impact non-projectiles (complete tools and trace), low-impact tools (complete and trace), and finally, lumps of adhesive material. Figure 3.4 and corresponding Table 3.5 describes these finds in detail.

The projectiles identified with adhesive remains in the late Holocene are composed of both organics (wood and bone) as well as inorganic stone. Some pieces are completely intact, with such notable finds including stone-tipped arrows from Faraoskop (though they lack specific stratigraphic provenience [Manhire, 1993]) and Adam's Kranz Cave (Binneman, 1994). Backed quartz pieces mounted in adhesive (reflecting two components of a composite projectile) from Andriesgrond

(Mazel, 1977; Anderson, 1991; pers. obs., 2016) have also been recorded. This specimen shows structural similarities to the arrows from Faraoskop, as well as those housed in the Pitt Rivers Museum, Oxford (No. 1887.1.700-705). Trace on stone tools of similar function has also been identified at Melkhoutboom Cave (segments [H. Deacon, 1976]), Makwe (segments [Phillipson 1976]), and Sehonghong (a pressure-flaked point [Mitchell, 1996b]). Bone and wooden points with either hafting adhesive or adhesive poison have also been described. These pieces are notably absent from the rest of the archaeological record, but appear in layers associated with the last 2000 BP of the ceramic final LSA or the final LSA, and in some instances are associated with historic assemblages. Such examples include a wooden projectile at Highlands, Eastern Cape Province (H. Deacon, 1976), and bone points from Collingham south of the Thukela Basin, KwaZulu-Natal (Mazel, 1992).

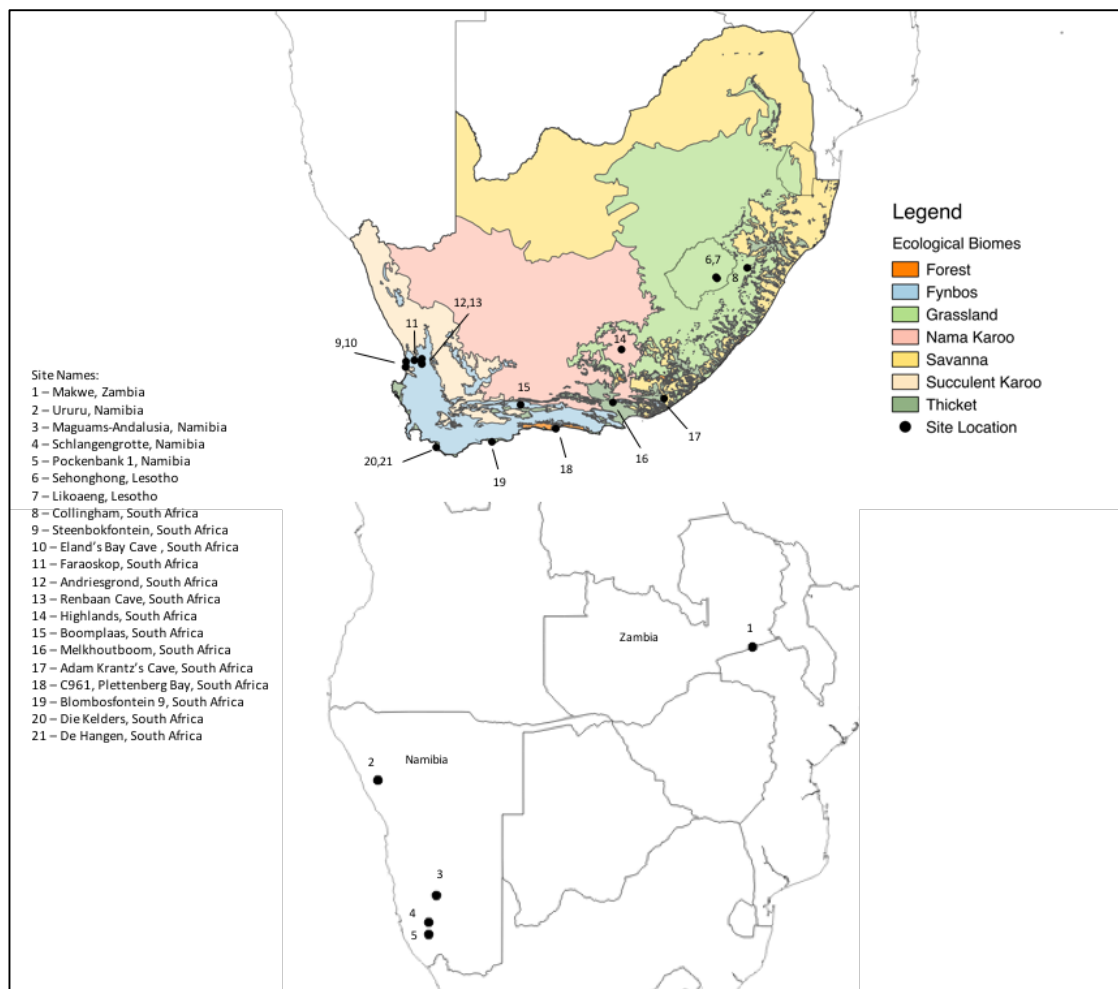


Figure 3.4. Late-Holocene sites with identified adhesive finds. The ecological Biomes of southern Africa are highlighted, as this region is the focus of the study. Vegetation Map of South Africa, Swaziland, and Lesotho 2012 available from the Available from the Biodiversity GIS website bgis.sanbi.org, downloaded Dec 5, 2016. African countries layer by Esri.

Table 3.5. Details of late-Holocene sites with adhesive finds, corresponding to site location points in Figure 3.4.

Site Names	Biome Type	Find Description	Associated Dates	References
1 – Makwe, Zambia	Woodland	Fifty-two tools with trace, especially on backed microliths	Multiple layers, dates ranging between 970 ± 70 BP (SR-206) and 1730 ± 80 BP (SR-207)	Phillipson, 1976
2 – Ururu, Namibia	Namib Desert	Lump of resin	Assemblage contained pottery	Wendt, 1972
3 – Maguams-Andalusia, Namibia	Nama Karoo	Trace on stone tools,	Likely associated with upper layers containing pottery	Wendt, 1972
4 – Schlangengrotte, Namibia	Nama Karoo	Lumps of mastic associated with an historic surface layer, containing glass beads, a European button and iron arrowheads	Assessment based on assemblage content, which included glass beads, a European button and iron arrowheads	Wendt, 1972
5 – Pockenbank 1, Namibia	Nama Karoo	Lumps of red resin and a scraper with adhesive trace	Likely associated with assemblage containing pottery, described separate from the overlying historic assemblage and the indeterminate assemblage below	Wendt, 1972
6 – Sehonghong, Lesotho	Grassland	Trace on stone tools, including a CCS pressure flaked point, adzes scrapers from DC layers	DC layer is younger than 1240 ± 50 BP (Pta-6084)	Mitchell, 1996b
7 – Likoaeng, Lesotho	Grassland	Trace evidence of hafting on stone tools	Radiocarbon dates from sites between 3110 ± 50 BP (GrA-13535) and 1285 ± 40 BP (GrA-23237)	Mitchell, 2009; M. Lombard pers comm.
8 – Collingham, South Africa	Grassland	Intact and broken points with adhesive trace lines, ochre stains, and adhesive or poison trace	Finds date between 1880 ± 45 BP (Pta-5101) to 1770 ± 50 BP (Pta-5274)	Mazel, 1992
9 – Steenbokfontein, South Africa	Fynbos	Adhesive mounted adze, and a lump of adhesive. Trace was also identified on stone tools.	Dates from associated layer, 2200 ± 50 BP (Pta-6136) and 2200 ± 60 BP (Pta-6424). Dates not given for the trace on tools	Jerardino, 2001; Jerardino pers comm.
10 – Eland's Bay Cave, South Africa	Fynbos	Adhesive handle, complete tool (adhesive with backed quartz microlith insert)	Two adhesives are either associated with a burial (8000 BP) or a later excavation that occurred at 3750BP**	Charrié-Duhaut <i>et al.</i> , 2016
11 – Faraoskop, South Africa	Fynbos	Trace on silcrete and quartz scrapers and adzes	Found in Layers 2 and 1, dates from Layer 2 4420 ± 60 BP (Pta-4809) to 2000 ± 70 BP (Pta-4955)	Manhire, 1993
12 – Andriesgrond, South Africa	Fynbos	Trace on CCS backed pieces, and on silcrete scrapers, adzes, and an awl	Material from layers 3, 2B, 2A, and 1. Dates for Layer 3 1640 ± 50 BP (Pta-2480), Layer 2B 430 ± 50 BP (Pta-2462), and Layer 2A 180 ± 50 BP (Pta-4026)	Anderson, 1991

13 – Renbaan Cave, South Africa	Fynbos	Trace on silcrete adzes and scrapers	Finds from Ash deposit, 1910 ± 60 BP (Pta-3783) and the Bedding units 1150 ± 50 (Pta-3768)	Kaplan, 1987; Parkington and Hall, 1987
14 – Highlands, South Africa	Nama Karoo	Wooden projectile with black resin or poison trace, and one adze with adhesive trace	Adze with trace related to the following dates: 3570 ± 50 BP (Pta-563), 4500 ± 60 BP (Pta-536)	H. Deacon, 1976
15 – Boomplaas, South Africa	Fynbos	Four lumps of adhesive, one mounted adzes and one mounted scraper	From the BLD member, 2000 BP	J. Deacon, 1984
16 – Melkhoutboom, South Africa	Thicket	Trace on chalcedony scrapers, segments, and silicified shale adzesborers from layers CAF, OMB, S	Finds date between 2870 ± 90 BP (Pta-706) and 250 ± 70 BP (Gak-1537)	H. Deacon, 1976
17 – Adam Krantz’s Cave, South Africa	Thicket	Complete stone tipped projectile	1760 ± 50 BP (Pta-6418)	Binneman, 1994
18 – C961, Plettenberg Bay, South Africa	Forest	Incomplete hafted tool, composed of a bird femur shaft and a lump of ochre stained adhesive	Object was described in associated with Cape Coastal pottery, <2000 BP	H. Deacon, 1966
19 – Blombosfontein 9, South Africa	Fynbos	Two lumps of adhesive	480 ± 45 BP on charcoal (Pta-6187)	Henshilwood, 2008
20 – Die Kelders, South Africa	Fynbos	Quartz adze mounted in adhesive	Found in Layer 12 dating to 1960 ± 85 BP	Schweitzer, 1979
21 – De Hangen, South Africa	Fynbos	Traces of adhesive on retouched and unretouched pieces	Association unspecified, dates span from 1850 ± 50 BP (Pta-127) to 90 ± 50 BP (Pta-167)	Parkington and Poggenpoel, 1971

Adhesives associated with high-impact non-projectiles, notably adzes, begin to appear with greater frequency after 4000 BP. Adzes mounted in adhesive were identified at Steenbokfontein, Boomplaas, and Die Kelders in the Western Cape Province, South Africa. Trace on adzes was identified at Faraoskop, Highlands, and Andriesgrond, and adhesive remnants on this tool type made up the majority of finds from the final LSA assemblages at Melkhoutboom (H. Deacon, 1976) and Andriesgrond (Anderson, 1991).

Low-impact tool types also continue to remain prevalent in this period, with adhesives on scrapers continuing in prominence. A mounted scraper from Boomplaas’ BLD member, dating to

~2000 BP (H. Deacon and J. Deacon, 1980; J. Deacon, 1984), remains the only complete composite example from this grouping with a secure function. However, H. Deacon and J. Deacon (1980) have suggested that the Albany Museum's specimen C961, an adhesive lump hafted to an incised bird femur with a fragment of a quartz insert imbedded in the adhesive (although missing in 2015) has a similar form, size and mounting orientation to the Boomplaas scraper. As such, they postulated that the fragment of stone is likely a scraper and served a similar function. Trace remains on scrapers have been identified at Faraoskop, Andriesgrond, Renbaan, and Melkhoutboom in South Africa, Sehonghong in Lesotho, and Pockenbank 1 in Namibia. Other tool types including awls and borers have also been recorded (see: Table 3.4).

Amorphous lumps of adhesive are also greater in number and distribution after 4000 BP. They make up the majority (three of four) of records in Namibia and were recovered from Schlengengrotte, Ururu and Pockenbank I. These specimens were described by Wendt (1972) as *mastic* or *resin*. A lump of red adhesive was identified at Steenbokfontein and its moulded form and tapered tip was described by Jerardino (2001). Further inland, a series of four amorphous lumps, one with evidence of having been wrapped around wood and another with impressions of the material to which it once adhered, were found at Boomplaas in the same BLD member as the mounted adze and scraper (J. Deacon, 1984). Finally, along the southernmost coastline of South Africa, two lumps of adhesive were found at Blombosfontein 9 (Henshilwood, 2008).

3.3.5. Visibility of Later Stone Age Finds

In summation of the sites and associated finds presented, two trends are apparent. Firstly, there is an increasing trend in the number of sites with records of hafting adhesives that mention trace on artefacts, lumps of adhesives (either as amorphous masses, or used components of tools with surviving impressions), or complete or relatively complete composite tools as we move from the Pleistocene and through the Holocene. Secondly, finds are geographically clustered, coming predominantly from the west coast of the Western Cape (within the Fynbos Biome), the

southernmost coast of South Africa below the Cape Folded Mountain Belt (encompassing Fynbos, Forest, and Thicket Biomes), and Lesotho (Grassland Biome). The lists and counts mentioned here are likely not exhaustive and I now put forward some reasons for these trends and discuss how this may reflect the datasets collated above.

Diagenesis has complex influences on the molecular components of organic archaeological materials and residual trace (Cattaneo *et al.*, 1993; Tuross *et al.*, 1996; Evershed *et al.*, 2001; Langejans, 2010). While the exact nature of those processes is not well-known in every depositional environment and for every class of organic material, it is certain that taphonomic processes influence preservation. This is the case for whole organic objects and for trace alike. The trace that has preserved on artefacts within archaeological assemblages is the result of a material contact and exchange process during the manufacture and use of that artefact (Hortolà [2002], conforming with Locard's [1920] principle). Some materials create closed systems, incorporating trace within the internal structure of the artefact and in doing so preserving it, as is the case with archaeological ceramics and their associated residues (Evershed, 2008; Roffet-Salque *et al.*, 2017). Other materials, however, including stone, bone and wooden artefacts are open systems, whereby the trace material remains on the surface of the tools are thus open to the diagenetic processes of the depositional environment. Geography and climate play a significant role in which molecular compounds remain; variability in factors including pH, temperature, microbial activity, aridity, and sediment composition also influences the nature of residue degradation (Denys, 2002; Langejans, 2010). A further influence on molecular residue preservation is the length of time since residue deposition that an artefact has been exposed to those taphonomic processes (Haslam 2006); the longer organic components of artefacts and residues are exposed to an environment unfavourable to preservation, the more complete the decay process is likely to be.

This assessment may hold true for hafting adhesive finds in southern Africa. Under ideal preservation circumstances one may put forward two hypothetical outcomes of find prevalence

through the LSA. The first suggests that the prevalence of archaeological hafting adhesives will correspond to lithic assemblage changes over time, with the microlithic assemblages of the Robberg (>19–12,000 years ago) and Wilton (8-4000 years ago), and some variants of the final LSA (4-1000 years ago) and ceramic final LSA (<2000 years ago) (Lombard *et al.*, 2012; Mitchell, 2013) producing higher numbers of adhesive finds compared to the non-microlithic Oakhurst, and temporally similar regional variants between 12 and 8000 years ago (Mitchell, 2002, Lombard *et al.*, 2012). Therefore, as the microlithic assemblages are generally described as hafted components of tools (Bousman 2005), adhesives use may thus have been more prevalent during this time. An example we can consider Sehonghong, Lesotho, where my screening of the lithic assemblages from the 1992 excavation showed that evidence of adhesive trace was prevalent in the layers corresponding to the Robberg, Wilton, and Late Holocene assemblages, while no such visible trace was identified in the Oakhurst layers (pers. obs. September 2015). Recovery and storage procedures were identical for all lithic assemblages, and as such these differences are not related to post-excavate curation. A second, though more tentative hypothesis follows from the characteristics of different LSA assemblages, taking into account the size of their flakes and retouched components. Orton's (2014) application of J. Deacon's (1984) scheme to defining the technocomplexes of the LSA highlights that these assemblages varied in size through time between microlithic forms (<30mm in length) and non-microlithic (in the range of 30-50mm). However, when considering the preference for the fixation of tool components in southern Africa with comparatively large masses of adhesive, both assemblage types can conceivably be hafted. Indeed, the stone component of AA1588 measures 54.98 mm x 53.86mm x 12.02mm, taking up much of the palm of the hand, and was hafted to a large mass of adhesive nearly twice its size in length. One may thus postulate that a constant prevalence of adhesive finds through time is not inconceivable. However, in fact, the frequency of adhesives at LSA sites increases from older to younger assemblages. It may thus be argued that this is more likely the result of find preservation (Figure 3.5).

An additional point may be raised with regard to adhesive find prevalence that ties into local environment and resource selection preferences for the manufacture of adhesives. The components selected to create adhesives are variable; organic and inorganic materials of a variety of chemical compositions. The molecular class of the constituents that making up the adhesives may thus have a range of differing chemical properties, including solubility and pH, that may adversely affect their preservation. For example, terpenoid-based plant resins are insoluble in water, while plant gums, composed of carbohydrates, are soluble in water (Langenheim, 2003). While gums can be identified in artists' materials and works of art (Lliveras-Tenorio *et al.*, 2012; Bonaduce *et al.*, 2016), they have yet to be identified in the archaeological record outside exceptionally arid environments (Dhakal and Armitage, 2013). As a local example, the prevalence of red ochre staining on Howiesons Poort segments at Sibudu was the only visual indicator preceding detailed analysis that hafting adhesives were present (Lombard, 2005, 2008), and while resins were identified, gums are still supposed to be the main source of the adhesive (Soriano *et al.*, 2015). It is plausible that resource selection and the composition of those resources would both affect the archaeological visibility of adhesive finds. Where resources are available whose composition can survive various taphonomic degradation processes, and those resources are selected for adhesive manufacture, it is more likely that they will be found in the archaeological record.

The geographical clustering of sites where adhesives and adhesive traces have been found likely represents the development of archaeological enquiry and output in southern Africa. In the majority of cases, the sites of interest were all components of larger LSA research programmes whether eastern Lesotho (Carter, 1977; Carter *et al.*, 1988; Mitchell 1993, 1995, 1996a, 1996b, 2009), Namibia (Wendt, 1972), the Western Cape coast (Parkington, 1976; Parkington and Poggenpoel, 1987; Jerardino and Yates, 1996; Jerardino, 1998,2010), the middle Olifant's River valley (Parkington and Poggenpoel, 1971; Parkington, 1977; Kaplan, 1987; Anderson, 1991), the Eastern Cape (H. Deacon, 1976), and along the southernmost coastline (Schweitzer, 1979;

Schweitzer and Wilson, 1982; J. Deacon, 1984; Inskeep and Avery, 1987; Henshilwood, 2008). It stands to reason that there is a greater likelihood of unique finds (hafting adhesives included) in such intensely researched localities.

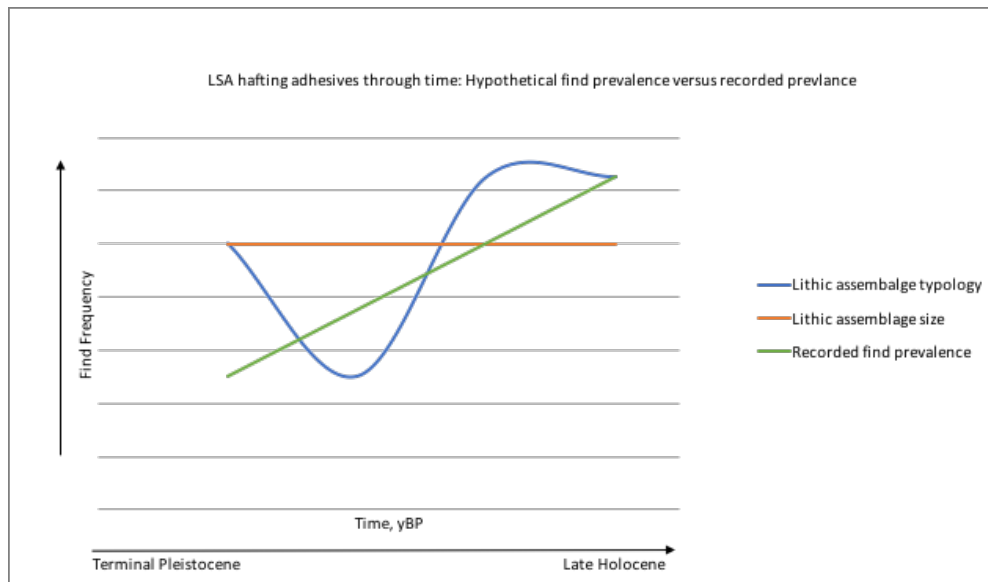


Figure 3.5. A representation comparing two hypothetical adhesive prevalence trends, based on lithic assemblage typology and assemblage size, to the frequency of reported LSA adhesive finds spanning the terminal Pleistocene to the late Holocene.

Another possibility is whether these finds survived excavation and subsequent curation. Rev. Paterson (Anon., 1949:121), while discussing various methods of sieving for an upcoming dig, noted that he had recovered implements with handles made of a clay-resin mixture and that in dry-sorting these would have been discarded as “one instinctively throws out any dollops of clay...” This brief missive highlights the relative ease with which these pieces may have been lost during the excavation process. From a curatorial perspective, there are records of whole masses of adhesive being removed from tools at Border Cave at some point in the past (Villa *et al.*, 2012). There are also noticeable alterations to museum specimens such as the new rhinoceros horn handle of A1543 at the Albany Museum (Deacon, 1966), and the dissection and subsequent repair of SAM AA5355 at the Iziko Museums (pers. obs., 2016), neither of which are noted in accession records. It is anticipated that specimens of rarity and interest may then be exhibited, either within museum

collections or in publication. It is however possible that finds of this kind remain inaccessible to wider audiences, and are limited to closed archives (i.e. as noted by A. Mazel, pers. comm., for adhesive finds within the Thukela Basin).

3.3.6. Later Stone Age Adhesive Recipes: Chemistry Studies

Chemistry-based studies to determine the source of organic and inorganic ingredients used in adhesives are not isolated to MSA case studies. Indeed, the first developments of archaeological chemistry to identify these materials began with LSA specimens. However, rather than serving to complement existing microscopy studies, as was the case for the MSA, analytical techniques are were frequently stand-alone.

Walker (1974) noted that the earliest chemical analyses were conducted in the 1950s, with a scraper with adhesive from Hewitt's (1931) excavations at Melkhoutboom, and samples from SAM AA1588 (the Knysna implement) being sent to several institutions, including the British Museum and the Colonial Products Laboratory, London (Corporation name from 1953-57, records held at The National Archives, Kew). However, the results of their analysis never made back to South Africa. Walker also describes the 1960s analysis of the hafted UCT specimens by Thin Layer Chromatography (TLC) at the UCT Department of Chemistry. A summary of these results suggested that some matched common resins (such as Mediterranean mastic, sandarac, and Southeast Asian dammar), confirming that they were likely resinous, but no South African species were used in the comparison.

Deacon (1966) reported on the Albany Museum specimens A1543 and C961, using a combination of X-ray photography and microscopy to begin the characterisation process of the adhesive components of these tools. He was able to comment on the composition of the A1543 and C961, discussing the predominantly resinous quality of the adhesives (though C961 also had vegetable fibres mixed within the adhesive [H. Deacon, 1966]), and noted both the missing haft component in A1543 as well as the broken 'quartzitic' insert in C961 based on the X-ray photographs.

The mottled surface of both specimens was also discussed, and thought to be the result of the application of an ochre to the surface of the tool (cf. Lombard, 2007).

Subsequently, Walker (1974) analysed the two pieces from Eland's Bay, SAM AA1588, and the hafted UCT specimens. Unlike the first attempt at TLC analysis, he collected an extensive collection of South African exudates to compare to the archaeological material and employed a multi-method approach that alongside TLC also included infrared spectroscopy and solubility tests. He concluded, however, that the analyses should be viewed as a trial with further required to make any headway in discerning with certainty the taxa utilised in the adhesive preparation process. Walker (1974) was nevertheless able to comment on additives, including plant fibres and inorganic material, that were present in the specimens analysed. Finally, in an appendix to the analysis of segments from the Zambian sites of Makwe and Kalembe, Phillipson (1976) described the infrared analyses of adhesive from four stone artefacts. The results, however, were deemed inconclusive, with Jean Langenheim (Phillipson, 1976: 215) reporting that "[they could] make no sense whatsoever out of the infrared spectra."

While from a positive standpoint, all these studies confirmed the use of resin during the LSA period as the main constituent of adhesives and were also able to identify additives that were present to change the functional or aesthetic properties of the adhesives (Deacon, 1966; Walker, 1974), they did not yield any specific results. It is therefore not surprising then that after several decades of such inconclusive and rather disappointing chemical analyses there was a hiatus in the application of such techniques to LSA hafting adhesives. Forty years, however, after the publication by Phillipson (1976), Charrié-Duhaut and colleagues (2016) released the results of their analysis of the Eland's Bay specimens, which included the handle and hafted insert described earlier in the chapter, as well as sealant on a fragment of ostrich eggshell. Their combined use of gas chromatography-coupled mass spectrometry and Fourier Transform Infrared spectroscopy successfully identified *Podocarpus* sp. resin as botanical components of the hafting adhesives and

sealant. This material was mixed with quartz sand to create a composite organic and inorganic adhesive, while the sealant showed evidence of fats also being present (Charrié-Duhaut *et al.*, 2016). The specific identification of the main and additive components in these objects from the Holocene assemblages at Eland's Bay Cave, goes beyond being the first chemical identification for the LSA since it provides the first glimpse of the procurement of a resource and its continued use from the MSA (Charrié-Duhaut *et al.*, 2013; Soriano *et al.*, 2015) into the ELSA (Villa *et al.*, 2012) and finally the Holocene LSA.

3.4. Concluding Remarks

In compiling instances of adhesive finds from the MSA through to recent times, it is evident that southern Africa has an extensive and variable record of adhesive use. The frequency of such finds increases with time through the LSA with the highest counts associated with the Holocene microlithic (Wilton) and late Holocene (final LSA and ceramic final LSA) technocomplexes. This trend is best explained by selective preservation rather than as an artefact of assemblage composition.

Find location is invariably associated with regions of southern Africa where significant archaeological surveys have been conducted since the 1960s. The present-day ecological breadth of such finds is impressive, emphasising the presence of adhesives in environments of varying floral, faunal, and mineral distributions. The majority of compositional information comes from disparate sources: a handful of archaeometric studies on chemical composition from MSA and LSA contexts and historic and ethnographic observations. What is most apparent upon evaluating these two is that there is a disconnect in the types of resources utilised in the deep-past of the archaeological record versus those of more recent times. Current and not-so-recent cases put forward by archaeologists highlight an over-reliance on ethnographic sources in understanding past hunter-gatherer behaviour and material culture (Wobst, 1978; Parkington, 1984; Mitchell 2002, 2017;

Hobart and Mitchell, 2004; Pargeter *et al.*, 2016a, 2016b). While southern Africa's rich ethnographic history and the analogies derived from it undoubtedly benefit archaeological enquiry in this region, it is becoming increasingly common that the boundaries of material culture and behaviour variability in the Kalahari and Karoo Biomes, and by extension the historic contexts of the 19th to 20th centuries, do not account for all the archaeological variability identified in less arid regions of southern Africa (Mitchell, 2017). The case of hafting adhesive composition further serves to accentuate this disconnect. The few chemical identifications of the constituents of adhesives from archaeological contexts and the means of their manufacture differ markedly from historic and ethnographic sources (Table 3.1) and instead highlight the breadth of resources that may be utilised for adhesive purposes. This is especially the case in the identification of pitch obtained from *Podocarpus* sp. conifers as a source of adhesive (Villa *et al.*, 2012; Charrié-Duhaut *et al.*, 2013, 2016; Soriano *et al.* 2015). The analogies of adhesive recipe preparation from the last two centuries may not serve the understanding of resource acquisition and production. Indeed, comparisons to case studies in experimental archaeology, particularly aceramic birch tar production, outside southern Africa may serve as a more apt comparison (Schenck and Groom, 2016; Kozowyk *et al.*, 2017a).

The adhesives of the LSA are by no means the first of the southern African archaeological record. However, unlike the periods that came before or after, the terms *breadth* and *variability*, in typology, ecology, and implied function, may best describe the LSA specimens highlighted in this chapter. While this review may not be complete, and possible limitations are highlighted in Section 3.3.5., it puts us in a better position to appreciate the potential compositional variety among adhesive recipes and how this may have been influenced by tool function, local environment, and the raw materials that make up the other components of composite technologies. I now go on to discuss the methods employed during this thesis in Chapter 4.

CHAPTER 4

MATERIALS & METHODS

Introduction

This chapter highlights the materials and methods associated utilised in this project. I first describe the strategies employed for the selection of specimens for analysis, followed by the microscopy. The analytical strategy employed in this thesis highlights the use of a multi-analytical approach to identify and characterise organic and inorganic materials. This practice is by no means uncommon or novel, and has been employed by research groups to identify amorphous materials or objects in both the archaeological science and conservation science disciplines (Marinach *et al.*, 2004; Regert *et al.*, 2005, 2008; Bradshaw, 2013; Rageot *et al.*, 2016)

To account for the varying types of archaeological adhesive finds represented within this study, the different ecological environments in which the find sites are situated, and the observed visual differences noted among the find types, a multi-method analytical approach encompassing well-established screening and chemical characterisation techniques was deemed to be essential. The primary aim of this strategy was to identify both organic and inorganic materials present in the adhesive samples (Figure 4.1).

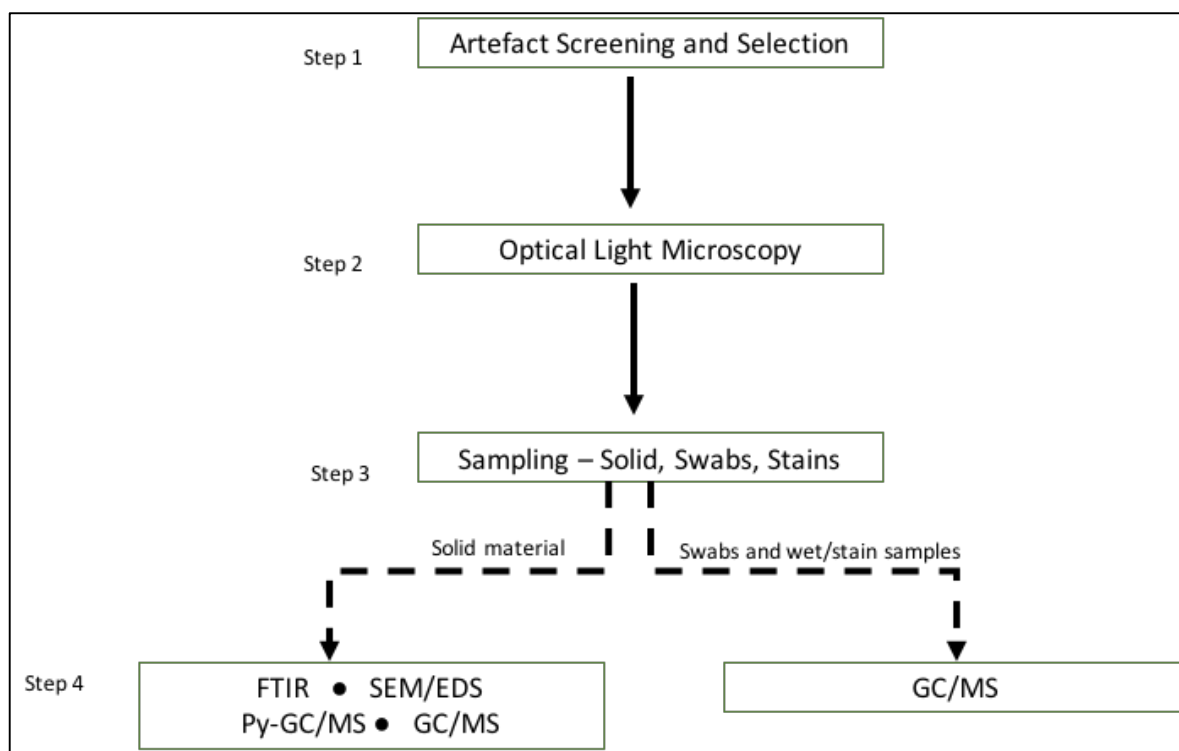


Figure 4.1. Flow chart highlighting the methodology strategy applied to characterize the organic and inorganic components of hafting adhesives.

4.1. Material selection strategy

The selection of materials for sampling varied depending on the location of the stored collections, the accessibility and state of these collections, the find type to be assessed, and whether past excavators had identified and separately stored ‘mastic’ finds from other materials. Easily accessible materials, particularly adhesive lumps and complete or incomplete hafted implements, were screened first, their dimensions measured with calipers, and any loosening fragments or completely detached material noted for ease of sampling. Selections of specimens containing macroscopically visible traces of residue on stone tools were made based on the following four criteria (adapted from Charrié-Duhaut *et al.*, 2013): that the residues were of a sufficient density that distribution patterns were clear to the naked eye; showed clear outlines that are delimited on the piece; covered the surface of the tool, opposite to the sharpened or utilised edge; and, as best as possible, residual trace was observed on both sides of the tool. Figure 4.2 provides examples of material that fits the listed criteria.

4.2. Microscopy

Optical light microscopy (OLM) was conducted on all material to qualitatively describe the nature of the adhesive, and in the case of trace on stone tools, to document its extent. This procedure followed those studies conducted by Lombard (2005; 2006; 2008) to plot the distributions of residues associated with hafting on stone tools. A low-powered stereomicroscope was used, with an objective magnification between 1X – 12X, depending on the instrument. Multiple microscopes were employed, based on the instruments available within a given institution, and whether microscopy was a necessary component to a permit application prior to export or sampling. Models included: Zeiss Discovery V8 stereo microscope (with a Nikon D5000 camera) and a Nikon SMZ-2T stereo microscope connected to a Canon Rebel XSi DSLR camera attached to an Amscope camera adaptor for a live feed, with the additional magnification of 2X for the camera mount lenses.

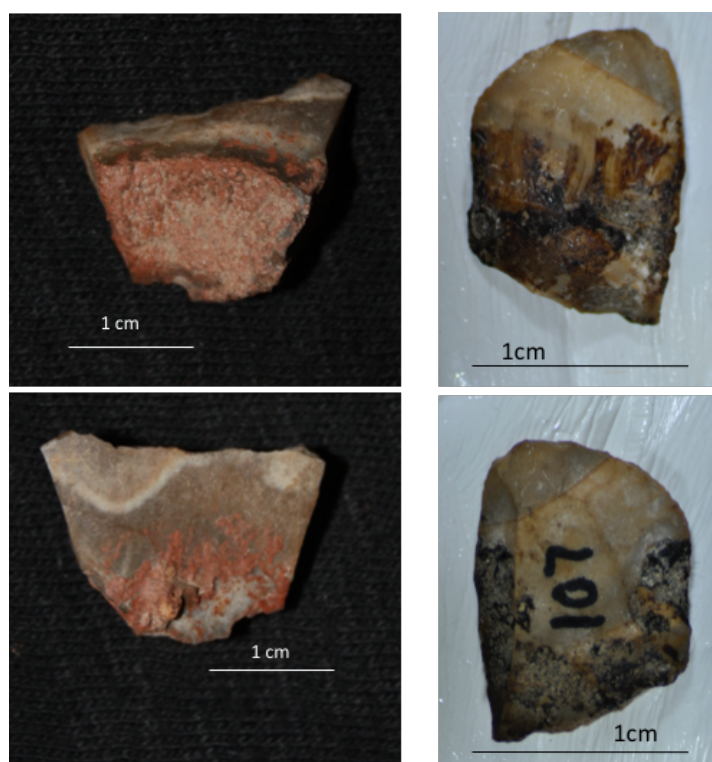


Figure 4.2. An example of artefacts selected for analyses based on residue criteria adapted from Charrié-Duhaut *et al.* (2013). Left. Adze, Renbaan Cave. Right. Scraper, MHB69/107. Photos taken by author.

4.3. Sampling methodologies

Two sampling protocols were employed, depending on the type of find and the relative amount of adhesive material available. Dry sampling was conducted on all hafted implements, lumps, and stone tools with sufficient trace that a fragment could be removed. The overall aim of the dry sampling strategy was to ensure that the specimens remain in their original condition, and as intact as possible. Depending on the permit requirements and the nature of the specimen, samples were obtained from the adhesive debris from the containers in which the specimens are held or from loose and fragmentary areas on the specimen. The samples were collected using a scalpel and forceps, with a total amount removed varying between 1-7mg. Wet removal was conducted on stone tools with adhesive trace or staining and insufficient quantities of material for dry sampling. This was accomplished in the field using a cleaned cotton swab dipped in a solution of 2:1 v/v dichloromethane: methanol, or in the laboratory by submerging a portion of the proximal end of a tool in the same solvent solution and sonicating 3 times (10mins) at 40°C.

4.4. Analytical Protocols and Instrumentation

4.4.1. FTIR Spectroscopy

Less than a milligram of dry material was placed on a diamond cell with a scalpel. Measurements were acquired on an Agilent Cary 640 spectrometer (Santa Clara, CA, USA) with a GladiATR Single Reflection diamond ATR accessory (PIKE technologies, Fitchburg, WI, USA). Analyses were performed in absorbance mode. Spectra were collected from 4000-400 cm⁻¹ with 64 acquisition scans, and a resolution of 4 cm⁻¹. Spectra were transformed from absorbance (A) to percent transmittance (%T) using the following equation:

$$\%T = 10^{-(A-2)}$$

4.4.2. SEM/EDS

A few micrograms of sample were placed on an iron planchet containing carbon tape. Samples were analysed using a Jeol JSM-6610LV Scanning Electron Microscopy (USA) with an Oxford Instrument EDS detector (UK). Imaging was conducted between 3-5kV, with a spot intensity of 53, in secondary electron detector mode (SED). Analyses were conducted at 20kV with a spot intensity of 53 using the backscatter electron detector (BSE). Spectra interpretation and image management were completed using Inca (Oxford Instruments, UK).

4.4.3. Chromatography

4.4.3.1. py-GC-MS

Sample preparation follows those details outlined by Ribechini *et al.* (2011) and Orsini *et al.* (2017). Solid material (~200µg) were placed into a cleaned metal holder with 5µL of hexamethyldisilane (HMDS) added as a derivatising agent and mounted into the pyrolyser injector for analysis. The 3030 multi-shot pyrolyser was coupled to a 6890N Agilent GC System coupled with an Agilent 5973 MSD single quadrupole mass spectrometer. The pyrolyser interface was kept at 250°C, the transfer line at 300°C. The GC system was equipped with an HP-5MS fused silica capillary column (5% diphenyl-95% dimethyl-polysiloxane, 30 m length x 0.25 mm ID x 0.25 µm supplied by Agilent Technologies, USA) with a de-activated silica pre-column (2m x 0.32mm I.D, Agilent Technologies, USA). Derivatised samples underwent pyrolysis at 550°C (20 seconds), and were injected in split mode (1:10). The chromatographic conditions were as follows: initial temperature 30°C (8 mins), 10°C/min up to 240°C and isothermal for 3min, 20°C/min up to 300°C and isothermal for 30min. The carrier gas (He, purity 99.9995%) was used in constant flow mode at 1.2mL/min). Underivatised samples instead underwent pyrolysis at 600°C and were injected in split

mode (1:10). The chromatographic conditions were as follows: initial temperature 40°C 2min isothermal, 10°C up to 140°C ; 6°C/min up to 280°C and isothermal for 3min, 10°C/min up to 300°C and isothermal for 30min. The carrier gas (He, purity 99.9995%) was used in constant flow mode at 1.2mL/min).

4.4.3.2. GC-MS

Sample preparation: dry samples

Samples were analysed using the protocol established by Colombini *et al.* (2003). This analytical procedure was adopted for its ability to characterise various natural products from archaeological and historical contexts, including resins, pitches, and lipid material found in waxes and oils (Andreotti *et al.*, 2006) outlines the sample preparation protocols employed.

Less than 2mg of sample was selected for analysis. Samples were submitted for saponification in a hydroalcoholic solution of potassium hydroxide (10% w/v KOH_{H2O} : 10% w/v KOH_{CH3OH} at a ratio of 3:2). The solution was incubated at 60°C for 3 hours. After saponification, the neutral organic components were extracted with n-hexane (400 µL, three times, combined into a single neutral fraction). Following the addition of 6M HCl to acidify the solution up to pH=2, the acidic organic components were then extracted from the solution using diethyl ether (400 µL, three times, combined into a single acid fraction).

Sample preparation: swab samples & reference pitch material

Material underwent a preliminary solvent extraction by sonication (3 x 10min) utilizing hexane, dichloromethane, and methanol in order of increasing polarity. These fractions were then combined for downstream analysis, with each aliquot dried under a stream of nitrogen in the same vial and weighed for a total extraction mass. These samples then underwent the saponification protocol highlighted above prior to undergoing derivatisation.

Sample preparation: wet samples

Material underwent a preliminary solvent extraction by sonication (3 x 10min) utilising hexane, dichloromethane, and methanol in order of increasing polarity. These fractions were then combined for downstream analysis, with each aliquot dried under a stream of nitrogen in the same vial prior to undergoing derivatisation.

Sample derivatisation

Aliquots (between 200 – 800µL depending on solution colour) were dried under a stream of nitrogen and underwent derivatisation. Added to the dried aliquots were 10 µL of internal standard (tridecanoic acid, 140µg/g, for samples analysed in Pisa and a combination of tridecanoic acid, 100µg/g, and hexadecane, 50µg/g for samples analysed in Oxford), 20µL of N,O-bis(trimethyl)silyltrifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS), and 150µL of isooctane or n-hexane as a solvent. The derivatisation reaction occurred at 60°C for 30min.

Instrumentation details and analytical conditions

Two GC/MS systems were used to acquire data:

The Pisa GC/MS instrumentation, analysing samples for extraction protocol optimization, utilized a Trace GC 2000 gas chromatograph system equipped with a PTV injection port and coupled to an ITQ 900 ion trap (Thermo Fisher, U.S.A.). Samples were injected in splitless mode at 280°C. GC separation was performed on a fused silica capillary column HP-5MS (J&W Scientific, Agilent Technologies, U.S.A (30 m length x 0.25 mm ID x 0.25 µm film thickness, 5% diphenyl / 95% dimethylpolysiloxane stationary phase). Chromatographic conditions were as follows: initial temperature 80°C, 2 min isothermal hold, 10°C/min up to 200°C, 4 min isothermal hold, 6°C/min up to 280°C, 40 min isothermal hold (adapted from Ribechini *et al.* 2009). The helium (purity 99.9995%) gas flow was set in constant flow mode at 1.2 mL/min. MS parameters were: electron

impact ionization (EI) of 70 eV; ion source temperature 230°C; interface temperature 280 °C; and, a scan range of 50-700 *m/z*. The injection volume was 2 µL.

The Oxford GC/MS system utilized an Agilent 7820A gas chromatograph equipped with a Restek Rxi-5ms column (30m length x 0.25mm ID x 0.25µm film thickness, 5% diphenyl/95% dimethylpolysiloxane stationary phase). Samples were injected in splitless mode at a temperature of 300°C. Chromatographic conditions were one of two protocols: 1) initial temperature 80°C, 2 min isothermal hold, 10 °C/min up to 200 °C, 4 min isothermal hold, 6 C/min up to 280°C, 40 min isothermal (adapted from Ribechini *et al.* 2009); or, initial temperature 50°C, 2 min isothermal hold, 50-300°C at 10°C/min with a 10 min isothermal hold at 300°C (Woodworth *et al.*, 2015). The helium (purity 99.9995%) gas flow was set in constant flow mode at 1.2 mL/min. The Agilent 5975 quadrupole mass spectrometer was set at the following parameters: operated in EI ionization mode at 70 eV; transfer line interface temperature of 280°C; and, a scan range of 50-650 *m/z*. The injection volume was 2 µL.

Peak assignment for all acquired data was based on comparisons to mass spectra libraries (NIST 11 main EI MS library and a prepared AMDIS library) and published data.

4.5. Materials

4.5.1. Chemicals

All solvents used were HPLC analysis or residue analysis grade. Water was obtained from a Milipore Milli-Q system (Merck, United Kingdom). N,O-bis(trimethyl)silyltrifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDS) was purchased from Sigma Aldrich (Milan, Italy and Loughborough, United Kingdom).

4.5.2. Standards

For those materials analysed in Pisa, the tridecanoic acid internal standards was purchased from Sigma Aldrich (Milan, Italy). In Oxford, the tridecanoic acid and hexadecane internal standards were purchased from Sigma Aldrich (Loughborough, United Kingdom).

4.5.3. Reference materials

Tables 4.1 and 4.2 highlight all the botanical, animal, and inorganic materials that make up the comparative reference collection.

Table 4.1. Reference botanical material from southern African plant species collected for analysis. Alongside details of each species collected are the analyses conducted on each specimen.

Name	Material Type	Source	Accession Number	Analyses Conducted	
				FTIR	GCMS
<i>Acacia karoo</i> (Hayne)	Exudate	Kew - Economic Botany Collections	58619	X	
			78706	X	
<i>Afrocarpus falcatus</i> (Thunb.)	Bark and wood tissue	Royal Botanic Gardens Edinburgh	20001613 A1	X	X
			20001613 A4	X	X
		University of Pisa, Italy	/		X
<i>Ammocharis coranica</i> (Ker Gawl.) Herb.	Bulb	Telos Rare Bulbs, Ferndale, California	/	X	X
<i>Asperagus densiflorus</i> (Kunnth)	Extract of bulb	Kirstenbosch Nursery, Cape Town	/	X	
<i>Boophone distcha</i> (L.f.) Herb.	Bulb	Telos Rare Bulbs, Ferndale, California	/	X	X
<i>Brunsvigia radulosa</i> Herb	Bulb	Telos Rare Bulbs, Ferndale, California	/	X	X
<i>Carissa macrocarpa</i> (Eckl.)	Extract of Branch clipping	Personal collection, Cape Town	/	X	
<i>Chasmanthe aethiopica</i>	Bulb extract	Personal collection, Cape Town	/	X	X
<i>Colophospermum mopane</i> (Kirk ex Benth.)	Exudate	Kew - Economic Botany Collections	59545	X	X
			59546	X	X
<i>Euphorbia ingens</i> (E. Mey. Ex Boiss)	Exudate	Personal collection, Cape Town	/	X	X
<i>Euphorbia tirucalli</i> (L.)	Exudate	Kew - Economic Botany Collections	44009	X	X
			43970		X

<i>Euryops</i> sp. (Cass.)	Exudate	Personal collection, Cape Town	/	X	X
<i>Ficus natalensis</i> (Hochst.)	Exudate	University of the Witwatersrand, Johannesburg	/		X
<i>Hartogia schinoides</i> (C. A. Sm)	Exudate	Newlands, Cape Town	/	X	X
<i>Hypoxis</i> sp. (L.)	Extract of bulb	Personal collection, Cape Town	/	X	X
<i>Juniperus procera</i> (Hochst. Ex Endl.)	Bark and woody tissue	Edinburgh Zoo	20080832G		X
			20080832H		X
			20080832I		X
<i>Ozoroa paniculosa</i> (Sond.)	Exudate from burned wood	Magaliesberg, Gauteng	/	X	X
<i>Pelargonium triste</i> (L.)	Exudate	Rondebosch, Cape Town	/		
<i>Podocarpus elongatus</i> (Aiton L'Herit. Ex Pers.)	Bark and wood tissue	Royal Botanic Gardens Edinburgh	20061205 A1	X	X
<i>Podocarpus henkelii</i> (Stapf ex Dallim. & A.B.Jacks.)	Bark and woody tissue	Royal Botanic Gardens Edinburgh	19710164 A6	X	X
			19710164 A7	X	X
<i>Podocarpus latifolius</i> (Thunb.)	Extract of bark	Personal collection, Cape Town	/		X
<i>Pterocelastrus echinatus</i> (N.E. Br.)	Exudate	Kew - Economic Botany Collections	75563	X	X
<i>Sarcocaulon partersonii</i> (DC.)	Exudate	Kew - Economic Botany Collections	64225	X	X
<i>Scilla natalensis</i> (Planch.)	Extract of bulb	Personal collection, Cape Town	/		
<i>Searsia lancea</i> (L.f.)	Extract of Branch clipping	Personal collection, Cape Town	/		X
<i>Terminalia sericea</i> (Burch. Ex DC.)	Exudate	Kew - Economic Botany Collections	78717	X	
<i>Widdringtonia cedarbergensis</i> (Marsh.)	Bark + Woody tissue + Exudate	Royal Botanic Gardens Edinburgh	19642703 A1	X	X
<i>Widdringtonia cupressoides</i> ((L.) Endl.)	Exudate	Kew - Economic Botany Collections	28866	X	X

Table 4.2. Reference animal and mineral material utilised for analysis.

NameSource		Analyses Conducted	
		FTIR	GC/MS
Animal –sourced material			
Beeswax	LiveMoor, Dartmoor, United Kingdom	X	X
Bovine liver – internal standard	RLAHA, Oxford, United Kingdom		X
Animal lard	Tesco, United Kingdom	X	X
Mineral Materials			
Hydroxyapatite	RLAHA, Oxford, United Kingdom	X	
Orange ochre	T Hodgskiss, South Africa	X	X
Red ochre	T Hodgskiss, South Africa	X	X
Yellow ochre	T Hodgskiss, South Africa	X	X
Other			
Humic acid	RLAHA, Oxford, United Kingdom	X	

4.5.4. Pitch preparation

Experimental pitch was made from botanical specimens of *Afrocarpus falcatus*, *P. elongatus*, *P. henkelii*, *J. procera*, and *W. cedarbergensis* in a controlled laboratory environment. Up to a gram of bark and woody tissue was added to a glass tube. This was purged with nitrogen gas, sealed, and inserted into the narrow opening of a muffle furnace and heated at 500°C for 30min (Figure 4.3).

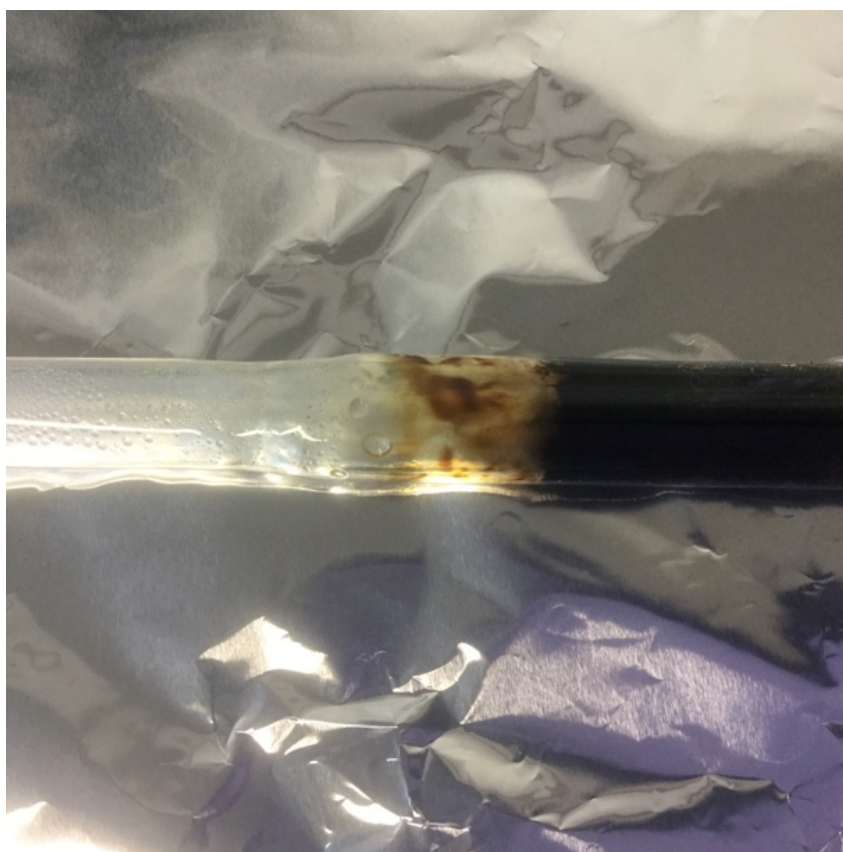


Figure 4.3. Production of experimental pitch from *P. elongatus*. Photo taken by author.

4.5.5. Preparation of bulb exudates

Amموcharis coranica, *Boophone distcha*, and *Brunsvigia radulosa* were acquired from Telos Rare Bulbs (Ferndale, California) for exudate preparation and analysis. Based on observations by Wadley *et al.* (2015) of the heat processing of *A. coranica* scales, the whole bulbs were processed by indirect heating by wrapping in aluminium foil, and placing samples adjacent to a propane gas burner, turning every three minutes until the bulbs were heated through and became plump and translucent. Bulbs were then crushed until an exudate was produce and the resulting material was left to dry on foil (Figure 4.4).



Figure 4.4. Heat processing of *A. coranica* bulbs. Left: young bulb specimens. Centre: foil packets heated by propane. Right: exudate produced. Photos taken by author.

CHAPTER 5

ARCHAEOLOGICAL MATERIALS & SITE OR ACCESSION DETAILS

Introduction: mastic find types analysed in this project

Chapter 3 provided a chronological and typological review of archaeological adhesive, or mastic finds, throughout the southern African LSA, highlighting the breadth of find types and associated composite technologies. These finds were grouped by associated archaeological context (technocomplex) and by ecological biome. To objectively address the proposed research hypotheses offered in the introductory Chapter 1, however, the adhesive specimens, and by extension their composition, are grouped together by object types rather than environmental landscape, cultural assemblage, or time period. They are thus divided into two main categories: stone tools bearing traces of adhesive and lumps of adhesive. When available, descriptions of excavations, local environment and calibrated ^{14}C determinations for the associated stratigraphic units are provided. The first section of this chapter highlights the archaeological context of the samples of trace adhesives from stone tools recovered from four archaeological sites - Melkhoutboom, Renbaan, Rose Cottage Cave, and Sehonghong (Figure 5.1). Its second section describes the archaeological contexts of from six amorphous adhesive masses. These specimens may either possess or lack characterising features or impressions, or be visible components of complete or nearly complete composite tools. Included here are the archaeological details on the material from Boomplaas (Figure 5.1), as well as the known object histories of three hafted implements (Figure 5.1) housed in museum collections. Details of all the selected material are found in Appendix I.

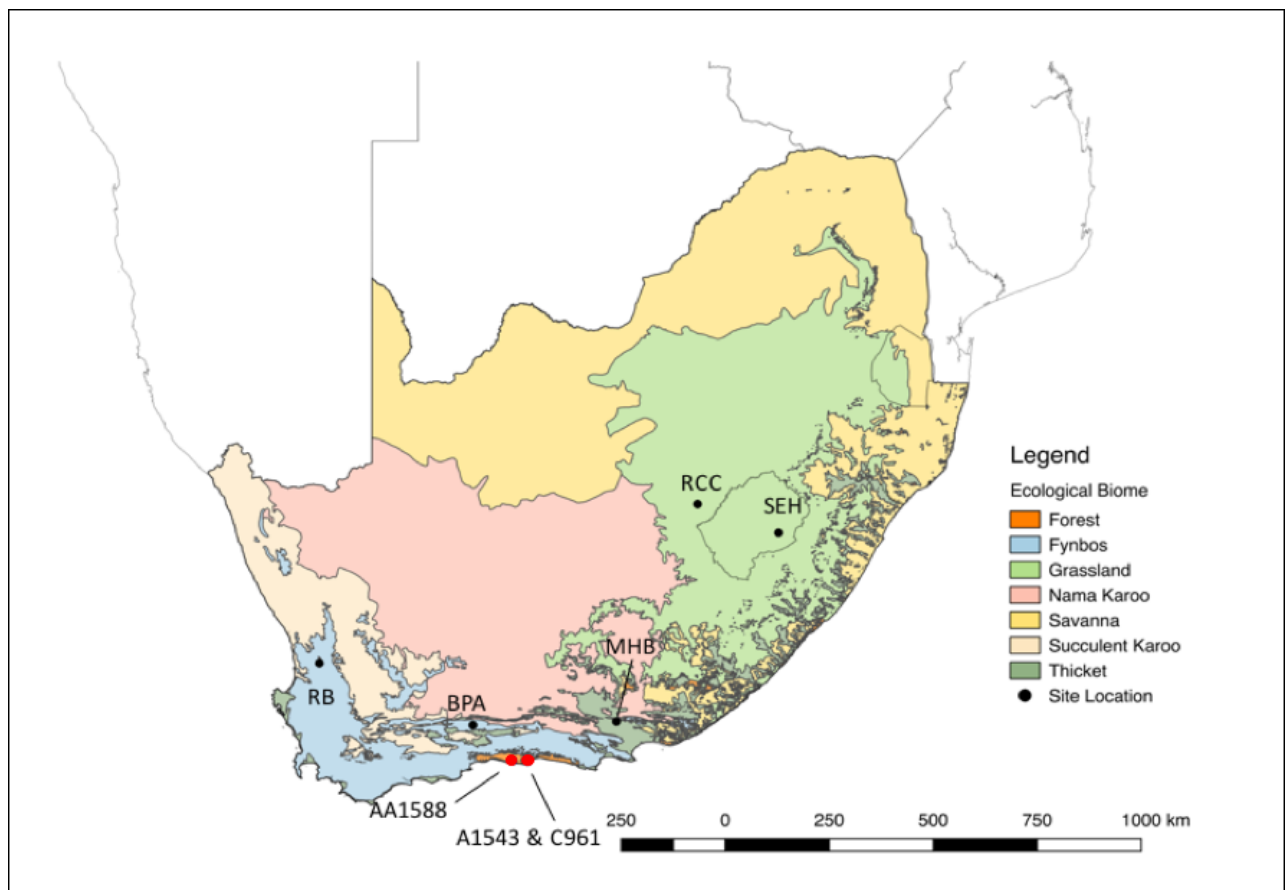


Figure 5.1. Ecological biome map of southern Africa, highlighting the locations discussed in this chapter. Sites in black include: Renbaan Cave (RB), Boomplass (BPA), Melkhoutboom Cave (MHB), Rose Cottage Cave (RCC) and Sehonghong (SEH). The geographic locations for the nearest towns associated with unprovenienced museum objects are highlighted in red. GIS layer of 2012 Vegetation Map of South Africa, Lesotho and Swaziland courtesy of South African National Biodiversity Institute, and the GIS layer of African countries by Esri.

5.1. Stone tools with trace: the archaeological sites and materials

5.1.1. Melkhoutboom, Eastern Cape Province, South Africa

This rockshelter is located in a sheltered forest kloof of the quartzitic Witteberg Series of the Zuurberg Mountain Range (33° 19'S; 25° 17'E) (Figure 5.2). The surrounding region may be described as an environmental mosaic, including *Podocarpus* sp.- dominated forests within the kloof, the bushveld of the adjacent Beans River Valley and the kloof boundary, sclerophyllous vegetation along the mountain ridge slopes, and the grassveld at the ridge peaks (H. Deacon, 1976). Preliminary excavations of the site began in 1930 by Hewitt and continued into 1931 (Hewitt, 1931; H. Deacon, 1969). Hilary Deacon re-excavated the site in 1967 and 1969, extending the cuttings in approximately the same area of Hewitt's original work (H. Deacon, 1969). The well-stratified sequence he found yielded cultural material ranging from the Robberg until the final LSA, with collections of well-preserved organic materials among the notable finds from the Holocene layers of the Wilton and final LSA (H. Deacon, 1976; Lombard *et al.*, 2012).



Figure 5.2. Melkhoutboom, June 2016. Left, photographed facing the mouth of the shelter. Right, photographing the shelter interior. Photograph taken by author.

The first adhesive finds were described in Hewitt's 1931 excavation report, with records of "patches of resinous material" on several scrapers (Hewitt, 1931: 544). H. Deacon also remarked on the presence of mastic on scrapers, adzes and segments from the site (H. Deacon, 1969; 1976), as well as mastic trace on a wooden artefact (H. Deacon, 1976: Fig. 25) and a lump of mastic on a

stick (Deacon, 1976: Fig 42). In total, 185 tools with adhesive trace have been identified from the material recovered from these excavations. This relatively large sample size, and range of adhesive trace on the tools discussed within the context of H. Deacon's (1969, 1976) lithic analyses made this collection a comparative benchmark when others discussed mastic finds within the context of the southern African LSA (e.g. Wendt, 1972; Phillipson, 1976; Binneman, 1983; Inskeep and Avery, 1987).

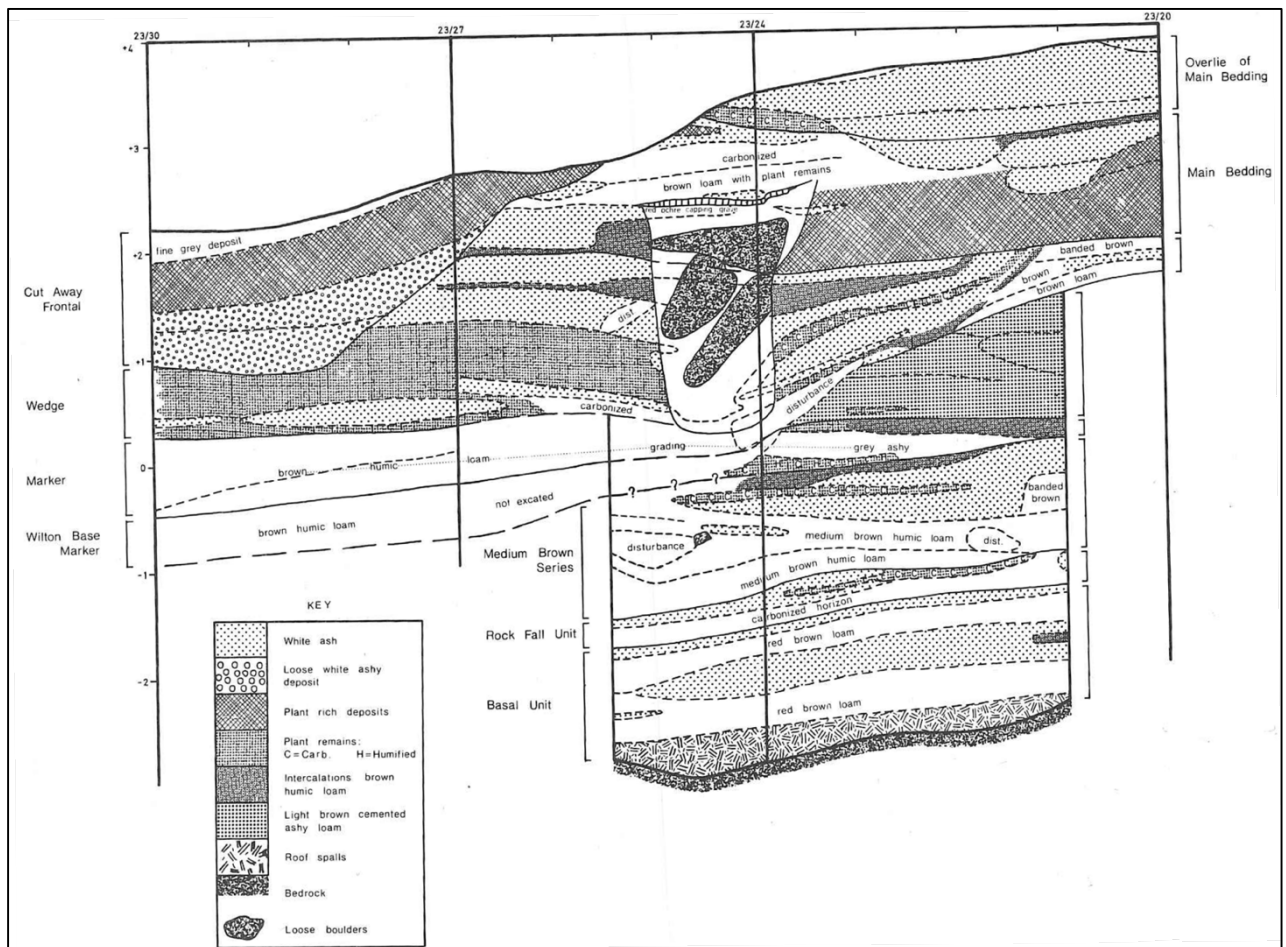


Figure 5.3. Melkhoutboom: Section along the grid line 23/20-30 from H. Deacon's 1969 excavation. Digitised and edited from H. Deacon (1976, Figure 9).

5.1.1.1. The associated archaeological context of selected finds

All specimens selected for adhesive analysis were recovered during H. Deacon's (1976) 1969 excavations. Radiocarbon determinations associated directly with a related stratigraphic layer (Figure 5.3) from which a find was recovered or from dated overlaying or underlaying layers were calibrated and are described in Table 4.1. No specimens from the Oakhurst or Robberg layers were available for analysis.

Specimens were acquired from the following layers:

- Marker (M) Unit, younger than 8311-7969 calBP (UW-234, based on a date from the Wilton Base Marker Unit below) and older than 7937-7686 calBP (Pta-668) from the W Unit above
- Wedge (W) Unit, with a date of 7937-7686 calBP at the base (Pta-668)
- Main Bedding (MB), 6945-6496 calBP at the base (Pta-680)
- Cut Away Frontal Unit (upper, and unspecified), the lowermost point of the unit is younger than 6945-6496 calBP of MB and the base of the upper unit (CAFu) dating to between 3235-2780 calBP (Pta-706)
- Overlie of the Main Bedding Unit (OMB), younger than 3235-2780 calBP (CAFu, Pta-706)
- Surface Unit (S), a pottery containing layer dating between 490 calBP (Gak-1537) to present

The sampled materials are housed in the collection of the Albany Museum, Grahamstown. The sampling permit was granted by the Eastern Cape Provincial Heritage Resources Authority under reference number 2/2/APM-PERMIT/15/11/001, while the export of the material was permitted by the South African Heritage Resources Agency under permit number 2166.

Table 5.1. ¹⁴C determinations from Melkhoutboom Cave in years BP, shown in sequence with stratigraphic context and cultural association. The uncalibrated dates were obtained from Deacon (1976). Associated dates were calibrated to two standards of deviation, with calibrations calculated with OxCal 4.2 (Ramsey, 2009) using SHCal13 calibration curve (Hogg *et al.*, 2013).

Lab No.	Unit	Cultural Association	Date (uncalibrated)	±	Date (cal BP)	
					from	to
Gak-1537	S	Ceramic Final LSA	250	70	490	...
Pta-706	CAF upper	Final LSA	2870	90	3235	2780
Pta-680	MB	Wilton	5900	90	6945	6496
Pta-668	W	Wilton	6980	65	7937	7686
UW-234	WBM	Wilton	7300	80	8311	7969

5.1.2. Renbaan Cave, Western Cape Province, South Africa

Renbaan Cave was excavated in 1979 as a salvage operation by Cedric Poggenpoel after notice was obtained of uncontrolled excavation of the site (Kaplan, 1984). It is situated approximately four kilometres from Clanwilliam in the Olifants River Valley in the Cedarberg region of the Western Cape Province (32° 14'S; 18° 52'E) (Kaplan, 1987). The valley is bounded by the Olifants River Mountains to the west and the Cedarberg range to the east. This region has a range of floral types, being a transition zone between the Fynbos and Karoo Biomes, although the Clanwilliam District itself is rich in Karoo species (Milton, 1978). Three main veld types have been identified in the region, namely Succulent Karoo, Broken Karoo, and Fynbos (Acocks, 1975).

