Multi-analytical characterisation of red colouration on decorated ostrich eggshells from the Middle Bronze Age in Bahrain

Gianluca Pastorellia\*, Mikkel Scharffb, Samantha Pressleec, Kirsty Penkmanc, Jane Richterb

aNational Gallery of Denmark / Statens Museum for Kunst (SMK), Sølvgade 48-50, 1307, Copenhagen K, Denmark

bRoyal Danish Academy, Institute of Conservation, Esplanaden 34, 1263 Copenhagen K, Denmark

cDepartment of Chemistry, University of York, York, YO10 5DD, UK

\*Corresponding author:

Gianluca Pastorelli

[gipa@smk.dk](mailto:gipa@smk.dk)

National Gallery of Denmark / Statens Museum for Kunst (SMK), Department of Conservation and Scientific Research (BENA), Conservation and Art Technological Studies Laboratory (CATS), Sølvgade 48-50, 1307, Copenhagen K, Denmark

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Abstract

In the early 1960s, a Danish archaeological team excavated a group of mounds in Bahrain dating back to 2000 BC. Among their finds were fragments of decorated ostrich eggshells that displayed rectangular engravings as well as red colouring on the outer surface and a uniform red tint on the inner surface. The unpigmented natural coloration of ostrich eggs is the result of adaptations to prevent overheating in the arid habitat, and therefore, the red hue was artificial. The aim of this research was to characterise this coloration. Elemental analysis revealed low iron content, ruling out the use of iron-rich pigments such as ochre, while analysis by molecular spectroscopy could not detect any compounds besides the characteristic constituents of the calcareous eggshell. Thermal experiments on modern eggshells, combined with chiral amino acid analysis, indicated that the red colour on the archaeological samples could have been due to exposure to moderate temperatures. This investigation provides valuable insights into the art and cultural practices of ancient Middle Eastern societies during the Middle Bronze Age, contributing to our knowledge of prehistoric archaeology.

Key words

decorated ostrich eggshell; ancient Near East; colour characterisation; elemental analysis; molecular spectroscopy; experimental archaeology; chiral amino acid analysis.

1 Introduction

Decorated ostrich eggshells (OES) from prehistoric times offer a unique window into the cultural and societal practices of ancient civilizations. These intricately engraved and often coloured eggshells were likely used as household, decorative and ceremonial items (Hodos, 2020; Texier et al., 2013). The study of decorated OES has been a subject of interest for archaeologists and scientists for many years, as it provides valuable insights into the symbolic, artistic and cultural importance of these objects in ancient societies (Hodos, 2020). The consistent motifs and styles found on these eggshells suggest that they had a specific meaning and were part of a complex system of visual and symbolic communication (Texier et al., 2010). Since the Middle Palaeolithic, ostrich eggs have been utilised as containers, jewellery and decorations in a large geographical area, comprising Africa, the Middle East (including the Arabian Peninsula and Bahrain), through to China (Gorzalczany and Rosen, 2022; Kandel and Conard, 2005; Laufer, 1926; Pitarch Martí et al., 2017; Wei et al., 2017). Some of the most well studied examples of decorated OES are those from southern Africa, with the earliest archaeological finds dating back to Diepkloof Rock Shelter, around 60,000 years ago (Texier et al., 2010). These decorated objects are considered among the earliest known examples of symbolic behaviour by prehistoric hunter-gatherers (Texier et al., 2010, 2013). When used as containers, the eggs were likely emptied for yolk and albumen through a hole in the apex, which was subsequently sealed with grass, bees wax or clay (Conwell, 1987). In Ethiopia, South Africa and Botswana, ostrich eggshell beads have been excavated (Clark and Williams, 1978; Orton, 2008; Tapela, 2001), further highlighting the importance of these artefacts in ancient cultures. In addition, decorated OES are believed to have been used as trade items and likely transported around the Mediterranean from the Middle East. For example, studies about the origin and production of decorated OES that were traded and exchanged during the Bronze and Iron Ages showed that these objects must have been imported from the Arabian Peninsula or North Africa, where ostriches were indigenous during those periods (Hodos, 2020).

