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# SR-FTIR microscopy for the study of residues on Palaeolithic stone tools: looking for a methodological protocol

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**Abstract.** In this paper, we use SR-FTIR microscopy to analyse residues identified on seven lithic artefacts from the Evolved Epigravettian layer 9c2 of the cave site of Grotta Paglicci (Apulia, southern Italy). Synchrotron radiation, thanks to its properties that particularly increase the sensitivity of FTIR microscopy, allows the analysis of samples of microscopic size and the characterisation of even highly degraded compounds, such as the residues of materials worked by Palaeolithic stone tools or complex compounds used for hafting. This pilot study has been carried out in the framework of a project concerning the reconstruction of hunting technologies between the Middle and Upper Palaeolithic. The preliminary results allowed us to focus on the issues of our methodological approach and to show the potential of the SR-FTIR microscopy for the analysis of residues on lithic implements.

## 1. Introduction

This work is part of a PhD project aimed at investigating the Middle and Upper Palaeolithic hunting technologies and strategies in southern Italy, funded by the Central European Research Infrastructure Consortium, CERIC-ERIC. The identification of hunting technologies is based on both the morphological and use wear study of stone tools and the chemical analysis of the substances used in hafting procedures and/or that came into contact with them during their use. These organic and inorganic residues, when preserved, consist of degraded traces of the original compounds not always easy to identify. The present contribution is to be considered as a preliminary step in framing the issues related to the chemical characterisation of residues on lithic artefacts, in relation to both archaeological evidence and depositional environment/post-depositional processes.

Several techniques for chemical characterisation meet the fundamental issue of being non-destructive for the integrity of the archaeological finds. Among these, FTIR microscopy is to be considered as a cutting-edge technique in the analysis of lithic residues [1], as it was applied in archaeology (except for a single case [2]) only from 2012 [3], thus opening a season of new studies [4], [5], [6], [7], [8], [9]. The use of this technique is however still sporadic in this field and not systematically performed yet [1].

The principal advantage of FTIR microscopy is its capability to study both organic and inorganic IR-active compounds from minute sample residues. FTIR microscopy in reflection mode allows *in situ* observation of the residue in its original micro-context, thus preserving its integrity, while eliminating the sample preparation [1], [10], [11]. Some methodological works on this approach in the analysis of



lithic residues have been produced [10], [11], [12] and several case studies are available [3], [4], [6], [7], [9]. On the other hand, FTIR microscopy in transmission mode eliminates the difficulties deriving from the interpretation of reflectance spectra, that can be often affected by diffuse reflection, refraction, or scattering effects due to the roughness of the stone tools surface [10], [11]. Thanks to the loading of the sample into a compression cell, the method requires very small quantities of sample, without further preparation. The high brightness of the InfraRed Synchrotron Radiation (IRSR) and the achievable spatial resolution close to the diffraction limit allow us to select different regions of the sample, according to their colour, for a finer discrimination between organic and inorganic residues. In addition to this, the use of the IRSR instead of conventional sources provides a faster spectra collection characterised by a higher signal-to-noise ratio, particularly useful in dealing with degraded or in traces organic compounds. Sample analysis obtained in this way is particularly suitable in our contexts, as demonstrated by the unique but remarkable case study with these characteristics currently available [9].

In our study, SR-FTIR microscopy in transmission mode has been applied to analyse seven lithic artefacts from layer 9c2 of Grotta Paglicci (Rignano Garganico, Foggia, Italy) attributed to the Evolved Epigravettian (18,002-18,956 cal yr BP [13]). In Mediterranean Europe, Grotta Paglicci is a key site for the Upper Palaeolithic, with a continuous stratigraphy from the Proto-Aurignacian to the Final Epigravettian currently undergoing a new set of investigations by the University of Siena.

## 2. Material and methods

The lithic artefacts labelled as 7, 15, 30, 32, 34, 43 and 47 were observed under Hirox KH-7700 3D digital microscope to localise residues on which FTIR analyses could be conducted (Table 1). All the examined artefacts are made of chert and four of them belong to the typological group of backed points [14]. These implements are on bladelets and were used as armatures. They are supposed to have functioned as part of composite weapon systems, on the basis of archaeological and ethnographic instances and the several use-wear studies that have been produced over the last years on this kind of tools [e.g., 15]. The other lithic artefacts analysed are common tools (i.e., a denticulate, a side-scraper and a bec) which were manufactured on blades (Table 1).

SR-FTIR measurements were performed at the Chemical and Life Sciences branch of the SISSI beamline at Elettra Sincrotrone, Trieste [16]. The residues were gently scraped off from each of the selected lithic tools by the tip of a needle under stereomicroscope observation and transferred onto a diamond compression cell (Diamond EXpress by S.T. Japan, clear aperture 2 mm) in order to flatten them to a thickness suitable for FTIR transmission measurements. The measurements were performed by a VIS-IR Bruker Hyperion 3000 microscope equipped with an MCT-A detector and coupled with a Vertex 70v interferometer operating in the MidIR range (4000 - 650  $\text{cm}^{-1}$ ). 15 to 25 spectra were collected for each residue on half compression cell, averaging 512 scans (scan velocity 80 KHz) at 4  $\text{cm}^{-1}$  and setting the lateral resolution at 20x20  $\mu\text{m}$  in order to select the most diagnostic sample regions according to observable differences in colour. Two samples were analysed from each stone tool, excepting for finding no. 30 on which only a single residue was available for sampling.

