Creating a reference collection of hafting adhesives to interpret some "black spot" residues on lithic artefacts

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1. Introduction

Tool hafting has been widely accepted as an important technical innovation, highly significant in terms of human behaviour evolution (e.g. Ambrose, 2010; Anderson-Gerfaud, 1990; Lombard, 2008; Rots, 2010; Stordeur, 1987; Wadley, 2010; Wilkins et al., 2012). However, handles, artefacts with handles or clear evidence of these are really scarce in Palaeolithic contexts. However, macro and microscopic use-wear on archaeological stone tools, and the identification of adhering residues can help to identify evidence for hafting.

Since organic materials degrade over time in most archaeological contexts, the identification of hafting adhesive residues on prehistoric artefacts is rare. However, some Near East and European Middle Palaeolithic and African Middle Stone Age sites have retained evidence for the use of adhesives. Additionally there is evidence for the use of birch bark pitch as an adhesive in hafting, from several Middle Palaeolithic sites including Campitello in Italy (Mazza et al., 2006), Inden-Altdorf and Königsaue in Germany (Pawlik & Thissen, 2011; Koller et al., 2001; Grünberg, 2002), and some Upper Palaeolithic sites as Les Vachons, in France (Dinnis et al., 2009). Bitumen has also been identified at the Paleolithic site of Gura cheii-Râsnov Cave, in Romania (Cârciumaru et al., 2012). In the Near East Middle Palaeolithic sites including Umm el Tlel and Hummal in Syria also have evidence for the use of bitumen for hafting (Boëda et al., 1996, 2007; Hauck et al., 2013; Monnier et al., 2013) while plant resins have been reported in South African MSA and LSA sites including Dieplkloof Rock Shelter and Border Cave (Charrié-Dunhaut et al., 2013; Villa et al., 2012) as well as more recent sites from the Yukon and Selwyn mountains, Canada (Helwig et al., 2014).

Nevertheless, hafting technology remains insufficiently documented. Apart from the issue of poor preservation of such a kind of residues, an additional problem is the lack of standardisation in analytical methods used. The aim of this project is to determine to what extent characterisation of a series of "black spots" identified on archaeological artefacts from different Palaeolithic sites in Spain, Nagorno Karabagh and Iran can be identified as adhesive residues. On the basis of our results, we will develop a multi-analytical protocol for similar cases.

2. Description of the "black spots"

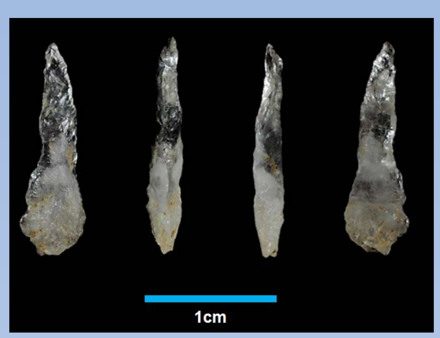
Residues considered here are brownish black stains that appear as isolated drops of dried liquid material, that can have the appearance of cracks on their surface.

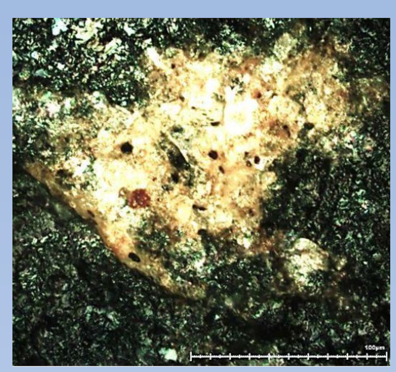
The residues occur on both faces, in many cases (but not all) distributed around those parts of the tool which were likely grasped or hafted. Although most of the hafting adhesives that are published, appear more conspicuous residues, their distribution on the artefacts suggest hafting residues.

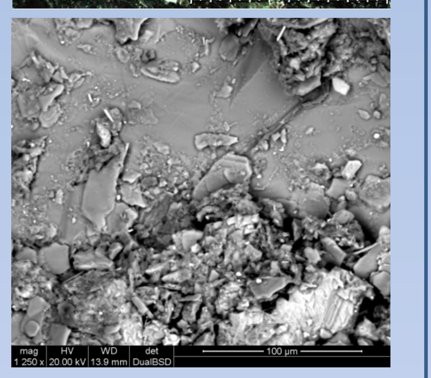
However, the fact that in most cases these residues were just a few microns and too small for standard chemical analysis (Pawlik & Thissen, 2011: 1701) guided our first set of analysis (OLM, SEM, EDX and Raman) all of which have been carried out without extracting samples. It is however, clear that a method that enables a more definitive characterisation is required. A reference collection is an essential starting point as it will provide a known context for the morphological and chemical fingerprints extracted. Once this is achieved, we plan to work other methods including GC-MS.

