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Radiocarbon-dating adhesive and wooden residues from stone tools by Accelerator Mass Spectrometry (AMS): challenges and insights encountered in a case study

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ABSTRACT

In this study we present and assess a process to enhance archaeological residue AMS dating by focusing on contaminant confinement. The sequence of methods applied consists of: 1) optical residue and use-wear analyses, 2) experimental designs addressing cleaning treatments to mitigate impact of contaminants, 3) preparation and extraction of residues from (mostly) previously dated stone artefacts, and 4) establishing the elemental characteristics of residues by using SEM/EDX as a final step to avoid sample contamination during analyses. We found the alkaline surfactant Decon 90 is a useful solution for removal of skin scales and fabric fibre but has limited effect on graphite contamination introduced by pencil lead. Adhesive residues were not affected by Decon immersion, however, wooden residues from bog sites were partly dislodged. While the methodological sequence was in general successful and some artefact residues were dated within the anticipated age range, difficulties were encountered with other lithic residues. Some artefact residues attained AMS dates which appear to be affected by modern contaminants and other residue radiocarbon dates were seemingly affected by fossil shell derived from flint stone, plasticizers or from a fixative substance older than the fabrication and use of the artefact. One outcome from this study is that performing chemical residue identification earlier in the method sequence using non-destructive and non-contaminating methods would guide the choice of residue treatment and improve reliability of age determination.

1. Introduction

Direct dating of artefact residues has the potential to provide archaeologists with new chronological information. Accelerator Mass Spectrometry (AMS) radiocarbon measurements can be made on samples containing as little as 5 μg or less of carbon ('μgC') (Smith et al., 2007, 2010a, 2010b; Yang et al., 2011) and in principle this allows very small amounts of residues from stone tools to be radiocarbon dated. In a pilot study, we demonstrated the feasibility of direct residue dating under laboratory conditions with only 10.5 μgC obtained from wooden residues (Yates et al., 2014). One of the key limitations, however, was the impact of contamination due to the extremely low mass used for the dating. Fungus and soil components can be easily transferred into archaeological residues during handling and storage (e.g. Barton, 2009: 134 Wadley and Lombard, 2007: 1003; Langejans, 2011). This highlights the need to develop preparation and removal protocols for accurate AMS dating.

In our pilot study, we also suggested that a next step after experimental residue dating should be to date well-preserved residues from artefacts that are stratified and well dated, so as to verify the methodology. For this study, we obtained seven stone

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tools with associated age determinations from three archaeological assemblages. Five artefacts from Friesack, Germany were selected for two reasons: first, a use-wear residue analyses conducted on 306 stone tools revealed frequent preservation of hafting residues (adhesives) along with plant remains from wooden shafts (Pawlik, 2011a); and second, Gas Chromatography Mass Spectroscopy (GC/MS) analyses on four samples (three pieces of tarry black material, two of which had chewing marks, and one sample of tarry dark material adhering to a bone point) revealed birch bark tar was used at the site (Baumer and Dietemann, 2008). This provided an indication of the likelihood of finding this hafting fixative on lithic tools. Two stone tools, one from Wesseling, Germany, and one from Yelgun, Australia, were chosen because they exhibited macroscopically visible dark residues resembling adhesive residues. This case study aimed to test the feasibility of radiocarbon dating adhesive and wooden residues from archaeological stone tools and at the same time to reduce contamination by finding adequate removal techniques.

Adhesive residues have the advantage of having a tough texture, and wooden residues have been dated successfully in the above mentioned study. Both residues have been found preserved under various conditions. However, adhesive residues are commonly preserved in higher quantities than other residues, allowing replicate radiocarbon dating. This fact is significant because different kinds of adhesive residues are preserved worldwide and the possibility of directly dating minute amounts would provide archaeologists with a new way of determining age. By choosing adhesive residues for radiocarbon dating, we aimed to establish protocols which then can be transferred and adjusted for other scarcer residues.

Archaeological adhesives function to a large extent as fixatives for lithics to hafts of wood, antler or bone. In Europe, birch bark tar (also known as birch pitch) is reported as a common hafting fixative. So far the oldest examples have been found at Middle Paleolithic sites (Mania and Toepfer 1973; Hedges et al., 1998: 229; Grünberg, 2002; Grünberg et al., 1999; Koller et al., 2001; Mazza et al., 2006; Pawlik and Thissen 2011), followed by Mesolithic sites (e.g. Aveling and Heron, 1998; Clark, 1954; Pawlik, 1997, 2004) and from sites from the Neolithic period onwards (Charters et al., 1993; Müller-Beck, 1965; Regert et al., 1998, 2003; Urem-Kotsou et al., 2002).

In the Near East, tar or pitch produced from naturally occurring bitumen is reported as hafting cement and is also evident from the Middle Paleolithic period (e.g. Boëda et al., 1996, 2008; 2009; Hauck et al., 2013; Monnier et al., 2013).

The use of *Podocarpus elongatus* (Yellowwood) with regionally different hafting technologies has also been documented in South African sites (Charrié-Duhaut et al., 2013). In the Diepkloof Rock Shelter, the adhesive was associated with the Howiesons Poort and was mixed with bone and quartz grains while in the Sibudu Cave, ochre was found as an additive (Lombard, 2006, 2007; Wadley et al., 2009). Underneath plant residues found on segments in the Sibudu Cave, 67% consisted of resin or gum (Lombard, 2008). Furthermore, there is variability in haft materials through time. These analyses suggest the oldest tools have been hafted to bone and the younger ones hafted to wood (Lombard and Wadley, 2009).

In Southeast Asia, resinous residues probably from *Shorea* spp., *Agathis* spp., or *Canarium* spp. were found on lithic implements from terminal Pleistocene layers at Ille Cave, Palawan (Pawlik, 2011b), and have also been identified on stingray spines used as hafted projectile points in the terminal Pleistocene at Niah Cave, Borneo (Barton et al., 2009).

In Australia, the use of various resin types is reported. Two of the more common ones were derived from a grass tree (*Xanthorrhoea*) (e.g. Cribb and Cribb 1982: 89; Leiper, 1982; Zola and Gott 1992: 59) and from Spinifex (*Triodia pungens*) (Gamage et al., 2012; Mondal et al., 2012), (*Triodia iiritans*), (e.g. Boot, 1993: 5). Other Australian resin types reported as cement for hafting stone implements to wooden handles include beefwood *(Grevillea striata)*, sugarwood (*Myoporum platycarpum*), cypress pine (*Callitris collumellaris*), and kurrajong (*Brachychyton populneus*) (e.g. as described in Boot, 1993: 5).

1.1. Archaeological study sites

1.1.1. Friesack 4

Friesack 4, a bog site located in Brandenburg (Germany), was occupied for approximately 3200 years and contains 100 Mesolithic layers identified in 6 different trenches. According to radiocarbon dates, Mesolithic settlement first began in the middle Preboreal period around 9000 cal BC and ended around 5800 cal BC during the Early Atlantic period (Gehlen, 2009; Görsdorf and Gramsch, 2004), with a hiatus of several hundred years during the middle Boreal period. To date, this represents the most detailed stratigraphy known from the Mesolithic period in Europe. The excellent preservation conditions revealed numerous wooden and antler objects as well as thousands of bones and 140,000 stone artefacts (Gehlen, 2009; Gramsch, 1990, 2001, 2006, 2009/2010, 2011).

1.1.2. Wesseling

The open site of Wesseling is located within an old channel of the Rhine River in the western part of Germany. Excavations revealed 6 activity zones with typical late Paleolithic stone tools such as backed points, backed knifes, scrapers and burins. The site also contains pebble plasters interpreted as working areas, several sandstone grinding plates and flat, geometrically-shaped, brown coal objects (Heinen, 2008; Heinen et al., 2010). Four AMS radiocarbon dates suggest an approximate date of ~11,500 BP for the site's occupation (AMS-Labor Erlangen, 2010).

1.1.3. Yelgun

Yelgun, in north-eastern New South Wales, Australia, is located on a ridgeline overlooking a coastal shoreline and plain. The site consists of a stone artefact scatter of 159 lithic tools and 60 ochre pieces. Artefacts include cores, flakes, scrapers, ground edge tools and are held in a private collection. Eight stone artefacts of the bungwall pounder type (e.g. Hall et al., 1989) possibly suggest a late Holocene age for the site.

