Characterisation of red colour on decorated ostrich eggshells from Bahrain.

Gianluca Pastorelli[1], Mikkel Scharff[2], Kirsty Penkman[3], Jørgen Wadum[1] and Jane Richter[2]

[1]*Centre for Art Technological Studies and Conservation – Statens Museum for Kunst (CATS-SMK), Sølvgade 48-50, 1307 Copenhagen K, Denmark*
[2]*School of Conservation, Royal Danish Academy of Fine Arts, Schools of Architecture, Design and Conservation, Esplanaden 34, 1263 Copenhagen K, Denmark*
[3]*Department of Chemistry, University of York, York, United Kingdom*

Introduction

- In 1962-63, a Danish archaeological expedition excavated a group of mounds in Bahrain dated to around 2000 B.C (Fig. 1). Among other objects, numerous fragments of decorated ostrich eggshells were unearthed
- The outer surfaces of these fragments bear engravings in the form of rectangular patterns and some areas coloured in a reddish hue on a white background (Fig. 2)
- Understanding the art of decorating common objects like these eggshells during the Late Bronze Age will allow us to bring a significant contribution to prehistoric archaeology
- The aim of this research is to investigate the process by which the ostrich eggshells were decorated, with particular focus on the characterisation of the reddish colour

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Methods

Optical imaging

A variety of optical imaging techniques, including UV-induced fluorescence photography, reflectance transformation imaging (RTI), optical coherence tomography (OCT) and cross-section optical microscopy, were used to obtain information on the surface properties of the fragments (Fig. 3-a)

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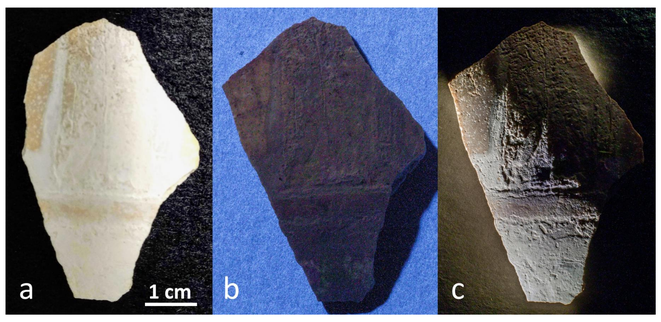

Results and discussion

- UV-induced fluorescence photography (Fig. 3-b) did not reveal the presence of any UV-sensitive colourants
- RTI (Fig. 3-c) showed that the white areas were carved on the red surface of the eggshells
- OCT (Fig. 4-a) indicated that a thin surface layer is present on the red areas (appearing smooth in cross section; Fig. 4-b) and absent in the white areas (appearing uneven in cross section; Fig. 4-c)

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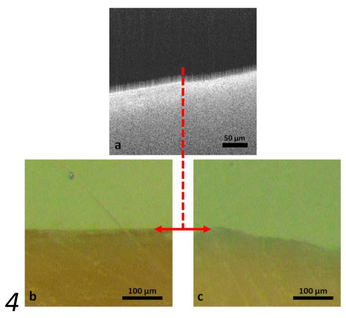

Elemental analysis

Since red colour on archaeological samples is often related to iron-containing pigments such as hematite and ochre, scanning electron microscopy (SEM)-energy dispersive spectroscopy (EDS) was used to detect the presence of iron in the eggshell fragments. Results were confirmed by X-ray fluorescence (XRF) spectroscopy and X-ray photoelectron spectroscopy (XPS)

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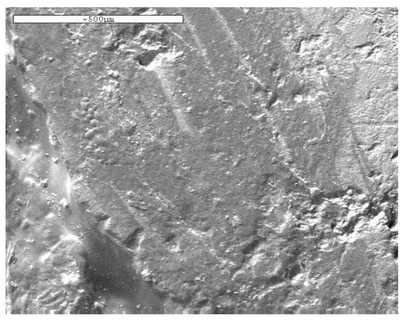

- Analyses carried out by SEM-EDS showed an average iron concentration of 0.207 wt% (2070 $\mu g \cdot g^{-1}$) in both the red and white areas (Fig. 6), while the natural iron content of ostrich eggshells is 2.89 $\mu g \cdot g^{-1}$
- Although the concentration of iron in the shells under investigation is much higher than the natural content, it is too low to be associated with an iron-based pigment like hematite or ochre, and is likely due to post-depositional processes

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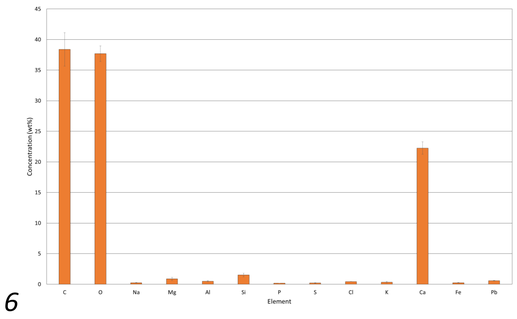

Molecular analysis

The absence of elements that are characteristic of red pigments suggested that an organic dye may have been used to paint the shells. Fourier transform infrared (FTIR) spectroscopy analyses were carried out to reveal the presence of organic compounds both on the surfaces and on the cross sections (Fig. 7) of the fragments. Results were confirmed by UV-visible-NIR spectroscopy, micro-Raman spectroscopy and surface-enhanced Raman spectroscopy (SERS)

