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## FIG. Holocene hunter—gatherers and adhesives manufacture in the West Coast of South Africa

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### ABSTRACT

Elands Bay Cave provides the opportunity to characterize Holocene technologies and hunter—gatherers adaptations in the West Coast of South Africa. In this paper, we discuss the question of adhesives uses and manufactures by applying a biomolecular and technological analysis to three unpublished organic artefacts recovered from the 1970s excavation. The first piece is a large handle made of adhesive and with a tear—drop shape (the 'handle'), the second piece is a kind of pencil grip wrapping a microlithic quartz segment (the 'grip'), and the last piece takes the form of a macro—residue likely sealing the perforation of an ostrich eggshell flask (the 'sealant'). The results of our study document the selection and transformation of *Podocarpus* resin, mixed with quartz sand to produce adhesive. One case study (the sealant) suggests that fat was added to the recipe in order to modify the adhesive's properties. The paper provides a unique insight into Holocene organic technologies and fuels ideas on how hunter—gatherers adapted and took benefit from local natural resources. We suggest that *Podocarpus*, in South Africa, has been specifically chosen for adhesive manufacture since, at least, the MIS4.

KEY WORDS: South Africa, Elands Bay Cave, Later Stone Age, Holocene, macro—residues, hafting, adhesive, Ostrich eggshell, backed tool, microliths, Podocarpus, Diterpenoids

The use of natural substances may represent a common practice among past hunter—gatherer societies, but archaeological evidences remain very limited. Natural substances encompass all sorts of plant and animal materials and there is sometimes confusion regarding the appropriate terminology. The first distinction to operate concerns the raw substances coming out of plant materials (exudates, gums, resins, saps) on the one hand, and the substances that have been “manufactured” (tar, pitch, adhesive) on the other. Basically, all these raw materials are exudates, liquids seeping from a plant. They include resins (mixture of terpenoids or phenolic structures), gums and mucilages (polysaccharides structures) and latex (Langenheim 2003). It is completely different from sap, an aqueous solution which carries nutrients through the phloem or xylem tissue of plants. As described below, following the family, genus or species of the plant, the corresponding resin has a diagnostic distribution of compounds called biomarkers allowing identification (Mills & White 1977, 1998). Some have special names: myrrhs from *Commiphora* species, Olibanum from *Boswellia* species, dammar for the resin of Dipterocarpaceae family or mastic from the trees mainly of the genus *Pistacia* of the Anacardiaceae family. Regarding the “manufactured” materials derived from plants, tars obtained by pyrolysis of wood are well known for their specific properties such as their viscous and sticky textures or their hydrophobicity. Birch bark tar and pitch (softwood tar from conifers) have been widely used in prehistoric times (Hayek et al. 1993; Pollard & Heron 1996).

In the present paper, we deal more specifically with the manufacture and use of adhesives. This is a material composed of one or several more organic natural substances, mixed or not with other components (mineral, fibrous, etc.), which has been shaped or intentionally applied to a surface in order to give it new properties. Adhesives could have been used for

different purposes, for example to seal or waterproof containers, but its main known use in prehistory relates to hafting technology (Helwig et al. 2014; Regert & Rolando 2002; Regert 2004).

Adhesives can be regarded as the first synthetic material produced in human history, i.e. the first natural substance chemically transformed to be used. The manufacture of an adhesive is a combination of different technological steps and know—hows, from the acquisition of the natural substances to their transformation and application. Such a manufacture implies complex cognitive capacities and requires a favorable context in terms of socio—economic structures and technical knowledge (Haidle 2010; Wadley 2010; Sykes in press).

The manufacture of an adhesive is a function naturally of the available resources but recipes reflect the types of property (or adherence) that were sought by the manufacturer. How the adhesive suits the need and how it resists through time are two of the main attributes that constraint the *chaîne opératoire* of an adhesive.

The oldest evidences of adhesives manufacture date back to the late Middle Pleistocene at the site of Campitello (Italy). There, two flakes have been found with a lump of birch bark tar at their base (Mazza *et al.* 2006). Following later examples date back from the Last interglacial. Another proof comes from the site of Königsau (Germany) where two pieces of birch pitch have been found (Koller et al. 2001; Grünberg 2002). The excavation of the site of Inden—Aldorf (Germany) has recovered 39 tools bearing residues and gives evidence for the use of an adhesive substance (Pawlik & Thissen 2011).

The other Middle Palaeolithic examples where adhesive has been found document the use of bitumen. This is the case at the site of Umm—el—Tlel (Syria) where several Levallois flakes and points showing basal bitumen imprints have been found (Boëda et al. 2008a, 2008b), together with a lump of oil—stained sands (Connan 1999). Evidence of bitumen use has also been observed in the Mousterian lithic assemblage from the nearby site of Hummal (Syria, Hauck et al. 2013). Another example is known from the late Mousterian site of Gura Cheii—Râsnov (Romania) where one flake has been found with a lateral imprint (Cârciumaru et al. 2012).