Cova Eirós

Cova Eirós is a small karst cave located in Mount Penedo (Triacastela, Galicia, NW Iberia) containing Middle Palaeolithic (levels 3 and 4) and Upper Palaeolithic (levels B, 1 and 2). The functional study of rock crystal implements from the UP levels documented the possible remains of adhesive substances in the proximal portions of some tools from the Final Magdalenian (Level B; 12.060±50 BP), Gravettian (Level 1; 17.000 BP), and Classic Aurignacian (Level 2; 31.690±240 BP) levels (Fábregas Valcarce et al., 2012; Fábregas Valcarce & de Lombera-Hermida, 2010; de Lombera-Hermida & Fábregas Valcarce, 2013).



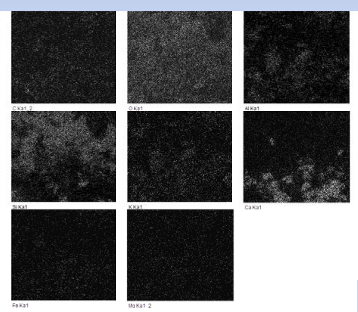


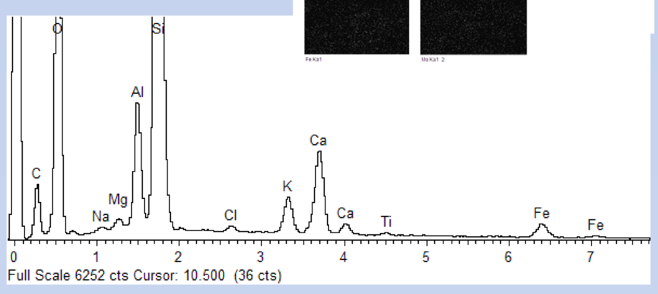


Preliminary interpretation
Possible presence of a composite adhesive including ochre. However, similarities with MIX1 (OLM and EDX) are not conclusive. Other apparent residues turn out to be abraded surfaces.

Apparent adhered black residue on a rock crystal flake fragment from level1 (OLM, above) which under SEM (BSD, bellow) revealed to be an eroded portion on dorsal face.

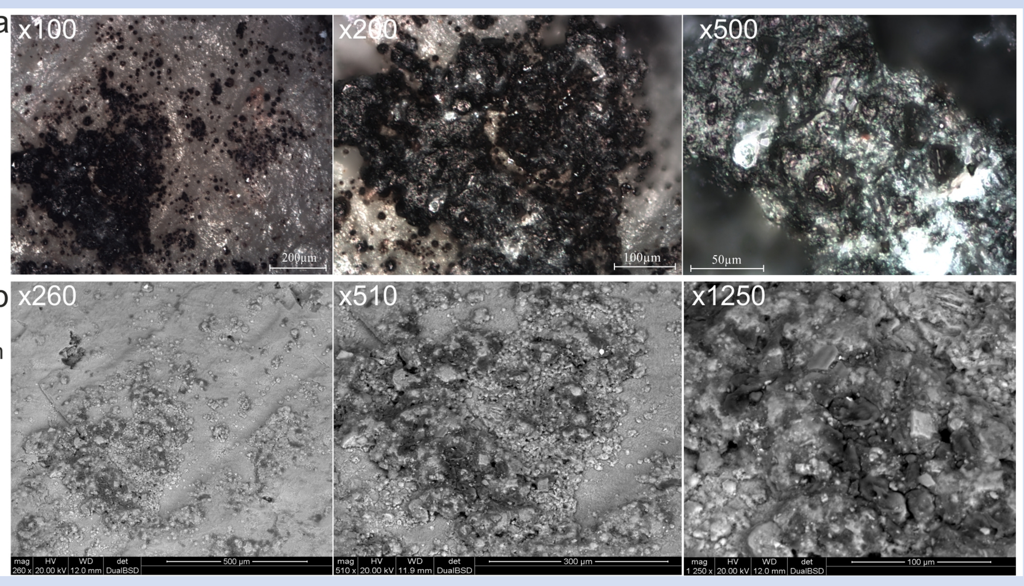
Small rock crystal point from level B with some residues on the proximal half. OLM and SEM image of the residue. EDX spectrum and maps of the principal elements (C, O, Al, Si, K, Ca, Fe and Mg)