2. Materials and methods

Seven stone tools from the three sites were analyzed in this study. Table 1 provides information about the lithic type, inherent residues and methods applied. In the following sections, these methods are described in the sequential order they were applied to the stone tools. An exception is the experimental design (Section 2.3) in which only modern fabricated artefacts were utilized.

2.1. Remarks on conditions of GC/MS analyses previously carried out on Friesack samples

From the four Friesack samples small fractions were gradually extracted using the solvents isooctane, methanol, chloroform and methanol-oxalic acid. The extracts were then injected directly and as a derivative (methylation with TMSH) into the gas chromatograph–mass spectrometer combination and subsequently analysed (Baumer and Dietemann, 2008).

An Agilent GC 6890 N gas chromatograph was coupled with an Agilent MSD 5975 quadruple mass spectrometer; the GC was equipped with J&W capillary column (DB5-ht, 30 m, 0.25 mm ID, film thickness 0.1 μm). Helium was used as the carrier gas at a flow

Table 1
Summary of archaeological samples and preparation protocol.

Archaeological sample/type	Origin/ID	(Anticipated) Age	Optical res. interpret.	Pre-treatment	Extraction/Removal by	ANSTO ID of AMS dated samples	SEM-EDX remain. residues
Water rolled cobble with dark residue patches	Yelgun, NSW, Australia	Late Holocene Late Holocene	Adhesive material	2% Decon90, 2 M HCl	Scalpel scrape off Scalpel scrape off	OZQ696-U1 OZQ696-U2	Yes
Flake with dorsal dark residue concentration	Wesseling, Germany (NW 2008/1001)	~11,500 BP ~11,500 BP	Adhesive material	2% Decon90	Scalpel scrape off DCM penetration	OZQ695-U1 OZQ695-U2	Yes
Flake fragment with dark residue concentration	Friesack, Germany (C3/S_9b)	9640 ± 60 BP 9640 ± 60 BP	Adhesive material (also Pawlik 2011a)	2% Decon90	DCM immersion, ultrasonication DCM immersion, AAA	OZQ694-U1 OZQ694-U2	No
Core axe with use-wear associated wood fibres on both working ends (Further wood and adhesive-wood mix discovered after Decon treatment)	Friesack Germany (D5/7)	Between 9000 and 9250 BP Between 9000 and 9250 BP	Adhesive material clinging to wood Wood	2% Decon90, AAA	Sample was tweezer picked from tool, immersed in DCM dried down in combustion tube Tweezer picked from beaker, after Decon cleanse	OZQ689-U1 OZQ689-U2	Yes
Core axe with use-wear associated wood fibres on both working ends	Friesack, Germany (B2/7)	~9200 BP	Wood, (also Pawlik 2011a)	2% Decon90, AAA	Pick out wood from Decon solution	OZQ690	No
Core axe with use-wear associated wood fibres on both working ends	Friesack, Germany (25_10b)	9–10,000 BP	Wood, (also Pawlik 2011a)	2% Decon90, AAA	Scalpel scrape off	OZQ691	No
Scraper with use-wear associated wood fibre	Friesack, Germany (CO15/8a)	9640 ± 60 BP	Wood	2% Decon90, AAA	Pick out wood from Decon solution	OZQ692	No

rate of 1.5 ml/min. Samples were introduced via splitless mode in the injection port at a temperature of 250 °C. The column temperature was initially held at 55 °C for 2 min then increased to 360 °C at a rate of 10 °C/min. The GC/MS interface temperature was set at 280 °C. The ionisation energy was 70 eV and the ion source was set at 250 °C under electron ionisation (EI) conditions. The scan range was from 40 to 500 m/z. The GC/MS interface temperature was set at 280 °C. Output files were analyzed using NIST98 Mass Spectral Database (further analysis details in Koller and Baumer, 2010).

GC/MS requires small amounts of pure organic material (~1–0.5 mg) (personal communication Baumer) that will be dissolved in the analyses process. The method is therefore considered destructive.

2.2. Optical residue and use-wear analyses

Initially, the seven stone tools were examined by using a low-power light microscope (stereo microscope, Olympus, CX40) with microscope photography (Olympus DP12) at 7× to 115× magnification ranges and high power light microscope (Olympus BX51) with microscope photography (MicroPublisher5.0 RTV) up to 1000× magnification ranges.

Edges, dorsal and ventral surfaces from flakes and at least two surfaces from core tools were examined. The occurrence of residues and use-wear traces was mapped, recorded, imaged and described.

After chemical treatment and removal methods were applied, each artefact was examined again to assess the quantity of residues left and potential changes to the stone tools' surfaces.

Visual residue and use-wear classification was conducted using established analytical criteria and compared with published material (e.g. Fullagar, 2006; Haslam et al., 2009; Hardy and Garufi, 1998; Lombard, 2008).

2.3. Experimental design to establish decontamination protocols

The optical analyses showed that besides archaeological residues, some artefacts exhibited pencil graphite markings that could potentially contaminate sampling for AMS dating.

To overcome graphite contamination an experiment was set up to test graphite removal methods which simultaneously preserve birch bark tar residue. This experiment involved the production of ten stone flakes and birch bark tar as well as the use of several cleaning methods.

Modern birch bark tar was produced by using sealed steel-sheet containers (5 cm diameter, 10 cm length), also known as retorts (e.g. Weiner, 1988, 1991), filled with birch bark rolls. The containers were placed in a charcoal fire for 15 min at 300–350 °C which transformed the bark into a viscous substance (~50% yield from original bark material). The still warm tar was then chewed to eliminate charcoal remnants and to homogenize the substance. The so processed substance was formed into lumps which were stored for further processing. This production procedure relied on inferred prehistoric conditions inspired by Mesolithic and Neolithic birch tar pieces with chewing marks and birch bark tar production experiments (Aveling and Heron, 1998, 1999; Charters et al., 1993; Palmer, 2007). Hardened modern birch tar was made viscous by holding it under a flame. The viscous mass was then deposited on the right margin of the proximal ventral surface of ten replicated chert flakes. In addition, five graphite marks were sketched onto the fabricated chert flakes – two from a 2B pencil, two from an HB pencil and one from a 2H pencil (using Faber Castell and Staedtler pencils). Pencil types were selected according to specifications given by stone tool graphic artists.

Decon 90 (2% + 5% diluted), acetone, 2 M hydrochloric acid (HCl), 2 M sodium hydroxide (NaOH) and an ultrasonic bath (LEO Ultrasonic Cleaner, LEO-50) were trialed for cleaning the artefacts prior to sampling. Decon is in common use in the ANSTO laboratories for cleaning equipment used in AMS radiocarbon sample preparation. With the exception of acetone (known for its degreasing properties, e.g. for removing finger grease), the remaining agents were chosen in accordance with research undertaken by Keeley (1980) and Loy (1987, 1990). While this previous research aimed to remove mineral, carbonate and extraneous organic deposits, our study aimed to understand the efficiency of each agent on graphite contamination as well as the potential damage to the deposited birch bark tar and to the stone surface. For

each method, two chert flakes were utilized. They were immersed in the respective liquid for two hours at room temperature, or sonicated in intervals up to 30 min.

2.4. Methodological approach on artefacts – preparation for AMS dating

2.4.1. Cleaning pre-treatment with Decon 90, 2% diluted

Because Decon 90 (2% diluted) delivered the best results in keeping birch tar and removing graphite in the above described experimental procedure, this agent was used on the seven archaeological stone tools to remove contamination. Each artefact was immersed in solution at room temperature for two hours.

The other methods applied to the archaeological samples are presented in Table 1.

2.4.2. Residue removal

Three removal methods were carried out: (1) removal by scraping with a fresh, unused scalpel under a microscope; (2) penetrating adhesive residues from Mesolithic and Late Paleolithic artefacts with dichloromethane (DCM), a known solvent for birch bark tar (Urem-Kotsou et al., 2002), and capturing the solution for later evaporation; and (3) some residues already dissolved in the Decon 90 (2% diluted) cleaning solution were centrifuged several times and rinsed with Milli-Q™ water.

2.4.3. AMS dating

Table 1 shows samples prepared with the acid-alkali-acid method (AAA) (2 M HCl, 1% NaOH, 2 M HCl) to remove carbonaceous contaminants such as carbonates and soluble organics. For a detailed description of the method, see Yates et al., 2014.

Residue samples were converted to CO_2 by combustion using the sealed-tube technique (Vandeputte et al., 1996) and then graphitized as outlined in Hua et al. (2001). Samples were then radiocarbon dated at the ANTARES AMS facility at ANSTO, Australia (Fink et al., 2004).