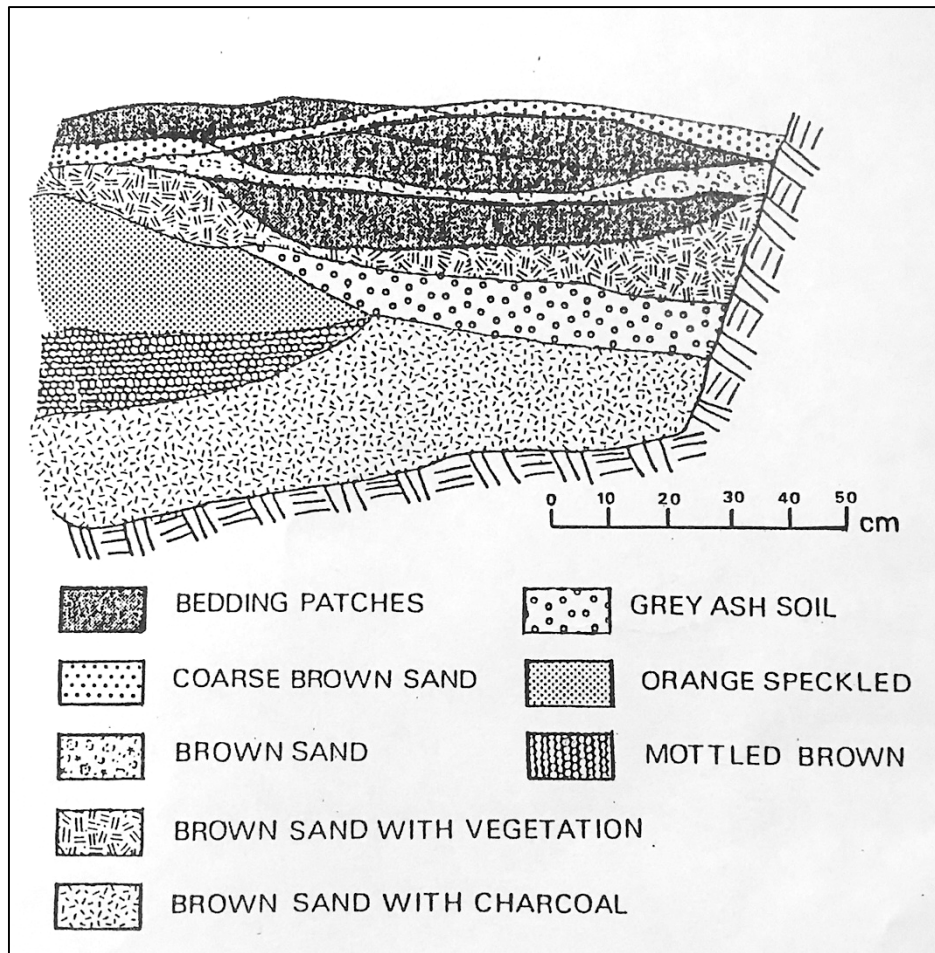


Figure 5.4. Renbaan: An illustration of the stratigraphy of the site from Kaplan (1987). Samples were recovered from the surface cleanings, the Bedding Patches, the Brown Sand with Vegetation, and the Grey Ash Soil. Digitised and edited from Kaplan (1987)

5.1.2.1. The associated archaeological context of selected finds

A total of twenty-nine tools were identified by Kaplan (1987) as bearing trace of hafting adhesives (Figure 5.4). The mastic-containing assemblages fall into two major phases: those before 2000 BP and those after. Those within the last two thousand years fit within a broader regional narrative of sites with a shift to high frequencies of adzes, edible plant material, and pottery in their assemblages which has been described as representing a response by hunter-gatherers to social and economic stress thought to be associated with arriving pastoralist populations (Parkington *et al.*, 1986.; Kaplan, 1987; Sadr, 1998; Sadr, 2015).

Selected material was recovered from the following stratigraphic units (Figure 5.4): Surface cleanings; Bedding (Pits 1,2,4, and 5); Brown Sand with Vegetation; Grey Ash Soil (GAS) (Kaplan, 1987). Only two dates are available for all the selected material (Table 5.2). The bedding units and the overlaying surface cleanings are associated with a date from 1172 to 925 calBP (Pta-3768) and younger. The Brown Sand with Vegetation unit underlays the Bedding units. Below this lies the GAS unit, which is associated with a date between 1992-1617 calBP (Pta-3783).

Table 5.2. ¹⁴C determinations from Renbaan Cave, including calibrated dates using OxCal 4.2 (Ramsey, 2009) ShCal13 (Hogg *et al.*, 2013). Determinations are at two standards of deviation. Uncalibrated dates obtained from Kaplan (1987) and Parkinson and Hall (1987).

Lab No.	Unit	Cultural Association	Date (uncalibrated)	±	Date (cal BP)	
					from	to
Pta-3768	Bedding Units	Ceramic final LSA	1150	50	1172	925
Pta-3783	Ash Deposit	Ceramic final LSA	1910	60	1992	1617

The sampled material is housed in the pre-colonial archaeology collections of the Iziko Museums, Cape Town, South Africa. The sampling permit was granted by Heritage Western Cape under reference number 16052308AS0523E, while the export of the material was allowed by the South African Heritage Resources Agency under permit number 2462.

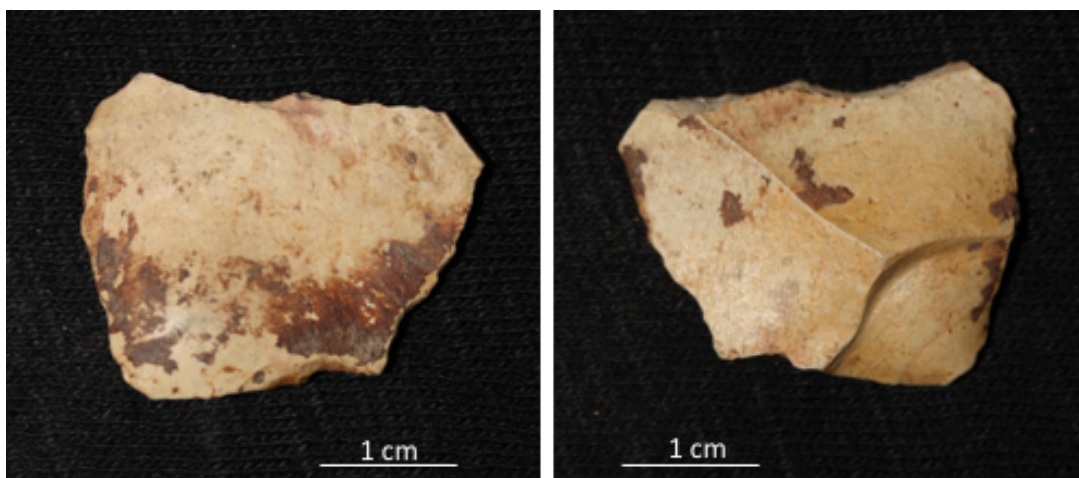


Figure 5.5. Renbaan: RB01, a silcrete adze with trace of hafting adhesive, from the surface cleanings. Photograph taken by the author.

5.1.3. Rose Cottage Cave, Free State, South Africa

The site of Rose Cottage Cave is located east of Ladybrand (29° 13'S; 27° 18'E; Williamson, 1996) and near the national boundary between South Africa and Lesotho. The first excavations were those of B.D. Malan in 1943 (Wadley, 1991). Following this, Rose Cottage was revisited firstly by Peter Beaumont in 1962 (Wadley, 1991) and then again by Lyn Wadley as one of ten sites excavated over a decade-long period between 1987 and 1997 in the eastern Free State, exploring the past material culture and the corresponding demographics of the region (Wadley, 2000). The cultural assemblages at this site spans the breadth of the LSA, as well as several MSA technocomplexes before this, as far back as the pre-Still Bay (Lombard *et al.*, 2012).

The stone tool assemblages and rock art pigments from Rose Cottage Cave underwent a significant amount of analysis by microscopy and several additional methods, notably by Bonnie Williamson (1996, 1997, 2000) and Johan Binneman (1997).

5.1.3.1. The associated archaeological context of selected finds

The material selected for analysis was recovered from three technocomplexes - the Oakhurst, Wilton, and the Final LSA (Table 5.3). The Oakhurst material was sourced from layers with dates spanning 9496-9127 calBP in the JaG unit to 9289-8775 calBP in Layer Ja. The underlying undated CM unit was described as likely dating between 9289-8775 calBP and 9623-9479 calBP based on the stratigraphic relationship described by Wadley (2000). Material from the only Wilton layer, Pt (Wadley, 2000b), spans 8548-8200 calBP at the base of the unit to 6945-6565 calBP at the top. Finally, the Final LSA material was sourced from the A2 (2344-2056 calBP) and A (669-547 calBP) units.

Table 5.3. ¹⁴C determinations from Rose Cottage Cave, including calibrated dates using OxCal 4.2 (Ramsey, 2009) and ShCal13 (Hogg *et al.* 2013), associated with the analysed material. Determinations are at two standards of deviation. Uncalibrated dates obtained from Wadley (2000, 2000b).

Lab No.	Unit	Cultural Association	Date (uncalibrated)	±	Date (cal BP)	
					from	to
Pta-5622	A	Final LSA (post-Classic Wilton)	680	50	669	547
Pta-7117	A2	Final LSA (post-Classic Wilton)	2240	60	2344	2056
Pta-5934	Pt (top)	Wilton	5970	70	6946	6565
Pta- 6783	Pt (base)	Wilton	7630	80	8548	8200
Pta-7122	Ja (upper)	Oakhurst	8160	70	9289	8775
Pta-5600	JaG (grey lens)	Oakhurst	8380	70	9496	9127
Pta-5560	H	Oakhurst	8614	38	9623	9479

5.1.4. Sehonghong, Thaba-Tseka District, Lesotho

Sehonghong is located in the Maloti Mountains of eastern Lesotho at approximately 1870m a.s.l., on the southern banks of the Sehonghong River (29° 46'S; 28° 47'E; Mitchell, 1995; Pargeter *et al.*, 2017). The MSA and LSA assemblages were excavated by Pat Carter in 1971 (Carter *et al.*, 1988), while the LSA layers were revisited by Peter Mitchell in the early 1990s. Brian Stewart and Genevieve Dewar are currently re-excavating and extending the MSA layers. The site has a long sequence extending from the late and terminal Pleistocene until the late Holocene, with historical sources recording the shelter's use into the beginning of the 20th century (Mitchell, 2010). The lithic assemblages have long provided a significant contribution to our understanding of hunter-gatherer populations in mountainous climatic refugia (Pargeter *et al.* 2017; Stewart and Mitchell, 2018). The archaeological and palaeobotanical assemblages highlight the ecological richness of the region (Mitchell, 1996c; Plug and Mitchell, 2008).

The site is located within the Grassland biome, with the climatic and local environment heavily determined by the high altitude, stable precipitation rates, and temperature fluctuations. Loftus *et al.* (2015) describes the local environment as a *Themeda-Cymbopogon-Eragostis* grassland, with trees and shrubs populating low altitude areas. It is unlikely that huge swaths of forested areas

covered Lesotho in the past, however, three main indigenous forests types have been documented and include *Leucosidea sericea* Forests, Mixed Forest and Thicket, and open Shrubland with Forest or isolated trees (Leslie, 1991).

5.1.4.1. The associated archaeological context of selected finds

Sehonghong is notable in that it is one of a few sites with both longstanding evidence of hafting adhesives in multiple LSA lithic assemblages, and a relatively high prevalence count. The assemblages of interest to this study were excavated by P. Mitchell in 1992 (Mitchell, 1995, 1996a, 1996b). Recent studies by Pargeter *et al.* (2017) and Loftus *et al.* (2015) have revised and expanded upon the existing chronology for the site's late Pleistocene and terminal Pleistocene sequence, re-calibrating existing dates of occupations and abandonment events. In doing so, they also included date re-calibrations using the SHCal13 calibration curve (Hogg *et al.*, 2013) to recalibrate the Late Holocene stratigraphic sequence (Table 5.4). The lithic assemblages are currently housed in the Department of Archaeology of the University of Cape Town, South Africa; selected material was transported to the Research Laboratory for Archaeology and the History of Art, Oxford, UK. The permit for the export of the associated material was issued by the Lesotho Protection and Preservation Commission, held by Prof. Mitchell, and stamped 28 June 1995.

The material selected for downstream analysis is from three distinct chronological and cultural episodes. The first set spans the Robberg, and involves bladelets originating from the RBL, RF and BARF layers. The use-wear based study on selected bladelets from these assemblages, published by Binneman and Mitchell (1997) and highlighted in Chapter 3, thus provided the temporal starting point for sample screening. The dates of these stratigraphic units span roughly three thousand years; 15,725 – 15,275 calBP (OxA-32922) in RBL to 13,395 – 12,559 calBP (Pta-6065) in BARF.

Table 5.4. ^{14}C determinations of units containing material associated with this study. The samples were obtained from the 1992 Sehonghong excavations by Mitchell, and are shown in sequence with stratigraphic context and cultural association. The uncalibrated dates were obtained from Mitchell and Vogel (1994) while the calibrated ages have been published previously by Loftus *et al.* (2015) and Pargeter *et al.* (2017).

Lab No.	Unit	Cultural Association	Date (uncalibrated)	$\pm$	Date (cal BP)	
					from	to
Pta-6084	GAP	Ceramic final LSA	1240	50	1265	980
Pta-6063	GAP	Ceramic final LSA	1710	20	1357	1180
Pta-6154	GWA	Wilton	5950	70	6931	6528
Pta-6278	ALP	Later Oakhurst	7290	80	8297	7879
Pta-6280	ALP	Later Oakhurst	7090	80	8007	7697
Pta-6072	ALP	Later Oakhurst	7210	80	8173	7839
Pta-6083	ALP	Later Oakhurst	7010	70	7942	7671
Pta-6368	SA	Oakhurst	9280	45	10 550	10 255
Pta-6057	SA	Oakhurst	9740	140	11595	10 588
Pta-6065	BARF	Robberg	11,090	230	13 395	12 559
Pta-6282	RF	Robberg	12,180	110	14 467	13 731
OxA-32926	RF	Robberg	12,010	50	14 020	13 745
OxA-32925	RF	Robberg	12,355	50	14 710	14 115
OxA-32924	RF	Robberg	12,420	50	14 880	14 185
Pta-6062	RBL	Robberg	12,410	45	14 735	14 125
Pta-6058	RBL/ CLBRF	Robberg	12,470	100	15 040	14 137
OxA-32923	RBL	Robberg	12,870	55	15 600	15 165
OxA-32922	RBL	Robberg	12,960	55	15 725	15 275

Lithics from the stratigraphic units containing Oakhurst and Later Oakhurst assemblages (SA and ALP layers, respectively) were then screened, but none were deemed suitable for further analysis. However, several specimens were selected from the GWA unit, which represents a Wilton assemblage (Mitchell, 1996) and dates to 6931-6528 calBP (Pta-6154).

A final set of specimens is associated with the three youngest units, GAP, DC, and SS (Mitchell, 1996), all of which are associated with the Ceramic Final LSA. Material was selected from all three units. The lowermost of these units, GAP, with a date range of 1357-1180 calBP (Pta-6063) from the bottom of the layer and 1265-980 calBP (Pta-6084) for the top. Above this, the DC unit, is younger than 980 calBP (970 AD). Oral histories from the region imply that after the death of the

San leader Soai ca. 1871, Sehonghong and other rockshelters like it may have been “occupied by residual hunter-gatherers at the very end of the 1800s/ start of the 1900s” (Mitchell, 2010: 164), although certainly not after the early years of the 1900s (Mitchell, 2010). The SS unit, the topmost layer, contains a combination modern material and LSA artefacts that may be associated with the DC layer below (Mitchell, 1996b), likely deposited since the 18th century. Only one specimen was analysed from this layer.

5.2. Amorphous adhesives from ‘mastic lumps’ and hafted implements

5.2.1. Boomplaas, Western Cape Province, South Africa

Boomplaas (33° 23’S; 22° 11’E) is located approximately 80 km from the southernmost coastline of South Africa, on the southern side of the Swartberg Mountains (the most inland range of the Cape Fold Mountain Belt), approximately 60m above the Cango Valley in a cavity in a large limestone outcrop (J. Deacon, 1984). The site straddles the boundary between the Fynbos and Karoo Biomes, and is uniquely situated in an area rich in fresh water resources from the Grobbellaars River and increased rainfall (~400mm annually), compared to the aridity of the Little Karoo to the south and the Great Karoo to the north. As such, the local environment is a composite

of fynbos and renosterveld vegetation, and home to a range of grazing mammals (Pargeter *et al.*, 2018).

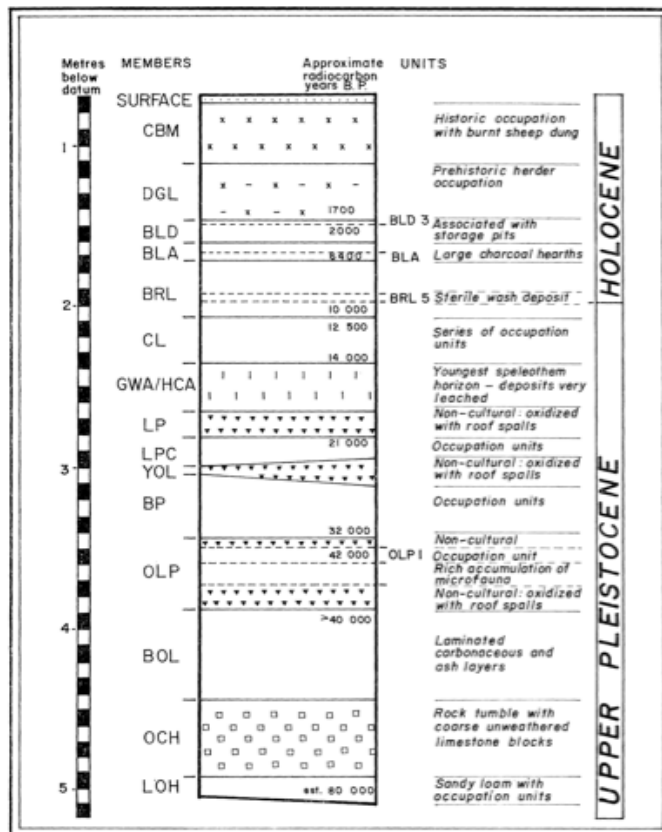


Figure 5. 6. Boomplaas: A summary of the stratigraphy and the associated interpretations from H. Deacon (1979). The BLD member is the third down from the Surface member. Digitised and edited from H. Deacon (1979).

The site was excavated as a component of a research programme sampling cultural and environmental assemblages to study human adaptations to the local environment through the Pleistocene (H. Deacon, 1979). Boomplaas also featured as a main component of J. Deacon's (1984) monograph on the Later Stone Age of southernmost Africa, highlighting the technological shifts that occurred in the late Pleistocene and through the Holocene. Today, it is also considered a key rockshelter site in understanding the finer nuances of the technological shift from MSA to LSA toolkits in this region, and considerable effort has been made to date the late/terminal Pleistocene layers to provide insight into variations in human behaviour and fill gaps in the site's chronological sequence (Pargeter *et al.*, 2018).

5.2.1.1. The associated archaeological context of selected finds

The material of interest was identified in a single stratigraphic layer near the top of the site's sequence, BLD. The BLD member, composed of two units, BLD3 and BL (Figure 5.6), and dates between 2004-1713 calBP (Table 5.5). It was described by H. Deacon (1979) as the most recent hunter-gatherer occupation layer. A total of 45 pits, deliberately made and some lined with *Boophone disticha* bulb leaves, were identified within this member. The lumps of hafting adhesive, identified by J. Deacon as 'mastic' (1984:174-175, 179) were found in four separate pits (7, 9, 15, 23). The lump from Pit 7 (Figure 5.7) was described as enveloping a small piece of wood, though lacking any tool impressions that might indicate that it was directly associated with composite tool. It was instead postulated that it may have been stored for future use. The specimen recovered from Pit 15 was identified as being a component of a composite tool, having evidence of breakage and impression of a handle. Two additional pieces of amorphous adhesive were found in Pits 9 and 23. However, they lack any distinguishing features, although the mass from Pit 9 has a distinct reddish color compared to the brown-grey appearance of the other specimens. These pieces were found in the same layer as an adze (J. Deacon, 1984: 107, Fig. 2) and a scraper (H. Deacon and J. Deacon, 1980) bearing evidence of hafting. The masses of adhesive are housed in the pre-colonial archaeology collections of the Iziko Museums, Cape Town. The necessary sampling permit was granted by Heritage Western Cape under the reference number 16052308AS0523E, while the export of the material was permitted by the South African Heritage Resources Agency under permit number 2462.

Table 5.5. ¹⁴C determinations of the unit containing material associated with this study. It is shown in sequence with stratigraphic context and cultural association. The uncalibrated dates were obtained from J. Deacon (1984). The date was then calibrated to two standards of deviation, with calibrations calculated with OxCal 4.2 (Ramsey, 2009) using SHCal13 calibration curve (Hogg *et al.*, 2013).

Lab No.	Unit	Cultural Association	Date (uncalibrated)	±	Date (cal BP)	
					from	to
UW-336	BLD	Final LSA	1955	65	2004	1713



Figure 5.7.Adhesive lumps from Boomplaas BLD Member. Left (top and bottom), an amorphous lump enveloping a fragment of wood, from Pit 7. Right (top and bottom), an amorphous lump, from Pit 9. Photographs taken by the author.

5.2.2. Hafted implements A1543 and C961, Albany Museum, Eastern Cape Province, South Africa

A1543 was acquired by the Albany Museum of Grahamstown in 1908 (Figure 5.8, middle frame). Recovered from a grave in a cave near Plettenberg Bay, it was described in museum records as a “stone implement fixed by means of resin to a wooden handle” (H. Deacon, 1966). The wooden handle appears not to have survived for long after acquisition; as early as 1912, Hewitt noted that the handle was composed of a rhinoceros horn that had been whittled down with a knife to fit the adhesive join and was hence described like this in all subsequent publications (Hewitt, 1921; Clark, 1958, 1959). The timing and nature of its recovery means that it is lacking provenience and direct association to any cultural technocomplex. Studies have described the structural alterations made to the object after its acquisition (Hewitt, 1912a, 1912b; H. Deacon, 1966), its possible function (Clark, 1958; Binneman, 1983), and have also attempted to explain the reddish appearance of its

outermost surface (H. Deacon, 1966; Lombard, 2007). Beyond this, however, it is difficult to place this object within the context of the southern African Stone Age sequence, limiting the contribution of this object to little beyond its value as a singular item and a potential analogue for tool design or appearance. No absolute dates are associated with this specimen.

C961 (Figure 5.8, bottom frame) was acquired in the same year as A1543 and was also recovered from a cave in the Plettenberg Bay area, although there is no indication that it came from the same location as A1543. It is a mass of adhesive, with a broken quartz insert, attached to an incised handle made of a bird long bone (H. Deacon, 1966, H. Deacon and J. Deacon, 1980). Both the adhesive and handle are coated in a reddish pigment. The nature of the mounting, nearly perpendicular to the handle, serves as a comparison to the mounted scraper from Boomplaas and emphasises the variety of function-dependent hafting orientations found in the southern African LSA record (H. Deacon and J. Deacon, 1980). Like A1543, the provenience of the specimen is also lacking, though it was found in association with “ground-bone, chisel-ended implements, and sherds of typical Cape coastal pottery” (H. Deacon, 1966: 89) and may tentatively be ascribed to the Ceramic Final LSA period (see: Chapter 3 for further discussion).

Studies contemporary with the acquisition of the objects narrows field of search for the place of origin. Peringuey’s (1911:159) note on an implement from “Rob Berg, acquired lately by the Graham’s Town Museum” likely places the location of either A1543 and/or C961 to a selection of caves located on the Robberg Peninsula. However, as the entry is a passing note and both specimens have the year 1908 fixed to their records, but only one being referred to in the 1911 publication, one cannot confirm with certainty to which Peringuey is referring.

The sampling permit for A1543 and C961 was granted by the Eastern Cape Provincial Heritage Resources Authority under reference number 2/2/APM-PERMIT/15/11/001, while export of the material was allowed by the South African Heritage Resources Agency under permit number 2166.



Figure 5.8. Implements: AA1588 (top) from the Iziko Museum; A1543 (middle), and C961 (bottom) from the Albany Museum. Photographs taken by the author.

5.2.3. Hafted implement SAM AA1588, Iziko Museums, Western Cape Province

SAM AA1588 (Figure 5.8, top) was recovered from a cave near Knysna by a Mr J. S. Henkel in 1912. It was first described in a letter from him to Louis Peringuey:

'I attach a sketch with measurements of an implement found in a cave. Undoubtedly it is of the same kind as figured in Plate xix, 150. I can give you no further particulars at present, but am sending this hurried note to report the find. As apparently, the implements are rare' (SAM, 11th October, 1912) – Goodwin 1929: 251-276.

The associated label describes the object only as a '[s]tone implement hafted in cement/Cave near Knysna/J.S Henkel'. Clark (1959) noted the concave working edge of the adze, suggesting that the piece may have been used to scrape wood or bone. Samples were taken for a chemical study by Walker (1974) in an attempt to identify the constituents of the adhesive.

On 20 May, 2016, observations and measurements were made the object to provide additional details it and its current state of preservation. SAM AA1588 comprises a silicified shale adze (54.98mm length x 53.86mm width x 12.02mm thickness) and one mass of adhesive (99.16mm length x 52.53mm width). The adhesive is very fragile and fragmented, having been glued back together from at least seven pieces, and appears to represent only half of the original adhesive mass. It has split along the coronal plane with the impression of the original handle clearly visible, although the handle itself is absent. Striations were also noted in the adhesive, with one set running parallel to the shaft impression on the left ventral surface, and the other perpendicular on the distal/medial right ventral surface just above the handle impression. The striations and the light coloured exposed inner ventral surface and edges may be accounted for by previous sampling. Walker (1974) notes that two samples each of 100g in size were obtained from the specimen. However, the exact sampling protocol and the instruments used, and whether the samples were obtained from fragmentary and detached material, was not specified.

The micro-sampling permit for AA1588 was granted by Heritage Western Cape under reference number 16052308AS0523E, while export of the material was allowed by the South African Heritage Resources Agency under permit number 2462.

CHAPTER 6 RESULTS

Introduction

This chapter highlights the collections screening, microscopy, and analytical results from the archaeological sites and non-provenienced specimens described in the previous chapter. The chapter begins with an overview of the screened collections, followed by the microscopic analyses, which includes a qualitative assessment of the residues types identified on the material and a corresponding frequency count. The largest component of the chapter includes the analytical results, whereby the materials are divided first by object type (as was seen in Chapter 5), and then laid out by residue type. Sites with multiple analytical techniques applied to the sampled material contain an interpretive summary section that aims to combine results from each analysis and provides an interpretation of the organic and inorganic components of the adhesive samples, where available.

6.1. Artefact Screening

A visual inspection (without microscopic lenses) was employed to screen through assemblage collections and select specimens that would be suitable for analysis. Table 6.1 highlights the total number of screened pieces (5911), and the number of artefacts (120) selected for characterisation by microscopy. The total collection counts and selected material varied from site to site, with the highest percentage of selected material derived from collections of adhesive lumps and complete implements (100% and 60% respectively). Artefacts selected for analysis among the sites having evidence of trace on stone tools ranged from 1.08% to 52.17%. The distribution of such

frequency percentages is accounted for by the accessibility of the material for screening. The entire lithic assemblages from specific excavations seasons (highlighted in Table 6.1) at Sehonghong (1.08%), Rose Cottage Cave (1.62%), and Melkhoutboom (4.00%) were available for screening, while at Renbaan Cave (52.17%), only a subset of artefacts that were previously identified as having adhesive trace were available for screening.

Table 6.1. Artefact counts for screening from the five sites, and the accessed museum implements.

Site	Total Counts of Screened artefacts	Total artefacts selected for microscopy	Selection frequency (%)
Boomplaas	4	4	100
Melkhoutboom (1969)	874	35	4.00
Renbaan Cave	23	12	52.17
Rose Cottage Cave (1987/88)	2219	36	1.62
Sehonghong (1992)	2786	30	1.08
Individual museum specimens	5	3	60
Total across all sites:	5911	120	2.03
Mean no. artefacts per study	20	Median	21
Standard deviation	15.43		

6.2. Low Powered Optical Light Microscopy

Eleven types of residue were identified by low-powered incident optical light microscopy (OLM). Table 6.2 provides a qualitative description of each of these types, alongside corresponding micrographs of each residue type in Figure 6.1 and 6.2.

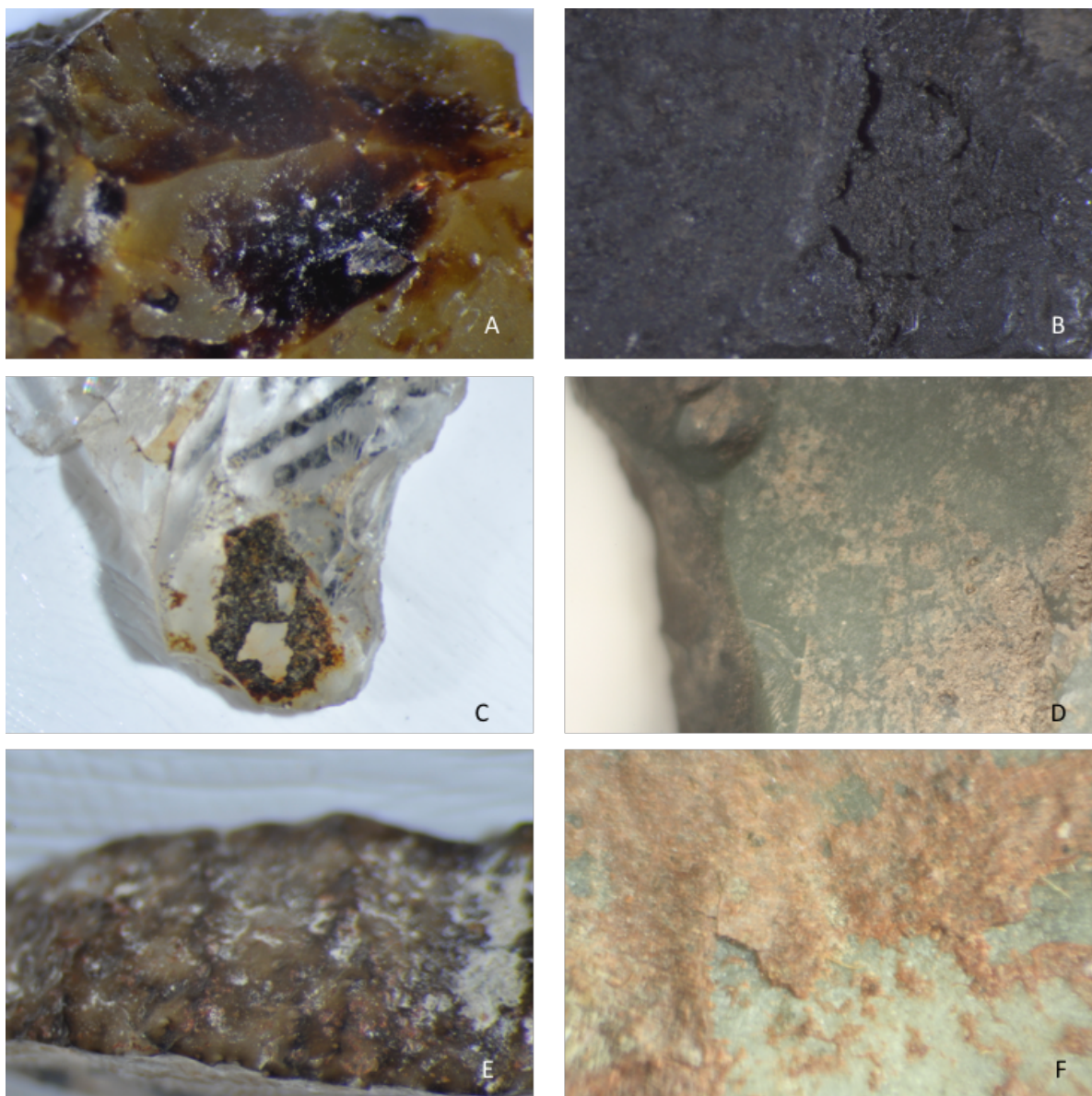


Figure 6.1. Identified residue types. A) Type 1A (25X), B) Type 1B (25X), C) Type 1C (20X), D) Type 2 (28X), E) Type 3A (20X), F) Type 3B (34X). The micrograph software utilised did not have the capacity to create scale bars, magnifications include the eyepiece and camera mounts. Photos taken by author.

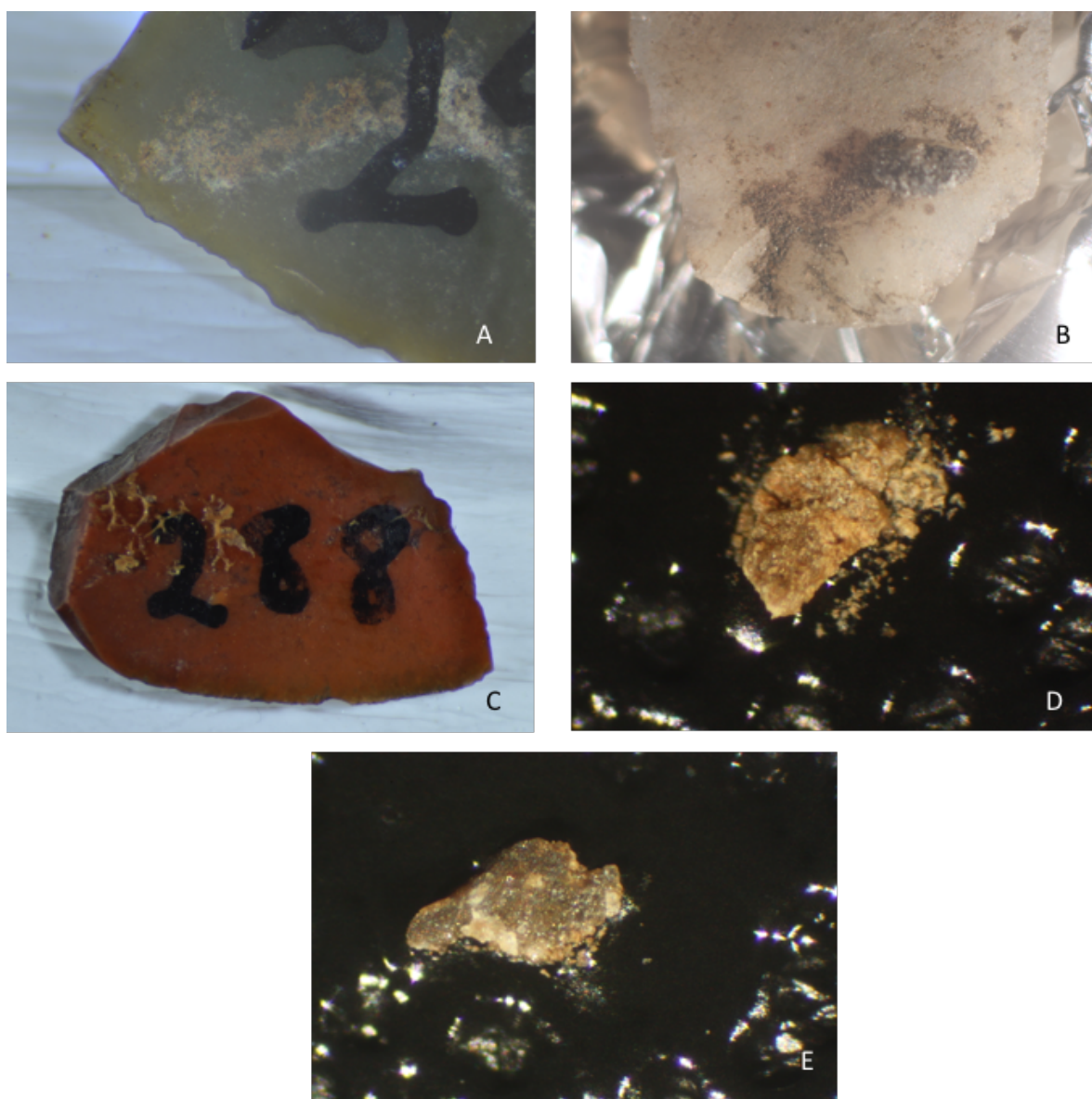


Figure 6.2 Identified residue types. A) Type 4 (30X), B) Type 5 (20X), C) Type 6 (20X), D) Type 7 (12.6X), E) Type 8 (20X). The micrograph software utilised did not have the capacity to create scale bars, magnifications include the eyepiece and camera mounts. Photos taken by author.

Table 6.2. Descriptions of the characteristic features of the observed adhesive residue types.

Residue Type	Qualitative Description	Distribution on Tool Surface
1A	Residue ranging in colour from a light to dark orange/brown, with a shiny, glassy surface. In low relief areas, these residues can appear as smears or dried droplets. Fragments have sharp rigid edges. They are relatively homogeneous in composition, with some low relief areas showing black flecks of material (possibly charcoal or burnt organics) with the residue. This residue type was associated with woody tissue or fibrous plant materials.	Distribution is dependent on tool typology. Orientations include: - Proximal end and surface to medial/distal surface
1B	Residues are dark brown in colour, with an overall granular texture, low relief and matte surface. Fragments crumble into smaller particles.	Distribution is dependent on tool typology. Orientations include: - Proximal end and surface to medial/distal surface - Medial surfaces only - Sporadically across tool surface
1C	This residue is an intermediary between Type 1A and Type 1B, and is lacking distinguishing feature of one or both types. Morphologically, they are described as amorphous, low relief smears, ranging between light brown and black in colour. The appearance of solid material from this category is rare. In some instances, this residue type may overlay other residues.	Distribution is dependent on tool typology. Orientations include: Orientations include: - Proximal end and surface to medial/distal surface - Parallel lines along the medial ridge (bladelets only)
2	White/beige residues, have an amorphous shape that can appear as a low relief smear and the edges. May be found on its own, or overlaying or underlying other residues.	This type was found to either indiscriminately covers artefact surfaces, or overlay the distribution patterns of another residue (i.e. Type 1A)
3A	Red/orange coloured residues that have a discrete particulate structure.	This type indiscriminately covers artefact surfaces, or appear in discrete patches.
3B	Red/orange coloured residues that are amorphous in appearance. Surfaces may appear either shiny, with fragments having rigid edges, or a more granular appearance. Low relief areas can look like a dried, smeared liquid (similar to Type 1A, though having an overall reddish colour), with black and red flecks. This residue type does not show indiscriminate distribution patterns.	Distribution is dependent on tool typology. Orientations include: - Proximal end and surface to medial/distal surface
4	White/beige particulate residues, fragments reflect under normal light, and have a sparkling quality.	This type was found to either indiscriminately covers artefact surfaces,

	Agglomerate particulate sizes vary from site to site, from relatively large quartz grains to fine crystals all embedded in concrete like matrix. Fibrous inclusions were noted in some cases.	or overlay particular residue types (i.e. Type 1C)
5	Residue colours range from light brown to black with a rough surface. Appears as a mixture of rough inorganic particulates. These may be agglomerated with a smooth, shiny matrix.	This type was found to either indiscriminately covers artefact surfaces
6	Yellow, low relief, smooth surface, waxy appearance. Color change to white at edges. Found with Type 1 residues or alone.	Extent of distribution could not be determined.
7	Granular, matte beige/light brown residue, amorphous in structure. Solid samples of this trace fragments easily, and has a powdery texture. Associated with Type 1A and Type 8 residues.	Identified only in lumps of organic material
8	Grey colour residues with white inclusions. Surface is uneven and matte. Associated with a Type 7 residue, found on its outer edge.	Identified only in lumps of organic material

The observed frequency of each residue type per site is described in Table 6.3. The listed values were compiled based on binary data (presence/absence count) obtained from the microscopic analysis of the dorsal and ventral surfaces of each tool specimen. It is possible that multiple residues types are present on a single tool surface, and as such, the frequency counts of the residues do not reflect the number of specimens analysed by microscopy.

Table 6.3. A frequency count of all observed residue types, from all sites and museum objects that underwent low-powered microscopic analyses. A count of n=1 signifies the presence of that residue on the surface of the tool. Site abbreviations: Melkhoutboom (MHB); Sehonghong (SEH); Rose Cottage Cave (RCC); Renbaan Cave (RB); Boomplaas (BPA); Museum implements (MUS).

Residue Types	Trace on Stone Tools				Lumps of Organics		All Sites	%
	MHB	SEH	RCC	RB	BPA	MUS		
1A	15	0	0	6	0	3	22	9.44%
1B	12	7	11	0	0	0	31	13.30%
1C	6	28	14	6	0	0	55	23.61%

2	3	7	5	0	0	0	15	6.44%
3A	11	13	7	0	0	2	33	14.16%
3B	0	0	3	7	0	0	10	4.29%
4	16	6	20	7	0	0	49	21.03%
5	0	8	1	0	0	0	9	3.86%
6	1	1	1	0	0	0	3	1.29%
7	0	0	0	0	4	1	5	2.15%
8	0	0	0	0	1	0	1	0.43%
Total	64	70	62	26	5	6	233	100.00%

6.2.1. Residue frequencies by type

6.2.1.1. Type 1A

This residue type was identified as trace materials on stone tools from Melkhoutboom and Renbaan Cave (see: Table 6.4 for details on associated typologies and raw material type), as well as being the main constituent of the museum specimens A1543, C961, and a component of AA1588 (Figure 6.3). At Melkhoutboom, this residue type was detected on 14 artefacts (38.89%) of varying attributed function, including scrapers, segments, and adzes, recovered from layers M, W, MB, CAF, OMB, and S. The highest frequency of identifications was found in the MB layer (n=7), and the most common typologies upon which this trace was found were on scrapers and segments. This residue type was also identified on several different raw material types, with chalcedony pieces appearing in the highest frequency. Plant tissues, including woody tissue (MHB 69/93 and reeds (MHB 69/134) were identified in several specimens.

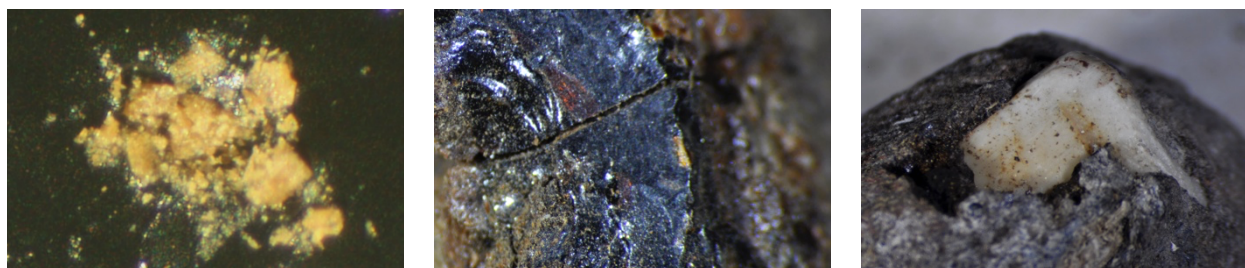


Figure 6.3 Hafted implements with Type 1A residues. Left: AA1588, with Type 1A mixed with Type 7 residues. Center: A1543. Right: C961. Photos taken by author.

At Renbaan Cave, 1A was detected on the dorsal and ventral surface from the proximal ends and surfaces to the medial and distal surfaces on scrapers, adzes, and a utilized flake. In total, Type 1A was identified on five artefacts (41.67%), from the surface cleanings, bedding, brown sand, and GAS layers. The sources of raw stone materials included silcrete, quartz, and cryptocrystalline silicates (CCS).

Table 6.4. Frequencies of Type 1A residues identified and categorised by tool typology and raw material.

Site	Category	Frequency
Melkhoutboom		
<i>Typology</i>		
	segment	7
	scraper	6
	borer	1
<i>Raw material</i>		
	silcrete	1
	chalcedony	11
	quartzite	2
Renbaan		
<i>Typology</i>		
	scraper	3
	adze	1
	utilised flake	1
<i>Raw material</i>		
	silcrete	1
	quartz	2
	CCS	1

6.2.1.2. Type 1B

Type 1B was found as trace on stone tools from Rose Cottage Cave, Sehonghong, and Melkhoutboom (Table 6.5). Trace was identified on 11 pieces including, segments, scrapers, blades, a bladelet, and a scraper/adze from Rose Cottage Cave. They are associated with the layers CM, Ph, A, and A2/A2(i); the highest counts were obtained from the A and A2/A2(i) layers (n=4 in both cases). At Melkhoutboom, Type 1B residual trace was detected on twelve of the thirty-five artefacts (34.3%). This type of trace was only identified on silicified shale and chalcedony materials, appearing most frequently on adzes and scrapers. These specimens were recovered from OMB, CAF, MB, W, and M layers, the highest count was recovered from layer W (n=4).

Table 6.5. Frequencies of Type 1B residues identified and categorised by tool typology and raw material.

Site	Category	Frequency	Site	Category	Frequency
Melkhoutboom			Rose Cottage cont.)		
<i>Typology</i>	segment	2	<i>Raw material</i>	quartz	2
	scraper	6		CCS	7
	borer	1		quartzite	2
	adze	4	Sehonghong		
<i>Raw material</i>	unknown	1	<i>Typology</i>	blade	3
	chalcedony	8		bladelet	2
	silicified shale	4		scraper	1
				adze	1
Rose Cottage			<i>Raw material</i>	adze	1
<i>Typology</i>	scraper	4		CCS	6
	segment	3		non-CCS	1
	bladelet	1			
	blade	1			
	backed blade	1			
	scraper/adze	1			

6.2.1.3. Type 1C

Identified as the most frequently counted residue (23.56%), this residue type was observed at all sites with trace on stone tools (Table 6.6). Five specimens (14.3%), which included a chalcedony borer and a quartz scraper from layer W, as well as two scrapers (chalcedony and silcrete) and a silcrete adze from the CAF layer were identified from Melkhoutbom.

A total of 14 specimens (38.9%) also exhibited this type of trace, found on scrapers, blades, bladelets, scraper/adzes, and an adze at Rose Cottage Cave. The material was associated with the layers CM, Ph, Ja, A, and A2/A2(i). Like the 1B residues identified at this site, the highest counts were obtained from the A and A2/A2(i) layer (n=4 and n=3, respectively). The co-occurrence of Type 1B and 1C residues were found on two specimens: a broken blade and a scraper/adze, both from the A2 layer. In two instances, tar-like Type 1C residues overlaid other residue types. This type of residue was also identified in small isolated patches.

At Renbaan Cave, the Type 1C residues co-existed with the Type 1A trace in all six identified specimens. The co-occurrence of 1C residues with 1A or 1B types may indicate that there is a relationship between the two groupings, with 1C being a more amorphous smearing with less residue density than the other two types. Similar to Rose Cottage, in two instances, tar-like Type 1C residues were identified in discrete patches overlaying other residues.

Sehonghong, by contrast to the other sites, is the only one whose residue trace is composed only of Type 1C. These residues were found on the dorsal and ventral surfaces (proximal, medial, and distal areas) of 28 (93.33%) artefacts. The tool typologies included blades, bladelets, scrapers, segments, and an adze, with the highest frequency identified on the bladelets (n=15, 100% frequency from this typology). Of particular note, the extent of trace on the bladelets and blades was concentrated along the medial surfaces and decreased in concentration as the residue approached the working edge. The artefacts were associated with stratigraphic layers spanning most of the LSA assemblage at the site, including the Robberg layers RF, BARF, and RBL; the

Oakhurst layer ALP (although trace on this specimen was lacking a defined residue extent); the mid-Holocene layer GWA; and, the SS and DC layers of the late Holocene.

Table 6.6. Frequencies of Type 1C residues identified and categorised by tool typology and raw material.

Site	Category	Frequency	Site	Category	Frequency
Melkhoutboom			Rose Cottage (cont.)		
<i>Typology</i>	adze	2	<i>Typology</i>	scraper	4
	scraper	3		adze	1
	borer	1		scraper/adze	2
<i>Raw material</i>	silcrete	2	<i>Raw material</i>	CCS	8
	chalcedony	2		quartzite	3
	silicified shale	1		quartz	3
	quartz	2	Sehonghong		
Renbaan			<i>Typology</i>	blackened blade	1
<i>Typology</i>	adze	3		bladelet	15
	scraper	3		blade	4
	utilized flake	1		unknown	1
<i>Raw material</i>	silicified shale	3		scraper	5
	CCS	2		adze	1
	quartz	2		segment	1
Rose Cottage			<i>Raw material</i>	CCS	18
<i>Typology</i>	blade	4		non-CCS	10
	bladelet	3			

6.2.1.4. Type 2

This residue type was identified at Melkhoutboom (8.57%), Sehonghong (23.33%), and Rose Cottage Cave (13.89%) (see: Table 6.7). At Melkhoutboom, it was isolated on three artefacts from the lower screened layers (M, W and MB), which included a scraper, a borer, and a segment. This residue type was not found in particularly high concentrations and never made up a majority extent of a residue. Sehonghong held the highest recorded residue count for this type found on

bladelets (n=4), a scraper, a segment, and an adze. The material was from the RBL, RF, GWA, DC, and SS layers.

Contrary to the aforementioned sites, specimens from Rose Cottage Cave did yield evidence of this residue type appearing in higher concentrations. Type 2 was identified as one of the main trace types on a scraper from the A2 layer, with residue present on both the dorsal and ventral surfaces but especially, on the former where it was found at the proximal end and continued up to the distal surface and was overlaid by Type 5 residues. Similarly, Type 2 was also found in high concentration on a bladelet from the same layer. The observed trace extended along both working edges of the piece, with the greater abundance on the right side of the dorsal surface.

Table 6.7. Frequencies of Type 2 residues identified and categorised by tool typology and raw material.

Site	Category	Frequency	Site	Category	Frequency
Melkhoutboom			Sehonghong		
<i>Typology</i>	segment	1	<i>Typology</i>	blackened bladelet	1
	borer	2		bladelet	3
<i>Raw material</i>	chalcedony	3		scraper	1
				adze	1
Rose Cottage				segment	1
<i>Typology</i>	bladelet	3	<i>Raw material</i>	CCS	5
	scraper	1		non-CCS	2
	scraper/adze	2			
<i>Raw material</i>	CCS	5			
	scraper	3			
	utilized flake	1			
<i>Raw material</i>					
	silicified shale	3			
	CCS	2			
	quartz	2			

6.2.1.5. Type 3A

Type 3A residues were detected on stone tools from Melkhoutboom (31.43%), Sehonghong (43.33%), and Rose Cottage Cave (19.44%) (Table 6.8). This residue was also found as the outermost layer covering the Type 1A residues on implements A1543 and C961 from the Albany Museum, giving the adhesives a reddish colouring.

Across all sites, Type 3A either indiscriminately covered the artefact, overlaying other residue types, or appeared in discrete low-relief patches or crystalline clusters across the tool surface. It does not, however, make up the majority of residue concentrations or their extent. At Melkhoutboom, this residue type appeared on eleven of thirty-five artefacts (34.3%), including scrapers, adzes, and segments from the M, W, MB, CAF, and OMB layers. The residue was also identified on a scraper, an adze, a point, a blade, a bladelet, and a miscellaneous piece at Rose Cottage Cave. The Sehonghong material held the highest counts of this type of residue, which was found on artefacts from the RBL/CLBRF, RF, BARF, ALP, and GWA layers. It was associated with bladelet, blade, and segment typologies but, occurs most frequently on bladelets (n=8).

Table 6.8. Frequencies of Type 3A residues identified and categorised by tool typology and raw material.

Site	Category	Frequency	Site	Category	Frequency
Melkhoutboom			Sehonghong		
<i>Typology</i>	scraper	5	<i>Typology</i>	backed bladelet	1
	segment	3		bladelet	7
	adze	3		blade	4
<i>Raw material</i>	chalcedony	7	<i>Raw material</i>	segment	1
	silcrete	2		CCS	11
	silicified shale	2		non-CCS	2
Rose Cottage					
<i>Typology</i>	bladelet	2			
	scraper	1			
	unknown	1			
	backed blade	1			
	point	1			
	adze	1			
<i>Raw material</i>	CCS	7			

6.2.1.6. Type 3B

This residue type was observed on artefacts from Rose Cottage Cave (8.33%) and Renbaan Cave (58.33%). It differs from Type 3A in that this residue tends to occur in higher concentrations on the dorsal and ventral surfaces and to have a more homogeneous and amorphous appearance (Table 6.9).

At Rose Cottage Cave, this trace was found on a scraper from layer A2, a broken flake from the Janice O/B layer, and an adze. On the scraper, the residue extended across the whole dorsal surface, from the proximal end up to the steep edge sloping toward the working edge. There was a notable high density of this residue noted on the broken flake on both the dorsal and ventral surfaces, extending up to broken edge on the left side.

As the majority residue type at Renbaan Cave, Type 3B was identified only on silcrete and CCS adzes on both dorsal and ventral surfaces. It extended from the proximal ends and surfaces to the medial or distal surfaces. Three specimens, RB01 and RB03 (silcrete) as well as RB05 (CCS),

contained fibrous material (likely hair) embedded in the residues. The appearance of these fibres was not discernible by incident light microscopy and a specimen from RB01 was mounted for SEM analysis (Section 6.3.2.2.).

Table 6.9. Frequencies of Type 3B residues identified and categorised by tool typology and raw material.

Site	Category	Frequency
Renbaan		
<i>Typology</i>	adze	7
<i>Raw material</i>	silcrete	6
	CCS	1
Rose Cottage		
<i>Typology</i>	scraper	1
	adze	1
	flake	1
<i>Raw material</i>	CCS	3

6.2.1.7. Type 4

This residue type was detected on 21.33% of all analysed materials, sourced from all sites with trace on stone tools (Table 6.10). It has been identified in isolation or overlaying other residues (i.e. Type 2 at Sehonghong and Rose Cottage Cave or Type 1A at Melkhoutboom).

At Melkhoutboom, it was observed on 15 (42.86%) of the 35 artefacts, including adzes, scrapers, segments, and a borer. Scrapers were found to have the highest abundance frequency compared to all other typologies (n=8). This residue type was identified in all layers, apart from the S (surface) deposit.

Table 6.10. Frequencies of Type 4 residues identified and categorised by tool typology and raw material.

Site	Category	Frequency	Site	Category	Frequency
Melkhoutboom			Rose Cottage (cont.)		
<i>Typology</i>	adze	3	<i>Typology</i>	blackened blade	1
	scraper	7		adze	2
	segment	4	<i>Raw material</i>	quartz	3
	borer	2		CCS	15
		quartzite		2	
Renbaan			Sehonghong		
<i>Typology</i>	adze	6	<i>Typology</i>	backed bladelet	1
	scraper	1		blade	1
<i>Raw material</i>	silcrete	5		bladelet	1
	CCS	1		scraper	1
	quartz	1		Segment	2
Rose Cottage			<i>Raw material</i>	CCS	5
<i>Typology</i>	scraper	8		non – CCS	1
	bladelet	4			
	scraper/adze	2			
	blade	3			

6.2.1.8. Type 5

Although also having an inorganic mineral-like appearance, this residue may be distinguished from Type 4 in that overall the particulates are larger in size. This type of residue was only identified at Sehonghong (26.67%) and Rose Cottage Cave (2.78%) (Table 6.11). At Sehonghong, it co-occurred with Type 1C and 3A residues and was found on bladelets, blades, and scrapers from the RF, BARF, ALP, GWA, and DC layers. The residue distribution on the artefacts' surfaces was sporadic. By contrast, a scraper from the A2 layer at Rose Cottage Cave had Type 5 residue extending along much of its ventral surface, overlaying a Type 2 residue.

Table 6.11. Frequencies of Type 5 residues identified and categorised by tool typology and raw material.

Site	Category	Frequency	Site	Category	Frequency
Type 5			Type 6		
Rose Cottage			Melkhoutboom		
<i>Typology</i>	scraper	1	<i>Typology</i>	segment	1
<i>Raw material</i>	CCS	1	<i>Raw material</i>	chalcedony	1
Sehonghong			Rose Cottage		
<i>Typology</i>	blade	3	<i>Typology</i>	unknown	1
	bladelet	3	<i>Raw material</i>	CCS	1
	scraper	2	Sehonghong		
<i>Raw material</i>	CCS	6	<i>Typology</i>	scraper	1
	non-CCS	2	<i>Raw material</i>	CCS	1

6.2.1.9. Type 6

This residue type was observed in three instances on single specimens from Sehonghong, Rose Cottage Cave, and Melkhoutboom. The Sehonghong piece was a scraper recovered from DC, the youngest layer below the surface deposits. The Rose Cottage Cave specimen was an unclassified stone tool from the CM layer. The Melkhoutboom specimen, a chalcedony segment from layer W, had Type 6 residue distributed along the medial surface. As it overlaid the labelling of the artefact, this trace is likely a modern contaminant.

6.2.1.10. Type 7 & Type 8

These two types were found exclusively on the Boomplaas amorphous lumps and AA1588, and are thus highlighted in tandem. Type 7 was considered the main component of these organic specimens in both instances. The Type 8 residues co-occur with Type 7 however, this was only found to be the case on the material from Boomplaas.

6.2.1.11. Modern residues

Modern residues were identified on stone tools from Melkhoutboom and Rose Cottage Cave. These were likely the result of assemblage curation, object labelling, and storage, and include trace derived from marker pens, varnish, and correction fluid as well as plant fibres resting on tool surfaces. Pen, varnish, and correction fluid, or a combination thereof, were detected on 20 (55.56%) of the 36 pieces analysed from Rose Cottage Cave. Based on this predominance and the lack of sufficient amounts of trace that could be isolated to acquire samples, it was determined that material from this site would be unsuitable for further analysis.

At Melkhoutboom, marker pen was the main modern residue identified and was present on all analysed specimens. One specimen, 69/288, a chalcedony segment recovered from layer W appears to have been coated with a thin metallic grey film, while the other side contains traces of synthetic adhesive that overlay the artefact label. Contrary to the Rose Cottage material, at Melkhoutboom there was sufficient amounts of solid material on several objects to carry on with further analysis.

6.2.1.12. Interpretive Summary

Three of the four sites with trace on stone tools - Melkhoutboom, Sehonghong and Renbaan Cave - yielded residue trace that conforms with criteria highlighted in Charrié-Duhaut *et al.* (2013) and modified in Chapter 3. These specimens were also either free of accession labels or where labels were present, had sufficient amounts of material for further analysis. At these sites, five residue types were identified as making up the bulk of the extent of trace that was consistent with hafting. These included: Types 1A, 1B, 1C, 2, and 3B. Based on orientation, the residue types identified were concentrated on the proximal to medial/distal surfaces of tools (with respect to the working edge) or ran medially in parallel with the working edge. The latter was especially the case with blades and bladelets.

In following Haslam's (2009) assessment of microscopic residue studies of stone tools, it is recognized that the sample sizes for each site are small (Table 6.1), especially for a quantitative assessment of the significance between the residue type, the raw material, and the ascribed tool typology. However, as the categories of raw material and tool typology are of benefit in testing the research hypotheses postulated in Chapter 1, those datasets are reiterated in the each interpretive summary and in the first sections of Chapter 6, which ties together aspects of the excavated material, the microscopy, and the analytical results.

A report was provided to the South African Heritage Resources Agency following the final condition of the export permit no. 2119 for Rose Cottage Cave, highlighting the results and the reasoning for not continuing further with additional analyses. A copy of this report is found in Appendix IV.

6. 3. Analytical results: adhesive trace on stone tools

6.3.1 Results from Melkhoutboom

6.3.1.1. FTIR Spectroscopy

Spectra were collected from eight solid samples, where sufficient amounts of material remained for SEM/EDS and chromatographic analyses. The IR spectra results are grouped into three residue types: Type 1A, Type 1B, and a mixture of Types 1A and 2.

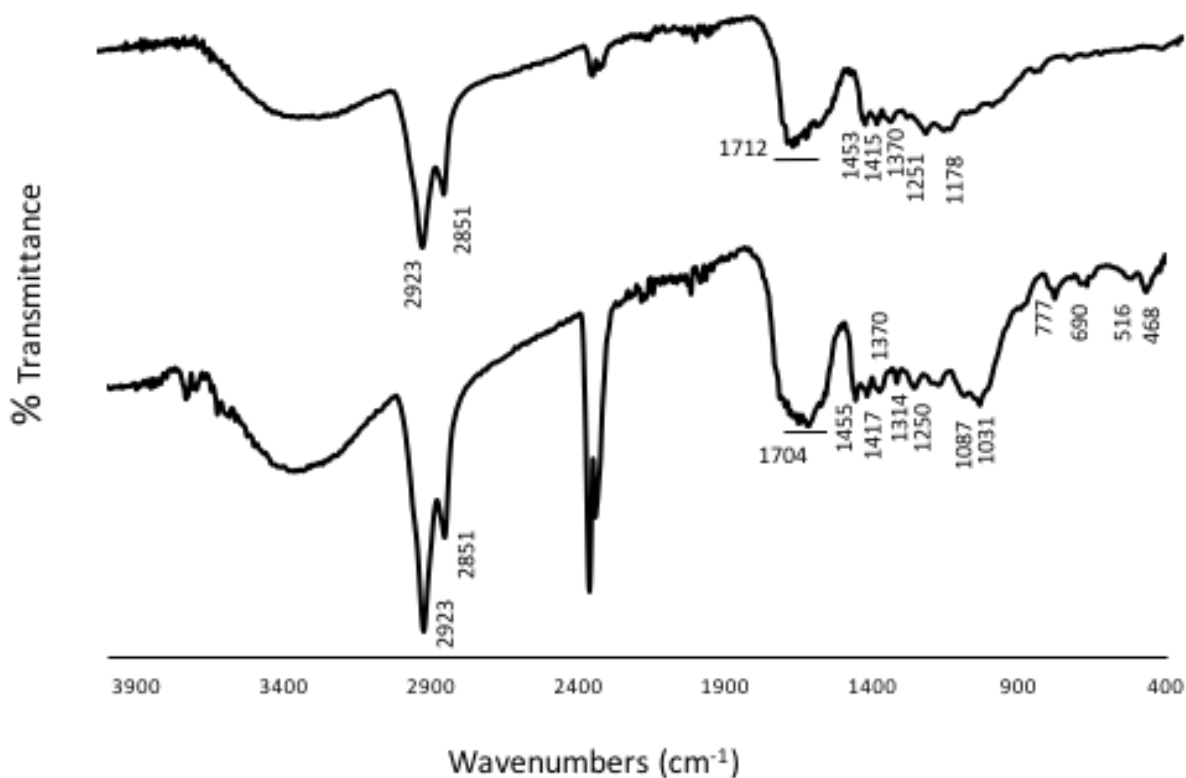


Figure 6.4. Melkhoutboom: IR spectra of two Type 1A residues, MHB03 (top) and MHB70 (bottom).

Spectra of Type 1A residues: MHB03, MHB70

Two samples of Type 1A residues, from MHB03 and MHB70, underwent analysis. The spectra from these specimens are presented in Figure 6.4 and the Table 6.12. The spectral features from both samples are very similar, containing organic components and possible traces of silicates in MHB70. Both spectra yielded broad O-H stretches between $3600\text{--}3000\text{ cm}^{-1}$, sharp peaks at the C-H stretch around ~ 2920 and 2850 cm^{-1} , medium intensity, multiple sharp peaks of carboxyl groups at approximately 1696 cm^{-1} and 1250 cm^{-1} (as well as the strong C=O stretching of a carbonyl at $\sim 1712\text{ cm}^{-1}$ in MHB03, less so from 1704 cm^{-1} in MHB70), an aromatic ring stretch at $1611/1613\text{ cm}^{-1}$, the C-H deformation of alkyl groups at $1453/1455\text{ cm}^{-1}$ and $1370/1372\text{ cm}^{-1}$, weak peaks at $1170/1178\text{ cm}^{-1}$, $1089/1091\text{ cm}^{-1}$ for the C-O-C ester stretch, a weak peak at $1031/1033\text{ cm}^{-1}$ that may be indicative of a C-O stretch (alcohols), and very weak bands that may indicate C-H

out-of-plane bending (alkenes) between 1000-700 cm^{-1} . Possible trace silica minerals (i.e. quartz) were identified in MHB70 based on the presence of a doublet peak at approximately 777 and 794 cm^{-1} (Russell and Fraser, 1994), however this signal was very weak.

Table 6.12. IR results from MHB03 and MHB70, two Type 1A residues.

Assignment*	Wavenumber (cm^{-1})	
	MHB03	MHB70
$\nu(\text{O-H})$, organics	3600-3000	3600-3000
$\nu(\text{C-H})$ aliphatic C-H stretch (long aliphatic chains, oils)	2921 / 2851	2923 / 2851
carbonates (calcite)	X	X
$\nu(\text{C=O})$ stretch of fatty acids	1712	X
carboxyl group	1694 & 1696	1692
$\nu(\text{COO}^-)$ anion or $\nu(\text{C=C-C})$ of an aromatic ring	1644	1556
$\nu(\text{C=C-C})$ of an aromatic ring	1611	1611
$\delta(\text{C-H})$ deformation (saturated aliphatic groups) or $\gamma(-\text{CH}_3)$ bending	1453 / 1370	1455 / 1372
Possible In-plane γ vinyl (C-H) of olefinic groups, or carbonate anion	1415	1417
γ (-OH), phenol or tertiary alcohol, or primary or secondary γ (-OH)	1314	1317
$\nu(\text{C-O})$ of esters and alcohols	1251	1250
$\nu(\text{C-O-C})$ of esters and alcohols	1178/1193	1087
$\nu(\text{C-O})$ or $\nu(\text{Si-O})$	shoulder	1031
Silicates	X	777
Silicates	X	524/468

*Assignments based on published literature: Russell and Fraser 1994; Colombini *et al.* 2003; Coates 2006; Helwig *et al.* 2008; Vahur *et al.* 2011. Peaks at $\sim 2370\text{cm}^{-1}$ are attributed to atmospheric carbon dioxide and are not included in the interpretations or listed data.

The presence of animal fats or raw beeswax making up a component of the IR spectra may be discounted based on the notable absence of a strong, sharp peak associated with the C=O ester stretching between 1735-1750 cm^{-1} (The National Archive, 2007; Vahur *et al.*, 2016). This same C=O stretching band is absent in heat altered beeswax. However, due to the absence of additional bands associated with hydrocarbon chains the presence of altered beeswax is unlikely as well (Regert *et al.* 2001).

When compared to plant reference materials analysed under the same conditions (Figure 6.5), the spectra of the archaeological specimens are not an identical match to any of the plant exudate types, including gum, resin, and pitch analysed as references. This is likely due to a single, very broad peak spanning $\sim 1700 - 1555\text{cm}^{-1}$, which complicates spectra comparisons. The presence of gum exudates may be excluded based on the absence of a strong broad peak at $\sim 1010\text{cm}^{-1}$, identified in the *Acacia karoo* specimen, which is associated with the alkene C-H bend of polysaccharides. Instead, the identification of strong C-H stretching vibrations, C=O stretching vibrations, and carboxylic acids highlighted in Table 6.13 would suggest that the sampled material is most likely derived from a plant pitch or resin (Hummel, 1988; Colombini *et al.*, 2003; Ribechini, 2006; Vahur *et al.*, 2011; Helwig *et al.*, 2014; Charri -Duhaut *et al.*, 2016).

Table 6.13. A comparison of the IR results of MHB70 and South African exudates.