A variety of analytical techniques, such as microscopy, chemical analysis, and radiocarbon dating have been used to understand the processes by which these eggshells were decorated and to learn more about the materials and techniques used by the ancient craftspeople. For instance, studies have determined that the eggshells were engraved using tools such as stone points and bone awls (d’Errico et al., 2012; Rigaud et al., 2006), and sometimes coloured with pigments made from ochre or charcoal (Lange, 2006; Pitarch Martí et al., 2017; Texier et al., 2010). In 1962-63, a Danish archaeological expedition excavated a group of mounds in Bahrain, dating back to around 2000 BC (Middle Bronze Age, MBA) (Højlund, 2007). Among the many artefacts discovered in the sediment-filled burial chambers of two partly deteriorated mounds, were numerous fragments of decorated OES, deposited on a layer of limestone covered with humus-rich soil. The shells from which these fragments derive are suggested to have been used as drinking cups, providing a glimpse into the funerary practices of the people who lived in the region during that time. The outer surfaces of the fragments bear engravings in the form of rectangular patterns, and some areas are coloured in a reddish hue on a white background (Fig. 1), while the inner surfaces are uniformly reddish. Natural ostrich eggs are glossy, cream-coloured or faintly yellow immediately after having been laid (Cramp, 1986; Deeming, 1993; Laufer, 1926) and are never pigmented (Mikhailov, 1997). This is thought to be an adaptation to the hot arid environment, to prevent the eggs from overheating and reaching a lethally high internal temperature—it only takes a slight artificial colouring of an ostrich egg to increase the internal temperature to a lethal level for the embryo (Bertram and Burger, 2008; Magige et al., 2008). Therefore, there can be no doubt that the reddish colour on the outer surfaces of the sub-fossil eggs is artificial. The characterisation of the reddish colour, as well as the process by which these eggshells were decorated, is the focus of this research. To investigate the surface properties of the archaeological decorated OES fragments, a broad range of imaging, chemical and biochemical analytical techniques, in addition to an experimental replication test were used. Imaging techniques for inspecting structural and compositional properties included ultraviolet-induced visible luminescence (UVL) photography, modified reflectance transformation imaging (RTI) and spectral-domain optical coherence tomography (SD-OCT). To examine the chemical properties of potential colorants, elemental and molecular analyses were carried out by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), fibre optic reflectance spectroscopy (FORS) and Raman spectroscopy. The experimental archaeological test on modern samples consisted of dry heating in an accelerated ageing test chamber, as well as CIE L\*a\*b\* spectrocolorimetry, which takes into account the “standard human eye response”. Several protein degradation reactions in modern OES samples occur at different temperatures; therefore, they may be used to identify sub-fossil samples that have been exposed to high temperatures (Crisp, 2013; Murray-Wallace et al., 2015). To determine whether the archaeological fragments had been heated, chiral amino acid (AA) analysis was conducted using reverse phase high pressure liquid chromatography (RP-HPLC).

2 Materials and methods

To characterize the red colour on the MBA decorated OES from Bahrain, 37 shell fragments, ranging in size from less than 1 cm2 to 10 x 7 cm2 and with a thickness of approximately 2 mm, were selected. The conservation state varied among the fragments, with the inner shell surfaces generally being well preserved while the outer surfaces displayed varying degrees of preservation. The inner surfaces exhibited a uniform reddish hue, while the well-preserved outer surfaces were white and reddish in colour. Unless otherwise specified, all selected eggshell fragments were inspected using a combination of imaging, spectroscopic and biochemical methods. All techniques were used to gather complementary information about the fragments’ surfaces, providing a comprehensive understanding of their structural and chemical properties.

