Journal of Human Evolution 194 (2024) 103578

Contents lists available at ScienceDirect

Journal of Human Evolution

journal homepage: www.elsevier.com/locate/jhevol

Adhesive technology based on biomass tar documents engineering capabilities in the African Middle Stone Age

Patrick Schmidt [a, b, *], Armelle Charrié-Duhaut [c], Edmund February [d], Lyn Wadley [e]

[a] Department of Early Prehistory and Quaternary Ecology, Eberhard Karls University of Tübingen, Germany
[b] Department of Archaeology, University of Cape Town, Rondebosch, 7701, South Africa
[c] Laboratory of Mass Spectrometry of Interactions and Systems (LSMIS), Strasbourg University, CNRS, CMC UMR 7140, France
[d] Department of Biological Sciences, University of Cape Town, Rondebosch, 7701, South Africa
[e] Evolutionary Studies Institute, University of the Witwatersrand, PO WITS, 2050, Johannesburg, South Africa

ARTICLE INFO

Article history:
Received 11 March 2024
Accepted 26 July 2024
Available online xxx

Handling Editor: Dr A Taylor

Keywords:
Early *Homo sapiens*
Transformative technology
Organic residues
Stone Age engineering
Complex behaviors

ABSTRACT

The foragers of the southern African Middle Stone Age were among the first humans to adapt their environment and its resources to their needs. They heat-treated stone to alter its mechanical properties, transformed yellow colorants into red pigments and produced moldable adhesive substances from plants. Until now, only *Podocarpus* conifers have been identified as the botanical origin of Middle Stone Age adhesives. This is curious as these conifers do not produce sticky exudations that could be recognized as potential adhesives. To obtain an adhesive, tar must be made with a technical process based on fire. However, the nature of these technical processes has remained unknown, hampering our understanding of the meaning of this adhesive technology for the cultural evolution of early *Homo sapiens*. Here, we present the first evidence of a technique used for tar making in the Middle Stone Age. We created an experimental reference collection containing naturally available adhesives along manufactured tars from plants available in the Middle Stone Age and compared these to artifacts using gas chromatography–mass spectrometry and infrared spectroscopy. We found that, in the Howiesons Poort at Sibhudu Cave, tar was made by condensation, an efficient above-ground process. Even more surprisingly, the condensation method was not restricted to *Podocarpus*. The inhabitants of Sibhudu also produced tar from the leaves of other plants. These tars were then used, either without further transformation or were processed into ochre-based compound adhesives, suggesting that people needed different moldable substances with distinct mechanical properties. This has important implications for our understanding of Middle Stone Age *H. sapiens*, portraying them as skilled engineers who used and transformed their resources in a knowledgeable way.

1. Introduction

Making substances that are not available in nature was a major achievement for humankind. The moment at which such materials appeared and the processes surrounding their invention have implications for our understanding of cognitive evolution. This is so because they must be produced, whereas most other substances can be collected. The procedures involved in producing materials may have required analogical reasoning (Wadley, 2023), forward planning (Kozowyk et al., 2017), technical skill, and cultural transmission (Schmidt, 2021). One example of manufactured materials is compound adhesives or adhesive substances requiring processing to make them usable. Such substances were used as moldable materials, prehistory's first plastic, to form grips and handles in the European Middle Paleolithic (Mazza et al., 2006; Niekus et al., 2019) and to haft stone tools to rigid shafts in the African Middle Stone Age (MSA; Lombard, 2005; Villa et al., 2009; Rots et al., 2011; Prinsloo et al., 2023).

In Africa, several authors have proposed hafting in the MSA based on the morphology of stone tools (e.g., Wilkins et al., 2012) or use-traces left by hafts (e.g., Rots et al., 2011), but analyses of the adhesives themselves are still extremely sparse. For the South African MSA, there are only three studies investigating the botanical origin of adhesives (Charrié-Duhaut et al., 2013; Villa et al., 2012, 2015). All three proposed that MSA adhesives are made from

---

[*] Corresponding author.
E-mail address: patrick.schmidt@uni-tuebingen.de (P. Schmidt).

https://doi.org/10.1016/j.jhevol.2024.103578

conifers, such as the evergreen *Podocarpus*. This is interesting as it has recently been found that South African *Podocarpus* does not produce visible exudations, such as resin, which could have been identified by foragers as potential adhesives (Schmidt et al., 2022). Rather, *Podocarpus* adhesives must be made by pyrolysis, most likely from leaves, and are therefore best called tars. The cognitive implications of MSA foragers making such tars from plants are therefore the same as those of European Neanderthals making birch tar (see, for example, the discussions in: Kozowyk, 2023; Schmidt et al., 2023b): they document creativity and the ability to innovate. This raises the question of how exactly tars were produced in the South African MSA and what the production method entails in terms of cognition, technical skill, and culture. Unfortunately, the available studies, all based on finding biomarkers specific to *Podocarpus*, were not successful in addressing this question. In this study, we aim to reconstruct the ancient production methods using an approach based on experimentation and the chemical analysis of residues on artifacts. For this, we analyze artifacts from the Howiesons Poort technocomplex of Sibhudu Cave on South Africa's eastern seaboard.

The Howiesons Poort technocomplex is widespread in South Africa and also occurs in southern Namibia (Wadley, 2015). When radiocarbon dates are excluded, most Howiesons Poort age estimates are quite tightly constrained between 65 and 60 ka ago (Jacobs et al., 2008a, 2008b), and sites crosscut a wide range of environments from arid semideserts to forests (Jacobs and Roberts, 2008). At Sibhudu, the rock shelter under discussion here, Howiesons Poort fauna predominantly comprises species that prefer closed environments, especially forests (Clark and Plug, 2008; Clark, 2011, 2013; Robinson and Wadley, 2018). Charcoal analysis at the site complements these data because *Podocarpus* (some species were formerly called *Afrocarpus*) was recognized as an important component of the wood brought into the rock shelter between ~65 and ~62 ka (Allott, 2006). This identification is particularly relevant for the study at hand because Villa et al. (2015) detected coniferous residue on two Sibhudu lithics from the Howiesons Poort and the adhesives on Diepkloof (Western Cape) lithics were made from *Podocarpus* (Charrié-Duhaut et al., 2013). The earliest Sibhudu adhesive use is not, however, in the Howiesons Poort but in the earlier ~71 ka Still Bay assemblage, where bifacial points were hafted with ochre-loaded, compound adhesives (Wojcieszak and Wadley, 2018). The organic components of the Still Bay adhesives have not yet been identified.

Howiesons Poort lithic assemblages are characterized by small blades and backed artifacts that include segments and other geometric forms. Short quartz segments may have been hafted transversely as arrow tips (Wadley and Mohapi, 2008; Lombard, 2011). Micronotches served as barbs demonstrating that projectile weaponry was composite (de la Peña et al., 2018). Quartz bifacial points are also part of the late Howiesons Poort at Sibhudu (de La Peña et al., 2013). Larger backed tools on hornfels, dolerite, and quartzite seem to have been designed for cutting (Soriano et al., 2015), and they, too, have traces of adhesives. Many Sibhudu lithic tools are likely to have been hafted, and they would have required adhesive for their attachment to shafts or handles. We suspect that different tools and weapons may have needed particular adhesive recipes and hafts, depending on whether robust or brittle mounts were required. Howiesons Poort hafting procedures were likely to have been innovative since innovation is evident in other technological contexts. Soriano et al. (2007) demonstrate, for example, that at Rose Cottage Cave, knappers used both hardstone and soft-stone hammers at different stages of knapping, resulting in distinct scarring on blade platforms. Clarkson (2010), using data from five sites, illustrates regional traditions of core reduction notwithstanding that similar backed tools were the endproducts. Regional differences in both lithic and nonlithic artifacts (Will and Conard, 2020) support an interpretation of technological individuality in the Howiesons Poort. Sibhudu, for example, has a large and varied bone tool assemblage (d'Errico et al., 2012a,b), whereas Diepkloof has a remarkable collection of decorated ostrich eggshell (Texier et al., 2010). Another innovation appears to be the production of several types of adhesives used for the mounting of the artifacts found in the Howiesons Poort. The site has yielded the largest corpus, so far, of adhesive materials in the African MSA, including compound adhesives that involved the mixing of organic substances with ochre (Wadley, 2005; Wadley et al., 2009). Such compound adhesives have been interpreted to contain information about cognitive evolution, e.g., they imply analogical reasoning (Hodgskiss, 2014; Wadley, 2010, 2023), and the willingness to invest relatively high provisioning and production costs (Schmidt, 2021). We therefore include single-component and compound adhesives from Sibhudu in our study to obtain a broader understanding of the MSA adhesive technology in the Howiesons Poort. Our study aims to identify materials and procedures for making adhesives in the MSA at Sibhudu.

2. Materials and methods

2.1. Samples

To investigate adhesive making at Sibhudu, we selected six stone tools made of quartzite and hornfels from layers GR, GR2, PGS, and PGS3 at the Sibhudu cave (Table 1). The PGS layer is dated by optically stimulated luminescence to 64.7 ± 1.9 ka, and GR2 is dated to 61.7 ± 1.5 ka (Jacobs et al., 2008a); see also Supplementary Online Material (SOM) Table S1. The artifacts were found in situ during the 2004, 2007, and 2009 excavations of the Howiesons Poort sequence. Technologically, these artifacts are backed tools and segments, supporting their attribution to the Howiesons Poort. To compare these residue samples of unknown composition with known materials, we built a reference collection of sticky substances and experimentally produced adhesives from materials that are naturally available in the Sibhudu environment. All plant materials were collected with permission from the landowners where the trees were sampled. All endangered species (South Africa's Red List) were planted garden trees that do not fall under protection in the Threatened Species Programme. During sampling, we selected multiple trees when possible, separating samples by individual plants.

Because three previous studies on the South African MSA (Villa et al., 2012, 2015; Charrié-Duhaut et al., 2013) identified the organic component of the adhesive as being derived from conifers, of which some residues were clearly identified as *Podocarpus*, we produced 48 tar samples from *Podocarpus* leaves (including all four species endemic to South Africa, *Podocarpus elongatus*, *Podocarpus falcatus*, *Podocarpus henkelii*, and *Podocarpus latifolius*, although *P. elongatus* does not occur on the eastern seaboard; SOM Fig. S1).