Assignment*	Wavenumber (cm^{-1})			
	MHB70	<i>Podocarpus elongatus</i> pitch	<i>Acacia karoo</i> gum	<i>Widdringtonia cupressoides</i> resin
v(O-H) (broad)	3600-3000	3600-3000	3600-3000	3600-3000
v(C-H)	2923 / 2851	2917/2847	2915	2926/shoulder
v(C=O) esters	X	1702	1714	X
v(COOH) of carboxylic acids	1694	X	X	1696
v(C=C-C) of an aromatic ring	1611	1595	1600	1594
(C=C)		1513		
δ (C-H) deformation (saturated aliphatic groups)	1455 / 1372	1459/1370	1370	1444/1382
γ (-CH ₃) in plane	X	X	1418	X
v (C-O), esters and alcohols	1250	1263/1230	1251	shoulder
v(C-O-C) esters and alcohols	1087	1199/1085	X	1087
v(C-O) or v(Si-O)	1031	1048	shoulder	1023
Alkene γ (C-H)	X	X	1010	X
γ (C-H) saturated aliphatic groups	X	X	X	1018
(C-H) wagging	X	728/719	X	X

*Assignments based on published literature: Russell and Fraser, 1994; Colombini *et al.*, 2003; Coates, 2006; Helwig *et al.*, 2008; Vahur *et al.*, 2011. Peaks at $\sim 2370\text{cm}^{-1}$ are attributed to atmospheric carbon dioxide and are not included in the interpretations or listed data.

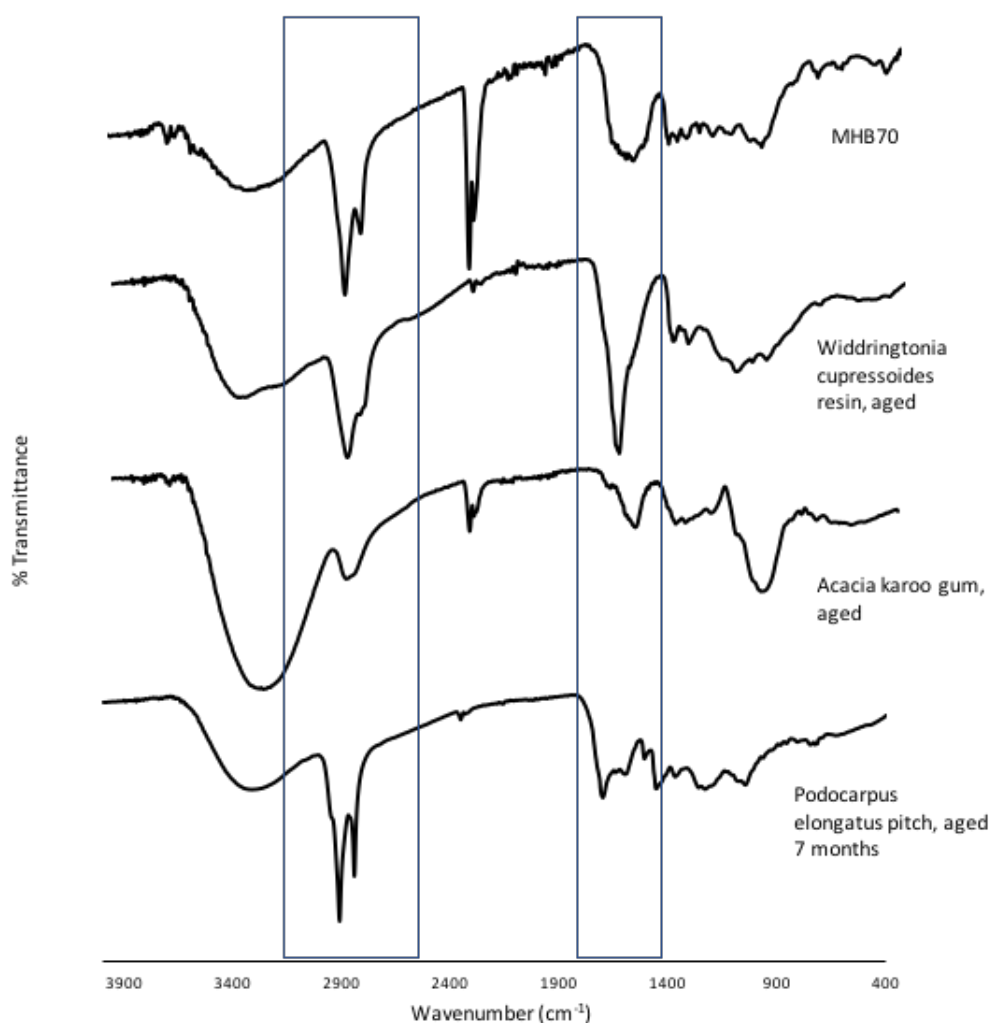


Figure 6.5. Melkhoutboom: IR spectra MHB70, compared to three types of exudates sourced from South African floral species.

Spectra of Type 1B residues: MHB16, MHB18, MHB22, MHB56, MHB77

The IR spectra from five Type 1B residue samples are described in Table 6.14 with corresponding examples in Figure 6.6. Alongside -OH and C-H stretches, additional organic functional groups included a broad peak with multiple maxima at ~ 1631 and $\sim 1555\text{ cm}^{-1}$ possibly indicative of C=O stretch, C=C stretch or an aromatic ring stretch, C-H deformation bands between $\sim 1460\text{ cm}^{-1}$ and 1340 cm^{-1} in all samples except MHB56, weak peaks at $\sim 1178\text{ cm}^{-1}$ and 1080 cm^{-1} for

the C-O-C ester stretch, and, weak peaks at $\sim 1033\text{-}1020\text{cm}^{-1}$ that are likely a C-O stretch. The presence of medium broad peaks at $1014\text{-}1004\text{ cm}^{-1}$ in MHB16, MHB18, and MHB56 may be indicative of either saturated aliphatic groups or phosphates ($-\text{PO}_4$) (Coates 2006). In addition to the above, an aromatic ring stretch at 1611 cm^{-1} was identified in MHB22. Peaks consistent with carbonates were identified in MHB22 and MHB18. Silicates were identified in all samples, except for MHB16. Based on the presence of peaks at $\sim 1033/1031$, $\sim 778/777$, $516/522$, and $464\text{-}460\text{ cm}^{-1}$, quartz minerals were identified as the best possible match (Russell and Fraser 1994: Fig. 2.25a). Sharp peaks at 873 cm^{-1} and 711 cm^{-1} are interpreted as corresponding to calcite (Russell and Fraser 1994: Fig. 2.26a).

All spectra show evidence of organic components, appearing visually similar to the Type 1A materials, particularly in the presence of a large broad peak associated with $\nu(\text{COO}^-)$ anion or $\nu(\text{C}=\text{C})$ of an aromatic ring and another $\delta(\text{C-H})$ deformation (saturated aliphatic groups) or $\gamma(-$

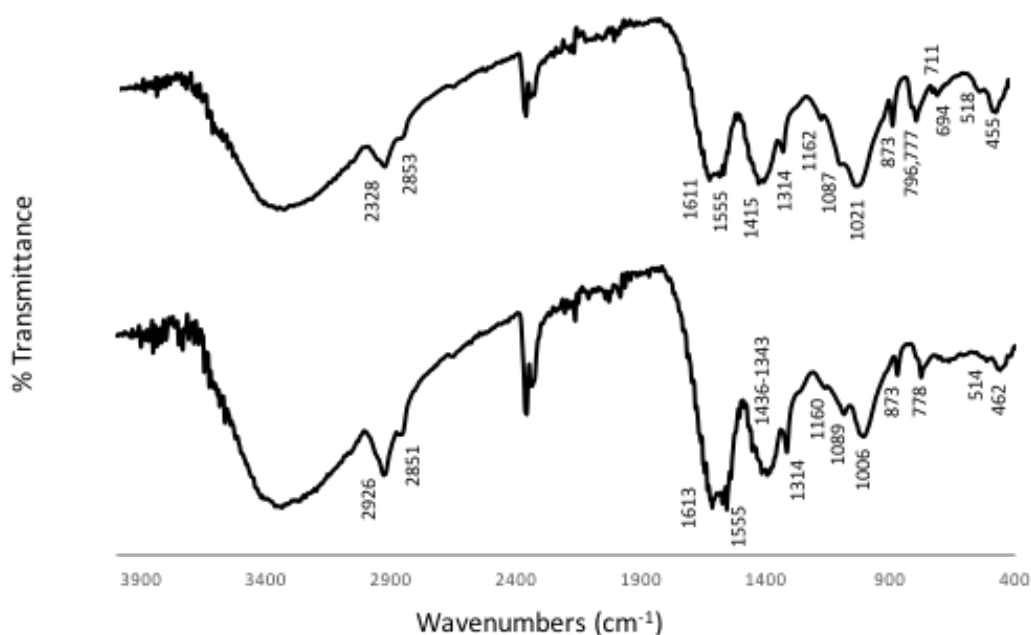


Figure 6.6. Melkhoutboom: IR spectra of two Type 1B residues, MHB56 (top) and MHB77 (bottom).

CH₃) bending. Inorganic minerals, including silicates and carbonates, are more well-defined in this residue type versus Type 1A.

Table 6.14. Melkhoutboom: The IR results from five Type 1B samples.

Assignment*	Wavenumber (cm ⁻¹)				
	MHB16	MHB18	MHB22	MHB56	MHB77
v(O-H), organics	3600-3000	3600-3000	3600-3000	3600-3000	3600-3000
v(C-H) aliphatic C-H stretch (long aliphatic chains, oils)	2924/ 2851	2928 / 2861	2924/ 2853	2926/2951	2919 / 2851
carbonate	X	X	X	1797	X
v(COO ⁻) anion or v(C=C-C) of an aromatic ring	1555	broad peak with maxima at 1611/1555	broad peak with maxima at 1631/1555	broad peak with maxima at 1631/1555	broad peak with maxima at 1613/ 1555
v(C=C-C) of an aromatic ring	X	X	1611	X	X
δ(C-H) deformation (saturated aliphatic groups) or γ(-CH ₃) bending	1384	1455	1465 - 1343	X	1436-1343
Possible in-plane γ vinyl (C-H) of olefinic groups, or carbonate anion	X	1415	X	1405	X
γ (-OH), phenol or tertiary alcohol, or primary or secondary γ (-OH)	X	1314	1314	1316	1314
v(C-O -C) of esters and alcohols	X	1162/1087	1089	1162/1089	1160/1089
v(C-O) or v(Si-O)	1033	1021	1033	X	X
Saturated aliphatic groups; - PO ₄ ; inorganic Si-O-Al groups	1012	1014	X	1008	1006
Carbonates	X	873/ 711	873/ 711	873	873
Silicates	X	796/777, 694	778	X	777
Silicates	X	518/455	460	516	514/462

*Assignments based on published literature: Russell and Fraser 1994; Colombini *et al.* 2003; Coates 2006; Helwig *et al.* 2008; Vahur *et al.* 2011. Peaks at ~2370cm⁻¹ are attributed to atmospheric carbon dioxide and are not included in the interpretations or listed data.

Mixture of 1A & 2 Residues

MHB38 (Figure 6.7, Table 6.15) was described by OLM as containing two discrete layers: a Type 1A residue, overlaid by a layer of Type 2. The IR spectrum of this sample was found to contain a weak, broad O-H stretch between 3600-3000 cm⁻¹, and weak C-H stretches around ~2921 and

2849 cm^{-1} , alongside a peak at 1584 cm^{-1} . This limited number of peaks related to organic functional groups is insufficient to determine the source of the sample. Notable in this specimen were carbonate peaks at 2514, 1793, 1405 (broad, strong), 871, and 711 cm^{-1} matching calcite minerals (Russell and Fraser 1994: Fig. 2.26a). Evidence of silicates, notably quartz is supported by a doublet at 796 and 777 cm^{-1} (Russell and Fraser 1994: Fig. 2.25a). This predominance of inorganics, alongside an organic component is consistent with the OLM results, describing two residues of different origins.

Table 6.15. Melkhoutboom: IR results from MHB38, a mixed Type 1A and 2, layered residue.

Assignment*	Wavelength (cm^{-1}) MHB38
v(O-H)	3600-3000
v(C-H) aliphatic lipids	2921/2849
carbonate (calcite)	2514
Carbonates (calcite)	1793
v(C=C-C) of an aromatic ring or v(C=C)	1584
Carbonates (C-O)	1405
v(C-O-C) of esters and alcohols	1087/1164
v(C-O) or v(Si-O-Si)	1018
Carbonates	871/ 711
Silicates v(Si-O)	796/777
Silicates γ (Si-O)	464

*Assignments based on published literature: Russell and Fraser 1994; Colombini *et al.* 2003; Coates 2006; Helwig *et al.* 2008; Vahur *et al.* 2011; van der Marol and Beutelspacher 1976. Peaks at $\sim 2370\text{cm}^{-1}$ are attributed to atmospheric carbon dioxide and are not included in the interpretations or listed data.

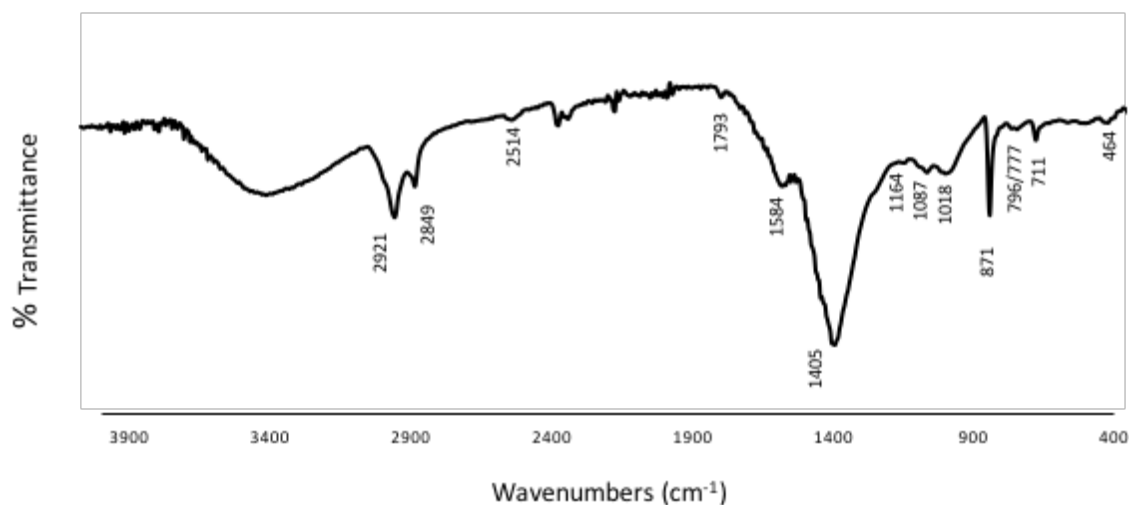


Figure 6.7. Melkhoutboom: IR spectra of MHB38, a combination of Type 1A and Type 2 residues.

6.3.1.2. SEM/EDS: Imaging and Elemental Composition

The images obtained by SEM were consistent with the qualitative characteristics of the OLM results. Most notable was the difference between the Type 1A residues and the Type 1B residues. At the same magnification, Type 1A material mounted for analysis was overall larger in size, holding up as bigger intact fragments and having a smooth textured surface with cracking visible in some areas; the Type 1B samples on the whole were smaller sized smooth-surfaced fragments with granular material interspersed throughout (Figure 6.8).

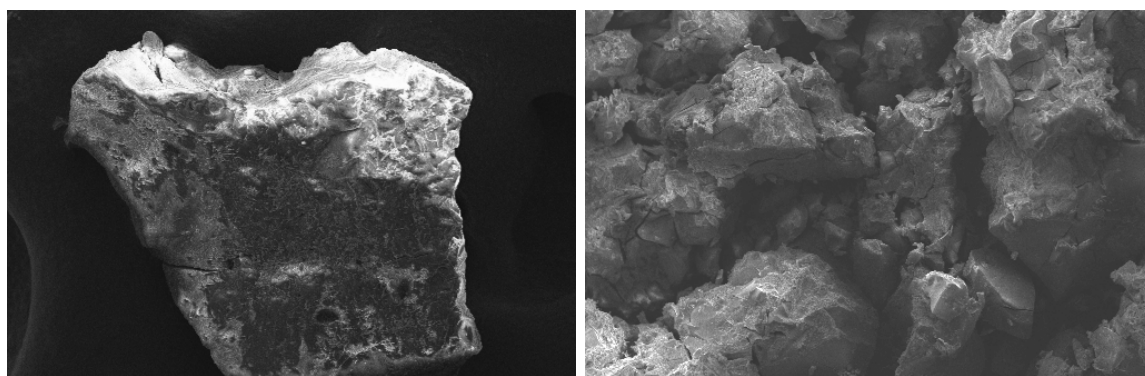


Figure 6.8. Melkhoutboom: SEM images in secondary mode of a MHB08 (left), a Type 1A residue, and MHB16 (right), a Type 1B residue.

Twelve samples yielded sufficient material for SEM/EDS analysis. Table 6.16 highlights the elemental composition of the solid adhesive samples from Melkhoutboom. Oxygen and carbon were identified as the main elements in all the analysed material, supporting the indicators of organics of plant origin from the IR analysis. Minor elemental components were identified in five samples, which include two Type 1B residues (MHB16, MHB18, MHB20), a Type 1C residue (MHB01), and a Type 1A/2 residue (MHB38). The presence of elemental silicon in MHB18 and calcium in MHB38 is consistent with the inorganic minerals identified in the IR spectra of these specimens. By contrast, elemental manganese was found in MHB16 and is notably absent in all other analysed samples. While manganese containing minerals were not identified in the IR spectra, it supports the overall inorganic appearance of this residues noted by microscopic analysis. There was insufficient material in MHB01 and MHB20 to acquire IR spectra. However, the presence of silicon and aluminium in MHB01 and calcium in MHB20 supports the presence of inorganic minerals in these residue samples.

The appearance of silicon and calcium as among the highest trace constituents in Type 1B samples (except for MHB77), supports the IR spectral findings that noted the prevalence of calcium carbonates and silicates in this material. The presence of silicate minerals in the IR spectra of MHB38, Type 2 residue, is also supported by the relatively high abundance of trace silicon. In contrast, Type 1A samples (MHB03, MHB05, MHB08, and MHB70), yielded sodium as the most relatively abundance trace element. It may be argued that the compositional differences between Type 1A materials, which has a more organic appearance, and those more inorganic adhesive residue types at Melkhoutboom show similar distinctions to the microscopic observations and the IR results.

The trace elements identified in eleven of twelve samples, irrespective of residue type, including sodium, chlorine, magnesium, iron, and aluminium may be the result of the depositional

environment surrounding the artefacts, indicating the presence of inorganic minerals and salts.

Phosphorus and potassium have been used as elemental markers to identify human activity as indicators of degradation of organic material (Price and Burton, 2011). Its presence in trace amounts in the majority of the MHB samples may be accounted for by degradation of organic phosphorus and potassium – containing compounds either related to the samples or the depositional environment.

Table 6.16. Melkhoutboom: Elemental composition of a selection of MHB adhesive samples.

Sample No.	Elemental Composition ¹ (Atomic %)		
	Major	Minor	Trace
MHB01	O (66.49) C (26.60)	Si (5.84) Al (1.06)	
MHB03	O (66.60) C (33.27)		Na (0.42)
MHB05	O (66.52) C (33.03)		Na (0.14) Si (0.01) Ca (0.09) Mg (0.06) K (0.05)
MHB08	O (66.54) C (33.12)		Na (0.15) Mg (0.09) Al (0.07) Ca (0.04)
MHB16	O (65.38) C (30.87)	Mn (1.10)	Ca (0.58) K (0.47) Si (0.41) Na (0.38) Mg (0.34) Al (0.18) Cl (0.18) Fe (0.11)
MHB18	O (65.96) C (29.34)	Si (2.42)	Al (0.72) Ca (0.71) Mg (0.33) K (0.25) Na (0.2) P (0.04) Cl (0.04)
MHB20	O (65.14) C (29.13)	Ca (2.95)	Si (0.9) Mg (0.52) Na (0.47) Al (0.31) P (0.31) K (0.28)
MHB22	O (66.48) C (32.96)		Si (0.15) K (0.12) Cl (0.1) Ca (0.09) Al (0.05) Mg (0.04) Na (0.03)
MHB38	O (65.65) C (31.09)	Ca (1.89)	Si (0.47) Na (0.34) K (0.18) Cl (0.13) Mg (0.12) Al (0.09) P (0.02) S (0.02)
MHB56	O (65.63) C (31.18)		Ca (0.89) Mg (0.47) K (0.45) Si (0.43) Na (0.41) Cl (0.23) Al (0.18) P (0.06) S (0.06)
MHB70	O (66.59) C (33.26)		Na (0.15)
MHB77	O (66.4) C (32.81)		Na (0.24) Si (0.12) K (0.12) Ca (0.12) Al (0.10) Mg (0.09)

¹ Qualitative analyses, and the terms major, minor, and trace components are subjective. Major is defined at more than 10 atomic%; minor as 1-10 atomic %; and, trace at less than 1 atomic%. These terms are defined in Goldstein *et al.* (2003)

6.3.1.3. Pyrolysis –Gas Chromatography/ Mass Spectrometry (py-GC/MS)

Py-GC/MS analysis was undertaken on ten solid samples from Melkhoutboom. This includes four Type 1A adhesive residues (MHB03, MHB05, MHB08, and MHB70), four Type 1B residues (MHB16, MHB18, MHB22, MHB77), as well as one Type 1C (MHB01) and one mixture of Type 2 and Type 1A (MHB38).

Table 6.17. Melkhoutboom: A summary of the results obtained by py-GC/MS analysis for a selection of Type 1, and mixed Type 1/2 residues from MHB.

Lab No.	Artefact No. (Unit)	Sample Amount	Main Identified Constituents	Additional Constituents
MHB01	Scraper 69/151 (W)	126 µg	-phenolic diterpenoids -conifer pitch	-polycyclic aromatic hydrocarbons -Cholesta-3,5-diene-7-one
MHB03	Scraper 69/93 (MB)	195 µg	-phenolic diterpenoids -conifer pitch	-aromatics related to pyrolysis -short chain dicarboxylic acids
MHB05	Scraper 69/107a (MB)	219 µg	-phenolic diterpenoids -conifer pitch	-aromatics related to pyrolysis
MHB08	Scraper 69/107b (MB)	195 µg	-phenolic diterpenoids -conifer pitch	-animal fat
MHB16	Scraper 69/150 L (W)	209 µg	-phenolic diterpenoids -oleanane triterpenoid	-polycyclic aromatic hydrocarbons
MHB18	Adze 69/75 (CAF)	228 µg	-phenolic diterpenoids -oleanane triterpenoid	-polycyclic aromatic hydrocarbons
MHB22	Adze 69/42L (OMB)	203 µg	- phenolic diterpenoids -conifer pitch -oleanane triterpenoid	-aromatics related to plant pyrolysis -polycyclic aromatic hydrocarbons
MHB38	Borer 69/100 (M)	146 µg	-phenolic diterpenoids -possible pitch	-animal fat
MHB70	Scraper 69/134 (MB)	219 µg	-phenolic diterpenoids -conifer pitch	-animal fat -aromatics related to plant pyrolysis
MHB77	Adze 69/48	409 µg	-phenolic diterpenoids -oleanane triterpenoid	-polycyclic aromatic hydrocarbons -diisooctyl phthalate

A summary of the components identified in each analysed sample is provided in Table 6.17.

Generally, the total ion current pyrograms can be clustered into two main groups based on the relative overall abundance yields. The first group, consisting of Type 1A and Type 1C adhesive

residues, had a higher relative abundance of pyrolysis products, while the second group, which includes Type 1B and mixed Type1A/Type 2 adhesives, had lower yields. These differences in relative abundance may either be attributed to overall lesser amounts of organics in the measured analysed material or the interaction between organic and inorganic materials, inhibiting derivatization yields (Bonaduce and Andreotti, 2009). This hypothesis may be supported by the presence of both silicates and carbonates in the IR spectra of MHB16, MHB18, MHB22, and MHB38 (Table 6.14, Table 6.15).

Type 1A & Type 1C

Figure 6.9 and the accompanying Table 6.18 highlight the constituents of a Type 1A adhesive residue, and the only Type 1C sample. All sampled material yielded series of saturated (C_6 to C_{22} chains) and unsaturated monocarboxylic fatty acids (C_6 to C_{18} chains) as well as a series of n-alkanes and n-alkenes (C_{11} to C_{31}). Fatty acids were identified based on the extracted ion m/z 117 and the combination of the M^+ and $[M-15]^+$ mass peaks. The n-alkanes and n-alkenes were confirmed by extracting the ions m/z 85 and m/z 83, respectively, alongside the presence of m/z decreasing in abundance every 14 mass units. The presence and carbon chain ranges of these constituents are similar to those ranges found in analysed archaeological birch bark tar and pitch (Ribechini *et al.* 2011), and is consistent with this manufactured product. The appearance of n-alkanes and n-alkenes is related to the breakdown of the macromolecule suberan, while the unsaturated monocarboxylic fatty acids are associated with breakdown by pyrolysis of the polymerised lipid, suberin (Tegelaar *et al.* 1995; Hamer *et al.* 2012). Ribechini *et al.* (2011) discussed the discrepancies in ranges of molecule sizes between modern reference material and archaeological samples, reflecting possible differences in the woody species to produce the tar and manner of production, as well as post-depositional alteration. The presence of pitch material is then confirmed by

identifying the presence of ω - hydroxycarboxylic and α,ω - dicarboxylic acids by GC/MS analysis in Section 6.3.1.4. (as discussed by Hamer *et al.* [2012] and Villa *et al.* [2012]).

The additional presence of aromatic phenols identified as pyrolysis products in plant material (Tamburi *et al.* 2014) further supports the evidence for a plant sourced in these analysed specimens. Several phenolic diterpenoids (i.e. totarol and semperviol) as well as their ketone derivatives (i.e. sugiol, totarol-7-one, and other related isomers), which are likely the result of oxidation, were identified. These components are consistent with the presence of an exudate derived from conifers, likely from the family Podocarpaceae (Cox *et al.*, 2007; Charri -Duhaut *et al.*, 2013; Villa *et al.*, 2012; Otto and Wilde, 2001). The presence of polycyclic aromatic hydrocarbons (pyrene and phenanthrene) may indicate that this material was associated with wood smoke (Khalili *et al.* 1995), and may further support the presence of a wood pitch product.

Saturated branched chain pentadecanoic and heptadecanoic acids are interpreted as being derived from a bacterial source (Corr *et al.*, 2008; Kedrowski *et al.*, 2009).

Type 1B & Mixed Type 1A& Type 2

The Type 1B and mixed Type 1A/2 samples (Figure 6.9) yielded similar components to the Type 1A and 1C material, including a series of saturated (C_6 - C_{16}) and unsaturated (C_8 - C_{16}) monocarboxylic fatty acids, a series of n-alkanes (C_{11} - C_{31}) and n-alkenes (C_{11} - C_{31}), polycyclic aromatic hydrocarbons, phenolic diterpenoids and associated oxidation products, and oleanane series triterpenoids. MHB77 yielded a notably smaller and relatively incomplete range of saturated and unsaturated monocarboxylic fatty acids, while MHB16 and MHB18 were lacking in unsaturated fatty acids. This absence was also the case for MHB38. With this in mind, although there was a prevalence of n-alkane and n-alkenes in all samples, only MHB22 and MHB77 are interpreted as having sufficient evidence of components related to a plant pitch.

Table 6.18. Melkhoutboom: Main pyrolysis products of the MHB specimens in Figure 6.9. No. refers to the peak numbers in figures

No.	Compound	No.	Compound	No.	Compound
<i>Monocarboxylic fatty acids and hydrocarbons</i>		31	1-octadecene	<i>Branched chain monocarboxylic fatty acids</i>	
1	hexenoic acid, TMS	32	octadecane	62	C15 branched unsaturated FAs, TMS
2	hexanoic acid, TMS	33	tetradecenoic acid, TMS	63	C17 branched unsaturated FAs, TMS
3	1-undecene	34	tetradecanoic acid, TMS	<i>Alcohols</i>	
4	undecane	35	1-nonadecene	64	1-docosanol, TMS
5	heptenoic acid, TMS	36	nonadecane	65	1-tetracosanol, TMS
6	heptanoic acid, TMS	37	pentadecenoic acid, TMS	66	glycerol, TMS
7	1-dodecene	38	pentadecanoic acid, TMS	<i>Polycyclic aromatic hydrocarbons</i>	
8	dodecane	39	1-eicosene	67	pyrene
9	octenoic acid, TMS	40	eicosane	68	phenanthrene
10	octanoic acid, TMS	41	hexadecenoic acid, TMS	<i>Terpenoids</i>	
11	1-tridecene	42	hexadecanoic acid, TMS	69	totarol, TMS
12	tridecane	43	1-heneicosene	70	unidentified ketone, first found in <i>Afrocarpus falcatus</i>
13	nonenoic acid, TMS	44	heneicosane	71	sugiol, TMS
14	nonanoic acid, TMS	45	heptadecenoic acid, TMS	72	ferruginol, TMS
15	1-tetradecene	46	heptadecanoic acid, TMS	73	2,3 - dehydroferruginol, TMS
16	tetradecane	47	1-docosene	74	oleanene triterpenoid
17	decenoic acid, TMS	48	docosane	75	Cholesta-3,5-dien-7-one
18	decanoic acid, TMS	49	octadecenoic acid, TMS	<i>Dicarboxylic fatty acids</i>	
19	1-pentadecene	50	octadecanoic acid TMS	76	heptanedioic acid, 2TMS
20	pentadecane	51	1-tricosene	77	octanedioic acid, 2TMS
21	undecenoic acid, TMS	52	tricosane	78	nonanedioic acid, 2TMS
22	undecanoic acid, TMS	53	1-tetracosene	<i>Phenols</i>	
23	1-hexadecene	54	tetracosane	79	hydroquinone, TMS
24	hexadecane	55	pentacosane	80	4-hydroxybenzoic acid, 2TMS
25	dodecenoic acid, TMS	56	hexacosane	81	vanillic acid, TMS
26	dodecanoic acid, TMS	57	heptacosane		
27	1-heptadecene	58	octacosane		
28	heptadecane	59	nonacosane		
29	tridecenoic acid, TMS	60	triacontane		
30	tridecanoic acid, TMS	61	hentriacontane		

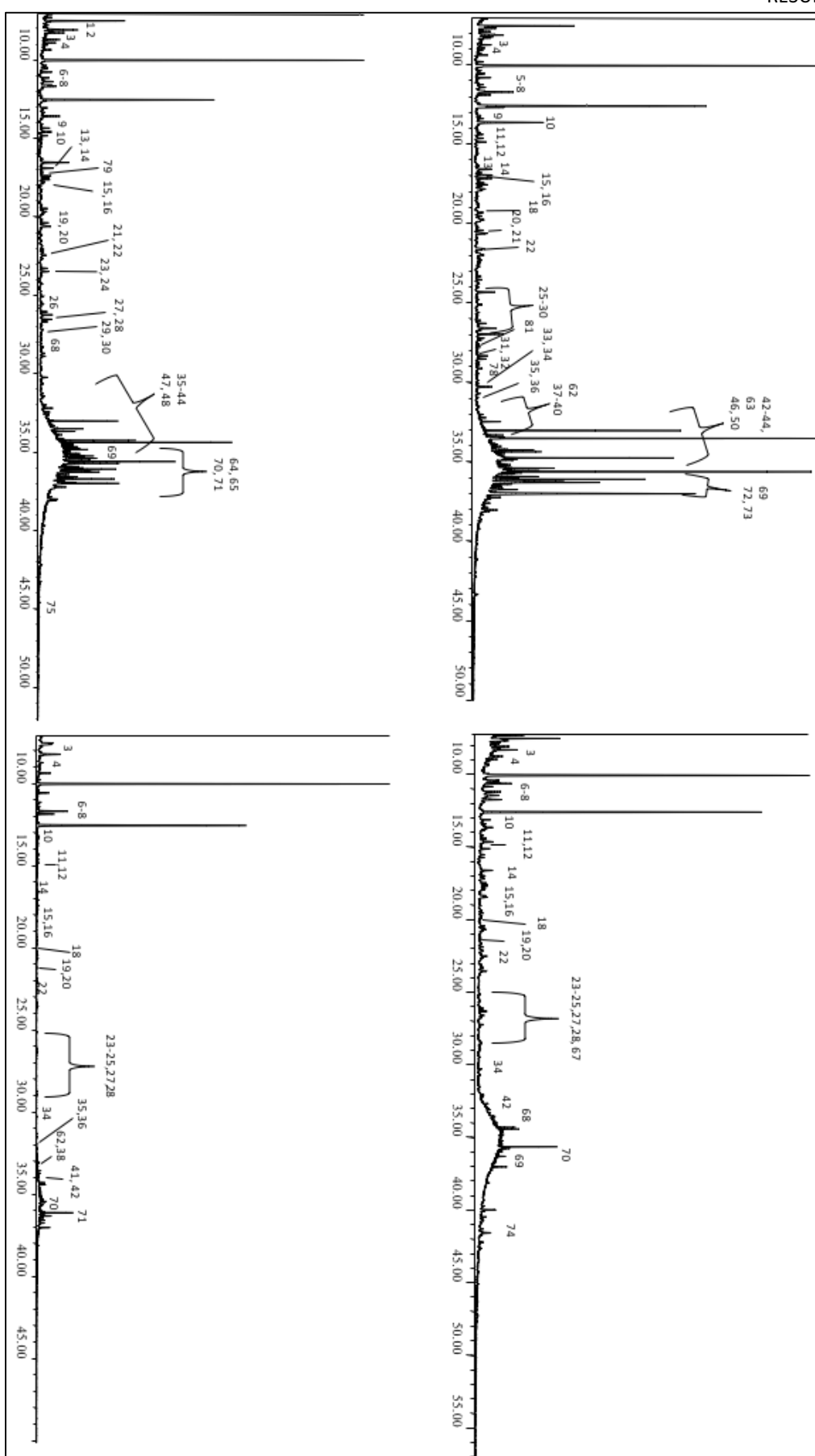


Figure 6.9. Pyrograms of the four adhesive residue types from Melkhoutboom. Top left: MHB08, Type 1A. Top right: MHB18, Type 1B. Bottom left: MHB01, Type 1C. Bottom right: MHB38, Mixed Type 1A/ Type 2.

The diterpenoid components from these samples are consistent with those listed in the Type 1A and 1C specimens, including the totarol, ferruginol, sugiol, and other totarol-derived ketones. Similarly, pyrene and phenanthrene were also identified in all Type 1B material. In MHB77, MHB22 and MHB18, there was also trace evidence of a possible triterpenoid component with prominent fragments at m/z 189, 203, and 218. The main peaks are consistent with members of the oleanane series of triterpenoids (Mathe *et al.* 2004) and may be indicative of a second exudate source being present in these residues. However, these triterpenoids are ubiquitous a number of southern African exudates sourced from members of the Euphorbaceae, Celastraceae, Amyrillidaceae, and Iridaceae families. Further analyses by GC/MS with comparison to reference triterpenoid containing plant material is thus necessary. In terms of contributions from animal-derived sources, MHB38 yielded C_{15} saturated monocarboxylic fatty acid, which may indicate the presence animal fats (Colombini and Modugno, 2009).

6.3.1.4. Gas Chromatography/ Mass Spectrometry (GC/MS)

Residue samples, obtained from swabs or solid material from 23 of the 36 tools, were analysed by GC/MS to ascertain the origin of each type of trace. In terms of sample sources, 15 of these specimens are solid fragments of adhesive residues, while the remainder are adhesives sampled with cotton swabs (Table 6.19). A summary of the components identified in the total ion current (TICs) chromatograms of each analysed sample is found in Table 6.21. The molecular constituents were identifiable in all residue types, except for the mixed residue from MHB38, the Type 1A residue, MHB34, and the Type 1B residue, MHB62.

A note on the constituents of swabs

There were several compound classes identified in the samples acquired by swabbing the tool surface that are associated with the cotton swabs themselves. Table 6.19 highlights the compounds identified in the eight swab samples. Triterpenoids and sterols appeared in all TICs. Birkemeyer *et al.* (2016) note that sterols included sitosterol, phytosterol and campesterol, as well as plant triterpenoids, especially those with an ursane skeleton can still be identified on swab blanks after a solvent pre-cleaning. This assessment was consistent with analysed material.

The analysis of the swabs from the MHB specimens also highlights the presence of a series of saturated monocarboxylic fatty acids between C₉ to C₂₅ and occasionally up to C₂₈, alongside the combined presence of C_{18:0}, C_{18:1}, and C_{18:2} monocarboxylic fatty acids. Additionally, swabs also contained even-numbered long chain alcohols (even numbered between C₁₈-C₃₀) and even-numbered long chain diols (C₂₀-C₂₄). These molecule classes are either absent in their entirety, or the range of chain lengths, especially fatty acids, is narrower in the samples of solid archaeological material. As such, a degree of caution was maintained in the interpretation of the swabbed material.

Table 6.19. Components identified in swab samples from Melkhoutboom.

Lab No.	Compounds Identified
MHB28	<ul style="list-style-type: none"> - Triterpenoids - Sterols (cholesterol, a related ketone derivative, and sitosterol) - Long chain alcohols ($C_{22} - C_{30}$)
MHB34	<ul style="list-style-type: none"> - Triterpenoids - Sterols (cholesterol, sitosterol) - Long chain alcohols ($C_{22} - C_{30}$)
MHB46	<ul style="list-style-type: none"> - Triterpenoids - Sterols (cholesterol, and a related ketone derivative) - Long chain alcohols ($C_{22} - C_{28}$)
MHB48	<ul style="list-style-type: none"> - 1,3, Ergost-5-ene, TMS - Sterols (cholesterol and sitosterol) - Long chain alcohols (even number only, $C_{22} - C_{30}$) - Monocarboxylic fatty acids, saturated ($C_8, C_9, C_{13}, C_{14}, C_{16} - C_{28}$) and unsaturated ($C_{18:1}$ and $C_{18:2}$) - Long chain diols (even numbered, $C_{20} - C_{24}$)
MHB50	<ul style="list-style-type: none"> - Triterpenoids - Sitosterol - Squalene - Monocarboxylic fatty acids, saturated ($C_9, C_{11}, C_{12}, C_{14}, C_{16} - C_{20}, C_{22}$) and unsaturated ($C_{16:1}, C_{18:1}$) - Long chain alcohols (even number only C_{22}, C_{24})
MHB54	<ul style="list-style-type: none"> - Triterpenoids - Cholesterol - Long chain alcohols (even number only C_{22}, C_{24}, C_{28}) - Squalene - Monocarboxylic fatty acids, saturated ($C_9, C_{11} - C_{19}, C_{22}$) and unsaturated ($C_{18:1}$ and $C_{18:2}$)
MHB62	<ul style="list-style-type: none"> - Triterpenoids - Sterols (cholesterol, a related ketone derivative, and sitosterol) - Squalene - Long chain alcohols (even number only C_{22}, C_{24}, C_{28}) - Monocarboxylic fatty acids, saturated ($C_9, C_{11}, C_{12}, C_{14}, C_{16} - C_{20}, C_{22}$) and unsaturated ($C_{18:1}$)
MHB67	<ul style="list-style-type: none"> - Triterpenoids - Long chain alcohols (even number only $C_{18}, C_{22}, C_{24}, C_{28}, C_{30}$) - Monocarboxylic fatty acids, saturated ($C_8, C_9, C_{13}, C_{14}, C_{16} - C_{20}, C_{22}$) and unsaturated ($C_{18:1}$ and $C_{18:2}$)

Type 1A residue samples

Nine Type 1A samples were analysed, with all but one (MHB34) yielding significant markers (Table 6.21). Two notable plant-derived compound classes were identified in this material. The first was a series of ω - hydroxycarboxylic ($C_{16} - C_{22}$) and α,ω - dicarboxylic acids ($C_{16} - C_{22}$) acids found in MHB03, MHB05, MHB08, MHB10, MHB33, and MHB70. These constituents were compared to

experimentally-made pitch sourced from South African conifers of the Cupressaceae and Podocarpaceae families. Overall, the modern pitch material yielded the same series of linear ω -hydroxycarboxylic and α,ω -dicarboxylic acids (ranging from C₁₆ to C₂₂) and a range of unsaturated ω -hydroxycarboxylic acids. These components are associated with the break-down of the lipid suberin, which, while remaining largely intact during the pitch production process, is broken down by alkaline hydrolysis during the sample preparation for GC-MS analysis (Ribechini, 2006). The presence of these same components in the archaeological material is consistent with both the modern pitch materials analysed and the constituents of birch bark tar, pine pitch, and *Podocarpus* sp. pitch identified in other archaeological materials (Ribechini 2006; Lucquin *et al.* 2007; Villa *et al.* 2012; Charri -Duhaut *et al.* 2013).

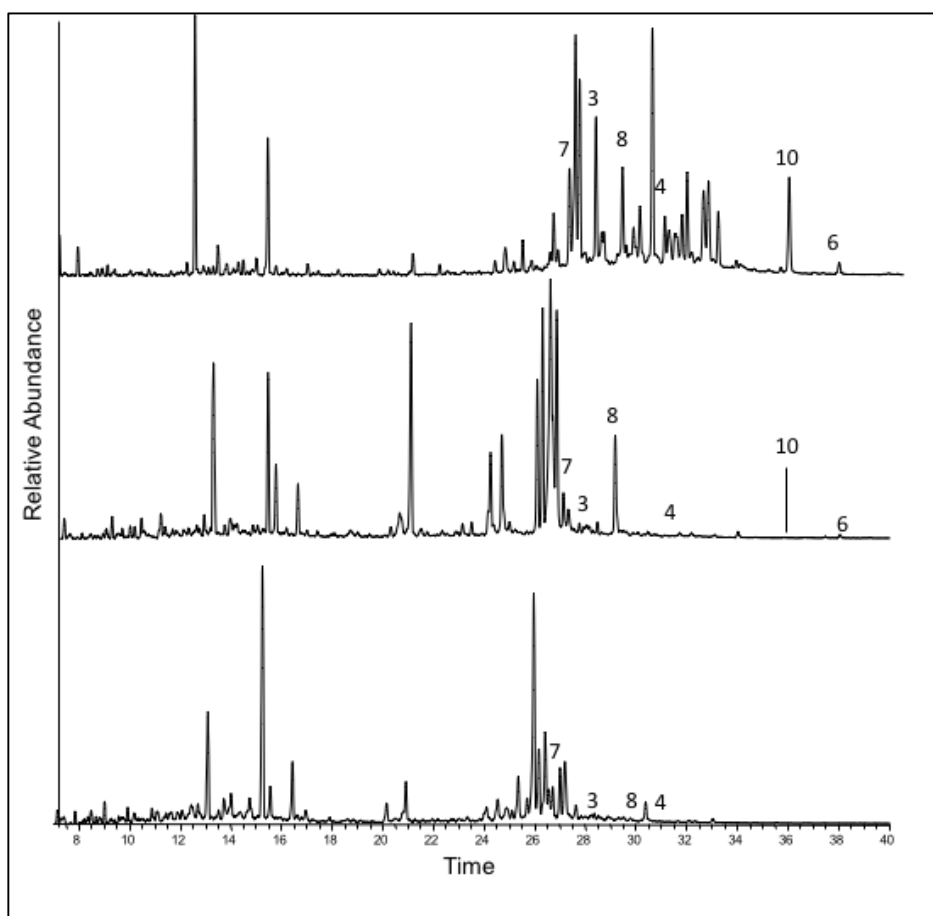


Figure 6.10. Melkhoutboom: Total ion chromatograms of the acidic fractions of MHB70 (top), *Afrocarpus falcatus* pitch (middle), and *Widdringtonia cedarbergensis* pitch (bottom) highlighting the mid- and long- chain hydroxy- and dicarboxylic constituents of each. Compound numbers refers to components in Table 6.20.

A number of diterpenoids were also present, notably phenolic diterpenoids and associated derivatives with points of unsaturation or hydroxyl, ketone and carboxylic acid functional groups (Figure 6.11). These may be divided into taxa-specific and non-specific components. One sample, MHB28, yielded silylated totarol and sugiol. Silylated totarol and sempervirol, alongside dehdrytotarol or dehydrosempervirol and 2,3-dehydroferruginol, were found in four samples (MHB03, MHB05, MHB08, and MHB10). These compounds are found in analysed reference material from the Cupressaceae and Podocarpaceae families, and are not specific to either taxa (Cox *et al.* 2007). Derivatives with a ketone, however, appeared most frequently among the analysed material, with sugiol being the most readily recognisable constituent. The prevalence of ketones derived from the phenolic structures totarol, sempervirol, and ferruginol is consistent with previously published analyses of compounds extracted from members of the Podocarpaceae family (Cox *et al.* 2007; Charri -Duhaut *et al.*, 2013, 2016). Sugiol is not taxon-specific, however, two other ketones, one with a prominent peak m/z 261 and the other at m/z 275, are found only in *Podocarpus elongatus* and *Afrocarpus falcatus* pitch and wood extracts. The position of the ketone functional group and the type of base structure could not be identified due to the structural similarities between totarol and sempervirol.

Table 6.20. Identified compounds in the MHB and reference conifer samples.

No.	Compound	No.	Compound
<i>α, ω - dicarboxylic fatty acids</i>		<i>phenols</i>	
1	nonadioic acid, 2TMS	18	4-hydroxybenzoic acid, 2TMS
2	decanedioic acid, 2TMS	19	vanillic acid, TMS
3	hexadecanedioic acid, 2TMS	20	syringic acid, TMS
4	octadecanedioic acid, 2TMS	21	unknown cinnamate #1, TMS
5	eicosanedioic acid, 2TMS	22	ferulic acid, TMS
6	dodecanedioic acid, 2TMS	<i>abietane diterpenoids</i>	
<i>ω hydroxy-monocarboxylic fatty acids</i>		23	DHA, TMS
7	15-hydroxyhexadecanoic acid, 2TMS	24	7-oxo-DHA, TMS
	17-hydroxyoctadecanoic acid, 2TMS	25	abietic acid, TMS
8	19-hydroxyeicosanoic acid, 2TMS	<i>phenolic diterpenoids</i>	
9	21-hydroxydocosanoic acid, TMS	26	totarol, TMS
<i>monocarboxylic fatty acids</i>		27	sempervirol, TMS
11	tridecanoic acid, TMS	28	sugiol, TMS
12	tetradecanoic acid, TMS	29	ketone, m/z 261
13	pentadecanoic acid, TMS	30	ketone, m/z 275
14	hexadecanoic acid, TMS	31	unidentified compound, m/z 362, 429, 444, 387, 401, 347
15	heptadecanoic acid, TMS		
16	octadecanoic acid TMS		
17	eicosanoic acid, TMS		

Trace amounts of 4-carboxynortotarol was found in MHB10. It was identified by mass spectrometry thanks to a prominent peak at m/z 327 associated with $[M-15-118]^+$ ion fragmentation (Charrié-Duhaut *et al.* 2016). This compound was found only the in pitch and wood extracts from *Podocarpus elongatus*, *Podocarpus henkelii*, *Podocarpus latifolius*, and *Afrocarpus falcatus*. An unidentified compound with a mass spectrum containing peaks at m/z 362 (relative abundance, 100), 429 (57), 444 (50), was found in MHB03, MHB05, MHB08, MHB33, and MHB70. This compound was also found in *Podocarpus elongatus*, *Podocarpus latifolius*, and *Afrocarpus falcatus*, and thus narrows down the source of the plant material. Based on the available markers, MHB03, MHB05, MHB08, MHB10, MHB33, and MHB70, are composed of pitch exudates from two possible species; both *Podocarpus elongatus* and *Afrocarpus falcatus* yielded a taxa-specific combination of ketones with base peaks at m/z 261 and 275 and an unidentified compound (base peak at m/z 362). MHB50 and MHB28 are lacking both pitch and taxon-specific diterpenoid markers, however, since both have the ketone derivatives sugiol and trace of another unidentified ketone, it is probable that they are also derived from members of the Podocarpaceae family.

One sample, MHB48, yielded dehydroabietic acid and α,ω - dicarboxylic acids and ω -hydroxycarboxylic acids. This was interpreted as being derived from a pitch manufactured from a species outside the family Podocarpaceae. This sample is closely related to three Type 1B specimens; the additional taxonomic interpretations are highlighted instead in the section below.

Branched-chain C_{15} and C_{17} chain monocarboxylic fatty acids were identified in MHB08 and are likely derived from a bacterial source (Corr *et al.*, 2008). The saturated, unbranched C_{15} and C_{17} fatty acids may however be sourced from animal-derived fats (Colombini and Modugno, 2009).

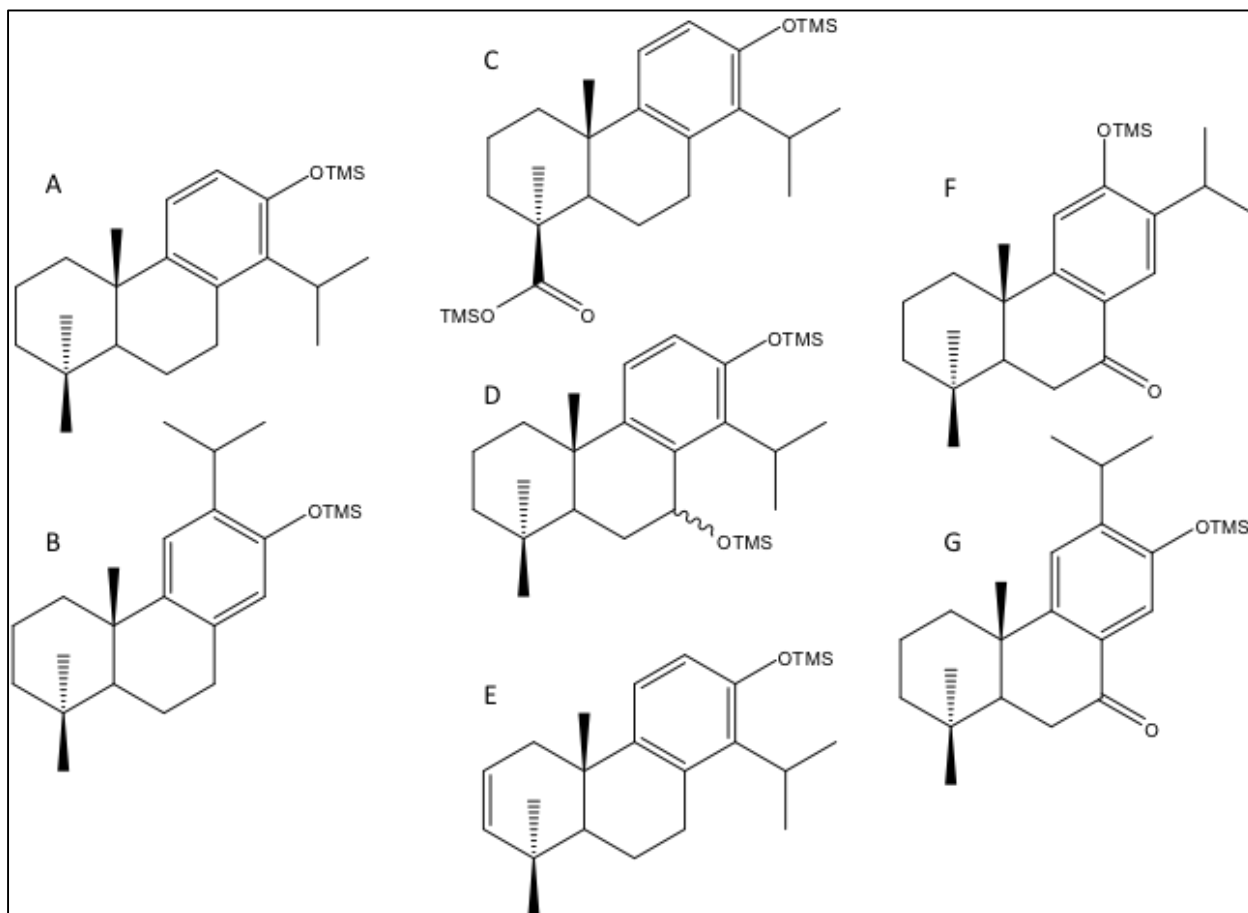


Figure 6.11. Phenolic diterpenoids and derived structures with known nomenclature identified in the MHB adhesive samples and reference collections from the Podocarpaceae family. A) Totarol-TMS. B) Semperviol-TMS. C) 4-carboxynortotarol-TMS. D) 7-hydroxytotarol-TMS. E) 2,3 – dehydrototarol – TMS. F) Sugiol-TMS. G) Totarol-7-one-TMS. TMS is the abbreviation of trimethylsilyl-

Type 1B residue samples

The Type 1B residues are notable in the breadth of terpenoids present in the analysed materials (Table 6.21). This includes monoterpenoids, diterpenoids, and triterpenoids. Markers associated with pitch production are also present in members of this group.

MHB13 and MHB18 both yielded the monoterpene camphene. This compound was only identified in extracts from *Podocarpus latifolius* wood. The presence of ω -hydroxycarboxylic (C_{16} only) and α,ω -dicarboxylic acids (C_{16} and C_{18} in MHB13) suggests that a bark pitch from this species may have been the source.

MHB16, MHB46, and MHB48 yielded only phenolic diterpenoid compounds. In MHB16, totarol, sugiol, an unidentified ketone related to sugiol, as well as an unidentified compound found in members of the Podocarpaceae family (possibly a dehydro-hydroxy-phenolic diterpenoid) was found in conjunction with the markers for pitch. This combination of compounds was identified in three species, *Podocarpus latifolius*, *Podocarpus elongatus*, and *Afrocarpus falcatus*. Only trace amounts of sugiol and an unidentified ketone were found in MHB48 and MHB46. The predominance of sugiol in all the analysed reference conifers from *Podocarpus* sp., *Afrocarpus* sp., *Widdringtonia* sp., and *Juniperus* sp. signifies that no particular taxonomic source can be determined.

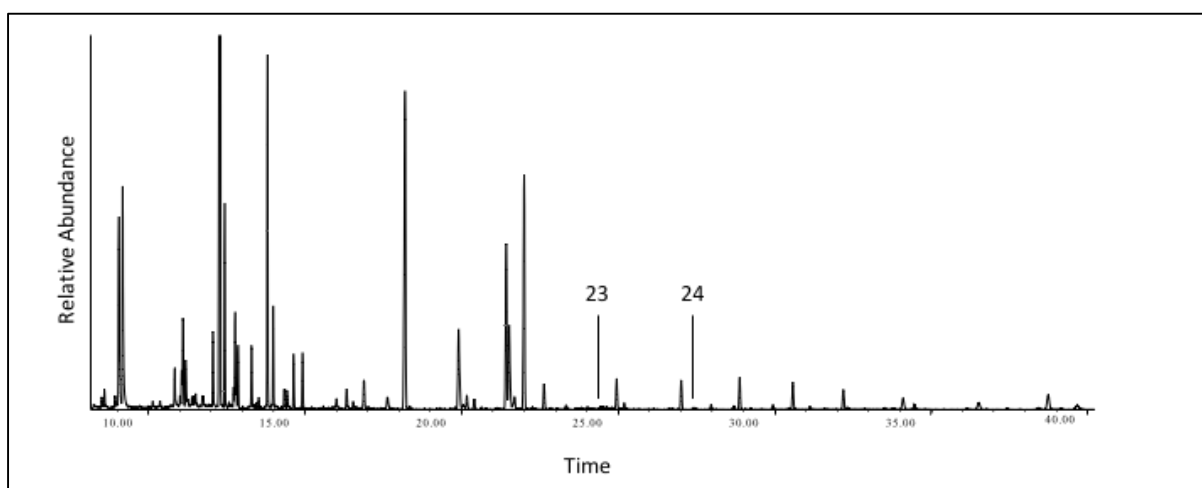


Figure 6.12. Melkhoutboom: Total ion chromatogram of the acidic fraction of MHB67, highlighting the abietane structures DHA (#23) and 7-oxo-DHA (#24) in low relative abundance. Compound numbers refer to Table 6.20.

Three samples (MHB32, MHB67, and MHB77) contained structural modification of abietic acid, notably dehydroabietic acid or DHA (found in all; #23 in Figure 6.12) and 7-oxo-DHA (MHB67 only; #24 in Figure 6.12). DHA and 7-oxo-DHA are common degradation products of abietic acid identified in conifer resins (Ribechini, 2006). Abietic acid was identified in the TICs from four southern African conifer references: *Podocarpus henkelii*, *Juniperus procera*, *Widdringtonia cederbergensis*, and *W. cuppresoides* (syn. *W. nodiflora*). Based on the current known geographic distributions of the aforementioned species the only likely candidate as the source for these

components would be *W. cuppresoides*, whose native distribution extends to the Eastern Cape Province (Coates Palgrave, 1977). The absence of sugiol in analysed members of the *Widdringtonia* genus, and the archaeological specimens MHB77 and MHB67 also supports this identification. MHB32, in contrast, yielded several derivative of phenolic diterpenoids, including sugiol, trace 7-hydroxytatarol (Figure 6.11), and an unidentified compound found in members of the *Podocarpaceae* family (possibly a dehydro-hydroxy-phenolic diterpenoid). Alongside these compounds, ω -hydroxycarboxylic (C_{16} , C_{18} , and C_{22}) and α,ω -dicarboxylic acids (C_{16} and C_{22}) were found in MHB77, indicating that in the case of this specimen, the material was a bark pitch. MHB32 also had ω -hydroxycarboxylic (C_{16} , C_{18} , and C_{22}) acids, which may also indicate that this adhesive was a manufactured pitch. No such components were found in MHB67.

The triterpenoids identified in the Py-GC/MS analysis of the Type 1B samples MHB77, MHB22, and MHB18 (all solid samples), were absent in the GC/MS analysis of the same samples. It is not inconceivable an additional plant source for these Type 1B adhesive residues cannot be excluded. MHB22 is notable in its complete absence of terpenoids. However, it does contain the markers associated with pitch production, alongside prominent short-chain dicarboxylic fatty acids between C_8 to C_{12} . It may thus be inferred that the adhesive from this specimen is derived from a bark pitch, however, its source is unknown.

Animal-derived compounds were identified in two Type 1B samples, MHB67 and MHB13. This assessment was made based on the presence of C_{15} and C_{17} monocarboxylic fatty acids (Colombini and Modugno, 2009); branched-chain of these fatty acids were also found, but are likely the result of bacterial action (Corr *et al.*, 2008).

Type 1C residue samples

MHB01 was the only Type 1C specimen from the analysed selection. In composition, it is similar to the other organic residue types. Notable constituents in the acidic fraction included nonanedioic and decanedioic acids, C_{16:0}, C_{16:1}, C_{18:0}, and C_{18:1} fatty acids, aromatics such as ferulic acid, vanillic acid, and cinnamic acid, an unidentified compound found in members of the *Podocarpaceae* family (possibly a dehydro-hydroxy-phenolic diterpenoid), and likely C₁₆, C₁₈ and C₂₂ ω - hydroxycarboxylic and α -, ω - dicarboxylic acids. The neutral fraction contained totarol and modified derivatives like dehydrototarol, sugiol, and the unidentified ketone with a base peak at m/z 275. As such, this combination of compounds is interpreted as originating from a bark pitch from the Podocarpaceae family with *Podocarpus elongatus* and *Afrocarpus falcatus* being the best matches.

Table 6.21. A summary of the main constituents identified in the TICs of the MHB samples.

Stratigraphic Context	Excavation No.	Lab No.	Residue Type	Typology	Main Components
OMB	69/42l	MHB22	Type 1B	Adze	- short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids
	69/48	MHB77	Type 1B	Adze	-abietane diterpenoids -short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids
	69/37	MHB28	Type 1A	Scraper	- phenolic diterpenoids (totaranes)
	69/30	MHB34	Type 1A	Segment	No identifiable components beyond swab constituents
CAFu	69/49	MHB56	Type 1B	Scraper	- mid-chain dicarboxylic acid
CAF	69/75	MHB18	Type 1B	Adze	- monoterpenes (champhene) - mid-chain hydroxyl-carboxylic acid
	69/61	MHB54	Type 1B	Adze	- triterpenoids -long chain saturated fatty acids, up to C ₂₈
MB	69/93	MHB03	Type 1A	Scraper	- phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - aromatics
	69/107a	MHB05	Type 1A	Scraper	- monoterpenes

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					<ul style="list-style-type: none"> - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - aromatics
	69/107b	MHB08	Type 1A	Scraper	<ul style="list-style-type: none"> - monoterpenes (champhene) (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - C₁₅ and C₁₇ branched chain monocarboxylic acids (animal fats)
	69/107c	MHB10	Type 1A	Scraper	<ul style="list-style-type: none"> - monoterpenes - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - aromatics
	69/132	MHB32	Type 1B	Segment	<ul style="list-style-type: none"> - monoterpenes - abietane diterpenoids - phenolic diterpenoids (totaranes) - abietane diterpenoids - mid to long chain hydroxy- carboxylic acids
	69/95s	MHB33	Type 1A	Segment	<ul style="list-style-type: none"> - monoterpenes - phenolic diterpenoids (totaranes) - mid chain dicarboxylic acids - mid chain hydroxy- carboxylic acids
	69/95l	MHB48	Type 1A	Segment	<ul style="list-style-type: none"> - abietane diterpenoids - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - sterols - long chain diols and alcohols, and a complete suit monocarboxylic fatty acids (C₈-C₃₀) (swab components)
	69/134	MHB50	Type 1A	Segment	<ul style="list-style-type: none"> - phenolic diterpenoids (totaranes)
	69/134	MHB70	Type 1A	Scraper	<ul style="list-style-type: none"> - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - aromatics
W	69/151	MHB01	Type 1C	Scraper	<ul style="list-style-type: none"> - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - aromatics - sterols
	69/150s	MHB13	Type 1B	Scraper	<ul style="list-style-type: none"> - monoterpenes (camphene) - C₁₅ branched and unbranched C₁₅ and C₁₇ chain monocarboxylic acids (animal fats) - short to mid chain dicarboxylic acids

	69/150I	MHB16	Type 1B	Scraper	- phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids
	69/238	MHB67	Type 1B	Segment	-abietane diterpenoids -short chain dicarboxylic acids -C ₁₅ and C ₁₇ straight and branched chain monocarboxylic acids (animal fats)
M	69/100	MHB38	Type 1A/4	Borer	No identifiable components.
	69/283	MHB46	Type 1B	Segment	- long chain alcohols - phenolic diterpenoids (totaranes) -sterols
	69/305	MHB62	Type 1B	Scraper	No identifiable components beyond swabs constituents

6.3.1.5. Interpretive Summary

A summary of all the results obtained from the multi-method analysis of the Melkhoutboom adhesive samples may be found in Table 6.22. The multiple lines of evidence suggest that the adhesives are either comprised of mixtures of organic materials and inorganic minerals (Type 1B) or dominantly organic materials (Type 1A; with a trace component of inorganics, i.e. in the case of the IR spectra of MHB70). FTIR and SEM/EDS analysis highlights the prevalence of inorganic minerals including silicates, carbonates, and manganese containing minerals in Type 1B adhesive residues. This may then be interpreted as the likely source of the compositional differences observed by microscopy between Type 1A and Type 1B material.

From an organic perspective, overall the IR spectra, and chromatography (GC/MS and Py-GC/MS) findings are consistent and highlight the presence of a plant-based source of adhesives, with animal fats a minor component in both Type 1A and 1B residues. The Py-GC/MS and GC/MS findings identified diterpenoids derived from southern African conifers and markers associated with the production of pitch. Phenolic diterpenoids with a totarane skeleton are identified in sampled material from the oldest through to the youngest analysed layers. These compounds

match best with *Afrocarpus falcatus*, *Podocarpus latifolius*, and *P. elongatus*, the former two found in the surrounding kloof of Melkhoutboom (Deacon, 1976). Abietane skeleton diterpenoids are identified from the second oldest (W) layer through to the youngest OMB layer, and represent a second botanical source. This source is most likely from *Widdringtonia cupressoides*, a conifer in the Cupressaceae family (Coates Palgrave, 1977; T. Dold, pers. comm.). Both totarane and abietane diterpenoid types appeared in conjunction with the markers from the manufacture of a bark pitch. This was identified in samples from the Wedge (W) layer through to the OMB layer. These markers are, however, absent in some samples, and when diterpenoids are present, was interpreted as indicative of a plant resin only. Triterpenoids were identified by Py-GC/MS in three solid samples, MHB77, MHB22, and MHB18, however, its source could not be identified. This does however indicate an additional exudate source for these samples.

Table 6.22. A summary of the results from the multi-method analysis at Melkhoutboom and the interpretation of the adhesive source for each specimen. Also included are details on stratigraphic context, ascribed tool typology and the raw material of the stone tool.

Stratigraphic Context	Excavation No.	Lab No.	Residue Type	Typology	Raw Material	Constituents (identified by py-GC/MS, GC/MS, IR, or SEM/EDS)	Interpreted Source
OMB	69/42l	MHB22	Type 1B	Adze	Silicified shale	<i>Organic</i> - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - triterpenoids (m/z 189, 203, 218) <i>Inorganic</i> - silicates - carbonates	<i>Organic</i> - pitch - exudate from an unknown source <i>Inorganic</i> - quartz - calcite
	69/48	MHB77	Type 1B	Adze	Silicified shale	<i>Organic</i> -abietane diterpenoids -short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - triterpenoids (m/z 189, 203, 218) <i>Inorganic</i> - silicates -carbonates	<i>Organic</i> - pitch, derived from <i>Widdringtonia cupressoides</i> - exudate from an unknown source <i>Inorganic</i> - quartz - calcite
	69/37	MHB28	Type 1A	Scraper	Chalcedony	<i>Organic</i> - phenolic diterpenoids (totaranes)	<i>Organic</i> - exudate from <i>Podocarpaceae</i> or <i>Cupressaceae</i> family
	69/30	MHB34	Type 1A	Segment	Chalcedony	No identifiable components beyond swab constituents	
CAFu	69/49	MHB56	Type 1B	Scraper	Silcrete?	<i>Organic</i> - mid-chain dicarboxylic acid <i>Inorganic</i> - silicates	<i>Organic</i> -possible pitch <i>Inorganic</i> - quartz

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						-carbonates	- calcite
CAF	69/75	MHB18	Type 1B	Adze	Silicified shale	<i>Organic</i> - monoterpenes (champhene) - mid-chain hydroxy-carboxylic acid - triterpenoids (m/z 189, 203, 218) <i>Inorganic</i> - silicates - carbonates	<i>Organic</i> -pitch, <i>Podocarpus latifolius</i> - plant exudate from an unknown source <i>Inorganic</i> - quartz - calcite
	69/61	MHB54	Type 1B	Adze	Silicified shale		No components identified that are associated with an adhesive
MB	69/93	MHB03	Type 1A	Scraper	Chalcedony	<i>Organic</i> - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - aromatics	<i>Organic</i> - plant pitch, derived from <i>Podocarpus elongatus</i> or <i>Afrocarpus falcatus</i>
	69/107a	MHB05	Type 1A	Scraper	Chalcedony	<i>Organic</i> - monoterpenes - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - aromatics phenols	<i>Organic</i> - plant pitch, derived from <i>Podocarpus elongatus</i> or <i>Afrocarpus falcatus</i>
	69/107b	MHB08	Type 1A	Scraper	Chalcedony	<i>Organic</i> - monoterpenes (champhene) - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids	<i>Organic</i> - plant pitch, derived from <i>Podocarpus elongatus</i> or <i>Afrocarpus falcatus</i> - animal fat

						- C ₁₅ and C ₁₇ branched chain monocarboxylic acids	
69/107c	MHB10	Type 1A	Scraper	Chalcedony	Organic	<ul style="list-style-type: none"> - monoterpenes - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - aromatic phenols 	Organic - plant pitch, derived from <i>Podocarpus elongatus</i> or <i>Afrocarpus falcatus</i>
69/132	MHB32	Type 1B	Segment	Chalcedony	Organic	<ul style="list-style-type: none"> - monoterpenes - abietane diterpenoids - phenolic diterpenoids (totaranes) - abietane diterpenoids - mid to long chain hydroxy- carboxylic acids 	Organic - plant pitch, derived from <i>Widdringtonia cupressoides</i> , and another species from the <i>Podocarpaceae</i> family
69/95s	MHB33	Type 1A	Segment	Quartzite	Organic	<ul style="list-style-type: none"> - monoterpenes - phenolic diterpenoids (totaranes) - mid chain dicarboxylic acids - mid chain hydroxy- carboxylic acids 	Organic - plant pitch, derived from the <i>Podocarpaceae</i> family
69/95l	MHB48	Type 1A	Segment	Quartzite	Organic	<ul style="list-style-type: none"> - abietane diterpenoids - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids 	Organic - plant pitch, derived from <i>Widdringtonia cupressoides</i>
69/134	MHB50	Type 1A	Segment	Chalcedony	Organic	<ul style="list-style-type: none"> - phenolic diterpenoids (totaranes) - polycyclic aromatic hydrocarbons (PAHs) 	Organic - exudate derived from a member of the <i>Podocarpaceae</i> or <i>Cupressaceae</i> family

							- wood smoke
	69/134	MHB70	Type 1A	Scraper	Chalcedony	<i>Organic</i> - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - aromatic phenols <i>Inorganic</i> - silicates, traces	<i>Organic</i> - plant pitch, derived from <i>Podocarpus elongatus</i> or <i>Afrocarpus falcatus</i> <i>Inorganic</i> - quartz
W	69/151	MHB01	Type 1C	Scraper	Quartz	<i>Organic</i> - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids - aromatics -sterols	<i>Organic</i> - plant pitch, derived from <i>Podocarpus elongatus</i> or <i>Afrocarpus falcatus</i>
	69/150s	MHB13	Type 1B	Scraper	Chalcedony	<i>Organic</i> - monoterpenes (camphene) - C ₁₅ branched and unbranched C ₁₅ and C ₁₇ chain monocarboxylic acids - short to mid chain dicarboxylic acids	<i>Organic</i> -pitch derived from <i>Podocarpus latifolius</i> - animal fat
	69/150l	MHB16	Type 1B	Scraper	Chalcedony	<i>Organic</i> - phenolic diterpenoids (totaranes) - short to long chain dicarboxylic acids - mid to long chain hydroxy- carboxylic acids <i>Inorganic</i> - manganese-containing mineral (identified by SEM/EDS)	<i>Organic</i> - pitch derived from a member of the <i>Podocarpaceae</i> or <i>Cupressaceae</i> family <i>Inorganic</i> - multiple sources, including manganese oxides and manganese dioxides

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	69/238	MHB67	Type 1B	Segment	Chalcedony	<i>Organic</i> -abietane diterpenoids -short chain dicarboxylic acids -C ₁₅ and C ₁₇ straight and branched chain monocarboxylic acids	<i>Organic</i> -pitch derived from <i>Widdrintonia cupressoides</i> - animal fat
M	69/100	MHB38	Type 1A/2	Borer	Chalcedony	<i>Organic</i> - C ₁₅ and C ₁₇ branched chain monocarboxylic acids	<i>Organic</i> - animal fat
	69/283	MHB46	Type 1B	Segment	Chalcedony	<i>Organic</i> - phenolic diterpenoids (totaranes)	<i>Organic</i> - exudate derived from a member of the <i>Podocarpaceae</i> or <i>Cupressaceae</i> family
	69/305	MHB62	Type 1B	Scraper	Chalcedony	No identifiable components beyond swabs constituents	

6.3.2. Results from Renbaan Cave

6.3.2.1. FTIR Spectroscopy

IR spectra were acquired for ten of the eleven samples, with only RB12 not producing sufficient amounts of material for analysis with the ATR accessory. The IR spectra results were grouped into three types: those derived from Type 1A adhesive residues; those from Type 3B; and, those derived from a combination of Type 1A and 3B (found in RB06_01 and RB06_02 only). The IR spectral results are thus subdivided based on these classifications and described in further detail below.