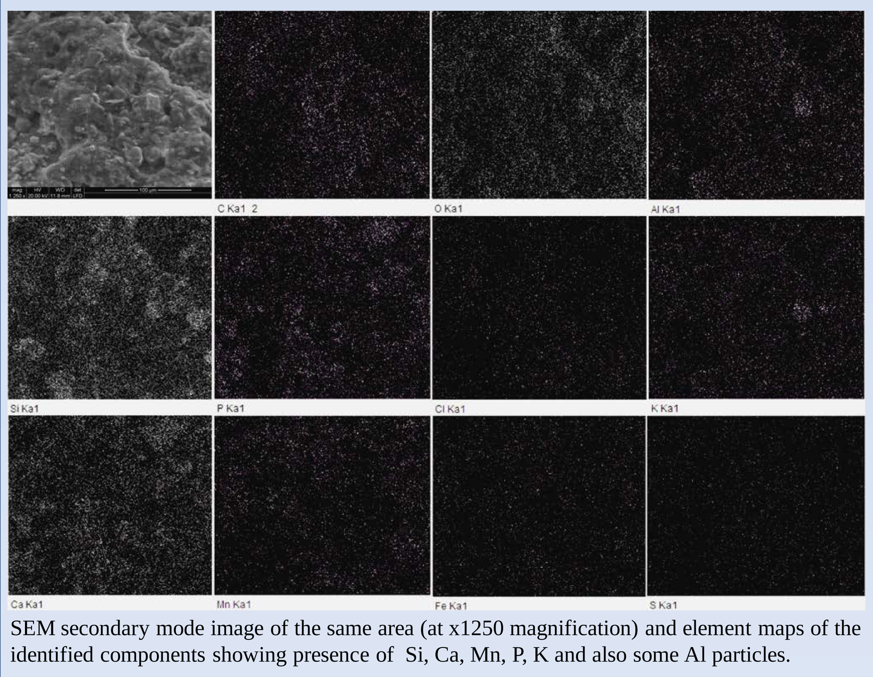


Azokh Cave

Azokh Cave is a Middle Pleistocene to Holocene site located in Nagorno Karabagh (Lesser Caucasus).Azokh 1 is a large cave with two geological sequences and nine geo-archaeological units of which only the upper (Units I to V) has a significant archaeological record (Fernández-Jalvo et al., 2010; Murray et al., 2010). The available chronological data indicates an age between 293 – 100 Ka for these units. Different local and non-local lithic raw materials were exploited in all units. Materials included here come from units V and II. While is still difficult to assign the assemblage from unit V to a techno-typological group, unit II assemblage is clearly associated with the Mousterian techno-complex (Asryan et al., 2014).



Flint artefact from Unit V. OLM (a) and SEM (DualBSD (b) images of an area with accumulated residues.



SEM secondary mode image of the same area (at x1250 magnification) and element maps of the identified components showing presence of Si, Ca, Mn, P, K and also some Al particles.

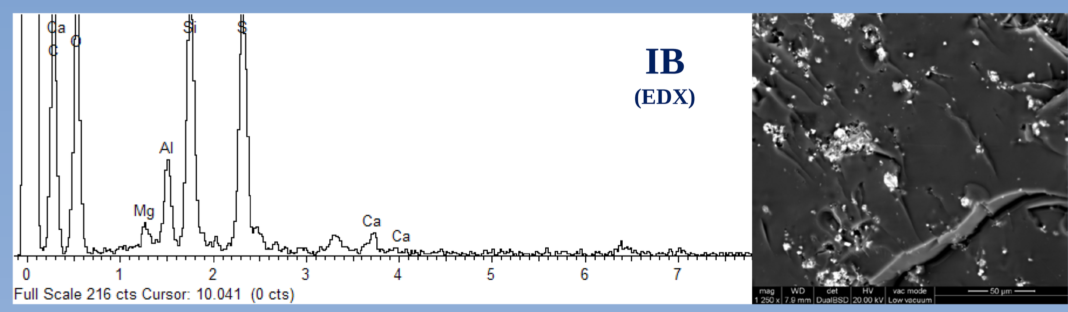
Preliminary interpretation
Morphology and elementary composition of the residues fit with results from post-depositional experiments involving bat guano (derived from the fact that the cavity hosts an important bat colony). The guano's highly acidic composition is likely the responsible of the "sparse drops", altogether with manganese oxide. However, bitumen cannot be still excluded.