2.5. Establishing elemental characteristics of residues

A Zeiss EVOLS/15 scanning electron microscope with attached EDX was used as a means to further interpret adhesive residues. Although considered non-destructive, the analyses had to be carried out after partial residue extraction for AMS dating on the remaining residues. This was required because of potential contamination from oil vapor or carbon particles in the SEM chamber.

X ray analyses were performed in High Vacuum SEM mode whilst using a Back Scatter Detector (BSD). The high vacuum analysis was preferred to enhance accuracy. The BSD allowed interpretation of the various residues present because the differential atomic weights of materials appear in varied shades of grey. The contrast is based on detecting areas with different atomic numbered elements, e.g. more carbon-based (organic) materials look darker, while silica (from a stone tool) appears lighter.

All samples were left uncoated to avoid destruction and to allow possible further analyses using other methods. Therefore, images were taken in Variable Pressure SEM to overcome the absence of a coating. Due to the size of some artefacts, residue samples had to be extracted for analysis and were placed on aluminum stubs. Other residues attached to smaller stone tools (OZQ695) were analyzed *in situ*.

3. Results and discussion

3.1. Optical residue and use-wear analyses

Three stone tools, OZQ695 (Late Paleolithic, Wesseling, Germany), OZQ694 (Mesolithic, Friesack Germany) and OZQ696 (Yelgun, Australia) showed macroscopically visible dark-blackish residues (Fig. 1, images 1–3). These were interpreted as a form of adhesive because of their mud-cracked and smooth-droplet appearance, some of which suggested embedded plant tissue (e.g. Fullagar, 2006: 218; Lombard, 2008) (Fig. 1, images 4–15). OZQ695 showed a black residue with a partial droplet-like appearance (Fig. 1, images 4–6). Non-use related residues on OZQ695 were interpreted as graphite overlaying putative adhesive residues, modern fabric fiber and a white round mass, possibly fungus (Fig. 1, images 7–9). Dark residue on artefact OZQ694 varied in color between dark brown (in the web version) and black. The brown colored residues often appeared to have a plant tissue structure, while the darker residues had more droplet patterns (Fig. 1, images 10–12). OZQ696 showed a homogenous black residue with a smooth surface and a mud-crack structure, in this case with sediment attached (Fig. 1, images 13–15).

Examination of OZQ694 showed wear-related scars which could indicate hafting (e.g. Odell, 1994; Rots, 2010), whereas OZQ695 and OZQ696 showed no such patterns.

Wooden residues in the form of wood fiber were observed within retouch bows of the 'working edges' (Fig. 2) of the Mesolithic stone tools from Friesack. The three core axes, (OZQ689, OZQ690 and OZQ691) showed working edges on both ends, confirming previous analyses by Pawlik (2011a). Wooden residues were identified predominantly in the retouched working edge of OZQ692 (scraper), and only occasionally on other parts of the tool edge. Traces of pencil graphite were observed on the edges and tool surfaces of all four artefacts. Modern fabric fiber and hair was also found on OZQ690 and OZQ692.

3.2. Experimental design to establish decontamination protocols

A 2% Decon 90 solution proved the most effective cleaning agent for maintaining the birch tar and for weakening all degrees of graphite hardness. However, a light wipe was necessary to complete the removal of graphite from the stone surfaces. The graphite marks in the 5% Decon 90 solution were visibly faded and some smaller parts of the birch tar were removed. Sonication removed graphite marks as well as all birch tar residues (on a stone flake lying face down in the floating boat). Sonication of another stone flake, lying face up and covered with Milli-Q™ water, had little effect on removing the graphite and no effect on the birch tar. Immersion of flakes in acetone resulted in the partial dissolution of both graphite lines and birch tar. The use of a 2 M HCl solution slightly weakened the graphite lines, while removing ~40% of the birch tar. Treatment with 2 M NaOH had no effect on the graphite marks and only small amounts of birch tar were removed on one flake, while on another flake graphite marks were weakened with no effect on the birch tar.

The limitations of these experimental procedures lies in the fixation of the birch tar deposit to the tool. The reproduced fixative appeared less solid and less strongly attached to the contemporary flakes than adhesive observed on archaeological stone tools. Therefore, the cleaning treatment effects on adhesives may be regarded as indicative only.

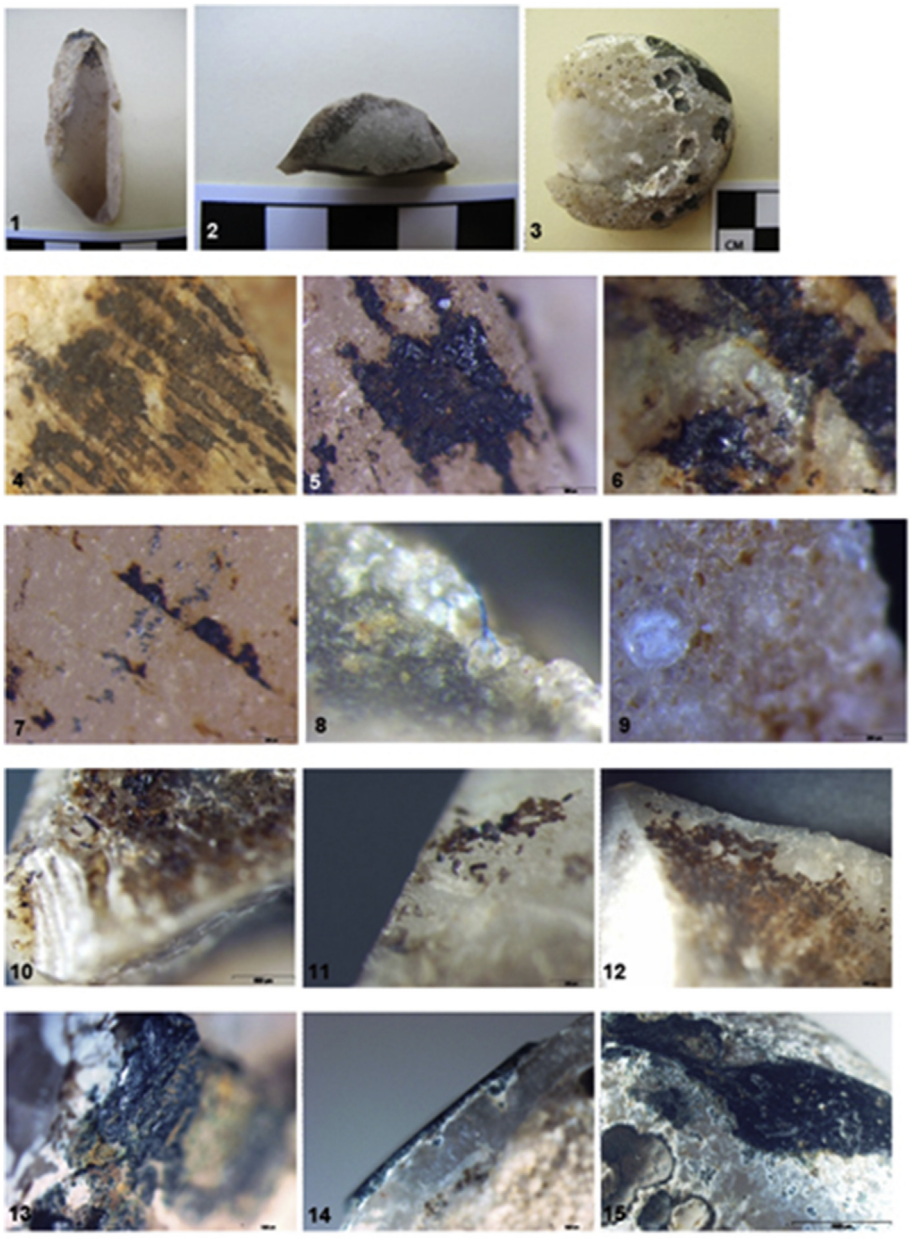

Fig. 1. Macroscopic and microscopic images of stone tools containing putative adhesive residues: **1** late Paleolithic flake (OZQ695), **2** Mesolithic flake fragment (OZQ694), **3** undated cobble fragment (OZQ696), **4**–**9** OZQ695: Microscopic images of **4** adhesive concentration 32× mag., **5** partially droplet appearance of adhesive, **6** white mass overlays adhesive, possibly bone collagen, 115× mag., **7** pencil graphite overlaying adhesive residue, **8** modern fabric fiber, **9** possible fungus contamination. **10**–**12** OZQ694: Microscopic images of **10** dark droplet appearance of adhesive with brown (plant) tissue, **11** edge area with fibrous (plant) material and dark droplet like adhesive spots 100× mag., **12** right margin edges damaged and fibrous (plant) material 20× mag., **13**–**15** OZQ696: Microscopic images of **13** presumably adhesive chunk mixed with sand 25× mag, **14** adhesive patch cross section at 20× mag., **15** adhesive chunks and mud cracked appearance of adhesive parts at 7× mag.