We used two different techniques to make tar from *Podocarpus* leaves: underground distillation and above-ground condensation (Schmidt et al., 2022; Fig. 1m, n; SOM Figs. S2 and S3). The underground distillation technique we used is closely related to the raised-structure technique (Kozowyk et al., 2017; Schenck and Groom, 2018), approximating an aceramic version of the double-pot technique (e.g., Kurzweil and Todtenhaupt, 1991). It aims at creating an underground oven-like heating environment where oxygen is limited. Tar drips down from an upper chamber containing the leaves, into a receptacle positioned in a separate lower chamber from where it can be collected after the fire burned out and the structure cooled down.

Table 1
Sample numbers, raw materials, and analyses performed on archaeological samples and results of experimental tar making. Sample masses are masses of powder scraped from the surface of artifacts. Averages for condensation method tars reported here are only those of 5-min-long runs.

Sibhudu accession number	Find layer	Raw material	Visibly compound?	Sample mass (mg)	IR/Raman	GC–MS	CT scan
CM-010	PGS	Hornfels	No	0.2	Yes		
MLG-001	GR2	Quartzite	Yes (red)	0.6	Yes		Yes
MLG-014	GR	Quartzite	No	0.4	Yes		
MLG-018	PGS	Quartzite	Yes (red)	0.6	Yes		
MLG-019	PGS	Hornfels	No	0.3	Yes	Yes	
MLG-022	PGS3	Quartzite	Yes (red)	0.3	Yes	Yes	Yes

Tar reference collection

Technique	Plant	Leaves (g)	Tar yield (g)	Tar/100 g leaves (g)	T_{max} recorded (°C)	Burning time (min)	Tar/h (g)
CM	*Podocarpus elongatus*	123	0.30	0.24	–	5	3.64
CM	*Podocarpus falcatus*	219	0.27	0.12	–	5	3.19
CM	*Podocarpus henkelii*	129	0.29	0.23	–	5	3.50
CM	*Podocarpus latifolius*	154	0.32	0.21	–	5	3.89
CM	*Dodonaea viscosa*	115	0.16	0.13	–	5	1.89
CM	*Pterocelastrus tricuspidatus*	159	0.11	0.07	–	5	1.35
CM	*Sideroxylon inerme*	71	0.09	0.11	–	5	1.02
CM	*Euclea tomentosa*	178	0.22	0.12	–	5	2.61
UD	*Podocarpus elongatus*	97	0.07	0.07	483	105	0.03
UD	*Podocarpus falcatus*	48	0.27	0.54	521	106	0.15
UD	*Podocarpus henkelii*	47	0.10	0.22	443	95	0.07
UD	*Podocarpus latifolius*	50	0.28	0.56	462	87	0.19

Abbreviations: IR = infrared spectroscopy, GC–MS = gas chromatography–mass spectrometry, CM = condensation method, UD = underground distillation, CT = computed tomography.

The condensation method (also see Schmidt et al., 2019) is an open-air technique that involves burning plant material near slightly tilted flat stone surfaces from where the tar that condensed onto the surfaces can be scraped off using a stone tool. Because some studies that had proposed a coniferous tree as the botanical origin of Sibhudu tars (Villa et al., 2015) could not confirm a *Podocarpus* identification (i.e., the biomarkers obtained were ambiguous), we also attempted to make tar from four other plant genera. These are *Pterocelastrus tricuspidatus* (Celastraceae family; SOM Fig. S4), a tree (up to 20 m tall) endemic to South Africa's eastern seaboard, *Sideroxylon inerme* (Sapotaceae family; SOM Fig. S5), a tree (10–15 m tall) from the same environment, and *Dodonaea viscosa* (Sapindaceae family; SOM Fig. S6), a shrub (up to 5 m tall) that can be found over large parts of South Africa, including around Sibhudu. To verify whether tar can be made from the leaves of almost any plant, we randomly chose a fourth genus from farther away from Sibhudu, *Euclea tomentosa* (Ebenaceae family; SOM Fig. S7), a shrub (1–2 m tall) endemic to South Africa's arid western seaboard. We made tar from the leaves of these four plants by condensation, following the same protocol as for *Podocarpus* leaves (Schmidt et al., 2022). To complete our adhesive reference collection, we sampled exudations that can potentially be used as adhesives from three plant genera (comprising nine species) that occur in the east coast environment near Sibhudu. We collected latex from five *Euphorbia* species (*Euphorbia mauritanica*, *Euphorbia ingens*, *Euphorbia cooperi*, *Euphorbia tetragona*, and *Euphorbia tirucalli*; SOM Fig. S8) because there are several ethnographic and archaeological records showing that *Euphorbia* latex was, and still is, used as an adhesive and sometimes as a poison (d'Errico et al., 2012a,b; Wadley et al., 2015). *Euphorbia mauritanica* is a bushy shrub yielding relatively little latex when injured. The other four *Euphorbia* species are tall, several-meter-high trees that yield abundant latex when their epidermis is pieced. There are ethnographic accounts from Ethiopia (Sahle, 2019) documenting that the latex of *Euphorbia abyssinica*, a species closely related to *E. ingens*, is cooked to obtain tar. We therefore cooked latex of *E. ingens* and *E. tirucalli* to obtain tar (under fully aerated conditions in an open crucible over a gas flame). Samples were regularly collected at various intervals during tar cooking, and the process was stopped when the tar overheated, losing its adhesive properties (the number of samples and cooking times are listed in SOM Tables S2 and S3). We also collected latex from three species of *Ficus*, Moraceae family (*Ficus bubu*, *Ficus burkei*, *Ficus sur*; SOM Fig. S9), because wood of *F. burkei* was found in the charcoal record at Sibhudu (Zwane and Bamford, 2021). We attempted to cook tar from *Ficus* latex but were unsuccessful (the latex quickly turned into a thick mass with a dry and tough appearance).

Additionally, we collected resin from *Widdringtonia nodiflora*, Cupressaceae family, a common shrub to small tree found throughout South Africa (SOM Fig. S10). We cooked *Widdringtonia* resin using the same protocol until it lost its adhesive properties (after 37 minutes), removing subsamples regularly (SOM Fig. S11). Our collection and tar production resulted in 97 reference samples, 90 of which were compared with the six Sibhudu adhesive residues chemically (SOM Table S3).

2.2. Analytics and data treatment

To analyze and compare archaeological and reference samples, we recorded infrared (IR) spectra from KBr pellets by direct transmission using a Bruker VERTEX 80v spectrometer, with spectral acquisition between 1800 cm^{-1} and 400 cm^{-1} and a resolution of 2 cm^{-1}. Transmission measurements were recorded in a vacuum chamber (at <4 hPa). Exact sample masses in each ~0.3-g pellet are summarized in Table 1. Principal component analysis (PCA) using a covariance matrix was performed on first derivative data of the spectral range between 1800 and 405 cm^{-1} (yielding 1447 variables, see SOM Table S4), following the methodology in Schmidt et al. (2023a). All spectra were first normalized to the highest and lowest points of the fingerprint region to reduce remaining differences due to variations in the slightly varying sample masses. Then, the first derivative was calculated over five spectral points to obtain data representing positive and negative slopes on the spectra that are only minimally influenced by band height.

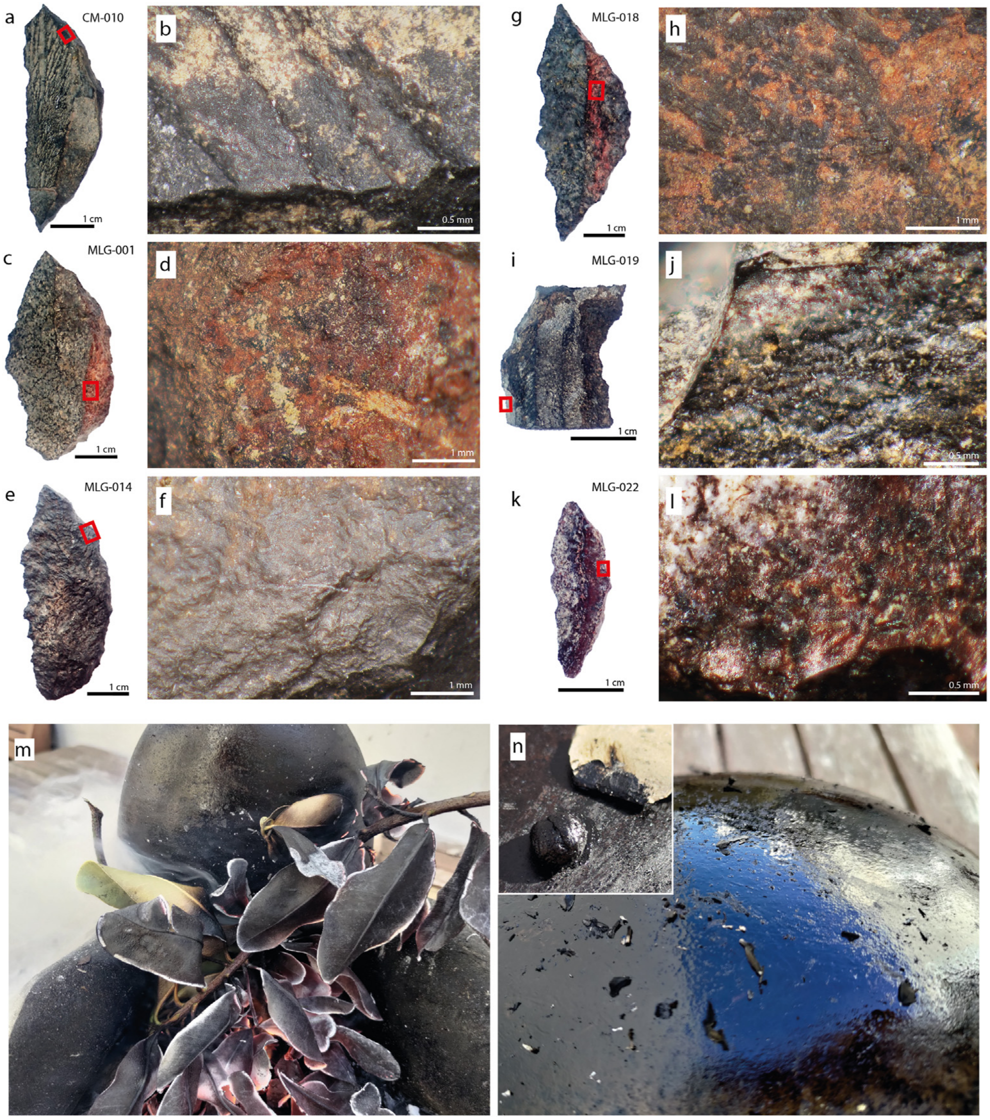

Fig. 1. Photos and details of Sibhudu adhesives. Red frames on the overview pictures (a, c, e, g, i, k) show the location where the detailed photos (b, d, f, h, j, l) were taken (a and b are pictures of the same artifact; c and d, etc.). Sample numbers are written between overview and detailed photos. m) Set-up of the condensation method using leaves of *Sideroxylon inerme*. Leaves are burned near the inclined stone surface. n) The surface of a cobble covered by biomass tar made with the condensation method. Tar condensed onto the stone surface from where it can be scraped off. Inset shows tar scraped off with a stone tool. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

We also conducted Raman spectroscopy on the six artifacts, using a dispersive Renishaw InVia Reflex Raman spectrometer. Backed tools and segments were directly placed under a 20× magnification microscope objective of the spectrometer. The excitation wavelength was 532 nm, spectral acquisition was between 1000 and 2000 cm^{-1}, and count times were between 5 and 15 minutes.