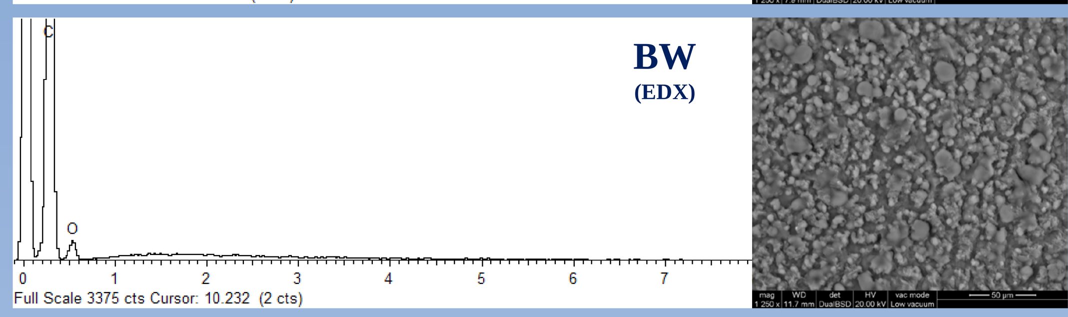
3. Methods

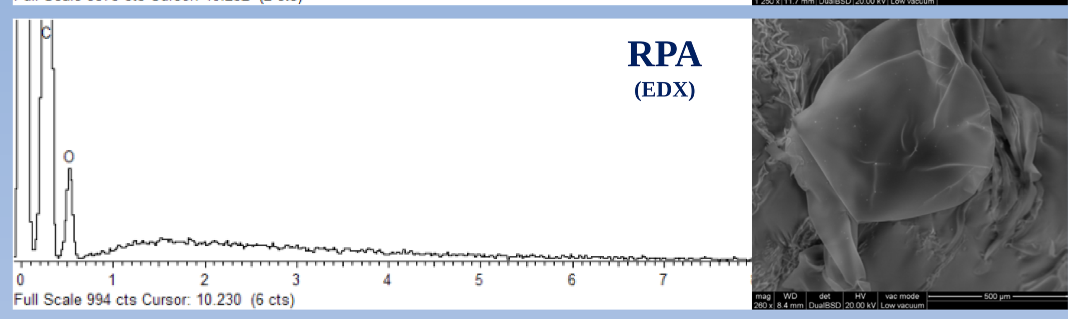
3.1.The reference collection

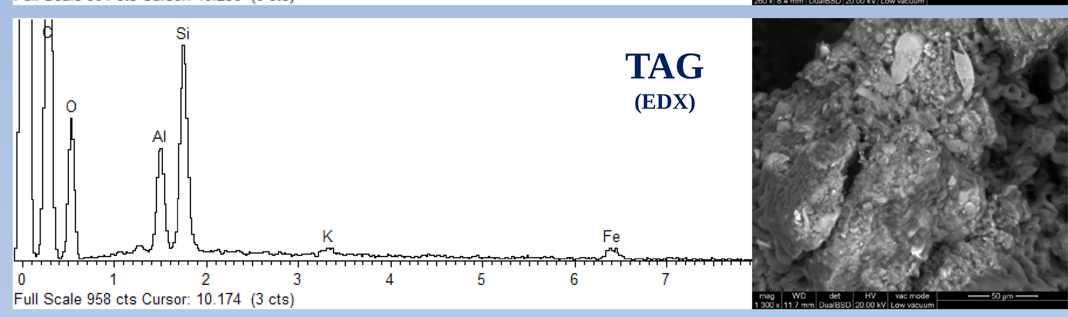
A reference collection has been started comprising a limited number of substances most likely present on some of the archaeological materials, and others commonly reported by other authors. Additional samples from well known archaeological Egyptian contexts have also been included.