3.3. Methodological approach on artefacts – preparation for AMS dating

3.3.1. Cleaning pre-treatment with Decon 90, 2% diluted

Loose graphite traces, skin scales, fabric fiber and fungi were removed from the tools, whilst ink writing was unaffected by the Decon 90 treatment. Faint graphite lines could be wiped off using a nylon cloth followed by Milli-Q™ water rinses. No changes on the stone tool surface were observed.

Putative adhesive residues: Two samples (OZQ695 and OZQ696) showed no macroscopically observable change. Sample OZQ694 showed residue dislodgement after 7 min of immersion. The artefact was therefore removed from the solvent and then oven-dried at 35 °C and freeze-dried at −52 °C. The centrifuged and Milli-Q™ water-rinsed solution was retained. Examination by light microscopy revealed that most of the residues on the ventral and on large parts of the dorsal surface had been removed.

Wood residues: All four samples (OZQ689, OZQ690, OZQ691, OZQ692) showed partial detachment of wooden residues. Microscopic examination showed some wooden residues were still present in retouched working edges of OZQ690 and OZQ692. From one Mesolithic artefact, further residues were uncovered which were previously trapped in a cavity. The Decon treatment washed out the material previously filling the rock cavity. Two samples, 1) wooden

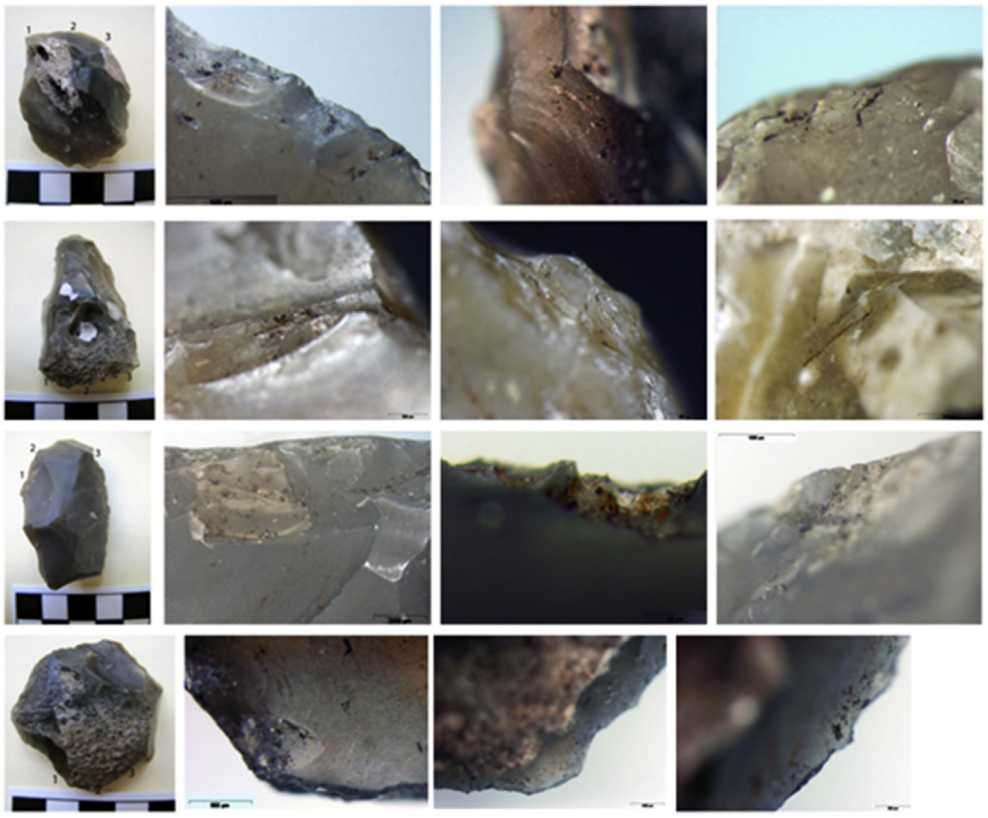

Fig. 2. Macroscopic and microscopic images of Mesolithic stone tools with identified wooden residues associated with use-wear traces. **1**st **row**: OZQ689 (Friesack, D5/7), Core axe, (Scale 1 = 1000 μm, 2 = 500 μm, 3 = 200 μm). **2**nd **row**: OZQ690 (Friesack, B2/7), Core axe (Scale, 1 and 2 = 500 μm, 3 = 2000 μm). **3**rd **row**: OZQ691 (Friesack, F25/10b), Core axe, (Scale 1and 3 = 1000 μm, 2 = 200 μm). **4**th **row**: OZQ692 (Friesack, CO15/8a), Scraper, (Scale 1 and 3 = 500 μm, 2 = 1000 μm).

residues (OZQ689-U2), and 2) wood mixed with dark substance residues (OZQ689-U1) (Fig. 3) were taken and processed for AMS dating.

Overall, these results show that along with some cleaning effect, the wooden residues did get dislodged from the stone tool. While this may be a desired effect when extraction is the aim, in this situation it is possible that graphite particles may have been transferred into the sample. On the other hand, as a substitute for the 'Alkali' step in the Acid-Alkali-Acid treatment, the solution is believed to be effective at removing fulvic and/or humic acid contamination. Wooden residues captured in the solution were rinsed with Milli-Q™ water, centrifuged and further treated as described in Table 1.

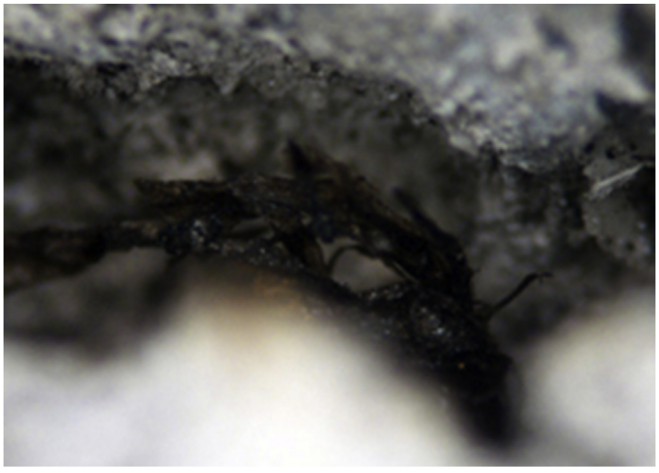

Fig. 3. Detailed picture of OZQ689 wooden residues intermixed with dark deposit from an unknown substance (possibly adhesive residue) (200× magnifications).

3.3.2. Residue removal

3.3.2.1. Scraping. Removal of residue deposits by scraping with a fresh scalpel blade was conducted on tools with putative adhesive residues. Two samples were taken from OZQ696, one from OZQ695, and one sample from OZQ691. The extracted residues were captured in centrifuge tubes. Powder-free gloves were worn at all times and changed between samples and intermittently.

3.3.2.2. Dichloromethane (DCM). On OZQ694 and OZQ695, extraction was trialed with dichloromethane (DCM) because the artefacts' find contexts suggested birch bark tar as a likely adhesive residue type.

Using a syringe containing ~1 mL of DCM, the adhesive deposit on OZQ695 was sprayed in two consecutive steps. The collected DCM was drawn up into the syringe and repeatedly re-applied to the stone tool deposit. The DCM was then transferred into a combustion tube. No change in color was observed in the DCM solution. There was little effect on the deposit.

For OZQ694, two sample fractions were obtained by using DCM. First, the captured residues from the Decon immersion were centrifuged and rinsed with Milli-Q™ water. The organic material was then treated with DCM followed by drying in a combustion tube. Second, the remainder of the residue which was still adhering to the tool was separated by immersion in DCM, followed by 20 min of ultrasonification. The solution was then evaporated on a hotplate and dried in a combustion tube.