To interpret some of the findings made with IR spectroscopy, we conducted gas chromatography–mass spectrometry (GC–MS) analysis on two artifacts (Table 1), four experimental tar samples made by condensations of *Podocarpus* (*P. latifolius* and *P. elongatus*), *S. inerme*, and *D. viscosa*, and one tar sample made by underground distillation (*P. latifolius*). We used an Agilent 8890 chromatographer coupled with an Agilent 5977B MSD. The temperature of the source was set at 220 °C. The mass spectrometer was operating in the electron impact mode at 70 eV. Gas chromatographic separations were operated on a HP-MS column (30 m × 0.25 mm × 0.25 μm film thickness), with He constant flow of 1.5 mL/min and a temperature gradient of 40 °C for 2 minutes, then 10 °C/min until 100 °C, then 4 °C/min up to 320 °C, and a hold time for 60 minutes. Samples were processed by ultrasonic-assisted extraction (Dichloromethane/methanol 60:40), filtration through diatomaceous earth, and trimethylsilylation using N,O-Bis(trimethylsilyl) trifluoroacetamide. To obtain a stronger signal of wax esters potentially contained in *Podocarpus* and *S. inerme* tars samples, we separated nonpolar and polar phases in two samples. This separation was conducted by fractionation using thin-layer chromatography (SiO_2, dichloromethane). This allows separation of the extract into a 'nonpolar fraction' ($R_f > 0.70$), a 'ketone–alcohol fraction' ($0.70 > R_f > 0.15$), and an 'acids and polyfunctionalized compounds fraction' ($0.15 > R_f$). This fractionation by polarity classes of underivatized extract makes it possible to enrich fractions into compounds that could have been hidden during the analysis of the complete extract. Only the GC–MS profiles of the nonpolar fractions will be discussed along total ion profiles that did not undergo thin-layer separation as the nonpolar fractions contain most wax-related molecules.

To understand the association of hematite and the organic phase in the two red compound adhesives (MLG-001, MLG-022), we obtained microcomputed tomography (μCT) scans. To obtain a baseline for density calculation, artifacts were scanned together with a small fragment of a quartz single crystal. Acknowledging a roughly linear relationship between gray values in our CT scans and density (Mull, 1984; Razi et al., 2014), the overall density of the adhesive can be calculated from its brightness value compared to the brightness value of this quartz reference. We recorded CT scans using a Nikon XT H 320 CT scanner, selecting resolutions between 2 and 6 μm (XrayA = 57 mA and ErayV = 110 kV). The reconstructed volumetric data (.vol) was sliced and the ISO surface of the pieces were generated using the VGSTUDIO MAX v. 3.5.1 (Volume Graphics, Heidelberg).

3. Results

3.1. Macroscopic observations

All six tools contain visible residues of adhesives, three of which appear red (most likely ochre-based compound adhesives); the other three are black (most likely single component adhesives; Fig. 1). In five of the six tools, the residues are located at the backed part, opposite to the cutting edge of the tools. If tar were deposited on the pieces during postdepositional processes, it would more likely be distributed randomly across the pieces. Instead, tar can only be found on the portions of the pieces that were presumably attached to hafts, strongly suggesting the distribution is related to hafting. One tool (MLG-019) shows adhesive remains on both sides, suggesting a different hafting scheme than for the other five tools.

3.2. Tar making

The two techniques we experimented with for making *Podocarpus* tar (condensation and underground distillation) resulted in different tar yields, depending on the mass of leaves used, and the processing time. *Podocarpus* tar made in 5 minutes using the condensation method produced 0.27–0.32 g of tar from 123–219 g of leaves, i.e., 0.12–0.24 g of tar/100 g leaves, depending on the species. Average values of tar yield, production time, and mass of leaves are summarized in Table 1, values separated by sample are recorded in SOM Table S2. *Podocarpus* tar made by underground distillation was slightly more efficient in terms of raw materials, yielding 0.03–0.28 g of tar from ~50 g of leaves, i.e., 0.07–0.51 g of tar/100 g leaves, depending on the species. However, the condensation method was substantially more efficient in terms of time. We conducted runs of 20 and 5 minutes (durations found to be most useful in previous experiments), which resulted in ~0.75 g and ~0.3 g of tar, respectively, i.e., 3.0–3.7 g/h. Underground distillation produced 0.03–0.28 g tar per run, which lasted ~100 minutes, i.e., 0.03–0.2 g/h. This lower time efficiency adds to the approximately 15-minute-long building time for each underground distillation structure and the need to wait until the structure cools down before tar can be collected. During experimentation, we also noted different success rates of both techniques. The underground distillation procedure failed nine times for a production of 23 tar reference samples, a success rate of 60%, whereas we had a 100% success rate during the production of the 25 condensation reference samples. The condensation method performed with the other four plants (*D. viscosa*, *P. tricuspidatus*, *S. inerme*, and *E. tomentosa*) yielded on average less tar than for *Podocarpus*. Five-minute runs allowed the production of between 0.09 and 0.22 g of tar (Table 1), i.e., 1–2.6 g/h. Tar production from leaves was 0.07–0.13 g/100 g leaves. The success rate during the production of 16 tar samples from *D. viscosa*, *P. tricuspidatus*, *S. inerme*, and *E. tomentosa* by condensation was again 100%.

3.3. Chemical analyses

To compare the six Sibhudu adhesive residues with reference materials, we first conducted nondestructive Raman spectroscopy. In three of the six Sibhudu samples, there are red areas in the otherwise black residues adhering to the tools. Raman spectra of these red areas are shown in Figure 2a. All three spectra acquired on red areas show bands at 226 cm^{-1}, 298 cm^{-1}, 412 cm^{-1}, 611 cm^{-1}, and 1319 cm^{-1}, characteristic of the hematite (Fe_2O_3) Raman spectrum. One spectrum also shows quartz bands (464 cm^{-1}), most likely caused by the underlying quartzite tool. Thus, the visibly red color of the adhesives is caused by hematite in all three cases. Raman analysis of the black areas of all six adhesives results in spectra that are flat between 150 cm^{-1} and 1000 cm^{-1} but show two broad bands near 1370 cm^{-1} and 1595 cm^{-1}. These bands are attributed to carbon–carbon vibrations and are sometimes called D- (lower wavenumber) and G-bands (higher wavenumber). They reflect the proportions of sp2-hybridized carbon (G-band) and sp3-hybridized carbon (D-band) in amorphous organic samples (see, for example, Sadezky et al., 2005) and result from pyrolysis (i.e., they are absent in terpenoid molecules as those that can be expected in natural resins, latex, and their tars; they are common in soot and organic matter transformed by heat). Their presence in all six Sibhudu samples suggests that the adhesives used for hafting the backed tools and segments are tars obtained by the pyrolysis of organic substances. However, a similar signal (D- and G-bands in the Raman spectrum only) would be expected if fine charcoal inclusions contaminate the residues. Whether this is the case or whether the six Sibhudu adhesives were produced by pyrolysis is best investigated by IR spectroscopy and the comparison with reference materials.

To obtain further insight into the nature of the natural substances used to produce these tars, we conducted transmission IR spectroscopy. All six Sibhudu IR spectra and all our reference spectra show sharp ν(CH) bands near 2900 cm^{-1} documenting that they contain an organic fraction (IR spectra of all artifacts and references are shown in SOM Figs. S12–S14; selected spectra are shown in Fig. 3). In their fingerprint region, the six artifact spectra show a weak C=O band at 1738 cm^{-1}. There are (sometimes weak, but present) C=O bands at this wavenumber in all reference substances except *Euphorbia* latex and tar. There is a broad $\delta(CH_{2+3})$ absorption envelope between 1500 cm^{-1} and 1340 cm^{-1}, which resembles that found in our *D. viscosa*, *P. tricuspitatus*, *S. inerme*, and *E. tomentosa* reference spectra in shape (see also SOM Figs. S13 and S15). There are also weak but sharp δ(CH) bands in this region that are present in these reference tar spectra and Sibhudu residues (Fig. 3a). The lower wavenumber range of the fingerprint region shows the bands of inorganic components: calcite ($CaCO_3$), quartz (SiO_2, likely contaminations), and hematite. The reference spectra of *Podocarpus, D. viscosa*, *S. inerme*, and *E. tomentosa* made by condensation also show calcite contaminations, most likely due to the incorporation of ash during the production process. Another feature common to all six Sibhudu IR spectra is the presence of a split CH_2 rocking band at wavenumbers 729 cm^{-1} and 719 cm^{-1} (Fig. 3b). The 10-cm^{-1} split of this methylene band is caused by chain packing of crystalline *n*-alkanes (Snyder, 1979). It is common in paraffin (Stein, 2004) and other waxes such as epicuticular waxes (Eglinton and Hamilton, 1967). In crystalline fatty acids and *n*-alkanes, such as those in waxes, this band spit normally occurs together with another methylene scissoring band near 1465 cm^{-1}