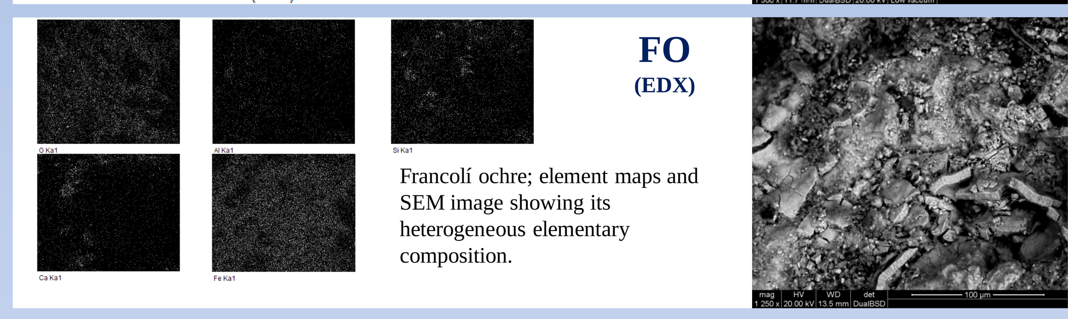
Pure products	Ref	Observations
Bitumen	IB-01	Untreated lump, Khorramabad valley outcrop (Lorestan, Iran)
Bitumen	IB-02	Iranian natural sources (Connan & Deschesne, 1996)
Ochre	FO	Untreated lump, Francolí river (Tarragona, Spain)
Beeswax	BW	Centre d'Interpretació Apícola Muria, el Perelló (Tarragona, Spain)
Pine resin(ext)	RPPe	*Pinus pinaster*, external secretion; Cangas (Pontevedra, Spain)
Pine resin (int)	RPPi	*Pinus pinaster*, internal secretion; Cangas (Pontecedra, Spain)
Pistacia resin	RPA	*Pistacia atlantica*, Khorramabad valley (Lorestan, Iran)
Yew pitch	TTB	*Taxus bacatta*, produced under laboratory conditions (Univ. of Bradford, UK)
Alder tree pitch	TAG	*Alnus glutinosa*, produced under laboratory conditions (Univ. of Bradford, UK)
Bat guano	BG	Azokh Cave (Nagorno Karabagh)
Archaeological reference product	**Ref**	**Observations**
Beeswax	EgyBW	Egyptian mummy of the Third Intermediate Period, c. 1069-664 BC
Pistacia resin	EgyRP	Egyptian coffins (c. 1400 BC)
Mixtures	**Ref**	**Observations**
Ochre + pine resin + beeswax + charcoal	MIX1	FO + BW + RPPi + pine wood charcoal