3.3.2.3. Decon 90, 2% diluted. OZQ690 and OZQ692 were extracted unintentionally by the Decon immersion. These samples were further prepared as described in the method section and Table 1. The wood-black substance mix from OZQ689-U1 (uncovered after Decon immersion) was removed from the tool using tweezers (Fig. 3). A second sample, OZQ689-U2, consisted of the wooden remnants picked out from the beaker after the tool was Decon-cleaned and desiccated.

In total, eleven residue samples were removed from seven stone tools. Three of these samples yielded less than 5 μgC, which was insufficient to proceed to AMS (Table 2).

3.3.3. AMS dating

The residue radiocarbon dates delivered mixed results. There were some agreement and also some significant deviations from the anticipated age (Table 2, Fig. 4).

3.3.3.1. Adhesive residues. Both adhesive residue samples from the Australian stone tool (OZQ696-U1/U2) dated within the expected Late Holocene time frame. The ages of ~2 ka BP correspond with dates reported for the 'bungwall pounder' type artefact (e.g. Hall et al., 1989: 155 and McNiven, 1992: 706 who suggest possible use from Mid Holocene), which were present at the site with OZQ696. As such, they provide a clue to the age of the assemblage. Discrepancies between the samples' ages may be related to differential treatment – for instance only one sample was acid treated (OZQ696-U2).

OZQ695-U1 yielded a surprising result. The sample measured a radiocarbon activity of 338.9 per cent of modern carbon (pMC) (corresponding to about 10 kA *in the future*) (Table 2). Even during the bomb pulse peak (~1963 AD), atmospheric CO_2 activity only doubled to about 200 pMC. Levels higher than this must be associated with nuclear technologies or ^{14}C tracers used in industry and medicine. We conclude, therefore, that this sample inadvertently came into contact with such materials. Our investigations have not revealed any clues as to how this might have occurred.

The two remaining adhesive residues from Friesack dated significantly older than the anticipated age.

The OZQ694 (Friesack C3/S_9b) residue's AMS date delivered an age of 14,130 ± 90 BP, which is at variance with the date of the stratigraphical position of the tool, 9640 ± 60 BP. In addition to the typological assignment of the residue-dated tool being a typical Mesolithic core-axe, the find circumstances within a bog site which developed after the Pleistocene and from the middle Preboreal Period onwards (Gramsch, 2001, 2006), somewhat exclude the occurrence of artefacts of this age on this site. Taphonomic processes or bioturbation as factors causing artefacts to move between soil layers would only be an explanation if, underneath the bog site layers, older Pleistocene archaeological deposits had been discovered. However, this is not the case. Therefore, one possible explanation is that the residue attached to the artefact consisted of a material that was older than organic material collected during the Mesolithic period. Although not previously reported in a Mesolithic context, the use of naturally occurring bitumen would be one potential explanation. Natural bitumen exists in the Nordhorn deposit, in the Northwest German basin (Clarke and Trinnaman, 2010:145), and reportedly is present e.g. in Wintjeberg near Braunschweig (~140 km distance to Friesack) and in Holzminden (~230 km distance to Friesack) (Danby, 2013). Here reported distances to sources lie well within known procurement ranges of hunter gatherer groups. Bitumen, as an additive to embalming resins, was previously found to be responsible for radiocarbon dates older than find circumstances suggested (e.g. Aufderheide et al., 2004).

Furthermore, two samples of bitumen adhesives were identified with birch tar hafting adhesives in a Neolithic French site (Regert et al., 1998). It is therefore important to consider the possibility that bitumen sources might have been used in the Mesolithic period.

Sample fraction OZQ689-U1 (adhesive mixed with wooden residues) also resulted in an age overestimation (18370 ± 140 BP) of around double the anticipated date. This supports the explanation about possible bitumen additions suggested above.

3.3.3.2. Wooden residues. In contrast, the second sample fraction of the core axe (OZQ689-U2) was dated to 7890 ± 180 BP, which is ~1000 years too young. The tool was excavated from layer 7 of section Z in Friesack. Layer 7 was not radiocarbon dated, however, layer 17, occurring underneath layer 7, delivered dates of 9180 ± 70 and 9240 ± 70 BP (Gramsch, 2001: 61). Layer 6c, present above

Table 2
Summary of residue sample dating by AMS. Radiocarbon ages are indicated in BP and previously obtained dates are from Görsdorf and Gramsch 2004 and Gramsch, 2000 and 2012. (Abbreviations: D = Decon90, 2% diluted, DCM = dichloromethane treated, AAA = Acid-Alkali-Acid, pMC = Percent Modern carbon).

ANSTO ID	Residue Interpretation	Pre-treatment	Carbon Mass	pMC	Radiocarbon age BP	Anticipated Age	SEM-EDX interpretation
OZQ696-U1 Yelgun, NSW	Adhesive material	D, scrape extract., untreated	44.38 μg	77.1	2089 ± 67	Late Holocene	Organic, substance
OZQ696-U2 Yelgun, NSW	Adhesive material	D, scrape extract., 2M HCl	33.30 μg	80.09	1783 ± 60	Late Holocene	
OZQ695-U1 Wesseling	Adhesive material	D, scrape extraction	35.30 μg	338.9	−9805 ± 14	~11,500BP	Inorganic substance, possibly Manganese Oxide/dendrites
OZQ695-U2 Wesseling	Adhesive material	D, DCM penetration,	4.87 μg	_	Insufficient carbon	~11,500 BP	
OZQ694-U1 Friesack	Adhesive material	D, DCM imm, ultrasonication	0.23 mg	17.4	14,130 ± 90	9640 ± 60 BP	N/a
OZQ694-U2 Friesack	Adhesive material	D, DCM, AAA	4.09 μg	_	Insufficient carbon	9640 ± 60 BP	
OZQ689-U1 Friesack	Adhesive material/wood	D, tweezer picked from tool, DCM,	137.14 μg	10.54	18,370 ± 140	Between 9000 and 9250 BP	Wood, amorphous, organic substance and shell
OZQ689-U2 Friesack	Wood	D, tweezer picked from beaker, AAA	18.97 μg	36.28	7890 ± 180	Between 9000 and 9250 BP	N/a
OZQ690 Friesack	Wood	D, Pick out wood, AAA	4.90 μg	_	Insufficient carbon	~9200 BP	N/a
OZQ691 Friesack	Wood	D, scrape extraction, AAA	9.20 μg	79.45	1848 ± 124	9–10,000 BP	N/a
OZQ692 Friesack	Wood	D, Pick out wood, AAA	8.68 μg	54.69	4848 ± 244	9640 ± 60 BP	N/a

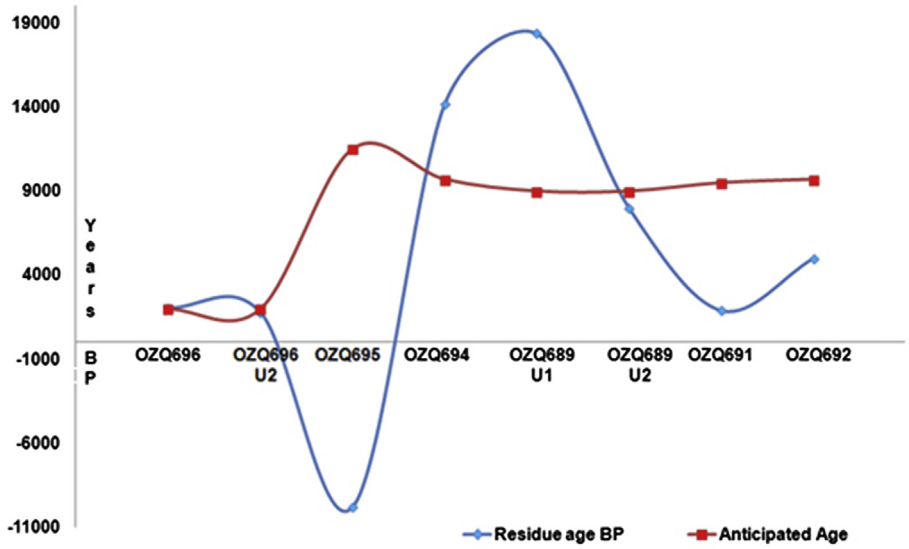

Fig. 4. Residue radiocarbon ages (rounded) plotted against anticipated ages. From left to right: Both samples of OZQ696 date within expected Late Holocene age range, OZQ695 significantly too young, OZQ694 and OZQ689-U1 significantly too old, 6 OZQ689-U2 dates close to anticipated age, OZQ691 and OZQ692 too young.

layer 7, yielded dates of 8980 ± 60, 9010 ± 70 and 9040 ± 70 years BP. In addition, layer 7 in section A was dated to 8850 ± 70 and 8975 ± 70 years BP (Gramsch, 2001: 61). These dates suggest an age between ~9000 and ~9250 years BP for artefact OZQ689. One possible explanation for this might be that the tool moved down from higher (younger) layers (e.g. through bioturbation or taphonomic processes). Furthermore, it is possible that the wooden residues (or parts of them) found in the cavity of the stone artefact were actually not use-related, but the result of root growth. In addition, contamination by modern carbon may be responsible for the age deviation of the small sample size consisting of 18.97 μgC.