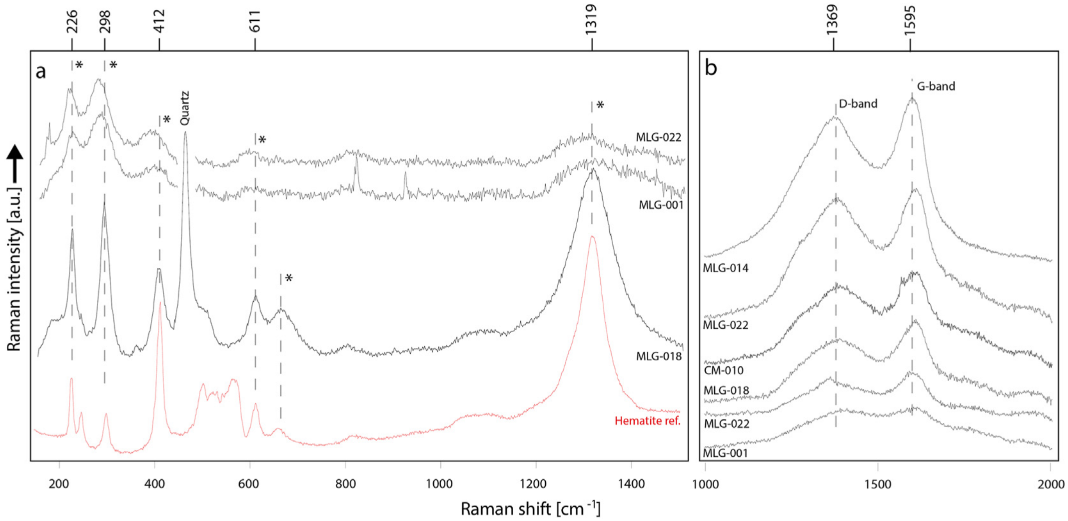

Fig. 2. Raman spectra of Sibhudu adhesives. a) Raman spectra acquired on red areas that are visible red filler on three Sibhudu adhesive samples compared to a hematite (Fe_2O_3) reference spectrum. Note that the three Sibhudu samples show the characteristic hematite Raman bands. Hematite bands are marked by asterisks. b) Raman spectra acquired on black portions of all six adhesive samples. Note the presence of characteristic D and G bands, indicating heat-transformation of the adhesives. Spectra are vertically offset. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(Li et al., 2004). This ~1465-cm^{-1} split band can also be distinguished as a weak band and shoulder on the high-frequency side of the $\delta(CH_{2+3})$ absorption envelope in all six Sibhudu spectra. All spectra of tars produced from leaves (by condensation and underground distillation; *Podocarpus, D. viscosa*, *P. tricuspitatus*, *S. inerme*, and *E. tomentosa*) show the same 10-cm^{-1} split methylene bands. These bands account for the strongest signal in the spectra of *Podocarpus* tar made by underground distillation. All other reference spectra acquired on naturally available adhesives (*Euphorbia*, *Ficus*, *Widdringtonia*) and their tars did not yield a wax signal. This can be expected because epicuticular waxes mainly occur on leaves; they are also called leaf waxes. Such waxes are generally absent in most tree parts other than leaves, so that the presence of these characteristic bands in the IR spectra of adhesives can be regarded as a good indicator that their production involved the use of leaves.

There are also several sharp bands in the IR spectra of artifacts and references adhesives that we do not attempt to assign to specific molecular vibrations. To interpret these spectral features in terms of the overall chemical similarity between samples, we conducted a PCA on the first-derivative spectrum calculated from spectral data between 1800 cm^{-1} and 400 cm^{-1}. This PCA contains

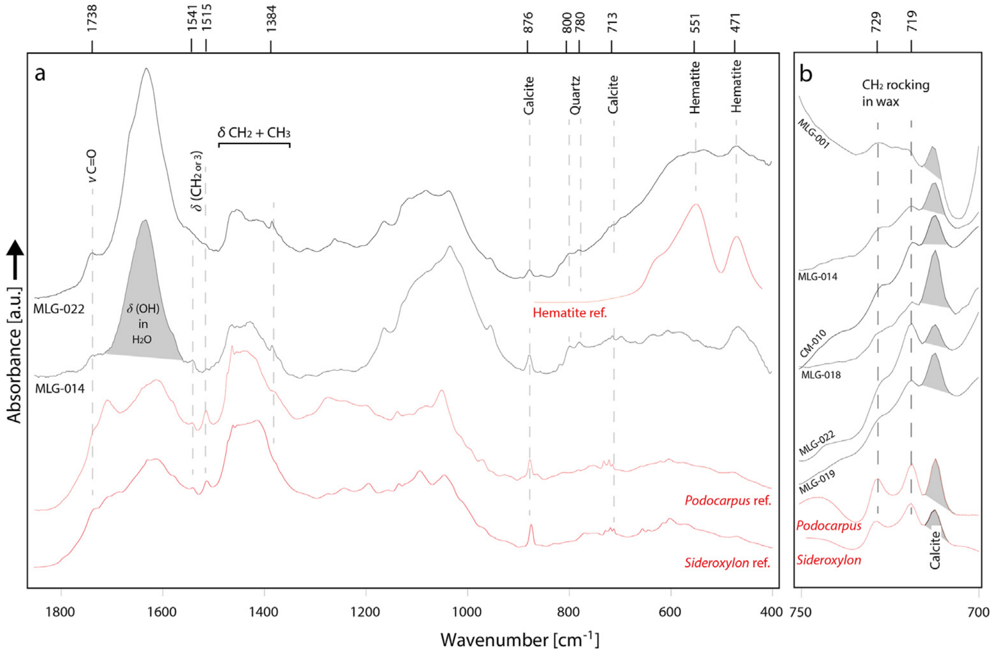

Fig. 3. Infrared transmission spectra of Sibhudu adhesives. a) Infrared spectra of one Sibhudu sample containing a red filler (MLG-022), one sample containing no filler (MLG-014), a hematite (Fe_2O_3) reference spectrum, and two reference spectra of *Podocarpus* and *Sideroxylon* tar made with the condensation method. Spectral features present in more than one spectrum are marked by dotted lines. Note the overall similarity of Sibhudu samples with condensation tars. b) Infrared spectra of all six Sibhudu samples in the range 700–750 cm^{-1}, compared to reference spectra of condensation *Podocarpus* and *Sideroxylon* tars. Note the presence of a CH_2 rocking band doublet characteristic of crystalized fatty acids and *n*-alkanes in waxes in all spectra. Spectra are vertically offset. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

information on how similar IR spectra are in terms of the presence/absence of absorption bands. In the PCA plot in Figure 4, all six Sibhudu adhesives plot in the same area as reference samples made with the condensation method (the data used to generate this plot can be found in SOM Table S4). Condensation tar made from different plants cannot be told apart in this graph. The plot shows a clear distinction between Sibhudu samples and all other reference substances (including *Podocarpus* tar made by underground distillation). Thus, the six adhesive artifacts are chemically most similar to the tar made with the condensation method.

To verify these findings, we conducted GC—MS on two Sibhudu samples (MLG-019 and -022), reference tars made by condensation (four samples: *P. elongatus, P. latifolius*, *S. inerme*, and *D. viscosa*), and tars made by underground distillation (one sample: *P. latifolius*). The chromatograms of both archaeological tars show strong markers of contamination, several short-chain fatty acids, phthalates, and cholesterol (Fig. 5; more chromatograms are shown in SOM Figs. S16—S20; a list of identified molecules is given in SOM Table S5), which most likely result from handling and storage. There are also characteristic wax esters in both Sibhudu samples, corroborating the finding of wax in their IR spectra. These wax esters contain a fragment at m/z 257, documenting that they are based on palmitic acid (C_{16}). There are several monoacylglycerols in both chromatograms, which may result from the decomposition of waxes (Li et al., 2007). However, monoacylglycerols may also result from the decomposition of triglycerides (possible contamination). There are no traces of diterpenoids, as would be expected in derivatives of conifers and other South African plant exudations, such as the latex of *Euphorbia* (see for example (Xu et al., 2021). Thus, our chromatograms do not allow us to make statements about the botanical origin of the Sibhudu tars, but they do confirm that they contain an important component of plant-related waxes. The chromatograms of reference tars made from *Podocarpus* by condensation are dominated by carbohydrates from the families of inositol and pinitol, natural cyclitols already described in leaves from other plants (Bieleski, 1994). They also contain polysaccharides and levoglucosan. These are common degradation products resulting from the pyrolysis of cellulose and/or lignin (see for ex: Zhang et al., 2013) and have entered the tar through burning of branches near the cobbles during condensation. These carbohydrates compose the majority of the condensation of the soluble phase of the tar samples. Similar carbohydrates can also be found in condensation tars made from *D. viscosa* and *S. inerme*, suggesting that the same processes were active as those causing the formation of *Podocarpus* tar. There are small concentrations of diterpenoids (typical biomarkers of gymnosperms such as conifers) in reference condensation tars made from *Podocarpus*, but biomarker totarol, which is often used for identifying the genus (Charrié-Duhaut et al., 2013, 2016; Veall, 2018), is absent in the condensation tar made from *P. elongatus*. The condensation tar made from *P. latifolius* contains a small quantity of totarol. In reference condensation tars made from *D. viscosa* and *S inerme*, there are triterpenoids (i.e., typical biomarkers of resin-producing angiosperms), including α- and β-amyrin, (Fig. 5; SOM Fig. S20). Their concentration varies from large amounts (*S. inerme*) to traces only (*D. viscosa*). The absence of terpenoid biomarkers in Sibhudu samples, therefore, cannot be understood to exclude or suggest the use of certain plants. Their concentration might simply be below the detection limit in the small sample masses used here. There are long-chain *n*-alkanes in all condensation tars, which likely result from the thermal decomposition of