The range of direct evidence seems to increase with the Upper Palaeolithic and, later on, with the Mesolithic. There are traces from three burins of the late Aurignacian of Les Vachons (Dinnis et al. 2009) where pitch resin has been recognized. A recent study on geometrics from the late Upper Palaeolithic site of Ohalo II in the Near East (Yaroshevich et al. 2013) indicates that both calcareous and organic substances were used as adhesives. And adhesives have also been macroscopically identified at Lascaux Cave (Leroi—Gourhan & Allain 1979) and in Mesolithic sites from Germany (Yates et al. 2015). There are a few other examples where shaft, adhesives and lithic tools have been found together. It is the case at the Magdalenian site of Pincevent (France) where two bladelets have been found attached with adhesive on an osseous point (Leroi—Gourhan 1983), and at the Mesolithic site of Tlokowo (Poland) where geometrics were found inserted and glued into the grooves of a bone point (Sulgostowska 1993). A final example is provided by the site of Loshult (Sweden) where lithic pieces have been found glued with birch tar onto a wooden arrow (Petersson 1951).

All these examples provide strong evidence that adhesive was part of the technological repertoire of hunter—gatherers since at least the MIS7. The set of evidences become even clearer if we open our argumentation to indirect hafting traces (e.g. Rots 2003; Rots et al. 2006; Conard et al. 2012), which suggest that adhesive might have been involved or required. One of these indirect evidences would be provided by the tang of the North African Aterian points (Tixier 1959; Iovita 2011).

In Africa, few studies have dealt with the question of adhesives technology. Adhesives imprints or residues presently known are documented in the Nubian site of Sodmein Cave in Egypte (Rots et al. 2011), in the Still Bay (SB) and Howiesons Poort (HP) of Sibudu Cave (Lombard 2006, 2008, Wadley & Mohapi 2008) and in the HP of Diepkloof Rock Shelter (Igreja & Porraz 2013) in South Africa, and have also been reported from the Early Later Stone Age

(LSA) site of Nasampolai in Kenya (Ambrose 1998). These evidences become more numerous through time, especially in South Africa, where adhesives have been reported in the Early LSA of Border Cave (Villa et al. 2012), in the Late Pleistocene Robberg of Elands Bay Cave (Porráz et al. this issue) and Sehonghong (Binneman & Mitchell 1997), as well as in the Holocene of Melkhoutboom (Deacon 1976) and Boomplaas (Deacon & Deacon 1980; Deacon 1984). So far, only few chemical analyses have been applied to such material. They concern adhesives from the HP of Diepkloof (Charrié—Duhaut et al. 2013) and Sibudu (Soriano et al. 2015) and from the Early LSA of Border Cave (Villa et al. 2012). All these studies indicate hunter—gatherers made use of a conifer resin, likely resin of *Podocarpus* (Yellowwood) as identified for the sites of Diepkloof and Border Cave.

This overview from the literature reports increasing evidence of the manufacture and use of adhesives from the Middle to the end of the late Pleistocene. This reflects that these organic materials could be preserved through time, but has also to be understood in the light of new (microlithic) technologies that have been adopted by hunter—gatherer groups. Our set of data suggests that at least from the MIS 2, the manufacture of adhesives was a familiar technological capacity among hunter—gatherers groups.

But the increasing set of archaeological evidences does not go together with a diversification in uses: in fact, all current evidence from the Pleistocene documents the use of adhesives in relation to hafting technologies. The diversification in uses seems only to develop from the Holocene. The Neolithic provides examples of ceramics being fixed with glue (Mitkidou et al. 2008); the Holocene LSA provides examples of ostrich eggshell (OES) containers being sealed with adhesive (Deacon & Deacon 1999; Henderson 2002). Other examples are derived from the historic period: bitumen has for example been used as a mortar in construction, to waterproof and seal containers, to caulk boats, and to create domestic and ornamental objects (Connan 1999).

In this paper, we aim to fuel the discussion on how adhesives were manufactured by hunter—gatherers and how this manufacture varied with uses. We focus on the Holocene sequence of Elands Bay Cave (EBC) where various organic artefacts have been found. Three different organic LSA artefacts have been selected for the study: 1) a large handle made of adhesive and with a tear—drop shape, 2) an adhesive pencil grip wrapping a quartz segment, and 3) a strip of adhesive circling the opening of an OES flask.

Most adhesives such as resin, tar or waxes are amorphous. These are substances without form, without crystalline structure or cellular organization and as such their identification requires chemical analysis. In this study, we provide results from both Fourier transform infrared spectroscopy (FTIR) and mass spectrometry analyses, together with a comprehensive description of the main technological steps and inferences involved in the adhesive's manufacture. We comment further on the technological implications of our study and argue that, in South Africa, *Podocarpus* was specifically chosen to produce adhesive since, at least, the MIS4.

## SITE AND MATERIAL

EBC is located on the West Coast of South Africa, about 200 km north of Cape Town (Fig. 1). The site has been excavated by John E. Parkington in the 1970s and exposes long and well—stratified deposits dominantly accumulated during the LSA. The upper part of the deposits represents a shell midden that started forming during the early Holocene (Parkington this issue). A relatively long suite of radiocarbon age determinations indicates the shell midden represents 3 main pulses of human occupation ranging from 11 000 to 8 000 b.p., 4 350 to 3 300 b.p., and 2 250 to 300 b.p. (Parkington this issue).

These upper deposits are characterized by substantial assemblages of archaeological materials including a range of terrestrial and marine fauna, lithic artefacts, ochre, worked wood,

worked bones, charcoals and seeds. Some pieces were individualized separated and labelled during excavation as they were showing evidences of organic macro—residues. Three of them have been selected for this study.