Remaining wooden residues dated significantly too young compared with the anticipated age (Table 2, Fig. 4). Residue from OZQ692 was removed unintentionally during the Decon clean and as such was intermixed with surface contamination including pencil graphite. Therefore, it is possible that contamination affected the radiocarbon date of the sample which was sized only 8.68 μgC. While graphite remains would have led to an older age, other unknown factors may have contributed to the younger age. The possibility of the tool having been moved through the sediment is unlikely as we are not aware of core axes typologically evident from ages as young as 4848 ± 244 years BP.

A microscopic image of wooden residue remains from OZQ691 suggested a possible precipitation of calcite on the artefact's wooden residue. For this possibility to exist, an older age would be expected (e.g. Long et al., 1992). In general, it was found that the influence on artefacts of carbon atoms from water in bog sites usually results in an age that is too old (Van der Plicht et al., 2004: 472, 473). However, any carbonate contamination deposited by groundwater should have been removed during the acid steps of the AAA pre-treatment. Long storage in a warm environment, inviting fungi and microbe development and decay, may introduce ^{14}C-rich CO_2 into the sample and may also result in radiocarbon dates that are too young – as has been suggested for pollen age deviations (Neulieb et al., 2013). We find it unlikely that contamination occurred during the scrape extraction as only fresh, unused scalpel blades were used. The dates yielded for OZQ691 and OZQ692 were not congruently "false" but showed a ~3000 year difference between them, while the anticipated age for both samples was between 9000 and 10,000 years BP (Table 2). For the above reasons, we suggest that the small sample size, and introduced atmospheric or modern carbon might be the more likely reason for the significantly younger age of the samples. The wide span of incongruence suggests an unknown amount of carbon as well as an unknown type of carbon introduced into the samples.

3.4. Establishing elemental characteristics of residues

Residues were still present on tools OZQ689, OZQ695, OZQ696 after the aforementioned treatment. This allowed the use of SEM-EDX analysis to establish the basic elemental composition. In addition, a modern *Xanthorrhoea* sample was analyzed for comparison.

3.4.1. OZQ689

On the one hand, we suspect that fossil bitumen might be responsible for the older radiocarbon age. On the other hand, however, SEM images also showed the presence of shell which was likely to have been formerly embedded in the flint stone matrix. This shell could also have contributed to radiocarbon age overestimations. In addition, wood fiber, silica and the putative adhesive (amorphous black substance) were observed by microscopy (Fig. 5). Published EDX data on archaeological bitumen residue show different elemental composition compared to the sample data (absence of P, Ca and Fe, but presence of Na, S and Zn) (Monnier et al., 2013: 3729–3732) (Table 3). However, elemental compositions of bitumen are known to vary from source to source (e.g. Brown et al., 2014). Also, addition of other materials to produce a fixative and the resultant differential decay may contribute to the differences. Further methods are required to clearly identify the nature of the residues.

3.4.2. OZQ695

The high levels of Manganese and the occurrence of Barium (Table 4) indicate that the black substance, mimicking the adhesive in appearance, might be a form of manganese dendrites (e.g. Potter and Rossman, 1979). A study analyzing manganese dendrites on different rock varieties by using SEM-EDX has identified Mn and Ba as major components (Xu et al., 2010). The non-organic nature of the dark residue is further suggested by the brighter appearance in the SEM images (Fig. 6).

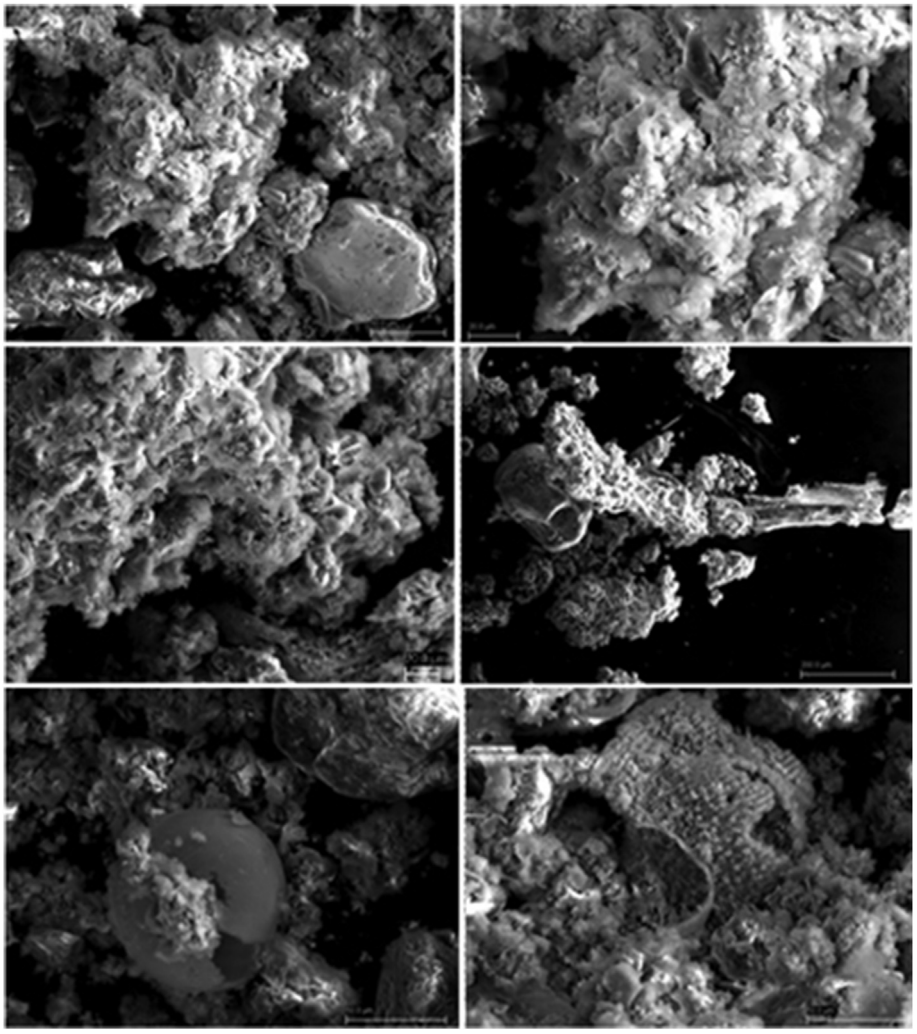

Fig. 5. SEM images from OZQ689 residue: **1** Unknown substance possibly adhesive material with silica chunk attached right side, (Scale = 50 μm); **2 and 3** Unknown organic substance (Scale = 20 μm); **4** from left to right: silica chunk, partially unknown substance and wood piece (Scale = 200 μm); **5, 6** shell with unknown residue (Scale = 50 μm).

Table 3
Extracted residue from cavity of OZQ689: Weight Percentages determined from EDX data for elements >1% average atomic weight.

Sample #	Description/Interpretation	Average atomic weight:									
		C	O	Si	P	Na	Mg	Al	S	Ca	Fe
1	Silica particle	35	53	41						1	
2	Black amorphous matter	22	37		8					12	
3	Black amorphous matter	22	37		9					15	
4	Black amorphous matter	40	32	3						1	
5	Black amorphous matter	105.19	80.91	11.41				3.32		3.92	2.85
6	Black amorphous matter	99.9	−11.91	4.19	1.1					3.6	1.06
7	Black amorphous matter	90.23	54.92	5.2						2.26	1.36
8	Black amorphous matter	52.67	61.31	7.31				2.58		2.22	2.23
9	Black amorphous matter	79.68	45.58	10.33						1.4	1.24
10	Wood fibre	52.38	24.83		1.24					2.53	
11	Wood fibre	95.51	29.65								
12	Shell	4.59	32.31	22.89							
13	Shell	15.02	60.69	26.85							

3.4.3. OZQ696

Two residue samples (A and B) were analyzed with A consisting of a chip scraped off the tool, and B being a scraping with powdery consistency. The SEM images show that both samples had a consistent fan-like plant structure which in sample A shines through the sealed part (Fig. 7, images 1–3). In contrast to this is the very dense and compact consistency and structure of the contemporary *Xanthorrhoea* sample. The beam caused cracks on the surface of the resin, probably due to the density of the material (Fig. 7, images 6).