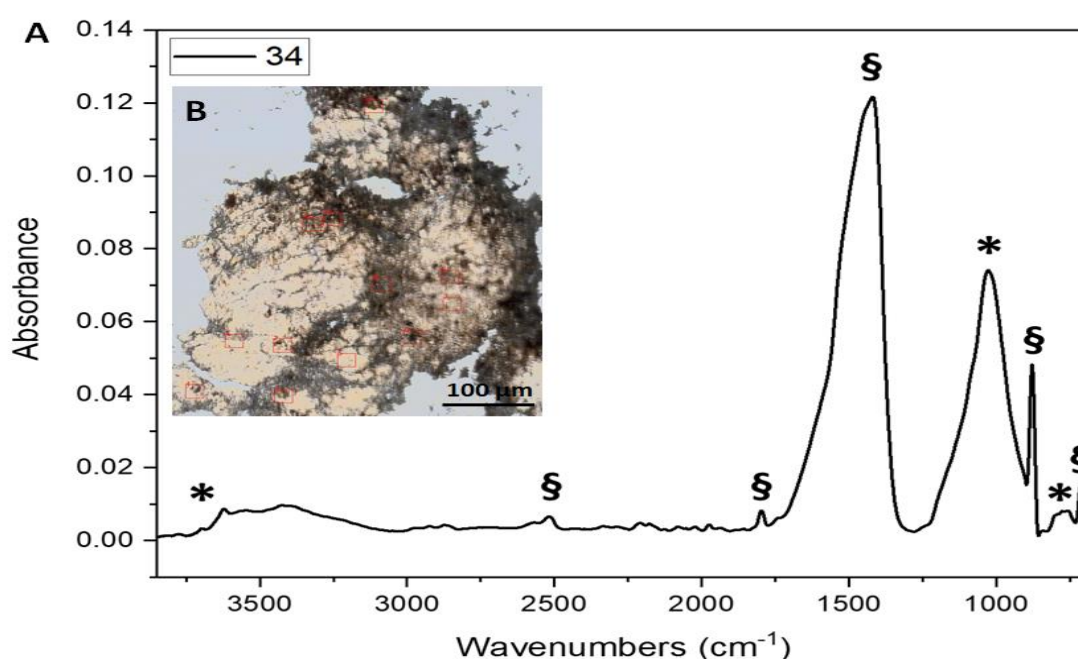
**Table 1.** – List of retouched artefacts analysed according to Laplace's typology [14] and residue sampling locations.

| ID | Retouched artefact | Sampling location                               |
|----|--------------------|---|
| 7  | Backed point       | dorsal face, proximal part                      |
| 15 | Backed point       | dorsal face, mesial and distal part             |
| 30 | Backed point       | back, proximal part                             |
| 32 | Backed point       | back, mesial part; dorsal arris, mesial part    |
| 34 | Denticulate        | ventral face, proximal and proximal-mesial part |

|    |              |  |
|----|--------------|--|
| 43 | Side scraper | ventral face, proximal part                            |
| 47 | Bec          | ventral face, distal part; dorsal surface, distal part |

### 3. Results

All the analysed samples showed very intense and broad signals at around  $1420\text{ cm}^{-1}$  and  $1030\text{ cm}^{-1}$ . The former, accompanied by weak spectral features at around  $2517$  and  $1795\text{ cm}^{-1}$  and by a sharp intense peak at  $877\text{ cm}^{-1}$ , are indicative of the presence of carbonates, while the latter is characteristic of silicates. Figure 1A shows a representative spectrum obtained from one of the residues collected on the finding no. 34 (figure 1B). The samples analysed from this specimen are mainly composed by inorganic fraction and can effectively represent the sediment from the burial environment.



**Figure 1.** - A. Example of IR spectrum of finding no. 34; silicates are indicated with \* and carbonates are indicated with §. B. Optical images of sample no. 34 with indication of the spots corresponding to the collected spectra.

In addition to the inorganic fraction presented above, all the studied findings from the layer 9c2 displayed well defined peaks in the range  $3000 - 2800\text{ cm}^{-1}$ , as shown in figure 2C. They can be attributed to the  $\text{CH}_2$  and  $\text{CH}_3$  stretching vibrations and are indicative of the presence of an organic fraction. The peak at around  $1740\text{ cm}^{-1}$  due to the  $\text{C}=\text{O}$  stretching vibration, even if very weak, is also widely observed in all the collected spectra. It is often accompanied by a characteristic double peak at around  $1577$  and  $1540\text{ cm}^{-1}$ . In some cases, a weak broad band with shoulders around  $1655$  and  $1630\text{ cm}^{-1}$  is also visible.