*The tear—drop shaped handle (Figure 2)*

This first piece studied by us is one of two hefty pieces described at the time of recovery as ‘mastic’ (see below for a description of the second piece). Both come from the lowermost unit (JOFR) in the fill of a sleeping hollow excavated about 3750 years ago into existing terminal Pleistocene deposits by mid Holocene cave occupants. This ‘excavation’ uncovered and disturbed an earlier human burial that might have been the original context of the pieces presently under study. It is possible but not demonstrable that these two artefacts are contemporary. The human remains are 8000 years old.

This organic artefact has a tear—drop shape and a hole on its truncated, narrower extremity. It has a size of a palm and presents attributes of a handle. It weighs 43.3 g and is 63 mm long, but is slightly damaged on one extremity. The base of the handle is 46 mm width and 26 mm thick, its top is 31 mm width and 22 mm thick.

The handle presents a homogeneous external surface of a brownish yellow color (Munsell soil color chart: 10YR6/8). The surface exposes multiple small cracks that make a pattern similar to desiccation features. Some of these cracks are filled up by secondary minerals. This external surface is locally smoothed at its base and presents vegetal imprints. Quartz grains are also visible.

The handle is composed of three distinct “layers”: an external layer of about 2 mm thick, a middle layer of 4 to 8 mm thick and an internal layer of 2 to 3 mm thick. The internal layer resembles the external layer but is slightly lighter in color. The middle layer has a dark color and is shiny, as if it was “vitrified”.

The hole is slightly off—centered and presents a diamond to circular shape. It is 43 mm deep and has a diameter of ca. 5 mm that seems to be constant throughout. The wall of the hole, as visible on its extremity, is not smoothed but present patterns on the form of “positive veins”, suggesting it has been formed in contact with an organic material such as a stick or a bone point.

Two main functional hypotheses can be proposed. One is to consider that the handle represents a reserve of resin that would have been collected around a stick and transported into the site for a future use. Such examples are reported from Melkhoutboom cave (Deacon 1976) on the form of a “stick with mastic”, as well as from Boomplaas cave (Deacon 1984) in the form of three lumps of adhesive, including one piece with wood attached on it. But the piece from EBC differs substantially from these examples. While the pieces from Melkhoutboom and Boomplaas caves have an irregular and asymmetric shape, the handle from EBC presents a symmetric shape and a set of technical stigmata suggesting it is a finished and desired form.

The organic tool inserted into the handle is not present anymore. But its imprint is the one of a regular artefact indicating it has been worked. The collection of EBC presents several organic tools, either in wood or bone. All of them are pointed. One identified wood tool presents an oval section and a diameter of 6 mm, suggesting that the variability of organic tools manufactured at EBC is compatible with the hypothesis that the piece was designed for handling such an artefact. The polished surfaces at the base of the piece suggest it was handled several times and also support this interpretation.

Though part of the extremity of the handle is missing, the absence of polishing at the side of the hole indicates the tool was well fixed into the handle and/or that no rotating motions were involved. The set of observations suggests the hole has not been drilled into the handle, but results either from the molding of the resin directly around the organic tool, or from the inserting of the tool into the resin while it was still plastic enough.

These observations, together with the presence of vegetal imprints, indicate that the resin was not liquid while it was worked, but malleable. The existence of three different layers could be indicative of different steps in the covering of the organic tool. But the contact between these

layers and their structure rather suggest they could represent different degrees of alteration or consolidation. The cracks that are observable on the external surface of the tear—drop didn't form on technical joints of manufacture, suggesting it was molded from one large piece of malleable adhesive. We observed no finger imprints, but several vegetal imprints are visible, indicating these plant parts were involved while the handle was being shaped. We consider four main hypotheses: 1) the vegetal substances/structures were used to maintain the soft resin, 2) the vegetal substance was used to help/control the drying of the resin, 3) the vegetal substance was part of the composition of the resin, or 4) the handle was held in a leaf package.

The macroscopic observation indicates the resin was mixed with millimetric quartz grains. One fragment of charcoal is present on the surface of the handle. Its isolation and position suggest this charcoal could be an indirect trace of manufacture, for example that could have occurred while the adhesive was (re—)heated.

### *The pencil—grip (Fig. 3)*

The pencil—grip adhesive, as well as a small collection of quite distinctive silcrete, ochre stained flakes, came from the excavated unit of the human burial immediately below JOFR. The piece is likely to have been placed in the burial at about 8000 years ago.

This piece is a small backed quartz segment held in place in an organic holder. The whole piece weights 2.3 g. The piece is complete, though the imprint still visible on the ventral face of the quartz tool might suggest the adhesive was a little bit more invasive.

The backed artefact is made of a quartz flake. This tool is 21 mm long, with a maximum breadth of 9 mm and a maximum thickness of 4 mm. It corresponds to a segment with a semi—lunate shape, the back having been partly shaped by bipolar percussion. The segment has a rectilinear profile and a sharp edge with an irregular delineation. The edge presents micro—scars localized toward the apex. The use—wear analysis shows the presence of a polish together with striations (Fig. 3) that indicate the tool was used as a knife in a longitudinal motion.

The adhesive forms a small piece of about 24 mm long, 10 mm width and 15 mm thick. It is of brown color (Munsell soil color chart: 10YR4/3) and is homogeneous at a macroscopic scale. On its thickest part, the adhesive presents a blackish and shiny color. Multiple small cracks are visible as well as many quartz grains and a few shallow vegetal imprints. Prominent surfaces are smoothed.

