

# Experiment Proposal

Experiment number GP2024010

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<b>Co-investigator</b>		
<b>Co-investigator</b>		
<b>Experiment title</b>	Understanding ritual practices in Neolithic Saudi Arabia on horn sheaths from Mustatils using Raman spectroscopy	
<b>MRF Instrument</b>	<b>AFM Raman</b>	<b>Days requested: 4</b>
<b>Access Route</b>	Direct Access	<b>Previous GP Number: GP2023065</b>
<b>Science Areas</b>	Cultural Heritage	<b>DOI: -</b>
<b>Sponsored Grant</b>	None	<b>Sponsor: -</b>
<b>Grant Title</b>	-	<b>Grant Number: -</b>
<b>Start Date</b>	-	<b>Finish Date: -</b>
<b>Similar Submission?</b>	-	
<b>Industrial Links</b>	-	
<b>Non-Technical Abstract</b>	Archaeological research in Saudi Arabia is going through a period of intense development that is constantly leading to important discoveries. Mustatils are massive stone structures serving ritual purpose that were built in hundreds in Northwest Arabia 7500 years ago by nomadic pastoral populations. An exceptional category of finds is represented by horn sheaths, made of the outer keratin shell of the horn. Due to its organic protein composition, the sheath is usually not preserved in archaeology and lacks research. To shed light on the horn treatment, desiccation through deliberate heating, colouring and degradation, we propose a surface characterization using Confocal Raman spectroscopy and, in a separate proposal, Fluorescence microscopy. A surface characterization via vibrational spectroscopy is expected to provide information on the materials applied on the horn outer layers which prevented degradation of keratin, and possibly explaining the sample colouring.	
<b>Publications</b>	Neutron-Enhanced Information on the Laboratory Characterization of Ancient Egyptian Leathers: Hydration and Preservation Status, G. Romanelli et al., Information, 13, 10, 2022	

<b>Instruments</b>	<b>TOSCA</b>	<b>Days Requested: 2</b>
<b>Access Route</b>	Direct Access	<b>Previous RB Number:</b>
<b>Science Areas</b>		<b>DOI:</b>
<b>Sponsored Grant</b>	None	<b>Sponsor:</b>
<b>Grant Title</b>	-	<b>Grant Number:</b>
<b>Start Date</b>	-	<b>Finish Date:</b>
<b>Similar Submission?</b>		
<b>Industrial Links</b>		



## Sample record sheet

**Principal contact** Dr Laura Strolin, Institut Català de Arqueologia Clàssica, SPAIN  
**MRF Instrument** **AFM Raman** **Days Requested: 4**  
**Special requirements:**

### SAMPLE

<b>Material</b>	Animal horn	-	-
<b>Formula</b>	Keratin	-	-
<b>Forms</b>	Solid		
<b>Volume</b>	5 cc		
<b>Weight</b>	5 g		
<b>Container or substrate</b>	-	-	-
<b>Storage Requirements</b>	-	-	-

### SAMPLE ENVIROMENT

<b>Temperature Range</b>	- K	-	-
<b>Pressure Range</b>	- mbar	-	-
<b>Magnetic field range</b>	- T	-	-
<b>Standard equipment</b>	None	-	-
<b>Special equipment</b>	-	-	-