Type 1A residue samples

Four specimens were classified as having predominantly Type 1A adhesive residues, namely, RB07-09. The results from these IR spectra and the associated peak assignments are highlighted in Figure 6.13 and Table 6.23. The main constituents of these specimens were identified as being organic in origin, with RB01 also containing a prominent organic component. Again, this assessment was firstly based on the prevalence of –OH stretching, C-H stretching, and C=C stretching regions, similar to the Type 3B residues. However, the Type 1A material does show some differences in the number and prominence of peaks associated with the –OH functional groups of phenols and alcohols (Table 6.23).

Based on the interpreted peak assignments, a component of this sample originated from a plant. Notable compared to other analysed specimens, RB09 contained a C-H stretching peak at 2971 cm^{-1} , two peaks associated with the C=C stretches of aromatics, and several peaks attributed to the –OH groups of phenols or alcohols.

The additional C-H stretch may be attributed to methyl groups found in saturated aliphatics. The source of this, however, could not be determined. The predominance of the –OH

and aromatic functional groups are interpreted as the presence of phenolic compounds, possibly associated with humic substances or tannins. These may be sourced from plant materials, and are present as breakdown products in woody tissues (Deviese, 2009). This combination of C-H and –OH functional groups may also be derived from waxes, including beeswax (Liang and Scott, 2014), however, these spectra do not match the typical spectra of beeswax (Stacey *et al.*, 2018) and it should be noted that there are significant alterations of IR spectra of this material after heating (Regert *et al.*, 2001), which may to some degree account for these differences.

Table 6.23. IR peak assignments for mixed 1A adhesive samples from Renbaan Cave.

Assignment	Wavenumber (cm ⁻¹)		
	RB09	RB08	RB07
v(O-H)	Max. at 3364	3389	3351
v(C-H)	2971/2917/2849	2946/2921/2849	2971/2917/ 2849
v(C=C-C) of an aromatic ring	1619 / 1602	1633/1613	1602
v(C=C-C) of an aromatic ring	1463/1453	1453	1453
δ(C-H) deformation (saturated aliphatic groups) or γ(-CH ₃) bending	1372	1374	1372
γ (-OH), phenol or tertiary alcohol, or primary or secondary γ (-OH)	1361 / 1338/ 1259	1301/1259	1338/1316/1259
In-plane γ(C-H) of aromatics (one of several)	1207	1205	1207
v(C-O -C) of esters and alcohols	1185	X	X
v(C-O) of tertiary alcohols	1147	1147	1147
v(C-O) or v(Si-O)	1116/ 1089	1114/1087	1114/1087
Kaolin minerals	1025/shoulder	1029/1008	X
In-plane γ(C-H) of aromatic groups	X	958	950
Out-of-plane γ(C-H) of olefinic or aromatic groups or kaolin minerals	910	912	910
Carbonates	875	875	X
Out-of-plane γ(C-H), aromatic ring groups	825	829	827
Silicates	X	796/771/692	X
Out-of-plane γ(C-H) or γ(-OH)	726	726	723
Kaolins, Silicates, Iron oxides	536/470	526/466	516
Unassigned	769	X	773/ 420

Weaker signals of kaolin and carbonate minerals indicating the possible presence of these materials were also noted. These peaks are interpreted as likely the result of the depositional environment or carry-over from excavations, based on the lower abundance and lack of several confirmatory peaks. This view is further supported by the optical microscopy findings, which identified Type 1A as the main residue type, with Type 4 (likely inorganic) residues overlaying the former.

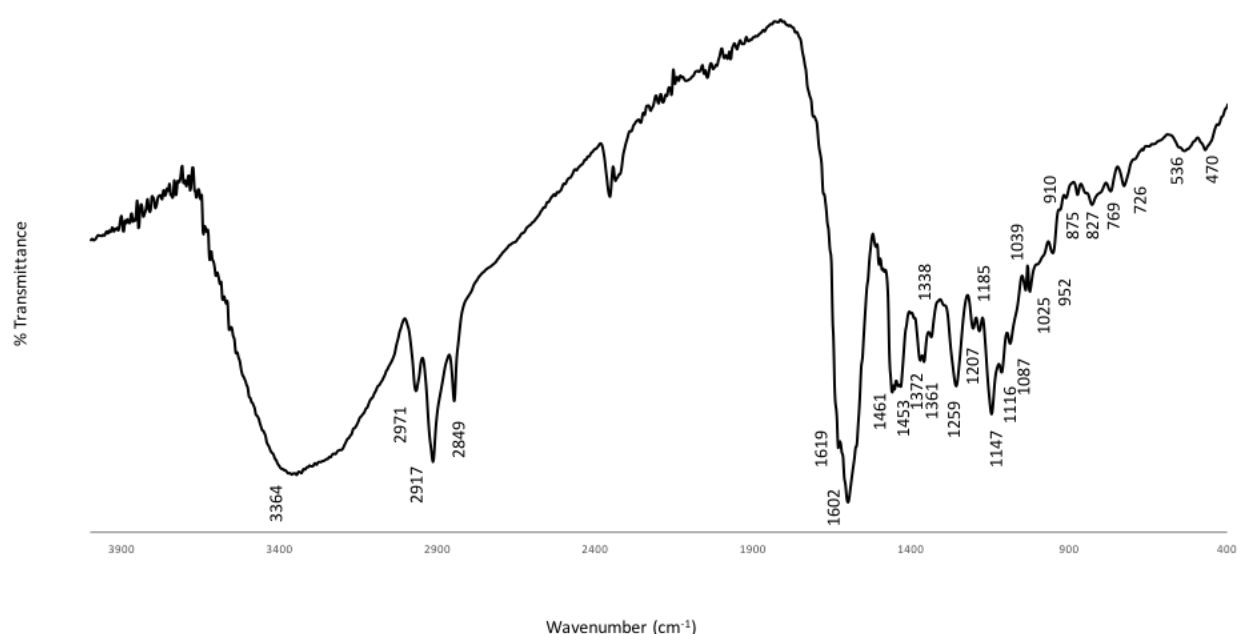


Figure 6.13. Renbaan Cave: FTIR spectra of RB09, a Type 1A adhesive.

Type 3B residue samples

The Type 3B residues identified show similar IR spectra and are interpreted as containing both organic and inorganic constituents (Table 6.24). Among those functional groups associated with organic constituents, all spectra demonstrate a broad and prominent –OH stretch spanning

between 3600-3000 cm^{-1} , two sharp C-H stretching peaks, and a broad peak with a maximum at 1555 cm^{-1} likely associated with carboxylic acid salts. Other identifiable group assignments include a C=O stretch around 1696 cm^{-1} (RB02) and 1694 cm^{-1} (RB03) associated with saturated aliphatic groups as well as $-\text{CH}_3$ bending at 1380 cm^{-1} in RB02 and RB05. These specimens also held bands associated with $-\text{OH}$ bending of phenols or alcohols, and a C-O-C stretching region. Furthermore, a peak at 1246 cm^{-1} in RB02 was attributed to the C-O stretch of alcohols and esters.

Table 6.24. Renbaan Cave: IR peak assignments for mixed 3B adhesive samples.

Assignment*	Wavenumber (cm^{-1})					
	RB01	RB02	RB03	RB05	RB10	RB11
v(O-H) inorganic (likely Al- OH)	3378	X	3730/3694		3686/3644/ /3615	3686/3644/ 3615
v(O-H)		Max. at 3372	Max. at 3343	Max. at 3372	Max. at 3374	Max. at 3347
v(C-H)	2917/2847	2917/2849	2915/2847	2917/2847	2817/2847	2915/2847
v(C=O)	X	X	X	X	X	X
carboxyl group	1644	1696	X	1694	X	X
v(C=C) stretch;	1571?	1644	1640	1644	X	X
v(C=C-C) of an aromatic ring	1453	X	X	X	X	X
Carboxylate anion	1413	1555	1557	1555	1555	1555
In-plane γ vinyl (C-H) of olefinic groups, or carbonate anion	1376	1415	1413	1413	1415	1415
δ (C-H) deformation (saturated aliphatic groups) or γ ($-\text{CH}_3$) bending	1376/1320	1380	X	1380	X	X
γ (-OH), phenol or tertiary alcohol, or primary or secondary γ (-OH)	1216	1322	X	1318	X	X
v(C-O) stretch of esters and alcohols	X	1247	X	X	X	X
v(C-O -C) of esters and alcohols		1183 (weak)	X	1195	X	X
v(C-O) or v(Si-O)	1164/1081	1162/1089/1039	1162	1164/1085	1160/1087	1162/1087
Kaolin minerals	1029/1008	1025/1002/912	1031/1012/912	1027/1008/912	1025/1002/910	1025/1000/910
In-plane γ (C-H) of aromatic groups	X	X	X	X	X	X

Out-of-plane γ (C-H) of olefinic or aromatic groups	913	X	X	X	931	935
Carbonates	875	875/715	873/711	873/713	875/711	875
Out-of-plane γ (C-H), aromatic ring groups		825	X	X	827	829
Kaolin minerals	790/755 (694)			790/755/692	792/750/692	792/751/690
Silicates	777 (694)	796/775	798/777, 692	777, 692	X	X
Iron oxides		X	X	X	643	X
Out-of-plane γ (C-H)	711	X	X	728	X	
Iron oxides, or kaolins	532/466	524/468	530/464	534/468	526/464	530/464

*Assignments based on published literature: Russell and Fraser 1994; Colombini *et al.* 2003; Coates 2006; Helwig *et al.* 2008; Vahur *et al.* 2011; van der Marel and Beutelspacher 1976. Peaks at $\sim 2370\text{cm}^{-1}$ are attributed to atmospheric carbon dioxide and are not included in the interpretations or listed data.

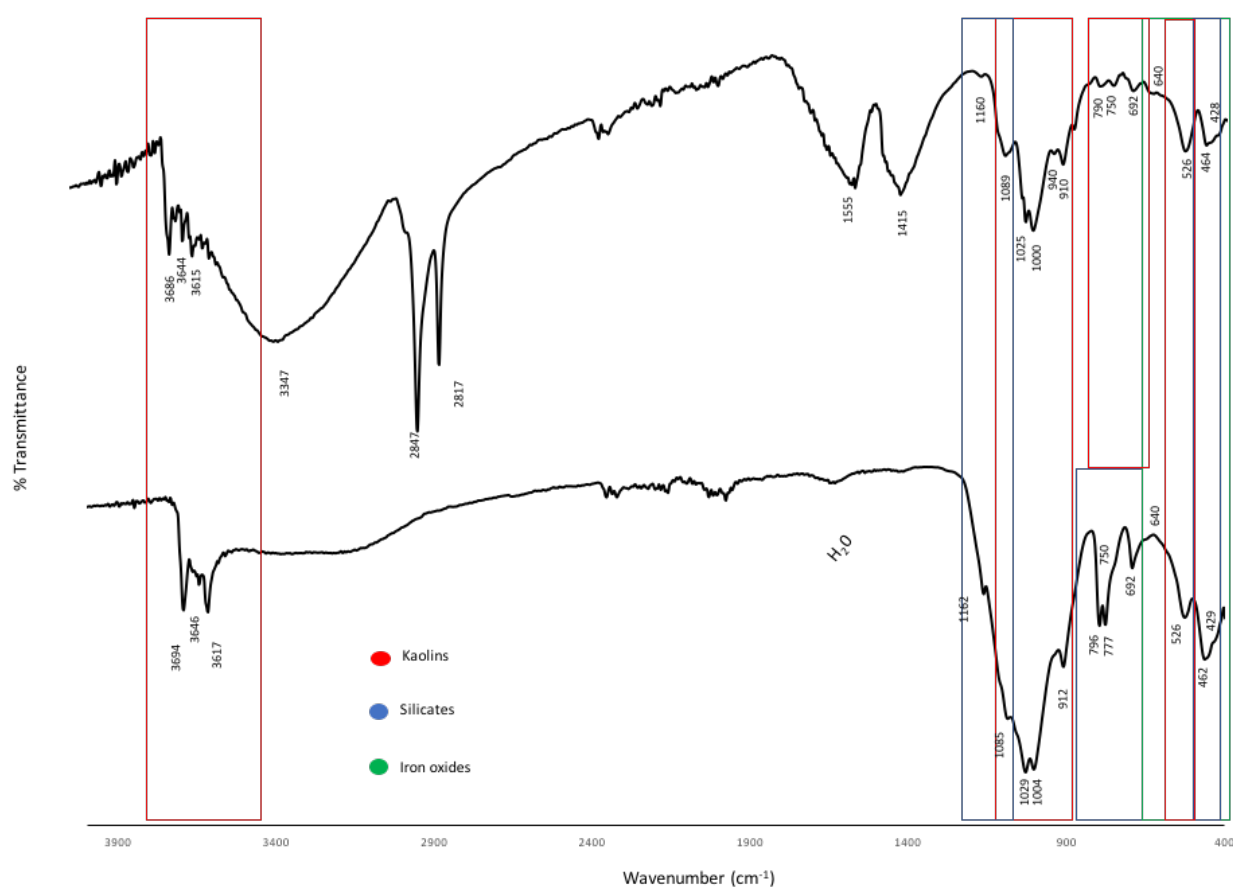


Figure 6.14. Renbaan Cave: A comparison of the IR spectra of RB11 (top) and orange ochre (bottom), highlighting the mineral types present in each spectrum.

The peak assignments in these materials, while organic in origin, are not uniquely associated with a source. The presence of strong peaks at 1555 cm^{-1} , assigned to carboxylates, may be indicative of the formation of metal carboxylates. Otero *et al.* (2014) describe the changing IR features of fatty acids in the presence of metal salts, whereby the distinctive C=O stretching region around 1700 cm^{-1} disappears, and COO^- stretching bands between $1600\text{--}1400\text{ cm}^{-1}$ are more pronounced. This reaction between monocarboxylic fatty acids with 7-22 carbon atoms (derived from fats, oils, etc.) and a metal salt has been identified as a reaction that is relatively common, occurring *in situ* on artefacts and works of art (Robinet and Corbeil, 2003).

Several inorganic mineral categories are identifiable in the Type 3B IR spectra. Calcium carbonates were found in all specimens based on the presence of bands at $1415/1413\text{ cm}^{-1}$, $875/873\text{ cm}^{-1}$ and $711\text{--}715\text{ cm}^{-1}$. RB11 is lacking a band between $711\text{--}715\text{ cm}^{-1}$, due to an overlapping peak at 690 cm^{-1} . Kaolin minerals ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) were also identified in all specimens (Figure 6.14). The strongest signals were noted in RB05, RB10, and RB11, with bands identified at $1027\text{--}1025$, $1000\text{--}1008$, $910/912$, 792 , $755\text{--}750$, and $690/692\text{ cm}^{-1}$. RB03, RB10, and RB11 also had --OH stretching peaks between $3700\text{--}3600\text{ cm}^{-1}$ consistent with this mineral type. The same peak distribution between $1030\text{--}912\text{ cm}^{-1}$ was also identified in RB02 and RB03, and thus also attributed to kaolin minerals.

Silicates, notably quartz, were identified in RB02 and RB03. This was confirmed based on the presence of a peak doublet at $775/777\text{ cm}^{-1}$ and $796/798\text{ cm}^{-1}$. The peak at 777 cm^{-1} in RB05 may also be attributed to silicates, however, the other component of the doublet is likely masked by the 790 cm^{-1} peak from the kaolin minerals. Peaks between $524\text{--}534\text{ cm}^{-1}$ and $464/468\text{ cm}^{-1}$ were found in all analysed specimens. This peak combination is found in kaolins, silicates, and iron oxides, though all at slightly different wavenumbers. Those peaks at $\sim 530\text{ cm}^{-1}$ could equally be attributed to iron oxides or kaolins, while those at $464/468\text{ cm}^{-1}$ may belong either to kaolins or silicates. A broad, weak peak at 640 cm^{-1} confirms the presence of iron oxides in RB11.

It is thus probable that all three mineral types are present in a mixture. This scenario for the Type 3B adhesives is plausible when the IR spectra are compared to a reference spectra of red ochre containing kaolin, silicates and iron oxides. The available reference spectra for red ochre (used for comparison in Figure 6.14), highlights components of IR spectra associated with some of the mineral components and the absence of others.

Overall, the Type 3B adhesive residues are interpreted as being composed of a mixture of organic and inorganic materials. The nature of the organic components cannot be elucidated from the IR spectra. It is noteworthy, however, that these materials are dominated by the presence metal carboxylates, possibly the result of the interaction between monocarboxylic fatty acids and metal salts. The source of the metal salts could be one of several possibilities, with a mixture of inorganic minerals, including silicates, kaolins, and iron oxides identified in the analysed material.

Mixed Materials: Type 1A and Type 3B residue samples

The IR spectra and associated peak assignments for RB06_01 and RB06_02 are highlighted in Figure 6.15 and

Table 6.25 and are consistent with the presence of organic and inorganic materials in both samples, although a more dominant inorganic mineral signature was identified in RB06_01.

Organics were identified based on the presence a broad –OH stretching region between $3400\text{--}3000\text{cm}^{-1}$ and two sharp C-H stretching peaks at 2915 and 2847cm^{-1} associated with saturated aliphatic groups, C=C stretching of aromatics at 1455cm^{-1} , various C-H deformation, bending, and stretching of aromatic and aliphatic groups, and -OH bending associated with phenols or alcohols

at 1318cm^{-1} . Differences were noted between RB06_01 and RB06_02 between $1700\text{--}1500\text{cm}^{-1}$; RB06_01 yielded peaks at 1706cm^{-1} and 1650cm^{-1} associated with C=O of carbonyls or with C=C of aromatics in the case of the latter; while RB06_02 yielded a prominent peak at 1644cm^{-1} which may also be indicative of C=O of carbonyls or with C=C of aromatics in addition to having peak at 1555cm^{-1} that has been assigned to a carboxylate anion group (COO^-).

The presence of a carboxylate anion in RB06_02 may be indicative of the presence of soaps (calcium, iron or aluminium soaps) in this sample. There were no consistent matches in the $\sim 1700 - 1200\text{ cm}^{-1}$ region in RB06_02 when compared reference exudate IR spectra (Appendix II). The spectra of RB06_01, notably the presence peaks at 1706 , 1455 , 1413 , 1376 , and 729 cm^{-1} is in distribution and intensity to those identified in the IR spectra of an altered beeswax (Stacey *et al.*, 2018; Regert *et al.* 2001) or a plant latex (Appendix II). Additionally, a shoulder at $\sim 1550\text{ cm}^{-1}$ was also identified and may be the result of an incomplete reaction between a metal cation and the carboxylate anion.

The presence of calcium carbonates, silicates, and other clay minerals including kaolin and iron oxides is suggested as inorganic mineral inclusions in the sampled material from RB06_01 and RB06_02. A peak at $1413/1417\text{ cm}^{-1}$, as well as relatively sharp, though weak, peaks at $877/875$ and 717 cm^{-1} are consistent with the presence of calcite in both samples. The combination of peaks likely associated with a Si-O bond stretching alongside the doublet at 798 and 777 and a peak at 694 cm^{-1} was identified in RB06_01. The best match for these peaks is to quartz grains (Russell and Fraser, 1994: Fig. 2.25.a). Additional clay minerals, either from kaolins or iron oxides (based on comparisons to reference spectra by Russell and Fraser (1994), Vahur *et al.* (2016) and mineral references described in Chapter 3), were also identified as being present. Similar minerals may also be present in RB06_02, however, the associated peak signals are considerably weaker, and in some cases, are absent entirely. The IR results for this RB06 (01 and 02) are consistent with the microscopy findings, which identified the predominance of Type 3B on the dorsal surface of this

tool (the sample location for RB06_01), while the Type 1A material was largely found on the ventral surface (sample RB06_02).

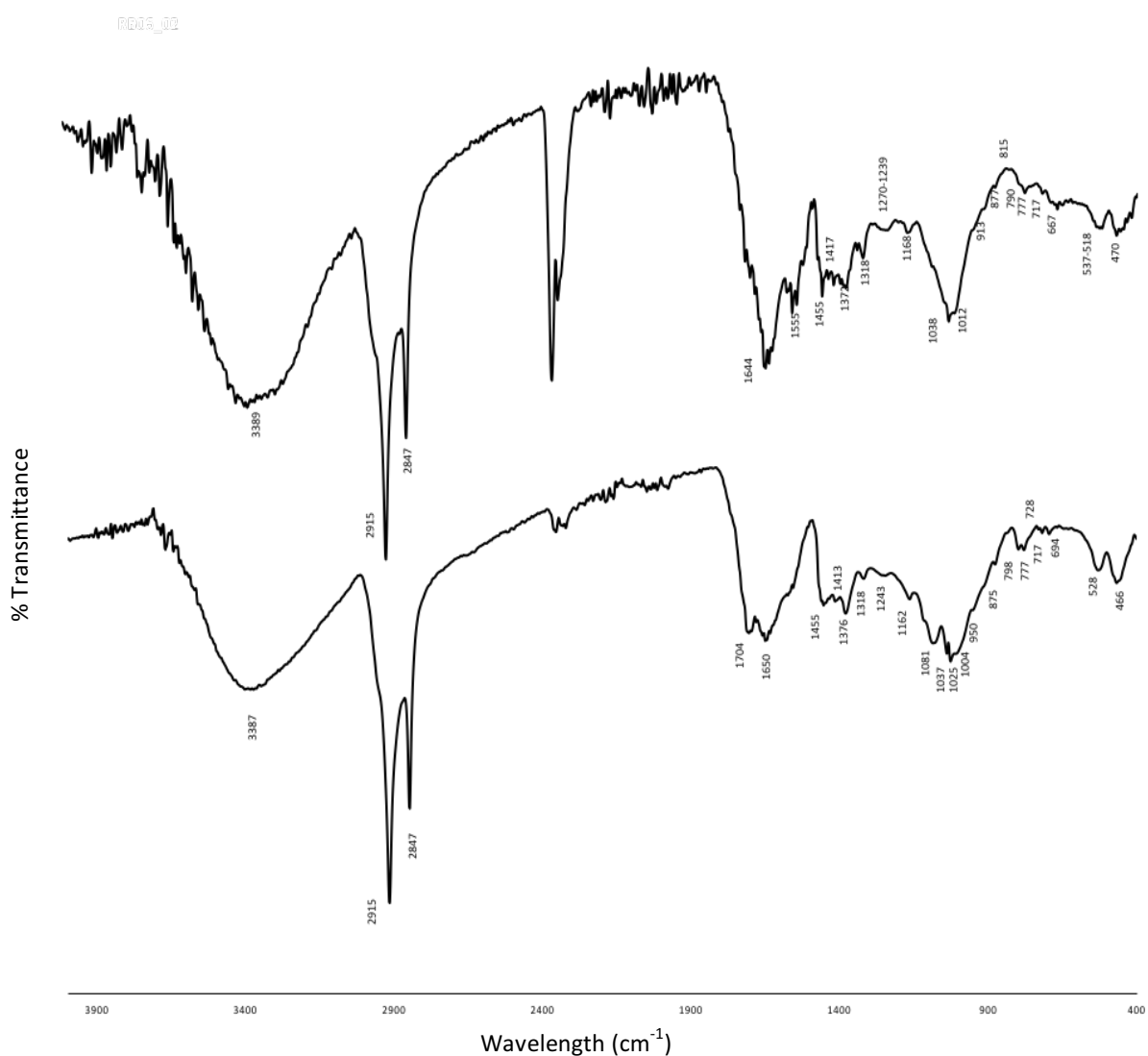


Figure 6.15. Renbaan Cave: IR spectra of two residue types from RB06: RB06_01, dorsal surface (bottom) and RB06_02, ventral (top).

Table 6.25. Renbaan Cave: IR peak assignments for mixed 1A/3B adhesive samples.

Assignment*	Wavenumber (cm ⁻¹)	
	RB06_01	RB06_02
v(O-H)	Max. at 3387	Max. at 3389
v(C-H)	2915/2847	2915/2947
v(C=O)	1706	X
v(C=C) or v(C=O)	1650	1644
v(COO ⁻) anion	X	1555
v(C=C-C) of an aromatic ring	1455	1455
In-plane γ vinyl (C-H) of olefinic groups, or carbonate anion	1413	1417
δ (C-H) deformation (saturated aliphatic groups) or γ (-CH ₃) bending	1376	1372
γ (-OH), phenol or tertiary alcohol, or primary or secondary γ (-OH)	1318	1318
v(C-O) of tertiary alcohols	1147	X
v(C-O) or v(Si-O)	1162/ 1081	1168
v(Si-O-Si) or v(C-O-C)	1037	1038
Kaolin minerals	1025/1004 (shoulder)	1012
In-plane γ (C-H) of aromatic groups	X	X
Out-of-plane γ (C-H) of olefinic or aromatic groups	X	913
Carbonates	875/717	877/717
Out-of-plane γ (C-H), aromatic ring groups	825	815
Silicates	798/777/694	777
Out-of-plane γ (C-H) or γ (-OH) out-of-plane bend	728	X
Kaolins	528/466	Broad, 537-518/ 470

*Assignments based on published literature: Russell and Fraser 1994; Colombini *et al.* 2003; Coates 2006; Helwig *et al.* 2008; Vahur *et al.* 2011; van der Marol and Beutelspacher 1976. Peaks at ~2370cm⁻¹ are attributed to atmospheric carbon dioxide and are not included in the interpretations or listed data.

6.3.2.2. SEM/EDS: Imaging and Elemental Composition

There was sufficient material for SEM/EDS analysis in ten of the eleven samples from Renbaan Cave, with the results highlighted in Table 6.26. The sampled material all appeared visually consistent with the optical light microscopy findings. Generally, samples had relatively smooth surfaces, with grains of material occasionally interspersed throughout that were especially apparent in backscatter detector mode (particularly in the case of RB10 and RB11).

RB01, RB03 and RB05 yielded additional evidence of structural additives included in the material. Animal hairs, identified as having a distinct cuticle pattern on their surface, were found embedded within the adhesive sample. Figure 6.16 highlights this structure, however, as the sample was uncoated during analysis there was insufficient resolution to acquire a cuticle pattern image that could be compared to a reference atlas.

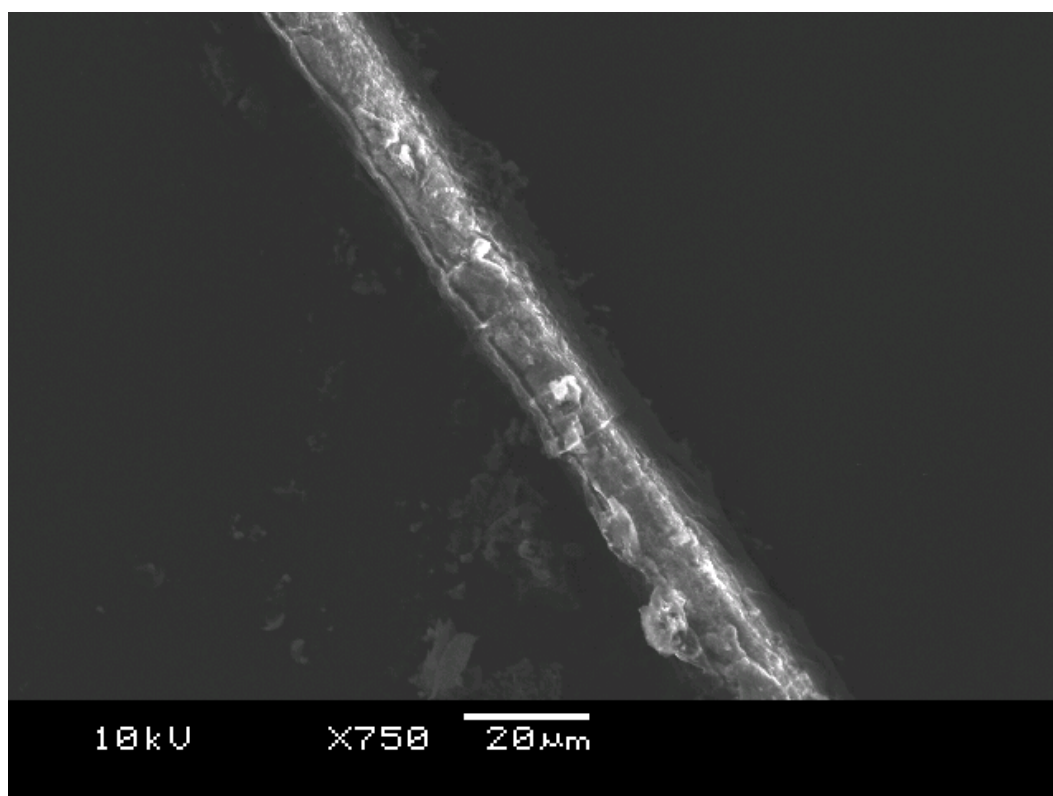


Figure 6.16. SEM image of a hair fragment from RB01.

Carbon and oxygen were identified as the main elemental components in all analysed material, confirming the presence of organic materials in these samples. Elemental phosphorus and potassium in the analysed materials, regardless of residue type, are interpreted as indicators of the degradation of organic material (Price and Burton, 2011). Alongside these elements, silicon, aluminium, calcium, and iron were also identified as minor components in specimens described as Type 3B or Type 1A/3B (RB06) residues, thus supporting the IR interpretations that indicate a significant contribution of inorganic minerals in these adhesive types.

Table 6.26. Renbaan Cave: The elemental composition of all adhesive samples.

Sample No.	Elemental Composition ¹ (Atomic %)		
	Major	Minor	Trace
RB01	C (61.27) O (31.27)	Si (2.10) Al (1.06) Ca (1.80)	Na (0.57) Mg (0.49) P (0.14) S (0.09) Cl (0.38) K (0.34) Ti (0.02) Mn (0.11) Fe (0.33)
RB02	C (72.91) O (23.38)	Ca (1.12)	Na (0.71) Mg (0.52) Al (0.21) Si (0.33) P (0.09) S (0.08) Cl (0.21) K (0.08) Fe (0.36)
RB03	C (69.28) O (25.25)	Si (1.28) Ca (1.31)	Na (0.35) Mg (0.57) Al (0.69) P (0.15) S (0.1) Cl (0.16) Fe (0.67)
RB05	C (63.07) O (28.42)	Al (1.71) Si (3.31) Ca (1.06)	Na (0.35) Mg (0.41) P (0.12) Cl (0.18) K (0.52) Mn (0.39) Fe (0.47)
RB06_01	C (73.26) O (22.87)	Si (1.57)	Na (0.22) Mg (0.16) Al (0.82) Cl (0.11) K (0.2) Ca (0.33) Fe (0.46)
RB06_02	C (54.40) O (38.99)	Al (2.02) Si (3.64)	Na (0.26) Mg (0.18) Cl (0.08) K (0.27) Ca (0.07) Fe (0.1)
RB07	C (80.09) O (17.83)		Na (0.41) Al (0.11) Si (0.14) Cl (0.07) K (0.15) Ca (0.10) Fe (0.09)
RB08	C (77.39) O (19.59)	Si (1.10)	Na (0.32) Al (0.47) P (0.04) S (0.03) Cl (0.08) K (0.13) Ca (0.42) Mn (0.03) Fe (0.16)
RB09	C (67.32) O (32.23)		Na (0.4) Mg (0.39) Al (0.33) Si (0.52) P (0.1) S (0.05) Cl (0.1) K (0.07) Ca (0.5)
RB10	C (71.9) O (23.98)	Si (1.3)	Na (0.06) Mg (0.27) Al (0.84) P (0.04) S (0.02) Cl (0.11) K (0.09) Ca (0.36) Ti (0.03) Fe (0.99)
RB11	C (68.95) O (25.42)	Si (1.01) Fe (1.74)	Na (0.24) Mg (0.47) Al (0.78) P (0.08) S (0.03) Cl (0.34) K (0.26) Ca (0.67)

Due to the input of inorganic minerals in these materials, several Type 3B samples underwent element mapping to determine the distribution of elements and possible element combinations. It was observed that aluminium and silicon (Figure 6.17), as well as silicon and oxygen, plotted together. The former combination, which appeared as a relatively homogeneous distribution, supports the IR findings, indicating the presence of kaolin minerals throughout the adhesive; the latter combination, appearing as larger structures dispersed in the material, is indicative of silicates also being present as a second additive. An appearance of elemental iron as a trace or minor element in the Type 3B residues supports the reddish appearance of this material.

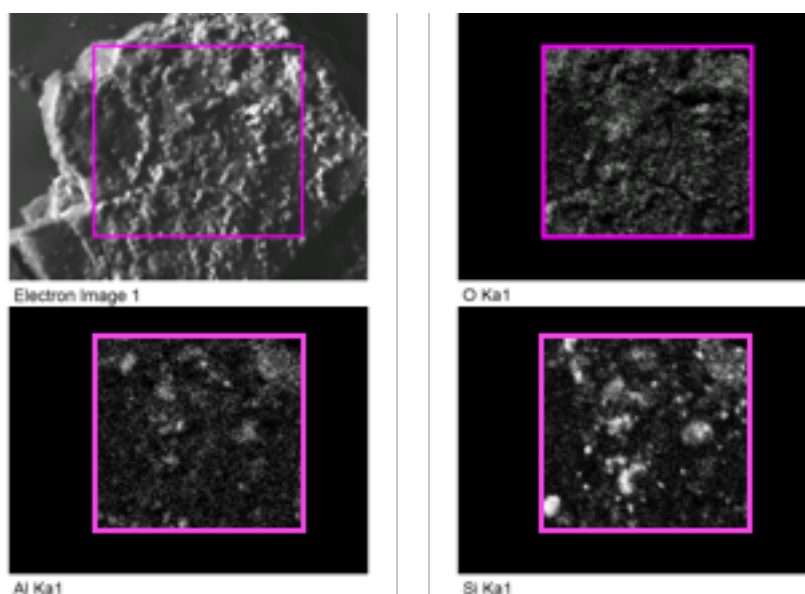


Figure 6.17. Renbaan Cave: An elemental of the surface of a fragment of RB01, highlighting the distribution of oxygen (O), aluminium (Al), silicon (Si).

Among the Type 1A residue samples (RB07-09), the presence of elemental aluminium, silicon, and calcium support the identification of weak kaolin and calcium carbonate signals in the IR spectra. The presence of silicon as a minor component also confirms the presence of silicates in RB08, a Type 1A specimen. The trace amounts of sodium, magnesium, chlorine, sulphur, iron, and manganese may be attributed to other mineral types, however, these could not be identified by IR.

The appearance of manganese (Mn) and iron (Fe) in RB08 and only iron in RB07 may indicate differences in mineral sources, despite both samples being derived from the same layer (Bedding; 1172-925 calBP).

6.3.2.3. Pyrolysis –Gas Chromatography/ Mass Spectrometry (Py-GC/MS)

Subsequent analysis by Py-GC/MS were then undertaken to more completely characterise the organic components. Samples from ten specimens underwent py-GC/MS analysis: RB01-03, RB05, RB06_02, and RB07-RB11. The component identified in the pyrograms are highlighted in the subsequent sections, divided by residue type.

Type 1A residue samples

Figure 6.18 and the corresponding Table 6.27 highlight the nature and composition of the pyrograms of the Type 1A residues. The main components of the pyrograms from RB07-09 were identified as being short to mid-chain saturated (C_8 - C_{26}) and unsaturated (C_8 , C_{16} , and C_{18}) monocarboxylic fatty acids, C_{16} and C_{18} ω -hydroxycarboxylic acids, and a series of n-alkenes (C_{11} - C_{23}) and n-alkanes (C_{23} - C_{30}). The carbon chain range of the components identified in these samples is less complete and of lower abundance than other analysed material from this site. Even-numbered long chain alcohols (C_{22} - C_{28}), phenolic compounds, phthalates, and short-chain dicarboxylic fatty acids (C_4 , C_8 , and C_9) were also detected.

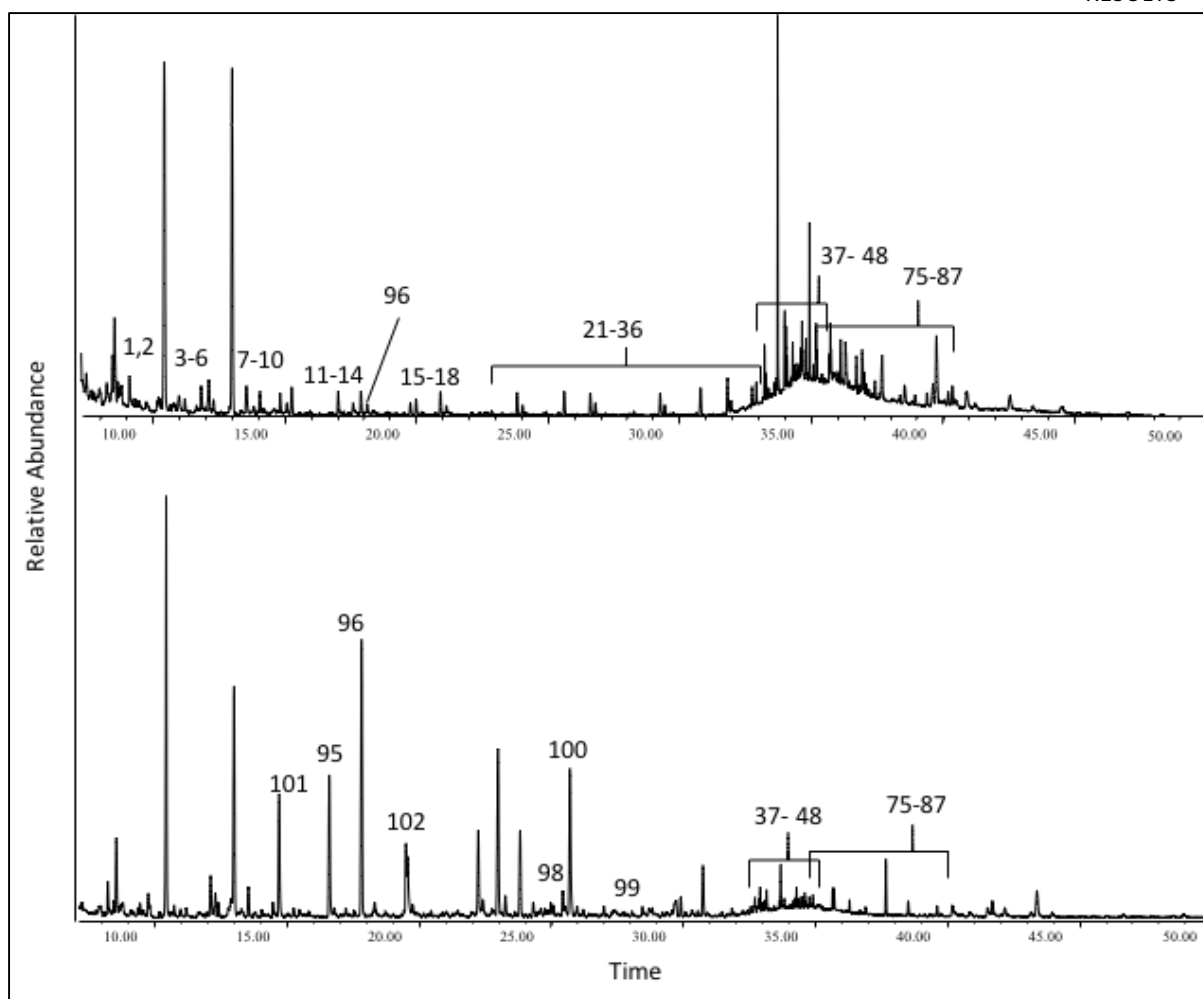


Figure 6.18. Renbaan Cave: Total ion chromatograms of RB09 (bottom), a Type 1A adhesive, and RB03 (top), a Type 3B adhesive.

14- and 15-hydroxyhexadecanoic acids, an abundance of hexadecanoic acid (C_{16} monocarboxylic fatty acid), and an n-alkane series of increasing intensity among odd-chain units between 25-33 carbon units were identified in RB07 and RB09. These markers are interpreted as belonging to beeswax (Ribechini *et al.*, 2009).

RB08, by contrast, differs from the other analysed material. It contains only a narrow range of n-alkanes (C_{23} - C_{29}) in relatively low abundance with an inverted U-shape. These compounds were found alongside a range of saturated (C_8 - C_{12} , C_{16} - C_{20} , C_{26}) and unsaturated (C_8 , C_{16} , and C_{18})

monocarboxylic fatty acids. These compounds could not be attributed to any definite source. This sample also yielded ricinoleic acid at 35.85min.

All samples of the residue type yielded a series of phenolic compounds. One main grouping includes phenolics associated with the pyrolysis of plant lignin and cellulose, notably silylated guaiacol, hydroquinone, resorcinol, 1,2,3-hydroxy-benzene, 4-hydroxybenzoic acid, and vanillic acid. Two pyrolytic markers of catechin tannins were also identified in the sampled material, namely 1,3,5-trihydroxy-benzene and 1,2 dihydroxy-4-propyl-benzene (RB07 and RB09 only) (Galletti and Bocchini, 1995; Marchetti, 2017). For these adhesive samples, the source of the plant material is interpreted as being derived from catechin containing plant material, however, these components are not taxonomically specific, and no further specifications can be made. RB09 also contained silylated 2-hydroxy-4-methoxyacetophenone, at 19.51min, a plant-based phenol.

Table 6.27. Renbaan Cave: Principal pyrolysis products found in RB03 and RB09 (Figure 6.17).

No.	Compound	No.	Compound
<i>Monocarboxylic fatty acids and hydrocarbons</i>		57	1-nonadecene
1	1-undecene	58	nonadecane
2	undecane	59	pentadecenoic acid, TMS
3	heptenoic acid, TMS	60	pentadecanoic acid, TMS
4	heptanoic acid, TMS	61	1-eicosene
5	1-dodecene	62	eicosane
6	dodecane	63	hexadecenoic acid, TMS
7	octenoic acid, TMS	64	hexadecanoic acid, TMS
8	octanoic acid, TMS	65	1-heneicosene
9	1-tridecene	66	heneicosane
10	tridecane	67	heptadecenoic acid, TMS
11	nonenoic acid, TMS	68	heptadecanoic acid, TMS
12	nonanoic acid, TMS	69	1-docosene
13	1-tetradecene	70	docosane
14	tetradecane	71	octadecenoic acid, TMS
15	decenoic acid, TMS	72	octadecanoic acid TMS
16	decanoic acid, TMS	73	eicosanoic acid, TMS
17	1-pentadecene	74	1-tricosene

18	pentadecane	75	tricosane
19	undecenoic acid, TMS	76	1-tetracosene
20	undecanoic acid, TMS	77	tetracosane
21	1-hexadecene	78	1-pentacosene
22	hexadecane	79	pentacosane
23	dodecenoic acid, TMS	80	1-hexacosene
24	dodecanoic acid, TMS	81	hexacosane
25	1-heptadecene	82	1-heptacosene
26	heptadecane	83	heptacosane
27	tridecenoic acid, TMS	84	octacosane
28	tridecanoic acid, TMS	85	nonacosane
29	1-octadecene	86	triacontane
30	octadecane	87	hentriacontane
31	tetradecenoic acid, TMS	88	dotriacontane
32	tetradecanoic acid, TMS	89	tritriacontane
33	1-nonadecene	90	dicarboxylic fatty acids
34	nonadecane	91	butanedioic acid, TMS
35	pentadecenoic acid, TMS	92	heptanedioic acid, TMS
36	pentadecanoic acid, TMS	93	octanedioic acid, TMS
37	1-eicosene	94	nonanedioic acid, TMS
38	eicosane	<i>Phenols</i>	
39	hexadecenoic acid, TMS	95	hydroquinone, TMS
40	hexadecanoic acid, TMS	96	resorcinol, TMS
41	1-heneicosene	97	1,3,5-hydroxy-benzene, TMS
42	heneicosane	98	4-hydroxybenzoic acid, TMS
43	heptadecenoic acid, TMS	99	vanillic acid, TMS
44	heptadecanoic acid, TMS	100	1,3,5-trihydroxy-benzene
45	1-docosene	101	guaiacol, TMS
46	docosane	102	2-hydroxy-4-methoxyacetophenone, TMS
47	octadecenoic acid, TMS	<i>Branched chain fatty acids</i>	
48	octadecanoic acid TMS	103	branched pentadecanoic acid, TMS
49	1-heptadecene	104	branched hexadecanoic acid, TMS
50	heptadecane	105	branched heptadecanoic acid, TMS
51	tridecenoic acid, TMS	<i>Phthalates</i>	
52	tridecanoic acid, TMS	106	diisooctyl phthalate
53	1-octadecene	<i>Hydroxy- fatty acids</i>	
54	octadecane	107	15-hydroxyhexadecanoic acid, TMS
55	tetradecenoic acid, TMS	108	14-hydroxyhexadecanoic acid, TMS
56	tetradecanoic acid, TMS		

Type 3B residue samples

All six of the Type 3B residue specimens were of a sufficient size for pyrolysis analysis. Figure 6.18 and the corresponding Table 6.27 highlight the nature and composition of the pyrograms of the Type 3B residues. The principal components of all pyrograms correspond to the pyrolytic markers of short to mid-chain saturated and unsaturated monocarboxylic fatty acids (C_7 - C_{20}), a series of n-alkenes (C_{11} - C_{23}), and n-alkanes (C_{11} - C_{33}). Long chain alcohols (C_{22} , C_{24} , and C_{28}), polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, phthalates, and short-chain dicarboxylic fatty acids (C_4 , C_8 , and C_9) were also identified.

The most common pyrolytic markers were identified as being derived from animal sources. The presence of $C_{15:0}$ and $C_{17:0}$ branched chain saturated monocarboxylic fatty acids indicate the presence of ruminant animal fat in five of the six analysed specimens (Colombini and Modugno, 2009), with the absence noted in RB03. Beeswax was identified in RB01-03 and RB05 based on the combined presence of short to mid-chain saturated and unsaturated monocarboxylic fatty acids (C_7 - C_{20}) with hexadecanoic acid being the most abundant and a series of n-alkenes (C_{11} - C_{23}) and n-alkanes (C_{11} - C_{33}), with an increasing intensity of odd-chain n-alkanes between 25-33 carbon units and C_{27} dominating (Bonaduce and Colombini, 2004; Ribechini *et al.*, 2009, Roffet-Salque *et al.*, 2015). The same markers were also detected in RB10 and RB11, however, C_{25} was the most dominant n-alkane. It is, however, possible that the same series of fatty acids, n-alkanes, and n-alkenes may also be derived from a plant pitch, as both products produce the same markers (see: Py-GC/MS sections of Melkhoutboom and the museum specimens). Analysis by GC/MS provides the additional confirmatory means to ascertain whether there is one or multiple sources present.

The additional presence of plant material is postulated for the adhesive samples RB01 and RB02. In RB02, a peak at 37.191 min corresponds to ferruginol, a phenolic diterpenoid identified in southern African conifers, which may be indicative of a likely plant source for the residue from this specimen. Additionally, phenolic compounds, including silylated hydroquinone, 1,2,3-hydroxy-

benzene (RB01), and 4-hydroxybenzoic acid (RB02) may be associated with the pyrolytic breakdown of lignin-containing plant material. PAHs, phenanthrene and pyrene were found in one sample (RB11). Although derived from several industrial sources, they are a product of the combustion of wood (Khalili *et al.*, 1995).

Mixed materials: 1A/3B Residues

Only one of the two mixed residue samples held sufficient material for pyrolysis analysis, RB06_02. Its constituents were found to be most comparable to the 3B adhesive samples. The principal components included short to mid-chain saturated and unsaturated monocarboxylic fatty acids (C_7 - C_{20}), a series of n-alkenes (C_{11} - C_{23}), and n-alkanes (C_{11} - C_{33}). Long chain alcohols (C_{22} , C_{24} , and C_{28}), phenolic compounds (cinnamic acid and 4-hydroxybenzoic acid), phthalates, and short-chain dicarboxylic fatty acids (C_4 , C_8 , and C_9) were also present. Beeswax was identified based on the combined presence of short to mid-chain saturated and unsaturated monocarboxylic fatty acids with hexadecanoic acid being the most abundant, alongside the series of n-alkenes and n-alkanes. C_{27} was the most prominent n-alkane. The presence of branched-chain C_{15} and C_{17} fatty acids indicates the presence of a bacterial source (Dudd *et al.*, 1998; Corr *et al.*, 2008; Kedrowski *et al.*, 2009).

An additional plant-based source may also be postulated, based of phenols associated with the pyrolytic breakdown of plant tissues (i.e. cinnamic acid and 4-hydroxybenzoic acid). Diisooctyl phthalate was identified in all analysed material and is interpreted as being a source of modern contamination associated with the long-term storage of the objects.

Protein analysis by pyrolysis

Four samples - RB05, RB06_02, RB09, and RB011 - were re-run for un-derivatised pyrolysis-GC/MS to assess for the presence of proteinaceous material. This class of molecule would otherwise not be assessed in the presence of a derivatising agent, as there is a solvent delay in place within the GC/MS protocol to allow solvent and derivatising agents to pass through the column prior to data collection by the mass spectrometer.

Table 6.28. Renbaan Cave: A selection of pyrolysis products and their mass spectra detected in the pyrograms of four adhesive samples.

Compound Name	Mass Spectra (m/z)	RB05	RB06_02	RB09	RB11
<i>Nitrogen containing compounds</i>					
Pyrrole	52 67	Y	Y	Y	N
<i>Aromatic hydrocarbons</i>					
Toluene	51 65 91	Y	Y	Y	Y
2,6, dimethyl phenol	51 77 107 122	Y	Y	Y	N
2-methyl-phenol	51 77 90 107 108	Y	Y	Y	Y
3-methyl-phenol	53 77 107 108	Y	Y	Y	Y
2,4 - dimethyl-phenol	51 77 107 122	N	Y	Y	N
4-ethyl-phenol	77 107 122	N	N	Y	N
methyl-indene	77 107 122	Y	N	Y	N
indene	89 115 116	Y	Y	Y	N

¹Masses in bold are the base peak. Compound and mass spectra information based on published results from Orsini *et al.* (2017).

Extracted ion chromatograms were obtained for selected m/z associated with proteinaceous material from archaeological and experimental contexts, based on those highlighted by Orsini *et al.* (2017). These included m/z 67 – pyrrole, m/z 91 – toluene, m/z 107- phenol derivatives, m/z 117- indole and benzeneacetonitrile, m/z 131- methyl-indole, m/z 70 and 154- diketopiperazines (DKPs), and m/z 186 - diketodipyrrole. The only markers of note in the four specimens were found in the early part of the chromatogram (between 0 – 11 mins) and are described in Table 6.28. The aromatic hydrocarbon content varied between samples. Toluene (m/z

91) was present in all sampled material, while methyl- and ethyl- phenols (m/z 107 and 122), and methyl-indene were identified in RB05 and RB09. Indene (m/z 115) was identified in three pyrograms, RB05, RB06_02 and RB09. Pyrrole (m/z 67) was the only nitrogen-containing aromatic ring structure discovered in the material, having been found in RB05, RB06_02, and RB09 (Figure 6.19). Based on the presence of pyrrole, the presence of proteinaceous material may be interpreted for these three specimens. However, due to the lack of DKPs, principal products associated with the pyrolysis of proteinaceous material such as collagen and casein, and an absence of heptadecanonitrile and octadecanonitrile, found in egg, no confirmation can be made as to the exact source of the proteinaceous material (Orsini *et al.*, 2017). It should be noted that a lack of DKPs in degraded material is expected, as a number of studies have identified an inverse relationship between the low DKP recovery and high degradation of protein chains (Poinar and Stankiewicz, 1999; Adamiano *et al.*, 2013; Orsini *et al.*, 2017; van der Werf *et al.*, 2017).

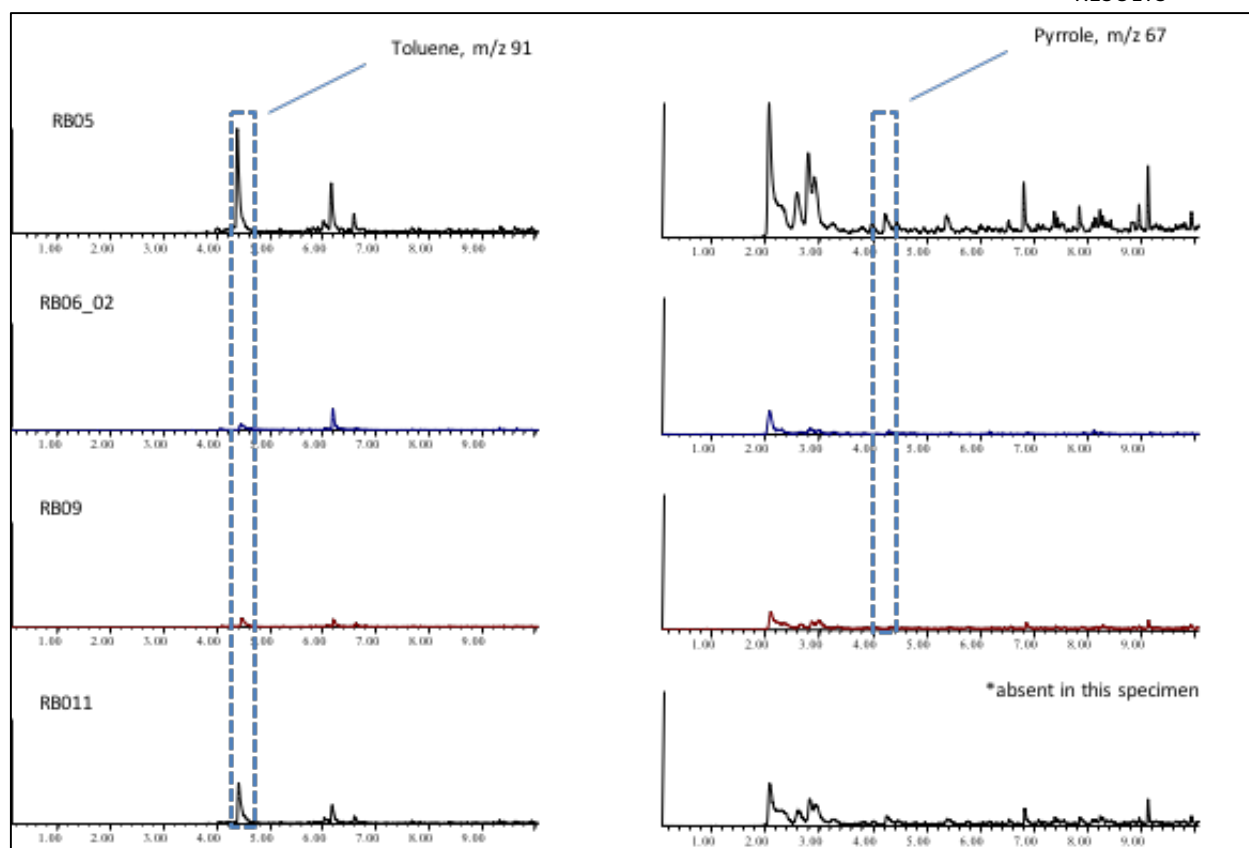


Figure 6.19. Extract ion pyrograms of four adhesive samples, highlighting the presence of toluene (m/z 91), and the protein marker, pyrrole (m/z 67).

6.3.2.4. Gas Chromatography/ Mass Spectrometry (GC/MS)

As a complement to the py-GC/MS analysis, all twelve samples underwent analysis and yielded markers from both plant and animal derived sources. The results are highlighted by residue type in the sections below. The constituents of wax esters (both plant and animal) appeared most commonly as identifiable compounds.

For the sake of eliminating repetition in all subsequent sections, the marker combinations utilised in the identification of waxes are described in Table 6.29. Both plant and animal waxes are identifiable based on the presence of long even-number chain alcohols and monocarboxylic fatty acids, and odd-chain *n*-alkanes (Roffet-Salque *et al.*, 2017). To distinguish between the sources two compound classes were assessed: *n*-alkane abundance and the presence or absence of hydroxy-

acids (C_{16:0}). In terms of n-alkane distributions the odd chain numbers are higher in abundance than the even-numbered chains (if even-number chains are present at all in the archaeological material), while C₂₇ (heptacosane) followed by C₂₉ (nonacosane) was noted as the most prominent of these. This distribution is consistent with known n-alkane distributions in beeswax from *Apis* sp. analysed from both recent and archaeological contexts (Ribechini *et al.* 2011; Was *et al.* 2014a, 2014b). By contrast, the n-alkane distribution in plant waxes tends to be dominated by C₂₉ or C₃₁ chain lengths as the most abundant depending on plant type (Kunst and Samuels, 2003; Bush and McInerney, 2013). For beeswax, 15-hydroxyhexadecanoic acid and 14-hydroxyhexadecanoic acid are used as the main confirmatory markers. These two compounds have been described as the resulting breakdown of wax esters by saponification and hydrolysis (Bonaduce and Colombini, 2004), and survive for identification in archaeological contexts (Ribechini *et al.*, 2009).

Table 6.29. Renbaan Cave: A selection of markers employed to determined the presence of plant and animal-derived waxes.

Compounds present	RB01	RB02	RB03	RB05	RB06-1	RB06-2	RB07	RB08	RB09	RB10	RB11	RB12
15-hydroxyhexadecanoic acid (TMS) and 14-hydroxyhexadecanoic acid (TMS)	✓	✓	✓	✓	✓	✓	—	—	—	✓	—	—
Odd chain n-alkanes (C ₂₅ -C ₃₁) *C ₂₇ alkane highest abundance unless specified	—	✓	✓	✓	✓	✓	✓	Low abundance	✓	✓ *C ₂₉	✓ *C ₂₉	—
Saturated even chain monocarboxylic fatty acids (C ₂₆ -C ₃₆)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	—
Even chain n-alkanols (C ₂₆ -C ₃₀)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	—

Type 1A residues

All Type 1A samples (RB07, RB08, RB09, and RB12) yielded organic constituents that may be attributed to plant or animal sources. Table 6.30 describes the main constituents of the GC/MS analysis. RB07 contained pitch derived from a conifer, with the possible addition of beeswax. The pitch material is suggested based on the presence of C_{16:0} and C_{18:0} dicarboxylic acids and the phenol hydroquinone, with its source as a conifer confirmed by dehydroabiatic acid at ~25min on the TIC. In support of the pyrolysis-GC/MS findings, beeswax is also a likely ingredient based on the combined appearance long chain even numbered alkanols (C₂₆-C₃₀), saturated monocarboxylic fatty acids (C₂₄-C₃₄), and n-alkanes (C₂₅-C₂₉, C₃₁).

Figure 6.20 compares the extracted ion chromatograms of RB07 to a modern beeswax reference, highlighting the abundance and distribution of the n-alkanes. It is possible that beeswax may have been a major constituent in this sample, as it is the only specimen at this site where even-numbered chains n-alkanes were present. The catechin tannins described in the pyrolysis results were not present in the GC/MS data.

RB08 yielded evidence of plant-based materials with the possible addition of animal fat. Plant materials include a wax, bark pitch, and ricinoleic acid – containing plant material. Long chain even-numbered alkanols (C₂₆-C₃₀) may be sourced to a wax. The combination of 15-hydroxyhexadecanoic acid, 17-hydroxyoctadecanoic acid, 17-hydroxyoctadecenoic acid, as well as C₁₆ and C₁₈ dicarboxylic acids, matches the known reference of a bio poly-ester, like pitch (see: Section 6.3.1.4; Villa *et al.*, 2012; Charrié-Duhaut *et al.*, 2013). The compound 1,3,5 – hydroxybenzene was also found; this was not identifiable in the pyrolysis results. The n-alkane stretch (C₂₅-C₃₀) were in abundance under 4000 for all chain lengths, and a source could not be identified. While identified in castor oil, *Ricinus communis* remains have only been recovered from Oliphant's River sites from the 18th century onwards (at De Hangan [Parkington and Poggenpoel, 1971] and Andriesgrond [Anderson, 1991]). Ricinoleic acid was identified based on the mass spectra

with prominent peaks at m/z 187 and 73, followed by peaks at 329, 411, and 427 (PubChem Compound Database, 2018). It is possible that this fatty acid is derived from an unknown plant source similarly containing high concentrations of ricinoleic acid. Animal fats are suggested based on the identification of $C_{17:0}$ and $C_{15:0}$, and the branched chain $C_{15:0}$ fatty acids.

Similar to RB08, pitch markers were also identified in RB09. The presence of 1,3,5 – hydroxybenzene and 1,2,4-hydroxybenzene indicates that the wood used in the production of this material contained tannins. Beeswax was also noted in this sample, as alongside the even-number chain n-alkanols (C_{26} – C_{30}) and monocarboxylic acids (C_{20} – C_{28} , with C_{26} the most abundant) there was a range of n-alkanes with C_{27} followed by C_{29} observed as having the highest abundance. It should be noted, however, that this identification is hypothetical due to an absence of the 14-hydroxyhexadecanoic acid and the 15-hydroxy acid being assigned to a plant pitch.

The only identifiable constituents of RB12 that could be attributed to a specific source were odd-chain saturated $C_{15:0}$ and $C_{17:0}$, derived from animal fat (Colombini and Modugno, 2009). The presence of branched-chain C_{15} and C_{17} fatty acids indicates the presence of a bacterial source (Dudd *et al.*, 1998; Corr *et al.*, 2008; Kedrowski *et al.*, 2009).

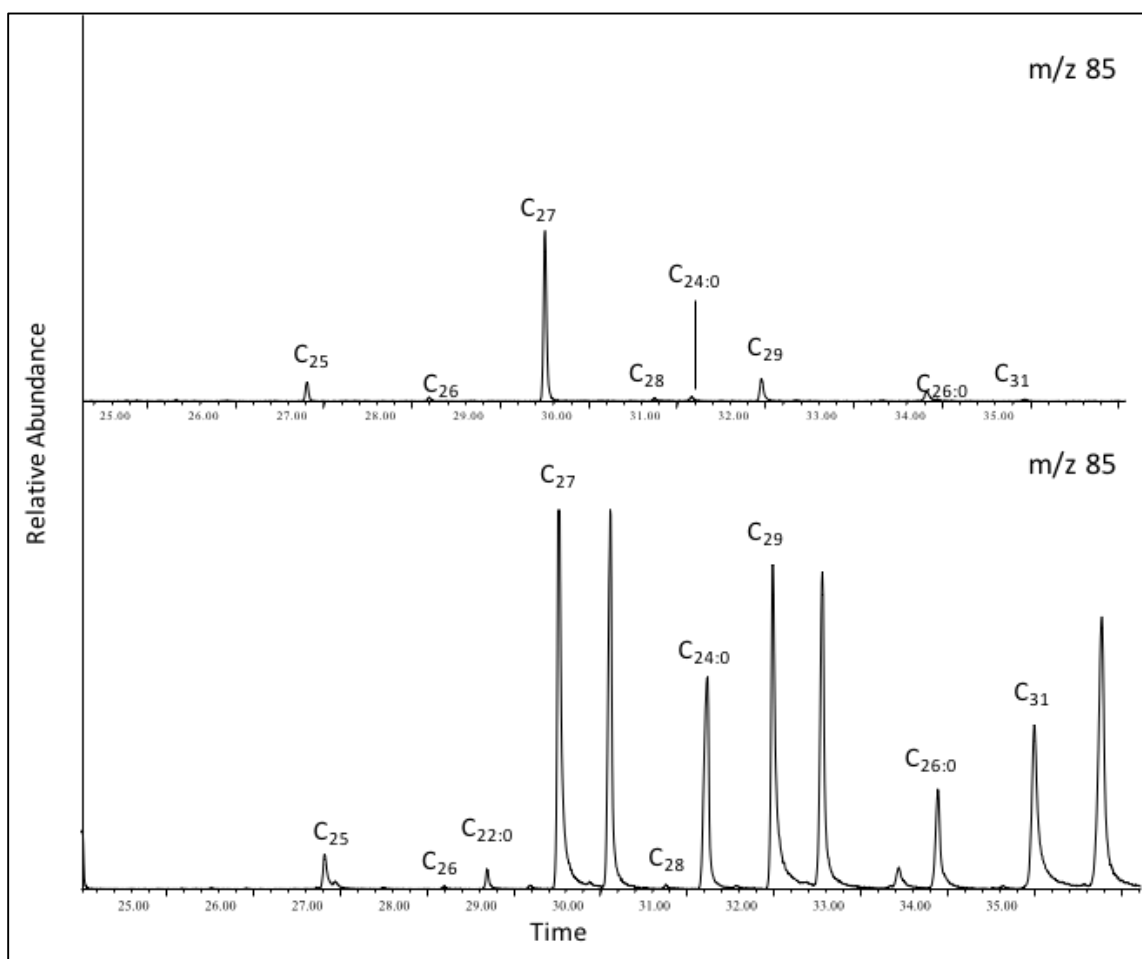


Figure 6.20. Extracted ion chromatograms (m/z 85) of RB07, a Type 1A adhesive from Renbaan (top) and modern beeswax (bottom).

