Elucidation of the Chemical Composition of Ancient Adhesives Present in Lithic Artefacts by Means of FTIR Spectroscopy

ICFO The Institute of Photonic Sciences

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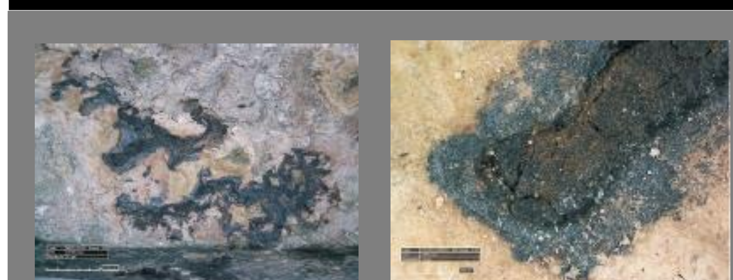
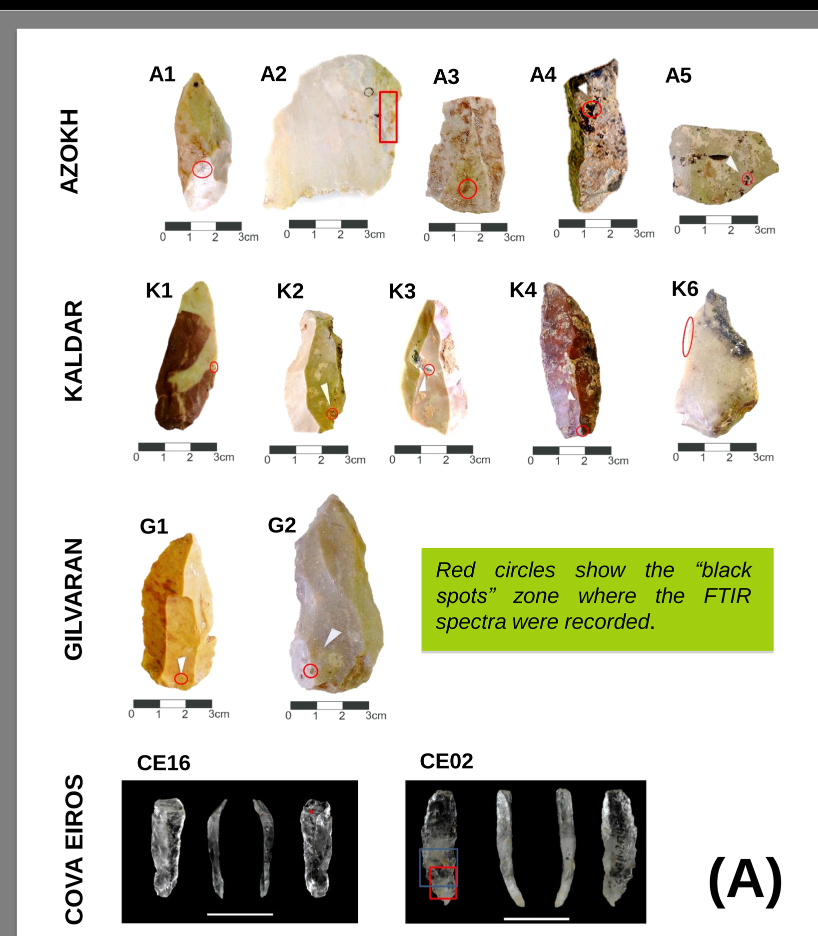
ABSTRACT