2.1 Imaging

UVL photography was used to capture images of the fragments’ surfaces under UV illumination (200-380 nm), allowing for the detection of potential luminescence signals emitted by UV-sensitive compounds present in the samples. The luminescence signals were captured using a high-end digital camera.

A modified version of RTI was used to acquire high-resolution images of the fragments surfaces, providing detailed information about their topography and surface features. A light source producing visible (400-700 nm) raking light illumination in equal steps around the object and a high-end digital camera were used. The samples were placed on a platform and illuminated with raking light, which was applied in 90⁰ steps over the surface of each sample. While standard RTI typically requires seven or more photographs, the camera only captured four images at different angles of illumination, which were then combined using specialised imaging software (nip2, version 8.7.0, © Imperial College, London).

Cross-sectional SD-OCT images of the fragments were collected using a Thorlabs Telesto OCT system, providing information about their sub-surface structure. The fragments were placed horizontally on a table and scanned at a distance of 43 mm using a low-coherence light source with a centre wavelength of 1300 nm. The images were obtained with an axial and lateral resolution of 5.5 and 13.0 µm in air, respectively.

2.2 Elemental analysis

Two representative samples were collected from the edges of one fragment using a scalpel. The samples were obtained by intersecting the horizontal fragment with the vertical scalpel blade, resulting in two sections that included either a reddish or white portion of the outer surface. The samples were embedded in Technovit 2000 LC light curing resin from Kulzer Technik (Wehrheim, DE) and prepared as cross sections by polishing the transverse plane. Afterwards, elemental analyses on one entire fragment and the two cross sections were carried out using a Hitachi S-3400N scanning electron microscope equipped with an energy dispersive X-ray spectrometer. The spectrometer is a Bruker Quantax 200 EDX system with two Peltier-cooled XFlash silicon drift detectors (SDD), which have an active area of 20 mm2 each. The fragment and the polished sections were mounted to a sample holder using non-porous double-sided electrically conductive carbon tape, with no additional preparation. Measurements were performed in variable pressure mode (30 Pa) using an accelerating voltage of 20 kV, a probe current of 50 µA in backscatter mode, and a working distance of 10 mm. Specific areas to be examined for elemental composition with point-and-shoot analysis were selected onto SEM backscattered electron (BSE) images manually. X-ray elemental mapping was used to visualise the distributions of the elements present in the samples. The acquisition times (live time) for analysing each selected area and for producing the elemental maps were 60 s and 600 s, respectively.

2.3 Molecular analysis

Fragments and cross-sections were analysed by micro-FTIR spectroscopy in ATR mode, using a Bruker Tensor 24 spectrometer coupled with a Hyperion 3000 microscope and equipped with a mercury cadmium telluride (MCT) detector. The ATR measurements were performed using a 20x objective and a Ge crystal with a refractive index of 4.01, which has an anvil design with an 80-µm tip. Spectra were acquired over the range of 3800-900 cm-1 with 128 scans at a resolution of 8 cm-1. Background spectra were run at hourly intervals.

FORS measurements on the fragments were performed with a FieldSpec 4 fibre optic spectroradiometer (PANalytical-ASD Inc., CO). Spectra were collected over the range of 350–2500 nm (i.e., from the near UV to the near IR according to the ISO 21348 and ISO 20473 schemes), with a spectral sampling of 1.4 nm to 2 nm. The spectral resolution was 3 nm at 700 nm, and 10 nm at 1400 nm and 2100 nm. Measurements were carried out using a bifurcated fibre optic probe, with each end comprising 78 fibres. All 156 fibres (with a core diameter of 2000 μm) are thoroughly mixed in the common end. The sampling spot was 4 mm in diameter and 64 spectra were averaged for each sample. The instrument was calibrated using a white reference panel from ASD, which is made of a totally reflective material.