There is no indication or marks that the adhesive was used to fix the tool into a wood or bone handle. The adhesive is complete and its shape suggests it was wrapped directly around the backed piece. Moreover, some surfaces of the handle are polished, suggesting a direct handling. Regarding the size of the piece and the types of functional traces, it is hypothesized that the lithic tool was involved in fine cutting or scribing activities.

The segment only fits in one way and so we have assumed that the tool was 'open' on one side (where the thumb presses) and that the segment could be easily changed. We see this as a kind of pencil grip that, in our case study, could only work if the object was held in the right hand with the right thumb doing the pressing.

The original morphology of the adhesive is the one of a foil that has been wrapped. It presents an irregular conic morphology with its maximum thickness being located on the contact with the tool. The morphology suggests that the foil, before being wrapped, had a pseudo—rectangular morphology and was about 25 mm width, 40 mm long and 2 to 4 mm thick. The quartz backed tool was positioned on the side of the adhesive foil and pinched by gripping until the two extremities recovered each other's marginally. The segment had been pressed into the mastic (and indeed there is an impression of one side of the segment in the mastic) and then held in place by the pressure of the thumb against it. A pleat was made at one extremity to adapt the global geometry of the handle and strengthen its adherence. It is a unique configuration of stone backed tool and holding device.

Our observations indicate the adhesive was moulded around the backed tool while it was plastic enough. Regarding the size of the piece and its nature, we expect that the adhesive has been moulded by hand, though no finger imprints are visible. One possibility is that those technical marks would have been erased with use. Alternatively, the craftsman may have made use of vegetation to manipulate the resin, explaining the presence of shallow vegetal imprints on the indurated adhesive (cf. the handle).

The macroscopic observation shows the adhesive has a rich load in quartz grains. No other additives, mineral or organic, are macroscopically visible.

#### *The OES sealant (Fig. 4)*

The third artifact is much younger than the other two and comes from a stratigraphic unit (DOLL) with an uncalibrated radiocarbon date of 950 years b.p.

The piece is an angular fragment of an ostrich eggshell water flask, with a maximum width of 36 mm and a maximum length of 25 mm. The light color of the surface of the eggshell suggests the OES has not been affected by post—depositional burning. Both perforation and macro—residue predate the breakage of the eggshell.

The presence of a perforation shaped by percussion indicates the OES was used as a flask or a container, presumably holding fresh water. The edge of the perforation is well polished, suggesting repeated contacts with another medium. The diameter of the perforation is estimated to be 10 to 12 mm. Although the fragment is small, its natural curvature suggests the hole was opened on the apex of the eggshell. No engravings or scratches are observed on the surface of the eggshell. So far, no engraved OES has been found in the related archaeological layers, which is consistent with the regional record. Generally in the Western Cape coastal region, terminal Holocene ostrich eggshell water flasks are not marked, although in the earlier Holocene such marking ('decoration') is more commonly found.

The macro—residue circling the perforation is of very dark grayish brown color (Munsell soil color chart: 10YR3/2), with a portion being even darker. The adhesive extends strictly on the external surface of the OES and almost reached the edge of the perforation. The macro—residue forms a strip with a regular width of about 10 mm. The maximum thickness of the macro—residue is on the middle of the strip and is about 2 mm. Some cracks are observable, as well as quartz grains and small fragments of shell (less than 2 mm).

Other examples of OES flasks with adhesive circling the perforation are known from the sites of Connies Limpet Bar (Parkington 2006) and Thoma's Farm (Henderson 2002). Some of them have even been found with a vegetal cork that was used to seal the flask. From that perspective, the role of the adhesive is to ensure the impermeability of the cork. In our studied case, this hypothesis is directly supported by the functional traces observed on the hole, which is well polished on its whole thickness, suggesting a cork was sunk inside the hole and removed several times.

The adhesive is well smoothed which indicates it was applied and manipulated directly by hand while the adhesive was still malleable. The adhesive looks very resinous and includes small quartz grains, shell fragments as well as one isolated small charcoal.

## ANALYTICAL METHODS

Having described the three organic artefacts under study, we propose to refer to them afterwards simply as: the 'handle', the 'grip' and the 'sealant'. We move from description of form to shorthand that refers essentially to the functional use of the pieces.

Protocols applied to archaeological pieces were adapted in order to minimize the quantity to be analyzed. For the handle, two samples were analyzed with the aim to highlight variations in manufacture or alteration. One of these two samples come from the outside layer and weight 5

mg, the other comes from the medium layer and weights 4.6 mg. Both samples originate from the top of the handle, already partly broken. For the grip, one sample of 4 mg was analyzed and for the sealant, one sample of less than 1 mg was analyzed. For these two specimens, samples were taken from broken parts.

#### *Recent resins*

The set of archaeological samples was complemented by a recent local resin originating from *Heeria argentea* (common name: Kliphout, Rockwood) that exudes spontaneously from the tree and by a dichloromethane/methanol (60:40 v/v) extract of recent bark from *Podocarpus elongatus* (common name: Yellowwood), both collected in South Africa. These two taxa are known sources of exploitable resin (Langenheim 2003): they still exist in the site area and were identified in the charcoal from both “Joe Frazer” (JOFR) and “Dolly” (DOLL) layers (Cartwright et al. 2014). They belong to two different plant families, easily distinguished based in their molecular composition in terpenic components (Mills & White 1977; Langenheim 2003). *P. elongatus* (Podocarpaceae family) is a part of Gymnosperm group (naked seed—producing plants) characterized by diterpene molecular markers (skeletal comprising 20 carbon atoms and up to three cycles). It is clear that the composition of the bark extract and the resin may differ, but the biomarker families of *P. elongatus* must be identical and present in each. *Heeria argentea* (Anacardiaceae family) belongs to dicotyledons Angiosperms (flowering plants), characterized by triterpene molecular markers (skeletal with four or five cycles comprising 30 carbon atoms).