Though the debate continues regarding whether the organic material on ancient lithic artefacts can survive and be microscopically identified, the study of residues is in fact already one of the key components of functional analysis. Indeed, the study of different kind of organic residues (e.g. bone, wood, plants, blood cells, starch granules etc.) on the archaeological lithic artefacts is currently being carried out by many authors. Here we focus on a particular type of residue, the "black spots" observed in some archaeological lithic artefacts from different sites (e.g. Umm El Tel and Hummal in Syria, Campitello in Italy, les Vachons in France, Königsaue and Inden-Altdorf in Germany, Diepkloof Rock Shelter in south Africa, some sites in the Yukon Territory, Canada, etc.) and interpreted most commonly by researchers as being residues of bitumen, tar or bark birch pitch, pine or other plants resin, used for hafting the lithic artefacts [1,2]. The most commonly employed methods for identification of these residues have been through use of optical and scanning electron microscopy to determine morphological features, and energy dispersive spectrometry (EDX) and the chromatography-mass spectrometry (GC-MS) for identification of chemical composition. However, all these techniques are considered as destructive and cannot provide information of the molecular composition and structure of the sample.On the other side, vibrational spectroscopies such as FTIR allow to obtain the molecular identity of materials in a reliable, reagent free and non-destructive way. Here we present the results obtained of the spectroscopic characterization of diverse organic residues (black spots) present on some lithic artefacts apparently related to projectile hafting. Samples were obtained from different Palaeolithic sites such as; Azokh Cave, in Nagorno Karabagh, Gilvaran and Kaldar in Iran and Cova Eirós, in Spain. 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. Results obtained of the analysis of the FTIR spectra recorded from the lithic artefacts here studied, suggest that one of the major components of the "black spots" has a bituminous origin, showing characteristic spectral signatures observed in these type of substances [3].

Characterization of "black spots" on the archaeological lithic samples



Black spots description: 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.



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).

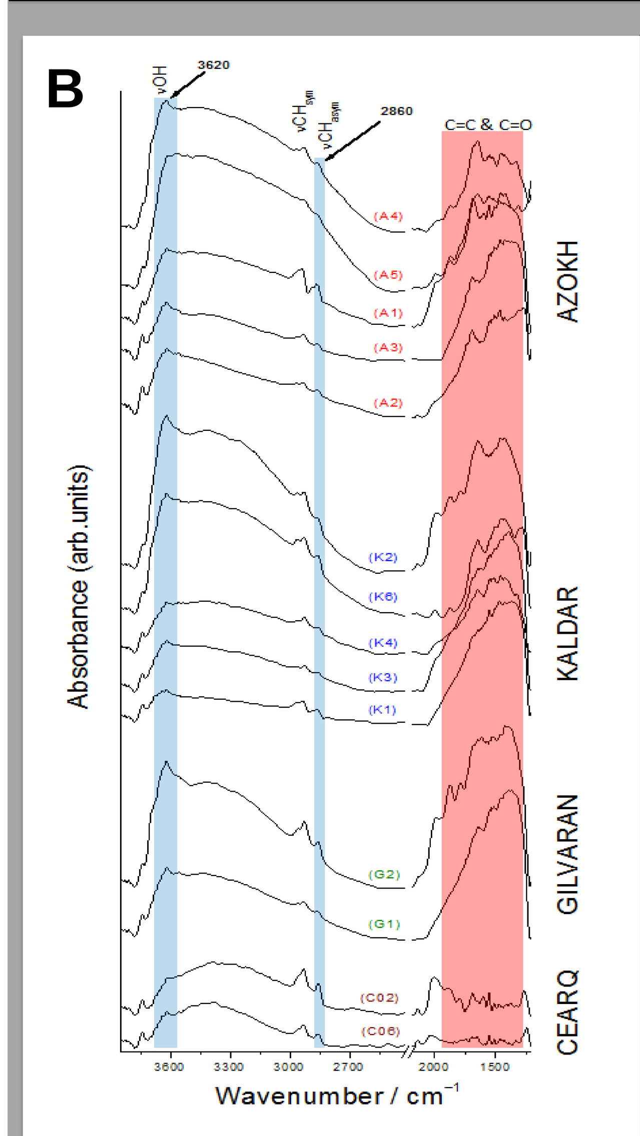
Kaldar cave

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.