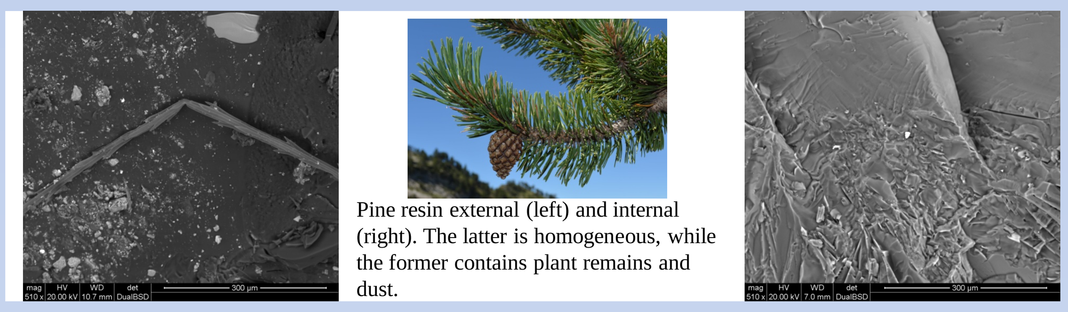




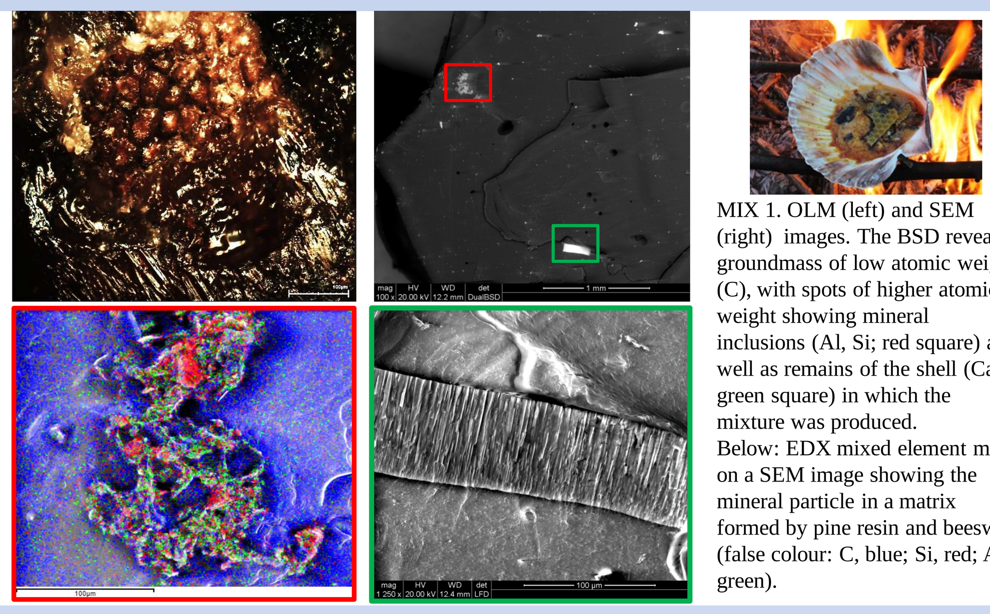




Francolí ochre; element maps and SEM image showing its heterogeneous elementary composition.

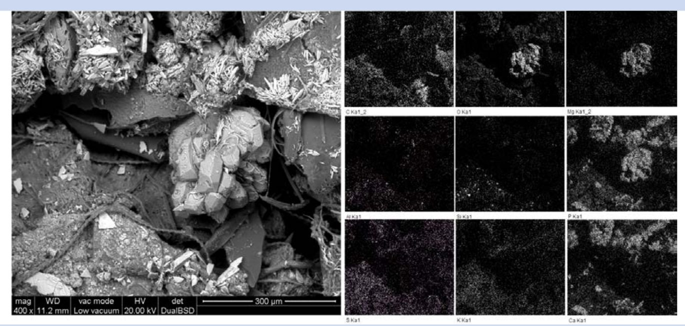


Pine resin external (left) and internal (right). The latter is homogeneous, while the former contains plant remains and dust.



MIX 1. OLM (left) and SEM (right) images. The BSD reveals a groundmass of low atomic weight (C), with spots of higher atomic weight showing mineral inclusions (Al, Si; red square) as well as remains of the shell (Ca; green square) in which the mixture was produced.
Below: EDX mixed element map on a SEM image showing the mineral particle in a matrix formed by pine resin and beeswax (false colour: C, blue; Si, red; Al, green).

Bat guano. SEM image (left) showing the animal and plant remains, altogether with chemically diverse particles (element EDX maps, on the right).



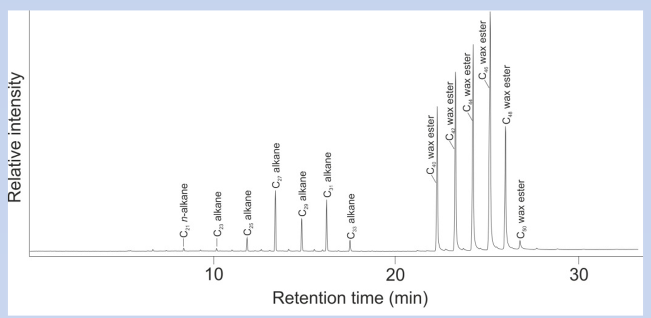
3.2. Techniques

Both the organic and inorganic residual components should be characterised and multi-analytical procedure is normally adopted (e.g. Charrié-Dunhaut et al., 2013; Cârciumaru et al., 2012; Cristiani et al., 2009; 2014; Evershed, 2008; Helwig et al., 2014; Mazza et al., 2006; Monnier et al., 2013; Pawlik & Thissen, 2011; Rigaud et al., 2013).