#### *Reagents*

All solvents were HPLC grade (Sigma Aldrich, purity: 99.9%) and were used without further purification. Pyridine and *N,O*—bis(trimethyl)silyltrifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) were purchased from Sigma Aldrich. To avoid any contamination, only dichloromethane cleaned glassware was used. Silica gel, cotton and Fontainebleau sand were extracted in soxhlet with dichloromethane.

#### *Extraction, purification, silylation*

The resins and the macroresidues finely ground in an agate mortar were fully solubilized ultrasonically for 5 min with dichloromethane. After concentration under nitrogen flow the organic extract was purified by gravity flow column chromatography (silica gel support, eluents: dichloromethane/ethyl acetate 50:50 v/v and dichloromethane/methanol 60:40 v/v). The combined elution fractions were again concentrated to dryness. Resulting extract was then engaged in the silylation reaction. 40 $\mu$ l pyridine and 200 $\mu$ l BSTFA with 1% TMCS were added. The reaction medium was heated for 2 hours at 70 °C and then evaporated to dryness before being injected in GC—MS.

#### *ATR — FTIR analysis*

Samples were directly deposited on the measuring cell. Absorbance was collected in the range of 4000 – 400  $\text{cm}^{-1}$  with 4  $\text{cm}^{-1}$  resolution at a temperature of 18°C. ATR cell of the Bruker Alpha spectrometer consists of a diamond platinum crystal.

#### *Mass spectrometric analysis*

GC—MS analyses were carried out using a Focus GC gas chromatograph interfaced with an ISQ mass detector ThermoScientific (splitless mode injector, HP–5 MS column, 30 m x 0.25 mm i.d., 0.25  $\mu$ m film thickness, temperature program: 40°C (1 min), 40–100°C (10°C/min), 100–320°C (4°C/min), isothermal 320°C (30 min). GC—MS interface was set at 320°C. Helium was used as carrier gas (1.5  $\text{mL}\cdot\text{min}^{-1}$ ). Mass spectra were produced at 70eV, source 180°C, in full detection mode over 40–800 amu. Peak assignment was based on interpretation of mass spectra and comparison with spectra available in literature and NIST library 2.0.

The matrix assisted laser desorption—ionization mass spectrometry (MALDI—MS) analyses were conducted on a Bruker Autoflex II MALDI — Time of Flight (TOF) — mass spectrometer (Bruker Daltonics, Bremen, Germany). The device was featured with a pulsed nitrogen laser emitting at 337 nm and operated at an extraction voltage of 20 kV. The samples were dissolved in a mixture acetonitrile/methanol 1:1 (v/v) with 0.1% trifluoroacetic acid (TFA) and deposited on a stainless steel target as dry droplets with a saturated solution of sinapic acid (SA) in the same mixture. Gated suppression was applied in order to prevent any saturation of the detector by matrix ions. A total of 1,000 laser shots were averaged for each spectrum and acquisitions were realized in reflector mode with positive ionization, with a laser power optimized and kept constant for the different samples. Bruker Pepmix II was used for calibration and spectra were processed with the Bruker FlexAnalysis software (version 3.4).

## RESULTS

### *Preliminary analysis by ATR—FTIR*

For a long time, FTIR has been used extensively in an archaeological context for the study of adhesives (e.g. Masschelein—Kleiner et al. 1968). Especially in ATR mode, this technique has the advantage of being non—destructive and the sample in powder form can be recovered. It is particularly suited to the analysis of pure organic materials with a low level of alteration. The presence of an inorganic base can indeed hide the organic signal and only the major components will be detected. Based on intermolecular bonds and on the presence of specific functional groups, it provides access to a diagnostic fingerprint of various natural substances such as resins or waxes and is useful for initial interpretations.

According to literature data and reference spectra available in the laboratory, the spectra of dichloromethane extract from *Heeria argentea* resin and samples from the handle and the grip show a typical absorbance profile of a vegetal resin (Derrick et al. 1999; Colombini et al. 2009). The carboxylic acids present in resins leads to strong C—H and C=O stretching vibration ( $\nu(\text{C—H})$  at 2927 and 2868 $\text{cm}^{-1}$ ,  $\nu(\text{C=O})$  at 1706 $\text{cm}^{-1}$ ). Other bands can be clearly assigned: O—H stretching at 3420  $\text{cm}^{-1}$ , aromatic ring stretching at 1607  $\text{cm}^{-1}$ , CH<sub>2</sub> and CH<sub>3</sub> bending at 1459 and 1367  $\text{cm}^{-1}$ , O—H bending at 1264  $\text{cm}^{-1}$ , C—O stretching and bending in the range 1281–1198  $\text{cm}^{-1}$ .

Unsurprisingly, the bands corresponding to oxygenated functionalities are more important in archaeological samples against fresh resins, reflecting a higher degree of alteration. They will also appear more clearly from the film surface than in the core of the handle.