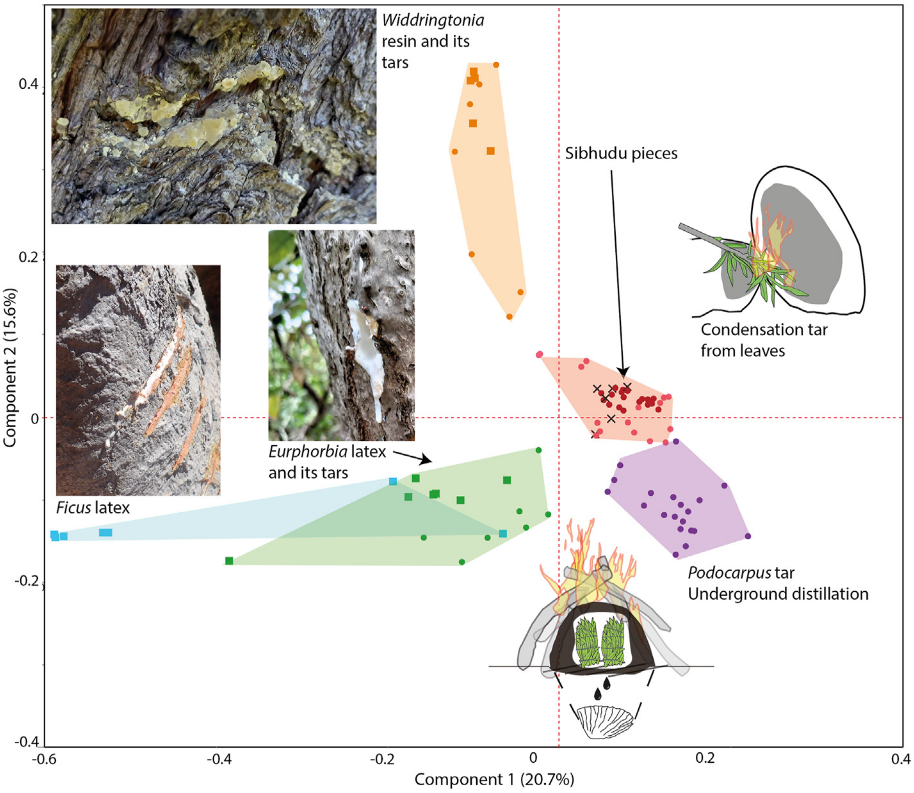

Fig. 4. Plot of a principal component analysis (PCA) comparing six Sibhudu residue samples (X) with different natural and produced substances in terms of similarities and differences of their infrared spectra. Squares are natural substances, resin, and latex; circles are tars, either made from leaves or cooked from latex and resin. Note that condensation tars made from *Podocarpus* leaves are darker dots than those made from other leaves. Data used to generate this PCA are all intensities between 1800 and 405 cm^{-1} in the first-derivative spectra calculated from transmission infrared spectra (covariance matrix) (For interpretation of the references to color in this figure, the reader is referred to the Web version of this article.).

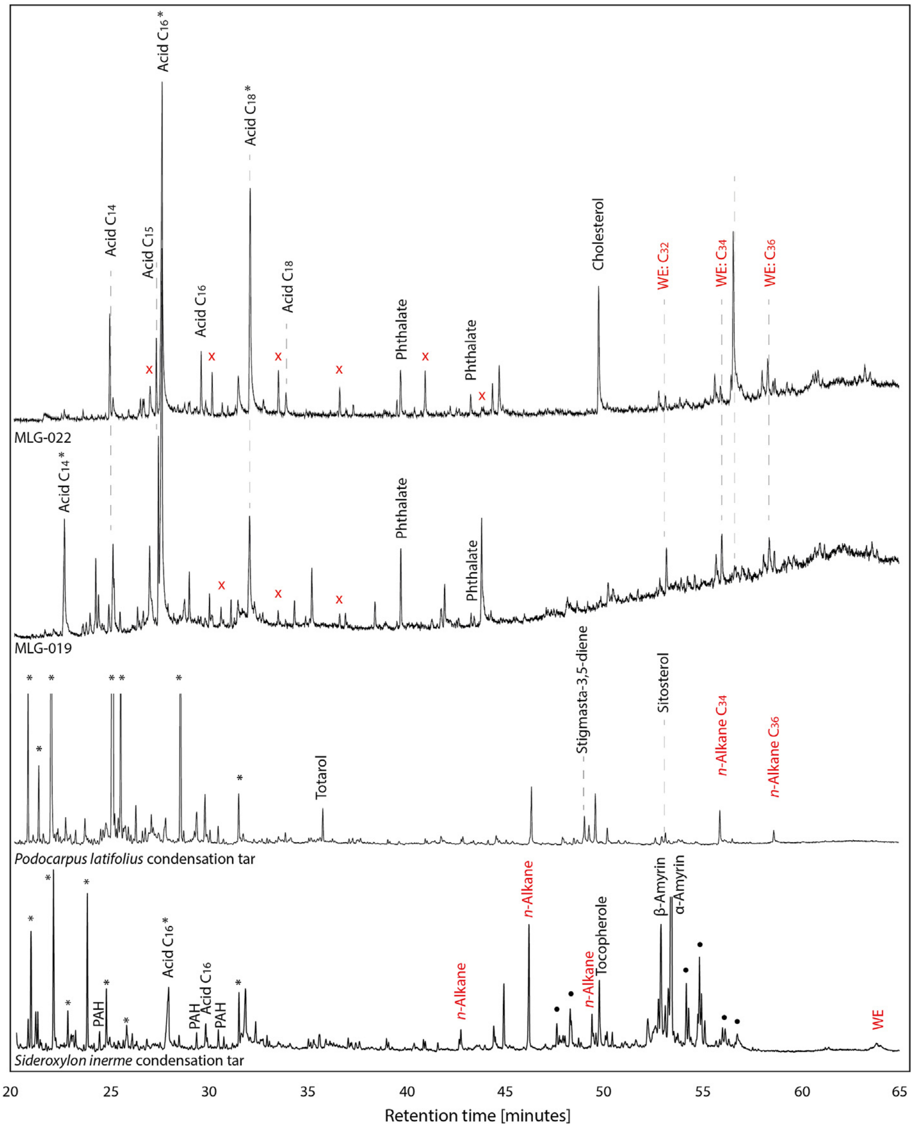

Fig. 5. Partial chromatograms of Sibhudu adhesives MLG-019 and MLG-022 compared to a tar reference made by condensation. Potentially wax-related molecules in red. x = monoacylglycerols; * = carbohydrates (inositol, pinitol, polysaccharides); ● = unidentified triterpenoid; WE = wax esters; PAH = polyaromatic hydrocarbon. Fatty acids marked with an asterisk after the number of carbon atoms were not successfully silylated. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

epicuticular wax in the samples. Reference tar made by underground distillation of *P. latifolius* leaves contains a substantially greater amount of such *n*-alkanes, corroborating the finding (IR spectroscopy) that underground distillation tar contains larger quantities of epicuticular wax. Tar produced underground contains no carbohydrates and a greater quantity of totarol. The profiles of condensation tars made from *Podocarpus* and *D. viscosa* do not show wax esters. However, after enrichment by thin-layer chromatography, we found wax esters with a fragment at m/z 257 in the apolar fractions of *Podocarpus* and *S. inerme* tar (SOM Figs. S17 and S18). The total mass of wax esters is different in artifacts and *Podocarpus* tar, despite both being based on palmitic acid. This might be due to postdepositional processes or different botanical origins. As it stands, Sibhudu and reference samples contain *n*-alkanes and wax esters with a fragment at m/z 257, documenting the presence of plant-related waxes. Whether wax esters can be used as biomarkers remains unclear for now and should be investigated in a dedicated study.

3.4. *Hematite content in compound adhesives*

Adhesives appear as thin discontinuous layers on the surfaces of the two samples. The adhesive coating on MLG-001 is not well preserved. Only ~15–20 μm thin surface coatings can be found in some of the depressions of the surface (Fig. 6a). This coating has a density of 3.26 g/cm^3 (as calculated from its mean brightness value, 11737 HU, compared to the brightness value of the 2.64 g/cm^3 quartz reference, 9541 HU). At a known density of hematite of 5.3 g/cm^3 and assuming a density of tar of 1.05 g/cm^3, the measured density value suggests that these zones consist of 77% ochre. However, because there is no continuous and intact adhesive layer found on this artifact, postdepositional loss of the adhesive's organic phase appears likely. Thus, 77% is likely an overestimate of the quantity of ochre mixed in this compound adhesive. MLG-022 contains a ~40- to 50-μm-thick patch of adhesive toward the center of the tool (Fig. 6b). An air bubble trapped between adhesive and stone surface can still be observed

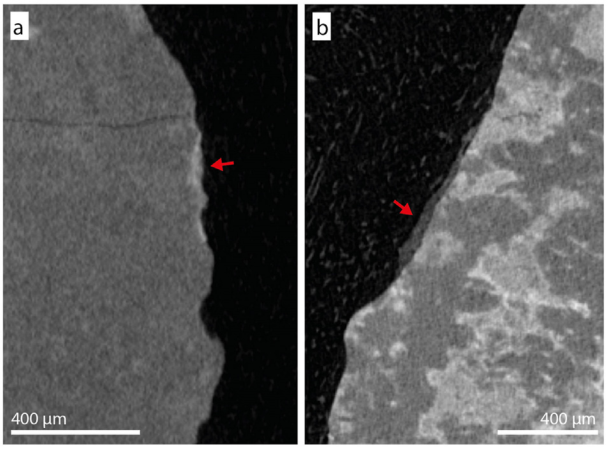

Fig. 6. Microcomputed tomographic slices of adhesives on MLG-001 (a) and MLG-022 (b). Adhesive coatings on the stone artifact are marked by red arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(Fig. 6b, upper part of the adhesive coating), suggesting good preservation. It is therefore likely that this patch of compound adhesive on MLG-022 is sufficiently well preserved to allow estimating the ratio by which biomass tar and ochre were mixed. There are only minor variations of the brightness, suggesting that hematite and the organic tar were homogeneously mixed. The adhesive's overall brightness value (17087 HU as compared to the quartz reference of 19909 HU) yields a density of 2.27 g/cm^3, indicating that the compound adhesive consists of 54% hematite ochre and 46 % tar.