Raman analyses were carried out using a Bruker Senterra dispersive Raman spectrometer coupled with an Olympus microscope and equipped with a thermoelectrically cooled charged-coupled device (CCD) detector. Raman spectra were recorded by focusing either a 785 nm or a 532 nm laser beam through a 100x objective. Gratings with resolutions of 400 lines/mm or 1200 lines/mm were used. The laser beam power incident on the surface of the fragment or cross section being analysed was maintained between 1 and 25 mW, with an acquisition time ranging from 1 s to 100 s per spot and 1 to 3 accumulations.

2.4 Thermal treatment and analysis of thermal degradation

Test pieces were produced from modern ostrich empty eggshells. In total, 84 fragments were prepared. Each of 28 triplets of fragments was placed in a glass Petri dish and subjected to dry heating at temperatures between 100 °C and 275 °C (in 25 °C increments excluding 125 °C), at which they were held for periods of 5, 10, 15 and 20 minutes, in the absence of light, in a Memmert UF160plus laboratory oven.

2.4.1 Colour measurement

Colour changes of the samples surfaces due to thermal treatment were evaluated by colorimetric measurements using a Konica Minolta CM-2600d portable spectrophotometer. Measurements were acquired referring to the CIE L\*a\*b\* colour space (Internationale Beleuchtungskommission, 2004), using a diffuse illumination/10° observation geometry and including the specular reflection component, through a measuring field of 5 mm in diameter and over the 400–700 nm spectral range. Standardized daylight at 6500 K (D65) containing 100% of UV radiation was used as the illuminant, CIE 1964 10° was used as the observer. The L\*, a\* and b\* values were measured at three random locations on each sample outer surface both on the modern test samples and two archaeological fragments, and the respective averages were calculated and used for data analysis. Colour measurements of the inner sides of the test fragments after heating may not have been accurate because of the presence of the degraded internal fibrous membrane (Deeming, 1993) and due to poor contact between the concave eggshell surface and the instrument. The colour difference between the test samples and the archaeological samples was calculated for each combination of temperature and exposure time using the CIEDE2000 (ΔE\*00) colour-difference index (Sharma et al., 2005).

2.4.2 Biomolecular analysis

With chiral AA analysis, different trends in amino acid racemisation (AAR), concentration, composition and peptide bond hydrolysis were used as indicators for exposure of the sub-fossil samples to increased temperatures. AAR refers to the post-mortem spontaneous conversion of amino acids from their laevorotary (L) configuration to their dextrorotary (D) configuration over time, until a one-to-one ratio of L to D is reached resulting in the fossil being fully racemised. The extent of amino acid racemisation observed is primarily used as a dating method to estimate the age of ancient biological materials (Bada, 1985). However, when combined with the aforementioned additional indicators in archaeological investigations, it can be used to gain insights into temperature-related effects. Samples from two archaeological fragments were prepared following the methods of Crisp et al. (2013) (Crisp et al., 2013); in brief, powdered eggshell samples were bleached for 72 hours using 12% (w/v) NaOCl to isolate an intra-crystalline fraction of protein. Two subsamples were then taken: one was gently demineralised in 2 M HCl (analytical grade) to provide the free amino acid (FAA) fraction; to the second 7 M HCl (analytical grade) was added and the sample was heated under N2 for 24 hours to provide the total hydrolysable amino acid (THAA) fraction. Both samples were then dried in a centrifugal evaporator. Samples were rehydrated for analysis by RP-HPLC using a modified method of Kaufman and Manley (1998) (Kaufman and Manley, 1998) and run alongside standards and blanks. During the preparation process, asparagine and glutamine deamidate to aspartic acid and glutamic acid respectively (Hill, 1965) and so these are referred to as Asx and Glx.