Type 3B residues

The results from the six analysed Type 3B residues indicated the presence of several organic sources from both plants and animals, supporting and providing additional detail to those findings from the pyrolysis-GC/MS results. Animal fats were identified in all samples of this residue type based on the appearance of saturated C_{15:0} and C_{17:0} fatty acids (Colombini and Modugno, 2009; Helwig *et al.*, 2014). Additionally, the presence of glycerol and cholesterol in RB10 may be attributed to this source. Beeswax was also present in all analysed material with the exception RB11, whose markers were interpreted as being derived from a plant wax (Table 6.29).

Plant material, both specific and non-specific, was identified in all specimens. The presence of phenols associated with lignin and cellulose, including vanillic and syringic acids, was evident in all samples. Ricinoleic acid was identified in RB02. Non-specific tannins with a m/z 193 base peak (Poulin, 2018) were found in RB02 and RB05. Diterpenoids derived from conifer resin were found in four of the six adhesive samples. The oxidation product of abietic acid, DHA, was the main diterpenoid component of these sample, while a derivative of this structure 7-hydroxy-DHA (Helwig *et al.*, 2014) was found in RB03. The pimarane 8, 15 - pimaradien-18-oate was identified in RB03 and RB11. These findings lend further support to the identification of ferruginol by Py-GC/MS in RB02, as the combination of abietanes, pimaranes and phenolic diterpenoids matches the exudates of the *Widdringtonia* genus (see Melkhoutboom results in Section 6.3.1.4.)

Markers associated that may be interpreted as sourced from a bark pitch were identified in RB01 and RB05; RB05 yielded 17-hydroxyoctadecanoic acid, and 21-hydroxydodecanoic acid while hexadecanedioic acid (C_{16} dicarboxylic acid) and octadecanedioic acid ($C_{18:0}$ dicarboxylic acid) were found in RB01.

Mixed Residues: Type 1A & 3B

The two samples from RB06 (RB06_01 and RB06_02) having Type 1A and 3B mixed residues yielded results that are consistent with the pyrolysis data from RB06_02. They contain essentially the same constituents including short and mid- chain dicarboxylic acids, monocarboxylic fatty acids (saturated, unsaturated, and branched), even-numbered long-chain alcohols, phenols, and the diterpenoid dehydroabietic acid (DHA). They are attributed to a combination of animal and plant sources.

Branched-chain C_{15} and C_{17} fatty acids indicates that ruminant animal fats were present in this adhesive. Beeswax was based on the combination of hexadecanoic acid, hydroxy- acids, even

numbered long chain alcohols and monocarboxylic acids, and odd chain n-alkanes (C_{27} , C_{29} , C_{31} , with C_{27} dominating) (Ribechini *et al.*, 2011; Roffet-Salque *et al.* 2017).

Plant material is also present, based on the identification of phenols associated with lignin, including 4-hydroxybenzoic acid, vanillic and syringic acids (Tamburini *et al.*, 2014). The identification of DHA highlights conifer resin as the source, likely from the genus *Widdingtonia*.

6.3.2.5. Interpretive Summary

Table 6.30 summarises all the results acquired from the Renbaan Cave adhesive samples. Evidence of mixtures of inorganic and organic materials were identified in the analysed adhesive specimens from this site. Inorganic minerals associated with laterite deposits (kaolins, iron oxides) were present in Type 3B residues. Of notable significance is the relatively complex mixture of organic materials identified, including waxes, oils, fats, protein, and plant exudates and pitch. In terms of overall organic constituents identified by chromatography, the composition of both Type 1A and Type 3B residues is very similar, with beeswax and animal fat being the main components with the addition in some instances of plant exudates and manufactured pitch (from a conifer or tannin-producing species, and a hitherto unknown species), as well as a ricinoleic acid containing plant (like castor oil), proteinaceous material, and hair.

This relatively consistent composition is notable, however, as the TICs of the chromatography results were strikingly distinctive based on residue type. When compared to a reference sample of beeswax, Type 1A residues yielded a lower range and abundance of monocarboxylic fatty acids with chain lengths stopping at $C_{28:0}$, while the results of Type 3B residues yielded fatty acids (up to $C_{36:0}$) that dominated the chromatograms. Long chain alkanols were present in both residue types, while n-alkanes were more prominent in the Type 1A than the Type 3B samples.

It is thus postulated that due to the sameness in organic sources found in the sampled material, the inorganic ochre minerals may have played a role in the differences in abundance and chain length in the identified constituents. Type 3B adhesives were found to contain the kaolin and iron oxide minerals of red ochre as well as calcite, with many samples yielding elemental aluminium, silicon, calcium, and iron as minor components in the adhesives. With the IR spectra of Type 3B yielding peaks associated with metal soaps, it is plausible that these metals may have played a role in differentially preserving some constituents over others.

While studies conducted on metal soaps have highlighted the reaction between a metal base and the ester or acid functional group of a triglyceride fat, reactions with beeswax have been studied in comparatively limited numbers (Daniels, 2007; Cotte *et al.*, 2016). Both Liang and Scott (2014) and Stacey *et al.* (2018) have described alterations in beeswax after its combination with metal salts to create paints. In a study of ancient Egyptian waxy pigmented material by Liang and Scott (2014), the authors highlight the differences in GC/MS constituents in comparing the results of red and green pigmented waxes to fresh beeswax under the same analytical conditions. Studies of encaustic paint and punic wax (Stacey *et al.*, 2018) are now beginning the process of understanding the reactions between metal salts (in the case of the study, sodium and lead salts) and beeswax, and highlight that a multi-method approach such as that employed herein improves measures to evaluate material of this kind.

Table 6.30. A summary of the results from the multi-method analysis at Renbaan Cave and the interpretation of the adhesive source for each specimen. Also included are details on stratigraphic context, ascribed tool typology and the raw material of the stone tool.

Layer	Sample No.	Residue Type	Tool Typology	Raw Material	Constituents (identified by py-GC/MS, GC/MS, or IR)	Interpreted source
Surface cleanings	RB01	3B	Adze	Silcrete	<i>Organic</i> - DHA - phenols - short and mid- chain dicarboxylic acids - even numbered long chain alcohols (C ₂₂ -C ₃₀) and monocarboxylic acids (C ₂₀ -C ₃₆) - saturated and branched chain C _{15:0} and C _{17:0} - 14- and 15-hydroxyhexadecanoic acid - long chain n-alkanes (C ₂₇ , C ₂₉ , C ₃₁) <i>Inorganic</i> - kaolin, iron oxide, silicate mixture - carbonates	<i>Organic</i> - bark pitch from conifer (likely <i>Widdringtonia</i> sp.) - beeswax - animal fat <i>Inorganic</i> - laterite soil, ochre - calcite
Bedding	RB03	3B	Adze	Silcrete	<i>Organic</i> -DHA, 7-hydroxy-DHA, 8, 15 - pimaradien-18-oate -phenols - even numbered long chain alcohols (C ₂₂ -C ₃₀) and monocarboxylic acids (C ₂₀ -C ₃₆) - saturated and branched chain C _{15:0} and C _{17:0} - 14- and 15-hydroxyhexadecanoic acid - long chain n-alkanes (C ₂₇ , C ₂₉ , C ₃₁) <i>Inorganic</i> - kaolin, iron oxide, silicate mixture - carbonates	<i>Organic</i> - plant material and conifer resin (likely <i>Widdringtonia</i> sp.) - beeswax - animal fat <i>Inorganic</i> - laterite soil, ochre - calcite
	RB05	3B	Adze	CCS	<i>Organic</i> -DHA, 8, 15 - pimaradien-18-oate -phenols -non-specific tannins - even numbered long chain alcohols (C ₂₂ -C ₃₀) and monocarboxylic acids (C ₂₀ -C ₃₄)	<i>Organic</i> - bark pitch, source unknown - beeswax - animal fat - non- specific protein <i>Inorganic</i>

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					<ul style="list-style-type: none">- saturated and branched chain C_{15:0} and C_{17:0}- 14- and 15-hydroxyhexadecanoic acid- long chain n-alkanes (C₂₇, C₂₉, C₃₁)- pyrrole, toluene, indene, methyl-indene, methyl- and ethyl- phenols (pyrolysis only) <i>Inorganic</i> <ul style="list-style-type: none">- Kaolin, iron oxide, silicate mixture- carbonates	<ul style="list-style-type: none">- laterite soil, ochre- calcite
RB06_01/ RB06_02	1A/3B	Adze	Silcrete	<i>Organic</i> <ul style="list-style-type: none">- DHA- phenols- non-specific tannins-short and mid- chain dicarboxylic (C₁₆ and C₁₈) acids- even numbered long chain alcohols and monocarboxylic acids- saturated and branched chain C_{15:0} and C_{17:0}- 14- and 15-hydroxyhexadecanoic acid- long chain n-alkanes (C₂₇, C₂₉, C₃₁)- pyrrole, toluene, indene (pyrolysis only) <i>Inorganic</i> <ul style="list-style-type: none">- Kaolin, iron oxide, silicate mixture- carbonates	<i>Organic</i> <ul style="list-style-type: none">- plant material and conifer resin (likely <i>Widdringtonia</i> sp.)- beeswax- animal fat- non-specific protein <i>Inorganic</i> <ul style="list-style-type: none">- laterite soil, ochre- calcite	
RB07	1A	Scraper	Quartz	<i>Organic</i> <ul style="list-style-type: none">- DHA- even numbered long chain alcohols (C₂₆-C₃₀) and monocarboxylic acids (C₂₀-C₂₈)-phenols- long chain n-alkanes (C₂₇, C₂₉, C₃₁)- 1,3,5-trihydroxy-benzene and 1,2 dihydroxy-4-propyl-benzene (pyrolysis only) <i>Inorganic</i> <ul style="list-style-type: none">- possible, kaolin minerals	<i>Organic</i> <ul style="list-style-type: none">-beeswax- plant material, sourced likely from a conifer (<i>Widdringtonia</i> sp.) and a plant with catechin tannins <i>Inorganic</i> <ul style="list-style-type: none">- possible, clay	
RB12	1A	Utilized flake	CCS	<i>Organic</i> <ul style="list-style-type: none">- saturated and branched chain C_{15:0} and C_{17:0}	<i>Organic</i> <ul style="list-style-type: none">-animal fat	

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Brown Sand with Vegetation	RB08	1A	Scraper	Quartz	<p><i>Organic</i></p> <ul style="list-style-type: none"> - ricinoleic acid - 1,3,5-trihydroxy-benzene - mid- chain dicarboxylic and hydroxy- acids (C₁₆ and C₁₈) - even numbered monocarboxylic acids (C₂₄-C₂₈) - long chain n-alkanes (C₂₅-C₃₁, even and odd chains) - saturated C_{15:0} and C_{17:0}, branched chain C_{15:0} monocarboxylic fatty acids <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - silicates, quartz - possible carbonates 	<p><i>Organic</i></p> <ul style="list-style-type: none"> - castor oil- type plant - catechin tannin - animal fat <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - quartz containing mineral or loose material
	RB02	3B	Adze	Silcrete	<p><i>Organic</i></p> <ul style="list-style-type: none"> - DHA - ricinoleic acid - phenols - non-specific tannins - short and mid- chain dicarboxylic (C₁₆ and C₁₈) acids - even numbered long chain alcohols (C₂₂-C₃₀) and monocarboxylic acids (C₂₀-C₃₆) - saturated and branched chain C_{15:0} and C_{17:0} - 14- and 15-hydroxyhexadecanoic acid - long chain n-alkanes (C₂₇, C₂₉, C₃₁) <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - kaolin, iron oxide, silicate mixture - carbonates 	<p><i>Organic</i></p> <ul style="list-style-type: none"> - bark pitch from conifer (likely <i>Widdringtonia</i> sp.) - beeswax - animal fat - castor oil- type plant <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - laterite soil, ochre - calcite
GAS	RB09	1A	Scraper	Quartz	<p><i>Organic</i></p> <ul style="list-style-type: none"> - DHA - 1,3,5-trihydroxy-benzene and 1,2 dihydroxy-4-propyl-benzene - phenols - mid- chain dicarboxylic and hydroxy- acids (C₁₆ and C₁₈) - even numbered long chain alcohols (C₂₂-C₃₀) and monocarboxylic acids (C₂₀-C₂₈) - long chain n-alkanes (C₂₇, C₂₉, C₃₁) 	<p><i>Organic</i></p> <ul style="list-style-type: none"> - bark pitch from a conifer (<i>Widdringtonia</i> sp.) and a plant with catechin tannins - possible beeswax - non-specific protein <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - possible, clay - multiple sources of carbonates

				<ul style="list-style-type: none"> - pyrrole, toluene, and methyl- and ethyl- phenols and indene, methyl indene (pyrolysis only) <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - possible kaolin minerals - possible carbonates 	
RB10	3B	Adze?	Silcrete	<p><i>Organic</i></p> <ul style="list-style-type: none"> -DHA - phenols - 14- and 15-hydroxyhexadecanoic acid - short chain dicarboxylic acid (C₆-C₁₀) - even numbered long chain alcohols (C₂₂ – C₃₀) and monocarboxylic acids (C₂₀- C₃₀) - long chain n-alkanes (C₂₇, C₂₉, C₃₁; C₂₉ most abundant) <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - Kaolin, iron oxide, silicate mixture - Carbonates 	<p><i>Organic</i></p> <ul style="list-style-type: none"> - beeswax - waxy plant and conifer resin (<i>Widdringtonia</i> sp.) <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - laterite soil, ochre - calcite
RB11	3B	Adze	Silcrete	<p><i>Organic</i></p> <ul style="list-style-type: none"> - phenols - short chain dicarboxylic acid (C₆-C₁₀) - even numbered long chain alcohols and monocarboxylic acids - long chain n-alkanes (C₂₇, C₂₉, C₃₁; C₂₉ most abundant) - saturated and branched chain C_{15:0} and C_{17:0} <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - Kaolin, iron oxide, silicate mixture - Carbonates 	<p><i>Organic</i></p> <ul style="list-style-type: none"> - waxy plant material and conifer resin (likely <i>Widdringtonia</i> sp.) - animal fat <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - laterite soil, ochre -calcite

6.3.3. Results and Interpretation of the analysis of the Sehonghong material

This section highlights only the chromatography analyses for the material from Sehonghong. As this material underwent only a single type of analyses, the interpretive summary is included within the chromatography section for readability and to reduce repetition.

6.3.3.1. Gas Chromatography/ Mass Spectrometry (GC/MS) & an Interpretive

Summary

Of the specimens analysed by optical light microscopy, twelve samples underwent solvent extraction and analysis by GC/MS. Due to the lack of material available for solid sampling, samples were acquired by submerging the tools in a solvent bath. Table 6.32, at the end of the section, describes the details of each specimen, the residue type, and the associated archaeological context.

Overall, the most frequently occurring constituents of the analysed specimens were saturated and monounsaturated carboxylic fatty acids and phthalates. The phthalates, diisooctyl phthalate in particular are common additives in plastics (Meeker *et al.*, 2009). These compounds are most likely to be modern contaminants associated with the storage of the archaeological collections.

The saturated fatty acids observed, including short chain and mid-chain lengths, are not diagnostic of a particular source (Devièse *et al.*, 2017). From samples SEH02, SEH03, and SEH09, hexadecenoic (both *cis*- and *trans*- isomers) and octadecenoic (oleic) acids were also found. These unsaturated fatty acids, in combination with a prominent peak of hexadecanoic acid (C_{16:0}), may suggested the presence of heated, plant lipids (Mills and White, 1994; Colombini and Modugno, 2009; Villa *et al.*, 2012).

A series of long-chain n-alkanes, with an abundance distribution that resembles a mineral-based hydrocarbon wax series was identified in SEH01 and SEH05 (Ng *et al.*, 1994). Due to the radiocarbon dates and the cultural affiliations of SEH01 to the Robberg period (14 735 – 14 125 calBP [Loftus *et al.*, 2015]), it is probable that the hydrocarbon wax is a modern contaminant from

excavation. In the case of SEH05, an artefact recovered from the DC layer and associated with occupations spanning 1265-980 calBP up to the very end of the 1800s/early 1900s (Mitchell, 1996; 2010), two hypotheses are suggested for its source. Such waxes, including paraffin, were not in manufacture until the mid-19th century (Sanderson *et al.*, 1988) and are relatively modern. The material is either the result of modern contamination, or is authentic.

Table 6.31. List of compounds corresponding to the marked peaks in Fig. 5.20. TMS signifies trimethylsilyl derivative.¹

Label	Compound Name	m/z values of characteristic fragment ions
<i>monocarboxylic fatty acids</i>		
C15:0 Br	pentadecanoic acid, branched chain TMS	299, 117, 73
C16:0	hexadecanoic acid, TMS	311, 117, 73
C17:0 Br	heptadecanoic acid, branched chain TMS	327, 117, 73
C18:1	octadecenoic acid, TMS	339, 117, 73
C18:0	octadecanoic acid, TMS	341, 117, 73
RA	ricinoleic acid, TMS	359, 187, 73
<i>sterols</i>		
	cholesterol, TMS	453, 443, 368, 353, 329, 129, 73
<i>diterpenoids</i>		
P	pimaric acid, TMS	374, 257, 256, 121, 105, 73
S	sandaracopimaric acid, TMS	374, 359, 257, 256, 121, 73
DHA	dehydroabiatic acid, TMS	372, 257, 239, 73
7-OH-DHA	7-hydroxyabiatic acid, TMS	460, 445, 237, 191, 73
7-oxo-DHA	7-oxo-dehydroabiatic acid, TMS	386, 268, 253, 187, 73

¹Identifications and m/z values from published source, including Helwig *et al.* 2008; Helwig *et al.* 2014; NIST Database library

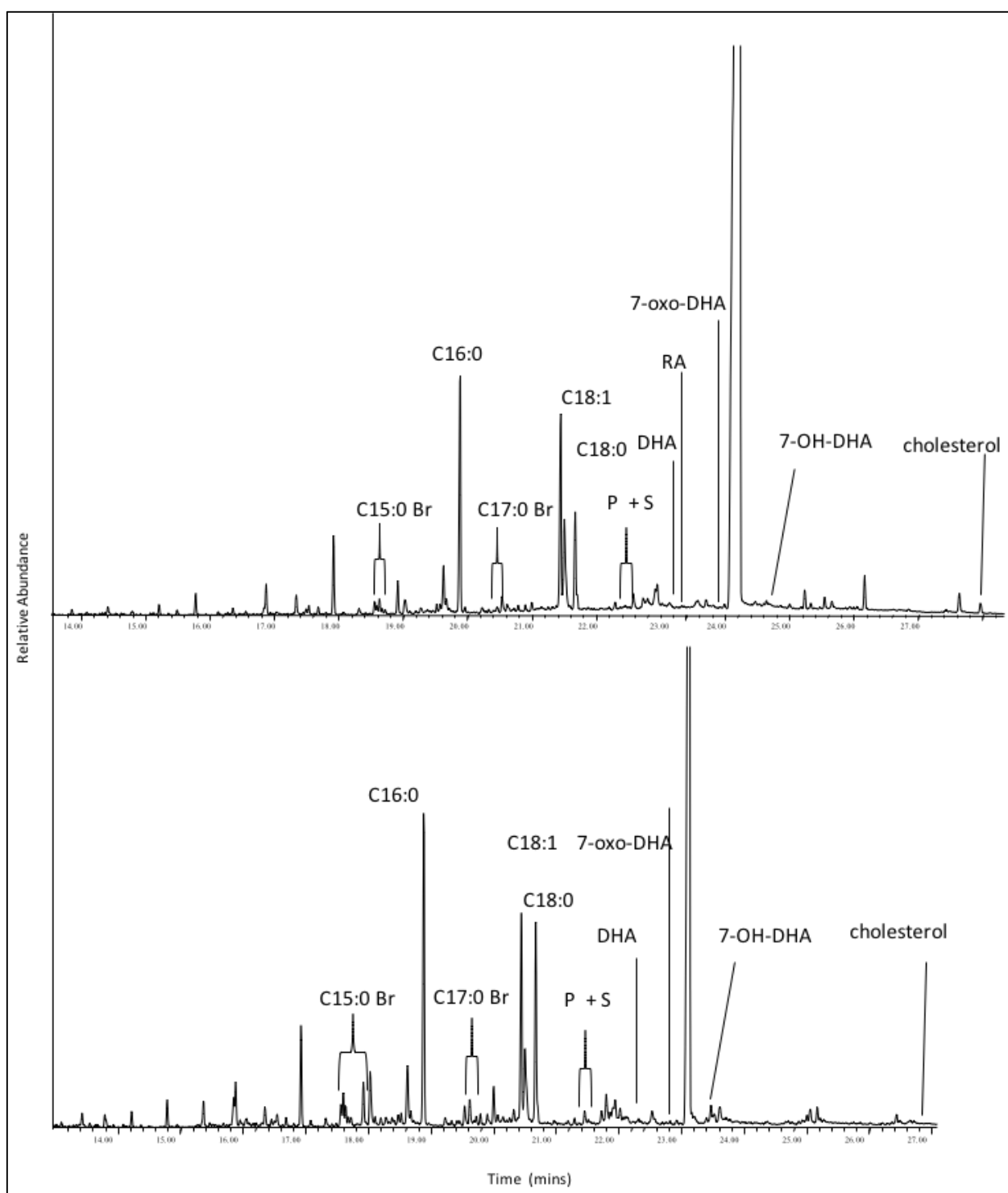


Figure 6.21. Sehonghong: Total ion chromatogram of SEH04 at a retention time between ~14 - 28min (top) and SEH05 between ~13-27min (bottom), highlighting a selection of components. All components are TMS derivatives.

Two scrapers from the DC layers, SEH04 and SEH05, yielded more complex chromatograms than all the other analysed materials from this site (Figure 6.21 and corresponding Table 6.31). Notable compounds from SEH04 include polycyclic aromatic hydrocarbons (PAHs) pyrene and phenanthrene, C_{15:0} and C_{17:0} branched chain fatty acids, cholesterol, cis- and trans- isomers of monounsaturated C_{16:1} and C_{18:1} fatty acids, ricinoleic acid, the abietanes, dehydroabietic acid (DHA), 7-hydroxy-DHA, and 7-oxo-DHA, and the pimaranes, pimaric acid and sandaracopimaric acid. The constituents of SEH05 are similar, with the exception that a paraffin series mineral hydrocarbon was present and ricinoleic acid absent in this sample.

The presence of the isomers of C_{16:1} and C_{18:1} fatty acids is indicative of the presence of a heated lipid material, likely plant in origin. A heated substance may also be supported by the presence of pyrene and phenanthrene, common PAHs in wood smoke (see Sections 6.3.1.4. and 6.3.2.4.). The combination of abietane and pimarane diterpenoids is indicative of the presence of an exudate of a conifer from the Pinaceae family (Mills and White, 1994; Otto and Wilde, 2001; Colombini *et al.* 2003). The abietane, dehydroabietic acid is a very stable derivative of abietic acid, and is present in hardened pine resins; its derivatives are also commonly identifiable in archaeological and art objects (Osete-Cortina *et al.* 2005; Helwig *et al.* 2008). The preservation of pimarane skeleton diterpenoids is rare in archaeological contexts (Colombini and Modugno, 2009), having been documented in instances of exceptional preservation (i.e. ice patch finds, Helwig *et al.* 2008). The identification of pimaric acid and sandaracopimaric acid in these samples, probably the result of the relatively recent age of the material, indicates that the most likely source of the resin was *Pinus* sp. rather than other genera from the Pinaceae family (Mills and White, 1994).

SEH04 also yielded ricinoleic acid (12-hydroxy-9-octadecanoic acid). This fatty acid is the main component of castor oil, making up between 83-89% of the total fatty acid content and is a marker for this material (Mills and White, 1994). The interpreted presence of castor oil in the residue from this specimen is consistent with the relatively recent age of this layer. It cannot be

discounted, however, that the presence of a hitherto unknown ricinoleic acid-containing plant product may also be the source of this compound.

The detection of cholesterol in combination with C_{15:0} and C_{17:0} saturated fatty acids in both SEH04 and SEH05 suggests the presence of animal fats (Colombini and Modugno, 2009; Regert, 2011). The presence of branched-chain C₁₅ and C₁₇ fatty acids commonly belongs to bacterial sources associated with this material (Dudd *et al.*, 1998; Corr *et al.*, 2008; Kedrowski *et al.*, 2009).

Table 6.32. A summary of the compounds identified in the SEH specimens, with information relating to the archaeological context of each sample.

Stratigraphic Context	Specimen Details	Lab No.	Residue Type	Typology	Main Components
SS	SEH92 L12-0003	SEH12	Type 1C	Adze	
DC	SEH92 N2 003 -1	SEH04	Type 1C	Scraper	- abietane and pimarane diterpenoids - polycyclic aromatic hydrocarbons (PAHs) - odd-chain branched and unbranched fatty acids (C ₁₅ and C ₁₇) - ricinoleic acid - mono unsaturated fatty acids (C _{16:1} and C _{18:1} , cis- and trans- isomers)
	SEH92 N2 003 -2	SEH05	Type 1C	Scraper	- abietane and pimarane diterpenoids - PAHs - odd-chain branched and unbranched fatty acids (C ₁₅ and C ₁₇) - long chain n-alkanes (hydrocarbon series) - mono unsaturated fatty acids (C _{16:1} and C _{18:1})
	SEH92 M12	SEH06	Type 1C	Scraper	- phthalates - monocarboxylic fatty acids (C _{8:0} , C _{9:0} , C _{14:0} -C _{18:0})
GWA	SEH92 M13 004	SEH07	Type 1C	Scraper	- phthalates - monocarboxylic fatty acids (C _{8:0} , C _{9:0} , C _{14:0} -C _{18:0})
	SEH92 M13 004	SEH08	Type 1C	Scraper	- phthalates - monocarboxylic fatty acids (C _{8:0} , C _{9:0} , C _{14:0} -C _{18:0})
	SEH92 N13 004	SEH09	Type 1C	Scraper	- phthalates - saturated monocarboxylic fatty acids (C _{8:0} , C _{9:0} , C _{14:0} -C _{18:0})

					- mono unsaturated fatty acids (C _{16:1} and C _{18:1})
SA	SEH92 K13 036A	SEH11	Type 1C	Bladelet	-phthalates
BARF	SEH92 H13 064	SEH10	Type 1C	Bladelet	- phthalates -monocarboxylic fatty acids (C _{14:0} -C _{18:0})
RF	SEH92 #2322	SEH13	Type 1C	Blade	-even number, mid chain monocarboxylic fatty acids (C _{14:0} -C _{18:0} , C _{18:1});
RBL	SEH92 I12 067 - 1	SEH02	Type 1C	Bladelet	- phthalates -saturated monocarboxylic fatty acids (C _{8:0} , C _{9:0} , C _{14:0} -C _{18:0}) - mono unsaturated fatty acids (C _{16:1} and C _{18:1})
	SEH92 L12 067- 2	SEH03	Type 1C	Bladelet	- phthalates -saturated monocarboxylic fatty acids (C _{8:0} , C _{9:0} , C _{14:0} -C _{18:0}) - mono unsaturated fatty acids (C _{16:1} and C _{18:1}), cis- and trans- isomers of C _{16:1}
	SEH92 J12 067	SEH01	Type 1C	Bladelet	-long chain n-alkanes (hydrocarbon series) - sterols -even numbered, mid and long chain alcohols (C ₁₈ -C ₃₀) - saturated monocarboxylic fatty acids (C _{8:0} -C _{22:0})

6. 4. Analytical results: adhesives from ‘mastic lumps’ & hafted implements

6.4.1. Adhesive Lumps from Boomplaas

6.4.1.1. FTIR Spectroscopy

The IR spectra of the four lumps of material described as ‘mastic’ from Boomplaas (J. Deacon, 1984) are described in Figure 6.22, with prominent peaks and associated functional group assignments highlighted in Table 6.33. Analyses of assigned peaks indicate the presence of mixtures of organic and inorganic minerals in all sampled materials, with a predominance of multiple inorganic minerals types identified in BPA03. Generally, organic materials were identified based on

the presence of broad –OH stretching regions between 3600-3000 cm^{-1} and sharp peaks at the C-H stretch around $\sim 2920 \text{ cm}^{-1}$ and a doublet $\sim 2870 \text{ cm}^{-1}$ and $\sim 2850 \text{ cm}^{-1}$ present in all spectra; these peaks, however, are noticeably weaker in BPA03.

The peak assignments, and by extension the functional groups, associated with organic components in BPA01, BPA02, and BPA04, are all relatively similar with strong bands associated with C=O stretching of carbonyl groups, C=C stretching, C-H deformation or -CH₃ bending, as well as C-O esters and alcohols. Weak to medium bands were also identified, and assigned to C-O-C stretches and various types of bending and stretching of C-H from olefinic and aromatic groups (between 1000-700 cm^{-1}). The only peaks that could be assigned to organic functional groups in BPA03, by contrast, were associated with the C-O-C stretching region at 1195 cm^{-1} of alcohols and esters, and C-H in plane bending of aromatics, aliphatic phosphates (P-O-C), or a phosphate ion at 1014 cm^{-1} (Coates, 2006).

When compared to reference materials analysed under the same conditions, the spectra of BPA01, BPA02, and BPA04 are qualitatively similar to latex derived from *Euphorbia tirucalli* (No. 43970, Kew Economic Botany Collections) with strong C-H stretching regions, alongside C=O stretching vibrations, C=C stretching, C-O-C and C-O bending associated with esters and alcohols, alongside weak C-H bending and stretching associated with olefinic and aromatic groups.

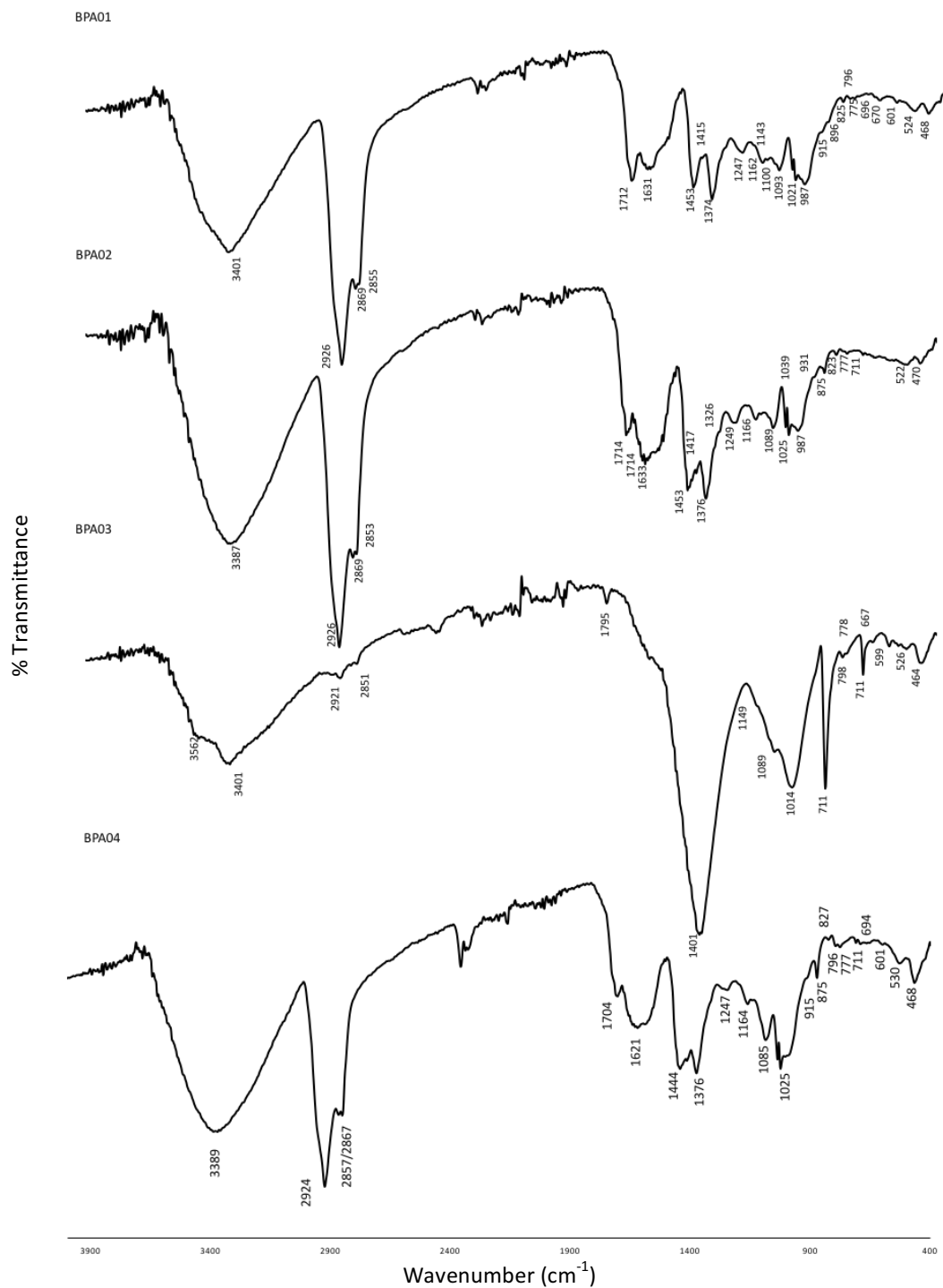


Figure 6.22. Boomplaas: IR spectra in % transmittance of the four Boomplaas adhesive lumps from the BLD member.

Table 6.33. A summary of the IR peak assignments for the adhesive specimens highlighted in Figure 6.21.

Assignment*	Wavenumber (cm ⁻¹)			
	BPA01	BPA02	BPA03	BPA04
ν(O-H)	Max. at 3401	Max. at 3387	3562/3401	Max. at 3389
ν(C-H)	2926/2869/2855	2926/2869/2853	2921/2851	2924/2867/2857
Carbonates	X	X	1795	X
ν(C=O)	1712	1714	X	1704
carboxyl group	X	X	X	X
ν(C=C) stretch;	1631	1633	X	X
ν(C=C-C) of an aromatic ring	X	X	X	1621 (broad)
δ(C-H) deformation (saturated aliphatic groups) or γ(-CH ₃) bending	1453 / 1374	1453/1376	X	1444/1376
In-plane γ vinyl (C-H) of olefinic groups, or carbonate anion	1415	1417	1401	1415
γ (-OH), phenol or tertiary alcohol, or primary or secondary γ (-OH)	X	1326	X	X
ν(C-O) stretch of esters and alcohols	1247	1249	X	1247
ν(C-O -C) of esters and alcohols	1183 (weak)	X	1195	X
ν(S-O)	X	X	1149	X
ν(C-O) or ν(Si-O)	1162/1093/1021	1166/1089/1039	1089	1164/1085/1025
In-plane γ(C-H) of aromatic groups	X	X	1014	
Out-of-plane γ(C-H) of olefinic or aromatic groups	X	987	X	996
Carbonates	X	875/711	871/711	875/711
Out-of-plane γ(C-H), aromatic ring groups	825	823	X	827
Silicates	796/775, 694, 524/468	777, 522/470	798/778, 526/464	796/777, 694, 530/468
Out-of-plane γ(C-H)	X	721	X	X
γ(S-O), possible	X	601	670/599	601

*Assignments based on published literature: van der Marel and Beutelspacher, 1976; Russell and Fraser, 1994; Colombini *et al.*, 2003; Coates, 2006; Helwig *et al.*, 2008; Vahur *et al.*, 2011. Peaks at ~2370cm⁻¹ are attributed to atmospheric carbon dioxide and are not included in the interpretations or listed data.

The inorganic mineral types identified in the Boomplaas specimens included calcium carbonates, silicates. Silicates were identified in all analysed samples based on the presence of a broad stretching region between 1087 - 1093 cm⁻¹ and peaks at 694cm⁻¹, ~520 and ~464cm⁻¹, with quartz determined as the most likely source in BPA01, BPA03, and BPA04 due to a doublet identified at ~778 and 800 cm⁻¹ (van der Marel and Beutelspacher, 1976). It is plausible that peak

shifting in BPA04 to 530cm^{-1} may be caused by the presence of iron oxides (Fraser and Russell, 1994). Calcium carbonates, with calcite providing the best IR match, were identified in BPA02-BPA04 based on weaker, sharp peaks at 875 cm^{-1} and 711 cm^{-1} , as well as the addition of a broad stretching region at 1401cm^{-1} and a weak peak at 1795 cm^{-1} in BPA03. Calcium sulphate dehydrate (gypsum) is also suggested as a possible inorganic mineral source in the adhesive from BPA03, with some peaks consistent with an IR reference of construction gypsum (Vahur *et al.*, 2016). This assessment was based on several factors, which include two peak maxima in the -OH stretching region at 3526cm^{-1} and 3389cm^{-1} , and peaks at 1141cm^{-1} , as well as 670 and 599cm^{-1} , associated with S-O stretching and bending, respectively.

6.4.1.2. SEM/EDS: Imaging and Elemental Composition

The results of the elemental composition analysis of the adhesive lumps from Boomplaas are highlighted in Table 6.34. Carbon and oxygen were identified as the main elemental components in all analysed material, with calcium appearing as an additional major component in BPA03 (Figure 6.23). These findings are consistent with the IR spectroscopic analysis, confirming the organic composition of BPA01, BPA02, and BPA04 (Figure 6.23) and a larger portion of inorganic materials present in BPA03. The presence of calcium in BPA02 and BPA04, and its relatively high abundance in BPA03, is consistent with the identified of calcium carbonate minerals in these samples. The abundance of calcium in BPA03 may also be attributed to calcium sulphate dehydrate; however, the absence of sulphur within the scanned area trace makes this hypothesis unlikely. The abundance of silicon, as a minor component in BPA02 and BPA04, as well as its presence as trace in BPA03, is consistent with the presence of silicate minerals in the IR spectra.

Table 6.34. The elemental composition of the Boomplaas adhesive samples.

Elemental Composition ¹			
Sample No.	Major	Minor	Trace
BPA01	C (88.3) O (11.7)		
BPA02	C (59.63) O (35.02)	Ca (1.52) Si (1.42)	Na (0.25) Mg (0.44) Al (0.6) P (0.18) Cl (0.34) K (0.29) Fe (0.08)
BPA03	C (23.86) O (58.69) Ca (15.92)		Mg (0.21) Al (0.21) Si (0.9) P (0.11) K (0.1)
BPA04	C (59.63) O(35.02)	Si (1.42) Ca (1.52)	Na (0.25) Mg (0.44) Al (0.6) P (0.22) S (0.18) Cl (0.34) K (0.29) Fe (0.08)

¹ Qualitative analyses, and the terms major, minor, and trace components are subjective. Major is defined at more than 10 atomic%; minor as 1-10 atomic %; and, trace at less than 1 atomic%. These terms are defined in Goldstein *et al.* (2003).

Aluminium and magnesium are likely derived from mineral types not identified in the IR spectra. This may similarly be the case with sodium and chlorine. Phosphorus and potassium have been used as elemental markers to identified human activity, as indicators of degradation of organic material (Price and Burton, 2011). Its presence in relatively low amounts in the BPA material may be accounted for by the degradation of organic phosphorus - and potassium – containing derived from the adhesive lumps or the depositional environment. The presence of iron in trace amounts in BPA02 – 04 may indicate of the presence of iron-containing minerals. This element may explain the reddish colour of BPA02. Their relatively low abundance makes it unlikely that iron oxides are present in any high abundance (as was the case in the material from Renbaan Cave).

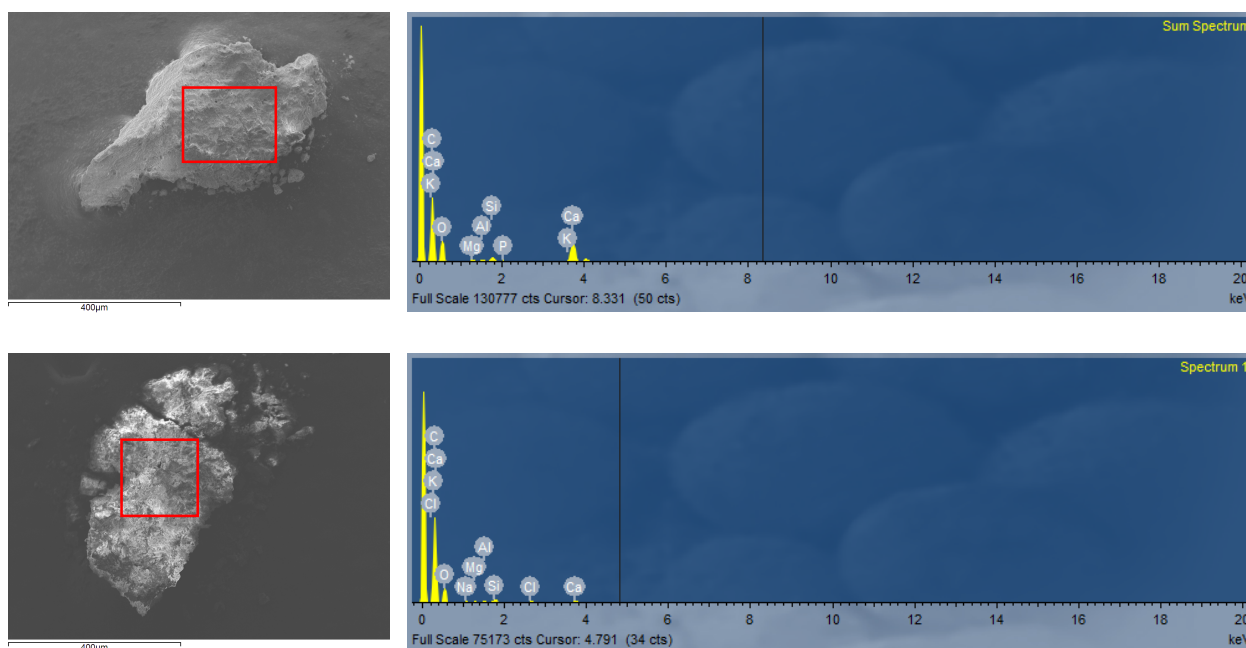


Figure 6.23. Boomplaas: Scanning electron microscope images of and elemental spectra of BPA03 (top) and BPA04 (bottom).

6.4.1.3. Pyrolysis –Gas Chromatography/ Mass Spectrometry (py-GC/MS)

Analyses by pyrolysis-GC/MS of the BPA01-04 further supported the findings by IR and SEM/EDS. Quantitatively, there are similarities in the pyrograms of the four samples (Figure 6.24), with a noted prevalence of compounds eluting between 40.5 – 55mins. These components (highlighted in blue) displayed in Figure 6.24 have a high abundance of m/z 218, 203, and 189, in varying ratios, and are thus classified as triterpenoids. BPA03 has a noticeably low abundance of organic constituents, despite having the highest amount of sample utilised for analysis (149µg). This may be accounted for by the mineral content identified in this sample.

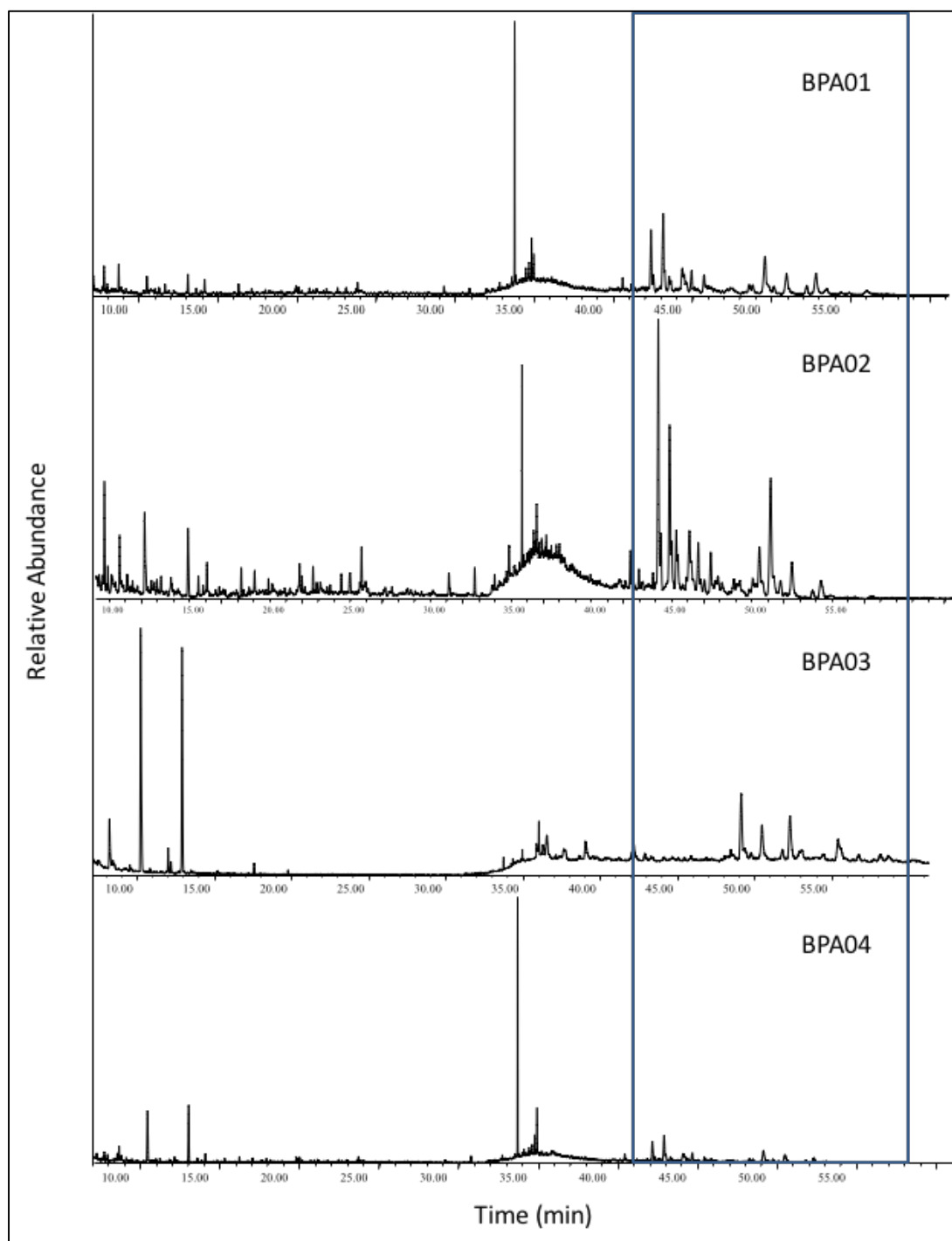


Figure 6.24. Boomplaas: Pyrograms of all adhesive specimens, highlighting the region between 40.5 – 55min. Several triterpenoid compounds were identified in this retention time range.

Table 6.35 summarises the molecular components detected by pyrolysis-GC/MS for all the BPA specimens. Notable components in BPA01, BPA02, and BPA04 were a series of saturated and unsaturated mono-carboxylic fatty acids ranging between six and twenty carbon units, a series of short to long chain n-alkenes and n-alkanes (in relatively low abundance in BPA04), and mid- to long- chain alcohols (again, in low abundance in BPA04). Also identified were several phenolic compounds, including vanillin (TMS) (BPA01 and 04), benzoic acid (TMS) (BPA01, 02, and 04), and 4-Z-isoeugenol (TMS) (BPA01). These compounds have been identified as products of lignin that are broken down during analytical pyrolysis Tamburini *et al.* (2014), and suggest the presence of these plant-derived macromolecular structures in three of the four analysed specimens. The combination of monocarboxylic fatty acids, n-alkanes and n-alkenes may also be indicative of the pyrolytic breakdown of suberin and suberan molecules.

Table 6.35. Boomplaas: A summary of the compound types identified in the BPA adhesive samples by py-GC/MS.

Sample No.	Pyrolytic components				
	Mono-carboxylic fatty acids (m/z117)	n-alkanes (m/z85) and n-alkenes (m/z83)	Alcohols (m/z75, 103)	Triterpenoids (m/z 189, 203, 218)	Phenolic compounds (multiple m/z)
BPA01	C _{8:0} – C _{18:0} C _{8:1} – C _{14:1} , C _{16:1} (cis- and trans- isomers) C _{18:1} (cis- and trans- isomers) Branched chain C _{15:0} , C _{16:0} and C _{17:0}	C ₁₁ –C ₃₁ , C ₁₁ –C ₂₁	C ₂₂ , C ₂₄ , C ₂₈	✓	✓
BPA02	C _{7:0} –C _{16:0} , C _{18:0} C _{16:1} , C _{18:1} Branched chain C _{15:0}	C ₁₁ –C ₂₉ , C ₁₁ –C ₂₃	C ₂₂ , C ₂₄ (low abundance)	✓	✓
BPA03	C _{16:0} and C _{18:0}	X	X	✓	X
BPA04	C _{6:0} – C _{18:0} , C _{20:0} (including iso- C _{16:0}) C _{6:1} – C _{18:1}	X	C ₂₂ and C ₂₄ (low abundance)	✓	✓

6.4.1.4. Gas Chromatography/ Mass Spectrometry (GC/MS)

The results from the four Boomplaas adhesive lumps yielded a combination of markers from plant and animal sources. The total ion current chromatograms (TICs) of BPA01, BPA02, and BPA04 were identical in their constituents. These samples all contained a series of short chain dicarboxylic acids ($C_6 - C_{12}$), even-numbered long-chain alcohols ($C_{24}-C_{28}$), even-numbered saturated long-chain monocarboxylic fatty acids ($C_{20}-C_{28}$) and unsaturated 11-eicosanoic acid ($C_{20:1}$), hexadecanoic acid ($C_{16:0}$) as the dominant fatty acid with both cis- and trans isomers of hexadecenoic acid present, octadecanoic acid ($C_{18:0}$) as the second-most abundant fatty acid with both isomers of octadecenoic acid present and the cis- isomer prominent (an abundance ratios of cis- $C_{18:1}:C_{18:0}$ was 0.76 [BPA01], 1.36 [BPA02] and 0.56 [BPA04], triterpenoids with lupane, cycloartane, oleanane and ursane skeletons structures, C_{29} and C_{31} long chain hydrocarbons (C_{31} only in BPA01), and the phenolic compounds 4-benzoic acid, vanillic acid, syringic acid and ferulic acid. These components are derived from plant material with the phenolics highlighting the presence of lignin breakdown. The heating of this plant substance is also suggested based on the presence of both cis- and trans- isomers of unsaturated $C_{18:1}$ (octadecenoic) fatty acids (Ribechini *et al.*, 2008b). The high abundance of saturated and unsaturated (both cis- and trans- isomers) C_{18} monocarboxylic fatty acids have also been identified in plant latexes and may indicate the type of exudate exploited as an adhesive. Indeed, both cis- and trans- isomers of $C_{18:1}$ are present in the acidic fractions of *Euphorbia tirucalli* and *E. ingens* latex samples. Based on the combined presence of odd-numbered long chain hydrocarbons (only C_{29} and C_{31} were identifiable), even-numbered long chain alcohols and fatty acids, it is also hypothesised that this adhesive material contained a waxy component derived from a plant as well (Kunst and Samuels, 2003; Roffet-Salque *et al.* 2017). Mid- and long chain dicarboxylic and terminal hydroxycarboxylic acids were identified in these specimens as well. BPA01 yielded C_{16} , C_{18} , C_{20} , and C_{22} chains, while BPA02 and BPA04 were limited to C_{16} and C_{18} . This is evidence of the presence of a bio-polyester derived from suberin, and is

consistent with a heated material (Villa *et al.*, 2012). These results are supported by the py-GC/MS results.

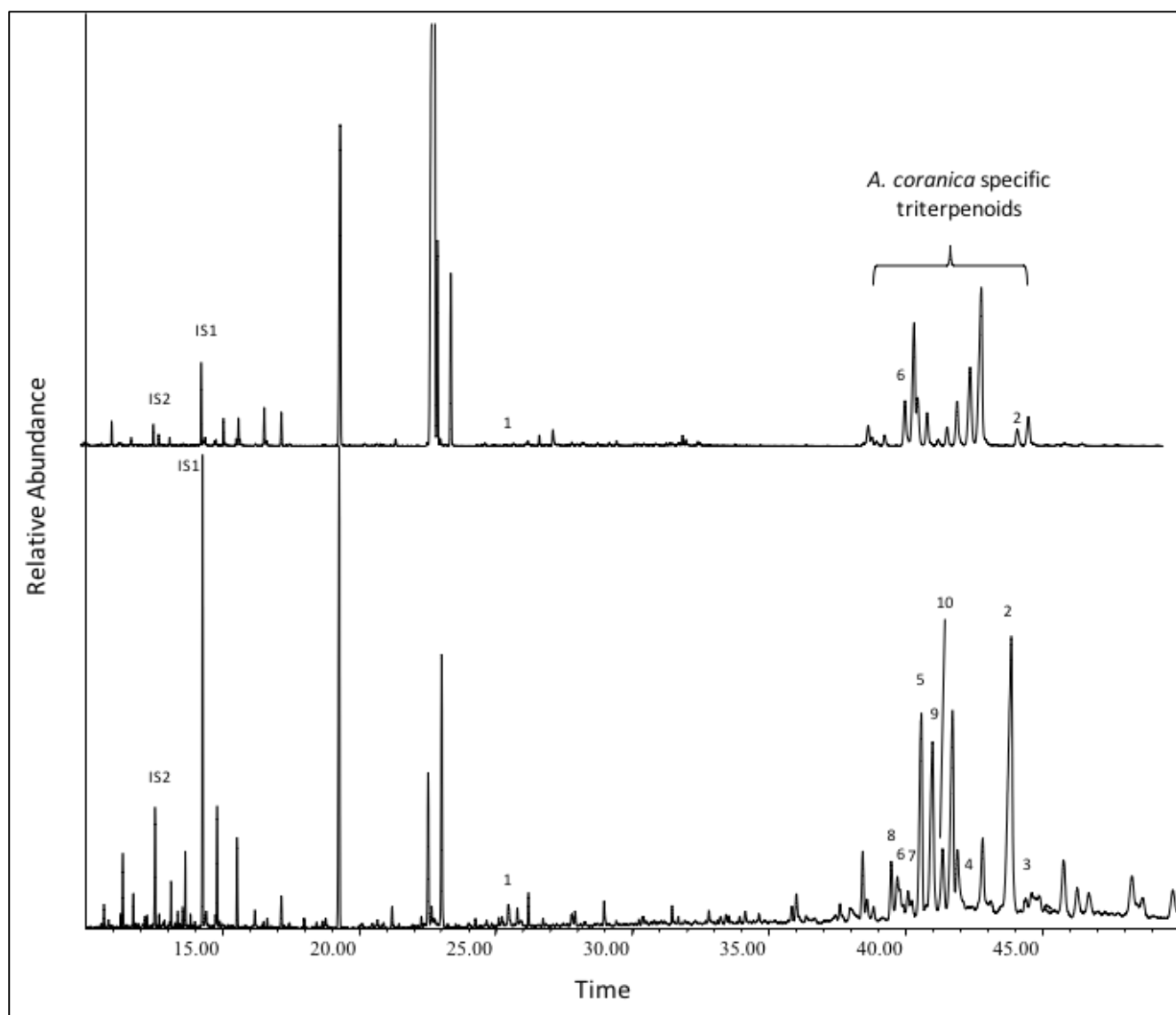


Figure 6.25. Total ion chromatograms from 10 to 50 min of acidic fractions highlighting sterol and triterpenoid constituents of the bulb of *A. coranica* (top) and BPA04 (bottom).

Table 6.36. Boomplaas: A summary of the compound types identified in the BPA adhesive samples by GC/MS.

No.	Compound Name
1	11-eicosanoic acid (gondoic acid), TMS
2	24-methylene-cycloarten-3-ol, TMS
3	Epi-lupeol, TMS
4	24-methylene-cycloarten-3-one, TMS
5	Lanosterol, TMS
6	β -sitosterol, TMS
7	β -amyrin, TMS
8	β - amyrone
9	α - amyrone
10	α – amyrin, TMS
IS1	Tridecanoic acid, TMS
IS2	Hexadecane

With the presence of triterpenoids, it is possible to narrow-down the taxonomic source. Among those triterpenoids identified included alpha- and beta-amyrin (TMS), beta-amyrone, epi-lupeol (TMS), lanosterol (TMS), as well as a number of unidentified ketones which are likely oxidation products (Mathe *et al.*, 2004). These components matched the constituents from *Euphorbia tirucalli* and *E. ingens* latex, particularly the prominent peak of lanosterol, while beta-amyrin (TMS) and beta-amyrone were also identified in the latex lump from Border Cave which was subsequently ascribed to *E. tirucalli* (d'Errico *et al.*, 2012). Due to the abundance of *Euphorbia* sp. in southern Africa, and only two such species represented, it would be inappropriate to narrow down the classification to species, and the identification thus remains at the genus level. The presence of these components is also consistent with published literature on modern *Euphorbia* sp. latexes (Gupta *et al.*, 2013). The compound 24-methylenecycloartan-3-one, a 3- ketone

structure, is not present in an analogous modern botanical source from the local region, however, 24-methylenecycloartenol was identified in the heated bulbs of *Ammocharis coranica* and bulb of *Chasmanthe* sp. This structural difference may be accounted for by an oxidization reaction of the 3-alcohol, a structural alteration that Mathe *et al.* (2004) discussed in the characterization of ursene, oleanene, and lupane triterpenoids to account for the presence of alpha- amyrone, beta- amyrone and lupenone in *Boswellia* sp. resin. The bulb of *A. coranica* also yielded 11-eicosanoic acid and was the only analysed specimen to have this combination of compounds. It is thus postulated that the due to the combination of these two components in three of the Boomplaas specimens, a member of this genus may be a likely second botanical source of the adhesive. Figure 6.25 and the corresponding Table 6.36 compares the TICs of BPA04 to the exudate obtained from a heated *A. coranica* bulb. It is also suggested that a third adhesive source is present in BPA02. Ricinoleic acid was also found in this sample. As previously discussed in Section 6.3.3.1, this fatty acid is the dominant constituent of castor oil (Mills and White, 1994), however the known age of the BLD member the source of BPA02 is not consistent with the recent arrival of the castor plant *Ricinus communis* (Mitchell, 2002). It is thus possible that an unknown ricinoleic acid-containing plant product may also be the source of this compound.

The combined presence of C_{15:0}, C_{17:0}, C_{19:0} fatty acids, glycerol and cholesterol are interpreted as derived from animal fat (Colombini and Modugno, 2009; Regert *et al.*, 2011; Helwig *et al.*, 2014). Branched-chain C₁₅ and C₁₇ acids are interpreted as likely derived from a bacterial source (Dudd *et al.*, 1998; Corr *et al.*, 2008; Kedrowski *et al.*, 2009). These compounds were found in BPA01, BPA02, and BPA04.

BPA03, by contrast yielded overall fewer markers and at relatively low abundance. The acidic fraction of the sample contained a series of short to mid- chain saturated monocarboxylic acids (C₉, C₁₁- C₁₈), branched chain C_{15:0} and C_{17:0} fatty acids, and vanillic acid. The branched chain fatty acids are interpreted as being derived from animal fat, while the vanillic acid combination with the presence of nonanedioic acid (azelaic acid) is interpreted as sourced from an unknown

plant material (Lucejko *et al.*, 2015; Luong *et al.*, 2017). This more limited range of compounds is consistent with the py-GC/MS, SEM/EDS, and FTIR results, which identified a mostly inorganic mineral source for this adhesive.

Diisooctyl phthalate was found in all samples. It is interpreted as a modern contaminant (Meeker *et al.*, 2009).

6.4.1.5. Interpretive Summary

A summary of the results and the interpreted sources of the adhesive is found in Table 6.37. At Boomplaas, the adhesive specimens may be divided into two groups based on the microscopy and analytical results. The first group includes BPA01, BPA02, and BPA04, which were microscopically classified as Type 7. They contain predominantly heated plant exudates derived from *Euphorbia* sp. latex as well as animal fat, and a minor inclusion of quartz and calcite. It is possible that an additional exudate is present in these three specimens. Similarities were noted between the analysed acidic fractions of the heated bulb of *A. coranica*, and the archaeological material. However, the main triterpenoid markers from this species were absent. Hence, this may suggest that the additional source could be from a relative of *A. coranica* (i.e. within the family of Amyrillidaceae). Further to this, BPA02, a fragment of adhesive bearing the impression of a tool, was unique among this group in that it contained castor oil.

BPA03 sits apart, classified as having a mixture of Type 7 and Type 8 residues, and when analysed by FTIR and SEM/EDS was found to have comparatively high amounts of inorganic calcium carbonate (matching calcite) in the sample. The analysis by chromatography of BPA03 identified animal fats and plant derived materials of an unknown source within this largely inorganic mixture.

Table 6.37. A summary of the results from the multi-method analysis at Boomplaas and the interpretation of the adhesive source for each specimen. Also included are details on stratigraphic context, ascribed tool typology and the raw material of the stone tool.

Layer	Sample No.	Residue Type	Constituents (identified by py-GC/MS, GC/MS, or IR)	Interpreted source
BLD	BPA01 (Pit 7)	7	<p><i>Organic</i></p> <ul style="list-style-type: none"> - triterpenoids (lupanes, oleanes, ursanes, cycloartanes) - phenols - short, mid-, and long chain dicarboxylic acids - mid- and long chain terminal hydroxycarboxylic acids - even numbered long chain alcohols (C₂₂-C₂₈) and monocarboxylic acids (C₂₀-C₂₈) - unsaturated 11-eicosanoic acid (gondoic acid) - saturated and branched chain C_{15:0} and C_{17:0} - long chain n-alkanes (C₂₉, C₃₁) - py-GC/MS: n-alkanes, saturated and unsaturated monocarboxylic acids <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - silicates 	<p><i>Organic</i></p> <ul style="list-style-type: none"> - heated plant material - <i>Euphorbia</i> sp. latex, and the exudate from <i>Ammocharis</i> sp. - animal fat <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - quartz
	BPA02 (Pit 9)	7	<p><i>Organic</i></p> <ul style="list-style-type: none"> - phenols - triterpenoids (lupanes, oleanes, ursanes, cycloartanes) - ricinoleic acid - short, mid- chain dicarboxylic acids - mid- chain terminal hydroxycarboxylic acids - even numbered long chain alcohols (C₂₂-C₂₈) and monocarboxylic acids (C₂₀-C₂₈) - unsaturated 11-eicosanoic acid (gondoic acid) - saturated and branched chain C_{15:0} and C_{17:0} - long chain n-alkanes (C₂₉, C₃₁) - py-GC/MS: n-alkanes, saturated and unsaturated monocarboxylic acids <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - silicates - carbonates 	<p><i>Organic</i></p> <ul style="list-style-type: none"> - heated plant material - <i>Euphorbia</i> sp. latex, and the exudate from <i>Ammocharis</i> sp. - animal fat - ricinoleic acid-containing plant <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - quartz - calcite
	BPA03 (Pit 15)	7/8	<p><i>Organic</i></p> <ul style="list-style-type: none"> - phenols - short chain dicarboxylic acids - saturated and branched chain C_{15:0} and C_{17:0} - long chain n-alkanes (C₂₇, C₂₉, C₃₁) <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - silicates - carbonates 	<p><i>Organic</i></p> <ul style="list-style-type: none"> - plant material - animal fat <p><i>Inorganic</i></p> <ul style="list-style-type: none"> - quartz - calcite
	BPA04 (Pit 23)	7	<p><i>Organic</i></p> <ul style="list-style-type: none"> - triterpenoids (lupanes, oleanes, ursanes, cycloartanes) - phenols - short and mid- chain dicarboxylic (C₁₆ and C₁₈) acids 	<p><i>Organic</i></p> <ul style="list-style-type: none"> - heated plant material - <i>Euphorbia</i> sp. latex, and the exudate from <i>Ammocharis</i> sp. - animal fat

- even numbered long chain alcohols (C ₂₂ -C ₂₈) and monocarboxylic acids (C ₂₀ -C ₂₈)	<i>Inorganic</i>
- unsaturated 11-eicosanoic acid (gondoic acid)	- quartz
- saturated and branched chain C _{15:0} and C _{17:0}	- calcite
- long chain n-alkanes (C ₂₉ , C ₃₁)	
- py-GC/MS: n-alkanes, saturated and unsaturated monocarboxylic acids	
<i>Inorganic</i>	
- silicates	
- carbonates	

6.4.2. Hafted Implements from the Iziko and Albany Museum Collections

6.4.2.1. FTIR Spectroscopy

The IR spectra of the three hafted implements are presented in Figure 6.26, with prominent peaks and associated functional group assignments highlighted

Table 6.38. Analyses revealed the presence of predominantly organic material in all three implement specimens. All three spectra are characterised by the presence of a broad band attributed to O-H stretching, peaks related to C-H stretching of long aliphatic chains, C=O stretching with C=O attributed to carboxylic acids at 1694 cm⁻¹ identified in A1543, C=C-C stretching of an aromatic ring; C-H deformation associated with aliphatic groups or -CH₃ bending, bending of O-H groups associated with phenols or alcohols, C-O-C and C-O stretches associated with alcohols and esters, and out of plane bending of C-H groups of aromatic, aliphatic or olefinic groups (Coates, 2006). C961 is lacking discrete peaks in the 1750 - 1500 cm⁻¹ region, and instead has a broad peak stretching between ~1720 and 1500cm⁻¹. The peak maximum at 1511cm⁻¹ may be associated with a carboxylate anion. AA1588 is distinctive from the Albany Museum implements (A1543 and C961)

in the relatively pronounced –OH stretching region and comparatively strong C-H, C=O, and C=C-C stretches.