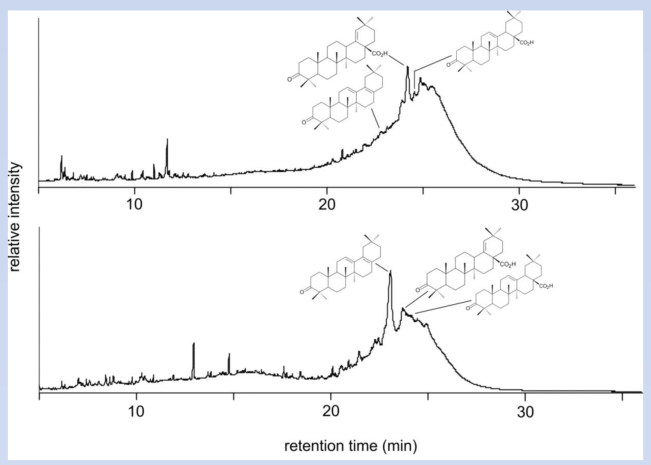
Our aim is to begin with the simpler techniques and explore the advantages and the limits of each, as well as evaluating how the results are complementary.

Eventually, we aim to create feasible and efficient protocols for residue characterisation (specially addressed to archaeologists focused on functional analysis).

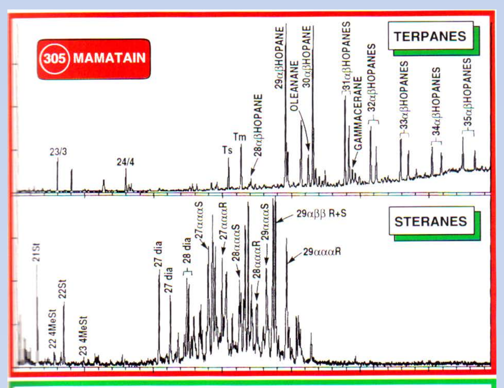
1. **Optical light micropscopy (OLM)**. Aims: residue location, residue limits, and main physical features (e.g. colour, texture, structure, homogeneity...).
2. **Scanning Electron Microscopy (SEM)**. Aims: detailed structural description, elemental characterisation and chemical composition.
3. **Energy Dispersive X-ray analysis (EDX).** Aims: composition spectra and element maps.
4. **Raman spectrometry**. Aims: Characterisation of minerals and some organic substances, providing molecular information with high specificity.
5. **Gas chromatography-Mass Spectrometry (GC-MS)**. Aims: composition -"chemical-fingerptinting"- of organic substances (archaeological biomarkers).
6. **Sequential thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) and pyrolysis-gas chromatography mass spectrometry (Py-GC-MS)** (Destructive). Aims: identification of chemical compounds and detailed characterisation of organic residues with a minimally destructive sampling.
7. **Fourier transform infrared spectroscopy (FTIR).** Aims: Identification of molecular compounds and minerals (technique considered but not still included).

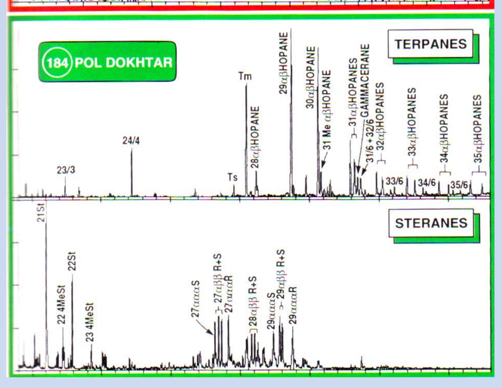


Total ion chromatogram from the GC-MS analysis or archaeological beeswax from an Egyptian mummy of the Third Intermediate Period, c. 1069-664 B.C.



Pistacia resin from Egyptian coffins (c. 1400 B.C.)