Gilvaran & Cova Eirós

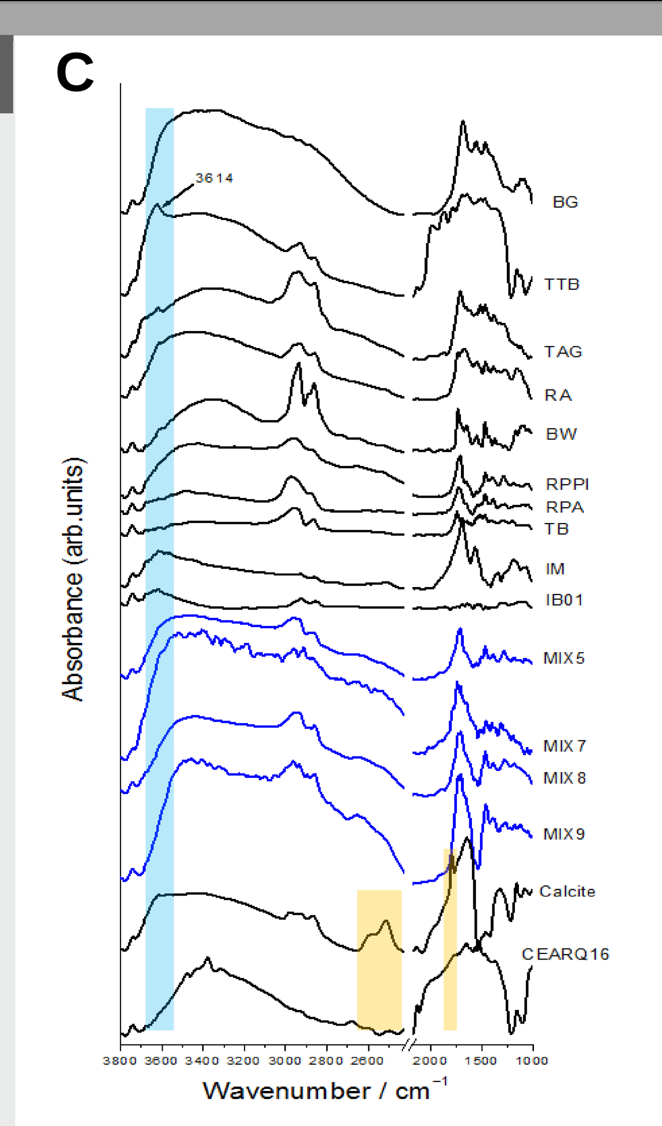
Cova Eirós is a small karst cave located in Mount Penedo (Triacastela, Galicia, NW Iberia) containing Middle Palaeolithic (levels 3 and 4) and Upper Palaeolithic (levels B, 1 and 2). The functional study of rock crystal implements from the UP levels documented the possible remains of adhesive substances 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).