### *Molecular analysis by GC—MS*

The biomolecular approach used in this study is based on the identification of diagnostic molecular markers also called biomarkers derived from naturally—occurring substances by the means of mass spectrometric techniques (Charrié—Duhaut et al. 2009). The resulting diagnostic molecular fingerprints permit us both to define the biological origin of pure natural products or in admixture (plant, animal, families, and species) and to evaluate states of alteration (natural ageing or anthropic transformations). In the particular case of resins, specific series of terpenic skeletons are characteristics of plants families, or even of genera and species (Mills & White 1977; Langenheim 2003). This will be illustrated below by comparing the molecular fingerprints of the two recent plant samples of known taxonomy and used as reference. This also explains why it is so essential to identify precisely the carbon skeleton of the components present in archaeological samples. Indeed, even if changes of functional groups occur, cyclic carbon structure is preserved. The latter can be used as a molecular marker to connect a degraded substance in archaeological context to its recent equivalent and to get an idea of the transformation processes that took place (Lampert et al. 2002; Burger et al. 2011; Charrié & Leprovost 2012; Charrié—Duhaut et al. 2013.).

### *Heeria argentea* and *Podocarpus elongatus*

*Heeria argentea* is a South African endemic, specifically in the Western Cape area. Few studies of this taxon are reported in the literature and no molecular markers are described to the best of our knowledge, unlike *Pistacia* genus which is another member of Anacardiaceae family but not native to South Africa. The GC—MS total ion current traces of the silylated total extract consist mainly of triterpenoid structures (Fig. 6). The presence of such tetra— and pentacyclic components with retention time greater than 50 minutes provides evidence for an Angiosperm contribution and is expected for a plant from the Anacardiaceae family. The major compounds are based on euphane skeleton with a hydroxyl group at position 3 and double bonds in the ring B and in the side—chain (Appendix A) such as lanosterol. The pentacyclic triterpenoids belong to both oleanane and ursane families ( $\beta$ —amyrin and  $\alpha$ —amyrin respectively). Stigmasterol derivatives ubiquitous in higher plants were also detected.

As expected, the GC—MS total ion current trace of the silylated total extract of bark from *Podocarpus elongatus* is more complex (Fig. 7). Linear structures (acids, alcohols) and components derived from sitosterol / stigmasterol generally observed in higher land plants such as stigmasta-3,5-dien-7-one, are present. Saccharides whose origin is certainly the cellulose of the bark are also detected. Concerning terpene skeletons, only phenolic diterpenic structures are present (retention times between 30 and 45 minutes). These latter compounds are used to precisely define the biological origin of natural substances. As mentioned above, diterpenic biomarkers indicate a Gymnosperm contribution, mainly conifer precursors. The specific molecular fingerprints of abietane skeletons are used to distinguish the different families in the group of conifers, especially of southern hemisphere conifers resins: Araucariaceae, Cupressaceae, Pinaceae, Podocarpaceae, Taxodiaceae (Mangoni & Caputo 1967; Bendall & Cambie 1995; Otto & Wilde 2001; Langenheim 2003; Cox et al. 2007). The basic principles are for instance: “phenolic” abietanes divided into three groups according to the position of substituents on the aromatic ring (totarol, sempervirol, ferruginol) are absent in Pinaceae, predominance of ferruginol derivatives associated with totarol and sempervirol derivatives characterize Cupressaceae family, totarol and ferruginol are biomarkers for Podocarpaceae. We should also mention that the distinction of compounds belonging to all three families of “phenolic” abietanes is not easy because of the similarity of mass spectra and therefore special care must be taken for precise structural identification (Enzell & Wahlberg 1970). As an example, according to Cox et al. (2007), the distinction between the three diagnostic unsubstituted phenols (totarol, ferruginol, sempervirol) is based on the intensity of the fragment  $m/z$  247 compared to the fragment  $m/z$  261 (Fig. 8), which is much more important for the totarol and this is indeed the case in this sample. The major components of the extract of present bark are totarol, 3-ketototarol (prominent M-57 ion in the fragmentation pattern *ie*  $m/z$  315), 3-hydroxytotarol (prominent M-15-90 ion in the fragmentation pattern *ie*  $m/z$  341), 4-carboxynortotarol (prominent M-15-118 ion in the fragmentation pattern *ie*  $m/z$  327), 3-hydroxy-4-carboxynortotarol and 3-hydroxyferruginol. This molecular fingerprint is that expected for *Podocarpus elongatus*.

### *The handle*

The GC—MS total ion current traces of both outside and medium layers display a relatively small number of compounds with similar retention time. The compounds are divided into two main groups. The first with retention time between 50 and 60 min corresponds to the compounds of the family of sitosterol and stigmasterol. As before, they are indicators of higher land plant material. The second consists of diterpene structures related to totarol (Fig. 9a–b). The distributions are, however, quite different from that observed in bark extract described above. Regarding first the middle layer, totarol is still detected but is not at all major as in the bark. Only another compound is common to both: 3-ketototarol. Other structures based on totarol

skeletons include more oxygen functionalities. Although little information on these oxidized components is available in the literature, structural proposals can be made on the basis of mass spectra. Derivatives with a carboxyl group at the 19-position and/or a ketone at the 7-position appear mostly (Fig. 9a–b). The major compound is the 4-carboxy, 7-ketototarol. From a chemical point of view, the benzylic position of phenolic structures (the 7-position) is extremely sensitive to oxidation. So it is no surprising to find such degradation byproducts, easily formed both by anthropogenic transformations or natural ageing. Although having a different physical appearance, molecular fingerprint corresponding to the outer layer has little difference with respect to the middle layer. Only small differences in intensity are visible. The material constituting the handle is therefore *Podocarpus* resin. No other component seems to be present as no other biomarkers appear on the GC—MS traces.