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- Micro-FTIR spectroscopy measurements only showed the typical spectrum of calcite (Fig. 8) and could not suggest the use of an organic dye
- Further analyses by means of UV-Visible-NIR spectroscopy, micro-Raman spectroscopy and SERS could not detect any compounds besides the characteristic constituents of the calcareous eggshell

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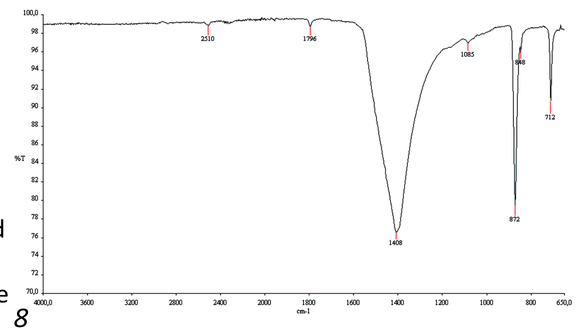

Thermal treatment experiment

As reported in similar research works [1,2], thermal experiments of fresh ostrich eggshells show that the range of colour found on archaeological samples is caused exclusively by the exposure to high temperature. Therefore, fragments of a modern ostrich eggshell (Fig. 9) were dry heated between 200 °C and 300 °C in a furnace, and their surface colour was measured subsequently

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- CIE L*a*b* colour measurements showed that the smallest surface colour difference (ΔE) between the archaeological fragments and the modern test pieces was obtained when the samples were heated at 225-250 °C for 7-8 minutes (Fig. 10)
- This supported the hypothesis that the eggshells might have been mildly heated with fire, in order to give them a reddish hue, and then engraved by removing the outer layer in certain areas, to re-expose the white colour

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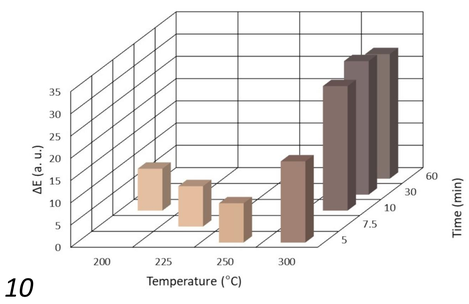

Amino acid racemization

Several protein degradation reactions in modern ostrich eggshell samples have different temperature dependencies, and therefore may be used to identify sub-fossil samples which have been exposed to high temperatures [2]. Different trends in relative rates of amino acid racemization, i.e. the conversion of pure laevorotary (L) amino acids into mixtures where both the L and the dextrorotary (D) forms are present, calculated after analysis by high performance liquid chromatography (HPLC) show a potential use as indicators for exposure to increased temperatures

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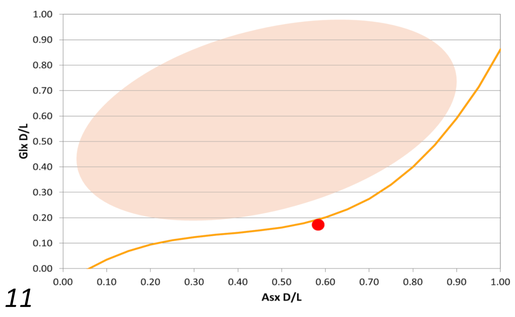

- Glutamic acid-glutamine (Glx) D/L ratios were calculated and plotted versus aspartic acid-asparagine (Asx) D/L (Fig. 11) and isoleucine (Ile) D/L (Fig. 12) ratios
- Modern samples heated at high temperatures have higher Glx D/L ratios for given Asx D/L and Ile D/L ratios than samples heated at lower temperatures. The archaeological samples (red dots) did not show any evidence of heating, as heated samples tend to fall off a reference line into the highlighted areas on the plots

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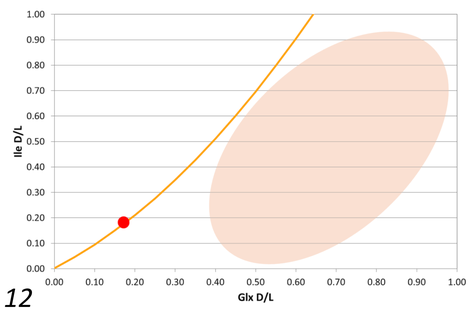

Conclusions

- There is no evidence that a colourant (pigment or dye) was used to produce the red areas on the decorated ostrich eggshells
- Similarly, there is no evidence that a firing/heating process was used to discolour the eggshells surfaces prior to engraving, although a very gentle heating cannot be excluded and might be proved with identification of characteristic degradation products by HPLC during future investigations
- It is also reasonable to assume that the eggshells were not originally coloured and the red colour is the result of differential alteration during the sub-fossilisation process – only the areas which were not engraved and contained significant amounts of organic material (e.g. external cuticle) underwent discolouration

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Contact

Email: gianluca.pastorelli@smk.dk ORCID iD:

References

1. Texier, P.J., Porraz, G., Parkington, J., Rigaud, J.P., Poggenpoel, C., Miller, C., Tribolo, C., Cartwright, C., Coudenneau, A., Klein, R. and Steele, T., 2010. A Howiesons Poort tradition of engraving ostrich eggshell containers dated to 60,000 years ago at Diepkloof Rock Shelter, South Africa. *Proceedings of the National Academy of Sciences*, p.200913047.
2. Crisp, M.K., 2013. *Amino acid racemization dating: Method development using African ostrich (Struthio camelus) eggshell* (Doctoral dissertation, University of York).

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