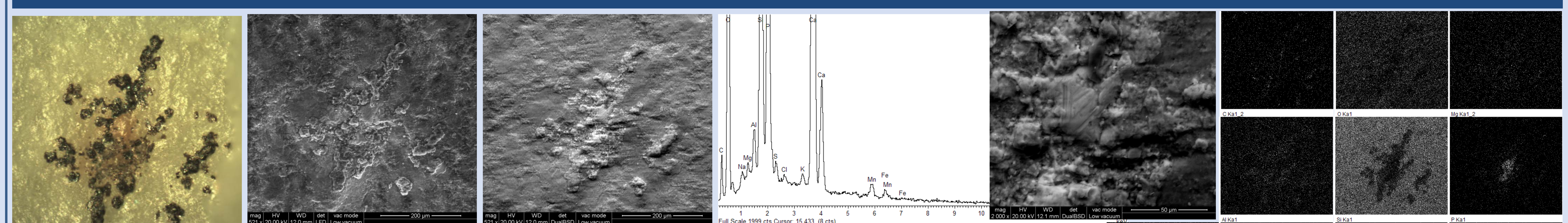


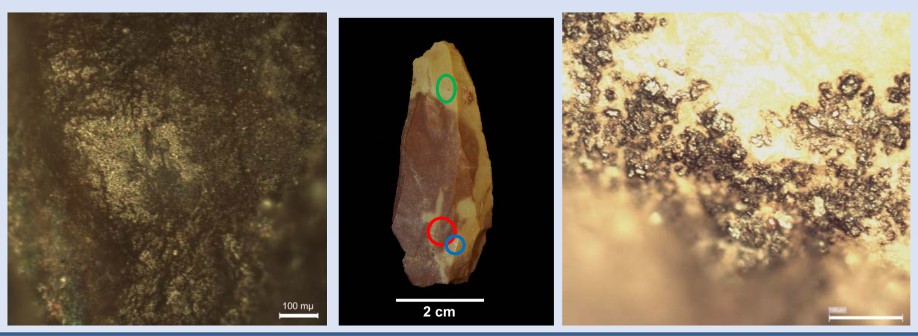


Terpanes (m/z 191) and steranes (m/z 217) from Iranian sources of natural bitumen (Connan and Deschesne 1996).

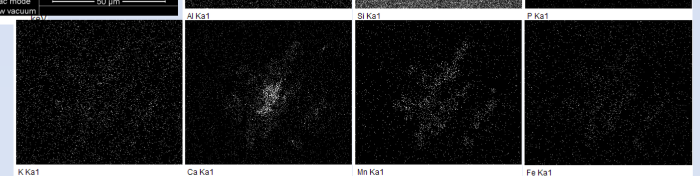
Kaldar Cave

Kaldar cave is situated in the north of Khorramabad Valley, western Iran. In 2010, an intensive and goal-oriented study of the Paleolithic sites led to excavations of several localities, notably Kaldar as which was excavated for the first time (Bazgir et al., 2014). Preliminary techno-typological analysis showed the site has been occupied at least from the late Pleistocene. Five cultural phases were recognised; levels 5 and 4 are attributed respectively to Middle and Upper Paleolithic. This is a very promising site, containing an undisturbed stratigraphy, very well-preserved lithic industry and faunal remains for the study of the transition between these two crucial periods of hominin occupation in western Asia.





The images above show the OLM, SEM (SE and BSD), EDX spectra and element maps of a bone residue (Ca + P) surrounded by Mn oxide on the spot highlighted by a green circle. Below, a spot with hafting traces (blue circle) and the OLM image (red circle) of black residues identified by Raman as bitumen.
We obtained the Raman reference spectra of two referential molecular substances: IB-01 and MIX1. Comparing these spectra with those on the archaeological residues (proximal part), we observed that the black stains spectra contain similar bands with bitumen Raman spectra. Specifically, we observed two bands (1330 and 1580cm^{-1}) that could correspond to the ones found in bitumen Raman spectra at 1360 and 1580 cm^{-1}.



Preliminary interpretation
In one of the analysed points two different residues have been identified. On its proximal portion the residues correspond to bitumen, whereas the stains on the tip turned to be manganese oxide precipitated around a bone residue.

Final remarks

· OLM as well as SEM provide morphological characterisation of residues. EDX can provide information on the appearance of the residues but do not allow accurate residue identification.
· Raman spectroscopy is a non-invasive and non-destructive promising technique, to be used as a fast analytical tool in situ of archeological residues.
· For accurate residue identification, precise chemical analyses as CG-MS are really convenient.
· Although the current reference collection is still in construction, the combined application of the different techniques demonstrated the feasibility of identifying some of the residues, while also of rejecting some of the spots as evidence of hafting.
· In some cases the association of residues with tool handling adhesive is clear. But there are other possibilities in which the tools' surfaces and the identified substances can come into contact. Therefore, only after large archaeological data sets and contextual studies will we be able to properly asses this aspect.

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