Finally, some spectra showed the characteristic features of organic acids with a broad and intense band at around  $1590\text{ cm}^{-1}$  that can be attributed to  $\text{COO}^-$  and/or  $\text{C}=\text{C}$  stretching vibrations in aromatic compounds. These could derive from the degradation of organic compounds of both animal and vegetal origin [17].

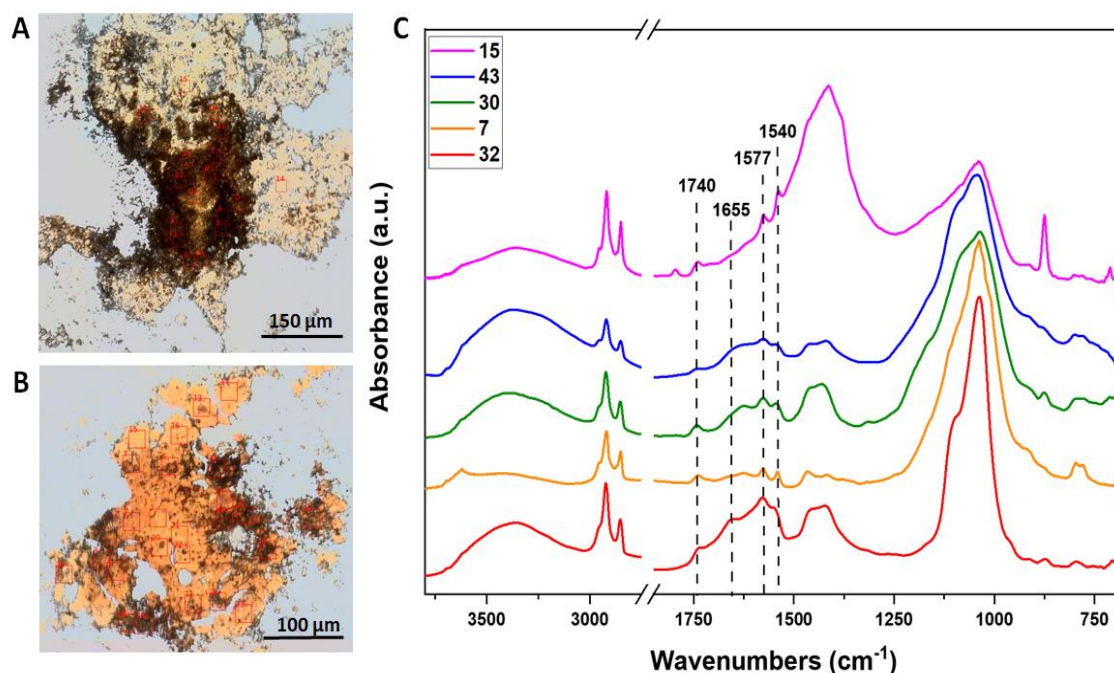


Figure 2. **A, B.** Optical images of samples no. 7 and 43, respectively, with indication of the spots corresponding to the collected spectra. **C.** Example of IR spectra of sample no. 15, 43, 30, 7, 32 showing the main peaks discussed in the text-

#### 4. Discussion and conclusions

A partial characterisation of the depositional context of layer 9c2 of Grotta Paglicci was carried out through the analysis of the mineral components of all the findings taken into consideration, including the one that did not yield any organic residue (finding no. 34). In fact, observation by FTIR microscopy made it possible to chromatically discriminate at general level organic residues (typically brown - reddish - orange - black in colour) from carbonates (dark grey in colour) and silicates (off-white in colour), commonly composing soils. The most relevant result from findings that yielded organic residues (findings no. 7, 15, 30, 32, 43 and 47) is the characteristic recurrence of the doublet at around  $1577\text{ cm}^{-1}$  and  $1544\text{ cm}^{-1}$ , which is due to the C-O stretching mode of fatty acid calcium salt carboxylate [18] [19]. A further peak at around  $1740\text{ cm}^{-1}$ , detected in all the findings, can be due to C=O moiety in free fatty acids, carboxylic acids or can be attributed to an incomplete triacylglycerol decomposition [19].

It is widely reported in literature that these infrared features are associated with the presence of adipocere, a wax-like compound originating from the anaerobic bacterial hydrolysis of fat tissues [20]. As far as we know, in only one case adipocere were detected on prehistoric lithic artefacts, consisting of a handaxe and a scraper from the Lower Palaeolithic of Revadim, Israel [7]. The authors suggest that this finding can be directly correlated with butchery and animal carcass processing. However, since the typical colour of adipocere is whitish and light, an interesting consideration should be made on the chromatic appearance of the samples analysed in this paper. In fact, just in a few cases the infrared spectra revealed the presence of adipocere in correspondence with clear spots, while quite often these compounds were detected in brownish and dark coloured regions. It must be taken into account that the archaeological residues under study can be composed by a complex mixture of substances or have undergone strong diagenetic processes. In our opinion this raises both theoretical and methodological issues that will need further investigations.

This case study lays the foundations for the design of a methodological protocol on SR-FTIR microscopy in transmission mode applied to residue analysis on lithic artefacts, taking into account both organic and inorganic contributions deriving from the sedimentary environment.

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