4. Discussion

4.1. Formation and composition of biomass tars from leaves

Before this study, only tar made from *Podocarpus* (or unidentified conifers) was known from the South African MSA (Villa et al., 2012, 2015; Charrié-Duhaut et al., 2013). It has recently been shown that *Podocarpus* tars were most likely produced from leaves (Schmidt et al., 2022). The mechanism leading to tar formation was presumed to be the distillation of resin contained in these leaves (Langenheim, 2003). Our results show that this view was incomplete at best. Tar can be made from the leaves of many plants. These tars may or may not contain resin-related terpenoid biomarkers. Even in those tars that contain terpenoid biomarkers, they only account for a small portion of the soluble fraction. The major part of these tars is most likely composed of polymerized molecules that are insoluble and therefore are not analyzed by GC—MS. This polymerized phase is likely structurally analogous to modern biomass tars that form during biomass gasification for the production of syngas (Font Palma, 2013). In fact, similar processes occur during heat treatment of silcrete, a process commonly practiced in the MSA (Schmidt et al., 2020). Here, wood tar condenses onto the surface of tool-stones during the treatment (Schmidt et al., 2016). Such tars form by pyrolysis of lignocellulosic biomass and consist of polymerized macromolecules based on aromatic and aliphatic carbon (Lu et al., 2020). In modern biomass gasification plants, such tars are considered an unwanted by-product that can be removed from the syngas by different processes, one of which is the condensation of the tars contained in the gas (Dafiqurrohman et al., 2020). Thus, the formation of our Sibhudu adhesives relied on the same processes as modern biomass tars. However, in the MSA, biomass pyrolysis was not controlled by regulating temperature and pressure, or by setting up oxygen-depleted environments. Consequently, these tars also contain inositol/pinitol derivatives and polysaccharides that entered the tar during incomplete pyrolysis. These carbohydrates typically do not preserve in MSA deposits and, thus, cannot be detected in archaeological adhesives. In fresh tars, they likely act as inert filler and do not contribute to the adhesiveness of the tar; in any case, they are not thermoplastic. Small amounts of thermoplastic epicuticular waxes also form part of these biomass tars. They most likely entered the tar during contact between burning leaves and the cobble surface onto which the tar condensed. This wax fraction can be expected to have similar properties as the polymerized insoluble fraction of the tar.

4.2. The chemical signature of biomass tars at Sibhudu

The reference tars we made by condensation contain polysaccharides. IR spectroscopy unambiguously shows that the six Sibhudu tar samples are chemically most similar to these condensation tars, notwithstanding that they contain no polysaccharides. While this might appear contradictory at first glance, a closer look at the expected IR spectroscopic signatures of polysaccharides reveals that they are not expected to yield a major contribution to the IR spectra of complex mixtures. They normally yield weak and broad bands (compare the spectra in: He et al., 2008; Hong et al., 2021), which are expected to underlie sharper bands in the spectra of *Podocarpus* biomass tars. Indeed, the spectra of *Podocarpus* tar made by condensation are overall similar to spectra of tar made underground that do not contain polysaccharides (SOM Fig. S9), with the exception of the wax signature that is significantly stronger in underground tars. Thus, IR spectroscopy is not particularly sensitive to the presence of polysaccharides in tar samples, at least not in such small quantities (it can be expected that the tar's soluble fraction containing these polysaccharides is only a small portion of the bulk tar samples), and our results appear not to be influenced by them. Not finding polysaccharides in Sibhudu tars is also expected and does not contradict our finding of it being most similar to tars made by condensation. Carbohydrates are highly water-soluble and cannot be expected to preserve over periods as great as 60 ka (the age of our Sibhudu samples). In the past (Charrié-Duhaut et al., 2013, 2016; Veall, 2018), totarol and related components were understood to be the best biomarkers for *Podocarpus* in South African archaeological adhesives. Our results show that this might not be true. Totarol was absent in condensation tar made from *P. elongatus* leaves, and only a small quantity was found in condensation tar made from *P. latifolius*. Similarly, the condensation tars made from *S. inerme* leaves contained triterpenoid biomarkers, but tar made from *D. viscosa* showed only small traces of triterpenoids. It therefore appears that the absence of specific biomarkers in Sibhudu tars is best interpreted as indicating the use of the leaves of plants that do not contain great amounts of identifiable terpenoid biomarkers.

The leaves of *Podocarpus* cannot be excluded as botanical origin of the tars based on the presence/absence of biomarkers. This is an interesting observation because previous work on adhesives from a close-find context at Sibhudu (Villa et al., 2015) identified diterpenoids in residues on stone tools, but those were derivatives of abietadienic acid not specific to *Podocarpus* (totarol was also not reported). Thus, our results imply that Sibhudu tars were produced by open-air pyrolysis of lignocellulosic biomass in leaves and collected by condensation. These leaves were not specifically those of *Podocarpus*, although it is possible that *Podocarpus* leaves were also used along with other plant species. The use of leaves is further supported by the presence of wax in reference tars and Sibhudu adhesives.

Epicuticular waxes are abundant on the leaves of South African plants (Bush and McInerney, 2013), and we found no wax signatures in the IR spectra of any reference adhesive made from other parts of plants (including resin, latex and their tars). The finding of epicuticular wax in tars made from leaves also means that there is a potential risk of erroneously assigning its spectral or chromatographic signature to beeswax in archaeological adhesives. Beeswax is normally identified through the presence of wax esters based on palmitic acid (causing a predominant fragment at m/z 257 in the esters' mass spectra). We found that the wax esters in epicuticular waxes of some South African plants also have a mass spectrum dominated by a fragment at m/z 257. Thus, the presence of long-chain *n*-alkanes and wax esters based on palmitic acid can no longer be considered an exclusive marker of beeswax in archaeological adhesives, at least not in contexts where adhesives were made from leaves, such as in the South African MSA. This might also have important implications for the debate surrounding compound adhesives said to contain beeswax in other parts of the world (Degano et al., 2019).

4.3. Implications for Middle Stone Age archaeology

Findings from this study have important implications for our understanding of the people living at Sibhudu in the Howiesons Poort. They chose to produce an adhesive substance from a raw material that does not have adhesive properties itself. They did this despite having access to other plants from which adhesive substances could have been collected with less investment. The reason for this may have been the superiority of such tars over these substances in terms of mechanical properties (this has recently been demonstrated for biomass tar made from *Podocarpus* (Schmidt et al., 2022). This behavior portrays the Sibhudu foragers as engineers with intimate knowledge of the available resources and an understanding of how to change their properties.

It has been suggested that underground distillation techniques document cumulative cultural transmission because some of the processes that take place below ground cannot be observed or discovered accidentally (Schmidt, 2021). Cumulative cultural transmission of technical procedures cannot be clearly demonstrated for open-air techniques, such as the condensation method, because condensed tar might also have been a by-product of other processes (e.g., fire lighting, see Schmidt et al., 2019) and therefore discovered or reinvented several times. In the case of European-birch tar, where the condensation method is substantially less efficient than underground distillation (Blessing and Schmidt, 2021; Koch and Schmidt, 2022), the implications of identifying the condensation method in the archaeological record would have been that cumulative cultural transmission was likely not involved in the Neanderthal adhesive technology (note that the contrary is the case, see Schmidt et al., 2023a). In the case of South African biomass tars, the implications are not so straightforward. The comparison between biomass tars made from *Podocarpus* leaves using underground distillation and condensation shows that for tars made from leaves, the condensation method is almost as efficient as underground distillation in terms of the quantity of leaves used (although it is expected that gathering enough leaves from prolifically leafy trees is not a major impediment for tar making in any case). Condensation is even substantially more efficient in terms of time invested (Table 1). Even more importantly, leaf-derived tar made by condensation is more than six times stronger than tar made by underground distillation (Schmidt et al., 2022). Thus, if South African MSA foragers had made biomass tar by underground distillation, this would have been counterproductive because it would have produced an inferior product. This means that for biomass tars made from leaves, a shift from a more obvious above-ground technique to underground tar making would not satisfy one of the core criteria proposed to be minimum requirements for a population to exhibit cumulative cultural evolution (Mesoudi and Thornton, 2018). While it might have been a change in a behavior (criterion one) that must be transferred via social learning (criterion two), it certainly did not lead to an improvement in performance (which would have been criterion three). Finding an above-ground tar-making technique in the Howiesons Poort at Sibhudu, therefore, does not detract from the meaning of the southern African adhesive technology. The MSA occupants of Sibhudu likely had a good understanding of the technical process of tar making (including its efficiency) and the mechanical properties of the tar produced. Further information comes from an observation we made when producing our reference tar collection. When we attempted to burn leaves directly after cutting them from the trees, it was impossible to keep them lit long enough to start condensation. Only after drying the leaves between three and five days in the sun were we able to make tar. While this was not a systematic observation, and we cannot make statements about the exact drying time necessary, it nonetheless suggests that forward planning must have been involved in tar making at Sibhudu.

Our results also raise another important question. Why are there single-component and compound adhesives made from the same tar? Understanding this is not straightforward because there is no obvious technical need for compound adhesives made from biomass tars. If such tars, which have excellent adhesive and elastic properties (Schmidt et al., 2022), could be used untransformed, why transform them into compound adhesive; and only in some cases but not others? Small quantities of loading agents such as ochre mixed with gum (a polysaccharide) increase adhesive strength, but high quantities of ochre, or any other type of loading agent, have been shown to reduce adhesiveness (Wadley, 2005; Wadley et al., 2009; Prinsloo et al., 2023; Schmidt et al., 2024). A possible explanation is that compound adhesives were used for different functions than single-component adhesives. Adding high ochre loads to otherwise sticky substances creates a moldable mass that can be used as a handle molded to a stone tool (Schmidt et al., 2024). Such use-types, commonly found in European sites associated with Neanderthals (Grünberg et al., 1999; Mazza et al., 2006; Niekus et al., 2019), are also known from the South African Late Stone Age (Charrié-Duhaut et al., 2016). The presence of two distinct use-types of adhesives at Sibhudu, one as hafting material in situations where stones are attached to rigid (perhaps wooden) hafts and one where the adhesive is used as a handle itself, could explain the otherwise curious finding of the addition of ochre to an adhesive that also works without it. An alternative interpretation is that some, but not all, of the backed tools were expected to remain in their hafts, whereas others were expected to break off after hitting their target (Wadley et al., 2009). This would explain the need of two different sets of mechanical properties.