Further clues suggesting different materials are found in the elemental composition of contemporary *Xanthorrhoea* which is

Table 4
Residue and rock matrix of OZQ695: Weight Percentages determined from EDX data for elements >1% average atomic weight.

Sample #	Description/Interpretation	Average atomic weight:									
		C	O	Si	P	Na	Mn	Al	S	Ca	Fe	Ba
1	Black substance on tool tip	10.34	48.99	1.45			38.65			1.66	10.2	7.48
2	Black substance on tool tip	7.37		1.14			36.38	1.04		1.56	9.01	8.93
3	Black substance on tool tip	6.92	56.56	1.13			46.11			1.52	7.41	11.45
4	Black substance on tool tip	−2.99	52.72	35.16							13	
5	Black residue streaks on tool		47.95				48.21			1.15	4.93	11.54
6	Black residue streaks on tool	2.48	36.92	2.73			36.99			1.16	13.18	8.86
7	Black residue streaks on tool	3.85	44.86	1.54			42.19	1.19		1.77	10.43	10.01
8	Black residue streaks on tool		34.48	3.6			11.4	1.87		1.13	36.06	
9	Black residue streaks on tool	3.16	35.56	2.98			18.26	1.47		1.59	30.97	3.24
10	Black residue streaks on tool		35.99	4.63			13.7	1.82		1.41	29.58	
11	Matrix of rock	4.46	71.98	52.55								
12	Matrix of rock	2.83	135.95	68.54								
13	Matrix of rock	14.89	58.63	40.46								
14	Matrix of rock	8.72	40.88	27.54								
15	Matrix of rock	11.69	73.07	48.67								
16	Matrix of rock	10.22	57.25	37.24								

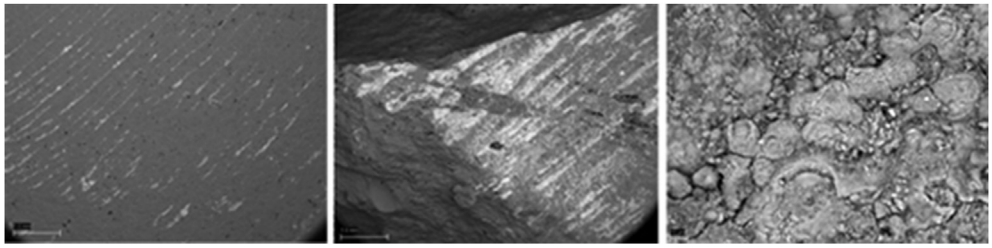

Fig. 6. SEM images of OZQ695 residue: **1** adhesive streaks (white); **2** adhesive streaks (white) and grey traces from scraping off adhesive; **3** residue on tip area of tool (Scale 1 + 2 = 1.0 mm, Scale 3 = 10 μm).

limited to high C and O fractions. By contrast, the black to dark green colored adhesive material in samples numbered 1 to 7 (Table 5) shows high average weights of O, and sequentially decreasing weights of Si, C, Fe and K. Except for samples 3 and 5, Mg is present in all other samples, while Al occurrence is limited to sample 7. Noteworthy are the clearly higher proportions of O, Si, K, Mg and Fe in sample B (6, 7) which had the more powdery consistency. This may indicate that the elemental composition within the material had changed because the outer layer, more exposed to weathering (sample A), contains less of these elements.

Comparing images and data of the archaeological adhesive residue material with the contemporary *Xanthorrhoea* sample does not provide great insight. Chemical modifications, decay, the presence of other materials (e.g. sand, animal fur) (e.g. Gamage et al., 2012; Rots, 2010) and weathering may have altered, partially or completely, the SEM surface aspect as well as the elemental composition. The differences in data between archaeological and contemporary material could, however, indicate two different materials.

4. Discussion

The detection of several shells by SEM in OZQ689 residue, interpreted as a constituent of flint stone (e.g. Pellant, 2000: 246), has important repercussion on inferences about the dates. The AMS age distortions obtained for OZQ689-U1 and OZQ694-U1 could well be explained by the presence of shells. In order to preserve the adhesive residue, both sample fractions were not AAA treated, the acid step of which would have removed shell remains and related age offsets. On the other hand, one cannot determine bitumen presence in the residue solely by SEM-EDX analyses and this could be another cause for age offsets.

Apart from the reasons described above, plasticizers may also be incorporated into the sample from storing the artefact in plastic bags. The GC/MS analyses on the four analyzed Friesack samples has shown every birch tar piece contained plasticizers (one example represented by Fig. 8) (Baumer and Dietemann, 2008). Due to the fossil origin of plastic materials, too old radiocarbon dates could be expected. We found diverse information about the effect of plasticizers on radiocarbon dates: First, direct contact with a wood sample caused a ~200 years age overestimations (Hyman and Rowe, 1997:64). Second, "… *a surprising level of plasticizer (as phthalate)*" was found in lipid samples, although it was considered "… *not enough to invalidate the dates*." (Hedges et al., 1992:911). — The obtained dates were ~5000 and ~10,000 thousands of years too old (Hedges et al., 1992:910). The authors suspect laboratory contamination as responsible for the age offsets, however more detail for this assumption was not provided. Third, *"considerable"* amounts of plasticizes found in birch bark tar sample Königsaue B may have contributed to a >4000 age overestimation compared with the stratigraphical younger sample Königsaue A, which had "*lesser impurities*" (Koller et al., 2001: 103). For the latter study it needs to be considered that both samples stratigraphical ages are older (80,000 years and older) than the age range obtainable with radiocarbon dating.

These examples indicate the potential effect of plasticisers on wood, lipid and birch bark tar samples. Yet, a more in-depth analyses, that demonstrates measurable evidence of plasticisers effect is missing. This shows that currently there are too many unknown variables possibly responsible for age offsets caused by plasticizers. These variables include residue type, length of storage, plastic type used for storage, heat exposure of sample in plastic bag. A specific radiocarbon dating series testing plasticisers effect with the combination of these variables would help to resolve the problem.