#### *The grip*

The GC—MS total ion current trace corresponding to the leaf handle is very similar to the preceding ones and is clearly related to *Podocarpus* resin (Fig. 9c). As mentioned above, no other biomarkers were detected, indicating the use of pure plant material. There is no indication of heating.

#### *The sealant*

Despite the small quantities available, the applied protocol allowed the precise molecular composition of this coating to be established. A diterpenic distribution related to the family of totarol similar to that presented above is clearly observed indicating once again the contribution of a *Podocarpus* resin. This sample differs from the previous as linear structures are clearly present (Fig. 10a). Their fingerprint is dominated by linear monocarboxylic acids (even predominance, ranging from C<sub>14</sub> to C<sub>18</sub>, presence of the mono—unsaturated C<sub>18</sub> acid) and linear alcohols (even predominance, ranging from C<sub>14</sub> to C<sub>18</sub>). Only one linear diacid ( $\alpha,\omega$ -dicarboxylic acid) is detected in low abundance: this is the term C<sub>9</sub> also called azelaic acid. Such structures are usually fat characteristics. Based on the GC/MS data, it is very difficult to accurately determine its biological origin. This is especially true when the level of degradation is high. Indeed alteration processes lead to the loss of molecular markers allowing for example to differentiate a plant oil from an animal fat (Bastien 2011). The hypothesis of an animal fat is however encouraged by the fact that very few unsaturated fatty acids and diacids (their degradation products) are present (almost absent). Contribution of external contamination cannot be excluded. This fingerprint is strongly different from the one observed in a hafting adhesive at Diepkloof Rock Shelter (Charrié—Duhaut *et al.* 2013), where linear diacids predominate linear monocarboxylic acids. It also doesn't correspond to the distribution of linear structures shown by Villa *et al.* (2012) suggesting the presence of bio—polyester derived from suberin. Further analysis would need to be undertaken to achieve for the biological origin of fat (measurement of carbon isotopic ratio <sup>13</sup>C vs <sup>12</sup>C of the fatty acids for instance).

#### *Resin or tar?*

The various studies on archaeological plant residues always raises the question of the use of an optionally heated resin or of making a tar? This is especially true when corresponding charcoals are found on the site. This involves different technologies, know—how and therefore cognitive functions. At the macromolecular as well as molecular level, it is difficult to distinguish. However some indications are in favor of one of the two assumptions. Plant tars are obtained by heating wood under reduced oxygen atmosphere. Some have been widely used since ancient times as the well—known pitch deriving from *Pinaceae* or the birch bark tar. The intense heating required to produce tar is accompanied by an aromatization of compounds through thermal dehydrogenation or decarboxylation (Robinson *et al.* 1987; Bailly 2015). This modification of the molecular composition demonstrated for pitch or birch bark tar should be present if *Podocarpus* wood was

intensively heated to produce tar. Such aromatic structures were not detected in the samples from EBC. Another clue for molecular characterization of tar is the identification of molecules resulting from thermal degradation of the cellulose and lignin such as phenolic dimers (Bailly 2015), which is not the case in this study. According to Villa et al. (2012), suberin—containing pitch is also characterized by the presence of linear monocarboxylic acids and  $\alpha,\omega$ -dicarboxylic acids. Low abundance of these compounds has been detected in the OES sealant, which also contains fat, and are absent in the two other samples. MALDI—MS analyzes were undertaken to provide additional data on this specific issue. The mass spectra acquired for tars (analyzes performed on reference and archaeological birch bark tar and ancient pitch) show a regular distribution typical of a polymer. This is probably a lignocellulosic polymer finding its origin in the use of wood as raw material. This distribution is not found in the resins or in the tear—drop shaped handle from EBC. In the mass spectrum corresponding to this sample only diterpenes, more or less oxidized, appear (Fig. 11). For the three samples from EBC, it is reasonable to conclude in favor of resin rather than tar, resin that could have been slightly heated to gain malleability. Indeed, moderate heating probably induces little change in the molecular composition of the resin and will be very difficult to demonstrate.

## SYNTHESIS AND MAIN IMPLICATIONS

Even if the pieces studied differ in terms of form, function and chronology, the *chaînes opératoires* present certain similarities. First of all, our results indicate a common use of *Podocarpus* to create adhesive. As charcoals from *P. elongatus* were found on the site (Cartwright et al. 2014), we hypothesize that this species likely provided the resin used. However, other species of *Podocarpus* exist in South Africa (*P. falcatus*, *P. latifolius*) and distinction between species on the basis of biomarkers needs further clarification. Furthermore, terpenoid resins are quite resistant to natural decay, which is not the case of other natural substances like proteinaceous binders or plant gums. This may result in a preferential preservation of the resins and we must keep in mind that the *chaînes opératoires* could be more complex.

The resin was mixed with a load of quartz grains in varying amounts. One fragment of shell found in the sealant would suggest the mineral load might have been acquired directly on the Atlantic beach at the foot of the shelter. Though we ignore the exact protocol, the transformation of the resin requires it to be heated for softening, until the right consistency and transformation are achieved. Our observations converge to recognize that the adhesive was malleable and not liquid when applied. Rare fragments of charcoals observed in two of the three artefacts might suggest the adhesive was heated during its application, possibly in direct contact with embers and purportedly to control softening. The application and shaping of the adhesive were likely made by hand. The presence of vegetal imprints on the two handles suggests their use was part of the process of modelling.