3 Results and discussion

In order to obtain information on the surface properties of the sub-fossil OES fragments and to understand the processes by which these eggshells were decorated, a variety of imaging, chemical and biochemical analytical techniques were used. UVL photography did not reveal the presence of any UV-sensitive colorants, while RTI showed that the white areas are at a lower depth than the reddish areas, suggesting that they were carved on the surface of the eggshells (Fig. 2). This assumption is supported by SD-OCT measurements, which indicated that a thin surface layer—probably corresponding to the fossilised external cuticle (Deeming, 1993)—was present on the red areas, appearing smooth in cross-section; however, this layer was absent in the white areas, which appeared uneven in cross-section and marked with abrasion lines in the fragment outer surface (Fig. 3). Elemental analysis was conducted using SEM-EDX. Results showed an average iron concentration of 0.207 wt% (2070 μg·g-1) in both the red and white areas (Fig. 4), which is much higher than the natural iron content of OES (2.89 μg·g-1 (Szczerbińska and Wiercińska, 2010)). However, this concentration is still too low to be associated with iron-based pigments such as hematite (Fe2O3) or ochre, which are typically characterised by iron contents of 17466 μg·g-1 or higher (based on the minimum iron oxide or oxy-hydroxide amount of 5%—in mass oxide—as reported by Dayet, 2021). Therefore, it is likely that the increased iron concentration is due to post-depositional processes related to the presence of humus-rich soil, particularly influenced by humic substances like fulvic acid and humic acid, which could potentially be bound to iron hydroxides/oxides (Ghabbour and Davies, 2001). The absence of elements characteristic of red inorganic pigments led to the hypothesis that an organic dye may have been used to paint the shells. FTIR spectroscopy, FORS and micro-Raman spectroscopy were used to analyse the presence of organic compounds on the surfaces and cross-sections of the fragments. However, these analyses only showed the typical spectrum of calcite (Fig. 5) and did not indicate the use of any organic dyes. To investigate the possibility that the reddish colour is the result of a heating process rather than the application of a colouring agent (Collins and Steele, 2017; Crisp, 2013; Texier et al., 2010), an experimental replication test was carried out. Fragments of modern OES were dry heated in an accelerated ageing test chamber, and the surface colour was subsequently measured and compared with that of the archaeological samples. CIE L\*a\*b\* colour measurements showed that the smallest outer surface colour difference between the sub-fossil fragments and the modern test pieces was obtained when the samples were heated at 200 °C for 15 minutes (ΔE\*00 = 3.43), while the smallest inner surface colour difference corresponded to heating at 275 °C for 5 minutes (ΔE\*00 = 3.35) (Fig. 6). Since the adiabatic flame temperature of common materials such as wood is within a narrow range around 1950 °C, these results supported the hypothesis that the eggshells were subjected to gentle heating, probably in the context of charring phenomena rather than combustion (Bartlett et al., 2019), in order to give them a reddish hue. It is likely that the eggshells were engraved by removing part of the outer layer in certain areas before or after the heating process. To test whether the archaeological samples had been exposed to relatively high temperatures, chiral AA analysis by RP-HPLC was used. Previous studies have established that modern OES samples subjected to high temperatures (>200 °C) exhibit a range of parameters indicative of heating (Crisp, 2013). These parameters include olfactory indicators, impacts on the chromatogram baseline, and differences in relative extents of racemisation. The two most sensitive markers, indicating heating at high temperatures, are when samples show higher Glx D/L values in relation to their Asx D/L and isoleucine (Ile) D/L values. The archaeological samples investigated in this study showed values that are similar to the range observed in unheated and moderately heated (i.e., up to 200 °C for a few minutes) modern samples (Fig. 7), which confirmed the hypothesis that the eggshells could only have been exposed to a moderately high temperature for a relatively short time. Since the fragments are reddish in cross section, it is plausible to assume that, similarly to Bronze Age decorated pottery in the Mediterranean (Swiny, 1981), the incised patterns appear white and calcareous because they were filled-in with a lime-based paste, which was visible as an extra layer in the BSE images of one cross section (Fig. 8). In summary, the decorative patterns on the OES from Bahrain were white-on-red and not red-on-white.