Indeed, there are observations from southern African hunter-gatherers, showing that elements were loosely hafted to arrows so that they would detach after hitting a target (Bradfield, 2015; Wadley, 2015), inflicting more severe injuries to the animals that were hit. As mentioned earlier, the Sibhudu Howiesons Poort assemblage contains lithics that were intended as barbs in addition to lithics intended as weapon tips, and others that were cutting tools. Clearly, it is necessary to study the adhesive residues on each category of artifact to answer questions about the functionality (or otherwise) of compound adhesive recipes. In addition, a thorough use-wear study looking for traces related to hafting (e.g., Rots, 2004) and those specific to the use as handles (Schmidt et al.,

2024) is needed to supplement the results from residue analysis. While understanding the rationale for compound adhesives may elude us for now, the imagination and forward planning needed for the manufacture of adhesives from leaves does suggest a high degree of analogical thought used by people in the South African MSA.

5. Conclusions

Our study implies that previous assumptions about MSA adhesives might have been too simplistic. Until the present study, only *Podocarpus* was chemically proven as the botanical origin of MSA adhesives. However, we found that tar can be readily made from a variety of plants, *Podocarpus* being only one of them. The reason for the focus on *Podocarpus* might have been due to a limited understanding of the processes involved in tar formation. At Sibhudu, these tars were made through the condensation method using leaves. This has important implications for our understanding of these foragers. They purposefully conducted an efficient production process to make their adhesives.

CRediT authorship contribution statement

Patrick Schmidt: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Armelle Charrié-Duhaut:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Edmund February:** Writing – review & editing, Resources, Investigation, Formal analysis. **Lyn Wadley:** Resources, Investigation.

Declaration of competing interest

The authors declare that they have no conflict of interest/competing interest.

Data and materials availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Information.

Acknowledgments

We acknowledge the South African Heritage Resources Agency for granting a permit (ID: 4026, CaseID: 21038) allowing transport and analysis of the six Sibudu artifacts. Part of the research equipment (Raman and IR spectrometers) was provided by K.G. Nickel and C. Berthold at Tübingen University's Department of Geosciences, Applied Mineralogy, and the Competence Center Archaeometry Baden-Wuerttemberg. We acknowledge A. Flicker (University of Tübingen) for assistance with the spectral acquisition; G. Ferreira (Senckenberg Centre for Human Evolution and Palaeoenvironment at the University of Tübingen; SHEP) for assistance with the microcomputed tomography scans. We also thank N. Allsopp and T. Koch for their assistance in sampling the reference plant material in South Africa. Furthermore, we thank E. Leize-Wagner, Head of the Laboratory of Mass Spectrometry of Interactions and Systems (Strasbourg, France), J.-L. Schmitt, Head of the analysis platform from ISIS, and W. Kazöne from Laboratory of chemical catalysis for providing access to the GC-MS system (Strasbourg, France). P.S. received funding from the Deutsche Forschungsgemeinschaft (DFG), grant SCHM 3275/4-1.

Appendix A. Supplementary Online Material

Supplementary Online Material related to this article can be found at https://doi.org/10.1016/j.jhevol.2024.103578.

References

Allott, L.F., 2006. Archaeological charcoal as a window on palaeovegetation and wood-use during the Middle Stone Age at Sibudu Cave. South. Afr. Humanit. 18, 173–201.

Bieleski, R.L., 1994. Pinitol is a major carbohydrate in leaves of some coastal plants indigenous to New Zealand. N. Z. J. Bot. 32, 73–78.

Blessing, M., Schmidt, P., 2021. On the efficiency of Palaeolithic birch tar making. J. Archaeol. Sci. Rep. 38, 103096.

Bradfield, J., 2015. Identifying bone-tipped arrow types in the archaeological record of southern Africa: The contribution of use-trace studies. J. Afr. Archaeol. 13, 135–147.

Bush, R.T., McInerney, F.A., 2013. Leaf wax n-alkane distributions in and across modern plants: Implications for paleoecology and chemotaxonomy. Geochem. Cosmochim. Acta 117, 161–179.

Charrié-Duhaut, A., Porraz, G., Cartwright, C., De Araujo, M., Conan, J., Poggenpoel, C., Texier, P.-J., 2013. First molecular identification of a hafting adhesive in the Late Howiesons Poort at Diepkloof Rock Shelter, Western Cape, South Africa. J. Archaeol. Sci. 40, 3506–3518.

Charrié-Duhaut, A., Porraz, G., Igreja, M., Texier, P.J., Parkington, J.E., 2016. Holocene hunter-gatherers and adhesive manufacture in the West Coast of South Africa. South. Afr. Humanit. 29, 283–306.

Clark, J.L., 2011. The evolution of human culture during the later Pleistocene: Using fauna to test models on the emergence and nature of “modern” human behavior. J. Anthropol. Archaeol. 30, 273–291.

Clark, J.L., 2013. Exploring the relationship between climate change and the decline of the Howieson's Poort at Sibudu Cave (South Africa). In: Clark, J.L., Speth, J.D. (Eds.), Zooarchaeology and Modern Human Origins: Human Hunting Behavior during the Later Pleistocene. Springer, Dordrecht, pp. 9–18.

Clark, J.L., Plug, I., 2008. Animal exploitation strategies during the South African Middle Stone Age: Howiesons Poort and post-Howiesons Poort fauna from Sibudu Cave. J. Hum. Evol. 54, 886–898.

Clarkson, C., 2010. Regional diversity within the core technology of the Howiesons Poort technocomplex. In: Lycett, S.J., Chauhan, P.R. (Eds.), New Perspectives on Old Stones: Analytical Approaches to Paleolithic Technologies. Springer, New York, pp. 43–59.

d'Errico, F., Backwell, L.R., Wadley, L., 2012a. Identifying regional variability in Middle Stone Age bone technology: The case of Sibudu Cave. J. Archaeol. Sci. 39, 2479–2495.

d'Errico, F., Backwell, L., Villa, P., Degano, I., Lucejko Jeannette, J., Bamford Marion, K., Higham Thomas, F.G., Colombini Maria, P., Beaumont Peter, B., 2012b. Early evidence of San material culture represented by organic artifacts from Border Cave, South Africa. Proc. Natl. Acad. Sci. USA 109, 13214–13219.

Dafiqurrohman, H., Bagus Setyawan, M.I., Yoshikawa, K., Surjosatyo, A., 2020. Tar reduction using an indirect water condenser and rice straw filter after biomass gasification. Case Stud. Therm. Eng. 21, 100696.

de la Peña, P., Taipale, N., Wadley, L., Rots, V., 2018. A techno-functional perspective on quartz micro-notches in Sibudu's Howiesons Poort indicates the use of barbs in hunting technology. J. Archaeol. Sci. 93, 166–195.

de La Peña, P., Wadley, L.Y.N., Lombard, M., 2013. Quartz bifacial points in the Howiesons Poort of Sibudu. South. Afr. Archaeol. Bull. 68, 119–136.

Degano, I., Soriano, S., Villa, P., Pollarolo, L., Lucejko, J.J., Jacobs, Z., Douka, K., Vitagliano, S., Tozzi, C., 2019. Hafting of Middle Paleolithic tools in Latium (central Italy): New data from Fossellone and Sant'Agostino caves. PLoS One 14, e0213473.

Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. Science 156, 1322–1335.

Font Palma, C., 2013. Modelling of tar formation and evolution for biomass gasification: A review. Appl. Energy 111, 129–141.

Grünberg, J., Gratsch, H., Baumer, U., Koller, J., 1999. Untersuchung der mittelpaläolithischen “Harzreste” von Königsaue, Ldkr. Aschersleben-Stassfurt. Jahresschr. Mitteldtsch. Vorgesch. 81, 7–38.

He, F., Yang, Y., Yang, G., Yu, L., 2008. Components and antioxidant activity of the Polysaccharide from Streptomyces virginia H03. Z Naturforschung C 63, 181–188.

Hodgskiss, T., 2014. Cognitive requirements for ochre use in the Middle stone age at Sibudu, South Africa. Camb. Archaeol. J. 24, 405–428.

Hong, T., Yin, J.-Y., Nie, S.-P., Xie, M.-Y., 2021. Applications of infrared spectroscopy in polysaccharide structural analysis: Progress, challenge and perspective. Food Chem. X 12, 100168.

Jacobs, Z., Roberts, R.G., 2008. Testing times: Old and new chronologies for the Howieson's poort and still bay industries in environmental context. S. Afr. Archaeol. Soc. Goodwin Ser. 10, 9–34.

Jacobs, Z., Roberts, R.G., Galbraith, R.F., Deacon, H.J., Grun, R., Mackay, A., Mitchell, P., Vogelsang, R., Wadley, L., 2008a. Ages for the Middle stone age of southern Africa: Implications for human behavior and dispersal. Science 322, 733–735.

Jacobs, Z., Wintle, A.G., Duller, G.A.T., Roberts, R.G., Wadley, L., 2008b. New ages for the post-Howiesons Poort, late and final Middle Stone Age at Sibudu, South Africa. J. Archaeol. Sci. 35, 1790–1807.

Koch, T.J., Schmidt, P., 2022. A new method for birch tar making with materials available in the Stone Age. Sci. Rep. 12, 413.

Kozowyk, P.R.B., 2023. Archaeological *Podocarpus* tar supports the cognitive complexity of Neanderthals. Proc. Natl. Acad. Sci. USA 120, e2221676120.

Kozowyk, P.R.B., Soressi, M., Pomstra, D., Langejans, G.H.J., 2017. Experimental methods for the Palaeolithic dry distillation of birch bark: Implications for the origin and development of Neandertal adhesive technology. Sci. Rep. 7, 8033.

Kurzweil, A., Todtenhaupt, D., 1991. Technologie der Holzteergewinnung. Acta Praehist. Archaeol. 23, 63–91.

Langenheim, J.H., 2003. Plant Resins – Chemistry, Evolution, Ecology, and Ethnobotany. Timber Press, Portland.

Li, H.-W., Strauss, H.L., Snyder, R.G., 2004. Differences in the IR methylene rocking bands between the crystalline fatty acids and n-alkanes: Frequencies, intensities, and correlation splitting. J. Phys. Chem. A 108, 6629–6642.

Li, Y., Beisson, F., Ohlrogge, J., Pollard, M., 2007. Monoacylglycerols are components of root waxes and can be produced in the aerial cuticle by ectopic expression of a suberin-associated acyltransferase. Plant Physiol. 144, 1267–1277.