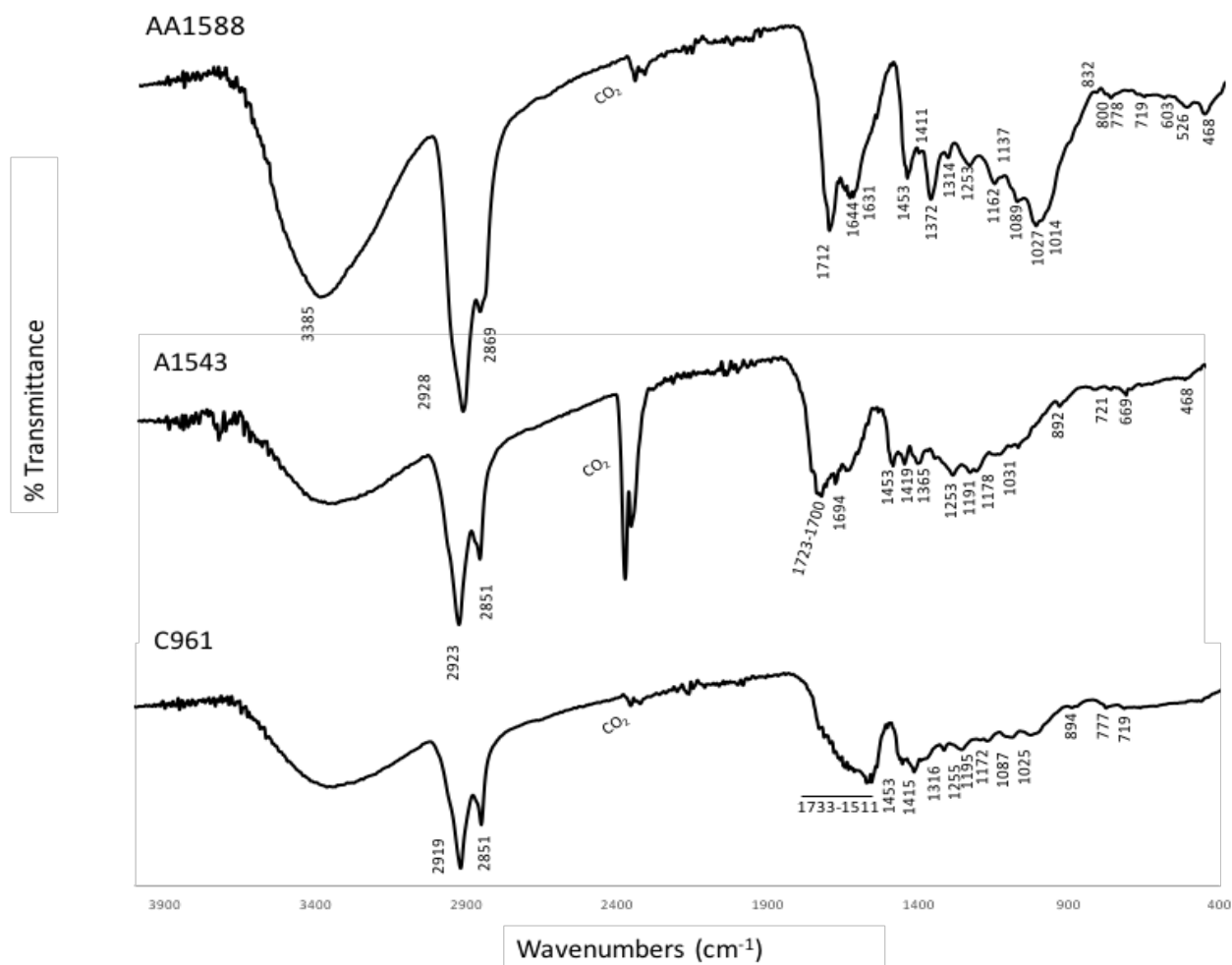


Figure 6.26. FTIR spectra (uncorrected) of the hafted implements AA1588, A1543, and C961 displayed in % transmittance, between 4000 – 400cm⁻¹.

Table 6.38. Peak assignments for the IR spectra of AA1588, A1543, and C961. Highlighted in Figure 6.26.

Assignment*	Wavenumber (cm ⁻¹)		
	AA1588	A1543	C961
$\nu(\text{O-H})$	3600-3000 (maximum at 3385)	3600-3000	3600-3000
$\nu(\text{C-H})$	2928 / 2869	2923 / 2851	2919 / 2851
$\nu(\text{C=O})$	1712	1700	X
carboxyl group	X	1694	X
$\nu(\text{C=C})$ stretch;	1644	1650	X
$\nu(\text{C=C-C})$ of an aromatic ring	1611	1604	X
$\delta(\text{C-H})$ deformation (saturated aliphatic groups) or $\gamma(-\text{CH}_3)$ bending	1453 / 1370	1453/1370	1453
γ (-OH), phenol or tertiary alcohol, or primary or secondary γ (-OH)	1314	1313	1316
$\nu(\text{C-O})$ stretch of esters and alcohols	1251	1257	1255
$\nu(\text{C-O-C})$ of esters and alcohols	1178/1193	1178/1191	1195
$\nu(\text{C-O})$ or $\nu(\text{Si-O})$	1162/1083/1027	1031	1087/ 1025
Out-of-plane $\gamma(\text{C-H})$ of olefinic or aromatic groups	X	892	894
Silicates	778/800, 526/468	X	778/800, 526/468
Out-of-plane $\gamma(\text{C-H})$	X	721	719

*Assignments based on published literature: Russell and Fraser 1994; Colombini *et al.* 2003; Coates 2006; Vahur *et al.* 2011.

Inorganic components were also identified in AA1588 and C961, likely derived from silicate minerals (Russell and Fraser, 1994), but the signals were weak. The sample from AA1588 is characterised by the presence of peaks at 1162, 1083, 800, 778, 526, and 468 cm⁻¹, and was interpreted as containing quartz minerals.

When compared to reference materials analysed under the same conditions (Figure 6.27), the results varied. The IR spectra from AA1588 matches well to the spectra of *Euphorbia tirucalli* latex obtained from the KEW Economic Botany Collections (No. 43970, acquired in 1893). Peak intensity and wavenumber in section B of both spectra were very similar, indicating the presence of similar organic functional groups in both samples.

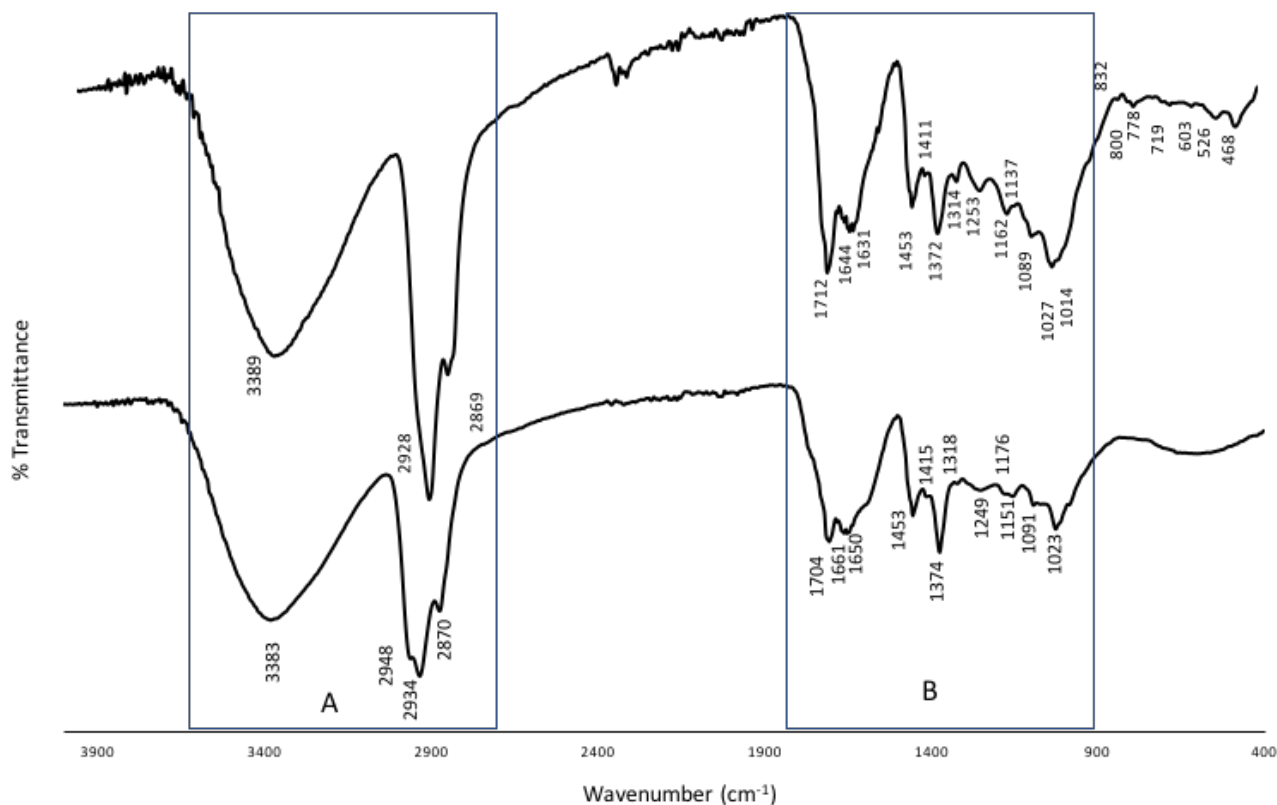


Figure 6.27. A comparison of AA1588 (top) and *Euphorbia tirucalli* latex (bottom), displayed in % transmittance, between 4000 – 400 cm^{-1} .

In contrast, the spectra of the samples from A1543 and C961 did not match any of the plant exudate types from southern African specimens, including latex, gum, resin, and manufactured pitch. However, the presence of strong C-H stretching vibrations, C=O stretching vibrations, and peaks associated with carboxylic acids (A1543) and carboxylate anions (C961) highlighted in

Table 6.38 are consistent with the sampled material being derived from a plant resin (Hummel, 1988; Colombini *et al.*, 2003; Ribechini, 2006; Vahur *et al.*, 2011; Helwig *et al.*, 2014; Charrié-Duhaut *et al.*, 2016).

6.4.2.2. SEM/EDS: Imaging and Elemental Composition

Table 6.39 describes the elemental composition of a sample of the three adhesive materials. Carbon and oxygen were identified as the main elemental components in these adhesive specimens. The elemental composition of all three samples is consistent with the presence of organic material and the IR results. Trace amounts of sodium, magnesium, calcium, chlorine, potassium, and aluminium are derived from the depositional environment. The trace amounts of silicon found in AA1588 and C961, which are absent in A1543, further support the IR interpretations indicating the presence of silicates in these specimens.

Table 6.39. The Albany and Iziko Museums: Elemental composition of the hafted implement samples.

Specimen No.	Elemental Composition ¹		
	Major	Minor	Trace
AA1588	C (79.93) O (18.95)		Cl (0.36) Mg (0.34) Na (0.19) Ca (0.14) Si (0.08)
A1543	O (65.92) C (32.43)		Na (0.59) Mg (0.35) Ca (0.30) Cl (0.29) K (0.08) Al (0.06)
C961	O (66.38) C (32.94)		Na (0.25) Mg (0.18) Ca (0.11) Cl (0.09) Al (0.05) Si (0.02)

¹ Qualitative analyses, and the terms major, minor, and trace components are subjective. Major is defined at more than 10 atomic%; minor as 1-10 atomic %; and, trace at less than 1 atomic%. These terms are defined in Goldstein *et al.* (2003).

6.4.2.3. Pyrolysis –Gas Chromatography/ Mass Spectrometry (py-GC/MS)

Subsequent investigations by Py-GC/MS further support the preliminary IR assessment of identifying predominately organic material in the sampled adhesives from the Albany and Iziko Museums. These analyses tend to produce mass spectra that were highly fragmented, however, three notable features were noted in the hafted implement samples.

The first feature, found in AA1588, was an abundance of compounds eluting between 42min and 54min. The mass spectra of these compounds have a high abundance of peaks at m/z 218, 203, and 189, in varying ratios. These peaks are common in the mass spectra of triterpenoids; however, due to the structural modification occurred due pyrolysis process (Bonaduce and Andreotti, 2009; Ribechini *et al.*, 2011), the source of these components is difficult to identify.

Two additional features were detected in the pyrograms from A1543 and C961 (Figure 6.28) from an abundance of compounds eluting between thirty- two minutes and thirty-eight minutes. Two compounds were identified based on their mass spectra: the trimethylsilyl derivatives of sugiol and a related isomer, totarol-7-one (Figure 6.11, Appendix III for relevant mass spectra). These components appear in relatively high abundance, along with other underivatised phenolic diterpenoids, in both A1543 and C961. The presence of these phenolic abietane diterpenoid structures (as well as their associated oxidisation products), whose retention time is approximately thirty-six minutes, indicates the presence of a conifer resin. The presence of underivatised diterpenoids in both may represent an incomplete derivatisation reaction or the unavailability of derivatisation sites. The pyrograms from A1543 and C961 also yielded series of saturated (C_6 to C_{18} chains) and unsaturated monocarboxylic fatty acids (C_6 to C_{16} chains) as well as a series of n-alkanes and n-alkenes, C_{11} to C_{20} in A1543 and C_{11} to C_{21} in C961. Figure 6.28 and the accompanying Table 6.40 highlight the presence of these components in the archaeological material, with fatty acids identified by the presence in their mass spectra of peaks at m/z 117 and 129 mass peaks and n-alkanes and n-alkenes determined by the prominent peaks at m/z 85 and m/z 83, respectively (decreasing in abundance every 14 mass units). Like the findings at

Melkhoutboom, the carbon chain ranges of these constituents are similar to those ranges found in archaeological and modern birch bark tar and pitch (Ribechini *et al.*, 2011) and is consistent production of a pitch. An assessment of the presence of pitch material is additionally confirmed by identifying ω -hydroxycarboxylic and α,ω -dicarboxylic acids by GC/MS analysis (as discussed by Hamer *et al.*, [2012] and Villa *et al.*, [2012]).

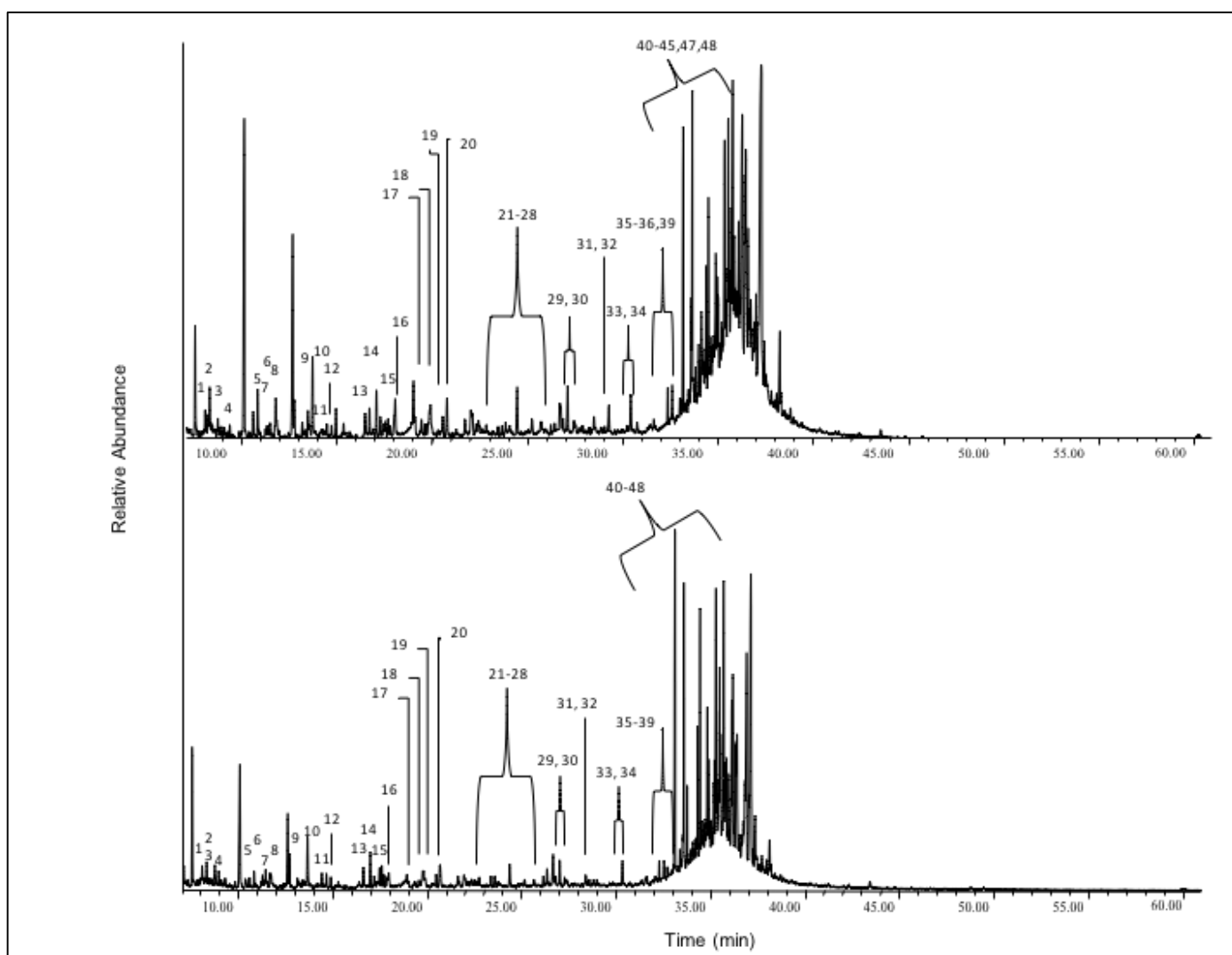


Figure 6.28. Albany Museum: TIC pyrograms of A1543 (top) and C961 (bottom), with labelled markers associated with pitch manufacture.

Table 6.40. Components identified in the pyrograms of A1543 and C961, Figure 6.28.

No.	Compound	No.	Compound
1	hexenoic acid, TMS	26	dodecanoic acid, TMS
2	hexanoic acid, TMS	27	1-heptadecene
3	1-undecene	28	heptadecane
4	undecane	29	tridecenoic acid, TMS
5	heptenoic acid, TMS	30	tridecanoic acid, TMS
6	heptanoic acid, TMS	31	1-octadecene
7	1-dodecene	32	octadecane
8	dodecane	33	tetradecenoic acid, TMS
9	octenoic acid, TMS	34	tetradecanoic acid, TMS
10	octanoic acid, TMS	35	1-nonadecene
11	1-tridecene	36	nonadecane
12	tridecane	37	branched chain pentadecanoic acids, TMS
13	nonenoic acid, TMS	38	pentadecenoic acid, TMS
14	nonanoic acid, TMS	39	pentadecanoic acid, TMS
15	1-tetradecene	40	1-eicosene
16	tetradecane	41	eicosane
17	decenoic acid, TMS	42	hexadecenoic acid, TMS
18	decanoic acid, TMS	43	hexadecanoic acid, TMS
19	1-pentadecene	44	1-heneicosene
20	pentadecane	45	heneicosane
21	undecenoic acid, TMS	46	branched chain heptadecanoic acids, TMS
22	undecanoic acid, TMS	47	heptadecanoic acid, TMS
23	1-hexadecene	48	octadecanoic acid TMS
24	hexadecane		
25	dodecenoic acid, TMS		

6.4.2.4. Gas Chromatography/ Mass Specrometry (GC/MS)

The total ion chromatograms (TIC) of the acidic and neutral fractions from AA1588 are highlighted in Figure 6.29 with the labelled identified compounds described in Table 6.41. This sample contained a series of short chain monocarboxylic fatty acids ranging from eight carbon units to 14 carbon units (C_{10} was not identified), hexadecanoic acid ($C_{16:0}$) as well as cis- (20) and trans- (21) isomers of palmitolaidic acid ($C_{16:1}$), octadecanoic acid ($C_{18:0}$), and cis- (25) and trans- (26) isomers of oleic acid, saturated and unsaturated (C_{16} , $C_{16:1}$, and $C_{18:1}$) terminal hydroxycarboxylic acids, saturated short chain (C_8 to C_{11}) and mid-chain (C_{16} and C_{18}) dicarboxylic fatty acids, long chain monocarboxylic fatty acids (C_{22} – C_{28}), sterols including cholesterol and beta-sitosterol, and even-number long chain alcohols (C_{22} – C_{30}). Two classes of terpenoids were also identified. The phenolic diterpenoid, totarol, was detected in the neutral fraction. Triterpenoids of differing structural types and their oxidisation products were also found. Alpha- amyrin (oleanene, $[M]^+$ at m/z 498) and beta- amyrin (ursene, $[M]^+$ at m/z 498), as well beta-amyrone (ursene ketone, $[M]^+$ at m/z 424) were characterised based on the prominent base peak at m/z 218 and relatively low ratios of m/z 203 and 189 (Mathe *et al.*, 2004). Lanostane and cycloartane triterpenoids and associated oxidization products were also identified in both acidic and neutral fractions of AA1588 (#48,49,51, 63,65).

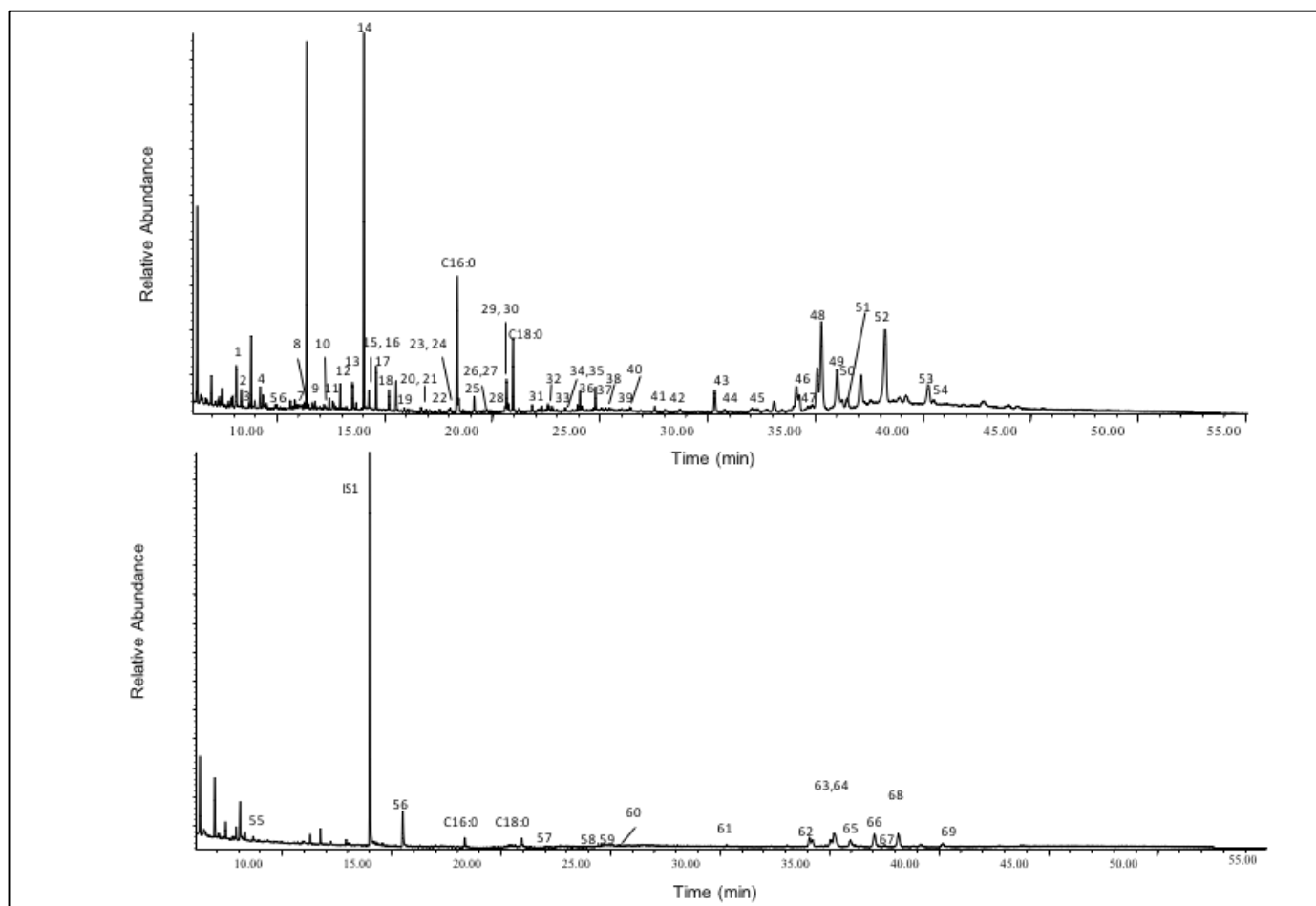


Figure 6.29. TICs of the extraction acidic (top) and neutral (bottom) fractions from AA1588.

Table 6.41. Peak assignment for the acidic and neutral fractions of specimen AA1588 shown in Figure 6.29. All compounds are trimethylsilyl (TMS) derivatives, unless otherwise stated.

Label	Compound Name
1	butyric acid
2	octananoic acid, TMS
3	butanedioic acid, TMS
4	nonanoic acid, TMS
5	Unidentified compound, possible sesquiterpene
6	Unidentified compound, possible sesquiterpene
7	malic acid
8	hexanedioic acid, TMS
9	undecanoic acid, TMS
10	heptanedioic acid, TMS
11	p-benzoic acid, TMS
12	dodecanoic acid, TMS

13	octanedioic acid, TMS
14	IS 1
15	vanillic acid, TMS (3-methoxy-4-[(trimethylsilyl)oxy]-,trimethylsilyl ester)
16	nonanedioic acid, TMS
17	tetradecanoic acid, TMS
18	decanedioic acid, TMS
19	undecanedioic acid, TMS
20	pentadecanoic acid, TMS branched chain (cis-)
21	pentadecanoic acid, TMS branched chain (trans-)
22	pentadecanoic acid, TMS
23	hexadecenoic acid, TMS (cis-)
24	hexadecenoic acid, TMS (trans-)
C16:0	hexadecanoic acid, TMS
25	ferulic acid, TMS
26	heptadecanoic acid, TMS branched chain (cis-)
27	heptadecanoic acid, TMS branched chain (trans-)
28	heptadecanoic acid, TMS
29	octadecenoic acid, TMS (cis-)
30	octadecenoic acid, TMS (trans)
C18:0	octadecanoic acid, TMS
31	C _{16:1} ω -OH dicarboxylic fatty acid, TMS
32	C ₁₆ ω -OH dicarboxylic fatty acid, TMS
33	eicosanoic acid, TMS
34	C _{18:1} ω -OH dicarboxylic fatty acid, TMS
35	hexadecanedioic acid, TMS
36	docosanol, TMS
37	docosanoic acid, TMS
38	octadecanedioic acid, TMS
39	tetracosanol, TMS
40	tetracosanoic acid, TMS
41	hexacosanol, TMS
42	hexacosanoic acid, TMS
43	octacosanol, TMS
44	cholesterol, TMS
45	octacosanoic acid, TMS
46	triacosanol, TMS
47	beta-sitosterol, TMS

48	1,3-[(trimethylsilyl)oxy]lanosta-8,24-diene (lanosterol, TMS)
49	Alpha or beta amyrin, TMS
50	Epi-lupeol, TMS (possible) (identified in <i>E. tirucalli</i>)
51	9,19-cyclo-9.beta.-lanost-24-en-3.beta.-yloxy, TMS (possible)
52	Unidentified triterpenoid, possible cyclolanostane skeleton, m/z 512 [M+] 497[M-15], m/z 379(100), 407(96), 422(85), 73(80), 95(76),
53	Alpha or beta amyrin
54	unidentified triterpenoid, possible lanostane skeleton, m/z 498 [M+] and 498[M-15],
55	glycerol, TMS
IS1	IS1
56	phthalates
C16:0	hexadecanoic acid, TMS
C18:0	octadecanoic acid, TMS
57	totarol, TMS
58	docosanol, TMS
59	diisooctyl phthalate
60	tetracosanol, TMS
61	possible octacosanol, TMS
62	beta-sitosterol, TMS
63	1,3-[(trimethylsilyl)oxy]lanosta-8,24-diene
64	beta-amyrone, underivatised
65	alpha or beta amyrin, TMS
66	24-methylenecycloartan-3-one, underivatised
67	Unidentified triterpenoid possible cyclolanostane skeleton, m/z 512 [M+] 497[M-15], m/z 379(100), 407(96), 422(85), 73(80), 95(76),
68	Unidentified triterpenoid ketone, lupane skeleton m/z 218(100), 203(70), 175(70), 95(37), 55(34), 424 [M+], underivatised
69	alpha or beta amyrin

The main organic constituent of this adhesive is plant material, with the addition of animal fats noted to a lesser extent. This is confirmed by the presence of beta-sitosterol (#62 and #47), several phenolic compounds likely derived from the breakdown of lignin (#11, #15, #25), an abundance of $C_{16:0}$ monocarboxylic fatty acids versus $C_{18:0}$ fatty acids, as well as the presence of oleic acid ($C_{18:1}$ fatty acid) and a series of short chain saturated dicarboxylic fatty acids, with azelaic acid (C_9) being the main constituent. The heating of this plant substance is also suggested based on the presence of cis- and trans- isomers of unsaturated $C_{16:1}$ (palmitolaidic) and $C_{18:1}$ (oleic) fatty acids. Similar to the material from Boomplaas, the high abundance of unsaturated (both cis- and trans- isomers) C_{18} monocarboxylic fatty acids, may be indicative of the presence of a latex exudate. It is likely that a wax originating from a plant source is also a component of this material, based on the even numbered long-chain alcohols and long chain fatty acids identified in the acidic fraction (Colombini and Modugno, 2009)

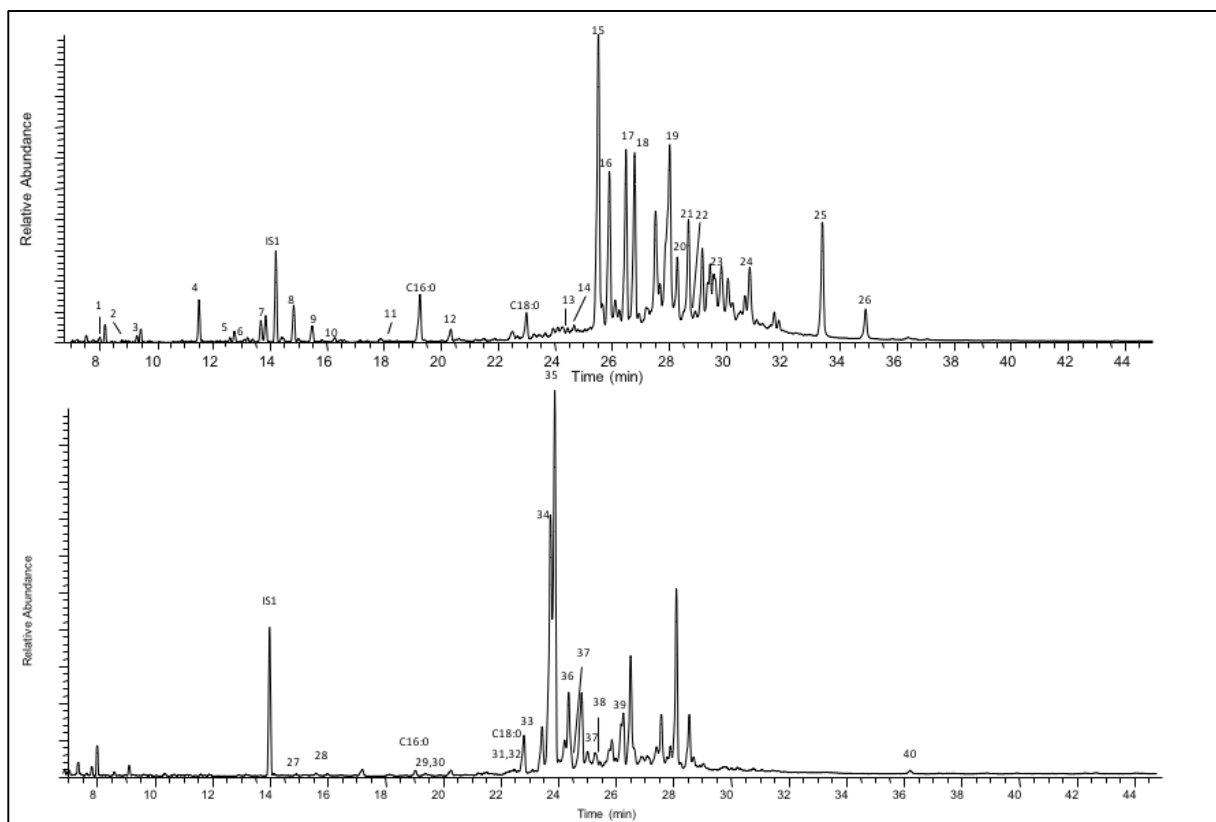


Figure 6.30. TICs of the extraction acidic (top) and neutral (bottom) fractions from A1543.

Table 6.42. Peak assignment for the acidic and neutral fractions of specimen A1543 shown in Figure 6.6. All compounds are trimethylsilyl (TMS) derivatives, unless otherwise stated.

Label	Compound Name
1	octanoic acid, TMS
2	butanedioic acid, bTMS
3	nonanoic acid, TMS
4	hexanedioic acid, TMS
5	heptanedioic acid, TMS
6	dodecanoic acid, TMS
IS1	IS 1
7	octanedioic acid, TMS
8	nonanedioic acid, TMS
9	tetradecanoic acid, TMS
10	decanedioic acid, TMS
11	undecanedioic acid, TMS
C16:0	hexadecanoic acid, TMS
12	unknown cinnamate (TMS), likely related to ferulic acid
C18:0	octadecanoic acid, TMS
13	totarol, TMS
14	unidentified ketone, m/z 275 (100), TMS
15	C _{16:0} ω-OH dicarboxylic acid TMS
16	unidentified compound, m/z 350(100), 363(41), 372(39), 351(33), 73(28) TMS
17	sugiol, TMS
18	hexadecanedioic, TMS
19	C _{18:1} ω-OH carboxylic acid, TMS
20	C _{18:0} ω-OH carboxylic acid, TMS
21	Unidentified compound, m/z 357(100) found in <i>Podocarpus</i> sp.
22	dodecanoic acid, TMS
23	octanedioic acid, TMS
24	C _{20:0} ω-OH carboxylic acid, TMS
25	C _{22:0} ω-OH carboxylic acid, TMS
26	docosanedioic acid, TMS
IS1	IS 1
27	possible polycyclic aromatic hydrocarbon
28	tetradecanoic acid, TMS
C16:0	hexadecanoic acid, TMS
29	abietatriene, TMS

30	isomer of abietatriene, TMS
31	dehydrosemperviol or dehydrototarol, TMS
C18:0	octadecanoic acid, TMS
32	sempreviol, TMS
33	underivatised dehydrototarol
34	underivatised totarol
35	totarol, TMS
36	ketone, possible totarol-7-one, TMS
37	underivatised phenolic diterpenoid, TMS
38	unidentified, possible dehydro-hydroxy phenolic diterpenoid, TMS
39	sugiol, TMS
40	BPA
41	unidentified compound, m/z 357(100) found in <i>Podocarpus</i> sp.
42	cholesterol, TMS

The presence of diterpenoid and triterpenoid compounds indicates an adhesive derived from multiple botanical sources. Totarol (TMS derivative), detected in the neutral fraction (#54), is derived from members of the conifers families Podocarpaceae and Cupressaceae. There are, however, insufficient biomarkers to identify the genus of the diterpenoid source.

The triterpenoids identified in the acidic and neutral fractions of AA1588 are the same as those found in the Boomplaas samples. They include alpha- and beta-amyrin (TMS), beta-amyrone, epi-lupeol (TMS), lanosterol (TMS), an unidentified lupane series ketone as well as 24-methylenecycloartan-3-one and acetylated 24-methylenecycloartenol. All compounds, with the exception of the cycloartanes were found in the latex of *Euphorbia* sp. The high abundance of saturated and unsaturated C₁₈ monocarboxylic fatty acids may also be attributed to the presence of a latex.

The compounds, 24-methylenecycloartan-3-one and acetylated 24-methylenecycloartenol, as well as an unknown cyclolanostane triterpenoid were not found in the analysed *Euphorbia* sp. specimens, despite being documented in published literature (Gupta *et al.*, 2013). AA1588 yielded both 24-methylenecycloartan-3-one and acetylated 24-

methylenecycloartenol. While the 3- position alcohol of the former was identified in the heated bulbs of *Ammocharis coranica* and bulb of *Chasmanthe* sp., the latter, along with an unidentified lanostane triterpenoid were identified in both *A. coranica* and the latex of *Hartogiella schinoides*. It is plausible that members of the Amaryllidaceae family to which *A. coranica* is a member, are the likely source of this adhesive. It should be noted, however, that a series of cycloartane triterpenoids (M⁺ ion of m/z 498, and a base peak at m/z 129) as well as gondoic acid identified in the *A. coranica* samples was absent in AA1588 (Table 6.41).

The presence of animal-derived fats in AA1588 was also identified as a minor component of the adhesive. This assessment was based on the presence of glycerol (#55), cholesterol (#44), as well as odd-chain saturated fatty acids with fifteen and seventeen carbon units and bacteria-derived branched-chain fatty acids (#20-22, #26-28). These components are present in lower abundance to the plant-derived components in the sampled archaeological material.

The total ion chromatograms of samples from the Albany Museum specimens A1543 (Figure 6.30 and Table 6.42) and C961 (Figure 6.31 and Table 6.43) were alike in composition. Both samples contained short chain monocarboxylic fatty acids (see Table 6.42 and Table 6.43 for ranges), short-chain dicarboxylic fatty acids ranging between C₄, and C₆-C₁₁, aromatic compounds including ferulic acid, vanillic acid, and other derivatised cinnamate structures, even-numbered mid- and long- chain dicarboxylic and hydroxycarboxylic acids, a several phenolic diterpenoids and their associated dehydro- and oxidization products (Cox *et al.*, 2007; Charrié-Duhaut *et al.*, 2016).

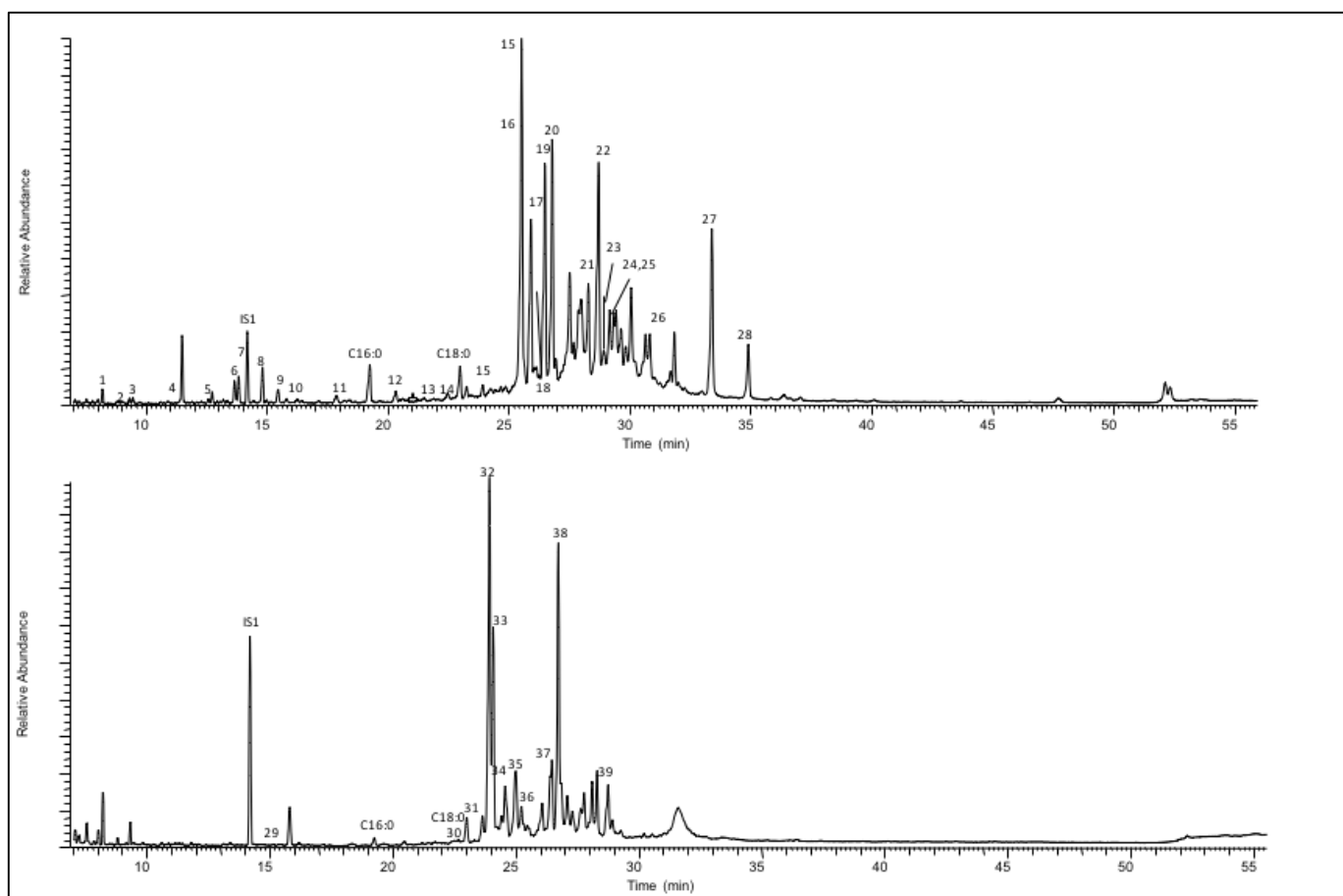


Figure 6.31. TICs of the extraction acidic (top) and neutral (bottom) fractions from C961.

Table 6.43. Peak assignment for the acidic and neutral fractions of specimen C961 shown in **Figure 6.7**. All compounds are trimethylsilyl (TMS) derivatives, unless otherwise stated.

Label	Compound Name
1	octanoic acid, TMS
2	glycerol, TMS
3	butanedioic acid, TMS
4	nonanoic acid, TMS
5	hexanedioic acid, TMS
6	heptanedioic acid, TMS
7	octanedioic acid, TMS
IS	IS1
8	vanillic acid, TMS

9	nonanedioic, TMS
10	decanedioic, TMS
11	pentadecanoic acid, TMS
C16:0	hexadecanoic acid, TMS
12	unknown cinnamate (TMS), likely related to ferulic acid
13	heptadecanoic acid branched chain, TMS
14	heptadecanoic acid, TMS
C18:0	octadecanoic acid, TMS
15	dehydrototarol, double bond location unknown, TMS
16	C _{16:0} ω-OH carboxylic acid, TMS
17	unidentified component (first identified in MHB10A) m/z 350(100), 363(43), 351(31), 378(28), 372(27), 343(16), TMS
18	eicosanoic acid, TMS
19	sugiol, TMS
20	hexadecanedioic acid, TMS
21	C _{18:0} ω-OH carboxylic acid, TMS
22	unidentified compound, m/z 357(100) found in <i>Podocarpus</i> sp.
23	docosanoic acid, TMS
24	unidentified oxidized diterpenoid, TMS
25	octadecanedioic acid, TMS
26	C _{20:0} ω-OH carboxylic acid TMS
27	eicosanedioic acid, TMS
28	docosanedioic acid, TMS
IS1	IS1
29	C _{14:0} monocarboxylic FA TMS
C16:0	C _{16:0} monocarboxylic FA (hexadecanoic acid) TMS
30	dehydrosempervirol, unidentified double bond location TMS
C18:0	octadecanoic acid, TMS
31	sempervirol, TMS
32	underivatised dehydrototarol
33	underivatised totarol ketone, base peak at m/z 261(100), 275(97), 372(38), 73(32), 262(28), 276(27), 357(22)
34	TMS
35	totarol, TMS

36	underivatised sugiol
37	underivatised totarol
38	sugiol, TMS
39	unidentified, ketone TMS

Similarly, A1543 and C961 are also composed of predominantly plant material, with the possible addition of animal fats in C961. This assessment is based the presence of diterpenoids, as well as short, mid and long chain dicarboxylic fatty acids, with azelaic acid (C₉) the most prominent of those short chain acids. There is a possible addition of animal fats, based on the presence of odd-chain saturated fatty acids in the acidic fraction of C961 (C_{15:0} and C_{17:0}), however, the sample is lacking cholesterol as confirmation. A1543, by contrast, only contains cholesterol.

The presence of the linear ω - hydroxycarboxylic and α,ω - dicarboxylic acid series in these samples is consistent with the modern pitch materials and heated bulb samples analysed, as well as the published data on manufactured heated plant products (Ribechini, 2006; Lucquin *et al.*, 2007; Villa *et al.*, 2012; Charri -Duhaut *et al.*, 2013) found in archaeological contexts. These components are associated with the break-down of the lipid suberin, which is broken down by alkaline hydrolysis during the sample preparation for GC-MS analysis (Ribechini, 2006). The range of mid- and long- chain ω - hydroxycarboxylic and α,ω - dicarboxylic acids (between 16 and 22 carbon units) was consistent with both prepared pitch manufactured under laboratory conditions and bulbs heated under open flame. The phenolic substances identified were likely derived from the break- down of lignin (#12 in A1543 and #7 and #11 in C961).

In terms of diterpenoid components, totarol, sempevirol and the dehydro- and ketone modifications of these structures were detected in the acidic and neutral fractions of both specimens. These components are consistent with those found in pitch and bark specimens from members of the *Afrocarpus falcatus* and *Podocarpus elongatus*, as well as in the Type 1A, 1B, and 1C adhesive samples at Melkhoutboom.

6.4.2.5. Interpretative Summary

The adhesives of A1543, C961, and AA1588 were identified as being composed of several sources of organics derived from predominantly plant material, with an addition of animal fats in AA1588 and C961. Evidence of the addition of silicate minerals was noted in AA1588 and C961 by IR and supported by the SEM/EDS results. This was in marked contrast to the red coloured mineral that comprised the outer-most layer of A1543 and C961, noted in the microscopy and published elsewhere (H. Deacon, 1966; Lombard, 2007).

All three specimens bore evidence of the presence of a conifer exudate. In the case of A1543 and C961, this was a manufactured pitch from either *Afrocarpus falcatus* or *Podocarpus elongatus*. These results are similar to those from Melkhoutboom. In AA1588, the mixing of more than one plant exudate, as identified by the chromatography results, is supported by the mixture of Type 1A and Type 7 residues identified by OLM. A heated plant bio-polyester (Villa *et al.*, 2012) was also present in AA1588, however, it may be attributed to multiple plant sources. The presence of the diterpenoid, totarol, alone in AA1588 was not diagnostic of a particular taxon of conifer. Triterpenoids recovered from the sample of AA1588 match two exudate sources. The most prominent, in terms of marker abundance, was from the latex of *Euphorbia* sp., with the compounds matching a reference of *Euphorbia tirucalli* and *E. ingens* latex. Similar to the Boomplaas specimens, the interpretation of the triterpenoid constituents remains at genus level, and are assigned to *Euphorbia* sp. The second source matched compounds identified in *A. coranica* bulbs, *H. schinoides* latex, *Chasmanthe* sp., bulbs. As a number of markers were lacking, it is not inconceivable that another member of either the Amaryllidaceae or Celastraceae families be a potential source. A significant point to note are the similarities in organic composition in the adhesive samples from AA1588, A1543, and C961 to the material from Boomplaas and Melkhoutboom.

CHAPTER 7 DISCUSSION

Introduction

In this chapter I consider the significance of the data presented in Chapter 6 within the context of the study of hafting adhesives in archaeology. I first present a summary of the materials identified as components of adhesives from each of the case studies, followed by a reassessment of each of the research hypotheses outlined in the Introduction to determine whether they may be accepted, rejected or re-evaluated. I then evaluate the role that some of the identified organic materials, including conifer pitches, toxic exudates, and the combination of animal fat and beeswax, have in current debates within the archaeological discipline in southern Africa.

7.1. A summary of the results

As a starting point, Table 7.1 provides a review of all the organic and inorganic materials identified in the analysis. The available data fit within the original aims of this project, although it is acknowledged that the project's scope narrowed from what was originally envisaged based on two factors, temporal breadth assessed by the available collections and the sample size of usable results. The research hypotheses are thus evaluated accordingly.

Despite sample screening and microscopic analysis being conducted on specimens spanning all technocomplexes of the LSA at multiple sites, adhesive sources were not identifiable from stone tools before the Wilton or Holocene microlithic (approximately 4000 – 8000 years BP); the majority of analysed specimens were sourced from deposits with cultural affiliations to the Final LSA (4000 BP to within the last one hundred years) or the Ceramic Final LSA (<2000 BP). Analysed specimens with results span multiple ecological contexts including the Grassland

(Sehonghong), Fynbos (Boomplaas and Renbaan Cave) and Thicket (Melkhoutboom) Biomes of southern Africa. It should be noted at this point that Rose Cottage Cave (Grassland Biome) did not produce any significant microscopy results, and it is not discussed in this chapter.

The final counts of the total number of specimens with viable data that may be used to test the research hypotheses is given in Table 7.2, with percentage frequencies compared to both the total number of specimens screened and the total number of specimens submitted for microscopy. Of all the analysed material, the solid samples from Boomplaas, the museum implements AA1588, A1543 and C961, and the artefacts from Renbaan Cave, yielded the highest frequency of viable datasets (those that produced results that differ to run blanks and/or background and are comparable to reference material). They were followed by Melkhoutboom and then Sehonghong with the lowest yield of all the sites examined. There appears to be a correlation between the amounts of material available for analysis and the frequency of usable results, with samples from the highest rates of success obtained from specimens with high amounts of adhesive remains and larger samples obtained (~2mg). The low yield at Sehonghong may be attributed to the nature of the adhesive remnants, with all screened specimens bearing only trace and staining and no significant amounts suitable for solid sample acquisition. The varying results at Melkhoutboom are likely due to the range in size of the solid samples (<1mg for many samples) and variable success in the use of cotton swabs (the majority of the unsuccessful analyses were from swab samples).

Table 7.1. A component summary list of all materials identified in the hafting adhesives described in the case studies presented in Chapter 6.

Sites			
Boomplaas	Melkhoutboom	Renbaan Cave	Sehonghong
<ul style="list-style-type: none"> - <i>Euphorbia</i> sp. latex - <i>Ammocharis coranica</i> bulb exudate - animal fat - calcite - quartz 	<ul style="list-style-type: none"> -conifer pitch and/or exudates (<i>Podocarpus elongatus</i>, <i>Afrocarpus falcatus</i>, or <i>Widdringtonia cupressoides</i>) -animal fat - quartz - calcite - manganese minerals 	<ul style="list-style-type: none"> -beeswax -animal fat - <i>Widdringtonia</i> sp. (likely <i>W. cederbergensis</i>) pitch/exudate - pitch/ exudate from a tannin-producing species - hair -proteinaceous material - ricinoleic acid-containing plant - red ochre - calcite 	<ul style="list-style-type: none"> - <i>Pinus</i> sp. resin - castor oil - animal fat - paraffin wax (possible)
Museum Implements			
AA1588		A1543 / C961	
<ul style="list-style-type: none"> - conifer exudate - <i>Euphorbia</i> sp. latex - exudate from the Amyrillidaceae or Celestraceae family -animal fat -quartz 		<ul style="list-style-type: none"> -pitch (<i>Podocarpus elongatus</i> or <i>Afrocarpus falcatus</i>) -animal fat (C961 only) - quartz 	

Bearing in mind the results frequencies of Table 7.2 and the screening and sampling strategies discussed in Chapter 5, the scales at which interpretations can be made vary between studies. Haslam's (2009) assessment of a trend to small sample sizes in residue studies rings true for the material I have analysed here, and is worth taking into account as I discuss the hypotheses below.

Table 7.2. Frequencies of specimens from the individual case studies which passed the screening protocol developed in Chapter 4; analytical results are highlighted in Chapter 6. The percentage frequencies describe each stage of the results acquisition process. Where two percentages are given, the first denotes the number compared to the total of screened specimens, while the second compares to the total number submitted for microscopy.

Site	Total Number of Screened Specimens	Total Number of Specimens Submitted for Microscopy	Total Number of Specimens Analysed	Total Count of Specimens with Viable Results
Boomplaas	4	4 (100%)	4 (100%, 100%)	4 (100%, 100%)
Melkhoutboom	874	35 (4%)	23 (2.63%, 65.71%)	20 (2.28%, 57.14%)
Renbaan Cave	23	12 (52.17%)	11 (47.82%, 91.66%)	11 (47.82%, 91.66%)
Sehonghong	2786	30 (1.08%)	12 (0.43%, 40%)	2 (0.071%, 6.66%)
Iziko and Albany Museum Implements	5	3 (60%)	3 (60%, 100%)	3 (60%, 100%)

7.2. Hypothesis 1: adhesive variability across time and space

The first hypothesis described in the Introduction is as follows:

Given the ecological mosaic of southern Africa's biomes, there will be variability in hafting adhesive formulae through time and across differing ecological spaces corresponding to differences in vegetation.

On the face of it, it may be argued that variations in adhesive recipes were identified between each independent case study. However, to have a better understanding of the nature of

this variability, this hypothesis may best be addressed by separating aspects of time and ecological region.

7.2.1. Time & adhesive formulae

Adhesive formulation variability by time may be assessed based on the results obtained at Melkhoutboom (Figure 7.1) and Sehonghong, at both of which chronological differences are notable. In the case of Melkhoutboom, we see relative stability in the use of organic adhesives and additives, with conifer exudates and pitch derived from species of *Podocarpus*, *Afrocarpus*, and *Widdringtonia*, as well as animal fats, identified throughout the sequence spanning the Holocene microlithic (Wilton) until the Final LSA (FLSA). There were, however, differences in the inorganic additives present in the analysed specimens. While the presence of quartz and calcite mixtures in the Type 1B adhesives extends from the FLSA layers CAFu and CAF into the youngest FLSA layer OMB, a second Type 1B adhesive with a manganese mineral component was identified on a chalcedony scraper from Layer W, the oldest analysed unit. Although represented by a single specimen, this may be evidence for the selection of a different filler in the mid-Holocene versus those selected by the shelter's inhabitants in the later Holocene.

At Sehonghong, there is limited evidence of the source of adhesive trace on the analysed stone tool specimens, however, the markers identified on the scrapers from the youngest DC layer (SEH04 and SEH05) derived from non-local materials including paraffin wax, castor oil, and *Pinus* sp. The known arrival of paraffin onto the commercial market in the mid-19th century (Sanderson *et al.*, 1988) and the movement of several species of *Pinus* across the Cape Province following the movement of the Boers northward and their subsequent spread into the KwaZulu-Natal region in the mid-19th century (Showers, 2010) means that these scrapers must have been made and used by some of the very last hunter-gatherers to occupy the shelter. This is supported by the historic records that note that people still inhabited the space in 1870/1871, and that people remained within the surrounding landscape making stone tools until as late as 1902 (Vinnicombe, 2009;

Mitchell, 2010). As these resources are not found locally before the arrival of European colonial influence in the region, they indicate a transition in the source of adhesives from local endemic resources, which unfortunately could not be identified in this analysis, during the 19th century.

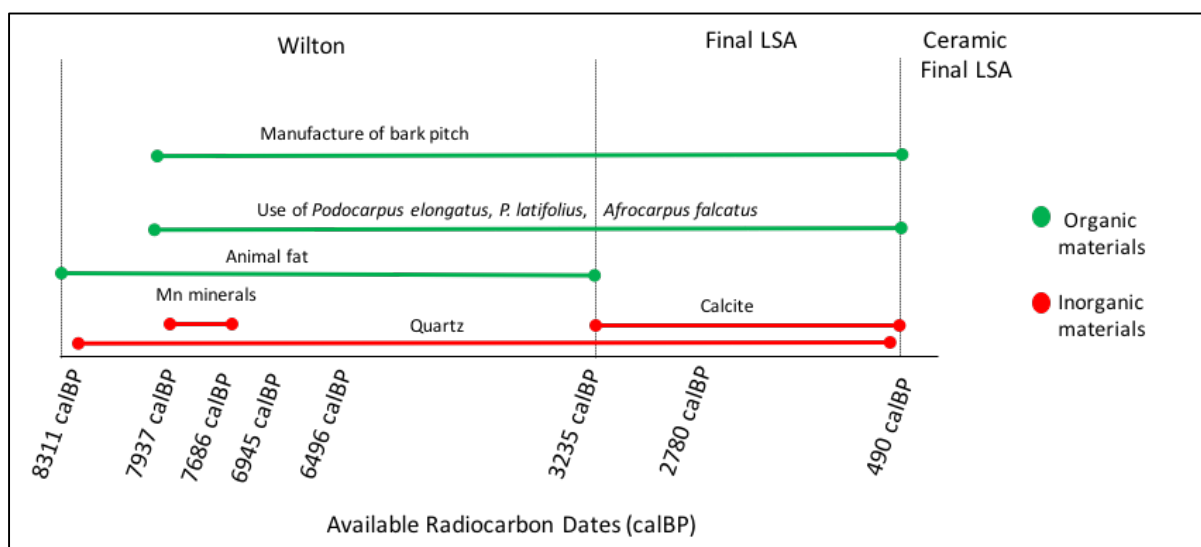


Figure 7.1. A depiction of the adhesive resources identified from Melkhoutboom spanning the Holocene assemblages in calBP. Mn – manganese.

7.2.2. Space and adhesive formulae

If we shift perspective to cover aspects of space and the associated ecology of the regions by limiting the timespan under consideration to late Holocene assemblages (Final LSA, <4000 BP), there are four cases available for assessment: Boomplaas, Melkhoutboom, Renbaan, and the hafted implements AA1588, A1543, and C961. Figure 7.2 highlights five sites (the four case studies and Eland's Bay [Charrié-Duhaut *et al.*, 2016] for comparison) alongside the relative provenance of the three hafted implements, listing the constituents of the adhesive recipes from each region. We see a transition from east to west in the types of organic materials utilised. The use of conifer pitch and exudates dominates the most easterly location, Melkhoutboom, as well as the implements A1543 and C961. The appearance of conifer pitch and exudate at Melkhoutboom is consistent with the known flora of the local kloof (H. Deacon, 1976) and the surrounding Zuurberg region (van Wyk *et al.*, 1988).

As we move westward toward the Knysna region of the southern Cape, where AA1588 was recovered, a mixture of conifer exudate (*Podocarpaceae* or *Cupressaceae*) and *Euphorbia* sp. latex was identified. The relative recovery locations of all hafted implements (A1543, AA1588, C961) are found within the Knysna Afromontane Forest biome. It is notable that, based on pollen analysis, the Knysna forest region is considered a mosaic of grassland/fynbos and Afromontane vegetation and members of the *Podocarpaceae* family as well as latex-producing *Euphorbia* sp. have been identified in the region (Duncan, 2006). The same latex source was also identified in the Boomplaas adhesive lumps, alongside the heated exudate from the bulbs of *Ammocharis coranica* (its most probable source). Moving further west into the Cedarberg region and to Renbaan, there is yet another transition, this time to the use of animal products (beeswax and animal fat) with plant material representing a minor component. Interestingly, the results from Renbaan are not consistent with the analyses conducted at Eland's Bay Cave, geographically, the closest site from which adhesives have been analysed (Charrié-Duhaut *et al.*, 2016), although it should be noted that the dates associated with the Eland's Bay specimen are not absolute. At Elands Bay, Charrié-Duhaut *et al.* (2016) identified *Podocarpus* sp. resin as the only source of the adhesive used, but this resource was not found in any of the analysed material from Renbaan. As both sites, as well as Boomplaas, occur in largely Fynbos vegetation dominated regions, within-biome variations here may be the result of what is locally available and preferred for adhesive production.

In contrast to the organic materials, however, there is evidence of the consistent use of inorganic minerals through time and across different ecological zones. The presence of quartz, likely sourced from sand, for instance, was identified in the adhesives at Melkhoutboom, A1543, C961, and Boomplaas. Its presence is consistent with findings from the MSA assemblages at Diepkloof and among the LSA finds at Eland's Bay Cave (Charrié-Duhaut *et al.*, 2013; 2016). As highlighted in Chapter 3, the widespread presence of such an additive among these case studies has interesting parallels in experimental work, as Zipkin *et al.* (2014) point out that ground quartz performs as well

on rough substrates as clay-sized minerals and may thus provide insight into the selection of this material in adhesives. Similarly, calcite was identified at Melkhoutboom, Boomplaas, and Renbaan. This is the first time that carbonates have been documented in adhesives from archaeological contexts in this region of the world. The calcium carbonate mineral calcite may be derived from a number of sources – all of them speculative in terms of availability and use by hunter-gatherer populations – including shells (aquatic and terrestrial) and geological deposits. Calcium-containing minerals are considered among the main geological cementation agents (Hodgekiss, 2006), and these properties may have been the selection basis for their use. They have been identified in archaeological case studies outside of South Africa, notably as a component of a composite adhesive on a Pre-Pottery Neolithic tool from Gesher, Israel (Shaham *et al.*, 2010).

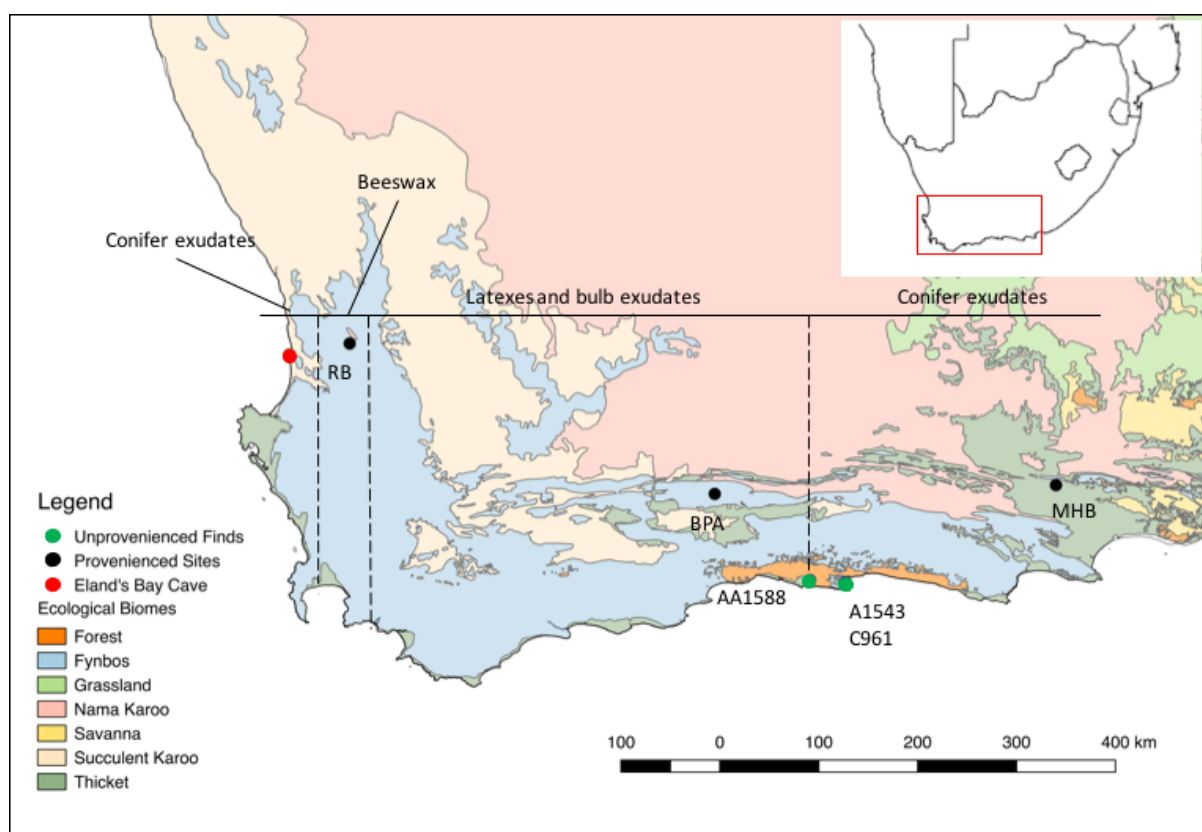


Figure 7.2. A depiction of the ecological distribution of the case studies alongside Eland's Bay Cave (Charrié-Duhaut *et al.* (2016), highlighting the transitions in main adhesive components in a west-east direction from during the late Holocene/Final LSA. Labels for case study sites: MHB, Melkhoutboom; BPA, Boomplaas; RB, Renbaan. GIS layer of 2012 Vegetation Map of South Africa, Lesotho and Swaziland courtesy of South African National Biodiversity Institute (downloaded Dec 5, 2016), and the GIS layer of African countries by Esri.

7.2.3. Summary

Overall, a great deal of complexity is associated with these case studies due to the composite nature of the adhesives and the combination of organic and inorganic materials present. Summing up, however, we can accept the hypothesis that adhesive formulae did indeed vary within and between different ecological environments. On aspects of time, it may be argued that there is evidence of both stability and variability in adhesives recipes depending on the archaeological case study. Melkhoutboom is a prime example since there is evidence of a roughly 7900-year-long tradition of the use of conifer exudates and the manufacture of pitch, albeit with a difference between the inorganic additives identified in the oldest analysed layer and those from the most recent layers. Additional datasets from material that spans several LSA technocomplexes within would lend further weight to this assessment.

7.3. Hypothesis 2: The continued use of plant sources as adhesives during the LSA

The second hypothesis put forward in the introduction is:

The geographic and temporal distance between molecular identifications of hafting adhesives in residues suggests a preference for and a continuity in the use of exudate-producing plant species as adhesives, despite the differences in technological industries and manufacturing processes. There will thus be similar continuity within LSA sites.

It is clear from the results in Chapter 5 that exudate- (and pitch-) producing plants have been utilised in LSA hafting adhesives, however this is by no means a complete picture. To fully address this research hypothesis, I highlight three chemically distinct adhesive sources, two derived from plants and the other derived from animals to emphasise the appearance of each of these

sources within the LSA contexts of this project and to attempt to shed light on aspects of their manufacture, acquisition, and reasoning for doing so.

7.3.1. Conifer Exudates and Pitch

Conifer exudates and/or pitch, sourced from endemic members of the *Podocarpus*, *Afrocarpus*, and *Widdringtonia* genera and the invasive *Pinus* genus, were identified in four of the five case studies. The appearance of products from members of the Podocarpaceae (Yellowwood) family in the material at Melkhoutboom and among the hafted implements (A1543 and C961) found in the Plettenberg Bay area expand their current geographic distribution to biomes in the southernmost regions of South Africa, below the Cape Fold Mountain Belt. Evidence from Melkhoutboom also confirms the use of this material in the Wilton period and throughout the Holocene – particularly as the archaeological association of the Eland’s Bay Cave specimen cannot be confirmed (Charrié-Duhaut *et al.*, 2016). The possible identification of *Widdringtonia* sp. provides evidence that the Podocarpaceae family was not the only favoured conifer; this genus, although rare nowadays due to its susceptibility to fire, is diagnostic to the Forest Fynbos biome of the Zuurberg around Melkhoutboom (van Wyk, 1988; Dold, pers comm.) as well as being found in the Cedarberg region around Renbaan; members of this genus are known to produce an aromatic resin (Coates Palgrave, 1977).

The presence of manufactured pitch deserves further mention. Resins and pitches are difficult to distinguish microscopically, but the presence of one material over the other has very different implications in resource acquisition. In terms of performing molecular characterisation, the identification of archaeological resins and pitch is well-established in the literature (Colombini *et al.*, 2003; Helwig *et al.*, 2008; Rageot *et al.*, 2015). Both conifer resins and pitches are taxonomically identified by their diterpenoid constituents with the relatively narrow range of indigenous South African conifers being composed of pimarane, abietane and phenolic abietane diterpenoids as highlighted in Chapter 6 and Appendix III. However, as seen in Chapter 6, a selection of additional

markers are utilised to identify the presence of a manufactured pitch or a heated plant material. According to Ribechini (2006) and Villa *et al.* (2012), suberin-containing pitch is characterised by the presence of linear α,ω -dicarboxylic acids and hydroxy-monocarboxylic acids when material is processed by alkali saponification and hydrolysis. It will also produce a series of linear saturated and unsaturated monocarboxylic acids and hydrocarbons (*n*-alkanes and *n*-alkenes) when it undergoes *in situ* pyrolysis (Ribechini *et al.*, 2011). Aromatic phenols, such as ferulic acid, and polycyclic aromatic hydrocarbons can further support the identification of this product.

The use of pitch in adhesives was identified at Melkhoutboom, Renbaan, and on the hafted implements A1543 and C961. It is significant to note that this type of adhesive involves significantly more planning and effort than that of tree resin, particularly within the context of the absence of ceramics. Our understanding of the production of such materials is gleaned from the experimental production of birch bark tar akin to that identified in Middle Palaeolithic contexts in Europe (Groom *et al.*, 2013; Groom and Schenk, 2016; Kozowyk *et al.*, 2017a). The first experiments describe the range of variables that may influence the success or failure of such production, including the reducing atmosphere, the form of the structure housing the material, fire temperature and exposure time (Groom *et al.*, 2013). It is possible to identify the time needed for pyrolysis by the odour of the fire and take the appropriate fire management measures. As such, once the relevant skillset is acquired and a successful structure to produce pitch has been identified, the technique may be maintained among tool producers (Groom and Schenk, 2015). Indeed, Kozowyk *et al.* (2017a) observe that the production of birch bark tar may have been a step by step process, with gradual improvements in yield and quality. The authors go on to postulate that the nature of the manufacture process and innovation in a step-wise fashion is such that it is possible that this technique was discovered and re-discovered through time (2017a: 6). If we return to southern Africa, the same conclusions drawn from European experiments may be equally applicable. The entirely organic nature of aceramic pitch-producing structures utilised in modern experiments implies that there will be no preservation of such components in the southern African

archaeological record beyond the products that were manufactured. It is conceivable that in southern Africa we see pitch manufacture appear in the MSA at Diepkloof in South Africa's Western Cape Province with either a continued use or separate loci of re-discovery at Border Cave on South Africa's border with Swaziland. By the Holocene (Wilton and Final LSA assemblages) at Melkhoutboom and among the Plettenberg Bay specimens, for instance, one may argue that there is evidence for either continued use or re-discovery of this technique, and that gradual improvements were made in the pitch distillation process that resulted in the high yields and adhesive-heavy composite tools seen in the Holocene record.