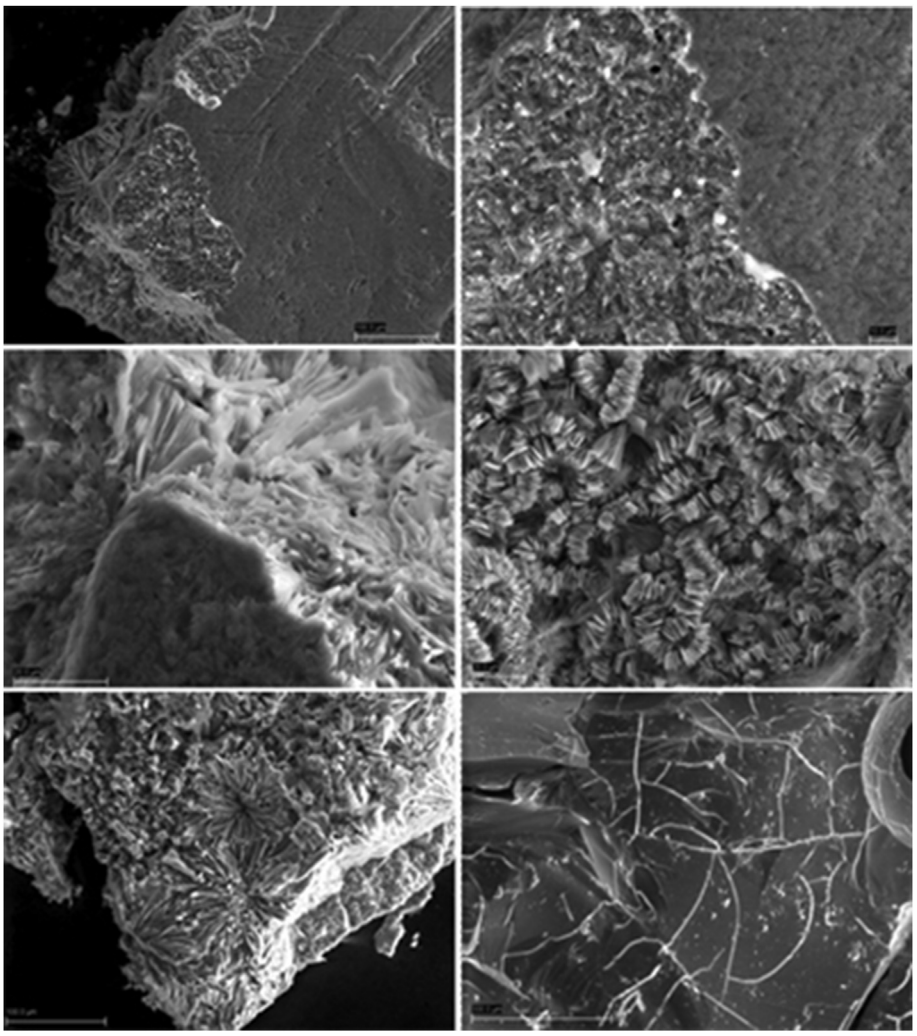

Fig. 7. SEM images from residue recorded on artefact OZQ696 (images 1–5) and a contemporary *Xanthorrhoea* sample (6): **1**–**3** transition from chipped part to more sealed part of sample A imaged in increasing magnification (Scale, 1 = 100 μm, 2 = 10 μm, 3 = 20 μm), **4**–**5** structure of sample B (Scale, 4 = 20 μm, 5 = 100 μm), in contrast: **6** dense and compact consistency of contemporary *Xanthorrhoea* sample, cracks here occurred through beam (Scale = 300 μm).

Table 5
Residue and rock samples of OZQ696, in comparison with contemporary *Xanthorrhoea* samples: Weight Percentages determined from EDX data for elements >1% average atomic weight.

Sample #	Description/Interpretation	Average atomic weight:									
		C	O	Si	K	Na	Mg	Al	S	Ca	Fe
1	Black-green substance, sample A	7.37	36.92	14.9	4		1.78				7.69
2	Black-green substance, sample A	2.28	30.48	12.92	3.45		1.49				9.8
3	Black-green substance, sample A	15.08	30.3	9.82	3.22						7.71
4	Black-green substance, sample A	5.53	32.42	13.95	4.18		1.65				8
5	Black-green substance, sample A		12.39	8.17	3.46						7.53
6	Black-green substance, sample B	4.44	90.98	32.43	7.03		5.17				15.84
7	Black-green substance, sample B	4.32	96.84	31.55	8.14		4.27	1.97			16.66
8	Silica particle	3.1	56.48	43.3							
9	Contemporary Xanthorrhoea	78.7	45.64								
10	Contemporary Xanthorrhoea	66.97	32.08								

Finally, graphite contamination needs to be taken into account for age overestimations, despite attempts to remove the material with Decon 90.

SEM-EDX analyses allowed discerning organic from inorganic residues, suggested the presence of manganese dendrites (OZQ695) and detected fossil shell (OZQ689) as a potential contamination source. The possibility to examine residues *in situ* can be applied as a preliminary step to validate their organic nature. In combination with optical light microscopy, the method demonstrated to provide mutual complementary results for understanding residue and use-wear (e.g. Pawlik, 1995, 2004; Jahren et al., 1997; Dinnis et al., 2009; Pawlik and Thissen 2011; Borel et al., 2014). EDX results need to be considered as an indication of the basic elemental composition and the data as qualitative

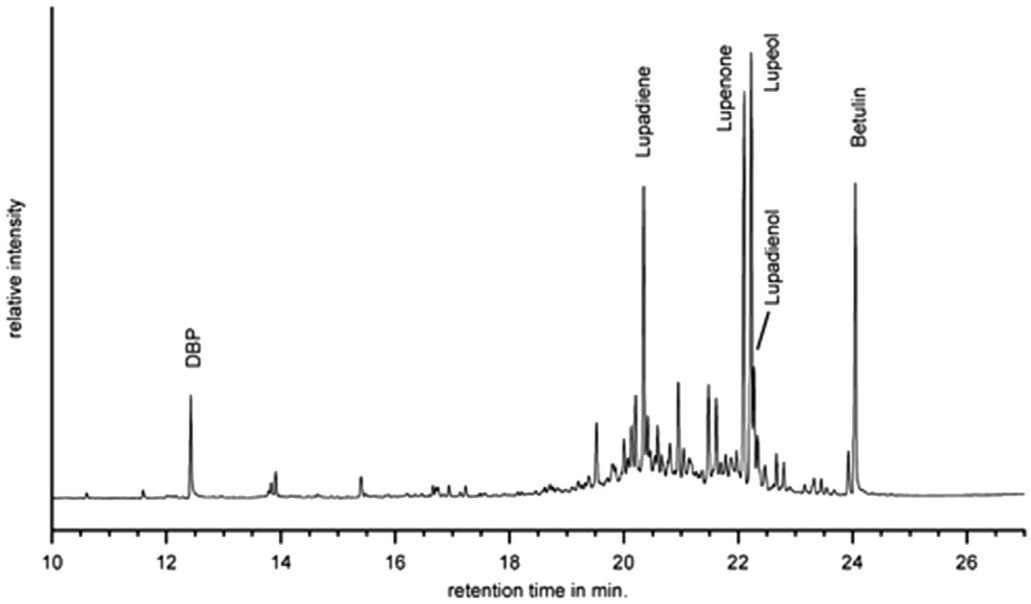

Fig. 8. Gas-Chromatogram from birch bark pitch of Friesack, find 1977:7/P4. Betulin, lupeol and lupenone, biomolecular markers of birch bark. Additionally plasticizers in form of Phtalatestern, Dibutylphthalat (DBP) (Courtesy of Baumer and Dietemann, 2008, Doerner Institute, Munich).

rather than quantitative. These results are further impaired by the uneven and rough surfaces of the samples.

Although accurate in results, sample amounts needed for GC/MS are larger than most lithic residues preserve. In addition, for our purpose, to radiocarbon date smallest residues we need to avoid sample destruction which is also desirable for replicate analyses. Vibrational spectroscopic techniques (e.g. Daher et al., 2013) might be the answer to assess the actual nature of residues. That said, a clear evaluation of the impact on the sample, such as damages by the beam or by pressure, the importance of plane surfaces as well as the need for reference material, is mandatory to validate its use (Cesaro and Lemorini, 2012: 300; Matheson and Mc Collum, 2014: 125; Prinsloo et al., 2014: 738). In addition, the application of techniques such as UV light irradiation and chemilumescene (e.g. Matheson, 2014; Lombard, 2014) may aid in residue detection and identification. A practicable workflow could then be as represented in Fig. 9.

In the context of dating, one can argue for the lesser role that residue type plays in the actual radiocarbon age as long as it is use-related. For example, stone tools are known to have been used for multiple tasks and therefore contain various residues. While this argument might be acceptable for certain types of organic residues (e.g. bone, blood, fat, protein, starch, or wood), adhesive residues might be intermixed with materials that distort the radiocarbon ages. We have pointed out the possibility of bitumen additions as one distorting factor, however, sand, dust, and ground shell might also lead to age deviations. This study has shown that the chemical signature is needed on such samples prior to AMS dating as it would have guided the choice of extraction and preparation protocol.

5. Conclusion

The aim of this study was to test the feasibility of radiocarbon dating residues of archaeological stone tools and at the same time to mitigate inherent contaminant impact. We have obtained modest, but encouraging AMS dates for one wooden residue and for one adhesive residue. This indicates the feasibility of residue AMS dating, but it also clearly shows we are still at an early stage of method development in this research field. In this study we demonstrate that successful residue dating requires a thorough identification of their type and the nature of potential contaminants. SEM-EDX and GC/MS were helpful in detecting potential contamination sources, such as fossil shell, and plasticisers, for age deviations. Further sample analyses from Friesack may reveal whether bitumen, or other sources, could explain the age over-estimations. Decon 90, 2% diluted, appears to remove graphite contamination while preserving birch bark tar, however, the effect on other adhesives is unknown and the agent is unsuitable for wooden residues. In general, the applied methodological sequence appears appropriate and led to successful outcomes. Additional characterisation methods at the beginning of the analyses, such as vibrational spectroscopic techniques or the application of biochemical substances, would be beneficial, especially for adhesive residues.

Fig. 9. Suggested workflow of method sequence for efficient residue AMS dating.

Future research needs to develop residue-specific sampling protocols for these non-destructive characterization methods to avoid contaminant transfer. In addition, a further protocol for artefact handling from excavation through to adequate storage is essential.

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