FTIR and EDX characterization



← FTIR spectra

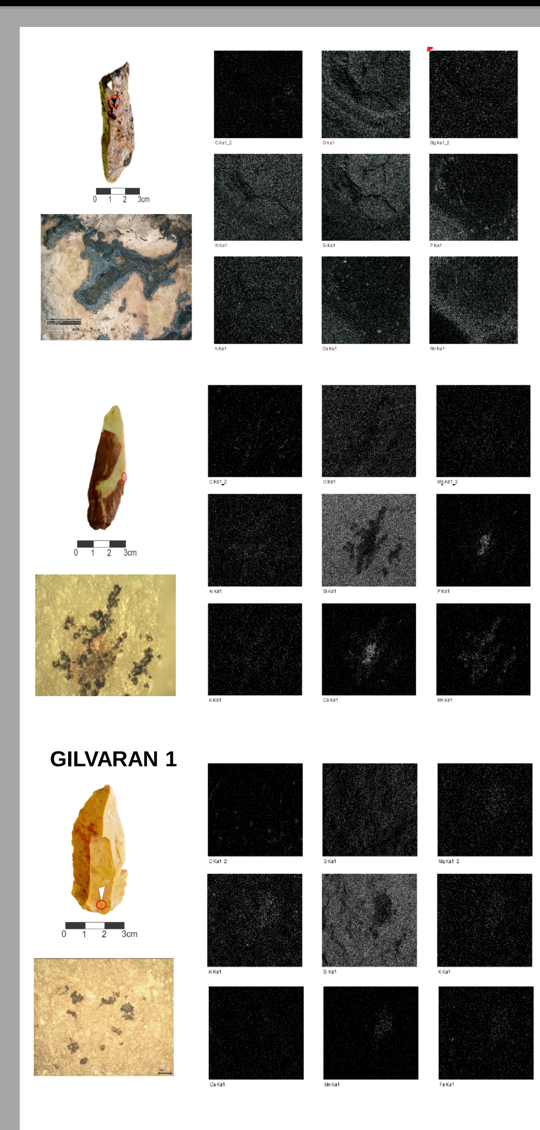
FTIR spectra were collected using a microscope FTIR Agilent model Cary 620 in reflection mode with a resolution of 4 cm^{-1} in a spectral range of 4000 to 650 cm^{-1}. Measurements were carried out over an area of 24x24 μm. Different "black spots" were analysed for each sample and an average of ten spectra were collected for each "black spot".
(**B**) Figure shows fourteen representative spectra of one black spot recorded for each sample. Spectral fingerprint of these samples shows a high overlap of bands which are mainly ascribed to C=C and C=O stretching vibrations, which can be related with the presence of organic substances present in the black spots as well as the bands at 2860 and 2925 cm^{-1} characteristics of the assymetric and symmetric C–H stretching modes, respectively. On the other hand, some authors have reported that band located at *ca.* 3617 cm^{-1}, ascribed to stretching mode of free OH, it is a distinctive band observed in bituminous materials [4].

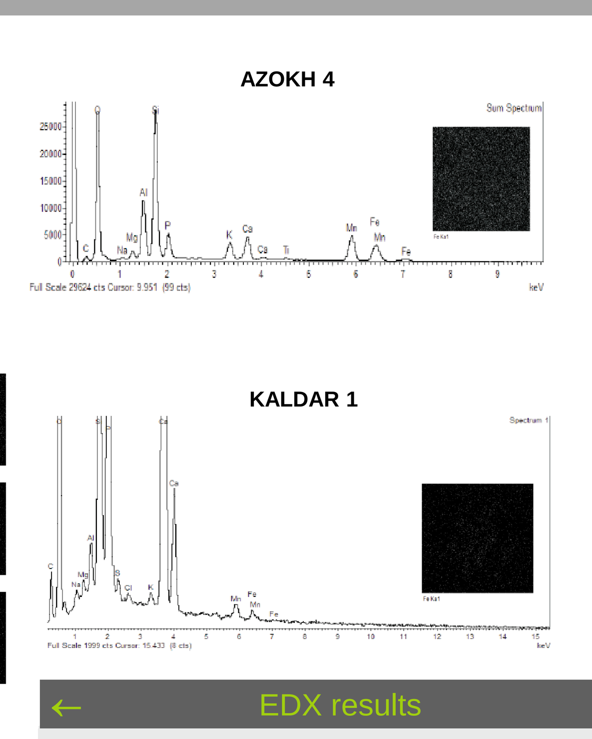


← FTIR Database

(**C**) 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.

Code	Substance
BG	Bat guano
TTB	Yew pitch/tar
TAG	Alder tree pitch
RA	Arjan tree
BW	Beeswax
RPPI	Pine resin
RPA	Pistacia resin
TB	Birch bark pitch
IM	Fine carbon powder
IB	Bitumen
MIX5	Pine resin + beeswax + ochre
MIX7	Pine resin + cow fat + ochre
MIX8	Pine resin + beeswax + ochre
MIX9	Pine resin + beeswax + ochre





← EDX results

Most of the information obtained from EDX analysis can be related with the substrate (rock) instead with the black substance present in the rock (i.e. Ca, P, K, Al, Fe). However it is posible to identify in some of elemental analysis the presence of high amounts of C and O, which can be associated with some bituminous substances.

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Fundació Privada CELLEX
European Regional Development Fund
European Social Fund