Although we can only speculate about how pitch was manufactured, based on the number of organic and inorganic materials identified in this analysis, it is one of many components of the composite adhesives found in the case studies. Figures 6.3 and 6.4 provide two such possibilities, depicting the complexity of the production of composite adhesives while taking into account the use of a pitch at Melkhoutboom and A1543 and C961, and Renbaan Cave respectively and utilising the pit roll method described by Kozowyk *et al.* (2017a). It is significant to note that, when visually depicted, the production of a pitch is among the more complex resource acquisition methods identified in these cases studies.

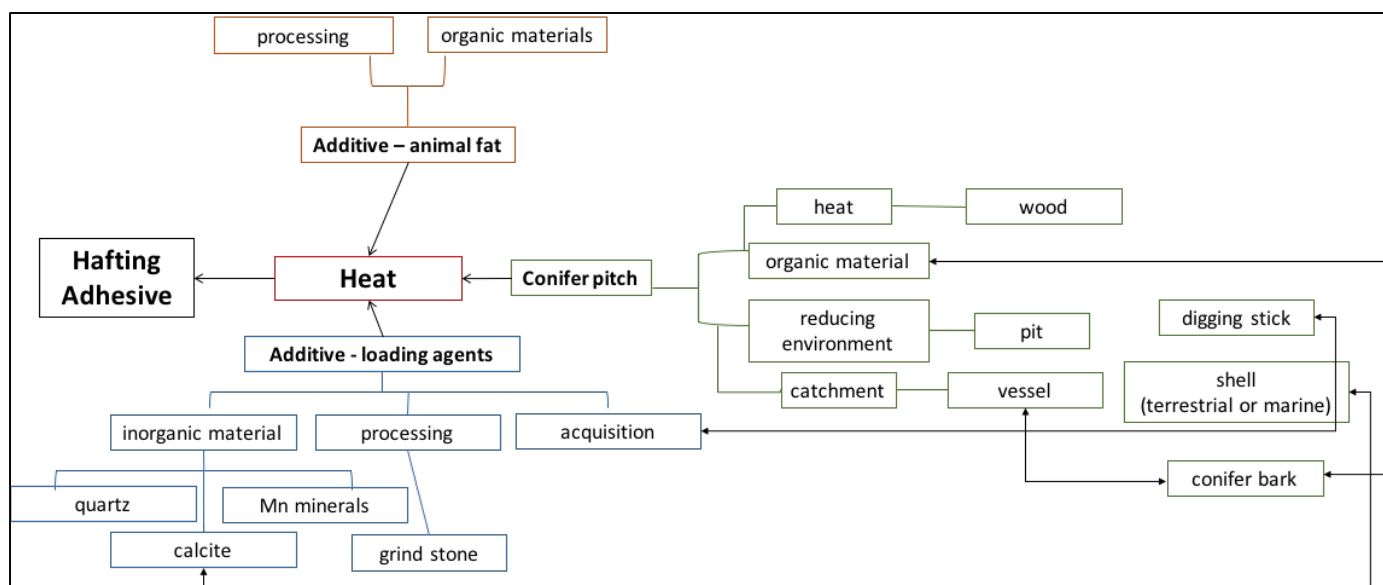


Figure 7.3. A depiction in modular form hypothesising the acquisition of resources to produce the composite adhesives at Melkhoutboom. The pitch processing portion of the diagram was based on those discussed by Kozowyk *et al.* (2017a).

The reasoning behind the longstanding use of the manufacture of such materials will likely vary on a case-by-case basis. However, it should be pointed out that during my visits to the Edinburgh Botanic Gardens (July 2015), Kirstenbosch Botanical Gardens in Cape Town (August 2015), and the Zuurberg region of the Eastern Cape (June 2016), it became apparent that members of the Podocarpaceae family did not exude large quantities of resin when the trees were in good health, unlike members of the Pinaceae family or the more local *Widdringtonia* sp., the bark of which glistens with fragments of resin. If *Podocarpus* sp. or *Afrocarpus* sp. were desired for the properties of their exudates, the distillation of bark to produce pitch may have increased yield volumes to more favoured quantities. Indeed, Kozowyk *et al.* (2017a) highlight how pitch yields can range between ~1 – 9g of pitch per 100g of bark. While significant for low yield conifer species, it should be emphasised that the acquisition of such quantities of material to produce the quantities of pitch found on hafting implements (notably those from the Final LSA) is economically costly, and these manufactured components should thus be viewed as high value commodities. Although speculation, this may also be the reason why AA1588 contained only a minor component of conifer exudate, compared to the latex-derived material that was its main compositional material.

7.3.2 Latexes, bulb exudates, and other processed plants

The triterpenoid-producing exudates (latexes, resins, and bulb exudates) are chemically very different from the conifers discussed in the section above. Contrastingly, the materials analysed as references were remarkably similar in chemical composition to each other, with α – and β - amyrin and their oxidised ketones common between many and specific markers utilised to distinguish between genera classified as ‘unidentified’ during this analysis.

The use of such exudates has been identified at Boomplaas and in the adhesive of Iziko’s specimen AA1588. The appearance of *Euphorbia* sp. latex is consistent with both historic records noting the uses of other members of this genus for their adhesive properties (Lloyd Notebooks [LL. VIII.1.6088-6091]; Walker, 1974; Webley, 1994). It is also consistent with the case study of the Early

LSA adhesive lump found at Border Cave (d'Errico *et al.*, 2012) and provides evidence of the use of such materials into the Holocene. As was argued for the manufacture of conifer pitch, the distance in time and geography means that one cannot distinguish between whether this was a continued use of this source as an adhesive or a reflection of punctuated periods of discovery and re-discovery. D'Errico *et al.* (2012) note that members of this genus, particularly *E. tirucalli* and *E. ingens*, are toxic and several species have been described for their medicinal benefit as well as for their use in poisons (Webley, 1994; H. Deacon and J. Deacon, 1999; d'Errico *et al.*, 2012). *Euphorbia* sp. have been identified in mixed bush vegetation within the surroundings of Boomplaas (Moffett and H. Deacon, 1970), and are likely to have been local resources.

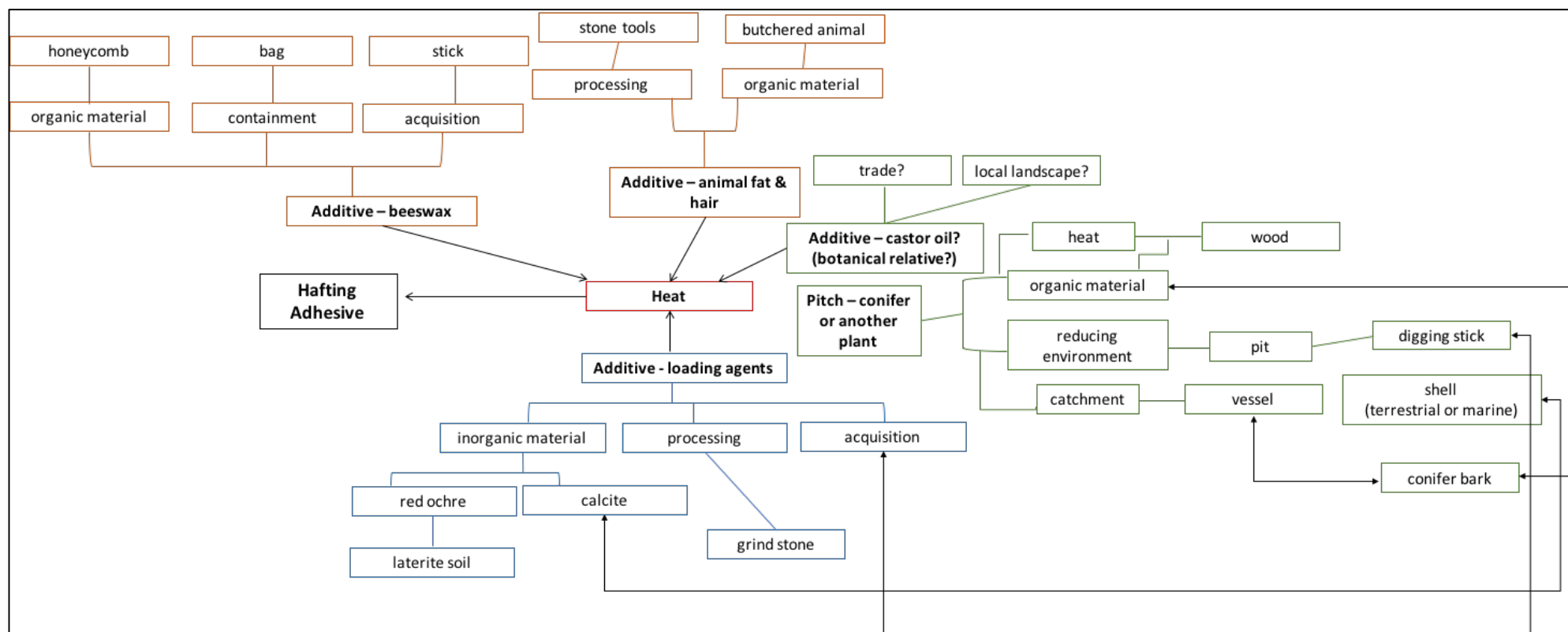


Figure 7.4. A depiction in modular form hypothesising the acquisition of resources to produce the composite adhesives at Renbaan. The pitch processing portion of the diagram is based on Kozowyk et al (2017b), while the beeswax acquisition was drawn from Russell and Lander (2015).

The material from Boomplaas marks the first time that the use of a heated plant bulb has been identified as a significant adhesive component in an archaeological context. The same markers indicative of the pyrolytic breakdown of the lipid suberin (Ribechini, 2006) were found in both the experimentally heated bulbs of *Ammocharis coranica*, *Boophone disticha* and *Brunswigia radulosa*, and in the samples from the adhesive lumps of Boomplaas. The triterpenoid constituents of these archaeological samples were most consistent with the exudate produced from heated *A. coranica*. Although never identified in the archaeological record, this plant exudate is one of several utilised among the Ju/'hoan San of Namibia to produce a composite adhesive for hunting weapons (Wadley *et al.*, 2015). Unlike the open savanna landscape of the case study area in Namibia, it is interesting to note that the landscape surrounding Boomplaas is richer in vegetation and annual rainfall, especially when compared to the Great and Little Karoo that surrounds it (Pargeter *et al.*, 2018). Being surrounded by several ecological biomes, it thus has a wider range of available species to choose from. *A. coranica*, although widespread, preferentially favours dry, sandy soils and can thrive in arid regions (South Africa National Biodiversity Institute, 2018). Whether this implies a purposeful excursion to a more arid environment to acquire this resource for its favourable properties or perhaps the materials were acquired by trade. Both instances have been recorded in ethnographic accounts. Joseph Orpen's 1874 article on the ethnographic data he collected from an informant (Qing) of the Southern San populations of the Maloti-Drakensberg, where in the myth of '[t]he creation and death of the first eland' (republished in McGranaghan *et al.* [2013: 155]) describes that Cagn (the first being) "...went to his nephew to get arrow-poison, and he was away three days", suggesting that travel is not inconceivable for other organic materials of composite tools. Further to this, instances of trade are noted among the /Xam dialect groups in their acquisition of *jo-/õä* or *sho:-/a*, a potentially psychoactive plant (Mitchell and Hudson, 2004).

The main argument discussed in Chapter 3 highlights a discontinuity between the ethnographic and historic records and the archaeological record, and further acknowledges the contextual limitations of those most recent sources in being suitable analogues for those in the LSA and MSA. The use of the latex-producing species highlighted in this section begins, however, to provide links between the recent past and the archaeological record. Our understanding of the relationship between how these items were acquired (i.e. trade) is nevertheless still comparatively limited.

7.3.3. Beeswax, animal fat, and other animal materials

Animal-based adhesives are comparatively uncommon in the archaeological record of southern Africa. While all case studies, with the exception of AA1588 from the Iziko Museums, yielded evidence of the use of animal fat among the adhesive samples, only the specimens from Renbaan Cave yielded multiple sources of animal products. The lump of *Euphorbia* sp. adhesive from an Early LSA context at Border Cave was found to be mixed with beeswax (d’Errico *et al.*, 2012), but this remains the only case known outside this project. Fats and waxes make adhesives less prone to breaking and improve their overall quality, especially when a resin or pitch has been over-heated (personal observation; Kozowyk *et al.*, 2017a).

Included within the Renbaan specimens, were beeswax, animal fat, hair fibres, and proteinaceous material. While the markers that allowed for the identification of proteinaceous material were non-specific, proteins can come from numerous plant and animal-based sources. Those animal-derived ones include milk, egg, and processed bone. The inclusion of such materials is not unknown in this region, though the exact source in this instance is speculative; milk was identified as a constituent of an ochre-based paint at Sibudu from 49 000 BP (Villa *et al.*, 2015), while egg was described as the possible proteinaceous material in the beeswax-containing adhesive lump from Border Cave (d’Errico *et al.*, 2012). The hair fibres may be sourced from any mammal,

humans not excluded, and may have acted like a filler, akin to plant fibres (as described by Charrié-Duhaut *et al.* [2016]).

The combination of beeswax and animal fat is unique among the case studies discussed here. While it is entirely likely that these resources were used for their utility as adhesive components and for their availability alongside two additional plant sources, beeswax, in particular, may have been a conveniently available by-product from honey procurement practices.

The combination of the two components, however, raises an interesting question. If we follow along the trajectory paved by authors including Russell and Lander (2015) and Hollmann (2015), who discuss the importance of bees, honey, as well as fat in the wider San cosmos and daily livelihood, may we draw upon some parallels that provide an alternative motive behind the selection of these resources in a hafting adhesive? Bees, honeycomb, and hives are among the motifs of rock art in southern Africa, a testament to the practice of honey gathering by hunter-gatherer/forager populations (Russell and Lander, 2015), and a number of researchers have interpreted these images as reference to the supernatural potency of bees and honey (Hollmann, 2015).

Fats are high quality nutrients and hugely important in the diets of hunter-gatherers (Speth, 2009). In southern Africa, depending on the environment, these may be difficult to come by. The fat of the eland has been described as supernaturally potent (Lewis-Williams, 1981), and its use outside people's diet has been described as giving potency to other materials (specifically paint) (Jolly, 1986; Russell and Lander, 2015). Animal fat has been identified as the carbon source for carbon-black paint at RSA TYN2 in South Africa's Eastern Cape Province (Bonneau *et al.*, 2012), while fat has also been identified in paint samples from Barnes Shelter in the uKhahlamba-Drakensberg (Prinsloo *et al.*, 2008). There is no means to ascertain the source of the fat from the paint, while the odd-numbered C₁₅ and C₁₇ saturated fatty acids found in the adhesives only narrows down the source to any number of quadrupeds (ruminant and non-) that call southern Africa home. Whether the presence of any fatty source is evidence of a link to potency or its use

based purely on its ability to alter adhesives and improve their overall quality remains an interesting point of speculation.

It has also been argued that fat and honey are alike, both of them being relatively scarce and - by extension - high value items (Russell and Lander, 2015). Is it possible then, that beeswax, being the foundation of honeycomb, was similarly of high value? Economically, it is plausible, as there are records outside of southern Africa, highlighting the trade value of bee products among hunter-gatherer groups, often describing honey and beeswax as a pair (Spielmann and Eder, 1994; Junker, 1996; Marlowe, 2002 [cf. Bleek, 1931]).

7.3.4. Summary

Based on the results, we can accept Hypothesis 2 on the basis that in all the case studies analysed, plant-based materials represented a component of the hafting adhesives examined, suggesting the continued use of such materials throughout the LSA. However, it is important to emphasise that these are by no means the only source of adhesives and that in the case of Renbaan animal-based materials were the dominant constituents.

In the assessment of this hypothesis, I have highlighted several aspects relating to the acquisition and manufacture of some components of adhesive. The presence of manufactured materials, like conifer pitch, as well as acquisition of toxic substances and of bi-products of highly valued goods (i.e. honey) suggests that the production of adhesives was a mindful and deliberate task involving, in many instances, multiple production steps (Figures 6.3 and 6.4). On that basis, these materials thus deserve to be considered high value goods in their own right. Further to this, it is of interest to point out, as suggested in Section 6.3.3, that different non-tool manufacture causes may relate to the selection of adhesive materials. These avenues, which find their basis in ethnographic and rock art studies, may be worth considering further in the future.

7.4. Hypothesis 3: adhesive composition and considerations on tool typology, function and raw material

The final hypothesis discussed in the Introduction is that:

The prevalence of single component adhesives versus composite mixtures will be influenced by tool function, typology and the raw material that make up a composite tool.

I highlight the case studies from Renbaan and Melkhoutboom to emphasise that there is variation between sites with known tool function, typology, raw material, and associated adhesive mixture. At Renbaan, all analysed specimens may be considered composite adhesives, having mixtures of both organic and inorganic materials present. If both the tool function or ascribed typology, and the raw material of the stone tool is taken into consideration, adzes (composed of silcrete or CCS) from this site appear visually similar (having Type 3B residues) and are composed of beeswax, animal fat, plant exudates/pitch, with the occasional addition of proteinaceous material and hair, as well as laterite-sourced ochres and calcite (source unknown). Of the scrapers and the utilised flake from the dataset, only one (RB09) yielded a weak mineral signal associated with the aforementioned material, while all exhibited the presence of Type 1A adhesives. The scrapers were composed of quartz, while the utilised flake was made from CCS. Despite this, the Type 1A materials are similar in organic composition to the Type 3B materials, and, as such, it may be suggested that the differences in inorganic composition may be based on functional implications, and perhaps to some extent raw material.

Within the Melkhoutboom dataset, the adhesive trace may be divided into two visually distinctive types, 1A and 1B. Based on the microscopy results, both residue types were identified on segments, scrapers, and borers alike, but only 1B was found on adzes. When raw materials are added for consideration, Type 1A was identified on silcrete, chalcedony, and quartzite, while Type 1B appeared on chalcedony (red coloured only), silicified shale, and an unidentified rock type. The

interpretive summary in 6.3.2.5 suggests that the Type 1A material is either a single component plant pitch or exudate adhesive or a composite organic adhesive with animal fat as an additive, while the Type 1B is a composite organic/inorganic adhesive. The chromatography results indicate that there is no difference in the organic materials utilised between adhesive type and, as at Renbaan, the inorganic additives are the defining characteristic that separates these types.

If, instead, we opt to take each archaeological context as well as the current theories on tool reliability into consideration, another possible correlation comes to mind. The process of hafting, and hafting adhesives appear in discussions of hunter-gatherer technological adaptations as both a quantifiable value of study (Collard *et al.*, 2005) and a conceptual module for multi-level cognitive operations (Lombard and Haidle, 2012). These components may be considered to be a means of constructing reliable and maintainable complex tools (Hiscock, 2006), and inversely a costly and risky innovation (Wilkins *et al.*, 2014). Bousman (2005) presents a hypothetical depiction of the design goals of composite tools, combining concepts of tool expediency, reliability, and maintainability. The nature of the adhesive procurement strategies (Figures 7.3 and 7.4) described from the results in Chapter 6 implies that these components are not expedient by any means and would better fit within Binford's (1973) assessment of a *curated* tool, thus falling more within the realm of reliable and maintainable tools, or components thereof. Bousman (2005) goes on to postulate that economic risk is the driving factor that dictates where tools fit within the realms of maintainability (moderate investment, renewable utility) or reliability (high investment, high utility).

It is difficult to ascertain where each adhesive recipe fits within these overlapping spheres, as the datasets of Chapter 6 reflect only the compositional characterisation of such substances and no testing of recipe efficacy. Figure 7.5, a modification of Bousman's (2005) hypothetical depiction of the goals of tool design, places these materials in the realm both maintainable and reliable design strategies. If this is the theoretical reasoning behind tool design, there must indeed be economic risks.

The narrow time range of the samples collected from Renbaan Cave and the archaeological context of the surrounding region provides the opportunity to test this alternate hypothesis related to adhesive complexity. The material from Renbaan Cave submitted for analysis is sourced from deposits dating to 1992-1617 calBP (Pta-3783) and 1172-925 calBP (Pta-3768) and younger and thus post-dates the arrival of populations of herders in the region, something thought likely to have imposed a degree of stress on hunter-gather populations by restricting their access to key resources (Kaplan, 1987). The adhesives identified on the adzes and scrapers from Renbaan are among the most complex analysed, containing beeswax, animal fat, hair fibres, proteinaceous material, and exudates/pitch from conifers and other plants and red ochre. Two additional lines of evidence support the likelihood of increasing risk and therefore adhesive complexity at Renbaan Cave. The first are the adhesive remains from Eland's Bay Cave, located along the Western Cape coastline in the same region at Renbaan. The adhesive handle and composite tool from this site pre-date the material from Renbaan and are composed of *Podocarpus elongatus* resin and quartz grains. During the period when Eland's Bay Cave was reoccupied from 4300 to ~3000 BP, a broad mix of marine and estuarine as well as terrestrial resources were consumed (Mitchell, 2002: 179). By 2000 BP, access to coastal resources became increasingly difficult with competition from herders and their livestock for access to more nutrient-rich landscapes, with inland sites located in areas uninhabitable by livestock and floral and faunal assemblages emphasising the consumption of terrestrial animals and geophytes (Mitchell, 2002: 249-251). This is similarly the case at Renbaan, where the post-2000 BP assemblage is dominated by adzes, geophytes and pottery, sharing features with many contemporaneous deposits at sites such as Diepkloof and Tortoise Cave, which highlight the transition to population reduction, isolation and a lack of mobility across the landscape (Kaplan, 1987). This incursion of a new population with a distinctive subsistence strategy was not identifiable at other sites included in this analysis. Melkhoutboom, in contrast, is described by H. Deacon (1976) as demonstrating a relatively stable period of technology and subsistence from ~6000 BP, consistent with the relatively stable environment of the close forested kloof surrounding

the site. The adhesives analysed during this time are similarly stable in their constituents (Figure 7.1) and more akin to those from the Wilton and/or Final LSA at Eland's Bay Cave in their composition.

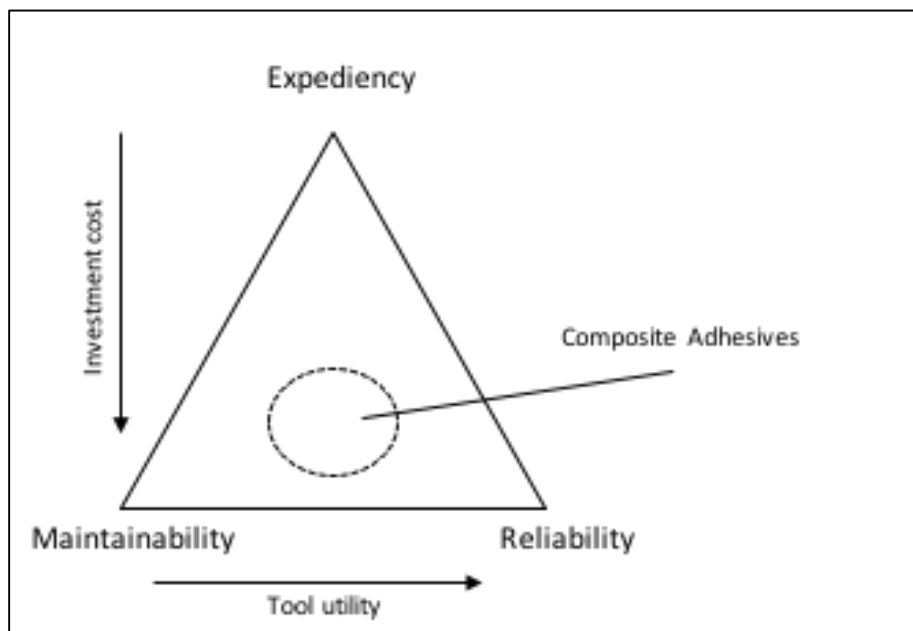


Figure 7.5. A modification of Bousman's (2005) hypothetical depiction of the goal of tool design, highlighting composite adhesives within this theoretical framework.

The multiple steps and acquisition requirements for each component of the Renbaan adhesives may thus reflect a need to produce a more maintainable and reliable tool, given the high cost of the components, some of which are materials that are of high value (see Section 7.3.3 on beeswax). Indeed, each realm of product type, faunal, floral, and mineral is represented in duplicate, derived from very different sources (i.e. calcite-containing minerals are found in high pH environment, where the opposite is the case for laterite soils containing red ochre, and as such these two materials would not be found together). It is interesting that Renbaan, like De Hangen and Andriesgrond in the Western Cape, bear evidence of the re-use of MSA assemblages and 'older' flakes post- 2000 BP, notably in adze manufacture (Kaplan, 1987). This may be a response to

minimising risk and economic cost to access stone, and is in contrast to the lengths the inhabitants of Renbaan went to acquire the adhesive resources.

An investment cost model may be more consistent with the similarities in adhesive composition, especially the organic component, found in samples from differing tool typologies and raw materials. While plausible, the small sample size and the absence of available specimens that pre-date the 2000 BP transition at Renbaan means that this assessment must remain speculative for now.

7.4.1. Summary

Presently, there may be a correlation between inorganic additives and tool typology and utilised raw material within the case studies examined for this project. While it would provide closure to the assessment of this research hypothesis, the sample sizes from both Melkhoutboom and Renbaan, despite being the largest sample sizes, are too small to comment in relation to a whole assemblage. Statistical analyses were not suitable to evaluate correlations on a case-by-case basis and, as such, I suggest that Hypothesis 3 cannot be fully evaluated with the sample sizes that were available from these case studies.

It is also worth noting that isolating factors associated with composite tool manufacture (i.e. function or raw materials used) and hafting adhesive production removes them from the context in which they were produced. We are thus in danger of ignoring extenuating circumstances and the underlying reasons for why such materials were made in the way they were, and thus not fully comprehending the lengths a manufacturer may go to produce such complex materials. I highlight the argument put forward in regard to reliable and maintainable tool design in Section 7.4.3 to emphasise this point.

7.5 A note on object histories and colonial archaeology

The contribution of this project to southern African archaeology and hafting adhesive studies in general is not the only value of this research. In this section, I will highlight a narrower field of view, namely how the kinds of analysis I have undertaken in this project can engage with the biographies of objects and contribute to specific cultural narratives that other archaeological and historic disciplines have already discussed in great detail. In this section I discuss two such examples using the case studies of the Albany Museum specimens and two scrapers from Sehonghong rockshelter.

The ability for scientific analysis to contribute to an object's history is perhaps best exemplified in the narrative of the hafted implement A1543 from the Albany Museum (Figure 6.6). First acquired by the museum in 1908, this "stone implement fixed by means of resin to a wooden handle" was recovered from a grave in a cave near Plettenberg Bay (H. Deacon, 1966; Binneman, 1983). The historical timing and nature of its recovery mean that it is lacking provenience and direct association to any cultural technocomplex. Studies have described the structural alterations made to the object after its acquisition (Hewitt, 1912a, 1912b; H. Deacon, 1966) and the possible function of the object (Binneman, 1983), and have also attempted to explain its reddish appearance (Deacon 1966; Lombard 2007). Beyond this, however, it is difficult to place this object within the context of the southern African Stone Age sequences, limiting its contribution to being little more than a singular item and a potential analogue for tool design or appearance. In the transition of archaeological theory and practice in South Africa to a more quantitative approach with an overhaul of excavation practices and a shift to place archaeological assemblages within a framework ground in palaeoenvironmental data and anthropological studies (Mitchell, 2002: 35), objects like A1543 were left behind to remain mere mentions in a museum accession register.

In revisiting A1543 to conduct chemical analyses, it has been possible to determine the

composition of the resinous adhesive component of this piece. The well-preserved markers from this material not only provided a baseline with which to assess the preservation of the other archaeological assemblages, but the constituents of this material now place A1543 into a larger narrative of the use of manufactured Podocarpaceae pitch across the southernmost coastline of South Africa, linking this specimen to the adhesive assemblages of Melkhoutboom and its counterpart from Plettenberg Bay, C961.

At Sehonghong, on the other hand, two scrapers yielded evidence of the use of non-indigenous pine resin (*Pinus* sp.) as an adhesive, with additives including the fat of an animal, castor oil, and possibly paraffin wax. Members of the *Pinus* genus first arrived in the Cape with *Pinus sylvestris* at the time of Van Riebeeck's initial colonisation, encouraged by the VOC and the Netherlands government to stave off a timber shortage; and, subsequent waves of *Pinus pinea* and *Pinus pinaster* arrived later in the 17th century. The spread of pine, however, did not establish itself until the 19th century (Showers, 2010). Pines were never documented as being planted under British colonial rule in the then Basutoland as part of government-implemented tree-planting programmes (Showers, 2006). However, the highly invasive nature of members of this genus suggests that it was not long before these trees would have spread beyond the colonial frontier.

The appearance of such materials at Sehonghong indicates that these tools must have been produced by some of the very last hunter-gatherer populations to occupy this part of southern Africa. Presented herein is another story, not told by people or by rock art imagery. The use and acquisition of resources that are not native to the region and not representative of a traditional repertoire of adhesive components may be an example of King's (2017: 14) assessment of the meaning of refuge during this time and part of a "complex and sustained series of engagements" in the 19th-century Maloti-Drakensberg Mountains. The historical narrative in the region begins in the early 1800s by describing relationships between hunter-gatherer groups (once described as the "Bushman raiders of the Drakensberg" (Wright, 1971; Mitchell, 2010) and Bantu-speaking and European farmers living east of the uKhahlamba-Drakensberg Escarpment in modern-day KwaZulu-

Natal and south into the Eastern Cape Province. Violence and extermination appears as the dominant subject-matter in historic records (Wright, 1971). However, oral histories recall the presence of hunter-gatherers at Sehonghong in the late-1880s/1890s (Vinnicombe, 2009; Mitchell, 2010). Conceivably, this puts the last hunter-gatherer populations of the rockshelter within contact distance with those parties wishing to bring order, spiritual or magisterial, to the Maloti-Drakensberg, and by extension their products (paraffin, castor oil, and pine products such as rosin soap, printing inks and varnish (Gibbs, 1939; Mills and White, 1987). The presence of such products in local hafting adhesives may thus be a reflection of the penetrability of such items at a time when colonial settlement encroached on the lifeways and movement of hunter-gatherers within a region that was still viewed at the time as largely untameable (King, 2017).



Figure 7.6. Photographs of the hafted implement A1543, taken in September 2015 at the Albany Museum. Left: Implement and rhinoceros horn handle. Right: Macro-image of the proximal end of the adhesive. Photographs taken by the author.

All cultural heritage objects have life-histories, the stories of their creation, use, and death. These biographies, however, extend beyond their purposeful lives which are book-ended by the manufacture of an object and their eventual disuse, discard, and deposition (Holtorf, 1998; Joy, 2009) and represent the varying relationships between objects and people depending on cultural context (Gosden and Marshall, 1999). These objects have the capacity to tell a story and lend a different perspective to long-established narratives. At Sehonghong, two scrapers lend to a historic record of the tense relationships between the last hunter-gatherer populations of the Maloti-Drakensberg, the Basotho, and British colonial rule, a sense of more peaceful exchange and

innovation that goes beyond simple (and arguably outdated) visions of 'cattle-raiders'. Among the Albany Museum collections it may be argued that the appearance of objects in museum exhibitions, in accession catalogues, and excavation reports offers multiple instances to reconnect with these specimens and give them the capacity to contribute to a new a body of research and extend the lives of objects and their contextually dependent value. The application of analytical techniques to better understand the composition of objects, especially those that are organic in composition, not only provides the opportunity to contribute to their life history, but also has the potential to re-engage with objects and re-establish their value to past users, current researchers and future audiences.

CHAPTER 8 CONCLUDING REMARKS

In the introductory chapter of this thesis I highlighted three main aims for my research: 1) to design a methodology that emphasises the potential for variability of hafting adhesives and characterises all organic and inorganic materials as best as possible; 2) to apply this methodology to larger collections of material spanning multiple sites and cultural sequences; and 3) to contribute to discussions on aspects of time and space in the manufacture of adhesives within the more constrained contexts of the archaeological case studies. To address the first point, the multi-method approach highlighted in Chapter 4 encompassed the use of four discrete steps including screening, optical light microscopy, sampling, and multi-method analytical analyses. The selection of each method was based on its suitability in the characterisation of micro-samples of either organic or inorganic materials. The application of such techniques on a combination of samples was successful in the analyses of solid samples obtained from museum specimens and four case study sites. Arguably, the application of swabs and solvent extractions to sample materials from two sites (Melkhoutboom and Sehonghong, respectively) was not as successful in the acquisition of results, nor could the samples be used for any other type of analysis beyond GC/MS. While acquiring solid samples is more invasive than using swabs or wet solvents (especially when fragments that have detached from objects are not available), it allows for the application of a wider range of analytical techniques. I thus suggest that greater efforts be made, especially when applying for sampling permits, to highlight the utility of such samples and the benefits it may have for answering compositional questions.

To move on to the second and third points, the selection of case studies discussed in this thesis is by far the largest and geographically most wide-ranging chemical analysis of hafting adhesives in southern Africa undertaken to date. As well as being new, the placement of emphasis

on LSA assemblages specifically contributes to narrowing the divide between the preference for the study of the MSA over the LSA highlighted in recent years (Wadley, 2014). The analyses conducted are centred mainly on Holocene assemblages (both the Holocene microlithic [Wilton] and the late Holocene assemblages [Final LSA and Ceramic Final LSA]), although datasets were also acquired from the late Pleistocene microlithic (Robberg) at Sehonghong. I argue that this may reflect differential preservation of younger material compared to older LSA material, as was also observed in Chapter 3.

Overall, the case studies I have investigated I have contributed to the current narrative of hafting adhesive production and use during the LSA, especially along the southernmost coast below Cape Fold Mountain Belt. However, I do emphasise that at present we still lack datasets that cover much of the late Pleistocene and early Holocene assemblages of the LSA and that we also lack concrete evidence for specific adhesive production processes through time. For now, we cannot therefore discern whether there was continued use of acquired and/or manufactured resources (i.e. conifer pitch) or whether these instances represent periods of punctuated discovery and re-discovery. Similarly, the case studies presented in this thesis are isolates and there are significant differences between each in terms of geography and ecology. Sites included within this study spanned the breadth of the southernmost coastline of South Africa, as well as the interior reaches of Free State (South Africa) and the highlands of Lesotho; the ecological biomes represented included the Fynbos, Afromontane Forest, Thicket, and Grassland. While evidence from the adhesives analysed herein supports Clark's (1958) hypothesis and emphasises the use of resources that are local to the vegetation biome in which the archaeological site is found, this is not the rule. The Boomplaas adhesive lumps highlight this point. A multi-site study in the Western Cape for example, including sites such as Faraoskop and Andriesgrond (the former having evidence of trace on late Pleistocene assemblages), may provide the scale necessary to more completely address aspects of adhesive resource choice within a defined region.

In addressing the three hypotheses, I discussed the main plant and animal constituents identified from this analysis and highlighted the inherent value of both the components - based on the complexity of their production or the nature of the resources (i.e. toxic or derived from bees) - and the adhesive as a whole, due to the multitude of resource sources and stages necessary to produce these composite substances. I also wish to emphasise that we need to take into further consideration the underlying reasons for the design of composite adhesives and how these components influenced the production of composite tools.

Pollard and Heron (1996: 2) emphasise the fundamental relationship in archaeology between “residues, artefacts, buildings and monuments, and human behaviour” with archaeological science now providing a means of elucidating aspects of human activity that, in the past, were merely speculative. Hafting adhesive analyses in southern Africa has tremendous potential to bring new perspectives to the underlying circumstances that drive tool system designs and how these systems fit into hunter-gatherer strategies to exist within a landscape of exploitable resources.

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APPENDIX I

LISTS OF ANALYSED SPECIMENS

Table I- 1. Details of the specimens from Boomplaas and Melkhoutboom analysed during this project.

Level	Excavation Details	Analysis No.	Object Details
<i>Boomplaas</i>			
BLD	Pit 7	BPA01	Lump
	Pit 9	BPA02	Lump
	Pit 15	BPA03	Lump
	Pit 23	BPA04	Lump
<i>Melkhoutboom</i>			
S	69/13	MHB41	Scraper, metamorphic
OMB	69/42l	MHB22	Adze, silicified shale
	69/37	MHB28	Scraper, silcrete
	69/37	MHB30	Segment, chalcedony
	69/30	MHB34	Segment, chalcedony
CAFu	69/48	MHB77	Adze, silicified shale
	69/42s	MHB20	Adze, silicified shale
	69/49	MHB56	Scraper, chalcedony
	69/49	MHB58	Scraper, silcrete
CAF	69/75	MHB18	Adze, silicified shale
	69/46	MHB52	Adze, silcrete
	69/61	MHB54	Adze, silicified shale
	69/93	MHB03	Scraper, chalcedony
MB	69/107a	MHB05	Scraper, chalcedony
	69/107b	MHB08	Scraper, chalcedony
	69/107c	MHB10	Scraper, chalcedony
	69/132	MHB32	Segment, chacedony
	69/95s	MHB33	Segment, quartzite (?)
	69/95l	MHB48	Segment, quartzite (?)
	69/134	MHB50	Segment, chalcedony
	69/134	MHB70	Scraper, chalcedony
	69/136	MHB72	Scraper, chalcedony
	69/151	MHB01	Scraper, quartz
	69/150s	MHB13	Scraper, chalcedony
	69/150l	MHB16	Scraper, chalcedony
	69/201	MHB24	Borer, chalcedony
	69/229	MHB26	Borer, chalcedony
	69/226	MHB64	Segment, chalcedony
	69/240	MHB66	Segment, chalcedony
M	69/238	MHB67	Segment, chalcedony
	69/100	MHB38	Borer, chalcedony
	69/283	MHB46	Segment, chalcedony
	69/276	MHB60	Scraper, chalcedony (?)
	69/305	MHB62	Scraper, chalcedony

Table I-2. Details of the museum specimens analysed during this project.

Object No.	Location	Object details
A1588	Iziko Museums	Hafting adhesive mass with silicified shale adze
A1543	Albany Museum	Complete implement with horn handle, adhesive mass, and quartz adze
C961	Albany Museum	Implement with bone handle, adhesive mass and quartz scraper

Table I-3. Details of the specimens from Renbaan Cave and Rose Cottage Cave analysed during this project.

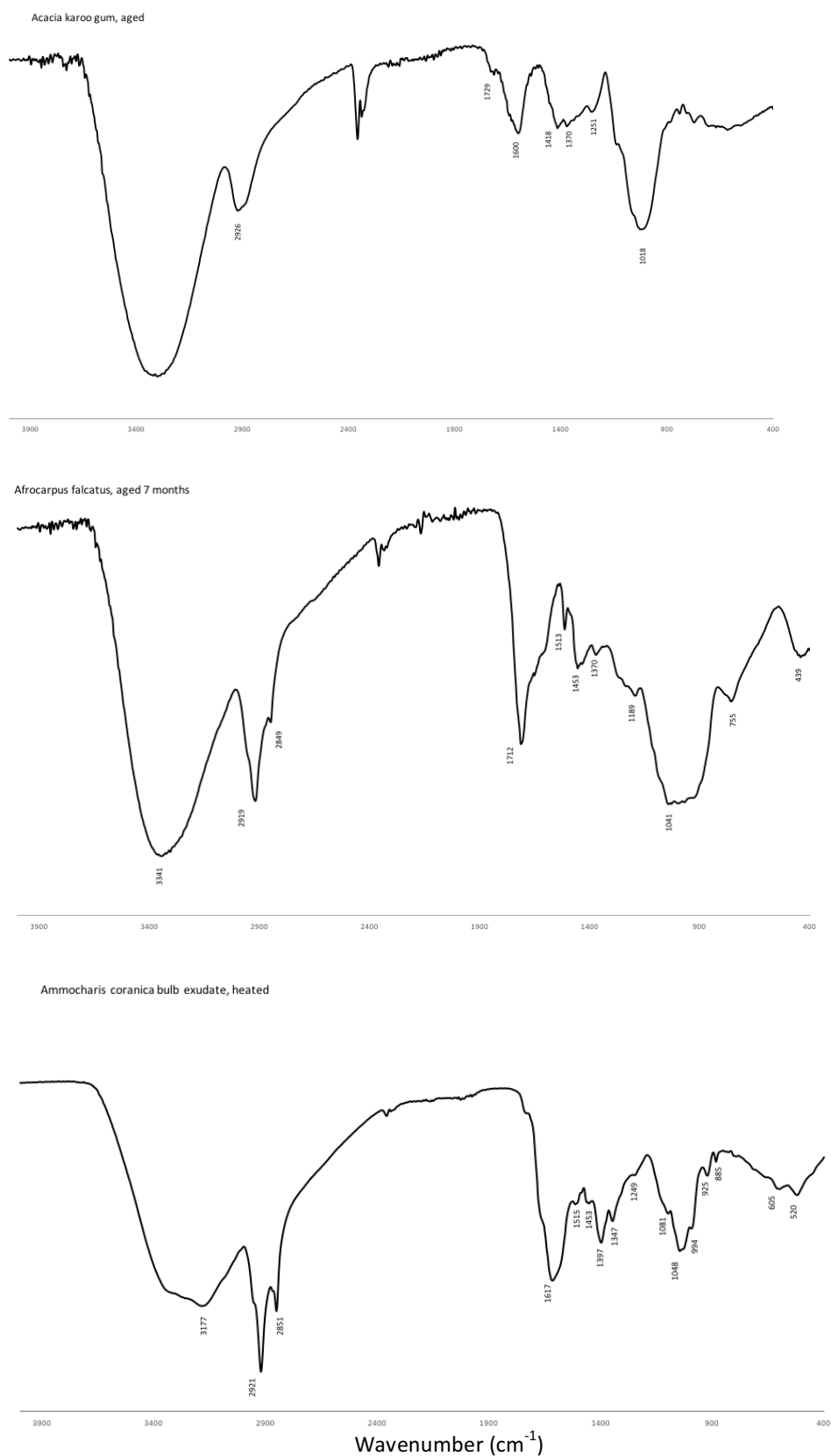
Level	Analysis No.	Object Details
<i>Renbaan Cave</i>		
Surface cleanings	RB01	Adze, silcrete
Bedding	RB03	Adze, silcrete
	RB04	Adze, silcrete
	RB05	Adze, CCS
	RB06_01/ RB06_02	Adze, silcrete
	RB07	Scraper, quartz
Brown Sand with Vegetation	RB12	Utilized flake, CCS
	RB08	Scraper, quartz
	RB02	Adze, silcrete
GAS	RB09	Scraper, quartz
	RB10	Adze, silcrete
	RB11	Adze, silcrete
<i>Rose Cottage Cave</i>		
A	RCC02	Scraper, quartz
	RCC06	Segment, quartzite
	RCC07	Bladelet, CCS
	RCC08	Scraper, quartzite
	RCC27	Blade, CCS
	RCC32	Segment, quartzite
	RCC36	Scraper, CCS
	RCC01	Scraper, quartzite
A2	RCC03	Segment quartz
	RCC04	Scraper, CCS
	RCC09	Scraper, quartz
	RCC10	Scraper, CCS
	RCC12	Blade, CCS
	RCC13	Blade, CCS
	RCC15	Scraper, quartz
	RCC16	Broken blade, CCS
	RCC20	Broken blade, CCS
	RCC21	Blade, CCS
	RCC24	Scraper, CCS
	RCC33	Adze, CCS

A2 (i)	RCC14	Scraper, CCS
Ja	RCC05	Bladelet, CCS
	RCC17	Bladelet, quartzite
	RCC35	Broken blade, CCS
Ph	RCC11	Scraper, CCS
	RCC26	Adze, CCS
	RCC28	Scraper, CCS
	RCC29	Scraper, CCS
	RCC31	Scraper, quartzite
	RCC34	Adze, CCS
CM	RCC18	Bladelet, CCS
	RCC19	Adze, CCS
	RCC22	Broken blade, quartz
	RCC23	Backed blade, CCS
		Miscellaneous
	RCC25	retouch, CCS
	RCC30	Point, CCS

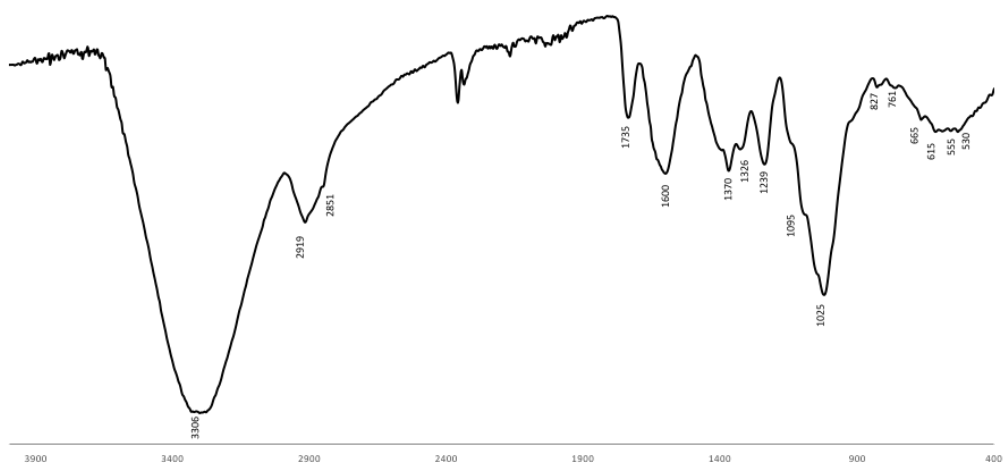
APPENDIX II

REFERENCE FTIR SPECTRA A SELECTION OF PLANT EXUDATES & INORGANIC MINERALS

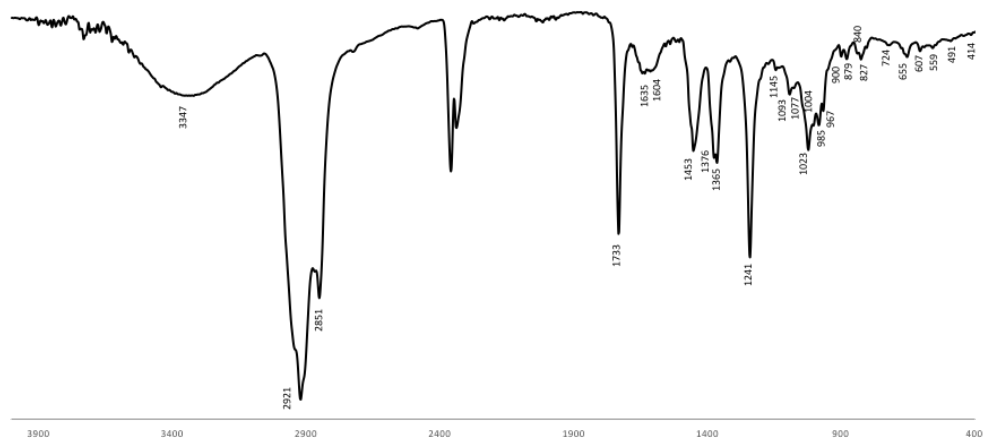
Reference IR spectra of plant exudates displayed in % transmittance



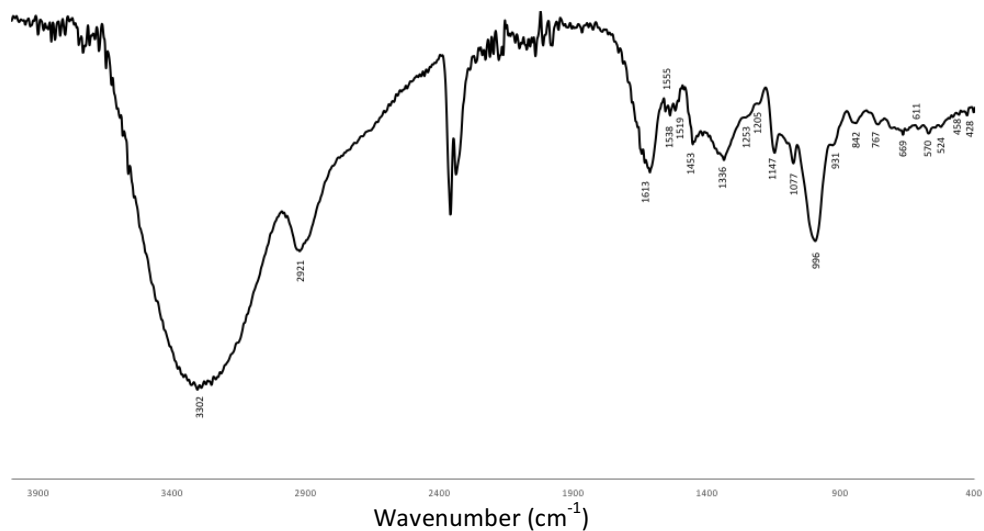
Asparagus sp. exudate



Carissa sp.

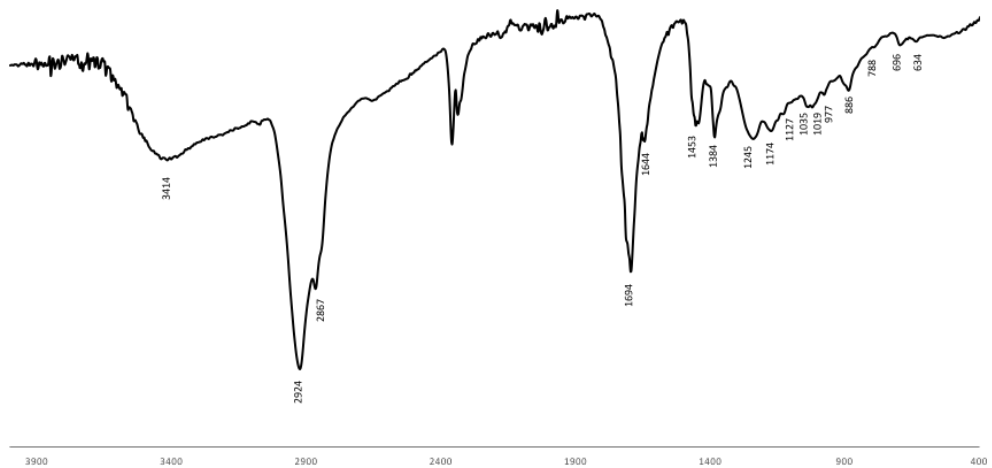


Chasmanthe sp.

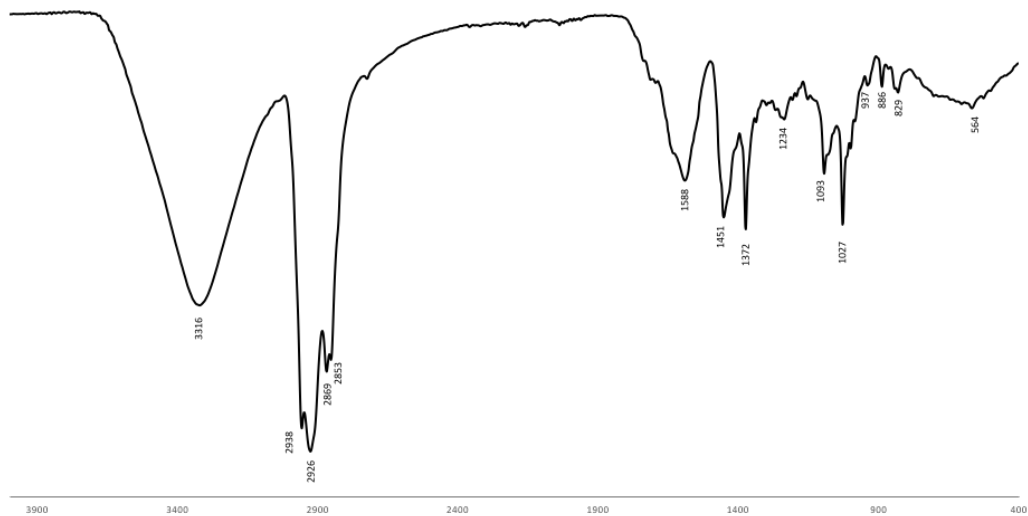


Wavenumber (cm⁻¹)

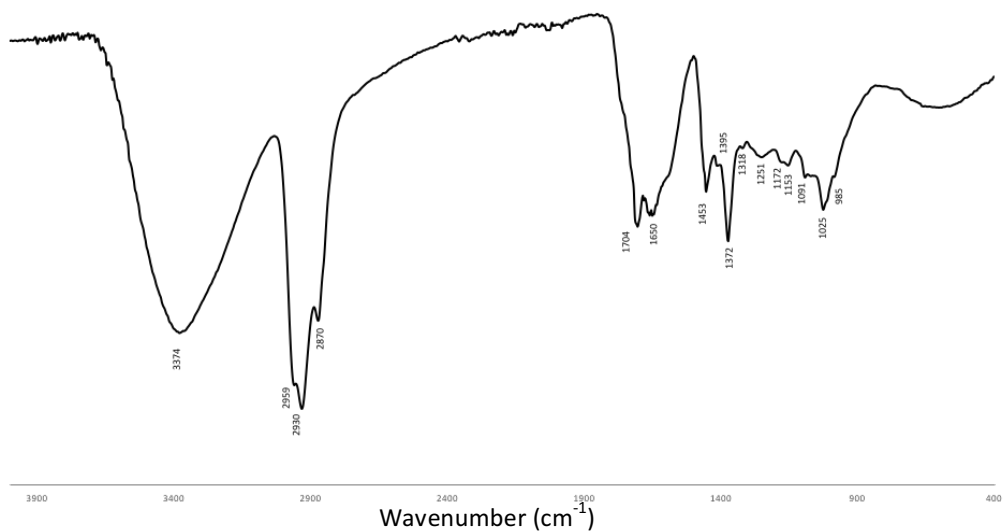
Colophospermum mopane resin

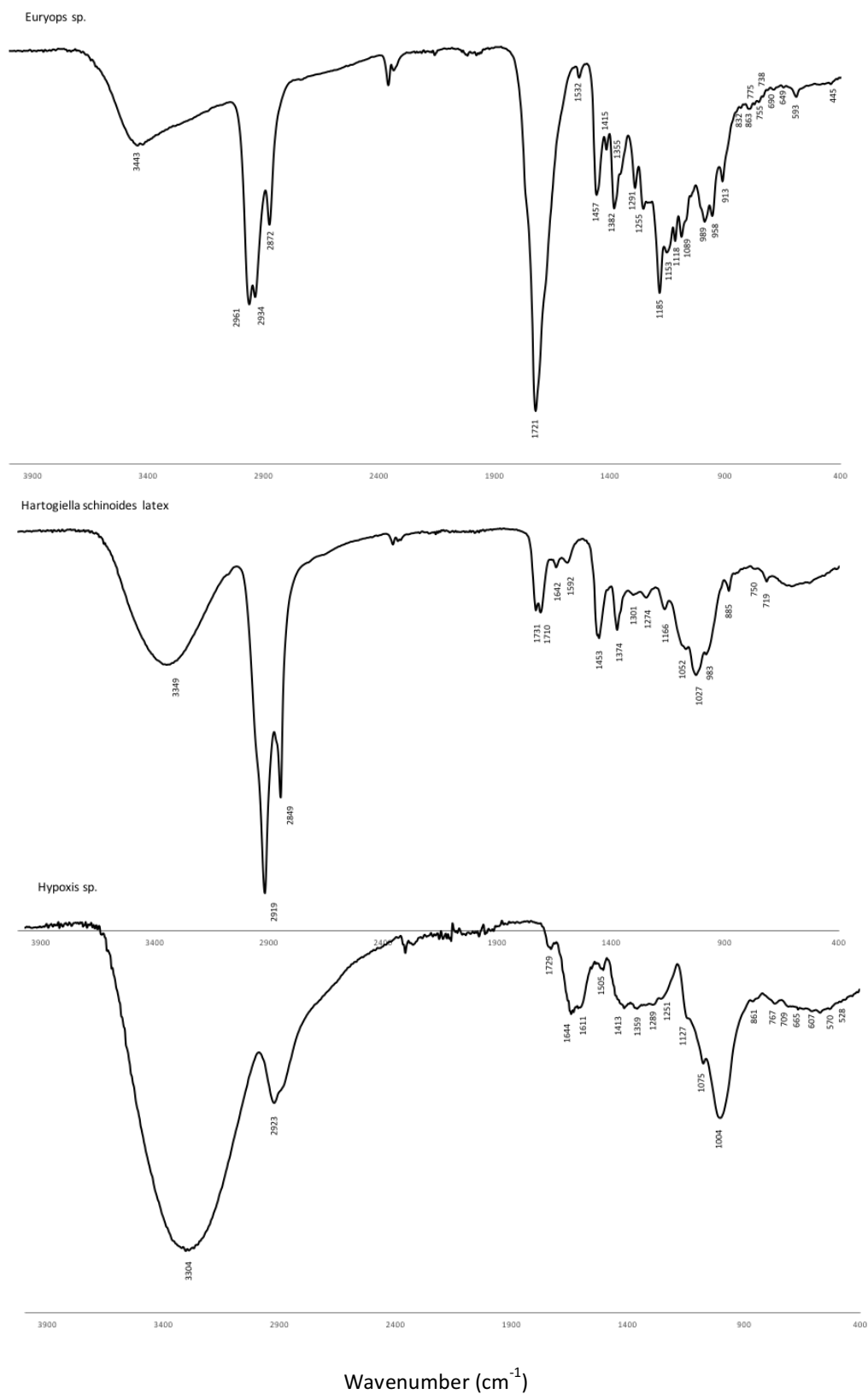


Euphorbia ingens latex

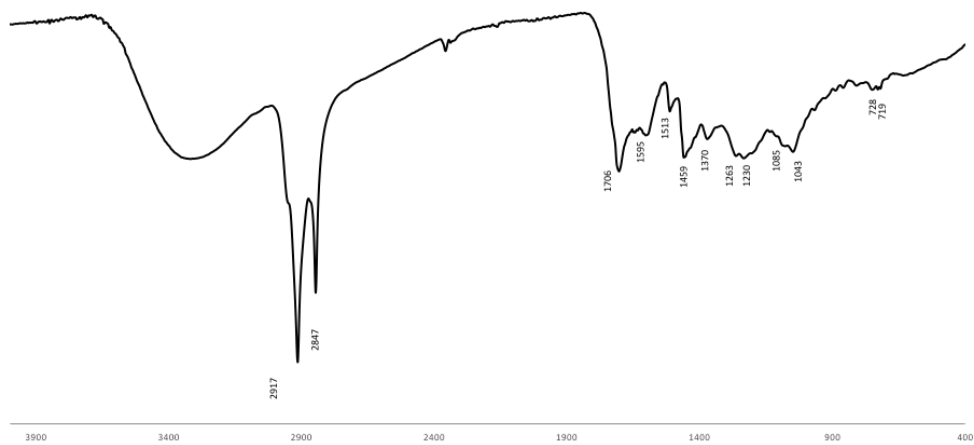


Euphorbia tirucalli latex, aged

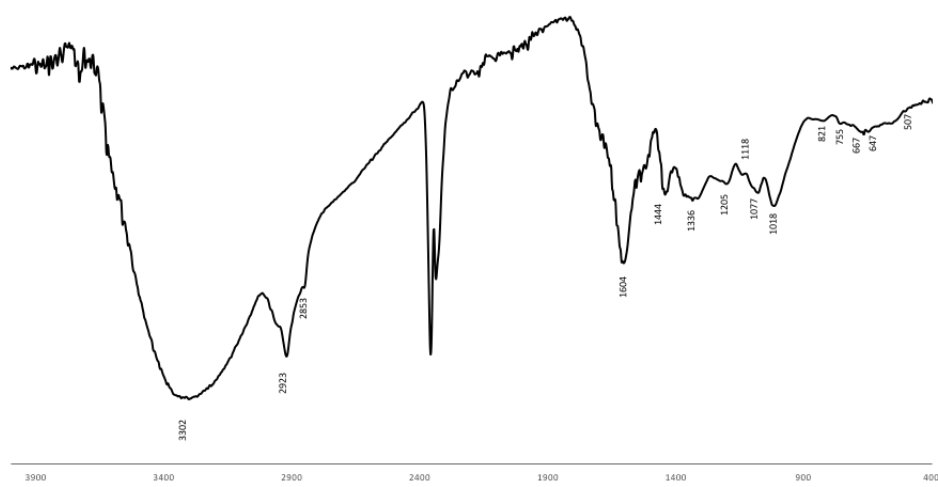




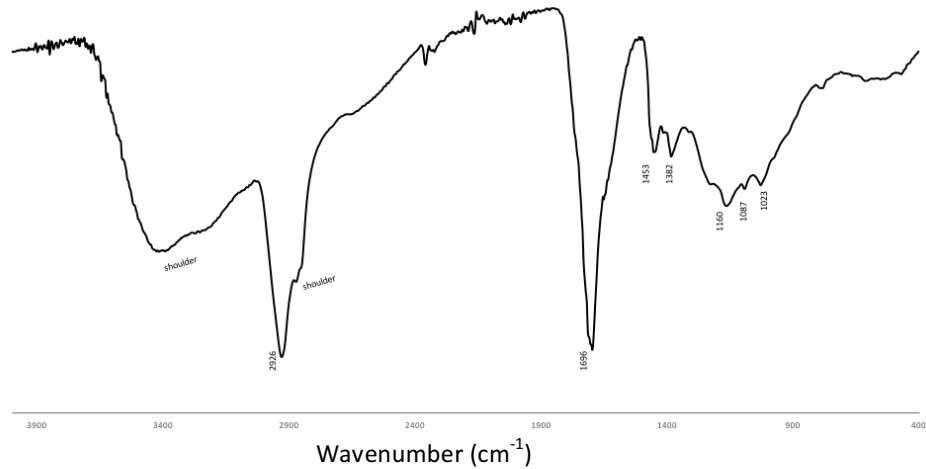
Podocarpus elongatus pitch, aged 7 months