Macroscopically, no ochre or bone fragment has been observed. But the fingerprint of the sealant indicates the presence of (animal?) fat. While we cannot avoid the possibility that this results from pollution, we have to acknowledge the peculiarities required by the process of sealing in terms of properties. Unlike the other two pieces where adhesive exist as a solidified form, the seal needed to be “sticky”. The addition of fat, during manufacture or during use, could have been part of the recipe to create and keep the properties of that adhesive.

There are other artefacts from EBC that reflect the use of adhesive. This is the case for a few adzes, which are tools that have supposedly been used in woodworking activities. The presence of macro—scars on the working edges suggests adzes were involved in a hard motion requiring the use of a haft. The manufacture and use of wood and bone handles and hafts are inferred from many archaeological contexts but direct observations are few. Part of the explanation for this might lie in our results here, as the Holocene record of EBC indicates that

hafting technology was commonly made up only of adhesive, at least for tools that were involved in (light) domestic activities such as cutting.

Our record adds substantial data to the discussion on composite technologies, microlithic and interchangeable tools. When there is use of a haft, the adhesive is here to ensure the good maintenance of the haft and the tool. In that case, the shape of the tool has to adapt to the handle, which contributes to normalize the production. In our examples, the grip adhesive and the microlithic backed piece form one single piece. In other words, the shape has not been influenced by the need of interchangeability: this was an ad hoc wrapping of adhesive finger protection around a specific quartz segment.

While there are many debates about microlithic backed tool manipulation and use, this piece provides a good example that microlithic and geometric tools do not need automatically implicate their use in projectiles. The microlithic backed tool from EBC described here was used as a knife, in longitudinal action, just being wrapped into an adhesive in order to protect the hand and facilitate its prehension. As emphasized in many other contexts, microliths are not monolithic tools used in only a limited way (Elston & Kuhn 2002; Wadley & Mohapi 2008; Porraz et al. this issue) and could have been involved in a whole range of activities including hunting and domestic tasks.

## CONCLUSION

South Africa is characterized by a rich ecological diversity and includes different ecozones that define a wide range of constraints and opportunities, fueling the question of how hunter—gatherers adapted and diversified their practices. Archaeologically, one scientific advantage lies in the quality of the organic preservation, with Late Pleistocene plant remains being well documented and studied.

The study of archaeological plant remains, predominantly found in the form of charcoals, seeds and more occasionally as leaves, allows different kinds of investigation and interpretation (Sievers & Muasya 2011; Wadley 2012; Lennox & Bamford 2015; Sievers 2015). While these plant remains are good indicators of past environments, they also document a suite of behaviors that can be interpreted with reference to their known properties (as poisons, repellants, medicines, hallucinogens, etc.). Although these interpretations are no demonstration, the set of archaeological observations grows and converges to indicate that some plants were preferentially selected, suggesting some properties were understood and researched by hunter—gatherer groups. Our study on Holocene adhesive brings a new kind of evidence on how hunter—gatherers used and took benefits from their environments.

There are uncertainties regarding the recipes, the exact nature of the *chaînes opératoires* as well as the importance of each step during the adhesive's manufacture. This process of clarification requires a large set of experiments in order to evaluate the nature of the pyrotechnic management and in order to discriminate what reflects choices and preferences and what relates to constraints. This process of understanding also requires a larger set of archaeological observations, starting with macroscopic descriptions. Adhesives are recorded in different sites of South Africa, with many examples found in LSA contexts. Presently, the use of adhesive has been recorded for three types of functional tasks: 1) to glue tools into their haft, 2) to create handles, 3) to seal OES containers (as strips to seal flasks, as cork or as spout). But within these broad categories, variability in recipes is expected.

The impact of mastering adhesive manufacture could have had major effects on other technologies and could represent one of the key innovations from the Late Pleistocene. Among the different properties that could characterize an adhesive, malleability appears to be a key property that could have durably influenced the technology of past hunter—gatherer groups.

One biomolecular analysis of adhesive presently done in South Africa relates to the Late HP of Diepkloof and dates back to ca 55,000 years ago, although evidence of adhesive use at the site goes back much earlier in time (Igreja & Porraz 2013). These analyses have recognized *Podocarpus resin* as the organic substance that was used to produce adhesive (Charrié—Duhaut et al. 2013). Similarly, 2000 km east of Diepkloof, the analysis of an adhesive coming from the Early LSA layers of Border Cave, dated to 43,000 BP, also demonstrates a composition based on *Podocarpus* (Villa et al. 2012). Our analysis from EBC expands this suite of observations and recognizes *Podocarpus* as the natural substance used to create adhesive during the Holocene of the West Coast of South Africa. These independent results converge to recognize that the resin of *Podocarpus* was preferentially collected by South African hunter—gatherers to produce adhesive since, at least, the MIS 4. We argue that the exploitation of *Podocarpus* may represent a lasting tradition and adaptation that is similar to the one recorded in Western Europe where birch is well known for having been used preferentially by prehistoric groups (Regert 2004). The use of *Podocarpus* resin would represent a knowledge that transcended changes in technological traditions.

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