### SAFETY

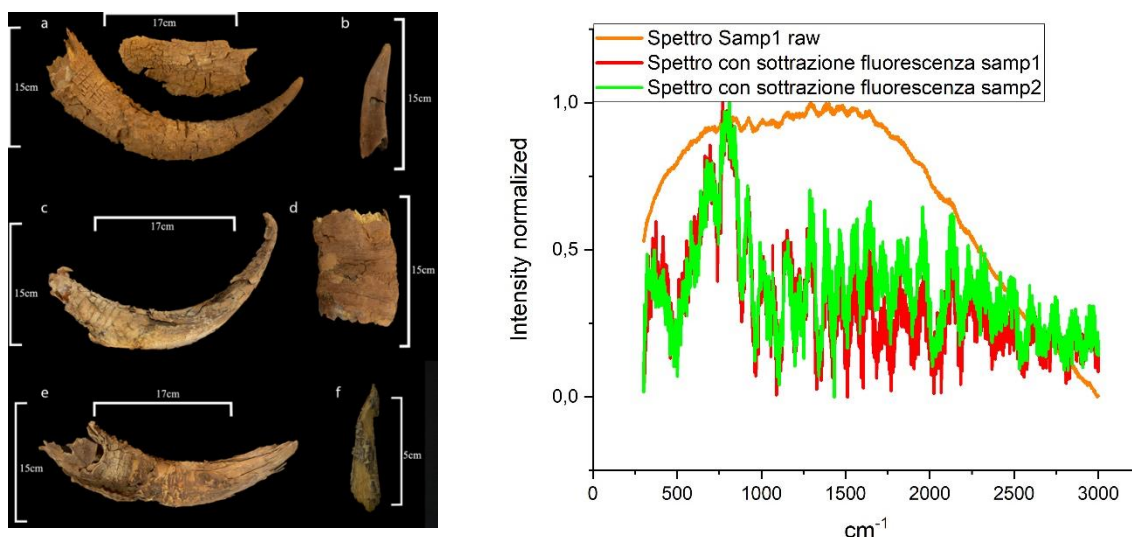
<b>Prep lab needed</b>	Yes	-	-
<b>Sample Prep Hazards</b>	-	-	-
<b>Special equip. reqs</b>	-	-	-
<b>Sensitivity to air</b>	No	-	-
<b>Sensitivity to vapour</b>	No	-	-
<b>Experiment Hazards</b>	-	-	-
<b>Equipment Hazards</b>	-	-	-
<b>Biological hazards</b>	-	-	-
<b>Radioactive Hazards</b>	-	-	-
<b>Additional Hazards</b>	-	-	-
<b>Additional Details</b>	-	-	-
<b>Sample will be</b>	Disposed by IS	-	-



## Background and Context

Archaeological research in Saudi Arabia is going through a period of intense development that is constantly leading to important discoveries. Namely, previously unknown monumental structures dating back to the Neolithic are being investigated for the first time: the 'mustatils'. Mustatils are massive stone structures serving ritual purpose that were built in hundreds in Northwest Arabia 7500 years ago by nomadic pastoral populations [1-3]. So far, little is known about their culture, economy, and habits. The main finds in mustatils are skulls of selected horned animals (cattle, goat, gazelle), intentionally deposited in specific offering chambers where hearths are also present [2, 4]. Moreover, these faunal remains are the most ancient attestation of domestic cattle and goat in Arabia.

An exceptional category of find is present, the horn sheath, that is the outer keratin shell of the horn. Due to its organic protein composition, the sheath is usually not preserved in archaeology and lacks research. Therefore, the exceptional preservation of horn sheaths in mustatils opens the unique possibility to investigate this material not only for better understanding the ritual universe and technical knowledge of Neolithic nomadic people of ancient Arabia, but also for clarifying the circumstances of sheath desiccation as related to paleoclimatic conditions. In addition, we target possible conservation methods as archaeological horn is a highly fragile and perishable material.



*Figure 1: a selection of the horn sheaths found in Mustatil IDIHA-F-0011081 (left); the preliminary Raman spectra obtained in the feasibility measurements, also suggesting to analyse the fluorescence signal (right).*

The research questions motivating this proposal are: were the sheaths treated prior to deposition in the mustatil (as part of the ritual, for preservation purposes) and how? Were some of the sheaths deliberately heated? Why do the sheaths present different colours and levels of degradation? What is their current state of desiccation and degradation?