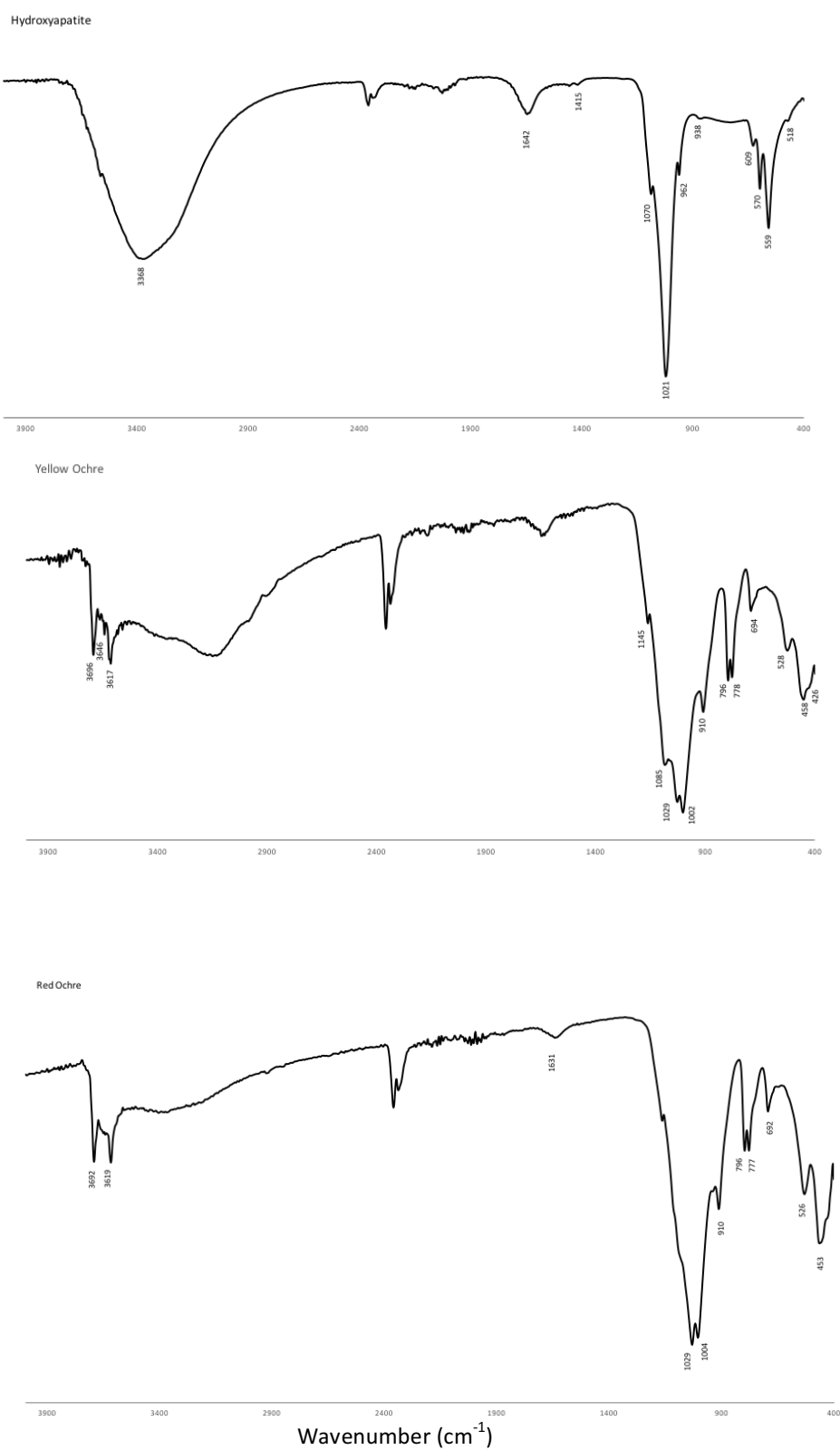
Ozoroa paniculosa exudate, heated

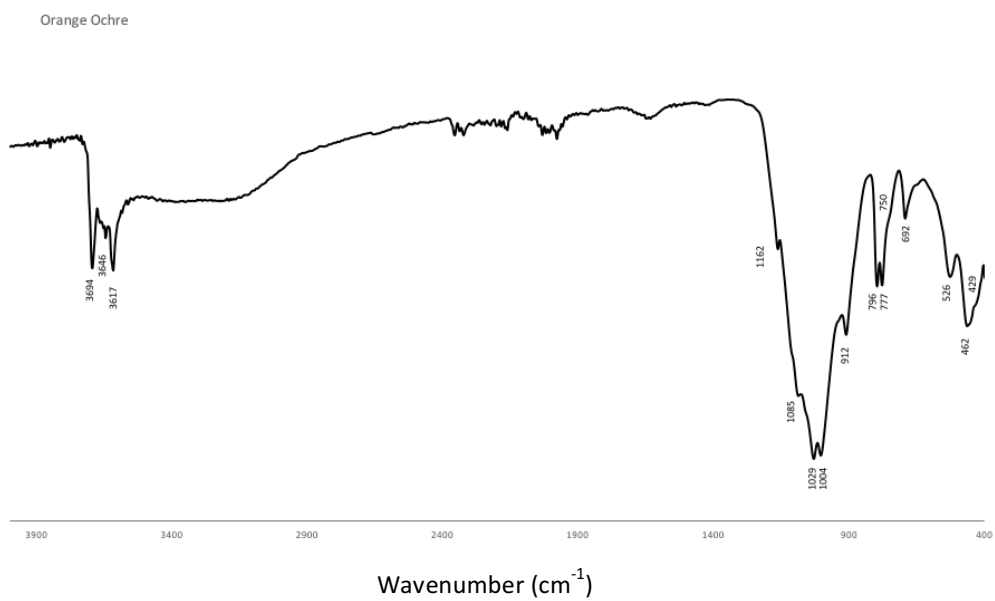


Widdringtonia cupressoides resin, aged



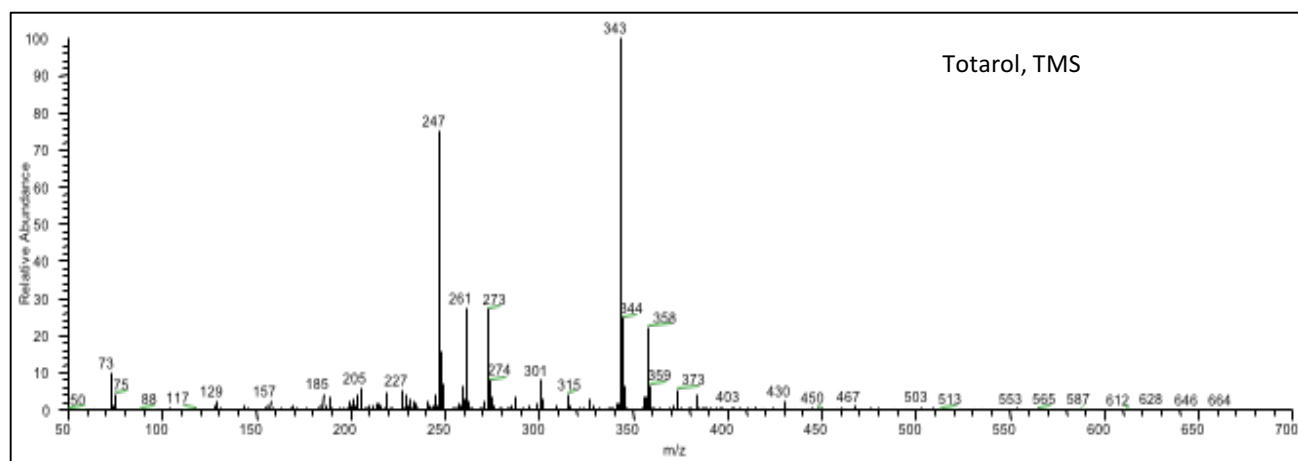
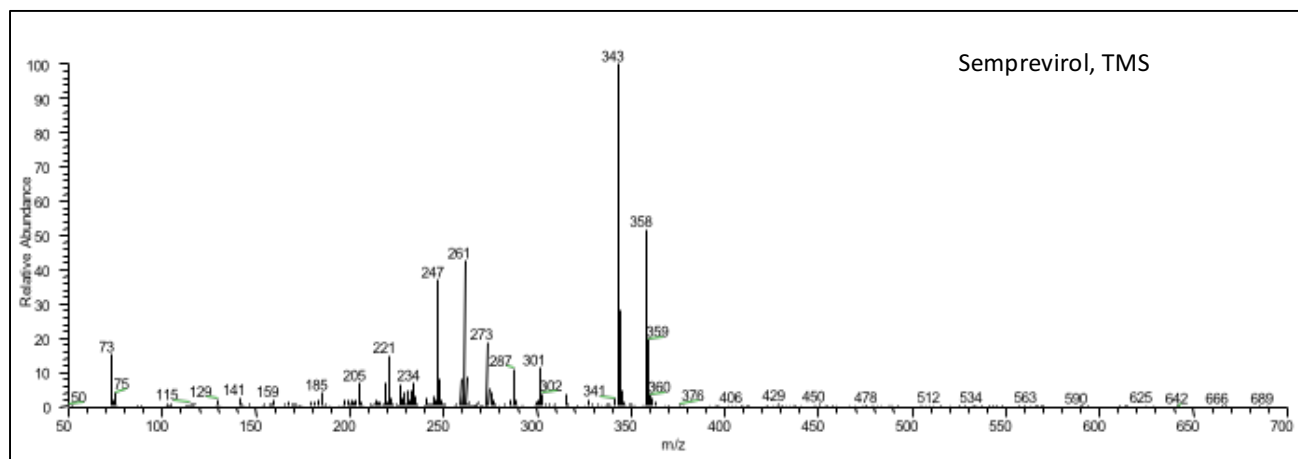
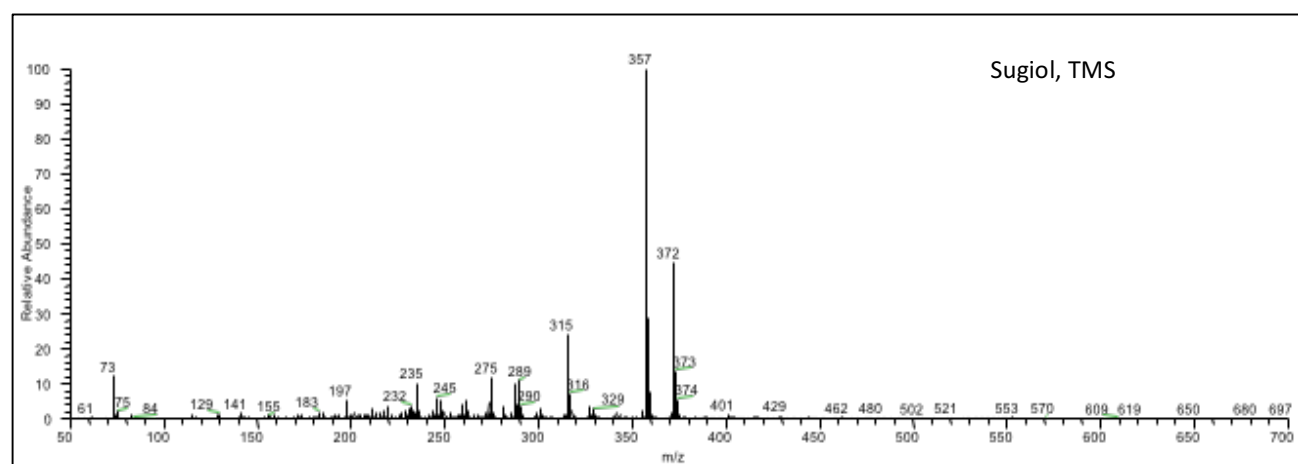
Reference IR spectra of inorganic minerals displayed in % transmittance

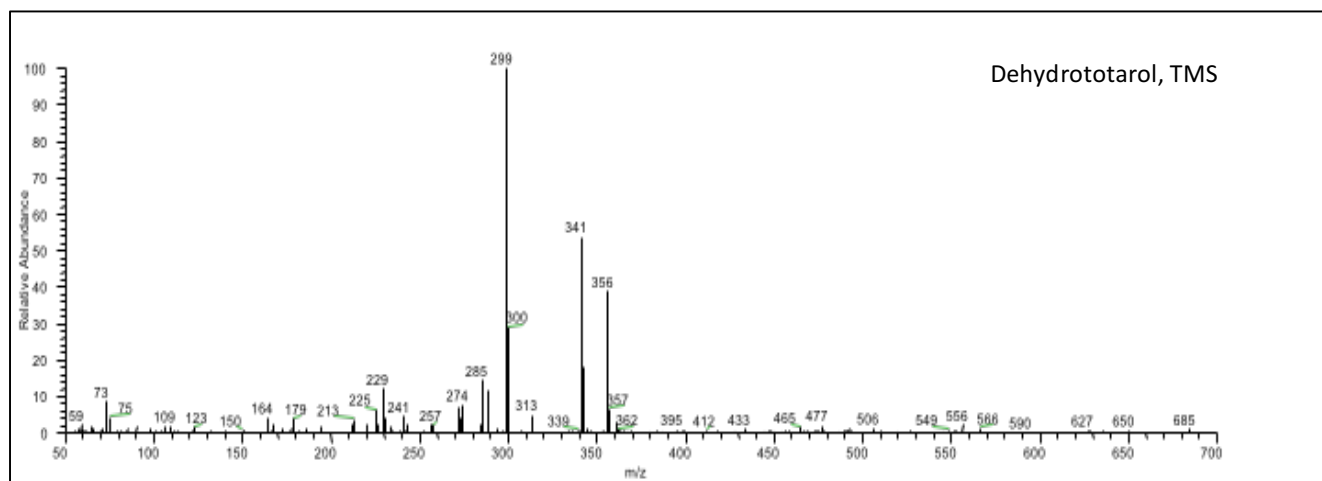
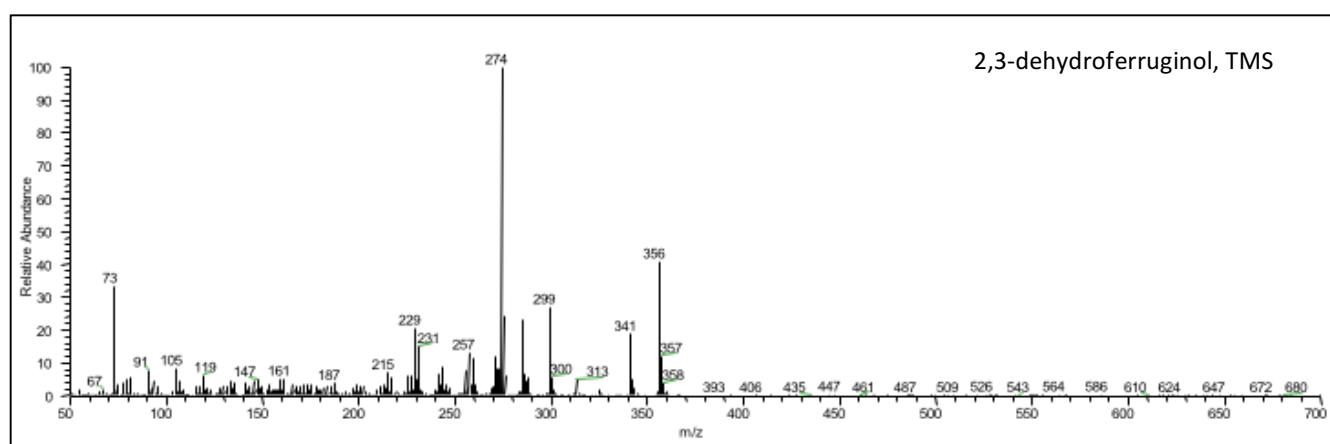
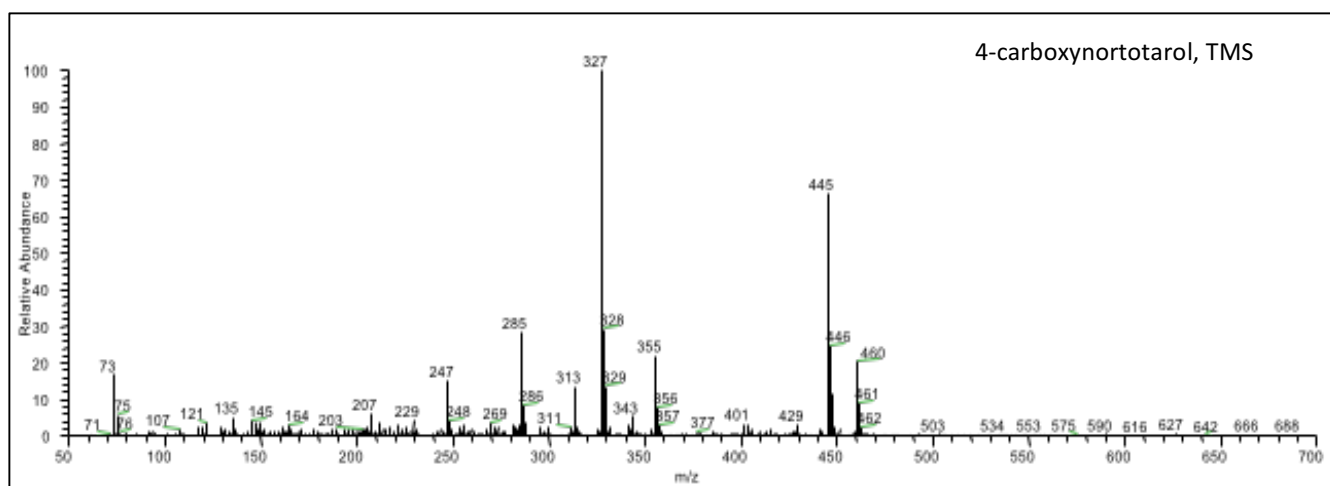


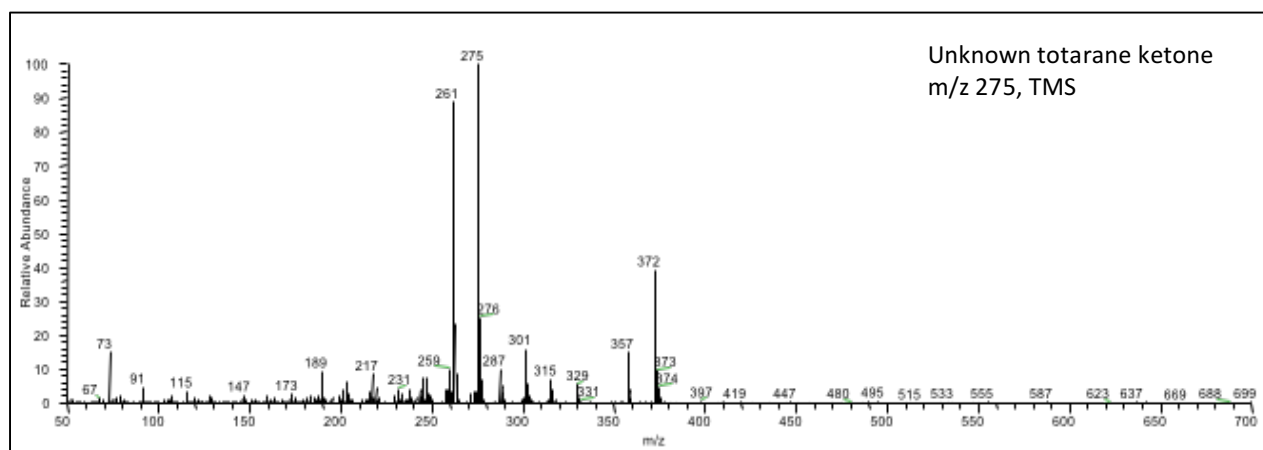
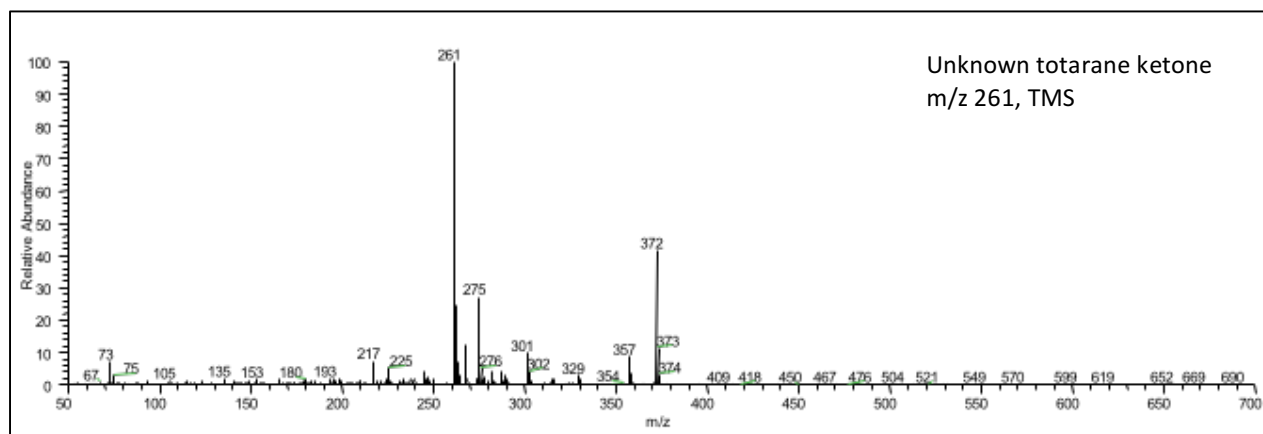
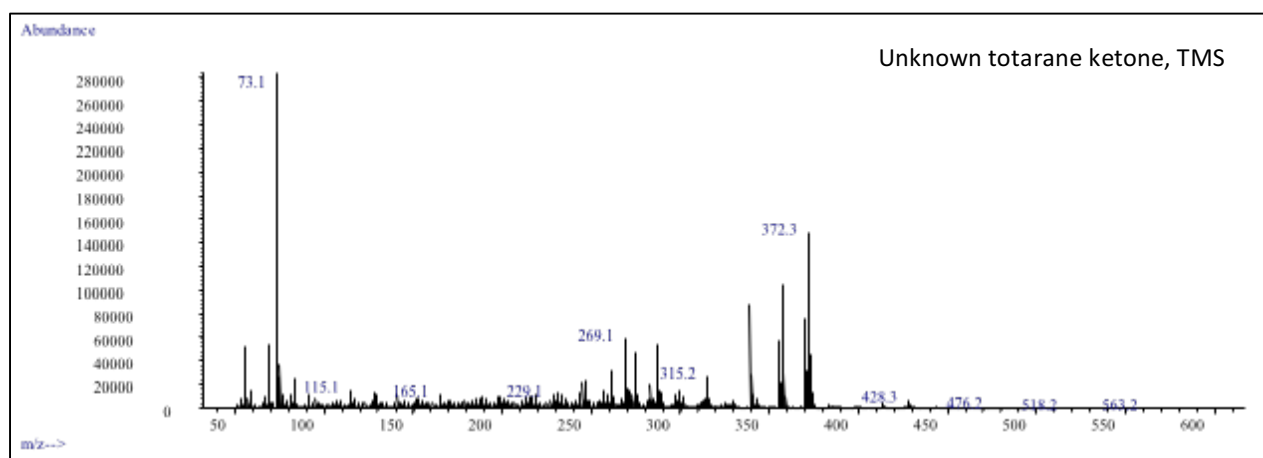


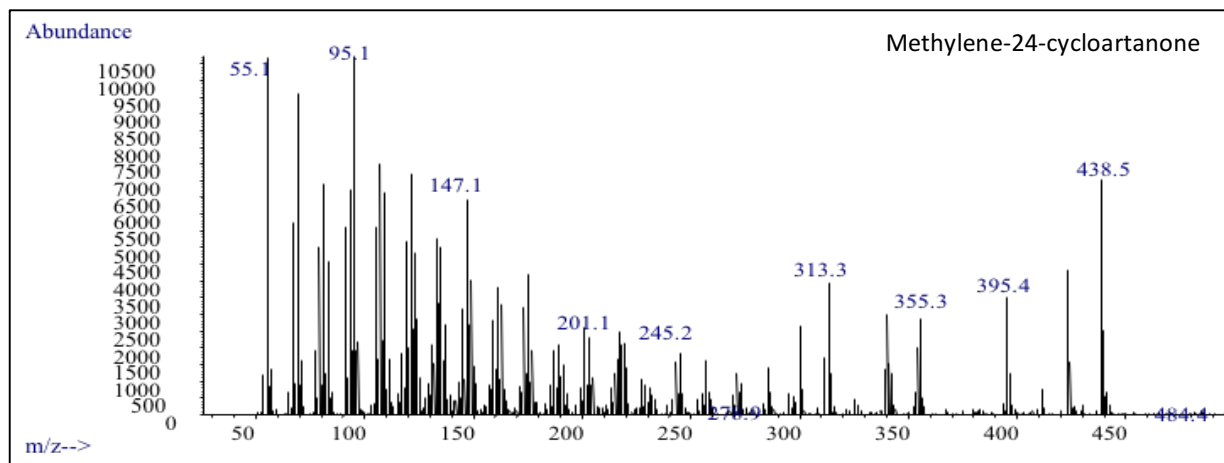
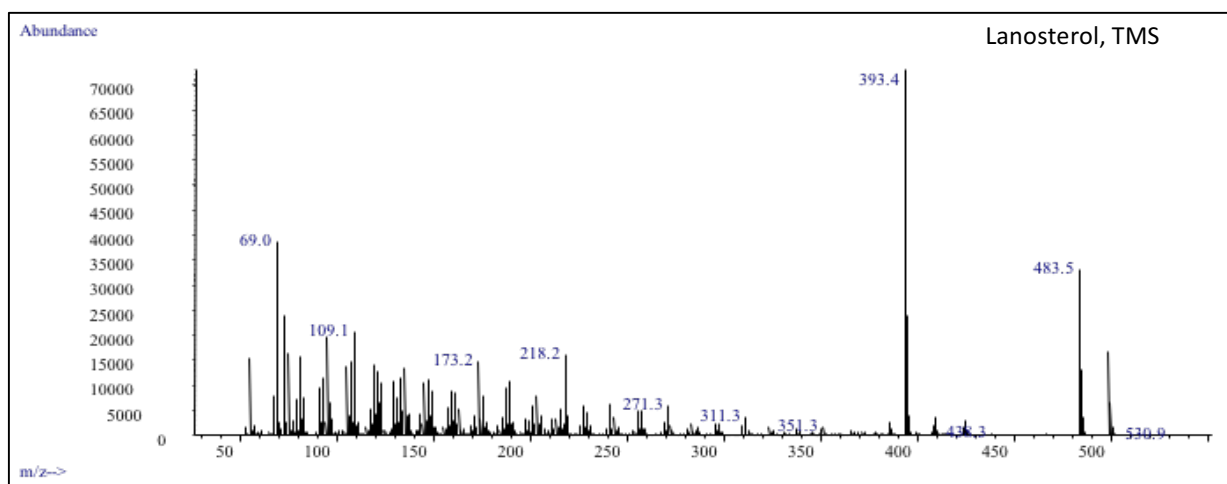
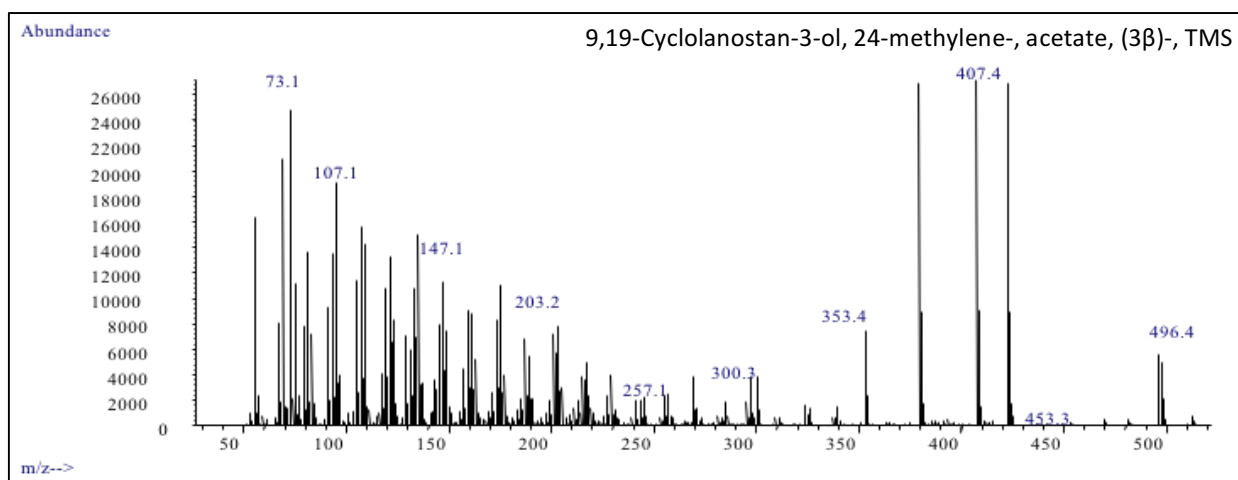
APPENDIX III

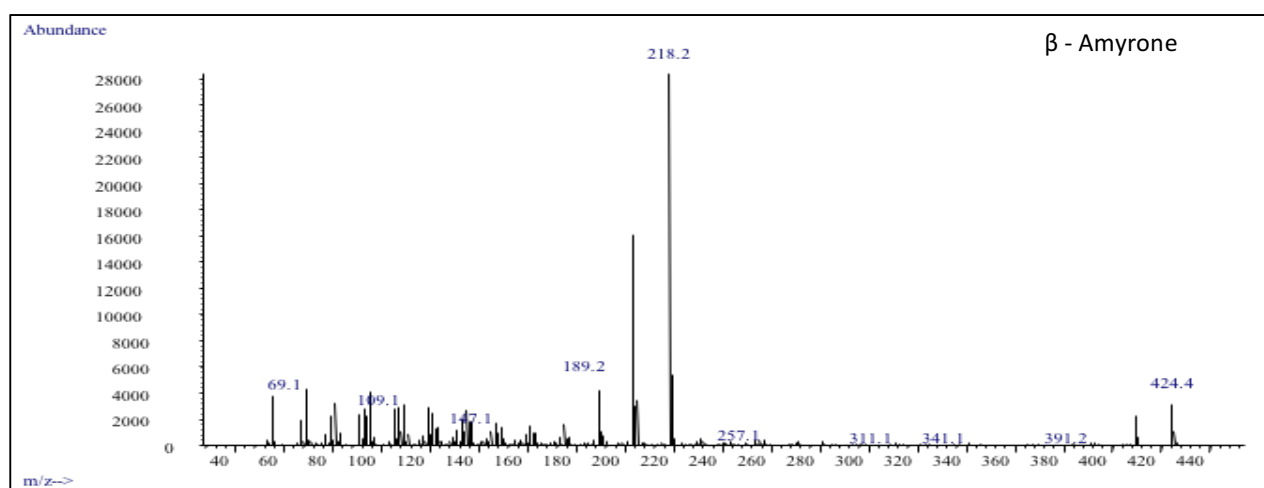
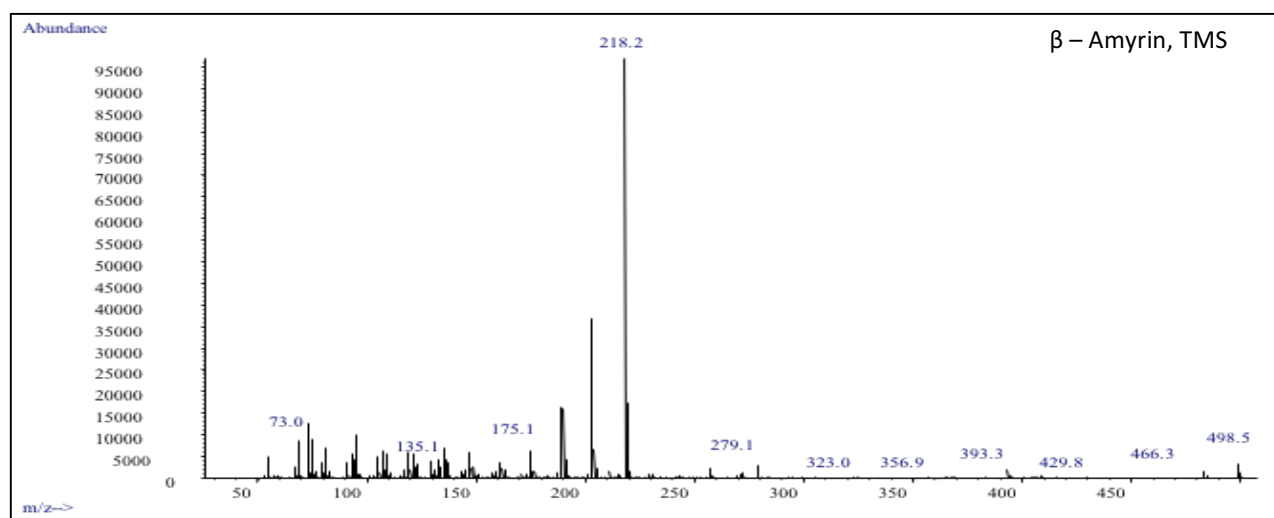
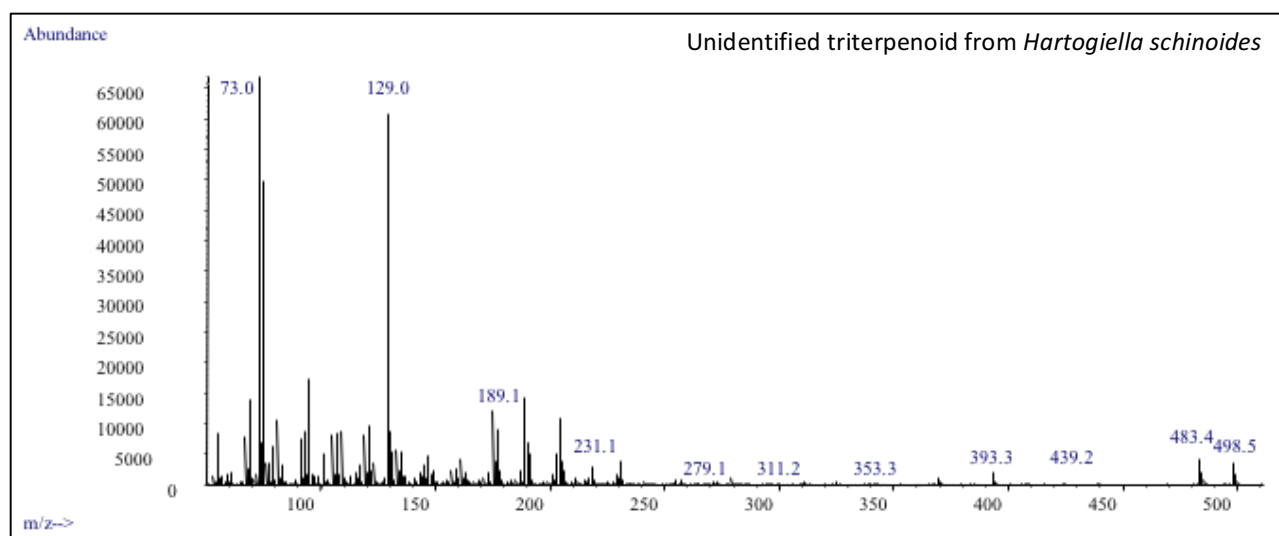
REFERENCE MASS SPECTRA
&
COMMENTS ON TERPENOID CONSTITUENTS











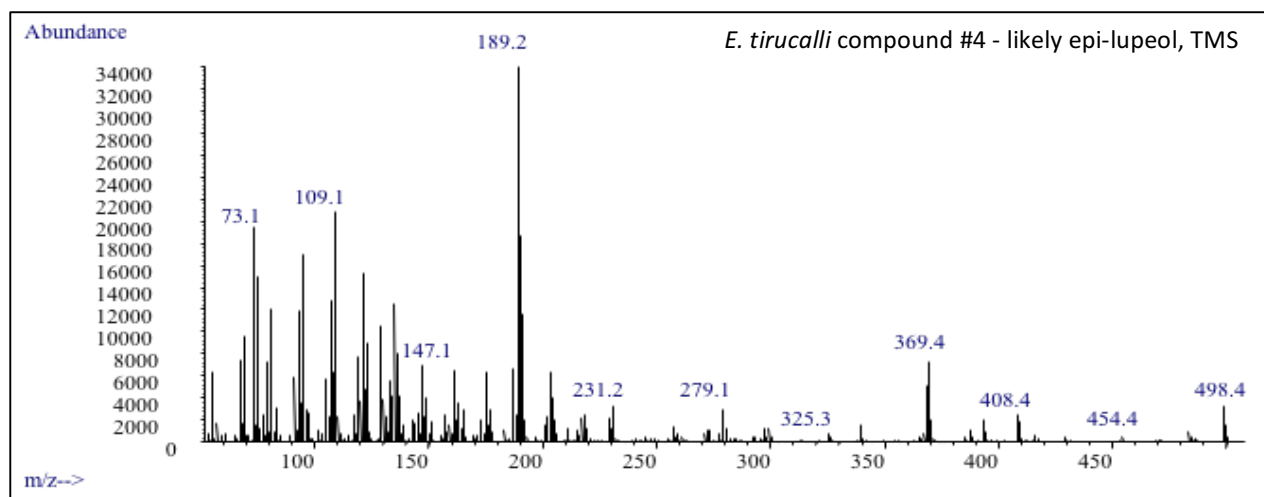


Table III-1. Percentage composition of a selection of diterpenoids of analysed wood, bark, and experimental pitch samples.

Species	Family	8,15-pimaradien-18-oate	levopimaric acid	sandaracopimaric acid	isopimaric acid	ferruginol	semperviol	totarol	abietol	communic acid	sugiol
A FALCATUS PITCH 1	Podocarpaceae	0.00	0.00	0.60	40.92	0.00	0.00	22.70	0.00	0.00	14.09
A FALCATUS PITCH 2	Podocarpaceae	0.89	0.00	20.85	43.18	0.00	24.67	0.70	0.00	0.00	6.63
P ELONGATUS PITCH	Podocarpaceae	0.00	0.00	0.00	0.00	0.00	6.01	4.69	0.00	0.00	52.68
P HENKELII PITCH 1	Podocarpaceae	13.95	0.00	15.75	0.00	0.00	20.85	38.21	0.00	0.00	0.00
P HENKELII PITCH 2	Podocarpaceae	40.90	0.00	55.93	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P LATIFOLIUS BARK	Podocarpaceae	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	24.04
J PROCERA PITCH 1	Cupressaceae	0.00	0.00	0.34	0.00	20.74	2.67	21.42	0.24	0.18	0.68
J PROCERA PITCH 2	Cupressaceae	0.00	0.00	1.32	0.00	10.34	16.18	16.18	15.91	20.14	0.00
W CEDARBERGENSIS PITCH 1	Cupressaceae	0.00	30.89	11.19	56.20	0.00	0.00	0.00	0.00	1.03	0.00
W CEDARBERGENSIS PITCH 1	Cupressaceae	0.00	7.85	68.53	4.35	0.22	4.65	2.90	4.58	4.35	0.00
P ELONGATUS WOOD	Podocarpaceae	0.00	0.00	0.00	0.00	6.50	0.09	0.00	0.00	0.00	20.01
A FALCATUS WOOD	Podocarpaceae	0.32	0.00	0.00	48.83	2.96	0.00	0.00	0.00	0.00	0.00
P HENKELII WOOD 1	Podocarpaceae	31.49	0.00	44.44	0.00	0.00	0.00	0.06	0.15	23.57	0.00
P HENKELII WOOD 2	Podocarpaceae	30.80	0.00	47.04	0.00	0.00	0.00	0.52	0.00	21.57	0.00
W CEDARBERGENSIS WOOD	Cupressaceae	0.00	0.00	72.16	14.73	0.00	0.00	0.00	0.00	13.11	0.00
A FALCATUS WOOD 2	Podocarpaceae	0.81	0.00	35.47	42.88	3.17	0.05	1.30	0.00	0.00	10.32
J PROCERA WOOD	Cupressaceae	0.00	0.00	0.00	0.00	6.35	0.00	0.97	2.47	89.66	0.14
J PROCERA WOOD 2	Cupressaceae	0.00	0.00	3.78	0.00	14.84	0.00	1.44	2.53	73.09	1.34

Table III-1 (cont.). Percentage composition of diterpenoids of analysed wood, bark, and experimental pitch samples.

Species	Family	unknown, A falcatus ketone 261 (100)	dehydro- sempervirol	dehydro- totarol	2,3- dehydroferruginol	7- hydroxytotarol	3- hydroxytotarol	4- carboxynortotarol	DHA	unknown dehydro- hydroxy- phenolic diterpenoid
A FALCATUS PITCH 1	Podocarpaceae	0.00	18.75	0.00	0.00	2.02	0.00	0.04	0.00	0.87
A FALCATUS PITCH 2	Podocarpaceae	0.00	2.46	0.00	0.00	0.47	0.00	0.14	0.00	0.00
P ELONGATUS PITCH	Podocarpaceae	0.47	24.37	0.00	0.00	1.92	0.00	3.51	0.00	6.36
P HENKELII PITCH 1	Podocarpaceae	0.00	0.00	0.20	0.00	0.63	0.00	10.41	0.00	0.00
P HENKELII PITCH 2	Podocarpaceae	0.00	0.00	0.00	0.00	0.00	0.00	3.17	0.00	0.00
P LATIFOLIUS BARK	Podocarpaceae	0.00	0.00	0.00	0.00	0.00	0.00	75.96	0.00	0.00
J PROCERA PITCH 1	Cupressaceae	0.00	17.60	2.66	31.83	0.00	0.00	0.00	0.00	1.66
J PROCERA PITCH 2 W	Cupressaceae	0.00	9.60	0.00	10.34	0.00	0.00	0.00	0.00	0.00
CEDARBERGENSIS PITCH 1 W	Cupressaceae	0.00	0.00	0.00	0.68	0.00	0.00	0.00	0.00	0.00
CEDARBERGENSIS PITCH 1	Cupressaceae	0.00	0.21	0.00	2.35	0.00	0.00	0.00	0.00	0.00
P ELONGATUS WOOD	Podocarpaceae	0.00	0.00	0.00	42.29	2.52	20.01	0.00	0.00	0.00
A FALCATUS WOOD	Podocarpaceae	0.29	41.33	1.06	4.25	0.22	0.00	0.62	0.00	0.00
P HENKELII WOOD 1	Podocarpaceae	0.00	0.00	0.00	0.00	0.00	0.00	0.29	0.00	0.00
P HENKELII WOOD 2 W	Podocarpaceae	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00
CEDARBERGENSIS WOOD	Cupressaceae	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
A FALCATUS WOOD 2	Podocarpaceae	0.00	0.00	0.00	0.00	0.32	0.00	0.27	0.00	0.00
J PROCERA WOOD	Cupressaceae	0.00	0.00	0.00	0.41	0.00	0.00	0.00	0.00	0.00
J PROCERA WOOD 2	Cupressaceae	0.00	2.19	0.00	0.00	0.00	0.00	0.00	0.80	0.00

Table III-2. Comments on the constituents of a selection of non-diterpenoid producing plants from the reference collection.

Specimen details	Comments
<i>Ammocharis coranica</i> heated bulb exudate	- Cycloartane, ergostane (m/z129), and lanostane triterpenoids
<i>Boophone disticha</i> heated bulb exudate	- Ergostane (m/z129) - Main components were alkaloids, including buphandrin and alpha-D-glucopyrnoside
<i>Brunswigia radulosa</i> heated bulb exudate	- No identifiable terpenoids
<i>Chasmanthe</i> sp.	- Cycloartane, ergostane (m/z129) triterpenoids - Monoterpenoids with m/z 119 and m/z 229
<i>Euphorbia ingens</i> latex	- Ursane, oleanane, lupane and lanostane triterpenoids - Prominent C _{18:0} and C _{18:1} fatty acid peaks
<i>Euphorbia tirucalli</i> latex	- Ursane, oleanane, lupane and lanostane triterpenoids - Prominent C _{18:0} and C _{18:1} fatty acid peaks
<i>Euryops</i> sp.	- Main peaks, all unidentified within 26mins
<i>Hartogiella schinoides</i>	- Two unidentified triterpenoids - Cycloartane, ursane, oleanane, lupane and lanostane triterpenoids
<i>Hypoxis</i> sp.	- No terpenoids present
<i>Ozoroa paniculosa</i>	- Main identified compounds, lanosterol (TMS) and an unknown compound with [M ⁺] m/z 525, m/z 511, 444, and 409, with base peak at 73 and a prominent 189
<i>Rhus undulata</i>	- Only contains phenols from lignin and cellulose

APPENDIX IV

COPY OF ROSE COTTAGE CAVE PERMIT REPORT

EXPORT PERMIT REPORT

The Analysis of Residues from Stone Tools from Rose Cottage Cave

for

The South African Heritage Resources Agency
111 Harrington Street, Cape Town 8000
PO Box 4637

by:

Margaret-Ashley Veall

May 30, 2018

Introduction

Thirty-six stone tools from Rose Cottage Cave were exported to the Research Laboratory for Archaeology and the History of Art, University of Oxford (UK), for analysis by a combination of microscopic and analytical techniques. The specimens were exported (transported by hand) from the RSA to Oxford, UK, under the CaseID 8599 and the PermitID 2119 in November 2015. Material was returned the Republic of South Africa November 2017.

Residues on stone tools from the LSA contexts of Rose Cottage Cave were previously studied and published by B. Williamson (1996, 1997). A black film was described on several specimens as possibly relating to plant resins (Williamson 1997) or manganese oxide (Williamson, 1996). Based on these findings and published discussions of hafting arrangement on several pieces (Williamson, 1997; Binneman, 1997), material from this site was thus deemed as a suitable candidate for further study as a component of a multi-site doctoral project identifying the composition of hafting adhesives from southern African Later Stone Age contexts.

The main aim of this study at Rose Cottage Cave was to: determine whether the residue traces were consistent with selection criteria for hafting adhesive residue trace set out within the larger doctoral project; if so, to identify whether this material were predominantly organic or inorganic in origin; and finally, whether these residues are consistent with hafting adhesive trace from other southern African LSA archaeological contexts. **Table 1** highlights the details of each exported specimen.

Table 1. Details of exported specimen highlighted in this report.

Laboratory No.	Level	Square	Typology	Max. dimensions H x L x W nearest mm	Raw material	Associated Dates (uncalibrated, Wadley 2000, 2000b)
RCC01	A2	L3	scraper	5 x 18 x 22	quartzite	2240 +/- 60 BP
RCC02	A	L3	scraper	6 x 13 x 16	quartz	680 +/- 50 BP
RCC03	A2	O4	segment	2 x 10 x 5	quartz	2240 +/- 60 BP
RCC04	A2	L4	scraper	5 x 5 x 20	crypto crystalline silicate	2240 +/- 60 BP
RCC05	Ja	Q3	bladelet	2 x 16 x 7	crypto crystalline silicate	8160 +/- 70 BP
RCC06	A	Q2	segment	3 x 11 x 7	quartzite	680 +/- 50 BP
RCC07	A	Q6	bladelet	3 x 25 x 11	crypto crystalline silicate	680 +/- 50 BP
RCC08	A	Q5	scraper	9 x 26 x 21	quartzite	680 +/- 50 BP
RCC09	A2	M3	scraper	9 x 13 x 14	quartz	2240 +/- 60 BP
RCC10	A2	L5	scraper	5 x 22 x 13	crypto crystalline silicate	2240 +/- 60 BP
RCC11	Ph	O4	scraper	6 x 18 x 20	crypto crystalline silicate	No direct dates from layer; range - 8614 +/-38 - 7630 +/- 80 BP
RCC12	A2	L5	blade	8 x 37 x 9	crypto crystalline silicate	2240 +/- 60 BP
RCC13	A2	O4	blade	4 x 25 x 11	crypto crystalline silicate	2240 +/- 60 BP

RCC14	A2 (i)	K5	scraper	3 x 13 x 17	crypto crystalline silicate	2240 +/- 60 BP
RCC15	A2	N4	scraper	5 x 13 x 13	quartz	2240 +/- 60 BP
RCC16	A2	L5	broken blade	4 x 18 x 7	crypto crystalline silicate	2240 +/- 60 BP
RCC17	Ja	Q5	bladelet	2 x 13 x 5	quartzite	8160 +/- 70 BP
RCC18	CM	Q4	bladelet	2 x 14 x 6	crypto crystalline silicate	No direct dates from layer; range - 8614 +/- 38 - 8380 +/- 70 BP
RCC19	CM	P4	adze	11 x 45 x 28	crypto crystalline silicate	No direct dates from layer; range - 8614 +/- 38 - 8380 +/- 70 BP
RCC20	A2	K5	broken blade	2 x 8 x 10	crypto crystalline silicate	2240 +/- 60 BP
RCC21	A2	N3	blade	3 x 24 x 10	crypto crystalline silicate	2240 +/- 60 BP
RCC22	CM	K3	broken blade	2 x 26 x 6	quartz	No direct dates from layer; range - 8614 +/- 38 - 8380 +/- 70 BP
RCC23	CM	Q4	backed blade	<1 x 20 x 9	crypto crystalline silicate	No direct dates from layer; range - 8614 +/- 38 - 8380 +/- 70 BP
RCC24	A2	J/K3	scraper	9 x 27 x 18	crypto crystalline silicate	2240 +/- 60 BP
RCC25	CM	K3	misc retouch	4 x 34 x 9	crypto crystalline silicate	No direct dates from layer; range - 8614 +/- 38 - 8380 +/- 70 BP
RCC26	Ph	M4	adze	8 x 45 x 25	crypto crystalline silicate	No direct dates from layer; range - 8614 +/- 38 - 7630 +/- 80 BP
RCC27	A	Q3	blade	7 x 27 x 11	crypto crystalline silicate	680 +/- 50 BP
RCC28	Ph	J3	scraper	10 x 19 x 14	crypto crystalline silicate	No direct dates from layer; range - 8614 +/- 38 - 7630 +/- 80 BP
RCC29	Ph	K4	scraper	8 x 18 x 15	crypto crystalline silicate	No direct dates from layer; range - 8614 +/- 38 - 7630 +/- 80 BP
RCC30	CM	N4	point	6 x 18 x 19	crypto crystalline silicate	No direct dates from layer; range - 8614 +/- 38 - 8380 +/- 70 BP
RCC31	Ph	K5	scraper	7 x 26 x 18	quartzite	No direct dates from layer; range - 8614 +/- 38 - 7630 +/- 80 BP
RCC32	A	P4	segment	3 x 12 x 11	quartzite	680 +/- 50 BP
RCC33	A2	K4	adze	10 x 19 x 25	crypto crystalline silicate	2240 +/- 60 BP
RCC34	Ph	N4	adze	9 x 29 x 18	crypto crystalline silicate	No direct dates from layer; range - 8614 +/- 38 - 7630 +/- 80 BP
RCC35	Ja	P4	broken blade	3 x 16 x 7	crypto crystalline silicate	8160 +/- 70 BP
RCC36	A	Q6	scraper	3 x 24 x 12	crypto crystalline silicate	680 +/- 50 BP

Methods

Optical Light Microscopy (OLM)

Microscopy was conducted utilising a low-powered stereomicroscope with a trinocular head, with an objective magnification of 1.4 - 3X, and an eyepiece magnification of 10X. Images were acquired with a Canon Rebel XSi DSLR camera attached to an Amscope camera adaptor for a live feed, with the additional magnification of 2X for the camera mount lenses.

Fourier Transform Infrared Spectroscopy (FTIR)

The measurements were acquired on an Agilent Cary 640 spectrometer with a GladiATR Single Reflection diamond ATR accessory. Analyses were performed in absorbance mode, with spectra collected from 4000-400 cm^{-1} with 64 acquisition scans and a resolution of 4 cm^{-1} . Figures are displayed in percent transmittance.

Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS)

A few micrograms of sample were analysed using a Joel JSM-6610LV Scanning Electron Microscope with an Oxford Instrument EDS detector. Images were acquired between 3-5kV, with a spot intensity of 53, in secondary detector mode (SED). Elemental composition analyses were conducted at 20kV with a spot intensity of 53 using the backscatter electron detector (BSE).

Results

Microscopy

All exported specimens underwent OLM microscopy using low-powered objectives. Visually, the main residues identified were classified into seven discrete categories (Veall, in prep.). **Table 2** highlights the residue features noted from the analysis, and the prevalence counts of each residue type.

Table 2. Qualitative features of eight residue types.

Residue Type	No. of Tools residue was identified	Qualitative Description
1B	11	Residues are dark brown in colour, with an overall granular texture, low relief and matte surface. Fragments crumble into smaller particles.
1C	14	Morphologically, they are described as amorphous, low relief smears, ranging between light brown and black in colour. The appearance of solid material from this category is rare. In some instances, this residue type may overlay other residues.
2	5	White/beige residues, have an amorphous shape that can appear as a low relief smear and the edges. May be found on its own, or overlaying/ underlying other residues.
3A	7	Red/orange coloured residues that have a discrete particulate structure. Tends to appear indiscriminately in clusters on a tool surface.
3B	3	Red/orange coloured residues that are amorphous in appearance. Surfaces may appear either shiny, with fragments having rigid edges, or a more granular appearance. This residue type does not show indiscriminate distribution patterns.
4	20	White/beige particulate residues, fragments reflect under normal light, and have a sparkling quality. Agglomerate particulate sizes, from relatively large quartz grains to fine crystals all embedded in a concrete like matrix, particularly notable when compared to the Type 2 residues. Fibrous inclusions were noted in some cases.
5	1	Residue colours range from light brown to black with a rough surface. Appears as a mixture of rough inorganic particulates. These may be agglomerated with a smooth, shiny matrix.
6	1	Yellow, low relief, smooth surface, waxy appearance. Colour change to white at edges.

Residues distributions varied across the analysed pieces. Five tools (13.89%) yielded residues that indiscriminately covered the tool surface. Contrastingly eight specimens (22.22%) did not yield sufficient amounts to discern the extent and nature of the residue distribution. One sample yielded no discernible residues. The most commonly identified residue type, Type 4, was found on 20 (55.55%) specimens. Most frequently, it was observed to cover the whole tool surface; it either overlaid other residue types or was overlaid by Type 1C residues (found on 14 [38.89%]).

Selected Samples

Of the analysed specimens, fifteen yielded residue trace that matched the criteria adapted from Charrié-Duhaut et al. (2013) as being suitable for further analysis of hafting adhesive presence. The criteria highlighted included: residues showed clear outlines that are delimited on the piece; covered the surface of the tool opposite to the sharpened or utilised edge (in the case of a complete tool); and, as best as possible, residual trace was observed on both sides of the tool. Of these however, only eight were deemed suitable for subsequent analysis. **Table 3** highlights these specimens in further detail.

Table 3. Residue distributions for the eight specimens that underwent additional analysis.

Lab No.	Extent of Major Residue Types
RCC02	Type 1B and Type 4 present. Residues found along the edge of tool with Type 4 predominating, absent in medial portion.
RCC08	Type 1C with Type 4 overlay running from proximal end to distal surface on dorsal surface with high relief at proximal end and left distal edge. On the ventral surface, the same is noted along the right proximal edge and surface and along the right medial and distal edge. Stops where pitting is present in the raw material.
RCC10	Type 2 present. Main distribution covering the dorsal and ventral surfaces. Extending on dorsal surface from proximal to the distal end. On the ventral surface, a Type 5 residue overlays Type 2.
RCC12	Type 2 runs parallel with the two working edges, with a greater prominence on the right side of the dorsal surface. Type 4 found across the surface of the whole tool.
RCC22	Type 1C smears noted on dorsal left broken surface, and on ventral right surface with Type 4 overlay (found in broken areas and micro-cracks)
RCC26	Type 4 present. Residue noted along proximal left side up to medial surface, high relief at proximal end on ventral surface. Dorsal has lacquer and label.
RCC34	Type 4 present on the ventral right side inside hinge fracture.
RCC35	Type 3 residues present (staining or higher relief) on both surfaces, with residue trace extending up to broken edge on left side.

FTIR Spectroscopy

IR spectra were acquired from eight Rose Cottage Cave specimens, and interpreted as containing mixtures of inorganic clay minerals, with quartz being the most common mineral type regardless of the residue type identified by microscopy. Three samples were found to have weak signals indicative of organics. **Table 4** highlights the spectral findings and the wavelength assignments, while spectral interpretations are described in the subsections below, by sample residue type.

Type 1B & 1C with Type 4 Residues

Three samples, RCC002 (1B), RCC008, and RCC022 (both 1C and 4 overlying) were analysed. The main constituent of all three of these samples were identified as quartz, based on

the 796 and 778 cm^{-1} doublet being the most identifiable feature when compared to reference spectra. Additional peaks associated with inorganics were identified in RCC008 and RCC022, however, the nature of the mineral type could not be ascertained. No organic signal was identified in analysed material. **Figure 1** highlights two of these spectra.

These findings are consistent with the microscopic data, which highlight the presence of inorganic particulates and account for the largely inorganic composition of the samples. Type 1B residues are described as having visible minerals homogeneously distributed within the residue. The prevalence of particulates in the Type 4 residues, which overlaid the relatively amorphous 1C trace, would also account for the prevalence of inorganics, particularly quartz crystals, in the IR spectra.

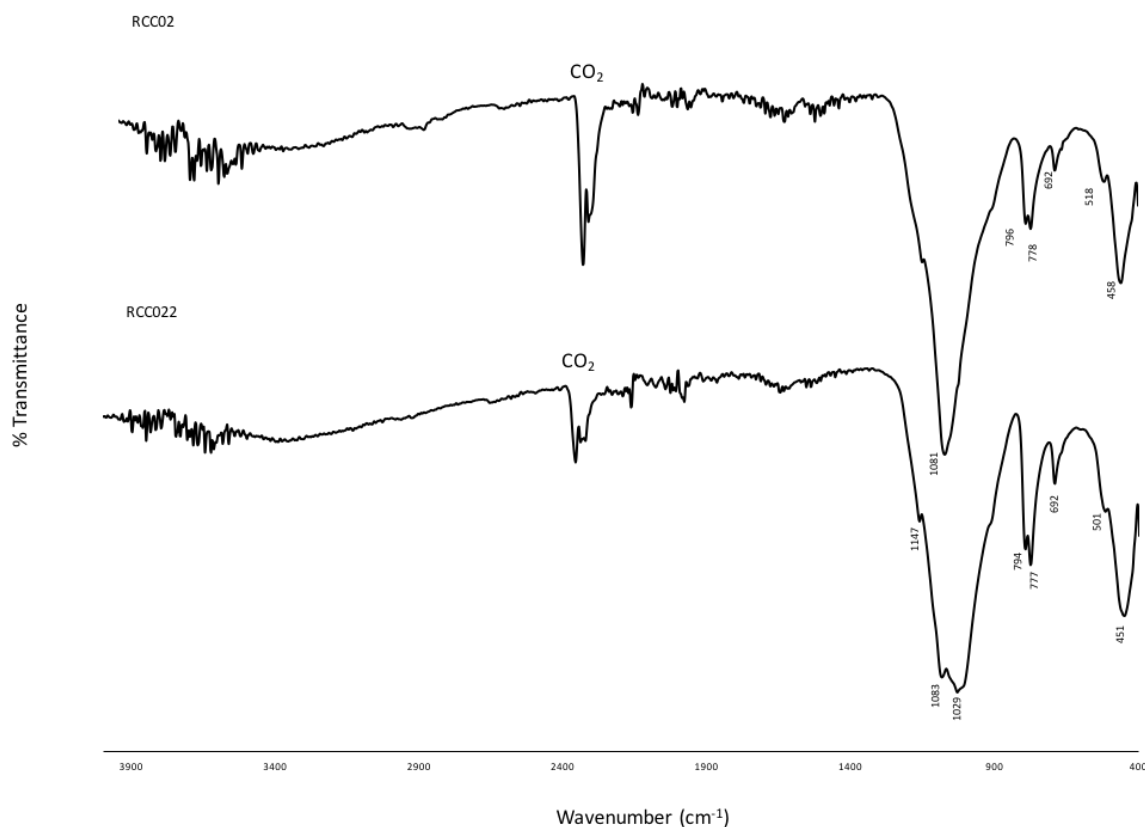


Figure 1. FTIR spectra of RCC002, a Type 1B residue and RCC022, a Type 1C residue with overlaying Type 4.

Table 4. Results and the associated peak assignments for the analysis residue specimens.

Assignment*	Wavenumber (cm ⁻¹)							
	RCC002	RCC008	RCC010	RCC012	RCC022	RCC026	RCC034	RCC035
v(O-H) inorganic (likely Al- OH)	X	X	X	3646/3624	X	X	X	X
v (-OH) organics	X	X	X	X	X	Max at 3341	X	X
v(C-H) aliphatic groups	X	X	2919	2921/2851	X	X	X	X
v(C=C-C) aromatic ring	X	X	X	X	X	1584	X	X
Aliphatic (C-H) deformation	X	X	X	X	X	1455	X	X
Phenolic –OH, or carbonates	X	X	X	X	X	1413*	X	X
v(S-O)	X	X	X	X	1147	X	1149	1149
v(C-O) or v(Si-O)	1079	1081/1057	X	1162/1085	1085	1162/1083	1083	1085
Si-O-Si, Si-O-Al vibrations, kaolin minerals	X	915	1031/1006 (shoulder)/ 912	1004/912	1031/917	1029	X	998/913
Carbonates	X	X	X	X	X	873 (shoulder)		
v(Si-O) silicates	796/778, 694	796/778, 694	794/778, 692	796/778	796/777/ 692	796/777/694	X	796/777 /692
Iron oxides	X	X	X	X	X	649/563	649/563	X
Possible interstratified or feldspar minerals	X	X	669/532/45 1/422	669/528/45 5	X	456	X	X
Si-O or Si-O-Al, silicates or kaolins/ iron oxides	518/458	522/464	X	X	X	522/458	522/456	526/441
Inorganic mineral, unknown	X	X	X	X	501/451	X	X	X

*Assignments based on published literature: van der Marel and Beutelspacher, 1976; Russell and Fraser, 1994; Coates, 2006; Helwig et al., 2008; Vahur et al., 2011, 2016. Peaks at ~2370cm⁻¹ are attributed to atmospheric carbon dioxide and are not included in the interpretations or listed data.

Type 2 Residues

Spectra from two type 2 samples, RCC010 and RCC012, were acquired. Both samples show evidence of inorganic material being present, as well as the addition of a trace organic component. RCC010 was identified as a mixture of inorganic minerals, composed of silicates, based on the presence of a doublet at 796 and 778 cm⁻¹ being the most identifiable feature when compared to reference spectra. Two additional minerals types are proposed as also being present in this sample. Kaolin minerals were identified based on the presence of peaks at 1031 cm⁻¹ (and a shoulder at 1006cm⁻¹), 649 and 532 cm⁻¹. Peaks in the –OH stretching region (associated with Al-O-H bonds) at 3646 cm⁻¹ and 3624 cm⁻¹, were identified as also belonging to kaolins. Additional peaks, that may be associated with feldspars or interstratified minerals are

also present, however, the spectrum is lacking the complexity associated with IR references for minerals of this type (Russell and Fraser, 1994, fig 2.13-15). A peak at 2919 cm^{-1} may be indicative of the presence of organics.

Similarly, RCC012 also contains evidence of silicates, notably quartz. Kaolin minerals are proposed based on the presence of strong peaks at 1004 and 912 cm^{-1} (Vahur et al. 2016), while interstratified minerals, such as aliettite, may be present based on peaks at 669 , 528 , 455 cm^{-1} (Russell and Fraser, 1994). Due to the absence of more diagnostic peaks between 3700 - 3600 cm^{-1} and 850 - 600 cm^{-1} , neither mineral type can be confirmed. Two weak peaks were also identified in this sample, 2921 and 2851 cm^{-1} , and may be attributed to the $-\text{CH}_2$ of saturated aliphatic groups (Coates, 2006).

The proposed co-appearance of kaolin minerals, having a small particle size, alongside silicates would support the qualitative characteristics observed in Type 2 residues by microscopy, and explain the relatively low-relief appearance of these residues.

Type 3B Residues

RCC035 was the only specimen identified as having a Type 3B residue among the sampled set. The presence of inorganic minerals, notably silicates with the possible addition of iron oxides and kaolins, were identified in the IR spectrum. Peaks at 1085 , 796 , 777 , 692 , and 458 cm^{-1} were attributed to the quartz (van der Marel and Beutelspacher, 1976; Vahur et al., 2011), while peaks at 649 , 526 , and 458 cm^{-1} , may be associated with iron oxides (Russell and Fraser, 1994). The broadness of the peaks between 600 - 400 cm^{-1} makes the confirmation of a mineral type difficult, and may be the result of band overlap from admixture. There are similarities in wavelength band locations in the IR spectra of iron oxides, kaolins, and silicates that are the result of Si-O and Fe-O bending, which occur in two separate, yet similar regions from between 600 - 400 cm^{-1} and inconsistencies between spectra (van der Marel and Beutelspacher, 1976; Fraser and Russell, 1994). Kaolin minerals are postulated, though not confirmed, as a source based on the presence of peaks at 998 and 913 cm^{-1} attributed to Si-O-Al and Al-OH bonding, respectively (van der Marel and Beutelspacher, and 1976).

The possible presence of iron oxides in the sampled residues would likely account for the red colour that is a hallmark feature of the 3B residue type, however, confirmatory peaks associated with iron oxides are notably absent, likely due to admixture from other mineral types. Evidence of organic admixture was absent in RCC035.

Type 4

Samples were obtained from two Type 4 residues, RCC026 and RCC034. Both were identified as being composed of inorganics, with RCC026 also having organic admixture. Quartz was identified in both samples, based on peaks at 1083 , 796 , 777 , 694 , and $456/458\text{ cm}^{-1}$. Strong, broad peaks were also identified at 1035 and 1029 cm^{-1} and may be attributed to Si-O and Si-O-Si bonding. The peaks at 649 and 563 are likely associated with another mineral class

(van der Marel and Beutelspacher 1976). RCC026 also yielded a weak peak 1413 cm^{-1} and a shoulder at 873 cm^{-1} , which may be indicative of the presence of carbonates such as calcite (Vahur et al., 2016), however additional confirmatory peaks are absent.

RCC026 yielded a weak, broad peak with a maximum at 3341 cm^{-1} which may be associated with the --OH stretch found in organic materials, alongside evidence of organic functional groups between 1600cm^{-1} and 1400cm^{-1} with weak peaks at 1584cm^{-1} (C=C-C aromatic ring stretching), and aliphatic C-H deformation at 1455cm^{-1} . The --OH groups may be indicative of the phenolic compounds (Devi  , 2009), although there are insufficient details in the IR spectra of RCC026 to ascribe the aforementioned to a particular organic source.

Scanning Electron Microscopy

Table 5 highlights the elemental composition of seven of the eight highlighted in the FTIR section above. Further details of each analysed sample is discussion by residue type category below.

Table 5. Elemental composition of a selection of RCC samples.

Sample No.	Elemental Composition ^{1,2} (Atomic %)		
	Major	Minor	Trace
RCC002	O (64.87) Si (28.25)	Al (3.74) Fe (1.26)	K (0.91) Ca (0.31) Mg (0.26) Na (0.22) Ti (0.19)
RCC008	O (64.26) Si (25.71)	Al (6.7) Fe (1.23) K (1.1)	Ca (0.51) Mg (0.48)
RCC010	O (63.95) Si (25.03)	Al (5.80) K (1.85) Fe (1.44)	Ca (0.81) P (0.60) Mg (0.53)
RCC012	O (66.42) C (15.07) Si (17.35)	Al (1.01)	K (0.15)
RCC026	O (64.44) C (19.02)	Ca (7.57) P (3.77) Si (3.53) Al (1.35)	Mg (0.32)
RCC034	O (65.50) C (25.75)	Ca (3.96) P (2.59) Si (1.15)	Al (0.61) Mg (0.28) K (0.16)
RCC035	O (63.09) C (18.26)	Fe (8.61) Si (6.43) Al (2.49)	K (0.48) P (0.24) Mg (0.16) Ti (0.13) Ca (0.12)

¹ Qualitative analyses, and the terms major, minor, and trace components are subjective. Major is defined at more than 10 atomic%; minor as 1-10 atomic%; and, trace at less than 1 atomic%. These terms are defined in Goldstein et al. (2003)

² Element names: O (oxygen), Si (silicon), C (carbon), Al (aluminium), Fe (iron), K (potassium), Ca (calcium), Mg (magnesium), Ti (titanium), P (phosphorus).

Type 1B & 1C with Type 4 Residues

RCC002 (Type 1B) and RCC008 (Type 1C and Type 4 overlying) were found to be composed of predominantly oxygen and silicon as major components. The minor and trace constituents were similar between the two samples, although the addition of trace titanium and sodium was recorded in RCC002 and potassium was a minor component in RCC008 rather than appearing in trace amounts.

The major constituents are consistent with the silicate signal identified by FTIR. The appearance of aluminum and iron as minor components indicate an additional signal of inorganic minerals. This is similarly the case for the presence of calcium, magnesium, and titanium. Potassium was interpreted as either a possible marker for the degradation of organic material, either from the residue itself or the depositional environment (Price and Burton, 2011) or sourced from a mineral type that was not present in the IR spectra. The absence of manganese in the Type 1B and Type 1C samples is suggestive, and counters the findings discussed in Williamson (1996), as a potential source of this black coloured residue.

Type 2 Residues

The presence of oxygen and silicon as major elemental components is consistent with the presence of silicates in the IR spectra of both specimens. Furthermore, of the Type 2 specimens, the presence of carbon in RCC012, may be considered consistent with the presence of organic components identified by FTIR, while carbon was not identified in any significant amounts in RCC010. The discontinuity between the weak organic signal identified in the IR results and the elemental composition may be indicative of the relative heterogeneity of the analysed residues from this residue type.

The presence of potassium and phosphorus in RCC010 and potassium in RCC012, were interpreted as markers for the degradation of organics, either related to the samples themselves or the depositional environment (Price and Burton, 2011). Similar to the Type 1B and Type 1C with Type 4 residues, however, the potassium may also be derived from inorganic minerals. The presence of aluminium, iron, calcium and magnesium, alongside potassium, may be sourced from types of interstratified minerals, and supports the presence of related peaks in the IR spectra of these samples.

Type 3B Residues

Carbon and oxygen were identified as the main constituents in RCC035, followed by iron, silicon and aluminium as minor components. The presence of iron supports the IR peaks that were possibly indicative of iron oxides, and supports the overall red colour of the residue observed by OLM.

Additionally, silicon and aluminium as minor components are consistent IR peaks ascribed to kaolin clay minerals and silicates. Trace potassium and phosphorus were also

present and, as in previous residue types, may be linked to the degradation of organics associated with either human activity or the depositional environment. This is a tentative hypothesis, however, as while carbon is present as a major component, it is lower than expected organics analysed under the same conditions where samples adhesives yielded elemental carbon composition between 29-80% depending on the degree of inorganic mineral contribution (Veall, in prep). This would be consistent with the FTIR results.

Type 4 Residues

Like other residue types, RCC026 and RCC034 also yielded carbon and oxygen as major components. The prevalence of carbon, albeit relatively low abundance, may support the presence of organic functional groups in the IR spectrum. The prevalence of phosphorus in both samples may also suggest the presence of markers associated with organic materials, although whether these are associated with the residue or the depositional environment it is not known (Price and Burton, 2011).

The abundance of silicon as minor components in both RCC026 and RCC034 are consistent with silicates, while calcium identified in RCC026 may also support the presence of calcium carbonates identified by FTIR.

Summary and Concluding Statement

A low-powered analysis by OLM identified eight residue types on the analysed tools, with Type 1B (22.58%), Type 1C (8.06%), and Type 4 (32.26%) residues appearing most frequently. Fourteen of the samples (38.89%) yielded either no trace, insufficient trace to determine residue extent, or the trace indiscriminately covered the tool surface. Pen, varnish and correction fluid, or a combination thereof, was detected on 20 of the 36 (55.56%) pieces analysed. Based on this prominence and the lack of sufficient amounts of trace that could be isolated to acquire samples, it was determined that much of the exported material was unsuitable for further analysis.

Eight of the thirty-six samples analysed by OLM matched some of the modified criteria highlighted by Charrié-Duhaut et al. (2013) in the selection of samples to characterise residues that are likely the result of the application of a hafting adhesive (see: Veall, in prep.). Of the material from Rose Cottage Cave, the main constituents identified from the IR and SEM analysis were predominantly inorganic in origin, with silicates and kaolin minerals the most common types found. Evidence of some organics in the Type 2 and Type 4 materials was identifiable by infrared spectroscopy, however, there were insufficient numbers of peaks to discern the nature of the source. The SEM/EDS elemental composition data supports the presence of inorganic minerals, with the presence of organics being largely a secondary component.

It was highlighted that the abundance of carbon in the analysed materials was comparatively less than analysed adhesives from other southern African LSA contexts (between

29-80% [Veall, in prep]). As such, analysis by chromatographic techniques would be unsuitable at this time. There is presently no evidence to suggest that the presence of organic materials is consistent with known hafting adhesive datasets acquired from other southern African LSA sites associated with this study.

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