4 Conclusion

Using a combination of optical imaging, elemental analysis, molecular analysis, thermal treatment experiments and AA analysis, this study of decorated OES fragments from the MBA in Bahrain provided new insights into the processes and materials used to create these objects. The results of the study showed that the red hue on the eggshells was likely due to gentle heating prior or subsequent to engraving, rather than the use of pigments or dyes, while the incised decoration was lime-filled for producing a white colouration. Considering that in addition to the thermal treatment, the creation of designs on the eggshells was accomplished by removing part of the outer layer, the research suggests that this process required significant skill and knowledge, as the eggshells were delicate and easily prone to damage. This is an important finding as it sheds light on how ancient craftspeople transformed their artistic ideas into physical objects and adds to our understanding of their level of artistic expertise and mastery of their craft. This research highlighted the potential of using multiple analytical techniques to study prehistoric objects and added to our understanding of the art and cultural practices of the MBA in the Middle East. Future research in this area has the potential to uncover more information about the creative process behind decorated OES, and to explore the relationship between artistic ideas, availability of materials and cultural significance of these objects more deeply.

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Figures & captions

R:\NEaar\Kirsty\OES\Bahraini samples\Fig_1.tif

Fig 1. Fragments of decorated OES from the MBA in Bahrain, displaying geometric designs and light tints of red (a, c – outer surfaces; b, d – inner surfaces).

SINGLE COLUMN, NO COLOR IN PRINT

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Fig 2. Comparison of visual representations of a decorated OES fragment surface using visible light illumination (a), UVL (b), and RTI (c).

SINGLE COLUMN, NO COLOR IN PRINT

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Fig 3. Comparative analysis of the surface structure and topography of a decorated OES: SD-OCT image of a fragment (a), and BSE images of sample cross sections (b and c). The thin layer indicated by the arrow on the left side of subfigure a (corresponding to a smooth profile in the cross section) is absent on the right side (corresponding to an uneven profile in the cross section). The inset in subfigure c shows the BSE image of a white portion of the fragment surface, displaying evident abrasion marks.

SINGLE COLUMN, NO COLOR IN PRINT

R:\NEaar\Kirsty\OES\Bahraini samples\Fig_4.tiffFig 4. Average elemental concentrations detected by SEM-EDX from different decorated OES areas. The y-axis scale is logarithmic for better readability. Error bars represent standard deviation.

SINGLE COLUMN, NO COLOR IN PRINT

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Fig 5. ATR-FTIR spectra of calcite in decorated OES fragments. Spectra A (white outer surface), B (reddish outer surface), and C (modern eggshell) show the characteristic peaks of calcite in the mid-infrared region, demonstrating the absence of other materials in the fragments.

SINGLE COLUMN, NO COLOR IN PRINT

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Fig 6. Colour measurements of the thermally-treated OES test samples compared with the colours of the archaeological samples (a – outer surfaces, b – inner surfaces). The size of the data points represents the ΔE\*00 colour differences between the thermally-treated OES test samples and the archaeological samples (the two blue-encircled points indicate the smallest ΔE\*00 values). The colour of the data points corresponds to the average CIE L\*a\*b\* values measured on each respective sample.

2-COLUMN, NO COLOR IN PRINT

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Fig 7. Glx D/L values plotted against Asx D/L (a) and Ile D/L (b) values can provide information on heating intensity. The archaeological OES samples (red dots) were consistent with gentle heating as it has been shown that samples heated at temperatures >200 °C for more than 5 minutes tend to fall off the curved unheated reference line (in orange) into the shaded areas on the plots.

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Fig 8. Macro-photograph showing the cross-sectional view of a decorated OES fragment (a) and BSE image showing, indicated by the arrow, a distinctive calcareous extra layer (b; the overlay displays the elemental distributions of Ca, P, Si, O and C).

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