## Previous characterizations

Mustatils are the object of a wide research programme carried out previously by the University of Western Australia and currently the University of Sydney (Prehistoric AIUla and Khaybar Excavation Project – PAKEP) with the support of the Royal Commission for AIUla. The research focuses on Neolithic mustatils and settlements, as well as on Bronze Age tombs. As such, it aims at enlightening all aspects of ancient societies in the area. It also includes remote sensing, helicopter photography, ground survey, excavation, and material analyses, with a special attention to outreach.



As suggested by the panel during our previous submission (2023065), we have carried out some preliminary measurements (Figure 1, right) showing that a Raman signal can be obtained, and it is accompanied by an intense fluorescence light. Given the limited amount of time to be used for just one sample and considering that other sample may have rather different fluorescence backgrounds, the promising results so far seem to suggest a spectroscopic investigation tackling both the vibrational and the fluorescence signal.

### **Proposed experiment**

We propose a surface characterization of a series of fragments and pieces from a selection of horn sheaths, i.e., smaller portions of the finds in Figure 1 (left), through confocal Raman spectroscopy at the Tor Vergata – IM@IT unit using the AFM Raman XploRA Plus. Vibrational spectroscopy of the sample surface will provide information on any materials applied on the horn outer layers which prevented degradation of the keratin organic material and on any desiccation and preservation processes related to such samples and on the reason why different colours are observed. Ancient samples will be compared with modern ones to facilitate the interpretation of the experimental data.

In addition to Raman spectroscopy, through separate proposals, we will request access to the Fluorescence Microscopy, located at the University of Milano Bicocca – IM@IT Unit, to better characterize the source of the fluorescence signal. This will, at the same time, provide an elemental analysis of the sample surface and suggest the best settings for the Raman characterization.

Finally, considering the importance of vibrational spectroscopy to assess the chemical composition of the samples, yet the challenge in using light-based instruments, we plan to submit a beamtime request for the TOSCA instrument at the ISIS Neutron and Muon Source (UK) to complement the surface characterization obtained in this IM@IT proposal.

### **Justification of experimental time requested**

We request 4 days of instrument time on the *AFM Raman* MRF located at the Tor Vergata – IM@IT unit, to be used as follows: up to 2 days for samples featuring the same colour, for a total of up to 6 fragments per day. While the preparation of the measurement is quick, to keep the fluorescence signal to a minimum the laser intensity needs to be highly attenuated and extra time needed.

### **References**

- [1] Kennedy D. 2017. ‘Gates’: a new archaeological site type in Saudi Arabia. *Arabian Archaeology and Epigraphy* 28: 153–74.
- [2] Thomas H., Kennedy M., Dalton M., McMahon J., Boyer D. and Repper R. 2021. The Mustatils: Cult and Monumentality in Neolithic north-western Arabia. *Antiquity* 95(381): 605–626.
- [3] Abu-Azizeh W., Studer J., Al-Ahmari S., Boyle A., Dausse L., Quartermaine J., Strolin L., Tombret O. and Zazzo A. 2022. The Horn Chamber Mustatil: A Neolithic open-air sanctuary evidencing pastoral nomadic ritual activity in the north-western Arabian Desert (al-‘Ulā [AlUla]). In Foote R., Guagnin M., Périsse I. and Karacic S. (eds.). *Revealing Cultural Landscapes in North-West Arabia. Proceedings of the Seminar for Arabian Studies* 51, 133–156.
- [4] Kennedy M., Strolin L., McMahon J., Franklin D., Flavel A., Noble J., Swift L., Nassr A., Fallon S. and Thomas H. 2023. Cult, herding, and ‘pilgrimage’ in the Late Neolithic of north-west Arabia: Excavations at a mustatil east of AlUla. *PLoS ONE* 18(3): e0281904.
- [5] Mattiello S., Guzzini A., Del Giudice A., Santulli C., Antonini M., Lupidi G., Gunnella R. 2022. Physico-Chemical Characterization of Keratin from Wool and Chicken Feathers Extracted Using Refined Chemical Methods. *Polymers*, 15(1):181