Lombard, M., 2005. Evidence of hunting and hafting during the Middle Stone Age at Sibidu Cave, KwaZulu-Natal, South Africa: A multianalytical approach. J. Hum. Evol. 48, 279–300.

Lombard, M., 2011. Quartz-tipped arrows older than 60 ka: further use-trace evidence from Sibudu, KwaZulu-Natal, South Africa. J. Archaeol. Sci. 38, 1918–1930.

Lu, Y., Li, D., Huang, X., Picard, D., Mollaabbasi, R., Ollevier, T., Alamdari, H., 2020. Synthesis and characterization of bio-pitch from bio-oil. ACS Sustain. Chem. Eng. 8, 11772–11782.

Mazza, P.P.A., Martini, F., Sala, B., Magi, M., Colombini, M.P., Giachi, G., Landucci, F., Lemorini, C., Modugno, F., Ribechini, E., 2006. A new Palaeolithic discovery: Tar-hafted stone tools in a European Mid-Pleistocene bone-bearing bed. J. Archaeol. Sci. 33, 1310–1318.

Mesoudi, A., Thornton, A., 2018. What is cumulative cultural evolution? Proc. Biol. Sci. 285, 20180712.

Mull, R.T., 1984. Mass estimates by computed tomography: Physical density from CT numbers. Am. J. Roentgenol. 143, 1101–1104.

Niekus, M.J.L.T., Kozowyk, P.R.B., Langejans, G.H.J., Ngan-Tillard, D., van Keulen, H., van der Plicht, J., Cohen, K.M., van Wingerden, W., van Os, B., Smit, B.I., Amkreutz, L.W.S.W., Johansen, L., Verbaas, A., Dusseldorp, G.L., 2019. Middle Paleolithic complex technology and a Neandertal tar-backed tool from the Dutch North Sea. Proc. Natl. Acad. Sci. USA, 201907828.

Prinsloo, L.C., Bordes, L., Mauran, G., Lombard, M., Wadley, L., 2023. Graphite and multilayer graphene detected on ~70,000-year-old stone tools: Geological origin or constituent of hafting resin? J. Raman Spectrosc. 54, 182–190.

Razi, T., Niknami, M., Alavi Ghazani, F., 2014. Relationship between hounsfield unit in CT scan and gray scale in CBCT. J. Dent. Res. Dent. Clin. Dent. Prospect. 8, 107–110.

Robinson, J.R., Wadley, L., 2018. Stable isotope evidence for (mostly) stable local environments during the South African Middle Stone Age from Sibudu, KwaZulu-Natal. J. Archaeol. Sci. 100, 32–44.

Rots, V., 2004. Prehensile wear on flint tools. Lithic Technol. 29, 7–32.

Rots, V., Van Peer, P., Vermeersch, P.M., 2011. Aspects of tool production, use, and hafting in Palaeolithic assemblages from Northeast Africa. J. Hum. Evol. 60, 637–664.

Sadezky, A., Muckenhuber, H., Grothe, H., Niessner, R., Pöschl, U., 2005. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. Carbon 43, 1731–1742.

Sahle, Y., 2019. Ethnoarchaeology of compound adhesive production and scraper hafting: Implications from Hadiya (Ethiopia). J. Anthropol. Archaeol. 53, 43–50.

Schenck, T., Groom, P., 2018. The aceramic production of Betula pubescens (downy birch) bark tar using simple raised structures. A viable Neanderthal technique? Archaeolog. Anthropol. Sci. 10, 19–29.

Schmidt, P., 2021. Steak tournedos or beef Wellington: an attempt to understand the meaning of Stone Age transformative techniques. Humanit. Soc. Sci. Commun. 8, 280.

Schmidt, P., Blessing, M., Rageot, M., Iovita, R., Pfleging, J., Nickel, K.G., Righetti, L., Tennie, C., 2019. Birch tar production does not prove Neanderthal behavioral complexity. Proc. Natl. Acad. Sci. USA 116, 17707.

Schmidt, P., February, E., Bretzke, K., Bellot-Gurlet, L., 2016. Tempering-residue on heat-treated silcrete: An experimental perspective and a potential analytical protocol. J. Archaeol. Sci. Rep. 15, 611–619.

Schmidt, P., Iovita, R., Charrié-Duhaut, A., Möller, G., Namen, A., Dutkiewicz, E., 2024. Ochre-based compound adhesives at the Mousterian type-site document complex cognition and high investment. Sci. Adv. 10, eadl0822.

Schmidt, P., Koch, T.J., Blessing, M.A., Karakostis, F.A., Harvati, K., Dresely, V., Charrié-Duhaut, A., 2023a. Production method of the Königsaue birch tar documents cumulative culture in Neanderthals. Archaeolog. Anthropol. Sci. 15, 84.

Schmidt, P., Koch, T.J., February, E., 2022. Archaeological adhesives made from *Podocarpus* document innovative potential in the African Middle Stone Age. Proc. Natl. Acad. Sci. USA 119, e2209592119.

Schmidt, P., Koch, T.J., Tennie, C., 2023b. Reply to Paul R.B. Kozowyk: Interpreting the complexity of archaeological adhesives may lead to misconceptions about early humans. Proc. Natl. Acad. Sci. USA 120, e2300325120.

Schmidt, P., Stynder, D., Conard, N.J., Parkington, J.E., 2020. When was silcrete heat treatment invented in South Africa? Palgrave Commun. 6, 73.

Snyder, R.G., 1979. Vibrational correlation splitting and chain packing for the crystalline *n*-alkanes. J. Chem. Phys. 71, 3229–3235.

Soriano, S., Villa, P., Delagnes, A., Degano, I., Pollarolo, L., Lucejko, J.J., Henshilwood, C., Wadley, L., 2015. The still bay and Howiesons Poort at Sibudu and Blombos: Understanding Middle Stone Age technologies. PLoS One 10, e0131127.

Soriano, S., Villa, P., Wadley, L., 2007. Blade technology and tool forms in the Middle Stone Age of South Africa: The Howiesons Poort and post-Howiesons Poort at Rose Cottage Cave. J. Archaeol. Sci. 34, 681–703.

Stein, R.S., 2004. Interaction of methylene deformation frequencies in paraffin crystals II. A theoretical treatment of the interaction of vibrations. J. Chem. Phys. 23, 734–736.

Texier, P.-J., Porraz, G., Parkington, J., Rigaud, J.-P., Poggenpoel, C., Miller, C.E., Tribolo, C., Cartwright, C., Coudenneau, A., Klein, R., Steele, T., Verna, C., 2010. A Howiesons Poort tradition of engraving ostrich eggshell containers dated to 60,000 years ago at Diepkloof Rock Shelter, South Africa. Proc. Natl. Acad. Sci. USA 29, 1001–1015.

Veall, M., 2018. Stuck like Glue': Assessing variability in hafting adhesives in the southern African Later Stone Age. Ph.D. Dissertation, University of Oxford.

Villa, P., Pollarolo, L., Degano, I., Birolo, L., Pasero, M., Biagioni, C., Douka, K., Vinciguerra, R., Lucejko, J.J., Wadley, L., 2015. A milk and ochre paint mixture used 49,000 years ago at Sibudu, South Africa. PLoS One 10, e0131273.

Villa, P., Soressi, M., Henshilwood, C.S., Mourre, V., 2009. The still bay points of Blombos Cave (South Africa). J. Archaeol. Sci. 36, 441–460.

Villa, P., Soriano, S., Tsanova, T., Degano, I., Higham Thomas, F.G., d'Errico, F., Backwell, L., Lucejko Jeannette, J., Colombini Maria, P., Beaumont Peter, B., 2012. Border Cave and the beginning of the later Stone Age in South Africa. Proc. Natl. Acad. Sci. USA 109, 13208–13213.

Wadley, L., 2005. Putting ochre to the test: Replication studies of adhesives that may have been used for hafting tools in the Middle Stone Age. J. Hum. Evol. 49, 587–601.

Wadley, L., 2010. Compound-adhesive manufacture as a behavioral proxy for complex cognition in the Middle Stone Age. Curr. Anthropol. 51, S111–S119.

Wadley, L., 2015. Those marvellous millennia: the Middle Stone Age of southern Africa. Azania 50, 155–226.

Wadley, L., 2023. Experimental archaeology enables inferences about human cognition. In: Wynn, T. (Ed.), The Oxford Handbook of Cognitive Archaeology. Oxford University Press, pp. C15S11–C15S15.

Wadley, L., Hodgskiss, T., Grant, M., 2009. Implications for complex cognition from the hafting of tools with compound adhesives in the Middle Stone Age, South Africa. Proc. Natl. Acad. Sci. USA 106, 9590–9594.

Wadley, L., Mohapi, M., 2008. A segment is not a monolith: Evidence from the Howiesons Poort of Sibudu, South Africa. J. Archaeol. Sci. 35, 2594–2605.

Wadley, L., Trower, G., Backwell, L., d'Errico, F., 2015. Traditional glue, adhesive and poison used for composite weapons by Ju/'hoan san in Nyae Nyae, Namibia. Implications for the evolution of hunting equipment in prehistory. PLoS One 10, e0140269.

Wilkins, J., Schoville, B.J., Brown, K.S., Chazan, M., 2012. Evidence for early hafted hunting technology. Science 338, 942–946.

Will, M., Conard, N.J., 2020. Regional patterns of diachronic technological change in the Howiesons Poort of southern Africa. PLoS One 15, e0239195.

Wojcieszak, M., Wadley, L., 2018. Raman spectroscopy and scanning electron microscopy confirm ochre residues on 71 000-year-old bifacial tools from Sibudu, South Africa. Archaeometry 60, 1062–1076.

Xu, Y., Tang, P., Zhu, M., Wang, Y., Sun, D., Li, H., Chen, L., 2021. Diterpenoids from the genus Euphorbia: structure and biological activity (2013–2019). Phytochemistry 190, 112846.

Zhang, X., Yang, W., Dong, C., 2013. Levoglucosan formation mechanisms during cellulose pyrolysis. J. Anal. Appl. Pyrol. 104, 19–27.

Zwane, B., Bamford, M., 2021. A reconstruction of woody vegetation, environment and wood use at Sibudu Cave, South Africa, based on charcoal that is dated between 73 and 72 ka. Quat. Int. 593–594, 95–103.